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^{234}U-^{238}U-^{230}Th-^{232}Th systematics in saline groundwaters from central Missouri

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ABSTRACT

Saline groundwaters with 4.7 to 26‰ total dissolved solids were sampled from springs and artesian wells in Mississippian and Ordovician carbonates and sandstones in central Missouri. U-Th isotopic variations provide a means of evaluating processes of water–rock interaction and fluid mixing and estimating the time scales of element transport. Recently developed mass spectrometric techniques are used to make isotopic measurements on small-volume groundwater samples (0.1–4 l) with high precision (e.g., $< \pm 5‰$ for ^{234}U/^{238}U activity ratios). The groundwaters have a wide range of ^{238}U concentrations, 50×10^{-12} to 200×10^{-12} g/g; ^{234}U/^{238}U activity ratios, 2.15–16.0; ^{232}Th concentrations, 0.10×10^{-12} to 33×10^{-12} g/g; and ^{230}Th concentrations, 0.91×10^{-17} to 26×10^{-17} g/g. Unfiltered and filtered (0.4 μm, 0.1 μm) aliquots of a saline sample have the same isotopic composition and concentration of U, indicating that ^{234}U and ^{238}U occur almost entirely as dissolved species. The concentration of ^{232}Th is up to seven times lower in filtered vs. unfiltered aliquots, indicating that ^{232}Th is predominantly associated with particulates in the groundwaters. In contrast, most of the ^{230}Th is in solution.

Previous geochemical studies indicate that: (1) the saline waters originated as meteoric recharge and evolved through halite dissolution, reactions with silicates and saline-dilute mixing processes during a long-distance flow history; and (2) interaction with limestone and dolomite aquifer rocks in central Missouri has been limited. A consistent relationship between U/Ca and ^{234}U/^{238}U activity ratio is observed in the groundwaters and provides constraints on the U/Ca ratios and ^{234}U/^{238}U activity ratios of end-member reservoirs and on the processes of isotopic exchange in this water–rock system. Model calculations that simulate (1) saline-dilute groundwater mixing and (2) limited extents of dissolution of carbonate aquifer minerals by the groundwaters can account for the variations in U/Ca, ^{234}U/^{238}U and ^{18}O/^{16}O in the suite of water samples. The model calculations demonstrate that dissolved U isotopic compositions can be a sensitive indicator of water–rock interaction, which in turn limits the usefulness of ^{234}U-^{238}U disequilibria for groundwater age determinations. The concentration of dissolved ^{230}Th in the groundwaters is (1) two to three orders of magnitude below ^{230}Th-^{234}U equilibrium activity levels, and (2) significantly in excess of concentrations estimated for the supply of Th to solution via desorption and dissolution. A model involving the derivation of the excess ^{230}Th from the *in situ* decay of dissolved ^{234}U in the groundwaters indicates the operation of an adsorption mechanism on the time scale of 10–10^3 years. The results reported here may have broader application to the assessment and management of hazardous chemical species in natural environments.

1. Introduction

Uranium-series disequilibrium measurements have been applied to subsurface brine and groundwater systems in order to constrain models for mixing of water masses, water–rock interaction, and estimating groundwater "ages", e.g., [1–3]. Such studies commonly find a large extent of ^{234}U-^{238}U disequilibrium in groundwaters. There is also interest in the use of U-Th isotopes in groundwaters as analogs for radionuclide migration in aquifers near ore bodies and waste disposal sites [4,5], and in the use of U-Th isotopes to examine element transport in and discharge histories of active hydrothermal systems [6,7]. In the present study, the principal nuclides of interest in the ^{238}U decay series are: ^{238}U (4.469×10^9 yr

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half life) → ^{234}Th (24.1 days) → ^{234}U (2.445×10^5 yr) → ^{230}Th (7.538×10^4 yr) → ^{206}Pb.

Previous studies have established the major and trace element and H, O, Sr and Nd isotope geochemistry of saline groundwaters in central Missouri [8,9]. Banner et al. [9] evaluated models for the origin and chemical evolution of the waters in the context of hydrologic models and processes of fluid mixing and water–rock interaction using isotopic data. in the present study, we examine the distribution of U and Th isotopes in the suite of central Missouri groundwaters studied by these workers. Pronounced fractionation among the isotopes ^{238}U-^{234}U-^{230}Th-^{232}Th is found within the groundwaters and between the groundwaters and their aquifer rocks in central Missouri. These data provide a means of further evaluating water–rock exchange and fluid-mixing processes, and a means to study mechanisms and time scales of element transport in this natural system.

Alpha-counting spectrometry has been the principal analytical method for the measurement of U and Th isotopic abundances in waters. Recent applications of thermal ionization mass spectrometric methods to U-series disequilibrium studies of seawater and corals have demonstrated that ^{234}U, ^{238}U, ^{230}Th and ^{232}Th can be measured on much smaller samples and with higher precision as compared with α-counting techniques [10–12]. In this study, we apply these technical advances to the analysis of groundwater. In order to evaluate the role of particulate matter on the U-Th isotope geochemistry of the central Missouri groundwaters, we present data for both filtered and unfiltered sample aliquots, ranging in volume from 0.1 to 4 l. Monitoring of U and Th contamination during field and laboratory filtration, preservation, chemical processing and filament loading was a critical part of the procedure.

2. Geochemistry and hydrogeology of central Missouri groundwaters

Saline groundwaters discharge from Mississippian carbonates and Ordovician sandstones and carbonates in central Missouri (Fig. 1). Early Paleozoic carbonates and sandstones in western Missouri and Kansas comprise the Western Interior Plains aquifer system. According to the hydrologic model of Jorgensen et al. [13], meteoric recharge in the Front Range of Colorado sustains the eastward migration of groundwaters in this aquifer system from Colorado to the central lowlands of Missouri. This is generally consistent with potentiometric surface data for the Ordovician in this area [14] and the geochemical and isotopic models of Banner et al. [9]. Eastward-migrating saline water (> 200‰ total dissolved solids) in the Western Interior Plains aquifer system mixes with locally recharged freshwater in the Ozark Plateaus aquifer system in central Missouri (Fig. 1), resulting in the discharge of Na-Ca-Cl waters with salinities of 1–30‰ from artesian wells and springs.

Data from previous work on the suite of groundwaters analyzed in this study are summarized in Table 1. Major and trace element data and correlated δD and $\delta^{18}O$ values are readily explained by the saline-dilute water mixing model. The saline end member has low δD and $\delta^{18}O$ values that lie approximately along the meteoric water line. These isotopic signatures and regional groundwater salinity distributions (Fig. 1) indicate that the subsurface dissolution of Permian halite in Kansas by far-travelled meteoric recharge has generated the high groundwater salinities in the Western Interior Plains aquifer system [9]. Subsequent water–rock interaction with predominantly silicate assemblages may have produced the Ca enrichments, high $^{87}Sr/^{86}Sr$ values (Table 1) and low $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ values in the waters. The isotopic characteristics were most likely acquired prior to the fluid's migration through the Mississippian carbonate aquifer in central Missouri, as the waters have significantly lower $\delta^{18}O$ and higher $^{87}Sr/^{86}Sr$ values and generally lower $^{143}Nd/^{144}Nd$ values for waters that would be in isotopic equilibrium with the carbonates. The trace element and isotopic composition of the Mississippian carbonates and their major constituent minerals, calcite and dolomite, is estimated from studies of the Burlington–Keokuk Formation [15–17], which is a principal water-bearing unit in the Mississippian in this region (Fig. 1A, [9]). The H, O, Sr and Nd isotope data and the results of quantitative modeling indicate that: (1) models involving ancient seawater cannot account for the origin of the salinity in the groundwaters; and (2) carbonate-groundwater interaction is limited during migration of central

