

A new explanation for extreme $^{234}\text{U}/^{238}\text{U}$ disequilibria in a dolomitic aquifer

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(Received January 1, 1993; revision accepted March 24, 1994)

Abstract

High $^{234}\text{U}/^{238}\text{U}$ activity ratios are found in the shallow groundwater of the phreatic Transvaal Dolomite Aquifer. The aquifer is uranium poor, while the waters are oxygen rich and young. Tritium and ^{14}C are used to show that the disequilibrium increases the longer the water resides in contact with the dolomite host. The ^{228}Ra and ^{222}Rn isotopes were used as supporting evidence that ion exchange between the ^{238}U series nuclides in the water and the carbonate wall rock is necessary in assisting in the fractionation process. The Wolkberg cave speleothems preserve a record of the uranium isotopic fractionations that evolved as water flowed through the aquifer. Extremely variable and elevated $^{234}\text{U}/^{238}\text{U}$ ratios (of 2–12) are characteristic. Individual caverns may exhibit very large $^{234}\text{U}/^{238}\text{U}$ variability in their drip water and in derivative carbonate precipitates (speleothems). Deeper chambers, where water has spent a longer time in contact with the aquifer, tend to exhibit a greater degree of uranium isotopic fractionation in their speleothems. The recorded fractionation process has been an ongoing one from at least the middle–late Pleistocene to the present. The speleothem study supports the contention that ion exchange processes that produce sufficient enrichment of uranium on carbonate can provide ideal conditions for generating uranium isotopic fractionation in the water of carbonate aquifers (in the absence of redox changes and within a uranium-poor environment).

1. Introduction

A study of the Transvaal Dolomite Aquifer was undertaken to investigate the isotopic changes in the ^{238}U decay series that accompany the evolutionary development of carbonate water over time. Among the isotopes investigated were ^{222}Rn , ^{226}Ra , ^{234}U , ^{238}U , ^3H and ^{14}C . Initially, the major springs were surveyed across this large karstic basin. However, as the rather unusual analytical

results started to come out, the sampling program was shifted to concentrate upon one specific region of the aquifer, centred around the Grootfontein compartment, where sufficient boreholes are available to yield depth profiles. A mode of fractionation of ^{234}U from ^{238}U in a well-oxygenated environment that has not been previously described is an outgrowth of this study. An isotopic study of speleothems from the Wolkberg Cave, within the aquifer, was carried out to corroborate the uranium isotope fractionation mechanism and to demonstrate that the process has been continuing for many thousands of years.

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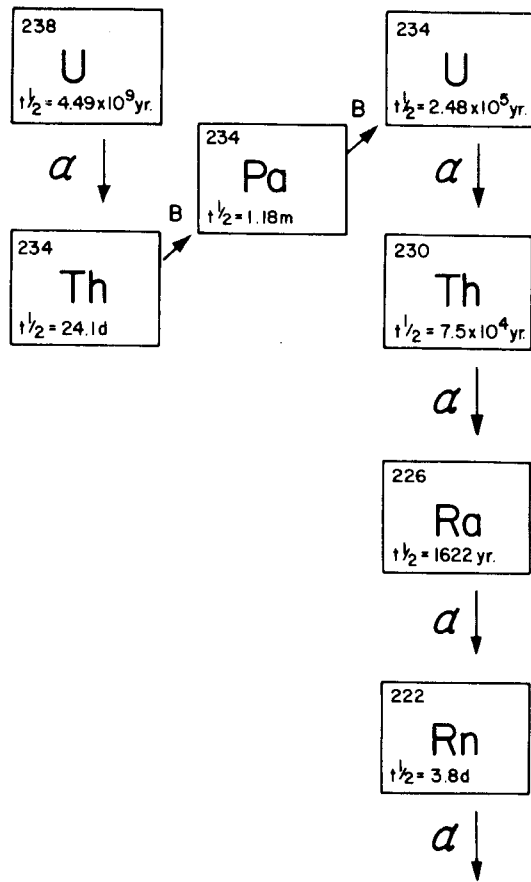


Fig. 1. The radioactive decay series of ^{238}U to ^{222}Rn , showing the half-lives of the isotopes.

Disequilibrium within the U series is the major topic of this investigation; therefore a few preliminary remarks concerning the solubility and fractionation mechanisms conventionally ascribed to uranium are in order. Uranium is generally considered to be soluble and to behave conservatively in groundwater rich in dissolved oxygen, especially where the U^{6+} ion is able to form complexes of the stable uranyl carbonate [1]. When the soluble uranium encounters reducing conditions, the soluble U^{6+} complex breaks down and the uranium precipitates as the insoluble U^{4+} species. The ^{234}U daughter (Fig. 1) can be separated by essentially two different mechanisms in natural water. One mechanism, which is particularly important when the water is oxidizing, effects the preferential leaching of ^{234}U from the mineral phase [2,3]. Another fractionation mechanism proceeds independently of environmental redox conditions. This involves the alpha-

recoil transfer of ^{234}Th from the grain to the water. ^{234}U is then formed in solution from the decay of the ejected ^{234}Th atom [4]. The $^{234}\text{U}/^{238}\text{U}$ disequilibria exhibited in nature are a result of either one or a combination of the two processes. It is the latter mechanism that is responsible for generating very high $^{234}\text{U}/^{238}\text{U}$ activity ratios in groundwater. This mechanism is most important for water where the dissolved ^{238}U concentration is low and relatively high uranium enrichments on the confining aquifer wall can contribute plentiful alpha-recoil products into the water [5]. A classic demonstration of this mechanism is the example of groundwater flowing through a uranium roll front deposit in sandstones [6]. In this case, uranium precipitates under reducing conditions along a redox boundary and the subsequent alpha-recoil injection of ^{234}U from the precipitated uranium to coexisting groundwater gives rise to low concentrations of dissolved uranium with a high $^{234}\text{U}/^{238}\text{U}$ activity ratio. In fact, waters with highly elevated $^{234}\text{U}/^{238}\text{U}$ are almost exclusively reducing.

