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REPORT**

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I: An analogue validation study of natural radionuclide migration in crystalline rock using uranium-series disequilibrium studies

II: A comparison of neutron activation and alpha spectroscopy analysis of thorium in crystalline rocks

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Part I
AN ANALOGUE VALIDATION STUDY OF NATURAL RADIONUCLIDE
MIGRATION IN CRYSTALLINE ROCK USING URANIUM-SERIES
DISEQUILIBRIUM STUDIES

Part II
A COMPARISON OF NEUTRON ACTIVATION AND ALPHA SPECTROSCOPY
ANALYSES OF THORIUM IN CRYSTALLINE ROCKS

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

A list of other reports published in this series during 1986 is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77), 1984 (TR 85-01) and 1985 (TR 85-20) is available through SKB.

Part I

AN ANALOGUE VALIDATION STUDY OF NATURAL RADIONUCLIDE MIGRATION IN
CRYSTALLINE ROCK USING URANIUM-SERIES DISEQUILIBRIUM STUDIES*

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Part II

A COMPARISON OF NEUTRON ACTIVATION AND ALPHA SPECTROSCOPY ANALYSES OF
THORIUM IN CRYSTALLINE ROCKS.**

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ABSTRACT

As part of a jointly-funded programme of research between the Swedish Nuclear Fuel and Waste Management Co (SKB) and the Swiss Nationale Genossenschaft für die Lagerung radioaktiver Abfälle (NAGRA), drillcore lengths intersecting suitable water-conducting fracture zones were chosen from three different hydrogeological environments; two in Switzerland

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(Böttstein and Grimsel) and one in Sweden (Kråkemåla), all located in granite bedrock. The samples represent profiles from the intersected fracture face into the bedrock. Sections cut from the profiles have been investigated using the uranium decay series ($^{238}\text{U} - ^{234}\text{U} - ^{230}\text{Th} - ^{226}\text{Ra}$), in conjunction with REE and $\text{Fe}^{2+}/\text{Fe}^{3+}$ analysis, alpha-track autoradiography, fission-track analysis and detailed mineralogy. The study has shown that radioactive disequilibria resulting from rock-water interactions were observed in two of the cores. These indicated uranium migration along distances of 40 cm or more on a timescale of 10^6 years in conjunction with thorium immobility under the same conditions. Fracture surface minerals showed a high affinity for radionuclide retardation and a limit of about 3 cm is suggested for the migration of radionuclides from fracture fluids into the saturated rock. This limit may correspond to enhanced matrix porosities resulting from earlier hydrothermal activity along the same channels.

The concentrations of Th in samples of crystalline rock from the three drillcore sections were analysed independently by instrumental neutron activation analysis and by chemical separation and alpha spectroscopy. The two methods show good general agreement over an approximate concentration range of 1 to 100 ppm Th. Variations in results between the two methods are not of a systematic nature and probably arise from sample heterogeneity. The results confirm the reliability of both methods and provide a useful comparison of the standards and reference materials used. The study indicates that, in cases where Th isotopic information is not required, the simpler and more rapid neutron activation analysis provides a satisfactory method.

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Part I

AN ANALOGUE VALIDATION STUDY OF NATURAL RADIONUCLIDE MIGRATION IN CRYSTALLINE ROCKS USING URANIUM-SERIES DISEQUILIBRIUM STUDIES.

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Concentrations and isotope ratios of natural decay series radionuclides have been studied in three contrasting crystalline rock drillcore sections intersecting water-conducting fractures deep in the bedrock. Radioactive disequilibria resulting from rock-water interactions were observed in two of the cores. These indicated uranium migration along distances of 40 cm or more on a timescale of 10^6 years in conjunction with thorium immobility under the same conditions. Fracture surface minerals showed a high affinity for radionuclide retardation and a limit of about 3 cm is suggested for the migration of radionuclides from fracture fluids into the saturated rock. This limit may correspond to enhanced matrix porosities resulting from earlier hydrothermal activity along the same channels.

INTRODUCTION

Safety assessment evaluations for the disposal of high-level radioactive waste characteristically assume a "worst case" situation. This usually means that progressive corrosion of the spent fuel metal container will occur, resulting in a slow release of radionuclide material into circulating meteoric waters present within the surrounding bedrock repository. It is highly probable that crystalline rocks at repository depths will be fractured, even prior to excavation, and that fracture permeability will be the dominant mode of flow. Thus, based on the premise that a cumulative failure

of the near-field engineered barriers will occur, far-field retardation processes in the geosphere would appear to be qualitatively the most important factor in controlling releases of radionuclides to the biosphere.

During far-field radionuclide transport along hydraulically connected fracture systems, radionuclides in solution will be subject to retardation mechanisms such as reversible and irreversible sorption onto fracture and fissure mineral coating phases. In addition, radionuclide diffusion into a water-saturated rock matrix could be an important retardation factor. To date, much of the work and model derivation involving radionuclide migration has been experimentally based. An obvious means of validating the experimental data is to examine naturally occurring radionuclide migration (or lack of migration) within the bedrock environment of the chosen repository. Such an analogue study allows, most importantly, an appraisal of migration on the scale of geological time.

Naturally occurring uranium and thorium are of particular interest in radioactive waste disposal since they represent useful analogues of the actinides. Furthermore, the daughter nuclides in the ^{238}U and ^{232}Th decay chains show ranges of chemical properties and half-lives such that the degree of equilibrium between parent-daughter pairs can be used to provide information about rock-water interactions. Such studies can indicate the degree of radionuclide mobility and can provide information on the rates of processes occurring over time intervals of up to 1 Ma.

As part of a jointly-funded programme of research between the Swedish Nuclear Fuel and Waste Management Co. (SKB) and the Swiss Nationale Genossenschaft für die Lagerung radioaktiver Abfälle (NAGRA), drillcore lengths intersecting suitable water-conducting fracture zones were chosen from three different hydrogeological environments; two in Switzerland (Böttstein and Grimsel) and one in Sweden (Kråkemåla), all located in granite bedrock.

The samples represent profiles from the intersected fracture face into the bedrock. Sections cut from the profiles have been investigated using the uranium decay series ($^{238}\text{U} - ^{234}\text{U} - ^{230}\text{Th} - ^{226}\text{Ra}$), in conjunction with REE and $\text{Fe}^{2+}/\text{Fe}^{3+}$ analysis, alpha-track autoradiography, fission-track analysis and detailed mineralogy.

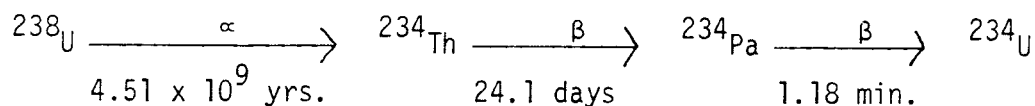
To the extent that the uranium-series disequilibrium is a product of rock-water interaction, these measurements may help to evaluate the effective addition or removal of uranium within the near vicinity of an open, water-bearing fracture zone. Evidence of such a migration profile occurring into the bedrock under ambient temperatures, should lend or detract support to models involving far-field radionuclide retardation processes.

URANIUM-SERIES DISEQUILIBRIUM IN ROCKS

Studies of the uranium decay series have now become a fairly standard investigative method within the field of geochemistry. Pioneered by Cherdynstev (e.g. 1955, 1971) the methods have been subsequently improved and applied by many workers to a wide range of geological environments and their related problems; see, for example, Rosholt (1959, 1983), Thurber (1962), Rosholt et al. (1963, 1966), Koide and Goldberg (1965), Kighoshi (1971), Kronfeld (1974), Osmond and Cowart (1976, 1972) and Fleischer and Raabe (1978).

In closed geological systems the nuclides $^{238}\text{U} - ^{234}\text{U} - ^{230}\text{Th}$ attain radioactive equilibrium after about 1.7 Ma, i.e. the respective activity ratios $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ all equal unity. However, if the systems are exposed to weathering and groundwater circulation, and assuming that ^{230}Th is immobile under normal groundwater conditions (Langmuir and Herman, 1980), the different physico-chemical conditions affecting ^{238}U and ^{234}U will result in their fractionation and thus isotopic disequilibrium. The respective activity ratios will therefore be greater or less than unity depending on whether there is an excess or deficiency of ^{238}U and/or ^{234}U .

Fractionation of ^{234}U and ^{238}U arises from the radiogenically produced ^{234}U daughter which originates through the three-step alpha and beta decay from its ^{238}U parent:



In general, the isotopic variation of uranium has been recognized as being produced by two mechanisms: (1) selective leaching of ^{234}U itself, (2) the direct alpha recoil transfer of a ^{234}U precursor (i.e. ^{234}Th), and a combination of these processes. For selective leaching to occur, ^{234}U atoms must be more susceptible to leaching and removal than ^{238}U atoms. This is facilitated by lattice damage resulting from the radioactive decay of ^{238}U . The resultant daughter atoms will be located in weakly bonded or interstitial sites, and oxidation of the daughter (i.e. ^{234}U) to the 6+ valency state as a result of the recoil within the lattice, will render it more vulnerable to removal by water. Direct alpha recoil of ^{234}Th can occur from near the surface of a mineral grain into the intergranular pore water, whereupon it is trapped and further decays to ^{234}U . This results in the enrichment of ^{234}U in water and a ^{234}U depletion in the mineral (i.e. solid to solution ^{234}U recoil gain). An additional mechanism recognizes the process of daughter product emplacement from pore waters containing dissolved ^{238}U and ^{234}U . Subsequent decay of these radionuclides results in the recoiling nuclides of ^{230}Th , ^{234}Th , ^{234}Pa and ^{234}U being absorbed or embedded in particulate matter at the solid-liquid interface. After sufficient geological time, this mechanism results in solids which are enriched in ^{234}U and ^{230}Th relative to ^{238}U (i.e. solution to solid $^{234}\text{U} + ^{230}\text{Th}$ recoil gain).

For crystalline rocks, such as these described in this paper, the uranium decay system has been used as a sensitive indicator of recent uranium

mobility (Zielinski et al., 1981; Schwartz et al., 1982; Rosholt, 1983; Gascoyne, 1983; Smellie and Rosholt, 1984). How recently this migration has occurred is determined from the half-life of the nuclide involved. In this present study the nuclides ^{238}U , ^{234}U , ^{230}Th and ^{226}Ra have been measured. Using the daughter/parent activity ratios $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{226}\text{Ra}/^{230}\text{Th}$, radionuclide migration over timescales of 1 million years, 300 000 years and 8 000 years respectively, can be evaluated.

SAMPLE SELECTION AND ANALYSIS

Drillcore lengths of 40 - 55 cm were chosen from the respective areas; these varied in diameter from 56 mm (Swedish sample) to 76 mm (Swiss samples). A thin rock slice was removed along the drillcore length for mineralogical and fission-track studies. A portion of the core was retained for reference and the remainder was sawn (Swiss samples) or cleaved (Swedish sample) into approximately 1 cm thick slices for analysis. The mineral coatings scraped from the inside surface of the fracture zone constituted another sample.

For uranium-series measurements samples of the powdered granite were spiked with ^{232}U in equilibrium with ^{228}Th and then digested with aqua regia and hydrofluoric acid and the small residue of insoluble material was further digested with nitric and hydrofluoric acids in a Parr high pressure digestion bomb. This process was repeated if necessary until the residue totally dissolved in 6 M hydrochloric acid. Uranium and thorium were recovered from half of the combined acid leachings by anion exchange techniques (Bacon and Rosholt, 1982) and were then electrodeposited onto stainless steel planchettes for alpha spectrometry measurements using silicon surface barrier detectors. The precision of the results is better than $\pm 4\%$ for the $^{234}\text{U}/^{238}\text{U}$ activity ratios, better than $\pm 7\%$ for the $^{230}\text{Th}/^{234}\text{U}$ and $^{230}\text{Th}/^{232}\text{Th}$ activity ratios and $\pm 15\%$ for the $^{226}\text{Ra}/^{230}\text{Th}$ activity ratio.

