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RADIOELEMENT MIGRATION IN NATURAL AND MINED PHOSPHATE TERRAINS

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FINAL REPORT

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ABSTRACT

The phosphatic strata of the Central Florida Phosphate District are enriched in uranium, along with all of its daughters, including thorium-230 and radium-226. Some of the surface and shallow aquifer waters have higher than average concentrations of radium, this being especially pronounced in the down-flow direction of aquifer water movement (towards the southwest). However, most of the shallow and deep aquifer waters of the mining district, as well as surface waters, are within normal range in terms of the radioelement content. We conclude that the phosphate and associated minerals tend to immobilize the radioelements, with the exception of radium.

In the course of mining operations, it appears that the natural pattern is not greatly altered, except in the immediate pit and spoil areas. The aquifers are not radiochemically disturbed, except possibly to a slight extent as a result of enhanced drawdown of the deep aquifer.

As a result of mining and processing operations, most of the radioelements accumulate in the waste clays. Radium and thorium also are present in the gypsum stacks and uranium is present in the acid products and fertilizer.

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1. INTRODUCTION

1.1 Background

1.1.1 Environmental Relationships

In west central Florida there are extensive phosphate mineral deposits contained within the Bone Valley and Hawthorn Formations. The deposits of this region, the land pebble phosphate district, occur at shallow depths. The phosphates are presently exploited by surface mining in the northeast portion of the district.

As a result of surface mining, the near surface physiographic and hydrologic systems are altered. In addition, phosphate ore constituents are redistributed both physically and chemically.

Phosphates have been observed to be significantly enriched in uranium (Cathcart, 1956). Early workers described the chemical fractionation and disequilibrium of uranium with its daughters as well as its mobilization from rock to groundwaters (Altschuler, et al. 1958). Uranium daughters may chemically fractionate due to differing chemical properties of the nuclides in the decay series. Physically, either physical ejection of daughters due to alpha decay recoil or changes of state as in the formation of gaseous radon may separate parents from daughters. The enrichment of uranium in phosphates, in combination with the ability of uranium and its daughters to fractionate, suggests that phosphates have the potential to act as a source of uranium series nuclides to groundwaters.

Although a number of radiological studies have been made within the land pebble district, most have primarily dealt with radium and only a few have examined the distributions of uranium series nuclides as a function of mining. No systematic uranium isotopic study has been undertaken to relate water, ore materials, and phosphate processing fractions.

1.1.2 Phosphorite

The Miocene phosphate deposits of Florida are not unique in that several similar deposits are known worldwide. However, there are no known contemporary environments where such deposits are forming today. At a few continental slope sites, where intense upwelling occurs, phosphate nodules are recognized which may be young; all other nodules from the sea floor have been shown, by uranium-series disequilibrium methods, to be old. (Veeh and Burnett, 1982).

Apparently, peculiar conditions of ocean currents, marine geochemistry, and climate are required to produce extensive phosphate deposition. The model involving movement of deep ocean water up and over shallow shelf areas must certainly have some validity, even though certain geochemical aspects of the proposed process have been refuted.

Collophanite, the "amorphous" form of apatite in sedimentary phosphorites, is more precisely identified as the mineral francolite. Whereas igneous fluorapatite has the formula:

$$Ca_5(PO_4)_3F,$$

francolite exhibits several kinds of ionic substitution, principally CO_3^{+2} for PO_4^{+3}, and Na and Mg for Ca, and perhaps OH for F. A general formula for francolite is:

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_yF_2$$

where a = x-y and x varies from 0 to 1.5. The operative substitution appears to be CO_3F for PO_4 (McClelland and Lehr, 1969). Presumably large ions like U^{+4} and Th^{+4} substitute for Ca^{+2}.

1.1.3 Phosphate mining

The phosphate ore in the land pebble district is excavated utilizing surface mining techniques. The overburden (Pleistocene sands and portions of the upper Bone Valley Formation) is stripped away and piled aside for use during reclamation. The ore, known as "matrix," is excavated, slurried with water and pumped to a beneficiation plant for concentration of the phosphate-bearing minerals, primarily apatite. Using various screens and washers, an initial size separation is effected between a clay fraction ("slimes"), a sand fraction ("tails"), and a phosphate fraction ("pebble").

During washing and screening the clays take up a great deal of water, increasing their volume in the process. As a result, the clay fractions are pumped to large settling areas to facilitate the de-watering process. The sand fraction is transported to a flotation plant to separate fine phosphate from the quartz. The phosphate fraction is sized and sorted for later chemical processing.

Flotation is a two step process, both steps involving surface tension fixing: first quartz, then phosphate. Initially, quartz dominant sands are reacted and frothed with a mixture of fuel oil and fatty acids. This process floats the phosphate fraction and allows most of the sand to sink. The now phosphate-dominant product is reacted with sulfuric acid to remove the organic reagents. The material is then frothed with amines to float the small quantity of quartz remaining. The fine phosphate fraction ("concentrates") is then stored for later chemical processing.

Phosphate pebble and concentrates are transported to a chemical plant for processing into super-phosphate or phosphoric acid. In both processes phosphate minerals react with sulfuric acid to produce a more concentrated product, super phosphate:

$$\mathrm{Ca_3(PO_4)_2 + 2H_2SO_4 + 6H_2O} = \underset{\text{super phosphate}}{\mathrm{CaH_4(PO_4)2}} + \mathrm{2H_2O} + \underset{\text{gypsum}}{\mathrm{2(CaSO_4 2H_2O)}}$$

or, phosphoric acid:

$$\underset{\text{phosphate rock}}{\mathrm{Ca_{10}F_2(PO_4)_6}} + \mathrm{10H_2SO_4} + \mathrm{20H_2O} = \underset{\text{gypsum}}{\mathrm{10CaSO_4 \cdot 2H_2O}} + \mathrm{2HF} + \underset{\text{phosphoric acid}}{\mathrm{6H_3PO_4}}$$

Phosphoric acid is either shipped out directly or sent first to a uranium recovery plant. The-waste gypsum is piled into "stacks" on site.

1.1.4 Previous Investigations

Much published attention has been given to the occurrence of uranium in phosphorites. The geochemistry of uranium in relation to apatite and phosphate rock was studied by McKelvey (1956) and Altschuler, Clarke and Young (1958). The occurrence of uranium in the phosphorites of the Bone Valley and Hawthorn Formations was described by Cathcart (1956), Altschuler, Jaffee and Cuttitta (1956) and Altschuler, Clarke and Young (1958). Uranium isotopes in sea-floor phosphorites have been investigated by Kolodny and Kaplan (1970), Burnett and Gomberg (1977) and Burnett and Veeh (1977). Radioactivity distributions in phosphate products and wastes were determined by Guimond and Windham (1975) and Roessler, et al. (1980).

Reviews of fractionation of uranium isotopes have been published by Cherdyntsev (1969) and Osmond and Cowart (1976, 1982). Application of uranium isotopic disequilibrium to groundwater studies has been discussed by Kaufman, Rydell and Osmond (1969), Cowart, Kaufman and Osmond (1978) and

Cowart (1980).

Concentrations and methods of extraction of radium in natural waters have been studied by Michel and Moore (1980) and Moore (1981). Radium-226 concentrations in groundwaters of west central Florida were investigated by Kaufman and Bliss (1977). Radon-222 and Ra-226 concentrations in sea water off the coast of west central Florida were reported by Fanning, Breland and Byrne (1982).

1.2 Uranium Series Geochemistry

1.2.1 Uranium Geochemistry

Among the many substitutions allowed in the francolite lattice, the trace element uranium is noteworthy. The U^{+4} ion has about the same ionic radius as Ca^{+2}, and Altschuler, et al. (1958) suggest that the incidental replacement occurs at the time of precipitation. The U^{+6} ion also occurs, to a lesser extent, in phosphorites, but its mode of incorporation is unclear. Normally only the UO_2^{+2} complex is available in natural waters, and this ion is too large to fit into the Ca^{2+} sites. Studies suggest that the redox conditions of the environment may determine which cation (+6 or +4) is substituted. Subaerial exposure of phosphate deposits may be the mechanism responsible for the oxidation of +4 to +6. The isotopic fractionation of ^{234}U and ^{238}U associated with the multi-valent occurrences suggested to Osmond and Cowart (1976) that secondary oxidation associated with alpha recoil processes is the explanation. In rare instances a separate uraninite phase (UO_2) has been observed in minute amounts in phosphorites (Veeh and Burnett, 1982).

In any event the uranium content of marine phosphorites is appreciable, ranging up to about 400 ppm for some samples from South Carolina which are stratigraphically equivalent to the Florida deposits (Menzel, 1968). The median value for Florida land pebble samples is from 100 to 200 ppm. The average values for samples from Morocco, Egypt, South America, and the Phosphoria Formation of the Rocky Mountains are similar. Tennessee brown rock, Russian and Turkish phosphorites, and Pacific guano deposits are generally less uraniferous (Menzel, 1968).

In the most reduced form uranium has an ionic radius of 1.05A and an ionic potential of 4. In the +4 state uranium is quite immobile and behaves as a large, lithophile cation. In this form uranium may substitute for calcium. In the +6 state, with a radius of 0.80A and an ionic potential of 7, uranium is relatively mobile as the uranyl ion, UO_2^{+2} (Langmuir, 1978). In oxidizing waters uranium forms uranyl di- and tri-carbonates at pH ranges of 7-8.

$$u^{+4} + 2H_2O = UO_2^{+2} + 4H^{+4} + 2e- \qquad E^o = 0.27\ V$$

Further complexing can occur depending on pH and the presence of other ions. The most stable uranyl carbonate complex in the pH range 4-10 is $UO_2(CO_3)_2^{-2}$ (Langmuir, 1978). In addition to carbonate, soluble uranyl complexes are also formed with phosphate, sulfate, fluoride, and silicate ions.

Uranium is normally mobile in the near surface environment but may be immobilized by reduction to the +4 oxidation state in humic soils, in anoxic basins, or in the down dip reducing zones of hydrochemically mature sandstone or carbonate aquifers (Cowart, 1980).

There are three naturally occurring isotopes of uranium: ^{238}U, ^{235}U, and ^{234}U. The first two of these are long-lived isotopes which accumulated with original earth forming materials. They are decaying at slow but differing rates so that the ratio $^{235}U/^{238}U$ has changed with geologic time but, because of their identical chemical properties, this ratio is everywhere the same throughout the earth at the present time (except for one anomalous but understood occurrence). The third natural isotope, ^{234}U , is far too short-lived to be a remnant of the earth's origin. As a daughter of ^{238}U its abundance is a function of (a) the abundance of its parent, and (b) its relative decay rate. Calculation of the Nd/Np relationship predicts a universal relative $^{234}U/^{238}U$ ratio of 0.000056 by atom count. More usefully, from our standpoint, the alpha ray activity ratio should be 1.0. Despite its chemical similarity to the other two isotopes, ^{234}U shows considerable natural deviation from the expected abundance and activity ratios, especially in weathered rocks and natural waters, the subjects of this research.

1.2.2 Thorium Geochemistry

Thorium occurs in the two decay series ^{238}U and ^{232}Th. ^{228}Th is a member of the ^{232}Th series whereas ^{230}Th is a member of the ^{238}U series. Thorium occurs in the tetravalent state in nature, forming sparingly soluble organic and inorganic complexes in aqueous solutions. As a result of its low solubility, thorium activities in groundwater are very low. Two isotopes of thorium, ^{228}Th and ^{230}Th, are observed more commonly in groundwaters than is ^{232}Th. Both of these isotopes are daughters of mobile parents which are soluble in water. Thorium activities in waters are generally too low to allow interpretations to be made although ^{230}Th activities in aquifer rocks may allow interpretations of previous flow conditions and may be an indicator of active leaching or accumulation of uranium.

The $^{230}Th/^{238}U$ activity ratio plays the most important part in determining the direction and magnitude of uranium mobilization in rock. Because ^{230}Th is immobile in groundwaters the activity ratio of $^{230}Th/^{238}U$ is diagnostic of uranium mobilization (high ratio) or accumulation (low ratio) (Osmond and Cowart, 1982).

1.2.3 Radium Geochemistry

There are four naturally occurring radium isotopes found in natural waters. We will be concerned with only ^{226}Ra of the uranium decay series in this investigation. Radium-228 of the ^{232}Th decay series is not considered because of the very low concentration of thorium in sedimentary phosphorites. Also deemed insignificant are the shorter-lived radium daughters of the two series, ^{223}Ra and ^{224}Ra.

The abundance of ^{226}Ra in ground water is a function of the ^{238}U and ^{234}U content of the aquifer materials and ground waters, the residence time of the ground water, and the chemical characteristics of radium itself.

High radium concentrations tend to indicate an enrichment of parent uranium within the aquifer matrix. However, enrichment may be only a secondary accumulation on grain surfaces as a result of precipitation under reducing conditions. The half-life of ^{226}Ra is 1620 years, so that in extremely transmissive aquifers or zones the radium may be transported a considerable distance from its source.

Radium is introduced into solution in part by alpha recoil and in part by selective leaching, the same as is ^{234}U. The rate at which any radioactive isotope is introduced into the aqueous phase is dependent on its half-life. Shorter-lived isotopes will be more rapidly introduced, in terms of activity units.

Ground water in a slow moving, low transmissivity aquifer or zone has a longer residence time within the aquifer, and will develop higher concentrations of ^{226}Ra, than in a fast moving system with comparable uranium concentrations in the aquifer materials. This is due to the fact that the slower moving water is in contact with the source for a longer period of time, and thus both recoil and leaching processes have more opportunity to operate (Section 1.3).

The geochemical character of the ground water may also influence ^{226}Ra concentrations. The leachability and the retention of ^{226}Ra in ground water may be enhanced by a solution of greater ionic strength, such as ground water with high total dissolved solids (TDS). In waters with low ionic strength, radium may be adsorbed on grain surfaces more readily than in more mineralized water, where many other ions are competing for adsorption sites.

Radium exists only as a divalent cation so that redox conditions do not directly affect its solubility. If concentrations of radium are high enough it may complex with sulfate, forming highly insoluble $RaSO_4$. The maximum concentrations of radium in ground waters, however, are much too low to reach the K_{sp} for radium sulfate of $10^{-10.4}$. High sulfate concentrations do not seem to affect radium solubility unless large amounts of barium are available for co-precipitation of the radium with barium sulfate.

1.3 Uranium Series Disequilibrium

1.3.1 Decay Chains and Radioactive Equilibrium

The three naturally occurring decay chains derive from the unstable but long-lived parents, ^{238}U($t^{1/2}$=4.47 billion years), ^{235}U($t^{1/2}$=0.713 billion years), and ^{232}Th($t^{½}$=13.9 billion years). Figure l-l shows the decay schemes in standard form, for ^{238}U--^{206}Pb, ^{235}U--^{207}Pb, and ^{232}Th--^{208}Pb. Some three dozen unstable daughters form temporarily during decay; that is, they represent channels of decay through which pass 99% of the nuclei which cascade from parent to ultimate stable daughter. Several other intermediate daughters which represent minor alternate decay paths and branching decay are not shown in Figure l-l.

Ten of the main scheme daughters are so unstable that their average lifetimes are less than 10 minutes. The most stable of all of the daughters is ^{234}U with an average lifetime of 350,000 years ($t^{½}$ =250,000 years). Only three other daughters have average lifetimes of a thousand years or more (^{230}Th, 108,000 years; ^{231}Pa, 50,000 years; and ^{226}Ra, 2,500 years). When these lifetimes are compared to those of the much longer lived parents, it means that eleven of the daughters have absolute abundances which are very much less than the parent nuclides in the series.

"Chemical uranium" neglects entirely the mass of all of the daughters which are inevitably present in varying proportions due to decay. On the other hand, because of this same instability, the radioactivity of these daughters cannot be neglected. In undisturbed systems, the radioactivity of each of the daughters is equal to that of the parent; the alpha radioactivity in old minerals is 10 times that of ^{238}U alone.

The decay rate (λ) of ^{238}U, for example, is about 1.5 x 10^{-10} and that of ^{234}U about 2.8 x 10^{-6}. The equilibrium rule for members of a decay chain states:

$$N_{238}\lambda_{238}=N_{234}\lambda_{234}$$

so that the relative abundance N_{234}/N_{238} =5.5 x 10^{-3} which is so small that the concentration of ^{234}U in any 'uranium' analysis can be neglected gravimetrically.

Accordingly, in the study of equilibrium conditions, the radioactivity is generally the parameter of interest. The undisturbed condition, wherein the radioactivity of the daughter is the same as that of either an immediate or ultimate parent, is termed secular equilibrium. If one considers the earth as a whole, or of large segments of the earth's crust, there is actually no such thing as disequilibrium. However since particular earth systems may be considered open or partially closed for times approximating or exceeding the half-lives (or average lifetimes) of certain nuclides they may be investigated with useful results.

1.3.2 Radioactive Disequilibrium

Disequilibrium occurs when a process acts to move a parent or daughter into or out of a system at a rate which is significant relative to the lifetime of the daughter, and over a distance which is significant relative to the size of the system.

The degree of disequilibrium produced is usually expressed as some ratio of activity, either A_d/A_p, the 'activity ratio' (A.R.), or $(A_d-A_p)/A_p$, the 'excess ratio' or 'deficiency ratio' where A_p and A_d are the radioactivity of the parent, and daughter respectively.

Once equilibrium is interrupted, decay processes begin to re-establish the equilibrium state again. Disequilibration is a transitory situation, just how transitory depending on the decay rates of the nuclides involved. The general equation is

$$A_d=(A_{p_o}e^{-\lambda_p t})+(A_{d_o}-A_{p_o})e^{-\lambda_d t})$$

where the original amounts of parent and daughter can have any relative values.

The verbal equivalent of such an equation is: whatever the original amounts of parent and daughter, the equal activity parts ($A_d=A_p$) will decay away in secular equilibrium fashion controlled by the decay rate of the parent. Any excess or deficiency of the daughter will be reduced, or, 'decay away', at a rate controlled by the decay rate of the daughter.

The most commonly encountered relationship in the study of natural processes is that of the longer lived parent and a much shorter lived daughter. In this case, the equation reduced to

$$A_d/A_p=1-e^{-\lambda_d t}$$

Figure 1-2 shows how the excess or deficiency of the daughter relative to the parent disappears with time.

The daughters in the three naturally occurring chains display a wide range of decay rates, over many orders of magnitude. For this reason, the schemes have different aspects, depending on the time scale of interest (Figs. 1-3, 1-4).

For most geochemical studies, including research on the migration of radionuclides near phosphate deposits, the uranium series decay chain can be regarded as a 5-member chain (Fig. 1-4). The shorter-lived intermediate daughters are, on a 10^3 year time scale, in equilibrium with their respective immediate parents.

1.3.3 Mechanisms of Disequilibrium

Disequilibrium results from geochemical sorting processes, or differentiation, whereby one daughter is more mobile than another. Solution and precipitation are important sorting processes, and the locales of disequilibrium production are primarily liquid/solid phase boundaries. However, some of the differentiation processes are physical, rather than chemical, so that isotopic, as well as elemental, fractionation can also be observed to occur at solid/gas or solid/solid phase boundaries (Osmond and Cowart, 1982).

A common differentiation process is selective leaching by ground water as it percolates past the solid mineral grains in an aquifer or soil. Some of the daughters of a series are more soluble than others under given conditions of Eh, pH, ions present, etc. The result is a liquid phase with excesses of the soluble daughters, and a solid phase with surfaces which are deficient in them. Subsequently, dissolved species produce daughters by decay, which may be less soluble than their mobile parent. Precipitation or adsorption processes then become disequilibrium producing processes. Chemical precipitates often exhibit the extreme states of disequilibrium which are characteristic of the hydrosphere.

The fact that a nuclide occurs as part of a radioactive series results in an amplification of its potential for dissolution. Even if a nuclide itself is not alpha radiogenic, to have had an ancestor decay in this mode is to increase its chances of residing in an unstable lattice site. Furthermore, if any of its precursors had been in solution, a daughter will either be formed in the liquid phase, or on a precipitation or adsorption surface where re-solution is facilitated.

The large excesses of ^{234}U over ^{238}U in many ground waters is a case in point. The intermediate daughter, ^{234}Th, is, at least in some instances, not present in solution, which has been cited as evidence that recoil mobilization is not the cause of fractionation (Hussain and Krishnaswami, 1980). However, it is appropriate in this situation to include the once-mobilized but subsequently lightly-absorbed ^{234}Th atoms as a part (essentially) of the aqueous phase. The lack of ^{234}Th ($t_{½}$ =24.1 days) in water samples is not a critical point.

There is another mechanism which can produce disequilibrium at phase boundaries of all kinds: recoil of daughter products in the process of alpha decay. In the case of a radioactive series, one can look at recoil displacement as a special kind of diffusion, which operates in even the most impermeable media, but which occurs only in the process of decay from one daughter to another. The rate of such 'diffusion' then is a function of (a) the number of decay events in the chain, (b) the energy of the individual decay events, and (c) the concentration gradient of the parent nuclides. The distance over which this kind of 'diffusion' operates is limited by the cumulative recoil ranges.

In geochemical systems, recoil displacement may be a significant process in causing disequilibria where phase domains are small in size, as for example in clay soils, or in the case of radioactive mineral grains in contact with ground water. Actually, this situation describes almost any mineral bathed by non-radioactive ground water. The recoil process must be taken into consideration, and especially if one is concerned with the 'mobility' of the later daughters in the series.

The well-known radon escape process in soils is not just a matter of true diffusion of one short-lived nuclide; rather it is the last step in a process that may involve recoil 'diffusion' of two or three preceding daughters.

It is difficult to isolate recoil displacement as a mechanism causing disequilibrium in natural processes because of the role of competing solution mechanisms. However, in one instance, the role of recoil in producing disequilibrium must be important. The disequilibrium of ^{234}U relative to ^{238}U, so universal in the hydrosphere and weathered rocks, is difficult to explain in other terms. The parent and daughter have the same chemical characteristics, and the intervening daughters, ^{234}Th and ^{234}Pa, are relatively insoluble and have short half-lives, so that leaching is an unlikely explanation. Furthermore, the disequilibrium in some cases involves solid phases only, or solid phases as the adsorbing or precipitating phase, so that leaching is not involved at all.

One other process has been suggested as the cause of natural disequilibrium, and is especially difficult to isolate and identify: The Szilard-Chalmers effect. Applied to the natural series, this translates to a 'vulnerability to leaching' condition. The process of decay, especially an alpha event (perhaps also a beta event), greatly disrupts the crystalline lattice along the path of recoil and in the neighborhood of the displaced daughter. The daughter nuclide itself is apt to lodge in an inhospitable lattice site, and may, as the result of its nuclear transformation, exhibit an unstable electronic configuration. In many ways, such a nuclide becomes more vulnerable to leaching than its neighboring atoms, including other longer lived members of the same series, and even other nuclides of the same chemical species (isotopes). This process is especially significant in such cases, as $^{234}U/^{238}U$ or $^{228}Th/^{232}Th$, where one of the isotopes has not experienced any decay event.

1.3.4 Geochemical Mobility and Range

An important determinant of the level of abundance of a given radionuclide in solution is its half-life. In the case of unsupported dissolved species, shorter-lived nuclides will decay away while longer-lived nuclides will persist. Even though two nuclides have similar chemical properties, the shorter-lived one will be scarce unless there is a continuing supply contributed to the water by the aquifer rock.

Figure 1-5 shows qualitatively how the various members of the natural decay series can be ranked according to the concept of 'range'. Range can be defined as a log-log product of both half-life and solubility (Osmond and Cowart, 1982). Uranium, radium and radon frequently occur in natural waters at the pCi/l level, and are thought of as geochemically soluble. Thorium and protactinium are seldom detected in solution and are essentially insoluble in natural waters. Lead, bismuth, actinium, and polonium may be found in solution under certain conditions. For those nuclides which are readily soluble, the factor which limits their occurrence in natural waters can be their average life times.

Unless supplied by decay from parents in solution, or in the immediate vicinity in the aquifer rock, short-lived nuclides will not be widely dispersed. Each nuclide, therefore, has its own geochemical mobility, which depends on its elemental solubility and its mode of radiogenesis; and its own geochemical range, which depends on its elemental solubility and half-life.

Range and mobility, as geochemical properties of nuclides, must be applied with caution inasmuch as the solubility of elemental species varies greatly depending on ground water composition. Nevertheless, even for very soluble nuclides, a short half-life is tantamount to a limited range; conversely, even very insoluble elements may be mobilized, although fleetingly, by recoil processes.

1.3.5 Surficial Disequilibrium

It is the geologic processes that occur at or near the surface of the earth (at the lithosphere/atmosphere or lithosphere/hydrosphere interfaces) which evolve fast enough to be timed or characterized by the decay and disequilibrium of daughters in the three naturally occurring series (Fig. 1-4).

Deeply buried rocks and minerals are generally in equilibrium, but where exposed at the earth's surface to attack by the corrosive agents of water and the associated dissolved species, differential mobility of the various daughters of the series can cause disequilibrium. As a result, soils typically display the disequilibrium pattern: $^{230}Th > ^{238}U > ^{234}U$. Even apparently unweathered rocks tens of meters below the earth's surface can be slightly altered by small amounts of percolating water. The best proof of this has been the occasional instance of marked disequilibrium shown by fresh-looking granites.

The primary agent of disequilibrium is percolating water, and all parts of the hydrosphere are out of equilibrium. Soil water usually shows the reverse pattern to that of soil: $^{234}U > ^{238}U > ^{230}Th$. This, of course, mainly reflects the different solubilities of the elements in aqueous media, and therefore their relative geochemical mobilities (Fig. 1-6). However, certain isotopic ratios, e.g, $^{234}U/^{238}U$ are unexpectedly variable, suggesting that more than simple solution is involved.

Rivers are the primary means of transport of elements through the external parts of their geochemical cycles, and the concentrations of elements in rivers relative to their abundances in crustal rocks is an indication of the rate at which they are being recycled. Among the natural series, uranium and radium are usually found to migrate ahead of thorium and lead in their cycles. With respect to the radioactive series, as with most elements, this disparity in mobility, and the resulting disequilibria, is balanced by the physical transport of sedimentary particles richer in the immobile elements, so that in sedimentary basins the various states of disequilibria tend to be redressed, both physically and chemically.

There are two circumstances of interest in disequilibrium research, corresponding to two kinds of geochemical problems to be solved.

The first kind of problem is that of age of the systems, which can be determined only if the time scale of the process and the decay rates are similar within an order of magnitude. Given the relatively poor definition of the systems, and the normal radioactive measuring techniques, changes of at least few per cent relative to equilibrium are required. For a nuclide with a half-life of 75,000 years (^{230}Th), an excess, or deficiency will disappear by about 5% in the first 7500 years. In a faster-changing system, ^{230}Th appears as an essentially constant activity species. At the other limit, if only 5% of excess or deficiency can be measured, this condition will be reached after about 4 half-lives, or 300,000 years. On any longer time scale the activity of ^{230}Th reflects that of ^{234}U.

As a rule of thumb, we can think of a process or system as being datable by the state of disequilibrium of a particular nuclide if its age, or rate of movement, is in the range of 1/10 to about 5 times the half-life of the nuclide. There are many factors which act to extend or, more often, contract this applicability range.

In another kind of problem, disequilibrium can be used as an isotopic characteristic to identify or "finger-print" a component of a system. For example, the ratios of dissolved isotopes of uranium or radium from groundwater from a given aquifer will likely be different from those of another. In such cases, once acquired, the disequilibrium state should be stable, which means the isotope of interest must have a half-life much longer than the time period of the process. The rule of thumb for this relationship is the opposite of that for dating: the mixing or separation process should be faster, by a factor or 10 or so, than the half-life of the isotope. For example, if diverse ground waters intermingle over a time period of 25,000 years or less, then their differing $^{234}U/^{238}U$ ratios can be used to calculate mixing volumes. If the percolation process is slower, then the evolution of the ratios with time, and the 'ages' of the ground water masses must also be considered.

In the phosphate deposits under study, the following conditions of disequilibrium are germane:

1) The age of the original Miocene deposition, or of the subsequent reworking to form 'pebble', is greater than 10^6 years. This means that any disequilibrium produced by the depositional process will long since have disappeared.

2) Contemporary weathering of surficial deposits will tend to produce disequilibrium conditions. Percolating ground waters are expected to carry uranium in excess of its less mobile daughter ^{230}Th, and because of recoil-related processes, ^{234}U is expected to exceed ^{238}U in activity. Unless the weathering process is quite rapid or extreme, ^{226}Ra, because of its shorter half-life, is expected to be close to equilibrium with its parent ^{230}Th in the solid

phase.

3) In deeper ground waters, the chemical disequilibrating processes are less potent but recoil related disequilibration is relatively more important. To the extent that uranium leaching might occur, the direction of disequilibration would be the same as in the weathering environment.

4) The mining operation produces extreme and abrupt disruptions of the natural order, and disequilibration at several levels can be effected. This includes the mobilization of radium, which can occur under conditions present in surface waters, and perhaps also of lead and polonium, daughters with even shorter lifetimes.

1.4 Area of Study

1.4.1 Geomorphology

The area of study is located within the Polk Upland and the DeSoto Plain, with a small portion in the Gulf Coastal Lowland. This is roughly coincident with the land-pebble phosphate district and corresponds to Polk and Hardee Counties as well as the eastern portions of Hillsborough and Manatee Counties (Fig. 1-7). Both plain and upland are marine terraces, the upland being broad and slightly dissected while the plain slopes gently to the south and is undissected.

1.4.2 Geology

Wells in the area which are developed in consolidated rocks produce water from limestones or dolomitized limestone of Eocene through Miocene age (Fig 1-8). At most locations in the area these rocks are covered by an unconsolidated sand-clay-phosphate unit which in turn is covered by surface sands.

The Avon Park Limestone, of Eocene age, is the lowest formation in the section in which wells are developed. The Avon Park primarily consists of fossiliferous limestones of varying character, typically containing a dolomitized zone. Color, hardness, and texture are quite variable. Permeability varies locally but in the unit as a whole it is high. It is highly transmissive and is a main producing unit of the Floridian Aquifer (Stringfield, 1966).

The Eocene Ocala Group, containing the Inglis, Williston, and Crystal River formations, overlies the Avon Park Limestone. The Inglis Formation consists of partially to highly dolomitized, fossiliferous limestones of variable composition. In some areas sand-filled cavities occur. The Williston Formation is typically a foraminiferal coquina with a chalky calcite matrix. Permeability is poor due to the nature of the matrix. Neither the Inglis nor the Williston Formation is a highly transmissive unit although some water can be produced from them. The Crystal River Formation, more transmissive than the other units of the Ocala Group, is not as transmissive as the Avon Park or Suwannee Limestones. A limestone, the Crystal River Formation is characterized by the presence of large foraminifers, Lepidocyclina, in a chalky carbonate matrix. Locally some dolomitized units are known to occur.

The Suwannee Limestone, of Oligocene age, unconformably overlies the Ocala Group. It occurs as a detrital limestone locally containing quartz sands, fossils (including bryozoa and echinoids) and cherts. It has a transmissivity between that of the Avon Park and the Crystal River Formations.

There are two formations within the Miocene Series, the Tampa Formation and the Hawthorn Formation. Although some workers group these units together for mapping purposes, others recognize them as being distinct units. In this study they are considered separately.

The Tampa Formation is exposed in pits in the northern part of the land pebble district, where the Hawthorn Formation is thin. Throughout most of the phosphate district the Tampa Formation is represented as having two units: a lower sandy-clay unit and an upper limestone unit. These units may grade together locally near appearances of limestones of the Hawthorn Formation.

