

THE HYRKKÖLÄ NATIVE COPPER MINERALIZATION: A NATURAL ANALOGUE FOR COPPER CANISTERS

NURIA MARCOS PEREA

Helsinki University of Technology, Engineering Geology & Geophysics Lab, FIN-02150 Espoo,
FINLAND

ABSTRACT

The Hyrkkölä U-Cu mineralization is located in south-western Finland, near the Palmottu analog site, in crystalline, metamorphic bedrock. The age of the mineralization is estimated to be between 1.8 and 1.7 Ga. The existence of native copper and copper sulfides in open fractures in the near-surface zone allows us to study the native copper corrosion process in conditions analogous to a nuclear fuel waste repository.

From the study of mineral assemblages or paragenesis, it appears that the formation of copper sulfide (djurleite, $\text{Cu}_{1.934}\text{S}$) after native copper (Cu^0) under anoxic (reducing) conditions is enhanced by the availability of dissolved hydrogen sulfide (HS^-) in the groundwater circulating in open fractures in the near-surface zone. The minimum concentration of HS^- in the groundwater is estimated to be of the order of 10^{-5} M ($\sim 10^{-4}$ g/l) and the minimum pH value not lower than about 7.8 as indicated by the presence of calcite crystals in the same fracture.

The present study is the first one performed on occurrences of native copper in reducing, neutral to slightly alkaline groundwaters. Thus, the data obtained is of most relevance in improving models of anoxic corrosion of copper canisters.

INTRODUCTION

In Finland and Sweden, disposed of spent nuclear fuel is planned to be in a repository to be constructed at a depth of about 300 - 800 m in crystalline bedrock. The nuclear waste will be isolated from the biosphere by multiple technical and natural barriers. In assessing the performance of the system, the corrosion of a copper canister (technical barrier) is considered.

The native copper mineralization at Hyrkkölä is related to the main uranium mineralization in granite pegmatites which occur as veins (0.05 - 5m thick) in quartz-feldspar gneisses and amphibolites. Petrological and mineralogical studies have demonstrated that this mineralization has many geological features comparable to sites being considered for nuclear waste disposal in Finland.

The evaluation of this native copper mineralization as a natural analogue for copper canister corrosion behavior under repository conditions is based on the study of the mineral assemblage native copper - copper sulfide occurring within open fractures in the near-surface zone. The occurrence of uranyl compounds in these fractures also allows consideration of the sorption properties of the engineered barrier material (metallic copper) and its corrosion product (copper sulfide).

A mineral assemblage at a given location may have been fixed by an externally controlled medium such as a moving fluid or pervasive atmosphere [1]. Therefore a detailed study of the fracture mineral assemblages may reveal the geochemical conditions (redox conditions, pH) in which they formed and the chemistry of the groundwaters in which they have been preserved. The hydrogeochemical conditions (water-rock interactions) that control the stability of the native copper and related fracture minerals are evaluated here.

MATERIAL AND METHODS

The fracture mineralogy assemblage of native copper-copper sulfide is present in an open fracture zone at about 8.3 m depth. So far, this fracture zone is the only one where, among other minerals, native copper and copper sulfides are known to be present. Gummities are also visible to the eye in these open fractures.

Fracture surfaces, polished sections and polished thin sections were examined using a stereomicroscope and polarizing microscope; α -particle autoradiography was used to determine the occurrences of radionuclides and their spatial relations to other fracture minerals. Spatial relation and quantitative and qualitative analyses of the native copper and copper sulfide in fractures were obtained using an electron probe microanalyzer (EPMA).

RESULTS

Copper sulfide composition

Table I shows the results of microprobe analyses from random points in copper sulfide grains. The calculated average of the Cu/S ratio is 1.934 and the standard deviation $\sigma_{n-1} = 0.033$. This result indicates that the copper sulfide phase is djurleite, $\text{Cu}_{1.934}\text{S}$, the upper thermal stability of which varies between 72 ± 2 and 93 ± 2 °C [2]. It has been found that djurleite is the solid phase precipitated at low temperatures under alkaline pH (pH ~ 8)[3] and reducing conditions (Eh < 0).

Table I. Chemical composition (weight %) of copper sulfide grains.

