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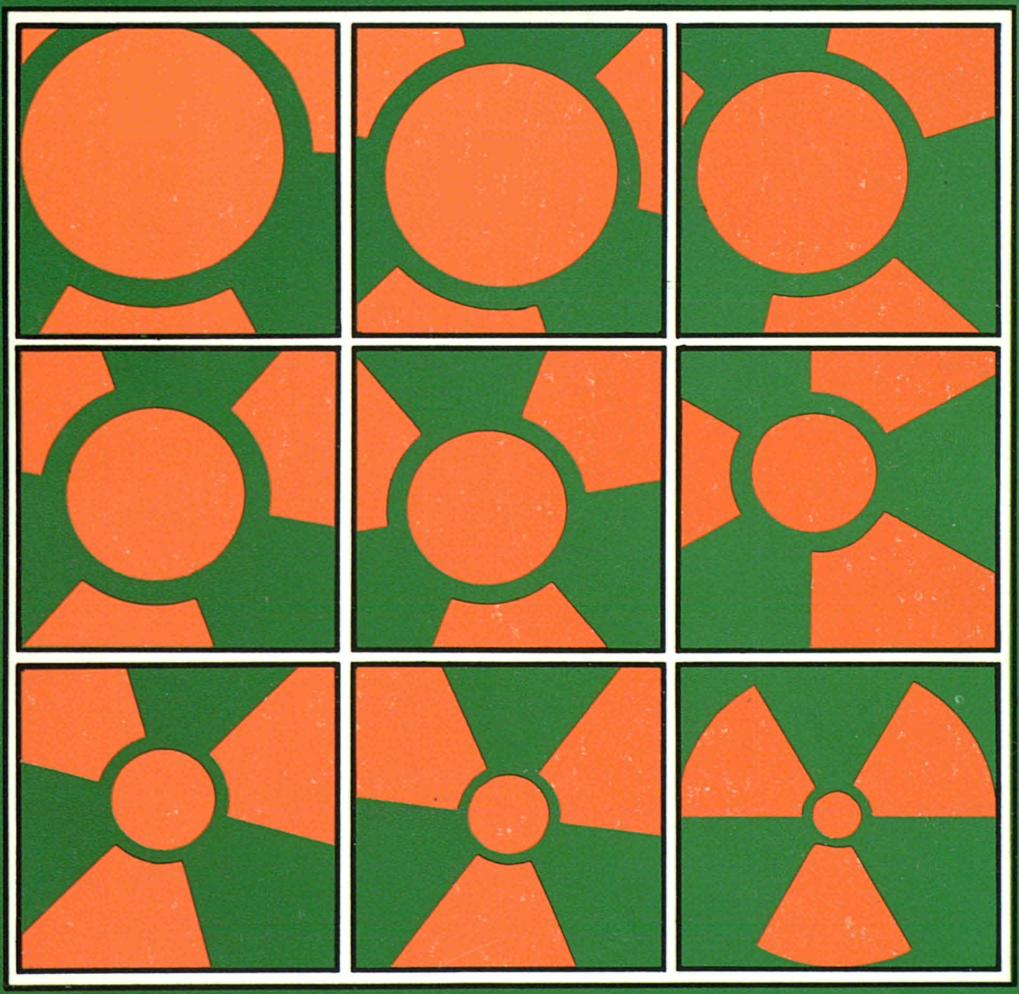

Report

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Geochemical modelling of the Broubster natural analogue site Caithness, Scotland

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EXECUTIVE SUMMARY

Anomalous uranium, thorium and rare earth element (REE) concentrations are associated with peat-rich soils at Broubster, Northern Scotland. The source of the anomaly has been traced to a mineralised hydrocarbon-containing zone in the underlying Devonian sedimentary rocks. From here the elements have been transported to and retained within a peat bog approximately 100 metres downslope. This report discusses the geochemistry of rock, soil and water samples collected from the Broubster site and the relationship of trace element distributions to actinide and lanthanide mineralisation. The results of a modelling study carried out to improve understanding of speciation and actinide migration mechanisms operating at Broubster are described.

Chemical speciation modelling indicates that natural organic acids compete successfully with inorganic ligands for uranium in the soil waters. The influence of humics is strongly pH dependent with a sharp "edge" at pH6. Under neutral to slightly alkaline conditions carbonate is the dominant complexant though elevated concentrations of phosphate may alter the inorganic speciation significantly. Reduction of U(VI) to U(IV) appears to play no part in uranium speciation at Broubster and levels are not constrained by solubility. Comparison with the results of a parallel experimental study suggests all the uranium to be in true aqueous solution.

The distribution of REE reflects the behaviour of uranium but the speciation of thorium is quite distinct; hydroxy species dominating throughout the pH range studied. All of the water samples are close to saturation with respect to amorphous ThO_2 suggesting precipitation or co-precipitation by iron oxy-hydroxides maintains concentrations at the values found. The poor mass balance obtained in experimental speciation work lends support to these findings. Taken together they indicate that a substantial proportion of the thorium in the Broubster waters is present in colloidal form.

The migration of transition metals both laterally and vertically within the soil zone has been investigated. Separate transport mechanisms are postulated for uranium and thorium. In the case of the former, chemical transport has been simulated using the directly coupled CHEMTARD program. A thermodynamic approach to quantifying uranium adsorption was followed, employing the Davis Leckie-triple layer model, as far as data availability allowed. Limited sensitivity studies were also performed to assess the effects of variation in key parameters.

In summary, the results of modelling are in very good agreement with experimental speciation data and the observed behaviour of uranium and thorium at the site. In the sense that field, laboratory and modelling aspects of the study were performed independently the results have, to an extent, validated the theoretical, thermodynamically-based approach. Recommendations are made in the report for further geochemical and hydrological investigations to allow better quantification of actinide mobilisation and fixation processes at Broubster.

1. INTRODUCTION

This report describes the results of a modelling study carried out, on behalf of the British Geological Survey (BGS), to aid interpretation of the Broubster natural analogue site, Caithness, Scotland (Figure 1). The work forms part of a co-ordinated project on natural radionuclide migration undertaken to improve confidence in predictive models used for radiological assessment [1].

Anomalous uranium concentrations were first discovered at Broubster in 1968 during a routine car-borne radiometric reconnaissance [2]. A preliminary soil survey in the same year, followed by more detailed investigations has traced the source to a mineralised vein in the Devonian (Middle Old Red Sandstone) Caithness Flags. From here uranium has been transported some 100m downslope into an adjacent peat bog. A number of other heavy metals including lead and zinc, do not appear to have been relocated to the same extent (Figure 2).

Recent advances in speciation and mass transport modelling [3, 4] provided an opportunity both to re-examine the geochemical system at Broubster and to attempt validation of thermodynamic models. Thus, the purpose of the present study has been to:-

- improve understanding of chemical speciation and migration mechanisms for uranium in peat-rich soils.

- test the applicability of current codes and data in a real field situation.

- highlight additional information required prior to further site investigation.

2. DESCRIPTION OF SITE

Broubster (Nat. Grid. Ref. N D 021 624) is located on an exposed "Flow" moorland about 10 miles south-west of Thurso (Figure 1). The regional topography is fairly flat with thick peat deposits and boulder clay concealing the underlying Caithness Flags. The uranium anomaly is transected by the minor north-south Shebster to Broubster road and marked, at its western end, by a lime kiln (Figure 3). Soils either side of the road are pedologically and geochemically distinct [5].

To the west the land rises as a grassy hummock about 10m or so above the plain. The soil here is well-drained consisting of silty, partly differentiated "Brown Earths". Development of leached ('E') and enriched ('B') horizons suggests the soil to be an <u>in-situ</u> deposit rather than resulting from disturbances associated with excavation of limestone for the kiln. Land to the east of the road is waterlogged with marshy vegetation and oily seepage. The soil comprises homogeneous peat, thickening from south to north and overlying a sharply differentiated boulder clay with a distinct 5cm gleyed horizon [5].

Bedrock has been examined at a pit excavated along the north bank of the kiln working. Laminated silty clay gradates into a weathered siltstone/fine-grained sandstone at 80cm depth. A 40cm bed of silicified limestone follows and at its base is the narrow mineralised zone; a 2-4cm thick calcite vein containing sphalerite, pyrite and galena. The lower surface of the vein is flecked with red-brown uraniferous hydrocarbon. A light-grey indurated siltstone with intercolated organic-rich laminations complete the sequence exposed. The rocks dip gently to the NNE [5].

3. ROCK AND SOIL CHEMISTRY

Recent analyses of rock, soil and water samples are available following detailed site investigations during the summers of 1986 and 1987 [6]. They have been re-examined during the present contract and the main features of the solid geochemistry are described below. Aqueous chemistry is considered further in the following section, in connection with the modelling exercise.

i) Rock samples

Eleven rock samples, collected from a pit dug into the limestone working west of the road (Figure 3), have been analysed by INAA for iron and 26 trace elements [6]. Values for U, Th, W,* Mo, As and five lanthanides are given in Table 1 where concentrations are compared with those of "average shale" [7,8].

Uranium is enriched in all the rocks with respect to shale, by at least a factor of four and, in the majority of samples, by an order of magnitude (Table 1). In contrast, thorium is depleted relative to shale, except in the silt fraction of JY6, where it reaches 24ppm. There is little correspondence between U, Th and the rare earths (REE). As these data show substantial concentrations of U in the limestone, this band itself is probably acting as a significant source for U mineralisation in addition to the hydrocarbon-rich zones.

REE patterns, normalised to average shale [8] are given in Figure 4. All show a strong relative enrichment of the heavy REE. Cerium concentrations are also higher than expected based on linear interpolation between lanthanum and the heavier elements. In the absence of data on Pr, Nd or Sm the existence of a positive Ce anomaly cannot be confirmed, however, and the possibility remains that artificially enchanced concentrations result from gamma spectral interference during analysis.

* The wide, and for soils (p4), systematic variation in values, suggests sample contamination during preparation for analysis is not the cause.

Other notable features of the rock analyses are the high concentrations of W*, enriched by a factor of 44 with respect to shale, Mo (x40) and As(x18.5). As with Th and the REE, higher values are associated with the sample of hydrocarbon-rich silt (JY6 SILT; Table 1). Although sphalerite has been detected [2], Zn levels are unremarkable.

ii) Soils

Soil traverses were carried out at Broubster in 1968, 1986 and again in 1987 [2, 6]. During the most recent survey three traverses were conducted, all at high angles to the anomaly. Samples of both surface and subsoils were taken.

Traverse 1 to the south-west of the kiln (Figure 3) encountered only shallow peat over boulder clay. Twenty surface and near-surface (<65cm) samples gave a pH range 4.2 to 6.2 and, with one exception, positive redox potentials. From the trace element analyses (Table 2) it can be seen that the majority of U and Th concentrations are less than 5ppm. Molybdenum levels are also lower than those found in the rocks of pit 1 (Table 1).

The soil encountered along Traverse 1 is not well differentiated in vertical section. This is reflected in the similar U concentrations for surface ($\leqslant$5ppm) and subsoils ($\leqslant$13ppm), close to the limit of detection.

Traverse 2, to the east and parallel to the road, extended over ground covered by peat and gleyed subsoil. The 28 samples collected show a wider variation in pH (3.7 to 6.5) and Eh (452 to -350mV) than obtained in 1968. This has been explained, in part, by seasonal factors and recent liming of the adjacent field [6]. Uranium concentrations are high (Table 3) but Th does not exceed 13 ppm along the traverse. Although the light REE La, Ce and Nd are at comparable or lower levels than in average shale (Table 1), Y displays up to a five-fold enrichment which may be indicative of heavy REE concentration. Indeed, the strong correlation between Y and U (Figure 5) suggests that the heavy REE may be similarly distributed. Zinc ($\leqslant$ 563ppm) is also enriched with respect to both the rocks ($\leqslant$ 136ppm) and "average shale" (90ppm).

The surface expression of the U anomaly is very sharp along Traverse 2 (Figure 6). High concentrations, in excess of 300ppm, are confined to a zone 20m wide with levels either side falling to those in the rocks (Table 1). The subsoil (>60cm) profile is more irregular (Figure 6), displaying a "blurred" reflection of the topsoil anomaly. This may be attributed to the fact that samples taken at 60-100cm depth contain variable proportions of organic material. The two samples of gleyed soil, however, are much lower in uranium (Figure 6).

Traverse 3, just to the north-east of the kiln and at roughly right angles to the anomaly, was underlain by peat at its extremities and brown earths in the centre. Analyses of seven paired surface/subsoil samples are shown in Table 4. All samples are strongly oxidising (390 to 507mV) and fall within a pH range of 4.4-6.5. Uranium concentrations increase slightly towards the centre of the traverse (Table 4) but do not exceed 15ppm in either surface or subsoils. Thorium levels are also low (≤13ppm) and show no correlation with uranium. Phosphate levels appear unrelated to U, Th or Y concentrations (Table 4).

Analyses of a soil profile taken from Pit 2 (Figure 3) 15m east of the road are shown in Table 5. The degree of concentration and fractionation of actinide and lanthanide elements is extreme. The waterlogged upper 30cm of peaty 'A' horizon [5] contains U levels far in excess of those found in the source rocks of Pit 1 (Table 1); the latter, themselves, enriched by an order of magnitude with respect to "average shale". Concentrations of U, the lanthanides and also Mo increase steadily from the surface to the base of the peat layer (Figure 7). High Th values, on the other hand, are confined to the lower 10cm, reaching only 2 to 3 ppm in the topmost peat. These results suggest upward diffusion or capillary transport of U and the REE with Th remaining fixed in the basal zone. Downward concentration of U, Th and REE by sorption and filtration is thought to be unlikely owing to exceedingly low Th levels in surface and near-surface soils.

The remainder of the profile comprises poorly differentiated boulder clay [5]. A 5cm leached 'E' horizon overlies a mottled silty clay (B/C) which, in turn, gradates into weathered rock (C/D). The sharp boundary with the peat is marked by a drastic change in trace element geochemistry (Figure 7). Uranium concentrations decrease with depth from only 15ppm to less than 4ppm and Mo to less than 3ppm. Thorium and the REE revert to levels similar to those of shale (Table 1). No downward diffusion occurs; all high U, Th, REE and Mo values being confined to the peat (Table 5).

