Radioactive disequilibria in mineralised drill core samples from the Björklund uranium occurence, northern Sweden

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RADIOACTIVE DISEQUILIBRIA IN MINERALISED DRILL CORE SAMPLES FROM

THE BJÖRKLUND URANIUM OCCURRENCE, NORTHERN SWEDEN.

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ABSTRACT

Forming the basis of a pilot study to investigate the natural mobility
of uranium and its daughter products within the geological environment,
a series of six samples, chosen from two mineralised fracture zones at
depths of 100-130m within a homogeneous leucocratic granite, were examined
mineralogically and isotopically to establish the presence or absence of
radioactive equilibrium that may indicate recent rock/water interaction
processes (i.e. during the last 0.5 m.y.).
The results show clear evidence of radioactive disequilibrium, and hence
recent rock/water interaction, in four of the six samples. Some is attribut-
able mostly to solution-solid ^{234}U recoil gain (weakly mineralised zones
adjacent to the main mineralisation) and others to solid-solution ^{234}U
recoil loss (moderate to highly mineralised zones). The richer type of
impregnation mineralisation indicates apparent radioactive equilibrium.

The absence of significant ^{238}U loss in the samples helps to underline
the reducing conditions prevalent within open fracture systems at these
depths. This has meant that uraninite, now found in fractured rock at
about 100m depth, has been chemically stable in its environment for most,
if not all, of its 1750 m.y. existence, including the last 0.5 m.y. when
it has been closest to the atmosphere. This could indicate that spent
nuclear fuel, which essentially is crystalline UO_2, and comparable to
uraninite once the main fission products have decayed, would also have
been stable in this environment for similar periods of time.

INTRODUCTION

One of the multitude of problems to be considered in the storage of high-level radioactive waste is the ability to try and predict the long-term effects on the geological environment in the event of a slow release of radionuclide material (e.g. through cannister corrosion) to circulating meteoric waters within the surrounding bedrock repository. Much of the work involving both the near field and far field radionuclide migration has been experimentally based, with computerised modelling to predict long-term effects on the geological environment. A rather natural and obvious complement to the experimental data is to examine naturally-occurring radionuclide migration (or lack of migration) within the geological environment of the intended repository. This allows, most importantly, an appraisal of migration within the limits of geological time, and thus negates the need for long-term prediction modelling.

Based partly on the proposals of the Ore Research Group, Stockholm University, and partly along the lines of research presently being conducted by the Uranium Prpospecting Section, SGAB, Luleå, a pilot study was initiated through the Division (KBS) of the Swedish Nuclear Fuel Supply Co. to examine the presence or absence of natural radionculide migration in a natural setting. This has involved mineralised fractures chosen from the Björklund uranium occurrence in S Norrbotten, which consist of uraninite impregnations and fracture infillings located within a homogeneous leucocratic (alaskite) granite. The object of the study is to investigate the extent (if any) of radionuclide migration within the mineralised fractures and within the host granite adjacent to the fractures.

Through collaboration with the USGS in Denver, USA, the uranium-disequilibrium system (^{238}U - ^{234}U - ^{230}Th) has been investigated from two mineralised fracture areas. This system has already been used as a sensitive indicator of geological recent uranium mobility during the last 0.5 m.y. (Zielinski et al., 1981; Rosholt, 1982; Schwarcz et al., 1982). To the extent that the uranium-series disequilibrium is a product of rock/water interaction, these measurements may help to evaluate the effective permeability of unfractured and macroscopically-fresh rocks, and they can be used to assess geologically recent uranium mobility in 'sealed' fracture zones.

GEOLOGY AND MINERALOGY

General Geology and Mineralogy of the Björklund Mineralisation.

The regional geological setting of the Björklund uranium mineralisation in S. Norrbotten has been described by Adamek and Wilson (1977; 1979) and the mineralogy by Guzman et.al. (1980) and Hålenius and Smellie (in preparation); prospecting and ore evaluation details have been described by Laurikko (1980).

The Björklund uranium mineralisation (Fig.1) is one of thirty known epigenetic occurrences characterising the Arjeplog-Arvidsjaur-Sorsele uranium province in N.Sweden, and believed to have been emplaced at the peak of metamorphism during the Svecofennian orogeny at about 1750 m.y. The rocks hosting the Björklund occurrence are granitoids considered to be older than 1840 m.y.(Wilson and Fallick, 1982). The mineralisation occurs within a leucocratic granite (alaskite) as uraninite disseminations together with fracture and fissure infillings. The granite is a medium to coarse grained variety with 5 to 7 vol.% mafic constituents. Quartz, plagioclase and potash feldspar dominate with the mafic phases occurring as interstitial aggregates of biotite and magnetite with accessory amounts of sphene (now mostly pseudomorphed to quartz and rutile), apatite and zircon. The normal unmineralised granite has average uranium and thorium values of 6.64ppm and 13.27ppm respectively, with a Th/U ratio of 2.0.

The mineralogy is described in detail by Hålenius and Smellie (in preparation) and briefly outlined here; the general paragenetic sequence of mineralisation at Björklund (Fig2) comprises six stages of development. Stage I, the primary crystallistion stage already described, is followed by a metamorphic episode. This has resulted in a series of deeply penetrating fracture systems which have provided access to the ensuing sequence of hydrothermal solutions and their precipitation products. Early processes (Stage II) within the fracture systems are initially characterised by localised albitisation of potassium feldspars and later by calcium-rich activity resulting in the formation of garnet I to the detriment of quartz, the sporadic formation of biotite and the precipitation of calcite. This is superseded (Stage III) by fracture

infillings, usually zoned, with amphibole, sphene and magnetite occupying the central infilled areas and epidote (with subsidiary calcite) occurring marginally.

Towards the end of this stage garnet II appears, most commonly forming a peripheral zone to garnet I within fractured feldspars. At the end of this stage, sporadic interstitial sulphide grains occur, comprising mostly pyrite, chalcopyrite, sphalerite and galena.

Hydrothermal calcium-rich, uranium-bearing solutions characterise Stage IV. These solutions, resulting in the precipitation of uraninite impregnations, have penetrated the rock fabric by way of:-
a) interstitial grain boundaries
b) pre-existing fracture zones infilled with Stage II amphibole, sphene, epidote and magnetite
c) Weak and irregular fractures within garnet I and II aggregates
The passage of the oxidising solutions has also resulted in the partial martitisation of magnetite causing some localised redox uraninite precipitation.

Later hydrothermal solutions (Stage V), now characterised by Ca, Ti and Fe, have resulted mostly in sphene formation with subordinate amounts of hornblende. When in contact with uraninite, reaction with these solutions has given rise to a series of complex uranotitanates and uraninite resorption textures. PbS, probably radiogenically derived and remobilised, is present as blebs, stringers, dustings and fracture infillings within and around the uraninite aggregates. Also characterising Stage V is the partial replacement of uraninite by coffinite and the precipitation of fine disseminations of sulphides, which may be newly introduced or remoblilised from Stage III.

Stage VI is characterised by late-stage low temperature hydrothermal activity resulting in the precipitation of FeOOH oxides. These have formed partly from the breakdown of Fe-Ti-Mn oxides but mostly from residual iron-rich solutions. These oxides are observed as zones marginal to mineralised fractures and along intergranular contacts. Further PbS remobilisation, the remobilisation of pyrite along small fractures, the formation of secondary uranium phases (e.g. uranophane, beta-uranophane and kasolite (Löfvendahl, 1981)) and continued calcite precipitation, also characterise this stage. The calcite, often together with chlorite,

is observed as infillings occuring interstitially and within small cavities and fractures.

Drill Core Selection

On the basis of gamma-ray log information from the drill holes, two suitable uranium-rich fracture and impregnation areas (approx. one metre in length) were selected for this investigation. A thin slice was removed along the length of each drill core for mineralogical and fission track studies. The remaining portions were sent to the USGS in Denver, USA, where final selection of the samples to be analysed was made. The location and size of the samples analysed are shown in Fig.3; the study was limited to six samples. The minimum sample size depends on the uranium content which in turn determines the counting times and ultimately the precision of the alpha spectrometry results. In general, a minimum size of 10 g.   is required to use both delayed neutron activation and alpha spectrometry so that sampling is limited by this size factor.

Mineralogy of the Selected Drill Core Samples.

The selected drill core samples are typical for the Björklund alaskite granite. Common to both sections is the superimposition on the primary rock fabric of a fracture zone accompanied by hydrothermal alteration and the crystallisation of new mineral phases. Both sections are mineralised with respect to uranium and minor sulphides.

