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URANIUM-SERIES DISEQUILIBRIUM INVESTIGATIONS OF THREE
SURFICIAL URANIUM DEPOSITS

presented by
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has been accepted towards fulfillment
of the requirements for

Masters degree in Geology

A handwritten signature in black ink, appearing to be "R. S. H.", written over a horizontal line.

Major professor

Date 12/12/77

**URANIUM-SERIES DISEQUILIBRIUM INVESTIGATIONS OF THREE SURFICIAL
URANIUM DEPOSITS**

By

Richard S. Lively

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ABSTRACT

URANIUM-SERIES DISEQUILIBRIUM INVESTIGATIONS OF THREE SURFICIAL URANIUM DEPOSITS

by

Richard S. Lively

^{230}Th and ^{234}U relations from three near-surface uranium deposits indicate that significant uranium accumulations have occurred during the Pleistocene. Data from these isotopes in conjunction with ^{238}U and ^{226}Ra have allowed calculations of mineralization ages and have furnished positive evidence of significant uranium migration in ground water, under near-surface conditions.

Analytical results from samples collected from deposit "K" in southern Africa indicates uranium mineralization took place approximately 40,000 years B.P. The results also indicates at least one and possibly more period(s) of post-depositional migration of uranium and radium. Samples collected from the uranium deposit at Yeelirrie, Australia resulted in inconclusive ages. Due to isotope movement within the system only two apparent: $^{230}\text{Th}/^{234}\text{U}$ ages could be calculated. A maximum age of 261,000 yr B.P. was established, but due to the extent of the deposit and the open system, this age does not represent the deposit as a whole.

Results from sample collected from Kelowna, British Columbia, (Lassie Lake), indicate a maximum mineralization age of 224,000 yr B.P. Other areas at Kelowna show evidence of significant uranium migration resulting in $^{230}\text{Th}/^{234}\text{U}$ ratios greater than unity, thus making age calculations impossible.

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INTRODUCTION

Presently there is an intense interest in uranium ore deposits because of their great economic value, In 1971 the average price per pound of U_3O_8 was \$6.20; in 1977 \$42.40 and the projected price for delivery in 1980 is \$51.05/lb. (U.S. Bureau of Mines). This represents an increase of 823% in less than ten years. Because of the rapid rate of appreciation, areas of low yield uranium which were previously uneconomical can now be profitably mined.

Aside from these economic aspects, uranium deposits present many interesting and important geochemical problems, some of which can be investigated by means of isotopic disequilibrium studies. While uranium and thorium isotopic disequilibrium is not in itself a direct exploration tool, results from such studies can be useful in terms of understanding exploration anomaly patterns and identifying the presence of chemical changes in the environment through changes in the isotope ratios. It is also possible under certain circumstances to derive an age of uranium mineralization as well as discern recent movements of uranium in the surficial environment.

Of specific interest in this study are three near surface uranium deposits from southern Africa, Western Australia and western Canada. The objective of the study is to analyze the isotopic disequilibrium within the deposits and where possible, establish an age of mineralization. Samples from these three areas were kindly provided by Professor A.A. Levinson of the University of Calgary.

Previous application of U-series disequilibrium studies to uranium deposits include Rosholt (1961), and Rosholt et al., (1961) who investigated uranium accumulations through the use of ^{231}Pa and ^{230}Th relationships with both parent and daughter isotopes. He concluded that the accumulations were recent and could be related to ground water movements. Rosholt et al., (1964, 1965) and Dooley et al., (1964), investigated isotope disequilibrium and fractionation in roll-front uranium deposits from sandstones in Wyoming and Colorado. They found that disequilibrium was related to changes in the water table and oxidation potential. Ostrihansky (1976), used U-series isotope relationships to classify periods of uranium accumulation in uranium ore deposits from the Elliot Lake region of Ontario, Canada. Cherdyntsev (1971) in his extensive review of ^{234}U noted extensive variations in isotope ratios derived from uranium minerals, uranium ore bodies and ground waters circulating through ores and crystalline rocks.

GEOCHEMISTRY AND ISOTOPE FRACTIONATION OF URANIUM

Uranium exists in nature in two stable valence states, U^{4+} and U^{6+} . Primary uranium, that found in crystalline rocks and the clastic sediments derived from them, usually is in the $4+$ state and as such is insoluble under near surface conditions. U^{6+} on the other hand, is soluble and is widely distributed throughout the surficial environment where oxidizing conditions exist.

Removal of uranium from crystalline rocks depends upon a number of parameters, including the geochemical nature of the weathering environment, the degree of weathering, and the amount of uranium present. Granites and pegmatites for instance, have much higher uranium concentrations (3-50 ppm), than do basalts or other basic rocks (1-3 ppm or less) resulting in higher uranium

concentrations for ground waters circulating through the former (Szalay and Samsoni, 1969; Handbook of Geochemistry, 1969).

The oxidation state of the uranium and therefore the oxidation potential of the weathering environment is probably the most important feature in the removal and transportation of uranium in the near surface environment. Beyond that however, the composition of the waters will influence both the amount of uranium in solution and its subsequent transportation. The bicarbonate (HCO_3^-) content of the waters has a large affect both on leaching and transportation because uranium $6+$ forms very stable uranyl carbonate complexes of the type $(\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2)^{2-}$ and $(\text{UO}_2(\text{CO}_3)_3)^{4-}$, which can exist over a wide pH range from about 3.5 to 8.0 (Hostetler and Garrels, 1962). These carbonate complex are the predominant form of uranium transport in the surficial environment (Grunner, 1956; Lisitsin, 1962; Hostetler and Garrels, 1962; Serebryakova, 1964; Kyuregyan and Kocharyan, 1969). Waters low in bicarbonate will then be less able to leach uranium from crystalline rocks and will also be less important in the subsequent removal of uranium from uranium minerals (Szalay and Samsoni, 1969; Grandstaff, 1976). Since most ground waters are within the pH range 4.5 to 8, (see Bass-Becking, et al. 1962), leaching and transportation of uranium should occur under oxidizing conditions.

Other types of complexes are also stable under near-surface conditions. These include uranyl and uraneous sulfates, chlorides, silicates and phosphates. Sulfide and chloride complexes form in a pH range below 3.5 and are unstable at higher pH values (Hostetler and Garrels, 1962). Uranyl silicate complexes are less stable than either the sulfate or chloride complexes and are found in waters of neutral to alkaline pH. They will rapidly decompose if a large decrease in pH is

encountered or the waters become concentrated in carbonate or sulfate ions where the uranium will form the more stable complexes (Yermolayev et al., 1965). Phosphates, when present in solution will also form very stable complexes with uranium (Langmuir and Applin, 1977). If no complexing ions are present in solution, uranium will occur as UO_2^{2+} or UO_2OH^+ , depending upon the pH of the waters (Hostetler and Garrels, 1962).

Fractionation of uranium isotopes and separation from their daughter nuclides is also related to the geochemistry of the ground waters. The excess is ^{234}U which is found in most ground waters (Cowart and Osmond, 1977) is thought to relate to a preferential oxidation of ^{234}U to the 6+ valence state, thus making it more easily removed into solution by circulating surface and ground waters. Thorium is very insoluble under near-surface conditions and thus not transported in aqueous solution (Dement'yev et al., 1965). It can, however, be transported adsorbed on clastic material.

A number of mechanisms have been proposed to account for the preferential oxidation of ^{234}U , most of which are related to radioactive decay. When an alpha particle is ejected from the nucleus of a ^{238}U atom, the resultant decay product undergoes a recoil, called the Szilard-Chalmers reaction (Friedlander, et al. 1955). Chemical bonds holding the atom in its lattice position are ruptured by the energy of the recoil, resulting in a dislocation of the atom, in this case ^{234}Th which rapidly decays to ^{234}Pa and ^{234}U . As the atom is no longer firmly bound, it can then be more readily removed into solution or migrate through the lattice until stopped by micro-cracks and fractures where it is easily available for oxidation and removal by ground waters (Cherdyntsev, 1971). Others argue that alpha decay is energetic enough to strip electrons from the atom during the recoil

process, producing ^{234}U which is already in the oxidized state (Rosholt et al., 1963, 1966). Cowart and Osmond (1977) feel that the resultant decay product will take on the oxidation state of the environment wherein it is located regardless of decay related phenomenon. Whatever the case, it is necessary for the environment to remain oxidizing to prevent the reduction of U^{6+} back to U^{4+} if significant uranium mobilization and transportation is to occur.

Another method of ^{234}U - ^{238}U fractionation resulting from alpha decay relates to recoil of ^{234}Th across a solid-liquid phase boundary. Alpha decay of ^{238}U 200-500 Å from such a boundary results in a recoil sufficiently strong to propel the ^{234}Th atom across the boundary, which then decays to ^{234}U producing an excess of ^{234}U in the waters (Kigoshi, 1971; Cowart and Osmond, 1977). Residence time of the waters within a formation is of importance here, because the amount of ^{234}Th produced in the waters will be related to the decay rate of ^{238}U . Fast moving waters will therefore not collect as much ^{234}Th as will slower moving or confined waters and which may have $^{234}\text{U}/^{238}\text{U}$ ratios as high as 15 (Cowart and Osmond, 1977).

Residence time and the degree of weathering will also affect the fractionation of uranium during the normal weathering and leaching processes. Syromyatnikov and Tolmachev (1962) reported a direct correlation between the uranium activity ratio and an increase in uranium from disseminated uranium in various rocks. This is to be expected, because, as weathering increases, more decay produced uranium will come into contact with the water. Continued removal of ^{234}U will leave the weathered material depleted in ^{234}U producing a $^{234}\text{U}/^{238}\text{U}$ ratio less than unity. Such a case has been found in the weathered zone of the Conway granite in New Hampshire (Cowart and Osmond, 1977).