In addition to U/Th partitioning and REE concentration in the 'A' horizon, there is evidence of REE fractionation between the peat and subsoil. From the shale normalised profiles (Figure 8), it can be seen that the heavier REE are relatively enriched in the peat (La/Yb=0.4) when compared to the flat pattern observed for the six boulder clay samples (La/Yb=1). No data are available for Pr, Nd or Sm but the peat analyses also appear to be enriched in Ce; normalised La/Ce=0.6 as opposed to ~ 1 in the clay. A similar fractionation of heavy REE and Ce has been observed in glacial soils from Central Wales [9]. There fractionation resulted from uptake by amorphous and concretionary iron oxides with Ce oxidised to Ce(IV). At Broubster, iron levels are comparable throughout the profile and organic matter is almost certain to be the main sink. The speciation of U and Th is discussed in section 4 below.

Although outside the remit of this work, mention is made here of iridium levels in the Broubster soil samples. The upper 10cm of the profile described contains more than 1ppm Ir, roughly 1000 times the crustal average [10]. The reason may be sample contamination but this is still uncertain.

4. AQUEOUS GEOCHEMISTRY

i) Soil water analyses

Eight soil water samples (Table 6) taken in 1987 and analysed for the major elements, traces, U and Th were used for speciation modelling. Earlier analyses were not considered as they had been acidified in the field [6]. All of the waters are strongly oxidising (Eh 201 to 419mV) and slightly acidic (pH 5.3-6.7). Uranium concentrations reach 21 ppb in BS3 but do not correlate with either Th levels or total organic carbon (Table 6). No data for U and Th were obtained for the three samples taken to the west of the site (BS4,5,8) but with so few analyses, at varying depths, no areal trend can be discerned.

The five waters with measurable quantities of the two actinides were passed through a sequential analyser [11], containing columns of ion-exchange resin and DEAE cellulose to differentiate polar inorganic and organically bound fractions. That portion associated with iron and manganese oxy-hydroxides (DEAE/HCl) was also analysed. The results (Table 7) show that, for all samples, the majority of the U (57-99%) is bound to organic matter with relatively minor concentrations in sesquioxide and cationic form. Uranium anions were not detected. The excellent mass balance obtained (Table 7) lends credence to the results.

In contrast to U, the bulk of the Th present is associated with Fe/Mn oxy-hydroxides (Table 7) and the total concentration measured by the analyser gives a very poor mass balance when compared to Th levels obtained by "whole element" groundwater analysis. The latter suggests an additional Th phase to be present, possibly colloidal, though ultra-filtration would be necessary to confirm this.

ii) Inorganic speciation of uranium

The speciation of each soil and peat water was modelled using the PHREEQE code [12] and two sets of thermodynamic data; the preliminary project database from CHEMVAL/MIRAGE [13] and an NEA compilation [14], based largely on the work of Schweingruber [15]. Results for uranium* are given in Table 8, from which the following points emerge:-

The dominant oxidation state is U(VI) for all samples

Measured electrode potentials range from 200-420mV (Table 6) and no reduction to a lower oxidation state is expected. It should be noted, however, that all water samples were taken from within about 1m of the surface and more reducing conditions are likely at depth.

Carbonate is the dominant inorganic complexant

Uranium(VI) carbonates are by far the most abundant species, hydroxy and sulphate complexes never exceeding 10% of the total speciation.

As shown in Table 8 results obtained using the two data sets are closely similar. With the CHEMVAL database, the 1:1 complex UO_2CO_3 appears relatively more important, comprising between 52% and 97% of the elemental concentration, but the difference is not great (NEA: UO_2CO_3 = 27-88%). Both predict sample BS8, which has the lowest pH (5.3), to contain a higher proportion of the cationic species, UO_2^{2+} (33%) and UO_2OH^+ (10%).

Phosphate levels are below detection limits [6] in most of the water samples and for this reason were not included in the above simulations. However, HPO_4^{2-} is known to bind strongly to uranium and could significantly alter its speciation even if present at low concentrations. To investigate possible effects, 1.7×10^{-6} $moldm^{-3}$ (160ppb) HPO_4^{2-} [6] were added to sample BS3 and U speciation modelled using the NEA/EIR database. Almost 95% of the U present was taken up as $UO_2(HPO_4)_2^{2-}$. This result suggests further work is required to determine low, but possibly significant, concentrations of HPO_4^{2-} in the other Broubster soil waters.

* For the three waters where no uranium value was available, concentrations were taken to be 8.9×10^{-8} $moldm^{-3}$, as in BS3, (Table 6).

Uranium levels are not solubility controlled

All waters are undersaturated with respect to the common uranium minerals uraninite*, coffinite and rutherfordine. The first and third columns of Table 8 show saturation indices, (lg ion activity product/solubility product) computed using the respective datasets; a value of zero representing a solution exactly at equilibrium with that mineral. As for aqueous speciation, the two sets of results compare very well. The saturation state of uraninite is pH dependent, values becoming less negative at lower pH. In contrast, rutherfordine (UO_2CO_3) has a saturation index of -3 for all samples. A single simulation performed on BS3 indicates that uranium phosphates do not approach saturation, though co-precipitation with corresponding lanthanide minerals has not been investigated.

iii) Speciation of uranium in the presence of organics

Uranium is known to interact strongly with natural organics and fixation of U in peat is common [16, 17]. The presence of oily seepages at Broubster suggests organic complexation may play a major role in determining soil and groundwater speciation. Although the Broubster organics have not yet been characterised, either in the soil or waters, measurements of total organic carbon are available (Table 6) allowing scoping studies to be carried out based on data obtained for "humics" from elsewhere.

A literature search was undertaken to obtain data for humic acid (HA) binding. Selected formation constants from four sources are shown in Table 9. It can be seen that the values are in surprisingly good agreement given the lack of detail concerning the structure of the HA molecule, type of complexation sites and, in some cases, the degree of ionisation.

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* The Ksp of uraninite in the CHEMVAL database corresponds to that quoted for $UO_2.2H_2O$ in the NEA/EIR.

Since the mechanism of U uptake by HA is poorly understood at present several assumptions need to be made when modelling uranium - humate speciation. Thus, for calculation purposes it was assumed that:-

- aqueous complexation takes place via a straightforward metal-ligand ion association reaction. This is known to be a gross oversimplification as large HA molecules are essentially colloidal organic substrates.

- the humic acid is completely dissociated (α =1), with a unit negative charge, at the soil water pH of 5 to 7. Values of α may be much lower, typically ~ 0.5 [18], and will vary with pH. The actual charge distributions are unknown.

- All organic carbon is present as "humic acid" with a molecular weight of 50,000 [19]. For sensitivity purposes a molecular weight of 10,000 was also adopted in some cases (below), increasing the effective concentration of HA by a factor of 5.

A number of simulations were carried out in order to assess whether "humic acid" could compete successfully for U with the major inorganic ligands in the Broubster peat waters (Table 6). Data for HA taken from Shanbhag and Choppin [19] were used in conjunction with the CHEMVAL database [13]. Constants for both the 1:1 and 1:2 species of U are available. No data were obtained for the majority of major and trace components, or Th, though additional information is expected from the CHEMVAL programme [13]. Results of the modelling exercise for each water sample are given in Tables 10 and 11. They are summarised below.

Humic acid complexes compete successfully with carbonates below pH6.

Uranium humate complexation is strongly pH dependent (Table 10). Above pH6 carbonates dominate the speciation but as acidity increases humates rapidly become more important, to the extent that 95% of U in sample BS8 (pH = 5.3) is predicted to be bound as UO_2HA^+. The pH "edge" (Figure 9) marks a sharp transition from neutral and negatively charged inorganic complexes to humates which may have a net residual positive charge dependent on the degree of ionisation and the relative abundance of adsorbed ions. Increasing the concentration of humic acid by a factor of 5 makes little difference to the speciation of uranium in near neutral solution (Table 10). The net effect is to shift the pH "edge" towards slightly higher pH (Figure 9).

Uranium levels are not solubility constrained in the presence of humic acids.

For the majority of samples saturation indices are unchanged from the corresponding inorganic speciation results presented previously (Table 8). In the case of BS8, however, binding by humates is sufficient to depress the saturation level of uraninite by more than an order of magnitude (Table 10).

As a check on the above calculations the modelling exercise was repeated using thermodynamic data supplied by the NEA [14] and constants for uranium-humic complexation taken from Kim [18]. Formation constants are available for the 1:1 and 1:2 complexes of both U and Th from which "representative mean values" were chosen based on the experimental details provided (Table 9).

Results of the simulations (Table 11) differ from those obtained using the CHEMVAL database (Table 10) in that humic complexes dominate the speciation throughout the pH range 5.3 to 6.7. A pH "edge" similar to that predicted using CHEMVAL data (Figure 9) does occur above pH7, however, and scoping studies based on sample BS1 suggest that U is quantitatively complexed by carbonate at pH 7.5 (Figure 10). As with the earlier cases, uranium is present exclusively as U(VI) and all uranium solids are strongly undersaturated (Table 11).

Taken together the results of modelling (Tables 8,10,11) compare well with the experimental speciation study (Table 7). The latter estimated the majority (57-99%) of U to be bound to organic matter with the remainder in sesquioxide and/or cationic form. Assuming these measurements are accurate, simulations employing the CHEMVAL database tend to slightly underestimate the strength of U-humic complexation or, conversely, overstate the importance of carbonate (Figure 10). In contrast, the NEA data would seem to overestimate organic interaction since computed saturation indices for uraninite and rutherfordine are much lower than expected in these waters (Table 11).

iv) Speciation of thorium

Thorium is not included in the preliminary CHEMVAL database [13] but speciation modelling has been carried out on the five samples with known Th levels (Table 6) using the NEA/EIR data. Results are presented in Table 12, from which it is apparent that only one species, $Th(OH)_4^{\circ}$, occurs at significant concentrations, accounting for almost 100% of the total Th present. Repeating the simulations in the presence of both phosphate and humic acid [18] was found to make no difference to the speciation results.

Amorphous $ThO_2.2H_2O$ is predicted to be slightly supersaturated in all samples (SI = 0.07 - 0.90) suggesting that Th levels are solubility controlled. In view of the saturation state of $Fe(OH)_3$ (Table 12), co-precipitation on amorphous iron oxides appears to be the most likely means of abstraction from solution.

The results of modelling are in excellent accord with the findings of the experimental speciation study. Thorium occurs only in the DEAE/HCl extract, corresponding to the Fe/Mn oxy-hydroxide phase. Further, the poor mass balance obtained for Th (Table 7) suggests that a large proportion (>60%) of the Th bearing oxides are colloidal. Sequential filtration of soil water samples below 0.45μm is required, therefore, in future work.

5. CHEMICAL TRANSPORT MODELLING

i) Approach

It was originally intended that the CHEMTARD coupled program [20] be used to quantify the rate and extent of uranium migration at Broubster. CHEMTARD is a directly coupled code which represents the one-dimensional transport of decaying chemical species while accounting for phase transfer via reversible precipitation-dissolution, ion-exchange and surface complexation. Unfortunately, however, no hydrogeological data are yet available from the Broubster site and none were measured during the period of the present study. This, together with the fact that the peaty soil and its sorptive properties have still to be characterised, precluded quantitative prediction. Nevertheless, a number of chemical transport simulations have been performed to demonstrate the capabilities of coupled modelling and to refine the approach to studying natural analogue sites.

Owing to uncertainties regarding the flow regime simplifying assumptions were made when constructing the conceptual models described below. Thus, differences in porosity, permeability and dispersivity between the boulder clay and peat (section 2) were ignored. Solute transport was assumed to be by advection only along a homogeneous flow path. Unsaturated flow in the boulder clay and seasonal effects were not considered.

On the basis of the speciation calculations described in the previous section, it has been assumed that uranium is transported from the mineralised zone, through the boulder clay, as neutral or negatively charged carbonate complexes (Table 8). As U-containing water enters the peat zone it encounters more acid conditions and a higher concentration of "humic acid" which competes with the carbonate to form a complex, represented as $UO_2HA^+(aq)$. The latter then sorbs onto the peat via the Davis-Leckie triple layer adsorption model [21]. This simple scheme (Figure 11) is felt to best reflect the body of experimental and theoretical data compiled to date. More exhaustive studies await the production of detailed hydrogeological analyses and adequate information concerning the specific interaction between groundwater solutes and the peaty substrate. No solute transport modelling was attempted for thorium owing to the likely role of colloidal particulates in its migration (section 4).

ii) Results of Coupled Modelling

Three sets of simulations were performed to investigate:-

- aqueous complexation of uranium as it moves from boulder clay to peat.
- formation and sorption of UO_2OH^+
- sorption of UO_2HA^+ in competition with Na^+, Ca^{2+} and H^+.

The calculation domain was 100m and the water velocity varied from $1myr^{-1}$ to $1cmyr^{-1}$. The former corresponds to the assumption that excavating the kiln (Figure 3) "triggered" uranium release whereas the latter represents a minimum velocity based on the inferred age of the peat (< 10,000 years). In either case decay of uranium is insignificant.

Competition between humic acid and carbonate for available uranium was first modelled for the case of rapid, "conservative" transport through the clay to the peat. Ten components were considered in the speciation calculations ($Na^+, Ca^{2+}, Mg^{2+}, H^+, CO_3^{2-}, SO_4^{2-}, Cl^-, OH^-, UO_2^{2+}$ and HA^-). Major element levels reflect those of groundwater BS8 in the peat (pH5.3; Table 6) and BS4(pH6.7) in the boulder clay. The input concentration of uranium was 8.9×10^{-8} $moldm^{-3}$, corresponding to the highest value found (Table 6).

Results at 20 years (Figure 12) and 100 years (Figure 13) clearly show the effect of competitive complexation as UO_2HA^+ progressively displaces $UO_2CO_3^{\circ}$, to become the dominant uranium species in the peat zone. The upper curve traces the decrease in total uranium from input to its background level of 1.4×10^{-8} $moldm^{-3}$ (Table 6), from which it is apparent that mass balance has been preserved.

The surface complexation model contained in CHEMTARD [20] is based on the Davis-Leckie triple layer approach [21] in which a neutral surface (SOH) can dissociate to give a negatively charged site:-

$$SOH = SO^- + H_s^+ \qquad K = \frac{[SO^-]\,[H_s^+]}{[SOH]} \quad *$$

or, conversely, react with a proton at the surface to form a positively charged site:-

$$SOH + H_s^+ = SOH_2^+ \qquad K = \frac{[SOH_2^+]}{[SOH][H_s^+]}$$

The activity of H^+ in the "surface plane" is related to the activity in the bulk solution by:-

$$[H_s^+] = [H^+] \exp\left(\frac{-e\psi_i}{kT}\right)$$

Where ψ_i is the change of potential when a species moves from the bulk solution to the solid phase, e is the electronic charge, k is the Boltzmann Constant and T, the temperature in Kelvin. The model is discussed in detail elsewhere [21,22].

