NEW DATA ON THE HYRKKÖLÄ NATIVE COPPER MINERALIZATION: A NATURAL ANALOGUE FOR THE LONG-TERM CORROSION OF COPPER CANISTERS

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ABSTRACT

The Hyrkkölä U-Cu mineralization located in south-western Finland is reassessed with reference to the corrosion mechanisms affecting the stability of native copper and the time-scales of corrosion processes. The mineral assemblage native copper – copper sulfide occurs in open fractures at several depth intervals within granite pegmatites (GP). The surfaces of these open fractures have accumulations of uranophane crystals and other unidentified uranyl compounds. The secondary uranium minerals are mainly distributed around copper sulfide grains. Microscopic intergrowths of copper sulfides and uranyl compounds also have been observed. Groundwater samples were collected from the vicinity of the Cu samples. The hydrogeochemical features of these samples indicate that the present conditions are oxidising. The minimum age of U(VI) transport and deposition is about 200 000 years. This age is indicated by $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ activity ratios of uranophane. The age of the hexavalent uranium precipitation may be somewhat later than the last influxes and/or demobilisation of sulfur.

The mineral assemblage native copper – copper oxide (cuprite) occurs only at one depth interval within altered granite pegmatite. The fracture surface was coated by smectite. The content of uranium in smectite was 69 - 75 ppm U. The $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ activity ratios of smectite showed that it has been exposed to recent groundwaters (e.g., during the last million years). The pH of the groundwater at this interval was near neutral (6.9). The copper grains present at this fracture surface were as large as 1 mm in diameter and had rims of cuprite of 0.01 to 0.1 mm thick. The smallest grains were totally oxidised.

INTRODUCTION

The Hyrkkölä U-Cu mineralization occurs within the Svecofennian schist belt (crystalline bedrock). Its mineralogical and geological characteristics [1] are similar to those of the sites considered for the actual disposal of nuclear waste in Finland and Sweden. In both countries, the planned disposal concept for spent nuclear fuel is based on encapsulation in copper-iron canisters and burial deep into the bedrock. According to theoretical calculations, the life-time of a thick-walled (50 mm) copper canister in oxygen free conditions is measured in millions of years [2]. The age of the Hyrkkölä mineralization is estimated to be between 1.8 and 1.7 Ga, and a special feature of the mineralization is the occurrence of copper as a native metal. Native copper and uraninite are the primary ore minerals within granite pegmatites. The aim of the present work is to study the long-term stability of metallic copper in the natural bedrock conditions.

It has been pointed out [3,4] that the geological association of native copper deposits corresponds mainly to basalts and to the surpergene weathering of copper sulfide deposits and that the hydrogeochemical environment of those native copper occurrences differ from that expected in the planned deep nuclear waste repository. Detailed studies on the behaviour of copper and its corrosion products in crystalline bedrock and in contact with groundwater are lacking to date.

Two new cored research boreholes were drilled to the Hyrkköla site in order to get groundwater samples in direct contact with metallic copper or in contact with drill-core samples containing metallic copper [5]. Both drillholes start from the same point, but are drilled in different directions to a depth of about 100 meters each. In order to evaluate the stability of native copper and its corrosion products in a fractured, water-saturated rock, the main fractures/fracture zones intersecting Cu-bearing GP were thoroughly examined. Rock and water samples related to open fractures and fractured zones at various depths/depth intervals were selected (Table I) for further mineralogical, isotopic, and hydrochemical studies. An intensively fractured zone was encountered in the bottom of both drillholes, and hydraulic observations during drilling indicated connection between the bottom part of the boreholes (distance about 10 - 15 m). Thus, the bottom parts of the both drillholes are considered to be similar with respect to their hydrogeochemical conditions.

The presence of uranium in the system allows us also to apply U-series isotope studies, which aim to determine whether or not native copper and related minerals have been in contact with groundwaters and to elucidate the time-scale of groundwater - rock/mineral interactions.

