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Uranium Mineralogy at the Askola Ore Deposit, Southern Finland

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ABSTRACT

Understanding uranium retention processes is essential when assessing the safety of a spent nuclear fuel repository as uranium forms over 95% of the spent fuel. It is crucial to establish whether migration mainly occurs continuously through slow diffusion, as usually postulated, or if groundwater-mediated transport occurs episodically, for example, during periods of intense, glacial recharge. This study provides insights into the principal retention mechanisms of natural uranium in granitic bedrock at Askola in Southern Finland.

The morphology and chemical composition of uranium minerals, found on the surfaces of water-conducting fractures ('open fractures') as well as in the matrix adjacent to fractures, were investigated in polished rock slabs and thin sections optically, by scanning electron microscopy (SEM) and by energy and wavelength dispersive spectrometers (EDS and WDS). In addition, the radiogenic isotopes were analyzed *in situ* by inductively coupled plasma mass spectrometry coupled to a high-performance Nd:YAG deep UV (213 nm) laser ablation system.

The predominant uranium ore mineral at Askola was identified as uraninite in studies carried out from 1963-1979, occurring as primary grains in the rock matrix. In the present study, abundant secondary uranium phases were found in micro-fractures, typically associated with goethite, pyrite and chalcopyrite. Chemical analyses indicate an assemblage of uranium (VI) silicates and hydroxides; phosphate is also present. Uranium (VI) hydroxides were found to fill micro-fractures propagating from open fractures to depths of several millimetres. If released into the bedrock, U would be expected to precipitate in such micro-fractures, preferentially in association with the various iron minerals present.

INTRODUCTION

It is planned to dispose of spent nuclear fuel from Finnish power plants deep in the bedrock at Olkiluoto (Western Finland). A comprehensive assessment of the future performance of the repository is required. Early failure of the engineered barrier system, in particular defects in the copper-iron canisters containing the fuel could lead to interactions with the local groundwater. On the longer term, glacial melt waters, which may intrude into the bedrock due to the high hydrostatic pressure under an ice sheet, have to be taken into account [1]. These conditions may lead to uranium migration and retention in the far field, i.e. the bedrock surrounding the repository and the local environment.

A variety of secondary uranium minerals have been identified at ore deposits in Finland [2, 3, 4, 5] and Sweden [6]. The topic is currently of interest from the perspective of both spent nuclear fuel disposal and the mining of uranium ores. It is essential to clarify which secondary

minerals are likely to precipitate under specific geochemical conditions. This information can then be used to predict uranium migration behaviour and to evaluate the capacity of the bedrock for uranium retention.

In this study, secondary uranium precipitates were investigated in samples from the Askola ore deposit, located 50 km north-east of Helsinki (Figure 1). As with other sites studied in the region [7], isotopic fractionation can be used to elucidate the conditions under which they were formed and the timescales over which migration occurred.



Figure 1. Askola uranium deposit is located ~50 km north-east of Helsinki.

EXPERIMENTAL

Samples

The samples were taken from two drill cores; DH303 at lengths of 15.55 m and 19.25 m and DH311 at 21.45 m, corresponding to vertical depths of 10.49 m, 12.98 m and 15.59 m, respectively (Figure 2).

Samples adjacent to open fractures were selected by α monitoring. Yellow crystals of uranophane can be seen with the naked eye. The samples comprise quartz (~40 % in DH303 and 20 % in DH311), K-feldspar (~20 % and 60 %, respectively), plagioclase and biotite; plagioclase is almost totally sericitized in DH303 samples (~20-25%). Fe-oxyhydroxide staining is common and apatite is present in sample DH303 at 19.25 m.