1) Drill core 77001.
Drill core 77001 represents a section taken across the transition from a highly mineralised impregnation-type zone to the weakly mineralised host granite (Fig.3a). From Table I, the variation in uranium and thorium values from A to D along the drill core length underline the sharp subdivision of the core into a highly mineralised impregnation zone (represented by analyses A and B) and a weakly mineralised impreg- nation zone (represented by analyses C and D). This subdivision is also mineralogically distinct.

The mineralogical contents of the drill core (Table II) clearly indicate that throughout the examined length (approx. 60 cm) the granite has

TABLE I: Analyses of drill core samples 77001 and 80003 from Björklund.

Sample number	U^+ (ppm)	Th^+ (ppm)	U^* (ppm)	$\dfrac{^{234}U}{^{238}U}$ §	$\dfrac{^{230}Th}{^{238}U}$ §	$\dfrac{^{230}Th}{^{234}U}$ §
77001 A	3918	32.9		0.995	1.013	
77001 A	3921	33.9		1.002	1.004	
ave	3920	33.4	4170	0.998	1.009	1.010
77001 B	997.4	17.8		0.930	0.957	
77001 B	982.1	16.4		0.931	0.944	
ave	989.8	17.1	1040	0.930	0.950	1.022
77001 C	157.6	14.8		1.267	1.127	
77001 C	158.3	16.2		1.204	1.107	
ave	158.0	15.5	165	1.235	1.117	0.904
77001 D	30.90	15.04	32.2	1.029	1.018	0.990
80003 A	6619	61.6		0.934	0.968	
80003 A	6709	46.1		0.935	0.970	
ave	6664	54	7160	0.934	0.969	1.037
80003 B	33.30	16.0	34.5	1.112	1.085	0.976

+ Analysis by radioisotope dilution with alpha spectrometry.
* Analysis by delayed neutron activation (DNA).
§ Analysis by high-resolution alpha spectrometry.

Table II: Modal analyses of representative samples from drill-cores 77001[+] and 80003[+]

Specimen / Mineral	77001:1	77001:2	77001:3	77001:4	77001:6	77001:8	80003:2	80003:3	80003:4	80003:6	BUAC81097[*]
Quartz	15.3	24.3	29.9	26.2	37.9	21.5	27.1	32.3	40.2	37.1	31.8
K-feldspar	1.0	1.8	3.0	3.2	2.3	1.9	0.3	1.2	13.8	25.5	29.1
Plagioclase	49.2	55.4	62.7	64.4	55.3	69.2	67.0	59.7	35.1	31.7	31.7
Epidote	2.3	1.8	1.0	0.8	0.1	1.6	1.1	2.1	2.2	1.6	1.2
Sphene	0.2	-	0.2	0.6	1.1	1.6	1.0	1.3	0.8	0.6	0.2
Garnet I	12.6	4.2	0.5								
Garnet II	15.0	7.4		-	-	-	-	-	-	-	-
Amphibole	0.2	1.1	0.3	1.1	0.5	3.3	-	0.3	0.6	0.4	0.2
Calcite	0.4	0.4	0.2	-	-	0.3	-	-	-	-	-
Biotite/Chlorite	-	-	-	-	0.2	-	0.4	2.0	2.0	0.5	3.5
Opaques	3.8	3.6	2.2	3.7	2.6	0.6	3.1	1.1	5.3	2.6	2.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Points counted	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000

+ See fig. 3 for sample location.

* Specimen BUAC 81097 is representative of the unmineralised normal granite.

been influenced by Na-metasomatism, seen commonly as an albitisation of K-feldspar. Phases such as amphibole (hornblendic in type), epidote, magnetite and sphene (i.e. Stage III minerals introduced during Ca-rich hydrothermal activity; Fig.2) also occur in varying proportions as interstitial and vein and fracture infillings throughout the core (Plate Ia). The highly mineralised section is further characterised by interstitial aggregates of garnet (andradite dominant) which has formed to the detriment of quartz (Table II; sections 77001:1 and 77001:2; Plates Ia and Ib).

The penetration of these metasomatising and Ca-rich solutions (and later U-rich solutions) has been facilitated by a system of microfractures which can be clearly observed traversing the primary rock fabric (Plate Id). These have probably formed coeval with the hydrothermal activity.

The later (Stage IV and V) uranium and calcium-bearing hydrothermal solutions have tended to permeate along those pre-existing channels and structural weaknesses, especially in the garnet-rich zones which have been more porous due to the replacement of quartz by garnet. This has resulted in the observed subdivision of a highly mineralised garnet-rich impregnation zone and a more weakly mineralised impregnation zone largely devoid of garnet.

Within the highly mineralised zone (approx. 4000ppm U), the uranium is mostly in the form of disseminations and aggregates of uraninite which occur as fracture infillings and interstitial aggregates within garnet (Plates Ic and IIa); minor quantities are associated with other Stage III minerals such as epidote and sphene, and some small uraninite disseminations exist interstitially within remnant portions of the quartz/feldspar rock fabric. Within the transition area between highly and weakly mineralised, the uraninite grains sometimes show partial replacement by coffinite and in some cases resorption textures are observed. Limited remobilisation of uranium due to oxidation has occurred forming   uranium secondary uranium silicate phases which are present in small amounts around the uraninite aggregates (Plate IIb). Small-scale remobilisation and precipitation of galena (probably radiogenic) is evidenced by the intergranular galena within the uraninite aggregates; galena also occurs as larger single grains (Plate IIb).

Within the weakly mineralised zone (approx. 30 to 200ppm U), garnet (both garnet I and II varieties) is largely absent and the much reduced uraninite content is sporadically associated with the other Stage III phases such as epidote, sphene and magnetite. Suitable nucleation and precipitation sites have been those in close association with the magnetite-rich mafic aggregates; the magnetites (both primary and Stage III varieties) have sometimes been partly martitised in the near vicinity to the uraninite precipitation.

The weakly mineralised zone has often been subjected to marked alteration and breakdown of primary and hydrothermally introduced silicate and Fe-Ti-Mn oxide phases. This has been due to the passage of oxidising solutions facilitated by the microfracture systems. The actual timing of these solutions is uncertain but are probably coeval and subsequent to uranium precipitation.

The minor uranium distributions (<10 to 500ppm U) in the core have been studied by the Fission Track method. Low to moderate concentrations (i.e. 50 to 250ppm U) are associated with epidote and sphene and low concentration (<10 to 50ppm U) are associated with apatite, magnetite, amphibole and garnet. Variable concentrations (250 to 1000ppm U) are contained in zircons and even higher concentrations may be associated with the formation of some complex uranotitanate phases. As most of these complex phases are the result of uraninite interaction with Ca- and Ti-bearing solutions, the close proximity of the reacting uraninite grains makes assessment of the U-contents difficult.

The uranium contents of the low U-bearing phases are fairly homogeneous along the drill core, so that their uranium contents mostly reflect primary compositions prior to the uranium mineralisation.

The fission track density maps show that interstitial and intergranular uranium distributions probably represent the impregnating distributions during mineralisation. There is no obvious mineralogical evidence of recent uranium mobility apart from the secondary uranium silicate phases at the margin of the highly mineralised zone.

2) Drill core 80003.
In contrast to Dh 77001, this section represents a fairly restricted fracture zone (approx. 30cm in width); the major mineralised portion

(approx. 7cm wide) is located towards the central area where the fracturing and hydrothermal alteration is most intense. The fracture zone is composed of a weakly orientated system of microfractures and veinlets ranging in width from 0.02 to 0.05 mm; small-scale crush zones up to 0.5cm wide and mostly containing recrystallised quartz also occur where fracturing has been most intense (Plates IIc and IId). The fracture infilling phases conform (with the exception of garnet which is absent) to those described above for Stage III of the paragenetic sequence of mineralisation (Fig.2) and are hydrothermal in origin. The most common assemblage is amphibole + magnetite + quartz $\pm$ albite $\pm$ epidote $\pm$ sphene. These phases are also common as sporadic matrix constituents.

Chemically, the zone is characterised by Na-metasomatism (mostly albitisation of K-feldspar) which is most apparent around the mineralised area but tends to weaken towards the edge of the fracture zone (see modal analyses presented in Table II).