Cu	Fe	Ca	S	U	O	Total
78.85	0.03	0.01	20.68	0.13	0.37	100.07
78.90	0.02	0.00	20.66	0.18	0.28	100.04
79.27	0.02	0.02	20.13	0.10	0.34	99.88
79.34	0.01	0.02	20.60	0.00	0.27	100.24
79.42	0.00	0.01	20.29	0.00	0.34	100.07
79.18	0.04	0.02	20.68	0.00	0.21	100.13
79.85	0.01	0.01	20.75	0.00	0.47	100.09
77.38	0.04	0.02	20.75	0.00	0.93	99.12

Native copper composition

The data of microprobe analyses of native copper (Table II) was normalized to 100%. Thus, the maximum Cu content obtained is 99.39%. These results are affected by the background "noise" produced by the surrounding silicate minerals, and the small grain size of the analysed copper. The true composition of native copper is estimated to be about 99.99% Cu.

Table II. Chemical composition (weight %) of metallic copper.

Cu	Fe	Ca	S	U	O	Total
99.33	0.05	0.01	0.00	0.00	0.60	100
99.39	0.03	0.02	0.02	0.08	0.45	100
97.46	0.09	0.02	0.00	0.06	2.37	100
97.36	0.08	0.04	0.02	0.00	2.50	100

Fracture surface mineralogy and uranium distribution

The X-ray spectrum in Figure 1b shows that the main mineral at the fracture surface is a silicate, rich in aluminum and magnesium, most likely a clay mineral of the montmorillonite group (smectites). Calcite (Fig. 1a) is also a common mineral on the fracture surface. The lighter zones in the backscattered secondary electron (BSE) image (Fig. 1a) correspond to a concentration of heavy materials, mostly metals. Figure 2b shows the X-ray spectrum at the center of a heavy mineral phase (Fig. 2a). The relatively high peaks of sulfur and copper are an indication that copper sulfide is underlying the U-rich silicate and that the maximum thickness of the U-rich clay layer is about 0.5 μm (depth from which X-rays emerge).

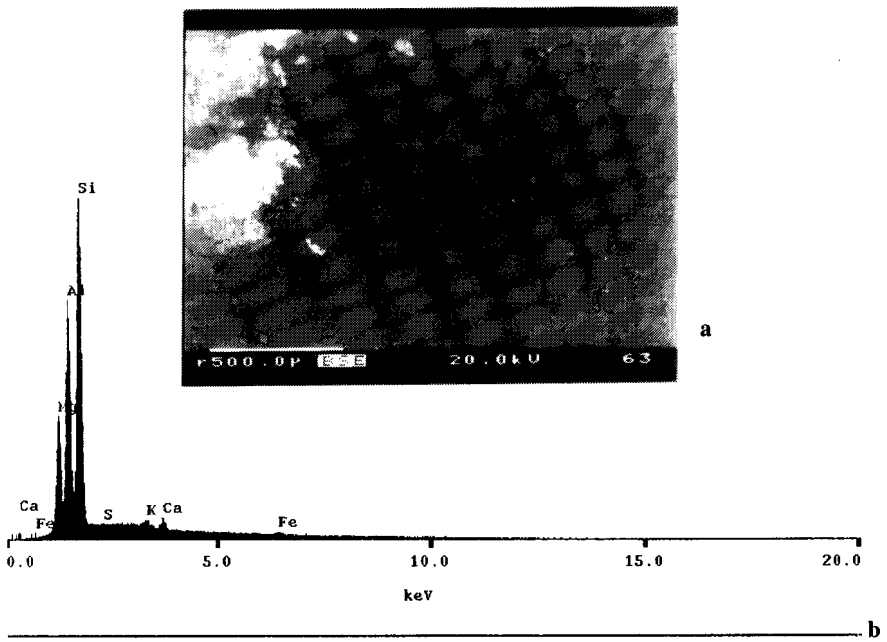


FIG. 1. a) Fracture surface. BSE image. b) X-ray spectrum at the center of the image.