Data requirements of the Davis-Leckie model are substantial, comprising the first and second deprotonation constants for SOH_2^+, the intrinsic adsorption constant for a given ion at the surface, effective area of sorbent, equivalent "concentration" of sites available for sorption and capacitance between the surface-beta plane and beta plane - "diffuse layer" [21]. In the absence of such data pertaining to either solution or solid species at Broubster, assumptions are necessary to allow scoping studies. Thus, intrinsic adsorption constants were taken from values quoted for sorption onto goethite (Table 13). Data for uranium humates are not known but the adsorption of UO_2OH^+ has been studied and constants for binding on goethite are available [23]. Although not of direct relevance these

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* The subscript 's' denotes an ion located at the surface plane [21].

are, nevertheless, useful for formulating and testing the surface complexation model and for estimating the likely uptake of uranium complexes in competition with major groundwater cations.

Preliminary calculations were performed in the presence of 0.1 molar NaCl solution to achieve convergence and optimise the grid spacing. The excess Na^+ and Cl^- ions appear to stabilise the numerical system such that in subsequent studies on actual groundwater compositions (Table 6) it was found necessary to allow anionic sorption of Cl^- to help maintain charge balance.

The equilibrium constant for sorption of UO_2HA^+ was first assumed to be equal to that of UO_2OH^+ ($10^{-2.2}$)and transport from the clay to the peat zone modelled using CHEMTARD. Concentrations of competing groundwater ions were those of BS8 (peat) and BS4 (clay), as before. The resultant concentration versus distance profile at 200 years is shown in Figure 14. It can be seen that the UO_2HA^+ "front" is extremely sharp, representing effective uptake on entry into the peat. The kink observed in the profile is probably a numerical artefact arising from quantitative retention of uranium close to the source. Two further simulations were carried out to investigate the effect on uranium uptake of decreasing the intrinsic adsorption constant (lg K_{ads}) for UO_2HA^+. The results, plotted in Figure 14 for comparison, demonstrate that as the lg K_{ads} decreases competition from other groundwater cations becomes more effective and the uranium plume spreads.

The above simulations are no more than example calculations and many alternative scenarios could be envisaged; for example, anionic sorption of $UO_2(CO_3)_2^{2-}$ [24], ion-exchange [17] and reduction of uranium to U(IV) [25]. Further sensitivity studies were not possible within the resources of the current contract. It is felt unlikely, however, that additional coupled transport modelling would lead to significant advances in quantifying U migration until the hydrogeology, soil and soil water chemistry of the Broubster site are better understood. Recommendations for future studies are made in the following section.

6. DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

Chemical speciation modelling has been carried out to investigate the behaviour of uranium and thorium at the Broubster natural analogue site. The results indicate that natural organic acids compete successfully for uranium with carbonates and other inorganic ligands in the peat-rich waters. The influence of humics rapidly becomes more marked as soil water pH drops below 6. Under more alkaline conditions carbonate is the dominant complexant, though elevated concentrations of phosphate (for example, from agriculture) could also have an effect.

Reduction of U(VI) to U(IV) appears to play no part in uranium speciation at Broubster. Thus, the situation differs substantially from that found in U "roll-front" deposits [25]. Further, U levels are not constrained by solubility in any of the waters modelled; its saturation state with respect to the more common minerals indicating true solution.

The speciation of thorium is quite distinct from that of uranium. Hydroxy species dominate throughout the pH range, even in the presence of high "humic acid" concentrations. All of the Broubster water samples are close to saturation with respect to amorphous ThO_2 suggesting precipitation and/or co-precipitation maintains Th concentrations at or near to the levels found.

The results of modelling are in very good agreement with experimental speciation data and the observed behaviour of U and Th at the Broubster site. Assuming the thermodynamic data employed are accurate, representative and can be independently confirmed, the above study constitutes a significant step in the direction of model validation. Given both theoretical and experimental evidence concerning the speciation of U and Th, an outline model may now be formulated for their transport and immobilisation.

Despite their common source and, ultimately, the same sink, migration pathways for U and Th are distinct. Uranium is transported in true solution as carbonate or, possibly, phosphate aqueous complexes. On the basis of the speciation studies described above, it appears that a pH "edge" marks a sharp transition from neutral to negatively-charged inorganic complexes of U to positively-charged humates. The latter then sorb onto the peaty substrate. Thorium, on the other hand is carried through the soil as a colloidal oxy-hydroxide phase and, given the slight supersaturation of amorphous iron hydroxides in Broubster waters, co-precipitation on finely-divided ferric flocs is highly probable (Figure 8).

The precise mechanism of fixation is unknown, but available data from electrode potential measurements (Eh>200mV), REE distributions, trace element correlations and aqueous speciation indicate that neither reduction nor precipitation reactions are involved in U uptake. Reversible ion-exchange of UO_2^{2+} has been suggested for other peaty soils [17] but is felt to be unlikely at Broubster owing to the following observations:-

- very little U exists in uncomplexed form (Table 10)

- sorption appears to be irreversible with little or no diffusion into underlying clay.

- the relative paucity of exchangeable cations in peats

- the peat shows no sign of becoming saturated with respect to U (levels in excess of 1000 ppm)

In the case of Th, retention by peat is thought to be partly a physical process; fixation arising from pore clogging by Th-bearing colloids. This would account for the observation that Th is restricted to the basal 10cm or so of the peat horizon whereas dissolved U is distributed vertically throughout the peat profile (Figure 7). However, since neither U nor Th is transported downwards into the clay, humic acids are obviously instrumental in the chemical retention of both actinides.

Coupled chemical transport programs now being developed [4] will help quantify the processes of actinide transport and fixation.

Progress in future work will depend, however, on adequate characterisation of site hydrology. In particular, estimates need to be made of:-

- soil water pathways and flow velocity
- diffusion rates in low permeability units
- dispersivity
- porosity
- cation-exchange capacity of soils, site "accessibility" and effective surface area available for sorption.

More detailed studies of soil and groundwater chemistry are also required, to include information on:-

- phosphate levels
- lanthanide element concentrations
- variation of soil water pH and Eh with depth
- change of water pH along a traverse from kiln to peat bog
- geometry and extent of the soil water anomaly
- U and Th activity associated with soil water filtrates at pore sizes down to 1nm.

Finally, the Davis-Leckie triple layer adsorption model has been used in preliminary coupled calculations with the CHEMTARD code [4]. The data requirements of this model have already been described and experimental data for key parameters would be needed in further work. However, some relatively simple experiments could also be undertaken to establish:-

- the size distribution and surface charge distribution of organic matter as a function of pH

- U speciation under controlled pH variation

- degree of U uptake before the peat becomes saturated

- adsorption/desorption rates and the extent to which U sorption is irreversible.

- the relative importance of physical and chemical processes in Th filtration. The latter may be assessed by passing coarse soil water filtrates though columns of Broubster clay and peat, respectively

- U and Th levels in local biota.

It is concluded that thermodynamic speciation modelling, used in conjunction with experimental studies and direct field observation has significantly improved understanding of the geochemical system at Broubster. Since the three aspects were carried out independently the results have also, to an extent, validated the theoretical approach. This suggests that future modelling exercises on natural geochemical analogues can be used to provide at least a qualitative guide to the behaviour of radioactive waste disposal systems.

ACKNOWLEDGEMENTS

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FIGURES

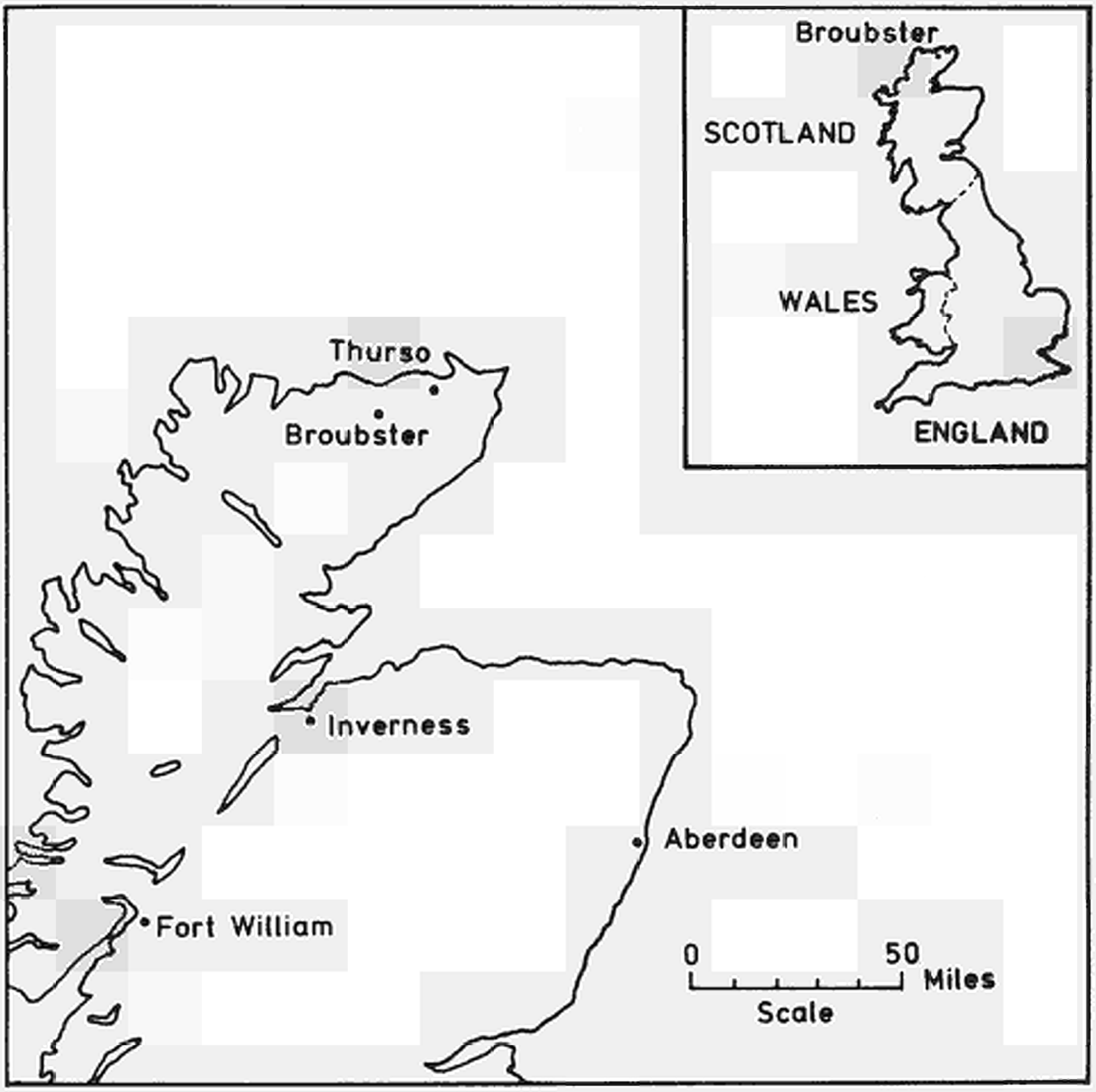

Figure 1 Location of the Broubster natural analogue site

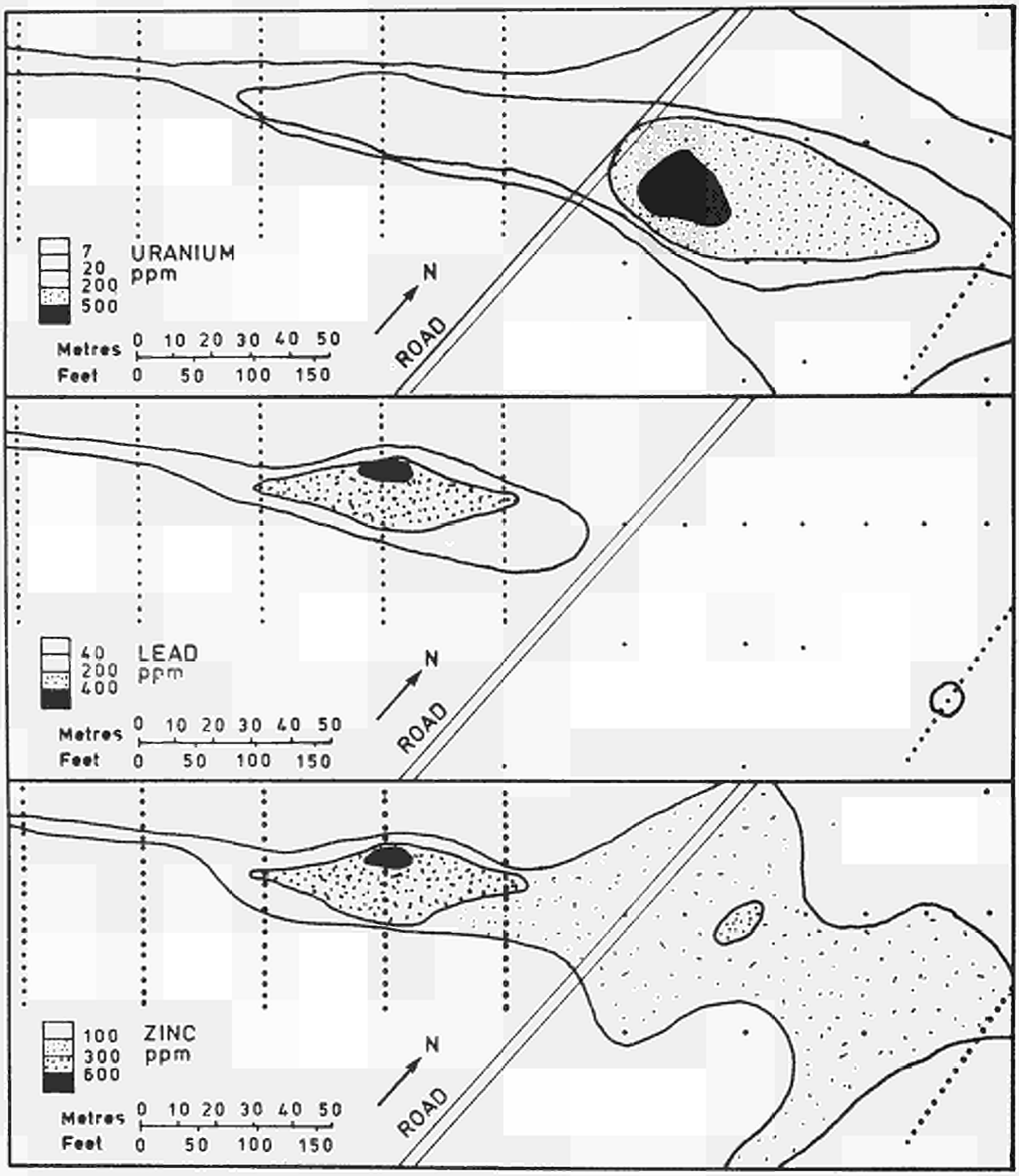

Figure 2 Uranium, lead and zinc distributions in the B and/or C horizons of Broubster soils (after [2])