Uranium mineralisation has been restricted to one main fracture and subordinate off-shoots of this; some sporadic impregnation concentrations are associated with mafic aggregates occurring interstitially in the rock matrix. The uranium is mostly in the form of uraninite disseminations which are surrounded or partly surrounded by a green silicate phase of chloritic composition. This has been observed from other parts of the Björklund mineralisation and may be a result of the breakdown of earlier silicate Stage III phases (probably amphibole) facilitated by alpha-particle decay from the uraninte. The green silicate phase is further surrounded by dispersed FeOOH-oxides giving these mineralised fractures a rust coloured appearance. Within the FeOOH-oxide envelope, especially peripherally, are fine disseminations of chalcopyrite, and larger single grains of galena (partly radiogenic ?) tend also to occur. Earlier Stage III magnetites have been partly to completely oxidised to hematite and resorption textures are not uncommon.
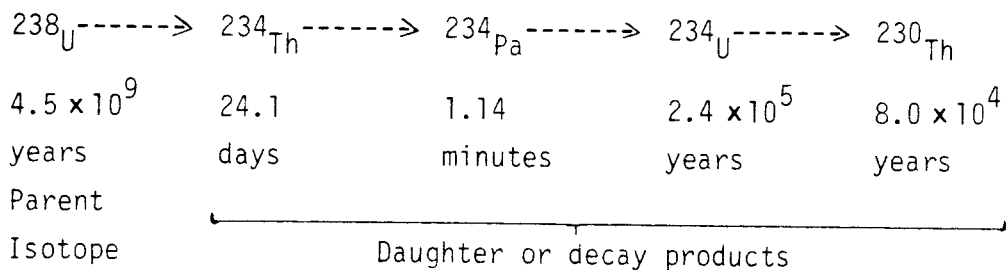
Fission track studies have shown that low to moderate uranium concentrations (approx. 50 to 250ppm U) are contained within epidote and sphene and low concentrations (<10 to 50ppm U) within magnetite, biotite and apatite. From those areas outside the mineralised zone, sporadic high

uranium concentration densities (up to 1000ppm U) occur associated mostly with Fe-Ti-Mn oxides and zircons. There is little evidence of subsequent uranium mobility; there are no secondary uranium phases and the fission track studies thus indicate no obvious recent interstitial movement of uranium outside the mineralised zone.

URANIUM-SERIES DISEQUILIBRIUM

Mostly based on the early work of Rosholt (1959) and more recently Rosholt (1982, investigations of the ^{238}U-^{234}U-^{230}Th system have been shown to provide a sensitive indicator of uranium mobility and rock/water interaction, during approximately the last 0.5 m.y.

Theoretical Basis.

$$^{238}U \dashrightarrow {}^{234}Th \dashrightarrow {}^{234}Pa \dashrightarrow {}^{234}U \dashrightarrow {}^{230}Th$$

4.5×10^9	24.1	1.14	2.4×10^5	8.0×10^4
years	days	minutes	years	years

Parent
Isotope   Daughter or decay products

Because ^{238}U and ^{234}U are isotopes of the same element, chemical differences are expected to be absent. In addition, because the intervening thorium and protactinium isotopes in the decay chain are so shortlived, little time for chemical separation is available. The $^{234}U/^{238}U$ activity ratios for geological materials should therefore be at equilibrium. Disequilibrium between ^{238}U and ^{234}U indicates migration of either radionuclide within the last 2.4×10^5y, that is, within the half-life of ^{234}U. Similarly, ^{234}U-^{230}Th can highlight migration within the last 8.0×10^4y. Non-equilibrium of $^{234}U/^{238}U$ activity ratios have for some time been reported from continental (e.g. Cherdyntsev, 1955; 1961) and oceanic environments (e.g. Thurber 1962; Koide and Goldberg, 1965; Kronfield, 1974). Furthermore, surficial weathering processes have also resulted in radioactive disequilibrium (e.g. Hansen and Scott, 1968; Rosholt et al, 1966).

Recently Rosholt (1982) has reported results from silicic crystalline rocks sampled both from the surface and at depth. This study has shown that drill core samples, which are unfractured and petrographically fresh, demonstrate that over a substantial vertical distance radioactive equilibrium has been maintained during the last 0.5 m.y. However, samples from surface and near-surface localities, and fractured samples at depth, all of which are in contact with water movement, most often demonstrate disequilibrium.

Radioactive disequilibrium is therefore more common than theoretically thought possible. The mechanisms giving rise to such anomalous $^{234}U/^{238}U$ activity ratios have largely centred on studies concerning alpha decay emission which is believed to play and important role. Several models have been postulated to explain these anomalies.

Model I (Rosholt et al, 1963): This model is based on the assumption that the ^{238}U atom within the atomic lattice of a mineral is commonly in the plus-4 valency state and therefore not particularly susceptible to dissolution. Following alpha decay, and subsequent beta decay, the resultant ^{234}U nuclide will occupy a more unusual lattice position because of the probability of its attaining a plus-6 valency state. As water preferentially dissolves uranium in a plus-6 valency state, this results in a depletion of ^{234}U in the mineral relative to ^{238}U.

Model II (Kigoshi, 1971): Consider a ^{238}U nuclide near to the surface of a mineral grain; the ^{238}U decays by alpha emission to ^{234}Th which subsequently recoils, and becomes ejected from the mineral into the intergranular pore water. Thus trapped, it further decays to ^{234}U which results in the enrichment of ^{234}U in water and a ^{234}U decrease in the mineral.

Model III (Kigoshi, 1971): Similar situation to Model II except that there is no pore water around the mineral grains. The recoiled ^{234}Th nuclide is therefore not trapped by the water but instead intersects the surface of an adjacent mineral grain causing a localised area of damage (i.e. alpha-recoil tracks). These tracks are considered to provide paths of rapid diffusion to allow the ^{234}U (subsequently formed from ^{234}Th decay) to move to the surface of the grain and be accessible to water that may later enter the pore spaces.

Model IV (Fleischer and Raabe, 1978): Similar to Model III with the addition of pore water around the mineral grains. The ^{234}Th recoiled nuclide still intersects an adjacent mineral grain and some or all of the damaged region (i.e. alpha-recoil tracks) is loosened or etched chemically by the intergranular liquid.

Model V (Rosholt, 1982): This model considers the process of daughter product emplacement from pore waters containing dissolved ^{238}U and ^{234}U. These radionuclides subsequently decay by alpha emission and the resulting recoiling nuclides of ^{230}Th, ^{234}Th, ^{234}Pa and ^{234}U are absorbed or embedded in particulate matter at the solid-liquid interface. After sufficient geological time, this mechanism (i.e. recoil gain) results in solids which are enriched in ^{234}U and ^{230}Th relative to ^{238}U. This is the only model which involves the transport of ^{230}Th.

All, or some combination of these models, may be active within a given rock complex of sufficient uranium content during recent geological time (i.e. the last 0.5 m.y.). Provided there is some circulatory movement of meteoric waters, the rocks should demonstrate a depletion of ^{234}U relative to the waters, and consequently both water and rock will be characterised by anomalous $^{234}U/^{238}U$ activity ratios. As expressed by Fleischer and Raabe (1978, p. 973), 'a first order, oversimplified, general description of the (published) observations is that ground water preferentially acquires ^{234}U, so that rocks through which such water flows are commonly, but not always, depleted in ^{234}U'.

Practical Applications.

As discussed by Rosholt (1982), evaluation of the ^{238}U - ^{234}U - ^{230}Th - ^{232}Th system can reveal geochemical and physiochemical processes that give rise to an open system behaviour of uranium and its daughter products in crystalline rocks, provided the disturbance occurred within the last 0.5 m.y. He recognised five important geochemical processes (based on the models described above) which served to produce isotopic disequilibria:-

1) Uranium leaching in which ^{238}U and ^{234}U are removed with little or no fractionation.
2) Preferential ^{234}U leaching following alpha-recoil displacement processes (^{234}U recoil loss) with lesser ^{238}U loss.
3) ^{234}U recoil loss with little or no ^{238}U loss.
4) Uranium assimilation in which both ^{238}U and ^{234}U were added with present-day $^{234}U/^{238}U$ activity ratios varying from 0.8 to 1.2.
5) Addition of ^{234}U and ^{230}Th by daughter emplacement processes (^{234}U + ^{230}Th recoil gain).

To assess the geochemical process, or combination of processes, which have produced isotopic disequilibrium in a given rock formation, the data are plotted on ternary diagrams whose apexes are ^{238}U, ^{234}U and ^{230}Th, expressed in percent of the combined activity (Fig.4). Various representative activity ratios of $^{234}U/^{238}U$ are shown by dashed lines. Rocks that are in equilibrium plot in the centre of the triangle, and areas that represent the commonly encountered types of isotopic fractionation are noted.

Rosholt (1982), in a study of 84 silicic crystalline rocks, found that ^{234}U recoil loss (i.e. solid to solution) is diagnostic of incipient weathering, whereas uranium assimilation and ^{234}U + ^{230}Th recoil gain (i.e. solution to solid), accompany substantial penetration of water into fractures and weathered zones.