A study of groundwater of the Transvaal Dolomite Aquifer presents an example which does not conform to the generally accepted redox-control mechanism described above and one which we suspect to be of wider occurrence. In this instance, the young, fresh water percolating through uranium-poor (less than 1 ppm) carbonate is rich with oxygen. However, it is found to lose soluble uranium rapidly (compared to average regional surface water [7]) while evolving very high $^{234}\text{U}/^{238}\text{U}$ activity ratios.

Other fractionations within the ^{238}U decay series, notably of ^{226}Ra and ^{222}Rn , are also found. In acidic and saline water high radium concentrations can accumulate [8,9], but in fresh water the mobility of radium is considerably reduced. Dissolved radium is chemically similar to Ca and it is very susceptible to sorption effects or ion exchange processes [10–13] that return it to the solid phase. In the aquifer, ^{226}Ra is largely generated from decay of the ^{230}Th parent that has precipitated along the aquifer walls.

The ^{230}Th is itself generated from the decay of soluble uranium (Fig. 1). The ^{222}Rn concentration in groundwater is governed by generation

from its parent ^{226}Ra in the water, or by recoil ejection directly from the solid phase, or through release by natural etching of alpha-recoil tracks [14]. Due to its short half-life of 3.8 d, high ^{222}Rn concentrations in groundwater imply high concentrations of the ^{226}Ra parent in the immediate vicinity, primarily on the aquifer rock surfaces.

2. Geohydrological setting

The Precambrian dolomites of the Chuniespoort Group (often referred to as the Transvaal Dolomite Aquifer) outcrop over large areas of the interior of South Africa. The crystalline dolomitic limestones, possibly exceeding 1200 m in thickness in the central part of the study area, are of considerable hydrologic interest [15]; they hold large quantities of fresh water. The dolomite is confined both below and in the west by the Pretoria Group quartzites and shales that dip to the east and northeast. Water is transmitted through the dolomite via cracks and solution channels, which may sometimes contain chert debris or a honeycomb of clay and other insoluble material of unspecified chemical composition that is locally called ‘wad’.

In the area under study (Fig. 2), the aquifer is

entirely phreatic. It is subdivided into separate groundwater compartments of irregular size by vertical, impermeable diabase dykes. Where the compartments overflow the dykes, the water is discharged at strong springs called ‘eyes’. The compartments are recharged by direct precipitation. Some compartments are partially recharged by spillage from springs situated at higher elevations.

The region centred around the Grootfontein (Western Transvaal) compartment was chosen for study because wells are relatively plentiful, some hydrologic information is available and the basic hydrology has been established [16]. The surface of the Grootfontein compartment and surroundings is uniformly flat, gently sloping westwards. There is virtually no drainage of surface water except via two small depressions that fill during periods of unusually heavy rainfall. Where the dolomite rock does not outcrop, it is covered by patches of soil that can reach up to 10 m in thickness. To insure that the Grootfontein area groundwater was representative of the processes taking place within the aquifer as a whole, springs and individual wells from other compartments were also analyzed (Fig. 2). Likewise, to evaluate the efficiency of the uranium isotopic fractionation process over time, speleothems from the

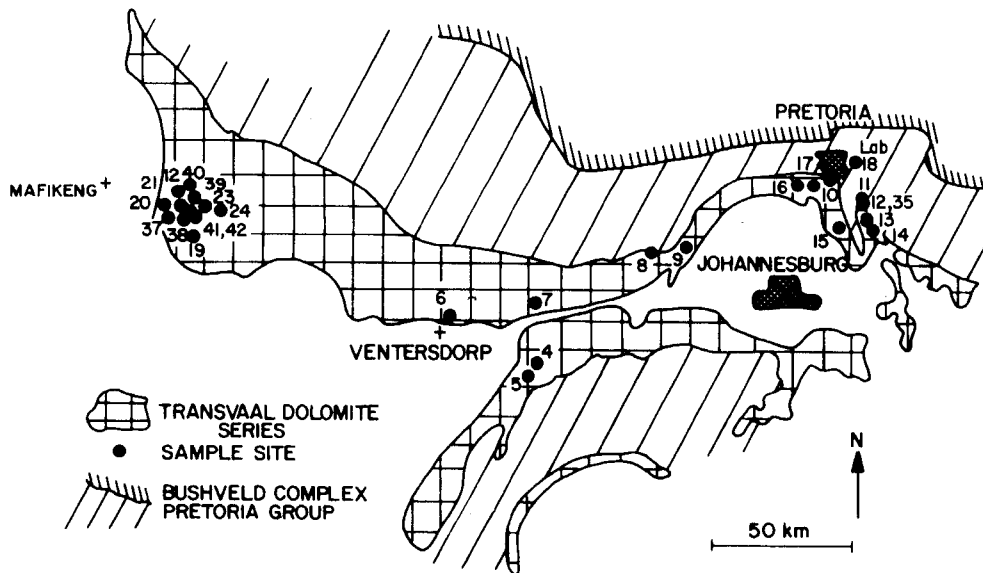


Fig. 2. Sample location map.

Wolkberg cave were studied. The uranium isotopic signature of drip water is preserved in pure speleothems that, in turn, can be dated by radiocarbon and by the $^{230}\text{Th}/^{234}\text{U}$ method. The Wolkberg cave, situated entirely within the Transvaal Dolomite, contains very high purity speleothems which a previous radiocarbon study has demonstrated to have formed from 1500 to over 45,000 yr B.P.

