The Palmottu Natural Analogue Project

Technical Report 99-11

Transport of Radionuclides in a Natural Flow System at Palmottu

3rd 12-monthly Progress Report 1998-02-01 –1999-01-31

Contract No FI4W-CT95-0010, DG 12-WSME

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I INTRODUCTION

The Palmottu project "Transport of radionuclides in a natural flow system at Palmottu" commenced on January 1st, 1996, as a research study agreed by the European Commission and the four contractors below:

- Geological Survey of Finland (GTK, coordinator),
- Svensk Kärnbränslehantering AB (SKB),
- Empresa Nacional de Residuos Radioactivos S.A. (ENRESA),
- Bureau de Recherches Géologiques et Minières (BRGM),

under the Nuclear Fission Safety research and training programme (Contract No FI4W-CT95-0010, DG 12-WSME).

The Contractors have agreed on associated contracts with the following five partners:
- Radiation and Nuclear Safety Authority, Finland (STUK),
- University of Helsinki, Laboratory of Radiochemistry, Finland (UHRAD),
- Technical Research Center of Finland, Nuclear Energy, Finland (VTT Energy),
- Technical Research Center of Finland, Communities and Infrastructure, Finland (VTT-CI),
- QuantiSci SL, Spain (QuantiSci),

and with the following subcontractors: Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Instituto de Medioambiente, (Ciemat), Universitat Politècnica de Catalunya (UPC) and Universidad de Oviedo (UO), all three from Spain, and Conterra AB, Geokema AB, Geosigma AB, Göteborg University, Intera KB (Intera), Kemakta Konsult AB (Kemakta) and ÅF-IPK AB Miljö, all seven from Sweden. Kivikonsultit Oy, Posiva Oy, PRG-Tec Oy, Suomen Malmi Oy and Technical University of Helsinki, have acted as the main subcontractors from Finland.

The project was originally subdivided into two Phases. Phase I studies which were focused on the hydrogeological assessment of the site, were commenced on January 1st 1996 and completed by May 31st, 1997. The following workpackages (WP) and major tasks (with WP and Task Leaders) were covered:

WP 1:   Understanding the natural flow system (GTK)
Task 1.1:   Up-dating the structural model of the site (GTK)
Task 1.2:   Hydraulic testing and interpretation (Geosigma)
Task 1.3:   Hydrochemistry as an indicator of groundwater flow (Conterra)
Task 1.4:   Flow modelling and integrated evaluation of hydraulic and hydro-geochemical results (VTT-CI)
Task 1.5:   Low-contamination drilling (GTK + Conterra)
WP 5:   Performance assessment exercise of Phase I (Kemakta)

The commencement of the Phase II was dependent on the successful completion of Phase I. Therefore, in order to offer the appropriate bases, a report on the hydrogeological evaluation of the Palmottu natural analogue study site was submitted to the European Commission in April 1997 and was published under EUR (18202) (Blomqvist *et al.* 1998). Based on an project evaluation, the European Commission supported to continue the Palmottu project for an additional 25 months with Phase II studies, with a starting from August 1st, 1997.

Phase II comprises the following major workpackages:

WP 2:   Geochemical evolution of the water-rock system (GTK)
WP 3:   Redox processes (QuantiSci)
WP 4:   Migration of radionuclides (VTT Energy)
WP 5:   Conclusions relevant to repository performance assessment (Kemakta/SKB)

In the following, the progress of the Phase II activities for the period 1998-02-01—1999-01-31 is described. The progress taken has been in good accordance with the plans of the project described in the Technical Annex (see Gantt chart, next page). Due to the delay in the starting of Phase II, the original flow chart of the project has slightly been modified for Phase II (with starting from August 1st 1997). The manpower usage of the project is in line with the plans (presented in a separate Annex).

III SUMMARY OF WORK CARRIED OUT 1998-02-01 – 1998-07-31

WP 2: Geochemical evolution of the water-rock system (GTK)

2.1. Objectives and main activities

The origin and evolution of the groundwater will be interpreted and conceptual evolutionary models tested. Hydrogeochemical interpretation will be supported by isotope studies of identified fracture-coating minerals known to be in contact with the sampled groundwater. As isotope signatures of recharge waters are climate-sensitive, the presence of isotopically light groundwater will be used as evidence for recharge during past cooler climates. Selected hydrogeological connections of the surface-close Eastern Flow System (EFS) will be tested. The target is to specify the EFS in such a detail that it will satisfy the needs of the on-going migration modelling exercise. WP 2 incorporates the following main tasks:

Task 2.1. Hydrochemical and geochemical data sets (GTK & others)
Task 2.2. Detailed characterisation of selected water-rock systems (Ciemat & GTK)
Task 2.3. Geochemical modelling of water-rock interaction (VTT CI, Ciemat, Intera, GTK)

2.2. Results

2.2.1. Hydrogeochemistry

The hydrochemical data set of Palmottu (Kaija *et al.*, 1999) consists of 214 water samples, and it includes precipitation, surface water, groundwater in the overburden, and groundwater from packed-off sections of boreholes. Additionally, a few samples from open boreholes were also included. Most of the chemical analyses have been done at the Geological Survey of Finland. For uranium series studies and other isotope measurements the following laboratories have been involved: BRGM, France; Centrum voor Isotopen Onderzoek, the Netherlands; Ciemat, Spain; IVO Technology Center, Power Plant and Environmental Chemistry, Finland; University of Helsinki, Laboratory of Radiochemistry, Finland; University of Uppsala, Tandem Accelerator Laboratory, Sweden; University of Waterloo, Department of Earth Sciences, Environmental Isotope Laboratory, Canada.

Based on this database, the following discussion highlights the major hydrogeochemical characteristics at Palmottu and presents preliminary geochemical evidence of likely processes affecting the water chemistry.

Palmottu waters have a varied range of chemical features from very dilute precipitation and actively recharging modern groundwater at shallow depths to slightly more concentrated saline groundwater types. A table summing up the chemical composition of the Palmottu waters with minimum and maximum extremes are presented in Table 2-1. The trilinear diagramme of the Palmottu groundwaters show that four main groundwater types are present (Figure 2-1):

1) Ca-HCO$_3$ water (near-surface, dilute)
2) Na-HCO$_3$ water (shallow)
3) Na-SO$_4$ water (intermediate, brackish)
4) Na-Cl water (deep, brackish)

The results of a standard multivariate analysis, called Principal Component Analysis (Figure 2-2), show that precipitation, surface water and groundwater in the overburden plot within the field of Ca-HCO$_3$ groundwater. The field of Na-HCO$_3$ groundwater partly overlaps with the previous one, but it also has an extension towards colder climate recharge. In contrast to the overlapping field of the various HCO$_3$ waters, the brackish Na-SO$_4$ and Na-Cl groundwaters form their own fields with a lack of continuous intermediate composition groundwaters to the HCO$_3$ waters, indicating that the brackish groundwaters are not likely to be simple further evolutionary steps of the HCO$_3$ waters, but rather that the brackish waters form genetically separate groups of waters.