Schwarcz et al (1982), have semi-quantitatively applied the uranium-series disequilibrium to granitic rocks. They have suggested a time-scale based on the fact that the $230_{Th}/234$ U activity ratios in rock varies with time, i.e. from the time of disturbance of radioactive equilibrium to the return to equilibrium of the daugther products. By measuring the various parent/daughter relationships, it is thus possible to determine so-called 'isotopic clocks' for every order of magnitude of time during the last 0.5m.y. Preliminary results from unmineralised granitic cores from Atikokan, Ontario, taken from depths ranging from 500m to 1000m, revealed recent disequilibrium effects, at least on a scale of a few centimetres. However, whether such displacements from equilibrium are uniformly present over large volumes of rock, or are locally compensated by complementary enrichments or depletions of isotopes in volumes of rock a few centimetres away, has still to be solved.

Because ^{234}U has a relatively high mobility during both endogenic and exogenic processes compared with its parent ^{238}U, such isotopic studies have been used for uranium exploration especially in sandstone terranes (e.g. Boyle, 1980; Osmond et al, 1981). For example, Cowart and Osmond (1977), working with sandstone-type uranium deposits, noted marked decreases in the uranium concentration and sometimes dramatic increases in the $^{234}U/^{238}U$ activity ratio in the water regime downdip from reduction (i.e precipitation) barriers. This was considered due to downdip precipitation of uranium at these reduction barriers coincident with an augmentation of ^{234}U to the downward moving water from the initial concentration of uranium at the barrier. Using $^{234}U/^{238}U$ activity ratios,accumulations of uranium in sandstone-type deposits can thus be detected isotopically for distances up to several kilometres in the direction of the water flow. Uranium-ore prospecting methods, based on uranium-series disequilibrium measurements, have been described and discussed by Ivanovich (1981).

However, the application of such techniques has its limitations. For example, it is not possible to distinguish between intense alteration (with large loss or gain of an isotope) a long time ago, from weak alteration a short time ago. In addition, rocks exhibiting profound alteration (e.g. many surface or crush zone samples) can appear to be isotopically in equilibrium. In this case, it can be inferred that whatever alteration processes have occurred, were completed more than 1 m.y. ago, i.e. outside the time-scale of this present study.

Sample Preparation and Analytical Procedures.

A total of six drill core samples were analysed for ^{238}U, ^{234}U and ^{230}Th by Dr. J.N.Rosholt using high-resolution alpha spectrometry at the USGS laboratories in Denver, USA. Details concerning sample preparation are outlined by Rosholt (1980b; 1982). Because of the small sample size used for the highly mineralised samples, duplicate analyses were made to check for splitting errors. For the most part, splitting errors were within the limits of analytical precision. The precision of the results is better than $\pm$2 percent for the $^{234}U/^{238}U$ and $\pm$3 percent for the $^{230}Th/^{238}U$ ratios.

RESULTS AND DISCUSSION

Results

The results of the uranium-disequilibrium series (^{238}U - ^{234}U - ^{230}Th) measurements are presented in Table I and Fig. 5.

Drill Core 77001

Sample A, from the highly mineralised impregnation zone (Fig. 2), indicates that apparent radioactive equilibrium has been maintained over the last 0.5 m.y. However, the very high uranium content in this zone (av. content 3920 ppm U) could very well mask significant amounts of disequilibrium ore, such as at crystal boundaries. Even considering this possibility, the result generally suggests that very little water movement is occurring relative to the high uranium content. This is to a large extent supported by the mineralogical observations.

Sample B, from the transition between the highly mineralised and weakly mineralised zones (av. content 989.8 ppm U), plots just within the field relating to ^{234}U recoil loss (i.e. solid to solution) thus indicating radioactive disequilibrium. This is partly reflected in the mineralogy where minor uranium remobilisation to form secondary uranium silicates has been noted.

Samples C and D, from the weakly mineralised impregnation zone (respective av. contents of 158 and 30.9 ppm U), both plot within the ^{234}U + ^{230}Th recoil gain field (i.e. solution to solid). This indicates that during the last 0.5 m.y. waters containing excess ^{234}U have permeated this zone causing enrichments of ^{234}U and ^{230}Th relative to ^{238}U in the rock. The greater enrichment reflected by Sample C, in comparison to D which is actually close to equilibrium, suggests that this effect decreases with increasing distance from the mineralisation.

Drill Core 80003

Sample A, representing the mineralised fracture (av. content 6664 ppm U) (Fig. 3) plots within the ^{234}U recoil loss field. This is comparable to Sample B from Dh 77001; both also exhibit a general absence of quartz replacement by garnet and the presence of a loose system of microfractures.

Sample B, from the weakly mineralised zone (av. content 33.3 ppm U), plots within the ^{234}U + ^{230}Th recoil field in accordance with Samples C and D from Dh 77001.

In general, the results show that two of the highly mineralised samples (i.e. Dh. 77001, sample B; Dh. 80003, sample A) are deficient in ^{234}U and that the weakly mineralised samples contain excess ^{234}U; only one sample indicates radioactive equilibrium (Dh. 77001, sample A). Rock/ water interaction processes therefore characterise all but one of the samples.

Discussion and Conclusions

A microscopic study of samples from depths of 100-130 m at the Björklund uranium occurrence show the presence of weak fracture systems mostly initiated prior to the mineralisation stage which has been dated to approx. 1750 m.y. (Adamek and Wilson, 1977). The uranium-rich mineralising fluids have followed these earlier textural and structural weaknesses and it is therefore reasonable to suppose that recent uranium mobilisation (i.e. during the last 0.5 m.y.) should also follow these same channels, and such mobilisations might be expected in those areas of highest permeability potential.

Dispite the fact that open microscopic fractures are still present, unaltred uraninite is found to be the main uranium-bearing phase. Other compounds of quadrivalent uranium, such as coffinite and complex U-Fe-Ti oxides, also occur, whereas secondary minerals of hexavalent uranium are rare and found in insignificant amounts only. Thus, the main conclusion to be drawn from the mineralogic evidence is that uraninite, now found in fractured rock at depths of 100-130 m, has escaped major oxidation and dissolution throughout the duration of its existence (i.e. approx. 1750 m.y.).

Studies of the uranium disequilibrium system (^{238}U-^{234}U-^{230}Th), which highlight developments during the last 0.5 m.y., show clear evidence of radioactive disequilibrium in four of six samples studied so far. In general, the two highly mineralised samples (i.e. Dh 77001, sample B; Dh 80003, sample A) are deficient in ^{234}U and that the weakly mineralised samples, located adjacent to the former, contain excess ^{234}U; only one sample indicated apparent radioactive disequilibrium (Dh 77001, sample A).

The limited isotopic data therefore suggests that at Björklund, during the last 0.5 m.y., weakly mineralised samples (represented by 77001 C) at depths of 100-130 m have been picking up ^{234}U nuclides from the surrounding pore solution, or still may be doing so. Less mineralised samples, 77001D and 80003 B, show similar though weaker effects. In the stronger mineralised samples, evidenced by 77001 B and 80003 A, local ^{234}U recoil losses (solid to solution) seem to dominate over any simultaneous pick-up of this isotope that may have taken place. The apparent radioactive equilibrium in sample 77001 A indicates that in the more extensive richer impregnation zones, the recoil-induced mobilisation of ^{234}U (solid to solution) does not appear to penetrate deep enough to affect the isotope ratio in the bulk of the sample. However, the very high uranium content in this zone (av. content 3920 ppm U) could have masked significant amounts of disequilibrium ore, such as at grain boundaries.

Comparison of the $^{230}Th/$ ^{234}U activity ratios indicates that five of the samples represent equilibrium within the limits of analytical precision. In one sample, 77001 C, however, the activity ratio is 0.904 which clearly implies a marked excess of ^{234}U. This, as shown by Osmond et. al. (1982; Figs. 6 and 8) places the sample in that part of a groundwater flow system which is distinctly downflow of any uranium redox front (i.e. Sector V in their notation), and which is characterised by reducing conditions where UO_2 is a chemically stable phase, and the content of dissolved uranium in the water is very low although the proportion of ^{234}U is high. This is supported by the fact that no loss of ^{238}U is evidenced in the other Björklund samples which infers that no oxidative bulk leaching of uranium has taken place during the last 0.5 m.y. It also confirms the microscopic and fission track evidence of insignificant uraninite dissolution and the lack of secondary minerals of hexavalent uranium.

Supportive conclusions are reported by Löfvendahl and Holm (1981) and Löfvendahl and Åberg (1982) who have made isotope studies of Swedish secondary uranium minerals (including some from Björklund) in samples collected at the surface or at shallow depths. They concluded that the great majority of minerals are all of Quarternary age, which means that they formed mainly after postglacial exposure of the primary minerals to the influence of the atmosphere. This also indicates that here the primary uraninite or pitchblende minerals had remained chemically stable for long periods of geo-

logical time since their formation, which in all cases exceeds 900 m.y.