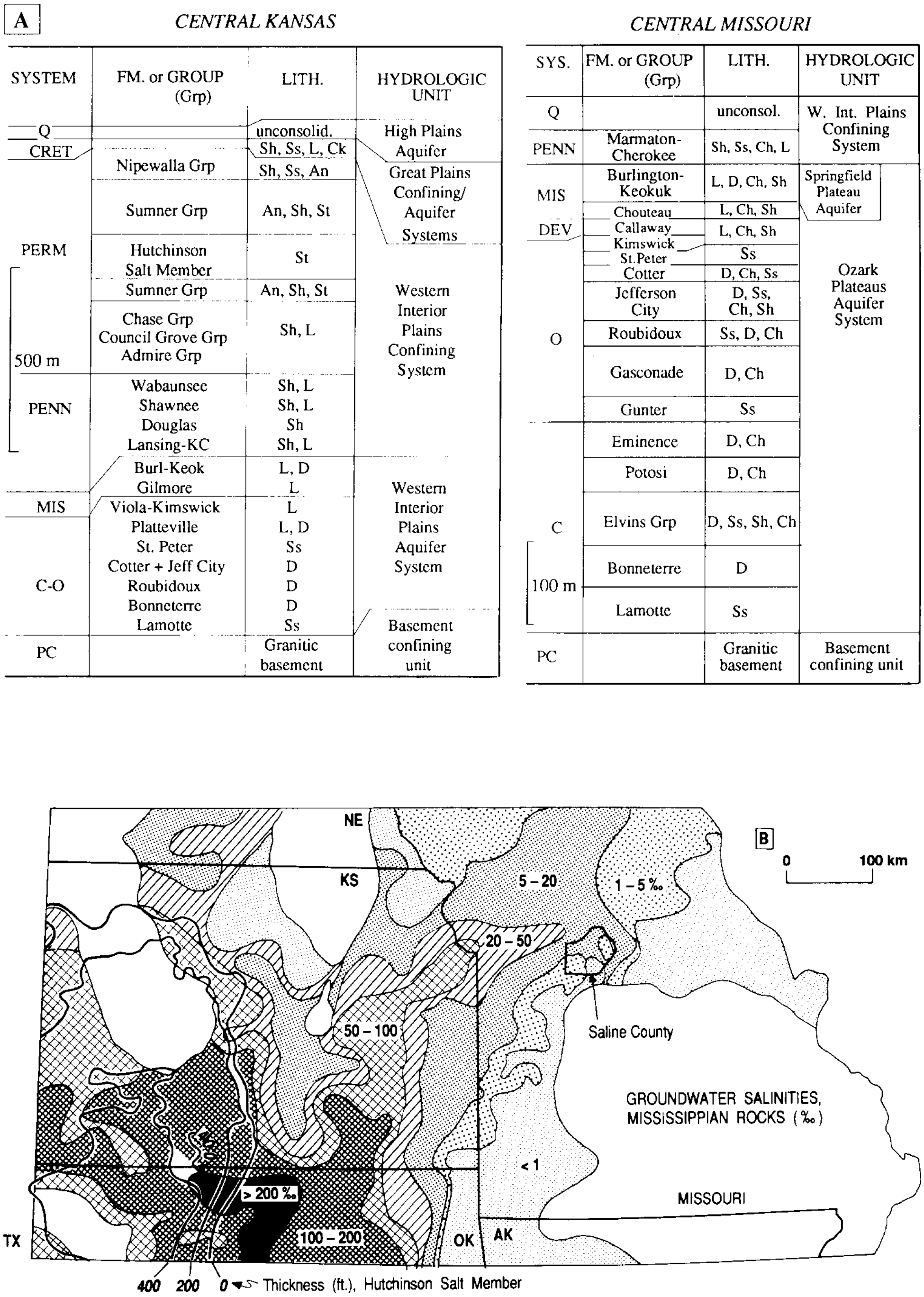

Fig. 1. (A) Lithostratigraphic section and major hydrologic units in central Missouri and central Kansas (after compilation in [9] and [36]). *Ss* = sandstone; *L* = limestone; *D* = dolomite; *Ch* = chert; *Sh* = shale; *An* = anhydrite; *St* = halite; *Ck* = chalk. (B) Salinity distributions in ‰ total dissolved solids for groundwaters in Mississippian rocks in Missouri and parts of Kansas, Oklahoma and Arkansas (after [37]). Mississippian rocks are not present in unpatterned areas. Also shown are contour lines of Permian Hutchinson Salt Member (see A) after [38].

TABLE 1

Ranges of geochemical data, isotopic compositions and trace element concentrations in central Missouri groundwaters [a]

pH	6.7	to	7.1
Eh (mV)	−95		−68
Salinity (%)	4.7		26
HCO_3 (mg/l)	225		293
T (°C)	13		15
δD (% SMOW)	−45		−108
δ^{18}O (% SMOW)	−6.5		−14.5
^{87}Sr/^{86}Sr	0.71551		0.71607
$\epsilon_{Nd}(0)$ (mg/l)	−8.1		−10.9
Sr (mg.l)	8.15		41.4
Nd (ng/l)	12.6		112

[a] Data from [9], except Eh and pH data for same localities from [8].

Missouri groundwaters to the surface through Mississippian aquifer rocks, such that marked Sr and O isotopic differences are maintained between the groundwaters and the carbonates.

3. Analytical methods

Spring and well-water samples were filtered either on site during collection (localities 1 and 4), or in the laboratory of Dr. P.I. Nabelek at the University of Missouri, Columbia, within several hours of collection. Filtrates were obtained using 0.4 μm and 0.1 μm filter pore sizes, and were subsequently acidified to pH < 2 with purified 10 N HCl. Unfiltered samples, both acidified and unacidified, were also collected at each site. Sampling procedures are detailed in Banner et al. [9]. This filtration and acidification scheme was followed so that direct comparison of isotopic data for unfiltered and filtered aliquots of groundwater from the same locality will yield information on the effects of particulates. ^{238}U, ^{234}U, ^{230}Th and ^{232}Th were measured on aliquots of the same samples reported in Banner et al. [9], using chemical separation and thermal ionization mass spectrometric procedures following Chen et al. [10] and Edwards et al. [11]. Enriched spikes of ^{233}U, ^{236}U (^{233}U/^{236}U $\sim$ 1) and ^{229}Th (^{230}Th/^{229}Th $< 2 \times 10^{-5}$) were added to samples at Caltech, about 21 months after sampling. No precipitates were observed in the waters during this storage period. U and Th were co-precipitated with Fe-hydroxide and separated using anion exchange chemistry.

Blank levels of U and Th for the field and laboratory filtration procedures and the acidification, co-precipitation, chemical separation and filament loading procedures were determined by treating distilled water in an identical manner to the water samples (Table 2). In particular, efforts were made to assess contributions to the blank levels from filtration and handling both in the field and laboratory. Uranium blanks for the complete procedure (including either lab filtration, no. 3, or field filtration, no. 4 in Table 2) are less than a factor of two higher than the blank for the combined co-precipitation, chemical separation and filament loading procedures (no. 2). The Th blanks determined for the complete procedure are slightly lower than the portion of the procedure without filtration. These results indicate that filtration of the groundwaters, on-site or in the laboratory, contributes a negligible portion of the Th blank level and a minor portion of the U blank level associated with sample treatment. Total U blanks for the complete sample treatment and analysis are negligible for the samples analyzed. The principal source of Th contamination is from the co-precipitation and chemical separation steps. The ^{232}Th blank constituted between 5×10^{-4}% and 12% of the samples analyzed. Appropriate corrections were applied to the ^{232}Th concentration data in Table 4.

Uranium isotopes were measured on the Lunatic I mass spectrometer using an electron multiplier in the analog mode with a gain of $\sim 4 \times 10^{3}$ and an electrometer with a 10^{9} Ω feedback resistor. 140–300 ^{234}U measurements are obtained at ion beam intensities of 700–4000 ions/s, in the sequence ^{236}U-^{235}U-^{234}U-^{234}U-^{233}U,

TABLE 2

Uranium and thorium blanks (pg) for water sample handling and analytical procedures [a]

Procedure	^{238}U	^{232}Th
1. Filament loading	0.28	0.22–0.46
2. Co-precipitation (co-ppt.) + chem. separation + loading	3.0	4.3, 4.7
3. Lab filtration + acidification + co-ppt. + chem. separation + loading	4.7	3.4
4. Field filtration + acidification + co-ppt. + chem. separation + loading	5.2	3.7

[a] Handling and analytical procedures performed on 175–220 ml distilled water. 1 pg $= 1 \times 10^{-12}$ g.

