

## THE THEORY AND USES OF NATURAL URANIUM ISOTOPIC VARIATIONS IN HYDROLOGY

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**ABSTRACT.** The dissolved concentration of uranium and the relative abundance of two uranium isotopes,  $^{234}\text{U}$  and  $^{238}\text{U}$ , vary over a wide range of values in natural waters. The concentration is controlled mainly by the redox potential of the environment and by  $\text{CO}_2$ . The mechanism of isotope fractionation is thought to be entrainment of  $^{234}\text{U}$  in the aqueous phase either by selective leaching of the solid phase or by direct recoil of the daughter nuclide. Ion exchange techniques and alpha-spectrometry permit the measurement of uranium at concentrations as low as  $10^{11}$  and the isotopic ratio to a few per cent. In oxidizing conditions the uranium isotopes behave in a chemically stable conservative manner such that separate groundwater sources may have identifiably different characteristics and mixing volume calculations may be made.

Other potential uses of these isotopes include radiometric dating, tracing of hydrologic systems, ore prospecting and earthquake prediction.

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### 1. INTRODUCTION

#### 1.1. General statement

This review is intended to summarize developments in the field of  $^{234}\text{U}/^{238}\text{U}$  disequilibrium studies since publication of Cherdyn'tsev's book, Uranium-234 [1], a period of roughly a decade. Our focus is on terrestrial hydrogeochemistry, so we will scarcely touch upon interesting allied topics such as  $^{230}\text{Th}/^{234}\text{U}$  age dating, marine geochemistry of uranium, and uranium ore geochemistry, except where they impinge on the principal subject.

A characteristic of this review is its emphasis on models: fractionation models, mass balance models, mixing models, uranium accumulation models, etc. Because we believe that the fullest application of uranium isotope geochemistry will require more than mere tabulation of data, we have endorsed or constructed models freely, with the hope that interest in disequilibrium methods will be stimulated and that both new models and new applications will be forthcoming.

#### 1.2. Radioisotopic geochemistry of uranium

There are three naturally occurring isotopes of uranium.  $^{235}\text{U}$  and  $^{238}\text{U}$  are unstable, but long-lived, isotopes formed in a primary stellar nuclear synthesis process. Because of their radioactivity, their abundances in the earth and the ratio  $^{235}\text{U}/^{238}\text{U}$  have been decreasing logarithmically through geologic time. Both isotopes are still easily detected and can be measured accurately in rocks

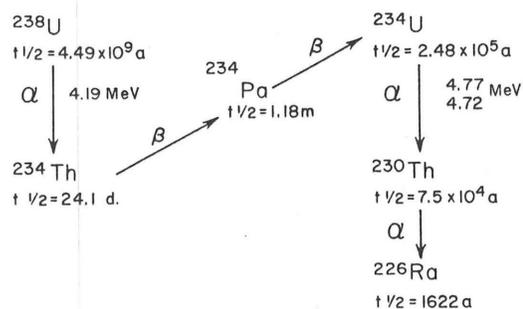


FIG. 1. The radioactive decay series of  $^{238}\text{U}$  through its first five daughters. Both  $^{238}\text{U}$  and  $^{234}\text{U}$  are alpha emitters and at secular equilibrium their alpha activity ratio is 1.00. The intervening daughters,  $^{234}\text{Th}$  and  $^{234}\text{Pa}$ , have a mean lifetime of about 36 days, which would appear to be too short to have any important role in the geochemical fractionation of the two uranium isotopes.

and in natural waters today. Because their minor mass differences preclude significant isotopic fractionation effects, their abundance ratio is everywhere the same: 1/137.5 [2]. Hamer and Robbins [3] found a maximum percentage deviation of 0.046 for this ratio in the samples they analysed. An interesting exception is the Gabon ore body in West Africa, where natural fission processes have resulted in a decrease in  $^{235}\text{U}$  [4, 5]. It is appropriate to begin our review with mention of this natural reactor, not only because of the presumed role of water in slowing the neutrons to energies suitable for fission, but also as the only example, by inference, of groundwater in which uranium occurs with an anomalous  $^{235}\text{U}/^{238}\text{U}$  ratio.

$^{234}\text{U}$ , the third naturally occurring isotope, is far too short-lived ( $T_{1/2} = 248\,000\text{ a}$ ) [6] to be a remnant of the earth's beginning. This isotope is regenerated in nature by decay from its parent  $^{238}\text{U}$  by way of the intermediate, short-lived nuclides,  $^{234}\text{Th}$  and  $^{234}\text{Pa}$  (Fig. 1). Therefore, the worldwide abundance of  $^{234}\text{U}$  is determined by the abundance of  $^{238}\text{U}$ .

The radioactivity of an unstable isotope is, by definition:

$$A = N\lambda \quad (1)$$

where  $A$  is activity in disintegrations per unit time,  $N$  is the number of atoms in the system, and  $\lambda$  is the decay constant, the fraction of atoms decaying per unit time. If secular equilibrium has been achieved between a radioactive parent and a radioactive daughter (a situation that has existed on a global scale for the uranium series since the earth was a few million years old), the activities of the two are equal:

$$A_p = A_d \quad (2)$$

where subscript  $p$  denotes parent and  $d$  denotes daughter. From Eqs (1) and (2)

$$N_p\lambda_p = N_d\lambda_d \quad (3)$$

and the abundance ratio, by atom count, of  $^{234}\text{U}$  to  $^{238}\text{U}$  is

$$N_d/N_p = \lambda_p/\lambda_d = 0.000056 \quad (4)$$

which is the relative peak height ratio expected on a mass spectrograph.

However, a more common measurement procedure is by alpha-ray pulse-height analysis, so that the relative abundance of these two uranium isotopes is usually expressed as 'activity ratio' (A.R. or  $\gamma$ ), which, according to Eq. (2), is exactly 1.00 for natural uranium in the world as a whole. Locally, closed systems older than  $10^6$  years also exhibit A.R.s of 1.00, e.g. unweathered igneous rocks or individual refractory crystals. Even in open systems, such as weathered minerals and in natural waters, significant deviations from this A.R. were not expected because of the small mass difference between the two isotopes (1.7%), and because of the very short half-lives of the two intervening daughters in the decay chain (Fig. 1). (The average lifetime of an atom in the interval between the decay from  $^{238}\text{U}$  to the birth of  $^{234}\text{U}$  is 36 days.)

Thus, interest was generated by the discovery two decades ago that large deviations in the A.R. commonly occur in nature [7]. The greatest variations were seen in ground and surface waters. Figures 2 and 3 display the remarkable variability of both uranium concentration and  $^{234}\text{U}/^{238}\text{U}$  isotope ratio in natural waters. The extreme variations in concentration reflect, in part, the fact that uranium occurs in two valence states with divergent solubility functions. The range of variation of the  $^{234}\text{U}/^{238}\text{U}$  ratio shown in Figs 2 and 3 can best be appreciated by contrasting with the variations observed in most naturally occurring isotopic pairs, usually measured in parts per thousand.

Groundwaters exhibit much greater variations in A.R., especially noticeable at low concentrations, than do surface waters. This suggests that the variations are related to a solid-liquid interface phenomenon, dependent in some way on the radioactive generation of  $^{234}\text{U}$  and the apparent capability of the surrounding water to promote isotope separation. The major sources of fractionated uranium appear to be pore waters in weathered rocks, soils and aquifers; each sub-surface system contributes its unique concentration and A.R. to the surface run-off systems, and finally to the major reservoir of dissolved uranium, the oceans. This last reservoir is very large, so that the discovery that it has an excess of  $^{234}\text{U}$  of about 15% was perhaps the most surprising aspect of all [24, 25]. We may infer, from Eq. (2), that the large accumulation of excess  $^{234}\text{U}$  in the oceans is balanced by an equal reservoir of  $^{234}\text{U}$ -deficient uranium elsewhere. We will discuss at length the causes of uranium isotopic fractionation and its significance to global uranium balances in later sections.

The unique behaviour of uranium in its isotopic geochemistry may be ascribed to two primary factors, one chemical and one radiological.

Chemically, uranium has two natural valence states, 4+ and 6+. In the 4+ state its ionic radius is about 1.05 Å, and its ionic potential (charge/radius) is about 4 [26]. This is its normal ionic condition within the solid earth, where it behaves as a large lithophile cation. The high concentration of uranium in the crust relative to its abundance in the earth's interior, despite its being the heaviest of all naturally occurring elements, is an important fact in geophysical considerations of the earth's heat balance. In the 6+ state, uranium's ionic radius is about 0.80, and its ionic potential is about 7 [26]. This is its normal ionic state in surficial oxidizing waters and in many secondary minerals. The greater solubility of the 6+ ion is due in part to its tendency to form uranyl di- and tri-carbonate anions and thus the boundary between the two ionic states on a fence diagram depends not only on redox conditions but also on the pH and the partial pressure of  $\text{CO}_2$  in the system [27–29]. Uranium is mobile under oxidizing conditions, but immobile under reducing conditions. Although the soluble and complexed condition is the normal state of uranium in surficial systems, a number of environments do exist in which uranium is reduced and immobilized: humic soils, anoxic basins and at the reducing and/or sorption barriers of sandstone aquifers.

Radiologically, all three naturally occurring uranium isotopes are alpha emitters. This means that uranium can be readily detected and accurately measured even at very low concentration levels. More significantly, the radiogenic origin of  $^{234}\text{U}$ , in concert with the alternative valence states, leads to unusual isotopic fractionation possibilities, which appear to be exploited quite efficiently by nature near and at the earth's surface.

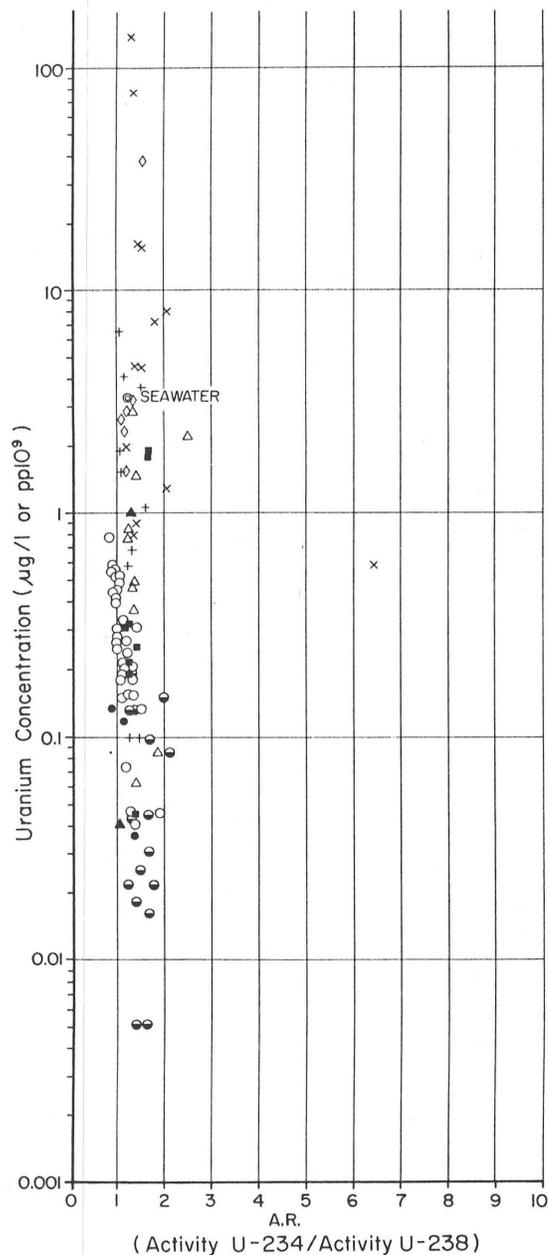


FIG. 2. Distribution of uranium concentration and  $^{234}\text{U}/^{238}\text{U}$  alpha activity ratio (A.R.) for most published analyses of surface waters. (Both parameters must have been determined on the same sample in order to be included here.) The purpose of the figure is to show the extreme variations in uranium concentration (shown on a log scale) and in the isotopic ratio (which can be compared with stable and/or non-radiogenic isotope variations). Nevertheless, these variations are less than those observed in groundwater (see Fig. 3).  $\circ$  [8];  $\bullet$  [9];  $\blacksquare$  FSU, rivers and lakes in North America, this review;  $\triangle$  [10];  $\times$  [11];  $\odot$  [12];  $+$  [13];  $\diamond$  [14];  $\blacktriangle$  [74];  $\bullet$  [192].

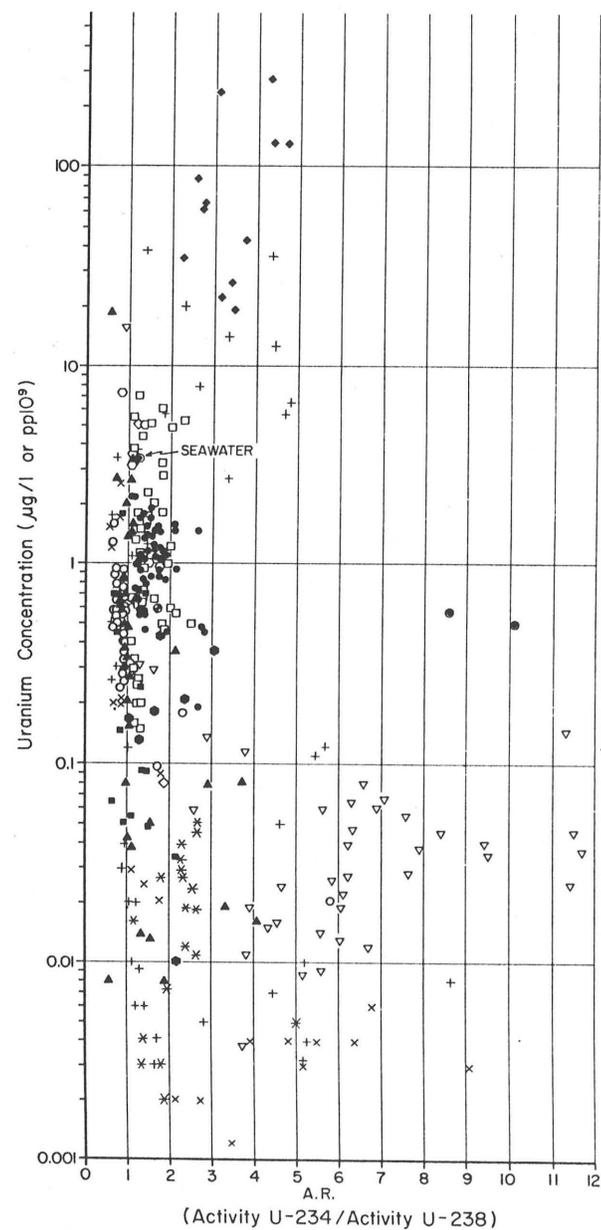


FIG. 3. Distribution of uranium concentration and  $^{234}\text{U}/^{238}\text{U}$  alpha activity ratio (A.R.) for most published analyses of underground water. (Both parameters must have been determined on the same sample in order to be included here.) The range of values in both parameters is greater than for surface water (see Fig. 2). It would appear to be of particular significance that A.R.s less than 1.00 are more frequent at medium concentrations, and that very high A.R.s occur at low concentrations.  $\circ$  [8];  $\bullet$  [15];  $\square$  [16];  $\blacksquare$  [17];  $\nabla$  [10];  $\blacktriangle$  [9];  $\diamond$  [11];  $\blacklozenge$  [18];  $\circ$  FSU, unpublished, Hosston Aquifer;  $\bullet$  [19];  $\times$  [20];  $\oplus$  brine [17];  $\otimes$  brine [21];  $\ast$  [22];  $+$  ore-bearing formation [23].

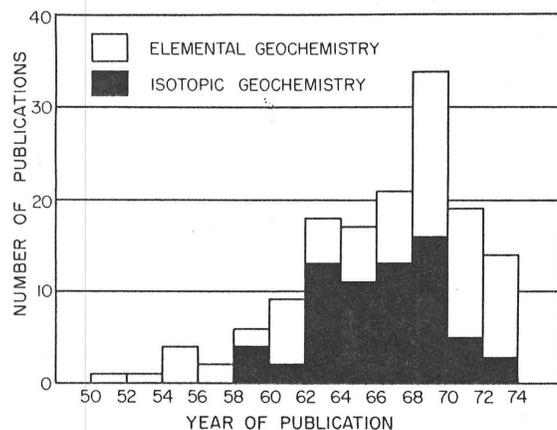


FIG. 4. Histogram showing the increase in interest in uranium hydrogeochemistry in the 1960s.

Finally, the average life of a  $^{234}\text{U}$  atom ( $1/\lambda$ ) is 360 000 years, which means radioactive decay is not a factor when A.R.s are used to trace fast-moving surface waters or shallow groundwaters; but it may be a useful indicator of time scales in studying very deep groundwater systems, certain sediments, and major steady-state reservoirs such as the oceans. The decay scheme and nuclear constants for uranium are summarized in Strominger et al. [6].

The general hydrogeochemistry of uranium has been reviewed by Adams et al. [30], Lisitsin [27], Vinogradov [31], Kolodny [32] and Rogers and Adams [2]. The most comprehensive discussion of the isotopic geochemistry of uranium, based on the international literature through about 1967, can be found in the book by Cherdyntsev [1], who is generally acknowledged to have been the discoverer and a leading investigator of the phenomenon of uranium isotopic disequilibrium.

Figure 4 gives a histogram showing the increasing interest in uranium hydrogeochemistry in the 1960s. Whereas the major increase in isotopic studies occurred in the early 1960s, the largest increase in elemental (non-isotopic) geochemistry occurred a few years later. The apparent decline in isotopic publications in the 1970s may be real in part, and in part due to the time lag in locating titles and translations.

### 1.3. Early studies

The fractionation of  $^{234}\text{U}$  and  $^{238}\text{U}$  in nature was first reported by Cherdyntsev et al. in 1955 [7]. Baranov et al. [33] and Starik et al. [34] were able to observe uranium isotope shifts produced by leaching under laboratory conditions. Chalov [35] noted the tendency of residual materials to be deficient in  $^{234}\text{U}$  and redeposited materials to contain excess  $^{234}\text{U}$ .

Thurber [24] found that the oceans, the ultimate destination of most surface waters, have a A.R. of about 1.15. This relative abundance ratio was found by many others to be essentially constant for all open ocean waters [36–40].

Consistent with the report of uranium disequilibrium in the oceans were the findings that an excess of  $^{234}\text{U}$  was also present in rivers [11, 41–45]. It had earlier been reported that small mountain streams had A.R.s greater than unity [46].

Lakes were sampled in the USSR [41–45] and attempts were made to determine the absolute age of the closed drainage basins of Lake Issik-kul, Lake Chatyr-kul and the Aral Sea. Values for lakes in the Great Basin area of the western United States of America were reported by Kaufman and Broecker [47] and by Thurber [11].

Groundwaters, sampled from both boreholes and springs, were studied in many different terrains: bedrock, detrital deposits, peat bogs, volcanic regions, and thermal regions by Cherdyntsev et al. [40, 44, 48], Hill and Crookall [49], Thurber [11], Kazachevskii et al. [41], Isabaev et al. [46], Rosholt et al. [50] and Sakanoue and Hashimoto [51].

The mechanism by which the two isotopes are separated under natural conditions was the subject of much discussion by these early workers as well as by others [52–63]. Interphase isotope equilibration between liquids and solids was studied by Syromyatnikov [64].

Investigations of uranium isotope variations associated with near surface accumulations of uranium were conducted by Syromyatnikov and Tolmachev [65], Ivanov and Kudryashova [18], Syromyatnikov [66], Rosholt et al. [50, 53–57] and Dooley et al. [60].

## 2. ANALYTICAL TECHNIQUES

### 2.1. Field and laboratory procedure

The acquisition of uranium isotope data from natural waters entails several steps that seem to be common in the procedures used by various investigators. First, because of the low abundance of uranium in all but a few subsurface waters, a **preconcentration** step must be used. Secondly, the **uranium** must be separated from those compounds or elements that would interfere with the uranium analysis. Finally, a **thin source** suitable for alpha counting must be prepared so that the relative abundances of  $^{234}\text{U}$  and  $^{238}\text{U}$  and the total uranium concentration can be determined.

An excellent recent review of the various procedures available for effecting each of these three steps is found in Veselsky [67]. Other more or less detailed outlines of specific procedures concerned with uranium isotopes in water have been reported by Umemoto [68], Edwards [69], Rydell [9], Van and Lalou [70], Korkisch and Godl [71], Mangini [72], Brown [73] and Briel [8].

Although some early workers attempted to extract and measure uranium from waters quantitatively, nearly all determinations made today use a yield tracer isotope, or 'spike', such as  $^{232}\text{U}$ . This spike, an alpha emitter that does not occur naturally, is added to the sample at the time of collection, or on arrival at the laboratory. Procedures that involve field extraction of uranium may be suspect unless care is taken to ensure spike equilibration with the natural uranium isotopes.

If a sample is not to be processed in the field, the water should have reagent grade hydrochloric or nitric acid added to prevent the precipitation of iron as ferric hydroxide in the collecting container. Addition of enough acid to cause a pH of approximately 1.0 is recommended.

It is the authors' observations that clear non-turbid well or spring water will give the same uranium data whether it is processed unfiltered, filtered with paper, or with millipore type (0.45  $\mu\text{m}$ ); filtering is usually a necessity for surface waters, however.