^{226}Ra analyses were initially attempted on the remaining half of the acid leaching solution by the standard technique of collection and alpha counting of the daughter ^{222}Ra (Scott and MacKenzie, 1984; Scott and MacKenzie, 1985). Since there is no spike available to act as a yield tracer in this method, the process depends upon 100% transfer of ^{226}Ra to the radon emanation vessel. Replicate analyses and analyses of samples to which a known quantity of ^{226}Ra was added indicated that the above condition was not being satisfied and that loss of ^{226}Ra was occurring before transfer to the emanation vessel. No satisfactory explanation is at present available for this loss but attempts at ^{226}Ra analysis by this method were abandoned in favour of direct counting of the 609 keV peak in the gamma spectrum of ^{226}Ra decay products in a subsample of the untreated powdered granite. This peak, produced by ^{214}Bi decay, can only be used if ^{222}Rn does not escape to any significant extent from the sample and initial results appear to justify this assumption.

REE and total Fe analysis were carried out on 0.1 g samples using instrumental neutron activation analysis (INAA). This involved a six hour irradiation in a thermal neutron flux of 3×10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. Gamma counting using co-axial and planar Ge (Li) detectors was performed at approximately 3 days and 3 weeks after irradiation (MacKenzie et al. 1983). Fe^{2+} was analysed using standard wet chemical techniques and fission-track distributions from polished thin sections of the granite were recorded on polycarbonate by thermal neutron irradiation (MacKenzie et al., 1984).

GEOLOGICAL SETTING AND MINERALOGY OF THE DRILLCORES

Kråkemåla Drillcore (K1: 317.85-318.40 metres)

The Kråkemåla specimen was selected at a depth of approximately 318 m from one of three test holes drilled in the Götömar granite, located along

the south-eastern coast of Sweden. The Kråkemåla area within the Göttemar granite has been the focus of geological investigations as part of an earlier programme concerning feasibility studies for the disposal of radioactive waste material in crystalline rocks (Scherman et al. 1977). The geology, geochemistry and geochronology of the Göttemar granite has been previously described by Kresten and Chyssler (1976), Åberg (1978) and Smellie and Stuckless (1985).

The sample location level is characterized by the coarse-grained granite variety which is macroscopically homogeneous. The chosen core is traversed by a single, open fracture zone at 45° to the vertical drillcore length; from geophysical logging investigations (Magnusson and Duran, 1982) the fracture zone is considered water-bearing. This is partly supported by fracture plane coatings of hematite and FeOOH-oxides. In addition, the feldspathic content marginal to the fracture zone shows evidence of alteration extending to 2-3 cm from the fracture plane.

The drillcore is representative of the Göttemar coarse-grained granite and is macroscopically homogeneous. At greater resolution the rock is mineralogically variable consisting primarily of quartz (15-45 vol. %), plagioclase (30-42 vol. %) and potash feldspar (30-50 vol. %) with subordinate biotite, muscovite and chlorite. The plagioclase (An < 10%) occurs mostly as euhedral to subhedral laths, as a matrix constituent, and included in potash feldspar. Accessory minerals include interstitial amounts of magnetite, apatite, zircon, fluorite, sphene and monazite; isolated grains of galena, pyrite, and more rarely molybdenite, also occur. The non-sulphide accessory phases usually occur as intergranular aggregates sporadically dispersed throughout the rock, resulting in considerable inhomogeneity on the scale of a thin section.

Throughout the length of the drillcore sample the granite is weakly but uniformly altered; this is generally typical to the depths of maximum

drilling in the massif (Smellie and Stuckless, 1985). In most sections the partial breakdown of the feldspars to muscovite/sericite with minor quartz occurs. Magnetite sporadically shows limited alteration to hematite, or partial to complete pseudomorphing by chlorite. Biotite is sometimes partly altered to chlorite, and muscovite, normally clear and unaltered, has occasionally altered to chlorite and less frequently to epidote and opaque phases (mostly Fe-Ti-oxides).

The fractured area occupies a width of about 1 cm and is composed of a series of parallel to sub-parallel micro-fissures easily distinguished by FeOOH-oxide coatings. The central and largest fracture (max. 1.5 mm wide) is also partly infilled with hematite and subordinate chlorite. Macroscopically the influence of the fracture zone extends up to 2 cm into the host granite. This is apparent as FeOOH-oxide dustings present both interstitially within the rock matrix and included within altered to partly altered potash feldspar phases; biotite and magnetite are also more markedly altered to chlorite and hematite respectively.

Böttstein Drillcore (BOE: 618.34-618.70 metres)

The Böttstein area is located in central northern Switzerland about 30 km north-west of Zurich and 5 km from the German border. Investigations carried out by NAGRA began in October 1982 and are still in progress. A major part of this work has involved the drilling of a deep borehole to some 1500 metres: the fracture sample selected for this study has been taken from approximately 618 m depth. The geology, geochemistry and geochronology of the intercepted granite, which forms part of a much wider complex, are summarised by NAGRA (Technical Reports: 84-25; 85-01). Essentially two hydrothermal events affected the granite: an early stage coeval with granite emplacement which occurred some 300 Ma ago, and a later (Permian ?) event which resulted in alteration along fracture and fault zones.

Drilling in the area encountered the crystalline basement at a depth of approximately 300 metres. Down to the final depth of 1501 metres the core consisted of the Böttstein granite. This granite is typically coarse-grained, rich in biotite, and porphyritic in texture accompanied by large phenocrysts of potash feldspar. The chosen drillcore section was selected from a fracture intersection which was suspected as being water-conducting. The fracture was located near the contact between the granite and thin intruded horizons of pegmatite (up to 40 cm wide) and aplite (up to 1.5 m wide); the fracture occurs in the pegmatite only a few centimetres from the granite contact. Intersection of the fracture with the core axis is 37° and its water-conducting properties were indicated by its open character and idiomorphic quartz fillings. Fluid logging identified a major water inflow between 618-621 m, a zone which comprises a potentially water-conducting kakirite horizon. Intersection between these two horizons at a short distance from the borehole is suspected as both exhibit similar dips combined with strikes perpendicular to each other.

The selected drillcore length investigated consists of about 7 cm of pegmatite in contact with 13 cm of biotite-rich granite which is representative of the Böttstein porphyritic granite variety; the granite at the pegmatite contact has been hydrothermally altered to the extent of some 8 cm. In terms of average modal content (vol. %), the granite comprises 27% quartz, 26% plagioclase, 38% potash feldspar and 8% biotite. The potash feldspar, which is seen as large phenocrysts in hand specimen, is perthitic in thin section and the plagioclase is normally zoned with a core of oligoclase (An 12-20) and a rim of albite. Some late magmatic muscovite has formed from the breakdown of potash feldspar and biotite, and pseudomorphs of pinite after cordierite are common. Apatite and zircon are the most frequent accessories present.

The pegmatite containing the fracture zone is fresh, coarse-grained, and consists of quartz, potash feldspar and albite, together with muscovite and tourmaline. Regarding the fracture faces, the dominant mineral phases

are calcite, fine-grained quartz and clays (mostly interlayerings of illite and smectite) and sporadic apatite. Hydrothermal alteration of the granite extends for some 8 cm from the pegmatite contact. This is characterised by strong argillisation with illite/smectite as the dominant alteration phases; some calcite is contained in potash feldspar and finely dispersed FeOOH-oxides give the rock a reddish tinge. A sealed fissure (0.5 - 2.0 mm wide) containing some calcite and clay minerals occurs at 8 cm and thereafter the granite is less altered (although the feldspars are still pigmented with iron-oxide) and the biotite content is higher. The granite contains two zones approximately 4 cm wide characterised by an increased mafic content. One of these zones constitutes the contact area with the pegmatite, and the other is located some 8 cm from the contact.

Grimsel Drillcore (FLG: 94.12-94.52 metres)

The Grimsel area is located near the Grimsel Pass situated in central south Switzerland some 15-20 km from the Italian border. The site, which now constitutes the NAGRA underground test laboratory, was initially developed as an underground hydroelectric power scheme which had tunneled through the Juchlistock mountain chain. In 1979 an exploratory drilling programme was started by NAGRA which was completed in 1984. The drillcore sample investigated was selected from a near-horizontal exploration borehole (SB 80.001: 94.12-94.52 m) drilled into the bedrock from the access tunnel to the power station: the altitude of the borehole level is 1730 metres.

The geology of the region is summarised in recent NAGRA publications (NTB 81-07; 85-34). The Aar massif of Hercynian age dominates the area; it is aligned in a SW - NE direction with a maximum extension of 115 km and a width of 23 km. This massif, which is the largest in the Swiss Alps, is surrounded by metasediments (mostly schists) and is itself mainly composed of plutonic rocks of granitic/granodioritic composition. These granitoid bodies were intruded during the Hercynian orogeny (approx. 280 Ma). The Eastern

granite was probably early Hercynian (located to the NW) and this was later followed by the Grimsel granite/granodiorite. The test site is located within the Central Aar granite which is thought to be late Hercynian. Soon after emplacement these granitoids were intruded first by aplitic dykes, and then by a variety of mafic lamprophyres. The interfaces between these latter dykes and the Aar granite mainly control the groundwater conductive system in the bedrock (Ohse, 1983).

The granite is typically grey-coloured, fresh, mineralogically homogeneous in hand specimen, and medium- to coarse-grained in texture; the granite is also characteristically gneissose. The chosen fracture is fresh and intersects the core axis at 40° ; no alteration on a macro scale was observed and there was no evidence of any fracture filling minerals. Its water-conducting properties are suspected on the basis of a large release of groundwater encountered while penetrating the fracture zone during drilling. This initially resulted in a flow of about 24 l/min which subsequently decreased to a steady rate around 2 l/min. However, the selected fracture was only one of several present over a short distance (frequency of fracturing in this part of the core is 10 fractures/metre). The age of these fractures is uncertain, at least late Alpine to recent; the area is still considered tectonically unstable and the continuous formation of new fractures/joints cannot be excluded.

Petrographical and mineralogical descriptions of the Grimsel area are given by Stalder (1964). The average modal content of the granite core (expressed in vol.%) is 33% quartz, 34% potash feldspar, 21% plagioclase, 7% biotite/chlorite, 1-2% muscovite, 1% hornblende and 2% epidote. The associated accessory phases are sphene, orthite, apatite, zircon, calcite and opaques. The feldspars have undergone some alteration to sericite, and the biotite to chlorite; magnetite is partly oxidised. These alterations are products of the complex metamorphic history of the area and should not be

considered as due to low temperature rock/water reactions during recent geological times.

CHEMISTRY OF THE DRILLCORES

Kråkemåla Drillcore

The drillcore contents and distributions of uranium and its daughter decay products, iron and the rare-earth elements (REE), La and Ce are listed in Table 1 and illustrated in Figure 1. Other elements analysed but not illustrated include Na, K, Sc, Rb, Cs, Ta and the remaining REE.

The uranium contents range from 12.51 to 23.26 ppm (mean 15.67 ppm) and the thorium from 46.37 to 89.42 ppm (mean 67.04 ppm); the mean Th/U ratio is 4.38. These uranium and thorium values, which are roughly in agreement with the average values from the granite as a whole (Smellie and Stuckless, 1985), are still anomalously high when compared to either the average contents for worldwide granites (Rogers and Adams, 1969 a, b) or a compilation of 2,500 granites mainly from the U.S.A. (Stuckless and Van Trump, 1982). Furthermore, in crustal rocks the average Th/U ratio is 3.5 (Rogers and Adams, 1969), i.e. thorium concentrations usually correlate with uranium by a factor of 3. Thus the high Th/U ratio recorded from the Götömar granite would suggest a general removal of uranium, which has also been demonstrated isotopically by Smellie and Stuckless (1985).

