Lessons from Nature – The behaviour of Technical and Natural Barriers in the Geological Disposal of Spent Nuclear Fuel

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ABSTRACT

This work deals with the study of the long-term performance of materials and elements involved in the near- and far-field of an underground nuclear waste repository. Materials and elements occurring in nature are similar, or at least analogous, to the materials and elements manufactured or processed by man. Also, natural processes may be similar to those envisaged as occurring in a nuclear waste repository. This similarity makes it possible to study the behaviour of those materials in nature and to compare it with the behaviour of the manufactured materials to be used in a repository. As many materials and elements have been in the natural environment for long time periods (thousands to million of years), the data obtained can be extrapolated to estimate the future evolution of similar components in a nuclear waste repository. Thinking by analogy is the process of comparison, with those materials, elements and environments used to perform the studies that allow the comparison to be regarded as natural analogues.

The Hyrkkölä U-Cu mineralisation (SW Finland) was studied as an analogue to the behaviour of copper canisters in crystalline bedrock. This analogue could also address the interaction between copper corrosion products and uranium. Copper sulphides are shown to retain up to 25% of uranium as U (IV) even if oxidizing conditions prevail. Furthermore, uranium was observed in smectite (main component of bentonite) associated with native copper and cuprite, which constitutes an analogue to the behaviour of the repository near-field materials in a natural oxidizing environment.

In addition to the Hyrkkölä analogue, the issue of irreversible sorption or uranium immobilization is also addressed, in the studies of the boulder rock near Hämeenlinna. The behaviour of U, Th, and rare earth elements (REE) as analogues to the long-lived actinides is also evaluated in groundwater and rock samples at Olkiluoto (SW Finland). U and Th were shown to be released more easily from clean fracture surfaces than from fracture surfaces covered with calcite or kaolinite.

From the studies presented here, it may be seen that the Hyrkkölä analogue has been applied so far in safety assessments, mainly to demonstrate the canister lifetime and to a lesser extent to confirm the interactions between copper corrosion products and uranium. Up to the present, the issues of irreversible sorption or immobilization and the analogy between REE and actinides have not been taken into account in safety assessments. The results of the studies presented here indicate strong prospects that these issues could be new and powerful tools indispensable to safety assessments. More research and understanding is required, however, to form them into operational tools for this application.

PREFACE

This work was started at the former Laboratory of Engineering Geology and Geophysics and was completed at the present Laboratory of Rock Engineering at the Department of Material Science and Rock Engineering of the Helsinki University of Technology. I am grateful to Professor Heikki Niini, who offered his invaluable assistance at the beginning of this work and pushed me to apply for a vacancy in the Graduate School of Rock Engineering. Special thanks go to Professor Markku Peltoniemi for his guidance and encouragement during the final stages of the work. I owe my thanks also to Professor Pekka Särkkä for giving me the opportunity to fully participate in the work of the Graduate School of Rock Engineering. Thanks are also due to Professor Timo Jaakkola for his support during my radiochemical studies. The financial support of the Academy of Finland through the Graduate School, the Finnish Ministry of Trade and Industry and Posiva Oy, all of whom made it possible to carry out this research. I also thank Dr. Juhani Vira and Ms. Margit Snellman at Posiva Oy for their keen interest and support during the initial stages of the study.

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LIST OF PUBLICATIONS

The thesis is based on the following publications:

I Marcos, N., 1997. *The Hyrkkölä native copper mineralization: A natural analogue for copper canisters.* Mat. Res. Soc. Symp. Proc. **465,** 1153-1160.

II Marcos, N., Ahonen, L., Bros, R., Roos, P., Suksi, J. and Oversby, V., 1999. *New data on the Hyrkkölä native copper mineralization: A natural analogue for the long-term corrosion of copper canisters.* Mat. Res. Soc. Symp. Proc. **556**, 825-832.

III Marcos, N., Suksi, J., Ervanne, H. and Rasilainen, K., 2000. *Fracture smectite as a long-term sink for natural radionuclides–Indications from unusual U-series disequilibria.* Radiochim. Acta **88**, 763-766.

IV Marcos, N., Siitari-Kauppi, M., Suksi, J., Rasilainen, K., Finch, R.J. & Hellmuth, K-H., 2001. *Discussion on the use of the matrix diffusion model after a multidisciplinary study of a granitic boulder sample.* Mat. Res. Soc. Symp. Proc. **663**, 1053-1063.

V Marcos, N., 2002. *Low-temperature mobility of rare earth elements, U and Th at the Olkiluoto site, SW Finland.* Mat. Res. Soc. Symp. Proc. **713**, 825-832.

Publications I to III deal with the Hyrkkölä natural analogue for copper canisters and interactions among the elements and materials involved in the near field of a nuclear waste repository. Publications IV and V deal with the behaviour of radionuclides and/or their chemical analogues in the bedrock or far field.

CONTENTS

1 INTRODUCTION

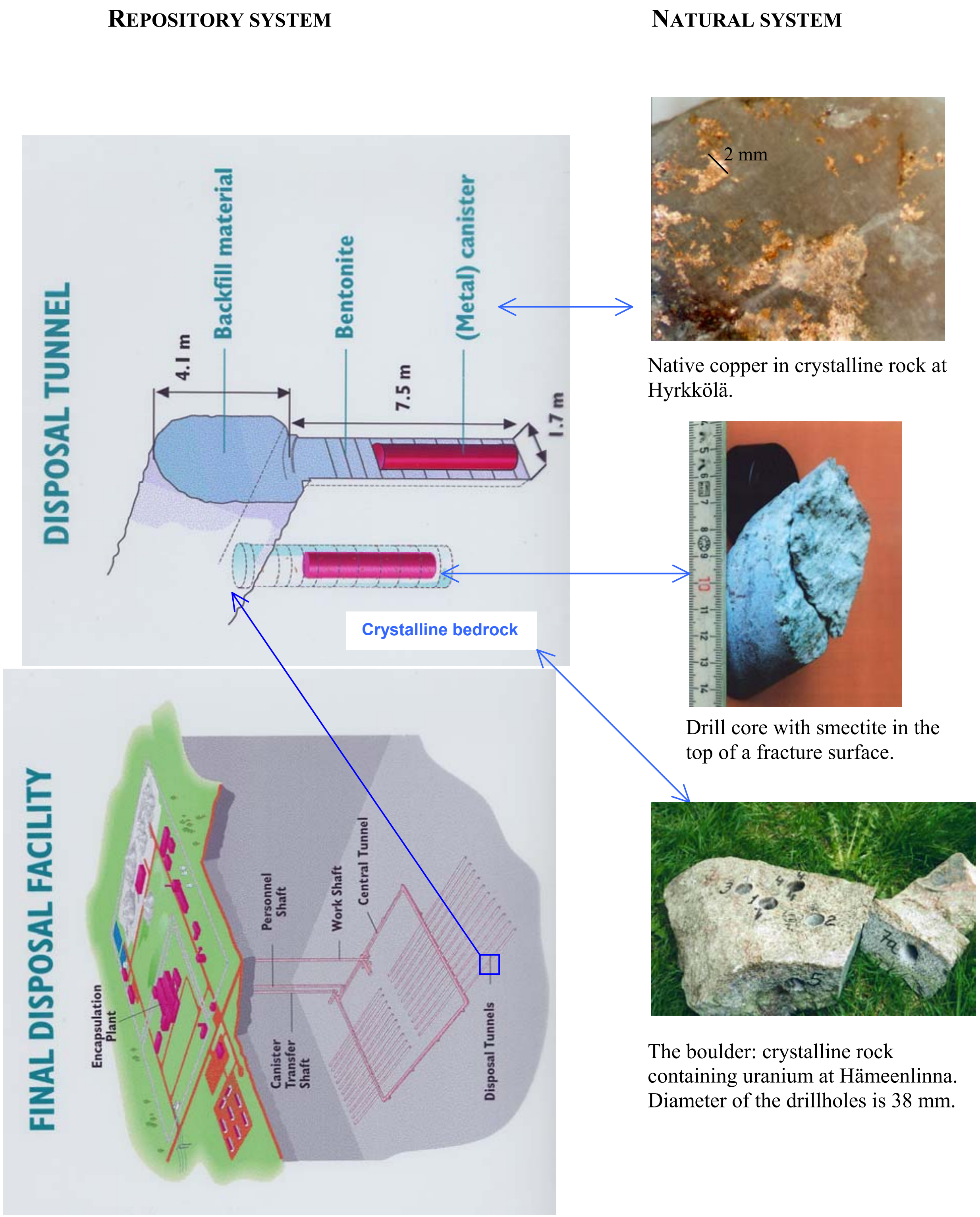
The disposal of spent nuclear fuel in a geological formation has been considered by many countries as the most suitable way to provide protection for the biosphere or living environment (e.g., IAEA 1982). Most national programs plan to isolate the waste using a system based on multiple barriers: 1) a near-field multibarrier engineered system composed of the waste itself, the canister containing the waste, the bentonite buffer surrounding and isolating the canister from the host bedrock, and 2) a far-field natural barrier composed of the host bedrock or geosphere, also called the geobarrier. The goal of the multibarrier system is to retain or delay the harmful long-life radionuclides long enough for substantial radioactive decay and/or dilution to occur.

It is necessary to predict the long-term performance and safety of the disposal system confidently. As no nuclear waste repository system that has evolved over long time of periods of time (i.e., 10^3-10^5 years) is yet available for any kind of study, natural analogues are used to demonstrate the long-term behaviour of parts of a repository system. Natural geological systems offer materials and processes occurring in time frames similar to those envisaged for the safety of nuclear waste repositories (i.e., thousands to million of years). The acceptability of a natural analogue, either for canister performance or for any other disposal component performance, is dependant upon estimating whether or not the natural conditions are sufficiently similar to those at disposal.

The philosophical concept of scientific reasoning by analogy (e.g., Niiniluoto 1988) in which the similarity between systems “A” and “B” allows the study of one of them and the extrapolation of the results to the other is used throughout this work. In the field of nuclear waste management studies Ewing and Jercinovic (1987) were the first to discuss the concept of analogy, and the benefits and limitations of applying it to long-term predictions of natural systems. Petit (1992) remarked on the use of analogy as a particular research methodology and its role in the process of scientific discovery. This work examines how the lessons learned from observation of materials and processes in nature can be transferred to an understanding and estimation of the long-term behaviour of similar (analogous) materials and processes involved in a high-level radioactive waste repository. Natural geological systems (materials and processes) are studied as analogues to canister corrosion (Publications I and II) and to radionuclide retention (or release) both in the near-field (Publication II to III) and in the far-field (Publications IV and V). Interactions between components of the system are also considered.

1.1 Setting the analogy

The analogy between the repository and natural systems is set here to give the frames and basis to the studies presented. Figure 1 shows the relation among components of the repository (Finnish concept) and components of the natural system used as analogues in this study. The processes common to the repository and the natural system that affect the behaviour of these components are listed in Table 1.