3. Description of the Wolkberg cave

The Wolkberg cave is situated in the eastern Transvaal province of South Africa (24°06'S, 29°53'E). The cave morphology has been described previously [17,18]. The cave is entered by a vertical shaft at an altitude of 1486 m. It consists of two upper chambers and a lower passage, located at altitudes of 1430 m, 1365 m and 1335 m, respectively, which cover a lateral distance of 720 m. The cave formation coincided with the pulsated lowering of the phreatic saturation level. After reaching its present level of between 1326 and 1365 m, large-scale roof collapse occurred. This was followed by a period of massive calcium carbonate deposition, during which the speleothems investigated formed.

4. Sample preparation

Groundwater samples were collected from springs and wells in the dolomite aquifer during the dry winter season, July–September, 1979 and 1980. The well sampling program was carried out after selection of the most suitable wells, on the basis of access, flow, depth and well condition, determined from the available data at the Department of Water Affairs, Pretoria. The sample description and pertinent well data are presented in Table 1. The sample sites are depicted in Fig. 2.

At each site 20 l of water were collected for radiocarbon analysis and uranium isotopic analysis. The pH and alkalinity were measured on site. Separate water samples of 1 l size were collected

for chemical and tritium analysis. In addition, two samples of approximately 400 ml of water were drawn into evacuated 500 ml flasks containing HgCl_2 and H_3PO_4 . The flasks were connected to a glass extraction line and the gas in the flask to be analyzed for dissolved oxygen was pumped through dry ice and liquid nitrogen traps with a Toepler pump. The concentration of the dissolved oxygen was measured using an Atlas M86 mass spectrometer.

CO_2 was added to the flasks containing the radon sample. The gases were pumped through a liquid nitrogen trap and the CO_2 and Rn mixture was transferred to a gas proportional counter, where the ^{222}Rn gas was measured. After a storage period of 1 month or more, the radon gas (generated by the radium in the water) was once again stripped from the flask and remeasured to yield the concentration of supporting radium parent.

The radiocarbon analyses of the water were carried out on the CO_2 gas that was liberated when the water was acidified in the laboratory. The method has been previously described by Vogel [20]. The acidified water remaining was spiked with ^{232}U . Uranium was concentrated by co-precipitation with $\text{Fe}(\text{OH})_3$ and purified by ion exchange and solvent extraction techniques [1] prior to analysis by alpha spectrometry.

Speleothems used in this study were taken from an assemblage that had been collected for a previous stable oxygen and carbon isotopic study [17]. They were cut along their axis to reveal their growth layers. Care was taken not to sample the outer layer, or rind, which had undergone obvious resolution, caused either by drip or meteoric water, or through the temporary elevation of the water table. Using a saw, cubes of between 25 g and 40 g were cut from the speleothem. Where feasible, samples of the outer and inner parts from the cross-section were taken and analyzed separately. Splits of each sample were analyzed by X-ray diffraction to determine carbonate mineralogy. The uranium concentration and uranium and thorium isotopes were determined by alpha-particle spectrometry using standard isotope dilution methods employing a $^{232}\text{U}/^{228}\text{Th}$ spike [1]. The radiocarbon dating of the speleothems was

performed on the CO₂ gas that was liberated when the carbonate was dissolved in phosphoric acid [21].

Representative samples of the dolomite country rock were taken, east to west, from Wolkberg, Sterkfontein and Zwartkops to determine the av-

Table 1
Sample description, hydrologic and isotopic data for the Transvaal Dolomite Aquifer

Sample Code No.	Regional locations/ sample name	Water level (m)	²³⁸ U dpm/kg	²³⁴ U/ ²³⁸ U activity ratio	Ra dpm/kg	Rn dpm/kg ±1%	¹⁴ C PMC	Tritium TU±1
<u>Turffontein</u>								
4	Turffontein Eye	Spring	0.19±0.01	5.47±0.41		630	89.7±0.6	
5	Gerhard Minnebron Eye	Spring	0.13±0.01	5.57±0.51		210	75.3±0.5	0
<u>Ventersdorp/Krugersdorp</u>								
6	Schoonspruit Eye	Spring	0.14±0.01	5.75±0.58	0.6±0.1		93.3±0.6	
7	Bovenste Eye	Spring	0.10±0.01	8.98±0.72		95	75.2±0.5	
8	Maloney's Eye	Spring	0.41±0.03	8.86±0.92		1090	55.9±0.5	
9	Sterkfontein Cave		0.10±0.01	5.2 5±0.59		240	73.9±0.5	1.4
<u>Pretoria: Irene/Erasmia</u>								
10	Pretoria Fountains	Spring	0.10±0.01	4.89±0.51		280	77.6±0.5	0
15	Sterkfontein Spring	Spring	0.088±0.008	5.31±0.46		230	80.5±0.7	
16	Erasmia	< 37	0.081±0.007	4.38±0.59	0.20±0.07	500	89.2±0.5	1.2
17	Valhalla Borehole #2	< 61	0.10±0.01	3.17±0.33	0.05±0.07	105	84.9±0.8	
<u>Pretoria: Elands</u>								
11	Willow	Spring	0.041±0.004	4.54±0.43	0±0.1		60.6±0.8	0
12	Van Reenen	Spring	0.035±0.002	1.93±0.12			74.3±0.7	0
13	Grootfontein	Spring	0.041±0.004	5.62±0.67	0.14±0.11	300	58.4±0.6	0
14	Erasmus	Spring	0.002±0.003	3.35±0.53	0±0.1	280	51.4±0.6	
35	Cuttings	Spring	0.027±0.005	1.89±0.45	0.19±0.10	1070	55.0±0.8	
<u>Grootfontein (West Transvaal)</u>								
19	BB17 Well	18	0.17±0.01	4.59±0.13	0.21±0.10	170	86.4±0.3	4.2
20	VF34 Well	1	0.18±0.01	2.76±0.14	0.34±0.10	1040	118.5±0.5	9.9
21	VF118 Well	6	0.14±0.01	4.41±0.22	0.18±0.07	17	85.1±0.4	2.4
22	Grootfontein (west) Eye	Spring	0.11±0.03	5.27±0.25	0±0.10	9	86.1±0.3	0.8
23	VL4 Well	23	0.069±0.003	4.56±0.22	0.09±0.06	230	96.9±0.6	5.9
24	E-28 Well	19	0.34±0.02	2.31±0.14	0.28±0.10	130		0.6
37	C-1 Well	4	0.09±0.01	2.16±0.24	0.20±0.07	190	119±0.5	7.2
38	S.S. Beyers Well	29	0.16±0.01	3.58±0.21		90	82.6±0.5	5.7
39	GN17 Well	"Deep"	0.14±0.01	5.75±0.39	0.50±0.10	110	74.4±0.5	0
40	Wondergat sinkhole	6	0.11±0.01	4.29±0.28		54	112.7±0.6	5.9
41	GN-3 Well	12	0.11±0.01	5.06±0.49		250	84.2±0.6	1.8
42	GN-32 Well	12	0.23±0.01	3.43±0.22	0.24±0.12	430	100.7±0.7	2.9