From fission-track studies of the Götömar granite (Kresten and Chyssler, 1976; Smellie and Stuckless, 1985) most of the uranium is associated with zircon and monazite with subordinate amounts contained in sphene, magnetite, hematite, and ilmenorutile-type phases. Small amounts are also associated with sericite, epidote and FeOOH-oxide dispersions. Although no data are available for minor thorium, the distribution of monazite, which can contain up to 10 wt.% Th and perhaps as high as 26 wt.% Th (Fronde! et al. 1967), almost certainly controls the thorium distributions in the Götömar granite.

The distribution of uranium and thorium along the drillcore from the fracture zone is shown in Figure 1. Apart from the fracture face which indicates an increase, the uranium content is fairly uniform for a distance of some 8 cm into the granite until a broad peak occurs over a length of 4 cm. In comparison, thorium indicates an antipathetic decrease at the fracture face, and then shows an extremely irregular fluctuation until it too forms a broad peak sympathetic to that observed for uranium.

On the basis of mineralogy, the known geochemical behaviour of uranium and thorium, and the similarity of the Th profile with those of the rare-earth elements (discussed below), these profiles suggest that thorium has remained relatively immobile throughout the history of the granite, and its irregular distribution thus reflects the irregular distribution of the dominant Th-bearing mineral phase, monazite, which is of primary origin. As the first sample represents fracture-surface scrapings of mostly hematite, chlorite, clay minerals and FeOOH-oxides, the lower thorium value recorded here is perhaps not so surprising. With regards to uranium, which in comparison is easily mobilized and leached from granite provided the system has been open to fluid movement, Figure 1 shows some interesting features. If the granite had remained a closed chemical system since crystallisation, then most of the uranium would be associated with primary resistate radioactive minerals (often together with thorium and REE) with more minor amounts along intergranular boundaries (Tieh et al., 1980). For the case in question therefore, the distribution of major uranium would be expected to be sympathetic to thorium which in turn would be a reflection of the monazite content in the rock, as suggested above. In fact there is a sympathetic increase in uranium and thorium from approximately 8 to 13 cm along the drillcore which shows that this part of the rock has probably retained its original uranium and thorium signature, although the intergranular labile uranium has almost certainly been removed. In contrast, the absence of any sympathetic uranium/thorium relationship within the initial

8 cm of the drillcore indicates that uranium has at some stage been leached from even the more resistate radioactive mineral phases possibly during some hydrothermal event, the suggestion of such a process being supported mineralogically by the partial alteration of monazite along this part of the core. However, uranium removal is not indicated from the fracture surface sample which instead shows a marked increase. This suggests that in the groundwater/fracture system uranium accumulation rather than leaching is taking place.

Similar marginal increases in uranium have been reported in altered and fractured samples of granite from the Eye-Dashwa Lakes pluton, Ontario (Kamineni, 1985) which has been interpreted as preferential sorption or co-precipitation of uranium with hematite.

Uranium-series disequilibrium

Plots of the activity ratios $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{226}\text{Ra}/^{230}\text{Th}$ are presented in Figure 1. The $^{234}\text{U}/^{238}\text{U}$ ratios indicate general disequilibrium within a 2σ analytical error, with values ranging from a maximum of 2.29 at the fracture surface to a mean value of 0.86 for the major length of the drillcore. In contrast, most of the $^{230}\text{Th}/^{234}\text{U}$ and $^{226}\text{Ra}/^{230}\text{Th}$ ratios lie within 2σ of secular equilibrium.

Considering the major length of the drillcore (i.e. excluding the fracture edge) the isotope data show depletions of both ^{234}U and ^{230}Th relative to ^{238}U . This indicates a significant ^{234}U loss (most likely by recoil processes) with little ^{238}U loss, followed by a re-equilibration of the ^{230}Th daughter with ^{234}U . In other words, throughout the granite represented by these samples, the loss of ^{234}U (probably continuous) has been occurring over at least one million years by solid to solution alpha-recoil processes.

In strong contrast, the granite marginal to the fracture zone is characterised by enrichments of all four isotopes (Table 1); these fall off rapidly over a distance of 1-3 cm into the granite. The $^{234}\text{U}/^{238}\text{U}$ ratios indicate an

accumulation of ^{234}U which must be occurring sufficiently rapidly to prevent re-equilibration of the ^{230}Th daughter with ^{234}U ; this would account for the overall isotopic disequilibrium observed between ^{234}U and ^{230}Th in the three samples comprising the marginal zone to the fracture.

The question now arises as to whether these observed isotopic values at the fracture/groundwater interface zone are due to continuous isotopic movement from the granite to the interface zone, followed by subsequent sorption and/or isotopic fractionation onto the fracture minerals or, if these isotopic products have been introduced from the groundwaters to the fracture face by direct sorption or through daughter emplacement processes (i.e. solution to solid $^{234}\text{U} + ^{230}\text{Th}$ recoil gain) as suggested by Rosholt (1983). Unfortunately it is not possible to say if one or a combination of these two processes is responsible. In any case it underlines the importance of the physico-chemical properties of the fracture minerals in radionuclide retardation processes. The work of Airey (1985) clearly illustrates that the subsequent immobility of the radionuclides after up-take from solution will largely depend on the isotopic fractionation between the fracture zone minerals. It was shown that uranium and thorium tend to concentrate principally on the iron phases, whilst radium seems to be more often in association with the clay/quartz fraction where its activity exceeds that of its parent thorium. Furthermore, radionuclides taken up by crystalline iron phases such as goethite are believed to be inaccessible to removal by solution. Work by Kamineni (1985) also records the importance of goethite to explain enrichments of thorium along fractured zones located in the Eye-Dasha pluton, Ontario.

Unfortunately, from Kråkemåla there is no isotopic analysis of the groundwater in contact with the fracture zone that might indicate which uranium daughters are being removed from or added to the solid fracture surfaces. Groundwaters at the depth of the drillcore sample (approximately 318 m) should be reducing in character. According to secondary uranium accumulation processes

as discussed by Osmond et al. (1983), the isotopic data from the fracture/groundwater interface sample indicates a position furthest down-flow whereupon the groundwater is strongly reducing and ^{234}U exceeds ^{238}U , as does ^{230}Th , its in-grown daughter. It would appear reasonable to assume, therefore, that the groundwaters at a depth of around 350-400 m at Kråkemåla are characterised by an excess of ^{234}U and are strongly reducing. Along the fracture surfaces sorption and/or co-precipitation of ^{234}U with iron oxides is taking place; solution to solid $^{234}\text{U} + ^{230}\text{Th}$ recoil gain processes may also be contributing. The continuous loss of ^{234}U suggested from the overall length of the drillcore indicates that there is also some radionuclide movement from the fracture edge to the groundwater. The degree of radionuclide retardation and retention from both processes will be dependent on the physico-chemical properties of the fracture zone minerals, which consist mostly of hematite, chlorite, FeOOH-oxides and clay minerals.

Iron oxidation states

Figure 1 illustrates the distribution of iron and the variation of the $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ oxidation ratio along the drillcore. Iron shows a slightly irregular but distinct increase towards the fracture face; this is apparent mineralogically by an increase of hydroxy Fe-oxide dispersions throughout the rock, together with the presence of chlorite and hematite at and near the fracture face. The similarity of the iron distribution pattern, excluding the fracture face, with that of thorium, is due to the presence of magnetite grains which often accompany the monazite aggregates in the granite.

An attempt to assess the extent of any oxidation effects in the rock was crudely made using whole-rock Fe^{2+} and Fe^{3+} analysis; the degree of oxidation is expressed as the ratio $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$. Towards the fracture face there is some suggestion of increased oxidation.

Rare-earth distributions

Plots of La and Ce (which illustrate those trends common to all the REE's and Ta) are presented in Figure 1. From the general similarity of the element distribution patterns within the drillcore, and in comparison with Th (Fig 1), it can be concluded that no obvious mobilisation of these elements has taken place, and that their distribution is dominantly a reflection of the occurrence of monazite in the granite.

Minor uranium distributions

The distribution of minor uranium (< 1 ppm) has been investigated by fission-track analysis. The results show that even though there is a background dispersion of matrix uranium (i.e. uranium present within and interstitial to the main rock-forming minerals) throughout the total length of the core examined, there is a significant increase in density and penetration within the approximately 3 cm wide margin adjacent to the fracture face; this corresponds to the observed uranium/iron-oxide increase described above. The impregnation pattern corresponds to the dispersion of FeOOH-oxides and mineral breakdown products such as sericite which in turn corresponds to the degree of alteration. Alteration is pervasive but irregular in extent due to microstructural controls on penetration, which progresses along structural weaknesses such as fissures, intergranular boundaries, and crystallographic planes (mostly affecting the feldspars).

Böttstein Drillcore

The distributions of uranium and its daughter decay products, iron and rare-earth elements La and Ce, are listed in Table 2 and illustrated in Figure 2.

Although not presented, higher amounts of Na and lower amounts of K and Rb support the mineralogical observations and help to distinguish the pegmatite from the granite. From Table 2 the pegmatite uranium contents range from 2.42 - 4.43 ppm and the thorium from 0.74 - 12.58 ppm (mean Th/U ratio

of 0.9). In the adjacent granite the corresponding ranges are 3.37 - 5.73 ppm U and 21.44 - 34.69 ppm Th respectively (mean Th/U ratio of 6.5). Compared to fresh, unfractured granite parts of the same drillcore (NAGRA 85-01), which records uranium values ranging from 8.6 - 10.4 ppm and thorium values from 19.8 - 29.3 ppm (mean Th/U ratio of 2.65), the sampled core section indicates a significant depletion of uranium; thorium appears to have been immobile. The fresh granite compares favourably with world-wide averages for normal granites. Although no further data are available for the pegmatite horizons, aplitic zones throughout the drillcore are characterised by exhibiting low thorium (7.61 - 16.62 ppm) and high uranium (10.88 - 29.88 ppm) with a mean Th/U ratio of 0.95. Fission-track analyses are not available, however most of the uranium and thorium is believed to be associated with the accessory mineral contents which include zircon and apatite. Minor amounts of uranium and thorium may be accommodated by the mafic constituents such as biotite/chlorite, or associated with finely dispersed iron-oxides.

The distribution of uranium and thorium along the drillcore is illustrated in Figure 2. Within the granite portion of the drillcore the uranium content is uniformly distributed until the pegmatite is approached whereupon a small increase is observed. In the pegmatite the uranium decreases only to increase again some 3 cm from the fracture surface; a small decrease occurs at the fracture surface. The thorium is essentially sympathetic to that of uranium except that in the pegmatite a continuous decrease is observed.

As inferred from the mineralogy, the granite represented by this part of the drillcore has been subjected to hydrothermal temperatures in association with the emplacement of the adjacent pegmatite and aplite horizons. This appears to have remobilised and removed part of the available uranium in the rock resulting in low but uniform levels within both the granite and pegmatite. The observed increase of uranium and thorium at the granite/pegmatite contact may be due to limited remobilisation and concentration

of both elements marginal to the pegmatite; this contact zone just within the granite is also characterised by an increase in mafic mineral content.