Native copper in crystalline rock at Hyrkkölä.

Drill core with smectite in the top of a fracture surface.

The boulder: crystalline rock containing uranium at Hämeenlinna. Diameter of the drillholes is 38 mm.

Figure 1. View of the Finnish final disposal facility (with the courtesy of Posiva Oy) and some of the samples used in this study.

Table 1. Elements, materials and processes in natural and repository systems concerning this study. The symbol ↔ indicates interactions between components of the natural system with relevance to the long-term behaviour of the repository.

	REPOSITORY SYSTEM	NATURAL SYSTEM	PROCESSES
Near field: the waste and technical barriers	Long-term durability of copper canister	Long-term durability of native copper ↕	Corrosion, sulfidation ↕
	Behaviour of bentonite in buffer and backfill	Smectite properties with respect to radionuclide retention	Retention of radionuclides Long-term retention of radionuclides
	Actinides	Rare-earth elements ↕	Interactions in the far-field
Far field: the geo-sphere	Crystalline bedrock	Crystalline bedrock	Matrix diffusion, precipitation, others

It is planned to dispose of the spent fuel from Finnish nuclear power plants in copper-iron canisters at a depth of about 500 metres in crystalline bedrock. The Finnish disposal concept aims at long-term isolation of the spent fuel from the biosphere and even from the geosphere. Hence, the role and behaviour of the copper canister is of primary importance. The major role of bentonite is to isolate and protect the canister from any disturbance in the geosphere and to fill possible fractures in the bedrock. The long-term evolution of the repository system is undertaken in performance assessment studies through “scenarios” (e.g., Vieno and Nordman 1999). One of them considers the consequences of the failure of the canister/s and of the radionuclides being released into the near field (canister corrosion products and bentonite) and the far field or geosphere. It is within this “scenario” that the studies on interaction of radionuclides with canister corrosion products, smectite and bedrock may give support and help in predicting with more confidence the long-term evolution of the repository system.

1.2 Background: previous studies

The requirement for a good analogue with respect to copper canister performance under conditions representative of a Finnish spent fuel repository is that metallic copper should be encountered in granitic rock and preferably in conditions that confirm the significant processes – e.g., sulphide attack, bacterially assisted or not – are those predicted (Vira 1996). Previous studies addressing the durability and longevity of metallic copper are those of Johnson and Francis (1980), Crissman and Jacobs (1982) and Marcos (1989). Miller et al. (1994, 2000) reviewed those works and remarked that metallic copper occurred in environments not totally similar to the near field of a repository. Miller et al. (2000) mention the studies at Hyrkkölä, SW Finland (Marcos 1996, Marcos and Ahonen 1999) but no remarks are presented on the meaning of the results in the study.

Johnson and Francis (1980) studied the corrosion and weathering of archaeological copper objects providing a good insight into the durability of copper over the last

8000 years, but the environment in which the objects had been preserved was either unspecified or irrelevant to the conditions expected in a spent fuel repository. Crissman (1982) and Crissman and Jacobs (1982) presented studies on the geohydrological conditions that control the stability of native copper deposits in the Keweenaw Peninsula (Michigan, USA). Native copper occurred within the Keweenawan basalts that are not analogous to crystalline bedrock. Recently, Milodowski et al. (2000) presented a study on a potential natural analogue for the long-term behaviour of copper canisters surrounded by a bentonite buffer. The native copper mineralisation surrounded by smectitic siltstones and mudstones is older than 176 Ma. The authors conclude that native copper can remain stable in a saturated and compacted clay environment for geological timescales (over 176 Ma) well in excess of the timescales considered for performance assessment, i.e., 100 000 years (e.g., Werme 1998). The possible water-rock interactions that caused changes in the composition of copper are deciphered through petrographic studies. No current analyses of the groundwater in the system are presented, but the environment differs from that expected in crystalline bedrock.

The ability of bentonite to expand or swell is the property that makes it a suitable barrier material. Most of the natural analogue studies of the long-term durability of bentonite are focused to highlight the processes that would affect the mineralogy of bentonite and thus any possible change in the swelling property. One of these processes is illitisation (i.e., the exchange of sodium (Na^+) in the clay for potassium (K^+) in the groundwater), a process dependent on the temperature and the availability of potassium (e.g., Push 1983, Push and Karnland 1988). Natural analogue studies of the interaction of bentonite with other repository materials, with copper, for example, have no straightforward carried away, although the studies on the Kronan cannon (Hallberg et al. 1988, King 1995), with a copper content of 96.3% found buried in marine clays, could, in this case, offer an analogy. In safety assessment, the expected role of bentonite is to protect the canister from mechanical damage and to serve as a barrier in case of a release of radionuclides. The uptake of radionuclides by bentonite has not been considered of much, if any, importance, so no natural analogue studies relating to this issue have been attempted prior to the study in Publication III.

With respect to the role of the barrier in the far field (i.e., bedrock), a lot of effort in the field of natural analogues or natural system studies has been devoted to interactions between the possible released radionuclides, groundwater and bedrock. Uranium deposits (e.g., Oklo in Gabon, Cigar Lake in Canada, Peña Blanca in Mexico, Palmottu in Finland, El Berrocal in Spain) have been used as natural analogues to assess radionuclide transport, retention, and spent fuel stability in geologic media (e.g., reviews and references therein by Chapman et al. 1984, Brandenberg et al. 1993, Miller et al. 1994, Smellie et al. 1995, McKinley and Alexander 1996, Smellie et al. 1997, Smellie and Karlsson 1999, Miller et al. 2000, Smellie 2002). The uraninite in several uranium orebodies at Oklo was rich enough in ^{235}U isotope to allow nuclear criticality about 2 billion years ago, and thus Oklo provides an opportunity to investigate the transport behaviour of transuranic radionuclides and the stability of uranium minerals that have undergone criticality (e.g., Curtis et al. 1989, Blanc 1996, to mention but two references concerning Oklo). Al-rich chlorite and Fe-oxides played a major role in the immobilization of U and other actinides (e.g., Eberly et al. 1996, Bros et al. 2002). The Cigar Lake orebody is located deep underground and has been considered as the natural system most similar to a whole repository (Cramer and Smellie 1994), but the main differences between the orebody and the Finnish repository are the host rock (sandstone in Cigar Lake) and the absence of an analogue for metal canisters. However, this analogue stresses the role of the low permeability clay in the isolation from the uranium deposit. The geological environment of the Peña Blanca uranium mine is silicic volcanic tuffs. The studies on the age of mineralisation and its alteration have been used to calculate radionuclide release rates (e.g., Murphy 2000) that have been applied in a performance assessment for Yucca Mountain (Nevada, USA). Both, the uranium orebodies at Palmottu and at El Berrocal occur within crystalline bedrock. At both sites mobilized uranium is mainly associated by sorption and co-precipitation with fracture coating minerals, especially calcite and iron oxy-hydroxides. These natural analogue studies also examined the stability and longevity of uranium minerals, the radionuclide transport by colloids, blind prediction tests of geochemical codes and radionuclide retardation by matrix diffusion. An overview of the results of the studies at El Berrocal is presented in Rivas et al. (1997). The latest results of the studies at Palmottu are summarized in Blomqvist et al. (2000).

Natural analogue studies focused specifically on the role of matrix diffusion as a radionuclide retardation mechanism in fractured bedrock have formed part of the studies mentioned above. Matrix diffusion is the process by which solutes, carried in groundwater flowing along fractures and fracture zones, penetrate the surrounding rock mass by diffusive processes. Rasilainen (1997) presented a review of this issue in his own work, and Miller et al. (2000) reviewed the investigations relating to this process both in sedimentary and crystalline rocks. Diffusion into the rock occurs in a connected system of pores and microfractures. The importance of the process is that it greatly enlarges the area of rock surface in contact with solutes and can delay releases of contaminants (e.g., Neretnieks 1980, Rasmuson and Neretnieks 1981, Hadermann and Roesel 1985). The measurement of uranium concentration and $^{234}U/^{238}U$ activity ratio distributions (usually along a profile in drill cores cut perpendicular to the fracture surface) is commonly used as an experimental reference to assess the migration of radionuclides in matrix diffusion models (e.g., Smellie et al. 1986, Rasilainen 1997 and references therein). Rivas et al. (1997) pointed out that the matrix diffusion process precedes not only reversible retardation of radionuclides but also their irreversible immobilization. Also, in the studies in Publication IV, matrix diffusion is considered to be the mechanism that "pushes" uranium within the rock prior to its precipitation as uranophane in tiny fractures. It is the relatively recent (postglacial) accumulation of uranium in the boulder that makes it an analogue suitable for the study of retention processes in a deglaciation scenario.

The works of Choppin (1983) and Krauskopf (1986) listed chemical analogues for the actinides from the lanthanide (REE) group, but Chapman et al. (1984) discussed the concept of chemical analogues for the elements relevant to radioactive waste earlier. As the most significant long-lived radionuclides present in spent fuel (e.g., technetium, neptunium, iodine, plutonium, americium and curium) do not occur in measurable concentrations in natural geological systems, suitable chemical analogues are required in order to study the behaviour of these radionuclides. The physico-chemical properties of these chemical analogues should be similar or analogous to the radionuclides. Chapman et al. (1984) listed several properties, such as similar valence state (similar redox behaviour), similar ionic radius, and similar complex formation among others. Eisenbud et al. (1984) discussed the use of Th (IV) as a chemical analogue for plutonium Pu (IV), although Pu occurs also as Pu (III) and Pu (V). The variable redox behaviour and complex chemistry of the radionuclides in spent fuel may be a major limitation in finding the adequate chemical analogue. The best chemical analogues for the americium (Am) and curium (Cm) are considered to be the REE with oxidation state III, but still there are differences in their ionic radius (e.g., Krauskopf 1986) Most of the recent studies of the behaviour of REE in variable environments (e.g., Wood et al. 1997, Johannesson et al. 1999, Biddau et al. 2002, to mention but a few) refer invariably to the pioneer work of these authors. In spite of the mentioned physico-chemical differences, the study of the behaviour of the chemical analogues in relevant environments can give indications of how the radionuclide might behave under natural conditions relevant to repository conditions. This has been one of the objectives of the studies in Publication V.

2 SAMPLING AND ANALYSES

The observations of materials in proper samples and processes from nature require the existence of both of them, the processes being past or actual. Knowledge of the existence of these prerequisites comes partly from detailed literature studies and partly from the experience of the researcher or research groups. Access to the materials and the examination of the processes will depend on economic and technical frames.