TABLE 3

Isotopic results for U and Th standards

Quantity analyzed (ng) [a]	$^{230}Th/^{232}Th$ [b] ($\times 10^5$)	$^{234}U/^{238}U$ ($\times 10^5$)	$(^{234}U/^{238}U)_{ACT}$
NBS SRM 960			
300		5.281 ± 0.032	0.9651 ± 0.0058
300		5.277 ± 0.040	0.9644 ± 0.0073
50		5.287 ± 0.033	0.9662 ± 0.0060
50		5.263 ± 0.032	0.9618 ± 0.0059
Average		5.277 ± 0.010	0.9644 ± 0.0018
Johnson Matthey ThO_2			
0.25	7.47 ± 1.25		
0.5	8.29 ± 1.38		
5	7.45 ± 0.25		
10	7.24 ± 0.20		
10	7.32 ± 0.25		
20	7.13 ± 0.19		
20	7.24 ± 0.11		
520	7.32 ± 0.19		
520	7.29 ± 0.13		
520	7.22 ± 0.14		
630	7.35 ± 0.15		
630	7.30 ± 0.16		
630	7.13 ± 0.34		
Average ($\geq$ 5 ng)	7.27 ± 0.06		

[a] Quantities of ^{238}U or ^{232}Th. 1 ng $= 1 \times 10^{-9}$ g.

[b] All errors are $2\sigma_{mean}$.

including zeros at 0.5 mass units above and below each mass. Data are normalized to the ^{233}U-^{236}U double spike composition. ^{238}U concentrations are calculated from the normalized $^{235}U/^{236}U$ ratios using $^{238}U/^{235}U = 137.88$ [10]. Ionization efficiencies for samples and standards range from 0.2 to 2‰ and are inversely correlated with the amount of U loaded.

$^{234}U/^{238}U$ ratios in a sample are also expressed as activity ratios, where

$$(^{234}U/^{238}U)_{ACT} = \frac{(^{234}U/^{238}U)_{sample}}{(^{234}U/^{238}U)_{eq}}, \quad \text{and}$$

$$(^{234}U/^{238}U)_{eq} = \lambda_{238}/\lambda_{234} = 5.472 \times 10^{-5}$$

which is the atomic ratio at secular equilibrium. The isotopic composition of U in NBS SRM 960 measured during the course of this study was $(^{234}U/^{238}U)_{ACT} = 0.9644 \pm 0.0018$ (Table 3), and is essentially identical to that obtained by Chen et al. [10], $(^{234}U/^{238}U)_{ACT} = 0.9625 \pm 0.0020$.

Thorium was measured in the sequence ^{229}Th-^{230}Th-^{230}Th-^{232}Th using the same instrumental setup as described for U, except that a 10^{10} Ω feedback resistor was used to increase measured voltages for some samples with low ^{230}Th abundances. Owing to the low $^{230}Th/^{232}Th$ ratios (8×10^{-6} to 1×10^{-4}) and low Th contents of the solutions, the number of ^{230}Th atoms loaded on the filament ranged from 2×10^7 to 4×10^9. As a result, $^{230}Th^+$ ion currents during analysis were extremely low, ranging from 2–5 ions/s above background currents for samples and 4–130 ions/s above background for standard runs of 20 ng or less of total Th. These $^{230}Th^+$ ion currents are up to 15 times lower as compared with previous ^{230}Th measurements on corals made in this laboratory [11,12]. Previous studies demonstrated the precision and accuracy that can be obtained by measuring low $^{230}Th^+$ ion currents. These are sensitive to uncertainties associated with electrometer noise, background currents resulting from the reflection of $^{187}Re^+$ and $^{185}Re^+$ ion beams off the flight tube and tailing from the large ^{232}Th beam. Scans at running conditions show that the baseline in the region of masses 228.5 to 230.5 is linear. Analyses were typically conducted at relatively low currents of 6–50 ions/s at masses 229.5 and 230.5 and required longer data acquisition times compared with the earlier studies quoted above. Ionization efficiencies for Th are between 0.2 and 0.9‰.

Analyses were conducted on a standard solution prepared from Johnson Matthey purified ThO_2 (as described in [11]). $^{230}Th/^{232}Th$ ratios for sample sizes of 5, 10, 20, 520 and 630 ng total Th for the ThO_2 standard were reproducibly determined with a precision of 1–4% ($2\sigma_{mean}$) for individual runs and an overall mean value of $(7.27 \pm 0.06) \times 10^{-5}$ (Table 3). Analyses of this ThO_2 standard were also made on much smaller loads of 0.25–0.5 ng of total Th, which are equivalent to 5×10^7 to 1×10^8 atoms of ^{230}Th. These experiments yielded ion currents of 4–8 ions/s for $^{230}Th^+$, and were performed in order to simulate analyses of the water samples. $^{230}Th/^{232}Th$ was determined on the small loads with a precision of ±15–20% and has values within uncertainty of the mean given by the analyses of the larger ThO_2 standard loads (Table 3). These results indicate that accurate $^{230}Th/^{232}Th$ isotopic measurements can be made on $^{230}Th^+$ ion currents as low as 4–8 ions/s with an analog multiplier. ^{230}Th/^{232}Th measurements on samples were determined with a precision of 8–40%, while only limits are given for samples that yielded the lowest ^{230}Th$^+$ signals (Table 5). ^{238}U and ^{232}Th concentration data for individual runs are determined to a precision of ± 2‰ and ± 1% respectively, although small samples have somewhat larger errors (Table 4), due to uncertainties in determining the ^{232}Th blank. The ^{234}U enrichments in several of the water samples (Table 5) permit the determination of ^{234}U/^{238}U ratios to ± 4‰ ($2\sigma_{\text{mean}}$) on less than 5×10^{-9} g of total U. Similar precision is obtained on 5×10^{-8} g of U in NBS SRM 960, which has a ^{234}U/^{238}U composition much closer to secular equilibrium (Table 3).

4. Results

^{238}U and ^{232}Th concentrations and salinity data are given in Table 4 and U and Th isotopic data are given in Table 5. The water samples have a salinity range of 4.7–26‰. ^{238}U ranges from 50 to 196 pg/g and ^{232}Th ranges from 0.100 to 33.4 pg/g. Comparisons are made between unfiltered and filtered aliquots in order to examine the extent to which various elements are associated with particulates in the groundwaters. For locality 4, unfiltered–filtered comparisons of ^{234}U, ^{238}U, ^{230}Th, ^{232}Th, Sm, Nd, Sr and Ca concentrations are shown in Fig. 2. The unfiltered aliquot (total sample) and the 0.4 μm and 0.1 μm filtrates all have the same ^{238}U concentration to within ± 3‰ and the same ^{234}U/^{238}U activity ratio to within ± 2‰ (Tables 4, 5). For locality 5, the 0.4 μm and 0.1 μm filtrates have ^{238}U concentrations that differ by 7% and ^{234}U/^{238}U activity ratios that differ by 7%. The near constancy of concentration and isotopic composition, independent of filtration, indicates that ^{234}U and ^{238}U occur almost exclusively as dissolved species and are not associated with particulates to any large extent.

In contrast to the U data, the results for ^{232}Th show significant differences between unfiltered and filtered aliquots and between different pore size filtrates. The filtered/unfiltered ^{232}Th concentration ratio is 0.30 for the 0.1 μm filtrate from locality 4 and 0.14 for the 0.4 μm filtrate (Fig. 2).