Uranium may be removed from solution by a number of means and under a variety of conditions. Changes in solubility correlated with changes in P_{CO_2} (see trends reported by Hostetler and Garrels, 1962), changes in salinity of the waters, or changes in Eh-pH related parameters can all cause direct precipitation of uranium bearing phases. Evaporation leading to an supersaturation of uranium in solution can also result in a direct precipitation of uranium, a process especially applicable to arid environments (Dall'Aglio, 1974). Uranium can also be removed from solution through dissociation of the U-bearing complexes under acid-reducing conditions, and resultant cation exchange onto clay materials, through absorption onto organic materials (Szalay, 1964), and through co-precipitation with other mineral phases (Hostetler and Garrels, 1962).

Uranium precipitated from solution will have the same uranium isotopic ratio as the 'parent' water. Due to the extremely small mass difference between ^{234}U and ^{238}U , fractionation is not temperature dependent as it is for the light stable isotopes, such as carbon or oxygen. Thus, differences which occur between the isotope ratios of U waters and a deposit must be the result of other processes.

For preexisting deposits, changes in the isotope ratios will result if the system is open to isotope migration. This usually occurs through a removal of uranium enriched in ^{234}U and results in a decrease of the $^{234}\text{U}/^{238}\text{U}$ ratio concomitant with an increase the $^{230}\text{Th}/^{234}\text{U}$ ratio. This results in 'apparent' ages which are older than the true age of the deposit or an excess of ^{230}Th such that it is impossible to calculate an age of deposition. If uranium enriched in ^{234}U is brought into a deposit, the opposite effect will be produced, resulting in higher $^{234}\text{U}/^{238}\text{U}$ ratios, lower $^{230}\text{Th}/^{234}\text{U}$ ratios, and younger 'apparent' ages. Analysis of a suite of samples from one area of a deposit often can establish the

presence of isotope migration, usually by identifying unsupported daughter products. Ages calculated from areas subject to isotope migration, should however, be viewed with extreme caution. The initial uranium ratios will also change through the decay of excess ^{234}U toward equilibrium, resulting in a lower $^{234}\text{U}/^{238}\text{U}$ ratio. Changes resulting from isotope migration will be superimposed on the ratios resulting from the decay of excess ^{234}U .

Identification of uranium isotope migration only on the basis of uranium and thorium isotope ratios is difficult because not all migrations result in distinct anomalies. It is useful, therefore, to employ when possible, a third isotope, ^{226}Ra , in identifying migration patterns. ^{226}Ra is the daughter product of ^{230}Th and has a half-life of 1622 years. Chemically, ^{226}Ra behaves differently than either thorium or uranium, although because of its low abundance in water, ^{226}Ra will remain dissolved (mobile) in natural waters of almost any composition. (Levinson and Coetzee, 1977). Due to its short half-life, ^{226}Ra should be in equilibrium with ^{230}Th within 10,000 to 12,000 years of deposition. Deviations from the equilibrium value for a deposit older than 10,000 years B.P. point to either a movement of radium or uranium.

GEOCHRONOLOGY

The $^{230}\text{Th}/^{234}\text{U}$ disequilibrium dating technique is based upon the radioactive decay law governing the formation of a 'daughter' from a 'parent' radionuclide. The assumption is made that, over a given period of time, a fixed amount of one nuclide will be formed by the radioactive decay of another and thus must be formed at a constant rate according to the expression:

$$N_t^p = N_0^p e^{-\lambda t} \quad (1)$$

where N_t^p is the number of atoms present at time (t) and N_0^p represents the number of atoms initially present. The decay constant, λ expresses the probability of a decay occurring within a given period of time. If, however, the daughter nuclide is itself unstable and undergoing radioactive decay, the general expression describing the parent-daughter relationship at some elapsed time (t) will be of the form:

$$N_t^d = \frac{\lambda^p}{\lambda^d - \lambda^p} N_0^p (e^{-\lambda^d t} - e^{-\lambda^p t}) + N_0^d e^{-\lambda^d t} \quad (2)$$

where the subscripts 'p' and 'd' represent respective amounts of parent and daughter nuclides. The first group of terms represents the growth of the daughter nuclide from the parent and the decay of the daughter atoms; the last term gives the contribution at any time from the daughter initially present (Friedlander et al., 1955).

In the ^{238}U series, the half-lives of the three major nuclides of interest to Pleistocene geochronology, ^{238}U , ^{234}U , and ^{230}Th are 4.51×10^9 years for ^{238}U , 2.47×10^5 years for ^{234}U and 7.8×10^4 years for ^{230}Th (USAEC Chart of the Nuclides, 1970). Measurement of all three nuclides is necessary to calculate an age as disequilibrium within the series is common in near-surface environments. In this case the decay equation is of the form:

$$\left[\frac{^{230}\text{Th}}{^{234}\text{U}} \right]_t = \left(\frac{1 - e^{-\lambda^{230} t}}{\left[\frac{^{234}\text{U}}{^{238}\text{U}} \right]_t} \right) + \left(\frac{\lambda^{230}}{\lambda^{230} - \lambda^{234}} \right) (1 - e^{-(\lambda^{230} - \lambda^{234}) t}) \quad (3)$$

When dealing with radioactive nuclides in geological samples, it is seldom possible to actually measure the number of atoms of a particular isotope of interest because of the low absolute abundances of the daughter nuclides. Instead, activity, i.e. decay per unit time, is measured. Ratios of the activities are then used in the decay equation to calculate an age. Equation 3 is based on measurement of $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios and assumes that there was no ^{230}Th initially present. This equation also takes into account any disequilibrium between ^{234}U and ^{238}U , which will affect the amount of ^{230}Th present (Broecker, 1963).

Ages calculated from equation 3, in order to be considered valid, must meet certain criteria. These are:

(1) There must be sufficient uranium and thorium present in the samples to provide accurate measurements of activities. This is not generally a problem for uranium ores, as alpha spectrometric techniques are capable of accurately measuring amounts of uranium as small as .05 ppm (Gascoyne, 1977). However, because of the extremely small amounts of thorium present in most samples, measurement of ^{230}Th activity can present difficulties in samples which are younger than 10,000 years unless uranium concentrations are high. Thus samples with very low activities may have large uncertainties in age.

(2) Ages are calculated assuming there is no thorium initially present in the system. Although thorium is insoluble under near-surface conditions and thus not present with uranium co-precipitated from a carbonate or sulfate solution or formed as a uranium mineral, contamination may result if

the deposit was formed containing a large amount of detrital material. Thorium readily adsorbs onto the surface of clay materials and is primarily transported as a clastic component. Measurement of the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio will however give an indication of the amount, if any, of a detrital component present, because detrital ^{230}Th will always be accompanied by 'common' thorium, ^{232}Th . $^{230}\text{Th}/^{232}\text{Th}$ ratios greater than about 20 indicate the absence of detrital thorium. Low $^{230}\text{Th}/^{232}\text{Th}$ ratios indicate the possibility of detrital thorium, therefore any calculated age will be a maximum age.

(3) Also inherent to age calculations is the assumption that the system has been closed to isotope migration, either into or out of the system, since the time of deposition. Young samples will naturally show some disequilibrium, but in a closed system, isotope ratios for a group of samples should all be close to the same value. If isotope migration is known to have occurred, calculated ages are only 'apparent' ages.

(4) Deposition of the uranium must have occurred within a relatively short period of time in relation to the half-lives of the isotopes, otherwise, the system must be considered 'open'.

METHOD

Isotope separation and chemical purification of the radioelements was accomplished using techniques developed by Thompson (1973) and modified for the present study. Below is a brief outline of the detailed procedure found in Appendix A.

Uranium-bearing sediments were dissolved first in HF followed by HNO_3 until all material was digested. Following addition of one ml of $^{228}\text{Th}/^{232}\text{U}$ spike, the radioelements uranium and thorium were co-precipitated with Fe in the form $\text{Fe}(\text{OH})_3$. The precipitate was dissolved in 9N HCL and the iron removed by extraction into isopropyl ether. U and Th are quantitatively separated by passing the solution through anion exchange resin conditioned in chloride form (Cl^-). Thorium is separated from interfering cations by anion exchange onto resin conditioned with a 10:1 mixture of methanol and nitric acid. Separately, U and Th are further purified by formation of TTA complexes and extraction into benzene. The organic phase containing the radioisotope is then evaporated onto a stainless steel planchet just prior to counting.

Activities of ^{238}U , ^{234}U , ^{230}Th , and ^{232}Th were measured using an Ortec 6240A multichannel analyzer and silicon depleted surface-barrier detector system. The total number of counts (one count = one alpha decay event) under each peak were summed and divided by the count time, resulting in count rates for each isotope. The count rates were corrected for background activity and processed using a computer program developed by Thompson (1973), which calculated isotope activities, activity ratios, uranium concentrations and a $^{230}\text{Th}/^{234}\text{U}$ age. Uncertainties in the age determinations are assigned based upon one standard deviation of the counting statistics. (For a review of the data processing and precision associated with this program, see Gascoyne, 1977). ^{226}Ra analyses reported in the following section were performed at the University of Calgary by Professor A.A. Levinson.