2.1 Samples and sample preparation

The first samples used in this work (Publication I) were drill cores collected during an ore exploration campaign in the beginning of the 1980's near the village of Hyrkkölä in Nummi-Pusula. The drill cores contained native copper within the rock matrix and in open fracture surfaces. The consideration of the occurrence of native copper as a potential natural analogue to the behaviour of copper canisters (Marcos 1989, 1996) led to a detailed rock and groundwater sampling in order to determine the actual physico-chemical conditions in which native copper occurs (Marcos and Ahonen, 1999).

Drill cores showing natural fracture surfaces were examined under a stereo-microscope to determine whether these surfaces showed interesting features (e.g., native copper, copper sulphides). Then, the drill core was sawn perpendicular to the fracture surface and prepared as polished and thin polished sections. Groundwater samples were collected from the drillhole sections corresponding to the observed open fracture surfaces.

Cores drilled from a boulder sample (see the boulder in Fig. 1, Chapter 1) were used for the studies in Publication IV and drill cores and groundwater samples collected for site characterization purposes at Olkiluoto in SW Finland were the materials used for the study in Publication V. Drill cores were prepared into thin sections. In the study of the samples at Olkiluoto, the drill cores were sawn into halves, one of them to prepare thin sections and the other to be used for chemical analyses.

2.2 Methods of research and analyses

This work has benefited from the integration of multiple investigation methods. Representative rock samples of the sites being considered were prepared as polished-thin sections and examined, first using reflected and transmitted-light microscopy. After this mainly qualitative mineralogical composition of the samples, the chemical composition of the minerals of interest (e.g., native, copper, copper sulphides, uranium phases) was investigated using a Cameca SX50 electron microprobe at the Geological Survey of Finland (GTK). The minimum size of the particles detected by the beam was $\varnothing = 5$ µm. In these studies the detection limits of quantitative analyses were 0.18 weight % (wt.%) for copper, 0.05 wt.% for sulphur, and 0.19 wt.% for uranium. The objective in getting qualitative and quantitative mineralogical compositions is to clarify the degree of "similarity" of materials and the distribution of phases in order to establish interrelationships between the observed changes and the possible processes that originated them. The fracture coating minerals were also examined under binoculars and analysed with X-ray diffraction (XRD) method if necessary.

The ^{14}C-polymethylmethacrylate (^{14}C-PMMA)-method (Siitari-Kauppi 2002, and references therein) was applied to physically characterize rock samples with respect to porosity and diffusivity (publication IV). The method employs the impregnation of vacuum dried rock samples by ^{14}C-PMMA, radiation polymerisation, autoradiography and digital image processing techniques.

Uranium series disequilibria (USD) studies in publications II, III, and IV were conducted to gain insights into the timescales and the nature of the processes considered to have affected the natural system (e.g., sulfidation of native copper and mode of retention or release of radionuclides). This is possible because USD have the capacity for yielding information on the removal and sorption of natural U and its daughters over geologically recent times (< 1 Ma), and because disequilibria are usually enhanced during water-rock interaction. Radionuclides were separated from the sample using total dissolution and sequential extraction (Yanase et al. 1991, Suksi et al. 1992) and measured by α-spectrometry. The reliability of the measurements is attained through the analysis of reference rock samples (Table 2). Suksi (2001) has recently reviewed the origin and uses of U-series disequilibria.

Table 2. Reference rock samples studied for quality assurance purposes. The first two samples are internationally certified reference samples. The third sample is provided by the Geological Survey of Finland (GTK) and represents its own reference material.

Sample code	Sample material	References
SY-2	Syenite	Abbey 1979
DL-1a	Uranium-thorium reference ore; U-series in radioactive equilibrium	Steger and Bowman 1980
RS 111	Granite	Backman 1991

Rock and groundwater samples were also chemically analysed by XRF (X-ray fluorescence spectrometry) and ICP-MS (Inductively coupled plasma mass spectrometry) at the Geolaboratory of the GTK.

The distribution of REE as a function of distance from fracture in Olkiluoto's drill core samples was obtained from slices parallel to the fracture surface. The readily leachable REE fraction of each slice was examined by reacting 0.5N ultrapure nitric acid ($HNO_{3)}$ solution with each crushed slice. The method is similar to that described by Johannesson and Zhou (1999), except that the rock-acid mixtures were allowed to react for 1 min (15 min with 1N HNO_3 in the experiment by Johannesson and Zhou, 1999), as the interest was in whether readily exchangeable REEs from the fractured bedrock could contribute to the REE signatures of the groundwater samples. The method is not likely to enhance reactions similar to those caused by high temperature fluids (hydrothermal and acidic conditions). The leachates were also chemically analysed by ICP-MS.

This work also benefited from the XPS (X-ray photoelectron spectroscopy) technique capable of detecting all elements and their oxidation state in the periodic table from the few top atom layers in a surface. The instrument used was a Kratos XSAM800 X-ray Photoelectron Spectrometer fitted with a dual Al/Mg X-ray source together with a Vacuum Generators imaging XPS instrument (ESCASCOPE). The instrument belongs to the Interface Analysis Centre at the University of Bristol. The technique is made quantitative by the application of sensitivity factors to the measured peak areas; the sensitivity for most elements is of 0.1% (1% for uranium).

3 MAIN RESULTS OF THE STUDIES

3.1 The outputs of the Hyrkkölä natural analogue

Publication I *"The Hyrkkölä native copper mineralization: A natural analogue for copper canisters"* shows the potential of the Hyrkkölä mineralization (Figure 2) as a natural analogue for the long-term performance of copper canisters. It was possible to establish the analogy due to the similarity between the composition of native copper at Hyrkkölä and the metallic copper to be used as a canister material (Marcos 1996). Also, as pointed out in Section 1.2, no previous studies had been conducted on the stability of native copper in crystalline bedrock. The long-term stability of metallic copper was assessed by the age of the mineralization (1800 – 1900 Ma). The most threatening process of metal corrosion was considered to be sulfidation (SKI Project-90, Werme et al. 1992), a process in which metallic copper reacts with dissolved hydrogen sulphide (HS$^-$). The possibility of this process being an ongoing one could be addressed by the occurrence of low-temperature copper sulphides altogether with metallic copper. Thermodynamic studies based mainly on mineralogical compositions envisaged the conditions under which sulfidation may occur (Marcos 1996). The minimum quantity of dissolved HS$^-$ was calculated to be of the order of 10^{-4} to 10^{-5} g/l (~ 10^{-5} to 10^{-6} M) within an Eh interval of about –350 to –248 mV at temperatures of 25 ºC and 5 ºC respectively, with a pH of about 7.8.

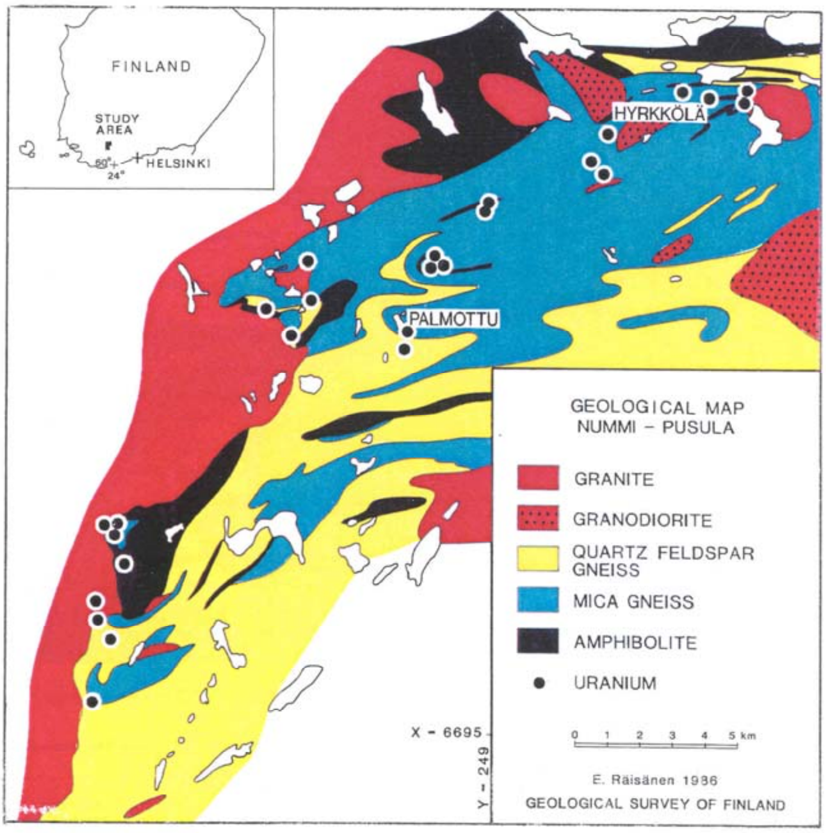


Figure 2. Geological map and the location of the Hyrkkölä study site (In Marcos and Ahonen 1999).

3.1.1 Behaviour of metallic copper and its corrosion products

The interest in making further studies at Hyrkkölä arose from the possibility that the sulfidation process could still be an on-going one. The results of these studies have been published in Marcos and Ahonen (1999) and compiled in **Publication II**.

The study of representative rock and groundwater samples revealed that the envisaged sulfidation process is not an actual one. Actual groundwater conditions are oxidizing, with the content of dissolved oxygen varying between 0.4 and 4 mg/l. The geochemical parameters at which the sulfidation process occurred could not be measured, and the validation of the results of thermodynamic studies for the sulfidation process is still open. However, it must be remembered that the process has occurred, and so cannot be ruled out. Moreover, it has implications for the interaction of copper corrosion products and uranium in present groundwater conditions.

Uranium and uranyl compounds occurred along silicate and sulphide grain boundaries (Fig. 3) and as intergrowths with Cu and Cu-Fe sulphides (Marcos and Ahonen 1999). The surface of the open fracture in Figure 3 exhibits β-uranophane (yellow) and calcite crystals around a copper sulphide (intergrowth djurleite and low chalcocite) grain. The small area marked with a square in Figure 2 was analysed with the XPS technique. The results showed that 25% of the uranium content in the area is U(IV) and 75% is in U (VI). As all the uranium within uranophane is as U(VI), U(IV) may correspond to the uranium content in calcite (Marcos and Ahonen 1999). The possible mechanism that allows the occurrence of U (IV) in calcite at the copper sulphide-groundwater interface will be discussed in Chapter 4.

A copper oxide, cuprite was observed to occur in a sample at a depth of about 97 m. The surface of an open fracture at this depth was coated with smectite. Small platelets of native copper with rims of cuprite occurred within the smectite (Figure 4). The most oxygenated groundwater sample (dissolved O_2 = 4 mg/l) occurred at the same depth interval.

How long the sulfidation process lasted could not be estimated in these studies, but the uranium series disequilibria (USD) studies performed of secondary uranium phases around copper sulphides give a minimum age for the end of the process. The maximum age of these secondary uranium phases was calculated to be about 200 000 years. The end of sulfidation can be much earlier than the precipitation of these U(VI) compounds in oxidizing conditions.