TABLE 4

U-Th concentration data for central Missouri groundwaters

Sample [a]	Salinity (‰)	Sample wt. (g)	^{238}U [b] (pg/g)	^{232}Th [c] (pg/g)	$\frac{^{232}\text{Th}}{^{238}\text{U}}$ ($\times 10^3$)	Ca (μg/g)	U/Ca molar ($\times 10^7$)
1. Sweet Springs							
UFA	4.7	117	50.0 ± 0.1	0.324 ± 0.009	6.65	338	0.249
2. McCallister Springs							
UU	6.3	263	92.6 ± 0.3	0.496 ± 0.011	5.49	305	0.510
3. Salt Branch Springs							
< 0.1 μm	7.9	224	196.3 ± 0.5	2.49 ± 0.02	13.0	407	0.811
4. Boone's Lick							
UFA	22	3.85×10^3	72.9 ± 0.2	0.728 ± 0.010	10.2	1120	0.109
< 0.4 μm		2.96×10^3	72.7 ± 0.3	0.100 ± 0.001	1.41	1110	0.110
< 0.1 μm		225	72.5 ± 0.2	0.216 ± 0.005	3.06	1110	0.110
5. Blue Lick							
< 0.4 μm	26	3.26×10^3	104.7 ± 0.3	33.4 ± 0.9	327	1310	0.134
< 0.1 μm		241	98.8 ± 0.3	8.91 ± 0.10	92.5	1330	0.125
< 0.1 μm replicate		247	97.4 ± 0.2	9.14 ± 0.05	96.3	1330	0.123
Seawater [d]	35	–	3238	0.092–0.145	0.029–0.046	415	13.1

[a] UFA = unfiltered, acidified; UU = unfiltered, unacidified. 0.4 μm and 0.1 μm filtrates were acidified upon filtration. Localities 1 and 4 are artesian wells; localities 2, 3 and 5 are natural springs. Details of each locality and salinity and Ca data given in [9].

[b] All errors are $2\sigma_{\text{mean}}$. Sources of uncertainties on U-Th isotope measurements discussed in Analytical methods section.

[c] ^{232}Th data corrected for blank of 4 ± 1 pg.

[d] Seawater data from [10]. Mean for U, range for Th for unfiltered, acidified samples.

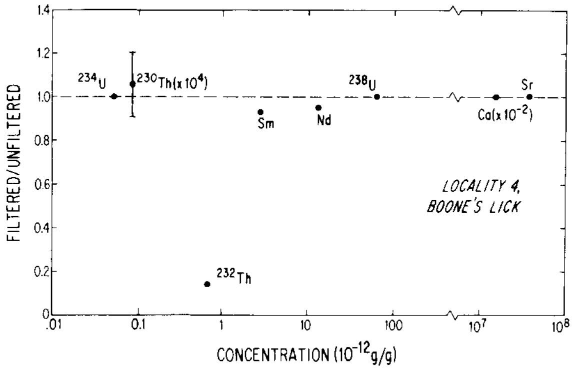

Fig. 2. Ratio of elemental and isotopic concentrations in filtered:unfiltered aliquots vs. concentration in unfiltered aliquot for groundwater sample from locality 4. U and Th data from this study; Sr, Nd, Sm and Ca data from [9]. Identical results are obtained using data for either the < 0.4 μm or the < 0.1 μm fraction as the filtered aliquot, except for Th isotopes (0.4 μm data shown here). Analytical uncertainties are smaller than size of symbols, except for ^{230}Th. ^{230}Th and Ca concentrations in unfiltered aliquot are multiplied by factor shown on the horizontal scale only.

These results imply that more than half, and as much as 80%, of the ^{232}Th in groundwater from this locality is associated with particulate matter greater than 0.4 μm in diameter. No unfiltered sample was analyzed for locality 5. A comparison of the 0.1 μm with the 0.4 μm filtrate shows close to the same ^{238}U and ^{234}U concentrations, but greatly decreased ^{232}Th in the finer filtrate (see Tables 4 and 5).

^{230}Th in the groundwaters ranges from 0.91×10^{-5} to 26×10^{-5} pg/g, which is equivalent to 2×10^4 to 7×10^5 atoms/g of ^{230}Th. As shown in Fig. 2, ^{230}Th concentrations are the same within analytical uncertainty for the unfiltered and filtered aliquots from locality 4, whereas the ^{232}Th is predominantly on particulates. ^{230}Th concentrations differ by a factor of two for the different filter sizes from locality 5 (Table 5). Thus, it appears that ^{230}Th is essentially in solution at sampling station 4. In contrast, the filtrates from locality 5 have higher Th contents and appear to show a correlation of ^{230}Th and ^{232}Th. These features may reflect a higher percentage of fine-grained particulates at locality 5.

It was found that ^{87}Sr/^{86}Sr ratios and the concentrations of Sr, Ca, Na, K, Mg, Li, Si and B in unfiltered and 0.4 μm, 0.1 μm and 0.025 μm filtrates are identical within analytical uncertainty for samples from each of the five central Missouri localities [9]. Results for Sm and Nd show that approximately 7% of the rare earth elements are on particulates in the waters. With the exception of ^{230}Th and ^{234}U, a general trend of increasing association with particulates with decreasing elemental concentration is observed for Ca, Sr, U, Nd, Sm and Th (Fig. 2).

The predominant particulates in the central Missouri groundwaters are iron sulfides and native sulfur, which form as precipitates from solution during and subsequent to ascent to the surface. X-ray diffraction studies indicate that the sulfides are predominantly greigite, with lesser amounts of mackinawite and other iron sulfides (A.B. Carpenter, pers. commun.). We note here that the particulates in the groundwaters may comprise any or all of the following: entrained mineral particles, suspended colloids, as well as precipitates from solution. The incorporation or formation of the particulates in the waters may have occurred along the flow path to a given locality, during ascent to the surface, and even during filtration. A thorough knowledge of the origin and composition of the particulate matter in this aquifer requires further study. Filter pore sizes less than 0.1 μm may be necessary to characterize the dissolved non-colloidal Th (e.g., [5,18]). In the present report, we take our analytical data for U and Th isotopes in the filtered aliquots to represent their dissolved distributions.

The ^{238}U concentrations in the groundwaters are two orders of magnitude lower than those in seawater and the ^{232}Th concentrations range from values similar to those in seawater up to two orders of magnitude higher. The ^{238}U concentrations are within a broad range of values for other groundwaters as compiled by Osmond and Cowart [19]. Compared with the few studies of ^{230}Th and ^{232}Th in groundwaters (e.g., [5,7]), the central Missouri samples have similar concentrations but a wider range of values.

The groundwaters have a large range of $(^{234}U/^{238}U)_{ACT}$ values of 2.15 to 16.0 (Fig. 3). The higher values represent pronounced ^{234}U-^{238}U fractionation relative to secular equilibrium or seawater. The $(^{234}U/^{238}U)_{ACT}$ values of the central Missouri groundwaters span a large portion of the range in values observed for previous studies of groundwaters [19]. $(^{234}U/^{238}U)_{ACT}$ values of up to

TABLE 5

U-Th isotopic compositions of central Missouri groundwaters

Sample	$\frac{^{234}U}{^{238}U}$ $(\times 10^5)$	$\left(\frac{^{234}U}{^{238}U}\right)_{ACT}^{a}$	$\frac{^{230}Th}{^{232}Th}$ $(\times 10^5)$	^{230}Th pg/g $(\times 10^5)$	$\left(\frac{^{230}Th}{^{234}U}\right)_{ACT}^{b}$ $(\times 10^4)$	$\left(\frac{^{230}Th}{^{234}U}\right)_{ACT}^{*c}$ $(\times 10^4)$	Model age ^{c}
1. Sweet Springs							
UFA	45.45 ±0.22	8.305±0.040	–	–	–	–	–
2. McCallister Springs							
UU	23.71 ±0.27	4.333±0.049	< 30	< 20	–	–	–
3. Salt Branch Springs							
< 0.1 μm	11.75 ±0.10	2.147±0.018	–	–	–	–	–
4. Boone's Lick							
UFA	87.27 ±0.37	15.95 ±0.07	1.26 ±0.28	0.91±0.20	4.8	3.1	34
< 0.4 μm	87.65 ±0.59	16.02 ±0.11	9.6 ±3.9	0.96±0.39	5.0	4.8	52
< 0.1 μm	87.52 ±0.37	16.00 ±0.07	< 200	< 50	–	–	–
5. Blue Lick							
< 0.4 μm	70.23 ±0.26	12.84 ±0.05	0.796±0.071	26.3 ±2.3	120	53	580
< 0.1 μm	74.51 ±0.31	13.62 ±0.06	1.21 ±0.46	10.7 ±4.1	48.9	31.0	340
< 0.1 μm replicate	74.85 ±0.25	13.68 ±0.05	1.17 ±0.14	10.6 ±1.3	48.6	30.1	330
Seawater ^{d}	6.258±0.012	1.14	2.0	0.39	0.65	–	–

Symbols as in Table 4.

[a] $(^{234}U/^{238}U)_{ACT}$ defined in text.