#### 2.1.1. Preconcentration methods

(1) *Co-precipitation.* About 15 milligrams per litre of iron in the form of nitrate or chloride is added to the sample.  $^{232}\text{U}$  spike is added in known quantity. The sample is shaken periodically for several days to promote isotopic equilibration. The sample is heated to boiling and the pH is then increased to approximately 10 by the addition of ammonium hydroxide. Uranium, as well as many other elements, co-precipitates with the ferric hydroxide. When cool, the floc is separated from the supernatant liquid by decanting and centrifuging. Separation of most of the

iron from the uranium and thorium can be accomplished by dissolving the floc in 8N HCl and extracting the iron with isopropyl ether.

The  $\text{Fe}(\text{OH})_3$  co-precipitation method of pre-concentration is currently the most widely used [8–10, 74–77].

Uranium can also be co-precipitated with aluminium phosphate in slightly acid conditions [69]. After decantation, the precipitate is dissolved in acid and the uranium and thorium are selectively extracted into ethyl acetate with magnesium nitrate being used as a salting agent.

(2) *Extraction.* Procedures for extracting uranium from natural waters with an ion exchange resin [13, 71, 78] and cation exchange resin have been used [52, 67, 79, 80].

Veselsky [67] reports a higher yield for this method than for co-precipitation methods. An advantage is that samples of large size (800 litres or more) can be processed at or near the site of collection, thus obviating the need to transport large amounts of water. A disadvantage is the problem of spike equilibration.

The use of charcoal to adsorb uranium from water is described by Van and Lalou [70], and Alekseev et al. [16].

### 2.1.2. Separation

In order to process a sample for alpha particle analysis it is necessary to separate the uranium from interfering elements, both radioactive (thorium and radium especially) and those that would cause decreased yield during the electroplating procedure and/or decrease the resolution of the alpha energy peaks (e.g. iron). The separation of the radioelements usually involves a method in which ion exchange resins are used. Many of the separation schemes include a step wherein uranium (and iron) are separated from thorium and radium by the adsorption of uranium on the anion resin in a strong hydrochloric acid environment (7–9N). Thorium, radium and various alkalis and alkaline earth elements are not adsorbed. Uranium is desorbed by washing with 0.1N HCl.

Alternatively, separation can be effected by solvent extraction using ethyl acetate [70, 81] or tri-butyl phosphate [22].

### 2.1.3. Alpha pulse height analysis

Thin sources of extracted and purified uranium are usually prepared by electrodeposition onto stainless steel or platinum planchets [82, 83] which are counted under vacuum. The uranium may also be extracted into an organic solvent, which is then evaporated to dryness on the planchet [70, 81].

In recent years solid-state semiconducting detectors have been used almost exclusively for the analysis of alpha-ray energies [84, 85], although scintillation spectrometers [86] and grid chambers [87] are adequate. Figure 5 shows a representative alpha spectrum obtained with a solid-state detector.

The ratio  $^{234}\text{U}/^{238}\text{U}$  may also be determined by mass spectrometry, with about the same degree of sensitivity and accuracy as alpha pulse height analysis [88–93].

## 2.2. Treatment of data

In looking for significant patterns of variation of uranium concentration and  $^{234}\text{U}/^{238}\text{U}$  alpha activity ratios, one must be aware of the uncertainty range of individual data points. These differ greatly from sample to sample, in part because of the extreme natural variations from very low to very high concentration, and also because the isotopic tracer method of analysis permits the use of data obtained even by low-yield extractions. The key factor in analysis of radioactivity data is the number of decay events counted for each isotope of interest. This means that

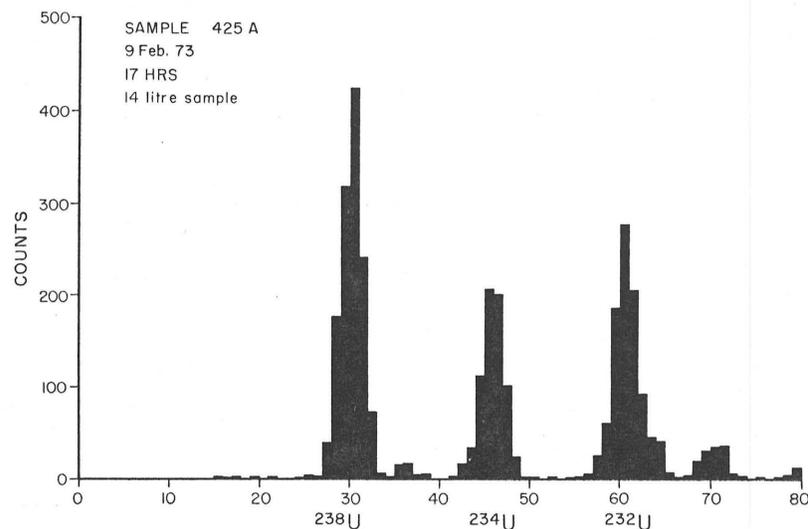


FIG. 5. Typical alpha energy spectrum of uranium extracted from groundwater which demonstrates the ease with which uranium isotope alpha peaks may be resolved. The  $^{232}\text{U}$  counts (5.3 MeV) are from the analytical tracer (spike) added to the sample at the time of collection. The small peak centred at channel 37 is  $^{235}\text{U}$  (4.5 MeV); that at channel 70 is  $^{224}\text{Ra}$  (6.1 MeV), a short-lived daughter of  $^{228}\text{Th}$  which develops radiogenically on the planchet after electrodeposition. The peak of  $^{228}\text{Th}$  (5.4 MeV) is obscured by the  $^{232}\text{U}$  peak. A number approximately equal to the  $^{224}\text{Ra}$  peak (=  $^{228}\text{Th}$ ) should be subtracted from the apparent  $^{232}\text{U}$  peak. This sample is characterized by relatively high concentration and low  $^{234}\text{U}/^{238}\text{U}$  alpha activity ratio.

determinations, in principle, can be made to almost any minimal uncertainty, providing that the background count rate is sufficiently low and stable, and also that one is willing to count the sample for a long enough period of time. In practice, however, most investigators count for a standard time interval, accepting whatever degree of uncertainty in data value this produces.

Background is usually a minor problem in alpha pulse height analysis. Even a well-used chamber/detector system will have a background rate in the  $^{234}\text{U}$  energy peak of less than 0.2 counts/h and in the  $^{238}\text{U}$  range of about 0.1 counts/h. The background in the  $^{232}\text{U}$  alpha energy envelope is more of a problem. This value increases with use of the detector due to the activity of  $^{228}\text{Th}$ , the daughter of  $^{232}\text{U}$ , which has a half-life of 1.9 years and an alpha energy of about 6.4 MeV, which means that its peak is not resolvable from that of  $^{232}\text{U}$  (Fig. 5). As  $^{232}\text{U}$  decays,  $^{228}\text{Th}$  is produced on the planchet, where its contribution to the count rate must be considered, especially if the time elapsed since plating is of the order of months. However, to the extent that this effect concerns only that particular planchet, it is not considered a part of the chamber background. That the chamber background itself increases is the result of  $^{228}\text{Th}$  atoms plating onto the detector and chamber walls by the process of alpha recoil. Only a small fraction of recoiling  $^{228}\text{Th}$  atoms cross the planchet-detector gap, but after a period of counting heavily spiked samples, the effect is noticeable. As a simple demonstration, one may clamp a clean planchet face-to-face with a planchet plated with  $^{232}\text{U}$ , unclamping at intervals of a month or so to test the alpha activity of the 'clean' planchet. The activity builds up on the unplated planchet in accordance with the radioactive growth equation. For an intermediate daughter

$$A_{228} = K \cdot A_{232} (1 - e^{-\lambda t}) \quad (5)$$

where  $A_{232}$  is the  $^{232}\text{U}$  activity of the plated planchet,  $\lambda$  is the decay constant of  $^{228}\text{Th}$ , and  $K$  is the factor that describes the probability of recoil transfer, in this case of the order of 0.05. This same equation describes the build-up of background activity in the  $^{228}\text{Th}$  peak ( $\approx ^{232}\text{U}$ ) of the detector chamber, except that the factor  $K$  is much smaller.

To lessen the effect of background build-up by recoil, one may increase the detector-planchet gap, which necessarily decreases the counting geometry of the system (although it increases the resolution), or decrease the vacuum of the chamber, which inhibits recoiling atoms without seriously decreasing the energy resolution of the alpha spectrum [94].

Simple statistical manipulations that will yield uncertainty ranges for radioactivity data have been described [95, 96]. If  $N$  is the total number of radioactive decay events observed, in time  $t$ , then the count rate is reported as  $R \pm r$ , where  $R = N/t$  and  $r = R^{1/2}/t$ . This is the 'standard error' of count-rate determinations. The propagation of such uncertainties is by means of the formula:

$$P = (p_1^2 + p_2^2)^{1/2} \quad (6)$$

where  $p_1$  and  $p_2$  are values of  $r$  when  $R$ 's are added or subtracted, as in determining net count rate by subtraction of background. When values of  $R$  are multiplied or divided, as in obtaining A.R. values, or concentration values, fractional uncertainties,  $r/R$ , are used as  $p_1$  and  $p_2$ .

Using these formulae, we can calculate some representative uncertainty ranges. Assuming 100 hours of counting time, counter geometry efficiency of 30% and analytical yield of 50%, 16 litres of sample, which contains  $0.1 \text{ pp}10^9$  of uranium with A.R. of 2.0, and spiked with  $11.25 \text{ dph}$  of  $^{232}\text{U}$  per litre of water, we have ( $1 \text{ pp}10^9 = 1 \mu\text{g}/1$  of  $\text{U} \approx 45 \text{ dph}$ ):

Isotope	Total dph in sample	total counts recorded	Uncertainty (counts/h)
$^{238}\text{U}$	$0.1 \times 16 \times 45 = 72$	$7200 \times 0.50 \times 0.30 = 1080$	$\pm 33$ (3.1%)
$^{234}\text{U}$	$2 \times 72 = 144$	2160	$\pm 46$ (2.1%)
$^{232}\text{U}$	180	2700	$\pm 53$ (1.9%)

The uncertainty in the A.R. is a propagation of that of  $^{234}\text{U}$  and  $^{238}\text{U}$  and calculates out to  $\pm 3.7\%$ , i.e. A.R. =  $2.00 \pm 0.07$ . Similarly, the concentration uncertainty is obtained by propagating that of  $^{238}\text{U}$  and  $^{232}\text{U}$ , and calculates out to  $\pm 2.8\%$ , i.e.  $C_u = 0.100 \pm 0.003 \text{ pp}10^9$ .

In a similar fashion we can calculate our detection limits for uranium in water, given reasonable limitations of counting time and sample volume. To measure uranium we need about 100 counts or more in the  $^{238}\text{U}$  peak. This gross count will have an uncertainty range of  $\pm 10\%$ , which will be increased somewhat when background counts accumulated in 100 hours are considered. Given the same yield and counting efficiency specified above, we can calculate that the minimum concentration of uranium that can be measured in a 16 litre sample (assuming we need one count per hour) is

$$1 \times 100/15 \times 1/45 \times 1/16 = 0.011 \pm 0.001$$

These detection limits and uncertainty ranges are for routine operation. They can be reduced by taking larger samples, and/or counting for longer time periods. Cowart [77] counted some of his planchets for a cumulative time of 35 days; Kigoshi [22] collected samples of 100 litres. Better yields, higher chamber efficiencies and lower backgrounds are also achievable. The methods that involve separation of uranium, or preconcentration, in the field are of course attempts to improve on these figures.

TABLE I. INTERLABORATORY URANIUM ISOTOPIC CALIBRATION EXPERIMENTS

A. Spergen Limestone			
(Samples supplied to interested laboratories by W. Sackett, 1963)			
U concentration (ppm)	Method	Activity ratio $^{234}\text{U}/^{238}\text{U}$	Reference
1.17	Fluorometric		Sackett, unpublished
1.09	Fluorometric	$1.02 \pm 0.02$	Veeh [97]
1.08, 1.12	Isotope Dilution	$1.01 \pm 0.01$	Thurber [11]
1.08	Isotope Dilution	$1.00 \pm 0.02$	Kolodny [32]
1.12	Isotope Dilution	$1.01 \pm 0.02$	Osmond, unpublished
B. IAEA Panel Standards			
(Solutions distributed to participants at the March 1973 Panel Meeting: 'Uranium Isotope Disequilibrium as a Hydrologic Tracer')			
$^{232}\text{U}$ tracer activity	U standard activity ratio: $^{234}\text{U}/^{238}\text{U}$	Investigators	
	$0.434 \pm 0.017$	J. Veselsky, IAEA, Seibersdorf Laboratory, Vienna, Austria	
1914 $\pm$ 3	$0.418 \pm 0.001$	C.V. Gaven, J.M. Martin, Univ. Paris, Paris 6 <sup>e</sup> , France	
1895 $\pm$ 20	$0.421 \pm 0.003$	J.K. Osmond, J.B. Cowart, Florida State Univ., Tallahassee, Fla., USA	

There have been only a few attempts to make systematic interlaboratory calibrations of uranium isotopic data. A solid limestone sample (Spergen limestone of Mississippian age) was used to make comparisons of uranium and thorium analytical methods by various US laboratories in the 1960s (Table I). Good agreement was achieved with respect to uranium concentration and  $^{234}\text{U}/^{238}\text{U}$  activity ratio, suggesting that analytical errors in both values were routinely of the order of a few per cent. Another such attempt, co-ordinated by R.S. Harmon and T.-L. Ku [98] is currently underway and involves laboratories from several nations. Preliminary results were presented at a symposium entitled "Rates of Climate Change during the Last Interglacial/Glacial Transition" which was held in conjunction with the 1976 Geological Society of America national meeting, and these also indicate good interlaboratory agreement.

In 1974 a liquid sample of  $^{232}\text{U}$  spike and one of unusual uranium A.R. were disseminated to participants of an International Atomic Energy Agency panel meeting on the use of uranium isotopes in hydrology. They were asked to calibrate, individually in their laboratories, these solutions against a gravimetric uranium standard. These results were also consistent (Table I).

No water sample has ever been designated as an interlaboratory standard, and in view of possible evaporation losses and shipping problems, perhaps none should be. However, the apparent uniformity of open seawater with respect to uranium concentration and A.R., as reported by numerous investigators, in effect provides a universal isotopic standard of the uranium isotopes.

TABLE II. REPLICATION OF URANIUM ISOTOPES IN GROUNDWATER

Sample	A.R.	Concentration	Date collected	Reference
Woodville Municipal Well, Leon Co. Fla., USA, T.D. 56 m, Floridan Aquifer, Tertiary 1s	0.523 ± 0.006	18.484 ± 0.954	Jan. 67	[9]
	0.503 ± 0.005	25.912 ± 1.450	Apr. 67	[9]
	0.506 ± 0.002	19.519 ± 1.069	Oct. 71	<sup>a</sup>
	0.507 ± 0.020	18.034 ± 0.794	May 75	<sup>a</sup>
Wakulla Spring, Wakulla Co., Fla., USA, Tertiary 1s	0.878 ± 0.020	0.584 ± 0.024	Sep. 66	[9]
	0.854 ± 0.028	0.608 ± 0.029	Apr. 67	[9]
	0.88 ± 0.05	0.58 ± 0.03	Oct. 71	<sup>a</sup>
	0.87 ± 0.04	0.50 ± 0.03	Dec. 74	<sup>a</sup>
Well, KB-68-58-401, T.D. 79 m, Frio County, Texas, USA, Carrizo ss, Eocene	0.69 ± 0.03	0.20 ± 0.01	Jul. 72	[20]
	0.68 ± 0.05	0.20 ± 0.01	Jul. 72	[20]
	0.70 ± 0.05	0.18 ± 0.02	Jun. 74	<sup>a</sup>
Well, AL-78-11-101, City of Charlotte, T.D. 576 m, Attascosa Co., Texas, USA, Carrizo ss, Eocene	6.55 ± 1.73	0.006 ± 0.002	Jul. 72	[20]
	6.68 ± 0.85	0.006 ± 0.001	Jun. 73	[20]
Well, City of Meridian, Bosque Co., Texas, USA, Hosston ss, Cretaceous	7.03 ± 0.30	0.067 ± 0.003	1970	[10]
	7.03 ± 0.75	0.087 ± 0.011	Jul. 74	<sup>a</sup>

<sup>a</sup> Previously unpublished, F.S.U. Laboratory.  
T.D. = total depth (metres).

A few water systems other than seawater have been subjected to replication measurements, in some instances by different investigators. Table II summarizes some of these results, which tend to confirm not only that analytical techniques are sufficiently reliable for the comparison of data from different laboratories, but also that at a given site uranium isotopes are apparently non-fluctuating constituents of the groundwater.

### 2.3. Presentation of data

The natural variation in the  $^{234}\text{U}/^{238}\text{U}$  activity ratio in nature indicates that, to some extent at least, the occurrences of the two isotopes are governed by different physico-chemical phenomena. In order to learn something about these phenomena, we present data on the two uranium isotopes in ways that display the degree of covariation of their abundances. Although basically only two parameters are measured,  $^{238}\text{U}$  activity and  $^{234}\text{U}$  activity, a number of variations of these parameters may be plotted:  $^{234}\text{U}/^{238}\text{U}$  activity ratio, excess  $^{234}\text{U}$  activity, reciprocal of  $^{238}\text{U}$  concentration, etc.

The  $^{238}\text{U}$  concentration may be expressed either in activity units, e.g. disintegrations per minute per litre (dpm/l), disintegrations per hour per litre (dph/l), or in mass units, usually micrograms per litre, which is equivalent to parts per  $10^9$ . If mass is reported, it makes no significant

difference whether 'total uranium' or just  $^{238}\text{U}$  is specified, since the concentration by weight of  $^{235}\text{U}$  in the total uranium is about two orders of magnitude less than that of  $^{238}\text{U}$ , and  $^{234}\text{U}$  alone is about four orders of magnitude less. For this reason,  $^{234}\text{U}$  is never reported in mass units such as micrograms per litre or pp10<sup>9</sup>. Where  $^{234}\text{U}$  (or excess  $^{234}\text{U}$ ) is to be plotted against concentration units of  $^{238}\text{U}$ , the  $^{234}\text{U}$  values are given in 'equivalent concentration units', i.e. the concentration of  $^{238}\text{U}$  that would be equivalent in activity to the  $^{234}\text{U}$  present. The excess  $^{234}\text{U}$  activity is defined as

$$X = (\text{A.R.} - 1) \cdot C \quad (7)$$

where C is uranium concentration, so that the units of excess are the same as concentration.

The concentration of  $^{238}\text{U}$  in water is, in effect, an intensive, or qualitative, property of that sample, which is obtained by taking the ratio of two extensive or quantitative properties of the water: mass of uranium and mass (or volume) of water. Similarly, specific activity (dpm/l) is an intensive property. Extensive properties are additive, whereas intensive, or qualitative, properties are not additive, but may be averaged. With respect to uranium isotopes we can write a simplified version of the standard isotope dilution equation:

$$V_1 A_1 + V_2 A_2 = V_3 A_3 \quad (8)$$

Where  $V_1$  and  $V_2$  are the extensive properties (volume of water) of two components, and  $V_3$  is the sum of the two.  $A_1$  and  $A_2$  are the intensive properties (activity of  $^{238}\text{U}$ ) of the two components, and  $A_3$  is the resultant activity. This equation has two important applications. It can be used in one form to determine the relative volume of a component in a system by measuring only the activities.

$$\frac{V_2}{V_3} = \frac{A_3 - A_1}{A_2 - A_1} \quad (9)$$

In another form it is used to calculate, or predict, the activity of a mixture of components:

$$A_3 = A_1 + (V_2/V_3)(A_2 - A_1) \quad (10)$$

These types of equations are the basis for the isotopic spiking procedures used in mass analysis and uranium alpha pulse height analysis. We can also apply them to mixing groundwater systems, and to erosional and weathering mass balance considerations.

To study the degree of covariance of two parameters, such as  $^{234}\text{U}$  activity versus  $^{238}\text{U}$  activity, it is necessary that they be averaged in terms of the same extensive property, e.g. volume of water. For example,

$$V_1 X_1 + V_2 X_2 = V_3 X_3 \quad (11)$$

and

$$\frac{V_2}{V_3} = \frac{X_3 - X_1}{X_2 - X_1} \quad (12)$$

where V is again the volume (or mass) of water, and X is the excess activity of  $^{234}\text{U}$  in equivalent  $^{238}\text{U}$  units. Combining this equation with Eq.(9), we can eliminate all extensive property considerations and relate one intensive parameter to another, e.g.  $^{238}\text{U}$  activity versus excess  $^{234}\text{U}$  activity:

$$\frac{A_3 - A_1}{A_2 - A_1} = \frac{X_3 - X_1}{X_2 - X_1} \quad (13)$$

Equations like this are the basis for the various plotting methods. For example Osmond et al. [99] plotted A.R. against S, the reciprocal of concentration. The use of S, in units of litres per microgram, was dictated by their choice of extensive property, mass of uranium, as the basis for averaging the intensive property of A.R. (Note that Osmond et al. used "A" in their equations to stand for A.R. Here we use it for specific activity, e.g. dph/l of  $^{238}\text{U}$ .)