As the partly and totally oxidised copper grains were embedded in smectite, USD studies were conducted on the smectite to estimate how long the oxidation process had been ongoing. An U-234/U-238 activity ratio (AR) of 0.29 to 0.39 was measured in the main U fraction in smectite. To attain and maintain such a low AR, oxidizing conditions and at least a time period comparable to the half-life of the U-234 isotope ($T_{1/2} = 2.44 * 10^5$ a) are required.

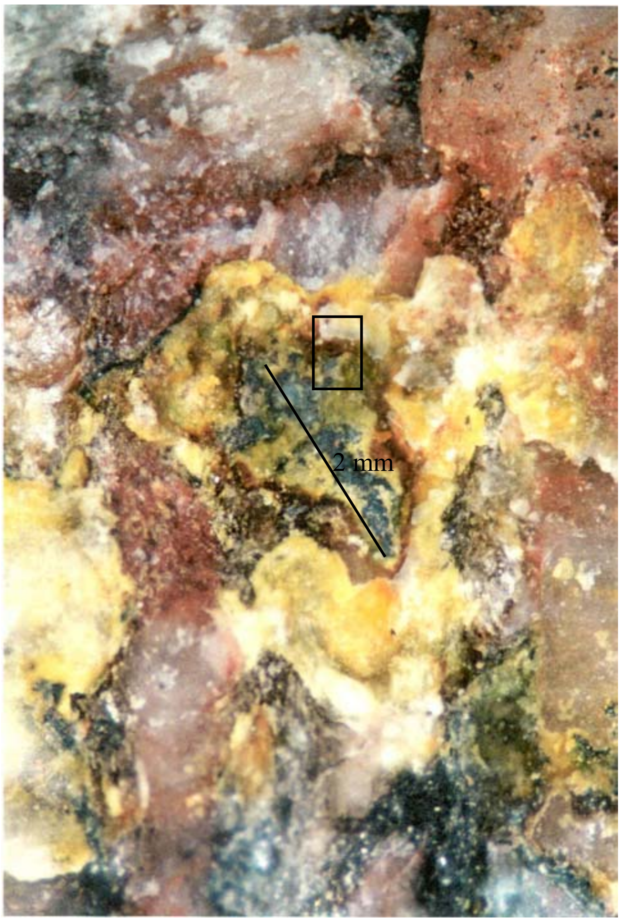


Figure 3. β-uranophane (yellow) and calcite (white) coats the fracture surface in a granite-pegmatite sample at 53.3 m depth. The length of the copper sulphide grain in the centre of the image is 2 mm.

Figure 4. Native copper grains embedded in smectite in a fracture surface at 98.8 m depth. Cuprite partially rims the biggest grain (see arrow). Width of view = 24 mm.

3.1.2 Radionuclide retention processes in smectite (~ bentonite)

The interest in doing further studies on the smectite sample above arose from the USD studies conducted on it to estimate how long the oxidation process had been active. **Publication III** gives explanations for the very low U-234/U-238 AR measured in the main U fraction in the smectite. This is the main mineral component of bentonite, the material proposed as a backfill barrier in the isolation of radioactive waste from the geosphere (e.g., Grauer 1994). The most important premises for the design and accomplishment of analytical work were 1) the smectite retains most of the uranium in the less soluble U (IV) form, 2) the low AR indicates preferential removal of U-234 from the sample, and 3) the preferential removal of U-234 is explained by changes in the valence state of U-234 due to recoil chemistry as suggested by Petit el al. (1985).

It could be confirmed through analytical methods that, indeed, well over 50% (62 to 88%) of the uranium in the sample occurs in the less soluble U (IV) form. By mathematical modelling, the age of the system (interaction between sample and oxidizing groundwater) was estimated to be about 300 000 a. Publication III remarks on the possible role of structural Fe (II) in the long term natural fixation of uranium within smectite. The radionuclide behaviour in the backfill will thus also depend on the chemical performance of the material.

3.2 The phenomena in the geosphere

The ultimate and natural barrier that will isolate the spent nuclear fuel from the biosphere is the host bedrock of the repository or geosphere. The most important phenomena in the geosphere are the transport and retardation of radionuclides (RN).

3.2.1 Transport and retardation in crystalline bedrock

Crystalline bedrock is a physico-chemical entity composed of rocks consisting of crystals or fragments of crystals (minerals) and the voids in and between them. Igneous and metamorphic rocks form the crystalline bedrock. The voids in and between the minerals may join each other and form a network of fissures and fracture zones. It is through and along such fissures and fracture zones that the transport and retardation of radionuclides will occur. The minerals that coat the fracture surfaces in the vicinity of groundwater flow routes/paths will play a special role in the release and retention of RN.

Miller et al. (2000) recently reviewed the phenomena of transport and retardation within fractured crystalline bedrock. The principal mechanism for radionuclide transport is advection along hydraulically active channels within the fracture network. The principal mechanism for transport of the migration of RN within the less fractured rock or intact rock is matrix diffusion, a process by which solutes in groundwater flowing in fractures, penetrate the surrounding rock mass by diffusive processes (e.g., Barenblatt et al. 1960, Neretnieks 1980, Grisak and Pickens 1980, Rasmuson and Neretnieks 1981, Hadermann and Roesel 1985). **Publication IV** deals with the issues of migration, matrix diffusion and precipitation of natural radionuclides in a boulder sample of granitic composition. The shortness of the period during which the retention mechanisms acted, and their situation in a recent deglaciation scenario, is of great and novel interest, as pointed out in Section 1.2.

The boulder, containing relatively high amounts of uranium (up to 300 ppm), was found on the top of a morainic hill in the Kolkanmäki area close to the town of Hämeenlinna in southern Finland. The study area is covered with glacial till and more sorted sediments (Figure 4). The mineralogy of the boulder was used in an effort to locate the parent rock; taking into account the known direction of ice flow at the site, 312–316° (NW-SE), the only reasonable granite outcrop with the same mineralogical composition (microcline granite) was found in Hirsimäki (Figure 5). The studied boulder exhibits an altered weathered zone on the upper part in contact with the air, whereas the lower part appears to be less altered. The lower part is the side of the boulder lying on the ground when found. A secondary U(VI) accumulation, mostly uranophane, was observed at the interface between the most and the least altered rock. Uranophane filled tiny fissures within the rock (Figure 6). USD studies indicate unambiguously that most of the U accumulation is recent, i.e., within the last 10 000 years (Rasilainen et al. 1996, Rasilainen and Suksi 1997).

The radionuclide migration in the rock boulder from any of the surfaces towards the fissures and voids within the rock is due to matrix diffusion processes. Matrix diffusion is considered the mechanism that triggers the precipitation of uranophane in voids and tiny fissures within the rock.

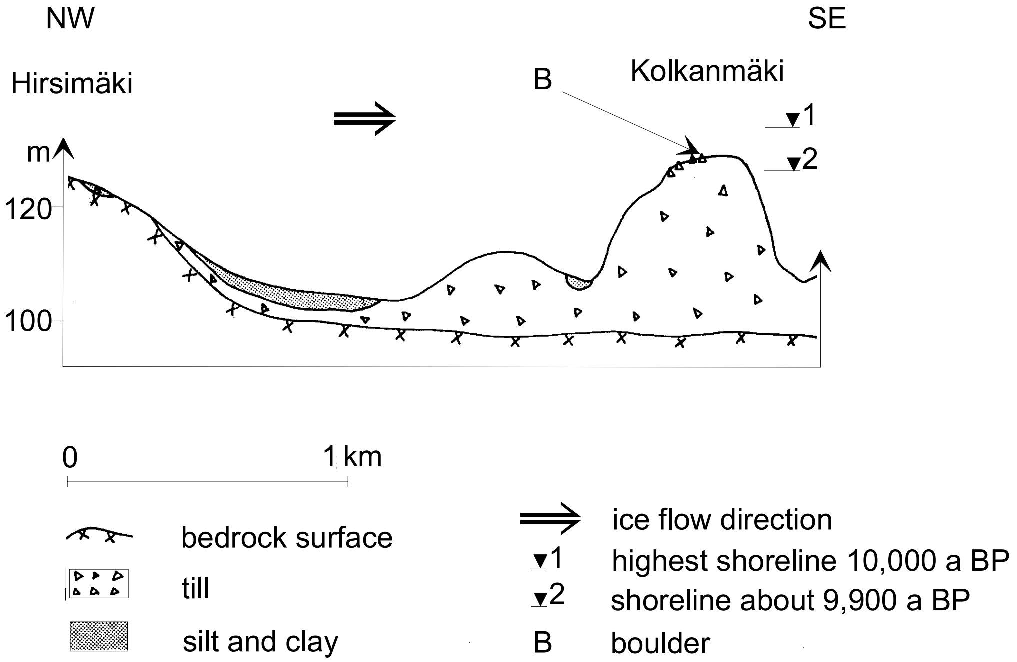


Figure 5. Cross-section of the geological surroundings of the boulder sample. The boulder (B) is assumed to have been transported by the ice to its current location. Rasilainen et al. 1996.

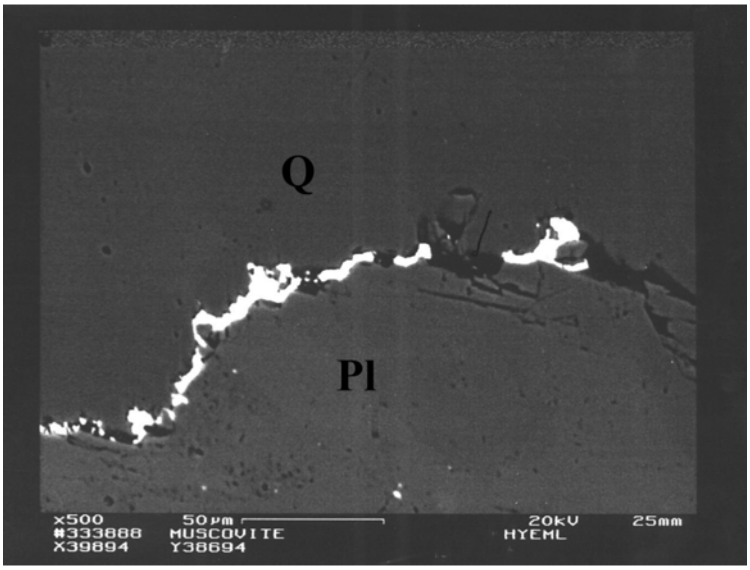


Figure 6. Uranophane (white) filling a tiny intergranular fissure between quartz (Q) and plagioclase (Pl) at about 20 mm from the upper surface of the boulder.