Uranium-series disequilibrium

Plots of the activity ratios $^{234}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{230}\text{Th}$ and $^{226}\text{Ra}/^{230}\text{Th}$ are presented in Figure 1. The $^{234}\text{U}/^{238}\text{U}$ ratio is unity for most of the core length although a slight increase to a maximum of 1.04 is observed close to the fracture face. The above discussion of the Kråkemåla $^{234}\text{U}/^{238}\text{U}$ ratio distribution can again be applied in this case but the degree of uranium mobilisation involved is obviously less. The $^{230}\text{Th}/^{234}\text{U}$ results for Böttstein exhibit a value slightly greater than unity except close to the fracture whereupon a significant decrease occurs. This presents an obvious contrast to the Kråkemåla core and suggests solution to rock transfer of ^{230}Th produced by the decay of ^{234}U in solution. The difference between the Kråkemåla and Böttstein $^{230}\text{Th}/^{234}\text{U}$ results could be partly explained by a much more rapid fluid transport through the Kråkemåla core than in the Böttstein core. In common with Kråkemåla, the $^{226}\text{Ra}/^{230}\text{Th}$ ratio is considered to represent equilibrium.

Iron oxidation states

Figure 3 illustrates the distribution of iron and the variation of the $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ oxidation states. The total iron contents are significantly higher in the granite than the pegmatite; their respective distributions are relatively homogeneous. These uniform distributions are supported mineralogically in that there is a fairly regular dispersion of FeOOH-oxides throughout the rock matrix.

The oxide ratios are almost all less than unity which indicates a fairly uniform degree of oxidation throughout both rock-types. This is in accord with this part of the Böttstein drillcore as a whole. It has been found (NTB 85-02) that Fe^{2+} minerals are common in fractures above 950 m, but are entirely absent below 1050 m.

Rare-earth distributions

Figure 2 presents data of La and Ce which illustrate the main REE and Ta trends encountered. Both La and Ce show fairly uniform distributions within the granite until some 7 cm from the pegmatite contact. At this point a systematic decrease occurs and then a very marked sharp increase just at the contact. This is followed by a gradual decrease through the pegmatite to the fracture edge. In addition to being typical of all the measured lanthanides (in contrast Sc, Co, Rb, Ba, Hf and Ta showed small increases) the La and Ce profiles are similar to that of thorium. The data strongly suggest that these increased concentrations are the result of limited remobilisation and concentration during hydrothermal activity coeval with the introduction of the pegmatites.

Grimsel Drillcore

The distributions of uranium and its daughter decay products, iron and rare-earth elements La and Ce, are listed in Table 3 and illustrated in Figure 3.

Most of the trace-element data are relatively homogeneous throughout the length of the drillcore specimen; there are no systematic trends that cannot be explained by mineralogical inconsistencies. A similar pattern is shown by uranium and thorium which vary from 5.26 - 9.25 ppm and 16.06 - 27.53 ppm respectively (mean Th/U ratio of 3.1). Only a few published analyses are available from the Aar granite as a whole (Rybach and Labhart, 1976); these record average uranium and thorium contents of 11 ppm and 27 ppm respectively (Th/U ratio of 2.4). Some auto-radiographic studies have been carried out on the Grimsel granite from specimens collected about 1 km from the test-site (Bajo, 1980). These have shown that the main uranium- and thorium-bearing mineral phases are allanite, thorite, zircon and apatite; polycrase is sporadically present sometimes included in feldspar. Although limited fission-track studies have indicated an absence of interstitial uranium, the slightly lower Th/U

ratios for the granite, in comparison with world-wide averages, suggests that small additions of uranium may have taken place.

From Figure 3 the uranium distribution varies irregularly between about 5 and 9 ppm and this is even more accentuated by the thorium which ranges from 16 to 28 ppm. This variation is not affected by the fracture and can be explained by mineralogical inhomogeneities. There is no obvious relationship between the uranium and thorium, which suggests that the uranium and thorium contents are controlled by radioactive minerals which are distinctly uranium or thorium-bearing. Alternatively, it may reflect a redistribution of uranium within the rock. In contrast thorium has probably been immobile and has retained its original signature.

Uranium-series disequilibrium

Plots of the $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{226}\text{Ra}/^{230}\text{Th}$ activity ratios are presented in Figure 3 and show secular equilibrium within the limits of analytical precision (2σ). This means an absence of rock/water interaction within the interval of at least the last 1 Ma.

Iron oxidation states

Figure 3 presents the distribution of total Fe and the iron oxidation ratios along the sampled drillcore. Approaching the fracture from both ends of the drillcore the total iron content increases and then decreases marginal to the fracture. The variation in the total iron content is considered to reflect the genetic inhomogeneities due to the primary mineralogy rather than any redistribution during rock/water interaction. The $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ oxidation ratios are generally uniform although there may be suggestion of slightly enhanced oxidation at one side of the fracture zone.

Rare-earth distributions

Figure 3 presents the distributions of La and Ce which are representative of the rare-earth elements as a whole. The patterns are irregular and reflect the distributions of rare-earth bearing minerals such as allanite and polycrase.

SUMMARY AND CONCLUSIONS

Drillcore sections traversing water-conducting fracture zones have been investigated from the Kråkemåla area (Götemar granite) in S.E. Sweden, the Böttstein area in north central Switzerland, and the Grimsel area in south central Switzerland. The cores have been examined using the uranium decay series together with the analysis of REE, Fe^{2+}/Fe^{3+} ratios, and other elements such as Na, K, Sc, Co, Rb, Cs, Ba and Ta. Fission-track analysis have been carried out on polished thin rock sections from the Kråkemåla granite.

Mineralogical studies of the Götemar sample (from approx. 380 m depth) have shown that at some stage the core has been subject to a weak, pervasive alteration throughout its length. A more intense alteration is evident within a marginal zone (3-5 cm wide) adjacent to the fracture zone. Here there is widespread alteration of feldspar and magnetite together with impregnations of FeOOH-oxides. The mineral coatings on the fracture face have not been quantitatively determined, but appear to be composed of a mixture of hematite, chlorite, clay minerals and FeOOH-oxides.

Of the elements measured, the variation of REE and thorium (together with Ta, Cs and Sc) appear to reflect the primary distribution of those radioactive refractory phases dominated by monazite. Uranium, on the other hand, shows evidence of mobilisation and leaching from monazite up to a distance of 8 cm from the fracture zone; for the remainder of the core length the uranium distribution is sympathetic with that of thorium and the REE. Work by Smellie and Stuckless(1985) showed a general loss of uranium in the Götemar granite as a result of large-scale hydrothermal alteration

processes some 420 ± 171 Ma. These processes may have contributed to the breakdown and removal of uranium from the monazite phases marginal to the fracture zone.

Isotopically the $^{234}\text{U}/^{238}\text{U}$ ratio along the major length of the drill-core is less than unity indicating uranium leaching. In strong contrast, the granite marginal to the fracture zone is characterized by a systematic increase in the $^{234}\text{U}/^{238}\text{U}$ ratio to a value of 2.29 at the fracture face which indicates an accumulation of uranium. The $^{230}\text{Th}/^{234}\text{U}$ ratio is unity throughout most of the core with a small decrease being apparent close to the fracture. The $^{226}\text{Ra}/^{230}\text{Th}$ ratio values are considered to indicate secular equilibrium.

The source of uranium giving rise to the enhanced concentrations and $^{234}\text{U}/^{238}\text{U}$ ratio values close to the fracture could be either uranium leached from the granite (as indicated by the $^{234}\text{U}/^{238}\text{U}$ ratios for the rest of the core), or from uranium transported in solution within the fracture migrating into the water-saturated rock. If the former process is responsible, then uranium migration over at least 40 cm is occurring whereas a constraint of about 3 cm can be applied if the latter process is taking place. The two processes are not mutually exclusive.

The $^{230}\text{Th}/^{234}\text{U}$ and $^{226}\text{Ra}/^{230}\text{Th}$ equilibrium and $^{234}\text{U}/^{238}\text{U}$ disequilibrium suggest that the process involved is either continuous or else indicates a time-scale long enough to allow re-equilibration of ^{230}Th with ^{234}U and ^{226}Ra with ^{230}Th but short enough to maintain ^{234}U disequilibrium with ^{238}U , i.e. a time-scale of about 10^6 years.

The mechanism giving rise to uranium deposition at and near the fracture could be due to any or all of: a) precipitation at a boundary between differing physico-chemical conditions, b) sorption on the fracture filling minerals, and c) solution to solid recoil transfer. The degree and retention of radionuclide retardation and retention from both processes will be dependent on the

physico-chemical properties of the fracture zone minerals.

The Böttstein sample is inconveniently located near the contact between a pegmatite and aplite horizon. As a result the granite has been subjected to hydrothermal temperatures which are reflected in the mineralogy and the chemistry. Uranium has been mobilised and depleted from the examined core which has resulted in a fairly uniform distribution both within the granite and pegmatite. In contrast, thorium and REE mobilisation has been restricted to a 7 cm zone in the granite adjacent to the pegmatite contact, with enrichment of these elements along a zone some 1 to 2 cm wide adjacent to the pegmatite contact.

The mineralogy of the fracture zone and the host pegmatite do not indicate any low temperature alteration processes which might have resulted in systematic compositional gradients around the fracture zone.

The $^{234}\text{U}/^{238}\text{U}$ ratio is unity for most of the core length although a slight increase is observed close to the fracture face; the $^{226}\text{Ra}/^{230}\text{Th}$ ratio suggests secular equilibrium. The above discussion of the Kråkemåla $^{234}\text{U}/^{238}\text{U}$ ratio distribution can again be applied in this case but the degree of uranium mobilisation involved is obviously less. The $^{230}\text{Th}/^{234}\text{U}$ results for Böttstein exhibit a value slightly greater than unity except close to the fracture. This presents an obvious contrast to the Kråkemåla core and suggests solution to rock transfer of ^{230}Th produced by the decay of ^{234}U in solution. The difference between the Kråkemåla and Böttstein $^{230}\text{Th}/^{234}\text{U}$ results could be partly explained by a much more rapid fluid transport through the Kråkemåla core than in the Böttstein core.

Contrastingly to Böttstein the Grimseil drillcore is located within a fairly homogeneous granite. Mineralogically and chemically there is no evidence of any systematic variations around the fracture that might be attributed to hydrothermal or low temperature processes (in fact the fracture faces are devoid of any mineral coatings). This is supported by the isotopic data which shows secular equilibrium for the uranium daughters measured. Two possibilities

therefore exist: either groundwater interactions at this depth are not occurring, or, the fracture is not water-conducting. Based on hydrogeological criteria the fracture is considered water-conducting. Thus, to take the first possibility, the groundwater believed to be in contact with this fracture zone is characterised by an excess of ^{234}U ($^{234}\text{U}/^{238}\text{U}$ activity ratio of 2.12 (Ivanovich and Wilkins, 1984)). Whether this is the result of chemical or recoil mechanisms, the fracture faces in contact with the groundwaters should reflect some isotopic discordance. As this is not the case, the isotopic equilibrium measured would lead one to suspect that the fracture is young, having occurred at any stage from Alpine to recent times. A fairly recent joint may not have had time to react sufficiently with the groundwater which is now characterised by a chemical and isotopic signature obtained from other parts of the granite bedrock.

In conclusion, the most important points resulting from this study are:

1. Two out of three of the investigated samples indicate that naturally-occurring uranium radionuclides have been remobilised by rock/water interaction processes within normal compact granite marginal to a water-conducting fracture zone at repository depths. Thorium does not exhibit mobilisation under the same conditions.
2. Rock/water interaction has taken place under predominately reducing conditions within measureable geological time, i.e. within the last 0.5 Ma as determined by the $^{238}\text{U} - ^{234}\text{U} - ^{230}\text{Th} - ^{226}\text{Ra}$ decay series and may still be active at the present time.
3. Isotopic movement has been mostly from the granite to the fracture zone through distances of at least 40 cm.
4. Some radionuclide movement has also taken place from the fracture zone (via the groundwater) into the granite; the extent of penetration has

been from 1-3 cm and this measure could therefore act as an upper limit in migration models. However, it may be an important prerequisite for penetration that the fracture system has been previously subject to hydrothermal processes resulting in a zone of enhanced porosity around the fracture. Furthermore, the mineralogical alteration products would make the rock more conducive to radionuclide sorption/retardation mechanisms.