Rosholt (1982) presents isotopic studies of uranium and thorium from 84 samples of silicic crystalline rocks in the USA. Few of these samples, if any, host actual uraninite/pitchblende mineralisation. The study has indicated that: 1) only unfractured rock from drillcores is in radioactive equilibrium, 2) ^{234}U recoil loss and preferential ^{234}U leach predominates in surface and near-surface rocks, and 3) $^{234}U + {}^{230}Th$ recoil gain and U assimilation occurs predominantly in drill core samples of fractured rocks. In addition, some rock samples show recoil losses whereas other samples from the same rock show actual gains of the same isotopes.

Schwarcz et al (1982) report on similar studies on eight unmineralised samples of granitic rocks from Canada. Preliminary semi-quantitative whole-rock samples have shown that some radioactive element migration on a scale of at least a few centimetres has occurred over the past few thousands to tens of thousands of years. They argue that these few results tend to raise some doubts about the short-term stability of crystalline rocks as storage media for nuclear waste disposal. This view is based on the idea that the solid to solution recoil-induced loss, and the subsequent migration or redistribution of certain isotopes leading to radioactive disequilibria, also signify transport of the chemical species in question from the host rock to the surficial environment. However, significant chemical transport of uranium, for example, may be expected only if the isotopic studies actually indicate a net shift of both ^{238}U and ^{234}U.

The overall conclusions suggested by the Björklund data is that rock/ water interaction processes, and therefore radioactive disequilibria, characterise most of the mineralised samples collected from fracture systems in a granite at depths of 100-130m. However, the physio-chemical environment at this depth has been, and probably still is, non-oxidative, as evidenced by uraninite which has remained chemically stable for most, if not all, of its 1750 m.y. existence, including the last 0.5 m.y. when it has been closest to the atmosphere (i.e. near the earth's surface). This could be taken to indicate that spent nuclear fuel, which is essentially crystalline UO_2, and comparable to uraninite once the main fission products have decayed, would also have been stable in this environment for similar periods of time.

ACKNOWLEDGEMENTS

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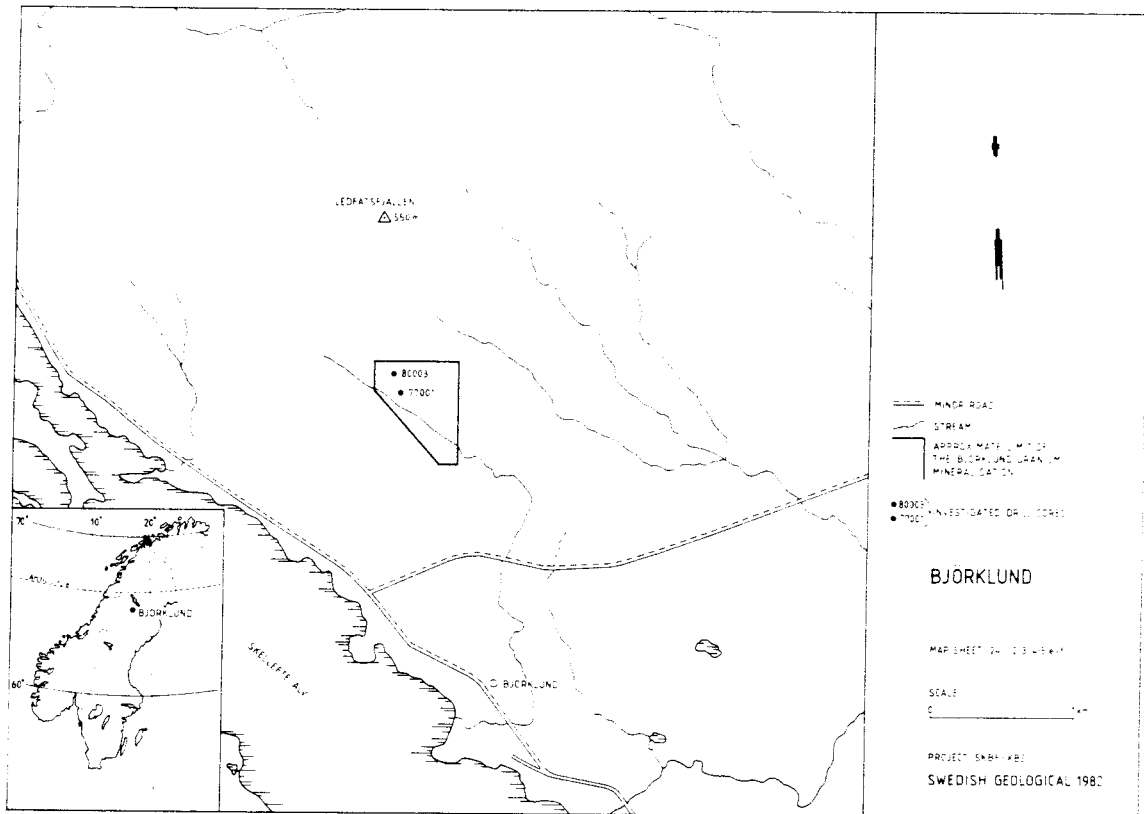
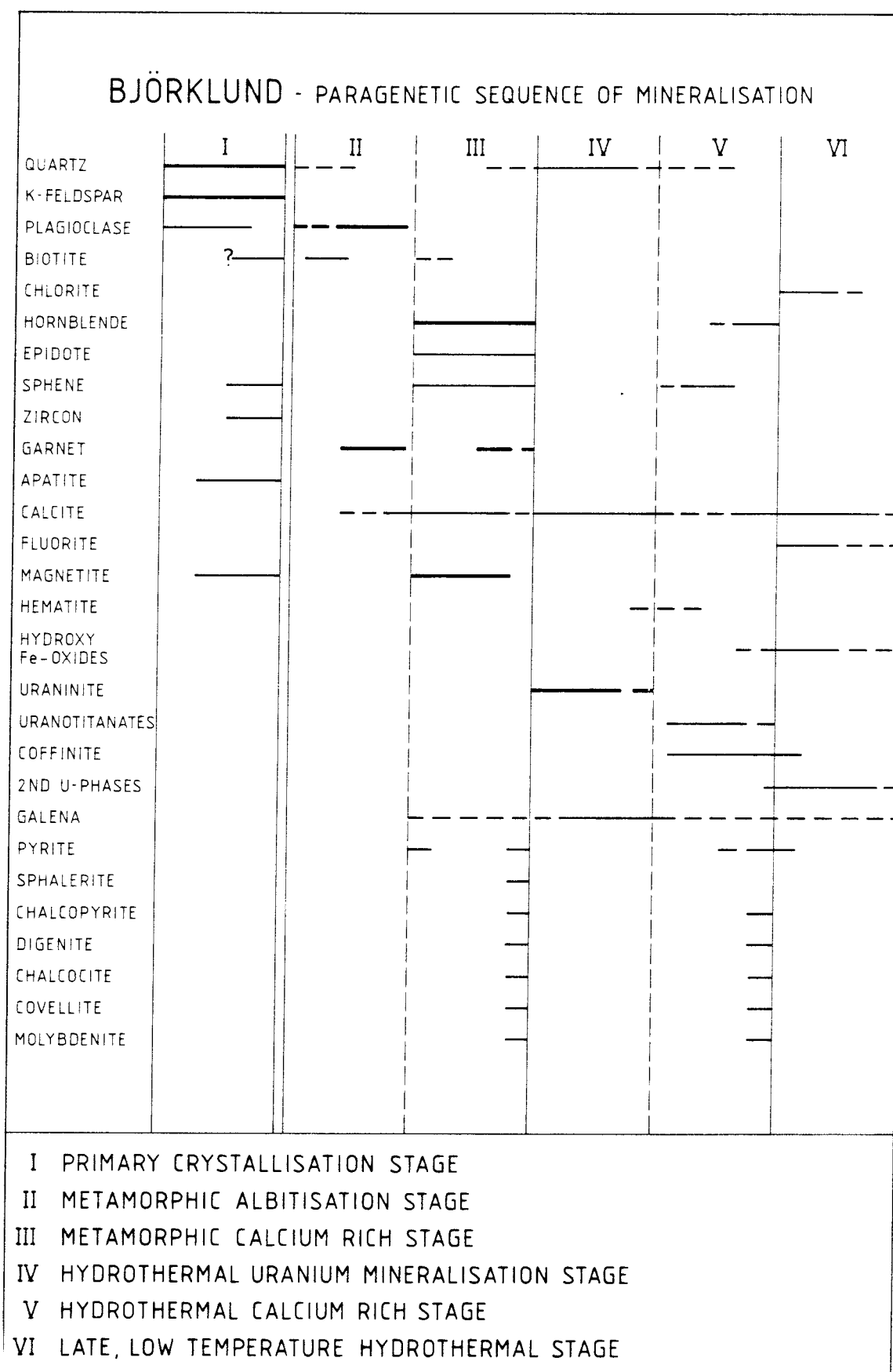Fig. 1 Map of the Björklund area showing location of the uranium mineralisation.