RESULTS AND INTERPRETATION

1. SOUTHERN AFRICA DEPOSIT "K"

The eight samples from "Deposit "K" are from an extremely arid area of southern Africa which has a mean annual rainfall of approximately 55 mm per year. Uranium mineralization is associated with a 1.5 meter thickness of diatomaceous earths, carbonaceous sands, silts and clays. These lacustrine sediments were deposited in an impeded drainage channel about 600 meters wide and some 5 km long, which is itself cut into a broad sand-filled valley several kilometers wide, draining an area of about 15,000 sq. km. The unconsolidated uranium-bearing sediments have the grey-green and yellow colors indicative of a reducing environment and stand in marked contrast to the red aeolian sands of the host valley. Overlying the sediments and the uranium deposit is a thin discontinuous layer of calcrete which in turn is partially concealed by recent windblown sand.

X-ray diffraction and microscope examination has identified the uranium minerals carnotite ($K_2(UO_2)_2V_2O_8 \cdot H_2O$), boltwoodite, ($K(H_3O)UO_2(SiO_4) \cdot nH_2O$), and zippeite, ($2UO_3SO_3 \cdot 4H_2O$). As these minerals account for only a small portion of the total uranium present, it appears that a majority is adsorbed as uranium cations onto the surface of clay particles, carbonaceous material and organic matter present in the deposit. The source of the uranium is uncertain, but it is thought to have been initially derived from abundant granites and pegmatites surrounding the area, where values up to 50 ppm have been found.

From stratigraphic correlation of the cross-sections of the four pits in Figure 1, it is observed that the uranium mineralization cross-cuts the major lithologies rather than being confined to particular horizon. Areal distributions of the pits as well as the locations of the samples within the stratigraphic units are shown in Figure 2. Isotopic activity ratios, uranium concentrations, and calculated ages are presented in Tables 1 and 2.

An inspection of the data in the tables reveals several important points:

1. $^{230}\text{Th}/^{232}\text{Th}$ ratios are sufficiently high, with the exception of sample 579, to indicate that relatively minor amounts of detrital thorium are present in association with the uranium.
2. Initial $^{234}\text{U}/^{238}\text{U}$ ratios exhibit only slight variations, having a standard deviation of .048, possibly indicating that the suite of samples are genetically related, i.e. derived from a common parent. If multiple source areas were involved, a greater variation in the initial ratios might be expected. The $^{234}\text{U}/^{238}\text{U}$ ratios indicate slight enrichment of the waters in ^{234}U , with no large scale post-depositional migration of ^{234}U having taken place.
3. Ages calculated on the basis of the isotope ratios are maximum ages and indicate that the deposit is geologically young, not more than about 50,000 years old.
4. Results of the ^{226}Ra analysis indicate some degree of isotope migration in three of the four sample pits. ^{226}Ra data also helps

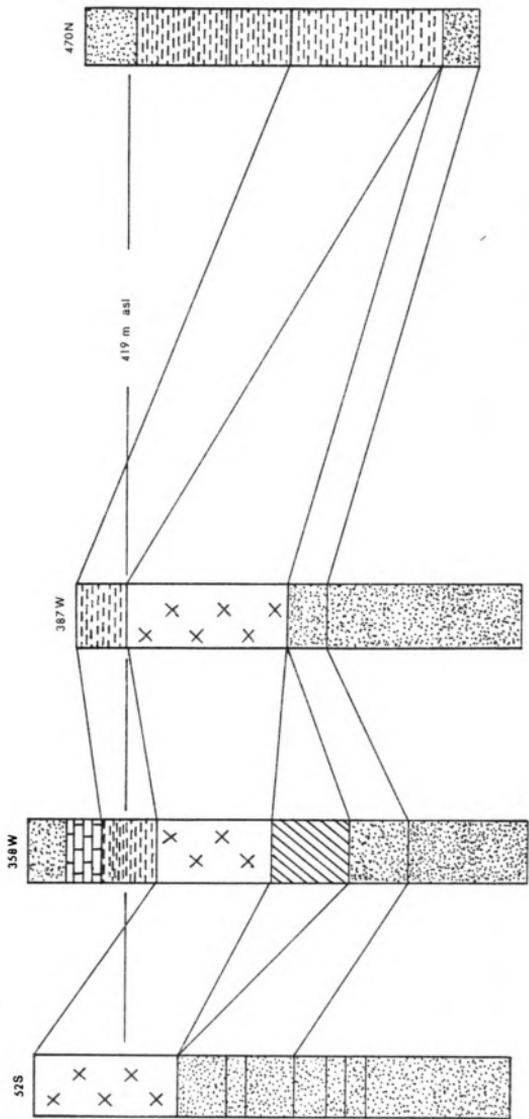


Figure 1
Stratigraphic Correlation - Deposit "K"

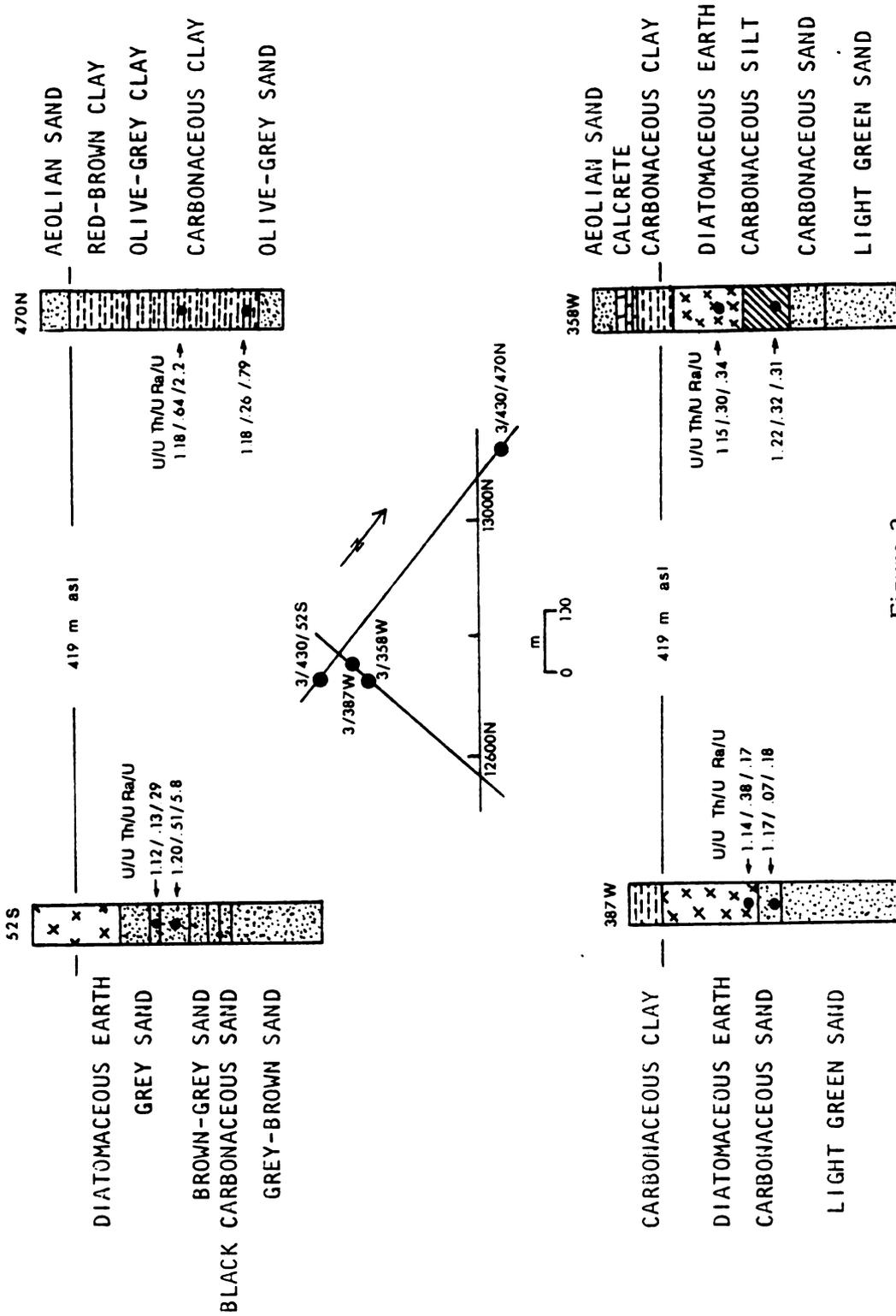


Figure 2

Sample Location and Isotope Activity Ratios

Table 1

URANIUM CONCENTRATIONS, ISOTOPE ACTIVITY RATIOS, AND CALCULATED AGES
FOR DEPOSIT "K"

Sample No.	$\left(\frac{^{230}\text{Th}}{^{234}\text{U}}\right)_t$	$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_t$	$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_b$	$\left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right)$	Calculated Age (years B.P.)
584	$.302 \pm .008$	$1.15 \pm .01$	$1.17 \pm .01$	133	$39,000 \pm 1300$
583	$.316 \pm .030$	$1.22 \pm .02$	$1.25 \pm .02$	160	$40,000 \pm 4000$
585	$.382 \pm .034$	$1.14 \pm .01$	$1.17 \pm .02$	130	$51,500 \pm 6000$
581	$.071 \pm .005$	$1.17 \pm .01$	$1.18 \pm .01$	58	$8,000 \pm 600$
578	$.643 \pm .028$	$1.18 \pm .03$	$1.25 \pm .05$	20	$108,000 \pm 8000$
580	$.257 \pm .012$	$1.18 \pm .02$	$1.20 \pm .02$	16	$32,000 \pm 1500$
582	$.126 \pm .006$	$1.12 \pm .02$	$1.12 \pm .02$	39	$15,000 \pm 800$
579	$.513 \pm .014$	$1.20 \pm .02$	$1.25 \pm .03$	7	$76,000 \pm 3000$
Mean Value	$.326 \pm .189$	$1.17 \pm .033$	$1.20 \pm .048$		42,000

Table 2

COMPARISON OF EQUIVALENT URANIUM FROM ^{226}Ra AND DETERMINED URANIUM

Sample No.	Equivalent U from ^{226}Ra (ppm)	Determined Uranium (ppm)	$\left(\frac{^{226}\text{Ra}}{^{238}\text{U}}\right)$
584	165	490	.34
583	700	2264	.31
585	263	1597	.17
581	320	1803	.18
578	153	70	2.19
580	163	206	.79
582	140	490	.29
579	175	31	5.79

confirm the reliability of the ages in pit 358W as well as provide some insights into the post-depositional migration which has occurred in the other pits.