5. Sorption and isotopic fractionation has occurred at the fracture/groundwater interface in association with fracture zone minerals such as hematite, chlorite, clay minerals and FeOOH-oxides. The major source of these radionuclides is believed to be the groundwaters which are either known or considered to contain excess ^{234}U .
6. Fission-track analysis of the Kråkemåla samples indicate that there was a significant increase in the amount and penetration of uranium within the approximately 3 cm wide margin adjacent to the fracture face. Penetration has been facilitated by micro-scale structural weaknesses such as fissures, intergranular boundaries and crystallographic planes, and further aided by pervasive alteration, especially of the feldspars. Radionuclide movements would appear to be the product of both fluid-flow and matrix diffusion processes.

However, many more similar studies need to be carried out within different geological and groundwater environments before any far-reaching conclusions can be drawn. Still, as demonstrated by the data, such analogue studies can play an important role in validating the importance of far-field radionuclide retardation mechanisms within the context of high-level radioactive waste disposal in crystalline bedrock, whereupon fracture permeability will be the dominant mode of groundwater flow.

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Table 1: Isotopic and chemical analyses of uranium and thorium from drillcore K 1, Kräkemåla, Sweden.

| Specimen | Distance from fracture face (cm) | Uranium ¹⁾ (ppm) | Thorium ¹⁾ (ppm) | Th/U | ²³⁸ U | ²³⁴ U | ²³⁴ U/ ²³⁸ U | ²³⁰ Th | ²³⁰ Th/ ²³⁴ U | ²²⁶ Ra | ²²⁶ Ra/ ²³⁰ Th | ²³² Th |
|----------|----------------------------------|-----------------------------|-----------------------------|------|----------------------|----------------------|------------------------------------|-------------------|-------------------------------------|-------------------|--------------------------------------|-------------------|
| KIA-1 | surface scrapings | 20.13±.54 | 46.37±2.07 | 2.3 | 14.8±0.4 | 33.9±0.8 | 2.29±0.51 | 31.9±1.0 | 0.94±0.06 | 32.7±4.9 | 1.03±0.15 | 11.2±0.5 |
| KIA-2 | 1 | 12.51±.41 | 57.96±1.24 | 4.6 | 9.2±0.3 | 16.7±0.3 | 1.81±0.05 | 14.8±0.3 | 0.89±0.05 | 16.6±2.5 | 1.12±0.17 | 14.0±0.3 |
| KIA-3 | 2 | 13.19±.27 | 74.52±2.07 | 5.6 | 9.7±0.2 | 10.9±0.2 | 1.12±0.02 | 9.3±0.3 | 0.85±0.05 | 9.7±1.5 | 1.04±0.16 | 18.0±0.5 |
| KIA-4 | 3 | 12.78±.41 | 65.83±.83 | 5.2 | 9.4±0.3 | 9.0±0.3 | 0.96±0.03 | 9.1±0.2 | 1.01±0.05 | 7.8±1.2 | 0.86±0.13 | 15.9±0.2 |
| KIA-5 | 4 | 12.92±.41 | 84.46±2.07 | 6.5 | 9.5±0.3 | 8.5±0.3 | 0.89±0.04 | 8.5±0.3 | 1.00±0.06 | 10.4±1.6 | 1.22±0.18 | 20.4±0.5 |
| KIA-6 | 5 | 13.46±.41 | 61.69±1.24 | 4.6 | 9.9±0.3 | 8.7±0.3 | 0.88±0.03 | 8.6±0.2 | 0.99±0.06 | 8.6±1.3 | 1.00±0.15 | 14.9±0.3 |
| KIA-7 | 6 | 13.46±.27 | 64.17±1.24 | 4.8 | 9.9±0.2 | 8.6±0.2 | 0.87±0.03 | 8.5±0.2 | 0.99±0.05 | 6.8±1.0 | 0.80±0.12 | 15.5±0.3 |
| KIA-8 | 7 | 12.65±.27 | 69.13±1.24 | 5.5 | 9.3±0.2 | 7.9±0.2 | 0.85±0.03 | 7.8±0.3 | 0.99±0.07 | 7.5±1.1 | 0.96±0.14 | 16.7±0.3 |
| KIA-9 | 8 | 14.55±.27 | 48.02±1.24 | 3.3 | 10.7±0.2 | 9.4±0.2 | 0.88±0.02 | 9.8±0.3 | 1.04±0.05 | 7.6±1.1 | 0.78±0.12 | 11.6±0.3 |
| KIA-10 | 9 | 14.42±.27 | 69.97±1.24 | 4.9 | 10.6±0.2 | 8.9±0.2 | 0.84±0.02 | 9.3±0.2 | 1.04±0.05 | 8.6±1.3 | 0.92±0.14 | 16.9±0.3 |
| KIA-11 | 10 | 18.63±.54 19.31±.41 | - - - - | - | 13.7±0.4 14.2±0.3 | 11.4±0.3 11.4±0.2 | 0.83±0.03 0.80±0.02 | -- -- | -- -- | -- 9.6±1.4 | -- -- | -- -- |
| KIA-12 | 11 | 23.26±.68 | 89.42±2.48 | 3.8 | 17.1±0.5 | 14.7±0.5 | 0.86±0.03 | 16.1±0.6 | 1.10±0.07 | 10.8±1.6 | 0.67±0.10 | 21.6±0.6 |
| KIA-13 | 12 | 19.31±.54 | 83.21±2.07 | 4.3 | 14.2±0.4 | 12.5±0.4 | 0.88±0.03 | 11.4±0.3 | 0.91±0.06 | 9.2±1.4 | 0.81±0.12 | 20.1±0.5 |
| KIA-14 | 13 | 14.14±.41 | 51.34±.83 | 2.7 | 10.4±0.3 | 8.5±0.3 | 0.82±0.03 | 8.8±0.2 | 1.04±0.06 | 8.7±1.3 | 0.99±0.15 | 12.4±0.2 |
| KIA-15 | 43 | 18.90±.27 | 72.45±2.48 | 3.8 | 13.9±0.2 | 12.1±0.2 | 0.87±0.02 | 11.4±0.4 | 0.94±0.06 | 9.2±1.4 | 0.81±0.12 | 17.5±0.6 |

1) Determined by radioisotope dilution and alpha spectrometry.

Table 2: Isotopic and chemical analyses of uranium and thorium from drillcore BOE (618.34-618.70 metres), Böttstein, Switzerland.

| Specimen | Distance from fracture face (cm) | Uranium ¹⁾ (ppm) | Thorium ¹⁾ (ppm) | Th/U | ²³⁸ U | ²³⁴ U | ²³⁴ U/ ²³⁸ U | ²³⁰ Th | ²³⁰ Th/ ²³⁴ U | ²²⁶ Ra | ²²⁶ Ra/ ²³⁰ Th | ²³² Th |
|----------|----------------------------------|-----------------------------|-----------------------------|------|------------------|------------------|------------------------------------|-------------------|-------------------------------------|-------------------|--------------------------------------|-------------------|
| BOE-3396 | Surface scrapings ²⁾ | 2.42 | 0.99 | 0.4 | 1.78 | 1.84 | 1.04±0.04 | 1.78 | 0.97±0.04 | -- | -- | 0.24 |
| BOE-1 | Fracture ³⁾ Slice | 4.20±.11 | 0.95±.12 | 0.2 | 3.09±0.08 | 3.17±0.08 | 1.03±0.04 | 3.00±0.12 | 0.95±0.07 | 2.2±0.3 | 0.73±0.11 | 0.24±0.03 |
| | | 3.98±.11 | 0.74±.25 | 0.2 | 2.93±0.08 | 2.65±0.08 | 0.90±0.05 | 2.82±0.11 | 1.06±0.08 | -- | -- | 0.18±0.06 |
| BOE-2 | 1.5 ³⁾ | 3.41±.08 | 3.27±.12 | 1.0 | 2.51±0.05 | 2.60±0.05 | 1.04±0.03 | 2.65±0.05 | 1.02±0.04 | 2.2±0.3 | 0.83±0.12 | 0.79±0.03 |
| BOE-3 | 3.0 ³⁾ | 2.68±.05 | 7.32±.29 | 2.7 | 1.97±0.04 | 2.01±0.04 | 1.02±0.03 | 2.23±0.08 | 1.11±0.06 | 1.9±0.3 | 0.85±0.13 | 1.77±0.07 |
| BOE-4 | 5.0 ³⁾ | 2.71±.04 | 12.58±.29 | 4.6 | 1.99±0.03 | 2.04±0.03 | 1.02±0.04 | 2.23±0.06 | 1.09±0.05 | 2.1±0.3 | 0.94±0.14 | 3.04±0.07 |
| BOE-5 | 6.5 ⁴⁾ | 5.73±.08 | 34.69±.87 | 6.1 | 4.21±0.06 | 4.15±0.06 | 0.99±0.02 | 4.63±0.14 | 1.12±0.05 | 4.7±0.7 | 1.02±0.15 | 8.38±0.21 |
| BOE-6 | 8.0 ⁴⁾ | 3.59±.07 | 23.27±.58 | 6.5 | 2.64±0.05 | 2.65±0.05 | 1.00±0.03 | 2.89±0.08 | 1.09±0.05 | 3.0±0.4 | 1.04±0.16 | 5.62±0.14 |
| BOE-7 | 10.0 ⁴⁾ | 3.60±.10 | 24.63±.75 | 6.8 | 2.65±0.07 | 2.67±0.07 | 1.01±0.04 | 3.01±0.12 | 1.13±0.07 | 2.8±0.4 | 0.93±0.14 | 5.95±0.18 |
| BOE-8 | 12.1 ⁴⁾ | 3.60±.10 | 21.44±.62 | 6.0 | 2.65±0.07 | 2.64±0.07 | 1.00±0.04 | 2.52±0.10 | 0.95±0.07 | 2.7±0.4 | 1.07±0.16 | 5.18±0.15 |
| | | 3.40±.14 | 23.52±.70 | 6.9 | 2.50±0.10 | 2.47±0.10 | 0.99±0.05 | 2.78±0.08 | 1.13±0.07 | -- | -- | 5.68±0.17 |
| BOE-9 | 13.9 ⁴⁾ | 3.55±.07 | 25.50±.75 | 7.2 | 2.61±0.05 | 2.63±0.05 | 1.01±0.03 | 2.99±0.12 | 1.14±0.06 | 2.7±0.4 | 0.90±0.14 | 6.16±0.18 |
| BOE-10 | 15.6 ⁴⁾ | 3.79±.05 | 22.27±.41 | 5.9 | 2.79±0.04 | 2.82±0.04 | 1.01±0.03 | 3.13±0.10 | 1.11±0.05 | 2.6±0.4 | 0.83±0.12 | 5.38±0.10 |
| BOE-11 | 17.6 ⁴⁾ | 3.37±.07 | 25.30±.50 | 7.5 | 2.48±0.05 | 2.46±0.05 | 0.99±0.03 | 2.70±0.07 | 1.10±0.05 | 2.6±0.4 | 0.96±0.15 | 6.11±0.12 |
| BOE-12 | 20.0 ⁴⁾ | 4.09±.08 | 24.18±.58 | 5.9 | 3.01±0.06 | 2.94±0.06 | 0.98±0.03 | 3.29±0.10 | 1.12±0.05 | 2.9±0.4 | 0.88±0.13 | 5.84±0.14 |

1) Determined by radioisotope dilution and alpha spectrometry.

2) Ivanovich and Wilkins (1984 b).

3) Pegmatite.

4) Granite.