erage uranium concentration by delayed neutron activation (DNA). This was carried out at the Nahal Soreq reactor.

5. Results

5.1. The groundwater analyses

The results of uranium isotopic analyses of the dolomite aquifer water are presented in Table 1. The associated statistical counting error is reported at the 1σ level of confidence. Also presented in this table are the concentrations of radium, radon, tritium and radiocarbon. The radiocarbon is reported as a percentage of modern carbon (PMC). Pertinent hydrological data are also reported in this table.

A detailed chemical description of the water will be presented in a separate report. The salient points are summarized here. The water is typical of that for dolomitic regions. It is fresh water, of Ca–Mg–HCO₃ composition. The total dissolved charged species range between 3 and 7 meq/l. The pH ranges between 7.2 and 7.7. The water is well oxygenated throughout. The dissolved oxygen concentration varies between 3 and 6 ml_n/kg [17]. Infiltrating water, in equilibrium with soil air, should contain 5–8 ml_n O₂/kg [19]. The exact value depends upon atmospheric pressure and temperature.

A high degree of uranium disequilibria in the dolomitic water is characteristic of the aquifer as a whole. The ²³⁴U/²³⁸U activity ratios range between 1.9 and 9.0 (Table 1). These ²³⁴U/²³⁸U activity ratios of the groundwater are consider-

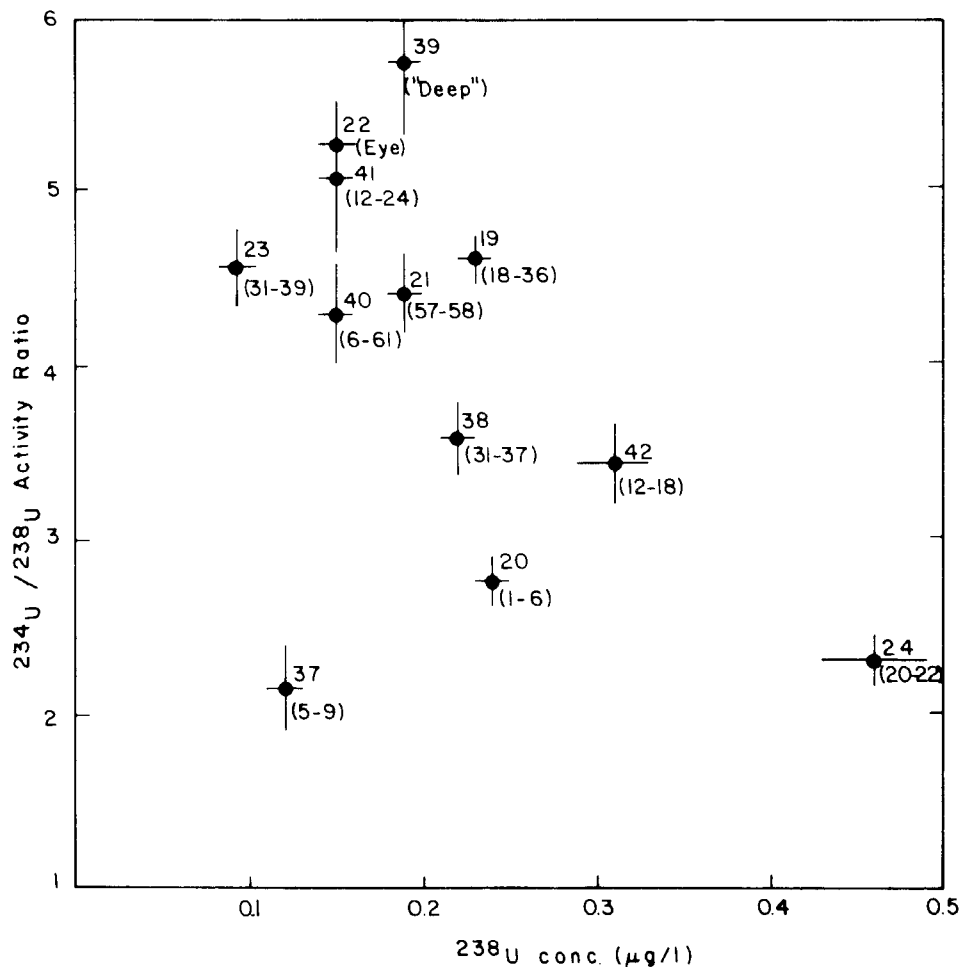


Fig. 3. Plot of the ²³⁴U/²³⁸U activity ratio against the ²³⁸U concentration for the waters in the Grootfontein compartment. The depths from which the waters are taken are in parentheses.

ably greater than the values of 1.5–2.7 that are characteristic of surface water in the semi-arid zone of southern Africa [7]. The youngest and shallowest borehole water (samples 20 and 37) are in this range. The deeper and older groundwater samples have higher activity ratios. The uranium concentrations of these shallow groundwaters as a whole (0.002–0.41 dpm/kg) are appreciably lower than the mean of the regional surface water (0.86 ± 0.74 dpm/kg) [7]. Fig. 3 plots the $^{234}\text{U}/^{238}\text{U}$ activity ratio against the ^{238}U concentration ratio. Fig. 4 plots the $^{234}\text{U}/^{238}\text{U}$ activity ratio against the tritium concentration and against the ^{14}C concentration. The uranium concentration of the aquifer dolomite is very low: the dolomite samples measured by DNA were all below 0.2 ppm.