Table I. Sample and location

Type of sample	Sample borehole/depth (or depth interval)	Sample code used hereafter	Other specifications
Rock/Mineral Sample	Hy325/68.25 Hy324/53.30 Hy324/97.85	GP1 GP2 SM	Fractured zone Open fracture open fracture
Water Sample	Hy325/67 – 68.5 Hy324/52.4 – 53.9 Hy325/90 – 104	S1 S2 S3	

MATERIAL AND METHODS

Native copper and copper sulfides occur in sample GP1. Copper sulfides and copper-iron sulfides occur in GP2. Uranyl compounds occur in both samples. Native copper and copper oxide occur within smectite in sample SM. Fracture surface materials and polished sections of the samples and adjacent rocks were examined using a stereomicroscope and a polarising microscope. The identification of minerals coating fracture surfaces was done by the XRD (X-ray diffraction) method. Quantitative analyses of native copper and related minerals were obtained using an electronprobe microanalyzer (EPMA) CAMECA SX 50 at the Geological Survey of Finland. The minimum size of the particles to be analysed is $\emptyset = 5$ µm. In this study the detection limit of quantitative analyses for copper was ~0.18 weight % (wt. %), for sulfur ~0.05 wt. %, and for uranium ~ 0.19 wt. %. Metallic uranium (U), metallic copper (Cu) and chalcopyrite ($CuFeS_2$) were used as standards for U, Cu, and S respectively. The detection limits for the other elements analysed may be considered 0.2 - 0.5 weight % depending on the element, current and voltage [6]. The uranium and copper contents of smectite was analysed by ICP-AES. Sulfur isotope determinations were performed at the Laboratory of Engineering Geology and Geophysics, Helsinki University of Technology, using the method described by [7].

Three subsamples of GP1 (a, b, and c), six of ß-uranophane crystals (UF1 to UF6) occurring on the open surface of GP2 and three fractions of smectite (SM1 to SM3) were selected as sample material for uranium-series disequilibrium (USD) studies. Radionuclides were separated from the sample material using total dissolution and sequential extraction [8,9] and measured by α-spectrometry. The analyses for uranophane and smectite were performed in two independent laboratories.

Groundwater sampling and associated measurements (e.g., Eh, pH) were carried out using the SKB mobile field laboratory [10]. The bedrock-fractures to be sampled were isolated by hydraulically expanded packers, and groundwater from the isolated drillhole section was pumped until the sample was considered to be representative. The flow rate was about 100 ml/min, and

pumping time about 2 - 3 weeks for each sampling section. Consequently about 2 - 3 m³ of water was extracted from each section.

In addition to the *on line* measurement of Eh and pH (in air-tight, overpressurized measuring chamber on the ground surface), also down-hole 'in situ' measurement of Eh and pH were done. The redox electrodes used were Pt, Au, and C, each both *in situ* and *on line*. The electrode potentials were measured against a silver chloride reference electrode. Before and after each measurement electrodes were calibrated in quinhydrone solutions at two different pH-buffer solutions (pH 4 and 7). Based on the known Eh of the quinhydrone solutions, measured redox potentials were recalculated to the Eh-scale. Other continuous *on line* measurements included electrical conductivity (EC) and dissolved oxygen concentration.

An additional measurement apparatus ('Ecolys') carried out automatic titration of alkalinity, measurement of pH and chloride concentration (ion-selective electrode). Dissolved sulfide, ferrous iron, total iron, and uranine tracer were analysed in the mobile laboratory immediately after sampling (uranine in concentration of 500 µg/l was used as a tracer in the flushing water during drilling). Other dissolved components were analysed in the Analytical Laboratory of the Geological Survey of Finland. Main cations and trace elements were analysed from filtered (0.45 µm), acidified (0.5 µl ultrapure nitric acid, HNO_3, in 100 ml) samples using ICP-MS, anions were analysed from unpretreated samples using ion chromatography. The $^{234}U/^{238}U$ activity ratios of the samples was measured by a-spectrometry.

RESULTS

Mineralogy of the samples

The sample GP1 is a granite pegmatite from a fractured zone. The rock forming minerals are quartz, K-feldspar and albite. Tourmaline is the main accessory. Copper occurs dispersed within K-feldspar and albite in excess of about 0.5 wt. %. Native copper seems to have been exsolved along cleavage planes of K-feldspar and albite. It also fills microfractures and voids. EPMA analysis of native copper grains gave a maximum Cu content of 98.85 wt. %. Sulfur was detected in maximum amounts of 0.10 wt. % at the same points. Copper sulfide occurred in close contact with native copper. The average of the Cu/S ratio for Cu-sulfide minerals is 1.8 − 1.86 (digenite) for points 1 to 6 and 1.93 (djurleite) for points 7 to 9 (Table II). The low analytical totals for points 3 through 9 may be due to continuous rearrangement of Cu atoms under the electron beam as found by [11] when studying the intergrowths between djurleite and digenite and between djurleite and low chalcocite. Lead (Pb) also occurs in copper sulfide in amounts of 0.5 wt. %.