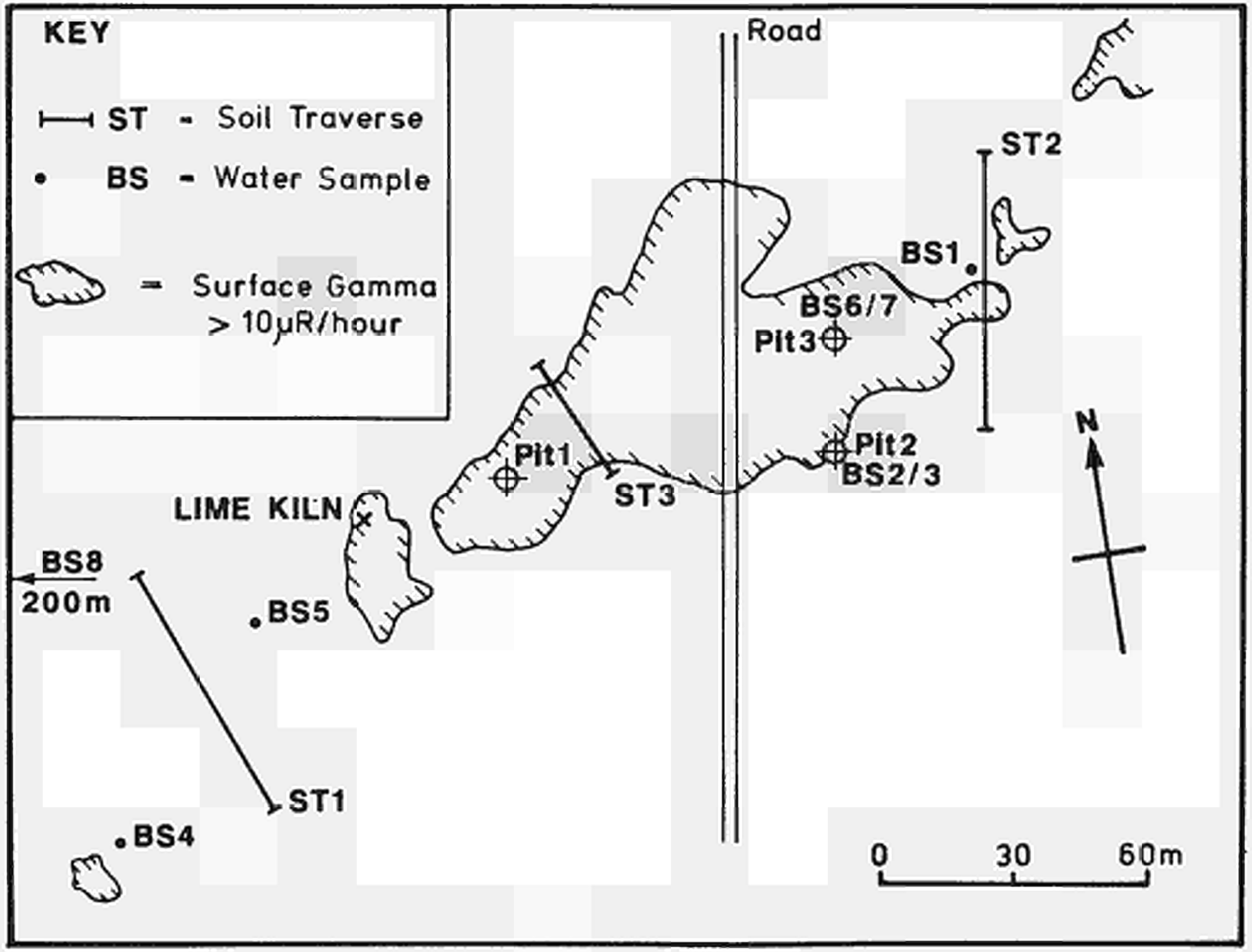

Figure 3 Location of soil and water samples

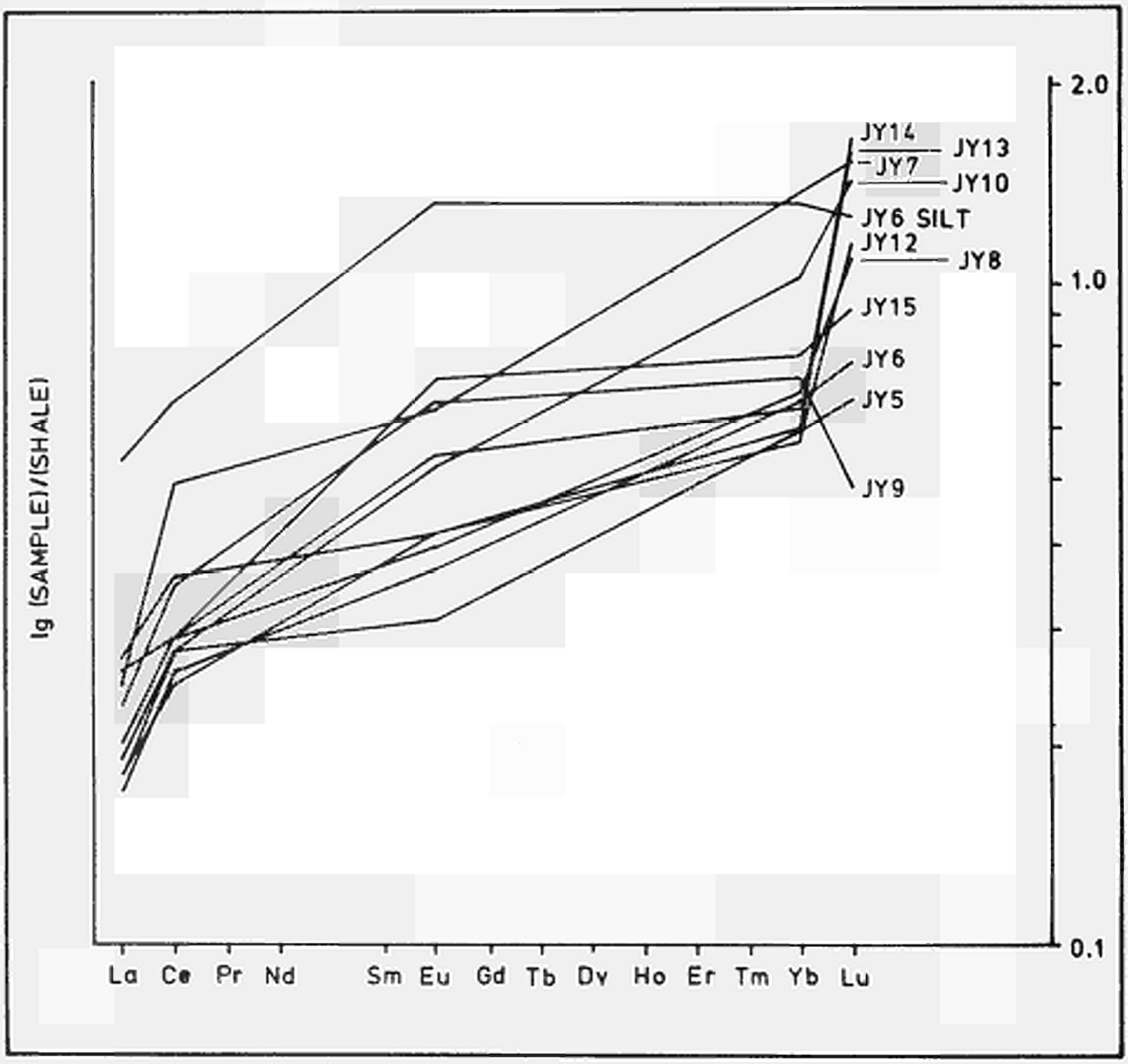

Figure 4 Shale normalised REE patterns for rock samples taken from Broubster Pit 1.