Detailed analysis of the ratios and anomalies provides some information about the post-depositional history of Deposit "K". Of particular interest, is pit 358W, containing sample 584, from the diatomaceous earth unit and sample 583 from the carbonaceous silt directly below. Both samples have equivalent $^{230}\text{Th}/^{234}\text{U}$ and $^{226}\text{Ra}/^{238}\text{U}$ ratios, (Figure 2); evidence that the uranium and daughter nuclides within this pit have remained undisturbed since mineralization. Thus the age of 40,000 years B.P. calculated for these two samples is considered to be representative of the age of the deposit as a whole and thus acting as a foundation upon which to draw conclusions concerning the isotopic disequilibrium observed in the other three pits. The differences in the uranium ratios between the two horizons can be explained in terms of either a different pre-depositional history and source area or a movement of uranium isotopes immediately after mineralization and prior to the formation of significant daughter products. Comparison with Figure 3, a modification from Ostrihansky (1976), indicates that the isotope ratios found in pit 358W are consistent with uranium accumulations during the last 10,000 to 400,000 years and which have undergone little or no post-depositional isotope migration.

Considering first pit 387W, which can be directly correlated to pit 358W, it is observed that the stratigraphically lower sand horizon (sample 581) has a slightly higher $^{234}\text{U}/^{238}\text{U}$ ratio and a much lower $^{230}\text{Th}/^{234}\text{U}$ ratio than that of sample 585. The low $^{230}\text{Th}/^{234}\text{U}$ ratio of .07 in sample 581 suggests recent uranium mineralization resulting from downward migration of ^{234}U -enriched

1. URANIUM ACCUMULATION OF YOUNG AGE ($\leq 10,000$ years).

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right) \gg \left(\frac{^{230}\text{Th}}{^{234}\text{U}}\right) > \left(\frac{^{226}\text{Ra}}{^{238}\text{U}}\right)$$

2. URANIUM ACCUMULATION OF INTERMEDIATE AGE (10,000 - 400,000 years)

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right) > \left(\frac{^{230}\text{Th}}{^{234}\text{U}}\right) \cong \left(\frac{^{226}\text{Ra}}{^{238}\text{U}}\right)$$

3. URANIUM ACCUMULATION OF OLD AGE ($> 400,000$ years)

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right) \cong \left(\frac{^{230}\text{Th}}{^{234}\text{U}}\right) \cong \left(\frac{^{226}\text{Ra}}{^{238}\text{U}}\right)$$

FIGURE 3

Relative Activity Ratios in relation to the age of Uranium accumulation

uranium from the diatomaceous earth into the sand horizon, thus resetting the 'clock' and producing an observed age of 8,000 years B.P. This is supported by the $^{230}\text{Th}/^{234}\text{U}$ ratio of .38 in sample 585 which indicates a uranium loss, relative to the undisturbed samples of pit 358W, i.e. higher than .31. As the uranium ratios are very close, fractionation of uranium during the migration was minimal. The small amount of thorium produced by decay over this short period has also resulted in a lower $^{230}\text{Th}/^{232}\text{Th}$ ratio relative to sample 585. The equivalent $^{226}\text{Ra}/^{238}\text{U}$ ratios observed in both horizons and which are lower than those in pit 358W suggest that either ^{226}Ra was present in both horizons when the uranium migrated downward, then left the system at some later time, or alternatively, ^{226}Ra may have moved downward from the area of sample 585 after uranium mineralization. This latter effect would decrease the $^{226}\text{Ra}/^{238}\text{U}$ ratio of sample 585, while at the same time, increasing the $^{226}\text{Ra}/^{238}\text{U}$ ratio in sample 581 above the equilibrium value it should have in a system 8,000 years old. Thus the latter alternative appears to be the most likely for the situation under consideration.

In pit 52S, a more complex isotope migration pattern is observed (Figure 2). The stratigraphically lower unit, sample 579, is a clear example of uranium removal resulting in a $^{230}\text{Th}/^{234}\text{U}$ ratio of .51, a value significantly greater than the undisturbed value of .31 (pit 358W). The low $^{230}\text{Th}/^{232}\text{Th}$ ratio in this sample indicates the possibility of some detrital ^{230}Th contributing to the observed $^{230}\text{Th}/^{234}\text{U}$ ratio. The high $^{226}\text{Ra}/^{238}\text{U}$ ratio can be attributed both to the loss of uranium, plus the addition of ^{226}Ra , although not necessarily at the same time. Stratigraphically above sample 579, is sample 582 with a $^{230}\text{Th}/^{234}\text{U}$ ratio of .13. This low ratio indicates a post-depositional migration of uranium, possibly either from the lower horizon or the result of lateral movements of ground water. The $^{226}\text{Ra}/^{238}\text{U}$ ratio of .29 is then greater than an equilibrium value of .13 and

indicates an addition of ^{226}Ra , in agreement with the ^{226}Ra addition noted in sample 579. The difference in the uranium ratios of the two horizons may be related to fractionation early in the deposits history, but more likely it is due to the remobilization which resulted in the observed $^{230}\text{Th}/^{234}\text{U}$ ratios.

Approximately 500 meters north from the other three pits, is pit 470N. This pit is difficult to correlate with the others (Figure 1), as it is composed of layers of clay, sandwiched between two thin sand units and contains no diatomaceous earth horizon. Samples 578 (upper) and 580 (lower) show isotopic variations similar to those in pits 387W and 52S. The high $^{230}\text{Th}/^{234}\text{U}$ ratio of .64 for sample 578 indicates a loss of uranium (possibly enriched in ^{234}U) from the immediate area. This interpretation is supported by the high $^{226}\text{Ra}/^{238}\text{U}$ ratio for that sample, also indicating a loss of uranium as well as a possible addition of ^{226}Ra . Sample 580, with a $^{230}\text{Th}/^{234}\text{U}$ ratio of .26 indicates that within this pit, also there has been a remobilization and deposition of uranium some time after the original deposition thus producing the younger age. The $^{226}\text{Ra}/^{238}\text{U}$ ratio of .79 is consistent with the addition of ^{226}Ra observed in sample 578 of this pit. The similarity in the uranium isotope ratios for both samples could be either the result of chance or due to the fact that uranium isotope fractionation did not occur during the remobilization.

Based upon the available geological evidence and results of the isotopic analysis, a tentative history of Deposit "K" can be formulated. During a pluvial period about 40,000 years ago the organic-rich lacustrine sediments were mineralized as ^{234}U -enriched uranium was stripped from ground waters moving laterally through the carbonaceous sediments; both by changes in the oxidation potential and ion exchange onto the clays. Shortly after deposition and before the

accumulation of significant daughter products, a small amount of isotopic fractionation and uranium migration may have taken place, resulting in different uranium isotope ratios between samples. These early migrations may have been associated with a lowering of the water table near the end of the pluvial period. Further ground water movements during a more recent pluvial period approximately 8,000 years ago resulted in localized movements of uranium and radium with the exception of pit 358W, which notably is capped by a layer of calcrete. Different $^{230}\text{Th}/^{234}\text{U}$ ratios in all of the pits indicate that other local uranium migrations may have occurred at later intervals but without further sampling no firm conclusions can be reached.

2. YEELIRRIE, WESTERN AUSTRALIA

Located in a semi-arid region of Western Australia, the Yeelirrie uranium deposit is found in an impeded drainage channel which has been incised into a Cretaceous plateau during Miocene or Pliocene time. Following the onset of arid conditions, the drainage channel became choked with sediments, finally resulting in a series of clay pans and salt lakes which now characterize that part of the state. Except for a narrow strip of Archaean greenstone along the western edge of the basin, the catchment area for the system is solely within the granitic terrain to the northeast.