Comparing the concentrations of the ^{234}U , ^{226}Ra and ^{222}Rn in the water, it can be seen that the three isotopes are not in secular equilibrium with each other. The activity sequence is seen to be: $^{222}\text{Rn} \gg ^{234}\text{U} > ^{226}\text{Ra}$. The amount of dis-

solved ^{226}Ra is small and often less than that which could be supported by the decay of ^{234}U in solution (Table 1).

5.2. Ages and isotopic data of the speleothems

The uranium content and uranium and thorium isotopes, along with the mineralogy, are reported in Table 2. The statistical error associated with the uranium series analysis is reported at the 1σ level of confidence. The uranium contents of the Wolkberg speleothems are low and variable (0.07–3.4 ppm). The variability in uranium concentration is both between different speleothems and within individual specimens. It is suggested that the differences are due to mineralogic changes as well as post-depositional interaction with cave water.

Aragonite is the initial carbonate mineral precipitated. Most of the speleothem aragonite is fine grained and dense but a coarse-grained, porous form is also present. Sample T-27, for

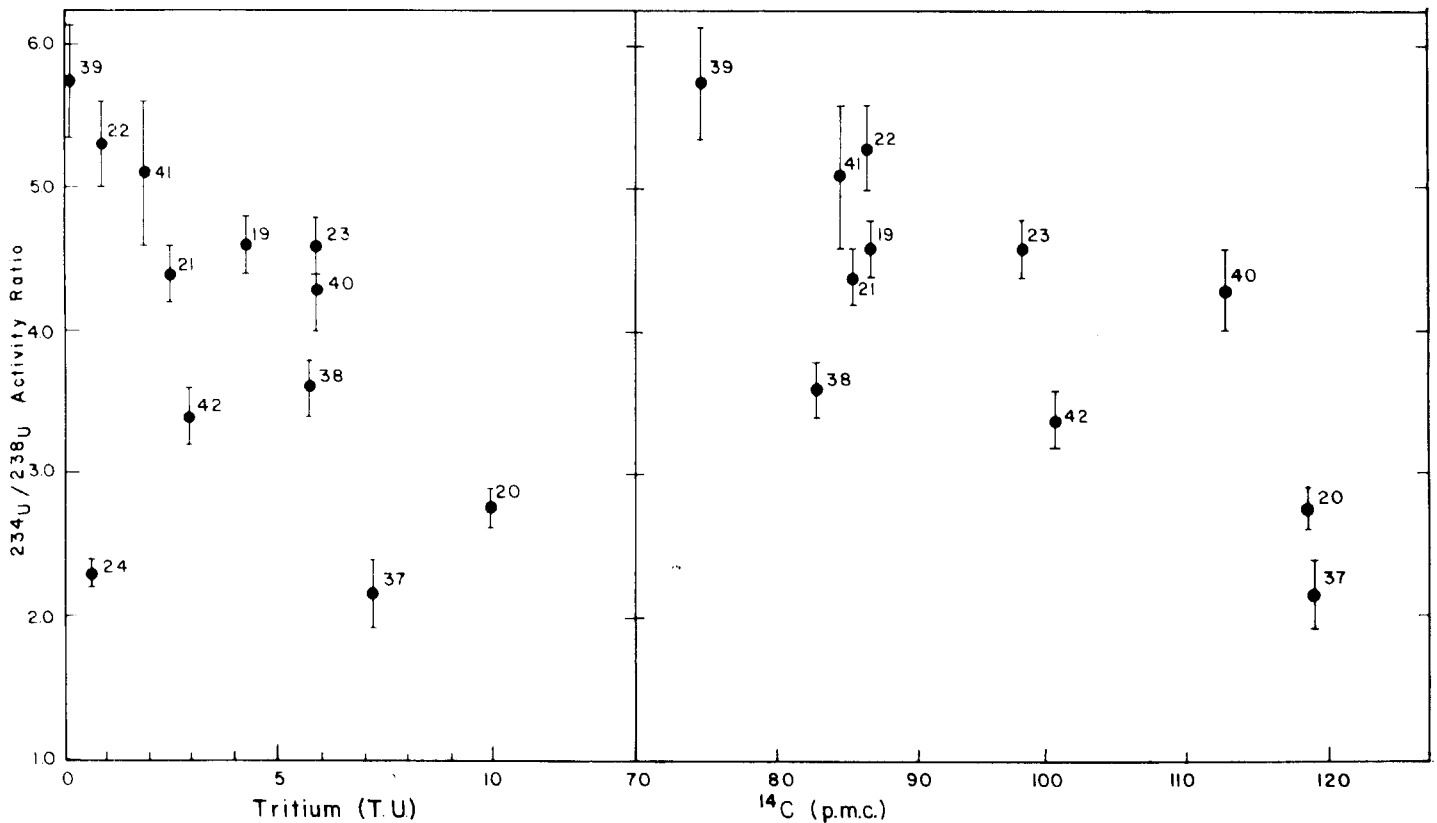


Fig. 4. Plot of the $^{234}\text{U}/^{238}\text{U}$ activity ratio against the tritium concentration and against the percent of modern ^{14}C in the waters of the Grootfontein compartment.

example, is all aragonite but comprises a dense core surrounded by coarse but more permeable crystals. Uranium is more concentrated in the dense form (0.5 ppm) than the outer layers (0.1 ppm). Large differences in uranium are noted between aragonite and calcitic layers within a single speleothem (e.g., T-23 and T-11). The cal-

cite can be found both surrounding and surrounded by the aragonite layers. In the latter case, the speleothems probably experienced a growth hiatus, during which time the primary aragonite altered to calcite, before resumption of the aragonitic deposition. The aragonite to calcite transformation may release uranium as the crys-