Table II. Values (wt. %) are from random points within copper sulfide grains in GP1.

Points	1	2	3	4	5	6	7	8	9
Cu	77.99	77.39	74.65	73.49	74.40	74.69	74.39	74.40	75.82
U	0.23	-	0.18	0.27	-	-	-	-	-
S	20.77	21.33	20.76	20.55	21.18	20.63	19.61	19.51	19.60
Th	0.34	-	-	-	0.37	-	-	0.47	-

The average content of U of this sample (ICP-AES) is 164 ppm. Uranium occurs as a non identifiable phase in microfractures and around grains of Cu sulfides.

The main accessory of sample GP2 is Mn-fluorapatite. Only Cu-sulfides (low chalcocite, djurleite) and Cu-Fe-sulfides (chalcopyrite) occur in this sample. ß-uranophane crystals and some calcite coated the surface of the fracture. Sulfides and uranyl compounds (Table III) occur along interconnected microfractures in apatite. Uranyl compounds also are distributed along silicate and sulfide grain boundaries. Calcite also occurs along sulfide grain boundaries where sulfides are close to the open surface.

Three sulfides, one of them low chalcocite in contact with native copper and the other two Cu sulfide and Cu-Fe-sulfide from sample GP2 were selected for sulfur isotope analysis. The $\delta^{34}S$

values fall in the narrow range of -5.0 ‰ to -5.7 ‰, thus suggesting a major component of sedimentary sulfur in these Cu and Cu-Fe-sulfides.

Native copper grains as large as 1 mm in diameter occur in sample SM. These native copper grains have rims of cuprite of 0.01 to 0.1 mm thick. Some of the smallest grains are totally oxidised. Figure 1 shows a native copper grain embedded in smectite. This grain was not discernibly oxidised. Smectite is the alteration product of K-feldspar in this GP. Two fractions of smectite were analysed for copper and uranium content. Concentrations of copper varied one order of magnitude from 33.8 to 342 ppm. The first fraction was less coherent than the second one. The uranium content was about 75 ppm in both samples.

Table III. Selected uranyl compound (u.c.) analyses (wt. %) in sample GP2. Ideal uranophane (I.U.) composition is included for comparison. Values marked with * are calculated.

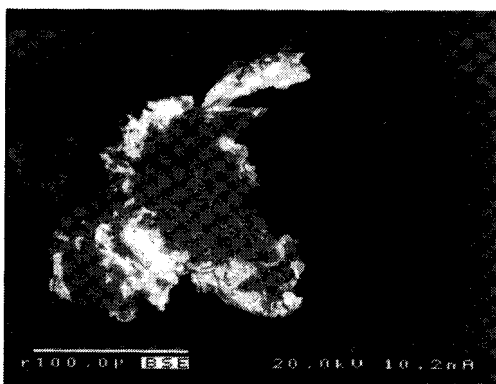|	SiO2	U_2O_3	Cu	CaO	S	PbO	H_2O
I.U.	14.03	61.21	-	6.54	-	-	18.22
u.c.1	14.12	74.77	1.32	5.96	-	0.20	3.63*
u.c.2	14.10	73.30	0.55	6.05	0.05	0.20	5.75*
u.c.3	13.50	72.20	0.75	5.60	-	0.24	7.71*

Figure 1. Native copper grain (light grey) embedded in smectite (medium grey). The background is conductive C-tape.

Radiochemical analyses

Table IV shows the radiochemical data of the samples. There are deviations from secular radioactive equilibrium in all the samples. The $^{230}Th/^{234}U$ activity ratio of all uranophane fractions is below unity (0.59 to 0.91), which indicates recent accumulation of uranium. The age was calculated assuming a thermodynamically closed system after uranophane formation. The ages estimated for groundwater circulation and oxidative precipitation of U(VI) in the form of uranophane range from 88 000 to 210 000 years. However, only minimum ages can be assigned using these data and the high $^{234}U/^{238}U$ ratios (up to 1.86 in UF4) may indicate recent accumulations of uranium from groundwater after the initial precipitation of uranophane (UF1).

The residual smectite after sequential extraction [12] has a very low $^{234}U/^{238}U$ activity ratio (0.29 to 0.39) and also a low $^{230}Th/^{234}U$ ratio (0.78).