The Hawthorn Formation forms the bedrock for the phosphate deposits. It has a variable lithology but generally there is a lower unit, dominantly limestone, underlying an upper clastic, non-calcareous unit (Bergendal, 1956). The Hawthorn is predominantly a sandy, phosphatic dolomite containing units of variable lateral extent consisting of sands, clays, limestones, and dolomites. The lower Hawthorn Formation limestones at some places are covered with a thin residual clay (locally known as bedclay) which may be included with the overlying Bone Valley Formation. The upper Hawthorn is absent in the northern part of the phosphate district.

The Bone Valley Formation is described as late Miocene in age (Bergendal, 1956). It contains two members: a lower phosphate member and an upper sand member. The lower unit has a variable composition whereas the upper unit is more uniform throughout the area.

Terrace sands of Pleistocene age blanket the Bone Valley except where cut by major rivers. These sands are undifferentiated by most workers.

1.4.3 Hydrology

In the area of study there are three, and in some areas four, recognized aquifers (Fig. 1-8).

Shallowest is the non-artesian or surficial aquifer. This aquifer includes the unconsolidated sands and clays at and just below the surface. It is underlain by impermeable clays of the Bone Valley Formation. Well depths are commonly in the range of 3 to 15 meters. Production from these wells rarely exceeds 100 gallons per minute (gpm). Waters from the surficial aquifer are typically acidic (pH = 4.0 - 6.5) and have low conductivity (100 microsiemen). The aquifer is generally oxidized but may be reduced locally due to the presence of organic materials or activity of iron-reducing bacteria.

The aquifer thickness varies from 0 to 80 meters, thickening near geomorphic ridges. The hydrologic properties vary laterally and seem to be a function of sand and clay content. The aquifer is recharged locally by rainfall and discharged by gravity flow to lakes and streams, recharge wells, percolation to underlying aquifers, pumping and evapotranspiration.

The uppermost artesian aquifer is located only in Polk County (Stewart, 1966). It is confined above by clays of the Bone Valley Formation and below by clays of either the Bone Valley or Hawthorn Formations. The aquifer thickens and the grain size becomes greater in the southern portion of the land pebble district; the upper confining beds become more porous and permeable towards the south so that they cease to be confining. Waters of the uppermost artesian aquifer tend to be similar in chemistry to those of the surficial aquifer.

The secondary artesian aquifer, located in the carbonate members of the Hawthorn Formation, is confined above by upper Hawthorn (or lower Bone Valley) Formation clays and below by clays of the Tampa Formation. This aquifer generally has a lower potentiometric head than the Floridian Aquifer, which it overlies. It occurs in the southern Polk, Manatee, Hardee, and portions of eastern Hillsborough Counties. The secondary artesian aquifer may hydrologically connect with the Floridian Aquifer where the underlying clays of the Tampa Formation are breached by faults, joints, sinks, or areas of low clay content. Wilson (1977) referred to this aquifer as the "upper unit of the Floridian Aquifer", connected with the lower (principal artesian) aquifer through a leaky aquiclude system. The aquifer is referred to as the secondary artesian in this investigation to conform with U.S. Geological Survey nomenclature. The pH of the secondary artesian aquifer is more alkaline than that of the surficial aquifer. Values tend to range from 6-7. The waters are generally more mineralized due to the carbonates present. In addition H_2S is present in the aquifer waters producing some reducing conditions.

The Floridan Aquifer exists within a series of Eocene to Miocene limestones. It was originally referred to as the Principal Artesian Aquifer. The term Floridian includes, "the Lake City Limestone, Avon Park Limestone, Ocala Group, Suwannee Limestone, Tampa Formation and perhaps the Hawthorn Formation where hydrologically connected" (Stringfield, 1966).

An area of recharge to the aquifer is located to the north of the study area (Fig. 1-7). Other sources of recharge include; sinkholes, fissure opening, recharge wells and some leaking from the secondary artesian where its potential is greater then that of the underlying Floridian Aquifer.

In some areas, the Floridian Aquifer behaves as a single unit. In others, low permeability zones may restrict vertical water movements. The Floridian Aquifer is the most transmissive aquifer in the area and the most extensively developed. In Manatee, Hardee, and Polk Counties it behaves as two units separated by a leaky aquitard, either lower Hawthorn or upper Tampa Formation clays (Stewart, 1966). In Hillsborough County the upper unit is not recognized because the Tampa Formation does not act as a confining unit there.

Waters of the Floridian Aquifer flow toward the southwest, trending with the dip of the units. These waters become more reducing and conductive toward the southwest as the ground water undergoes hydrochemical evolution in a Chebotarev sequence. Generally pH tends to be more alkaline than in any other water units (7.0-8.5). Conductivity is also high, a function of the total dissolved solids reaching levels of 1000 mg/l or more.

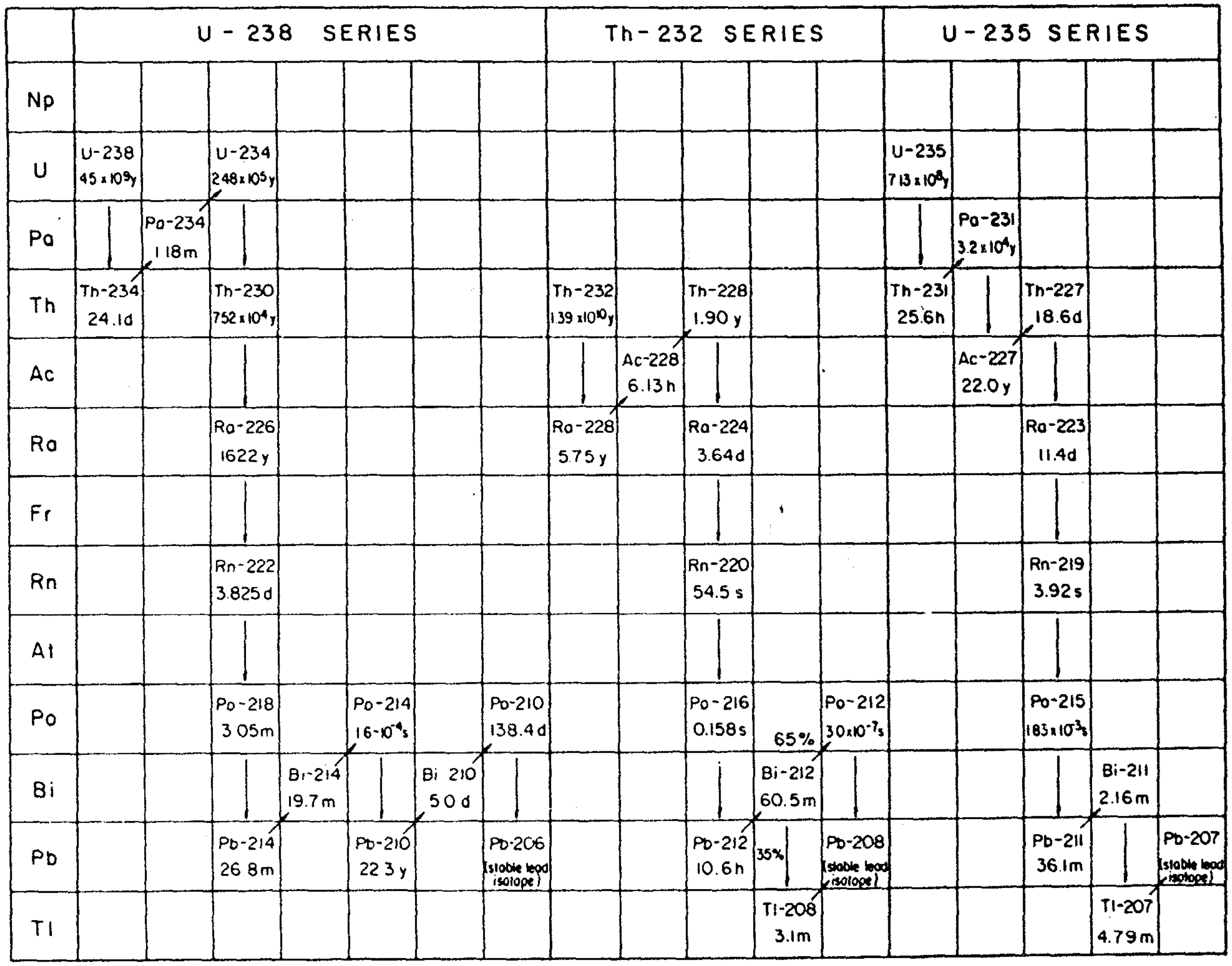

Fig. 1-1 The three naturally occurring radioactivity series

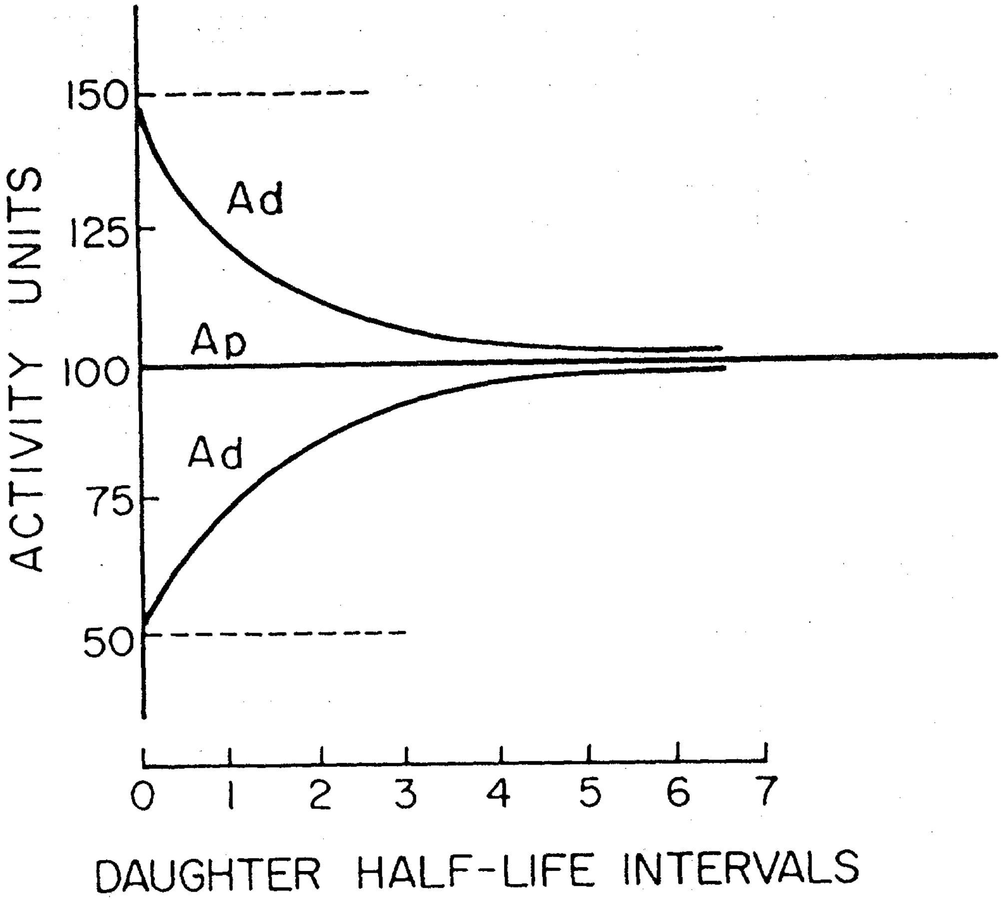

Fig. 1-2 Re-equilibration of daughter activity (Ad) after being initially out of equilibrium with its longer-lived parent (Ap)

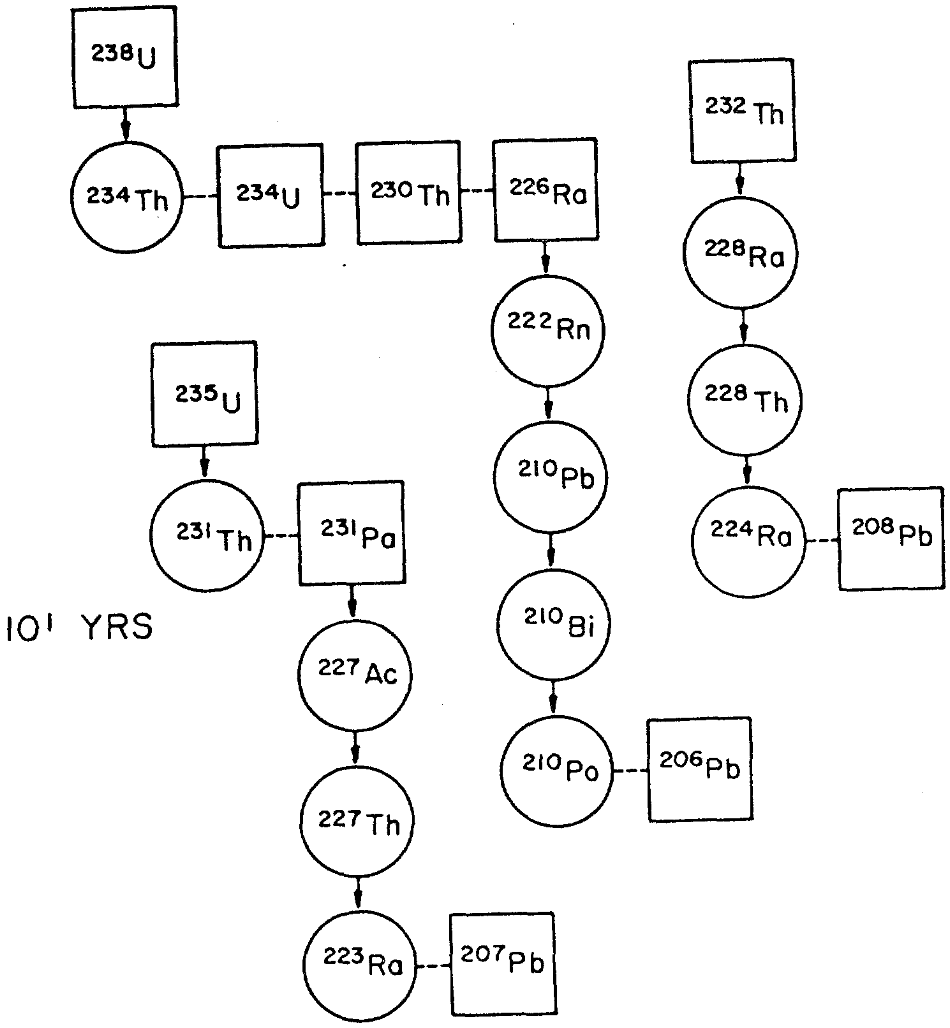

Fig. 1-3 "Geochemically practical" version of the decay series for time periods of days to years. Circled nuclides are variable and boxed nuclides are stable in this time frame. Arrows: alpha decay; dashes: beta decay.

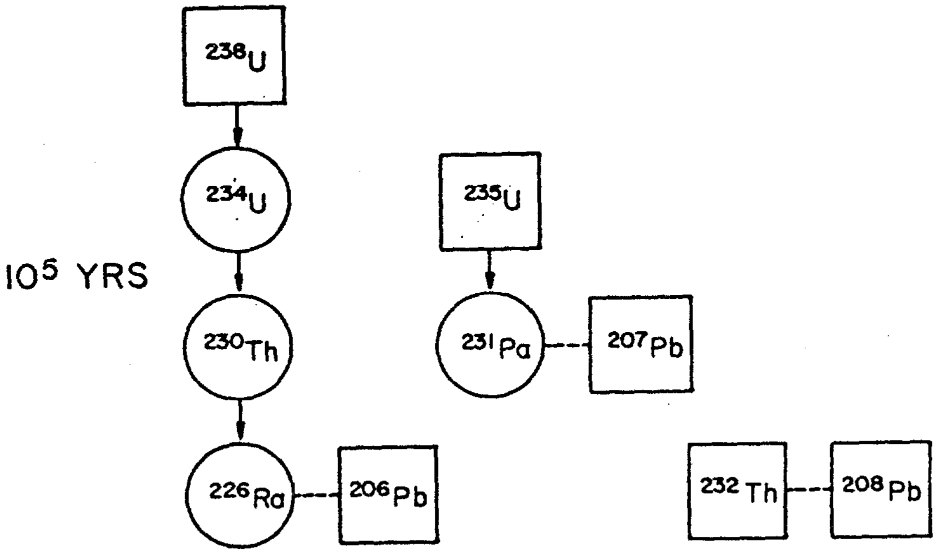

Fig. 1-4 "Age dating" version of the decay series. Circled nuclides have half lives in the range 10^3 to 10^5 years.

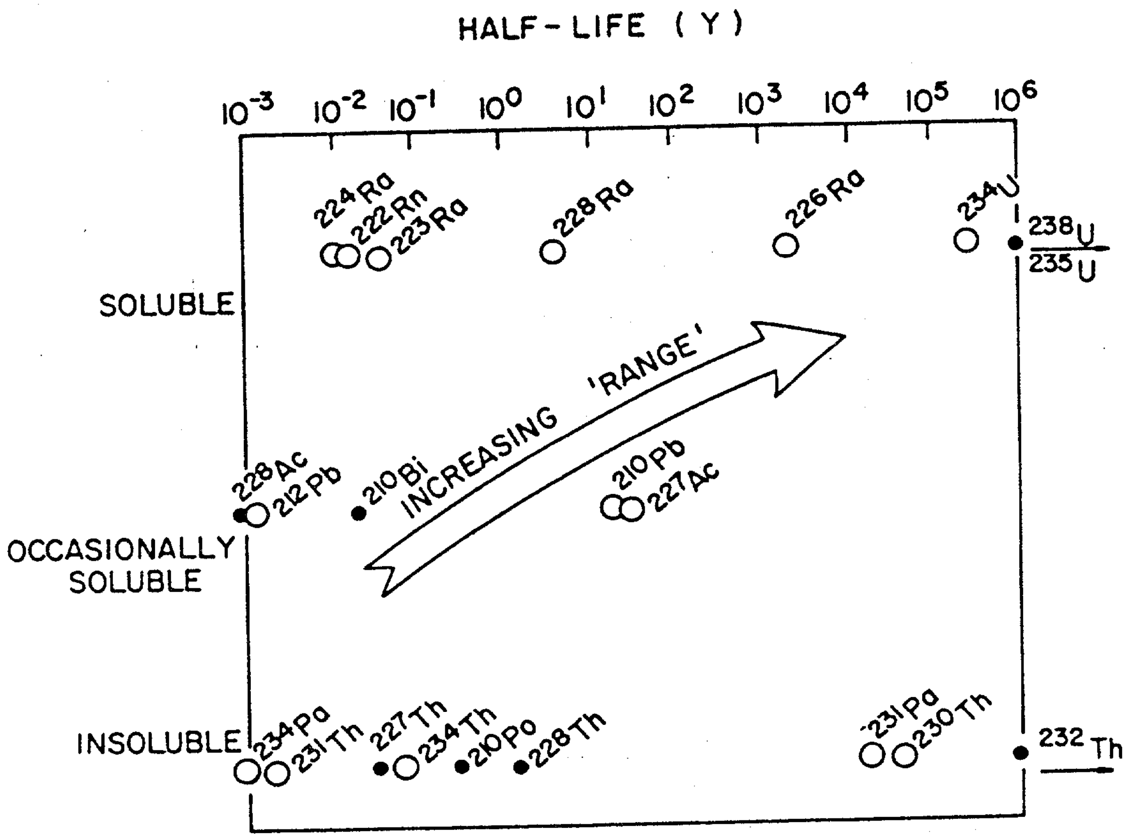

Fig. 1-5 Range concept for natural radionuclides. Increasing range depends on chemical mobility, half-life, and decay mode.

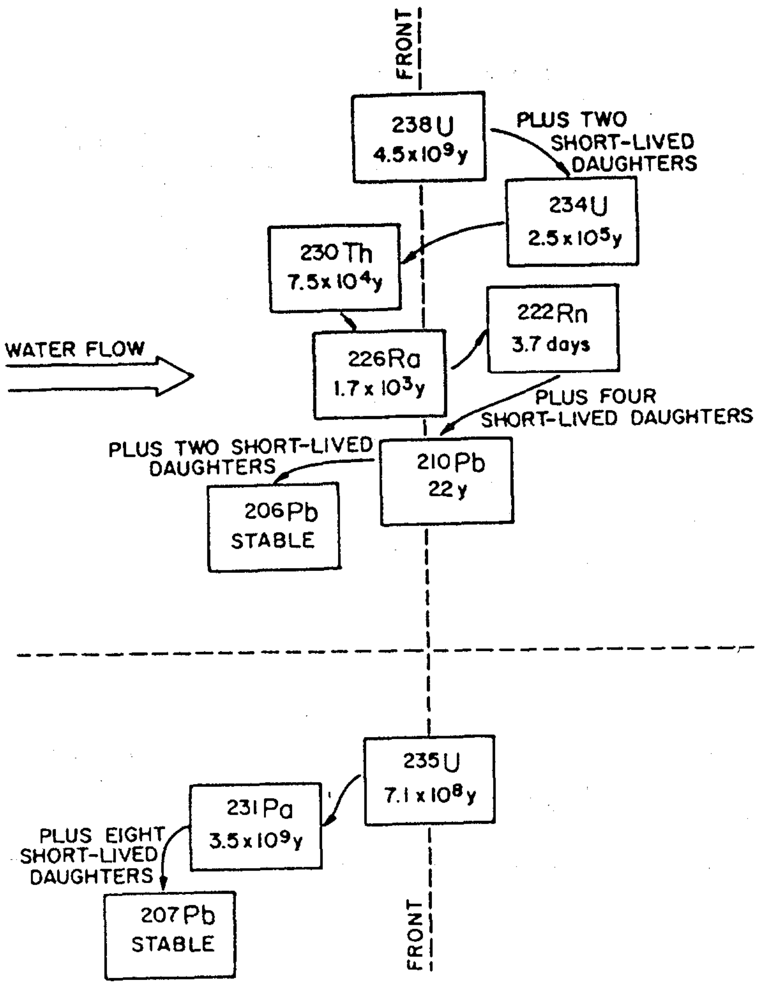

Fig. 1-6 Natural disequilibrium in rocks near an oxidizing/reducing ground water boundary (front). U-234 moves ahead while Th-230 lags behind with respect to water movement.

Fig. 1-7 Phosphate region of Peninsular Florida.

GEOLOGY and HYDROLOGY of WEST CENTRAL FLORIDA

AGE	FORMATION	AQUIFER		ASSOCIATION with PHOSPHATE	MINING TERMINOLOGY
Pleistocene	terrace deposits		surficial	none	overburden
Pliocene	Bone Valley Formation	upper	surficial	usually depleted in phosphate due to weathering	overburden
		lower	uppermost artesian (Polk Co.)	phosphate pebble cgl.; enrichment due to reworking of Hawthorn Fm.	matrix
Early and Middle Miocene	Hawthorn Formation	upper	confining unit	source of Bone Valley phosphate; may contain minable ore	possible matrix
		lower	secondary artesian	parent material for reworked Bone Valley Fm.	bedrock
Early Miocene	Tampa Formation		secondary artesian		
Late Oligocene	Suwannee Limestone		Floridan		
Late Eocene	Ocala Limestone		Floridan		
Middle Eocene	Avon Park Limestone		Floridan		

from: Cathcart (1966) and Kaufman and Bliss (1977)

Fig. 1-8 Relationship of aquifers to stratigraphy in Central Florida.

2. METHODS

2.1 General

Analytical methods for geochemical studies of the uranium series elements are characterized by simplicity and accuracy. The diagnostic elements in the series are separated from other constituents, and from each other, with relative ease. Also relatively simple is the measurement by alpha ray methods, including isotope dilution.

More detailed descriptions of the field and analytical procedures used in this investigation can be found in Wagner (in preparation) and Humphreys (1984).

General discussions of analytical techniques for uranium and thorium are also available in Gascoyne (1982) and Lally (1982).

2.2 Field Collection

Groundwater samples were collected from domestic, industrial and municipal wells in mineralized regions from both mined and unmined terrains as well as unmineralized regions. Phosphate recharge and production wells were also sampled in mined terrains.

Surface waters were sampled by hand bailing from the center of stream channels.

Sample sizes of 17.5 liters and one liter were collected for uranium and radium analyses, respectively. Field measurements of Eh, pH, and specific conductivity were made at the site. Wells were pumped for a period of time before sampling, depending on the size of the holding tank and the depth and diameter of the well, to assure representative measurements.

If samples appeared turbid they were filtered using Whatman #1 Qualitative filter paper. At the time of collection, or after filtration if needed, each sample was acidified and spiked with a known amount of ^{232}U, an artificial isotope of uranium used as an internal tracer.

Solid samples, including natural materials and mine products, were collected from mining sites and phosphate chemical plants. A number of cores from the Florida Bureau of Geology were also sampled and analyzed.

2.3 Laboratory Procedure for Water Samples

2.3.1 Uranium Analyses in Water

Recovery of uranium from natural waters requires that three basic steps be followed.

Pre-concentration: this may be accomplished in the laboratory or the field and is necessary due to the extremely low concentrations of uranium in natural waters.

After spiking, samples were allowed to equilibrate for 48 hours. The samples were placed in a water bath and boiled for 8-10 minutes to remove dissolved gases such as CO_2. In a basic solution any CO_2 would be present as CO_3^{-2} and might react with uranium to form a uranyl-carbonate complex.

Each sample was removed from the bath and transferred to a magnetic stirrer to ensure complete mixing as concentrated NH_4OH was slowly added, until $Fe(OH)_3$ flocculated. After decanting, the precipitate was then dissolved in 8N HCl. Concentrated HNO_3 was added to break down any organics and the sample was evaporated to dryness.

Separation: This step involves solvent extraction and ion exchange to separate uranium from chemical species or radionuclides that may interfere with analysis.

Samples were redissolved in 40 ml of 8N HCl, heated to boiling and added to a separatory funnel containing 50 ml of isopropyl ether. The funnel was shaken and vented until the buildup of pressure ceased. The acid and uranium portion was drained off and the extraction repeated. The acid phase was then evaporated to dryness in preparation for the ion exchange procedure.

Ion exchange columns were filled with Dowex AG 1-X8, anion exchange resin, 100-200 mesh, chloride form, which had been immersed in 0.1N HCl. The columns were then loaded with 8N HCl and the sample. The uranium-bearing elutant was evaporated to dryness and any remaining iron was removed by a second ion exchange using 8N HNO_3.

Electrodeposition: Uranium is reduced to a thin source by electroplating onto a stainless steel planchet. The sample was dissolved in 10 ml 2M NH_4Cl solution and poured into an electroplating cell. The cell consisted of a glass chimney fastened to a 2.5 cm diameter stainless steel planchet by rubber cement and an elastic band.

The uranium in solution was electro-deposited on the planchet for 30 minutes at 12 volts and 1 ampere. At the end of this time, a few drops of concentrated NH_4OH were added to the cell to inhibit the reaction. The solution was discarded and the planchet rinsed with distilled water. The planchet was flamed to drive off any remaining NH_4Cl and to harden the uranium deposit.

The uranium isotopes are identified and counted using a 2.5 cm^2 silicon barrier detector in a 10^{-5} torr vacuum chamber connected to a 100 channel pulse height analyzer. Count rates are typically on the order of a count per minute in the peaks of interest so that counting times are a day or so (solid samples may require less) (Figs. 2-1, 2-2). As many as four samples may be counting simultaneously.

2.3.2 Radium Procedures for Water Samples

The ^{226}Ra in water samples was concentrated by co-precipitation with $BaSO_4$. Two ml of $BaSO_4$ (16 mg/ml) solution were added along with 25 ml of concentrated HCl to a one liter sample which was stirred and heated to boiling. At this time, 20 ml of 18N H_2SO_4 were added to the sample to form a precipitate. The sample was allowed to stir for 5-10 minutes longer to aid in the formation of the precipitate.

The precipitate was allowed to settle overnight and the supernatant discarded. The precipitate was centrifuged and washed in 0.1N H_2SO_4. Twenty-five ml of a 0.25 M basic EDTA solution and several drops of 6M NaOH were added to the precipitate. The sample was then placed in a water bath on a magnetic stirrer/hot plate and heated and stirred until dissolution of the precipitate occurred.

The concentrated sample was loaded into a bubbler apparatus and de-gassed with helium to remove any residual ^{222}Rn. The sample was allowed to remain in the bubbler for at least 96 hours for sufficient ingrowth of ^{222}Rn to occur (Fig 2-3).

After ^{222}Rn had grown to partial equilibrium with its parent ^{226}Ra it was purged from the sample using the radon-emanation technique. This method involved de-emanating the sample with helium which transported the radon to a cold trap filled with brass filings. The filings were then heated, releasing the radon gas which was further transported by helium to an evacuated scintillation cell.

The scintillation cell was stored for 4 hours to ensure equilibrium between ^{222}Rn and its daughters ^{218}Po and ^{214}Po (Fig 2-3). The alpha scintillations were counted using a photomultiplier tube.

The radon system was calibrated frequently using a ^{226}Ra standard acquired from the National Bureau of Standards. An over-all efficiency is measured which encompasses the efficiency of the collection system itself in addition to the counting efficiency of the scintillation cell.

2.4 Laboratory Procedure for Solid Samples

Uranium

All solids were powdered, dried, weighed and dissolved in concentrated HCl, HNO_3 and $HClO_4$. The insoluble residue was filtered using a 0.45 micron millipore filter and leached with 8N HCl.

A hydroxide precipitate was formed by adding concentrated NH_4OH and adjusting the pH to 7. The supernatant was discarded and the precipitate centrifuged and washed using distilled water. The precipitate was then prepared for ion exchange by dissolving in 8N HCl.

Uranium is separated from thorium using AG1-X8, 100-200 mesh, chloride form, anion exchange resin. The uranium bearing elutant is evaporated to dryness, picked up in 8N HCl and extracted with ether until no color is remaining in the acid fraction. The sample is evaporated to dryness, picked up in saturated $Al(NO_3)_3$ in 4 N HNO_3, extracted in ethyl acetate and back extracted into distilled water.

The sample was evaporated to dryness, extracted in ether twice and evaporated again. The dried sample was picked up in 2M NH_4Cl and electroplated.

Thorium

Thorium accompanies uranium through the preconcentration and solvent extraction steps of the radiochemical procedure (Section 2.3.1 above). During the ion exchange step thorium passes through the resin bed in 8N HCl solution whereas the uraniun attaches to the resin. Thorium is further purified by a subsequent ion exchange separation using 7N HNO_3. The electrodeposition of thorium onto stainless steel planchets was effected in the same manner as was uranium.

Radium

After powdering, drying, weighing and dissolving the solid sample, each was filtered to remove insolubles. The sample was evaporated to dryness, picked up in 20 ml 0.1 N HCl and loaded into a bubbler for ingrowth of ^{222}Rn. At this point the procedure was the same as followed for water samples.

2.5 Data Reduction

Uncertainty in the reporting of disequilibrium data has two sources: statistical and analytical.

Statistical uncertainty is always a factor in reducing radiometric data. It depends on the number of decay events counted, which depends on the duration of the counting period and the count rate. The later, in turn, depends on the concentration of the radionuclide in the sample, the sample size, analytical yield, and counting efficiency.

For a single isotopic count rate measurement:

$$dA = 100 \sqrt{N}/N$$

where dA is the percent uncertainty of the count rate, and N is the total number of counts registered.

In the case of uranium and thorium ratio data, the uncertainty of the ratio depends on combining two counting uncertainties. This is calculated by:

$$dR = ((dA)^2 + (dB)^2)^{1/2}$$

where dA and dB are the uncertainties of the two isotopic count rates, and dR is the calculated uncertainty of their ratio. Because isotope dilution procedures are used, extraction and counting efficiencies are cancelled.

A similar argument applies to concentration values as well as to ratios, in the case of uranium and thorium. This is because isotope dilution analyses depend on a simple ratio of natural versus spike isotope count rates (Figs 2-1, 2-2).