Table 2-1. Summary of selected analytical data of Palmottu waters (Kaija *et al.*, 1999).

|	pH	TDS	Ca	Mg	Na	K	Cl	SO$_4$	HCO$_3$	Si	Br	Sr	B	Mo	U
		mg/l	Mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	µg/l	µg/l	µg/l	µg/l
Precipitation															
Min	4.1	4.6	0.11	0.03	0.13	0.1	0.2	0.53	0.61	0.02	0.03	0.44	0.5	0.03	0.01
Med	5.5	9.5	0.22	0.1	0.44	0.31	0.41	1.13	2.75	0.6	0.1	0.71	1.79	0.06	0.03
Max	6.0	18	0.52	0.1	1.65	1.25	2.61	6.81	13.42	0.6	0.1	1.16	2.84	0.17	0.2
Water in bedrock hollows															
Min.	4.1	3.6	0.11	0.03	0.13	0.1	0.2	0.53	0.61	0.02	0.03	0.21	0.5	0.03	0.01
Med	4.2	9.1	0.26	0.18	0.6	0.16	0.44	4.98	0.61	1.69	0.1	2.84	3.61	0.04	3.67
Max	4.7	17.1	0.52	0.29	1.19	0.35	0.97	10.8	1.22	3.38	0.1	4.65	4.55	0.05	4.35
Surface water															
Min	6.1	24	3.1	0.89	1.85	0.14	1.55	5.61	7.3	1.74	0.03	19.1	2.48	0.16	0.1
Med	6.4	29	3.73	0.93	1.95	0.42	1.61	5.9	10.4	1.76	0.1	20.8	2.97	0.89	0.12
Max	6.5	29.1	3.8	1.06	2	0.5	1.7	6.5	12.2	1.9	1	22.1	3.49	0.93	0.25
Overburden groundwater															
Min	6.2	36	1.5	0.6	1.5	0.5	1.4	0.1	8.5	3.1	0.03	17.1	2.2	0.04	0.1
Med	7.0	125.8	16	3.5	5.1	1.7	1.6	8.4	73.2	7.3	0.03	55	12.2	1.1	0.2
Max	8.0	153	20.5	5.5	8	3.2	1.8	11.7	91.5	14.4	0.11	65.7	19.7	1.5	11
Ca-HCO$_3$-type															
Min	6.2	63.9	10	1.2	1.8	0.9	1	4.8	30.5	0.1	0.03	25.6	5.7	0.6	2.2
Med	7.7	156.7	22.8	3.9	5	1.7	1.4	10.8	99.5	3.9	0.1	62.2	20	4.8	110
Max	8.7	265.6	48.4	7.6	25.6	4.1	15	28	165.4	5.7	1	139	96.5	176	880
Na-HCO$_3$-type															
Min	6.5	142.7	1.7	0.6	16.2	0.7	1.1	1.1	85.4	1.2	0.03	16	50	3.5	0.6
Med	8.2	210.5	15.3	3.2	36.8	2.1	6.5	21.1	115.9	4.3	0.1	53.5	134	35.2	38.1
Max	9.4	426.5	34.2	8	114	3.6	55	118	184.3	5.6	1	148	838	301	363
Na-SO$_4$-type															
Min	7.5	323.4	4.1	1	66	0.5	1.5	107	40.3	1.7	0.2	22.2	210	30	1.2
Med	8.8	1106	24.5	5.3	340	3.4	89	570	73.2	3.5	1.2	210	528	59.8	5.6
Max	9.4	1687	40	14.9	506	6.7	315	838	119.5	5.4	5	469	657	86	18.9
Na-Cl-type															
Min	7.4	305.9	5	1.2	84	2.6	69.4	18	31.7	2.6	1	27	191	14.1	0.3
Med	8.6	632.9	36.8	8.1	235	3.1	188	53.6	78.8	3.7	2.1	340	249	29	4.3
Max	9.1	1625	88.8	15.8	514	5.9	901	198	110.4	4.3	8.4	1140	345	324	8.2
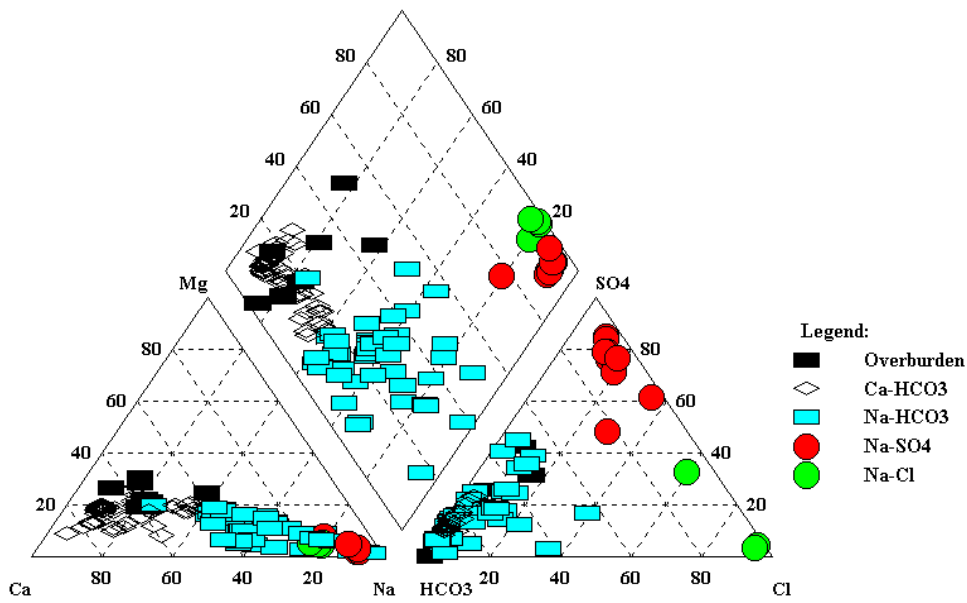
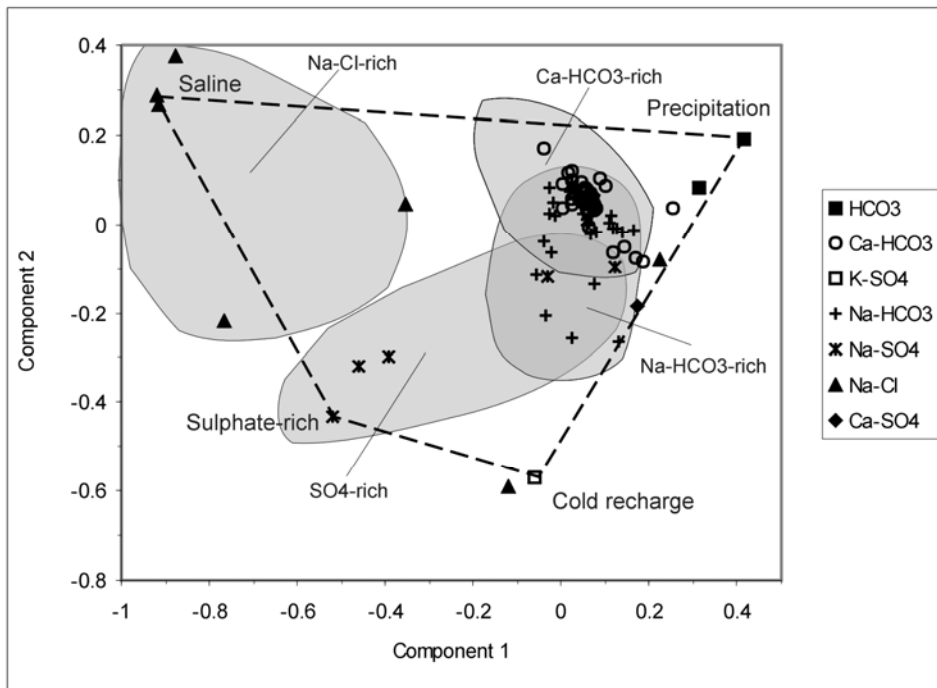Figure 2-1. Trilinear diagramme of groundwater samples (including overburden) at Palmottu (Kaija *et al.*,1999).