The process is benefited by the physical properties of the rock involving porosity, which is partly due to old hydrothermal events ($\delta^{18}O$-values for quartz vary from 10.9 to 12‰, and $\delta^{2}H$-values vary from -37 to -63‰) affecting the rock on both sides of a pre-existing fracture zone up to a depth of 8 mm. The history of the geological environment in which the boulder was found gives the boundaries within which to estimate the timescales of the processes. In the Hämeenlinna region, deglaciation started about 10 000 years ago. The highest shoreline of the subsequent Yoldia sea stage at Hämeenlinna was 133 m above current sea level. As the location of the boulder is only 2–3 m lower, it can be approximated that the boulder was below the Yoldia sea level for 50–100 years. Estimates of ice velocities towards the margin vary from a few to tens of m/year. This rate means a travel time of 50–500 years for the boulder over the estimated distance of 1–2 Km. For at least part of this time, the boulder was in saturated conditions near the basal layers of the ice (Rasilainen et al. 1996).

The granitic boulder sample, studied specifically as a matrix diffusion and sorption analogue, has shown that matrix diffusion alone is not enough to reconstruct the past U accumulation in the rock. The classical matrix diffusion model using the K_d approach, although conservative in overestimating the mobility of radionuclides in nature, is not realistic in estimating the retention capacity of the bedrock.

Publication V deals with the behaviour of REE, U and Th in the still relatively undisturbed system at Olkiluoto (SW Finland), the place selected as the final disposal site for the spent nuclear fuel repository in Finland. Olkiluoto is not a natural analogue study site in any strict sense and site characterization data do not replace analogue information (e.g., Miller et al. 2000), but, as the emphasis of the study is on the processes that may affect the behaviour of the mentioned elements, the relevant point is not about the site itself, but about the fact that the site is in crystalline bedrock.

Regarding the transport and retardation of RN, the results of this work confirm the important role of fracture surface coating minerals and of the quality of the rock in the vicinity of water-conducting fractures in the uptake/release of the elements in consideration.

Landström and Tullborg (1990) attempted a similar work, but the analysis of the bulk of rocks and fracture coating minerals gives no hints on the low-temperature mobility. The importance of these studies relied on the record of a suite of fracture minerals, but not on their specific role in low-temperature water-rock interaction. The main problems in trying to separate the effects of recent low-temperature processes with earlier high-temperature events remain. Later, at the Äspö Hard Rock Laboratory in Sweden the same authors (Landström and Tullborg 1995) investigated the sorption capacity of the fracture coating phases using sequential extraction methods, but still attempts to clarify whether the processes of uptake or release of elements were of low-temperature proved to be difficult.

Although the leaching method (mild nitric acid, 0.5 M HNO_3) employed in the studies in Publication V cannot assure that the mobility of the elements could be of the same extent as in low-temperature processes, it highlights the identities of the elements that are the more susceptible to being released in changing the physico-chemical conditions in the groundwater system. It is likely that this method simulates the effect that would cause the fast inflow of reactive waters in the bedrock.

For the sake of clarity, only a few leachate samples were shown in Figure 4 of Publication V. Figures 7 and 8 give a better insight into the rock-normalized leachate patterns of granite-pegmatite and migmatite samples, respectively. The leachate patterns of the granite pegmatite sample OL3/6K (Fig. 7) show moderate enrichment of the intermediate REE (IREE) except for the pattern of the outermost slice of this sample, which also displays a negative Eu anomaly probably due to kaolinite, as when two samples of this mineral were analysed separately depletion in Eu was shown. Kaolinite partially coated this slice. The Er negative anomaly of slice OL3/6KS2 is most probably an artifact. The leachates of two of the migmatite samples (Fig. 8 a, c) also exhibit rock-normalized patterns moderately enriched in the IREE. The other two samples (Fig. 8 b, d) represent the palaeosome, or dark-coloured part, of the migmatite, rich in biotite. Although selective analyses of biotite in these samples are lacking, it is probably that this mineral might be enriched with light REE (LREE). The fracture surface of sample OL3/5 was partially coated with calcite, the mineral responsible for the IREE and heavy REE (HREE) pattern of the leachate of the first slice (Fig. 8 b). McLennan and Taylor (1979) demonstrated a strong correlation between HREE and U during transport and ore deposition in a low temperature hydrothermal system where uranium deposition was accompanied by the precipitation of calcite.

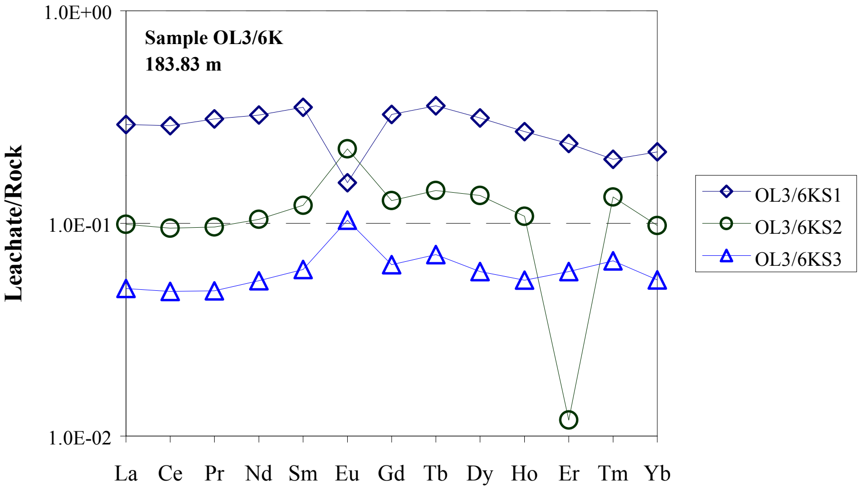


Figure 7. REE concentrations of leaching solutions normalized to the REE concentrations in the corresponding granite-pegmatite. S1…S3 are slices of drill core cut parallel to the open fracture surface. Length of drill core is about 6 cm.

Although the results of this work (Publication V) pointed to the possible past intrusion of acidic waters in the system, this cannot be so; the possibility of the origin of groundwater at Olkiluoto being the result of various mixing processes as remarked by Pitkänen et al. (1999) should not be ruled out. The intrusion of acidic waters (also possibly oxygenated) in the deep bedrock in the recent past (< 300 000 years) should also leave imprints in the fractured rock adjacent to water conducting fractures. The imprint of a fast intrusion of reactive waters may result in huge uranium series disequilibria between U-234 and U-238 with activity ratios (AR) usually below 0.5

(e.g., Suksi et al. 2001), but, to the knowledge of the author, no data of AR of rock samples from Olkiluoto exist to date.

3.2.2 The behaviour of REE as chemical analogues for actinides

The need to search chemical analogues for the waste elements arose from the fact that most of the waste elements (e.g., actinides) do not occur naturally in measurable quantities (Section 1.2). The analogy is based on the premise that a different naturally occurring element may behave in a chemically similar manner to the waste element. As for the chemical analogy between the transuranic elements or actinides and the lanthanides, the best chemical analogues for the americium (Am) and curium (Cm) are considered to be the REE with oxidation state III (see Krauskopf 1986 and Miller et al. 2000 for further discussions) because Am and Cm are not redox-sensitive elements in natural waters present also only in the III oxidation state.

With respect to the analogical behaviour between REE and the above mentioned actinides, the studies in Publication V show that the REE III (La, Nd, Sm, Gd, Dy, Er and Dy) concentrations in the current groundwaters at Olkiluoto are low and that the fracture coating minerals, especially calcite, limit the mobility of these elements from the fractured bedrock.

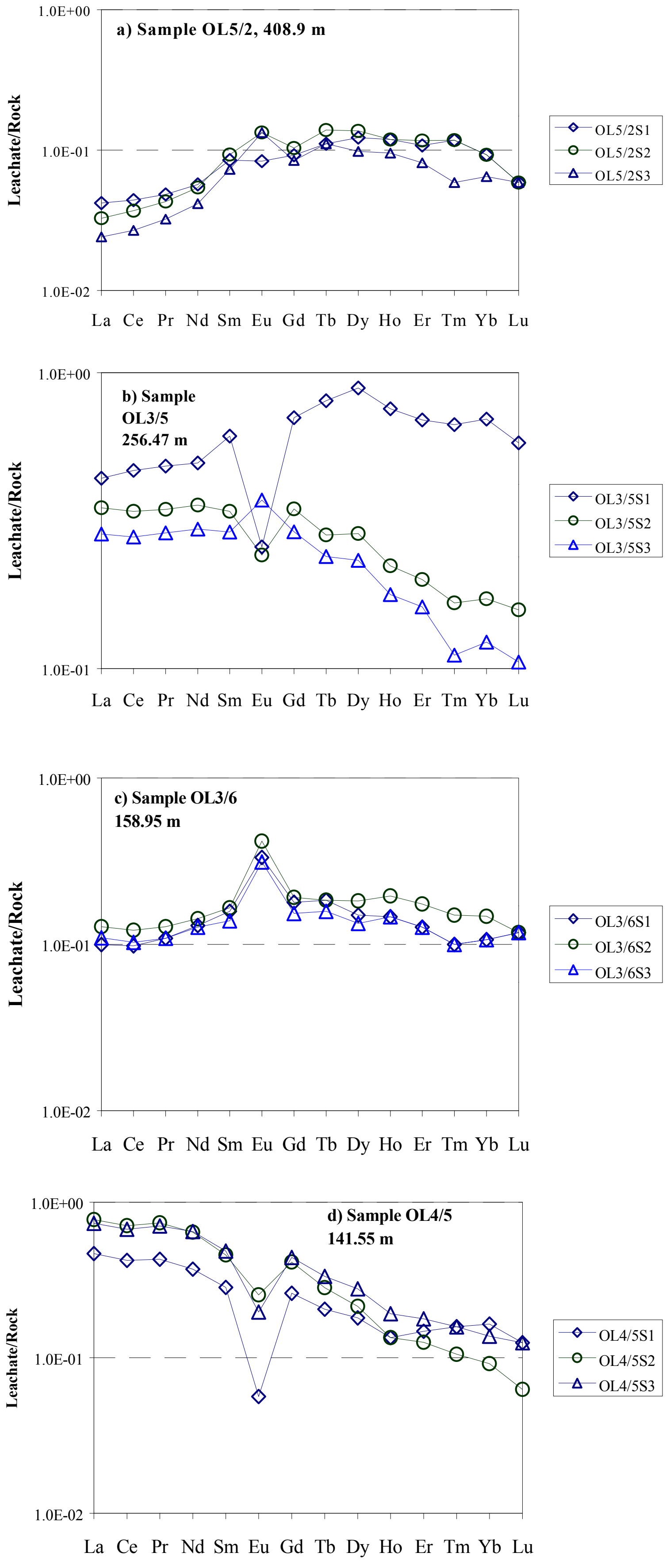


Figure 8. REE concentrations of leachate solutions of migmatite samples normalized to the REE concentration of the corresponding rocks.