These statistical calculations are all made using net count rate, i.e., with background counts subtracted. If the sample count rate is not appreciably greater than the background count rate, then the background uncertainty must also be taken into account. For most phosphorites and associated waters sampled for this study, this was not a problem.

In the case of radium analysis, isotope dilution was not used because there are no convenient tracer isotopes. Instead, the extraction and counting efficiencies for ^{226}Ra (actually the daughter, ^{222}Rn) must be determined by replicate analyses of standards. We attempted to achieve a consistent uncertainty level by (a) checking standards at frequent intervals, and (b) varying counting times so as to achieve a fixed count total.

In the data tables, uncertainty ranges are reported for uranium and thorium based on counting statistics only, with systematic errors assumed to have been compensated for by the isotope dilution procedures. An average uncertainty value for most uranium and thorium analyses was about 5 per cent. A few samples of lower concentration had uncertainties somewhat higher. Radium-226 data are generally reported without uncertainty values. One can assume for these data an uncertainty of 5-10% based on the considerations described in the previous paragraph.

The uncertainty of the radium/uranium ratio is governed primarily by the fixed radium uncertainty; consequently, a standard ratio uncertainty value of about 10-15% can be assumed.

In the study of disequilibria in the phosphate strata and associated waters, the variations in concentration and isotope ratios among suites of samples are significantly greater than the calculated uncertainty of any individual sample. This means that inferences regarding the processes of disequilibration and geochemical balances are generally not limited by analytical uncertainties.

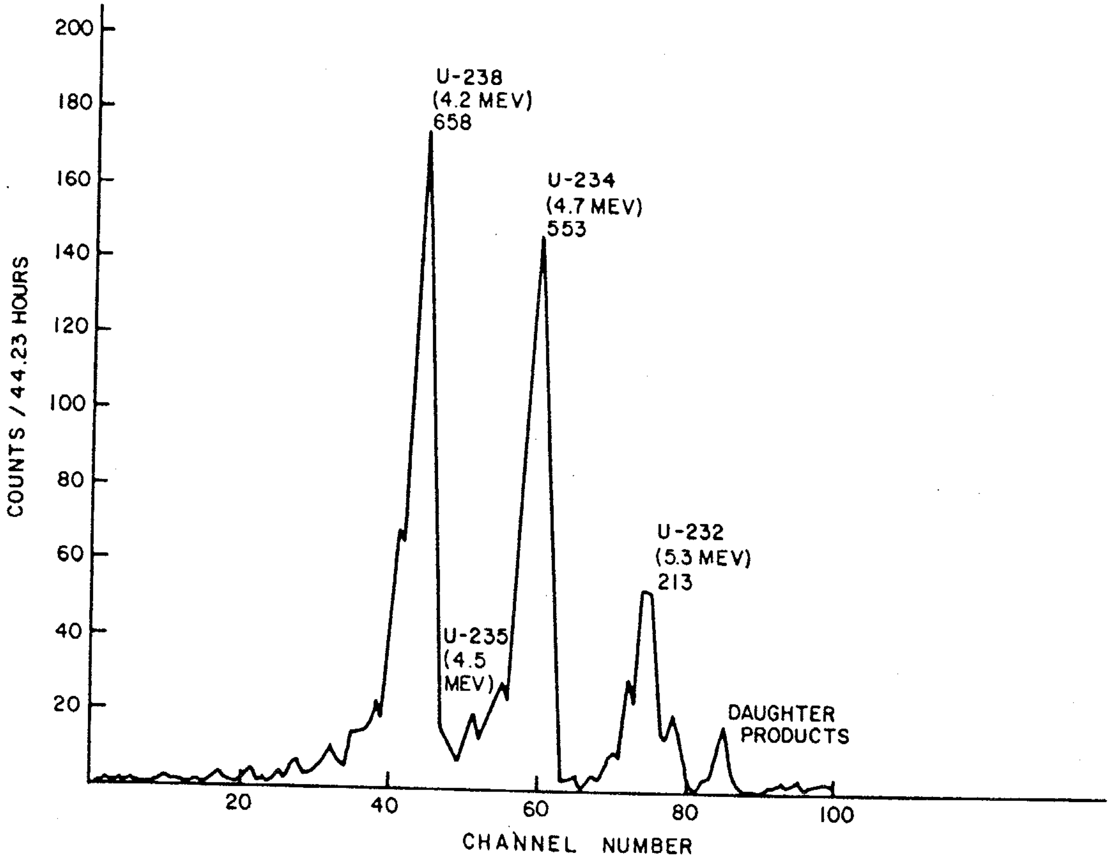

Fig. 2-1 Typical uranium alpha spectrum of ground water samples
U-234/U238 activity ratio can be determined by inspection.
U-232 is the yield tracer.

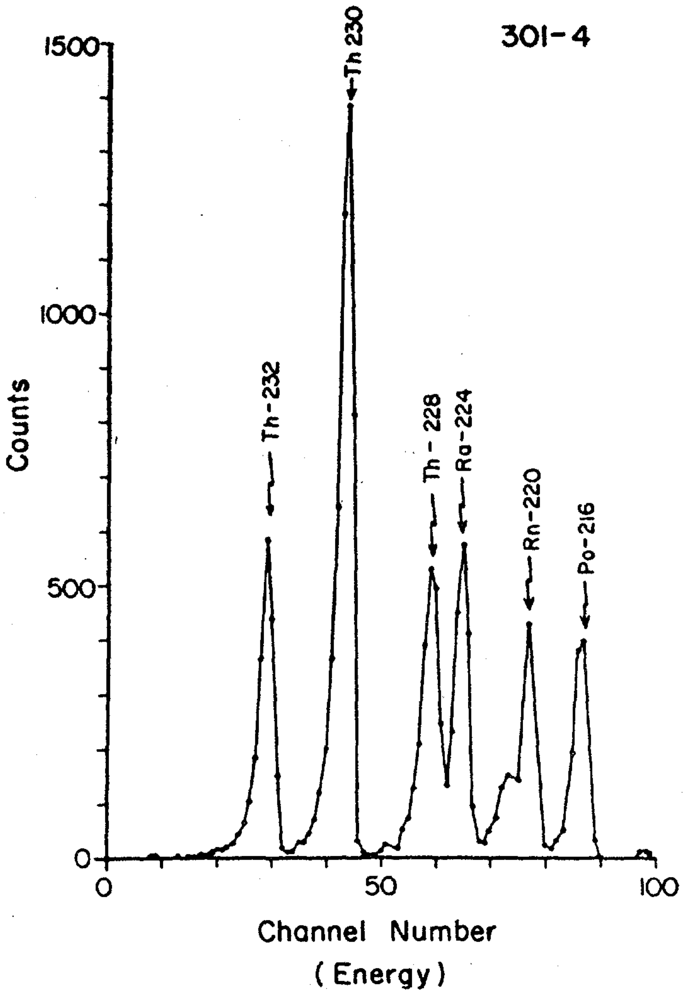

Fig. 2-2 Typical thorium spectrum of uranium bearing rocks. Th-228 and its daughters may be derived from either natural Th-232 of from the yield tracer.

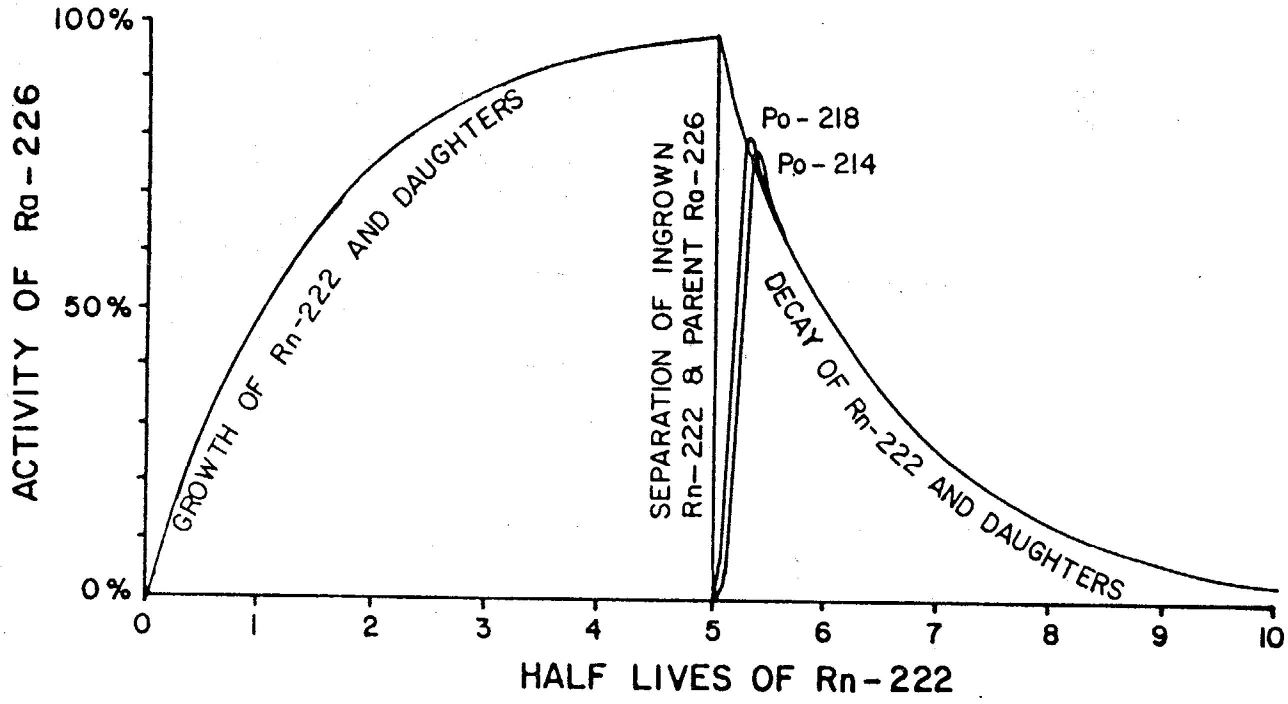

Fig. 2-3 Systematics of determination of Ra-226 by radon counting. Sample is stored while radon and daughters come to equilibrium; after separation, they must be counted before they decay.

3. RESULTS

In the course of this investigation we collected 114 rock samples, 150 water samples, and 29 mine product and effluent samples. Figures 1-7 and 3-1 show the region where these samples were taken. In the laboratory most samples were analyzed for more than one element; 335 separate analyses were made for ^{238}U and ^{234}U, along with 110 analyses for ^{230}Th and 152 for ^{226}Ra.

Prior to the time of this investigation, nearly fifty ground water samples from the Floridian Aquifer of the central Florida phosphate district had been analyzed for uranium concentration and uranium isotope ratios. These data, generated by the F.S.U. uranium/thorium geochemistry group, are presented in Table 3-1. Though not obtained with the objectives of the present study in mind, such data do help present a regional background basis with respect to uranium occurrences. Several of the samples cited in Table 3-1 would be classified, in terms of this study, as from 'mined' areas.

About 20 groundwater samples were taken from the phosphate mining district (Figures 3-2 through 3-6); of these, many were labeled 'proximate' to operations (Table 3-2) (Figures 3-7 through 3-15).

More than 100 ground water samples from the mining district were analyzed for both uranium and radium isotopes. In table 3-2 and Figures 3-7 through 3-15 the proximity to mining operations is indicated. Fourteen surface water samples were also analyzed for uranium and radium isotopes (Table 3-3).

The correlative water quality data for most of these groundwater and surface samples is shown in Table 3-4.

Over 100 rock samples were obtained from five cores collected by the Department of Natural Resources (Tables 3-5 through 3-9). In Figures 3-16 through 3-25 the stratigraphic position and the uranium/thorium isotopic character of these samples is shown. Eleven other rock samples were taken from two cores in Sarasota County and a stratigraphic section in Polk County; these were analyzed for both uranium and radium isotopes (Tables 3-10 and 3-11).

Seven miscellaneous solid samples from near the W.R. Grace property at Hooker's Prairie were analyzed for uranium and thorium, as listed in table 3-12. Another 14 samples of various mine products were analyzed for radium and uranium, and also listed in Table 3-12, while the radium and uranium isotopic data in eight mine water samples are presented in Table 3-13.

Table 3-1 Uranium Isotopes in Floridan Aquifer Water (Previous Data)

Sample No.	Location	Depth (A)	Activity Ratio	Concentration	Reference (B)
440	City of Lakeland (#10)	CSG 323' TD 1216'	2.38 ± .37	.009 ± .001	2
441	Kaiser (Mulberry)	(2775'- 2788')	2.05 ± .15	.040 ± .003	2
442	Kaiser (Mulberry)	(1254'- 1264')	3.22 ± .35	.036 ± .004	2
443	City of Lake Wales		1.23 ± .18	.040 ± .004	3
444	City of Avon Park	TD 1200'	1.31 ± .16	.045 ± .004	3
446	Sarasota Alameda Way	CSG 300' TD 570'	1.76 ± .21	.116 ± .012	2
501	Pinellas Co. Well Field	TD 330'	1.24 ± .21	.041 ± .005	2
701	Tropical River Groves	CSG 164' TD 1361'	2.14 ± .32	.031 ± .004	2
702	Tropical River Groves	CSG 150' TD 300'	.89 ± .05	.326 ± .018	2
703	Arcadia	CSG 900' TD 1410'	1.61 ± .29	.037 ± .006	2
711	Riverview	CSG 210' TD 750'	2.75 ± .50	.008 ± .001	2
712	Sun City	CSG 240' TD 700'	1.57 ± .35	.011 ± .002	2
715	Gibsonton (Claude Tanner)	CSG 32' TD 250'	.88 ± .04	.688 ± .04	2

Table 3-1 (Cont.) Uranium Isotopes in Floridan Aquifer Water (Previous Data)

Sample No.	Location	Depth (A)	Activity Ratio	Concentration	Reference (B)
719	Gen. Dev. Corp. DeSoto Co.	CSG 1326' TD 1411'	2.01 ± .24	.022 ± .002	2
720	Oscar Scherer St. Pk.		1.54 ± .18	.130 ± .015	2
721	Sarasota-Verna Field #38	CSG 173' TD 602'	1.09 ± .13	.023 ± .002	3
909	Sulphur Spgs Spa		.88 ± .04	1.91 ± .12	3
910	Sulphur Spgs (Mineral Spg)		.88 ± .04	.781 ± .040	3
2517	City of Lakeland (#1)		1.09 ± .41	.036 ± .010	3
2518	City of Lakeland (#3)		1.24 ± .18	.429 ± .062	3
2992	Blue Sink - Pinellas Co.		0.77 ± .05	2.44 ± .23	3
956	Crystal Spgs - Pasco Co.		0.72 ± .05	0.50 ± .03	3
489	Warm Mineral Spg., Sarasota Co.		1.49 ± .05	0.12 ± .01	2
912	Lithia Spg., Hillsborugh Co.		0.67 ± .04	0.71 ± .04	3
1259	Health Spg., Pinellas Co.		0.75 ± .03	1.73 ± .11	3
152	Winter Haven #2	CSG 138' TD 816'	1.58 ± 1.34	.013 ± .009	1
122	Brewster (Amer. Cyn.)	CSG 337' TD 950'	3.33 ± 1.15	.019 ± .006	1
442	Mulberry	CSG 330' TD 833'	1.34 ± .46	.014 ± .004	1
132	Wauchula	CSG 404' TD 1103'	4.07 ± 1.30	.016 ± .005	1

Table 3-1 (Cont.) Uranium Isotopes in Floridan Aquifer Water (Previous Data)

Sample No.	Location	Depth (A)	Activity Ratio	Concentration	Reference (B)
2993	Private well, Clearwater	TD 15'	1.05 ± .15	.175 ± .021	3
4811	Hot Spa - Charlotte Co.	CSG 648' TD 1900'	.94	.024	2
4821	Herren State Nursery Charlotte Co.	CSG 648' TD 1454'	1.19	.038	2
7061	"Old Faithful" Charlotte Co.	CSG 124' TD 1454'	3.68	.010	2
8871	Anderson Groves, DeSoto Co.	TD 1540'	3.15	.038	2
8891	Burtscher Ranch, DeSoto Co.	CSG 100' TD 1325'	2.73	.077	2
8901	Avant - DeSoto Co.	CSG 1100' TD 1447'	1.82	.039	2
4901	Sarasota USGS	1118'-1232'	1.40	.388	2
6941	Sarasota USGS	2008'-3513'	2.39	.065	2
6541	McKay Creek Monitor - Pinellas Co.	820'-840'	2.06	.043	2
6551	McKay Creek Monitor - Pinellas Co.	990'-1010'	2.15	.056	2
4921	McKay Creek Monitor - Pinellas Co.	1250'-1730'	1.99	.043	2

Table 3-1 (Cont.) Uranium Isotopes in Floridan Aquifer Water (Previous Data)

Sample No.	Location	Depth (A)	Activity Ratio	Concentration	Reference (B)
5411	South Cross Bayou - Pinellas Co.	960'-1080'	3.58	.035	2
5101	South Cross Bayou - Pinellas Co.	1850'-3260'	2.59	.017	2

(A) TD= total depth of well CSG= depth of casing

(B) References:
1. Osmond, Kaufman and Cowart, 1974
2. Osmond and Cowart, 1976
3. Unpublished, FSU Laboratory

Table 3-2 **Uranium and Radium Data for Groundwater Samples**

Sample Number	Uranium ppb	Conc. pCi/l	Ra-226 pCi/l	U-234 / U-238	Ra-226 / U-238	Aquifer[1]	Proximity[2] to Mining	Location
3008	.178 ± .016	.060	.254	1.04 ± .11	4.27	S	U	Hardee Co.
3011	.036 ± .01	.012	.299	1.45 ± .48	24.8	S	U	Manatee Co.
3013	.053 ± .008	.018	9.67	2.74 ± .47	545.88	S	U	Hardee Co.
3018	.008 ± .003	.003	.658	1.70 ± .90	246.08	SA	U	Hardee Co.
3037	.014 ± .002	.0057	3.46	4.90 ± .94	739.43			
3042	.008 ± .004	.0037	.380	.727± .647	142.12			
3045	.670 ± .111	.224	1.80	2.94 ± .34	8.04	SA	M	Polk Co.
3047	.129 ± .019	.043	5.25	1.85 ± .30	121.76	F	M	Polk Co.
3050	1.13 ± .007	.378	1.40	1.51 ± .07	3.71	F	M	Polk Co.
3080	1.43 ± .14	.478	8.80	.747± .005	18.41	S	M	Polk Co.
3141	.327 ± .041	.109		1.18 ± .15		SA	M	Polk Co.
3143	1.08 ± .014	.361	.338	1.33 ± .01	.936	S	M	Polk Co.
3144	2.36 ± .21	.789	7.95	1.99 ± .09	10.08	S	M	Polk Co.
3146	.146 ± .014	.048	.425	1.04 ± .12	8.892	F	M	Polk Co.
3147	2.55 ± .34	.852	4.14	.947± .074	4.857	F	M	Polk Co.

Table 3-2 (Cont.) Uranium and Radium Data for Groundwater Samples

Sample Number	Uranium ppb	Conc. pCi/l	Ra-226 pCi/l	U-234/U-238	Ra-226/U-238	Aquifer[1]	Proximity[2] to Mining	Location
3148	.058 ± .027	.019	.321	2.65 ± 1.36	16.56	F	M	Polk Co.
3150	.0126± .005	.004	3.49	5.50 ± 2.50	878.7	F	M	Polk Co.
3151	.017 ± .023	.057		1.21 ± .02		SA	U	Polk Co.
3155	.042 ± .072	.134		1.05 ± .072		S	U	Polk Co.
3156	.103 ± .024	.034		1.70 ± .46		F	U	Polk Co.
3158	.612 ± .008	.205		1.00 ± .098		F	U	Polk Co.
3161	.392 ± .127	.131		1.12 ± .37		S	M	Polk Co.
3163	.173 ± .025	.058		3.11 ± .45		SA	M	Polk Co.
3164	.044 ± .015	.015	1.94	1.44 ± .63	131.9	F	U	Polk Co.
3166	.106 ± .02	.035		2.07 ± .45		S	U	Polk Co.
3167	.032 ± .008	.011	2.32	1.33 ± .45	214.9	SA	U	Polk Co.
3168	.043 ± .012	.014	4.54	.615± .271	315.9	SA	U	Polk Co.
3172	.475 ± .067	.159	2.18	1.16 ± .16	13.73	SA	M	Polk Co.
3173	.185 ± .014	.062	4.29	1.40 ± .016	69.38	S	M	Polk Co.
3174	.067 ± .011	.022	.121	1.93 ± .36	5.403	S	M	Polk Co.

Table 3-2 (Cont.) Uranium and Radium Data for Groundwater Samples

Sample Number	Uranium ppb	Conc. pCi/l	Ra-226 pCi/l	U-234 / U-238	Ra-226 / U-238	Aquifer[1]	Proximity[2] to Mining	Location
3175	1.88 ± .014	.627	.169	1.30 ± .009	.2690	S	M	Polk Co.
3179	.009 ± .004	.003		2.56 ± 1.48		F	U	Polk Co.
3180	.020 ± .004	.007	1.76	1.02 ± .31	263.3	SA	U	Polk Co.
3181	.074 ± .002	.025	2.16	1.85 ± .66	87.33	F	M	Polk Co.
3184	.010	.003	3.46	1.30	1035.2	SA	U	Polk Co.
3185	.005 ± .003	.002		7.83 ± 6.65		S	U	Polk Co.
3186	.239 ± .054	.080		1.21 ± .31		F	U	Polk Co.
3231	.009 ± .004	.003	.753	2.57 ± 1.59	250.3	S	U	Polk Co.
3232	.475 ± .150	.159	.175	.907± .298	1.102	S	U	Manatee Co.
3233	.047 ± .022	.016	.952	2.63± 1.39	60.60	S	U	Manatee Co.
3234	.507 ± .065	.170	19.1	2.13± .23	112.7	S	M	Hillsborough Co.
3235	.154 ± .024	.051	4.86	2.85± .46	94.42	S	M	Hillsborough Co.
3237	.305 ± .067	.102	1.44	1.39± .31	14.13	F	M	Hillsborough Co.
3238	-----	----	.362	----	------	S	M	Hillsborough Co.
3240	.007 ± .002	.002	4.11	1.92± .91	1756.7	F/SA	U	Sarasota Co.

Table 3-2 (Cont.) Uranium and Radium Data for Groundwater Samples

Sample Number	Uranium ppb	Conc. pCi/l	Ra-226 pCi/l	U-234 / U-238	Ra-226 / U-238	Aquifer[1]	Proximity[2] to Mining	Location
3339	.032 ± .012	.011	2.48	2.00± .90	231.9	SA	U	Sarasota Co.
3340	.164 ± .021	.054	.243		4.433	SA	U	Sarasota Co.
3342	.008	.003	.460	4.36	172.0	SA	U	Sarasota Co.
3343	.005 ± .004	.002	8.25	4.20± .41	4936.7	SA	U	Sarasota Co.
3344	.10 ± .005	.003	1.49	4.13± 2.33	459.42	SA	U	Sarasota Co.
3347	.072 ± .511	.024		1.11± .22		SA	U	Sarasota Co.
3348	.038 ± .010	.013	17.78	5.84± 1.64	1399.0	SA	U	Sarasota
3349	.009 ± .004	.003		4.64± 2.68		S	U	Sarasota Co.
3350	.015 ± .002	.005	11.59	5.27± .99	2311.8	SA	U	Sarasota Co.
3351	.017 ± .006	.006	13.17	2.37± 1.07	2317.9	SA	U	Sarasota
3352	.213 ± .029	.071	.545	1.93± .27	7.655	SA	M	Polk Co.
3353	.015 ± .006	.005	8.23	3.09± 1.45	1641.6	SA	M	Polk Co.
3355	.007 ± .003	.002	3.50	3.81± 1.64	1495.9	SA	M	Polk Co.
3358	.002 ± .001	.001		----		SA	U	Sarasota Co.
3368	.011 ± .007	.004	7.14	3.56± 2.63	1942.0	F/SA	U	Sarasota Co.

Table 3-2 (Cont.) <u>Uranium and Radium Data for Groundwater Samples</u>

Sample Number	Uranium ppb	Conc. pCi/l	Ra-226 pCi/l	U-234 / U-238	Ra-226 / U-238	Aquifer[1]	Proximity[2] to Mining	Location
3369			7.70			F	U	Sarasota Co.
3370	.005 ± .001	.002		2.24± 1.05		SA	U	Desoto Co.
3371	.003 ± .001	.001	8.46	2.27± 1.61	8437.2	S	U	Manatee Co.
3372	.087 ± .016	.029	4.09	1.20± .27	140.7	F/SA	U	Manatee Co.
3373	.004 ± .003	.001	1.41	1.50± .015	1054.6	SA	U	Manatee Co.
3429	.091 ± .025	.030	.634	1.44± .47	20.84	F	M	Polk Co.
3430	.031 ± .006	.010	.109	1.42± .36	10.52	S	M	Polk Co.
3434	.088 ± .014	.029	1.09	1.17± .25	37.06	S	M	Polk Co.
3435	.551 ± .065	.184	1.15	2.87± .27	6.244	S	M	Hardee Co.
3437	.0019± .007	.001		1.34± .65		SA	M	Hillsborough Co.
3438	.054 ± .015	.018		1.31± .49		F	U	Hillsborough Co.
3439	2.34 ± .274	.782		1.03± .071		S	U	Hillsborough Co.
3440	.027 ± .013	.009	8.52	2.06± 1.19	944.1	SA	U	Manatee Co.
3441	.239 ± .023	.080	1.83	1.53± .16	22.91	S	U	Manatee Co.
3443	.381 ± .052	.127	4.43	2.29± .28	34.79	S	U	Manatee Co.

Table 3-2 (Cont.) <u>Uranium and Radium Data for Groundwater Samples</u>

Sample Number	Uranium ppb	Conc. pCi/l	Ra-226 pCi/l	U-234/U-238	Ra-226/U-238	Aquifer[1]	Proximity[2] to Mining	Location
3445	.460 ± .047	.154	1.84	.90± .09	11.97	S	M	Polk Co.
3446	.049 ± .014	.016	2.05	1.98± .67	125.2	F	M	Polk Co.
3448	.104 ± .033	.035	3.89	.95± .39	111.9	S	M	Polk Co.
3449	.444 ±	.147	2.92	.833±	19.86	S	M	Polk Co.
3450	.016 ± .006	.005		1.96± .94		SA	M	Hillsborough Co.
3451	.546 ± .068	.183	1.31	.96± .11	7.178	S	U	Manatee Co.
3452	.007 ± .003	.002	.354	3.88± 2.13	151.3	S	M	Hardee Co.
3454	.019 ±	.006	1.62	2.20±	255.1	S	M	Hardee Co.
3455	.302 ± .021	.101	.309	1.23± .09	3.06	S	M	Polk Co.

Notes
1. F: Floridan, SA: Secondary Artesian, S: Surficial
2. Proximity to Mining. U: Unmined M: Mined

Table 3-3 Uranium and Radium Data for Surface Water Samples

Sample No.	Uconc ppb	U-234/U-238	Ra-226 pCi/l	Ra-226/U-238	Location
FLW 3192B	.042 ± .008	1.18 ± .29			Peace River
FLW 3196B	.126 ± .008	1.18 ± .09	.350	8.31	Peace River
FLW 3456	.344 ± .028	1.10 ± .09	.236	2.05	Alafia River
FLW 3457	.052 ± .023	1.05 ± .62	.228	7.22	N. Prong Alafia
FLW 3458	.088 ± .006	1.12 ± .09	.306	10.31	S. Prong Alafia
FLW 3459	.173 ± .017	1.09 ± .13	.279	4.83	S. Prong Alafia
FLW 3460	.025 ± .006	1.30 ± .42	.167	19.99	Little Manatee River
FLW 3461	.200 ± .013	1.29 ± .09	.603	9.02	Payne Creek
FLW 3462	.014 ± .009	1.60 ± .47	.576	86.74	Payne Creek
FLW 3463	1.43 ± .11	1.16 ± .06	.416	.870	Little Payne Creek
FLW 3464	.111 ± .022	1.37 ± .32	.105	2.38	Saddle Creek
FLW 3465	.891 ± .125	1.02 ± .12	.465	1.56	Peace River
FLW 3466	.002 ± .0006	1.61 ± .69	.279	4.83	S. Prong Alafia
FLW 3467	.038 ± .005	1.89 ± .30			Little Manatee River

Table 3-4

Water Quality Data

Sample #	Eh millivolts	Ph	Conductivity siemen	Temperature °C	Sample #	Eh millivolts	Ph	Conductivity siemen	Temperature °C
3141	+200	7.0	210	27	3230	-210	7.7	---	23
3143	----	4.7	270	23	3231	-240	7.4	---	25
3144	----	5.2	280	26	3232	-35	7.1	---	24
3145	----	6.9	400	31	3233	-90	6.9	---	130
3147	----	7.1	480	26	3235	-100	4.39	140	--
3148	----	7.4	560	27	3237	----	7.6	340	27
3149	----	6.8	650	--	3238	----	5.27	60	--
3150	-260	7.5	200	27	3240	-250	7.4	570	25
3151	-280	7.2	170	24	3339	-280	7.9	350	25
3155	+155	4.8	200	25	3340	-163	7.3	300	24
3156	+160	6.9	130	28	3342	-80	7.7	660	22
3158	-200	7.1	320	25	3343	-250	7.9	420	22
3161	+128	7.1	100	25	3344	-250	7.9	380	24
3163	+173	7.8	220	26	3347	-260	7.5	----	25
3164	+190	8.0	160	25	3348	-230	7.2	600	26
3166	+400	4.1	250	25	3349	-140	5.2	----	27
3167	-75	7.4	200	27	3350	-260	7.5	----	25
3168	-80	7.3	230	25	3351	-230	7.3	----	24
3172	----	5.4	210	24.5	3352	+69	8.0	190	21
3179	+200	7.3	310	25	3353	58	7.7	340	22
3180	-240	8.0	160	26	3355	-100	7.6	380	24
3181	----	7.6	380	25	3356	30	7.7	280	23
3182	----	7.0	480	--	3357	-70	7.7	360	24
3183	----	7.1	540	--	3358	-100	7.5	300	26
3184	-150	7.5	290	25	3359	-220	7.6	800	24
3185	-120	7.6	200	26	3360	-265	7.4	800	24
3186	-50	7.7	210	27	3365	-248	7.2	1000	23
3188	----	9.4	430	--	3366	-278	7.2	470	24
3189	----	6.8	500	--	3367	-120	7.5	----	23
3192B	+170	9.0	350	25	3368	-240	7.3	740	26
3196B	+200	7.1	210	24	3369	-230	7.3	----	25

Table 3-4 (Cont.) **Water Quality Data**

Sample #	Eh millivolts	Ph	Conductivity siemen	Temperature °C
3370	-250	7.1	---	24
3371	-220	7.1	---	24
3372	-250	7.2	---	25
3373	-200	7.3	320	22
3429	-170	7.8	---	24
3430	-80	5.7	---	24
3434	+150	5.6	---	26
3435	+100	5.5	---	24
3437	-125	7.6	210	24
3438	-200	7.4	360	24
3439	+100	5.7	100	24
3440	-200	7.5	290	25
3441	+150	5.1	100	26
3442	+90	7.7	240	25
3443	+215	4.9	82	26
3444	----	6.2	140	23
3445	----	5.7	100	24
3446	----	7.8	310	26
3447	----	7.6	410	260
3448	----	5.6	140	24
3449	----	5.6	220	23
3450	+100	7.7	---	22
3451	-70	4.7	---	24
3452	-50	5.2	---	24
3453	+18	7.8	---	22
3454	+120	5.4	---	23
3455	-50	5.6	---	28
3456	+220	7.6	350	24
3457	+220	6.8	160	22
3458	+220	8.0	160	23
3459	+250	7.1	260	25
3460	+300	6.4	120	23
3461	+260	7.2	160	28
3462	+270	7.3	180	23
3463	+260	7.5	240	25
3464	+225	7.4	280	23
3465	+220	7.4	300	25
3466	+210	7.2	700	34
3467	+270	6.8	110	25