Figure 2-2. Principal Component Analysis of Palmottu waters based on major components and ^{3}H, ^{2}H and δ^{18}O (Laaksoharju *et al.*, 1999).

Precipitation at the Palmottu drainage area is dilute (TDS from 4.6 to 18.0 mg/l) and acidic (pH from 4.1 to 6.0). In general, Na is the prevailing cation and HCO_3 most frequent anion, but the composition of the precipitation is highly variable from precipiation to another (Table 2-1), especially with respect to anions Cl, SO_4 and HCO_3. 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. NO_3 concentrations are elevated as NO_3 could be detected in all samples, in contrast to the site-specific groundwaters (also in the overburden) where NO_3 concentrations usually are below the detection limit.

Rain water taken from shallow hollows on the outcropping eastern is likewisely dilute, but its composition tend to change soon after being in contact with the rock surface. Samples taken from the bedrock surface after the rain (4 and 24 hours), show higher concentrations of SO_4, Si, Fe and Mn compared to the original rain water. 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).

When recharging dilute water percolates in fractures of the upper bedrock it evolves towards a more mature $Ca-HCO_3$-type. Generally, there is an increase in dissolved solids and pH, and a decrease in Eh with depth. The plot of pH vs. depth (borehole length) reveals clearly the typical behaviour of pH with depth (Figure 2-3). Low-pH precipitation evolves in the overburden to medium-pH groundwaters of a $Ca-HCO_3$ type with pH from 7 to 8. At depths from 50 to 130 m, a more mature $Na-HCO_3$ type groundwater frequently prevails with pH values from 7 to 9. Deeper down the $Na-HCO_3$ type is followed by a $Na-SO_4$ groundwater down to 200 – 300 m, followed by a Na-Cl type. Presently no hydrochemical information is available from depths deeper than 350 m at Palmottu, however, as deeper saline groundwaters tend to be Ca-(Na)-Cl dominant in the Fennoscandian Shield (Blomqvist 1989, Nurmi 1988) an expert judgement would predict a Ca dominant groundwater at depth in Palmottu, too.
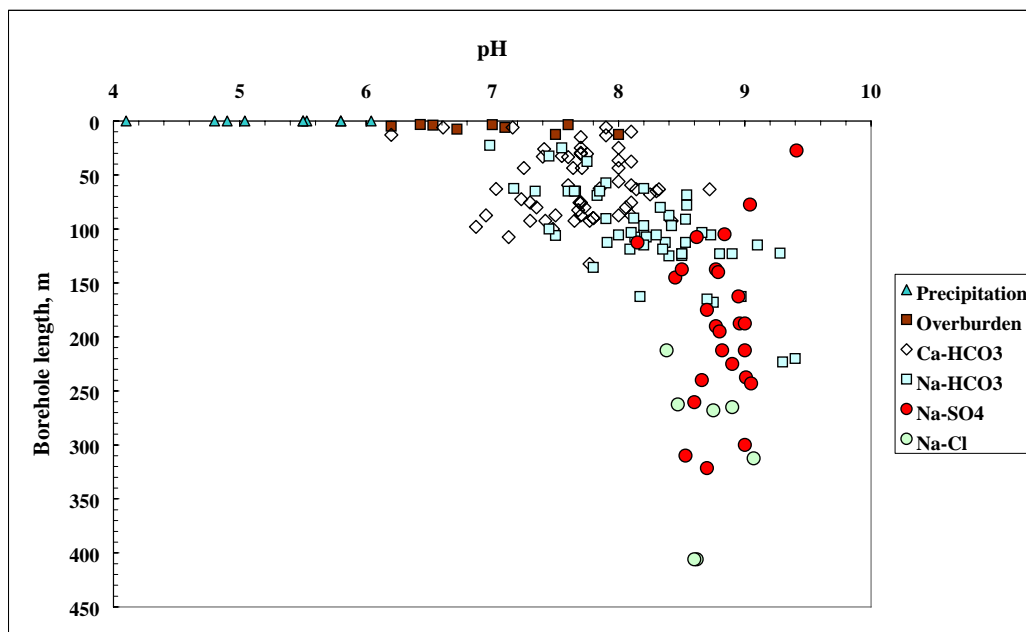

Figure 2-3. Variation of pH *versus* borehole length (Kaija J. *et al.* 1998).