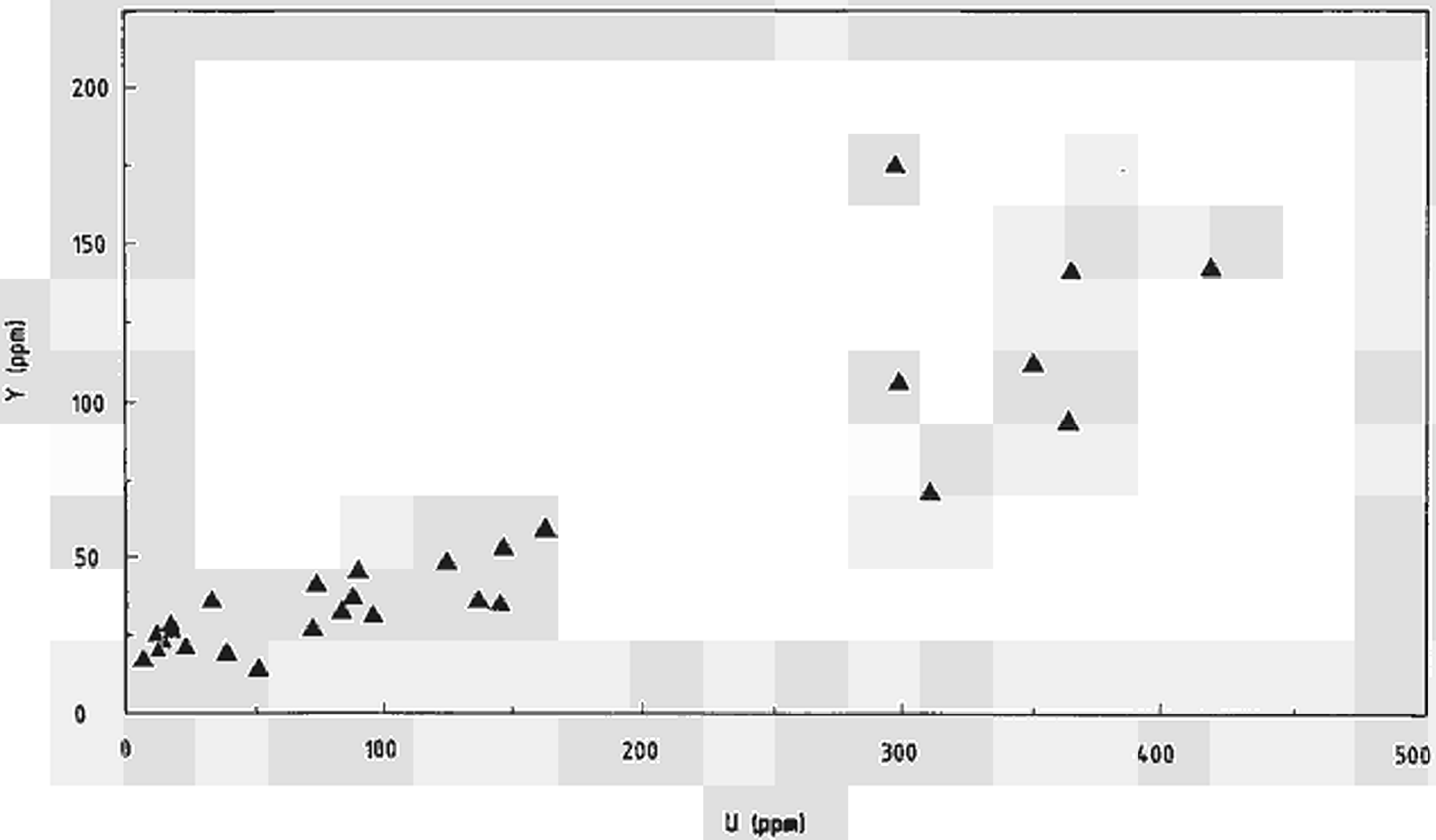

Figure 5 Correlation of uranium with yttrium along Broubster soil traverse 2

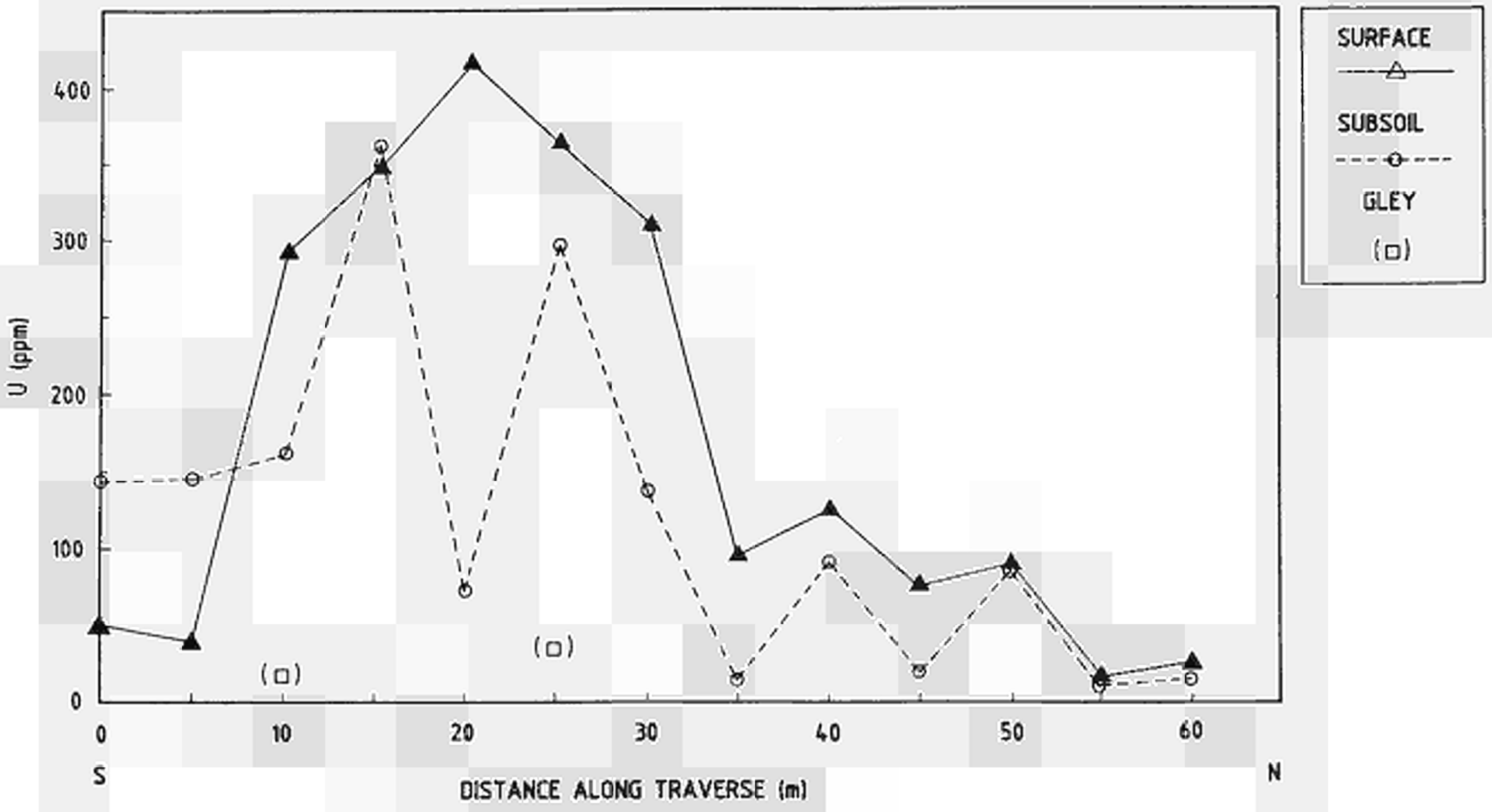

Figure 6 Variation in uranium concentrations along Broubster soil traverse 2

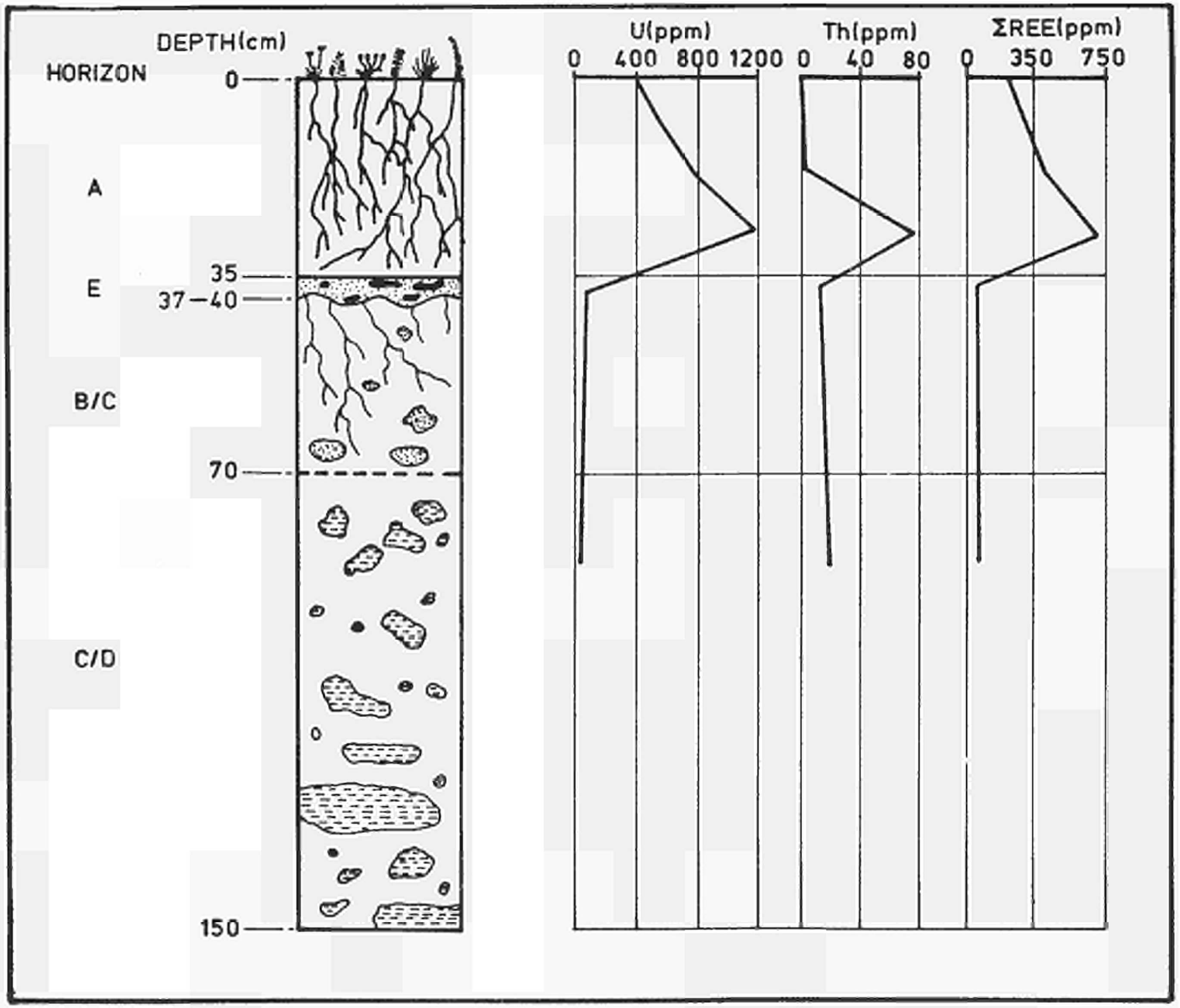

Figure 7 Soil profile at Broubster Pit 2 : Analysis for U, Th and REE (ppm)

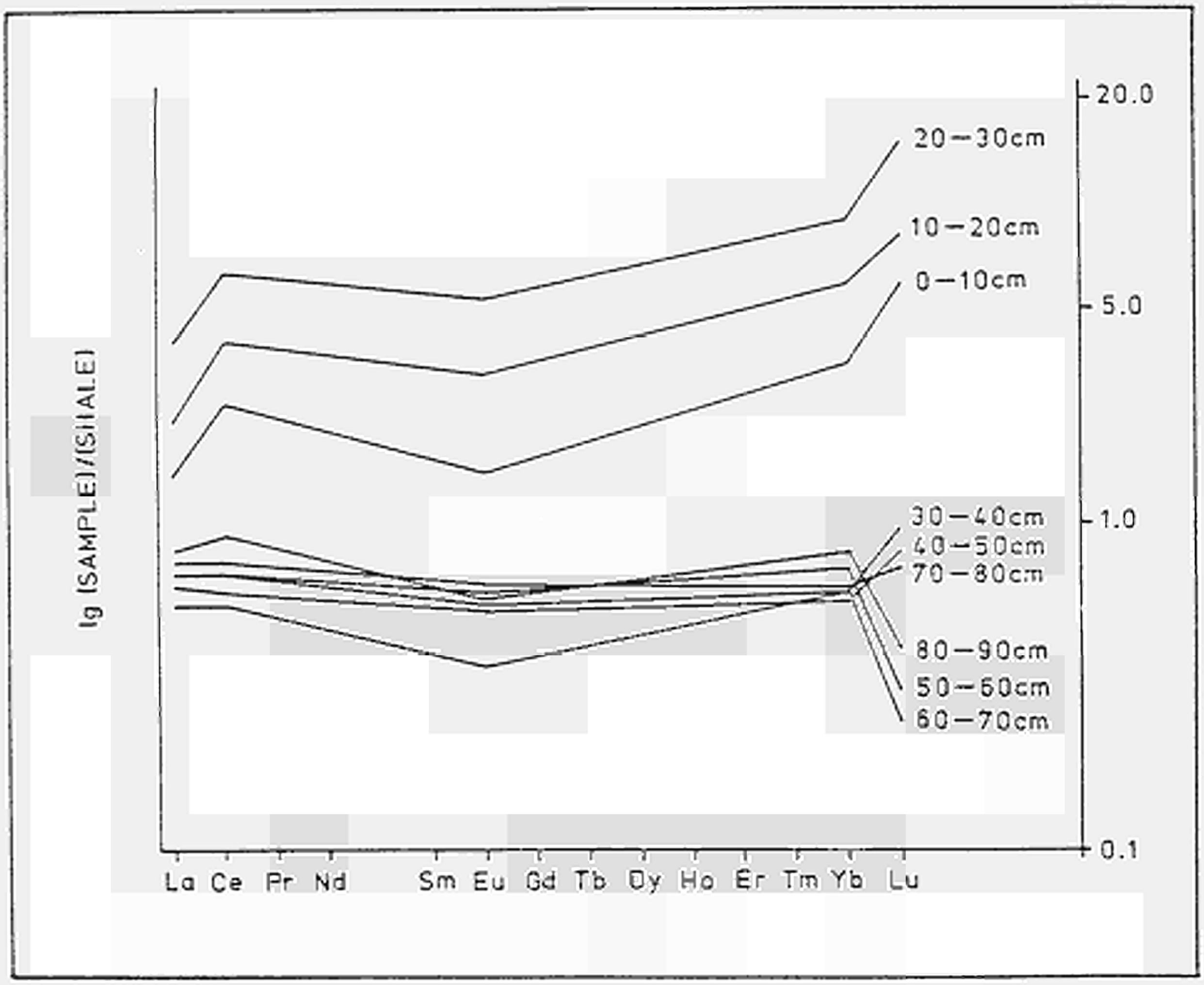

Figure 8 Shale normalised REE patterns for the soil profile exposed in Broubster Pit 2

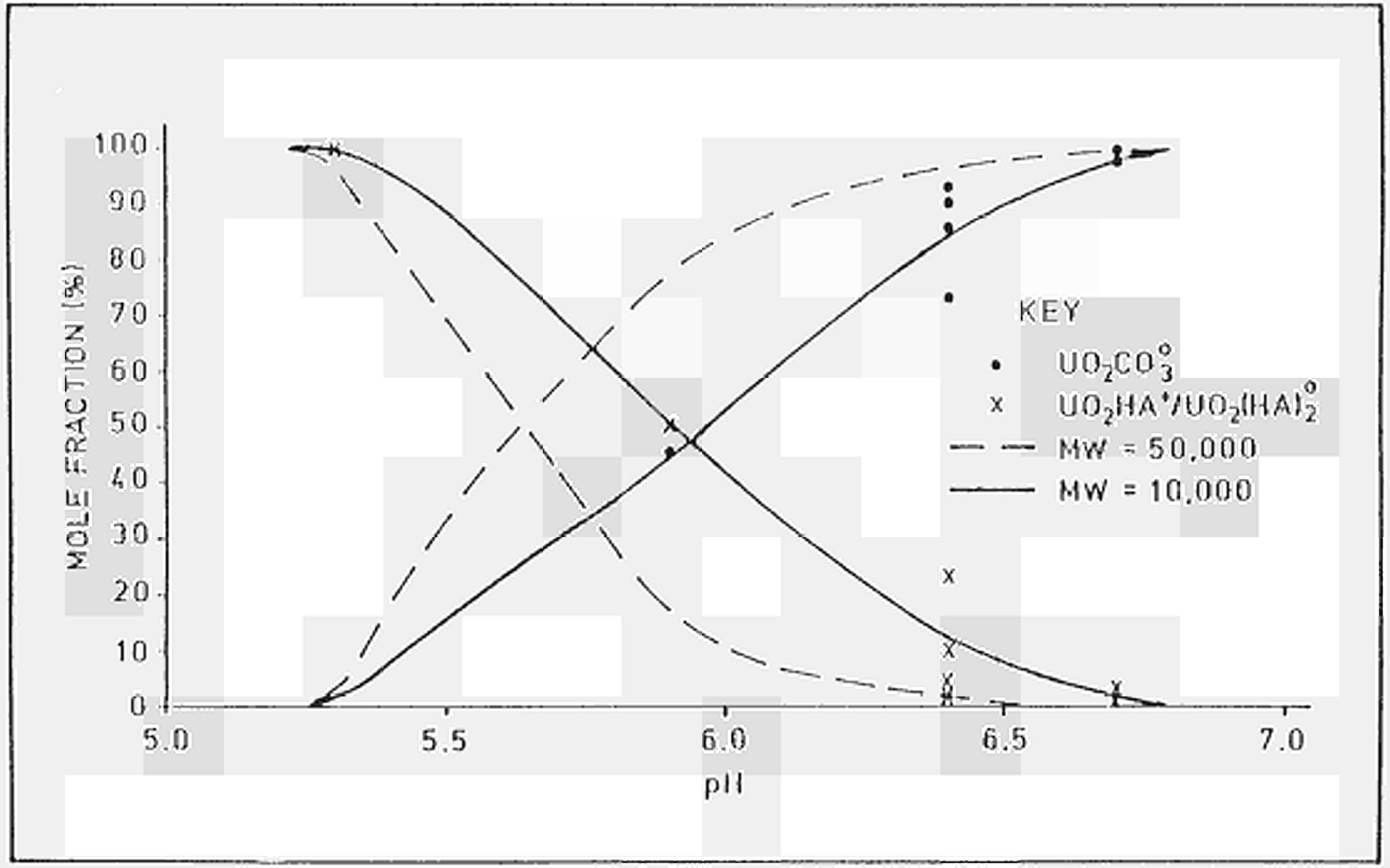

Figure 9 Relative percentage of U-carbonates and humates in Broubster soil waters. Variation with pH