Table IV. Radiochemical data of the rock and mineral samples and ages for ß-uranophane fractions.

	Total U (ppm)	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	Age (ka)
GP1-a	278	1.08±0.01	0.93±0.03	no estimations
GP1-b	197	0.94±0.01	0.98±0.03	- " -
GP1-c	182	1.18±0.01	0.81±0.04	about 300
UF1	≥ 5*10⁵	1.34	0.91	210 ± 15
UF2	– " –	1.46	0.81	155 ± 11
UF3	– " –	1.33	0.87	188 ± 12
UF4	– " –	1.86	0.59	88 ± 10
UF5	– " –	1.35	0.90	203 ± 14
UF6	≥ 2*10⁵	1.43	0.91	204 ± 15
	Total U (ppm)	U-content after sequential extraction [11]	$^{234}U/^{238}U$	$^{230}Th/^{234}U$
SM1	90.5	70.5	0.39 ± 0.02	-
SM2	92.5	81.4	0.36 ± 0.01	0.79 ± 0.03
SM3	53	41	0.29 ± 0.02	0.78 ± 0.07

Groundwater analyses

The hydrogeochemical parameters of the groundwaters associated with the studied fractures are summarised in Table V. With respect to the main components, the samples are classified as Ca-HCO3 waters, Mg and Na being the other main cations. The waters are slightly acidic, pH around 6.5. The calculated saturation indices (SI) for calcite show undersaturation, indicating relatively short water-rock interaction time, while the carbonic acid supersaturation with respect to air (i.e., with a gas phase having log PCO2 = -3.44) is probably due to biological activity (respiration). The waters also contain dissolved oxygen (about 1 - 3 mg/l).

Redox-potential measurements show quite similar patterns in all three cases. The Eh-value measured with Pt-electrode stabilised within about 5 to 50 hours to about 500 - 530 mV and 400 - 450 mV in surface and in situ electrodes, respectively. The Eh measured by Au-electrode on the surface was about 400 mV in all cases, while the in situ Au-electrode show 10 - 100 mV lower potentials. The C-electrodes stabilised to Eh values of about 300 - 340 mV. Dissolved (particle Ø < 0.45 µm) ferric to ferrous ratio of about 3:1 of the sample S3 also indicate oxidising conditions.

Due to the oxidising conditions, uranium concentrations in all three samples are relatively high (of the order of 10-6 M). Another factor affecting high uranium concentrations is the availability of secondary U(VI) minerals on the fracture surfaces and within interconnected microfractures. The copper concentrations analysed in Hyrkkölä are below the average copper concentration (0.4 µM) in Finnish wells drilled in bedrock comparable to the host rocks of the Hyrkkölä U-Cu occurrences [13].

Table V. Chemical composition in µM and other hydrogeochemical parameters of the water samples.

	Ca	Mg	Na	K	Cl	SO4	HCO3	NO3
S1	484	282	258	80.8	105	106	1400	173
S2	506	298	314	57.0	95.1	117	1400	116
S3	359	177	311	72.6	108	104	940	161

	Si	F	Fe_{tot}	Fe(II)	Mn	Cu	U	Diss. O_2
S1	170	10.0	<0.2	<0.2	1.8	0.071	1.77	30
S2	117	12.6	<0.2	<0.2	1.9	0.054	2.68	50
S3	210	10.5	0.90	0.23	0.8	0.20	0.39	90

	Charge Balance (%)	pH	pE	Uranine (µg/l)	E.C. (mS/m)	$^{234}U/^{238}U$	$SI_{calcite}$	SI_{atm}
S1	-0.8	6.6	6.5 ± 1.5	11	20	1.26±0.06	-1.7	+1.9
S2	3.2	6.8	6.5 ± 1.5	5	15	1.20±0.06	-1.5	+1.7
S3	1.0	6.6	6.5 ± 1.5	15	20	1.45±0.09	-2.1	+1.8

DISCUSSION

The present groundwater conditions are oxidising and would not allow the sulfidization of native copper. Therefore, sulfidization may be considered as an old phenomenon, older than the precipitation of non-identified uranyl phases in GP1 (e.g., more than about 300 000 years ago) and ß-uranophane in GP2 (~ 200 000 years ago).