Table 2
Mineralogy, isotopic data and ages of the Wolkberg Cave speleothems

Sample	Mineralogy	Uranium ppm	$^{234}\text{U}/^{238}\text{U}$ Activity Ratio	$^{230}\text{Th}/^{234}\text{U}$ Activity Ratio	$^{230}\text{Th}/^{234}\text{U}$ Ages x 10^3y	^{14}C Conventional Ages x 10^3y
Chamber I (altitude: 1486-1400 m)						
T-2	A	0.70±0.04	6.80±0.36	0.094±0.004	10.6±0.5	9.1
T-3	A	0.30±0.01	3.27±0.16	0.281±0.023	34.5±3.1	-
T-23a (outer)	A	0.33±0.03	2.76±0.19	1.18±0.10	368 ±154	≥42.4
b (inner)	C	0.066±0.004	2.40±0.15	1.11±0.08	302 ±77	≥44.0
T-27a (outer)	A	0.11±0.01	2.99±0.25	1.07±0.10	251 ±64	≥43.2
(grey blades)						
b (mid)	A	0.54±0.003	2.16±0.13	0.92±0.05	189 ±24	
(grey blades)						
c (inner)	A	0.42±0.02	3.57±0.13	0.99±0.08	202 ±34	
(dense white)						
Chamber II (altitude: 1400-1350 m)						
T-5 I	A	0.12±0.01	10.8±0.5			
II	A	0.12±0.01	10.7±1.0	0.018±0.005	2.0±0.5	recent
T-6 I	C	0.19±0.01	10.1±0.5	0.42 ±0.02	54.0±3.1	>48.0
II	C	0.12±0.01	9.80±1.01			
T-10	A	0.24±0.02	9.91±0.61	0.020±0.001	2.2±0.2	1.5
T-11a (outer)	A	0.78±0.03	10.8±0.2	0.059±0.003	6.5±0.3	3.4
b (inner)	C	0.34±0.01	9.79±0.25	0.52±0.03	71.5±4.6	29.8
T-12	C	0.20±0.01	8.23±0.54	0.54±0.06	75.2±10.5	
T-13	-	0.34±0.02	6.36±0.22	0.16±0.01	18.6±1.0	15.5
T-14 I	A	0.15±0.01	6.08±0.31	0.12±0.01	13.3±1.0	6.0
II	A	0.15±0.01	6.16±0.32	0.12±0.01	13.2±0.7	
T-24a (outer)	A+(trace C)	2.99±0.16	1.01±0.05	0.67±0.05	120 ±18.4	
b (mid)	C+A	3.37±0.22	1.01±0.03	0.80±0.06	173 ±29.7	
c (inner)	C	3.09±0.15	1.15±0.06	0.77±0.05	153 ±21.9	39.0
Lower Passage (altitude: below 1350 m)						
T-18	A	0.53±0.02	7.47±0.22	0.041±0.003	4.5 ±0.3	4.6
T-19	C (trace A)	0.29±0.02	8.04±0.51	0.86 ±0.06	147 ±10.9	40.2
T-20	A	0.39±0.02	7.56±0.28	0.16±0.01	18.4±1.0	19.8

tal is compacted; however, redistribution of elemental uranium should not lead to uranium isotopic fractionation [1]. Replicate analyses from a calcite speleothem (T-6) exhibited differences that are greater than warranted by the statistical error attributed to the measurement. In contrast, two sets of replicate analyses of aragonite speleothems (T-5 and T-14) yielded identical reproducibility. This indicates that more inhomogeneity in the uranium exists within the calcite. The redistribution of uranium was produced as recrystallization proceeded in the presence of water. Additional

interaction of drip waters, or rising groundwaters, with the already precipitated carbonate is evidenced by a thin secondary resolution rind on the surface of many fossil speleothems.

The speleothems are pure calcium carbonate: virtually no insoluble residue was present. In all cases the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio was greater than 100. Calculated $^{230}\text{Th}/^{234}\text{U}$ ages and radiocarbon ages are presented in Table 2. The radiocarbon ages are based on an initial ^{14}C content of 85% of that of modern organic carbon. The maximum error that can be caused by the inaccuracy