Environmental isotopes (^3H, $\delta^{18}O$, $\delta^{13}C$ and ^{14}C) reveal that at least two different meteoric groundwater components are involved: a meteoric water comparable to present day recharge and a glacial meltwater indicative of substantially colder climatic conditions values (Blomqvist *et al.*, 1995, 1998; Pitkänen *et al.* 1997). The latter is most typically observed in the Na-SO$_4$ groundwater, but the Na-Cl type and some Na-HCO$_3$ type groundwaters also show depleted $\delta^{18}O$ values (Figure 2-4).
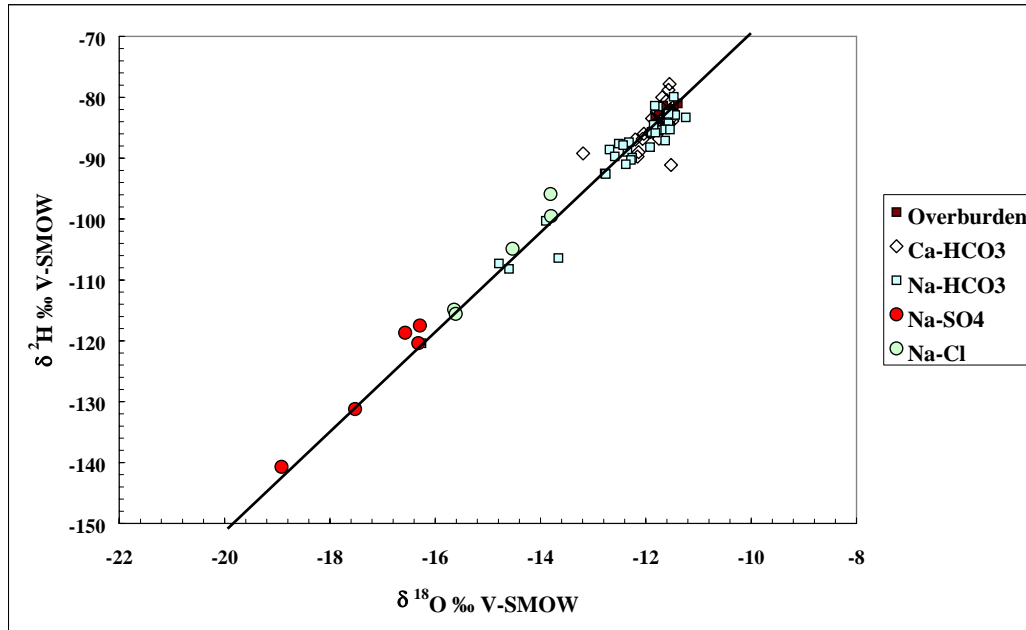

Figure 2-4. δ^2H *versus* $\delta^{18}O$ of groundwater at Palmottu (Kaija J. *et al.* 1998). Global meteoric water line ($\delta^2H = 8\delta^{18}O + 10‰$ SMOW, Craig, 1961) added.

2.2.2. Geochemical evolution modelling

The Principal Component Analysis (Laaksoharju *et al.*, 1999) was utilised to classify the various groundwater types present at Palmottu and a geochemical modeling study was applied to characterise the evolution of the Palmottu groundwaters (Gimeno *et al.*, 1999). In this latter study a statistical approach to the chemical data was first applied as a part of a conventional interpretation process, followed by a reaction-path approach where both inverse and forward simulation techniques were used, all with the code PHREEQC. Mineralogy, redox pairs, and isotopic data were taken into account as a support to the modeling work Based on the modelling results, the following conclusions were drawn (Gimeno *et al.*, 1999), (Figure 2-5):

(a) Three end member waters are involved in the system: recharge water, Na-HCO$_3$ and saline waters (Na-SO$_4$ and Na-Cl types);

(b) Two main hydrogeochemical processes dominate: weathering of minerals (Water-rock interaction), and conservative mixing of end member waters. The first is responsible for converting precipitation to Na-HCO$_3$ water, whereas the latter produce a variety of mixed groundwaters. The weathering processes is characterised by dissolution of calcite and plagioclase, activated by biogenic CO$_2$ uptake, biotite alteration, oxidation of iron sulphides and precipitation of silica, kaolinite, smectite, illite and iron oxyhydroxides.

In the report summing up the hydrogeochemical conditions at Palmottu (Pitkänen *et al.*, 1999), the role of carbon cycling in water-rock interaction is emphasised. Biogenically produced CO_2 promotes silicate weathering and dissolution of calcite at shallow depths. That is shown by the heavy $^{87}Sr/^{86}Sr$ ratios (Negrel and Casanova, 1999) measured from the Ca-HCO_3 waters which indicate dissolution of Rb-rich silicate phases such as K-feldspar and biotite. The Ca to Na ion-exchange, that occurs deeper in the bedrock, maintains continuous calcite dissolution and calcite becomes saturated in Na-HCO_3 type water. Minor calcite precipitation and silicate dissolution are likely to take place in the brackish groundwater types, thus buffering pH to values between 8 and 9. Anaerobic oxidation of organic matter in the lower part of the Na-HCO_3 layer using SO_4 (or eventually U(VI)) as an electron acceptor seem likely. Likewise CH_4 oxidation in the brackish NaCl groundwater layer is considered probable according to C and S isotope data. The fields of occurrence of the various water-rock interaction processes are schematically shown on the hydrogeological model of the site (Figure 2-6).
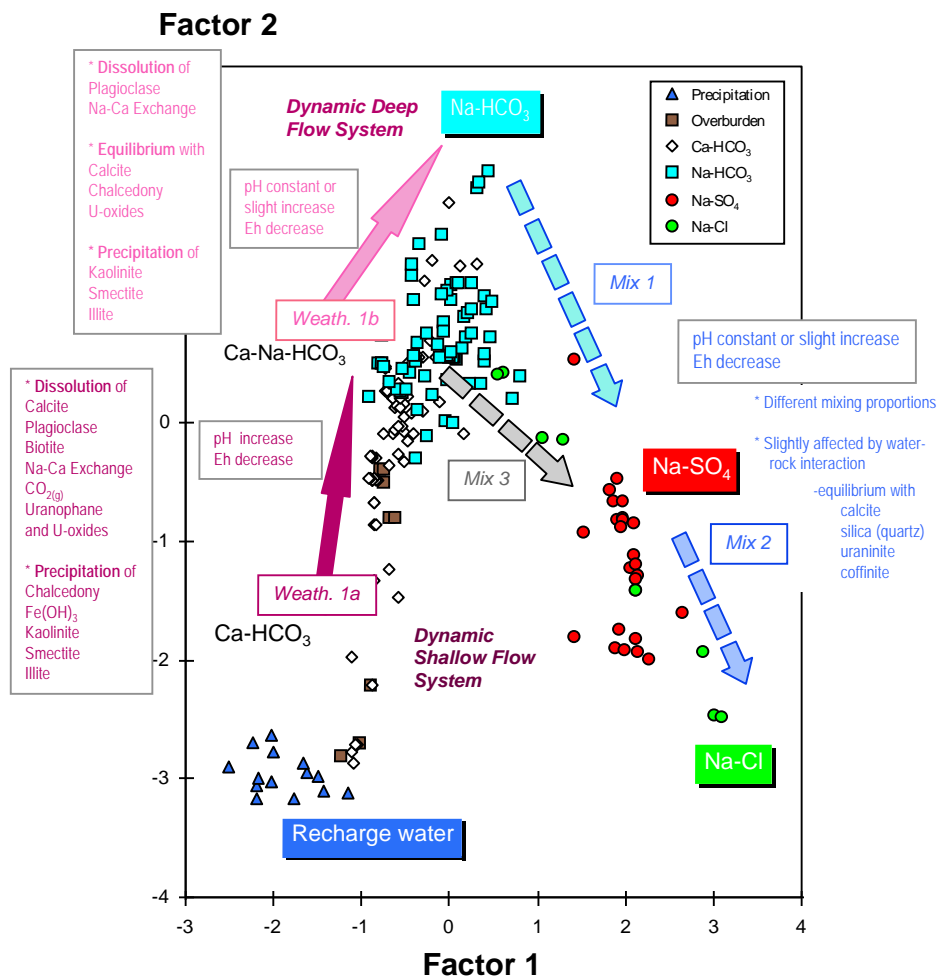