Table 3-5 <u>Uranium and Thorium Isotopes in Core W12942</u>

Sample #	Depth (ft)	U-234/U-238	Uconc (ppm)	Th-230/U-238
192	35-40	1.29 ± .61	13.6 ± 6.6	
193	40-45	.99 ± .05	61.7 ± 4.4	
194	45-50	1.01 ± .06	63.9 ± 6.0	
195	50-55	.93 ± .25	1.53 ± .29	3.89 ± .97
196	60	1.03 ± .12	18.5 ± 1.9	1.27 ± .46
197	65	1.04 ± .11	13.1 ± 1.3	1.18 ± .15
198	70-71	1.04 ± .06	36.8 ± 2.9	1.45 ± .18
199	76	1.04 ± .05	24.1 ± 1.7	1.17 ± .11
200	80	1.01 ± .10	11.5 ± 1.2	1.34 ± .19
201	121	1.07 ± .08	19.1 ± 1.6	.34 ± .11
202	125	.96 ± .08	12.9 ± 1.0	.92 ± .11
203	130	1.03 ± .08	22.8 ± 1.9	1.14 ± .15
204	140	.99 ± .04	15.1 ± .8	.08 ± .06
205	145	1.03 ± .12	8.32 ± .79	.93 ± .14
206	150	.98 ± .05	16.8 ± .9	.82 ± .15
207	155	.94 ± .09	21.8 ± 2.9	.86 ± .14
208	160	.93 ± .10	9.1 ± .9	.51 ± .29

Table 3-6 Uranium and Thorium Isotopes in Core W13078

Sample #	Depth (ft)	U-234/U-238	Uconc (ppm)	Th-230/U-238
217	5-10	1.16 ± .13	7.55 ± .75	.76 ± .44
218	20	.90 ± .06	24.9 ± 2.5	.87 ± .13
219	30	.95 ± .04	29.1 ± 2.3	.82 ± .14
220	40	.98 ± .08	11.9 ± 1.0	
221	50	.92 ± .10	7.64 ± .85	
222	60	1.00 ± .07	15.8 ± 1.2	
223	70	.99 ± .05	38.0 ± 2.2	
224	80	.96 ± .05	23.7 ± 1.3	1.29 ± .43
225	90	1.08 ± .05	8.99 ± .48	1.29 ± .17
226	100	.95 ± .05	31.0 ± 2.9	
227	110	.96 ± .06	16.5 ± 1.42	1.44 ± .20
228	120	.99 ± .05	8.75 ± .67	.79 ± .56
229	130	1.03 ± .10	22.5 ± 2.3	1.37 ± .20

Table 3-7 Uranium and Thorium Isotopes in Core W13107

Sample #	Depth (ft)	U-234/U238	Uconoc (ppm)	Th-230/U-238
230	3-5	.99 ± .12	6.44 ± .84	
231	5-10	.99 ± .12	8.13 ± .89	
232	16	.97 ± .07	14.4 ± 1.2	1.43 ± .65
233	20	.94 ± .08	14.1 ± 1.2	.91 ± .15
234	25	.96 ± .08	6.09 ± .61	.99 ± .45
235	30	.97 ± .50	1.72 ± .65	
236	35	1.48 ± .66	2.77 ± 1.04	
238	45	.58 ± .45	4.68 ± 2.30	
239	50	.96 ± .08	11.9 ± 1.3	
240	60	.98 ± .09	9.73 ± .96	.92 ± .30
241	70	1.01 ± .09	12.2 ± 1.4	
242	80	1.02 ± .09	15.6 ± 1.5	.85 ± .16
243	90	1.03 ± .12	2.48 ± .24	
244	95	1.01 ± .07	9.12 ± .61	
245	100	1.07 ± .03	15.3 ± .5	1.26 ± .27
246	105	.97 ± .06	12.2 ± .7	

Table 3-7 (Cont.) <u>Uranium and Thorium Isotopes in Core W13107</u>

Sample #	Depth (ft)	U-234/U238	Uconoc (ppm)	Th-230/U-238
247	109	.95 ± .06	43.9 ± 4.0	.83 ± .12
248	120	.99 ± .09	17.3 ± 1.5	
249	130	1.02 ± .09	15.4 ± 1.5	
250	135	1.03 ± .04	19.7 ± 1.0	.79 ± .24
251	140	1.03 ± .08	39.9 ± 3.2	
253	150	1.00 ± .05	9.51 ± .51	
256	180	1.05 ± .06	23.5 ± 1.4	1.06 ± .19
257	190	1.08 ± .15	1.72 ± .19	1.02 ± .20
258	200	.97 ± .07	4.22 ± .32	

Table 3-8 Uranium and Thorium Isotopes in Core W13237

Sample #	Depth (ft)	U-234/U-238	Uconc (ppm)	Th-230/U-238
146	15-20	.96 ± .06	129 ± .14	1.23 ± .21
147	20-25	.97 ± .03	54.9 ± 2.5	1.09 ± .44
148	25-30	.99 ± .09	43.8 ± 5.2	1.88 ± .28
149	30-35	.91 ± .04	29.1 ± 1.2	1.40 ± .13
150	35-40	.97 ± .07	40.5 ± 3.6	
151	40-45	.96 ± .05	31.3 ± 2.0	
152	45	.98 ± .04	18.7 ± .76	
153	50	1.01 ± .06	28.0 ± 2.3	
154	53-56	.91 ± .05	30.7 ± 2.0	
157	70	.99 ± .07	26.8 ± 2.2	1.12 ± .36
158	80	1.10 ± .06	54.1 ± 5.1	1.09 ± .17
159	90	.99 ± .06	34.2 ± 2.8	.94 ± .18
160	100	1.13 ± .09	31.4 ± 3.6	1.05 ± .24
162	120	1.00 ± .06	25.7 ± 2.2	
163	130	1.00 ± .06	12.9 ± .78	
164	140	1.05 ± .04	27.4 ± 1.0	

Table 3-8 (Cont.) Uranium and Thorium Isotopes in Core W13237

Sample #	Depth (ft)	U-234/U-238	Uconc (ppm)	Th-230/U-238
166	160	1.10 ± .14	3.78 ± .43	.52 ± .14
167	170	1.01 ± .03	108. ± 7.	1.52 ± .20
168	175	1.04 ± .17	28.5 ± 6.4	1.67 ± .43
169	180	.98 ± .11	15.7 ± 1.9	1.02 ± .19
170	190	1.10 ± .13	15.7 ± 1.9	.75 ± .29
171	200	.98 ± .08	94.3 ± 17.6	

Table 3-9 <u>Uranium and Thorium Isotopes in Core W13331</u>

Sample #	Depth (ft)	U-234/U-238	Uconc (ppm)	Th-230/U-238
172	15-20	.95 ± .12	8.89 ± .95	
173	20-25	.81 ± .04	89.1 ± 6.2	1.16 ± .31
174	25-30	.99 ± .07	29.1 ± 2.0	1.29 ± .59
175	30-35	1.14 ± .34	2.24 ± .50	4.42 ± 1.73
176	35-40	1.13 ± .17	17.0 ± 2.7	
177	40-45	.91 ± .15	10.5 ± 1.4	
178	55	1.09 ± .09	23.7 ± 2.2	.94 ± .37
179	64	.95 ± .14	.70 ± .08	
180	71	1.00 ± .09	12.0 ± .9	
181	75	1.03 ± .07	10.4 ± .7	
182	80	1.31 ± .07	5.29 ± 1.38	
183	85	1.07 ± .08	26.3 ± 2.4	.27 ± .07
184	90	.99 ± .05	27.9 ± 1.4	1.13 ± .39
185	100	.97 ± .07	8.14 ± .53	2.10 ± .24
186	110	.97 ± .08	5.46 ± .35	1.03 ± .18
187	118	.90 ± .23	2.46 ± .45	4.43 ± 1.47

Table 3-9 (Cont.) Uranium and Thorium Isotopes in Core W13331

Sample #	Depth (ft)	U-234/U-238	Uconc (ppm)	Th-230/U-238
188	130	1.32 ± .47	8.74 ± 2.80	2.32 ± .77
189	140	.96 ± .07	10.9 ± .9	1.06 ± .12
190	150	1.02 ± .04	18.8 ± 1.1	.28 ± .03
191	160	.95 ± .07	46.2 ± .07	.86 ± .24

Table 3-10

Uranium and Radium Data for Two Cores in Sarasota County

Sample No.	Uconc ppm	U-234/U-238	Ra-226 Ueq.	Ra-226/U-238	Depth	Well No. and Formation
FLR 307	378.38	1.02	131.	0.349	16-20'	W-11908 Bone Valley Fm
FLR 308	73.27	.885	27.	0.370	25'	W-11908 Hawthorn Fm
FLR 309	139.95	.988	133.	0.964	328'	W-11908 Hawthorn Fm
FLR 310	16.28	.972	16.	.97	111-114'	W-12983 Hawthorn Fm
FLR 311	19.21	.997	13.6	0.715	148-152'	W-12983 Hawthorn Fm
FLR 312	33.56	1.01	13.8	0.417	170-176'	W-12983 Hawthorn Fm

Table 3-11 **Uranium and Radium Data for Solid Samples from a Stratigraphic Section at USS Rockland Mine**

Sample No.	Uconc ppm	U-234 / U-238	Ra-226 Ueq.	Ra-226 / U-238	Stratigraphic Horizon
FLR 289	476 ± .203		4.9	1.03	Upper Bone Valley Leached Sandstone
FLR 291	116.60	1.01	167.20	1.43	Middle Bone Valley
FLR 292	189.39	.955	196.96	1.04	Lower Bone Valley
FLR 293	261.54	.951	157.97	.604	Upper Hawthorn Leached
FLR 294	65.51	1.02	67.4	1.03	Upper Hawthorn

Table 3-12 Uranium, Thorium and Radium Isotope Data for Mine Products

Sample #	Uconc. ppm	U-234 / U-238	Th-230 / U-238	Ra-226 / U-238	Sample Type	Mine
FLR 132A	52.25 14.00	1.034 ±.09	1.531 ±.342		Matrix	WR Grace Hookers Prairie
FLR 134	31.04 ±2.30	.991 ±.05	.159 ±.036		Debris Feed	WR Grace Bonnie Lake
FLR 136	2.43 ±.36	1.086 ±.18			Organic	WR Grace
FLR 137	65.40 ±6.25	1.035 ±.04	.934 +.146		Clay Organic	WR Grace Hookers Prairie
FLR 138	24.19 ±2.48	1.087 ±.06	.140 ±.033		Unmined Organic	WR Grace Hookers Prairie
FLR 140	57.53 ±3.68	1.029 ±.03	5.392 ±1.779		Primary Slime	WR Grace Bonnie Lake
FLR 286	15.03 ±.50	.99 ±.02			Matrix	IMC Noralyn
FLR 298	6.66 ±.30	.94 ±.04			Matrix	Mobil Nichols
FLR 296	208.89 ±3.59	.981 ±.015		1.04 ±.02	Pebble 60 BPL	USS Rockland
FLR 288	65.56 ±1.0	1.05 ±.02			Pebble	IMC Noralyn
FLR 299	138.53 ±2.0	.92 ±.02			Pebble	Amax Big Four

Table 3-12 (Cont.) Uranium, Thorium and Radium Isotope Data for Mine Products

Sample #	Uconc.	U-234	Th-230	Ra-226	Sample Type	Mine
		U-238	U-238	U-238		
FLR 297	105.53	1.04		.31	Concentrate	USS Rockland
	±2.0	±.02		±.02	68 BPL	
FLR 300	88.70	.99		.53	Concentrate	Amax Big Four
	±2.0	±.02		±.03		
FLR 290	5.62	.99		1.09	Overburden	USS Rockland
	±2.54	±.10		±.17		
FLR 287	61.31	1.00			Overburden	IMC Noralyn
	±2.0	±0.02				
FLR 303	79.45	.81			Slime	IMC Noralyn
	±2.0	±.02			(from pond)	
FLR 304	66.49	.96			Slime	IMC Noralyn
	±2.0	±.02			(from pond)	
FLR 305	301.66	.48			Slime	USS Rockland
	±5.0	±.01			(from pond)	
FLR 301	5.08			29.5	Phosphogypsum	IMC New Wales
	±.35			±1.5	(from stack)	
FLR 302	34.40			2.55	Phosphogypsum	USS Rockland
	±1.63			±0.70	(from stack)	

Table 3-13

Mine Waters

Uranium and Radium Isotope Data for Mine Waters

Sample No.	Uconc ppb	U-234 / U-238	Ra-226 Ueq	Ra-226 / U-238	Sample Type	Mine
FLW 3145	2.35 ±.32	6.62 ±.41	.56	.24	Slime Water (from return ditch)	IMC Phosphoria
FLW 3177	1.43 ±.07	1.15 ±.09	1.4	.99	Slime Water (from slime pond)	Mobil Nichols
FLW 3236	1.05 ±.13	1.45 ±.13	1.56	1.51	Slime Water (from slime pond)	Amax Big Four
FLW 3182	36.68 ±1.50	.62 ±.02			Slime Water (from plant)	USS Rockland
FLW 3149	1.25 ±.10	1.47 ±.12	1.36	1.105	Slime Water (from plant)	IMC Noralyn
FLW 3176	4.22 ±.91	1.04 ±.10	3.69	.89	Recirculating Water	Mobil Nichols
FLW 3183	1.16 ±.17	1.08 ±.021	.54	.48	Recirculating Water	USS Rockland
FLW 3447	1.32 ±.09	1.12 ±.05			Recirculating Water	Mobil Ft. Meade

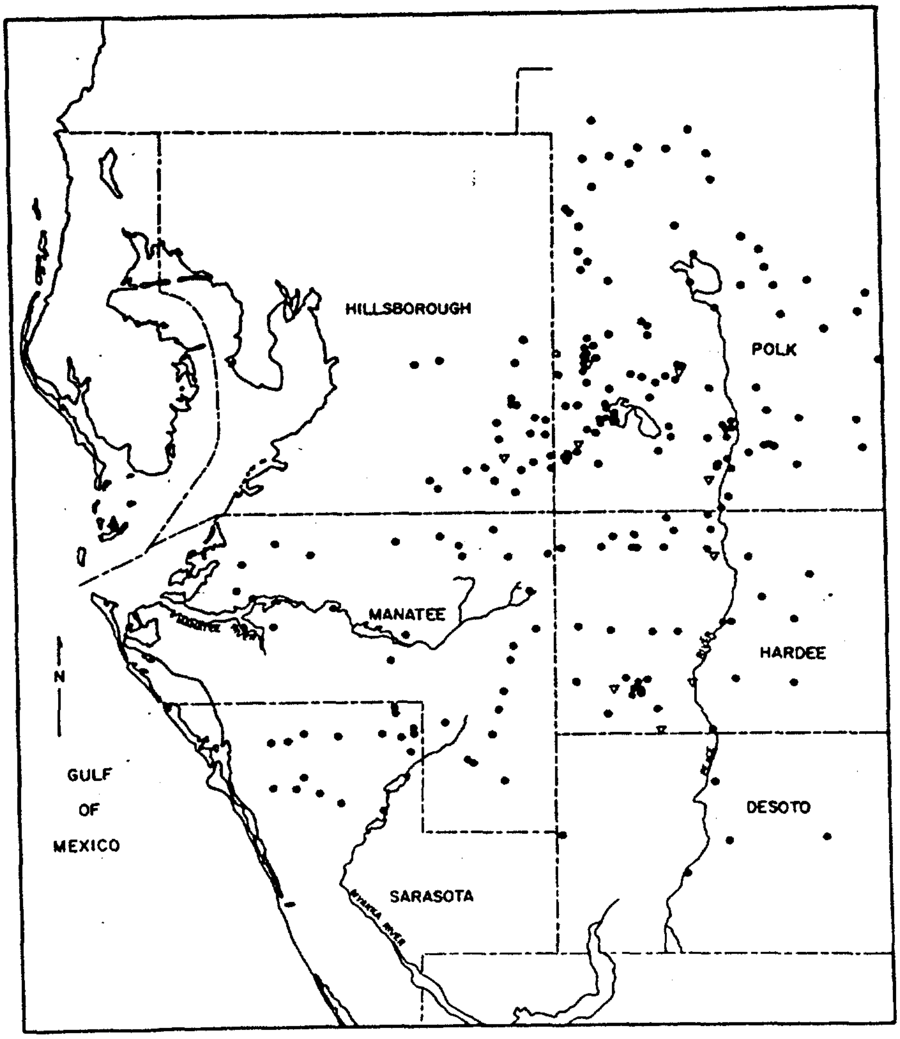

Fig. 3-1 Distribution of samples collected for this study. Dots: waters; triangles: rocks.

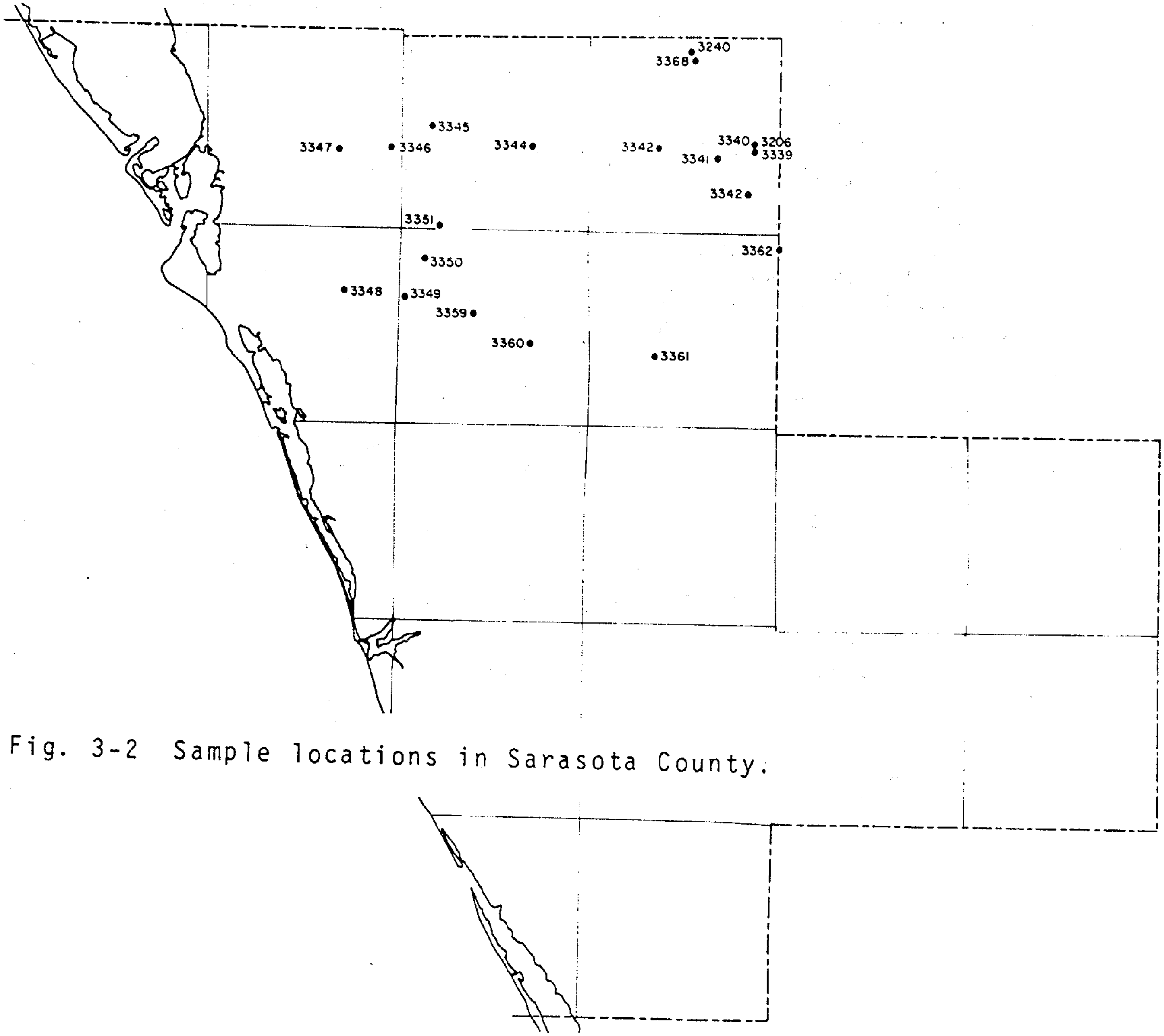

Fig. 3-2 Sample locations in Sarasota County.

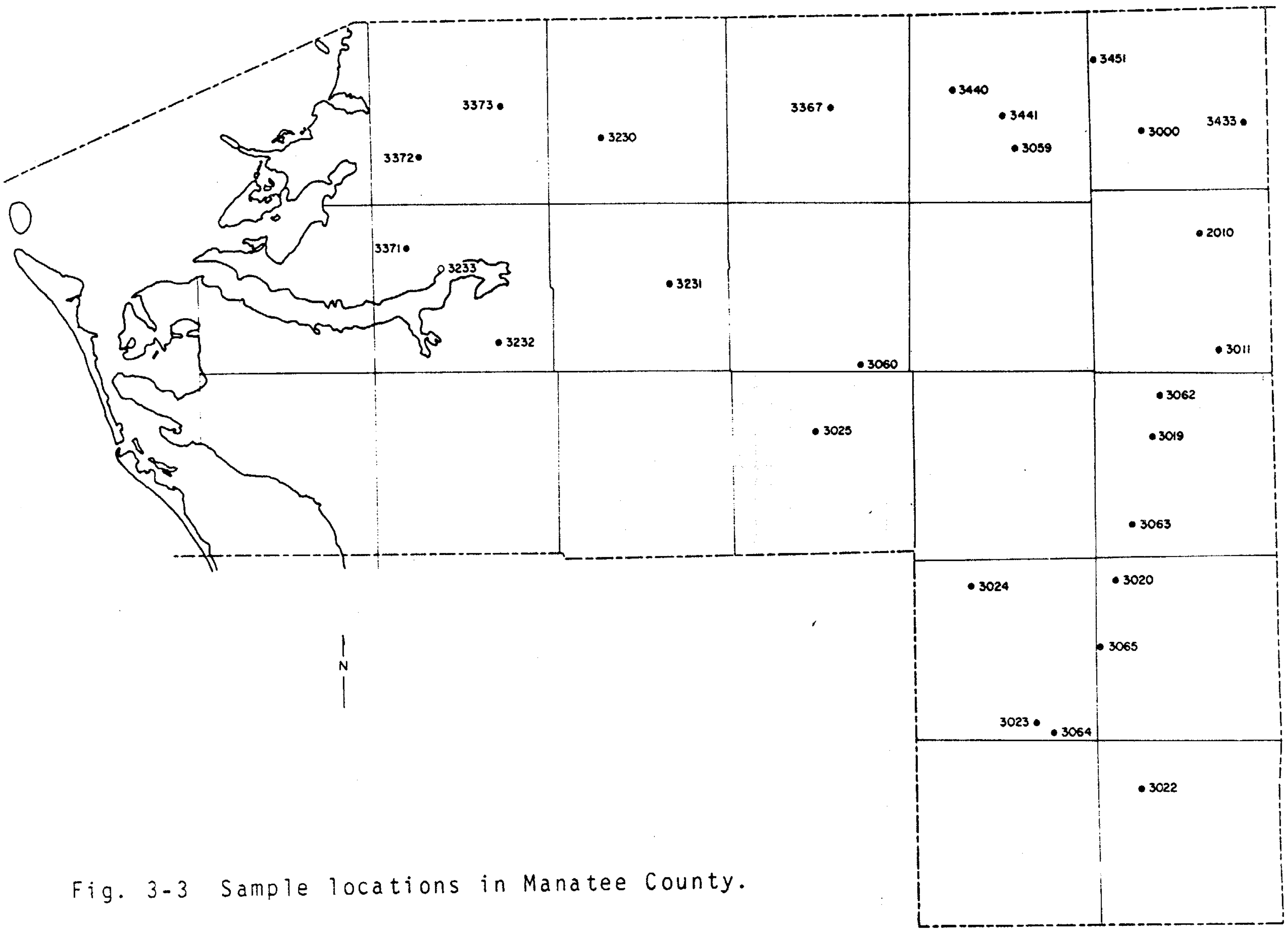

Fig. 3-3 Sample locations in Manatee County.

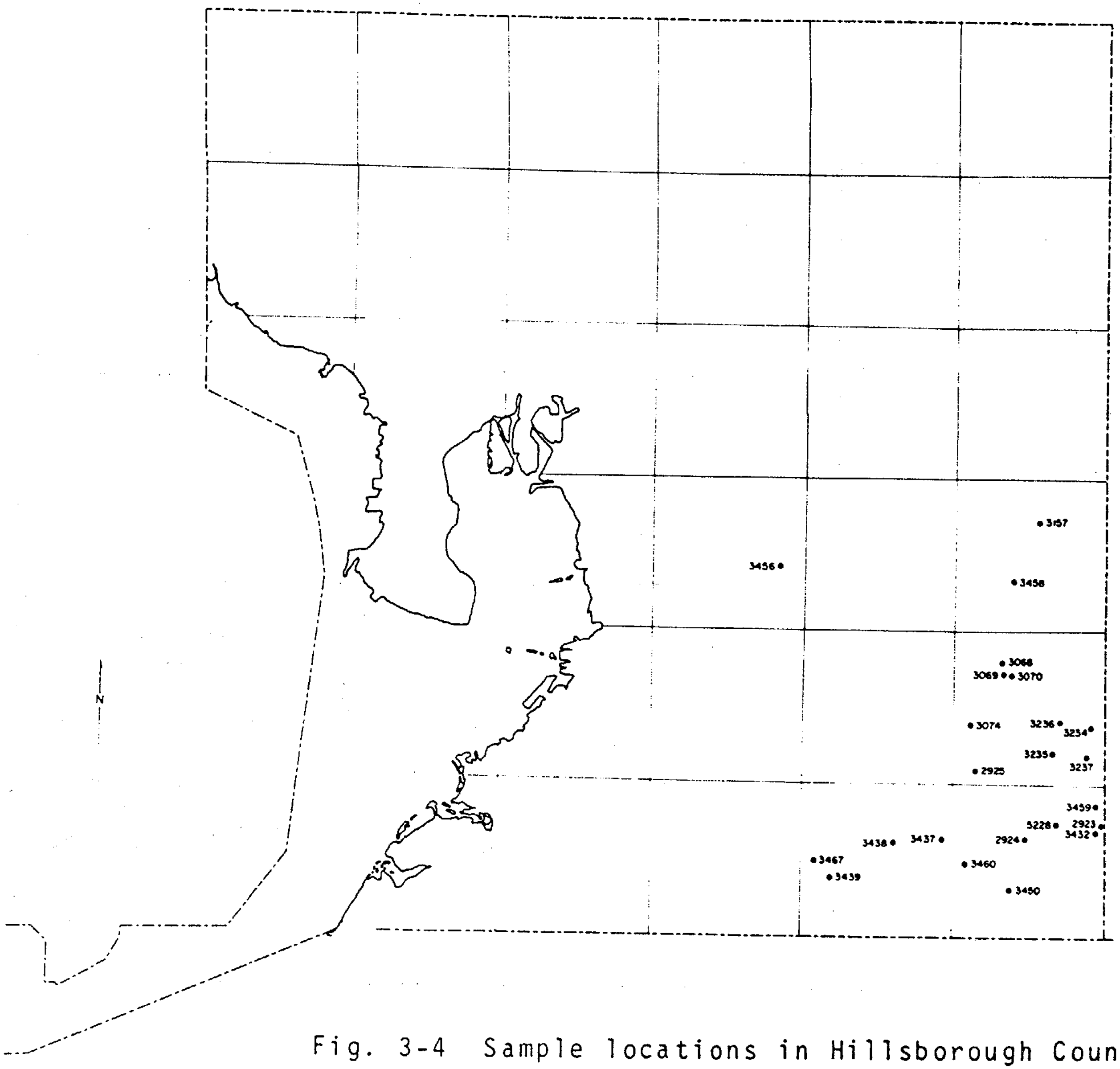

Fig. 3-4 Sample locations in Hillsborough County.

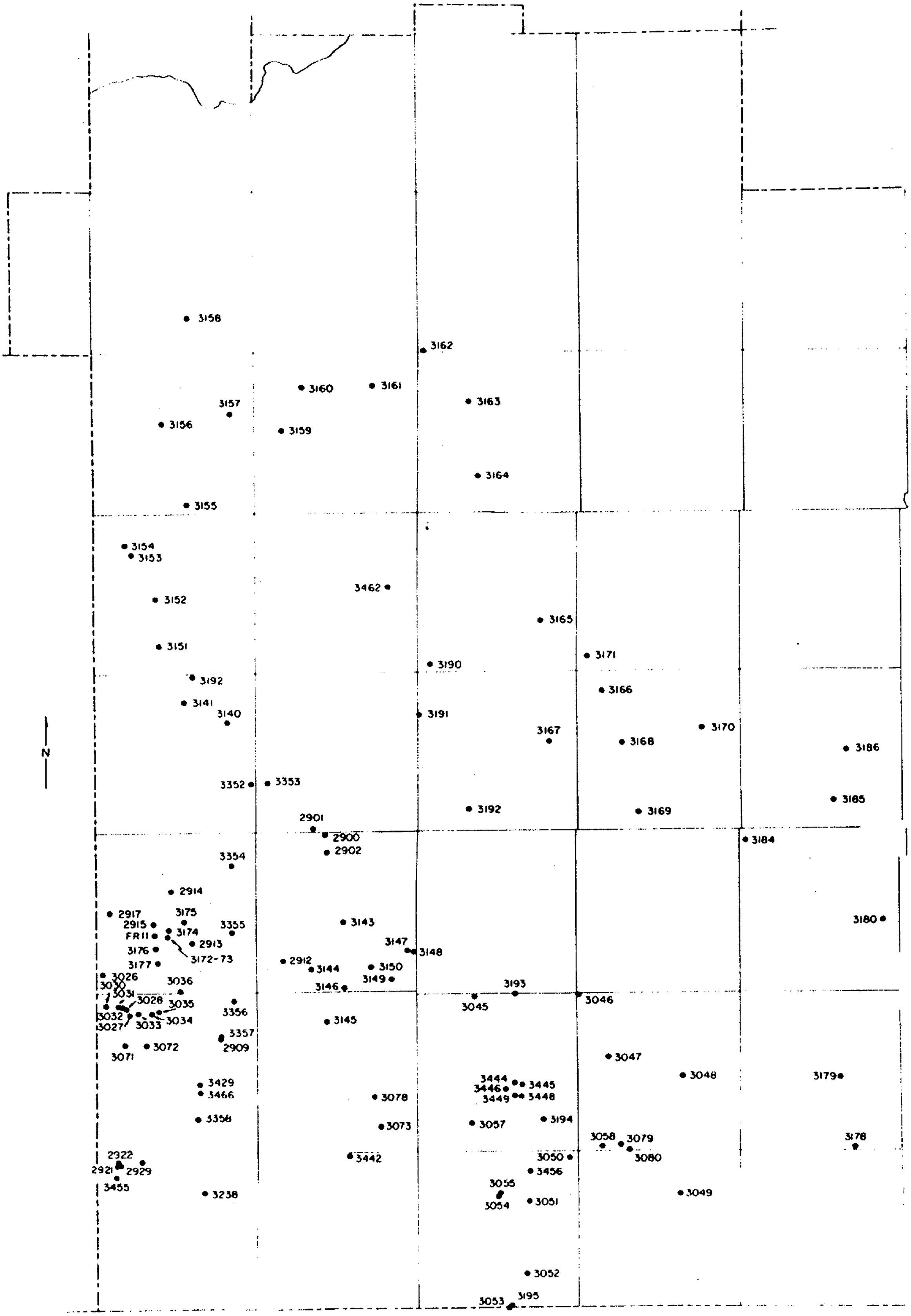

Fig. 3-5 Sample locations in Polk County.