4 SUMMARY AND PERFORMANCE ASSESSMENT IMPLICATIONS

4.1 Summary

The results obtained during the studies at the Hyrkkölä site addressed the long-term behaviour and interactions of the materials involved in the near field of a nuclear waste repository, i.e., metallic copper, smectite and uranium.

The long-term durability of metallic copper in fractured crystalline bedrock where the main threat is sulphide-induced corrosion is assessed by the Hyrkkölä analogue as being the fact of metallic copper having been, and still being, in contact with groundwater since it precipitated within the granite pegmatite about 1700 Ma ago. The long-term durability is indicated even though the sulfidation process is not a current one, because it has already occurred and because there is still copper in its native state in the system. Moreover the stability of native copper is assessed even in oxidizing conditions, as these have prevailed at least for 300 000 years, and yet there is still native copper in the system.

It has to be remarked that the aim of the studies at Hyrkkölä was to address the long-term behaviour of metallic copper as an analogue to copper canisters, and, given this aim, the studies were successful. The fact that current conditions are oxidizing and not reducing as expected after the mineral paragenesis (metallic copper coexisting with copper sulphides djurleite and chalcocite) made impossible the measurement of the parameters (e.g., Eh, pH, sulphide content) that allow sulfidation to occur. But what matters is that sulfidation has occurred and the minimum contents of sulphide in groundwater could be estimated (Marcos 1996).

Although current conditions in the groundwater in the vicinity of fracture surfaces exhibiting native copper are not as expected in the repository, i.e., reducing and alkaline, the issue of the interaction of corrosion products and uranium could be addressed at Hyrkkölä. In the current highly oxidizing conditions, it was found that copper sulphide (djurleite), the secondary alteration product from the past sulfidation process has the ability to immobilize migrating uranium most probably by electron exchange between Cu^+ in the external layers of copper sulfide and U (VI) sorbed as uranyl (UO_2^{2+}) on the mineral surface. Cu (I) oxidizes to Cu (II), whereas U (VI) is reduced to U (IV) through the following reaction:

$$2Cu^+ + UO_2^{2+} = + 2[Cu^{2+}, O^{2-}] + U^{4+}. \qquad (1)$$

Although U (VI) is likely to be present as the carbonate complex $UO_2(CO_3)_2^{2-}$ in the groundwater conditions at Hyrkkölä (Hsi and Langmuir 1985, Ahonen et al., 1994), the dissociation of this complex through a decrease in the activity of CO_3^{2-} due to precipitation of calcite (Reaction 2) along the path of groundwater flow may occur before the reaction above:

$$2Ca^{2+} + UO_2(CO_3)_2^{2-} = 2CaCO_3 + UO_2^{2+}. \qquad (2)$$

It is possible that U^{4+} in (1) is incorporated in the structure of calcite as suggested by the studies of Sturchio et al. (1998). These authors point out that the uptake of U^{4+} in the calcite structure explains the anomalous high concentrations of U observed in calcite from reducing environments (Israelson et al. 1996). The current conditions at Hyrkkölä are oxidizing, but the finding of U (IV) close to copper sulfide may be explained by the occurrence of a reducing microenvironment around copper sulphide grains. This finding provides insight into the interactions of copper sulphide and uranium in a repository evolving from reducing to oxidizing conditions.

The long-term durability of smectite as an analogue for bentonite is not addressed in a straightforward way by these studies. However it can be inferred that smectite has been at the site more than 300 000 years and since then it has been acting as a sink for uranium. The studies of the smectite sample directly demonstrate the important role of structural Fe (II) in the long-term retention or fixation of radionuclides. Indirectly it is shown that small grains ($\varnothing \approx 1$ mm) of copper within smectite persist in its metallic state even in oxidizing conditions. That is, structural Fe (II) in smectite may also retard the oxidation of metallic copper by uptaking the oxygen dissolved in groundwater in contact with smectite.

The results obtained during the studies at the granitic boulder at Hämeenlinna showed that although sorption is an important retardation process, precipitation is able to retain greater quantities of radionuclides.

The studies of the rock samples at Olkiluoto also show up the important role of the bedrock as a natural barrier and show up that the understanding of the past evolution and behaviour of the system is a key issue in predicting with confidence the future evolution of the repository. Although the long-term evolution cannot be reproduced in short term laboratory experiments, a lot of work with the application of methodologies used in natural analogues studies can still be conducted at repository sites already selected or in the process of selection.

4.2 Performance assessment implications

Miller et al. (1994, 2000) and Murphy (2000) have widely discussed and summarized the application of natural analogues in performance assessments for several nuclear waste disposal programs in Europe and in the United States, respectively. Other applications include non-technical demonstrations of safety and the extension of natural analogue studies to toxic waste disposal (e.g., Chapman 1994, Côme et al. 1997, Bowell et al. 1997).

From the studies presented here, only the Hyrkkölä native copper occurrence has been used in performance assessment for data provision with respect to canister lifetime (IAEA 1999) in TILA-99 (Vieno and Nordman 1999). Vieno and Nordman (1999) also remark that the role of the copper sulphides is relevant in the retardation of radionuclides (e.g., U). The importance of this process should not be underestimated because of the fact that larger volumes of iron will occur in most repository sites, and that iron is more reactive than copper.

The role of iron oxyhydroxides as scavengers of natural radionuclides has been highlighted in many previous studies elsewhere (e.g., Smellie et al. 1986, Guthrie 1989, Landström and Tullborg 1990), but the role of iron Fe (II) within smectite as a reducing agent for uranium in groundwater was pointed out in the present studies for the first time.

Many natural analogue studies have demonstrated the influence of the physical and mineralogical characteristics of the fracture surfaces on the retardation of natural radionuclides and of chemical analogues. The studies in Publication V attempted also to link the activity of the fracture (with respect to groundwater flow) to the behaviour of the elements in the fracture surface and its immediate bulk rock with respect to elemental retardation or release. So far, qualitative results were obtained revealing that clean fracture surfaces do not retain elements from groundwater as effectively as fracture surfaces with mineral coatings.

These studies, although they show the benefits of the role of iron and fracture surfaces with respect to the attainment of reducing conditions and the effects of sorption and precipitation processes, do not provide the kind of data that up to now has been used in performance assessment. But this fact should not diminish the utility of these observations from nature; on the contrary, improvements in performance assessment methodologies including realistic natural processes such as the studies of the boulder question, confronting conservatism in safety assessment and the realism of natural processes, should be developed and implemented. Models of sorption preceding precipitation could be integrated into safety assessment without great effort, at least for the sake of credibility and acceptance, by broader audiences, of the geological disposal of nuclear waste.

The site selection process could take into account natural analogues studies. The processes in the natural environment that are already understood could help to select the most appropriate site where the processes that are envisaged to occur are most similar to the natural ones already observed.

4.3 The Finnish case

Murphy (2000) claims: “the utility of analog studies as a deductive tool in performance assessment is enhanced by specificity of the analog system to the repository system.” At the time most of the works presented here were initiated and carried out, the site selection process in Finland was still going on, so the specific site conditions which could help to chose the type of analogue were not strictly defined.

The long-term performance of copper canisters is a central issue in safety assessment of the Finnish repository concept (cf. Section 1.2 and Vieno & Nordman 1999). The long-term durability of metallic copper as a canister material was assessed by the Hyrkkölä native copper occurrence. As long as the site for repository construction had not been selected, the main threat for the integrity of the copper canister had been mostly sulphide (e.g., Vira 1996). The studies at Hyrkkölä also showed up that, although sulfidation is a process that has occurred and that may affect the integrity of the canister, the process is beneficial with respect to the retention of radionuclides. Now, when the site has been selected, it has been found that the main threat to the integrity of copper canisters may be the groundwater salinity at Olkiluoto (Vieno 2000). Although recent thermodynamic considerations on the influence of the salinity on metallic copper at repository depth (King et al. 2002) show that canister lifetime will exceed 100 000 years, there have not been, up to now, examples from nature where copper is found in its native state in an environment which is saline and reducing at the same time. Posiva (2001) has remarked that the Hyrkkölä natural analogue cannot be applied to assess the integrity of copper canisters at the Olkiluoto site and at repository depths. However, the long-term durability of metallic copper as a material for the canister to be placed in Finnish bedrock remains as one of the main outputs of the studies at the Hyrkkölä site. With respect to the durability of metallic copper in conditions similar or analogous at repository depths, it is not ruled out that such conditions could be also encountered at deeper levels in Hyrkkölä.

King et al. (2002) pointed out that, although existing thermodynamic data support the stability of metallic copper, the possibility that copper will corrode cannot be totally excluded. A possible corrosion product may be solid cuprous chloride (nantokite, CuCl). To date, no examples from nature have been found that could show the benefit of this compound with respect to the retention of radionuclides, either in repository relevant conditions or in an oxidizing environment.

In the Finnish (and other) repository safety assessments, the development of reference scenarios is a common practice in analysing particular cases in the evolution of the repository. One of the reference scenarios is that of the failure of the canister and the release and transport of radionuclides to the near- and far-field. It is within this scenario that the results of the studies of the smectite, the boulder and rock and groundwater samples at Olkiluoto could have a major role in the understanding of the processes involved.

As mentioned before (Section 1.2), the uptake of released radionuclides by bentonite is not accounted for in the modelling of transport in safety assessment. However, this process has been identified as occurring in the studies of smectite. The nearly irreversible sorption of uranium by smectite is an important process in the retention of radionuclides in the near field, as smectites are the main component of the bentonite in the buffer and may be also a component in the backfill.

In a scenario where, besides the canister failure, bentonite performs poorly as a release barrier, the radionuclides will reach the geosphere. The studies of the boulder show up the processes of radionuclide retention by matrix diffusion and precipitation in a relatively short time and after the last glaciation. These studies illustrate the interactions of radionuclides and bedrock in near-surface oxidizing conditions.

The concentration of REEs was obtained from groundwater samples at Olkiluoto in relevant repository conditions. The behaviour of the bedrock with respect to the release/retention of REEs was also addressed. Further studies should be attempted to clarify the conditions in which these mechanisms/processes take place. It was also found that the REE patterns in the examined groundwater samples could be due to recent (< 1Ma) intrusion of acidic and, possibly, oxygenated waters. This is an important finding to be further studied. Information could be obtained into the processes to consider in a glacial scenario where glaciation and deglaciation periods alternate.

As a whole, and in general terms, the results of these studies have contributed to the process of increasing confidence in the safety of spent fuel disposal in crystalline rocks. As the radioactive wastes have a strong emotive connotation (Chapman 1994), the selection of the disposal site is not only made on a scientific basis; socio-political pressures are of great influence in the final approval of the site. In the process of selecting of Olkiluoto this can be seen to be true, taking into account the fact that the lessons learnt from at least the Hyrkkölä analogue are not being used to illustrate the long-term performance of copper canisters at the Olkiluoto site (Posiva 2001).