Table 3: Isotopic and chemical analyses of uranium and thorium from drillcore FLG (94.12-94.52 metres, exploration borehole SB 80.001) Grimsel Test-site, Switzerland.

| Specimen | Distance from fracture face (cm) | Uranium ¹⁾ (ppm) | Thorium ¹⁾ (ppm) | Th/U | ²³⁸ U | ²³⁴ U | ²³⁴ U/ ²³⁸ U | ²³⁰ Th | ²³⁰ Th/ ²³⁴ U | ²²⁶ Ra | ²²⁶ Ra/ ²³⁰ Th | ²³² Th |
|----------|----------------------------------|-----------------------------|-----------------------------|----------|------------------------|------------------------|------------------------------------|-------------------|-------------------------------------|-------------------|--------------------------------------|-------------------|
| FLG-1 | 2.0 | 6.62±.12 | 23.06±.66 | 3.5 | 4.87±0.09 | 4.72±0.09 | 0.97±0.03 | 5.42±0.16 | 1.15±0.06 | 5.2±0.8 | 0.96±0.14 | 5.57±0.16 |
| FLG-2A | 3.9 | 7.15±.15 | 19.25±.75 | 2.7 | 5.26±0.11 | 5.21±0.11 | 0.99±0.03 | 5.36±0.21 | 1.03±0.06 | 5.3±0.8 | 0.99±0.15 | 4.65±0.18 |
| FLG-3A | 5.0 | 6.99±.18 | 23.14±.54 | 3.3 | 5.14±0.13 | 5.15±0.13 | 1.00±0.03 | 5.66±0.13 | 1.10±0.05 | 5.1±0.8 | 0.90±0.14 | 5.59±0.13 |
| FLG-4A | 7.0 | 8.38±.08 | 27.53±1.28 | 3.3 | 6.16±0.06 | 6.22±0.06 | 1.01±0.02 | 6.46±0.31 | 1.04±0.06 | 5.6±0.8 | 0.87±0.13 | 6.65±0.31 |
| FLG-5A | 8.8 | 5.26±.14 | 17.10±.50 | 3.3 | 3.87±0.10 | 3.79±0.10 | 0.98±0.03 | 4.21±0.12 | 1.11±0.06 | 4.4±0.7 | 1.05±0.16 | 4.13±0.12 |
| FLG-6A | 10.8 | 6.47±.23 | 18.96±.54 | 2.9 | 4.76±0.17 | 4.66±0.17 | 0.98±0.04 | 4.91±0.14 | 1.05±0.06 | 5.5±0.8 | 1.12±0.17 | 4.58±0.13 |
| FLG-7A | 13.0 | 9.25±.14 | 22.65±.87 | 2.4 | 6.80±0.10 | 6.78±0.10 | 1.00±0.02 | 7.28±0.30 | 1.07±0.06 | 6.2±0.9 | 0.85±0.13 | 5.47±0.21 |
| FLG-8A | 15.8 | 6.15±.07 | 21.20±.41 | 3.4 | 4.52±0.05 | 4.58±0.05 | 1.01±0.02 | 4.91±0.10 | 1.07±0.04 | 5.8±0.9 | 1.18±0.18 | 5.12±0.10 |
| FLG-9A | 18.6 | 6.69±.15 | 16.06±.83 | 2.4 | 4.92±0.11 | 4.82±0.11 | 0.98±0.03 | 4.27±0.21 | 0.89±0.07 | 5.6±0.8 | 1.31±0.20 | 3.88±0.20 |
| FLG-2B | 0.4 | 7.36±.15 | 25.67±.50 | 3.5 | 5.41±0.11 | 5.40±0.11 | 1.00±0.02 | 5.69±0.12 | 1.05±0.04 | 6.5±1.0 | 1.14±0.17 | 6.20±0.12 |
| FLG-3B | 0.6 | 7.60±.15 | 25.83±1.28 | 3.4 | 5.59±0.11 | 5.59±0.11 | 1.00±0.02 | 5.89±0.31 | 1.05±0.07 | 6.9±1.0 | 1.17±0.18 | 6.24±0.31 |
| FLG-4B | 2.2 | 5.86±.08 | 18.92±.54 | 3.2 | 4.31±0.06 | 4.29±0.06 | 1.00±0.02 | 4.12±0.12 | 0.96±0.05 | 6.2±0.9 | 1.50±0.22 | 4.57±0.13 |
| FLG-5B | 3.4 | 6.80±.18 6.77±.27 | 21.49±.83 -- | 3.2 - | 5.00±0.13 4.98±0.20 | 5.23±0.13 4.91±0.20 | 1.05±0.03 0.99±0.03 | 5.04±0.20 -- | 0.96±0.07 1.03±0.08 | 5.7±0.9 -- | 1.13±0.17 -- | 5.19±0.20 -- |
| FLG-6B | 4.8 | 7.44±.12 | 23.68±.58 | 3.2 | 5.47±0.09 | 5.53±0.09 | 1.01±0.02 | 5.91±0.14 | 1.07±0.05 | 5.7±0.9 | 0.96±0.14 | 5.72±0.14 |
| FLG-7B | 6.4 | 6.94±.20 | 20.12±.66 | 2.9 | 5.10±0.15 | 5.02±0.15 | 0.98±0.03 | 5.09±0.17 | 1.01±0.06 | 5.7±0.9 | 1.12±0.17 | 4.86±0.16 |
| FLG-8B | 7.8 | 6.31±.16 | 18.96±.54 | 3.0 | 4.64±0.12 | 4.66±0.12 | 1.00±0.03 | 4.36±0.13 | 0.94±0.06 | 5.0±0.8 | 1.15±0.17 | 4.58±0.13 |
| FLG-9B | 9.2 | 6.38±.15 | 20.66±.70 | 3.2 | 4.65±0.11 | 4.60±0.11 | 0.98±0.03 | 4.91±0.17 | 1.07±0.06 | 5.1±0.8 | 1.04±0.15 | 4.99±0.17 |
| FLG-10B | 10.8 | 7.29±.14 | 22.65±.54 | 3.1 | 5.36±0.10 | 5.32±0.10 | 0.99±0.03 | 5.88±0.14 | 1.11±0.05 | 5.9±0.9 | 1.00±0.15 | 5.47±0.13 |

1) Determined by radioisotope dilution and alpha spectrometry.

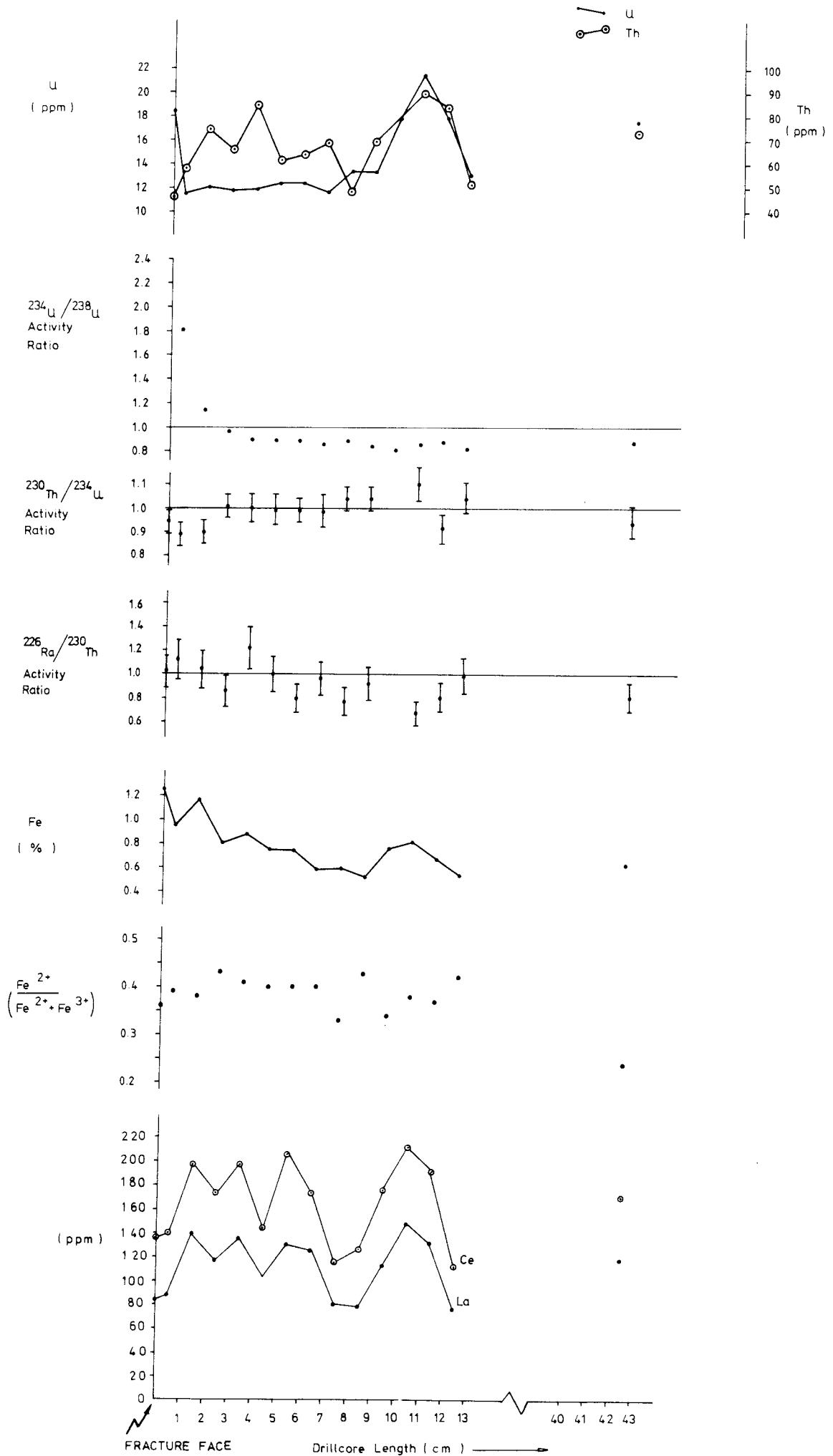
Figure Texts.

Figure 1: Distribution of uranium and its daughter decay products, thorium, REE (La and Ce), total iron and iron-oxide ratios characteristic of the K1 drillcore from Kråkemåla, Sweden.