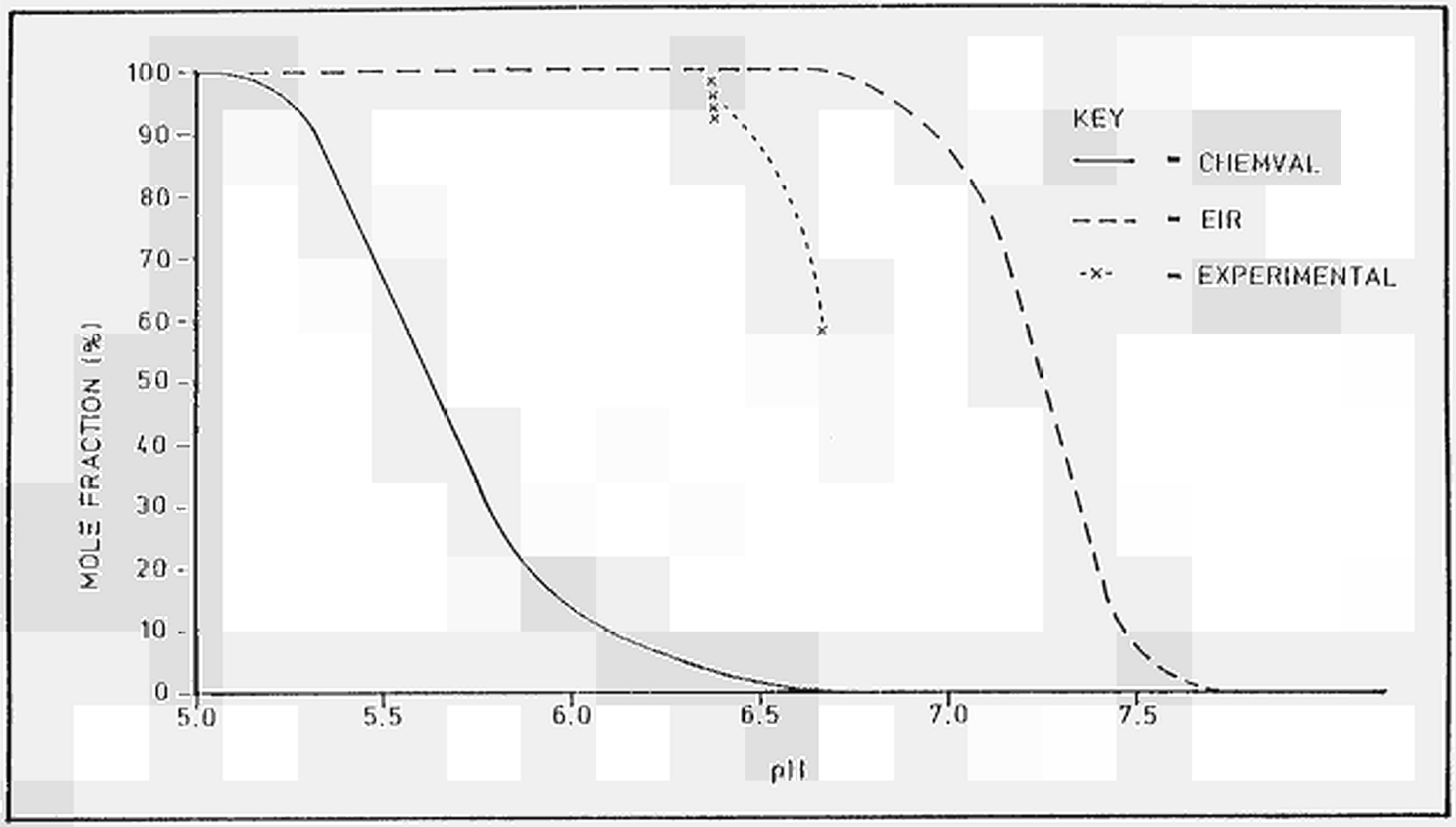

Figure 10 Uranium humates in Broubster soil waters : Variation with pH

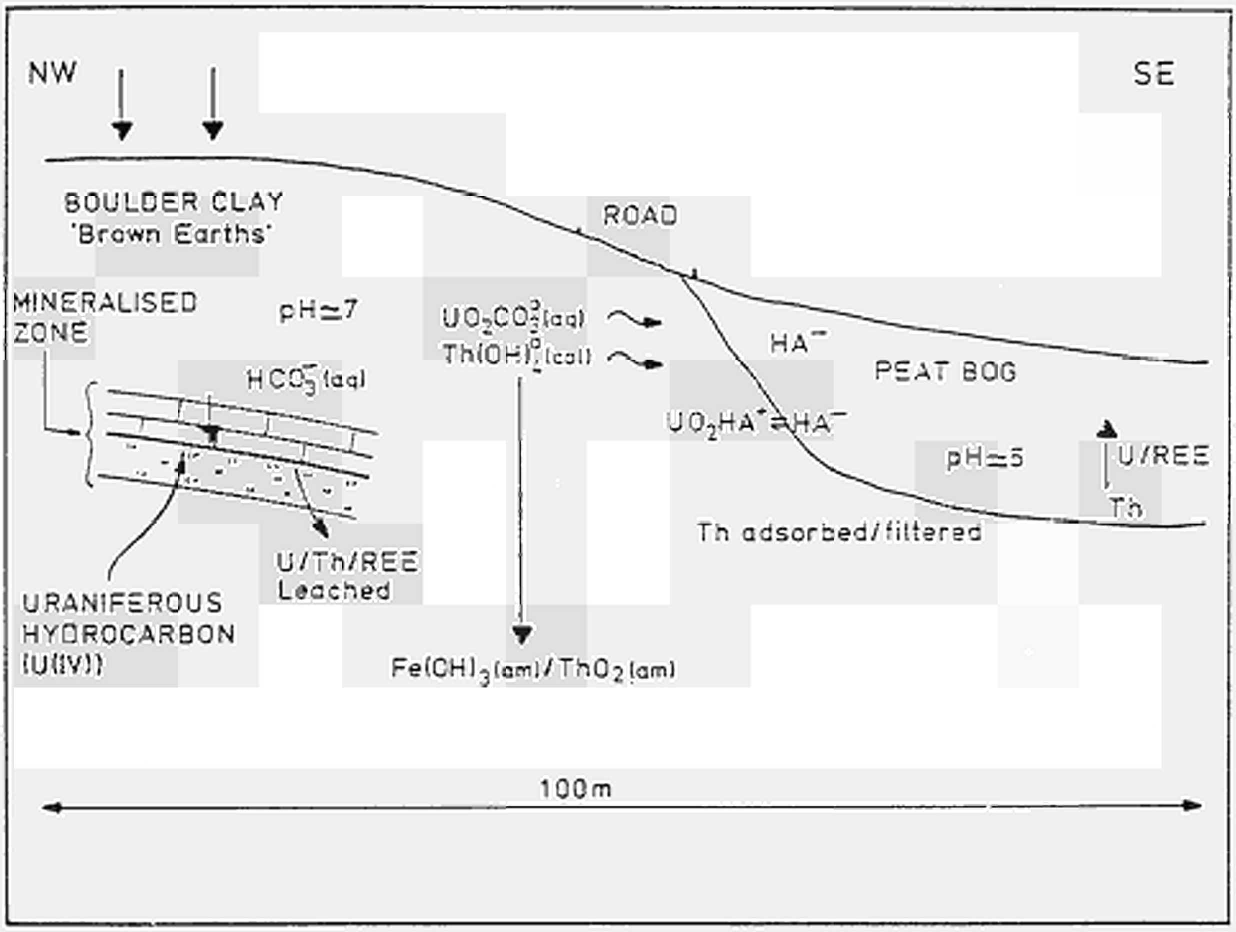

Figure 11 Conceptual model of U and Th transport in Broubster soils

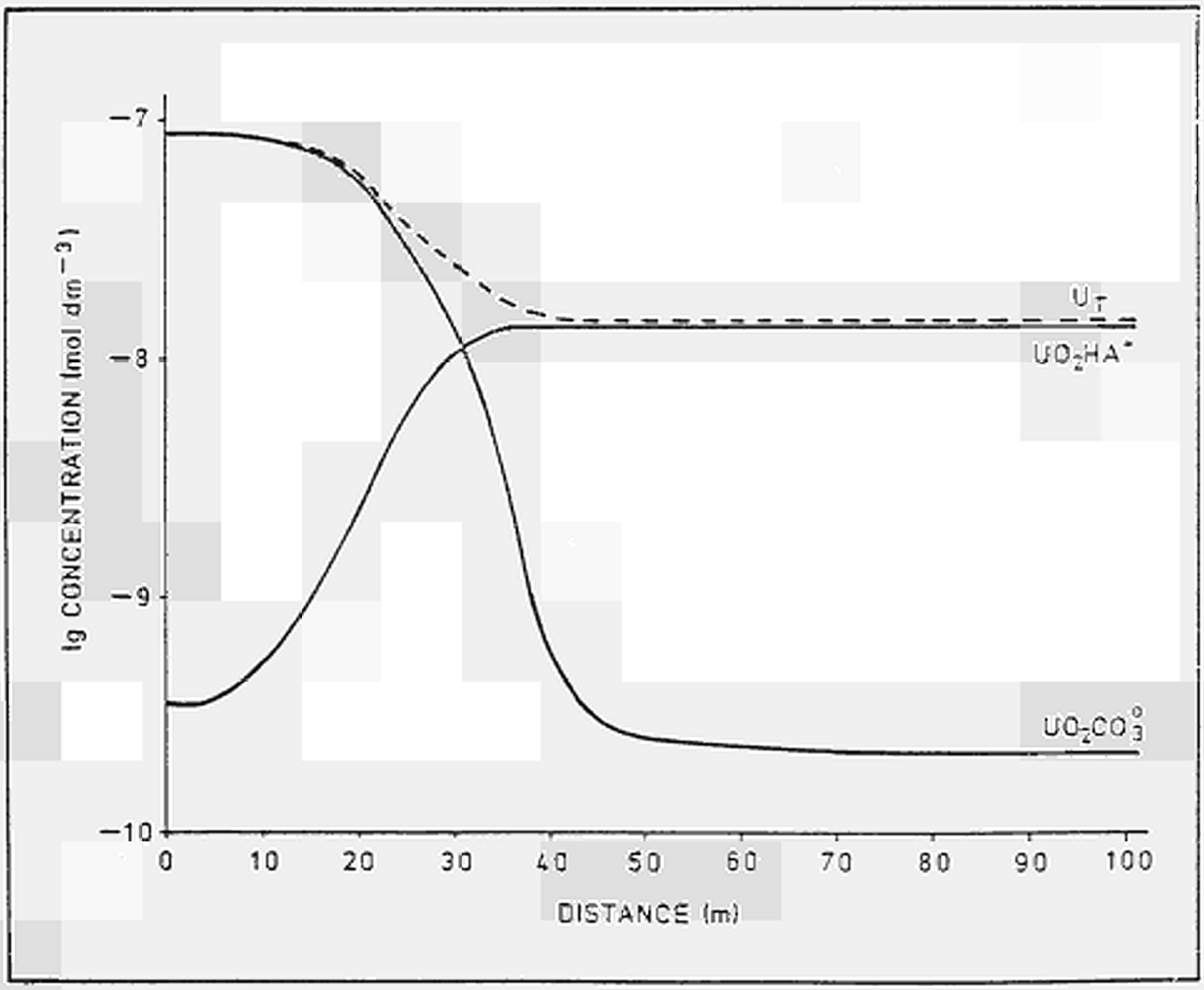

Figure 12 "Conservative" transport of U through peat: Effect of competitive complexation. Profile at 20 years. Velocity = 1myr^{-1}

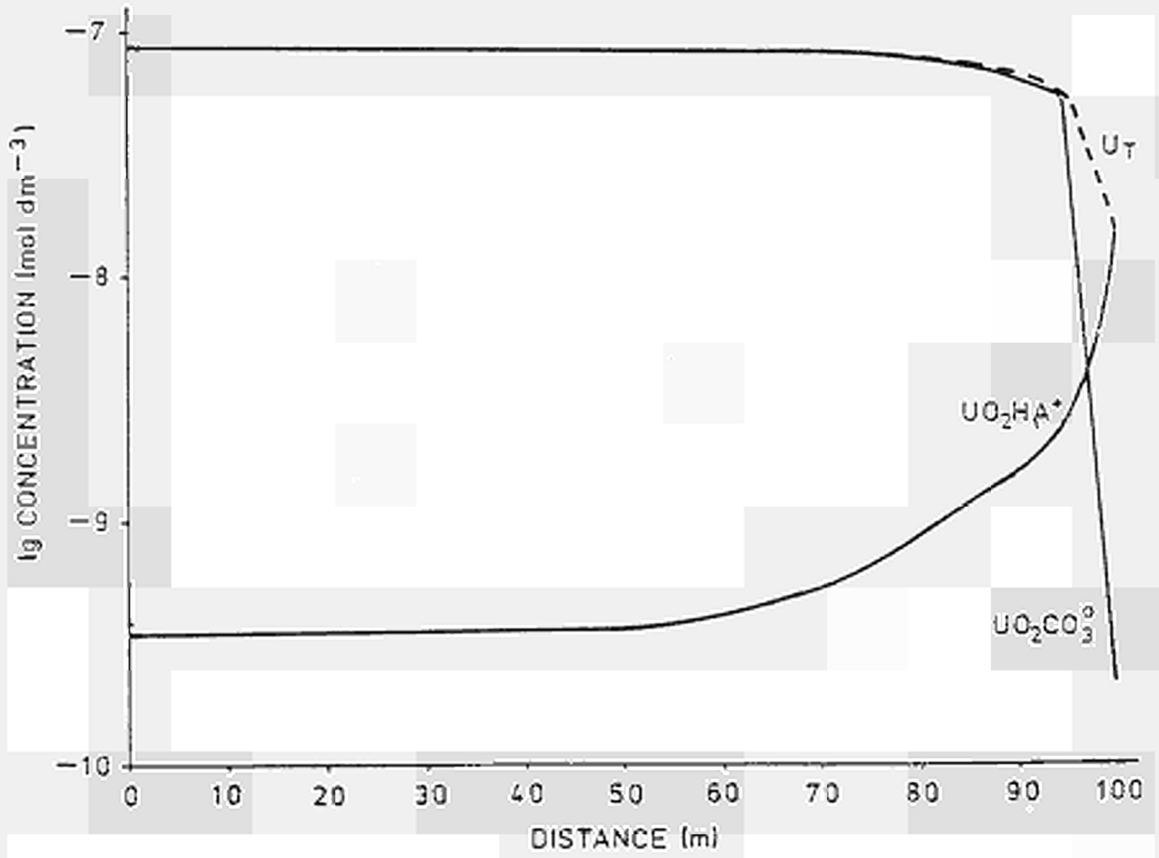

Figure 13 "Conservative" transport of U through peat. Profile at 100 years. Velocity = 1myr^{-1}