As pointed out by Briel [8], these equations are also the basis for the well-known Gibbs phase diagrams, in which the composition-related properties of intermediate phases plot along straight line segments joining two end-member components; intermediate phases of three-component systems have compositional properties proportional to the three altitudes of the resultant point relative to the triangle joining the three components (Fig.6). On a two-dimensional diagram the proportions of no more than three components can be specified by a single plotted phase.

Figures 7 to 9 illustrate some of the various uranium isotopic phase diagrams that have been used. Each of the plotting techniques can serve to interpret mixing proportions, as shown in Fig.6. (Actually, this particular plot is of less use than the other two in this regard because the components are averaged in proportion to unit weights of uranium. In the A-234 versus A-238 and the X-234 versus  $^{238}\text{U}$  methods the line segments are directly proportional to water volumes.) Most of the data plots of this review are of one of these types, though some of them may be modified so that at least one axis is on a log scale. This permits analysis of data relationships over wide ranges of

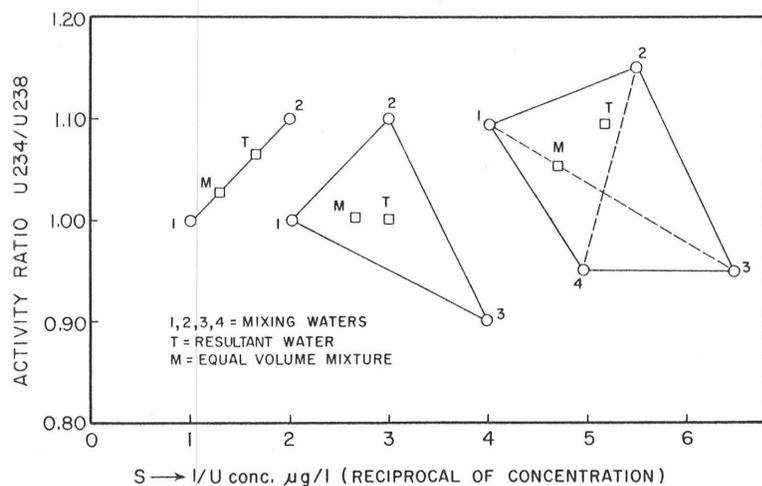


FIG. 6. One of the ways that natural variations in uranium isotope data can be presented: activity ratio of  $^{234}\text{U}/^{238}\text{U}$  (A.R.) versus the reciprocal of concentration (S) [99]. In this form straight line arrays of plotted points result from various volume mixtures of two end-member waters. In the three examples pictured M is the resultant plot of the equal volume mixture of two, three and four-component waters respectively. T is some other set of mixing proportions of the same components. Whereas the mixing volumes can be computed for the two and three-component systems (given the uranium isotopic data for the components and the resultant), the four-component system does not yield a unique volume solution to the mixing equations. At least two other plotting methods also yield straight line and triangular loci of mixing components (see Figs 8 and 9).

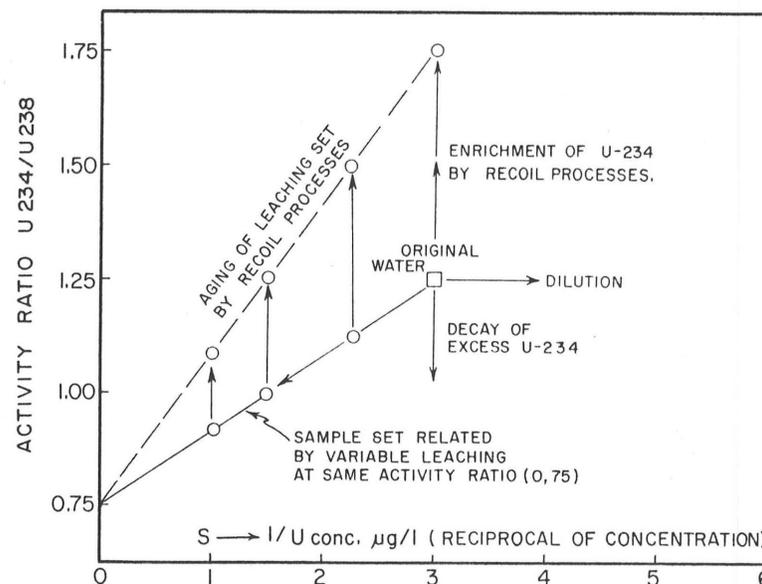


FIG. 7. Some possible evolutionary trends of uranium isotope variations in groundwater on a plot of reciprocal concentration against  $^{234}\text{U}/^{238}\text{U}$  activity ratio. If the A.R. is other than 1.00, the excess (or deficiency) of  $^{234}\text{U}$  will change at a rate governed by its half-life of 250 thousand years. Conversely, confined waters may accumulate more excess  $^{234}\text{U}$  by recoil processes. Dilution or precipitation moves the point to the right without changing A.R. On the other hand, leaching of uranium from the reservoir rock is likely to cause both concentration and A.R. to change. Note that the leaching trend line can also be thought of as a two-component mixing system with one end-member the original water and the other an infinitely concentrated water of a different A.R. [99].

concentration. In such cases the linear relationships are modified, and leaching and mixing interpretations are more difficult to make. Chemical abundance variations may also be plotted on a log-log scale, where concentration ranges of two elements are both extreme. On such a plot iso-ratio lines form diagonal parallels. We have used this type of plot to illustrate fundamental differences in groundwater systems (Fig.18), but it is worth noting that this approach would be of no value were it not for the very extreme divergence of A.R.s from unity in the low concentration waters of some systems.

It is unfortunate that the casual reader of papers on uranium isotopes in natural waters should be forced to adjust to so many different graphical ways of presenting the data. This is in part a symptom of the newness of the field, wherein the various investigators are attempting to find the best way to show the significance of their data. Perhaps with time one or two plotting methods will become standard. However, in assembling this review, we are impressed by the very wide range of problems that can be studied: mixing, leaching, aging, system categorization; each of which appears to be best analysed in a different plotting format.

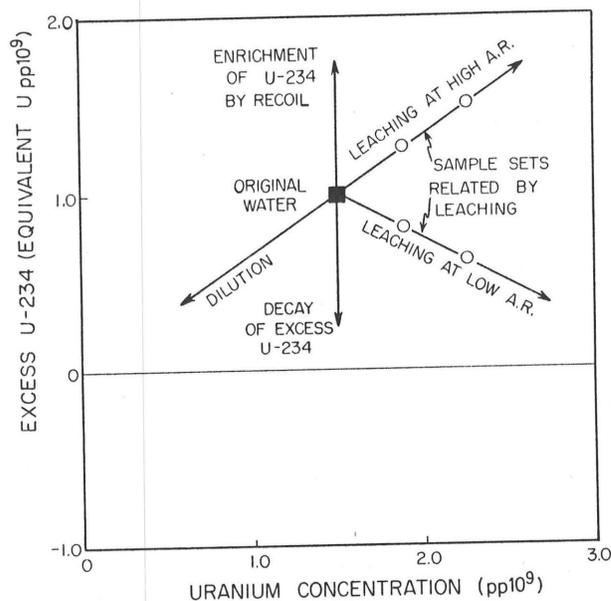


FIG. 8. A second way to plot uranium isotope data in water samples. The abscissa is uranium concentration ( $C$ ) and the ordinate is 'excess  $^{234}\text{U}$ ', which is equal to  $C(A.R. - 1.00)$ . Excess  $^{234}\text{U}$  means the amount that is in excess or deficit of that which would be in equilibrium with the associated  $^{238}\text{U}$ ; its units are in 'equivalent' parts per  $10^9$  of  $^{238}\text{U}$ . Alternatively, both the  $^{238}\text{U}$  and the excess  $^{234}\text{U}$  could be expressed in activity units. As pictured on the diagram, straight trend lines may be drawn similar to those of Fig. 7, except the directions and slope are different. Mixing proportions can also be shown to fall on straight line segments between component points. This plot is superior to the A.R. versus  $S$  plot in that mixing volumes are proportional to line segment lengths.

### 3. FRACTIONATION OF URANIUM ISOTOPES

#### 3.1. Fractionation mechanisms

Although the large variations in the  $^{234}\text{U}/^{238}\text{U}$  ratio found in nature were unpredicted, ex post facto analysis of the subject makes selective mobilization of  $^{234}\text{U}$  almost inevitable. We will use the customary term 'isotopic fractionation' to refer to the process causing such variations, although perhaps we should use the term 'radiogenic fractionation' so as to avoid confusion with mass effect fractionation, a type of differentiation not significant for the two uranium isotopes. Because there is some confusion as well as considerable disagreement about the mechanism of uranium isotopic fractionation, we begin by classifying the possible processes that might favour preferential mobilization of the daughter  $^{234}\text{U}$ :

- (A) Direct transfer of the atom by alpha recoil across the solid/liquid phase boundary.
- (B) Increased vulnerability to solution resulting from:
  - (1) Recoil displacement
    - (a) lattice destruction and bond breakage
    - (b) unstable location, e.g. interstitial lattice resting sites

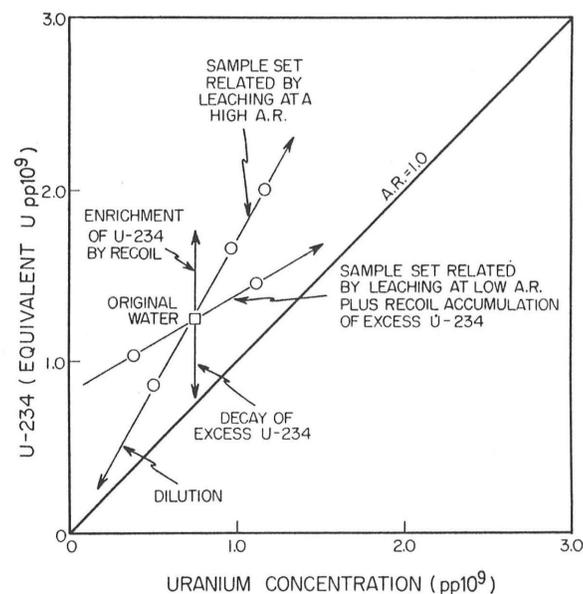


FIG. 9. A third way to plot uranium isotope data in waters.  $^{234}\text{U}$  activity is plotted against  $^{238}\text{U}$  activity. If the  $^{238}\text{U}$  activity is expressed in uranium parts per  $10^9$ , then the  $^{234}\text{U}$  activity is termed equivalent parts per  $10^9$  (meaning the amount of  $^{238}\text{U}$  that would have the same activity). As in the two previous methods, trend lines and mixing components appear as straight line segments.

- (2) Oxidation from  $\text{U}^{4+}$  to  $\text{U}^{6+}$ 
  - (a) related to oxidation potential difference between displaced site and original site
  - (b) related to the decay process itself.
- (C) Chemical fractionation of  $^{234}\text{Th}$ .

This classification scheme attempts to distinguish between direct and indirect effects of decay on the daughter. If we assume (C) is of only minor importance, the major distinction is between (A) and (B), i.e. whether or not alpha recoil causes the daughter to be propelled out of the solid grain entirely and directly into the surrounding pore water. If not, the effect of decay is to make the daughter vulnerable to subsequent leaching processes (extraction without gross lattice destruction). This may be due either to the severe dislocation effects of decay in the case of alpha recoil (about 70 keV [100]), or in the case of beta decay, mild disruption. However, even the latter involves more than enough energy to break chemical bonds. Oxidation of the daughter uranium may simply be the result of differences in the oxidation potential between the original crystal site of  $^{238}\text{U}$  and the host environment of the  $^{234}\text{U}$  after displacement. On the other hand, oxidation may be the result of the decay process itself, e.g. the stripping of electrons in the course of alpha recoil, or energetic beta decay.

Most early investigators favoured some form of the (B) category processes, those which are sometimes termed the 'Szilard-Chalmers' or 'hot atom' effect. For example, Cherdyntsev [1] stated, "... the recoil atom leaves its original position and becomes embedded in another part of the mineral, which has different properties and in which the neighboring atoms are usually no longer uranium atoms. It remains a foreign body, which tends to migrate into dislocation zones, and which is liable to be more readily eliminated out of the mineral than the parent isotope  $^{238}\text{U}$ .

The oxidative atmosphere of the surface layers of the earth converts tetravalent uranium atoms to the hexavalent state. Clearly, the migrating atoms ... i.e.,  $^{234}\text{U}$  in preference to  $^{238}\text{U}$  ... are converted to hexavalent uranium in the first place."

Rosholt et al. [53, 54] appealed to a combination of recoil-related factors: recoil caused radiation damage, formation of  $\text{UO}_2^{2+}$  before in situ reduction back to  $\text{U}^{4+}$  and chemical differences of intermediate daughters. Dooley et al. [58, 59] point out that the isotope fractionation effects are most pronounced in moderately acid waters, or those containing carbonate ions, and where the dissolved concentration of uranium is low. Van et al. [101] suggest that the presence of complexing ions in solution such as  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  greatly favours selective leaching of the vulnerable  $^{234}\text{U}$  atom.

An interesting phenomenon studied by Chalov and Merkulova [61, 102–104], Chalov [62], Kolodny [32] and Rydell [9] has been cited as lending credence to the oxidation effect as dominant in uranium isotopic fractionation. If one carefully separates by chemical means  $\text{U}^{4+}$  from  $\text{U}^{6+}$  in secondary minerals, the  $\text{U}^{6+}$  has a higher A.R. than the  $\text{U}^{4+}$ . Kolodny [32] suggests the distribution is such as to indicate that about one third of all decay-generated  $^{234}\text{U}$  atoms have been oxidized. This seems to support the decay related oxidation theory of fractionation, but inasmuch as only secondary minerals such as oxidized ores and submarine phosphorites exhibit the valence related fractionation, Chalov and Merkulova [61] and Kolodny [32] both conclude that something in the environment must be the actual agent of oxidation.

The simplest view of the  $4^+/6^+$  data would be that all daughter isotopes take on the oxidation state dictated by their environment after recoil displacement. If the reduced regimes have higher  $^{238}\text{U}$  concentrations than the oxidized regimes, then the net gain of  $^{234}\text{U}$  atoms by recoil displacement into the oxidized regimes will exceed their loss of  $^{234}\text{U}$  atoms by recoil displacement out. The reverse will be true of the reduced regimes. None of the studies cited has determined specifically the concentration of uranium in the two phases so that this model might be tested; however, certain of the data presented by Kolodny ([32] p. 68) are consistent with it.

In an effort to duplicate the  $^{234}\text{U}/^{238}\text{U}$  fractionation phenomenon observed in nature, Umemoto [105] and Moreira and Lalou [106] conducted leaching experiments in the laboratory. Both investigations produced inconsistent results. Umemoto observed moderate fractionation (A.R. = 1.3) in a sedimentary ore, the maximum A.R. occurring only after about 10% of the ore had been dissolved. From monazite he obtained almost no fractionation, which to him indicated annealing. Moreira and Lalou achieved appreciable fractionation (A.R.s = 2–3) in a basalt, but fractionation for uranium leached from a granite was minor (A.R. = 1.12) and in the uranium leached from several sedimentary rocks the A.R. was less than unity (0.8–0.9).

Earlier Syromyatnikov and Tolmachev [65] reported by far the highest A.R.s derived from the leaching of solids; in the case of uranium-molybdenum ores of hydrothermal-metasomatic origin a value as high as 7.5 was reported (A.R. as high as 10 in waters) and as high as 5.7 was reported for crushed samples of phosphate-zirconium mineralization with dispersed uranium (A.R. as high as 8 in waters). Most of their leaching A.R.s were lower, ranging to about 1.5. Their average values for leaching and for associated waters for igneous rocks were 3.0 and 3.5; for sedimentary rocks they report 3.0 and 1.8 respectively. For uranium ores they report values of unity for both leaching and associated waters.

Other high 'leaching ratios' obtained from natural solid materials have been those of Ku [63] and Immel and Osmond [107]. Their subject material was deep-sea sediment, which requires no grinding; interestingly, these high ratios (2 to 5) are found only in the deeper layers of sediment cores. Immel and Osmond believe that these leachates are derived from coatings on the sedimentary particles where they have precipitated from pore water. The inferred high ratios of pore water, which have been only partially confirmed by direct analysis [108, 109], are interpreted by Immel and Osmond as being the result of accumulation of recoil-generated  $^{234}\text{U}$ .

A very significant laboratory experiment, in our opinion, was that performed by Kigoshi [110]. He showed that immersing uraniferous zircon grains in water produced a time-related increase of  $^{234}\text{U}$  atoms in the water without significant leaching. He deduced that the process of alpha recoil

(which he took to involve a range of 550 Å in zircon, but according to Huang and Walker [100] should be about 200 Å) causes the recoiling daughter to be ejected out of the crystals into the water. He surmised that the same process occurs in groundwater and in pore water and that subsequent decay to  $^{234}\text{U}$  produces the observed excess of  $^{234}\text{U}$  in waters.

Sakanoue and Komura [111] report a very high  $^{234}\text{U}/^{238}\text{U}$  activity ratio of approximately 15 for a small sample of maghemite from an ore zone. They suggest that selective leaching and alpha recoil contributed excess  $^{234}\text{U}$  to the dissolved uranium in the interstitial water, which later precipitated during the formation of this mineral.

The extreme A.R.s observed by Cowart [77], Cowart and Osmond [20, 23], Kronfeld [10], Kronfeld and Adams [112] and Kronfeld et al. [21] are difficult to reconcile with any leaching/oxidation model when the sedimentary environment, infiltration source of water and large areal extent are considered.

An even higher A.R. is exhibited by a previously unreported sample (FSU) from a well in another south Texas aquifer which was collected in 1974 and again in 1975; the A.R.s are  $19.76 \pm 2.83$  and  $15.73 \pm 2.45$  respectively. In the case of the Carrizo sandstone aquifer [20, 23] a large increase in A.R. occurs at the same location as the decrease in total uranium concentration, a situation that should work against selective leaching mechanisms and for interphase isotope exchange. This suggests that some other mechanism is apparently overriding these. This observation in the field is contrary to the data of Syromyatnikov and Tolmachev [65], which indicated that the A.R. increases with increased leaching of uranium from disseminated uranium rocks. The zone of uranium concentration decrease and A.R. increase in the Hosston aquifer [10, 112, 113] is apparently more diffuse than that of the Carrizo but the same general characteristics hold. The brines studied by Kronfeld et al. [21] come from depths (2 km) that are unlikely to be oxidizing and are evidently quite old. That recoil  $^{234}\text{U}$  is the cause of the high A.R.s is the conclusion of the investigators.

Perhaps the strongest evidence that recoil across phase boundaries is an important agent in the production of uranium isotopic disequilibrium in nature is provided by data reported by Rosholt (personal communication). He describes a radioactive slurry from an ore-processing plant that exhibits a low A.R. for uranium in solution, and at the same time a high A.R. in the fine-grained suspended sediment, which has a concentration of uranium that is considerably less than that of the liquid. Here the donor phase (high concentration) is non-crystalline, so that all 'vulnerability' models become inoperative. The receptor phase, in this case a solid (like the oxidized regime in secondary minerals), exhibits a high A.R. because, according to Rosholt's interpretation, it is receiving more  $^{234}\text{U}$  atoms (via  $^{234}\text{Th}$ ) by recoil displacement across the phase boundary than it is donating in the opposite direction.

The slightly elevated A.R.s of volcanic sublimates, as reported by Gaven [114], are also, in our view, supportive of alpha recoil as the fractionation mechanism.

Figure 10 is a diagrammatic summary of the various competing processes between uranium series atoms in pore water and those on or just within the grain surfaces. Both leaching and recoil displacement occur in nature, and both processes take on greater importance in fine-grained systems such as soils and sediments.

Aside from the probability of its importance in nature, the recoil model of fractionation is attractive because it allows quantitative predictions to be made of the solid and liquid A.R.s to be expected in aquifer and pore water systems.

The basis for these calculations is another variation of the mass averaging formula (notation is that of Cherdyntsev [1]).

$$M_1 \gamma_1 + M_2 \gamma_2 = M_t \gamma_t \quad (14)$$

where  $M_1$  and  $M_2$  are the masses of uranium in two mixing components ( $\approx$  the masses of  $^{238}\text{U}$ ), and  $M_t$  is the sum of the two.  $\gamma_1$ ,  $\gamma_2$  and  $\gamma_t$  are the corresponding  $^{234}\text{U}/^{238}\text{U}$  alpha activity ratios.