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BJÖRKLUND - PARAGENETIC SEQUENCE OF MINERALISATION

	I	II	III	IV	V	VI
QUARTZ						
K-FELDSPAR						
PLAGIOCLASE						
BIOTITE	?					
CHLORITE						
HORNBLENDE						
EPIDOTE						
SPHENE						
ZIRCON						
GARNET						
APATITE						
CALCITE						
FLUORITE						
MAGNETITE						
HEMATITE						
HYDROXY Fe-OXIDES						
URANINITE						
URANOTITANATES						
COFFINITE						
2ND U-PHASES						
GALENA						
PYRITE						
SPHALERITE						
CHALCOPYRITE						
DIGENITE						
CHALCOCITE						
COVELLITE						
MOLYBDENITE						

I   PRIMARY CRYSTALLISATION STAGE
II METAMORPHIC ALBITISATION STAGE
III METAMORPHIC CALCIUM RICH STAGE
IV HYDROTHERMAL URANIUM MINERALISATION STAGE
V   HYDROTHERMAL CALCIUM RICH STAGE
VI LATE, LOW TEMPERATURE HYDROTHERMAL STAGE

Fig. 2   Paragenetic sequence of mineralisation for the Björklund
uranium occurrence. Line thickness corresponds to abundance:
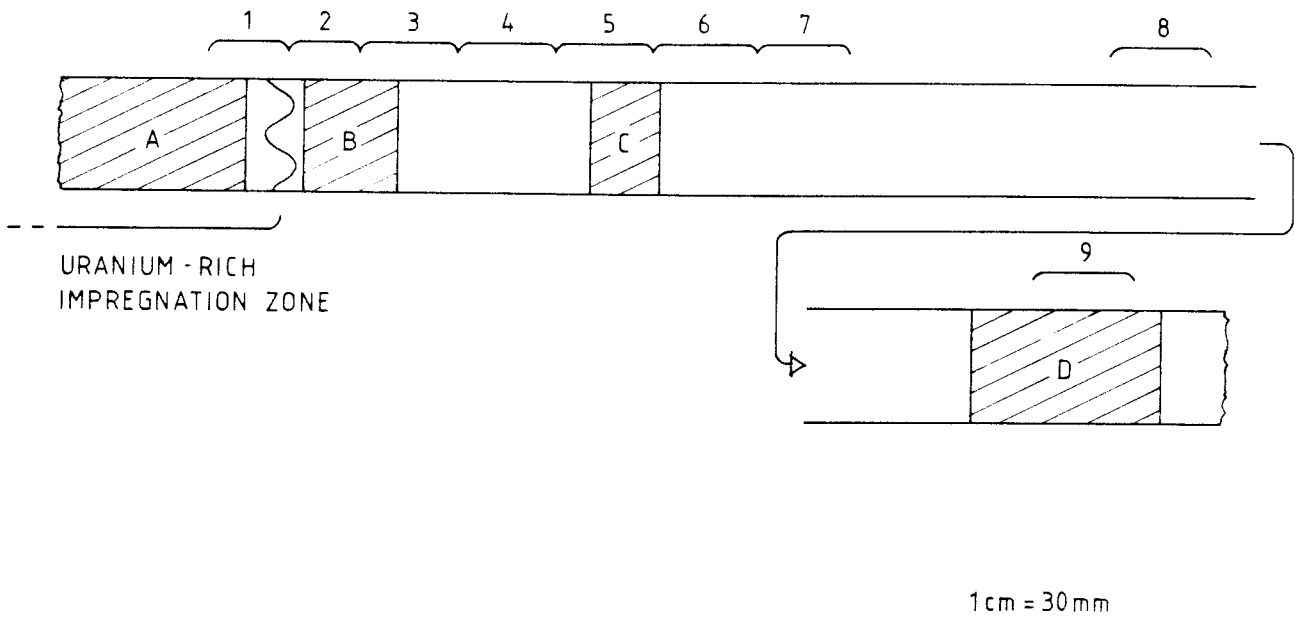broken lines indicate uncertain times of deposition.

1 cm = 30 mm

Fig. 3a Drill core 77001 showing location of analysed samples A to D
and thin section samples 77001:1 to 77001:9. Sample from
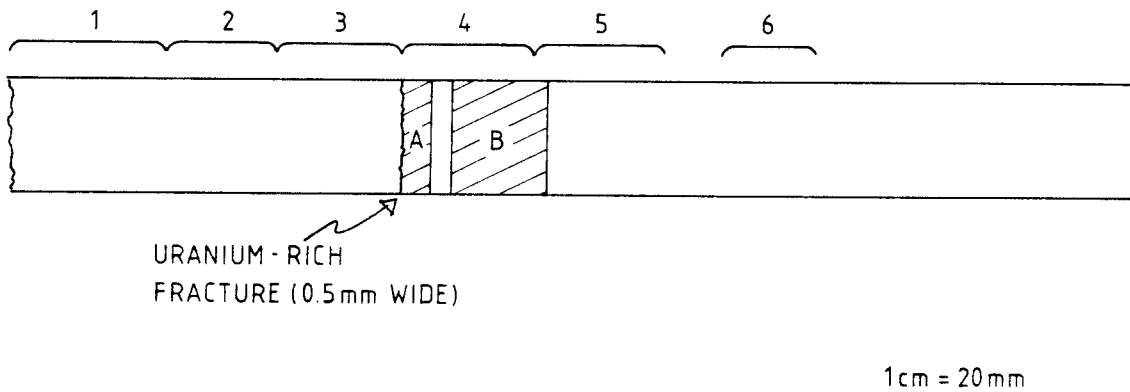approx. 100 m depth.

1 cm = 20 mm

Fig. 3b Drill core 80003 showing location of analysed samples A to B
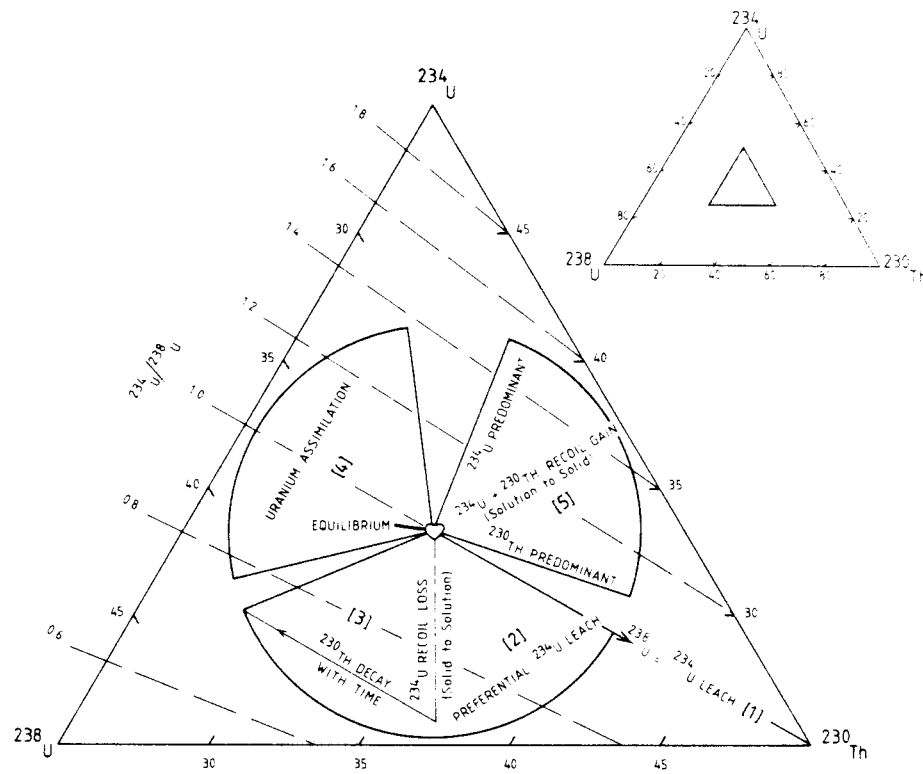and thin section samples 80003:1 to 80003:6. Sample from
approx. 128 m depth.