[b] $(^{230}Th/^{234}U)_{ACT} = (^{230}Th/^{234}U)_{atomic} \times (\lambda_{230}/\lambda_{234})$; $\lambda_{230} = 9.195 \times 10^{-6}$ yr^{-1}; $\lambda_{234} = 2.835 \times 10^{-6}$ yr^{-1}.

[c] Model ages calculated using $(^{230}Th/^{234}U)^*_{ACT} \equiv (^{230}Th/^{234}U)_{ACT}$ corrected for particulate ^{230}Th input, as discussed in text.

[d] U isotope data for average seawater from Pacific and Atlantic [10]. Th isotope data for seawater from 3000 m depth, Panama Basin [35].

15.6 have been reported for waters from lower Paleozoic aquifers in southwestern Missouri [20,21]. No consistent relationship between U concentrations and U isotopic composition is observed in this study or for groundwater samples from the other studies cited in Fig. 3A. To evaluate the possibility that U and Ca in the groundwaters are derived from the same source, we examine the relationship between U/Ca ratio and $(^{234}U/^{238}U)_{ACT}$ (Fig. 3B). Data from this study show a consistent inverse relationship. U/Ca-$^{234}U/^{238}U$ data from the other studies shown in Fig. 3A (for which Ca concentrations are reported) are not correlated.

$(^{230}Th/^{234}U)_{ACT}$ values in both filtered and unfiltered water samples range from 4.8×10^{-4} to 120×10^{-4} (Table 5). These values are two to three orders of magnitude lower than the near-equilibrium activity ratios that would be produced from the *in situ* decay of ^{234}U in the waters on a time scale of 10^4 to 10^5 years.

5. Discussion

The main features of the U-Th isotope data that provide insight into the processes of water–rock interaction and the time scales of nuclide transport in the central Missouri groundwaters are: (1) the wide range of ^{234}U enrichment relative to secular equilibrium; (2) the U/Ca-$^{234}U/^{238}U$ correlation; (3) the extremely low $(^{230}Th/^{234}U)_{ACT}$ values; and (4) the occurrence of ^{238}U and ^{234}U as dissolved species and the predominant association of ^{232}Th with particulates.

In this section, we evaluate the potential effects of several processes on the ^{234}U-^{238}U-^{230}Th-^{232}Th systematics in the groundwaters:

(1) It is assumed that the ^{234}U enrichment commonly observed in groundwaters results from the effects of α-recoil of ^{234}Th during the decay of ^{238}U [22,19] The enrichment can arise by either of two processes: (a) the direct ejection of ^{234}Th from an aquifer mineral into solution followed by *in*

situ decay to ^{234}U; or (b) the creation of a recoil-damaged lattice site for ^{234}Th (and thus for ^{234}U) in an aquifer mineral, which would be susceptible to preferential leaching. The mineralogic sources containing the parent uranium are assumed to comprise surfaces in the aquifer or particulates transported in the migrating fluid.

(2) Dissolution–recrystallization of aquifer minerals having $(^{234}\mathrm{U}/^{238}\mathrm{U})_{\mathrm{ACT}} \approx 1$ will change groundwater U isotopic compositions towards this value for secular equilibrium. Such isotopic equilibration via reactions with aquifer minerals has been proposed to account for the limited ^{234}U enrichments in Gulf Coast hydrothermal fluids (Fig. 3A, [3]). The same near-equilibrium $(^{234}\mathrm{U}/^{238}\mathrm{U})_{\mathrm{ACT}}$ values in these hydrothermal fluids may also be attained if α-recoil processes were limited in this system, or if the fluids ceased reaction with the host rock on a time scale that is long compared with $1/\lambda_{234}$.

(3) An increase in Eh in an aquifer will increase U solubilities (as the divalent uranyl ion, UO_2^{2+}, in carbonate, phosphate or sulphate complexes) and decrease Th solubilities through the stabilization of Fe and Mn hydroxides.

(4) Sorption processes involving suspended particulate matter, chemical precipitates and the surfaces of aquifer minerals can play an important role in retarding or enhancing the transport of radionuclides in aqueous regimes [4,23]. In particular, several studies have shown that the isotopes of Th are highly particle reactive in the marine environment [24,25].

(5) The relative rates of α-recoil injection, adsorption of radionuclides on particulates, and dissolution–recrystallization of aquifer minerals, as compared to the decay rates of the U-series nuclides, will determine the evolution of the radioisotopic signature of groundwaters during transport in an aquifer system.

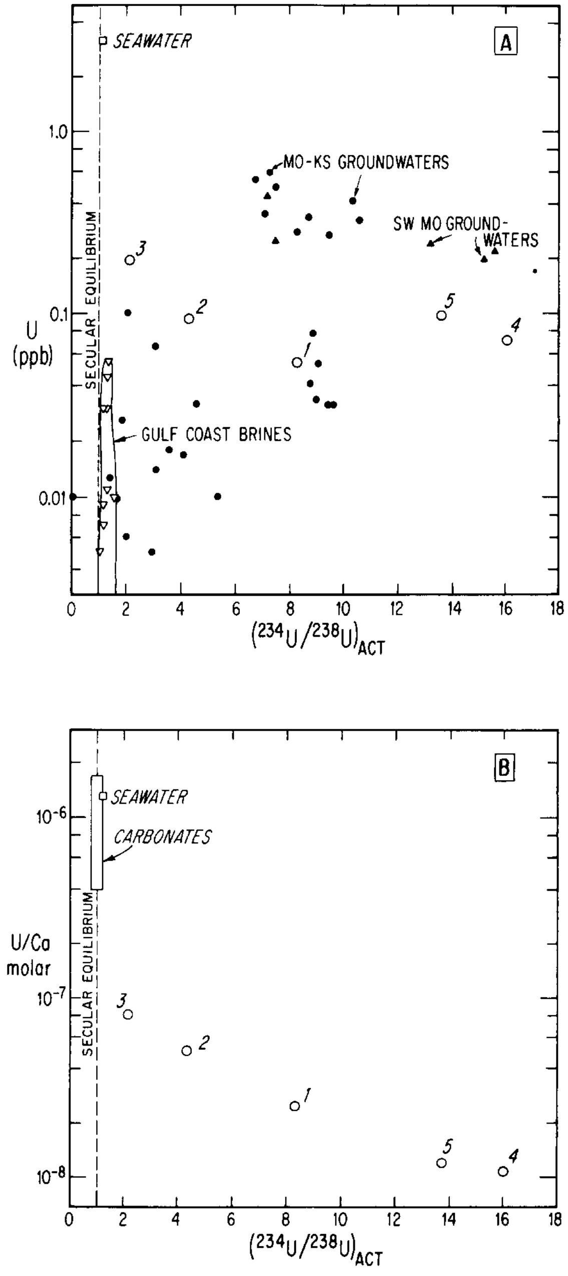

Fig. 3. (A) Variation of U concentrations and U isotopic compositions, expressed as activity ratios, in central Missouri groundwaters (numbered open circles). Central Missouri data are numbered by locality (Tables 4, 5) in all figures, corresponding to increasing salinity. Also shown are data for spring waters from southwestern Missouri (solid triangles, [20]), subsurface groundwaters from southwestern Missouri and southeast Kansas (solid circles, [21]), and brines from the Gulf Coast of the United States (open triangles, [3]). Seawater data as in Tables 4 and 5. (B) U/Ca molar ratio vs. U isotopic composition for central Missouri groundwaters. Plotted range in carbonate values include data for modern carbonates [11,39,40] and Mississippian carbonates of the Burlington–Keokuk Fm. [17].