4.4 Use of these studies in public perception

Photographic material and data on the long-term durability of metallic copper provided by the studies at Hyrkkölä has been used in brochures and exhibitions in Sweden (SKB Ab) and in Finland (Posiva Oy). It is a relatively easy way to show to the general public that metallic copper is also found in crystalline bedrock in evolving groundwater conditions, in which it is long-lasting. However, the environment in which metallic copper has been found and the processes that it has undergone should not be forgotten. The processes affecting the behaviour of copper at the analogue site, and those affecting the copper canister at the repository site, will be natural. The analogy will be given through the similarity of the environments (current or past) in which the processes take place.

5 CONCLUSIONS

The long-term behaviour of the materials, elements and processes involved in the near- and far-field of an underground nuclear waste repository can be demonstrated by both laboratory and natural analogue studies. The major advantage of natural analogues is the provision of experiments operating over time-scales of thousand to millions of years, time-scales that laboratory experiments cannot cover. In this work, the studies of the natural materials and processes at Hyrkkölä, Hämeenlinna and Olkiluoto have offered insights into 1) the long-term performance of native copper as an analogue for copper canisters, 2) interactions between copper corrosion products and uranium, 3) interactions between uranium and smectite and 4) the important role of the bedrock with respect to the transport and retardation of radionuclides.

The past sulfidation process that native copper has, indeed, undergone at Hyrkkölä, influences current conditions. The result of the past process (copper sulphide) is able to retain up to 25 % of uranium as U (IV). That is, a past process has implications for the current behaviour of the elements in the system. Although the retention process occurs on a microscopic scale, it is not less important in assessing the long-term behaviour of the disposal system, in particular if conditions are to evolve from reducing to oxidizing.

The studies of the smectite sample demonstrate the important role of structural Fe(II) in the long-term retention or fixation of radionuclides. It was also observed that small grains ($\varnothing \approx 1$ mm) of copper within smectite persist in its metallic state even in oxidizing conditions. That is, structural Fe(II) in smectite may also retard the oxidation of metallic copper by uptaking the oxygen dissolved in groundwater in contact with smectite.

It was observed that the processes of sorption, precipitation and incorporation of radionuclides in fracture coating minerals (e.g., calcite) have a major role in the long-term retention of radionuclides. These processes occurring in the geosphere or natural barriers should not be neglected in more realistic performance assessment methodologies in the future.

The lessons we learn from nature could be taken into consideration in the selection process of the site for an underground nuclear waste repository. The past and present natural phenomena in the geosphere should be understood to predict the future evolution of the repository with realism and confidence.

The Hyrkkölä natural analogue promotes confidence in the long-term performance of copper canisters in crystalline bedrock. However, the geochemical conditions prevailing at Olkiluoto (i.e., salinity) differ from that of Hyrkkölä. It follows that further studies are needed to assess the integrity of the technical barriers at Olkiluoto. Saline and reducing conditions could be encountered deeper (> 100 m) at Hyrkkölä.

5.1 Final remarks

Olkiluoto has been selected for the construction of the final repository. It is improbable that another site will ever be subjected to characterization by such an intense level of research due to economic and socio-political constraints. The integrity of the technical barriers is threatened due to the salinity at the site. It may be difficult to find native copper in repository-relevant conditions (saline and reducing). For the sake of acceptability of the actually selected disposal system at Olkiluoto, more research in understanding the phenomena in the geosphere is required. This would promote more confidence in the performance of the disposal concept and in the selected site.

6 REFERENCES

Abbey, S., 1979. Reference material–Rock samples SY-2, SY-3, MRG-1. Canmet Report 79-35 (Energy, Mines and Resources Canada, 1979), p. 66.

Ahonen, L., Ervanne, H., Jaakkola, T. and Blomqvist, R., 1994. Redox Chemistry in Uranium-rich Groundwater of Palmottu Uranium Deposit, Finland. Radiochim. Acta **66/67**, 125–128.

Backman, C., 1990. Sampling and data evaluation of 13 rock samples for internal quality control (internal report). Geological Survey of Finland.

Barenblatt, G.I., Zheltov, I.P. and Kochina I. N., 1960. Basic concepts in the theory of seepage of homogeneous liquids in fissured rock. Journal of Applied Mathematical Mechanics, **24**, 1286.

Biddau, R., Cidu, R. and Frau, F., 2002. Rare earth elements in waters from the albitite bearing granodiorites of Central Sardinia, Italy. Chemical Geology, **182**, 1–14.

Blanc, P.-L., 1996. Oklo – natural analogue for a radioactive waste repository (Phase 1). Volume 1: acquirements of the project. EC Nuclear Science and Technology Report, EUR 16857, EC, Luxemburg.

Blomqvist, R., Ruskeeniemi, T., Kaija, J., Ahonen, L., Paananen, M., Smellie, J.T.A., Grundfelt, B., Pedersen, K., Bruno, J., Pérez del Villar, L., Cera, E., Rasilainen, K., Pitkänen, P., Suksi, J., Casanova, J., Read, D. and Frape, S., 2000. The Palmottu Natural Analogue Project–Phase II: Transport of radionuclides in a natural flow system at Palmottu. European Commission, Report EUR 19611 EN, 192 p.

Bowell, R.J., Chapman, J., Connelly, R.J., Cowan, J., Dodds, J.E., Hockley, D., Sadler, P.J.K. and Wood, A., 1997. Natural analogues for toxic waste disposal: a mining perspective. In: von Maravic, H. and Smellie, J., (eds.) Natural analogue working group, 7th meeting, Stein am Rhein, October 1996. CEC Nuclear Science and Technology Report, EUR 15176, 225–247, CEC, Luxembourg.

Brandenberg, F., Grundfelt, B., Höglund, L-O., Karlsson, F., Skagius, K. and Smellie, J., 1993. Studies of natural analogues and geologic systems – their importance to performance assessment. Nuclear Waste Commission of Finnish Power Companies. Technical Report YJT-93-07, Helsinki, Finland.

Bros, R., Kamei, G., and Ohnuki, T., 2002. Radioelement transport in the Bangombé nuclear reactor zone (Gabon) – Evidence from U and Sm isotopes. Mat. Res. Soc. Symp. Proc. **713**, 817–824.

Chapman, N.A., McKinley, I.G. and Smellie, J.A.T., 1984. The potential of natural analogues in assessing systems for deep disposal of high-level radioactive waste. SKB Technical Report TR 84-16, Stockholm

Chapman, N.A., 1994. The geologist's dilemma: predicting the future behaviour of buried radioactive wastes. Terra Nova, **6**, 5–19.

Choppin, G.R., 1983. Comparison of solution chemistry of the actinides and the lanthanides. J. Less-Common Metals, **93**, 232–330.

Côme, B., Piantone, P. and Revin, P., 1997. Natural analogues in toxic waste disposal: an example in the French context. In: von Maravic, H. and Smellie, J., (eds.) Natural analogue working group, 7th meeting, Stein am Rhein, October 1996. CEC Nuclear Science and Technology Report, EUR 15176, 257–266, CEC, Luxembourg.

Cramer, J.J. and Smellie, J.A.T., 1994. Final report of the AECL/SKB Cigar Lake Analog Study. AECL Technical Report, AECL-10851, Whiteshell, Canada and SKB Technical Report, TR 94-04, Stockholm, Sweden.

Crissman, D.P., 1982. Groundwater geochemistry in the Portage Lake Volcanics, Hancock, Michigan, and implication of native copper stability. Unpub. MSc. Thesis, Houghton, Michigan Technology Univ. 112 p.

Crissman, D. and Jacobs, G., 1982. Native copper deposits of the Portage Lake Volcanics, Michigan: their implications with respect to canister stability for nuclear waste isolation in Columbia River basalts beneath the Hanford site, Washington. Rockwell Hanford Operations, Technical Report, RHO–BW–ST–26P.

Curtis, D.B., Benjamin, T.M., Gancarz, A.J., Loss, R., Rosman, J.K.R., DeLaeter, J.E., and Maeck, W. J., 1989. Fission product retention in the Oklo natural fission reactors. Journal of Applied Geochemistry, **4**, 49–62.

Eberly, P.O., Ewing, R.C., Janeczek, J., and Furlano, A., 1996. Clays at the natural nuclear reactor at Bangombé, Gabon: Migration of actinides. Radiochim. Acta **74**, 271–275.

Eisenbud, M., Krauskopf, K., Penna Franca, E., Lei, W., Ballard, R., Linsalata, P. and Fujimori, K., 1984. Natural analogues for the transuranic actinide elements: an investigation in Minas Gerais Brazil. In Smellie J.A.T. (ed.) Natural analogues to the conditions around a final repository for high level radioactive waste. SKB Technical Report, TR 84-18, SKB, Stockholm, Sweden.

Ewing, R.C., and Jercinovic, 1987. Natural analogues: their application to the prediction of the long-term behaviour of nuclear waste forms. Mat. Res. Soc. Symp. Proc., **84**, 67–86.

Grauer, R., 1994. Bentonite as a backfill material in a high level waste repository. MRS Bulletin, **19**, 43–52.

Grisak, G.E. and Pickens, J.F., 1980. Solute transport through fractured media, Part I: the effect of matrix diffusion. Water Resources Research, **16**, 719–730.

Guthrie, V.A., 1989. Fission-track analysis of uranium distribution in granitic rocks. Chemical Geology, **77**, 87–103.

Hadermann J. and Roesel, F., 1985. Radionuclide chain transport in homogeneous crystalline rocks: limited matrix diffusion and effective surface sorption. Nagra Technical Report, NTB 85-40, Nagra, Wettingen, Switzerland.

Hallberg, R.O., Östlund, P., and Wadsten T., 1988. Inferences from a corrosion study of a bronze cannon, applied to high level nuclear waste disposal. Applied Geochemistry, **3**, 273–280.

Hsi, C.-K. and Langmuir, D., 1985. Adsorption of uranyl onto ferric oxy-hydroxides: Application of the surface complexation site-binding model. Geochim. et Cosmochim. Acta, **49**, 1931–1949.

IAEA 1982. Radioactive waste storage and disposal. Excerpts from major technical reports by National and International Organisations 1975-1891. Vienna, 1982.

IAEA 1999. Uses of natural analogues to support radionuclide transport models for deep geological repositories for long-lived radioactive wastes. IAEA Technical Report 1109, International Atomic Energy Agency, Vienna, Austria.

Israelson, C., Halliday, A.N. and Buchardt, B., 1996. U-Pb dating of calcite concretions from Cambrian black shales and the Phanerozoic time scale. Earth Planet. Sci. Lett., **141**, 153–159.

Johannesson K.H. and Zhou X., 1999. Origin of middle rare earth element enrichments in acid waters of a Canadian High Artic lake. Geochim. Cosmochim. Acta, **63**, 153–165.