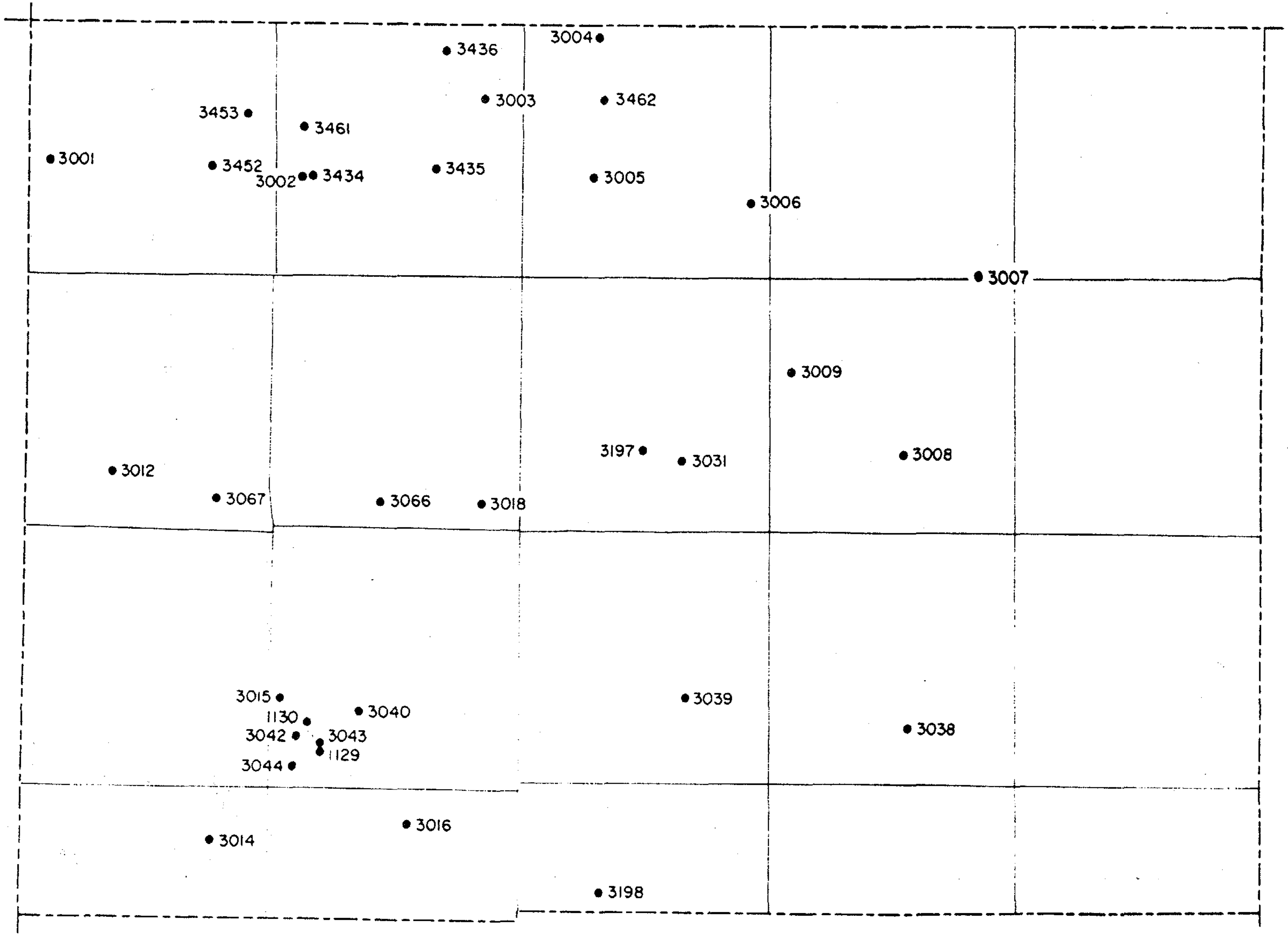

Fig. 3-6 Sample locations in Hardee County.

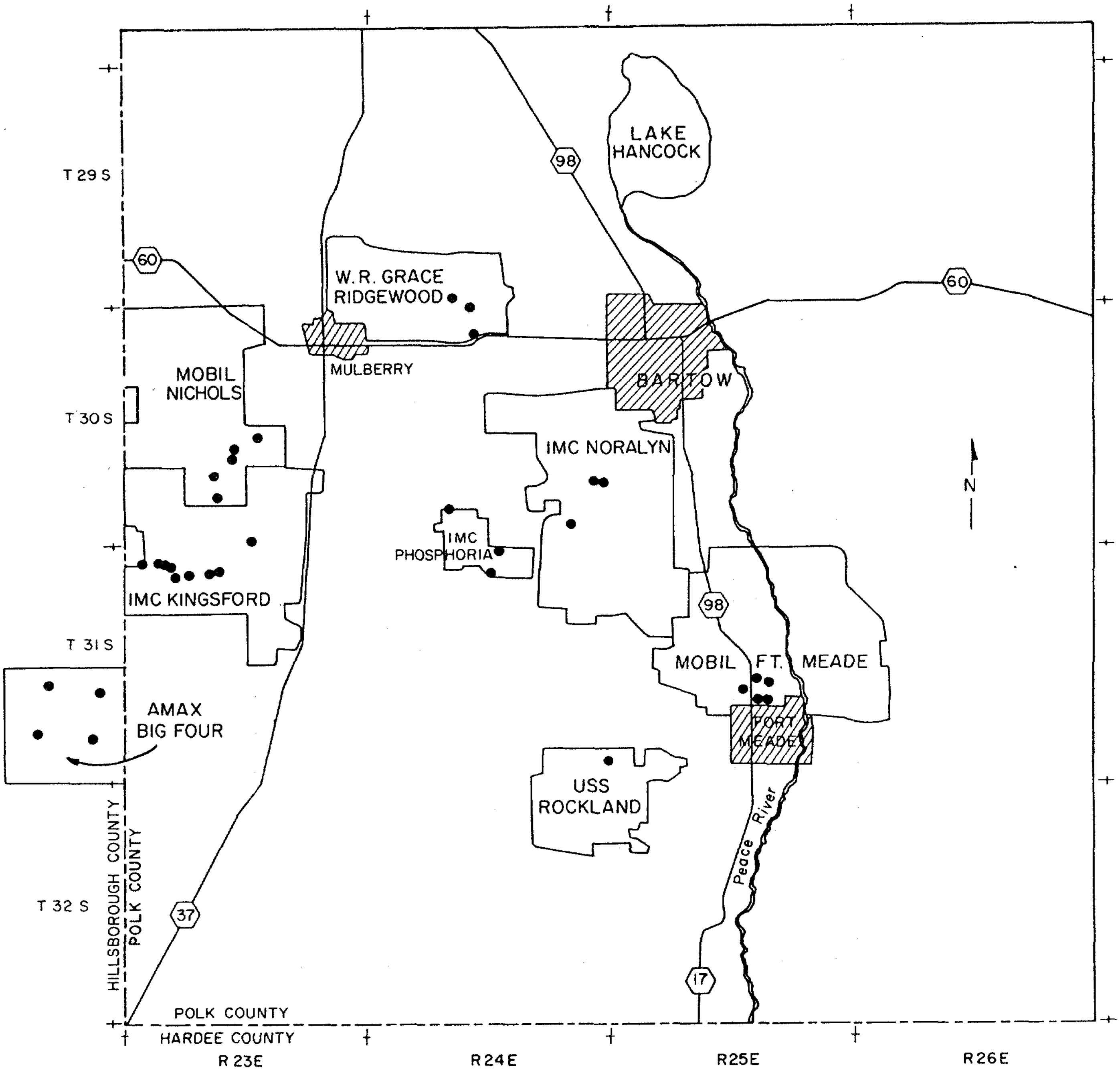

Fig. 3-7 Phosphate mines from which samples were obtained.

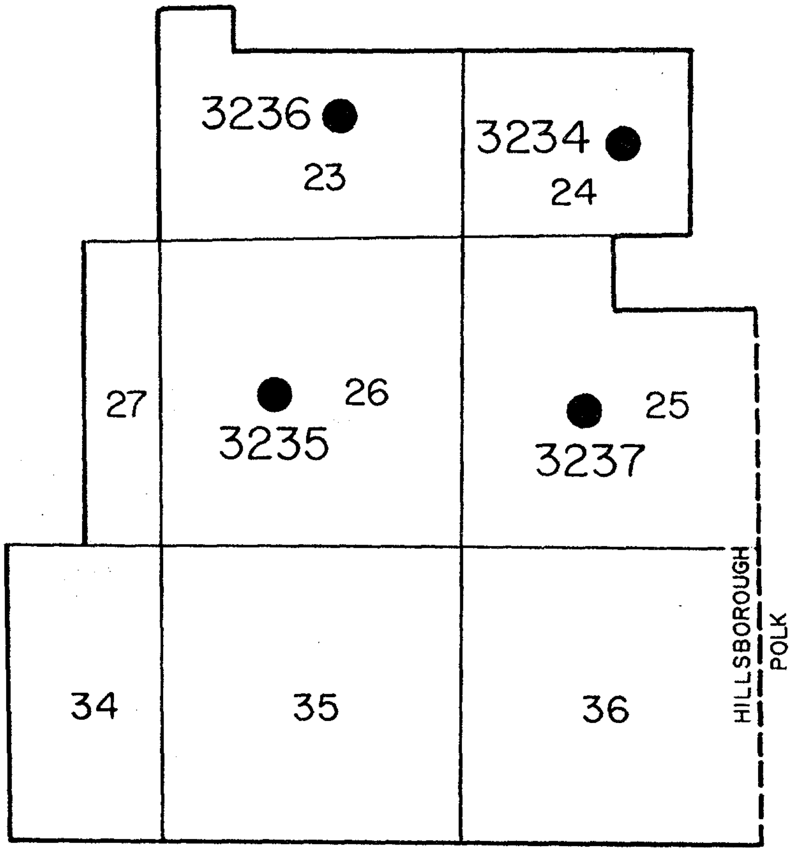

Fig. 3-8 Sample sites, Amax Big Four mine.

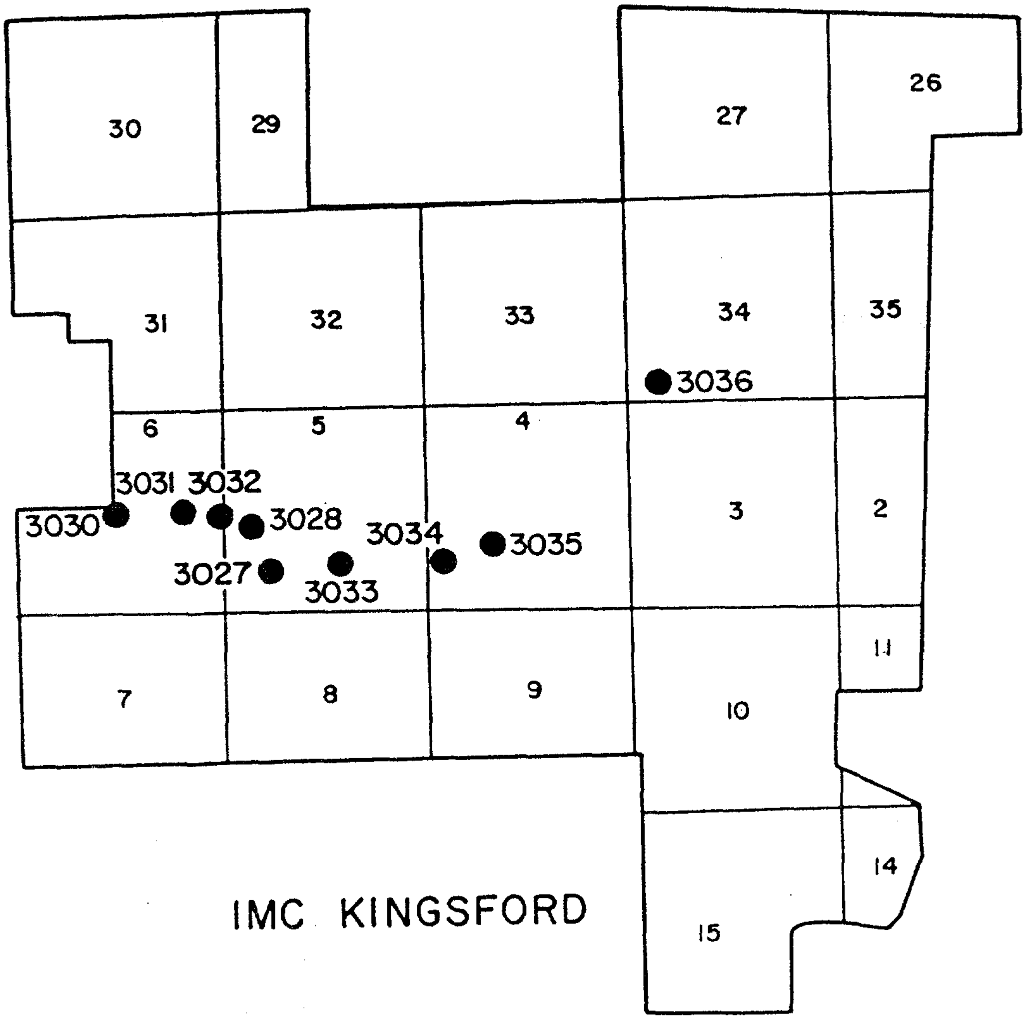

Fig. 3-9 Sample sites, IMC Kingsford mine.

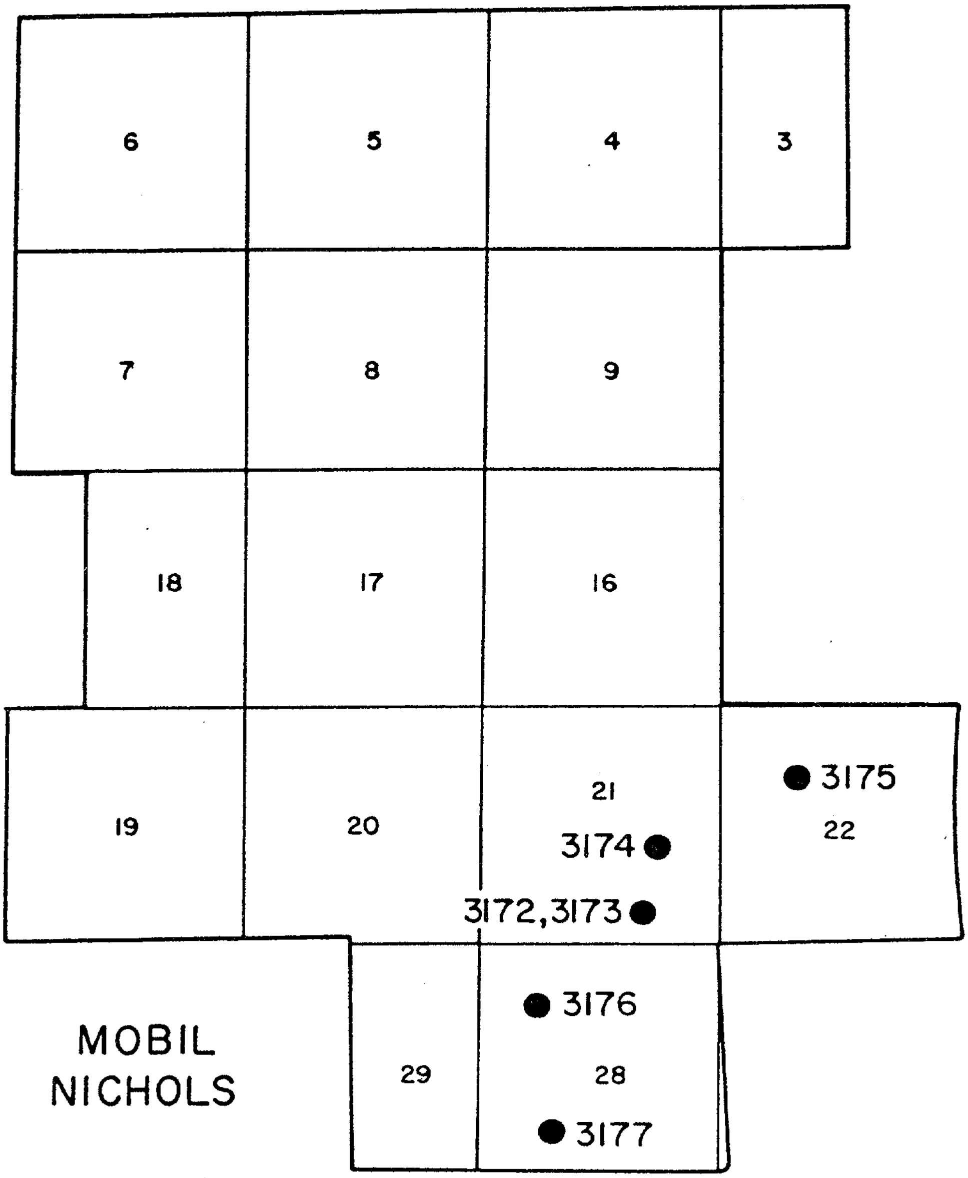

Fig. 3-10 Sample sites, Mobil Nichols mine.

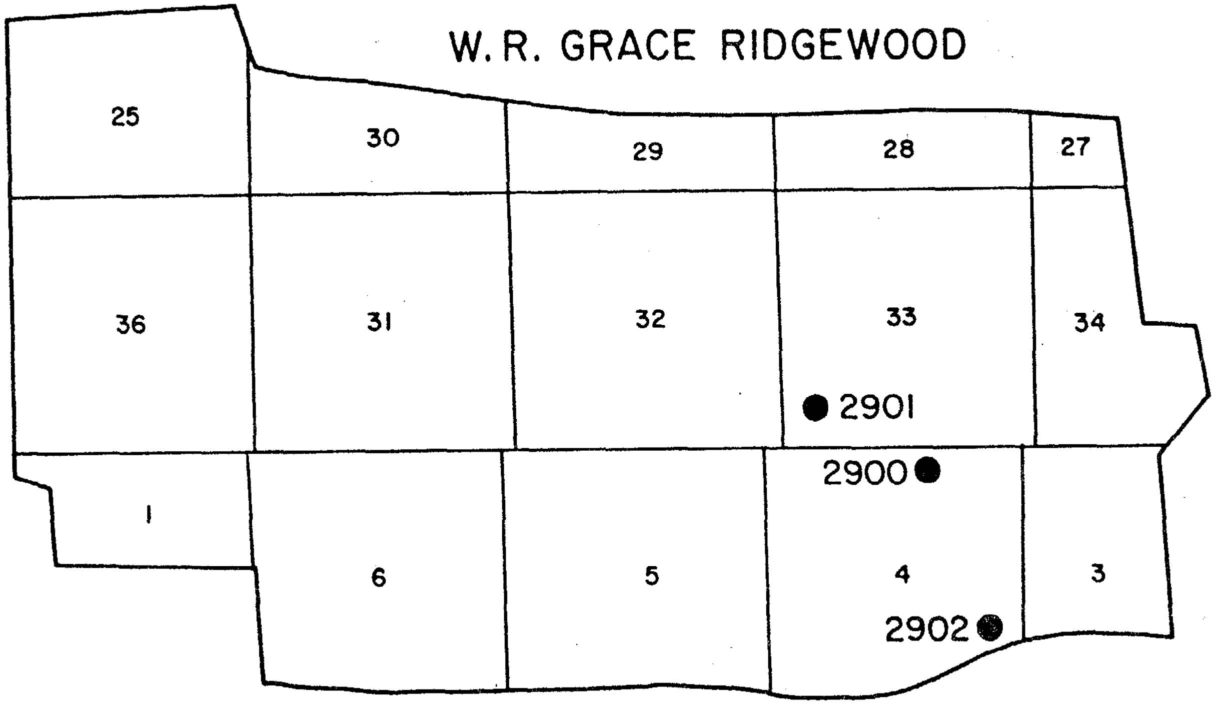

Fig. 3-11 Sample sites, W.R. Grace Ridgewood mine.

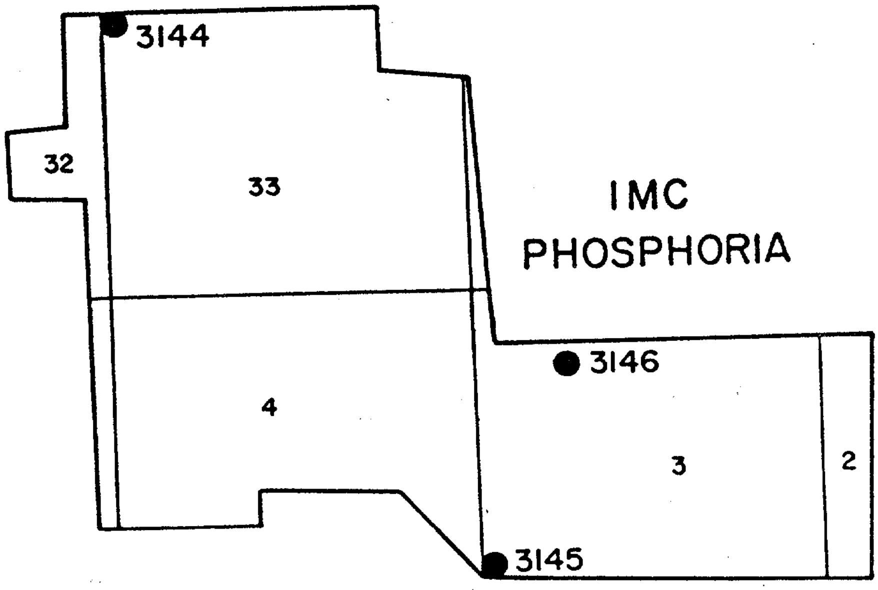

Fig. 3-12 Sample sites, IMC Phosphoria mine.

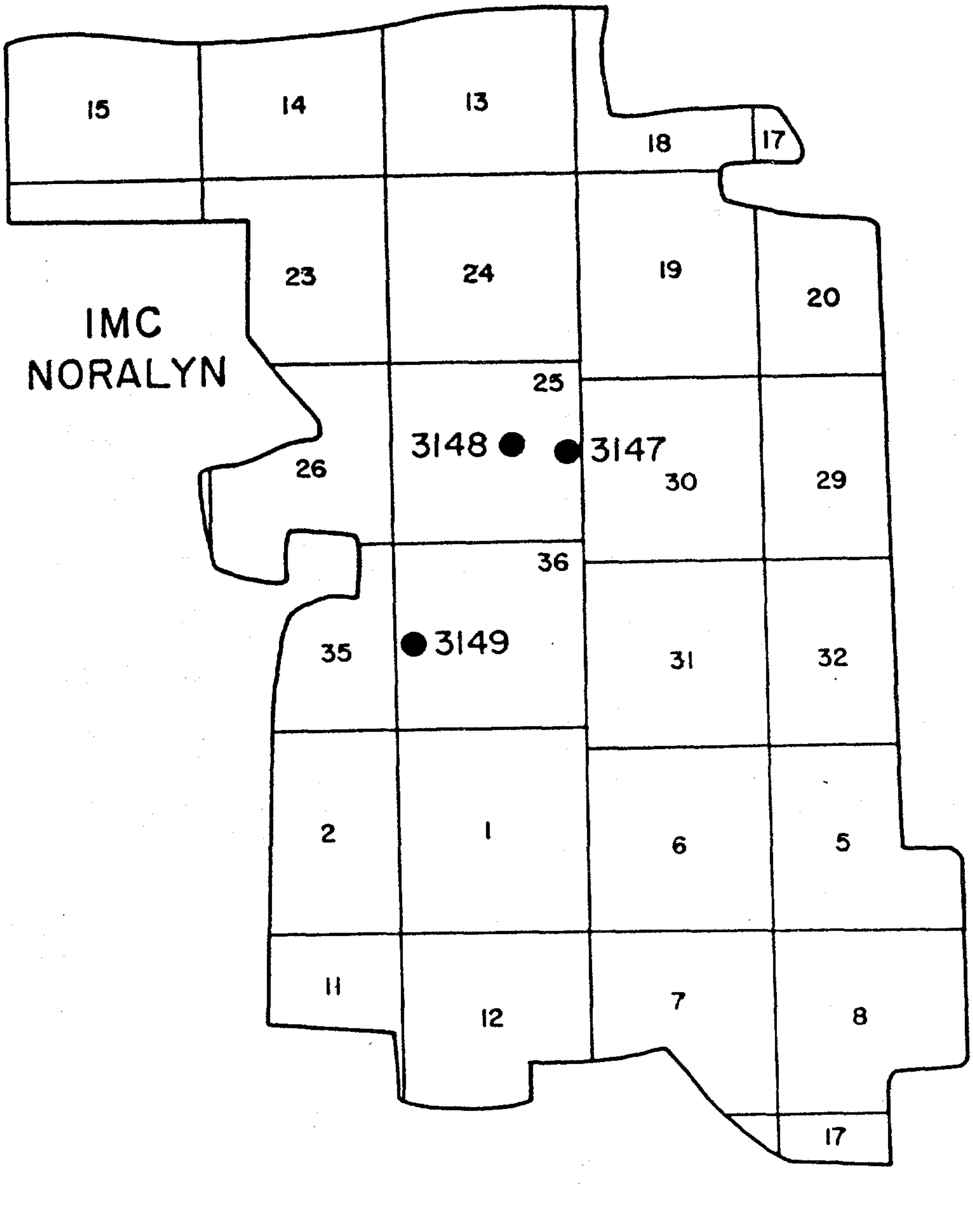

Fig. 3-13 Sample sites, IMC Noralyn mine.

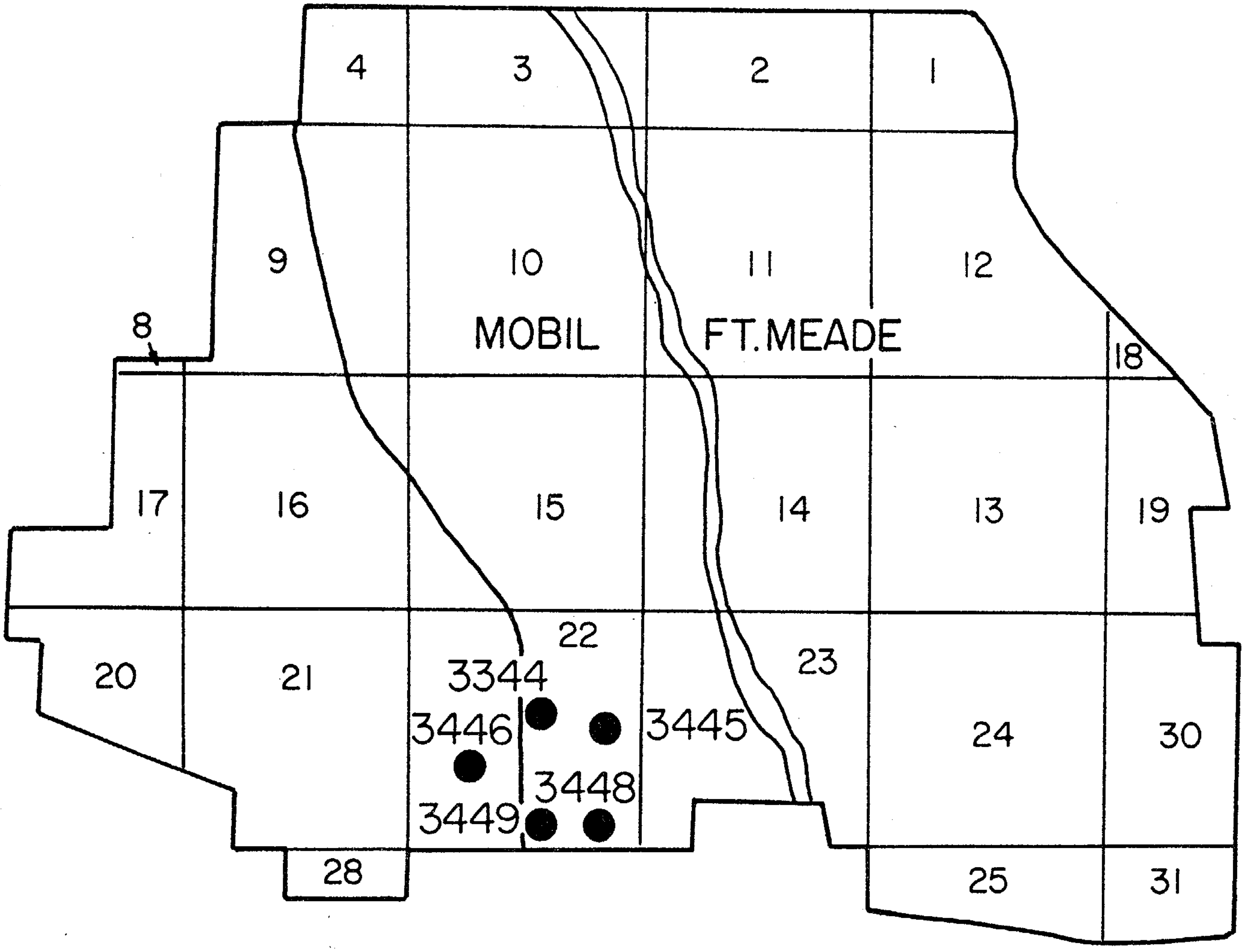

Fig. 3-14 Sample sites, Mobil Ft. Meade mine.

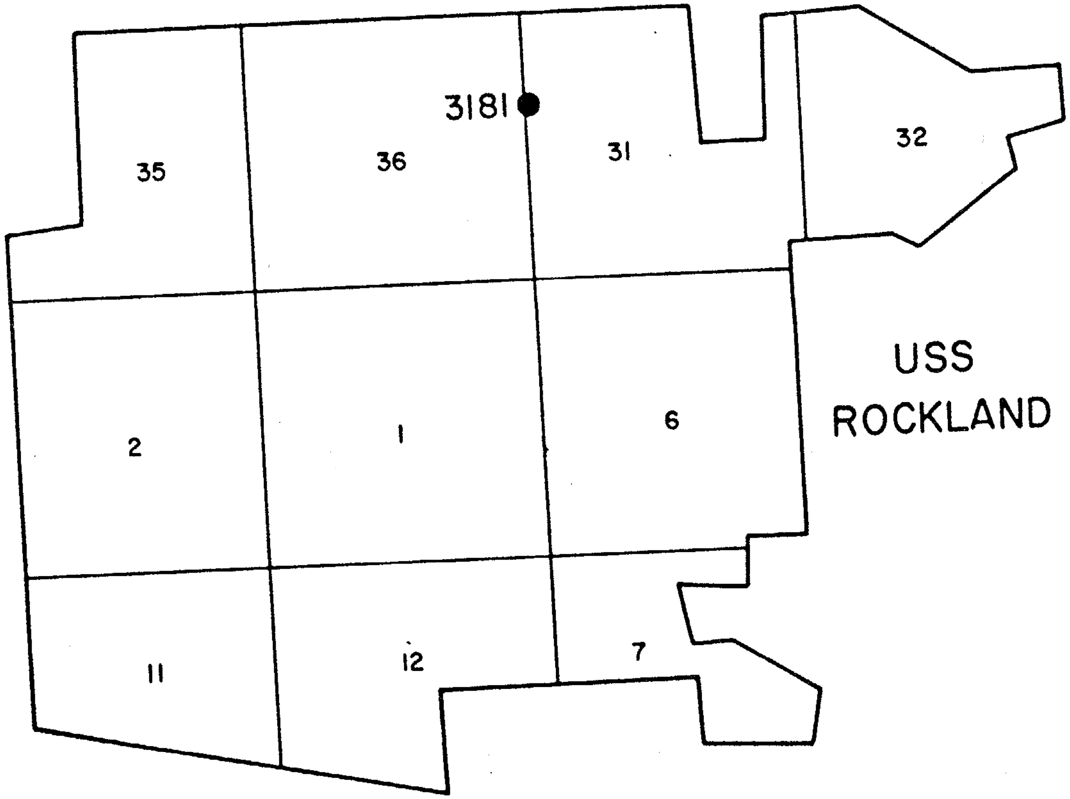

Fig. 3-15 Sample sites, USS Rockland mine.