5.1. ^{234}U-^{238}U distributions

Redox control on ^{234}U-^{238}U distributions has been documented in both limestone and sandstone aquifers, whereby oxidizing waters near recharge zones have high ^{238}U contents and low ^{234}U/^{238}U activity ratios. Groundwaters further along the flow path, under more reducing conditions, have lower solubilities of ^{238}U and higher ^{234}U/^{238}U activity ratios. A two-stage mechanism is used to explain these data, whereby ^{238}U and ^{234}U precipitate from solution under reducing conditions and ^{234}U is preferentially injected into solution by α-recoil processes [19,26]. Changes in the ^{234}U/^{238}U activity ratio along flow paths in the reduced portions of aquifers have been used in attempts to "date" groundwaters (e.g., [27]). The central Missouri groundwaters have a narrow range of Eh and pH values (Table 1) and the compositions of these groundwaters lie in the stability field for crystalline UO_2 on an Eh–pH diagram [26]. The observations of the present study are in contrast to other groundwater studies reporting a wide range of U isotopic compositions and concentrations that are coupled to a wide range of redox conditions (e.g., [19,2]). The wide range in $(^{234}U/^{238}U)_{ACT}$ values and ^{238}U concentrations under a narrow range of relatively reducing conditions for the central Missouri groundwaters suggests that U distributions in the portion of the aquifer sampled are not governed by large changes in redox conditions. The two saline samples (4,5) have significantly higher $(^{234}U/^{238}U)_{ACT}$ than the three dilute samples (1–3, Fig. 3A). However, within the dilute group, an inverse correlation between salinity and $(^{234}U/^{238}U)_{ACT}$ is observed. Thus, although the range in many elemental and isotopic parameters in the central Missouri groundwaters can be explained by a saline-dilute water mixing model [8,9], the ^{234}U-^{238}U systematics are controlled by an additional process.

The saline end member of the central Missouri groundwater suite, as represented by samples from localities 4 and 5, has high $(^{234}U/^{238}U)_{ACT}$ and intermediate ^{238}U concentrations. It also has had a longer flow history compared with the dilute end member [9]. The dilute end member can be represented by local meteoric recharge in central Missouri, based on δD-δ^{18}O variations (Table 1 and [9]). Estimation of $(^{234}U/^{238}U)_{ACT}$ in this end member is discussed below. Most studies of U isotopes in groundwaters conclude that α-recoil of ^{234}Th is critical for the attainment of high $(^{234}U/^{238}U)_{ACT}$ in groundwaters. However, distinguishing the processes controlling the ultimate distribution of U isotopes in any given aquifer is subject to uncertainties in data for surface-fluid sorption coefficients, mineral-fluid distribution coefficients, flow rates and the degree to which the system approaches steady-state conditions. Depending on the values of these parameters, $(^{234}U/^{238}U)_{ACT}$ values can either increase or decrease as a function of groundwater age or length of flow path [27].

The inverse correlation between U/Ca and $(^{234}U/^{238}U)_{ACT}$ in the central Missouri groundwaters (Fig. 3B) may reflect exchange between two distinct U reservoirs in this system: one end member with high $(^{234}U/^{238}U)_{ACT}$ and a low U/Ca ratio; the other end member with $(^{234}U/^{238}U)_{ACT}$ ~ 1 and a high U/Ca ratio. The first end member may be represented by one of the saline groundwater samples. Calcite and dolomite, the predominant minerals in the Mississippian aquifer, will have ^{234}U-^{238}U-Ca compositions similar to the second hypothetical end member (Fig. 3B). Preliminary work by Hoff and others ([17] and in progress) on Burlington–Keokuk dolostones (Fig. 1) indicates that a significant portion of the total U in some of these samples is associated with fine-grained coatings on dolomite rhombs, while in other Burlington–Keokuk samples nearly all of the U resides within the rhombs. Understanding the distribution of U and Th in carbonate rocks that comprise aquifers warrants further investigation. We consider here that isotopic and elemental exchange between the two reservoirs described above may be accomplished via limited dissolution of carbonate minerals in the aquifer by an end member groundwater composition.

Model calculations were used to simulate and quantify isotopic and elemental variations (^{234}U, ^{238}U, U and Ca) in a groundwater as it migrates through an aquifer and dissolves calcite and dolomite. It is assumed that a thermodynamic drive for calcite or dolomite dissolution exists in the model system, such as that produced by minor fluctuations in P_{CO_2} in waters at or near carbonate saturation. The distribution of uranium in a closed system comprised of groundwater and limestone (calcite) can be represented by the mass balance relationship:

$$C^{\mathrm{U}}_{\text{system}} = F \times C^{\mathrm{U}}_{\mathrm{f}} + (1 - F)C^{\mathrm{U}}_{\mathrm{s}} \qquad (1)$$

where f and s designate fluid and solid phase U concentrations (C^{U}) prior to any water–rock interaction, and F and $(1 - F)$ are weight fractions of the fluid and solid phases. "System" subscripts the U concentration in the entire water–rock system considered, which is equivalent to the U concentration in the groundwater upon calcite dissolution. A similar expression may be written for calcium concentrations. The distribution of uranium isotopes in the same system is given by (following [28]):

$$\left[\left(\frac{^{234}\mathrm{U}}{^{238}\mathrm{U}}\right)_{\mathrm{ACT}}\right]_{\text{system}} = \left\{\left[\left(\frac{^{234}\mathrm{U}}{^{238}\mathrm{U}}\right)_{\mathrm{ACT}}\right]_{\mathrm{f}}(C^{\mathrm{U}}_{\mathrm{f}})(F) + \left[\left(\frac{^{234}\mathrm{U}}{^{238}\mathrm{U}}\right)_{\mathrm{ACT}}\right]_{\mathrm{s}}(C^{\mathrm{U}}_{\mathrm{s}})(1 - F)\right\}\Big/C^{\mathrm{U}}_{\text{system}} \qquad (2)$$

The rock : water mass ratio is given by R/W = $(1 - F)/F$, and the molar ratio, $(\mathrm{R/W})_{\mathrm{m}}$, is given by $[(1 - F)FW_{\mathrm{f}}]/[F(FW_{\mathrm{s}})]$, where FW denotes formula weight. Through progressive changes in the amount of calcite introduced into the system and dissolved, the simultaneous chemical and isotopic evolution of a groundwater may be calculated. This modeling assumes that the time scale of the interaction process is significantly shorter than $1/\lambda_{234}$ (i.e., $\ll$ 350 kyr).

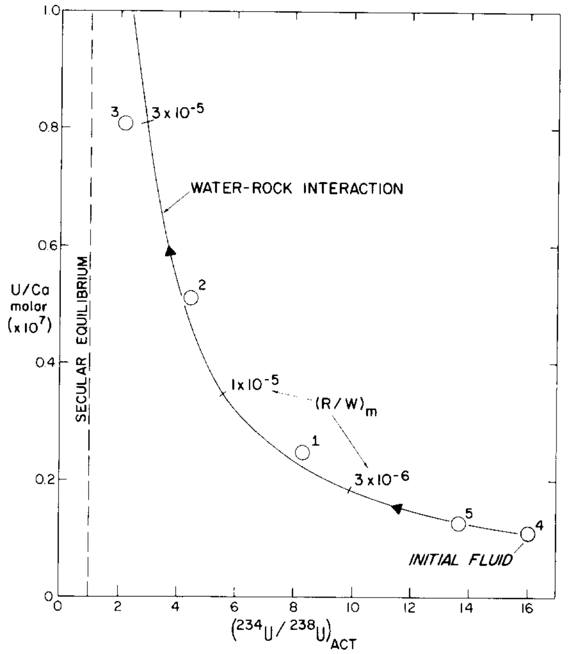

Fig. 4. Curve illustrates results of model calculations simulating evolution of groundwater compositions during progressive dissolution of calcite in aquifer. Compare model curve with central Missouri groundwater data (numbered open circles, as in Fig. 3). Initial compositions of end members used in model are: $(^{234}\mathrm{U}/^{238}\mathrm{U})_{\mathrm{ACT}} = 1.0$, U = 3 ppm for limestone; $(^{234}\mathrm{U}/^{238}\mathrm{U})_{\mathrm{ACT}}$, U and Ca data for groundwater from locality 4. Arrows indicate direction of changing groundwater compositions from initial fluid value with increasing rock : water ratio, $(\mathrm{R/W})_{\mathrm{m}}$. Method of curve calculation discussed in text.