Figure 2-5. The studied samples presented on the plane defined by factors 1 and 2. The end-members and possible evolutionary processes affecting the water chemistry are shown (Gimeno *et al.*, 1999).
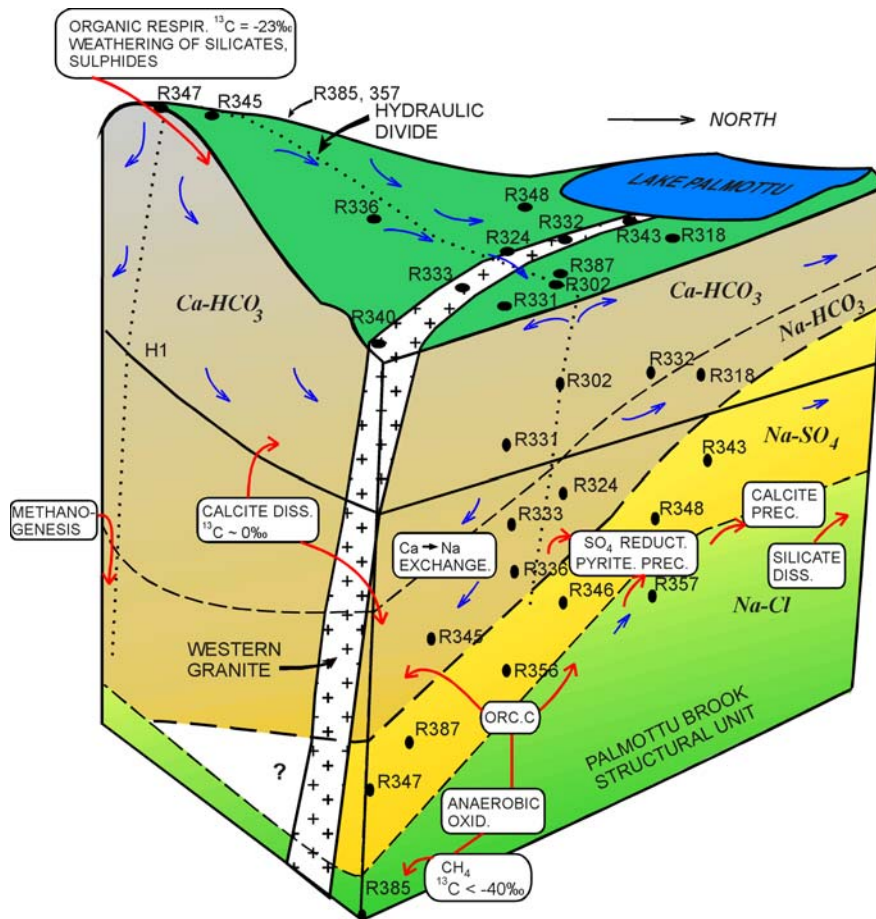
Figure 2-6. The hydrostructural model and the fields of occurrence of the various water-rock interaction processes at Palmottu (Pitkänen *et al.*, 1999).

The distribution of dissolved uranium is clearly controlled by the mineralised uranium bearing zone. High dissolved uranium concentrations (generally from 100-500 ppb) are linked with the HCO_3 groundwaters around the uranium bearing mineralisation down to depths of 130 m. At greater depths clearly reducing conditions prevail, around -300 mV, with $Na-SO_4$ / $Na-Cl$ groundwaters. Here the dissolved uranium concentrations non-frequently exceed 10 ppb. Groundwaters in the western part of the site, outside the mineralised rock types, show low uranium concentrations independent of the prevailing Eh values or groundwater types. Summing up, the upper uranium-rich groundwater body around the mineralised zone forms a horizontal, channel-like system with an approximate width and depth of 100 m and a horizontal extension of at least 300 m. Presently, it is open whether this uranium rich plume has a further extension towards SE along the direction of groundwater flow.

2.2.3. Geometry of fracturing

Fracturing as such is rather uniform in the different parts of the study area. A typical observed fracture density is 4-5 fractures/m. In highly fractured zones the number of fractures exceed 10 fractures/m. These zones are usually only few metres thick and they are difficult to follow from one borehole to another. In most cases these zones are healed by the formation of fracture infilling and only rarely open fracturing is observed.

The situation is completely different if only open, water-conductive fractures are taken in account. In general, not more than 10 % of all fractures of the core sample are open and the number of highly conductive water-bearing fractures is only 2-3 %. A major part of the open fracturing is found in the upper 100-130 m part of the bedrock (Stråhle 1996; Rouhiainen 1996, 1998; Paulamäki *et al.* 1997, Ruskeeniemi *et al.*, 1999). The lower boundary of this bedrock part is defined as the subhorizontal structure H1, an important hydrological and hydrogeochemical boundary at the site (Ludvigson, 1997, Blomqvist *et al.*, 1998). Below H1 open fracturing is far less common, as is also indicated by hydraulic results from the flow meter results (Rouhiainen 1996, 1998).