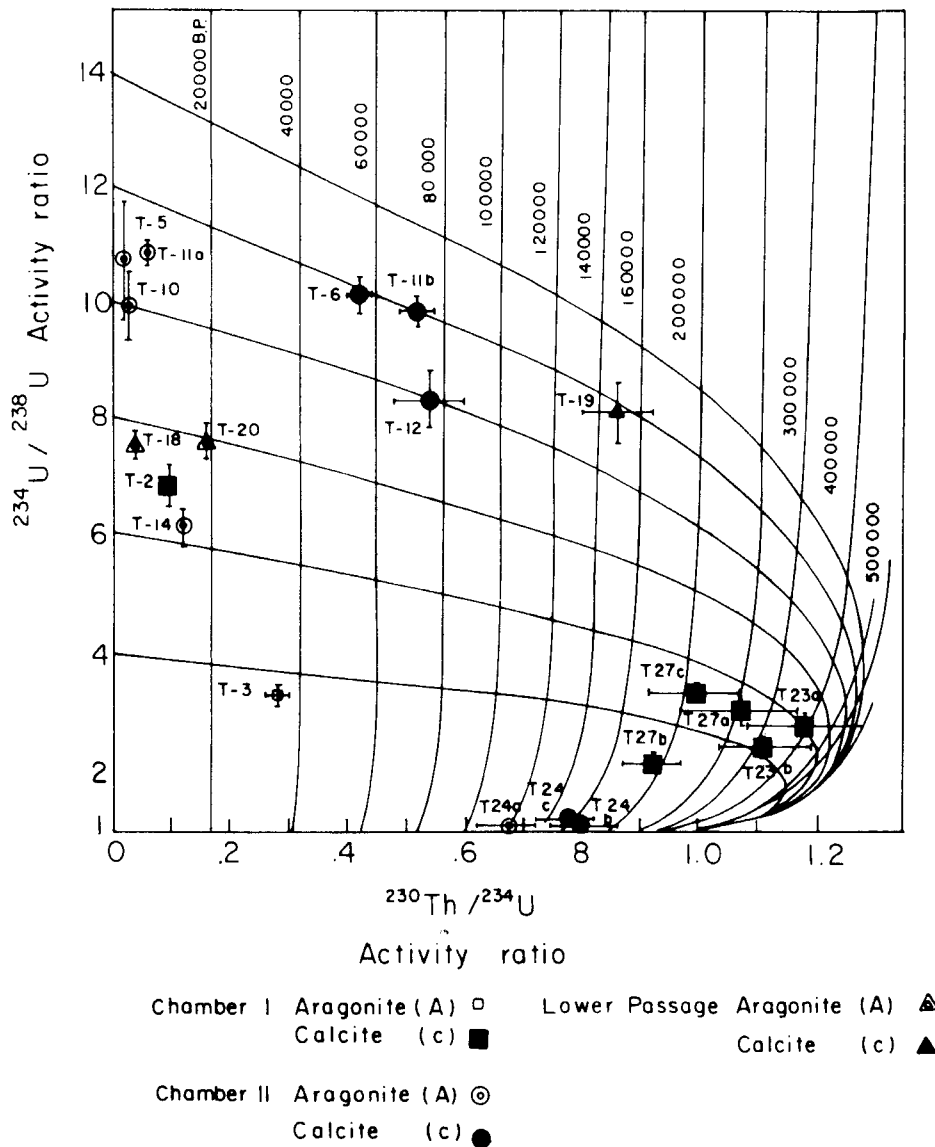


Fig. 5. Variation of $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios with time. The nearly vertical lines are isochrons. The nearly horizontal lines show how the activity ratios evolve, in a closed system, with increasing age for various initial $^{234}\text{U}/^{238}\text{U}$ activity ratios.

of this assumption is considered to be ± 1500 yr. The standard deviation of the age determinations ranged from 50 yr, for young samples, to between 3000 and 4000 yr for samples of 45000 yr B.P.

The age determinations demonstrated that speleothem deposition has been continuing since the middle–late Pleistocene to the present. Recrystallization or post-recrystallization alteration may be responsible for discrepancies between the ^{14}C and $^{230}\text{Th}/^{234}\text{U}$ dating methods, particularly for calcite speleothems. If elemental uranium is lost the $^{230}\text{Th}/^{234}\text{U}$ age will increase. An alternative possibility is that the drip water introduces young carbon to the fossil speleothems, causing the apparent ^{14}C age to be too young. A wide range in $^{234}\text{U}/^{238}\text{U}$ activity ratios is encountered in speleothems from different chambers of the cave, as well as in a specific chamber.

Fig. 5 plots the $^{230}\text{Th}/^{234}\text{U}$ activity ratios of the speleothems against their $^{234}\text{U}/^{238}\text{U}$ activity ratios. In a closed system, samples of different ages, derived from a single initial $^{234}\text{U}/^{238}\text{U}$ activity ratio, should fall along a single curve (or near-horizontal line). Each curve represents the evolution over time of the set of activity ratios from a specific starting $^{234}\text{U}/^{238}\text{U}$. Fig. 5 indicates that, in the Wolkberg cave, apparent initial ratios of $^{234}\text{U}/^{238}\text{U}$ in speleothems ranged between 4 and 12. In chamber II, for instance, the ^{14}C and $^{230}\text{Th}/^{234}\text{U}$ ages are in close enough agreement to indicate that the initial $^{234}\text{U}/^{238}\text{U}$ activity ratios ranged between 6 and 12 in contemporaneously deposited speleothems.

6. Discussion

6.1. Uranium isotopic fractionation

In the phreatic Grootfontein compartment the water enters the aquifer solely from the surface. It percolates downwards at varying rates, depending upon the extent to which the fissure network has been locally developed. It can be seen (Table 1) that the degree of uranium isotopic fractionation is highly variable, even between closely spaced sampling sites. The activity ratios tend to increase roughly as a function of depth (Table 1).

Since the aquifer is a secondary one, the age/depth relationship is not necessarily identical for all portions of the aquifer.

Fig. 4 presents a plot of the $^{234}\text{U}/^{238}\text{U}$ activity ratio as a function of age. The youngest and shallowest waters (samples 20 and 37) have uranium isotopic activity ratios that most closely approximate the regional surface $^{234}\text{U}/^{238}\text{U}$ disequilibria values. The uranium fractionation tends to evolve with increasing time spent in contact with the enclosing carbonate aquifer. Likewise, there is a sympathetic trend for a decreasing uranium content downwards from the surface. The evolution of the uranium isotopic fractionation within the groundwater takes place in the absence of a change in redox conditions. The tritium data (Table 1) indicates that the fractionation has progressed steadily over an approximate time span of only 20 yr. No chemical reducing barrier exists to precipitate uranium and act as a site for the generation of the alpha-recoil product ^{234}U . Another explanation is needed to explain the elevated $^{234}\text{U}/^{238}\text{U}$ in these waters.

As the uranium concentration of the water is low (< 0.5 mg/l) and exhibits no tendency to increase with depth, no leaching process can be evoked. The dolomite itself is of low uranium content, as the DNA analyses show. No anomalous uranium mineralization within the carbonate rock has ever been reported, which could have served as a source for ^{234}U derived from alpha-recoil. Rather, ion exchange/sorption processes best explain the distribution of the $^{234}\text{U}/^{238}\text{U}$ activity ratios and uranium concentrations.