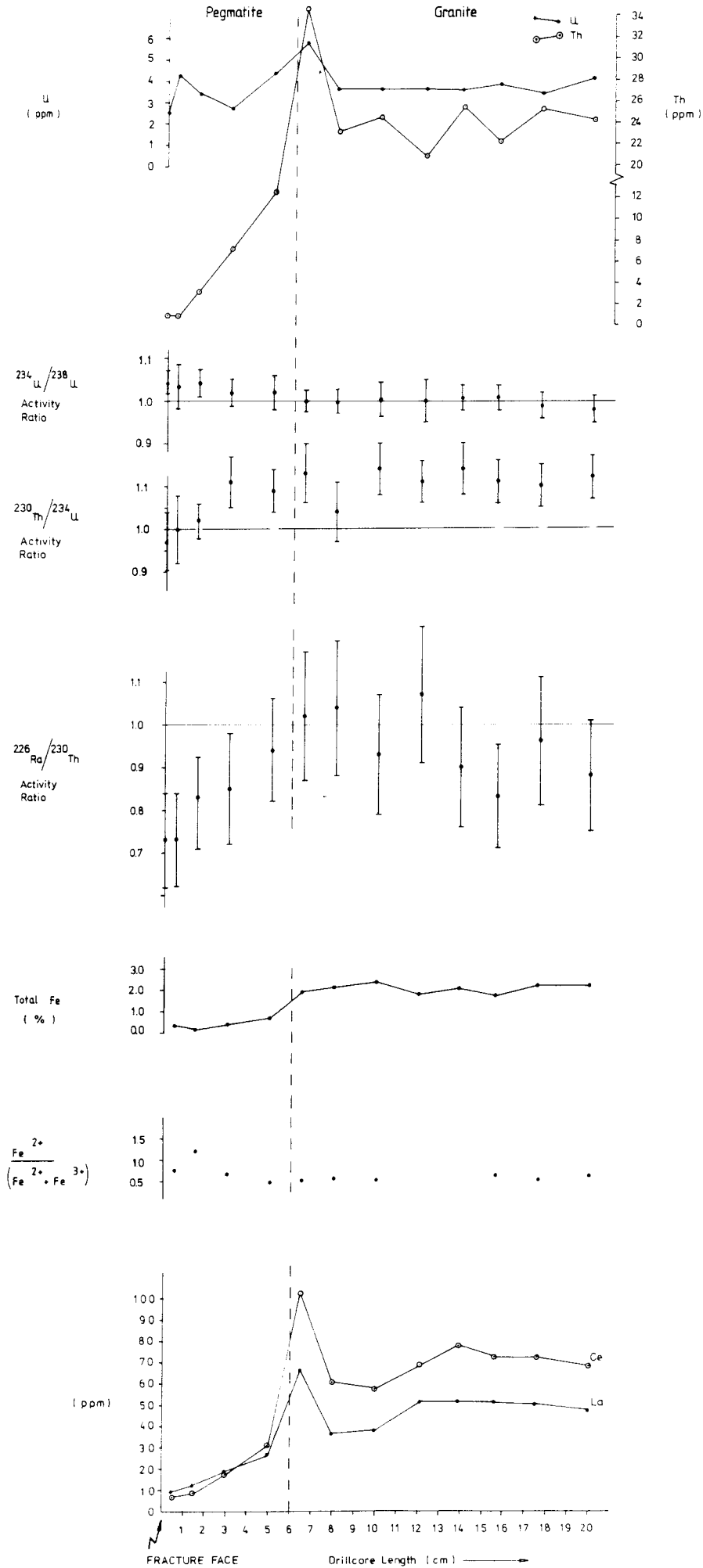
Figure 2: Distribution of uranium and its daughter decay products, thorium, RRE (La and Ce), total iron and iron-oxide ratios characteristic of the BOE drillcore from Böttstein, Switzerland.

Figure 3: Distribution of uranium and its daughter decay products, thorium, REE (La and Ce), total iron and iron-oxide ratios characteristic of the FLG drillcore from Grimsel, Switzerland.

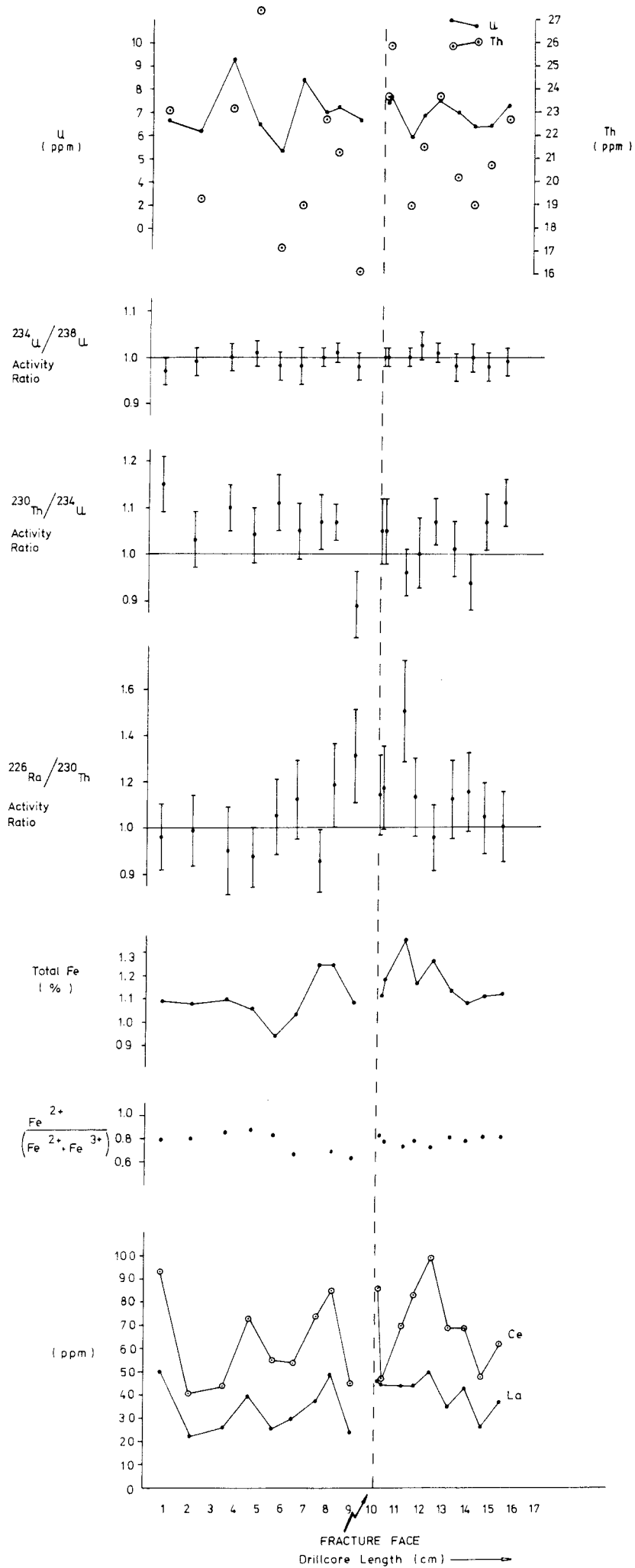
Kråkemåla Drillcore (K1:317.85-318.40 m)



Böttstein Drillcore (BOE: 618.34-618.70 m)



Grimset Drillcore (FLG: 94.12-94.52 m)



Part II

A COMPARISON OF NEUTRON ACTIVATION AND ALPHA SPECTROSCOPY ANALYSES OF THORIUM IN CRYSTALLINE ROCKS.

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The concentrations of Th in samples of crystalline rock from three drillcore sections were analysed independently by instrumental neutron activation analysis and by chemical separation and alpha spectroscopy. The two methods show good general agreement over an approximate concentration range of 1 to 100 ppm Th. Variations in results between the two methods are not of a systematic nature and probably arise from sample heterogeneity. The results confirm the reliability of both methods and provide a useful comparison of the standards and reference materials used. The study indicates that, in cases where Th isotopic information is not required, the simpler and more rapid neutron activation analysis provides a satisfactory method.

INTRODUCTION

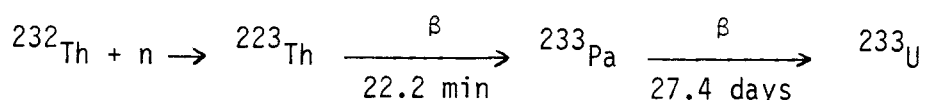
The analysis of Th in geological samples is routinely performed by either instrumental neutron activation analysis¹ or chemical separation and alpha spectroscopy^{2, 3}. As part of a study of the migration of natural radionuclides within crystalline rocks, we have analysed the Th content of a series of granite and pegmatite samples by both methods. The results presented below provide a useful comparison of the two methods and of the standards and reference materials used.

The samples analysed were taken from three drillcore sections and a full description of the geochemistry and geological context of each core is provided in detail by Smellie et al³. The samples were taken from 1 cm segments along the cores and the main characteristics of the samples are shown in Table 1.

EXPERIMENTAL METHODS

The experimental methods summarised below are based upon well established procedures which are described in detail elsewhere^{1, 2}. The 1 cm rock slices were powdered by using a jaw crusher and a Tema mill after which 0.2 g subsamples were taken for activation analysis and 5 g for chemical separation and alpha spectroscopy analysis of U and Th. The samples for activation analysis were irradiated in batches of about 10 in a thermal neutron flux of 3×10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. The USGS reference material GSP was used as a multi element standard and samples of AGV-1 (USGS) and SOIL-5 (IAEA) were included as reference materials. Flux variations between samples were corrected for by the use of Specpure Fe wires as flux monitors. As part of a sequence of counts for multi element

analysis, the samples were counted on a co-axial Ge(Li) detector (resolution 1.8keV at 661 keV) approximately 2 weeks after irradiation. Spectra were recorded on an EG and G Ortec 7032 analyser and were analysed by the Ortec programme GAMMA2. Neutron activation analysis calculations were performed by the SURRC programme NAA (I.A. Harris, 1981). The Th concentration in the samples was determined from the induced ^{233}Pa activity:



The ^{233}Pa activity was determined by using the gamma photopeak at 311.9 KeV (34 % intensity)⁴.

The samples for U and Th analysis were spiked with a fixed aliquot of the $^{232}\text{U}/^{228}\text{Th}$ equilibrium solution prepared by the isotope production unit of AERE Harwell (Harwell spike solution: Oct 81). The spiked samples were dissolved by a sequence of acid digestions using HCl, HNO₃, and HF with intermediate leachings of soluble material into 9M HCl. Teflon apparatus was employed throughout and a high pressure digestion in a Parr 'bomb' was used for dissolution of obdurate minerals. U was removed from the 9M HCl on Bio-Rad AG1X8 resin after which the residual solution containing the Th was reduced to a volume of about 20 ml by heating. A mixed hydroxide precipitate was produced by addition of NH₄OH to scavenge the Th from solution and, after washing, the precipitate was re-dissolved in a small volume of concentrated HNO₃ and made up to a volume of about 75 ml with 10M HNO₃. Th was extracted from this solution on AG1X8 resin and was eluted from the column with 0.1 M HNO₃. A repeat ion exchange separation of Th was performed prior to electrodeposition of the Th onto a stainless steel disc from slightly acidified NH₄Cl solution. Silicon surface barrier detectors were used to obtain the α-spectra from which the Th concentrations were calculated by hand.

RESULTS

The results for the analysis of 44 samples by both methods are shown in Table 2. All of the results are expressed in ppm, assuming a conversion factor of 4.12×10^{-6} g as the weight of Th giving rise to 1 dpm ^{232}Th . The results of 3 separate analyses of the reference materials AGV-1 and SOIL-5 performed along with the analyses of the granites and pegmatites by INAA are shown in Table 3. The uncertainties are those arising from counting statistics at the 1σ level and include, in the case of the α -spectrometry results, the effects of background caused by the accumulation of recoil nuclei on the faces of detectors.

DISCUSSION

The results obtained by radiochemical separation and α -spectroscopy are plotted in Figure 1 against those obtained by activation analysis. A weighted least squares linear regression analysis was performed for the results from each of the drillcores, and for the total set, and the best-fitting straight lines are also shown in Figure 1. Expressing the results in the form

$$\alpha = mN + C, \text{ in an obvious notation,}$$

the analysis yields:

| | | | |
|-------|---|----------------------|---------------------|
| KIA | : | $m = 0.88 \pm 0.15,$ | $C = 7.5 \pm 9.5$ |
| BOE | : | $m = 1.00 \pm 0.06,$ | $C = -0.2 \pm 0.4$ |
| FLG | : | $m = 0.56 \pm 0.40,$ | $C = 10.6 \pm 7.2$ |
| Total | : | $M = 1.05 \pm 0.04,$ | $C = -0.04 \pm 0.4$ |

where the uncertainties are those arising from the deviations of the experimental points from the best lines.

It is immediately evident that the overall agreement between the two methods of analysis is very good and that only in the case of the FLG set is there much evidence of a departure from ideal behaviour. This circumstance is probably due to the very small spread of the results: 70 % of them lie within ± 10 % of the weighted mean for the set so that the range is comparable with the analytical uncertainty. The uncertainties in m and c suggest that it is hardly appropriate to try to fit a straight line under these conditions.