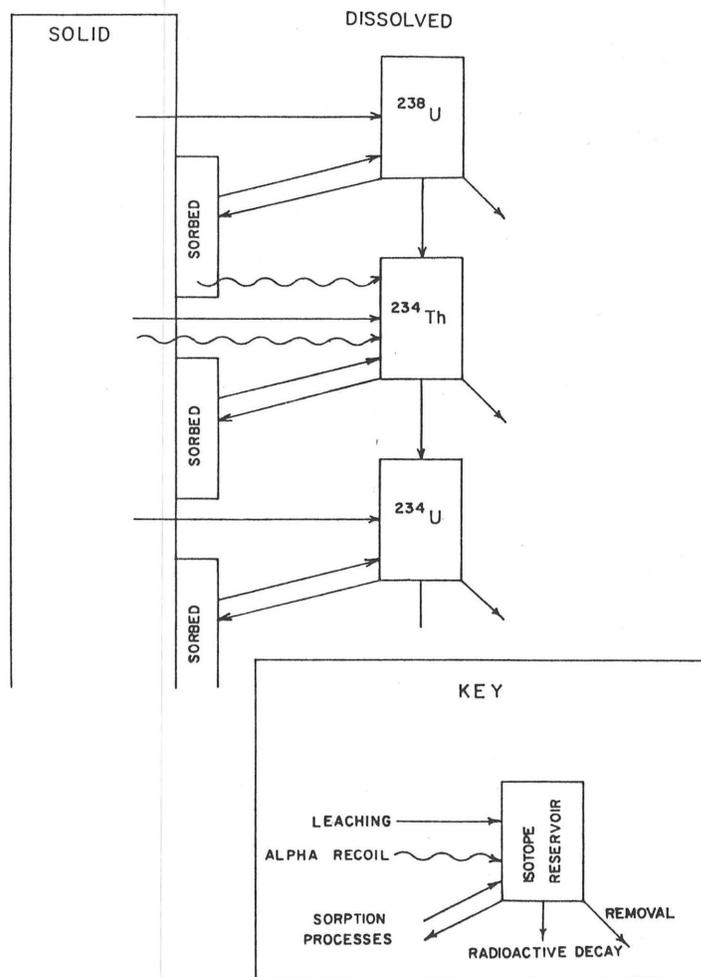


FIG.10. Diagrammatic figure showing the competing processes of leaching, sorption, recoil and decay in aquifer-uranium systems. Dissolved  $^{238}\text{U}$  is always a leaching product, but dissolved  $^{234}\text{U}$  may result from either leaching or as a result of recoil ( $^{234}\text{Th}$  followed by decay to  $^{234}\text{U}$ ). Sorption and precipitation affect  $^{238}\text{U}$  and  $^{238}\text{U}$  identically, but leaching may dissolve  $^{234}\text{U}$  preferentially (because of its common occurrence in unstable lattice sites as a result of radiogenic origin). In old groundwaters the amount of  $^{234}\text{U}$ , but not  $^{238}\text{U}$ , may be diminished or enhanced by decay processes (from [77]).

Rearranging terms, we have

$$\frac{M_1}{M_2} = \frac{\gamma_2 - \gamma_t}{\gamma_t - \gamma_1} \quad (15)$$

which, as in Eqs (9) and (12), yields the ratios of extensive properties (masses) by measuring the intensive properties (A.R.s).

Alternatively, one may calculate the fraction of one component in the resulting mixture:

$$\frac{M_1}{M_t} = \frac{\gamma_2 - \gamma_t}{\gamma_2 - \gamma_1} \quad (16)$$

For example, in a sediment-water system, if one assumes uniform distribution of uranium atoms within grains, the proportion of uranium atoms within recoil distance of grain surfaces is roughly  $L/R$ , where  $L$  is recoil distance, and  $R$  is average grain radius ( $L < R$ ). The proportion of  $^{234}\text{Th}$  atoms that will recoil from this surface zone varies linearly from zero on the inside (at  $L$  distance from the surface) to 50% on the surface, and the average A.R. of this zone may become 0.75. By the mass averaging formula (Eq.(14)) the A.R. of uranium in the grains as a whole, i.e. of the solid reservoir ( $\gamma_s$ ), is:

$$(L)(0.75) + (R-L)(1.0) = (R)(\gamma_s) \quad (17)$$

and

$$\frac{L}{R} = \frac{1.0 - \gamma_s}{1.0 - 0.75} \quad (18)$$

and

$$\gamma_s = 1.0 - (L/R)(0.25) \quad (19)$$

which shows that in order for the solid phase to develop an appreciable relative deficiency in  $^{234}\text{U}$ , the average grain size must be small; if  $L \approx 200 \text{ \AA}$  [100],  $\gamma_s$  will be as low as 0.95, provided  $R$  is not larger than  $1.0 \text{ \mu m}$ . Spongy materials and solids with extensive microfissures may effectively serve as very small grains.

Assuming equilibrium is approached, the A.R. ( $\gamma_w$ ) of uranium in the pore water may be arrived at by another application of the mass balance equation (Eq.(14)):

$$M_s \gamma_s + M_w \gamma_w = M_t \gamma_t = 1.00 \quad (20)$$

and

$$\gamma_w = 1.0 + (M_s/M_w)(1.0 - \gamma_s) \quad (21)$$

where  $M_s/M_w$  is the ratio of  $^{238}\text{U}$  in the solid phase relative to that in the liquid phase, which in turn is dependent on the relative concentrations in the two phases and also the relative amounts of the two phases (i.e. porosity).

These equations would seem to have potential value in the analysis of pore water systems, whereby the uranium isotopic properties are measured and inferences made regarding the porosity and effective grain size in the system. In our own tentative efforts to apply them to



As the crust of earth is regenerated and uplifted from below, the atmospheric and hydrospheric attack from above creates the weathered zone. We may think of this zone as a steady-state system, with inputs of fresh rock from below, and outputs of dissolved constituents and weathered rock fragments at the surface. Residual soils would appear to be open, rather than closed, systems; yet if one expands the system boundaries to include the departing components, sediment and water, then the equilibrium argument can be applied: the low A.R. in the sediment should be balanced by high A.R.s in the water (quantification being dependent on the relative rates of egress).

The time scale of this process is such that in mildly positive tectonic regions several centimetres of fresh rock enter the zone of weathering each thousand years. If the zone itself is a few metres thick, then the time it takes to change uranium in the isotopically equilibrated state into two states of disequilibrium is of the order of  $10^5$  years. Because this is of the same order of magnitude as the average lifetime of a  $^{234}\text{U}$  atom ( $3.6 \times 10^5$  years), conditions are favourable for the development of disequilibrium.

Among many studies of the general chemical evolution of soils, only a few have been concerned with the long-lived natural radioisotopes of the uranium series. Rosholt et al. [124] made such a systematic investigation in 1966. They measured the uranium and thorium isotopes in a series of soil profiles, extending through the A, B and C horizons. A few of their conclusions are illustrated diagrammatically in Fig. 11. In general, they found that the B and C horizons exhibit large deficiencies of  $^{234}\text{U}$  relative to  $^{230}\text{Th}$  (active ratio  $^{234}\text{U}/^{230}\text{Th}$  as low as 0.6) and moderate deficiencies of  $^{234}\text{U}$  relative to  $^{238}\text{U}$ . This they interpret to be due to the greater leachability of uranium over thorium and of  $^{234}\text{U}$  over  $^{238}\text{U}$ . Uranium does not accumulate in the B horizon, as iron and aluminium sometimes do; as long as conditions are oxidizing, uranium remains mobile. In the A horizon, however, humus may produce a reducing condition where uranium accumulates. This explains in part the reversal of the U/Th trend lines (arrows) in Fig. 11 from uranium loss to uranium gain. Similarly, the uniform trend toward lower  $^{234}\text{U}/^{238}\text{U}$  A.R.s in the B and C horizons sometimes reverses toward high A.R.s in the A horizon. We conclude from inspection of Fig. 11 that sediment eroded from a mountainous region with only primitive soil development will not have a very low  $^{234}\text{U}/^{238}\text{U}$  A.R. (nor a very low  $^{234}\text{U}/^{230}\text{Th}$  A.R.). The lowest A.R.s will be found in sediments eroded from maturely weathered regions with well-developed B and C horizons. However, a very deeply weathered region is not apt to yield sediments from the C or lower B horizons; rather, what little mechanical sediment is eroded from such a region may display the equilibrium or high A.R.s found in the A horizon.

According to this model, seasonal variations in the uranium isotopic character of suspended sediments might be expected. Lewis [192] in fact finds that the A.R. of suspended sediments in the Susquehanna River of Pennsylvania, USA, varies with the amount of suspended sediment in the river. At high loads the A.R. of suspended sediment at two sites was low; at the same sites under low load conditions the A.R. was high (Table II). We interpret this data to mean that at low stages only A horizon soil is eroded, but at higher sediment loads, B horizon soil is being removed.

Hansen and Stout [125] found no consistent  $^{234}\text{U}/^{238}\text{U}$  disequilibrium in the soils they studied.

Although, to our knowledge, uranium in the pore water of soils has not been directly studied, one might infer from the work of Kigoshi [22] and Kronfeld et al. [21] that the A.R.s of underground waters may be a function of residence time of water in the aquifer. Lewis [192] believes the difference in A.R. between uranium dissolved in the Susquehanna River and that in one of its tributaries is due to this factor.

However, a different conclusion can be reached if we emphasize that the mass averaging considerations mentioned above apply; namely, where the soil particles and sediments are developing low or very low A.R.s, the waters draining from such soils are developing high, or very high, A.R.s respectively. With respect to the A.R. of uranium in groundwater and rivers, the most important factor may be the relative amount of soil and sediment developed, as much as the degree of weathering. Consider Fig. 12, which is a graphical solution to the mass balance equation (Eq. (21)). This shows that the A.R. of water is a function of both parameters: the degree of

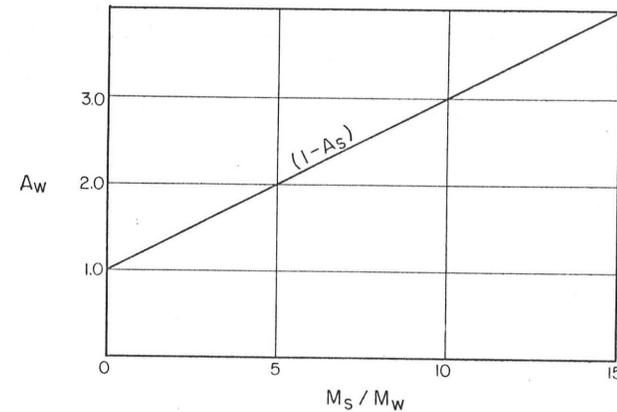


FIG. 12. A graphical solution of the uranium isotope mass balance equation (Eq. (21)), where  $\gamma_w$  is the expected A.R. of dissolved uranium and  $M_s/M_w$  is the ratio of uranium eroded as detritus ( $M_s$ ) to that transported in solution ( $M_w$ ). The slope of the mass balance solution is a function of the A.R. of the eroded sediment ( $\gamma_s$ ). The typical  $\gamma_s$  value is taken to be 0.80, so that the slope of this line is 0.20.

deficiency of  $^{234}\text{U}$  in the sediment,  $1-\gamma_s$  (the slope); and the ratio of the amount of uranium in the two phases, weathered sediment and water,  $M_s/M_w$  (the abscissa).

Noting that slow erosion rates and mature soils go together, we may generalize regarding the relationship of dissolved uranium in regional waters, either rivers or groundwaters. High A.R.s are characteristic of tectonically active regions, areas of high relief and/or arid climates, where soils are poorly developed and the ratio of chemical to mechanical erosion is small; low A.R.s are characteristic of areas of moderate relief and appreciable chemical erosion.

Figure 13 shows the trend lines of water samples from three regions plotted on the  $^{234}\text{U}$  versus  $^{238}\text{U}$  diagram. The lines indicate the regional A.R.s and are seen to exhibit the hypothesized relationship: waters from the arid and topographically youthful region (Galilee-Jordan) have uniformly higher A.R.s than those from the humid, low-lying Florida region, and an intermediate area (Great Lakes). The Galilee-Jordan samples are groundwater, the Great Lakes samples are surface water, and the Florida karstic terrain samples are a mixture; but each group is representative of the surface or shallow groundwater drainage system. These particular sample systems were chosen for display in part because they exhibit rather uniform A.R.s within each group, and in part because they have concentration values suitable for comparison on a linear scale. The factors of climate and topography are not distinguishable in this small group but, in principle, it should be possible to do so with a larger number of sample sets. The Galilee-Jordan sample group is one of four Israeli systems studied by Wakshal and Yaron [15], each of which has a different A.R. trend line. An analysis of the erosion rates versus climate of the four areas would perhaps be useful.

Perhaps the epitome of predominance of mechanical over chemical weathering, and immaturity of soil development, is the Dry Valley region of Antarctica. In fact, both dissolved uranium and that recovered from evaporites in the Dry Valley lakes do have high A.R.s, in the range of 2 to 4 (Christopher Hendy and David Thurber, personal communication).

The very low A.R.s exhibited by the Florida karstic area (Fig. 13) require a somewhat different origin. Neither selective leaching nor alpha recoil can explain, in a straightforward way, the regional occurrence of waters with A.R. < 1.00. At Wakulla Springs, in this North Florida

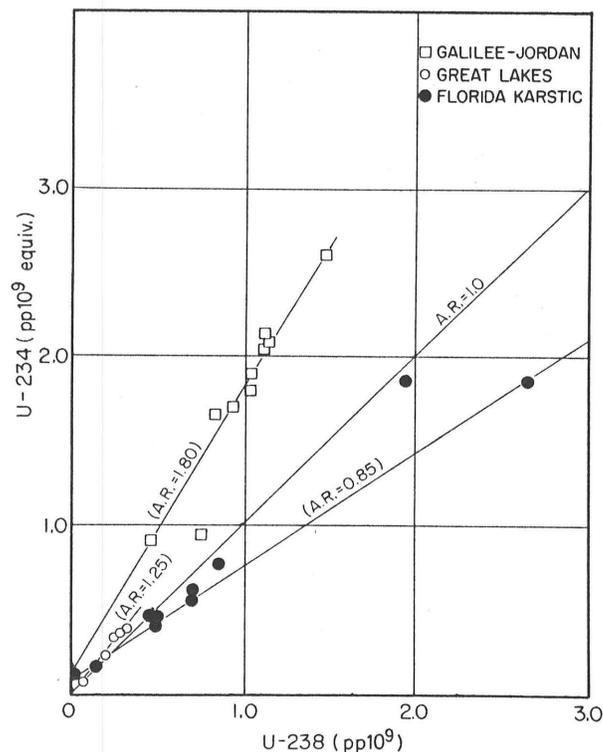


FIG. 13. Three sets of water samples illustrating the effects of different fractionation environments. The Galilee-Jordan group [15] represents a relatively shallow, oxidized aquifer in a region where mechanical weathering predominates over chemical weathering. The Florida karstic terrain samples [9] reflect the presence of a reducing and intense chemical weathering. The Great Lakes waters (FSU, previously unpublished) are homogenized mixtures of several temperate environments. Although the latter samples are from surface run-off, they are assumed to be representative of shallow groundwaters in the region.

area, an average of  $11 \text{ m}^3/\text{s}$  of water emerges from the ground and flows to the sea. Its dissolved uranium has a concentration of  $0.6 \text{ pp}10^9$  and an A.R. of 0.85. Nearby, another major discharge, Spring Creek, is located just offshore; its multiple boils discharge an estimated  $57 \text{ m}^3/\text{s}$  of water with similar concentration and isotopic values. Altogether, this calculates out to about 1.3 metric tons of uranium per year, only 85% of which has the equilibrium proportion of  $^{234}\text{U}$ . Where are the other 0.2 ton-equivalents of  $^{234}\text{U}$ ?

Extensive sampling of the karstic terrain soils and near-surface rocks in this region by Rydell [9] failed to reveal any large reservoir of high  $^{234}\text{U}$  solids. He concluded that flushing of the low A.R. uranium from the surface aquifer was a temporary condition caused by (a) development of grain-surface deficiencies of  $^{234}\text{U}$  by preferential leaching, which occurred under previous conditions of drier climate and lower water table, followed by (b) vigorous non-preferential leaching associated with post-glacial rise of the water table. He points out that such a low A.R. "rind" on massive, as opposed to fine-grained, aquifer rock surfaces would not produce a noticeable low A.R. for bulk rock samples.

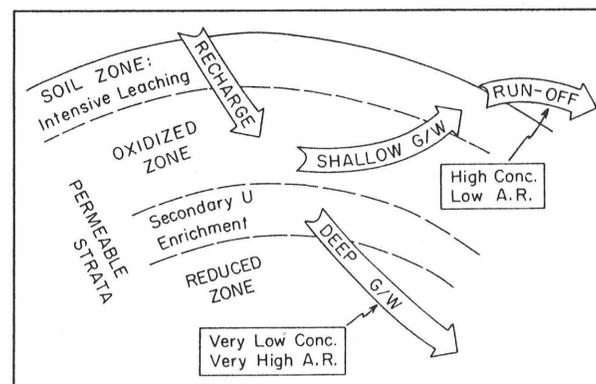
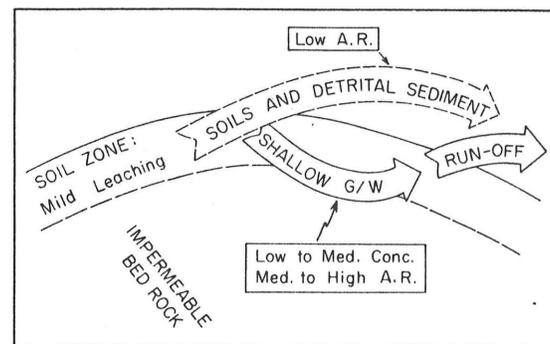


FIG. 14. Models for uranium isotope fractionation in regions of impermeable and permeable bedrock. Impermeable bedrock and/or mountainous terrain (top) causes groundwater regimes to be shallow and oxidizing. Leaching and recoil processes result in dissolved uranium having low to medium concentration and high A.R. The soil particles and eroded sediment have A.R.s less than 1.00. In regions of permeable rocks and/or aquifer recharge (bottom) infiltration becomes more important. As groundwaters penetrate the substrate, the uranium leached from oxidized regimes above accumulates at the reducing barrier below. The water that penetrates to great depth is consequently very low in uranium concentration, but has a high A.R. because of the recoil of  $^{234}\text{U}$  generated by the uranium coatings in the zone of enrichment. This accumulating uranium develops a low A.R. Shallow waters, which may escape to the surface, may be found to carry uranium in high concentrations and low A.R.s.

Subsequent investigations have shown that other aquifers with up-dip regions of low A.R. water exist [20], and also that the down-dip portions of these same aquifers are characterized by high A.R. water. The model developed by Cowart [77] and Cowart and Osmond [20] appears to have general applicability: when uranium is mobilized from oxidized weathered zones the dissolved uranium ( $6^+$ ) migrates as a carbonate or sulphate complex [27, 28, 129, 130] and it tends to remain in solution until it reaches the sea (Fig. 14, top). However, if the leaching water is part of a recharging system, lowering of the Eh by about 500 millivolts occurs at depth [131] and

uranium precipitates (Fig. 14, bottom). This may occur in a sharply defined zone of the type that has produced the sandstone ore bodies [54, 132–134] or it may be more diffuse geographically, as seems to be the case in limestone aquifers [131].

Szalay [135] showed that the process of uranium precipitation may be due to ion exchange adsorption of the  $\text{UO}_2^{2+}$  ion. Dement'yev and Syromyatnikov [29] hold a similar view, and suggest that decreasing the pH value of a carbonate solution to a value of about 6.0 will favour the formation of reducing and sorption barriers simultaneously.

At such a barrier uranium accumulates, adsorbed on the available surfaces. Such an accumulation of uranium as thin surface coatings makes an ideal condition for the process of selective leaching of  $^{234}\text{U}$  or recoil mobilization of  $^{234}\text{U}$ . The water that circulates through the reducing barrier, and on to greater depths in the aquifer, is characterized by having very low uranium concentration and very high  $^{234}\text{U}/^{238}\text{U}$  A.R. These high A.R.s [20, 77, 112], occurring as they do in the zone of low concentration, provide strong evidence for recoil as the dominant fractionation process in such conditions.

The uranium isotopic mass balance equation (Eq. (16)) requires that such high A.R.s in the transmitted water be balanced by low A.R.s in the surface coatings of uranium. Given that the landscape as a whole may be lowering by erosion at a rate of a few centimetres per thousand years, the uranium in the accumulation zone may be repeatedly recycled on the time scale of the average lifetime of  $^{234}\text{U}$  atoms. This recycling phenomenon, involving mobilization near the surface, immobilization at the reducing barrier and then remobilization as the weathering surface is lowered by regional erosion, is akin to the well-known formation of supergene ore deposits. By this model the very high A.R.s and low concentration values of down-dip dissolved uranium are explained and also the up-dip values of the recycled uranium, high in concentration and low in A.R.

We have now identified four principal pathways by which uranium passes through the weathering-erosion part of its geochemical cycle:

- (1) As weathered rock fragments, where  $^{234}\text{U}$  is deficient relative to equilibrium
- (2) Dissolved in oxidized surface and shallow groundwaters, where  $^{234}\text{U}$  is present in excess of equilibrium
- (3) Dissolved in deep reduced groundwaters, where  $^{238}\text{U}$  is very low in concentration, but where  $^{234}\text{U}$  is much in excess over equilibrium
- (4) Trapped in the recycling system by downward percolating oxidized waters and a reducing barrier, where dissolved concentrations may be high and  $^{234}\text{U}$  can be much below equilibrium.

Routes 1 and 2 may be considered normal, whereas the amount of uranium reaching the sea by 3 must be small. The same may be said of route 4, because if the recycling uranium escapes, the process will cease. In this sense the large amounts of low A.R. uranium escaping from the North Florida karstic region, referred to earlier, may indeed be, as postulated by Rydell, anomalous and temporary. It is also understandable that in early collections of data on uranium in surface water very low A.R. values were rare to non-existent.

The isotopic mass balance implications of the recoil-fractionation reducing barrier model for such topics as groundwater analysis, ore deposition, and continental erosion rates are discussed in later sections of this review.