Based upon close-grid diamond drilling and airborne radiometric surveys, a general outline of the area of mineralization has been identified (Figures 4 and 5). Mineralization occurs over an area 6 kilometers in length and .5 kilometers in width and to an average depth of 8 meters. Three distinct, but gradational stratigraphic layers have also been identified from the drilling: (1) the overburden, composed of loam and carbonated loam, (2) the calcrete and transition

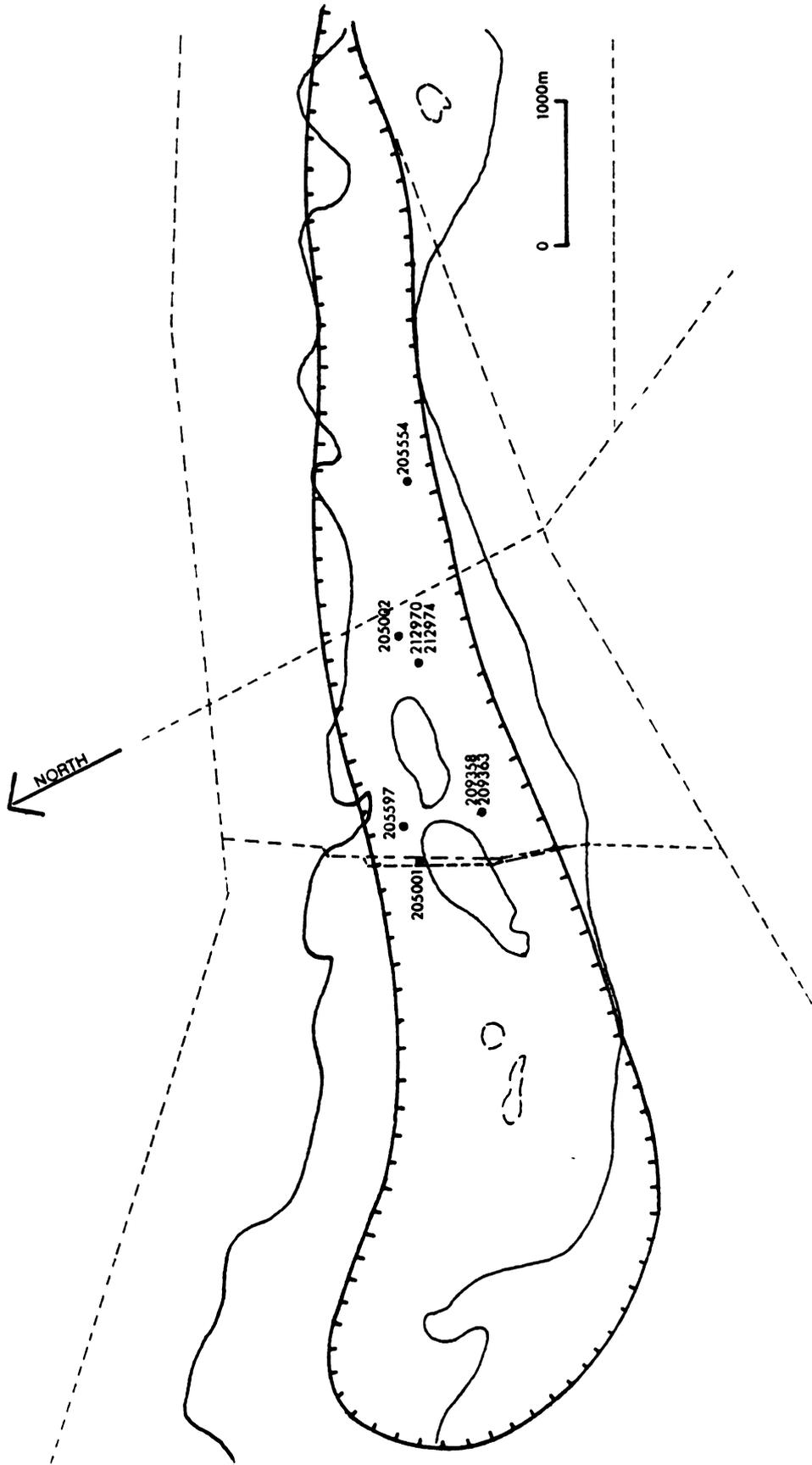


Figure 4

Sample Location and Outline of the Ore Deposit Based on Diamond Drilling

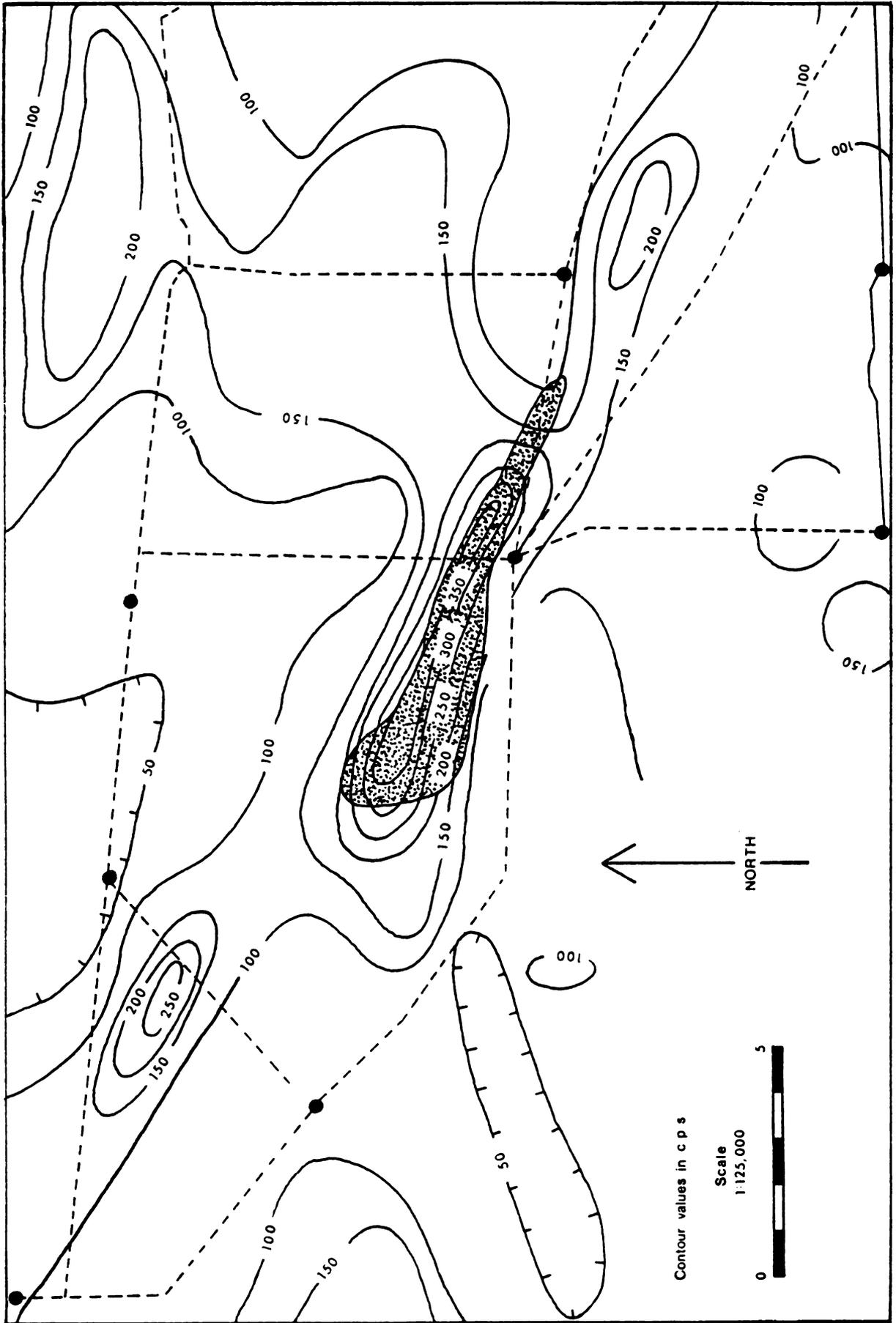


Figure 5

Outline of Yeelirrie from Radiometric Survey

calcrete, and (3) the clay-quartz unit, composed of clay-quartz and carbonated clay-quartz. Gypsum and celestite also occur in the overburden, along with calcite, but are not restricted to it. The calcrete layer contains both calcite and dolomite as dominant forms of carbonate, with calcite being more abundant in the upper transition zone and dolomite being more abundant in the calcrete proper. Silica and montmorillonite are also found in the calcrete, resulting in a large degree of variability, ranging from a white, hard, porcellaneous carbonate to a soft friable form. The clay-quartz unit is composed predominantly of quartz and kaolinite.

Uranium mineralization occurs primarily in the calcrete unit, both as coatings on cavity walls in the porcellaneous calcrete and as uranium dispersed throughout the earthy calcrete. It also occurs as grain coatings and disseminations in much of the clay-quartz as well as linings on fractures and small faults in all lithologies. Only minor amounts of clay and silica within the calcrete are demonstrably later than the uranium mineralization, indicating that the uranium is secondary and not associated with clastic deposition of the sediments. X-ray diffraction has identified carnotite as the only uranium mineral present. Both ground radiometric surveys and laboratory analysis indicate that no thorium is present in the deposit. The quantity of ore in the deposit is estimated to be over 30 million tons with an average grade of .15%, resulting in over 46,000 tons of U_3O_8 (Western Mining Corp., 1975).

Yeelirrie and surrounding areas receive an average of 20 cm of rainfall per year, usually in the form of high intensity storms, while at the same time having an evaporation rate of approximately 250 cm per year. Ground water flow begins at the granite breakaways, flows through the piedmont and alluvial plain, and into

the calcrete blocked drainage channel (Figure 6). Present estimates indicate the water table in the calcrete is at a depth of 5-6 meters (Western Mining Corp., 1975). Tests from one excavation in the channel indicate an average transmissibility of 55,000 imperial gal./day/ft., producing a yield of approximately one million imperial gal./day. Preliminary surveys of water salinity indicate less than 750 ppm TDS in the channel near the breakaways, increasing to 5000 ppm on the edge of the calcrete, and rising to over 20,000 ppm in the ore zone (Western Mining Corp., 1975). While tests of uranium concentrations in the water are limited, early figures from boreholes find values greater than 50 ppb and as high as 450 ppb. Analysis for potassium and vanadium are not available.