The following factors controlling the accuracy and precision of the two methods could influence the results in such a comparison: the accuracy of the reference values for the standards, interferences under the peaks used in the α - and γ -spectroscopy, variations in counting geometry in INAA, incomplete dissolution of the samples during chemical separation, non-equilibration of the ^{228}Th spike with the sample and heterogeneity of the samples and standards. On the basis of the above analysis there appears to be no systematic difference between the two sets of results such as would result from an inaccurate value for one or both of the standards. Also $^{230}\text{Th}/^{234}\text{U}$ activity ratios and replicate radiochemical analyses of some samples suggest that incomplete dissolution and spike equilibrium are not significant³ while repeated counting of a source showed that variations in counting geometry in the INAA result in uncertainties of <2 %.

Turning to the remaining possibilities, interferences under the peaks used in the α - and γ -spectroscopy constitute a source of systematic deviations and there is one such interference in the α -spectroscopy which has to be eliminated. This arises because ^{224}Ra , which grows in from its

parent ^{228}Th during the course of the measurement, has a small (5 %) component indistinguishable from the ^{228}Th α -peak. However, since the ^{228}Th and the main ^{224}Ra α -peaks are well separated the effect is calculable and has been allowed for. As far as ^{232}Th is concerned, the α -energy is 4.01 MeV and the nearest possibility for interference would arise from ^{238}U at 4.20 MeV (77 %) and 4.15 MeV (23 %), which should be excluded by the chemistry, and if not, would be very obvious in the spectrum. In the γ -spectroscopy, the only species than can be identified from γ -energy tables⁶ as possibly interfering with the ^{233}Pa photopeak at 311.9 keV is the weak (0.89 % intensity) 309.6 keV γ -ray of ^{160}Tb ($T_{1/2} = 72.1$ days) but comparison with the more intense lines at 298.5 keV (30 %) and 879.3 keV (31 %) indicates a maximum interference of <1 %. Any significant interference in the γ -spectra would also result in obvious discrepancies between reference values and the measured values for the reference materials but Table 3 shows the good agreement obtained for AGV-1 and Soil 5.

This leaves only sample or standard heterogeneity as the likely cause of discrepancies between the two analyses and the results in Table 3 suggest that the fine-grained standard and reference materials are suitably homogeneous. The samples were, however, relatively coarse-grained with the Th concentrated in particular minerals such as monazite and zircon, and this is bound to lead to a sampling uncertainty which increases for smaller samples. Thus the 5g samples used in the radiochemical analysis are more likely to provide a representative sample of the Th-bearing minerals than are the 0.2g samples used in the INAA, and this difference in sample size coupled with the heterogeneity could easily account for the observed results.

CONCLUSIONS

This comparison indicates that both methods produce generally reliable analyses for Th. The major source of variations between the two methods probably arises as a result of the heterogeneous distribution of Th bearing minerals in the samples. The INAA technique uses a much smaller sample than does the radiochemical analysis and is therefore more susceptible to error as a result of sampling. The INAA method is significantly simpler and faster than the radiochemical method and, in cases where Th isotope ratios are not required, INAA provides an adequate form of analysis. The analytical results presented indicate an acceptable accuracy on the basis of standard reference materials and confirm the compatibility of the reference Th value for the Harwell spike solution with the three geological reference materials used.

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Table 1: Characteristics of the samples analysed.

| SAMPLES | SAMPLING LOCATION | DEPTH (m) | ROCK TYPE |
|---------------|-------------------------|-----------|-----------|
| KIA-KIA.15 | Kråkemåla (Sweden) | 318 | granite |
| BOE.1-BOE.4 | Böttstein (Switzerland) | 618 | pegmatite |
| BOE.5-BOE.12 | Böttstein (Switzerland) | 618 | granite |
| FLG.1-FLG.10B | Grimsel (Switzerland) | ---* | granite |

* The FLG samples were taken from a horizontal borehole in the
Grimsel underground rock laboratory.

Table 2: Results of Th analyses in granites and pegmatites.

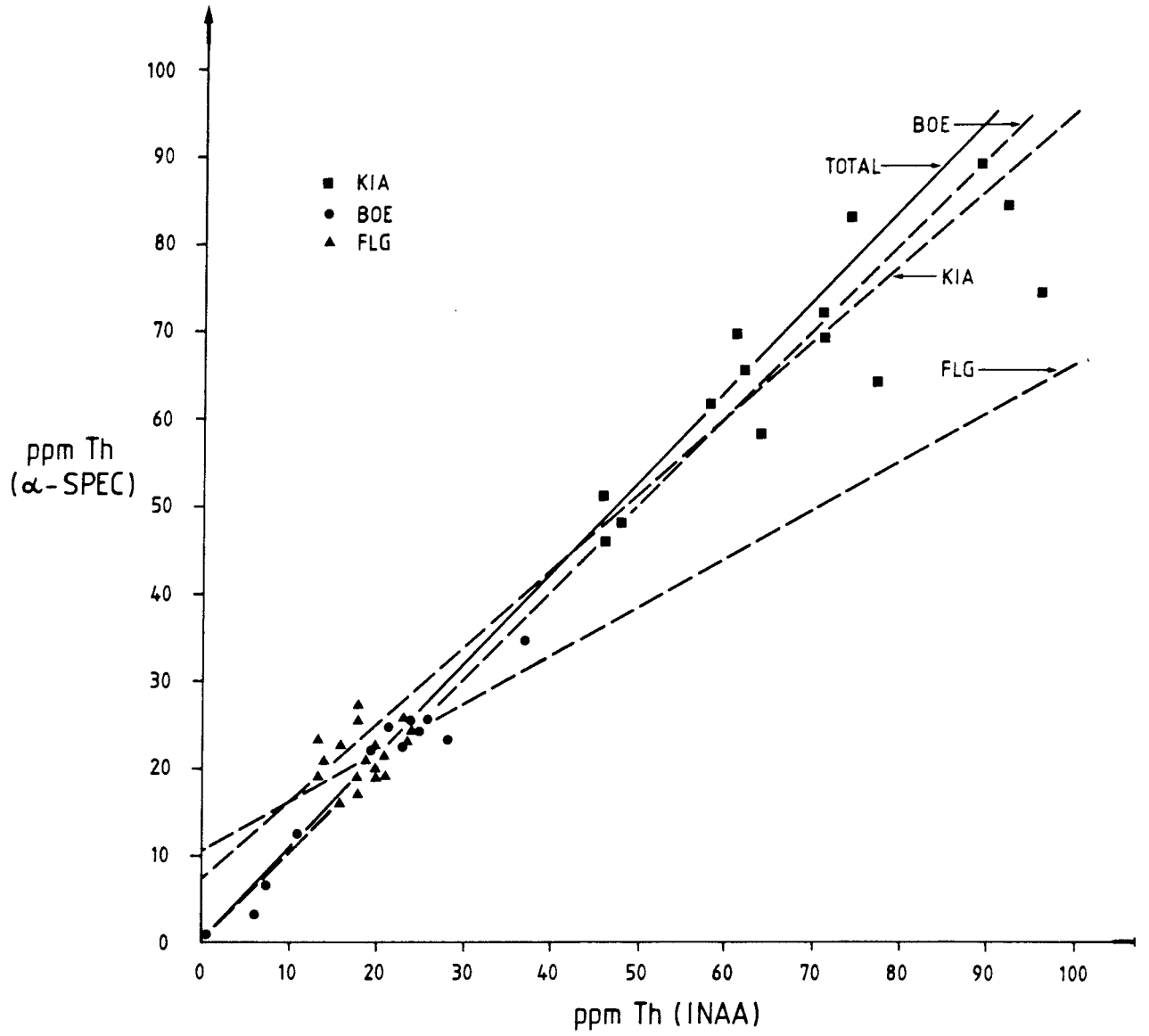
| SAMPLE | INAA Th ppm | RADIOCHEMICAL Th ppm | SAMPLE | INAA Th ppm | RADIOCHEMICAL Th ppm |
|--------|----------------|-------------------------|---------|----------------|-------------------------|
| KIA.1 | 46 + 2 | 46.1 + 2.1 | BOE.9 | 23.7 + 0.8 | 25.4 + 0.7 |
| KIA.2 | 64 + 2 | 57.7 + 1.2 | BOE.10 | 19.6 + 0.7 | 22.2 + 0.4 |
| KIA.3 | 96 + 3 | 74.1 + 2.1 | BOE.11 | 25.3 + 0.9 | 25.2 + 0.5 |
| KIA.4 | 62 + 2 | 65.5 + 0.8 | BOE.12 | 24.8 + 0.8 | 24.1 + 0.6 |
| KIA.5 | 92 + 3 | 84.0 + 2.1 | FLG.1 | 23 + 1 | 22.9 + 0.7 |
| KIA.6 | 58 + 2 | 61.4 + 1.2 | FLG.2A | 13 + 1 | 19.2 + 0.7 |
| KIA.7 | 77 + 3 | 63.8 + 1.2 | FLG.3A | 13 + 1 | 23.0 + 0.5 |
| KIA.8 | 71 + 2 | 68.8 + 1.2 | FLG.4A | 18 + 1 | 27.4 + 1.3 |
| KIA.9 | 48 + 2 | 47.8 + 1.2 | FLG.5A | 18 + 1 | 17.0 + 0.5 |
| KIA.10 | 61 + 2 | 69.6 + 1.2 | FLG.6A | 18 + 1 | 18.9 + 0.5 |
| KIA.12 | 89 + 3 | 88.9 + 2.5 | FLG.7A | 16 + 1 | 22.5 + 0.9 |
| KIA.13 | 74 + 3 | 82.8 + 2.1 | FLG.8A | 19 + 1 | 21.1 + 0.4 |
| KIA.14 | 46 + 2 | 51.1 + 0.8 | FLG.9A | 16 + 1 | 16.0 + 0.8 |
| KIA.15 | 71 + 2 | 72.1 + 2.5 | FLG.2B | 23 + 1 | 25.5 + 0.5 |
| BOE.1 | 0.58 + 0.03 | 0.86 + 0.12 | FLG.3B | 18 + 1 | 25.7 + 1.3 |
| BOE.2 | 5.9 + 0.2 | 3.2 + 0.1 | FLG.4B | 20 + 1 | 18.8 + 0.5 |
| BOE.3 | 7.4 + 0.3 | 7.3 + 0.3 | FLG.5B | 21 + 1 | 21.4 + 0.8 |
| BOE.4 | 11.0 + 0.4 | 12.5 + 0.3 | FLG.6B | 24 + 1 | 23.6 + 0.6 |
| BOE.5 | 37 + 1 | 34.5 + 0.9 | FLG.7B | 20 + 1 | 20.0 + 0.7 |
| BOE.6 | 28 + 1 | 23.2 + 0.7 | FLG.8B | 21 + 1 | 18.9 + 0.5 |
| BOE.7 | 21.4 + 0.7 | 24.5 + 0.7 | FLG.9B | 14 + 1 | 20.6 + 0.7 |
| BOE.8 | 23.1 + 0.8 | 22.5 + 0.7 | FLG.10B | 20 + 1 | 22.5 + 0.5 |

Table 3: Instrumental neutron activation analysis results for the concentrations in reference materials.

| Reference material | Th concentration ppm | Reference Value ⁵ |
|--------------------|-------------------------|---------------------------------|
| USGS AGV-1 | 6.2 ± 0.2 | 6.4 |
| USGS AGV-1 | 6.3 ± 0.2 | 6.4 |
| USGS AGV-1 | 5.6 ± 0.2 | 6.4 |
| IAEA SOIL-5 | 10.4 ± 0.3 | 11 |
| IAEA SOIL-5 | 10.2 ± 0.3 | 11 |
| IAEA SOIL-5 | 10.3 ± 0.4 | 11 |

CAPTION FOR FIGURE

Figure 1. Plot of alpha spectroscopy results against INAA results for Th analysis of granites and pegmatites.



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