#### 4. GROUNDWATER SYSTEMS

Groundwaters originate by infiltration through soils and weathered zones, which are the principal loci of uranium isotopic fractionation. Thus we may anticipate that groundwaters will exhibit uranium isotopic variations that are dependent on conditions in the recharge region, and that occasionally reach extreme degrees of fractionation.

Early studies showed that groundwaters as well as surface waters exhibit wide variations in uranium content and  $^{234}\text{U}/^{238}\text{U}$  ratio. Most of this early data is tabulated by Cherdyntsev [1].

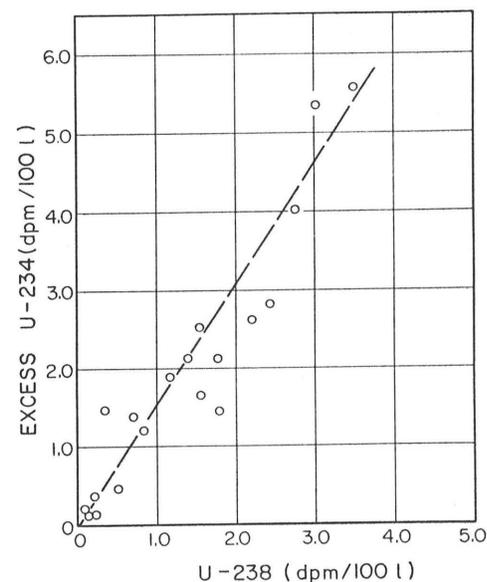


FIG. 15. Uranium isotopic variations in the underground waters near Tokyo. Kigoshi [22] interprets this trend pattern to be due to a continuous combination of two processes: non-selective leaching of uranium with an A.R. of 1.00; and simultaneous recoil ejection into the water of  $^{234}\text{U}$  (via  $^{234}\text{Th}$ ). By this interpretation the relative underground ages of the water samples run from lower left to upper right on the diagram.

Later investigations of groundwaters include those by Gottikh et al. [136], Syromyatnikov [137], Sultankhodzaev et al. [138], Spiridonov et al. [139], Rydell [9], Kaufman et al. [140], Kadyrov et al. [141], Zverev and Kuptsov [142], Alekseev et al. [16], Kigoshi [22], Wakshal and Yaron [15], Osmond et al. [143], Kronfeld and Adams [112], Cowart and Osmond [20, 23] and Knauss et al. [144].

We will consider groundwater systems to be of three types, each characterized by a particular uranium isotopic pattern: (1) open systems, entirely oxidized; (2) closed systems, confined aquifers reduced in the down-dip region; and (3) 'flooding' systems, which are like closed systems except for the escape of appreciable volumes of water to the surface from the upper part of the aquifer. Other groundwater types, such as geothermal, will be discussed as a separate topic in a later section.

The simplest groundwater systems, with respect to uranium isotopic character, are the open systems. These are aquifers in which the uranium, once leached, is conservative. The entire circulation system is sufficiently oxidized and/or with a high enough  $\text{pCO}_2$  to prevent precipitation of uranium. This includes most surface aquifers and in arid limestone terrains may include deeper aquifers as well.

An aquifer near Tokyo, although 150 metres deep, exhibits a fairly uniform pattern of increasing excess  $^{234}\text{U}$  with increasing uranium concentration. This is shown in Fig. 15, which is taken from a report by Kigoshi [22]. This aquifer system, according to Kogoshi, more or less continuously leaches uranium from its volcanic host rock, while accumulating excess  $^{234}\text{U}$  at the same time by the recoil process. The result is a fairly uniform A.R. of about 2 to 3 over the concentration range from 0.1 to 3.5  $\text{pp}10^9$ .

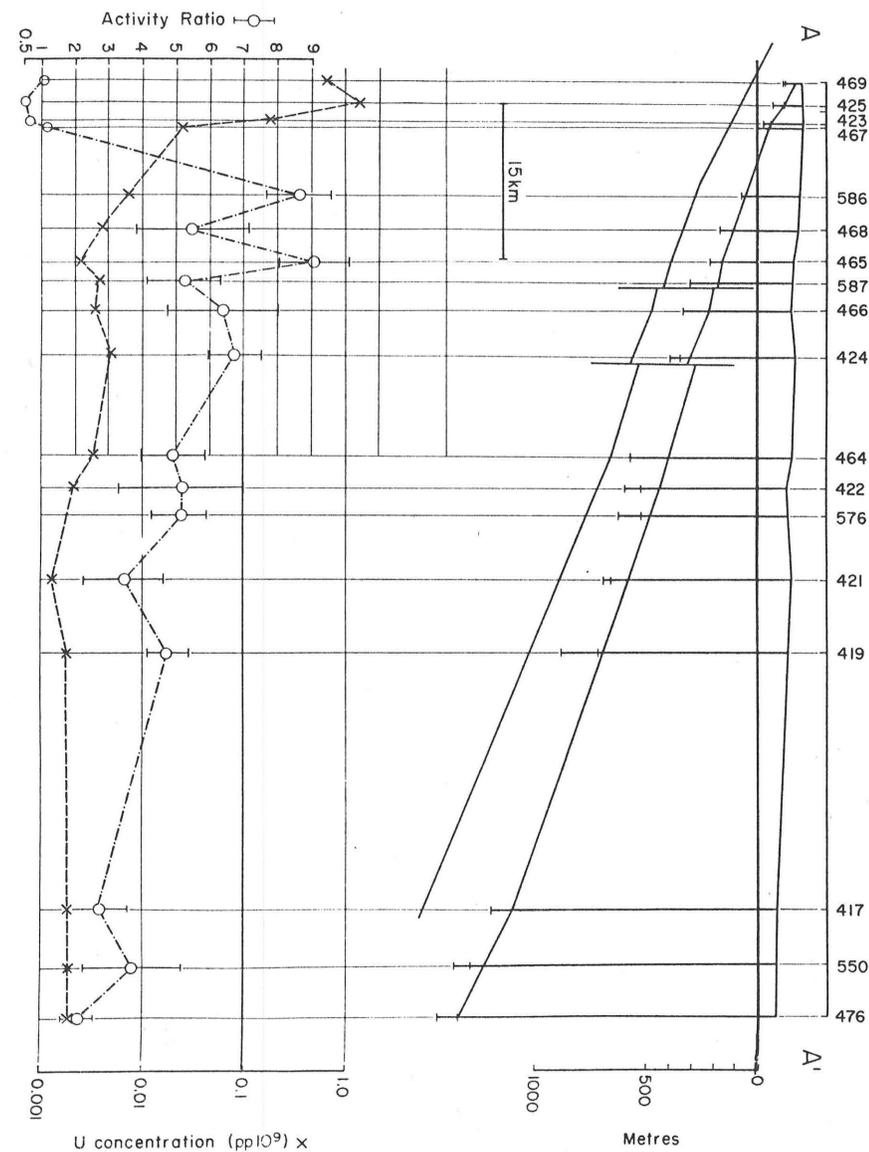


FIG.16. Uranium isotope variations in the Carrizo sandstone aquifer of Texas [20]. Top: Cross-section of the dipping aquifer showing locations of wells sampled. Bottom: Variations of uranium concentration (right-hand scale) and  $^{234}\text{U}/^{238}\text{U}$  A.R. (left-hand scale). The precipitous decrease of dissolved uranium concentration is interpreted as due to a reducing barrier, where uranium is accumulating on grain surfaces. The high A.R.s down-dip are due to the addition of  $^{234}\text{U}$  as the water flows past this accumulation zone. The sorbed uranium because of this loss of  $^{234}\text{U}$  develops a low A.R.; when it is later remobilized up-dip it contributes a low A.R. to the water. The decreasing A.R. far down-dip is discussed in Fig.17, and in the text.

Similarly, the four aquifer systems described by Wakshal and Yaron [15], each characterized by its own A.R., appear to be the open system types.

The underground artesian waters of two large basins in central Asia, the Pritashkent and the Bukharo-Karshinski, have been studied by Alekseev et al. [16]. These basins exhibit medium to high A.R.s associated with concentration values that are unusually high for deep groundwater systems (these data are included in the generalized plots of Fig.3). Since there are no low A.R. values anywhere in the two systems, we conclude that these artesian aquifers are uranium conservative, although the investigators describe certain of the aquifer zones as "stagnant". The A.R.s of the uranium in these zones are somewhat less than the values of the source waters up-dip. This decrease in A.R. with flow direction is attributed by the investigators to decay of excess  $^{234}\text{U}$ , and the calculated flow rates, 9 to 18 cm/a, seem to be in agreement with hydrodynamic data.

A very different isotopic characterization pertains to what we call closed-system aquifers. Alternatively, we might use the phrase, 'reducing barrier-recharge systems'. The essential feature, from our standpoint, is that in the course of flow to greater depths the water becomes reducing and the dissolved uranium precipitates and accumulates along a front that uranium-ore exploration geologists have called the 'reducing barrier'. Such an aquifer displays extreme variations in the uranium isotopic character of its water: high concentration and low A.R.s. up-dip, and low concentration and high A.R.s down-dip. The 'trapped and recycled' uranium model, which explains these isotopic values, was discussed in the previous section.

Only two such closed systems have been investigated in detail, both in Texas. However, we anticipate that many other artesian systems will be found to have a similar pattern.

The variations in the uranium isotopic character of the Eocene Carrizo sandstone aquifer of South-central Texas, both along strike and down-dip have been delineated by Cowart and Osmond [20,23]. This particular aquifer was chosen for study because it had previously been investigated extensively by geologists, hydrologists and isotope geochemists. Pearson and White [145] have determined its water flow rate by  $^{14}\text{C}$  techniques. The basic pattern of change of uranium isotopes down-dip is shown in Fig.16 (the changes are less extreme but still well defined for other cross-sections drawn further east).

Although there is no direct evidence, Cowart and Osmond believe that the sharp decrease in uranium concentration at about 5 km down-dip marks a uranium accumulation zone similar in nature (but not necessarily in economic value) to the well-studied sandstone ore bodies of Wyoming, and perhaps also to the Karnes County, Texas, ore body in Miocene sands located a few tens of kilometres southeast. They are unsure about the explanation for the gradual decrease in A.R. further down-dip. From the rate of flow, determined by  $^{14}\text{C}$  dating of the  $\text{CO}_2$  dissolved in the water and in agreement with the value arrived at independently by hydrologic studies [146], this cannot be due simply to decay of excess  $^{234}\text{U}$ ; the time scale is too short (Fig.17). Among the possibilities are: (1) re-equilibration of the dissolved uranium isotopes with those of the host rock, a process that would be favoured by the somewhat elevated temperature of the water at depth ( $66^\circ\text{C}$  at location 476, Fig.16); (2) rapid increase in size of the accumulation zone within the last 20 000 years — the down-dip waters are, by this view, pre-accumulation waters; (3) changes in the reducing barrier accumulation zone relationship. Recoil-model considerations suggest that if reducing and accumulation are now occurring further up-dip than formerly, the earlier accumulations will cause larger relative inputs of  $^{234}\text{U}$  in low concentration water, with a greater effect on the A.R. (Fig.29). Conversely, a shift by the barrier down-dip will result in the recoil, from the earlier accumulation zone, having a smaller effect on the A.R. because leaching and concentration are high. Among the factors that might have caused such shifts in the reducing barrier, Cowart and Osmond [20, 23] suggest a change in climate, which by a change in recharge rate might tend to cause the lower edge of the oxidized zone to shift somewhat up-dip.

In the Hosston sandstone aquifer, some 300 km to the northeast of the Carrizo, Kronfeld [10,113] and Kronfeld and Adams [112], have studied the very high A.R. waters of a similar system. No extensive collection of up-dip samples was done and so the accumulation zone was

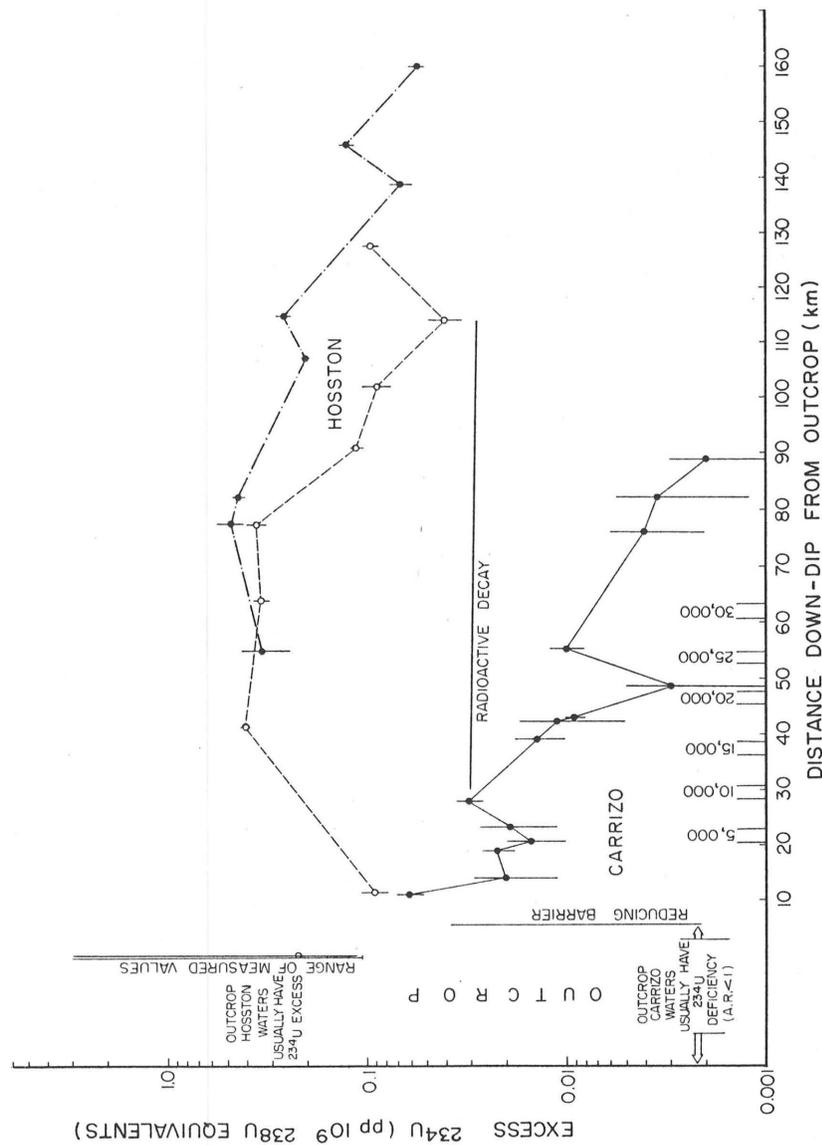


FIG. 17. Uranium-234 excess as a function of down-dip water flow in two Texas aquifers. Both the Hosston and Carrizo sandstone aquifers are characterized by water with low uranium concentration and very high A.R. down-dip. The Hosston pattern (drawn from the data of Kronfeld and Adams [112]) is shown along two flow lines and has been interpreted as the result of  $^{234}\text{U}$  accumulation by recoil followed by decay of the excess. The Carrizo curve (from Cowart and Osmond [20]) falls more steeply and the radiocarbon dating of the water (bottom scale) shows that the flow rate here is too fast for the decay of  $^{234}\text{U}$  to be important. The line labelled "radioactive decay" indicates the rate of decrease of the dissolved excess  $^{234}\text{U}$  if water in the Carrizo continued to travel at the rates indicated by radiocarbon investigation and decay was the only process causing the decrease.

not delineated, nor did the investigators consider it to be a factor in the decreasing A.R.s found down-dip (Fig. 17). It was concluded that the flow rate is slow enough for decay of  $^{234}\text{U}$  to be the explanation for the observed A.R. decrease; this has not been tested by  $^{14}\text{C}$  dating. Extensive faulting present in down-dip reaches of the Hosston may be a factor that obviates closed-system analysis. We believe, as suggested by Fig. 17, that the two Texas aquifers are exhibiting the same isotopic pattern, which, on further study, will turn out to have a single explanation.

A third type of aquifer system, as characterized by uranium isotopes, is represented only by the limestone aquifer of the karstic region of Florida. It is unique in that it underlies the only large area thus far identified having low A.R.s. in the regional run-off (discussed in the previous section). This region is a major groundwater recharge area, with many sinks and caverns which once served as conduits to the water table below. Now, however, the groundwater table is high, the caverns are flooded and many former sinks have become major springs. Thus it is that the regional run-off may be considered to be escaping aquifer water. (There are today 25 first magnitude springs in Florida with discharge of 2.85 or more cubic metres per second.)

Such a 'flooding' aquifer has similarities to the closed-system aquifers described above. However, we will discuss it here as if it were a separate category because: (a) the Floridan system has been studied so extensively with regard to its dissolved uranium isotope variations [8, 9, 99, 140, 143, 147] and (b) we expect that, in time, similar examples will be identified elsewhere.

In at least some limestone aquifers the water tends to be oxidized to great depths and appears to be uranium-conservative throughout. An example is the Paleozoic carbonate aquifer of Southern Nevada (Cowart and Winograd, unpublished data). However, we believe the Floridan system is so thick that as upper aquifer horizons funnel water to lower aquifer horizons reducing barriers are encountered. Thus, isotopically speaking, two distinct aquifers are present, a lower zone with low uranium concentration and high A.R.s, and an upper zone with higher uranium concentrations and low A.R.s. These are, of course, the same zones identified in the closed-system aquifers such as the Carrizo and Hosston of Texas. Whereas in sandstone aquifers the reducing barrier may be fairly shallow and well defined, the zone of reduction in limestone aquifers is probably indistinct and quite deep [148]. In Florida some of the formations associated with the aquifer system are highly phosphatic and somewhat uraniferous. This causes the concentration level of uranium in the entire upper zone to be especially high, but we believe that the same two sub-systems, oxidized and reduced, would be recognizable isotopically in any thick limestone system. A preliminary investigation of the Cretaceous Edwards limestone near San Antonio, Texas, tends to confirm this (Cowart, unpublished).

An important question is whether the Floridan flooding aquifer represents a 'steady-state' system. Arguing against this is the known extensive rise in water table, related to increasing eustatic sea level in the period 10 to 5 thousand years ago, and the large quantities of low A.R. uranium being flushed out of the system. On the other hand, the water doing the flushing is not relic but is water that has a residence time in the upper aquifer of a few days to a few years. If sea level and the groundwater table were now to remain stable, lowering only slowly as regional erosion (mostly chemical) progressed, and if the process of regional recharge continued, the model suggests that the upper aquifer would continue to serve as a zone of uranium accumulation and recycling with its low A.R. and high concentration values. However, with continued flooding and escape of water to run-off these values might be less extreme.

It was unexpected when Cowart et al. [17] discovered in the lower peninsula of Florida zones of the aquifer with A.R.s less than 1.00. Inasmuch as these waters (about 300 metres deep) must be old and far removed from their point of infiltration [148], their accumulation-zone isotopic character was puzzling. But an important clue was noted: the low A.R. water is associated with zones of unusually high permeability; in fact, the deep aquifer in some places is cavernous. This leads to at least two possible explanations: (1) although the deep aquifer is isolated from the surface today, at a time of greatly lowered sea level there may have been conduits

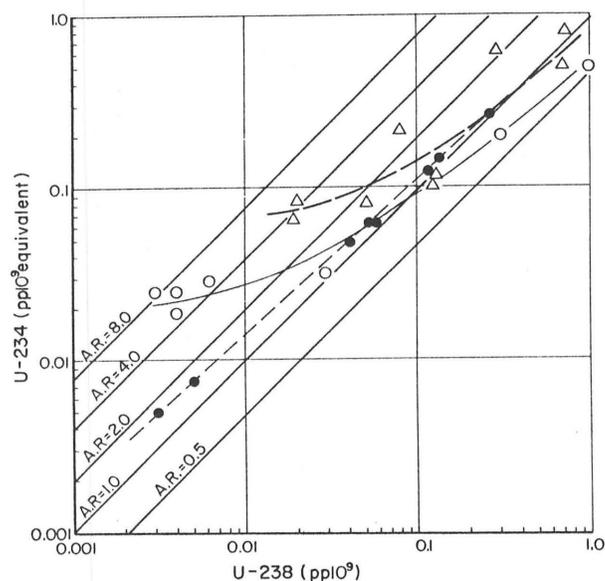


FIG. 18. Uranium isotope trend patterns in three groundwater systems. In this type of diagram the log of  $^{234}\text{U}$  ( $\text{U pp}10^9$  equivalent) is plotted against the log of  $^{238}\text{U}$  ( $\text{pp}10^9$ ). A.R. values appear as parallel lines. The log scales are required because of the large variation in concentration between oxidized and reduced parts of the systems. The dashed lines are rough trend lines for the three systems. (On an arithmetic scale these trend lines would appear as straight lines.) The open triangles are Florida karstic terrain waters [99], where physical weathering is minimal and the leaching ratio is moderately low. The high excess  $^{234}\text{U}$  probably results from the abundant uranium in the phosphatic aquifer. The open circles are the Carrizo aquifer waters, with very low leaching ratio (Fig. 16). The solid circles are geothermal waters at Yellowstone Park, USA. Geothermal waters are characterized by low concentrations of  $^{238}\text{U}$  and low amounts of excess  $^{234}\text{U}$ ; presumably high temperatures and reducing conditions favour precipitation and isotopic equilibration.

of leakage of upper aquifer waters downward through the aquiclude or the rate of water movement from the recharge area down-dip may have been much greater; or (2) there may be, even at great depths, minor accumulation zones brought about by local reduction barriers as a result of marked differences between the more and the less permeable parts of the aquifer. In this view, there would be two stages of uranium precipitation, one near the surface, and a second at greater depths, and each would result in an accumulation zone. Such a system might be related to changes in flow conditions brought about by changes in sea level and potentiometric head.