Fig. 4   Ternary diagram of percent relative activities of ^{238}U, ^{234}U and ^{230}Th showing selected lines of activity ratios of $^{234}U/^{238}U$ and areas of specific variations in isotopic fractionations (after Rosholt, 1982).
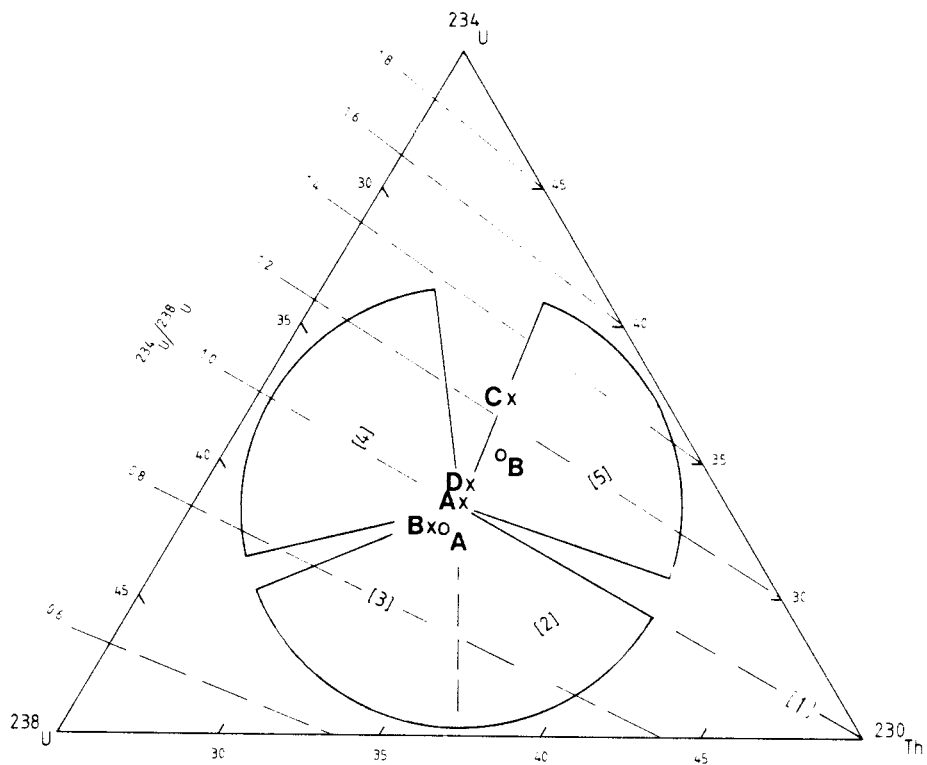
Fig. 5 Ternary diagram of relative activities of ^{238}U, ^{234}U and ^{230}Th in six samples from Björklund. Drill core 77001 is denoted by (X) and drill core 80003 by (0). Numbers 1 to 5 refer to the five geochemical processes producing radioactive disequilibrium illustrated in Fig. 4.

APPENDIX

Plate I a: Stage III amphibole, magnetite and epidote contained within
a fracture cross-cutting an albitised K-feldspar. Plane
polarised light.

b: Garnet I (Stage II) and II (Stage III) varieties showing
penetration and replacement of the rock fabric. Plane polarised
light.

c: Garnet I with subordinate garnet II. The dark fracture
infillings traversing the garnets are due to Stage IV uraninite
precipitation. Plane polarised light.

d: Intersecting microfractures within a K-feldspar crystal.
Infilling phases comprise Stage III magnetite and epidote
with subordinate amphibole and biotite. Plane polarised
light.

Plate IIa: Interstitial uraninite grains (U) within garnet I aggregates
(G). Note some replacement of uraninite to coffinite (C).
Reflected light under oil.

b: Uraninite aggregates (U) in association with Stage III epidote
(E). Within and peripheral to the uraninite is PbS (bright
white in colour) which may be partly   radiogenic. Marked
X on the photograph are areas containing finely dispersed
FeOOH oxides and small amounts of secondary uranium silicates.
Reflected light under oil.

c: Fracture/crush zone with uranium mineralisation (black)
confined to the intergranular matrix. Plane polarised light.

d: Fracture zone: note the fracturing of the rock fabric (mostly
quartz) now sealed by fine-grained recrystallised quartz. The
mineralised veinlets, together with some earlier Stage III
silicate phases, are mostly confined to a central crush zone.
Crossed polarisers.