Figure 4 illustrates the results of such a model calculation using a saline groundwater with high $(^{234}\mathrm{U}/^{238}\mathrm{U})_{\mathrm{ACT}}$ and a low U/Ca ratio (locality 4), and a Mississippian limestone of the Burlington–Keokuk Fm. During the progressive dissolution of calcite, as monitored by the increasing rock : water ratio, the groundwater evolves toward higher U/Ca ratios and lower $(^{234}\mathrm{U}/^{238}\mathrm{U})_{\mathrm{ACT}}$. Similar results are obtained using a dolomite dissolution model. The disparity in the U and Ca concentrations and U/Ca and $(^{234}\mathrm{U}/^{238}\mathrm{U})_{\mathrm{ACT}}$ values between the fluid and solid phases in this system governs the shape of the calculated water–rock interaction pathway shown in Fig. 4. As a consequence, this model curve is relatively independent of the reaction mechanism used. For example, if chemical and isotopic exchange are calculated using repeated dissolution–recrystallization steps in an open system model (as in [9,28]), a nearly identical curve to that shown in Fig. 4 for the closed-system process is produced.

Excellent agreement is found between the model curve and the groundwater data, suggesting that reactions with carbonate phases in the aquifer are important processes in controlling $^{234}\mathrm{U}$-$^{238}\mathrm{U}$ variations in this suite of waters. The molar rock : water ratios required (10^{-6} to 10^{-5}) to give the spectrum of groundwater U isotopic compositions shown in Fig. 4 represent the dissolution of 0.005 to 0.2 g of $\mathrm{CaCO_3}$ per liter of fluid. These rock : water ratios are significantly lower than those required to reset $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ or $\delta^{18}\mathrm{O}$ values in

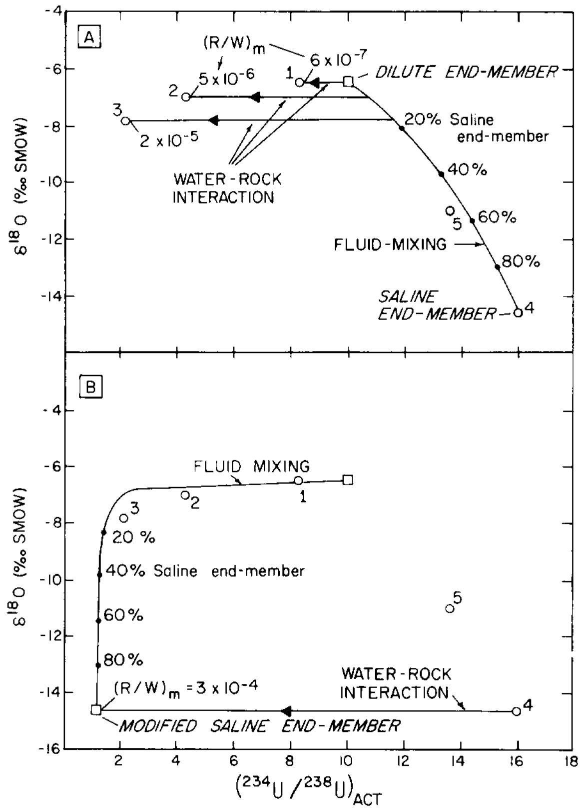

Fig. 5. $\delta^{18}O$ vs. $(^{234}U/^{238}U)_{ACT}$ variations in central Missouri groundwaters (numbered open circles, as in Fig. 3), and model calculations simulating evolution of groundwater compositions during mixing of two end-member fluids and water–rock interaction (via calcite dissolution). Estimation of end-member water compositions (open squares) discussed in text. Numbers on tick marks on water–rock interaction pathways indicate rock : water ratio, as in Fig. 4. Numbers on fluid-mixing lines indicate percentages of saline end-member fluid in saline-dilute fluid mixtures. (A) Model calculations for saline-dilute mixing followed by water–rock interaction. Mixtures in the range of 0–20% saline end member produce moderately saline groundwaters with low $\delta^{18}O$ values and high $(^{234}U/^{238}U)_{ACT}$. Specific mixture compositions then dissolve calcite to produce low $(^{234}U/^{238}U)_{ACT}$ with unchanged $\delta^{18}O$ at low $(R/W)_m$ values. (B) Model calculations for water–rock interaction between calcite and the saline end member (locality 4), followed by fluid mixing. Calcite dissolution produces a modified saline end member with low $(^{234}U/^{238}U)_{ACT}$ and high U/Ca (see Fig. 4). This modified saline water then mixes with the dilute end member to produce moderately saline groundwaters with high $\delta^{18}O$ values and low $(^{234}U/^{238}U)_{ACT}$.

the waters by the same process, as shown in Fig. 5 and discussed in [9]. The gross Sr and O isotopic differences between the groundwaters and the carbonates would be maintained at such low rock : water ratios, and these isotopic differences are therefore consistent with the model presented.

Based on these results and those of earlier studies on these groundwaters [8,9], both fluid mixing (with major effects on most geochemical parameters) and water–rock interaction (with minor or negligible effects on most parameters except U) may be operable in this aquifer system in central Missouri. The effect of each process is difficult to discern on the U/Ca-$(^{234}U/^{238}U)_{ACT}$ diagram, as fluid mixing between appropriate saline and dilute end members will define a similar curve to that shown for water–rock interaction in Fig. 4. Figure 5 portrays the combined effects of water–rock interaction and fluid mixing on the $(^{234}U/^{238}U)_{ACT}$ and $\delta^{18}O$ values of the groundwaters. Two end-member hypotheses that can account for the range of U and O isotopic compositions are illustrated: (a) saline-dilute fluid mixing precedes water–rock interaction between the mixed fluids and the Mississippian limestone, and (b) water–rock interaction between the saline end member and Mississippian limestone precedes mixing between a dilute end member and the modified (by calcite dissolution) saline end-member fluid. The dilute end-member composition of $(^{234}U/^{238}U)_{ACT} = 10$, U = 40 pg/g, $\delta^{18}O = -6.5‰$ and 336 μg/g Ca, is estimated by extrapolation from the trend given by the dilute sample group (localities 1–3) in Fig. 3, A and B from this study and in fig. 5 from [9]. The high $(^{234}U/^{238}U)_{ACT}$ of both fluid end members are indicative of water–rock interaction vs. fluid mixing as a mechanism to achieve low $(^{234}U/^{238}U)_{ACT}$ and high U/Ca ratios in the water samples of intermediate salinity (localities 2 and 3). While interactions with minor non-carbonate phases in the aquifer may also produce low $(^{234}U/^{238}U)_{ACT}$ values in the groundwaters, these phases are less likely to provide the requisite narrow range of either U concentrations or U/Ca values in the solid end member.

If water–rock interaction precedes fluid mixing in this system [model (B)], one would expect to find saline fluids with $(^{234}U/^{238}U)_{ACT}$ near unity. Relevant to model (A), mixing of two end-member fluids (each saturated or supersaturated with respect to calcite) with different ionic strengths can produce mixture compositions that are calcite undersaturated [29,30]. Such a scenario would be consistent with the model presented in Fig. 6A, wherein saline-dilute mixing produces mixed fluids with a capacity for carbonate dissolution. In order to test this hypothesis, the chemical equilibrium model PHREEQE [31] was used to determine the saturation states of calcite and dolomite in calculated mixtures of saline and dilute end-member water samples from central Missouri [8,9]. While the end-member waters are approximately saturated with respect to calcite and dolomite [9], modeled mixture compositions have saturation indices (= log[ion activity product/equilibrium constant]) for calcite and dolomite that are equal to or greater than the end-member indices. The mixed fluids of intermediate salinity therefore would not have an enhanced capacity for carbonate dissolution, such that the mixing process is apparently not the driving mechanism for water–rock interaction in this system. It is concluded that models involving both fluid mixing and limited extents of water–rock interaction can quantitatively account for the ^{234}U-^{238}U-Ca systematics and many other geochemical features of the central Missouri groundwaters. However, the specific mechanism and timing of water–rock interaction are unclear and are probably governed by minor fluctuations in P_{CO_2}, Eh, pH and temperature during the migration history of the waters.

The $(R/W)_m$ values determined in this model are similar to or greater than those required to reset ^{143}Nd/^{144}Nd and ^{147}Sm/^{144}Nd values in the same waters [9]. The generally lower ^{143}Nd/^{144}Nd and markedly lower ^{147}Sm/^{144}Nd in the groundwaters compared with the carbonates may reflect preferential control on dissolved rare earth elements by minor silicate minerals in the aquifer. Additional uncertainties for water–rock interaction models result from the narrow range of Nd isotopic variations in this system, which is only slightly larger than the analytical precision. In contrast, the pronounced fractionation of ^{234}U-^{238}U between the central Missouri groundwaters and constituent minerals in the aquifer makes this isotopic system a potentially sensitive indicator of small but significant extents of water–rock interaction. The recognition of the operation of such processes compromises the use of U series disequilibrium for estimating groundwater ages, because such dating schemes typically require reducing aquifer systems in which large changes in groundwater $(^{234}U/^{238}U)_{ACT}$ values result only from the *in situ* decay of dissolved ^{234}U on a time scale of 10^4 to 10^6 years (e.g., [27]).