In summary, we have categorized groundwater systems in terms of their uranium isotopic character, i.e. uranium concentration and  $^{234}\text{U}/^{238}\text{U}$  activity ratio. A more formal isotopic approach, and one that to us has a greater meaning phenomenologically, is that suggested by the trend lines of the various plotting techniques. If one plots a large number of samples from a given aquifer on such a diagram, a linear trend is usually displayed, e.g. the aquifer near Tokyo (Fig. 15), the Floridan aquifer of Florida (Fig. 13) and the Carrizo aquifer of Texas (Fig. 18). Significantly, in the latter case, a closed system aquifer, the contrasting isotopic values for up-dip and down-dip waters turn out to be opposite ends of the same linear trend.

In such cases either simple mixing of observable components may be inferred, or we may be justified in evaluating the role of hypothesized extreme end-member components.

TABLE IV. TREND LINE PARAMETERS

Y and X axes	Intercept (b)	Slope (m)
A.R. versus S	A.R. at infinite concentration (leaching term)	$^{234}\text{U}/\text{litre}$ at zero concentration (recoil term)
A-234 versus A-238	$^{234}\text{U}/\text{litre}$ at zero U concentration (recoil term)	A.R. at infinite concentration (leaching term)
X-234 versus A-238	Excess $^{234}\text{U}$ at zero concentration (recoil term)	X-234/ $^{238}\text{U}$ at infinite concentration (leaching term)

The equation of such a trend line is

$$y = mx + b \quad (22)$$

where  $b$  is the ordinate intercept and  $m$  is the line slope. The units of  $b$  are given by the ordinate, and the units of  $m$  are given by the ordinate/abscissa ratio. In all three of the plotting methods described previously  $b$  and  $m$  have the same (or inverse) end-member components, terms that are equivalent to (1)  $^{234}\text{U}/^{238}\text{U}$  alpha activity ratio at high  $^{238}\text{U}$  concentrations, and (2)  $^{234}\text{U}$  activity per litre at low concentrations. To the extent that these parameters are related to real fractionation phenomena, they may be called 'the leaching ratio term' and 'the  $^{234}\text{U}$  recoil term' respectively. (The  $^{234}\text{U}$  intercept is always positive or zero in systems we have reviewed or studied.) Table IV identifies these terms for the three plotting systems.

The leaching ratio may be any value from a high of 3 or 4 down to a low of about 0.5. In the case of high concentration values we are inclined to accept Kigoshi's view [22] that this involves simultaneous recoil and non-selective leaching. The recoil term, however, represents 'pure' recoil, completely independent of any leaching process, and is determined by extrapolation of the trend line to very low concentration values. A significant pure recoil term would be expected to result only from a high concentration of uranium in the aquifer rock and/or a long residence time of water in the aquifer. Consistent with this is the report of very high A.R.s (8–10) in brines from a deep oil test in Israel [21].

Figure 19 shows a plot of the  $b$  versus  $m$  parameters of several regional aquifer systems (as derived from A-234 versus A-238 plots), including many of those discussed in this review. They can be grouped into four categories corresponding to subdivisions of the aquifer types discussed above:

- (1) High  $m$  and low  $b$ : open system (oxidized) aquifers, and most regional run-off systems;
- (2) Low  $m$  and high  $b$ : closed system aquifers, involving recharge to lower depths through reducing barriers; by this analysis, the Floridan karstic system is considered a special case of closed system aquifers;
- (3) Low  $m$  and low  $b$ : the only examples to date are high temperature (geothermal) systems, which appear to result from some combination of factors: reducing conditions throughout (leaching is suppressed), rapid circulation and short time scale (recoil processes are suppressed), and high temperature isotope equilibrium with aquifer minerals (earlier leaching and recoil characteristics of circulating water are erased);
- (4) High  $m$  and high  $b$ : systems that have large excesses of  $^{234}\text{U}$  in both leaching and recoil terms are likely to be associated with high uranium concentrations in the aquifer rock exposed to circulating waters.



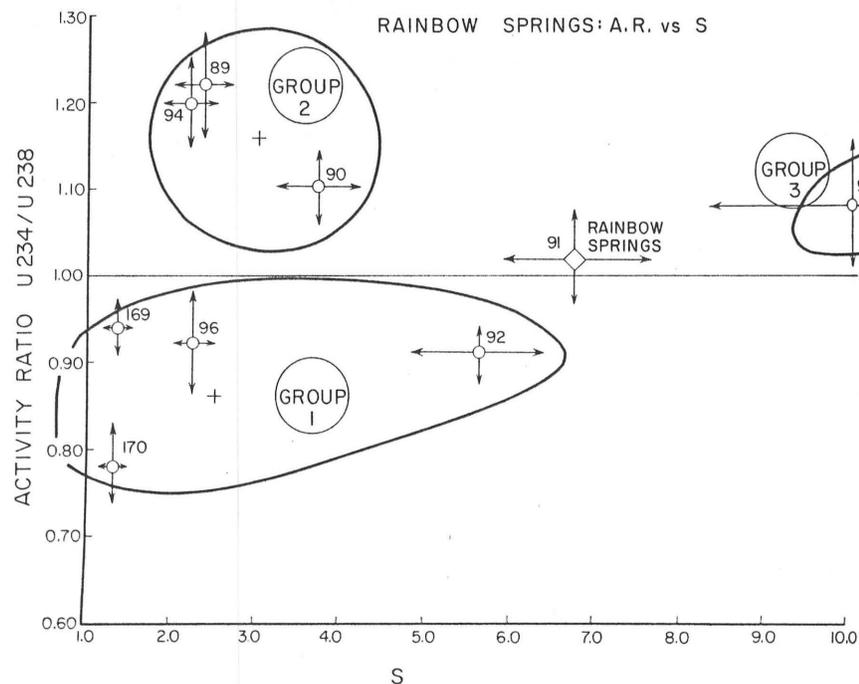


FIG. 21. Plot of uranium isotopes in possible component waters flowing to Rainbow Springs, Florida (see map, Fig. 20).  $S = 1/C$  (where  $C$  is uranium concentration in  $\text{pp}10^9$ ). + indicates the representative values used to compute the three-component mixing proportions (Eq. (24)). Group 3, consisting only of sample 95, was, as expected, the major contributing type (80%). Group 2, however, was calculated to be less important (6%) than Group 1 (14%). (From Osmond et al. [99].)

We presented in an earlier section a discussion of the appropriate parameters to measure and plot in order to have the linear mixing lines of a standard phase diagram. In summary, if the two intensive parameters can be balanced, or averaged, in terms of the same extensive parameter, the linear phase diagram requirements are met, and mixing equations can be used. For example  $A^{234}$  (activity of  $^{234}\text{U}$  in  $\text{dph/l}$ ) and  $A^{238}$  ( $\text{dph/l}$ ) are two such commensurate parameters, and

$$\frac{V_1}{V_2} = \frac{A_2^{234} - A_t^{234}}{A_t^{234} - A_1^{234}} = \frac{A_2^{238} - A_t^{238}}{A_t^{238} - A_1^{238}} \quad (23)$$

where  $A_1$ ,  $A_2$  and  $A_t$  are the activities of the two components and the resultant mixture respectively. For a three-component system

$$\frac{V_1}{V_2} = \frac{(A_t^{238} - A_3^{238}) \left( \frac{A_3^{234} - A_2^{234}}{A_3^{238} - A_2^{238}} \right) - (A_t^{234} - A_3^{234})}{(A_t^{238} - A_3^{238}) \left( \frac{A_3^{234} - A_2^{234}}{A_3^{238} - A_2^{238}} \right) - (A_1^{234} - A_3^{234})} \quad (24)$$

where  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_t$  are the activities of the three components and the resultant mixture respectively.

Because of the phase rule considerations discussed previously, a two-parameter system does not provide a unique solution to mixing problems involving more than three components. The equations used and derived by Osmond et al. [99] are essentially the same as Eqs (23) and (24), except that an extra term was required to convert one extensive parameter ( $\mu\text{g}$  of  $^{238}\text{U}$ ) into the desired extensive parameter (litres of water).

Figures 20 and 21, from the paper by Osmond et al. [99], show how the mixing equations are applied to Rainbow Springs in Central Florida. The possible sources of spring water consist of three shallow groundwater flow azimuths. The distinct isotopic character of these three components is thought to be due to their slightly different recharge conditions. This example, though interesting, is only illustrative of the technique. A complete study would have required more sampling so as to demonstrate that only three distinctive components were involved.

A truly definitive application of the mixing equations was the goal of Briel [8], who investigated the interaction of ground and surface waters of a karstic terrain river in Florida. He recognized three sources of water types, based on uranium isotopes, which contribute to the river flow volume as it traverses a region of numerous springs. The cavernous nature of the limestone country rock permits a large fraction of downstream flow to be underground; in fact the entire river disappears along one 5 km reach.

TABLE V. URANIUM ISOTOPES IN THE GREAT LAKES, NORTH AMERICA

Sample location	FSU sample number	Identifier in Fig. 23	Uranium conc. ( $\text{pp}10^9$ )	Activity ratio $^{234}\text{U}/^{238}\text{U}$	Excess $^{234}\text{U}$ ( $\text{pp}10^9$ equivalent)
L. Superior, at Keewenaw Peninsula	805	3	$0.048 \pm 0.002$	$1.33 \pm 0.06$	$0.016 \pm 0.003$
L. Superior, at Keewenaw Bay	806	3	$0.046 \pm 0.002$	$1.29 \pm 0.07$	$0.014 \pm 0.003$
L. Superior, at Sault Ste. Marie, Mich.	809	4	$0.045 \pm 0.002$	$1.30 \pm 0.06$	$0.014 \pm 0.003$
L. Michigan, at Green Bay	804	5	$0.293 \pm 0.006$	$1.28 \pm 0.03$	$0.081 \pm 0.010$
L. Michigan, at St. of Mackinac	810	6	$0.251 \pm 0.004$	$1.27 \pm 0.03$	$0.068 \pm 0.007$
Blind River, Ontario	807	1	$0.019 \pm 0.002$	$1.24 \pm 0.12$	$0.004 \pm 0.003$
Mississagi River, Ontario	808	2	$0.155 \pm 0.004$	$1.05 \pm 0.03$	$0.008 \pm 0.006$
Lake Huron, at St. Claire River	811	-	$0.151 \pm 0.003$	$1.22 \pm 0.03$	$0.042 \pm 0.004$
Lake Erie, at Monroe, Michigan	812	8	$0.156 \pm 0.003$	$1.16 \pm 0.03$	$0.032 \pm 0.004$
Nagara River (Lake Erie)	813	7	$0.316 \pm 0.006$	$1.13 \pm 0.03$	$0.057 \pm 0.010$
St. Lawrence River at Ogdenburg, N.Y.	814	10	$0.343 \pm 0.014$	$1.16 \pm 0.04$	$0.055 \pm 0.018$

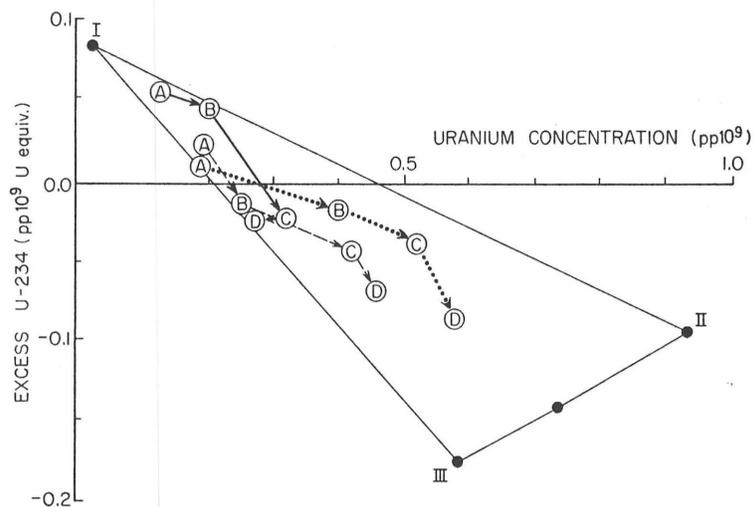


FIG. 22. Seasonal uranium isotopic variations in a river in karstic terrain (after Briel [8]). The Sante Fe River of Central Florida is a tributary of the Suwannee River, and in its lower reaches is fed by numerous springs. In this figure excess  $^{234}\text{U}$  is plotted against uranium concentration. Sequential locations A, B, C and D were sampled at low discharge ( . . . ), medium discharge ( - - - ), and high discharge ( — ) stages of flow. The uranium isotopic character of the water permits the calculation at any location and stage, of the three volume components: upstream water (type I), spring water of type II, and spring water of type III. A two-component analysis, using a point between II and III, is also possible. Because the volume contribution of the springs is less variable than run-off, higher stages of flow are characterized by enhancement of the up-stream-like component.

By computerized application of two and three-component mixing formulae, Briel was able to calculate, at each sampling site, the relative contributions of an 'upstream' and two 'underground' water component types, and to trace the main flow lines of the river in its underground reaches. He was also able to define quantitatively the relative run-off and groundwater contribution to the river at various flood stages. Figure 22 shows how the underground components B and C increasingly contribute to the stream discharge downstream, and how these contributions decrease relative to the surface component, A, during the rainy seasons.

A preliminary and tentative application of the mixing concept is offered by data from the Great Lakes system of the USA and Canada. Table V and Fig. 23 show the results of our analyses (not previously published). We hesitate to draw any conclusions about such a vast and complicated system on the basis of a few data points, inasmuch as we are stretching the requirements for well-defined components and completely conservative conditions. Nevertheless, it appears that parts of the system (e.g. Lake Superior + Lake Michigan = Lake Huron) are behaving like a simple mixing system. The isotopic changes across Lake Erie, however, are not consistent; considerable evaporation, leaching, or mixing with unknown components (industrial effluents or remobilized uranium from the bottom sediments) is indicated.

## 6. URANIUM ISOTOPES AND GEOCHEMICAL BALANCES

In this section we will regard the various occurrences of uranium in natural waters as parts of the general geochemical cycle of uranium. Uranium in unweathered rock is at radioactive

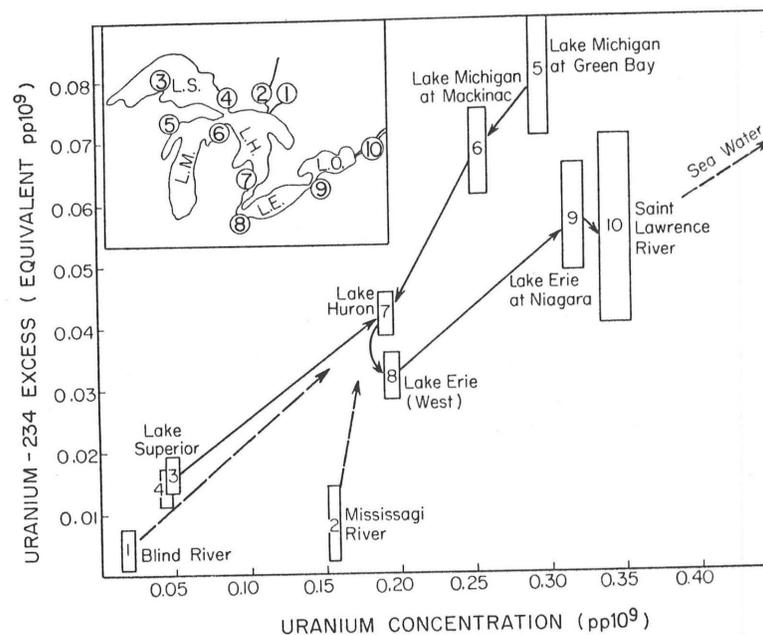


FIG. 23. Uranium isotopic variations for the Great Lakes of North America (Table V). Excess  $^{234}\text{U}$  is plotted against uranium concentration so that the variations in A.R. can be emphasized and the mixing proportions easily visualized (rectangles are data uncertainty limits). Geographically we know that Lake Superior water joins with Lake Michigan water to form Lake Huron. Isotopically, the plotted position of Lake Huron suggests that there is roughly a 50/50 mixture of Michigan and Superior water types (the effects of other sources such as the Mississagi and Blind Rivers are probably not significant). Lake Superior appears to be homogeneous with respect to uranium isotopes. The cause of the isotopic change across Lake Erie may be any one, or some combination, of the factors: inhomogeneity of lake waters, evaporation, other natural sources, or pollution. The uranium isotopic values for the St. Lawrence River are typical of continental waters draining into the sea (Conc. =  $0.35 \text{ pp}10^9$ , A.R. = 1.25).

equilibrium (A.R. = 1.00), and after burial and lithification uranium returns to the equilibrium state. In between uranium-238 and uranium-234 proceed through the external cycle by somewhat different pathways and at somewhat different rates (Fig. 24). However, the laws of radioactivity are not abrogated simply because the parents and daughters become separated and, indeed, the induced localized disequilibria and their drive toward equilibrium are the source of much of our interest.

Several geochemists have noted the unique insight offered by uranium isotope variations with regard to global balances of, not just uranium, but associated sediments and waters as well. Among these are Veeh [150], Bhat and Krishnaswamy [13], Baturin and Kochenov [151], Sackett and Cook [127], Heye [152], Sackett et al. [153], Turekian and Chan [154], Baturin [155] and Ku et al. [12].

Uranium is transported to the sea via three pathways: dissolved in surface run-off water, dissolved in groundwater which percolates into the sea below the strand-line, and incorporated in detrital sediments. The A.R. of surface and groundwater uranium is generally high and the A.R. of detrital sediments is generally low. The amount of uranium transported in solids is greater than that in solution by an amount which we will be able to calculate below. The amount in surface water is greater than that in groundwater, to the extent that we may be justified in neglecting the latter.

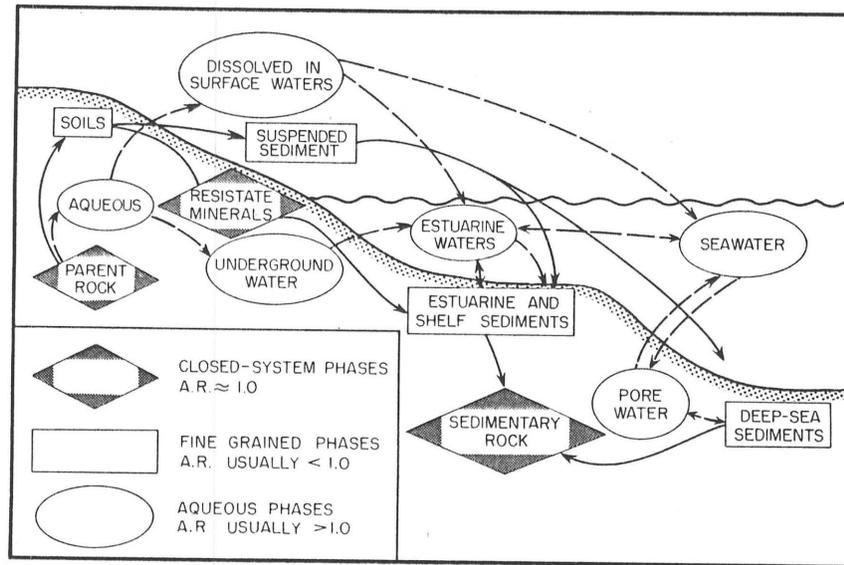


FIG. 24. Geochemical cycle of uranium near the earth's surface. Disequilibrium is initiated by water-mineral interactions in soils and weathered rock, and in aquifers where the surface to volume ratio is high. In general, a fine grained solid phase will exhibit  $^{234}\text{U}/^{238}\text{U}$  activity ratios less than 1.00 due to grain surface leaching and/or alpha recoil. Aqueous phases, including groundwater, surface water and ocean water, generally exhibit ratios greater than 1.00. In some parts of the cycle, e.g. soils, seawater and sediments, the uranium residence time is long enough so that the decay of  $^{234}\text{U}$ , with a half-life of 250 thousand years, can affect the A.R.

Garrels and MacKenzie [156] have analysed the dissolved and suspended load of rivers and concluded that the world's land masses are being eroded by chemical versus physical processes in the ratio of 4.7:1.0. Related estimates of sediment and chemical erosional fluxes by Judson and Ritter [157], Horn and Adams [158] and Holeman [159] are similar. Relatively insoluble elements like iron and manganese are concentrated in or on the surfaces of hydrolysis minerals, and are being transported in pathway proportions (chemical to mechanical) that are smaller. Uranium, being soluble and solution-conservative under most normal surficial conditions, should be transported via the two pathways in the same proportions calculated by Garrels and Mackenzie.