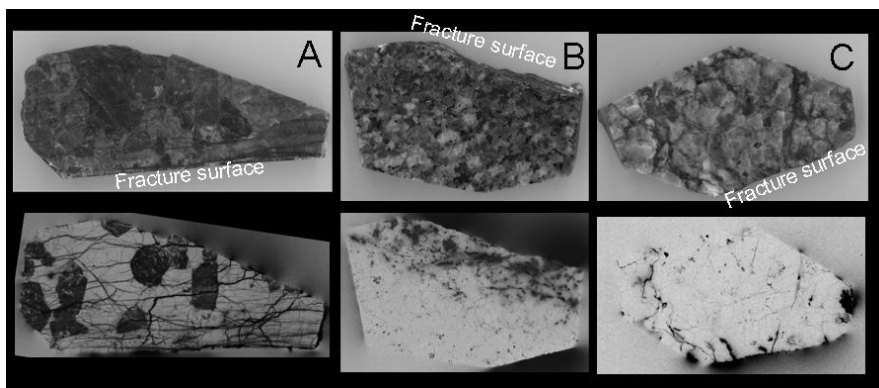


Figure 2. Photograph of A) drill core sample DH303 15.55 m, B) DH303 19.25 m, D) DH311 21.45 m and corresponding autoradiographs. Dark areas correspond to PMMA porosity and radioactive mineral phases. Width of samples: A 4.9 cm, B 4.1 cm and C 4.3 cm.

Autoradiography

The samples were impregnated with ^{14}C labelled polymethylmethacrylate (PMMA) to reveal the pore structure and porosity of the granites. The method [8, 9] involves impregnating centimetre-scale rock cores with ^{14}C labelled methylmethacrylate (^{14}C -MMA) in vacuum. This is followed by irradiation polymerization using a ^{60}Co -source, sample partitioning and autoradiography. In the case of samples containing loosely bound mineral phases or clay, the PMMA prevents the samples from crumbling and the water-soluble secondary uranium phases from dissolving during preparation. The distribution of radioactive minerals and pores in the selected rock slab samples were visualized on roentgen film (Figure 2). The sawn and slightly polished rock surfaces were exposed on Kodak X-omat MA roentgen film for 7-14 days. The film darkens in areas which are porous such that inter- and intra-granular fissures are clearly visible. Mineral phases containing natural radioactivity also cause film darkening but the U phases can be distinguished from the porous network in the autoradiograph images by the halos they produce around the darkened features.

Microscopy

The mineralogical composition of the samples is evident from thin sections under the polarizing microscope. Smaller scale observations were made on polished sections of the PMMA impregnated rock samples using a Hitachi FE-SEM S-4800 field emission scanning electron microscope. The elemental composition of mineral phases was determined semi-quantitatively using a INCA350 EDS system with a UTW Si(Li) detector operated in the backscattered electron mode (BSE). The operating conditions were 20 kV acceleration voltage and a 10 μA beam current. Wavelength Dispersive (WDS) analyses were performed with a Cameca SX100-type microprobe with 15 keV acceleration voltage and 10-25 nA beam current.

Laser ablation mass-spectrometry

Uranium minerals with radius more than 25 μm were chosen for LA-ICP-MS analyses using an Agilent 7500ce, quadrupole ICP-MS with an Octopole Reaction System coupled to a high-performance Nd:YAG deep UV (213 nm) laser ablation system. The latter provides flat craters with a diameter from 10 to 100 μm and high absorption for the analyses. The ablation frequency was 15 Hz, laser beam size from 20 to 55 μm , laser efficiency 65 % and ablation time 10 sec. The laser was focused manually. The isotopic mass ratio $^{234}\text{U}/^{238}\text{U}$ was measured to calculate corresponding activity ratio. No internal or external calibration was used.

RESULTS AND DISCUSSION

Emphasis in earlier studies at Askola [2] was placed on the primary uranium phases in order to determine ore potential. In the present study, samples were taken close to the surface, as the aim was to investigate secondary uranium phases formed by precipitation in a relatively open oxidized system.

Samples from core DH303 are altered and highly porous. Only a few radioactive minerals were detected in the sample from 15.55 m, mostly next to open fractures. Uranium content is high (UO_3 ca. 55 wt.%) due to co-precipitation at the rims of goethite nodules (Figure 3); levels

decrease towards the interior. Formation of the nodules may well be microbially mediated. Similar goethite nodules are found deeper in the matrix, but U rich rims do not occur.