Plate I

Plate II
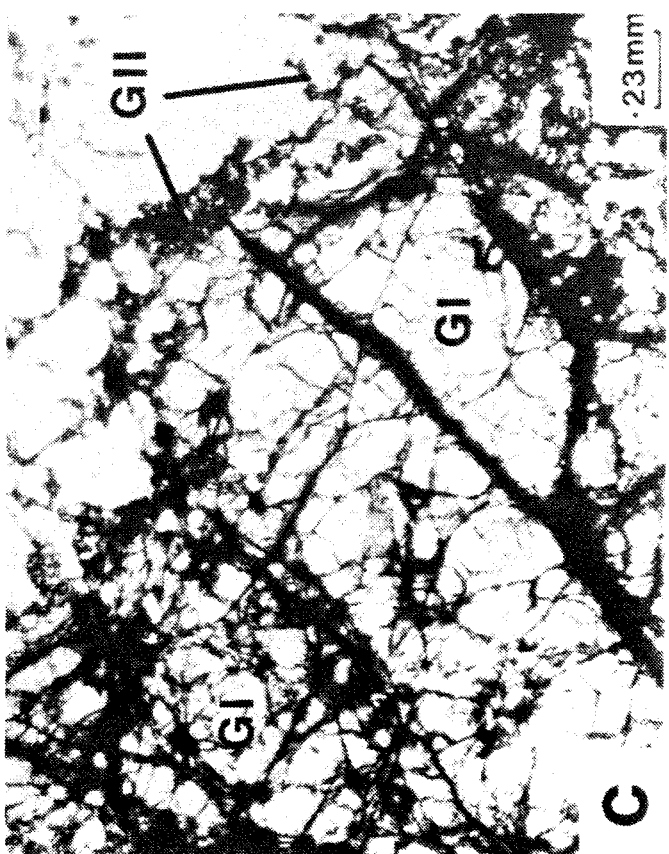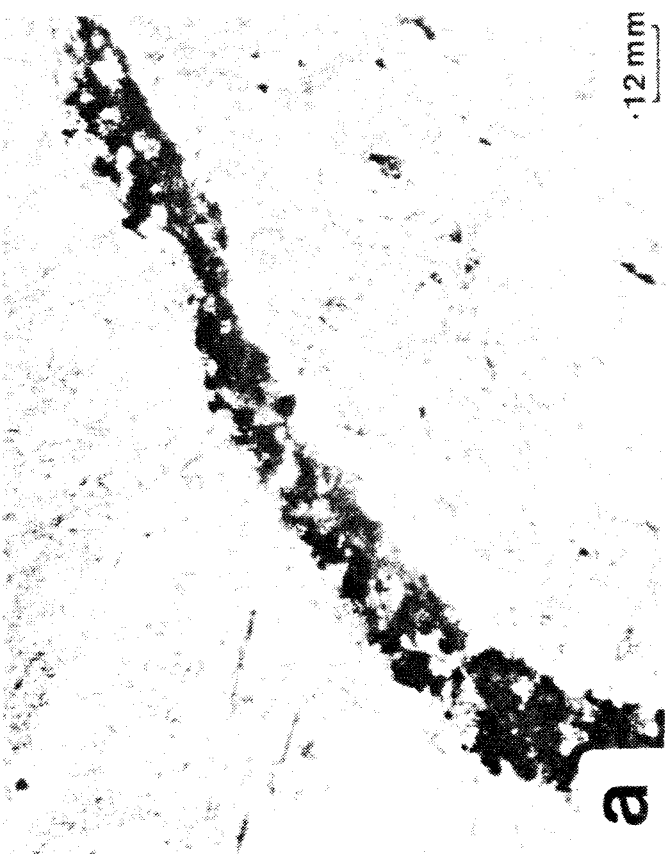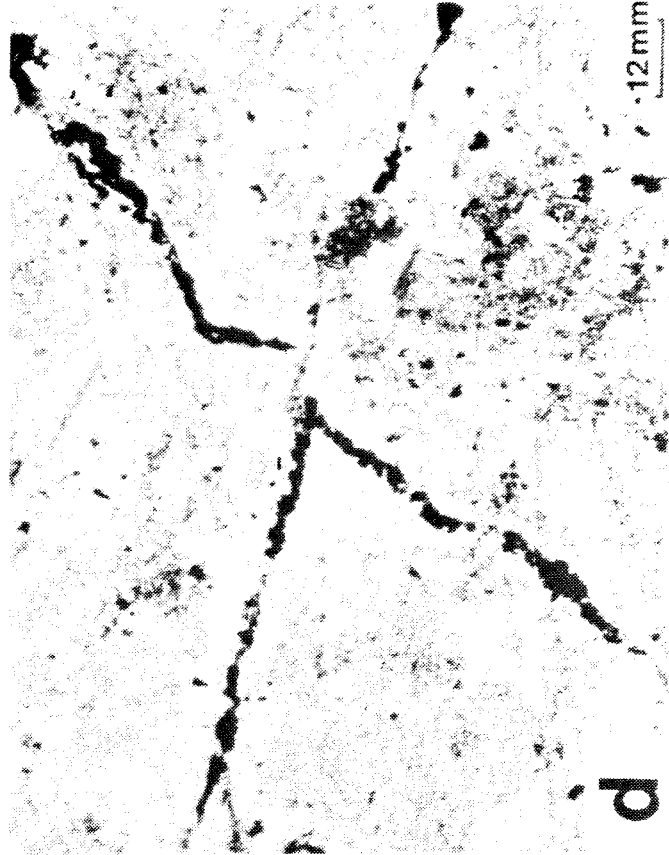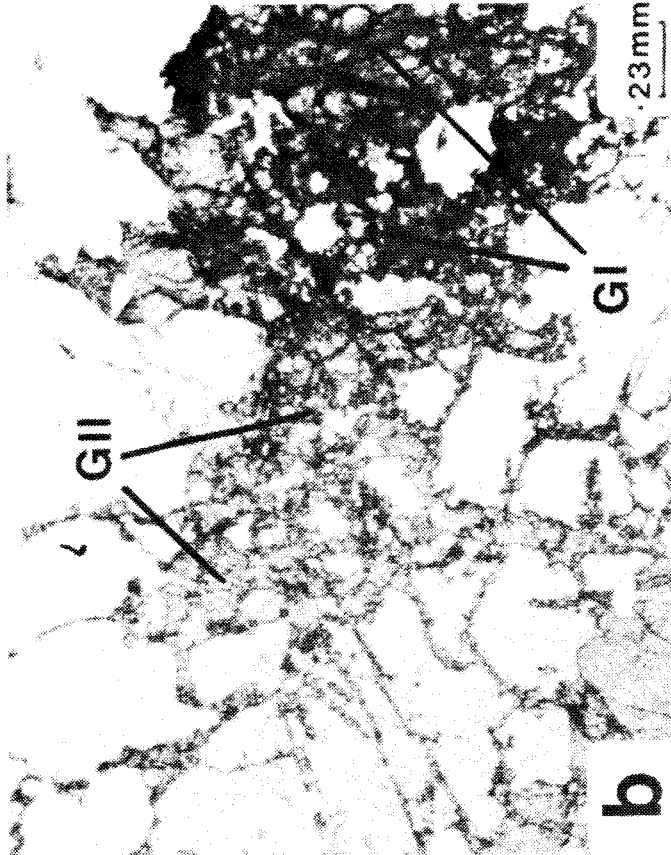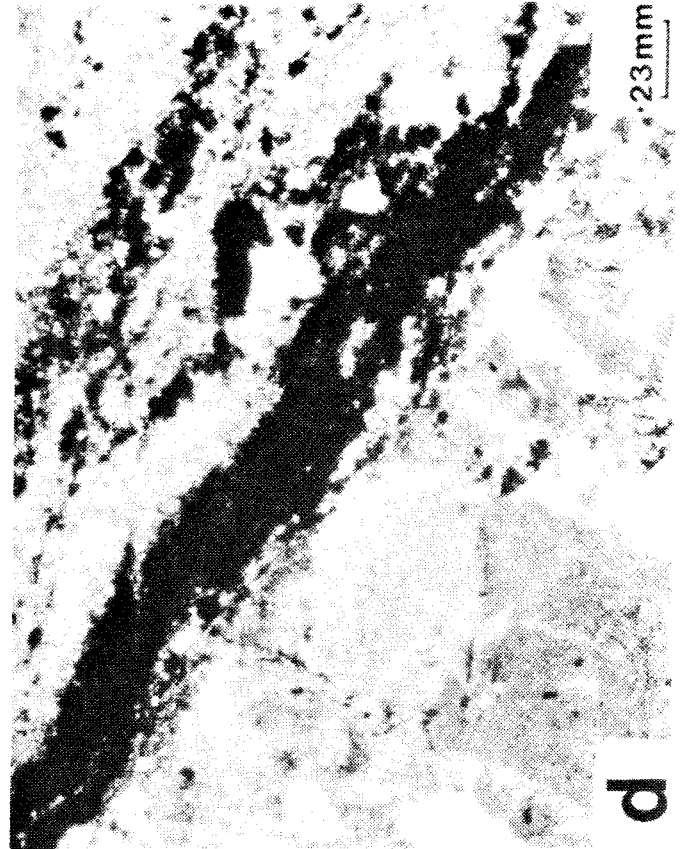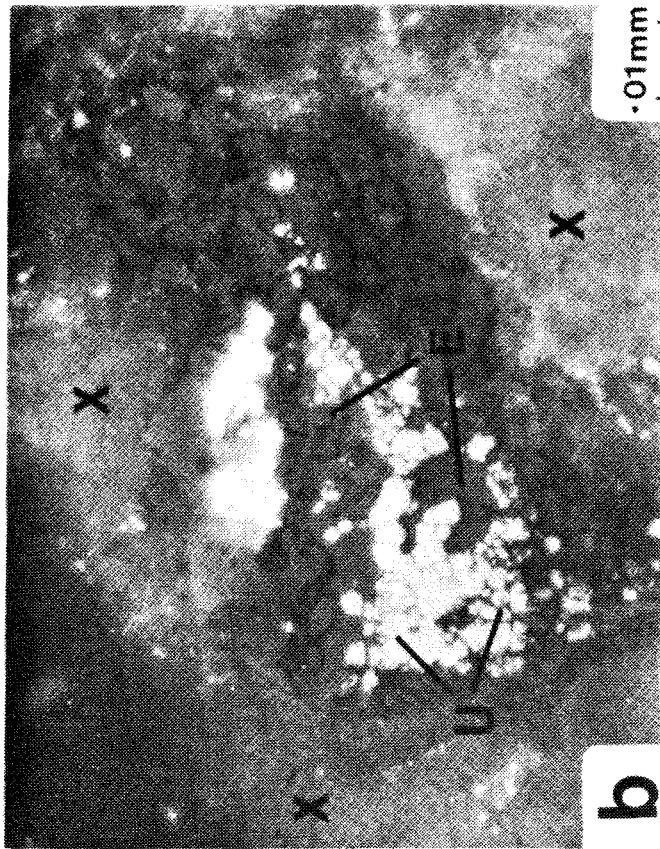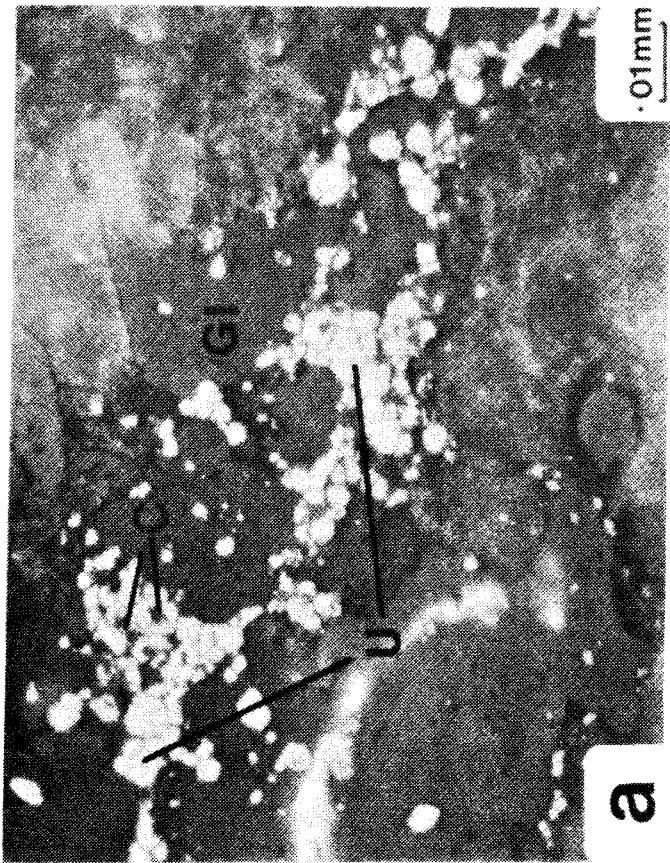
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