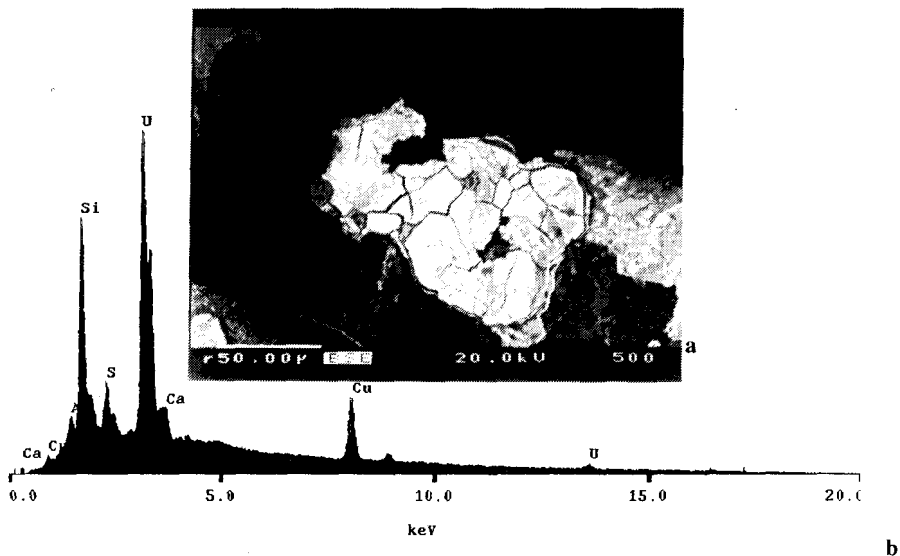


FIG. 2. a) A heavy mineral phase, BSE image. b) X-ray spectrum at the center of the image.

Figure 3 shows the BSE image of a copper sulfide grain. The X-ray spectrum at the center of the grain showed a small peak of uranium, indicating that uranium is not significantly adsorbed in the bulk of copper sulfide grains, but adsorbed around the grain boundaries. This was also shown by the results of α -particle autoradiography.

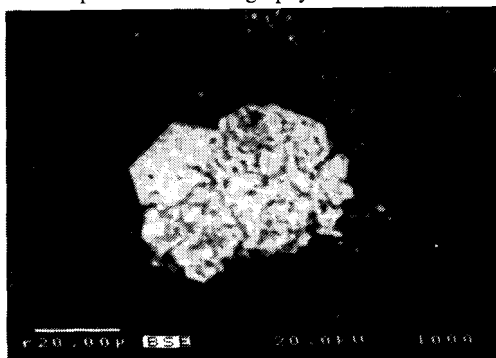
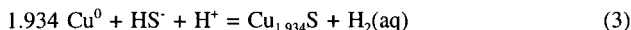
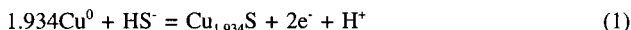


FIG. 3. Grain of copper sulfide, BSE image.

DISCUSSION

Of the various corrosion processes which may affect the stability of metallic copper in deep bedrock [4], sulfidization, a process in which metallic copper reacts with dissolved sulfide forming a solid sulfide phase, is considered the most important one at Hyrkkölä. The secondary

sulfidization of native copper in fractures is dependent on the availability of hydrogen sulfide (HS⁻) in the groundwater. Water acts as an electron acceptor (oxidant) in the corrosion reaction (3), a summation of (1) and (2):



Djurleite $\text{Cu}_{1.934}\text{S}$ is a mineral of low temperature supergene origin formed by sulfidization of native copper. It is a mineral phase of the system copper-sulfur. The phase boundaries of this system have been represented in pE - pH diagrams (Figs. 4 and 5; Eh = 59.155pE at 25 °C and at 5 °C Eh = 55.164pE). The occurrence of calcite crystals at the fracture surface indicates a minimum pH value of about 7.8 (25 °C; [5]) for circulating groundwaters in the fractures.

Figure 4a shows that at 25 °C, and a pH ~ 7.8 the minimum concentration of HS⁻ for the stability of djurleite is of the order of 10⁻⁵ M ~ 10⁻⁴ g/l. At the same values of temperature and pH, and a [HS⁻] = 10⁻⁶ M, the stability limits of djurleite lie outside the range to which water can act as an oxidant (Fig. 5a). At lower temperatures (Figs. 4b and 5b) and the same pH, the stability limits of djurleite lie within the range at which water can act as an oxidant even at concentrations of HS⁻ of the order of 10⁻⁶ M ~ 10⁻⁵ g/l.