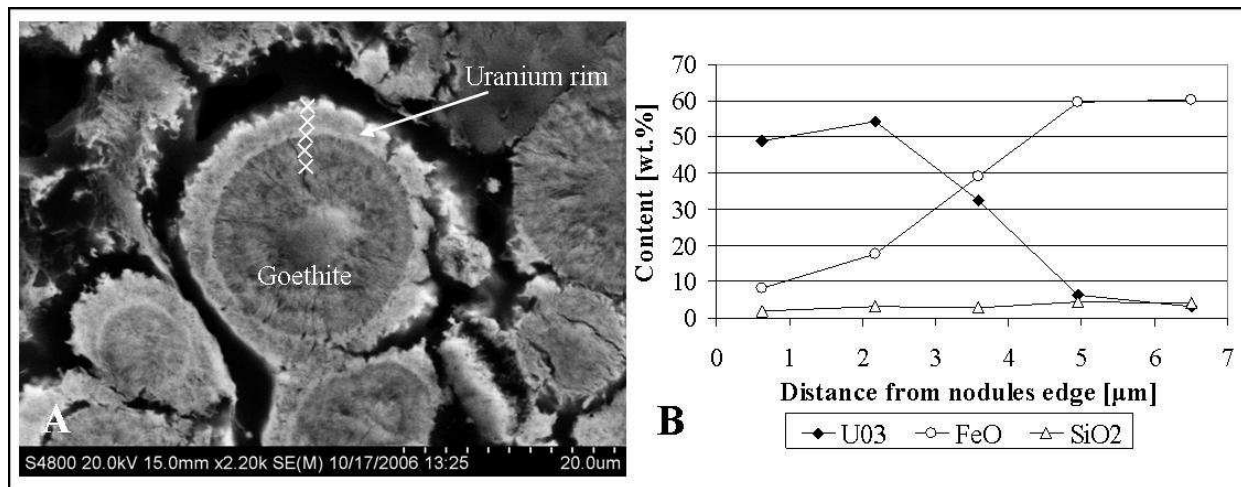


Figure 3. A) BSE image showing goethite nodules in sample DH303 15.55 m. Uranium is enriched (ca. 55 wt.%) at the edge of the nodules shown as a white rim. B) Uranium and iron content as wt.% in a line scan crossing the rim and the inner parts of the nodule as marked in A.

At 19.25 m autoradiography shows clearly that uranium is enriched in a 1 cm wide zone extending from an open fracture, indicating widespread penetration by oxidising waters. Uranium is associated with pyrite and chalcopyrite (Figure 4 A) in the form of a silicate-phosphate(s) (Table I). The uranium content (UO₃) is greater than 40 wt.%. Silica (SiO₂) content varies from 10 to 20 wt.% and calcium content is around 2% indicating uranophane as the dominant silicate phase. Phosphorus (P₂O₅) content varies from 4 to 6 wt.%.