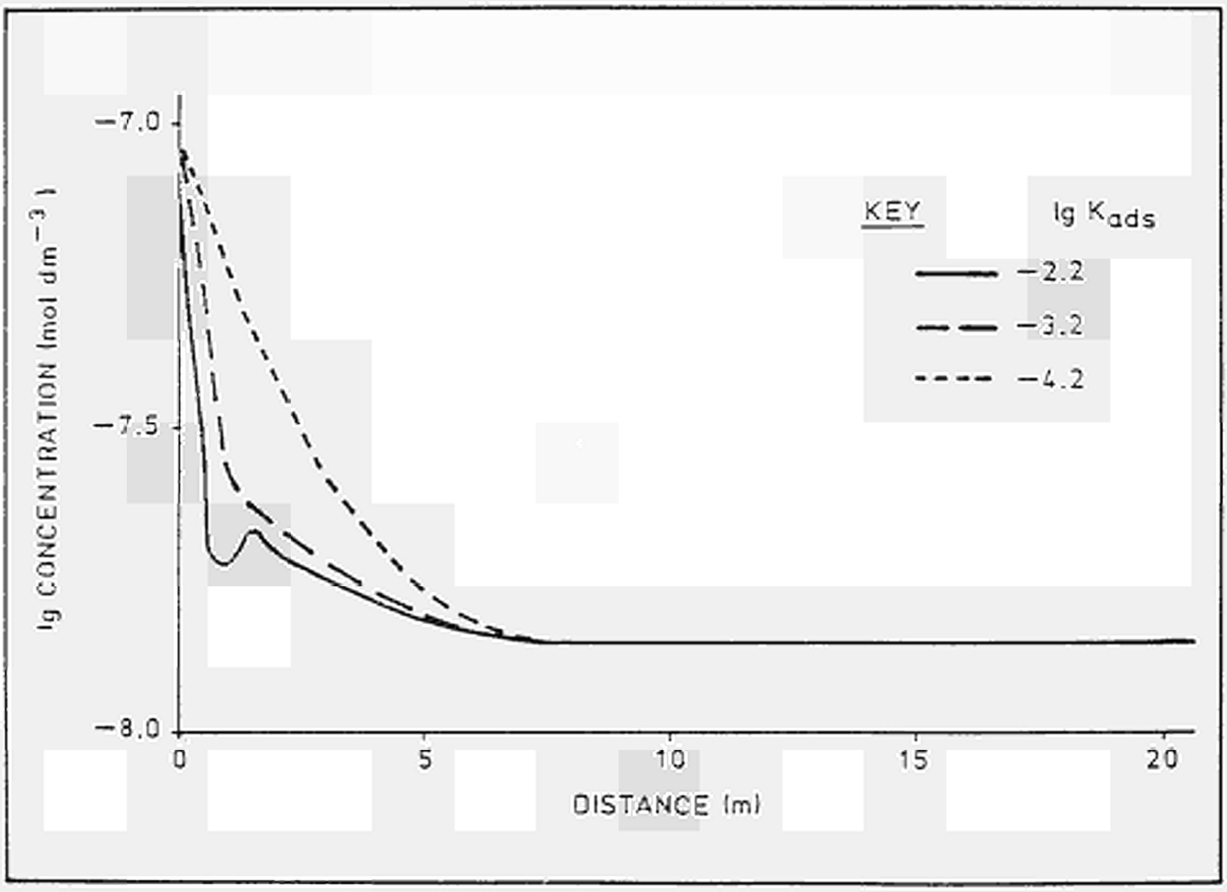

Figure 14 Transport of uranium through peat with sorption ($UO_2HA^+_{(aq)}$) by Davis-Leckie surface complexation. Effect of varying lg K_{ads}. Profile at 200 years

TABLES

Table 1 Trace element concentrations in rocks from Broubster Pit 1 (ppm w/w)

	JY5	JY6	JY6 SILT	JY7	JY8	JY9	JY10	JY12	JY13	JY14	JY15	Average shale (Krauskopf, 1979 except REE, Gromet, 1984)
U	25.5	28.3	44.3	76.7	26.0	49.9	27.1	23.1	28.5	30.4	14.0	2.66
Th	3.60	4.81	24.2	11.4	6.10	8.36	7.09	5.48	4.01	5.59	3.45	12.3
La	7.23	7.07	22.1	10.1	8.00	9.51	7.72	8.10	7.43	10.9	10.7	31.1
Ce	23.1	21.5	55.7	41.5	24.0	28.9	22.8	23.8	20.7	29.9	24.0	66.7
Eu	0.50	0.60	2.14	1.05	0.64	1.06	0.85	0.88	0.67	0.68	1.15	1.18
Yb	2.10	2.36	4.67	4.82	2.43	2.54	3.65	2.30	2.04	2.10	2.74	3.06
Lu	0.41	0.47	0.78	0.93	0.67	0.30	0.87	0.70	0.96	1.00	0.56	0.456
W	13.1	16.4	79.0	16.3	18.2	17.9	14.3	33.8	21.8	31.0	16.9	1.8
Mo	28.3	32.7	67.4	79.6	29.5	52.1	30.9	26.8	34.6	<4	17.3	2.0
As	56.8	62.6	185	56.9	59.6	61.6	52.7	22.7	34.1	28.2	12.8	10.0
Zn	56.9	84.2	85.7	109	51.3	136	30.6	<40	30.5	<60	30.7	90.0
(Fe(%)	0.85	0.83	2.01	1.09	0.75	0.93	1.76	0.80	0.78	1.13	0.27	4.7)
Y												35.0

Table 2 Trace element concentrations (ppm) in Broubster Soil Traverses, 1987: Traverse 1

Assay No ST1-	-3	-9	-7	-18	-8	-5	-12	-15	-1	-16	-2	-20	-11	-19	-13	-17	-14	-10	-4	-6
Field Sample No-	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B	6A	6B	7A	7B	8A	8B	9A	9B	10A	10B
U	<1	4	<1	4	2	5	4	3	<1	4	3	13	2	4	<1	4	5	1	4	2
Th	3	4	5	9	4	8	4	6	<1	7	4	15	6	13	4	9	5	8	7	6
La	<4	20	<4	23	5	20	14	26	<4	25	<4	35	11	21	14	16	19	26	22	20
Ce	<7	46	<7	38	<7	37	26	48	<7	50	<7	135	12	49	39	46	53	57	40	51
Nd	3	13	4	14	3	16	7	12	6	16	<1	39	9	18	7	15	21	19	21	16
Y	2	15	1	17	1	14	13	16	3	17	3	27	10	17	13	14	16	16	17	17
Mo	1	4	2	5	<1	3	2	4	7	6	4	15	1	3	5	4	4	2	3	3
Zn	18	59	4	59	20	51	11	56	45	60	11	54	10	62	120	62	48	64	39	41

Note The field sample numbers represent ten paired samples taken at 5m intervals along the traverse from south-east to north-west. Suffix A denotes surface samples and B, subsoil taken at >30cm depth.

Table 3 Trace element concentrations (ppm) in Broubster Soil Traverses, 1987 : Traverse 2

Assay No ST2 -	17	15	7	16	14	9	18	20	2	12	23	10	1	3	11	6	13	25	8	22	24	5	4	28	26	27	19	21
Field Sample No	1A	1B	2A	2B	3A	3B	3C	4A	4B	5A	5B	6A	6B	6C	7A	7B	8A	8B	9A	9B	10A	10B	11A	11B	12A	12B	13A	13B
U	51	144	39	145	293	161	17	348	362	416	72	362	296	33	309	136	95	12	123	89	73	17	87	83	14	7	23	12
Th	2	5	3	6	5	2	8	4	<1	6	6	5	4	9	4	6	6	13	8	7	5	8	7	8	6	8	8	9
La	5	14	7	16	56	32	25	31	30	28	14	52	33	32	13	27	18	26	32	23	23	30	24	19	21	24	24	21
Ce	10	<7	10	8	18	27	53	26	9	8	43	56	28	67	9	43	11	53	54	38	39	45	48	35	58	35	58	66
Nd	6	14	8	22	53	27	23	31	25	29	19	45	37	27	19	18	12	21	29	21	19	19	28	18	18	15	22	23
Y	14	35	19	53	174	59	28	112	94	142	27	141	106	36	71	36	31	25	48	45	41	26	37	32	23	17	21	20
Mo	<1	12	9	15	31	16	5	32	27	32	9	39	28	6	38	19	24	4	29	34	10	6	21	25	7	6	5	3
Zn	113	100	22	230	220	164	60	563	348	555	113	277	308	113	261	117	435	39	170	114	357	89	460	57	38	31	61	71

Note The field sample numbers represent soils obtained at 5m intervals along a 60m traverse from south to north. Suffix A denotes surface samples, B and C subsoils taken at >60cm and >130cm depth, respectively.

Table 4 Trace element concentrations (ppm) in Broubster Soil Traverses, 1987 : Traverse 3

Assay No ST3 -	16	4	10	13	5	9	6	8	14	15	7	17	11	12
Field Sample No	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B	6A	6B	7A	7B
U	<1	5	3	6	15	11	8	5	12	11	12	9	2	<1
Th	4	9	9	9	11	9	8	8	6	10	13	13	4	6
La	<4	17	11	12	22	21	23	16	22	20	6	17	<4	18
Ce	8	65	19	36	55	48	52	57	41	38	24	<7	<7	50
Nd	4	22	9	7	16	17	17	19	20	14	13	4	6	21
Y	4	16	14	14	17	21	19	18	23	26	15	20	9	14
Mo	<1	3	3	4	9	7	5	3	5	6	15	8	<1	2
Zn	17	60	31	56	118	119	85	72	131	167	195	140	20	66
P_2O_5(%)	0.58	0.19	0.24	0.22	0.27	0.20	0.28	0.18	0.26	0.16	0.29	0.19	0.56	0.14

Note The field sample numbers represent soils taken at 5m intervals along the traverse from south-east to north-west. Suffix A denotes surface samples and B, subsoil taken at >30cm depth.

Table 5 Trace element concentrations in soils from Broubster Pit 2 (ppm w/w)

Depth (cm)	0-10	10-20	20-30	30-40	40-50	50-60	60-70	70-80	80-90
U	553	766	1252	15.6	8.24	6.74	3.78	5.66	3.91
Th	2.05	3.27	79.7*	6.11	9.50	10.0	10.2	8.90	8.75
La	58.5	83.6	148	23.4	26.7	28.8	28.6	31.4	34.6
Ce	194	303	490	46.4	51.5	58.9	60.1	64.2	76.0
Eu	2.35	4.64	7.91	0.60	0.89	1.01	0.92	1.06	0.97
Yb	11.2	19.2	30.3	2.20	2.05	2.61	2.20	2.21	2.92
Lu	3.35	4.74	8.89	0.60	0.51	0.19	0.15	0.45	0.25
W	<10	<10	<15	<4	<5	<5	<6	<6	<6
Mo	642	887	1446	<3	<3	<3	<3	<3	<3
As	128	169	110	<2	<2	<2	<2	<3	<2
Zn	299	56.4	132	38.0	158	112	27.8	55.0	133
Fe(%)	4.57	6.00	2.68	1.23	3.13	2.96	3.23	3.55	3.87

* Datum to be confirmed.

Table 6 Broubster soil and groundwater analyses

(mol dm^{-3})	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8
Ca	6.0×10^{-4}	4.5×10^{-4}	1.1×10^{-3}	6.2×10^{-4}	2.8×10^{-4}	8.0×10^{-4}	9.5×10^{-4}	8.5×10^{-5}
Mg	1.4×10^{-4}	7.7×10^{-5}	1.3×10^{-4}	8.5×10^{-5}	2.4×10^{-4}	5.8×10^{-5}	6.4×10^{-5}	5.9×10^{-5}
Na	7.4×10^{-4}	1.1×10^{-3}	9.5×10^{-4}	7.8×10^{-4}	7.5×10^{-4}	6.9×10^{-4}	7.1×10^{-4}	6.5×10^{-4}
K	5.0×10^{-5}	2.8×10^{-5}	$<2.6\times10^{-5}$	$<2.6\times10^{-5}$	$<2.6\times10^{-5}$	$<2.6\times10^{-5}$	$<2.6\times10^{-5}$	$<2.6\times10^{-5}$
Fe	3.3×10^{-6}	7.1×10^{-6}	9.1×10^{-6}	$<3.6\times10^{-7}$	5.8×10^{-5}	6.8×10^{-6}	6.5×10^{-7}	1.5×10^{-5}
HCO_3	1.3×10^{-3}	1.3×10^{-3}	3.0×10^{-3}	1.5×10^{-3}	9.4×10^{-4}	2.2×10^{-3}	2.5×10^{-3}	2.2×10^{-4}
SO_4	1.6×10^{-5}	5.5×10^{-5}	3.0×10^{-5}	9.6×10^{-5}	8.0×10^{-5}	2.6×10^{-4}	1.3×10^{-5}	1.5×10^{-4}
Cl	1.3×10^{-3}	1.3×10^{-3}	1.0×10^{-3}	9.9×10^{-4}	8.3×10^{-4}	1.1×10^{-3}	1.1×10^{-3}	1.6×10^{-3}
pH (field)	6.7	6.4	6.4	6.7	5.9	6.4	6.4	5.3
Eh (mV)	278	383	383	419	201	238	238	-
U	1.4×10^{-8}	6.1×10^{-8}	8.9×10^{-8}	-	-	2.1×10^{-8}	5.1×10^{-8}	-
Th	5.2×10^{-10}	2.0×10^{-9}	6.7×10^{-10}	-	-	1.3×10^{-9}	3.4×10^{-10}	-
Mn	5.3×10^{-5}	3.2×10^{-6}	2.3×10^{-5}	5.2×10^{-5}	2.1×10^{-6}	4.4×10^{-6}	1.1×10^{-5}	2.0×10^{-5}
TOC (mg dm^{-3})	20.3	21.7	24.9	12.7	24.2	95.6	15.3	142
Si	1.1×10^{-5}	6.8×10^{-5}	8.0×10^{-5}	6.0×10^{-5}	1.1×10^{-5}	8.1×10^{-5}	7.0×10^{-5}	-

Table 7 Uranium and thorium speciation in Broubster waters - experimental results. Concentrations in μg dm^{-3}

	BS1		BS2		BS3		BS6		BS7	
pH	6.7		6.4		6.4		6.4		6.4	
TOC	20.3		21.7		24.9		95.6		15.3	
FRACTION	U	Th	U	Th	U	Th	U	Th	U	Th
Cation	1.4	0.01	0.2	0.02	0.46	<0.006	0.17	<0.006	0.16	<0.006
Anion	<0.01	<0.02	<0.01	<0.02	<0.01	<0.02	<0.01	<0.02	<0.01	<0.02
DEAE/HCl	0.03	0.008	0.04	0.099	0.16	0.039	0.09	0.019	0.56	0.028
DEAE/NaoH	1.90	<0.02	16.4	<0.02	18.5	<0.02	3.8	<0.02	10.2	<0.02
Total (speciation)	3.33	0.018	16.64	0.119	19.12	0.039	4.06	0.019	10.92	0.028
Total (groundwater analysis)	3.22	0.12	14.4	0.47	21.1	0.155	5.0	0.3	12.22	0.078
Error on mass balance (± %)	3%		16%		9%		19%		11%	