Only few water-conductive zones can be located in the deeper parts of the bedrock, generally with tens of metres of intact rock between them. A water-conductive zone may have one or a few open fractures with apertures from of 3 to 15 mm (occasionally also larger apertures have been observed). These fractures control the groundwater flow at the site. Additionally, the water-conductive zones may incorporate a large number of small fissures with apertures of 1 mm or less. Their main role, however, seem to be related to water-rock interaction processes rather than to groundwater flow.
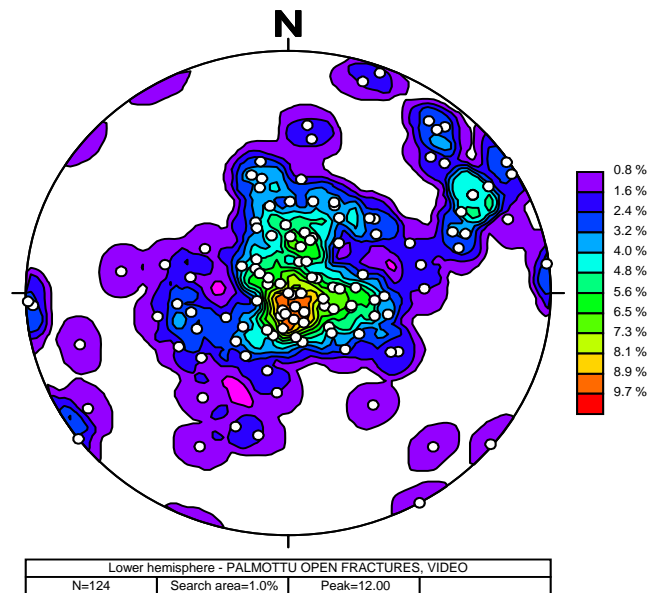

Figure 2-7. Orientation of open fracturing at Palmottu. Altogether 124 observations is collected from 9 boreholes down to the depth of 450 m. The dominant fracturing is subhorizontal or gently dipping towards S, SW and NE (Ruskeeniemi *et al.*, 1999).

The analysis of the orientation of the open fracturing shows that a few fracture systems clearly dominate at the site (Figure 2-7).

(Sub)horizontal or gently dipping fractures to S, SW or NE (10-30°) are common to all boreholes. Fracturing parallel to the schistosity is less common, but dominate in some boreholes (Figure 2-8).

The Eastern Flow System was selected as the main target for migration modelling at Palmottu. Here a roughly orthogonal network of fracturing was found to be characteristic for the flow system. The fracturing incorporates a steeply dipping fracture zone perpendicular to the strike of schistosity that effectively interconnect (sub)horizontal fractures located at different depths along the flow route (Paulamäki *et al.* 1997, Read *et al.* 1998, Ruskeeniemi *et al.* 1999). This implies that the groundwater along its flow route cross-cuts different bedrock units, which may have a pronounced effect on the water-rock interaction behaviour of the flow system.
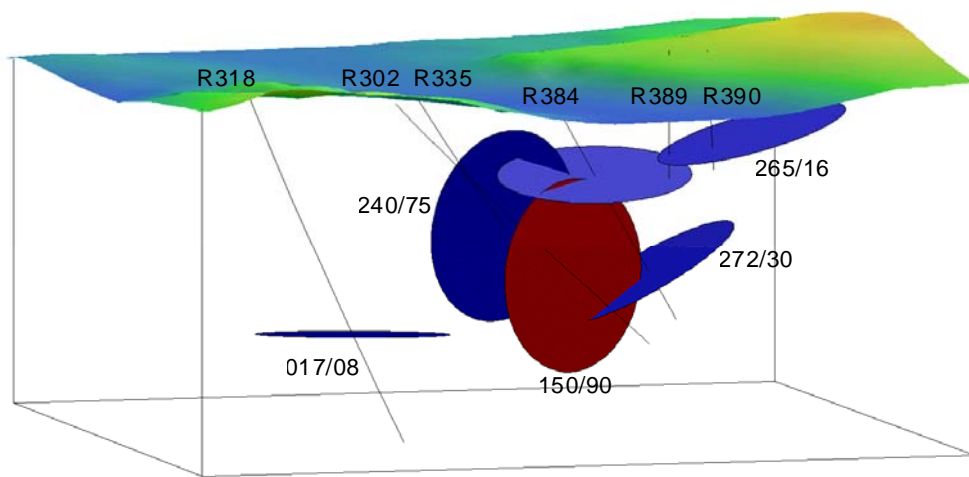

Figure 2-8. Visualisation of the major water-conducting fractures of the Eastern Flow System at Palmottu. A roughly orthogonal network of fracturing can be seen with (sub)horizontal fractures and 2 cross-cutting steeply dipping fracture systems (Paulamäki *et al.*, 1997).

2.2.4. Fracture infilling and fluid inclusion analyses

The studies of fracture infilling at Palmottu have been continued to understand the geological evolution of the site. Special attention has been devoted to the characterisation of the migration route of the Eastern Flow System (EFS) and to transport of uranium along the fracture system. The groups involved in this work are as follows: Geological Survey of Finland; Ciemat, Spain; University of Waterloo, Canada, Terralogica Ab, Sweden and Geokema Ab, Sweden. University of Helsinki, Laboratory of Radiochemistry and BRGM, France have been involved in uranium series studies.

Genetically the secondary minerals in the fractures at Palmottu can be divided into two categories: in-situ weathering/alteration products and mobilised infilling. The first group comprises minerals that are related to dissolution of the wall-rock minerals. Kaolinitisation of plagioclase, oxidation of sulphides to iron oxyhydroxides and alteration of Fe-Mg silicates to smectites are common examples of these processes. The formation of the second type is characterised by the transport of components before precipitation on a remote surface. Most

of the fracture infillings at Palmottu belong to this type, and calcite and kaolinite are typical examples of this group.

Some genetical assumptions can be made based on the fracture mineralogy. Weathering or alteration of primary silicates to kaolinite takes place already in slightly acid conditions. However, either very acid (pH<4) or alkaline (pH>9) conditions are needed to mobilise aluminium. In the type of bedrock encountered at Palmottu, acid conditions are more probable. The evolution of the fluids to more alkaline after the formation of kaolinite is readily seen in the infillings by the crystallisation of calcite upon kaolinite. The stability limit of kaolinite, 270°C, gives an approximate upper limit of the formation temperatures.

Fluid inclusion analyses of representative Palmottu calcites was done to aid in calculating paleofluid temperatures and isotopic compositions (Blyth and Frape, 1999). Palmottu fracture calcites proved to be very difficult to work with because of opaque surface coatings and a general lack of useful primary fluid inclusions.