In carbonate-rich groundwater, uranium forms stable uranyl carbonate complexes. However, Morse and co-workers [20] have demonstrated that UO_2^{2+} in solution can be efficiently adsorbed on to carbonate mineral surfaces, due to the formation of hydroxyl-carbonato species. This mechanism alone, or in conjunction with uranium removal by adsorption onto clay or wad, would provide an extensive thin uranium source on carbonate rock surfaces. This surface coating of uranium would be an effective medium for transferring alpha-recoil products into the co-existing aqueous phase. The alpha-recoil transfer of ^{234}U should generate progressively higher $^{234}\text{U}/^{238}\text{U}$

activity ratios with increasing rock/water interaction. The ^{234}U activity ratios should thus increase with residence time of the water within the aquifer (roughly as a function of depth).

Evidence that extensive ion exchange or sorption removal is occurring as the water filters through the dolomite is also provided by examining the radium and the radon concentrations. Part of the soluble ^{234}U decays to insoluble ^{230}Th , which precipitates on the aquifer rock face and, in turn, decays to ^{226}Ra (Fig. 1). The relatively high ^{222}Rn concentrations, which are in extreme excess to dissolved radium, are the alpha-recoil decay product of ^{226}Ra on the aquifer face. Ion exchange processes can account for the effective fixation of radium from the Ca-Mg-HCO_3 solution at concentration levels below saturation for radium carbonate [12].

6.2. Hydrologic deductions

The depth profiles established in the Grootfontein area suggest that the groundwater maintains a vertical stratification following recharge from the surface. Young, recently recharged water, characterized by moderately elevated $^{234}\text{U}/^{238}\text{U}$ activity ratios, overlies older water with higher activity ratios (Figs. 3 and 4). Very little mixing disturbs this stratification. Only where the water is discharged at the spring is it mixed. It is probable that the springs represent a mixture of water derived from different levels within the compartment.

6.3. $^{234}\text{U}/^{238}\text{U}$ in the speleothem record

The Wolkberg cave speleothems preserve a record of the uranium isotopic fractionations that were present in the cavern drip water. The outstanding degree of uranium isotope fractionation in groundwater is produced as the recharged water seeps down through the dolomitic fracture system.

The ion exchange, that we propose occurs between the uranium in solution and the carbonate rock walls, can lead to the deposition of a thin

film of uranium on the rock surfaces lining the aquifer. Alpha-recoil from the uranium source preferentially ejects ^{234}U into the water. This leads to the rapid development of higher $^{234}\text{U}/^{238}\text{U}$ activity ratios. A wide range of $^{234}\text{U}/^{238}\text{U}$ activity ratios are possible in the chemically similar waters that pass through a cavern. The longer the water remains in contact with the aquifer walls, the greater the opportunity for uranium isotope fractionation. Cave deposits at different levels provide a time-averaged record of the isotopic composition of descending groundwater. In the deeper chambers, speleothems generally record higher $^{234}\text{U}/^{238}\text{U}$ activity ratios than the upper chambers. Higher ratios correlate with greater (on average) amounts of water-rock interactions. Large variations in $^{234}\text{U}/^{238}\text{U}$ activity ratios at a given level (Fig. 5) reflect the variety of flow paths, channel geometries and flow rates that bring water to a particular point in the cave. The Wolkberg cave records that the fractionation process has been active for at least the past 350,000 years (Fig. 5).

$^{234}\text{U}/^{238}\text{U}$ disequilibrium dating is attractive because it provides ages that can extend back over a million years and it is based on only a single element. However, this method has not been conclusively evaluated for speleothem dating. A serious limitation to this method is the need to estimate the starting value of $^{234}\text{U}/^{238}\text{U}$. P. Thompson and co-workers [23] have demonstrated that drip water in a cave can vary and that speleothems depositing contemporaneously may incorporate different initial values. G. Thompson and co-workers [24] feel that the fluctuations in the original $^{234}\text{U}/^{238}\text{U}$ at a site can be considered to be normally distributed and averageable if the cave deposits formed slowly over a long period. They report the successful use of the method extending beyond 750,000 yr. Our data demonstrate that very large differences in $^{234}\text{U}/^{238}\text{U}$ activity ratios are recorded within a specific cavern. The assumption that an initial $^{234}\text{U}/^{238}\text{U}$ activity ratio can be derived for chronologic purposes in speleothems and then extrapolated as a constant value [24] over tens or hundreds of thousands of years is tenuous at best.

7. Conclusions

The process that gradually fractionates the uranium isotopes and causes disequilibria among the various daughter nuclides is an ongoing one that acts ubiquitously throughout the carbonate aquifer. This observation favours an ion exchange process [22] over a sorption process, because the latter would tend to be more effective where clays and 'wad' are concentrated. The isotopic fractionation process encountered within the Transvaal Dolomite Aquifer is undoubtedly not restricted to southern Africa but probably also operates in other dolomitic terranes. We believe that the Cotter Dolomite of the Cambro-Ordovician aquifer in the Tri-State area of the United States [25] presents another example where the ion exchange mechanism may explain the high (6.5–10) $^{234}\text{U}/^{238}\text{U}$ activity ratios, which are generated within the fresh recharge waters of dolomite in the absence of a reducing barrier.

Uranium isotopes can be used as a tool in hydrogeochemical reconnaissance prospecting for uranium. Abrupt decreases in uranium concentration, combined with high $^{234}\text{U}/^{238}\text{U}$ activity ratios may signal concentrations of uranium ore in reduced zones up dip [6]. However, the similar effects described here are entirely unrelated to any known economic accumulations of uranium. The interpretation of uranium disequilibria, specifically in dolomitic terranes, should be treated with circumspection when prospecting.

Acknowledgements

We would like to thank Dr. Robert Zielinski for his comments, which have improved this manuscript, and Mr. Even Ovadia for performing the DNA analyses.

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