In any case, the temperature at which Cu sulfides formed after sulfidization of native copper (GP1) and the precipitation of sulfides in GP2, was relatively low, as indicated by the mineralogy, composition, and the d34S values of the Cu and Cu-Fe sulfides. The upper thermal stability of digenite, djurleite and low chalcocite is between 72 ± 2 °C and 103.5 ± 0.5 °C [13]. The pH value at the time of sulfide-calcite precipitation in GP2 would have been about 7.8 (25 °C; [15]).

The mineral assemblage native copper-cuprite in sample SM is representative of the current groundwater conditions, as oxidation is like to be an on-going process, especially where dissolved oxygen is measurable (Table V). Native copper grains with rims of cuprite are in close contact with smectite, and native copper grains are also embedded in it (Fig. 1). USD studies on smectite showed a very low $^{234}U/^{238}U$ activity ratio (0.29 - 0.39) and a low $^{230}Th/^{234}U$ ratio (0.78). Such a disequilibrium pattern indicates that α-recoil-related preferential mobilisation of ^{234}U occurred from non-exchangeable sites of smectite, and the rate of mobilisation can be estimated with some confidence. The $^{230}Th/^{234}U$ is not far from unity, indicating that the rate of uranium removal has been sufficiently slow to allow ^{230}Th to grow back into near secular equilibrium with its immediate precursor ^{234}U, requiring at least from 350 000 to one million years. That means that smectite – groundwater interactions have been on going during at least the same period of time. Therefore, the native copper grains within smectite have also been and still are in contact with circulating groundwater (S3).

It has been stated above that the measured copper concentrations in the water samples at Hyrkkölä are below the average of copper concentrations in Finnish drilled wells. This may be due to the apparently short water – rock interaction time and also to the sorption and/or coprecipitation of copper into and/or with uranyl compounds and smectite. The concentration of copper in uranyl compounds varies between 0.55 and 1.32 wt. % in sample GP2 (Table III). In smectite the copper concentrations were also relatively high from 33.8 to 342 ppm. Native copper may get into solution through cuprite alteration (samples SM & S3).

CONCLUSIONS

Native copper has been (and is) in contact with evolving groundwaters (or different groundwater types) during long periods of time since it precipitated within granite pegmatites about 1700 Ma ago. This is assessed by USD studies, as native copper occurs in the same microfractures, where uranium is leached from and accumulated in alternately, due to mineral/rock-groundwater interactions.

Copper sulfides, copper-iron sulfides, and copper oxides also have been (and are) in contact with groundwater. The chemistry of groundwater at the time of sulfidization can be estimated through thermodynamical considerations [1], as sulfidization is not an current process.

The timing of the processes (e.g., sulfidization, oxidation) can be estimated either considering the system as a whole (all fractures/fractures zones belong to the same groundwater system) or as two different subsystems (Samples GP1 and GP2 representing one system and sample SM the other one). Considering the system as a whole, the end of sulfidization and/or remobilization of sulfide may be earlier than precipitation/leaching of uranium in smectite, that is, earlier than 350 000 years ago and even earlier than one million years ago.

Considering the subsystem represented by samples GP1 and GP2, the end of sulfidization and/or demobilisation of sulfide may be earlier than the precipitation of ß-uranophane and other uranyl (U6+) compounds in GP2 and GP1 (~ 200 000 years ago) on fracture surfaces and around the boundaries of copper sulfide grains.

The subsystem represented by sample SM may be considered as an independent system that is not related to any previous sulfidization process. Then the oxidation process may have been active since at least 350 000 years ago.

This work contributes not only with data on the timing of corrosion processes (sulfidization, oxidation) that may happen in the final nuclear waste repository, but also addresses the influence of these corrosion products on the release and transport of uranium and thorium. The interactions of uranium, copper and smectite in samples such as SM could be worthy of further studies, as new data could be obtained to clarify processes in the near-field environment.

ACKNOWLEDGEMENTS

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12. The uranium in samples SM1 and SM2 was selectively extracted by 1. NH4 acetate, 2. NH4 oxalate and the uranium in the residue for $^{234}U/^{238}U$ activity ratio was extracted by dissolution with HF-HNO3-HCl mixture. The uranium in sample S3 was selectively extracted by 1. Allard water, 2. NH4 acetate, 3. Tamm's reagent, and then, the uranium fraction for $^{234}U/^{238}U$ activity ratio was extracted by HNO3 (1M). The meaning of the sequential extraction methods for smectite is discussed in [5,16]. This discussion was not considered to be within the scope of this paper.

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