A plot of the homogenisation temperature (Th) vs. the final melting temperatures (Tm) coded for calcite type is shown on Figure 2-9. There are two distinct fluid inclusion groups. The first group has a Th range of 93 to 285°C (mean 162.5°C) and a Tm range 0 to -10°C (mean of -3.1°C). This group would have crystallisation temperatures of 93 to 285°C and are from low salinity NaCl fluids according to the Tm results. The second group has a Th range of 136 to 141°C (mean of 138.2°C) and a Tm range of -18 to -22°C (mean of -20.1°C). This group has a very narrow crystallisation temperature range of 136 to 141°C and the source fluid would be interpreted as a high salinity brine dominantly a Ca-Cl fluid.
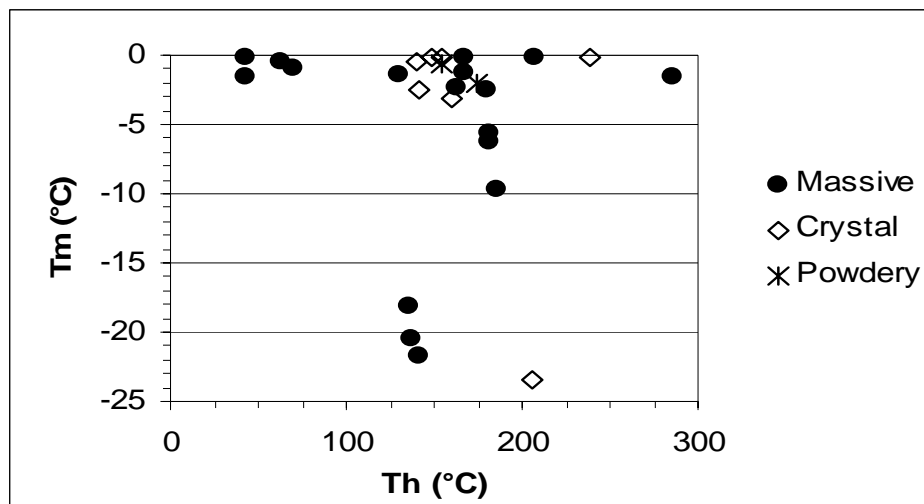

Figure 2-9. Plot of homogenisation temperature (Th) vs. the final melting temperatures (Tm) coded for calcite type at Palmottu (Blyth and Frape, 1999).

The $\delta^{18}O$ signature of the water from which the calcite was precipitated can be calculated using fluid inclusion homogenisation temperatures and the fractionation equations of Friedman and O'Neil (1977).

Petrographically five groups of calcites were found at the Palmottu site: massive calcite with low salinity fluid inclusions, massive calcite with high salinity fluid inclusions, crystalline calcite with low salinity fluid inclusions, crystalline calcite with high salinity fluid inclusions, and powdery calcite with no visible inclusions. The massive calcites with low-salinity inclusions show a very clear cooling trend under conditions of a low water/rock ratio

(Figure 2-10). The solid line is the theoretical composition of a water that equilibrated with a high temperature (286°C) magmatic calcite ($\delta^{18}O$ = -9 ‰ PDB and $\delta^{13}C$ = -9 ‰ PDB) and cooled to 25°C while precipitating calcite in a rock dominated system. In such a system, the isotopic composition of the water will be highly affected by the precipitation of calcite. On Figure 2-10 the bold numbers beside the line are the theoretical temperatures (°C) at which water would have given the isotopic signatures shown by the line.
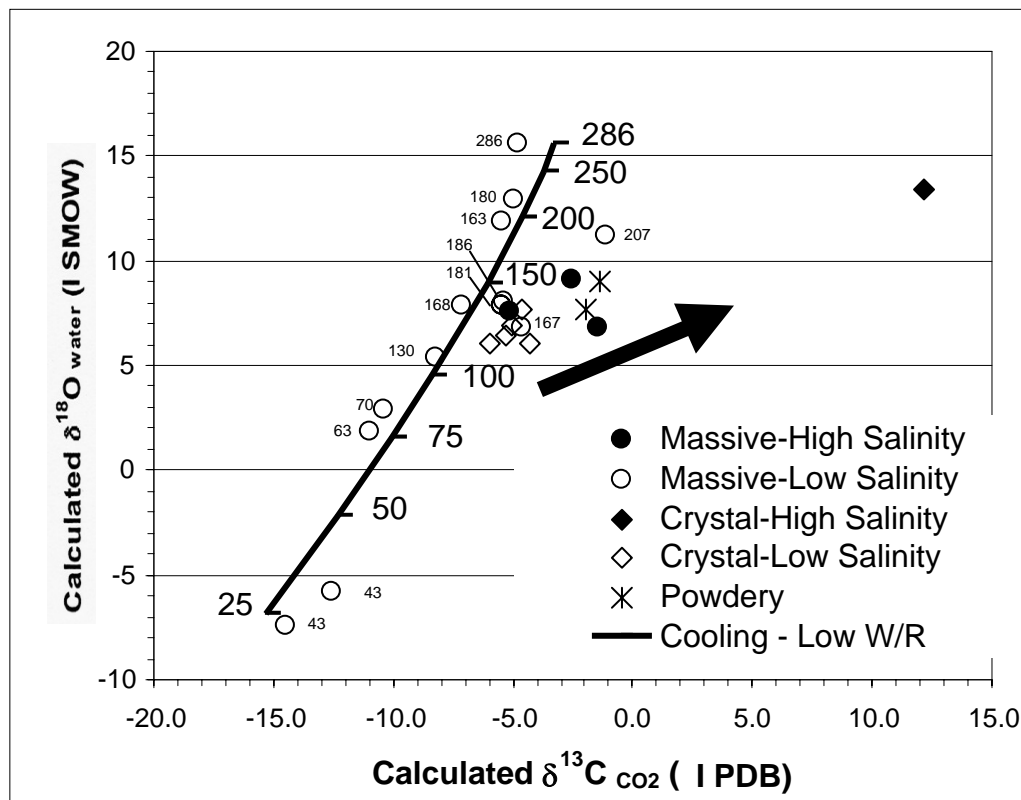

Figure 2-10. Massive calcites with low-salinity inclusions at Palmottu showing a clear cooling trend under conditions of a low water/rock ratios (Blyth and Frape, 1999).