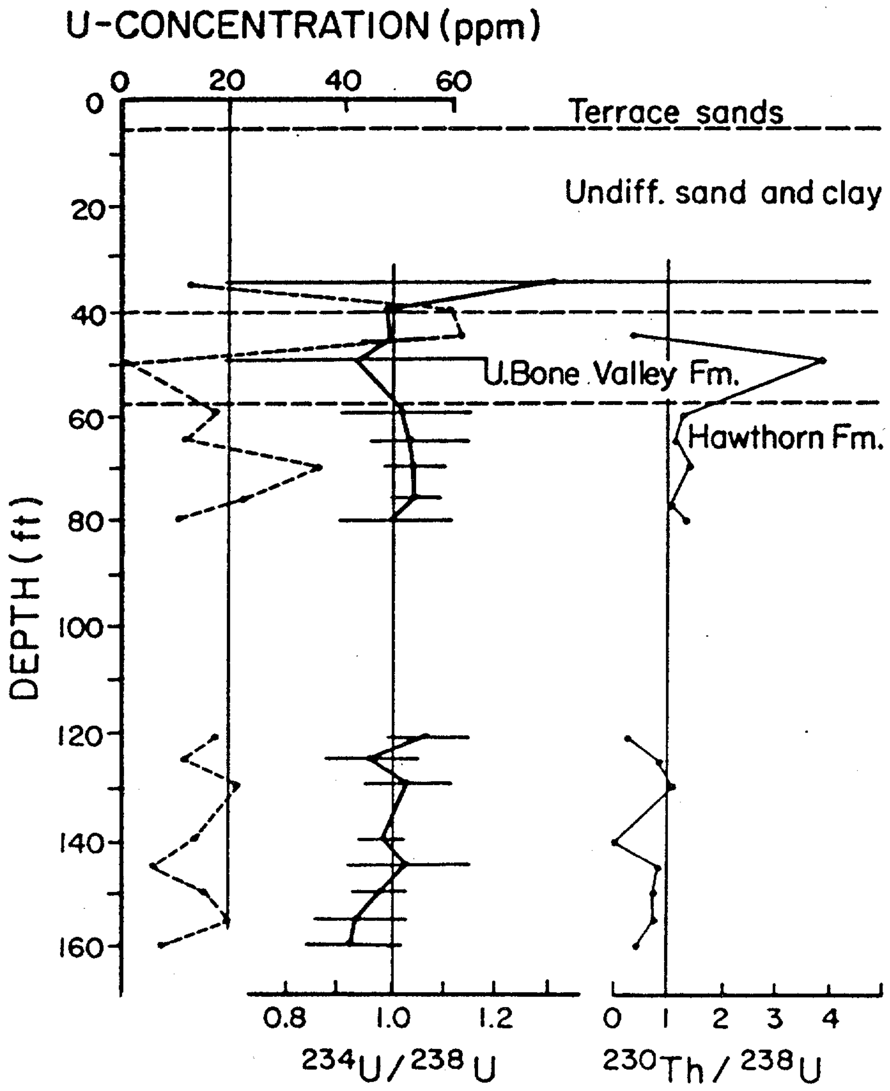

Fig. 3-16 Uranium concentration and isotopic ratios in core 12942

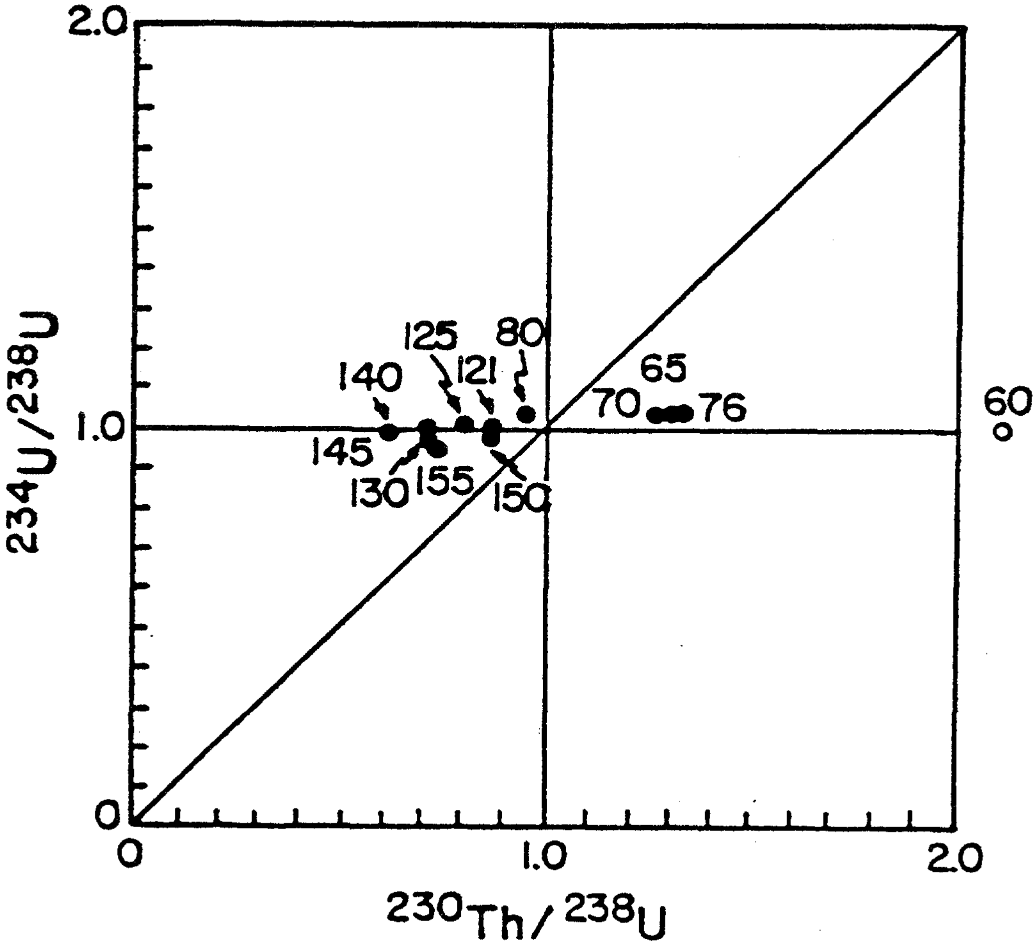

Fig. 3-17 Isotope ratios, running average with depth, in core 12942

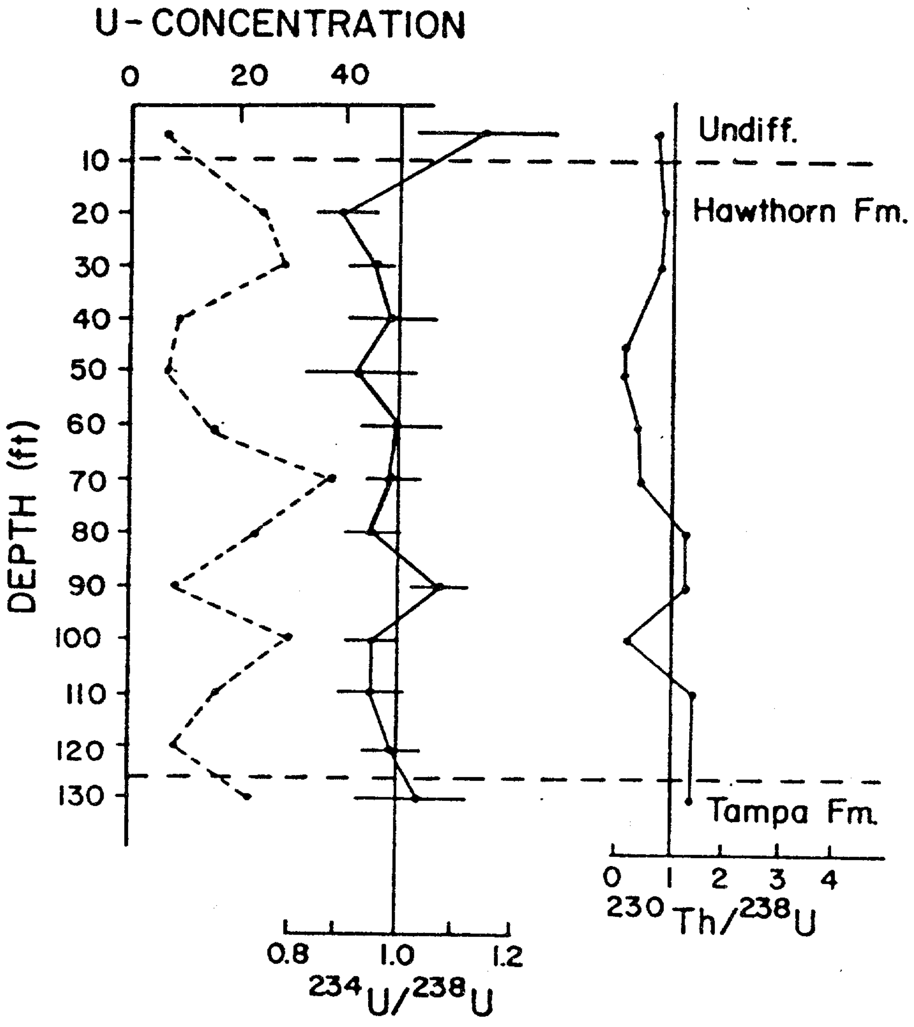

Fig. 3-18 Uranium concentration and isotopic ratios in core 13078.

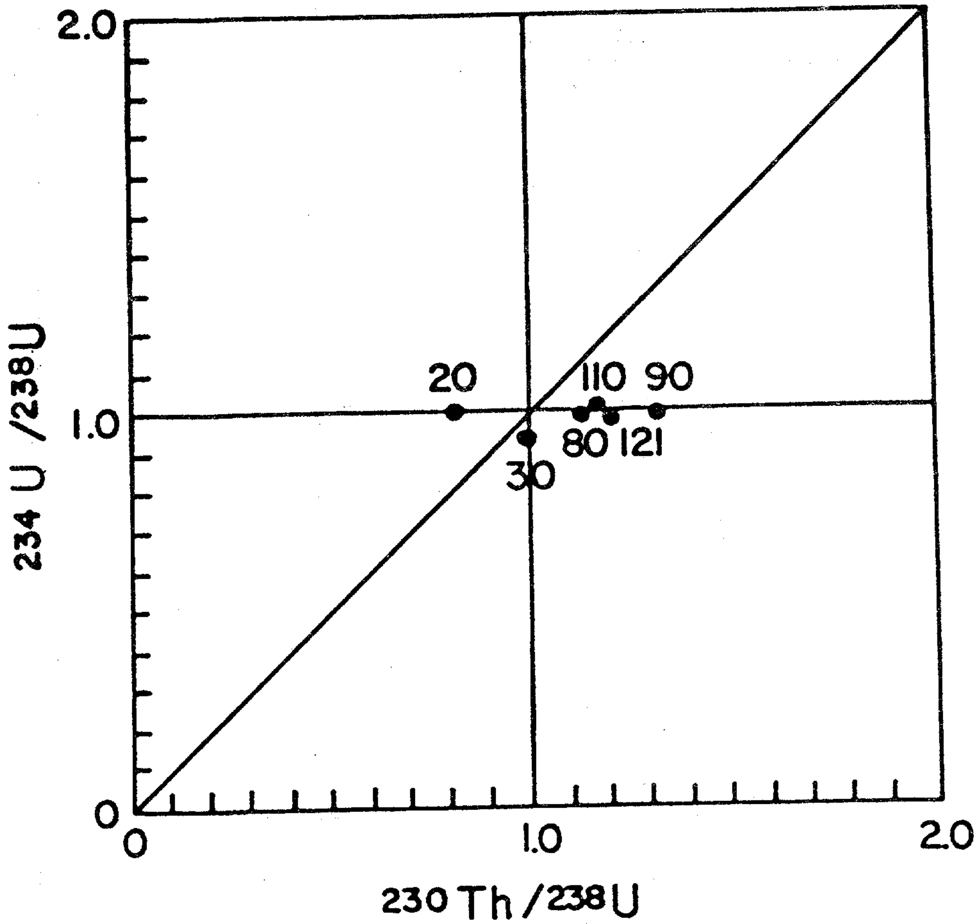

Fig. 3.19 Isotope ratios, running average with depth, in core 13078.

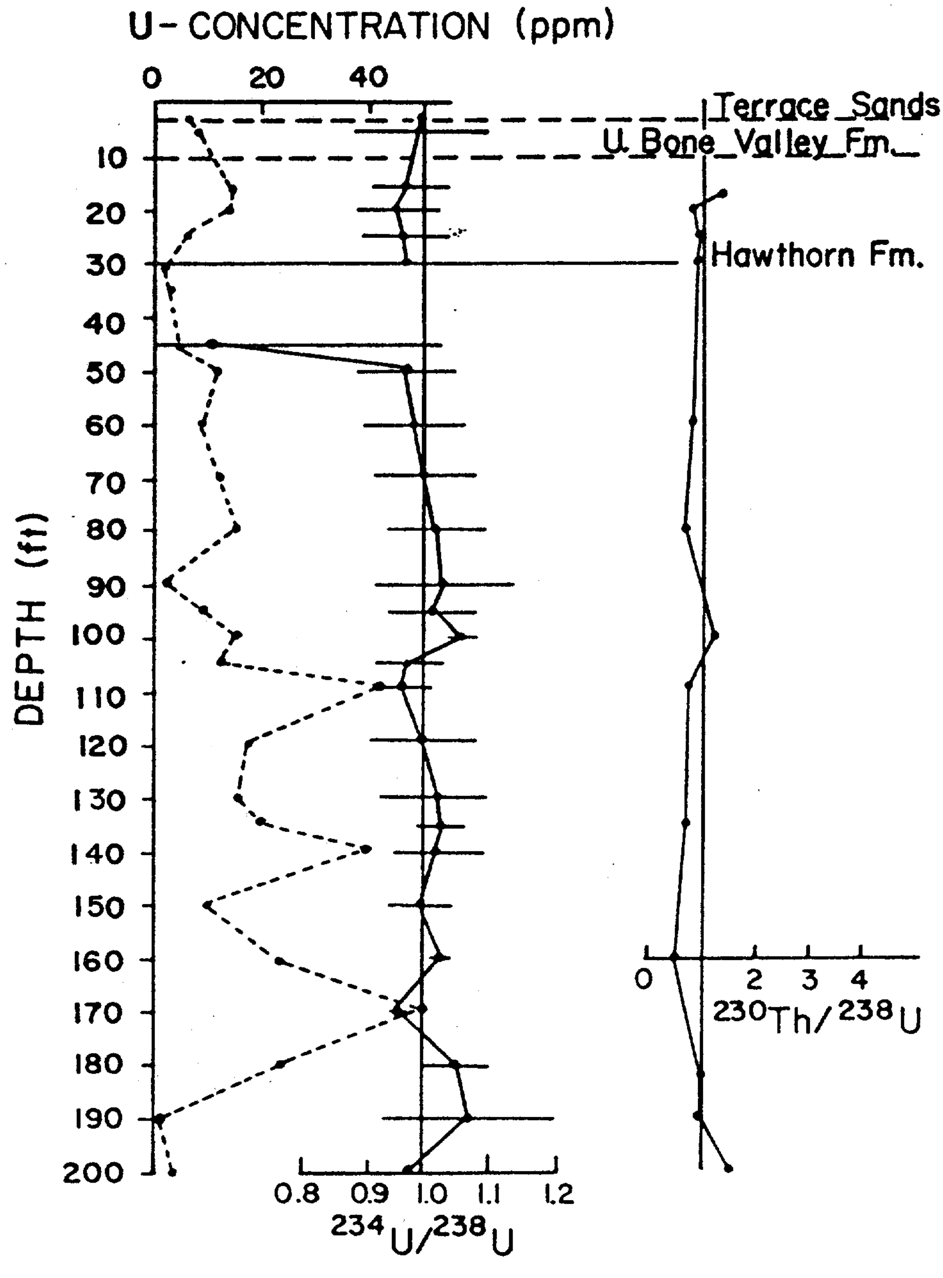

Fig. 3-20 Uranium concentration and isotopic ratios in core 13107.

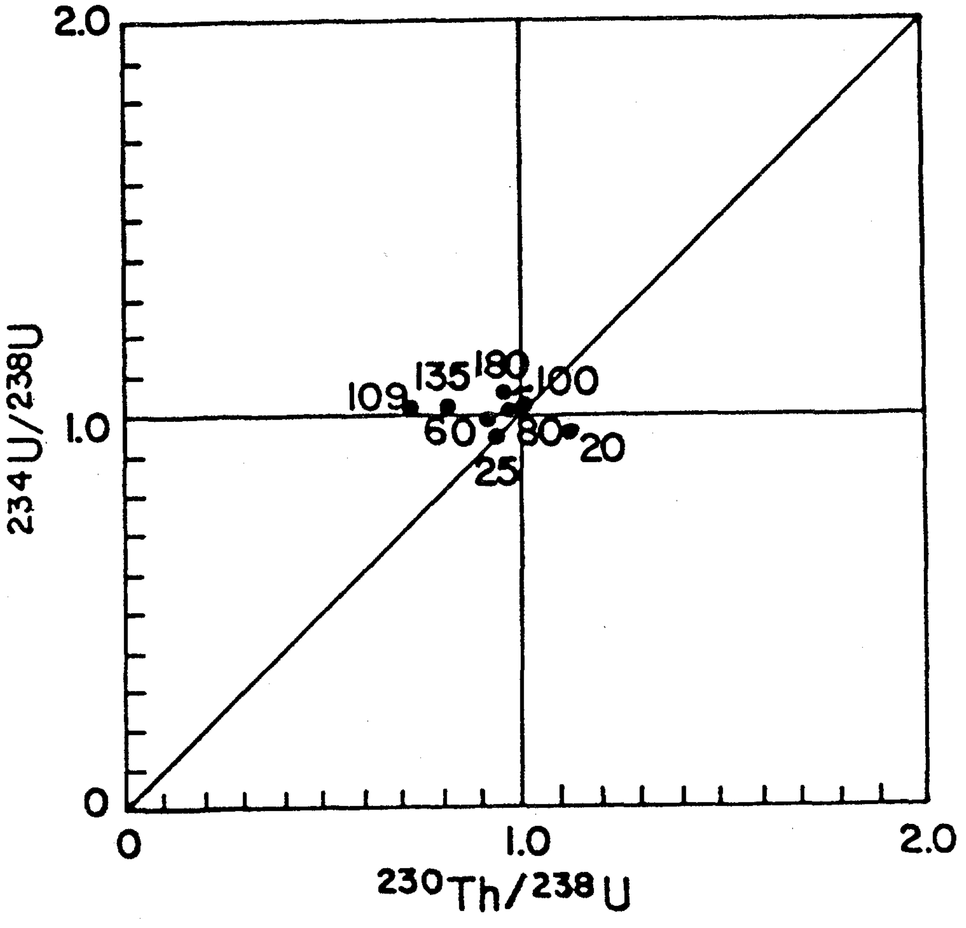

Fig. 3-21 Isotope ratios, running average with depth, in core 13107.

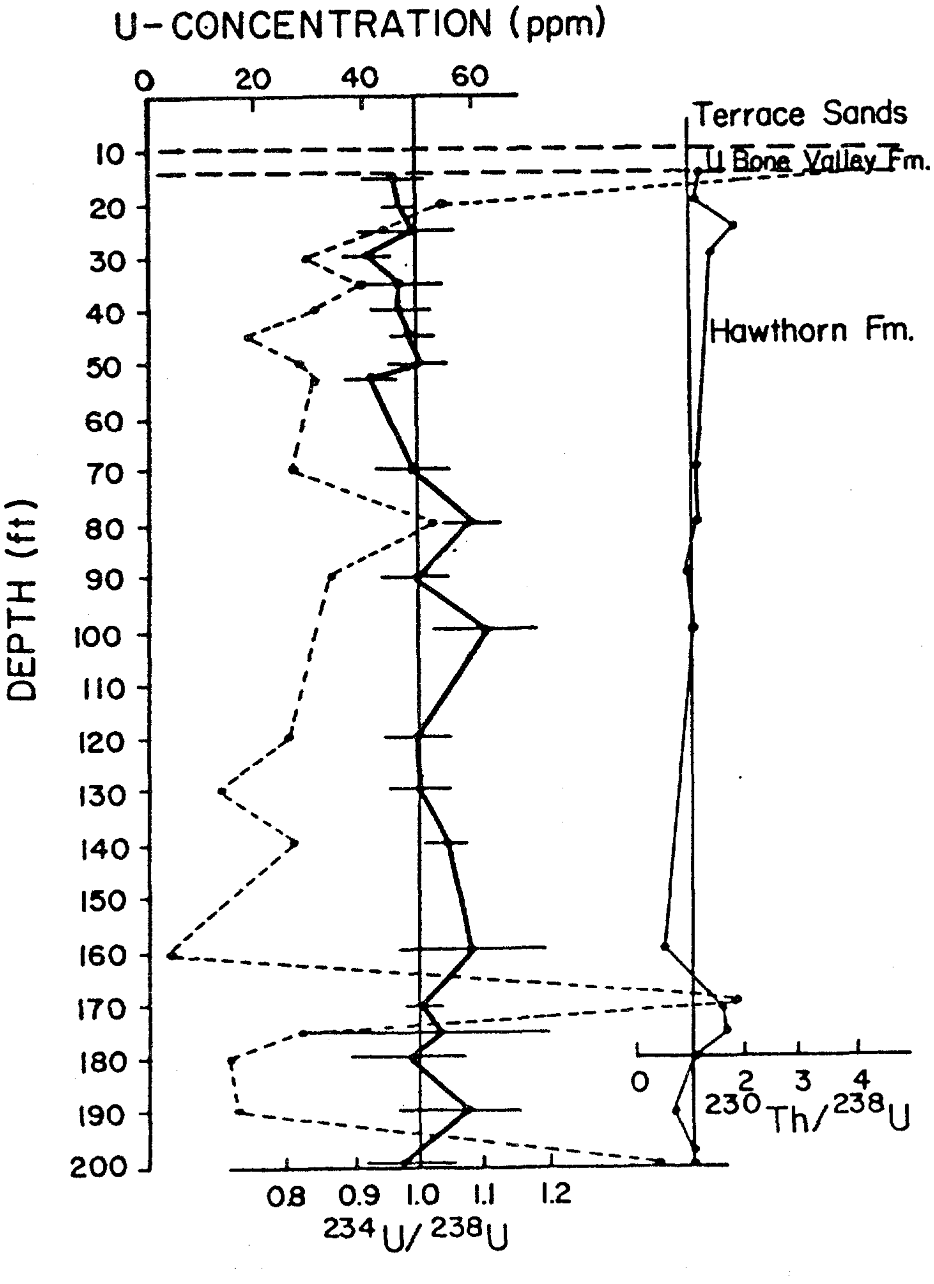

Fig. 3-22 Uranium concentration and isotopic ratios in core 13237.

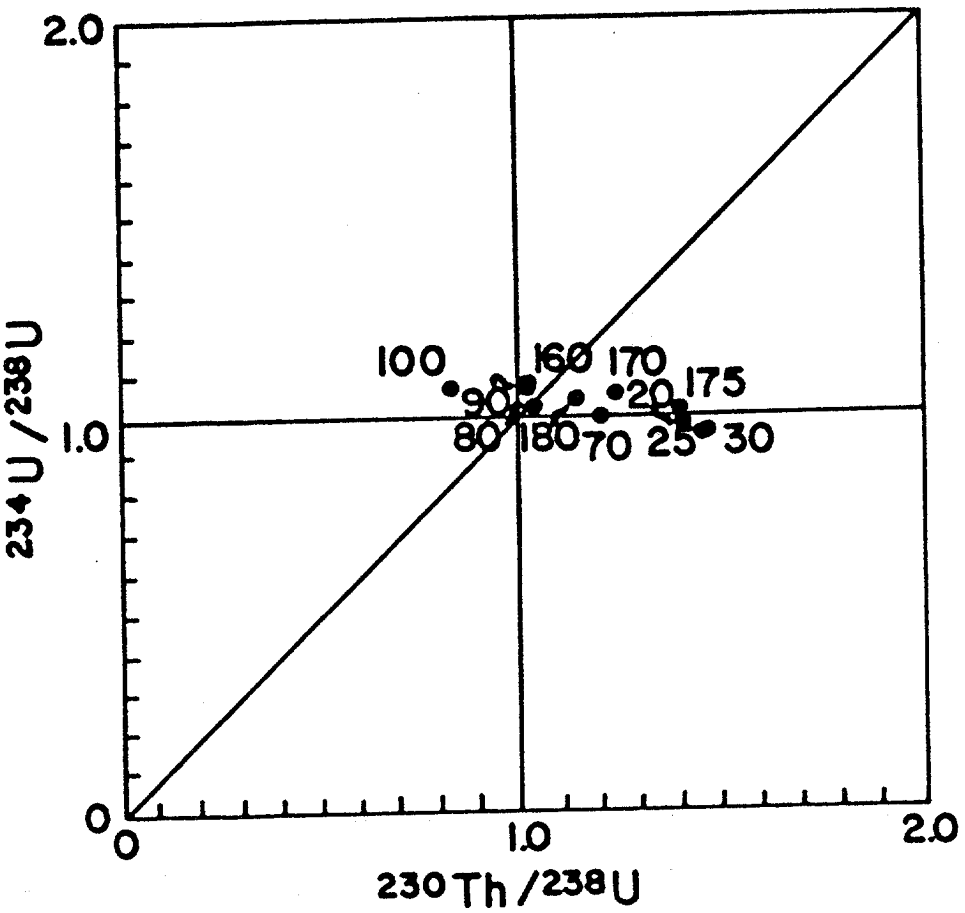

Fig. 3-23 Isotope ratios, running average with depth, in core 13237.

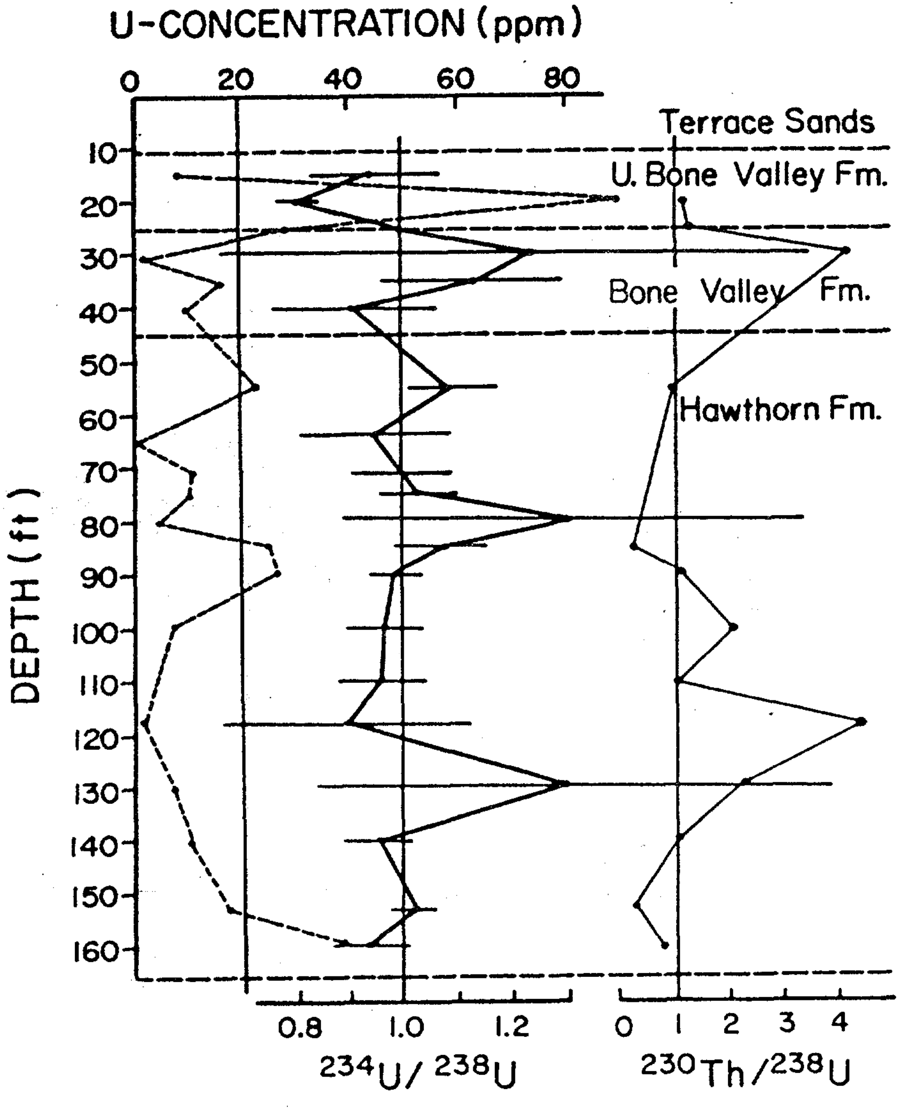

Fig. 3-24 Uranium concentration and isotopic ratios in core 13331.