In the case of uranium we can calculate these proportions by use of a form of the mass balance equation:

$$\frac{M_s}{M_r} = \frac{\gamma_r - 1.0}{1.0 - \gamma_s} \quad (25)$$

where components s and r are detrital (sediment) and dissolved (river) transported uranium respectively. The value for  $\gamma_r$ , the A.R. in average run-off, can be estimated to be about 1.3 based on the data plotted in Fig. 2, plus a few hundred surface water A.R.s not plotted because of a lack of concentration data (mostly by early Russian investigators). The value for  $\gamma_s$ , the A.R. of average river sediment, is a little harder to determine; Table III lists some of the data, which can be used to calculate an average. In arriving at a figure of about 0.94, it is assumed that

suspended and bottom load sediments of a river have about the same A.R., and that both are roughly equivalent to that in the B horizon of soils. Using these values in Eq. (24), we calculate that  $M_s/M_r$  is about 5, i.e. there is 5 times as much uranium transported with the sediment as in the dissolved state, a value that is in good agreement with the Garrels and McKenzie estimate for erosion as a whole.

An important assumption of this balance calculation, based on a steady-state system, is that  $\gamma_t = 1.00$ , i.e. although this is not a closed system, the escaping components are in balance at equilibrium. However, the uranium in and on the soil particles may be held back by as much as  $10^5$  years or so relative to the dissolved uranium, which is washed away immediately. The low A.R. in soils will tend to revert toward equilibrium by the decay function, which leads to an underestimation of the deficiency of  $^{234}\text{U}$  in the detrital phase and makes the calculated  $M_s/M_r$  ratio an upper limit.

Conceivably, changes in pH conditions may cause the dissolved uranium to be reabsorbed on particulate matter in rivers. Lewis [192] suggests that this is a normal occurrence, and cites uranium/calcium mixing diagrams for the Susquehanna River system as evidence.

One of the useful features of the use of Eq. (25) is that if  $M_s/M_r$  for uranium can be taken to be equivalent to the ratio of chemical to mechanical weathering erosion and if the uranium content of continental rocks is known, then global crustal erosion rates can be calculated from either (a) the flux of dissolved uranium in rivers, or by (b) the flux of uranium in sediments, or (c) by some combination of the two.

For example, we use as an average uranium concentration for rivers 0.4 ppb, taken from the data of Fig. 2, and an average uranium concentration for crustal rocks of 3 ppm, Rogers and Adams [2], and a continental water run-off of 25 cm/a. With an  $M_s/M_r$  ratio of 5, we calculate a world average erosion rate of 6 g/cm<sup>2</sup> per thousand years. This is in the lower range

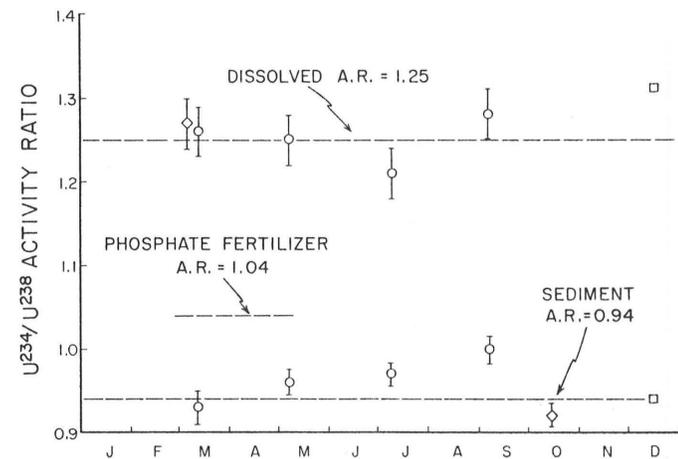


FIG. 25. Seasonal variation in  $^{234}\text{U}/^{238}\text{U}$  activity ratio in the water and sediment of the Mississippi River, as determined by Kaufman [126]. Neither the water nor sediment uranium shows major fluctuations with river discharge stage, whereas the uranium concentration values are more variable. Some investigators have suggested that the addition of uraniumous phosphate fertilizer has changed the balance of uranium by increasing the dissolved component. If this possibility is assumed to be negligible, the ratio of dissolved uranium to sediment-carried uranium in the Mississippi River can be calculated to be about 1 to 4 (Eq. (25)).

of estimates made by standard methods [157]. It would appear that this crude analysis is capable of considerable refinement, and that reliable determinations of regional, if not global, erosion rates are possible. A study of the uranium balance relationships of the Mississippi River drainage area is being made by Kaufman [126]. His calculations are at this writing, incomplete, but among his tentative conclusions are the following: (1) A.R. data for dissolved uranium is more consistent seasonally than is uranium concentration; (2) the widespread use of uraniumiferous phosphate fertilizer has not ruled out the making of this kind of calculation (contrary to the fears of Sackett et al. [153]); and (3) the Mississippi River drainage area calculations of  $M_s/M_r$  and regional erosion rates by the use of uranium isotopes are in general agreement with world-wide estimates (above). Some of Kaufman's uranium data for the lower Mississippi River are shown in Fig. 25.

It was assumed for the sake of the mass balance calculation above that the only pathways for transport of uranium to the sea are via run-off and water-transported sediment. The role of underground water flowing into the sea was neglected, as it usually is in balance problems involving the hydrologic cycle. It is possible that a refined analysis of uranium isotope balances could help answer questions concerning the quantitative role of underground water seepage into the seas. Globally, the wide range of uranium concentration and A.R. displayed by underground water (Fig. 2) would make average values difficult to estimate, and such an estimate of concentration would be quite low. The flux of neither  $^{238}\text{U}$  nor  $^{234}\text{U}$  could be very significant along this pathway. Locally, however, as along parts of the Florida coast, high groundwater flow rates and high uranium concentration values may make such a calculation worthwhile.

Another pathway of uranium transport, not usually considered to be significant, is through the atmosphere. Although evaporation should yield atmospheric water of zero uranium content, aerosol and dust particles have been increasingly recognized as carriers of heavy metals. The average concentration of uranium in rain water due to this factor is hard to estimate. Alekseev et al. [16] report a uranium concentration in one sample as  $1.0 \text{ pp}10^9$ . The A.R. of this sample was  $1.06 \pm 0.01$ . For glacial ice they report a uranium concentration of  $4 \text{ pp}10^9$  at an A.R. of  $1.00 \pm 0.05$ . Zverev and Spiridonov [160] determined the A.R. of rain water to be  $1.08 \pm 0.08$  and  $1.06 \pm 0.01$  at two places, but did not determine the absolute concentrations.

The fate of uranium after arrival at the sea, although not a major concern of this review, illustrates the potential value of uranium isotopic studies and also enables us to estimate average river concentration and A.R. values. For example Ku [161], Sackett and Cook [127], Sackett et al. [153] have observed that the accumulation rate of uranium in deep-sea sediments is too small to account for that amount of uranium calculated to be eroding from the continents. Speculation as to the location of the necessary sinks to balance the cycle have tended to focus on localized basins of reducing sediments such as the Black Sea [162], on the continental shelf and slope [150] and in estuaries. Among early studies was that of Koczy et al. [163] albeit without the use of isotopic ratios, wherein the importance of the reducing sediments of the North Sea were emphasized. More recently Kolodny and Kaplan [164] have come to similar conclusions regarding the muds of anoxic fjords.

Marine phosphorites of authigenic origin are uraniumiferous and may also play a role in the geochemical balance of uranium [165-167].

A study of the movement of dissolved uranium through Tampa Bay, Florida, using uranium isotopic data from both waters and sediments is being investigated by Kaufman (unpublished). He recognizes three sources of uranium: in-flowing streams, mixing marine waters, and effluent from a phosphate treatment plant. By use of uranium concentration versus salinity plots (Fig. 26) and uranium isotopic plots (not shown), he concludes that Tampa Bay sediments, though not markedly reducing, are indeed behaving as a uranium sink and that the uranium in such sediments is derived not only from river and pollution influx but from the sea as well. Other studies concerned with uranium isotopes in coastal and shelf sediments include those of Blanchard [37], Bernat and Allegre [168], Lopatkina [169], Joshi and Ganguly [170] and Aller and Cochran [171].

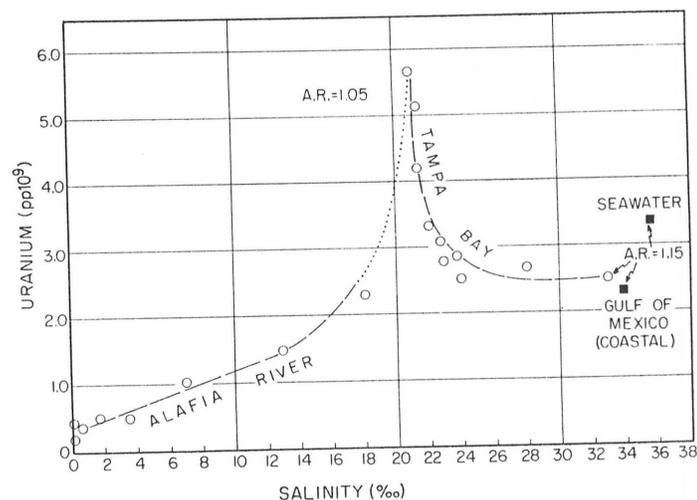


FIG. 26. Variations in uranium relative to salinity in a river-estuary system, at Tampa, Florida (Kaufman, unpublished). In the Alafia River estuary the straight line plot suggests that the increase in uranium downstream is due to mixing with seawater and that the uranium is conservative, i.e. remains soluble. A phosphate processing plant near the mouth of the Alafia releases uranium to the river and to Tampa Bay. However, the water of the bay does not show a straight line plot of uranium concentration versus salinity. This suggests that uranium may be accumulating in the sediment of the bay.

The residence time of uranium in the ocean may be calculated, like any other element, by use of the relationship

$$\tau = Q/I \quad (26)$$

where  $\tau$  is the residence time,  $Q$  is the mass of uranium in the oceans, and  $I$  is the annual dissolved influx from rivers, a steady-state ocean being assumed.

The calculation is simplified if the relationship of the residence time of the dissolved species,  $\tau_u$ , to that of water itself is considered, so that

$$\tau_u = \tau_w (C_o/C_r) \quad (27)$$

where  $\tau_w$  is the residence time of water in the ocean, known to be about 45 000 years and  $C_o$  is the concentration of uranium in the ocean water, well documented to be  $3.35 \text{ pp}10^9$  [12,36,80]. The value for  $C_r$ , the concentration of uranium in rivers, however, is not agreed upon. The value varies widely from river to river (Fig. 2) and from season to season; estimates for the world average range from a low of  $0.03 \text{ pp}10^9$  by Moore [74], to  $0.6 \text{ pp}10^9$  by Sackett et al. [153]. A median figure of  $0.3 \text{ pp}10^9$  [154] yields by calculation a uranium residence time of 500 000 years.

Uranium is unique among elements in that it offers the possibility of calculating its residence time in the ocean isotopically. Such a calculation has been made by Bhat and Krishnaswamy [13], Moore [74], Ku et al. [12] and others. It is based on two unique circumstances: (1) the high A.R. of uranium in continental run-off has created a vast reservoir of excess  $^{234}\text{U}$  in the ocean, and (2) the rate of removal of uranium by sedimentary processes is in the same time frame as the

decay rate  $^{234}\text{U}$ . For a steady-state ocean the annual increment of excess  $^{234}\text{U}$  from rivers is balanced by the annual decay of excess  $^{234}\text{U}$ . Measured in equivalent uranium activity units, annual decay of excess  $^{234}\text{U}$  is

$$-\Delta X = (Q)(\gamma_o - 1.0)(\lambda) \quad (28)$$

where  $Q$  is the mass of uranium in the ocean,  $\gamma_o$  is the A.R. in the ocean, and  $\lambda$  is the decay constant of  $^{234}\text{U}$ . The annual increment of excess uranium is

$$+\Delta X = (I)(\gamma_r - \gamma_o) \quad (29)$$

where  $I$  is the annual flux of dissolved uranium in rivers, and  $\gamma_r$  is the A.R. of uranium in rivers. For a steady-state ocean and substituting the known value for  $\gamma_o$ , 1.14, we have

$$(Q)(0.14)(\lambda) = (I)(\gamma_r - 1.14) \quad (30)$$

but  $Q/I$  is the residence time,  $\tau$ , so

$$\tau = (\gamma_r - 1.14)/0.14\lambda \quad (31)$$

This elegant equation calculates the residence time of uranium in the ocean without the use of any concentration data and without the necessity of knowing the water residence time itself. Using the average A.R. for run-off, approximated by use of Fig.2 (1.30), we calculate a  $\tau_u = 2800$  years for uranium. This value, we observe, is in the lower range of estimated residence times based on river concentration data (Fig.28).

The value of 1.30 for  $\gamma_s$  (river uranium), arrived at by averaging reported data, can be checked in an interesting way by use of Eq.(25). In this case we use a value for  $\gamma_s$  taken from the soil data of Rosholt et al. [124] and also estimate the ratio of soluble to detrital uranium from the same data. This is done by assuming that no thorium is chemically transported, so that the activity ratio  $^{238}\text{U}/^{230}\text{Th}$  ( $\psi$ ) is a measure of the immobile uranium (this ratio also is 1.00 before weathering and erosion). If it is further assumed that the time scale of soil erosion is not too long compared to the average life of  $^{230}\text{Th}$  atoms ( $1/\lambda = 108\,000$  years):

$$M_s/M_r = \psi/(1.0 - \psi) \quad (32)$$

and from Eqs (25) and (32)

$$\gamma_r = 1.0 + (1.0 - \gamma_s)(\psi)/(1.0 - \psi) \quad (33)$$

From Fig.11 we note that  $\gamma_s$  and  $\psi$  decrease together along a line so that the ratio  $(1-\gamma_s)/(1-\psi)$  is nearly constant at a value of 0.5. Thus river A.R. may be theoretically determined by the single parameter  $\psi$  in the following equation:

$$\gamma_r = 1.0 + 0.5 \psi \quad (34)$$

A typical value for  $\psi$  for the B horizon of soils is 0.6 to 0.8, which computes to river A.R.s of 1.3 to 1.4. This independent approach gives us confidence that the average A.R. for rivers as used above, 1.3, is reasonable.

Inasmuch as the uranium A.R.s of rivers are better known than the uranium concentration, it is useful, and germane to this review, to take the residence time for uranium calculated above and calculate backward in Eq.(27) to find what must be the average concentration of uranium in rivers

$$C_r = C_o(\tau_w/\tau_u) = (3.35)(45/280) = 0.54 \text{ pp}10^9$$

which is higher than the estimates of many investigators. The 'isotopic' continental erosion derived from this figure is about  $9 \text{ g/cm}^2$  per  $10^3$  years.

Pertinent to this entire balance analysis, Ku [63] has reported evidence for an alternate source of excess  $^{234}\text{U}$  in the oceans. The pattern of  $^{234}\text{U}/^{238}\text{U}$  A.R.s in deep-sea sediments suggests to him that  $^{234}\text{U}$  is mobilized after deposition and diffuses into the sea. Kigoshi [110] suggests that this is to be expected in light of his recoil experiments. Ku [63] speculates that the global average river concentration is in the lower range of those proposed, that the residence time of uranium is thus in the upper range of those proposed, and that the large excess of  $^{234}\text{U}$  in the ocean is due only in part to the A.R. of river waters.

The mobilization of  $^{234}\text{U}$  in sediments, however, may be quite irregular, depending on sediment type and particle size, and on the Eh conditions of the sea floor and within the sediments. Immel and Osmond [107] studied the A.R.s of uranium in the authigenic fraction of three deep-sea cores; two of these gave evidence of reducing conditions, and the pattern of increasing A.R.s (up to 4) with depth in the core suggests uranium immobility (Fig.27).

So until we have a better estimate of the role of deep-sea sediments in supplying  $^{234}\text{U}$  to seawater, the isotopic residence time calculation must be made with caution. Figure 28 shows how this factor modifies the calculation based on river A.R.s.

## 7. OTHER APPLICATIONS

With respect to uranium isotopic hydrology, most of the efforts of researchers to date have been directed toward gaining understanding. As far as applications are concerned, the field must still be considered in its infancy. However, it is clear that the uranium isotopes are potentially useful indicators of aquifer-water interactions. This is especially true if quantitative formulations can be substantiated. Among many promising applications of the study of uranium isotopes in water we will describe five briefly.

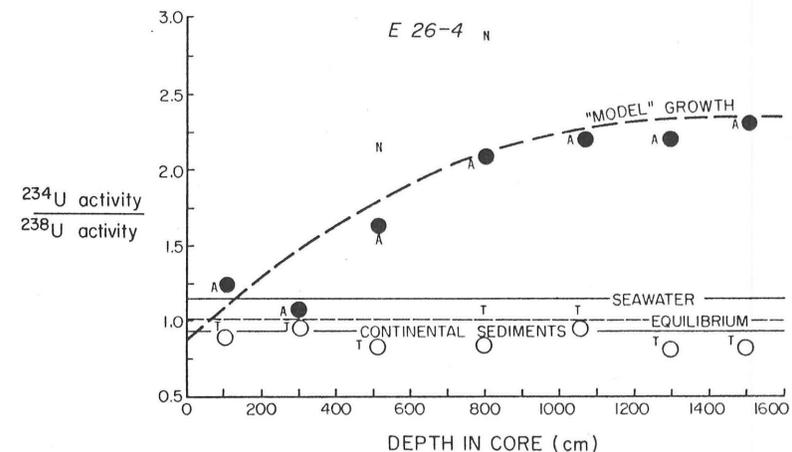


FIG.27. The variations of A.R. of authigenic uranium in a deep-sea core (Immel and Osmond [107].  $N$  = micro-nodule fraction;  $A$  = adsorbate;  $\bullet$  combined  $A + N$ ;  $\circ$  clay residue (the original detrital phase). If recoil-generated  $^{234}\text{U}$  is not diffusing out of the system, but rather accumulates in the pore water and authigenic phases, i.e. solid circles, the A.R.s of the latter would be expected to follow the dotted line.

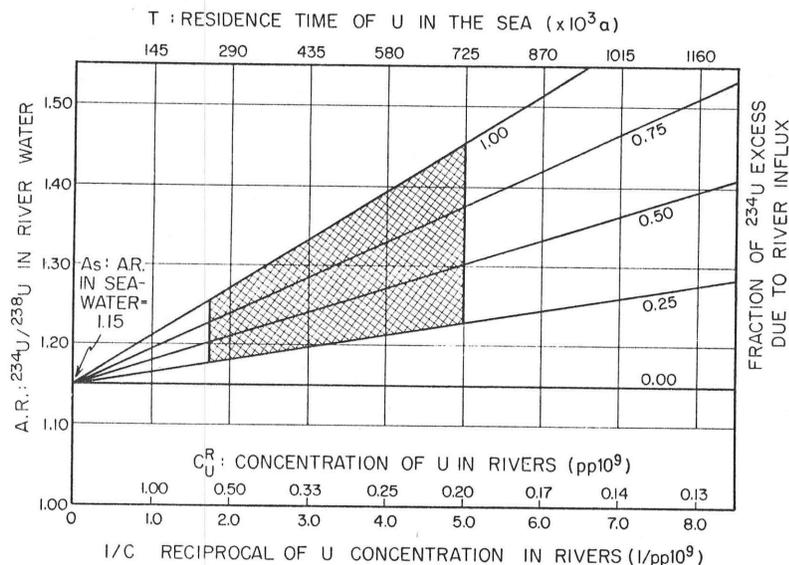


FIG. 28. Residence time of uranium in the ocean as a function of (a) the concentration of uranium in rivers, and (b) the activity ratio of  $^{234}\text{U}/^{238}\text{U}$  in rivers, in conjunction with the fraction of excess  $^{234}\text{U}$  in seawater due to river influx. The most direct calculation is based on river concentration (lower scale versus top), but various estimates for  $C_U^R$  are in poor agreement. The calculation of residence time based on the  $^{234}\text{U}/^{238}\text{U}$  ratio is promising because estimates of the average A.R. in rivers is more reliable (read right from A.R. to the 1.00 line, then up to  $T_u$ ). However, an appreciable fraction of the excess  $^{234}\text{U}$  in the oceans may be from some other source than rivers, such as diffusion out of deep-sea sediments (read right from A.R. to the line which corresponds to the estimated  $^{234}\text{U}$  excess in the sea due to rivers, then up to  $T_u$ ). The shaded area marks the region in which most investigators find a solution to the balance equations: river concentration from 0.2 to 0.6  $\text{pp}10^9$ ; A.R. from 1.2 to 1.4; and fraction of excess supplied by rivers from 25 to 100%.

### 7.1. Age determinations

The absolute ages of Pleistocene events are poorly known, because there are few radioisotopes with half-lives between those of carbon-14 ( $5.7 \times 10^3$  a) and potassium-40 ( $1.3 \times 10^9$  a).  $^{234}\text{U}$  with a half-life of 250 thousand years would be an ideal clock for the period between  $10^5$  and  $10^6$  years and soon after the discovery of the natural variations of  $^{234}\text{U}$  relative to  $^{238}\text{U}$  attempts were made to utilize it.

A standard form of the radioactivity decay formula is

$$A = A_0 e^{-t/T_v} \quad (36)$$

where  $A_0$  and  $A$  are the initial activity and the activity at time  $t$  respectively, and  $T_v$  is the average life of the radioactive species (the reciprocal of the decay constant).