Several calcite samples were selected for cathodoluminescence analysis (Blyth and Frape, 1999). Most of the samples showed homogeneous luminescence indicating only one fluid were involved in the deposition of the calcite. However, two samples showed multi-coloured luminescence, indicating a more complex depositional history. The sample from R387/124.65 m showed an euhedral calcite core with two generations of overgrowth (Figure 2-11). This calcite corresponds to the sample with an unusually enriched calculated $\delta^{13}C_{CO2}$ signature. Another sample from R325/68.50 m showed luminescence layers ranging from red to orange, indicating a change of fluid conditions during growth. This sample yielded two distinct groups of fluid inclusion temperatures over a very short distance. The higher temperature inclusions (163 to 180°C) were smaller and had yellow luminescence while the lower temperature inclusions (63 to 70°C) were larger and had orange to red luminescence. Drastically different fluid inclusion temperature over a very small distance is reasonable in light of the cathodoluminescence evidence that indicated a change in fluids.
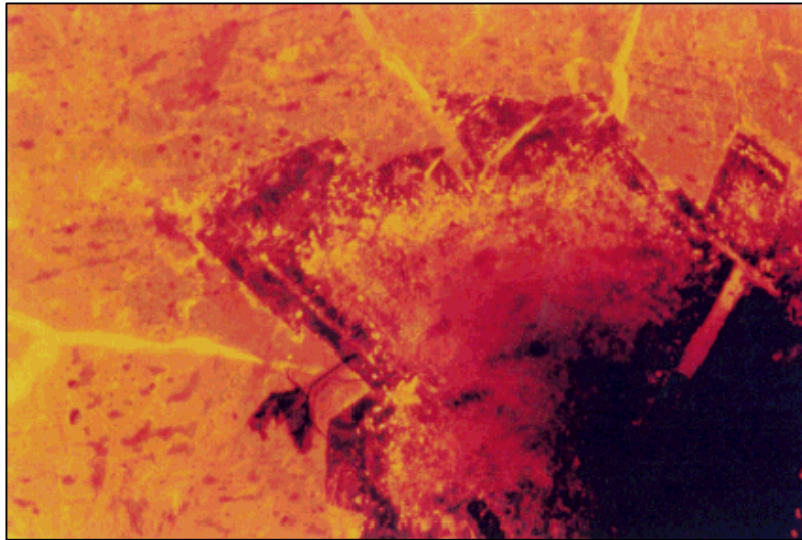
Figure 2-11. Cathodoluminescence showing euhedral, but corroded calcite crystals (red angular area) covered by younger, massive calcite generations (orange mass). Note also the youngest generation (yellow veinlets) filling microcracks in the massive part. Thin section, R387/124.65 m, magnification 25 x (Blyth and Frape, 1999).

The fluid inclusion work indicate that the major part of the studied calcites have crystallised at temperatures of 120 to 300°C either from a low salinity NaCl fluid or a high salinity brine, dominantly a Ca-Cl fluid (Blyth and Frape, 1999). The massive calcites with low salinity inclusions showed a clear cooling trend from 286°C to 25°C (Figure 2-9). The upper formation temperatures of the calcite are indicative of hydrothermal temperatures which persisted in the bedrock not more than few hundred millions years after the peak of the main metamorphic processes at the site, roughly at 1.5 Ma ago. Even these calcites that crystallised at relatively low temperatures, at 43°C, have to be very old. The present geothermal gradient is less than 15°C/km, and the erosion has generally considered very small since 1.2 Ma, only of the order of a few hundred metres (Gaal, 1986). However, the results of the fluid inclusion work do not prevent lower temperature calcites from being crystallised during later epochs, in fact, the low-temperature calcites do not even contain fluid inclusions suitable for geothermometric measurements.

Uranium concentrations associated with calcite infilling are very high especially in the fractures of the Eastern Granite (Ruskeeniemi *et al.*, 1999; Perez del Villar, 1999). The highest recorded values exceed 2000 ppm. High uranium concentrations with calcite infilling only prevail in upper part of the bedrock, and below a threshold of about 100 to 120 the uranium concentrations drop drastically. A very similar trend can be seen in the uranium concentrations of groundwaters, too (Blomqvist *et al.* 1998). In detailed studies small amounts of uranium silicate or possibly uranium silicophosphate has been detected from calcites (Ruskeeniemi *et al.* 1999).The common association with pyrite bearing calcite infillings and the chemical similarity with coffinite suggest that uranium is dominantly in the reduced form. Therefore, it is suggested that the major mobilisation of uranium from mineralised zones took place during the coffinitisation of uraninite under hydrothermal conditions (Ruskeeniemi *et al.*, 1999). This is supported by fluid inclusion data from a calcite infilling that contains more than 1000 ppm of U. The formation temperature was 285°C (Blyth and Frape, 1999).

Recently secondary uranium minerals have been detected from the upper part of the Eastern Granite at depths from 0 to 30 m. Uranophane, U(VI)-Ca-silicate, occurs in tight fractures together with minor calcite and/or smectite in boreholes R384, R389 and R390 (Ruskeeniemi *et al.*, 1999). Detailed microprobe analyses of the delicate uranophane needles failed to reveal any signs of corrosion structures of the crystals. Based on 3 uranium series measurements, the following dates were obtained: 90-120 ka, 189-240 ka and > 400 ka (*i.e.* beyond the upper limit of the dating method). Conventional U/Pb dating techniques support the young dates, giving results that show that upper limit of the uranophane crystals is 1-2 Ma. During the last one million years, the uranium has been mobilised under more oxidising conditions, leading to the precipitation of U(VI) silicates. The uranophane occurs in dilational fractures which could be related to crustal unloading during deglaciation.

The 1,800 ma old uranium deposit at Palmottu has been subjected to a long-term alteration history over hundreds of millions of years. A proportion of the original ore has been altered by hydrothermal processes resulting in an extensive mass of the U(IV) silicate, coffinite, formed around the primary uraninite crystals. However, reworking of uranium mobilisation has continued ever since, as evidenced by high concentrations in groundwater, and uranium sorbed onto iron oxyhydroxides and clays in open fractures. Despite several reactivation periods during the long history of the site, many fractures have remained tight and preserved their hydrothermal infilling mineralogy and the associated uranium concentrations. This indicates that fracture-filling may act as an effective non-reversible sink for uranium in geologically stable crystalline shield areas.

It is apparent that the major flux of uranium into the fracture system is related to the hydrothermal alteration of the uranium mineralisation. As apparent is that the reworking of uranium has continued ever since. This is evidenced by the high concentrations of U in groundwaters and the presence of sorbed uranium in iron oxyhydroxides and clays in presently open fractures. Despite of the reactivation mechanisms most fractures have remained tight for extremely long periods maintaining their hydrothermal features. This suggests that it is rather difficult to disturb the stability of a fracture system in the geologically calm Fennoscandian Shield.

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