The eight Australian samples analyzed were collected from an area near the center of the ore body (Figure 4). An inspection of the data presented in Table 3 indicates some of the trends associated with the isotope ratios:

1. $^{230}\text{Th}/^{232}\text{Th}$ ratios are high in all of the samples, with the exception of 212970, which has a lower but still acceptable ratio. Combined with data from the company surveys, these ratios confirm that only thorium produced from radioactive decay is present in the ore body.
2. $^{230}\text{Th}/^{234}\text{U}$ ratios in all but two of the samples are greater than unity indicating a post-depositional loss of uranium. The range of ratios observed may indicate differing amounts of ^{234}U loss, different ages for each sample, or both.

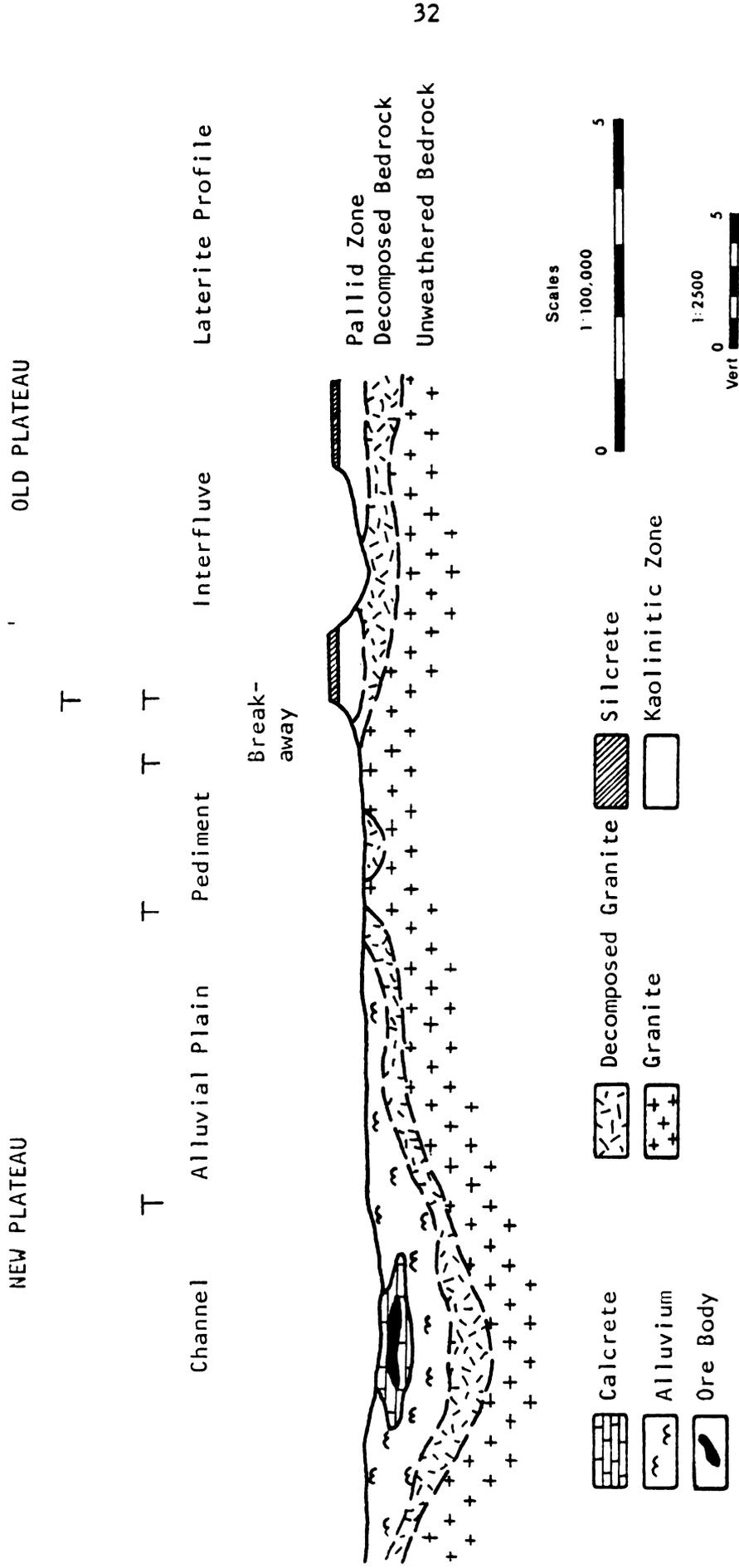


Figure 6

Geomorphological Profile of the Yeelirrie Drainage Basin

Table 3

URANIUM CONCENTRATIONS, ISOTOPE ACTIVITY RATIOS, AND CALCULATED AGES FOR
YEELIRRIE

Sample No.	Depth meters	$\left(\frac{^{230}\text{Th}}{^{234}\text{U}}\right)$	$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)$ t	$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)$	$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)$	$\left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right)$	Uranium Concentration (ppm)	Calculated Age (years B.P.)	Comments
209358	3.5	$1.345 \pm .147$	$1.324 \pm .022$	---	---	220	10903	---	same bore
209363	5.7	$1.279 \pm .049$	$1.231 \pm .039$	---	---	110	546	---	hole
205001	10.0	$1.231 \pm .081$	$1.121 \pm .019$	---	---	215	8348	---	
212970	4.0	$.966 \pm .031$	$1.281 \pm .036$	$1.582 \pm .127$	---	48	721	$261,100 \pm 31,000$	
212974	5.5	$1.035 \pm .035$	$1.128 \pm .017$	---	---	380	2819	---	same bore
205592	6.5	$1.087 \pm .087$	$1.139 \pm .079$	---	---	1000	196	---	hole
205002	6.0	$.750 \pm .022$	$1.374 \pm .011$	$1.547 \pm .027$	---	117	56413	$136,600 \pm 7600$	
205554	5.3	$1.086 \pm .024$	$1.152 \pm .011$	---	---	221	7800	---	

3. $^{234}\text{U}/^{238}\text{U}$ ratios of the samples are all greater than unity. The implications are that (1) initial uranium ratios were very high and a preferential loss of ^{234}U was insufficient to reduce the $^{234}\text{U}/^{238}\text{U}$ ratios to values below unity, or (2) there was little or no preferential loss of ^{234}U , instead a non-fractionated loss of both ^{234}U and ^{238}U occurred resulting in $^{230}\text{Th}/^{234}\text{U}$ ratios and $^{234}\text{U}/^{238}\text{U}$ ratios both being greater than unity.
4. Assuming that no ^{230}Th migration has taken place, the two ages calculated can be considered maximum ages, thus allowing for any loss of ^{234}U .

Although two ages were calculated, it is not possible to actually determine the time of mineralization of the deposit as a whole, as the $^{230}\text{Th}/^{234}\text{U}$ ratios are larger than unity for six of the eight samples and indicate that open system conditions have prevailed and thus a "true" age of deposition cannot be calculated. While loss of uranium from most of the samples is indicated by the $^{230}\text{Th}/^{234}\text{U}$ ratios, there is a possibility that uranium may have been added to some of the samples, (212970, 205002), thus lowering the $^{230}\text{Th}/^{234}\text{U}$ ratios and producing 'apparent' rather than true ages.

The formation of the uranium deposit at Yeelirrie appears to be related to the strong evaporitic conditions, resulting in supersaturation and precipitation from solution of uranium, potassium and vanadium (Dall'Aglio, 1974). The original source area from which ^{234}U -enriched uranium, vanadium and potassium, were leached is evidently the surrounding granitic rocks and greenstones. The present deposit may have formed through a multi-stage accumulation process from previous uranium deposits, (Grunner 1956, Rosholt, 1961), or it could be the result

of a single-stage accumulation from the granitic source area. The mobility of uranium and the evidence of recent uranium migrations within the present ore body tend to support a multi-stage accumulation process. The presence of a fluctuating water table plus the high evaporation rate and oxidizing conditions readily lend themselves to uranium migration within and out of the deposit. Post-depositional migrations of uranium apparently have not resulted in significant fractionation of ^{234}U as the majority of the $^{230}\text{Th}/^{234}\text{U}$ ratios and all of the $^{234}\text{U}/^{238}\text{U}$ ratios are greater than unity. This could result from the fact that in carnotite both uranium isotopes are already in the 6+ oxidation state, thus preventing preferential oxidation and removal of ^{234}U . While alpha recoil can significantly change the $^{234}\text{U}/^{238}\text{U}$ ratio in the liquid phase (Coward and Osmond, 1977), the ratio in the solid phase will be relatively unchanged, especially in area of higher concentration. It is hoped that when the ^{226}Ra data becomes available, more definite statements can be made about the extent of recent uranium migrations.

3. KELOWNA, BRITISH COLUMBIA

The third group of uranium samples analyzed are from the Kelowna area of south-central British Columbia, which presently, has a temperate, humid environment. Uranium mineralization in the area is associated with organic-rich sediments near the contact zone between the unconsolidated sediments and underlying granitic rock. In some areas, the deposit is presently overlain by a basalt caprock. An idealized section of this uranium deposit is shown in Figure 7. The flood basalts which overlie the sediments are thought to act as a relatively impermeable caprock, protecting the mineralized sediments from downward percolating waters.