CONCLUSIONS

The presence of native copper and copper sulfide within open fractures in the near-surface (8.3 m depth) implies the existence of reducing conditions, which are also predicted to prevail between 300 and 800 m depth in granitic bedrock. This finding allowed the study of native copper corrosion process in anoxic conditions.

It has been estimated that the formation of copper sulfide (djurleite, $\text{Cu}_{1.934}\text{S}$) after native copper (Cu^0) under anoxic (reducing) conditions is enhanced by the availability of dissolved HS⁻ in continuously or intermittently circulating groundwaters. The minimum quantity of dissolved HS⁻ has been calculated to be of the order of 10⁻⁴ to 10⁻⁵ g/l (Eh of about -350 to -248 mV), at temperatures of 25 °C and 5 °C respectively, with a pH of about 7.8. These values are not exceptional in granitic groundwaters, such as [6], [7].

Secondary uranium compounds were observed to be significantly adsorbed at the djurleite grain boundaries. Sorption was not significant in the bulk of copper sulfide grains nor in the bulk or boundaries of native copper grains.

The scale of the processes considered is still unclear. Further hydrogeochemical studies would provide a unique opportunity to determine the scale of the phenomena and to test the thermodynamic models (and their associated databases) used for copper corrosion analyses in performance assessment.

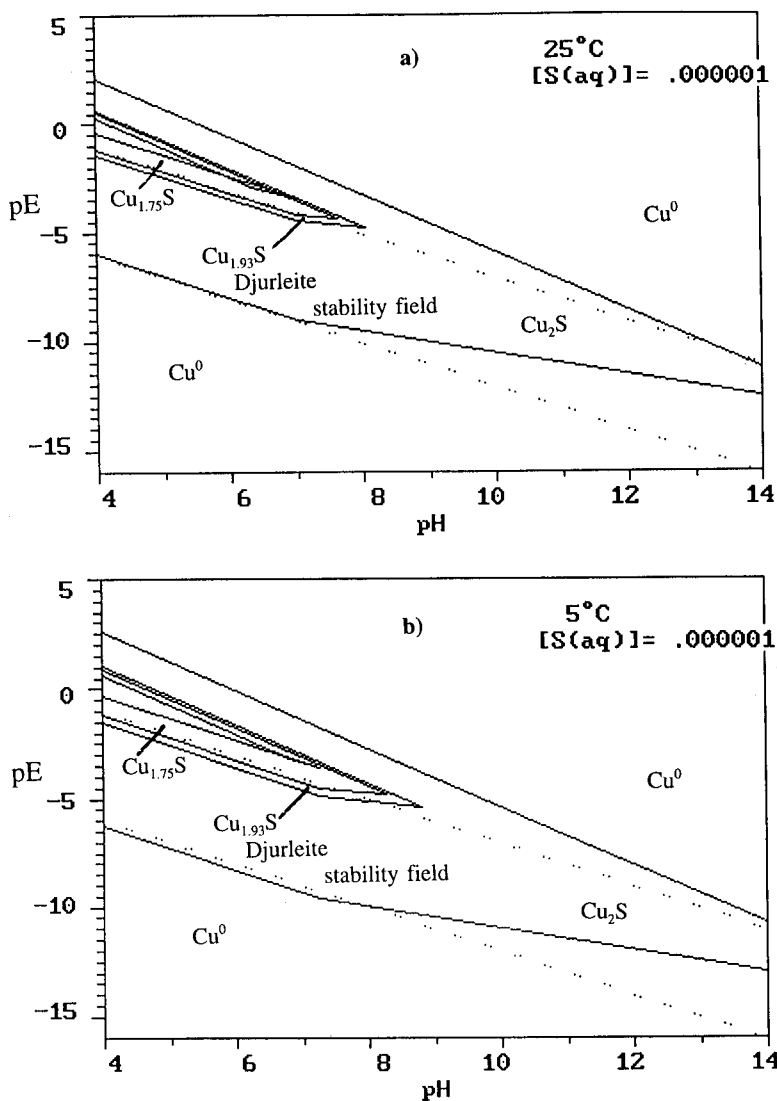


FIG. 5. Stability fields of metallic copper and copper sulfides. a) $T = 25^\circ\text{C}$, b) $T = 5^\circ\text{C}$. Activity of dissolved sulfur $[S] = 10^{-6}$ M (either as HS^- or SO_4^{2-}). Dotted lines indicate the pE-range at which water can act as an oxidant, upper limit ($[\text{H}_2] = 10^{-9}$) corresponds to the estimated lowest concentration of $\text{H}_2(aq)$, lower limit corresponds to the $\text{H}_2(aq)$ activity of 1.

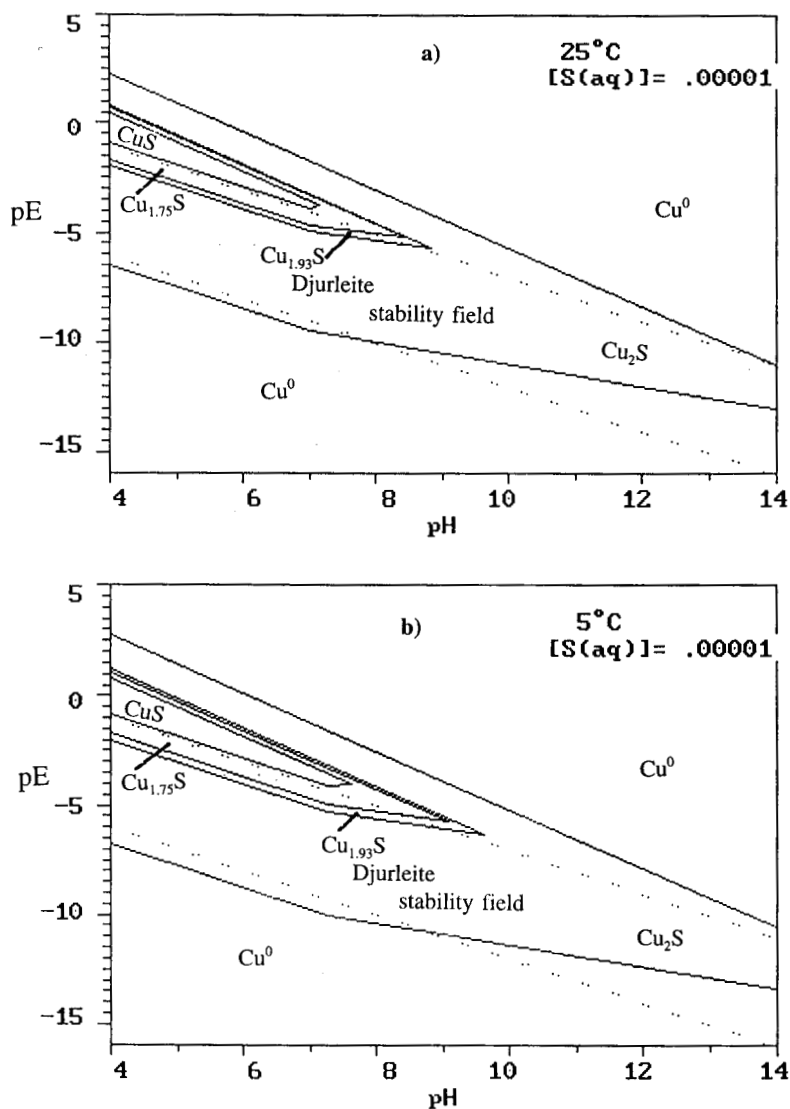


FIG. 4. Stability fields of metallic copper and copper sulfides. a) $T = 25^\circ\text{C}$, b) $T = 5^\circ\text{C}$. Activity of dissolved sulfur $[S] = 10^{-5}$ M (either as HS^- or SO_4^{2-}). Dotted lines indicate the pE-range at which water can act as an oxidant, upper limit ($[\text{H}_2] = 10^{-9}$) corresponds to the estimated lowest concentration of $\text{H}_2(aq)$, lower limit corresponds to the $\text{H}_2(aq)$ activity of 1.

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