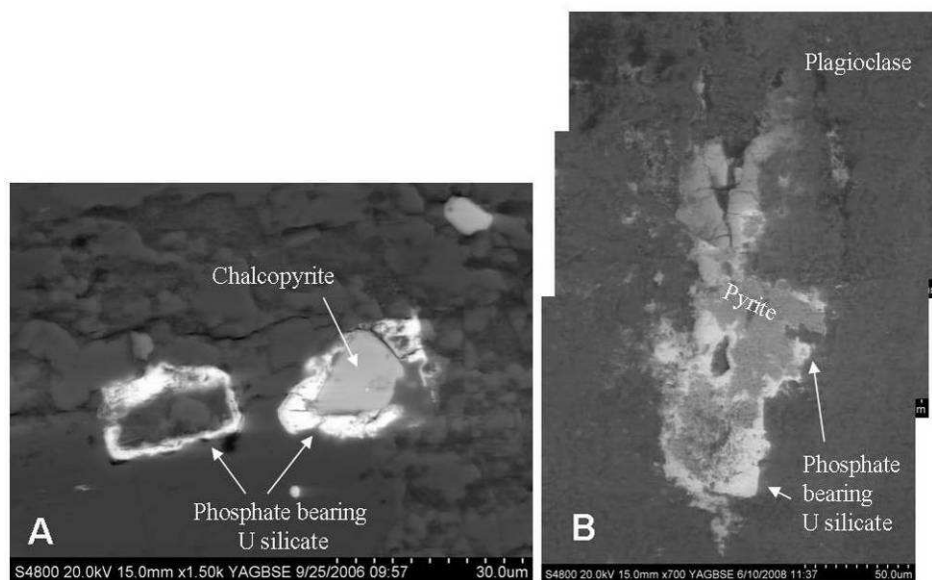


Figure 4. A) BSE image of a phosphate-bearing uranium silicate surrounding an euhedral chalcopyrite grain in sample DH303 19.25 m. B) BSE image of a phosphate-bearing uranium silicate surrounding a weathered pyrite grain in sample DH311 21.45 m.

Table I. Elemental analysis with EDAX of the uranium precipitates associated with chalcopyrite and pyrite seen in Figure 4.

Elements as oxides	Na ₂ O	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	UO ₃
Figure A	-	2.69	21.32	3.69	-	1.67	64.75
Figure B	0.42	2.34	13.26	5.89	0.60	3.37	45.04
Inferred mineral	Uranophane Ca(UO ₂) ₂ SiO ₃ (OH) ₂ ·5(H ₂ O) with possible apatite inclusions						

The sample from core DH311 is significantly less altered and grain boundary porosity dominates. At 21.45 m the uranium phases occurs associated with pyrite and filling micro-fractures. In addition to uranophane (Figure 4 B), uranium occurs as (hydr)oxides (Figure 5).

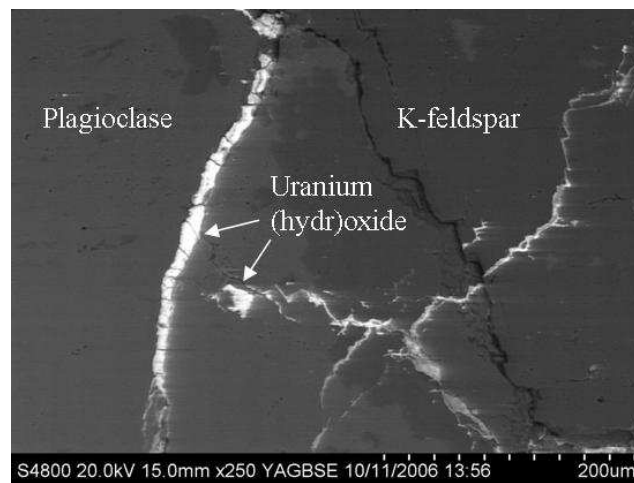


Figure 5. BSE image of uranium (hydr)oxide filling a micro-fracture in sample DH311 21.45 m.

Part of the 20 mm micro-fracture which cuts the whole of sample DH311 21.45 m is filled with uranium (hydr)oxide (Figure 5). Silica (SiO₂) and calcium (CaO) contents are ca. 4 wt.% and the uranium (UO₃) content more than 80 wt.%.

The isotopic mass ratio ²³⁴U/²³⁸U was measured in the secondary uranium silicates from DH311 21.45 m (e.g. Figure 4 B) to establish whether it represents direct precipitation from groundwater or an earlier hydrothermal event. The LA technique allows *in situ* measurements from precipitates a few micrometers in size. Mass ratios were converted to activity ratios (ARs); information needed for later age determination. Average ²³⁴U/²³⁸U activity ratios at three measurement positions were 1.4, 1.7 and 1.9 confirming that the uranium precipitated from groundwater [10], in the geologically recent past.

CONCLUSIONS

At Askola, uranium is associated with goethite nodules in open fractures, with pyrite and chalcopyrite grains in the matrix, possibly acting as local reducing agents, and in micro-fractures. The precipitates were observed to a maximum depth of one centimetre from the water-conducting zones. Fracture fillings were found to be principally uranophane and uranium

(hydr)oxides with some U-bearing phosphate also present. Activity ratios of the uranophane indicate relatively recent precipitation from groundwater. The formation of secondary uranium minerals in oxidizing conditions is the primary retardation mechanism for uranium released into groundwater.

ACKNOWLEDGMENTS

Financial support for this study was provided by the Finnish Research Programme on Nuclear Waste Management (KYT).

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