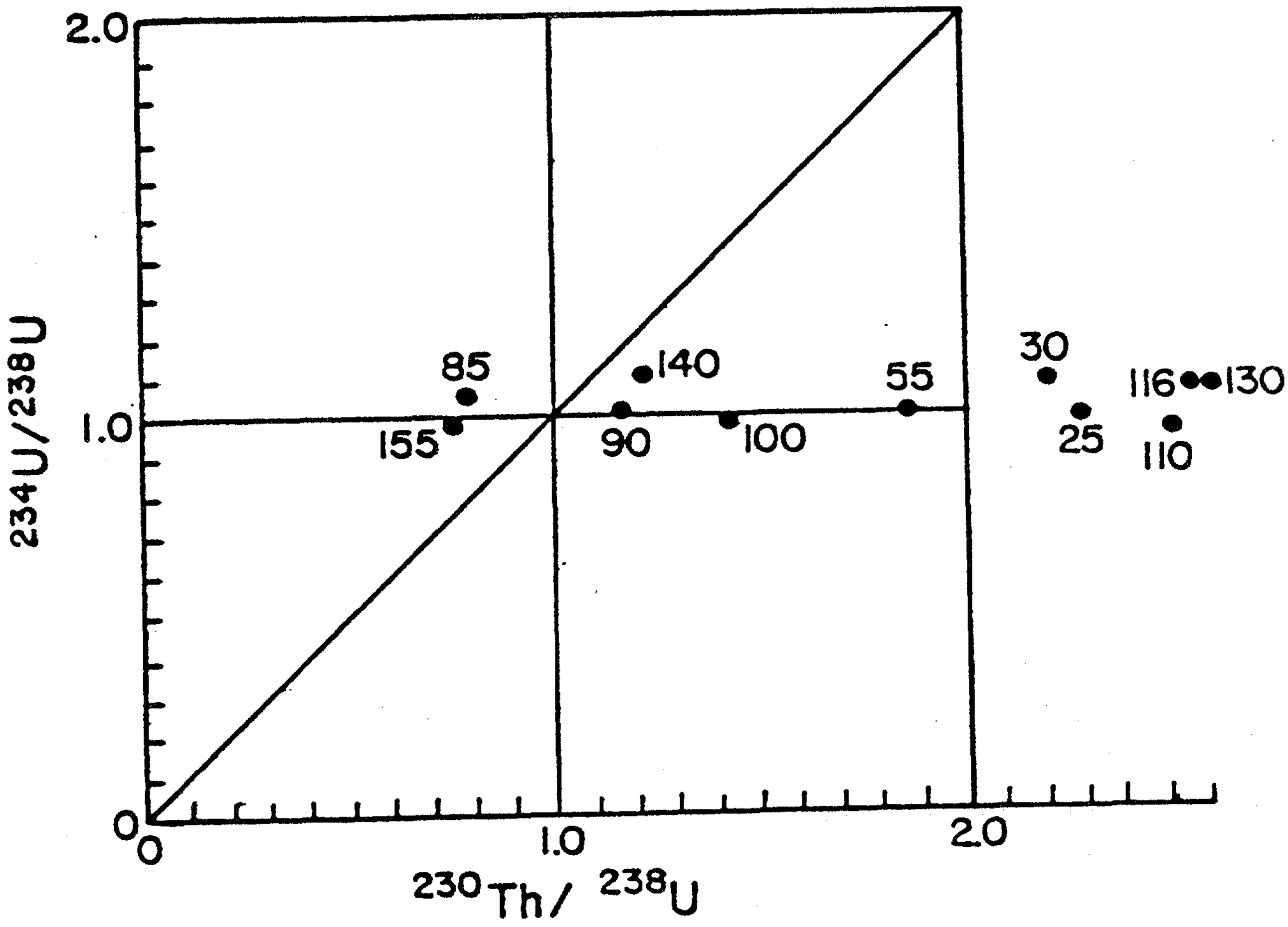

Fig. 3-25 Isotope ratios, running average with depth, in core 13331.

4. DISCUSSION

4.1 Ores and Rock Samples

Of the rock samples analyzed for this project, nearly all were collected from cores or from stratigraphic sections. As a result, in addition to a general collection of various horizons, we have a basis for drawing conclusions regarding radioelement mobilizations resulting from groundwater infiltration.

Of the five cores analyzed for thorium and uranium (Polk and Hardee Counties), the majority of samples were in the Hawthorn Formation; four cores were drilled through the Bone Valley Formation, and four included the overlying Terrace Sands. Considerable variation in uranium and thorium concentrations and isotopic ratios is apparent (Figures 3-16 through 3-25).

There appears to be no consistent trend of isotopic ratios in these cores, although somewhat higher uranium concentrations are apparent in the Bone Valley Formation relative to strata above and below. This supports the general view that the Bone Valley is an accumulation zone in which phosphorite is leached from above and redeposited below. To the extent that uranium is indicative of redistribution, we must conclude that the process is not uniform; various sections and various horizons have accumulated more uranium than others, in what appears to be an unpredictable manner.

In a general way, redistribution of uranium is indicated by the ^{230}Th/^{238}U ratio. Thorium-230 being the immobile daughter of parent uranium, a high ratio (greater than unity) denotes uranium leaching, and a low ratio uranium accumulation. (More precisely, the ratio of thorium daughter to its immediate parent uranium-234 should be used; however, the much greater variation between thorium and uranium as opposed to the variation between the two uranium isotopes makes this point somewhat academic.)

Because ^{234}U has a long half-life and is more mobile than ^{238}U (because of recoil-induced mobilization, discussed earlier) a low $^{234}U/^{238}U$ ratio may be taken to mean that there has been long-term stability in a zone of slight leaching, whereas its counterpart, a zone of slight accumulation, is indicated by a high $^{234}U/^{238}U$ ratio. A low $^{234}U/^{238}U$ ratio may also occur in a reducing environment if ^{234}U is being recoiled into solution.

Therefore a self-consistent pattern may be exemplified by zones of high $^{230}Th/^{238}U$ with low $^{234}U/^{238}U$ (leaching), and other zones of low $^{230}Th/^{238}U$ with high $^{234}U/^{238}U$ (accumulation). Plots of these ratios for the five cores (Figures 3-16 to 3-25) and for the aggregate (Figure 4-1) show no such consistent pattern, except in isolated zones.

The many samples in the 'inconsistent sectors' of the isotopic plots (Figure 4-1) must have a more complicated history. For example, samples in the lower left sector (low $^{234}U/^{238}U$ and low $^{230}Th/^{238}U$) may have experienced a relatively recent (on a time scale of 10^4 years) accumulation of uranium which had previously experienced a long period (on a time scale of 10^5 years) of slight leaching.

Given the climate, geomorphology, and stratigraphy of the central Florida phosphate district, such a history, or its converse, long term accumulation followed by more rapid leaching, is to be expected.

Similar scenarios are indicated by comparing the uranium concentration data with $^{234}U/^{238}U$ plots. In a long-term, stable, slightly leaching system, recoil-enhanced mobilization of ^{234}U would be the dominant factor in uranium isotopic variations, We would expect, in such a case, that the higher concentration phases would tend to have lower activity ratios, whereas the lower concentration phases would tend to have higher activity ratios. In other words, recoil-related processes should tend to cause the daughter to be more evenly distributed than the parent. In core W13078 (Figure 4-2) such a pattern is approximated, but at a relatively low confidence level. In the other cores a more inconsistent pattern is displayed; this is not so much an indication of randomness, but rather changes in the general geochemical leaching conditions at any one zone during the last 10^4 years.

In other stratigraphic sections (Tables 3-10 and 3-11) radium data as well as uranium data were obtained. Considerable disequilibrium is observed, in part because of the differing leaching characteristics of radium and uranium, and in part because of the immobility of the intervening daughter, ^{230}Th.

Low ^{226}Ra/^{238}U ratios occur in sediments from the Bone Valley and Hawthorn Formations in Sarasota County in conjunction with high concentrations of uranium. Disequilibrium may be expected on sediment surfaces while the interior would be expected to be in secular equilibrium. Whole rock analyses were performed on moderately-and-well indurated carbonates from these two formations. A sand-sized phosphate fraction was present in the samples but never exceeded 5%. Uranium concentrations in these sediments averaged 110 ppm and ranged from 16 to 378 ppm. Concentrations of this magnitude are seldom found incorporated within primary carbonates and the small phosphate fraction would not be expected to make such a large contribution. High uranium concentrations, coupled with extreme radium-uranium disequilibrium (^{226}Ra/^{238}U average is 0.551, suggest that the uranium has been adsorbed onto sediment grains as a secondary accumulation. Radium generated by decay of this accumulation is then recoiled into solution, or is preferentially leached. The ^{234}U/^{238}U ratios for these sediments are very close to unity, averaging 0.98.

Sediments analyzed from the Bone Valley and Hawthorn Formations obtained from a mine face at U.S.S. Rockland mine in Polk County (Table 3-11) show that approximate secular equilibrium exists between radium and uranium and between ^{234}U and ^{238}U, with activity ratios averaging 1.04 and 0.99 respectively. One sample from a leached zone in the upper Hawthorn shows marked radium-uranium disequilibrium ($^{226}Ra/^{238}U=0.60$). This zone is local and is not mined due to intense weathering. Another sample taken from the middle Bone Valley shows a radium excess with a $^{226}Ra/^{238}U$ ratio of 1.43. Uranium concentrations average 130 ppm for these sediments, and are attributable to phosphate mineralization. That samples showing both radium deficiency and excess are found suggests that both mobilization and adsorption of ^{226}Ra are occurring in this area.

4.2 Chemical Characteristics of Groundwater

The main factors controlling the chemical character of groundwater are the composition of soils, sediments and rocks that the water must pass through while recharging the aquifer or while flowing through the aquifer. The solubilities of these materials as well as the residence time of the water in the subsurface are other major factors. The presence of some constituents may also be attributed to human activities.

The length of time water is in contact with the aquifer material, the residence time, affects the amount of dissolved mineral constituents or total dissolved solids (TDS) in the water. Water just entering an aquifer or traveling through a highly transmissive portion of an aquifer, such as a cavernous zone, will not have been in contact with the aquifer materials long enough to develop a high total dissolved solids concentration. Water traveling downflow for a long distance from the recharge area in a slow flow system will show higher concentrations of dissolved chemical constituents. Water with a TDS concentration of over 500 mg/l is generally considered unpotable.

The Eh or oxidation-reduction potential of groundwater is mainly influenced by the rate of introduction of oxygen to an aquifer system in addition to the amount of circulation of oxygen and consumption of oxygen by bacterially controlled reactions. The rate of oxygen introduction depends on the oxygen content of recharge waters. If water enters the aquifer by percolating through an organic-rich soil it may be oxygen-poor by the time it reaches the aquifer. Because bacterially mediated reactions tend to occur very slowly, the circulation rate or residence time is important. In general, longer residence times mean a lower Eh.

Dissolved solid (TDS) concentrations in the surficial aquifer vary due to the open nature of the system and also due to its variable composition., It can generally be said that TDS concentrations are less than 200 mg/l in the northeastern portion of the study area and surficial waters exceed 200 mg/l TDS in the southwest. Near the coast and in tidally affected streams, concentrations may be quite elevated. Eh values are also quite variable depending on the nature of the soil; organic-rich soils or wetland areas produce reducing conditions in the surficial aquifer.

Groundwater within the secondary artesian aquifer shows an increase in total dissolved solids from northeast to southwest. TDS range from about 100-300 mg/l in Polk County and increase to between 300-1500 mg/l in Sarasota County. Eh values also vary from northeast to southwest. The majority of wells show oxidizing conditions within the aquifer in the northeast and oxidizing waters are less frequently found in the southwest. In Sarasota County all wells sampled in the secondary artesian aquifer show reducing conditions with most measurements giving readings of less than -200 millivolts.

The Floridian aquifer is, in general, more mineralized than overlying aquifers (Stewart, 1966). Total dissolved solids increase within the aquifer with depth. In Polk County, concentrations range from about 50 to 350 mg/l. Concentrations increase towards the southwest away from areas of direct recharge. In Sarasota County the Floridian is highly mineralized with total dissolved solids ranging from about 600 to over 2000 mg/l (Stewart, 1966).

Eh values in the northeastern part of the area where substantial recharge occurs show that oxidizing conditions exist in the upper zones of the Floridian. Waters become less oxidizing with depth. As water travels down dip to the south and southwest away from areas of direct recharge the upper zones of the Floridian become reducing. In Sarasota County, Floridian water is very reducing showing Eh values less then -250 millivolts.

4.3 Uranium and Radium in Ground Waters of the Phosphate District

The general pattern of uranium series nuclides in groundwater is somewhat variable, depending on particular geochemical conditions. However, a 'standard' pattern is well known:

1. Uranium itself tends to become less abundant in deeper aquifers and in the down-flow direction, primarily because of increasingly reducing conditions.

2. Insoluble daughters, such as thorium, are rarely present in solution in detectable amounts. (The accumulation of secondary thorium daughter down-flow, resulting from decay of mobile parent is of course not precluded.)

3. Soluble daughters such as ^{234}U and ^{226}Ra, tend to increase in relative abundance down flow, This is only partly the result of solubility differences. An important

factor in daughter nuclide solubility is what might be termed "recoil enhanced mobilization" (See earlier discussions, 1.3.3).

Given that the various members of the uranium series, including ^{238}U itself, tend to have a mobile history, much of their accumulation in aquifer rocks is located on grain surfaces. At such a site the alpha decay process tends to 'propel' a proportion (up to fifty per cent) of daughters into the aqueous phase. In the case of ^{234}U, the magnitude of this effect is quantified by the $^{234}U/^{238}U$ activity ratio, which in the absence of such recoil effects, would be 1.00.

Previous studies (Osmond and Cowart, 1976; Cowart, et al., 1978) have shown that the concentration and isotopic variations of uranium in groundwater are affected by the recharge rate of the local region. In highly transmissive areas, uranium concentration values decrease somewhat while the $^{234}U/^{238}U$ ratio remains near equilibrium. (The mobilization of previously ^{234}U-depleted uranium is indicated.) In less transmissive areas, the diagrammatic trajectory of uranium isotopes on a diagram like that of Figure 4-3 is toward lower concentration values and much higher A.R. values. Under such conditions, the recoil effects are more pronounced than the solubility effects.

The phosphate mining district is for the most part representative of a less transmissive region, as indicated in Figure 4-4. In fact, it appears that the more phosphatic the rocks ('mined region') the less transmissive the groundwater regime. In Figure 4-4 what appear to be anomalously low A.R. values for surface waters in both mined and unmined evolutionary curves are actually normal relative to statewide surface waters in low transmissivity regions. It is the deeper samples which exhibit a combination of somewhat higher than average A.R. values and higher than average concentration values.

The mining process itself appears not to have had a profound affect on the uranium mobilization system, as revealed by the isotopic trends. The exception to this statement might be with regard to the Floridian Aquifer in the immediate areas of phosphate mining, where enhanced concentration values appear to occur, both with respect to the general low transmissivity curves, and with respect to the secondary confined aquifer in the same areas. A possible explanation for this might be that general potentiometric draw-down, prevalent in the mining districts, has caused enhanced lateral flow and a corresponding increase in leaching of the aquifer rocks (not particularly phosphatic).

One way to look at the curves of uranium activity ratio versus uranium concentration is as an evolutionary system in which the daughter-to-parent ratio increases. This may be the result of recoil effects as the parent concentration decreases, the result of lesser solubility in less oxidized parts of the aquifer. Another way to look at the pattern is as a mixing system, in which the proportions of two end-member waters vary, these two being (1) the low concentration, high A.R. component, ever present in ground waters, and (2) the high concentration, low A.R. component produced by leaching where the waters are less reducing.

In Figure 4-5, where A.R. is plotted against reciprocal concentration, three flow systems exhibit similar patterns which fit precisely the mixing model. The curves of Figure 4-5 would appear as straight lines on arithmetic graph paper, thus satisfying the two-component mixing model equation. (Osmond et al., 1974).

However, the mixing and the evolutionary models are not mutually exclusive. In each of the three systems graphed, West and East Polk systems, and the Manatee-Sarasota system, there is some tendency for the down-dip samples to have the lowest concentration and highest A.R. values, consistent with the evolutionary model.

Radium concentration values in the phosphate areas exhibit more extreme variations than do uranium values

(Table 3-2). One generalization that can be made is that the amount of radium in groundwaters of this area is on average higher than normal, although not by any means extreme.

Figure 4-6 shows how both ^{234}U and ^{226}Ra increase relative to ^{238}U in the down flow direction. The effect is more pronounced for radium than for ^{234}U . This is in accordance with the standard daughter-parent model described previously, and can be taken to be indicative of a long-standing flow system in strata with dispersed phosphorite, especially in the surficial and secondary artesian aquifers. The variations in activity ratios displayed in Figure 4-6 are more affected by decreasing ^{238}U concentrations down flow than by increases in the daughter isotopes. The ^{226}Ra contents vary from 12 to 120 picocuries per liter.

Radium concentrations in the surficial aquifer average 3.5 pCi/l for mined areas in Polk County as compared to 2.5 pCi/l for mineralized/unmined areas and 5.3 pCi/l for unmineralized/unmined terrains. In the secondary artesian aquifer values average 2.9 pCi/l, 4.5 pCi/l and 6.0 pCi/l for mined, mineralized/unmined and unmineralized terrains, respectively. The majority of samples from unmined and unmineralized areas were located down gradient from mined areas. These higher concentrations along with excesses of ^{226}Ra seems to indicate that groundwater chemistry changes (i.e. higher TDS and more reducing conditions) down gradient have a greater mobilizing effect on radium than do mining operations.

4.4 Isotopic Balances

4.4.1 Principles

An important objective of this research project, and perhaps its most unique contribution, is to use the constraints imposed by the laws of radioactive equilibrium to quantify the distributions and mobilizations of uranium, thorium, and radium in both the natural and disturbed phosphorite terrains.

The guiding principle is simple: in any closed system (the laws of radioactive decay being immutable) the decay rate of each member of the series must be equal to that of the initial parent, and to each other (see section 1.3.2).

In the simple case of a dense uraniferous phosphorite nodule in impermeable strata, the result is equilibration of all daughters, given enough time relative to their half-lives. But in disseminated phosphorite subjected to leaching by groundwater, preferential loss of parent or daughter will produce disequilibration. This is not a case of violation of the laws of radioactivity; rather it means that three systems must be recognized: the leached system, in which the radioactivity of the parent exceeds that of the daughter(s), or vice versa, the leachate, in which the opposite disequilibration occurs; and the total system, including both the leached and the leaching phases, in which equilibrium is maintained. If the leached nuclide is redeposited elsewhere, then a fourth system, the accumulation phase, must be considered. By expanding the total system to include all of the disequilibrated parts, equilibrium can be assumed.

As an example, consider a leached zone above and an associated enrichment zone below, one in which the aqueous residence time is negligible. A balanced equation can be written:

$$M_l/M_2=AR_2-AR_t/AR_t-AR_1$$

which states that the amount of uranium in the one zone relative to the other zone is equal to the excess daughter activity ratio (e.g., $^{234}U/^{238}U$) of the second zone divided by the deficiency activity ratio of the first zone. AR is the total activity ratio, usually 1.00.

Less quantitatively, we can quickly recognize implausible geochemical models by use of such an equation. If the excess ratio of one phase is not reasonably in balance with the deficiency ratio of the other phase, then either (1) other significant phases have been overlooked, e.g., groundwater, or (2) the total system was out of equilibrium initially. But this has only a finite window of time in which it is applicable.

We will use this concept to test hypothesized models of natural and processed phosphorite disequilibration, to refine our estimates of representative elemental compositions and isotope ratios of various phases, and, ultimately to define geochemical processes of mobilization.

4.4.2 Elemental and isotopic balances in the natural system.

We can recognize several phases of the natural uraniferous phosphorite system in central Florida: the original phosphatic Bone Valley and Hawthorn formations (the possible origin of Bone Valley as an alteration phase of the Hawthorn is a topic beyond the scope of this study, at least to the extent that it may have occurred more than 10^6 years ago); leached Bone Valley and/or Hawthorn (undifferentiated here), enriched Bone Valley and enriched Hawthorn (where uranium and phosphorite, leached above have been redeposited below), and various leachate phases, including surface run-off, shallow groundwaters, and deeper groundwaters.

The uranium, thorium, and radium elemental and isotopic data for these phases are found in Tables 3-5 through 3-11 and in Figures 3-16 through 3-25. Some of this data is from previously published sources (Roessler, et al., 1979), but most is the result of analyses done as part of this project by Wagner and Humphreys. Other data, previously accumulated in the FSU uranium/thorium laboratory, some published and some unpublished (Kaufman, et al., 1977, Osmond et al., 1974, Cowart et al., 1978) are also included in the tables.

The natural disequilibration budget, Figure 4-7, was developed by an iterative process: first, setting up a plausible disequilibration model, second, averaging all available concentration and isotopic data for each unit, (Table 4-1) third, identifiying imbalances, fourth, revising the budget model, fifth, revising representative concentration and ratio data, and sixth, repetition of steps 4 and 5 until a consistent balance is achieved.

The model diagramed in Figure 4-7 is essentially unchanged from one initially proposed; the basic leaching and reaccumulation processes have been well studied by previous workers (Altschuler, et al., 1956; Altschuler, et al., 1958; Cathcart, 1956). The possibility of distinguishing between leached Bone Valley and leached Hawthorn was considered and rejected as being not only difficult to achieve but not particularly useful to an understanding of on-going geochemical processes. Whereas 'enriched' Bone Valley and Hawthorn could be identified by uranium concentration values, if not stratigraphically, both formations would be expected to yield similar low concentration values after leaching. With respect to model testing, we were better served by uranium values than by stratigraphic identification.

We actually identified 'original' Bone Valley and Hawthorn samples by a combination of stratigraphic position, uranium concentration, and isotopic ratios. Any sample that exhibited marked disequilibria was automatically assigned to another category rather than 'original'. A number of samples do exhibit the slightly daughter-deficient activity ratios (0.98) assigned the original Bone Valley and original Hawthorn in the model. This is not an uncommon situation; a slight loss of ^{234}U by recoil-related processes in the presence of ground water is often observed on a 10^6 year time scale, even in relatively impermeable rocks. The shorter-lived daughters, ^{230}Th and ^{226}Ra would, on this long time scale, be in equilibrium with ^{234}U.

Under near-surface leaching conditions of the sort currently prevailing in the central Florida region, uranium is geochemically mobile while thorium is not. This results in a decrease in uranium concentration, and an increase in the Th/U ratio in the leached zone ("aluminum phosphate beds"). At the same time, reaccumulation below results in enriched beds high in uranium and low with respect to the Th/U ratio. To the extent that this has been a long-term process, the ^{230}Th tends to re-establish equilibrium. This means that the uranium concentration is a better indication of the total amount of leaching or enrichment than is the ^{230}Th/^{238}U ratio.

The radium ratios suggest that radium is more mobile than thorium, and may in fact be leached to some extent in the enriched uranium zones as well.

The aqueous phases (right side of Figure 4-7) are characterized by normal uranium concentration values and not unusual daughter-to-parent activity ratios (the ^{226}Ra values for the deeper groundwater are on the high side of normal). The excess ^{234}U is the expected counterpart of the deficiency of ^{234}U in the solid phases. The same, in a more extreme way, is true for ^{226}Ra. The opposite holds for immobile ^{230}Th, which is only occasionally detectable in groundwater.

On the basis of the isotope-consistent model shown in Figure 4-7 we can conclude:

1. Uranium, on scales involving long times and short distances, is mobilized by groundwater, but little uranium is leaving the phosphate region in surface or groundwater.

2. Thorium is essentially immobile; the observed excesses and deficiencies in rocks result from the leaching and deposition respectively of parent uranium, followed by decay of these excesses or deficiencies at a rate governed by the ^{230}Th half-life, 75,000 years.

3. Radium tends to be leached from solid phases, with

the result that all leachate phases have significant excess of ^{226}Ra relative to uranium. This is especially true of the deeper phosphorite phases and the deeper aquifers.

4. Uranium-234 is in general deficient in the rocks and in excess in the leachate phases. This is primarily the result of recoil-related phenomena (see section 1.3.3). The resulting deficiency in the leached. zone is mostly balanced in the depositional zones below. However, the very long time required for development and decay of this disequilibrium (because of the ^{234}U half-life of 250,000 yrs) means that movement of elemental uranium from leached to accumulation zones will tend to 'transfer' the 'leached' activity ratio to the enriched phase.

4.4.3 Elemental and isotopic balances in phosphate mining and processing

Uranium series balance calculations for the mining and processing of phosphorite can be made more quantitative than the natural rock/groundwater system for several reasons: the elemental fractionations are more extreme, estimates of the amounts of the various phases are available, and on this time scale, decay and re-equilibration are not factors.

In this study, with its geochemical emphasis, we did not sample the mining and manufacturing phases as systematically as we did the natural phases (for example we analyzed many surface and groundwater samples near mined areas, but only a few clay settling area samples. Certain of the process samples we did study exhibited wide isotopic variations. Partly offsetting these negative factors in modeling mining effects was the positive factor that considerable published data were available.

The uranium series elements are budgeted in two ways in Table 4-2: (1) uranium concentration in parts per million and daughter nuclides in uranium-equivalents in parts per million. Uranium equivalent is an activity function: it is the ratio of the amount of daughter present to the amount that would be in equilibrium with one ppm of uranium. In the table, 80 ppm of uranium is present in the matrix, and the $^{230}Th/^{238}U$ ratio is 1.25, therefore the amount of ^{230}Th can be given as 80 x 1.25 or 100 ppm, U-eq;

(2) budget units of uranium equivalents, as distributed among the various phases. Plant input, matrix, is assigned 100 initial budget units of ^{238}U, with 105 and 125 units of ^{226}Ra and ^{230}Th respectively (corresponding to 1.05 and 1.25 activity ratios). Given that about 10% of matrix material is pebble feed (Roessler, et al., 1980) with a uranium concentration of 152 ppm, then the uranium budget amount in pebble is 100 x .10 x 152/80, or 19. This means that 19 units of the original 100 units of uranium in matrix are in the pebble phase. Similarly, the budget amount of ^{230}Th in the clay is 125 x .30 x 180/100 = 67.

All of the matrix material ends up as pebble, concentrate, clay, or sand, so that the distribution of radioelement budget units in these phases should add up to 100 in the case of uranium, and 105 and 125 in the cases of radium and thorium, respectively. Any left-over budget units must be assigned to effluent.

The concentration and budget values assigned to the various phases in Table 4-2 and Figure 4-8 were arrived at by reiterative modification of the original average concentration and activity ratio values. That there remained some uranium and radium budget units, but no thorium, in the effluents was in part a forcing requirement of the model. That more uranium than radium was left over, however, was a result and not a requirement, of the model. The data of Roessler, et al. (1980), when budgeted in this way, result in an unreasonably large amount of radium (40%) unaccounted for in the solid phases.

The available data for manufactured products, e.g., fertilizer and acid, are rather variable, but using pebble plus concentrate in a 1:2 ratio, and assuming that about half of the solid product ends up as gypsum, a reasonable balance can also be developed for this secondary stage of processing. The principal constraints here are the rather high Ra/U and Th/U ratios in gypsum, and the corresponding low ratios in the products.

In this secondary stage of processing, like the first, a larger proportion of uranium than radium ends up in effluent.

Figure 4-8 is a diagrammatic summary of the mining and processing radioelement budgets. Of 100 units of uranium in the matrix, 45 units ends up in clay, 8 in sand, 14 in effluent, and (by way of pebble plus concentrate) 30 units in products and 3 units in gypsum. Of 105 units of radium in matrix, 46 end up in clay, 10 in sand, 10 in products, 32 in gypsum, and 7 in effluents. Of 125 units of thorium-230 in matrix, 67 end up in clay, 10 in sand, 4 in products, and 44 in gypsum. Although not budgeted, the stable and more abundant ^{232}Th (present in matrix at about five ppm) would exhibit a budget unit distribution similar to ^{230}Th.

Table 4-1 Uranium Series Isotopes in Ores and Products of Phosphate Mining and Processing

Material	Uranium (ppm)	Radium (Ueq,ppm)	Ra-226/U-238 Activity Ratio	Th-230/U-238 A.R.	U-234/U238 A.R.
Overburden	4.8, 5.6, 61 (3)	4.9,6.1(3) 14 (2)	1.03,1.09(3)		.99,1.00(3) .85,1.3(4)
Hawthorn	16,19,34 (3)	14,14,16 (3)	.42,.72,.97 (3)		.97,.98,1.01 (3)
Matrix	113(1) 52(4) 7,15,65, 74,117,140, 189,378 (3)	116(1) 105(2) 67,131(3)	103(1) 1.03,1.04, .35,.96(3)	1.03(1) 1.53(4)	1.03(4) .88,.96,.99 .98,1.01, 1.02,1.03 (3)
Pebble	66,138, 209(3)	157(2) 214(3)	1.04(3)		.92,1.04, 1.05
Concentrate	89,106 (3)	96(2) 33,47(3)	.31,.53(3)		.99,1.04 (3)
Phosphoric Acid, Fertilizer	151,160, 173(1) 30,38(5)	15,14,58, 69(1)	.09,.09, .34(1)	.08,.15(5) .82,1.03(1)	1.04,1.05 (5)
Gypsum	5,34(3) 17(1)	88,151(3) 91(1)	2.6,30(3) 5.5(1)	2.2(1)	1.03(1)
Sand Tailings	15(1)	21(1) 14(2)	1.41(1)		
Organic Deposits	24,65(4)			.93,.14(4)	1.04,1.09 (4)

Table 4-1 (Cont.) Uranium Series Isotopes in Ores and Products of Phosphate Mining and Processing

Material	Uranium (ppm)	Radium (Ueq,ppm)	Ra-226/U-238 Activity Ratio	Th-230/U-238 A.R.	U-234/U238 A.R.
Clay	12(1) 66,79,302 (3) 9,57(4)	124(1) 88(2)	1.03(1)	1.09(1) .16,2.7,5.4 (4)	.99,1.03, 1.07(4) .81,.48,.96 (3)
Recycle Water from mining	1084,1818, 2874,5019, (1) 1.2,1.3,4.2 (3)	152,153, 226,237(1) .55,3.7(3)	.05,.08,.08 .14(1) .48,.88(3)	.013,.07 .22,.26 (1)	1.04,1.08, 1.12(3)

KEY:
(1) Roessler, et al.
(2) Guimond and Windham
(3) Humphreys, unpub.
(4) Wagner, unpub.
(5) Kaufman, unpub.

Table 4-2 <u>Uranium-Series Balances: Mining and Processing</u>

Material (Budget)	Uranium Conc. (ppm)	Budget	Ra-226 Conc. (U-eq)	Budget	Ra/U	Th-230 Conc. (U-eq)	Budget	Th/U
Matrix (100%)	80	100	84	105	1.05	100	125	1.25
Pebble (10%)	152	19	157	20	1.03	160	20	1.05
Concentrate (20%)	97	24	106	26	1.10	110	28	1.13
Clay (30%)	120	45	124	46	1.03	180	67	1.50
Sand (40%)	15	8	21	10	1.40	20	10	1.33
Sub-Total		96		102			125	
Effluent (1)		4		3	.75		0	.00
Second Feed (100%)	115	43	123	46	1.07	127	48	1.10
Products (phosphoric acid, fertilizer) (50%)	160	30	53	10	.33	20	4	.10
Gypsum (50%)	18	3	170	32	8.40	230	44	10.1
Sub-Total		33		42			48	
Effluent (2)		10		4	.40		0	.00

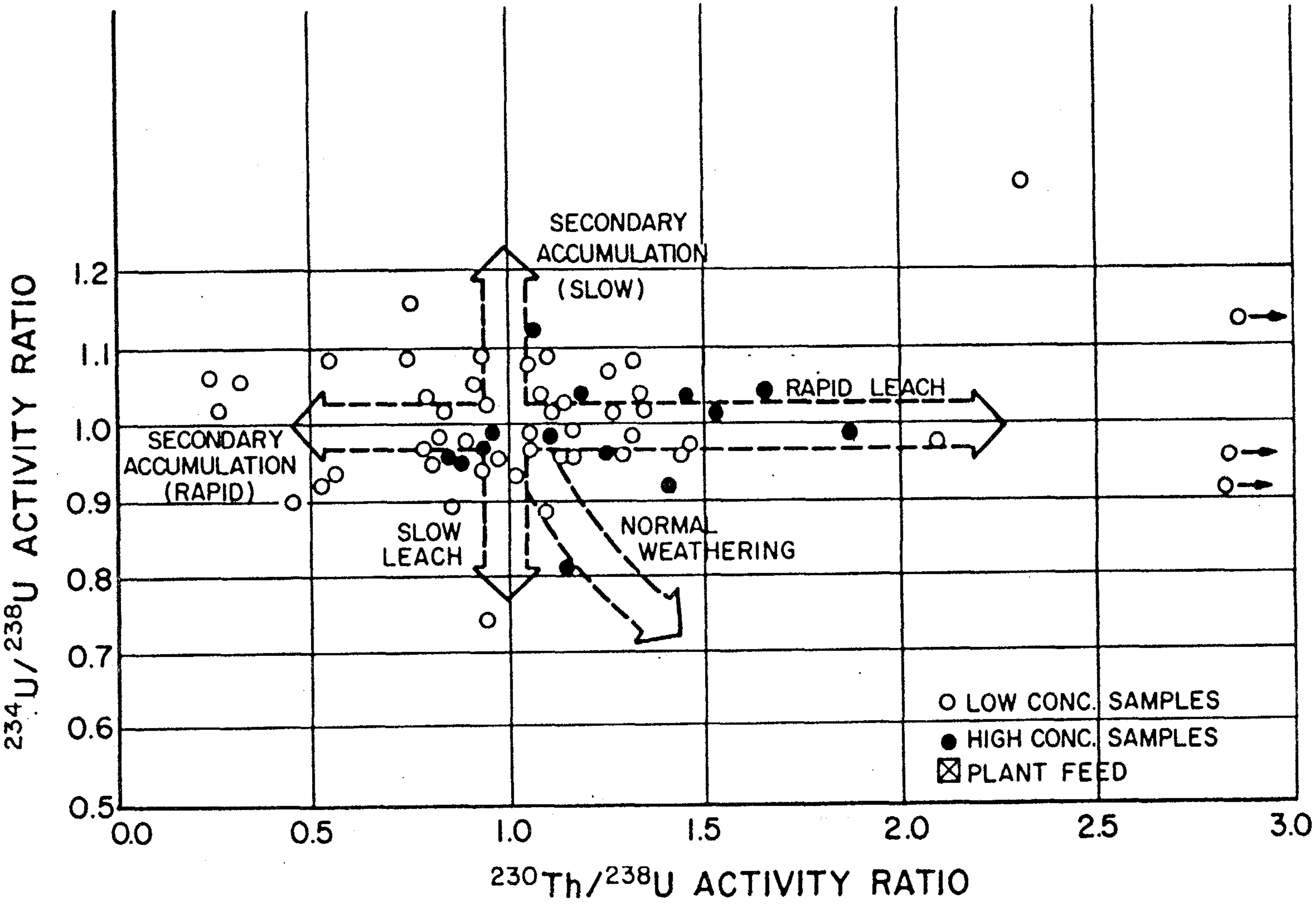

Fig. 4-1 Isotopec ratios in all rock samples, showing geochemical processes responsible for disequilibration. Equilibrium is at 1.0, 1.0.