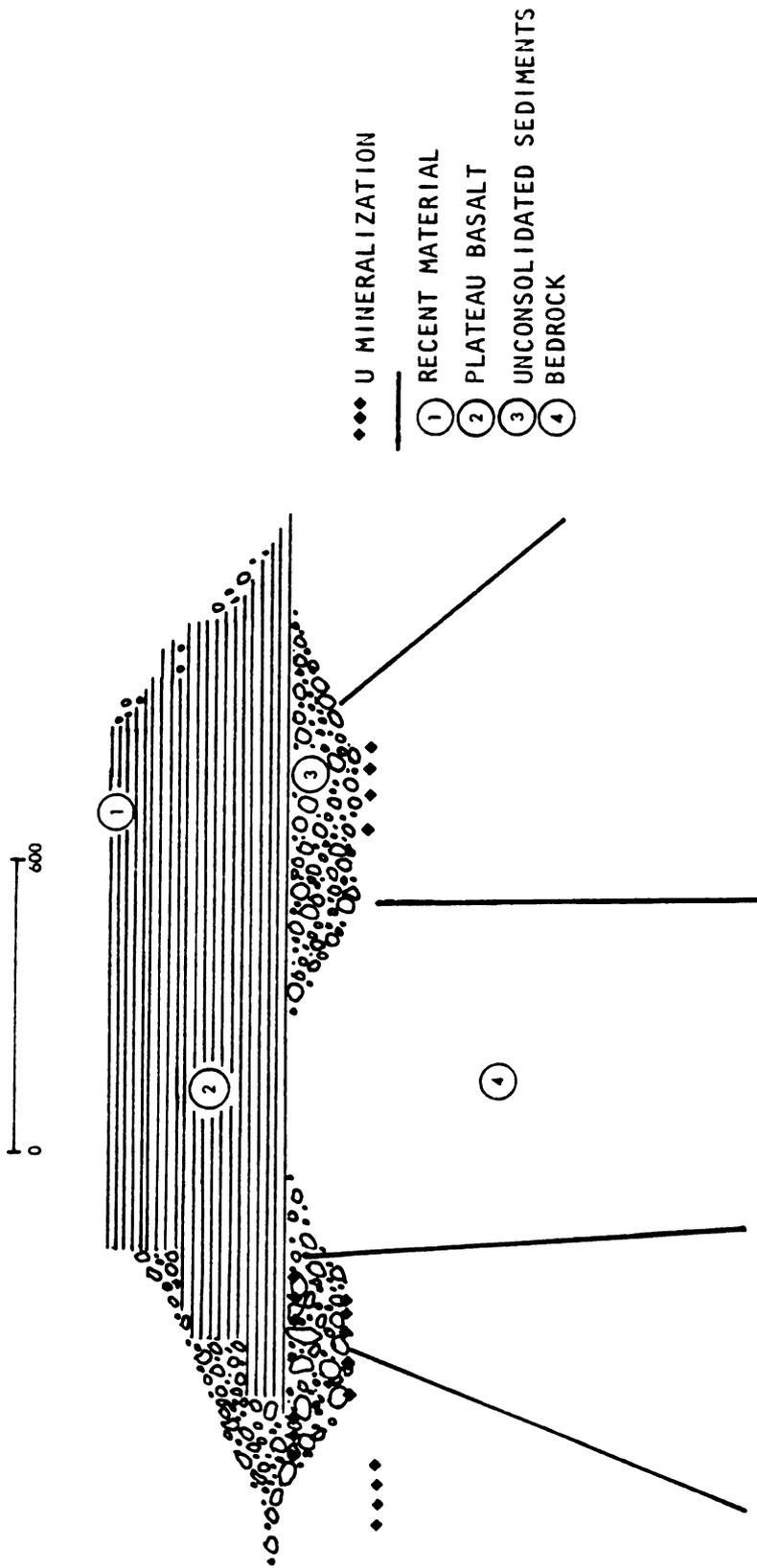


Figure 7

Idealized Section-Showing the Setting of Basal Type Uranium Deposits at Kelowna

Analytical data are shown in Table 4. $^{230}\text{Th}/^{232}\text{Th}$ ratios in all of the samples from this area are high indicating that no significant detrital thorium is present in any of the samples.

The samples from Lassie Lake are composites, each representing ten feet of core, covering a total of thirty feet of mineralized sediments. Sample 76-1-a represents the top ten feet, 76-1-b the middle ten feet and 76-1-c the bottom ten feet; all are presently under the basalt caprock. The ages calculated for the three samples range from 110,000 to 224,000 years B.P. As the oldest age is from the middle sample, it is evident that some migration of uranium has taken place, although not enough to raise the $^{230}\text{Th}/^{234}\text{U}$ ratios above unity. The similarity of the $^{230}\text{Th}/^{234}\text{U}$ ratios for samples 76-1-a and 76-1-b and the lower ratio for 76-1-c suggests a downward migration of uranium slightly enriched in ^{234}U about 110,000 years ago. The migration could have been in response to a lowering of the water table soon after deposition, or the result of water infiltrating through the caprock. The true age of the deposit is unknown, but mineralization appears to have taken place at sometime later than 224,000 B.P.

The single sample from Hydraulic Lake presents little possibility for accurate interpretation. It is not possible to determine if the sample is (1) truly at equilibrium as the ratios imply, or (2) if the ratios are the result of uranium migration. In view of the samples from Lassie Lake showing uranium movement, the latter alternative is the most likely.

Two samples were analyzed from the Fuki outcrop, resulting in similar ratios (Table 4). The samples are from channel sediments exposed in a road cut and are therefore near the surface. In the humid environment and lacking the

Table 4

URANIUM CONCENTRATIONS, ISOTOPE ACTIVITY RATIOS, AND CALCULATED AGES FOR KELOWNA

Sample No.	$\left(\frac{^{230}\text{Th}}{^{234}\text{U}}\right)$	$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)$ †	$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_0$	$\frac{^{230}\text{Th}}{^{232}\text{Th}}$ ($\frac{^{230}\text{Th}}{^{232}\text{Th}}$)	Uranium Concentration (ppm)	Calculated Age (years B.P.)	Comments
76-1-a	.853 ± .020	.987 ± .013	.976 ± .022	228	1022	209,600 ± 15,200	same bore hole
76-1-b	.874 ± .025	1.001 ± .026	1.002 ± .05	75	183	223,900 ± 21,700	10' composites
76-1-c	.633 ± .023	.983 ± .021	.976 ± .028	107	482	109,100 ± 6,900	over 30 ft.
Fuki (1)	1.542 ± .133	.770 ± .009	---	198	---	---	
Fuki (2)	1.44 ± .049	.857 ± .016	---	102	794	---	
Hyd. Lake	.988 ± .055	1.035 ± .039	---	20	127	---	
Okanagan Falls Rd.	3.370 ± .215	1.883 ± .190	---	69	26	---	

basalt cover, it is not surprising that there has been removal of ^{234}U -enriched uranium resulting in the relatively high $^{230}\text{Th}/^{234}\text{U}$ and low $^{234}\text{U}/^{238}\text{U}$ ratios observed.

The single sample from Okanagan Falls Road was taken from a conglomerate also exposed in a roadcut not covered by the basalt cap. The very high $^{230}\text{Th}/^{234}\text{U}$ ratio indicates a substantial loss of ^{234}U , while the high $^{234}\text{U}/^{238}\text{U}$ ratio indicates either a bulk removal of uranium, or a very high initial $^{234}\text{U}/^{238}\text{U}$ ratio.

Without more samples and data, little can be said to explain the low uranium ratios observed in five of the six samples, from Kelowna, other than that they could be the result of low uranium ratios in the water, leaching of ^{234}U , or a combination of both.

CONCLUSIONS

The results represent samples from Africa, North America and Australia each reflecting a different geologic and chemical environment.

Deposit "K" in southern Africa, consists of a uranium deposit formed by ground water migrating downdip through carbonaceous sands, clays and organic trash pockets (diatomaceous earth). The deposit formed as a result of changes in the oxidation potential resulting in precipitation of uranium from solution and cation exchange of uranium onto favorable material. Isotopic analysis of eight samples show that the deposit was formed about 40,000 years ago. Post-depositional migration of uranium most likely in response to water table

fluctuations, was shown to have occurred as recently as 8,000 years B.P. and a possibility exists that other migrations may have occurred previous to that.

The second uranium deposit, Yeelirrie, in Western Australia, consists of uranium mineralization in association with oxidized calcrete channel sediments. The deposit is thought to have formed through evaporation of groundwater, resulting in a concentration of uranium, potassium and vanadium and other salts in solution leading to the precipitation of carnotite. Isotopic analysis of eight samples from this deposit indicate significant uranium isotope migration. Six out of eight $^{230}\text{Th}/^{234}\text{U}$ ratios are greater than unity, allowing only two possible ages to be calculated. Evidence of uranium loss in the system indicate that the ages 261,000 and 137,000 years are maximum ages and represent areas of local uranium mineralization equal to or younger than those ages. Due to the extent of uranium migration noted these calculated ages cannot be considered reliable and do not reflect the age of the deposit as a whole. Fluctuations in the water table, presently at a depth of 5-6 meters is thought to be responsible for post-depositional uranium migration.

Kelowna, British Columbia, the site of the third deposit, has a humid climate, in contrast to the extremely arid climates of the two previous deposits. The uranium was deposited from solution under chemically favorable conditions associated with organic-rich sediments which in some instances are covered by flood basalts and which overly granitic basement rocks. Isotopic analysis of three samples from Lassie Lake indicate a maximum age of mineralization locally of 224,000 years B.P. About 110,000 years ago the $^{230}\text{Th}/^{234}\text{U}$ ratio indicates that a remobilization of uranium took place resulting in a minimum age for the deposit. Single samples from Hydraulic Lake and Okanagan Falls Rd. and two from Fuki,

all show varying degrees of isotope migration resulting in $^{230}\text{Th}/^{234}\text{U}$ ratios greater than unity, and require additional sampling before more definite conclusions can be reached about the age of each deposit.