Johannesson K.H., Farnham I.M., Guo C., and Stetzenbach K.J., 1999. Rare earth element fractionation and concentration variations along a groundwater flow path within a shallow, basin-fill aquifer, southern Nevada, USA. Geochim. Cosmochim. Acta, **63**, 2697–2708.

Johnson, A.B. and Francis, B., 1980. Durability of metals from archaeological objects, metal meteorites and native metals. Battelle Pacific Northwest Laboratory, PNL-3198.

King, F., 1995. A natural analogue for the long-term corrosion of copper nuclear waste containers – reanalysis of a study of a bronze cannon. Applied Geochemistry, **10**, 477–487.

King, F., Ahonen, L., Taxén, C., Vuorinen, U. and Werme, L., 2002. Copper corrosion under expected conditions in a deep geologic repository. POSIVA 2002-01. Helsinki, Finland.

Krauskopf, K.B., 1986. Thorium and rare-earth metals as analogues for actinide elements. Chemical Geology, **55**, 323–335.

Landström, O. and Tullborg, E.L., 1990. The influence of fracture mineral/groundwater interaction on the mobility of U, Th, REE and other trace elements. SKB Technical Report TR 90-37, SKB, Stockholm, Sweden.

Landström, O. and Tullborg, E.L., 1995. Interactions of trace elements with fracture filling minerals from the Äspö Hard Rock Laboratory. SKB Technical Report TR 95-13, SKB, Stockholm, Sweden.

Marcos, N., 1989. Native copper as a natural analogue for copper canisters. Nuclear Waste Commission of Finnish Power Companies, Technical Report, YJT-89-18.

Marcos, N., 1996. The Hyrkkölä native copper mineralization as a natural analogue for copper canisters. Helsinki. Posiva Oy. Report Posiva 96-15.

Marcos, N. and Ahonen L., 1999. New data on the Hyrkkölä U-Cu mineralization: The behaviour of native copper in a natural environment. Helsinki. Posiva Oy. Report Posiva 99-23.

McKinley, I.G. and Alexander, W.R., 1996. The uses of natural analogue input in repository performance assessment: An overview. In: H. von Maravic and J.A.T. Smellie (Eds.), Proceedings of the Sixth EC Natural Analogue Working Group (NAWG) Meeting, Santa Fe, New Mexico, USA, Sept. 12-16, 1994. EUR 1671 EN, 273-282 Luxembourg.

McLennan, S.M. and Taylor, S.R., 1979. Rare earth mobility associated with uranium mineralization. Nature, **282**, 247–250.

Miller, W., Alexander, W., Chapman, N., McKinley, I. and Smellie, J., 1994. Natural analogue studies in the geological disposal of radioactive wastes. Studies in Environmental Science 57, Elsevier, pp. 395.

Miller, W., Alexander, W., Chapman, N., McKinley, I. and Smellie, J., 2000. The geological disposal of radioactive wastes: Lessons from nature and archaelogy. Waste Management Series, Vol 2, Pergamon.

Milodowski, A.E., Styles, M.T. and Hards, V.L., 2000. A natural analogue for copper waste canisters: The copper-uranium mineralized concretions in the Permian mudrocks of south Devon, United Kingdom. SKB Tech. Rep. TR-00-11, Stockholm, Swedish Nuclear Fuel and Waste Management Co.

Murphy, W.M., 2000. Natural analogs and performance assessment for geologic disposal of nuclear waste. Scientific Basis for Nuclear Waste Management XXIII, Smith, R.W., and Shoesmith, D.W. (eds.) Materials Research Society Symposium Proceedings, **608**, 533-544.

Neretnieks, I., 1980. Diffusion in the rock matrix: an important factor in radionuclide migration? Journal of Geophysical Research, **85**, 4379–4397.

Niiniluoto, I., 1988. Analogy and Similarity in Scientific Reasoning, in D.H. Helman (ed.), Analogical Reasoning: Perspectives of Artificial Intelligence, Cognitive Science, and Philosophy, Kluwer Academic Publishers, Dordrecht, 1988, 271–298.

Petit, J.-C., 1992. Reasoning by analogy: rational foundation of natural analogue studies. Applied Geochemistry, **1**, 9–12.

Petit, J.-C., Langevin, Y. and Dran, J.-C., 1985. U-234/U-238 disequilibrium in nature: theoretical reassessment of the various proposed models. Bull. Minéral, **108**, 745–753.

Pitkänen P., Luukkonen A., Ruotsalainen P., Leino-Forsman H., and Vuorinen U., 1999. Geochemical modelling of groundwater evolution and residence time at the Olkiluoto site. Posiva Oy, Report POSIVA-98-10.

Push, R., 1983. Stability of deep-sited smectite minerals in crystalline rock: chemical aspects. SKB Technical Report, TR 83-16, SKB. Stockholm, Sweden.

Push, R., and Karnland, O., 1988. Geological evidence of smectite longevity. The Sardinian and Götland cases. SKB Technical Report, TR 88-26, SKB. Stockholm, Sweden.

POSIVA, 2001 (on line). Posiva kommentoi STUK:in lausunto. Tiedotteet, 2001, 29.11.2001. [Refered 12.6.2002]. Available: http://www.posiva.fi/cgi-bin/itemcart.cgi?action=spdf&name=STUK_vastine.pdf&path=raportit.

Rasilainen, K., Suksi, J., Hellmuth, K.-H., Lindberg, A. and Kulmala, S., 1996. Postglacial matrix diffusion in a boulder sample. Mat. Res. Soc. Symp. Proc. **412**, 885–862.

Rasilainen, K. and Suksi, J., 1997. On the accuracy of uranium-series dating: A comparison with a known matrix diffusion case. Mat. Res. Soc. Symp. Proc. **465**, 1177–1184.

Rasilainen, K., 1997. Matrix diffusion model–In situ tests using natural analogues. VTT Publications 331, pp. 81.

Rasmuson A. and Neretnieks I., 1981. Migration of radionuclides in fissured rock: the influence of micropore diffusion and longitudinal dispersion. Journal of Geophysical Research, **86**, 3749–3758.

Rivas, P., Hernán, P., Bruno, J., Carrera, J., Gómez, P., Guimerá, J., Martín, C. and Pérez del Villar, L., 1997. El Berrocal project. Characterization and validation of natural radionuclide migration processes under real conditions on the fissured granitic environment. CEC Nuclear Science and Technology Report, EUR 17478, CEC, Luxembourg.

Siitari-Kauppi, M., 2002. Development of ^{14}C-Polymethylmethacrylate method for the characterization of low porosity media. Report Series in Radiochemistry 17/2002. Academic Dissertation, University of Helsinki, 156 p.

SKI Project-90, 1991. Stockholm, Swedish Nuclear Power Inspectorate, SKI Technical Report 91:23.

Smellie, J.A.T., McKenzie, A.B., & Scott, R.D., 1986. An analogue validation study of natural radionuclide migration in crystalline rocks using uranium-series disequilibrium studies. Chemical Geology **55**, 233–254.

Smellie, J.A.T., Karlsson, F., and Grundfelt, B., 1995. The potential use of natural analogue studies in radioactive waste disposal: A review. Geoval '94: Validation through model testing. Proceedings of a NEA/SKI Symposium, Paris, France, 11-14 October, 1994. NEA/OECD, Paris, 1–26.

Smellie, J.A.T., Karlsson, K. and Alexander, W.R., 1997. Natural analogue studies: Present status and performance assessment implications. J. Cont. Hydrol., **26**, 3–17.

Smellie, J.A.T. and Karlsson, F., 1999. The use of natural analogues to assess radionuclide transport. Eng. Geol., **52**, 193–220.

Smellie, J.A.T., 2002. Solute Immobilisation: Observations from Natural Analogue Studies. Geotrap Project: Radionuclide Retention in Geologic Media. Proceedings of a NEA Workshop, Oskarshamn, Sweden 7-9 May, 2001. NEA/OECD, Paris, 155–162.

Steger, H.F. and Bowman, W.S., 1980. DL-1a: A certified uranium-thorium reference ore. Canmet Report 80-10E, (Energy, Mines and Resources Canada, 1980), p.12.

Sturchio, N.C., Antonio, M.R., Soderholm, L., Sutton, S.R. and Brannon, J.C., 1998. Tetravalent Uranium in Calcite. Science, **281**, 971–973.

Suksi, J., Ruskeeniemi, T. and Rasilainen, K., 1992. Matrix diffusion – Evidences from Natural Analogue Studies at Palmottu in SW Finland. Radiochim. Acta **58/59**, 358–393.

Suksi, J., Juntunen, P., Pitkänen, P., Rasilainen, K., Ruskeeniemi, T. and Casanova, J., 2001. Application of uranium-series disequilibrium data to the interpretation of oxygen intrusion in rocks. Cidu, R. (ed.): Proceedings of the 10th international symposium on water-rock interaction WRI-10. A.A. Balkema Publishers, **2**, 1395–1398,

Suksi, J., 2001. Natural uranium as a tracer in radionuclide geosphere transport studies. Report Series in Radiochemistry 16/2002. Academic Dissertation, University of Helsinki, 54 p.

Vieno, T. and Nordman, H., 1999. Safety Assessment of Spent Fuel Disposal in Hästholmen, Kivetty, Olkiluoto and Romuvaara, TILA-99. POSIVA 99-07. Posiva Oy, Helsinki, Finland.

Vieno, T., 2000. Groundwater salinity at Olkiluoto and its effects on a spent fuel repository. POSIVA 2000-11. Posiva Oy, Helsinki, Finland.

Vira, J., 1996. Natural analogues for canister performance. In: H. von Maravic and J.A.T. Smellie (Eds.), Proceedings of the Sixth EC Natural Analogue Working Group

(NAWG) Meeting, Santa Fe, New Mexico, USA, September, 1994. CEC Nuclear Science and Technology Report, EUR 16761, 163–174, Luxembourg.

Werme, L., Sellin, P. and Kjellbert, N., 1992. Copper canisters for nuclear high level waste disposal. Corrosion aspects. Stockholm, Swedish Nuclear Fuel and Waste Management Co (SKB), Technical Report 92-26.

Werme, L., 1998. Design premises for canister for spent nuclear fuel. SKB Tech. Rep. TR-98-08, Stockholm, Swedish Nuclear Fuel and Waste Management Co.

Wood, S.A., van Middlesworth, P.E., Gibson, P. and Ricketts, A., 1997. The mobility of the REE, U and Th in geological environments in Idaho and their relevance in radioactive waste disposal. J. Alloys Compounds, **249**, 136–141.

Yanase, N., Nightingale, T., Payne, T. and Duerden, P., 1991. Uranium distribution in mineral phases of rock by sequential extraction procedure. Radiochim. Acta, **52/53**, 387–393.

APPENDIX 1

Publications I – V

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