Table 8 Uranium Speciation - Broubster Groundwaters
Inorganic ligands only

Sample	CHEMVAL Database		NEA/EIR database	
	Saturation indices(lgIAP/Ksp)	Dominant species (%)	Saturation indices(lgIAP/Ksp)	Dominant species (%)
BS1	Uraninite -6.85 $UO_2CO_{3(s)}$ -3.54 $UO_2(OH)_{2(s)}$ -3.40 Coffinite -7.23	$UO_2CO_3^\circ$ (94%) $UO_2(CO_3)_3^{4-}$ (3%) $UO_2(OH)_2^\circ$ (1%) $UO_2(CO_3)_2^{2-}$ (1%)	$UO_22H_2O_{(s)}$ -7.35 $UO_2CO_{3(s)}$ -3.96	$UO_2(CO_3)_2^{2-}$(69%) $UO_2CO_3^\circ$ (30%)
BS2	Uraninite -9.36 $UO_2CO_{3(s)}$ -2.89 $UO_2(OH)_{2(s)}$ -2.95	$UO_2CO_3^\circ$ (96%) $(UO_2)_2(OH)_3CO_3^-$(1%)	$UO_22H_2O_{(s)}$ -9.62 $UO_2CO_{3(s)}$ -3.09	$UO_2CO_3^\circ$ (53%) $UO_2(CO_3)_2^{2-}$(46%)
BS3	Uraninite -9.55 $UO_2CO_{3(s)}$ -2.73 $UO_2(OH)_{2(s)}$ -3.14	$UO_2CO_3^\circ$ (95%) $UO_2(CO_3)_3^{4-}$ (2.5%)	$UO_22H_2O_{(s)}$ -10.0 $UO_2CO_{3(s)}$ -3.15	$UO_2(CO_3)_2^{2-}$(67%) $UO_2CO_3^\circ$ (32%)
BS4	Uraninite -10.9 $UO_2CO_{3(s)}$ -2.76 $UO_2(OH)_{2(s)}$ -2.68	$UO_2CO_3^\circ$ (89%) $UO_2(CO_3)_3^{4-}$ (3%) $(UO_2)_2(OH)_3CO_3^-$(3%)	$UO_22H_2O_{(s)}$ -11.4 $UO_2CO_{3(s)}$ -3.22	$UO_2(CO_3)_2^{2-}$(72%) $UO_2CO_3^\circ$ (27%)
BS5	Uraninite -2.09 $UO_2CO_{3(s)}$ -2.73 $UO_2(OH)_{2(s)}$ -2.84	$UO_2CO_3^\circ$ (96%) UO_2^{2+} (1%) $UO_2(OH)^+$ (1%)	$UO_22H_2O_{(s)}$ -2.13 $UO_2CO_{3(s)}$ -2.71	$UO_2CO_3^\circ$ (88%) $UO_2(CO_3)_2^{2-}$ (8%) UO_2OH^+ (1%)
BS6	Uraninite -5.12 $UO_2CO_{3(s)}$ -3.35 $UO_2(OH)_{2(s)}$ -3.63	$UO_2CO_3^\circ$ (97%)	$UO_22H_2O_{(s)}$ -5.51 $UO_2CO_{3(s)}$ -3.68	$UO_2(CO_3)_2^{2-}$(60%) $UO_2CO_3^\circ$ (39%)
BS7	Uraninite -4.79 $UO_2CO_{3(s)}$ -2.97 $UO_2(OH)_{2(s)}$ -3.30	$UO_2CO_3^\circ$ (96%) $UO_2(CO_3)_3^{4-}$ (2%) $UO_2(CO_3)_2^{2-}$ (1%)	$UO_22H_2O_{(s)}$ -5.22 $UO_2CO_{3(s)}$ -3.33	$UO_2(CO_3)_2^{2-}$(63%) $UO_2CO_3^\circ$ (36%)
BS8	Uraninite -1.87 $UO_2CO_{3(s)}$ -3.00 $UO_2(OH)_{2(s)}$ -2.58	$UO_2CO_3^\circ$ (52%) UO_2^{2+} (33%) UO_2OH^+ (10%) $UO_2SO_4^\circ$ (3%) UO_2^+ (2%)	$UO_22H_2O_{(s)}$ -1.87 $UO_2CO_{3(s)}$ -2.94	$UO_2CO_3^\circ$ (51%) UO_2^{2+} (33%) UO_2OH^+ (9%) $UO_2SO_4^\circ$ (3%) UO_2^+ (2%)

Table 9 Formation constants of U(VI) and Th(IV) humates

Source	U(VI)		Th(IV)	
	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_1$	$\lg\beta_2$
Kim, 1986 [18][1]	6.3	10.2	12.0	17.1
Shanbhag and Choppin, 1981 [19]	7.67	11.57	-	-
Choppin, 1980[2]	8.2	11.55	10.9	16.4
Li et al, 1980[2]	6.7	-	-	-

[1] Values quoted are mean of range

[2] Shown for comparison - constants not used in speciation calculations

Table 10 Uranium Speciation - Broubster waters
CHEMVAL database + Humic Acid from AERE (Shanbhag & Choppin)

Sample	Molecular Weight = 50,000		Molecular Weight = 10,000	
	Saturation indices	Dominant species (%)	Saturation indices	Dominant species (%)
BS1	Uraninite -6.85	$UO_2CO_3^{\circ}$ (93%)	Uraninite -6.87	$UO_2CO_3^{\circ}$ (90%)
	Coffinite -7.23	$UO_2(CO_3)_3^{4-}$ (3%)	Coffinite -7.25	UO_2HA^+ (4%)
	$UO_2CO_3(s)$ -3.54	$UO_2(CO_3)_2^{2-}$ (1%)	$UO_2CO_{3(s)}$ -3.56	$UO_2(CO_3)_3^{4-}$ (3%)
		$UO_2(OH)_2^{\circ}$ (1%)		
BS2	Uraninite -9.37	$UO_2CO_3^{\circ}$ (94%)	Uraninite -9.40	$UO_2CO_3^{\circ}$ (86%)
	Coffinite -8.95	UO_2HA^+ (2%)	Coffinite -8.99	UO_2HA^+ (10%)
	$UO_2CO_3(s)$ -2.90	$(UO_2)_2(OH)_3CO_3^-$(1%)	$UO_2CO_{3(s)}$ -2.94	
BS3	Uraninite -9.56	$UO_2CO_3^{\circ}$ (94%)	Uraninite -9.58	$UO_2(CO_3)^{\circ}$ (90%)
	Coffinite -9.08	$UO_2(CO_3)_3^{4-}$ (3%)	Coffinite -9.09	UO_2HA^+ (5%)
	$UO_2CO_3(s)$ -2.74	UO_2HA^+ (1%)	$UO_2CO_{3(s)}$ -2.75	$UO_2(CO_3)_3^{4-}$ (2%)
BS4	Uraninite -10.92	$UO_2CO_3^{\circ}$ (88%)	Uraninite-10.92	$UO_2(CO_3)^{\circ}$ (87%)
	Coffinite -10.56	$UO_2(CO_3)_3^{4-}$ (3%)	Coffinite-10.56	$UO_2(CO_3)_3^{4-}$ (27%)
	$UO_2CO_{3(s)}$ -2.76	$(UO_2)_2(OH)_3CO_3^-$(3%)	$UO_2CO_{3(s)}$ -2.77	$(UO_2)_2(OH)_3CO_3^-$(3%)
				UO_2HA^+ (2%)
BS5	Uraninite -2.18	$UO_2CO_3^{\circ}$ (79%)	Uraninite -2.41	UO_2HA^+ (51%)
	Coffinite -2.56	UO_2HA^+ (17%)	Coffinite -2.79	$UO_2CO_3^{\circ}$ (46%)
	$UO_2CO_{3(s)}$ -2.81	$UO_2(OH)_2^{\circ}$ (1%)	$UO_2CO_{3(s)}$ -3.04	
BS6	Uraninite -5.15	$UO_2CO_3^{\circ}$ (91%)	Uraninite -5.24	$UO_2CO_3^{\circ}$ (74%)
	Coffinite -4.66	UO_2HA^+ (6%)	Coffinite -4.75	UO_2HA^+ (22%)
	$UO_2CO_{3(s)}$ -3.37		$UO_2CO_{3(s)}$ -3.47	$UO_2(HA)_2^{\circ}$ (2%)
BS7	Uraninite -4.80	$UO_2CO_3^{\circ}$ (95%)	Uraninite -4.81	$UO_2CO_3^{\circ}$ (92%)
	Coffinite -4.37	$UO_2(CO_3)_3^{4-}$ (2%)	Coffinite -4.39	UO_2HA^+ (4%)
	$UO_2CO_{3(s)}$ -2.97	UO_2HA^+ (1%)	$UO_2CO_{3(s)}$ -2.98	
BS8	Uraninite -3.44	UO_2HA^+ (95%)	Uraninite -4.17	UO_2HA^+ (90%)
	Coffinite*	$UO_2(HA)_2^{\circ}$ (2%)	Coffinite* -	$UO_2(HA)_2^{\circ}$ (9%)
	$UO_2CO_{3(s)}$ -4.56	$UO_2CO_3^{\circ}$ (1%)	$UO_2CO_{3(s)}$ -5.30	

* No silica analysis

Table 11 Uranium Speciation - Broubster waters
NEA/EIR database + Humic Acid from Kim (1986)

Sample	Molecular Weight = 50,000		Molecular Weight = 10,000	
	Saturation indices	Dominant species (%)	Saturation indices	Dominant species (%)
BS1	$UO_22H_2O_{(s)}$ -12.57 $UO_2CO_{3(s)}$ -9.20	UO_2HA^+ (100%)	$UO_22H_2O_{(s)}$ -13.29 $UO_2CO_{3(s)}$ -9.91	UO_2HA^+ (99%) $UO_2(HA)_2°$ (1%)
BS2	$UO_22H_2O_{(s)}$ -18.10 $UO_2CO_{3(s)}$ -8.94	UO_2HA^+ (99%) $UO_2(HA)_2°$ (1%)	$UO_22H_2O_{(s)}$ -16.23 $UO_2CO_{3(s)}$ -9.70	UO_2HA^+ (99%) $UO_2(HA)_2°$ (1%)
BS3	$UO_22H_2O_{(s)}$ -15.34 $UO_2CO_{3(s)}$ -8.46	UO_2HA^+ (100%)	$UO_22H_2O_{(s)}$ -16.12 $UO_2CO_{3(s)}$ -9.24	UO_2HA^+ (98%) $UO_2(HA)_2°$ (2%)
BS4	$UO_22H_2O_{(s)}$ -16.17 $UO_2CO_{3(s)}$ -7.95	UO_2HA^+ (100%)	$UO_22H_2O_{(s)}$ -17.03 $UO_2CO_{3(s)}$ -8.81	UO_2HA^+ (99%) $UO_2(HA)_2°$ (1%)
BS5	$UO_22H_2O_{(s)}$ -9.17 $UO_2CO_{3(s)}$ -9.74	UO_2HA^+ (100%)	$UO_22H_2O_{(s)}$ -9.95 $UO_2CO_{3(s)}$ -10.52	UO_2HA^+ (98%) $UO_2(HA)_2°$ (2%)
BS6	$UO_22H_2O_{(s)}$ -11.72 $UO_2CO_{3(s)}$ -9.89	UO_2HA^+ (99%) $UO_2(HA)_2°$ (1%)	$UO_22H_2O_{(s)}$ -12.45 $UO_2CO_{3(s)}$ -10.62	UO_2HA^+ (94%) $UO_2(HA)_2°$ (6%)
BS7	$UO_22H_2O_{(s)}$ -10.46 $UO_2CO_{3(s)}$ -8.58	UO_2HA^+ (100%)	$UO_22H_2O_{(s)}$ -11.23 $UO_2CO_{3(s)}$ -9.34	UO_2HA^+ (99%) $UO_2(HA)_2°$ (1%)
BS8	$UO_22H_2O_{(s)}$ -11.26 $UO_2CO_{3(s)}$ -12.33	UO_2HA^+ (98%) $UO_2(HA)_2°$ (2%)	$UO_22H_2O_{(s)}$ -12.0 $UO_2CO_{3(s)}$ -13.07	UO_2HA^+ (91%) $UO_2(HA)_2°$ (9%)

Table 12 Thorium Speciation - Broubster Groundwaters
NEA/EIR database + Humic Acid from Kim (1986)

Sample	Saturation Indices (lg IAP/Ksp)		Dominant Species (%)	
BS1	$ThO_2\ 2H_2O$ $Fe(OH)_{3(am)}$	0.30 0.83	$Th(OH)_4^\circ$	(100%)
BS2	$ThO_2\ 2H_2O$ $Fe(OH)_{3(am)}$	0.90 1.02	$Th(OH)_4^\circ$	(100%)
BS3	$ThO_2\ 2H_2O$ $Fe(OH)_{3(am)}$	0.44 1.12	$Th(OH)_4^\circ$ $Th(OH)_3^+$	(99%) (1%)
BS6	$ThO_2\ 2H_2O$ $Fe(OH)_{3(am)}$	0.71 0.00	$Th(OH)_4^\circ$ $Th(OH)_3^+$	(99%) (1%)
BS7	$ThO_2\ 2H_2O$ $Fe(OH)_{3(am)}$	0.07 -1.01	$Th(OH)_4^\circ$ $Th(OH)_3^+$	(99%) (1%)

Table 13 Intrinsic equilibrium constants for sorption onto α FeOOH (Balistrieri and Murray (1981) except *, Hsi and Langmuir (1985))

Reaction	$\lg K^{INT}$
$SOH + Ca^{2+} = SO\text{-}Ca^+ + H^+$	-5.00
$SOH + Mg^{2+} = SO\text{-}Mg^+ + H^+$	-5.45
$SOH + Na^+ = SO\text{-}Na^+ + H^+$	-8.40
$SOH + K^+ = SO\text{-}K + H^+$	-8.40
$SOH_2\text{-}Cl = SOH + Cl^- + H^+$	-7.00
$^*SOH + UO_2OH^+ = SO\text{-}UO_2OH + H^+$	-2.2

* surface deprotonation constants used in the modelling study were 5.7 (pK_1) and 11.5(pK_2). Interlayer capacitances (140 and 20 µF cm^{-2} respectively) correspond to those in [23,24].

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