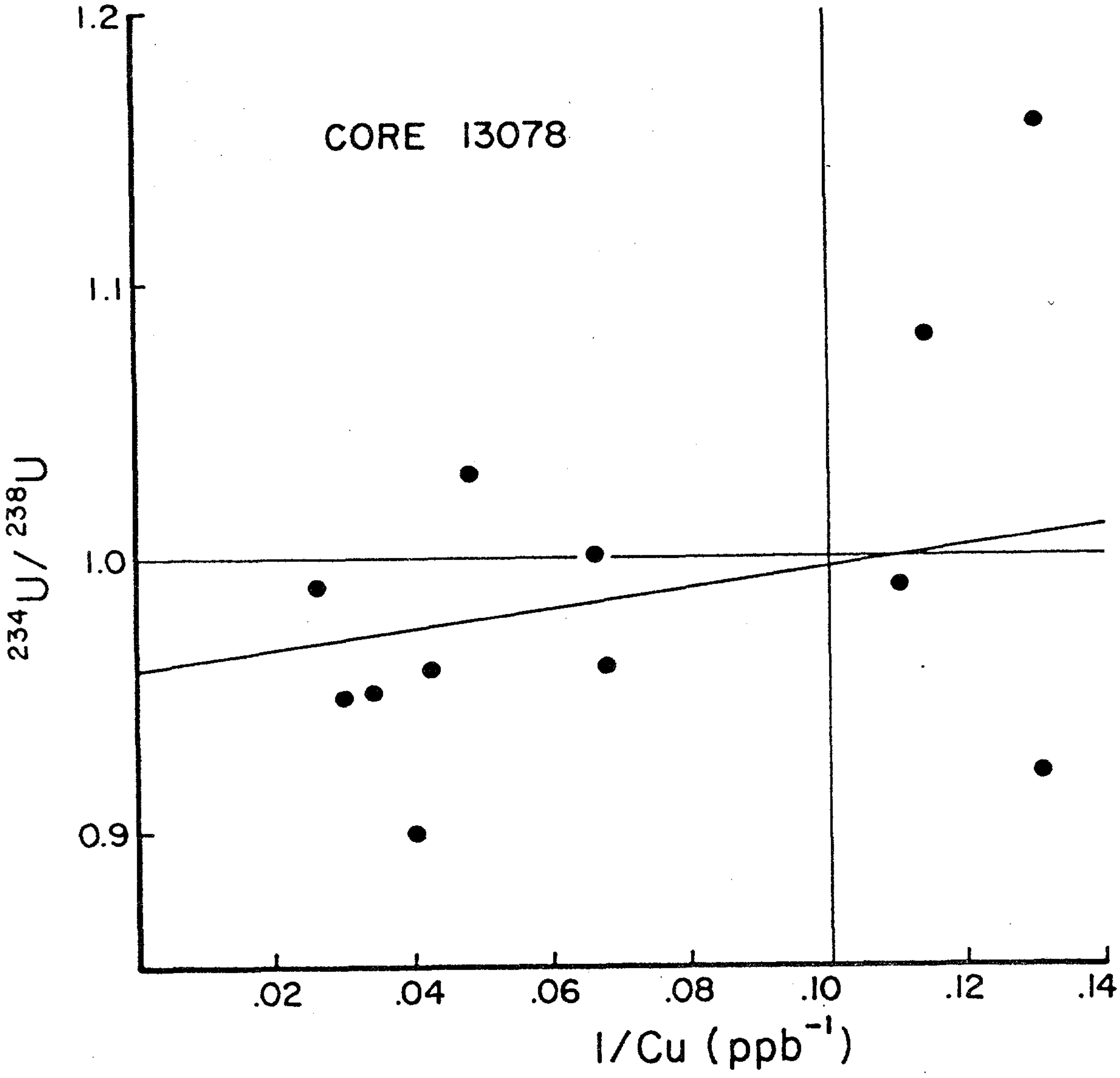

Fig 4-2 U-234/U-238 vs. uranium concentration in core 13078. Diagonal line is least squares fit.

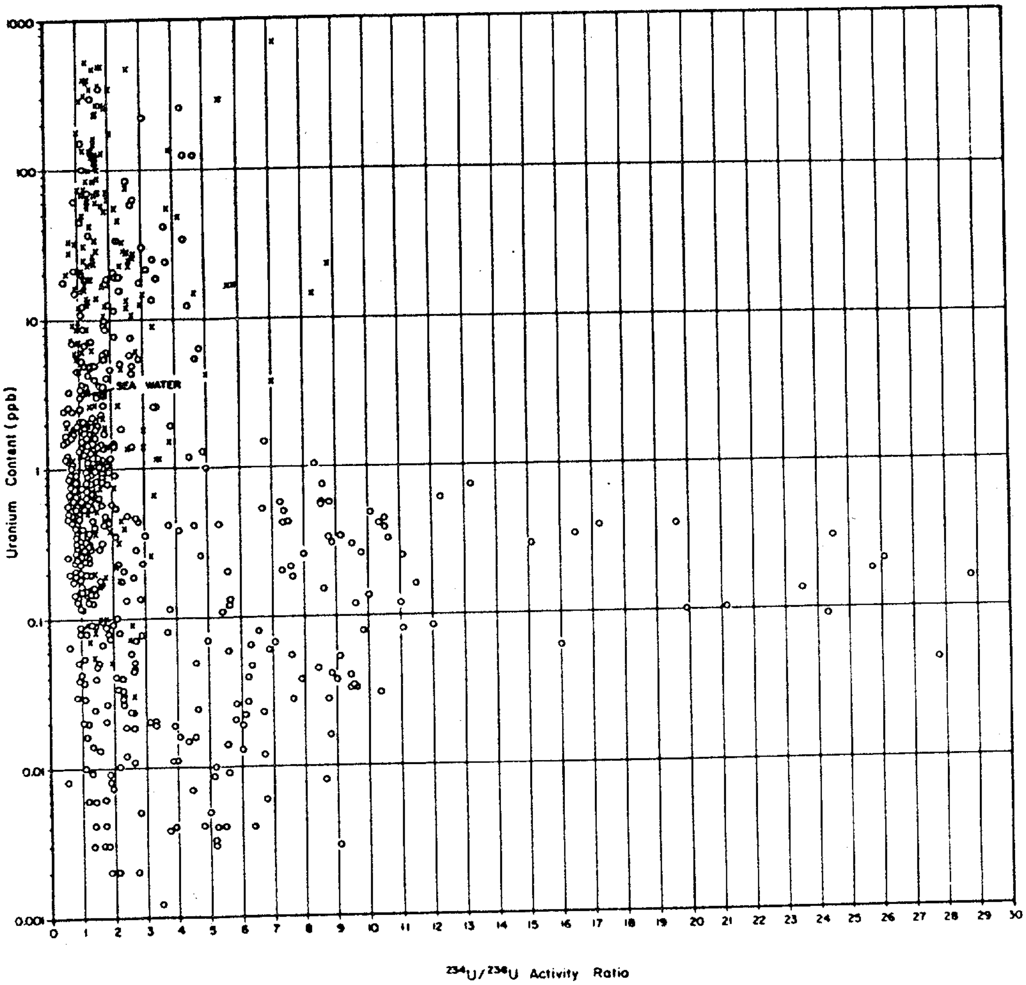

Fig. 4-3 U-234/U-238 vs. uranium concentration for water samples from all parts of Florida.

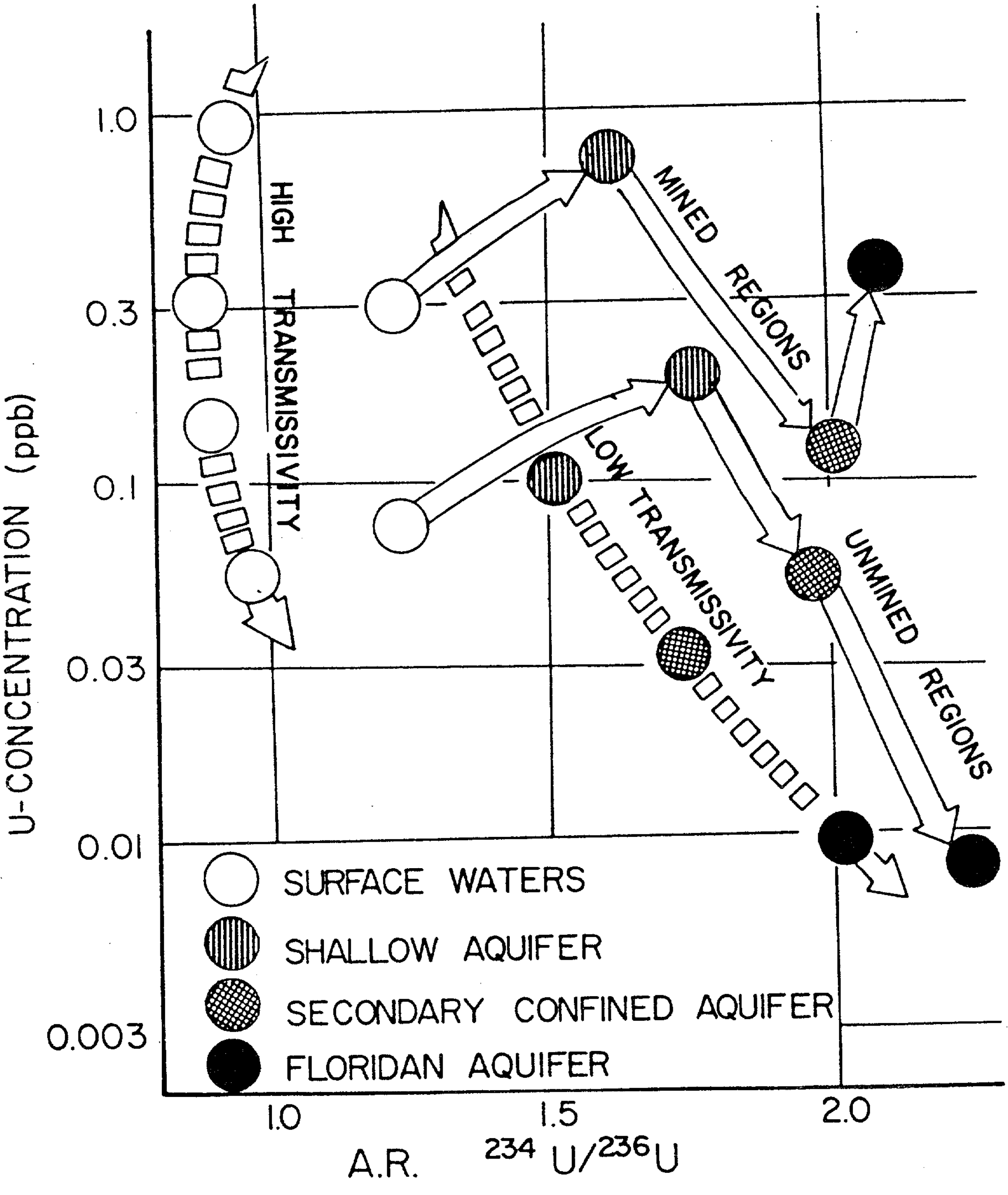

Fig. 4-4 Isotopic evolution of uranium isotopes in natural waters of Central Florida. Dotted lines: regional study of Kaufman, et al., 1977. Open arrows: this study.

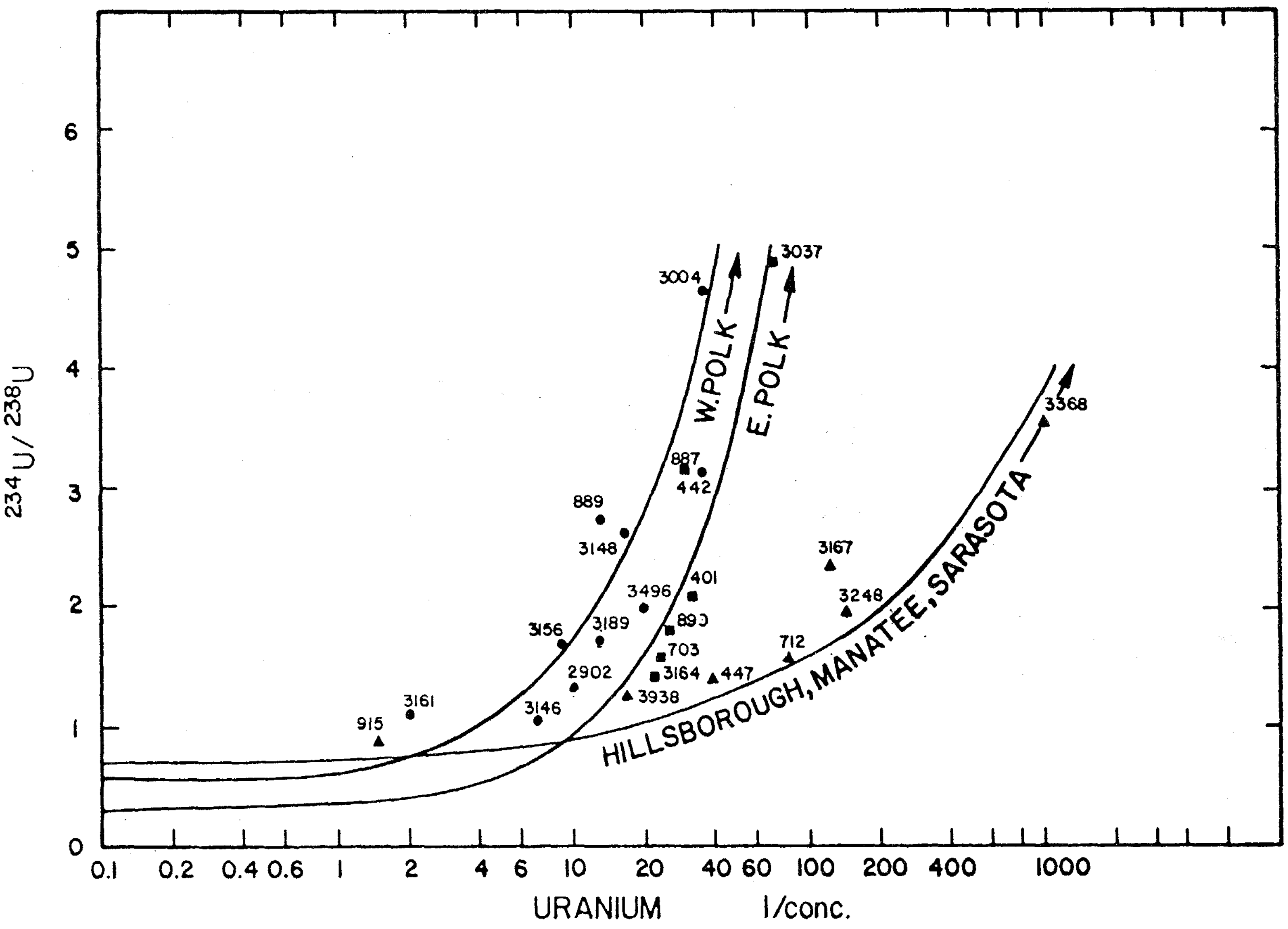

Fig. 4-6 Uranium concentration vs. U-234/U-238 trends in the Floridian Aquifer along three flow lines.

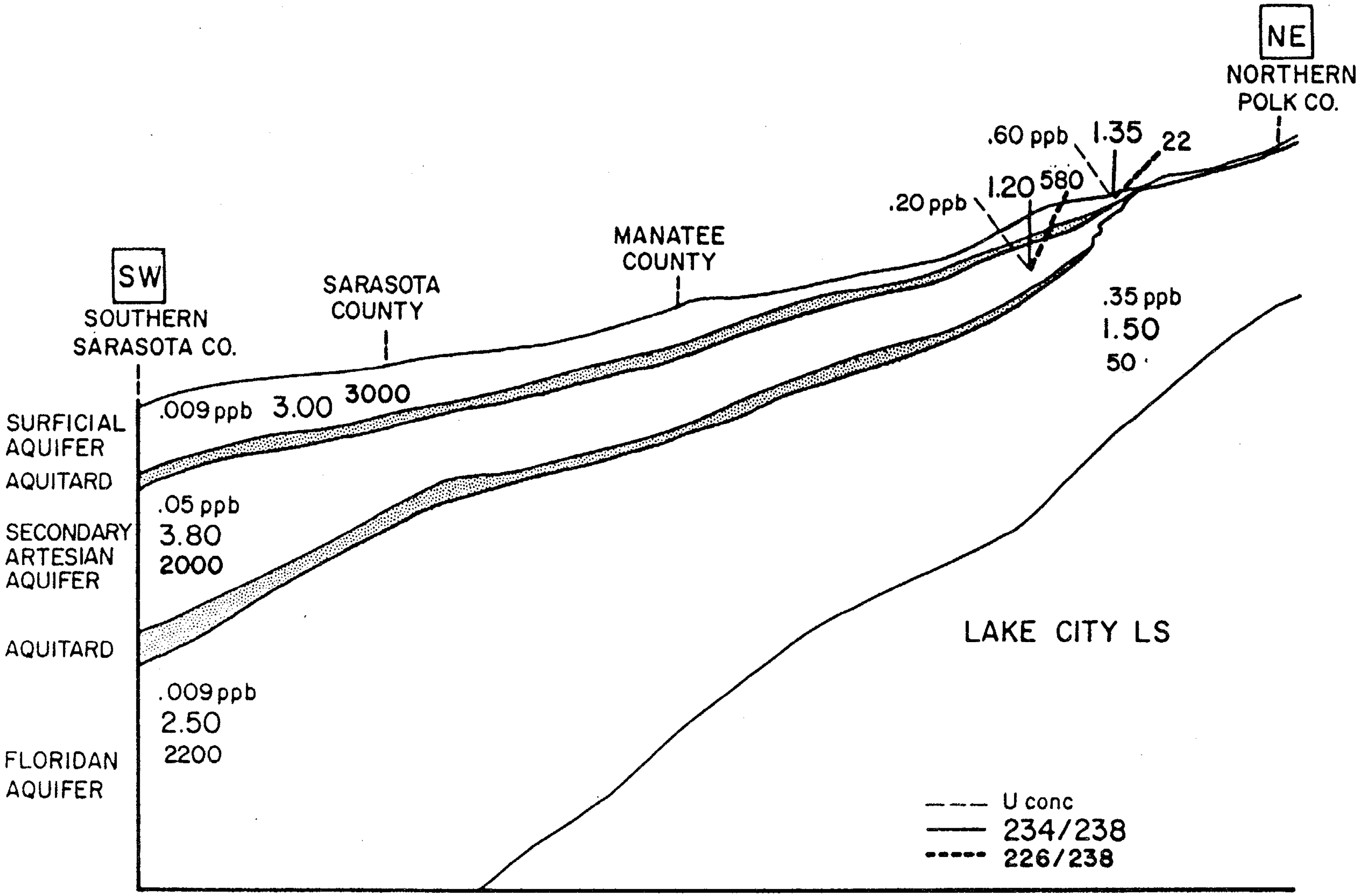

Fig. 4-6 Uranium and radium concentration and isotopic evolution along a NE to SW flow direction in three aquifers.

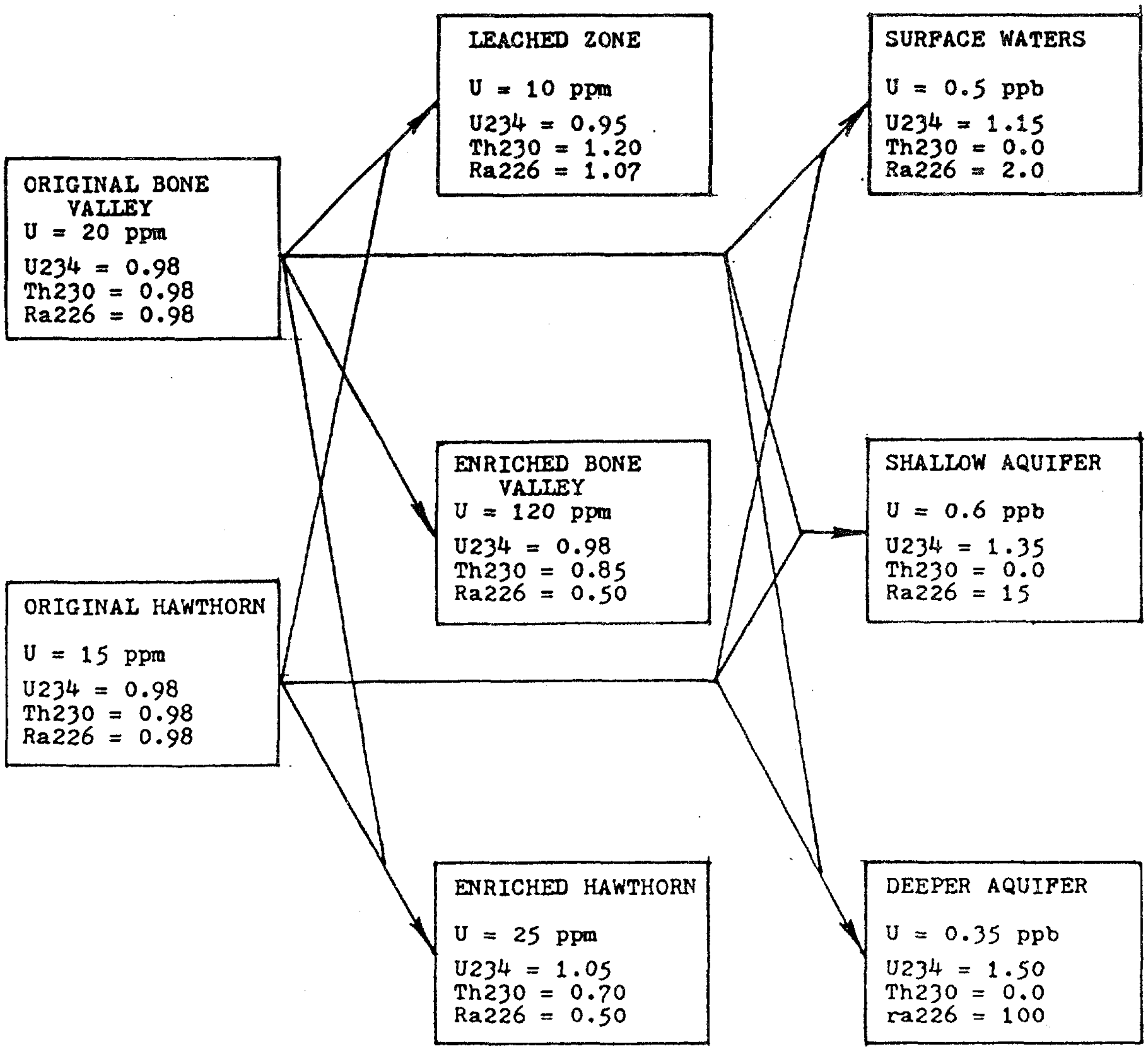

Fig. 4-7 Uranium concentration and uranium, thorium, and radium activity ratios in five phosphatic rock types and three aquifers. Representative values were obtained by iterative balancing of equilibrium equations.

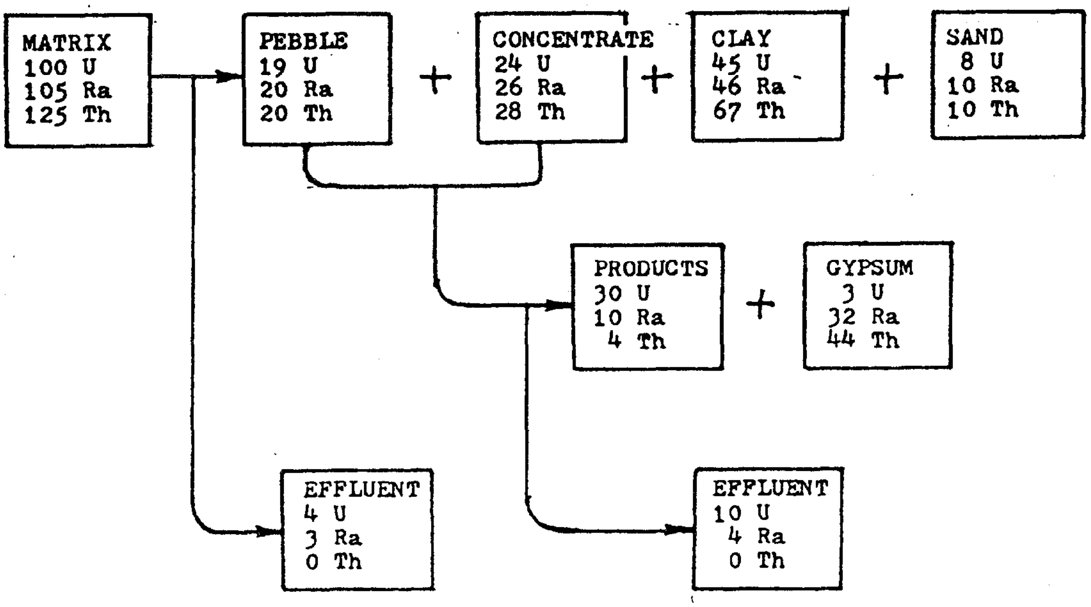

Fig. 4-8 Uranium, thorium, and radium balances in matrix, products, waste, and effluent. Values were obtained by iterative balancing of equilibrium equations.

5. SUMMARY

5.1 Rock Strata

Uranium is present at higher than normal concentration levels in the rocks of the phosphate mining district, the phosphatic strata, the Bone Valley and Hawthorn Formations. In a general way the uranium content is covariant with phosphorite content. In the calcium phosphate (apatite) horizons the uranium content is higher than in the aluminum phosphate horizons and in the overburden. Where the overburden includes an organic-rich soil horizon, elevated uranium concentrations are found.

The modest variability in $^{234}U/^{238}U$ activity ratios in all strata, and the extreme values in some horizons, show that these formations have been subjected to incipient weathering, i.e., gentle leaching by percolating waters on a time scale of 10^5 years at least. Uranium-234 has been mobilized by recoil-related processes in a slightly permeable hydrologic environment. For the most part, such mobilization is local, with some horizons serving as sources and others as sinks for the mobilized ^{234}U. On balance, however, more ^{234}U than ^{238}U is carried out of the rock system via flow-through groundwater, leaving a net average low activity ratio of about 0.98 in the rock column.

At some horizons, most notably in the overburden and Bone Valley horizons, uranium is being mobilized. This is indicated by the wide variation in $^{230}Th/^{238}U$ activity ratio. In general, a high ratio results from leaching (commonly in the overburden) and a low ratio results from re-accumulation (commonly in parts of the Bone Valley and Hawthorn formations). Whereas thorium is insoluble and immobile, uranium is mobilized, at least locally, by oxidized ground water. The bulk of the dissolved uranium is re-precipitated in nearby phosphatic strata, but a minor amount is carried away by percolating groundwaters.

Radium is also mobile in both the weathered and "unweathered" phosphatic strata, as shown by the extreme variability of both the Ra/U and Ra/Th ratios. To some extent these variations reflect daughter/recoil effects, rather than intrinsic solubility. The overall balance suggests a net loss of radium relative to uranium.

The mixed pattern of isotopic ratios and elemental concentrations together suggests that considerable mobilization is occurring in these horizons during the current geologic epoch (the last 10^3-10^4 years), but that for individual horizons, the geochemical circumstances have changed. Some zones that are currently being leached were previously (10^5-10^6 years ago) accumulation zones, and vice versa.

5.2 Regional Hydrology

While thorium is immobile and accumulates in weathered horizons, there is a net loss of uranium and radium to the hydrosphere. These losses are not great in the immediate areas of highly phosphatic strata; local groundwaters and surface waters have only moderate contents of dissolved uranium and radium, and the $^{234}U/^{238}U$ activity ratio is also quite moderate.

With respect to regional groundwater patterns, especially in the medium to deep aquifers, the leaching of radium is significantly higher than in average strata, especially in downdip portions of the aquifer where high ionic strengths (TDS) increase radium solubility. This, combined with the normal immobility of uranium in deep aquifers, results in very high Ra/U ratios. The $^{234}U/^{238}U$ ratios are also higher in the deeper aquifers, but this is consistent with ground waters in general.

5.3 Mining Operations

There is little hydrologic evidence that mining operations have caused significant increases in mobility of the uranium-series radioelements. The regional distribution of uranium and radium in groundwaters and surface waters appears not to have been disturbed. The one possible exception is in the Floridian Aquifer in the immediate areas of mining.' Higher than normal, though not exceptionally unusual, uranium concentration values are observed. We speculate that this may be related in some way to enhanced industrial water useage. Lowering of the regional potentiometric surface of the Floridian Aquifer (Stewart, 1966; Wilson,1977) may have promoted leaching of uranium from host rocks. The mining process does appear, on balance, to release uranium, and to a lesser extent radium from the matrix materials. However, such effluents are held in confining basins and the radioelements are ultimately coprecipitated on clay particles and sediment. A large proportion of the radioelements in phosphate ore ends up in the clay even before the adsorption process hypothesized above. We calculate that approximately 45% of the uranium and radium, and 55% of the thorium in the original matrix is in the clays that are removed by the washing process. In the gypsum residue resulting from further treatment stages are found 3% of the uranium, 30% of the radium, and 35% of the thorium of the original matrix. Less than 10% of the radium and thorium end up in fertilizer and chemical products, but as much as 30% of the uranium does.

Effluent waters, on average, are characterized by much lower Ra/U and $^{234}U/^{238}U$ ratios than the natural waters of the phosphate district. The lack of isotopic signals in water samples taken from the mining district is further evidence that the mining operations are not significantly upsetting the natural radioelement cycles.

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