The conclusions reached based on this preliminary study are that surficial uranium deposits of Late Pleistocene age have formed economic concentrations under both oxidizing and reducing conditions in climates ranging from humid to extremely arid. Once formed, environmental and chemical changes can lead to removal and relocation of uranium into, through, and out of a deposit. It has been shown that uranium accumulations and migrations have occurred during Pleistocene and Recent times and that unless the deposit is sealed from further interactions with ground water it will function as an open system resulting in anomalous isotope ratios, unsupported decay products and uranium removal or redeposition. It is felt that if preliminary study indicates an open system, as at Yeelirrie, much more isotope analysis is needed to establish an understanding of the systematics of uranium movement. While uranium migration occurred in Deposit "K", use of ^{226}Ra data not available for the other areas clearly established that one pit had undergone no post-depositional migration and thus presented a valid age for the deposit as a whole.

The broad conclusions reached regarding U-series disequilibrium and surficial uranium deposits are that under favorable conditions, it is possible to calculate an age, or range of ages of uranium mineralization. When conditions are not favorable for an age calculation, isotope disequilibrium can result in interpretation of uranium migrations and indicate periods of uranium movement.

APPENDIX

APPENDIX AANALYTICAL PROCEDUREA. DISSOLUTION AND PRIMARY PRECIPITATION STEPS

1. Crush the sample to a fine powder; approximately 300-400 mesh.
2. The amount of sample used depends upon the concentration of uranium in the ore. For most ores, one gram is sufficient. Samples which have a known concentration require an amount sufficient to provide 80-100 mgr. of separated uranium.
3. The dissolution technique is dependent upon the composition of the ore. Originally, samples were dissolved in a mixture of HF + H₂SO₄, but this was later abandoned in favor of hot HF, followed by treatment with concentrated HNO₃. Fifty milliliters of HF were used for every 0.5 gram of ore material. The samples are placed in teflon beakers with teflon covers and heated to just below boiling, for an 8-12 hour period. Samples which were dissolved after this period were evaporated to complete dryness to drive off fluorine. Fifty mls of concentrated HNO₃ was added, the beaker covered and heated until the residue was completely dissolved. Occasionally, a small amount of HF was added, which necessitated evaporation to dryness again, followed by another treatment with HNO₃. Samples which did not initially dissolve in HF were fumed again for an additional 4-6 hours and then evaporated to dryness, treated with concentrated HNO₃ and fumed for 2 hours. These were evaporated to dryness and redissolved in concentrated HNO₃, if any residue remained at this point, the above steps were repeated.

4. The nitric acid is then evaporated to a volume of 50 ml and placed in a graduated cylinder. The beaker is rinsed with a small amount of HNO_3 which is added to the solution raising the volume to 65 mls. Place the solution in a large beaker and dilute to 500 mls with distilled water, forming a 2N nitric acid solution.
5. The high uranium activity of uranium ore samples requires that one milliliter of spike (25.5 ug/l) be added to the solution, along with one ml of iron chloride solution (FeCl_3). Samples were then stirred for a short time either with a glass rod or magnetic stirrer then allowed to equilibrate for an 18-24 hour period.
6. While stirring the solution, concentrated ammonium hydroxide is slowly added to the solution, until a reddish-brown precipitate forms, usually at a pH between 6 and 7.
7. After flocculation and settling of the precipitate, it is separated from the solution by filtering with Whatman #1 filter paper and rinsing with distilled water.

B. IRON CARRIER REMOVAL BY ISOPROPYL ETHER EXTRACTION

8. Place the funnel containing the filter paper over a vycor beaker, and dissolve the filtrate using about 50 mls of 9N HCL. Rinse the filter paper with 9N HCL to ensure complete dissolution of all of the precipitate. About 10 mls of concentrated HCL is added to the solution to return the solution to 9N.
9. Removal of iron is effected by adding an equal volume of isopropyl ether to the solution in a separatory funnel. This is shaken vigorously, for about a minute, stopping periodically to release the vapor pressure. After allowing the phases to separate, drain the bottom layer containing the uranium and

thorium into the vycor beaker. The yellow ether layer containing the iron is discarded. Repeat the extraction until the yellow color disappears and the ether becomes colorless, usually about three extractions.

10. Gently heat the acid-ether solution to boil off dissolved ether; until cloudiness disappears and the acid phase is clear.

C. SEPERATION OF URANIUM AND THORIUM ISOTOPES BY ION EXCHANGE

RESIN

11. When the solution has cooled, it is placed on an anion-exchange resin column, which has been preconditioned with 50 mls of 9N HCL. Rinse the beaker with 9N HCL, also adding this to the column. Adjust the column to allow a drip rate of about 50 ml/hour. Once the solution has passed through, the column is rinsed with 100 mls of 9N HCL, and collected in the same vycor beaker. This beaker now contains the thorium, while the uranium has been adsorbed onto the resin.
12. Uranium is eluted into another vycor beaker by rinsing the column with 100 mls of 0.1N HCL.
13. Evaporate both solutions to complete dryness, on low heat. The uranium is now ready for plating and counting, while the thorium must be purified further.
14. In order to separate thorium, prepare another column of anion-exchange resin, by conditioning the resin with 50 mls of a 90% methanol-acid solution (45 mls of methanol and 5 mls of 5N HNO_3) (Tera et. al., 1961). Convert the thorium residue to nitrate salts by dissolving it in 10 mls of 8N HNO_3 , followed by evaporation to dryness. Redissolve the residue in 10 mls of 5N HNO_3 and dilute to 100 mls with 90 mls of methanol. When conditioning of

the resin is complete, add the solution containing the thorium and allow to flow through the column at the rate of 50 mls/hour. Following this, rinse the column with 50 mls of the 90% solution. The rinse may be discarded, as the thorium is adsorbed onto the column.

15. Thorium is eluted from the column by adding 100 mls of 1N HNO_3 and allowing the solution to drip into a vycor beaker. Once the elution is completed, slowly evaporate to dryness, removing the beaker from the stove just as it reaches dryness. If the thorium is allowed to heat beyond this stage, it tends to become insoluble, thereby interfering with the following procedures.

D. FINAL PURIFICATION BY SOLVENT EXTRACTION.

URANIUM EXTRACTION

16. Examine the residue in the uranium beaker, if it has a yellow-brown or dark brown color, substantial amounts of iron, are present which will interfere with the solvent extraction. To remove the iron, dissolve the residue in 3-4 mls of 9N HCL, place the solution in a test tube and add an equal volume of isopropyl ether. Mix the phases thoroughly and allow to separate, removing and discarding the ether phase. Repeat until the ether is colorless. Remove the acid into the beaker and evaporate to dryness.
17. Dissolve the residue in 5-7 mls of 0.1N HNO_3 , heating gently until all of the residue is in solution. Adjust the pH of the acid to 1.2 and place it into a test tube. To this, add one ml of 0.2 TTA (25 grams of 2-Thenoyltrifluoroacetone dissolved in 500 mls of benzene) and mix for one minute.

18. Centrifuge to completely separate the phases, then remove the layer of TTA and discard it. This step removes any thorium or protactinium which may have been present.
19. Transfer the acid phase to a clean test tube and raise the pH to 3.5 by dropwise addition of 0.3N NH_4OH . Add 2 ml of the TTA solution and mix for one minute. Centrifuge to separate the phases, and remove the TTA layer, containing the uranium, placing it into a 10 ml micro-beaker. Repeat the extraction with one ml of TTA and add it to the micro-beaker.
20. A dark red color in the TTA indicates the presence of iron, a light red color the presence of much less iron, usually not enough to interfere with the spectrum. A bright yellow color to the TTA indicates a large concentration of uranium, the brighter the color the higher the concentration. In this case, only a portion of the TTA is used, to avoid a thick source which will produce large tails on the spectrum.
21. Slowly evaporate the TTA solution, reducing it to a volume of approximately 0.25 ml. Further evaporation will cause crystallization, which can be remedied by adding more TTA and heating.
22. Remove the TTA from the beaker with a disposable pipette. Slowly drip the solution onto the center of a hot stainless steel planchet and allow it to evaporate in concentric rings.
23. Flame the planchet to red heat for about 10 seconds, thereby removing any volatile ^{210}Po which could interfere with the uranium spectrum. Count the disc on an alpha spectrometer immediately.

THORIUM EXTRACTION

24. Dissolve the thorium residue in 5-7 ml of 0.1N HNO_3 and heat gently to dissolve all of the residue. If the residue was on the stove for a long period after dryness, this may first necessitate a dissolution with a few ml of 8N HNO_3 , followed by evaporation just to the point of dryness, then followed by the 0.1N HNO_3 .
25. Adjust the pH of the acid to 1.2, with the addition of small amounts of 0.3N NH_4OH .
26. To the acid, add 2 ml of TTA and mix for one minute. Centrifuge to separate the phases and transfer the TTA phase, with the thorium, to a 10 ml micro-beaker. Repeat the extraction using 1 ml of TTA and add to the micro-beaker.
27. Evaporate the TTA solution to a volume of approximately 0.25 ml and plate onto a planchet as directed above. Flame the disc for a few seconds and then count immediately on an alpha spectrometer.

NOTES:

1. During the purification and extraction process, rinse all glassware with distilled water or the appropriate acid and combine with the solution to ensure the highest possible yields.
2. Wash all glassware in hot water, using a phosphate-free soap, followed by a wash with 8N HNO_3 , another wash with soap and water, then a rinse with hot water followed by a rinse with 8N HNO_3 and completed by a rinse with distilled water.
3. Vycor beakers are soaked in a 1:1 solution of nitric acid and then washed as in step 2.

LIST OF REFERENCES

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