In the case of members of a decay series headed by a long-lived parent, this equation must be modified to take into account the fact that decay tends to eliminate only that portion of the radioactive species that is out of equilibrium. In terms of  $^{234}\text{U}$ , we are familiar with the concept of 'excess  $^{234}\text{U}$ '. The age dating equation in this case is

$$X = X_0 e^{-t/T_v} \quad (37)$$

where  $X$  is defined as  $(A.R. - 1) \cdot A$ , and  $A$  is the activity of  $^{238}\text{U}$ .  $X$  may be either a positive or negative quantity. The age is determined by rearranging terms and eliminating the exponent.

$$t = T_v \ln(X_0/X) \quad (38)$$

The principal difficulties are two: (1) the isolated systems that have experienced fractionation are few in number, and (2) the initial A.R. of the system cannot usually be inferred with confidence. One system for which long-term stability might be assumed is that of the oceans, but the excess of  $^{234}\text{U}$  is not great relative to the precision of measurement. The excess of  $^{234}\text{U}$  in activity units is  $0.14 \pm 0.013$  [12]. Given that the uncertainty of a sample may be somewhat larger, the combined uncertainty of the decaying excess is apt to be  $\pm 0.03$ . This amounts to an age uncertainty of 100 000 to 200 000 years for marine samples even under the best of circumstances. Nevertheless, determinations of this 'seawater excess' has been useful in confirming ages based on Th/U or Pa/U ratios in corals [97, 172] and manganese nodules [173].

Deep-sea carbonates contain less uranium than do corals, and this fact, combined with evidence for fractionation and diffusion of  $^{234}\text{U}$ , led Ku [63] to the conclusion that this parameter could not be used to date deep-sea sediments. However, both the diffusion curves plotted by Ku and the secondary accumulation curves depicted by Immel and Osmond [107], Fig. 27, are time-related functions, which could be used in theory to deduce accumulation rates of the sediments. Krishnamurthy et al. [174] report success in dating a marine core by use of a selective leach of the carbonate phase.

Other systems have been studied that are more promising with respect to the degree of disequilibrium produced, but suffer from initial value uncertainties. For example, secondary deposits from limestone caves have been successfully dated by  $^{230}\text{Th}/^{234}\text{U}$  methods for intervals back to about 300 000 years. High  $^{234}\text{U}/^{238}\text{U}$  ratios are also present in speleothems (1.5 to 2.5). Some investigators [93, 175] conclude that the initial A.R.s have been constant in certain deposits, and that age determinations are possible to about 700 000 years. The evidence from other speleothems is that the A.R.s have been fluctuating [176].

Whenever uranium is found to be at equilibrium in deposits where an initial excess (whatever its value) may be assumed, then a lower limit for the age of the deposits may be determined. This approach has been used for certain of the Antarctica dry valley evaporites (Hendy, personal communication) and for iron nodules in an Alabama river terrace [177].

Chalov et al. [45, 102, 178, 179] estimate the ages of some major Kazakhstan lakes including Aral and Balkhash by a residence-time analysis similar to the one used for the oceans. They observed that the A.R. of uranium in the lake waters was lower than that of incoming rivers. The difference, they believe, is due to decay of excess  $^{234}\text{U}$  during the residence time of uranium in the lake. This leads to estimates of the minimum ages of the lakes. Alekseev et al. [16, 180] have revised the Chalov et al. calculations, making major changes with respect to the effects of rainfall and atmospheric fall-out (as identified by Zverev and Spiridonov [160]). They obtain a new age for Lake Issik-kul of  $220\,000 \pm 30\,000$  years.

Kaufman and Broecker [47] determined the uranium A.R.s for 50 carbonate and marl samples from the Pleistocene basins of Lakes Lahonton and Bonneville, in western USA. Their conclusion was that the initial uranium A.R.s were too varied, or that the systems analysed too 'open', to be useful in geochronological interpretation. A similar conclusion is implied by the data and discussion of Van et al. [101] of travertine deposits in Afghanistan.

In at least three investigations the ages of underground water itself (time since infiltration) is inferred from the observed decrease in uranium A.R. in the flow direction. Kronfeld and Adams [112] (Fig. 17), Alekseev [16] and Knauss et al. [144] noted isotopic ages that were consistent with plausible flow velocities. Additionally, Syromyatnikov [137] suggested that the migration and fractionation of the isotopes in groundwater basins are related to geological time. However, this application of uranium isotopes must be regarded as only an interesting idea.

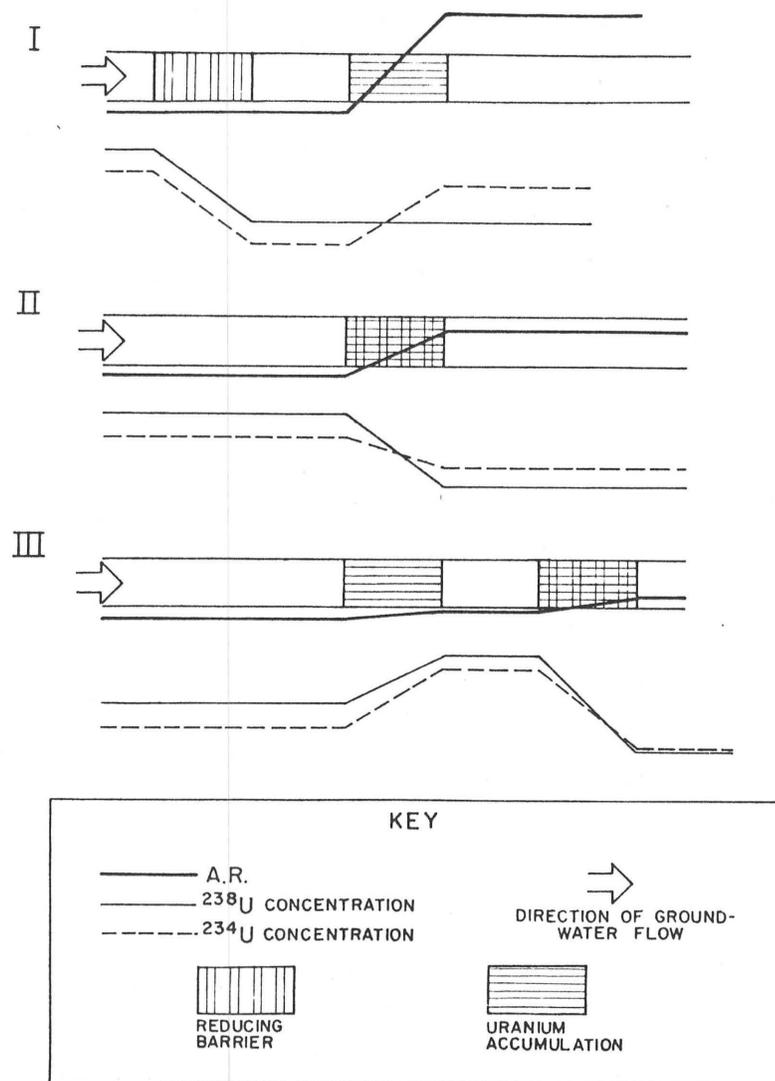


FIG. 29. Isotopic indications of uranium accumulations in a sandstone-type aquifer [77]. In all cases the groundwater flows from an oxidizing regime to a reducing regime past a reducing barrier, and causes uranium to accumulate at the boundary. In condition I the modern reducing barrier is up-dip from an earlier reducing barrier and accumulation zone. Water flowing past the earlier accumulation zone has a low uranium concentration, thus the addition of  $^{234}\text{U}$  by recoil processes greatly increases its A.R. Condition II indicates that the reducing barrier has remained fixed at one position; the down-dip water has a somewhat elevated A.R. Condition III illustrates the condition in which the reducing barrier has moved down-dip. Uranium in the earlier accumulation zone is now being remobilized up-dip and redeposited at the modern barrier. The water down-dip has only a moderate A.R. value.

## 7.2. Uranium prospecting

Syromyatnikov [64] mentioned the relationships between the relative migration of  $^{234}\text{U}$  and  $^{238}\text{U}$  and the possibilities of using the A.R. for interpreting radiohydrochemical anomalies. The prospects of this isotopic method were confirmed for uranium ore prospecting by the hydrochemical dispersion ratio, as reported by Ivanov and Kudryashova [18]. Syromyatnikov [66] concluded that A.R. determination of waters and of solids and extracts from soils and zones of cementation enable one to establish the nature of the uranium accumulation and to estimate the time of accumulation. The criterion for the non-metalliferous (i.e. non-economic) uranium anomalies in friable surface environments is the lack of any significant change in A.R. relative to the background.

Rosholt and co-workers [55] measured the variation of the uranium A.R. of sandstone ore bodies. In general, the unoxidized uranium ores were deficient in  $^{234}\text{U}$ , whereas the altered ores had an excess of  $^{234}\text{U}$ . Cowart and Osmond [23] also suggest that isotope signals may be generated at the site of some uranium accumulations. The signal is the excess  $^{234}\text{U}$  added to the groundwater as it flows through the accumulation. Sakanoue et al. [181] have observed just such an occurrence in a Japanese ore body. For an accumulation still being formed a downflow high uranium concentration would not be expected; however, at the site of accumulation recoiled atoms would produce a large relative excess  $^{234}\text{U}$  in the circulating water (Fig. 29). If substantiated, this method may be of use for reconnaissance of areas where sufficient water sampling locations are available.

## 7.3. Geothermal systems

Uranium isotopes in volcanic and fumarole waters from Kamchatka and the Kurile Islands and in thermal and related waters found in a neovolcanic area of the Caucasus have been studied by Kuptsov et al. [182], Kuptsov and Cherdyntsev [183] and Cherdyntsev [19]. They concluded that thermal waters from neovolcanic regions have, on average, higher A.R.s than waters from active volcanic regions and that this, in conjunction with other radioisotope data, indicates the age of these thermal waters is considerable (compared with the waters in volcanically active area) and that they have not travelled far from the heat source.

Our own unpublished uranium isotope analyses of water from Yellowstone National Park, Mt. Lassen, Imperial Valley and various thermal springs are generally consistent with the conclusion regarding the A.R. differences between 'actively volcanic' and 'neovolcanic' regions. Figure 18 shows the lowered concentration and A.R.s of hot waters sampled at Yellowstone as compared with non-geothermal groundwater systems elsewhere. Geothermal waters from Mt. Lassen and Imperial Valley also fall near the Yellowstone trend line.

Heated waters from deep wells (up to 2000 m) in areas of near average geothermal gradient also have rather low uranium concentration but have A.R.s of 2 to 3.5; the same is true for thermal and warm springs that are not associated with near surface magmas.

All of this suggests, as pointed out by Wollenberg [184], a hydrologic system wherein the dissolved uranium carried down by infiltrating water is precipitated in the hot reducing environment associated with the heated rocks. We can surmise that the elevated temperature promotes a liquid-solid isotope equilibration which counteracts the selective leaching and recoil processes and results in a near equilibrium A.R. as well as low concentration waters.

## 7.4. Reservoir analysis

The disposal of waste waters (sewage or industrial effluents) by means of injection into underground zones is being done or is being considered in a number of locations [185]. A requirement of this procedure is that it be capable of isolating the waste water and preventing contamination of other hydrologic systems.

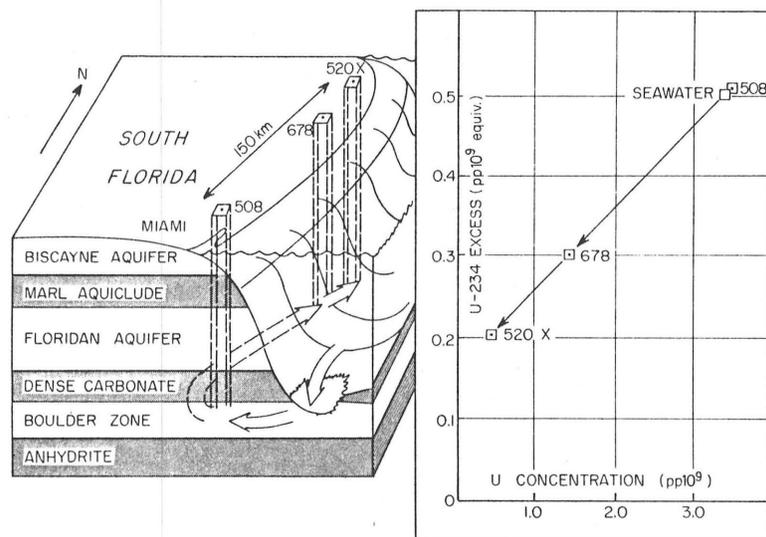


FIG.30. Uranium isotopic evidence for inland flow of seawater 1000 m underground through the cavernous "Boulder Zone" aquifer in southeast Florida. On the basis of temperature anomalies, Kohout [186] has suggested that seawater is entering the aquifer from a basin in the Florida Straits (solid arrow) and flowing in response to a convective circulation system. A plot of excess  $^{234}\text{U}$  against uranium concentration for three samples from along the coast suggests to Cowart et al. [17] that the movement has a northward component (dashed arrow). So far, samples from further inland have not been obtainable for uranium isotopic analysis.

In southeast Florida several wells are injecting waste waters into a cavernous dolomitized zone about 1000 m below the low-lying land surface. This cavernous zone contains water that is similar to seawater. Additionally, it has a temperature lower than expected and in fact a reverse geothermal gradient exists in several locations. Kohout [186] has attempted to account for these phenomena by hypothesizing that cold seawater flows inland from a subaqueous outcrop of the cavernous zone under the Straits of Florida as part of a geothermally driven convection system.

Three wells penetrating the cavernous zone have been sampled and the waters analysed for uranium isotopes by Cowart et al. [17]. The well closest to Kohout's hypothesized seawater intake location has uranium concentration and A.R. values virtually identical to seawater. The locations further away from the intake area showed decreasing uranium concentration and increasing A.R. (Fig.30). Analyses of other constituents (by US Geological Survey) are consistent with the hypothesis of inflowing seawater.

If the seawater is entering the cavernous dolomitized zone at one location, then it follows that water is leaving at some other location. Thus, the waste water may not be sequestered by this strategy of disposal. However, travel through this inferred flow system may render the effluent innocuous by the time it exists by a process of dilution and/or chemical degradation. Not enough data are available for judgement at this time, but the uranium isotope pattern is consistent with a circulation model hypothesized on the basis of very different parameters.

### 7.5. Dilatency phenomena

A causal relationship between seismic activity and variation of radon, helium and uranium in groundwater has been reported for the Tashkent region, Uzbek, USSR, for the series of earthquakes

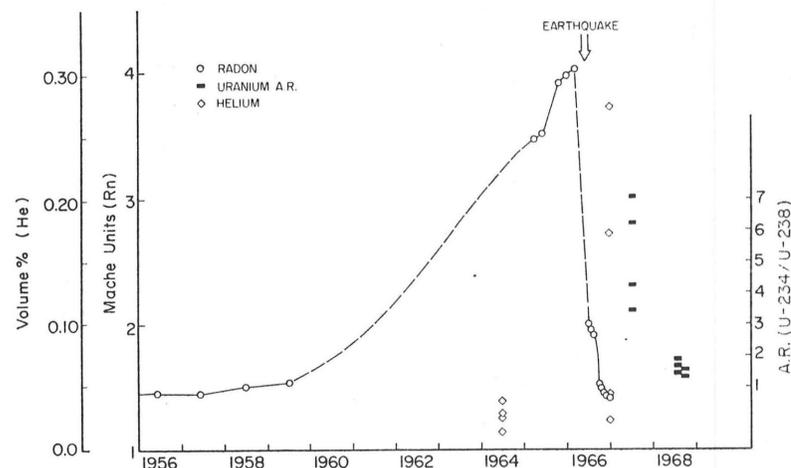


FIG.31. Activity ratio variations in dissolved underground uranium in response to earthquake activity. The pattern of radon concentration in the Tashkent Basin groundwater has been cited to support the dilatency model of earthquake precursor phenomena. Inasmuch as the uranium A.R.s were not determined before the earthquake period, two interpretations of the uranium isotopic data are possible: (1) there was a rise in the  $^{234}\text{U}$  input (increase in A.R.) during the precursor period, similar to the increase in radon concentration; and (2) the groundwaters of the Tashkent Basin are normally high in A.R. and the earthquake caused a re-equilibration during the post-quake period (modified from Ulomov and Mavashev [187]).

beginning 26 April 1966 [187, 188]. Observation wells in this region yielded samples in which the radon and helium concentrations increased during the period of increasing rock strain preceding the earthquakes (Fig.31). The mechanism of concentration is hypothesized by the investigators to have been dominantly ultrasonic elastic vibrations produced by rock deformation which sweep loosely bonded or adsorbed constituents into the groundwater. An abrupt decrease in radon concentration occurred during the protracted period of seismic events.

Analysis for A.R. of the groundwater was not done prior to the earthquakes. However, samples taken after the major tremors (July 1967) but presumably before quiescence have rather high A.R.s ( $7.0 \pm 0.3$  to  $3.9 \pm 0.1$ ) (Fig.31). These values are considerably greater than the investigators consider normal in a sedimentary-metamorphic terrain.

With time (samples taken August 1968) the A.R.s (and concentrations) decreased to levels consistent with the type of terrain and are presumed to be similar to those obtaining before the onset of rock-deforming forces. The decrease of A.R. is thought to be a function of interphase isotope equilibration.

Chalov et al. [189] believe that variations of the  $^{234}\text{U}/^{238}\text{U}$  activity ratio are not useful as an earthquake prediction parameter, but rather as a method for determining the flow rate and direction of water in strata after an earthquake.

Dolidze et al. [190] report anomalously high A.R. values in the groundwaters in the seismically active regions of Southern Georgia, USSR.

In an earlier section of this review we showed that high A.R.s would be favoured by high surface-area-to-volume ratios in the aquifer rock. It should not be surprising then if it turns out that dilatency phenomena, which tend, by fracturing, to increase surface areas, produce anomalous A.R.s in the circulating water system.

The understanding of radiological precursors can be of great significance for the prediction of earthquakes. The relative worth of uranium isotopic data as compared with radon, helium and other elemental concentration variations for earthquake prediction is not known at this time.

Gorbushina et al. [191] make the point that such uranium isotope changes as discussed above could be useful in paleotectonic studies, although they did not elaborate further. We might speculate that if uranium A.R. variations are indeed a function of the stress state of the solid earth in areas of seismicity and if such variations are recorded in some way, such as in a given lamina of a spring deposit, then the variations could be useful in determining the frequency of earthquakes at a given location. The 'normal' laminae between the seismically affected laminae perhaps could be radiometrically dated and used for bracketing the age of the paleoearthquakes.

## 8. SUMMARY

The International Atomic Energy Agency sponsored a panel meeting in Vienna in 1973 concerned with the "interpretation of uranium isotope disequilibrium as a hydrologic tracer". In an unpublished summary statement the panellists concluded that the two principal obstacles to greater utilization of this new hydrogeochemical tool were: (1) a lack of uniformly reliable analytical techniques, especially as regards very low concentration waters, and (2) a lack of universally accepted models for understanding isotope fractionation and uranium-aquifer interactions. Our own view is that there will be no serious obstacles to the solution of analytical problems as more research is done, and that our understanding of fractionation processes is improving.

Investigations in recent years have brought out evidence that tends to support the following conclusions regarding the variations in uranium isotopes in natural waters.

(1) The primary factors determining the concentration of uranium in natural waters are the oxidation potential and the partial pressure of carbon dioxide.

(2) Many naturally occurring uranium isotope variations can be explained on the basis of simple alpha-recoil displacement across a solid/liquid phase boundary. The solid phase with higher uranium concentration develops a deficiency of  $^{234}\text{U}$  (low A.R.) and the liquid phase with lower uranium concentration develops an excess of  $^{234}\text{U}$  (high A.R.).

(3) Leaching of uranium by groundwater may be generally non-selective, in which case the A.R. of the leached uranium is approximately the same as encountered in the surface layers of aquifer grains.

(4) Reducing barriers in circulating aquifer systems produce uranium accumulation zones as coatings on aquifer grains. These coatings are potent sources of non-equilibrium uranium.

(5) At high temperatures isotopic effects of fractionation tend to be eliminated by the process of isotopic equilibration.

The above conclusions regarding the fractionation process can be used to interpret and classify groundwater systems. Where aquifer waters display considerable variation in concentration and/or activity ratio, two kinds of dissolved uranium can be identified in theory: the 'leached' term is composed of a mixture of  $^{238}\text{U}$  and  $^{234}\text{U}$ , and the 'recoil' term consists of  $^{234}\text{U}$  only. Oxidized aquifers and many regional run-off systems are characterized by a predominance of the leached term with a medium to high A.R. Artesian aquifers with reducing barriers have a more dominant recoil term and a lower leaching A.R. Mineralized aquifers are apt to be high in both terms, while high temperature (geothermal) aquifers are usually low in both terms.

With respect to regional run-off waters, the A.R. values are characteristic of the weathering regime. A high A.R. (>1.5) is characteristic of run-off where the ratio of chemical to mechanical weathering is low. Medium or low A.R.s are characteristic of regions where chemical weathering is more important.

Where oxidizing conditions prevail and uranium remains conservative isotope dilution equations can be applied to deduce mixing proportions of groundwater sources. These same isotope dilution equations can be used to calculate the balances of  $^{238}\text{U}$  and  $^{234}\text{U}$  as they move via different pathways through the external parts of the geochemical cycle.

A few of the other applications of uranium isotope disequilibrium to practical problems include: age determination, ore location, geothermal circulation, aquifer waste injection, and earthquake precursor phenomena.

It is our hope that this review will help in the recognition and development of these and other uses of uranium isotopic variations to hydrologic and related sediment-water interface problems.

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