5.2. ^{230}*Th*-^{232}*Th distributions*

Both unfiltered and filtered aliquots of central Missouri groundwaters have much higher ^{232}Th/^{238}U ratios (1.4×10^{-3} to 0.33) than seawater (2.9×10^{-5} to 4.6×10^{-5}, Table 4). These results probably are due to both the stabilization of the uranyl ion in oxidizing marine waters, which leads to higher dissolved ^{238}U concentrations, and the stabilization of Fe-Mn hydroxides in oxidizing marine waters, which leads to the efficient scavenging of ^{232}Th. The ^{232}Th/^{238}U ratios of the groundwaters are orders of magnitude lower than a representative crustal, or detrital, value of 3.8 [32]. If such a crustal source provided the Th and U for the groundwaters, then the low Th/U ratios in the waters must reflect the low solubility (and high association with particulates) of Th relative to U in aqueous systems.

The filtration results for the central Missouri groundwaters may be used to estimate ^{234}U-^{238}U-^{230}Th-^{232}Th distributions in the particulate phase of the water samples. For locality 4, the results show that essentially none of the U is on particulates (Tables 4, 5). For locality 5, if we assume that the 0.4 μm filtrate represents the bulk sample and the 0.1 μm filtrate represents the dissolved phase, then differences in isotope abundances between bulk and dissolved phases represent U and Th isotope abundances on the particulates. Using the two 0.1 μm filtrate replicates and the 0.4 μm filtrate gives calculated ^{232}Th/^{238}U ratios of 4.2 and 3.3, and near-equilibrium values of $(^{234}U/^{238}U)_{ACT}$ and $(^{230}Th/^{234}U)_{ACT}$, for the particulate phase at locality 5. The similarity of these values to typical crustal values may be indicative of the transport of detrital Th and U on particulates in these waters.

The ^{232}Th concentrations of bulk and filtered central Missouri groundwater samples are 1–3 orders of magnitude higher than the calculated solubility of 0.01 pg/g for thorianite (ThO_2) in pure water [5,33]. The absence of a correlation between ^{232}Th concentration and any major dissolved species in the central Missouri groundwaters suggests that mechanisms other than inorganic complexing (see [33]) are operative. The filtration results of this study demonstrate the predominant association of Th with particulates in the waters, and it is likely that sorption processes control dissolved Th levels.

The major inputs of ^{230}Th into solution are (1) desorption from particulates, mineral dissolution or α-recoil, and (2) the *in situ* decay of dissolved ^{234}U. Adsorption on the surfaces of aquifer minerals and suspended particulates and radioactive decay are the principal removal processes. The particulate Th/U ratios estimated above suggest a predominantly non-carbonate source of particulate U and Th. We estimate the ^{230}Th/^{232}Th ratio of Th that is injected by sorption processes into the aquifer by assuming a particulate ^{232}Th/^{238}U of 3.8. At secular equilibrium, the ^{230}Th/^{232}Th ratio in this source, $(^{230}\text{Th}/^{232}\text{Th})_c$, can be expressed as:

$$(^{230}\text{Th}/^{232}\text{Th})_c = \left(\frac{^{238}\text{U}}{^{232}\text{Th}}\right)_c \times \left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right)_c$$

$$= \frac{1}{3.8} \times \frac{\lambda_{238}}{\lambda_{230}} = 0.44 \times 10^{-5} \quad (3)$$

^{230}Th/^{232}Th ratios for bulk and filtered central Missouri groundwaters range from 0.80×10^{-5} to 9.6×10^{-5} (Table 5), which are significantly in excess of the calculated crustal value determined by eqn. (3). Thus, the majority of ^{230}Th in the groundwaters may be derived from the *in situ* decay of dissolved ^{234}U. We estimate a correction for the input of particulate ^{230}Th by using the measured ^{232}Th concentration in each sample, and the $(^{230}\text{Th}/^{232}\text{Th})_c$ value from eqn. (3) to determine $^{230}\text{Th}_c$. Subtracting this calculated $^{230}\text{Th}_c$ from the measured ^{230}Th concentration for each water sample gives a corrected ^{230}Th concentration, which is used to calculate a corrected $(^{230}\text{Th}/^{234}\text{U})_{\text{ACT}}$ value, expressed as $(^{230}\text{Th}/^{234}\text{U})^*_{\text{ACT}}$ in Table 5.

For the case of a closed system in the age range of much less than 3×10^4 yr and having no initial ^{230}Th, the solution to the ^{238}U-series radioactive production and decay equations can be closely approximated by (see [34]):

$$(^{230}\text{Th}/^{234}\text{U})_{\text{ACT}} = 1 - e^{-\lambda_{230}T} \quad (4)$$

Assuming that the $^{230}\text{Th}_c$ concentrations in the water samples have resulted from the ingrowth from dissolved ^{234}U, the $(^{230}\text{Th}/^{234}\text{U})^*_{\text{ACT}}$ value for each sample gives the time required for this ingrowth by eqn. (4). The results of these calculations are given in Table 5 as model ages, which range from 30–600 yr for samples from localities 4 and 5.

These model ages may represent the time scale of the removal of ^{230}Th from solution by adsorption and precipitation. This scavenging process by which Th is removed from solution onto particulates or mineral surfaces may be episodic or continuous, and it may vary in its efficiency. As such, the model ^{230}Th ages represent the time of the most recent major adsorption event in a simple episodic removal model. For a model involving a steady-state balance between supply and removal of ^{230}Th in solution, the model age range of 30–600 yr for the central Missouri groundwaters can be taken as the mean residence time of ^{230}Th in solution in this aquifer. For deep-sea environments, residence times of 20–40 yr are determined from water column profiles of ^{230}Th [24]. Much shorter residence times of minutes or less are estimated from ^{234}Th measurements on Connecticut groundwaters [4]. Both of these studies concluded that desorption of thorium from particulate surfaces must play a significant role in governing dissolved thorium isotopic abundances. On the other hand, Short et al. [5], in a U-Th isotope study of groundwaters and particulates in an aquifer near a uranium ore body, suggest that Th adsorption is not reversible. If the model ^{230}Th ages are representative of the time of Th adsorption in the aquifer, then the relatively high ^{232}Th levels in some of the groundwaters must result from more recent desorption processes (<30 years).

Significant uncertainties are associated with the application of the above models of Th isotope behavior in the central Missouri groundwater system. These include the uncertainties involved in determining: (1) the extent to which steady-state conditions exist; (2) the potential association of Th with particulates of less than 0.1 μm diameter; (3) the timing of α-recoil injection of ^{234}U into solution relative to the injection or removal of ^{230}Th by sorption processes; and (4) contributions to the ^{230}Th budget from carbonate aquifer minerals by α-recoil or dissolution. Clearly, future studies involving experiments and theoretical modeling of solid–fluid actinide exchange, and studies involving other daughter actinides and ultrafiltration techniques in the central Missouri waters, will further constrain the role of particulates and the time scales of radionuclide sorption processes in this aquifer.

In the case of the central Missouri groundwaters, it is possible that these sorption processes have a direct relation to the dissolution, recrystallization and fluid-mixing processes that were implicated above to account for the $^{234}U/^{238}U$-U/Ca systematics in the waters. The mixing of particulates between two water masses, the release of particulates to solution during calcite dissolution, and the formation of new surfaces during calcite precipitation may all serve to create new adsorption sites for Th. If the same mechanisms govern both U and Th distributions in an aquifer, then unique information concerning the time scales of mineral-solution equilibria and fluid mixing may be obtained from U-series disequilibrium measurements on groundwaters in that aquifer. As an example, if we consider the range of model ^{230}Th ages for the two central Missouri groundwater localities as representative of the other three localities, then the model ages may constrain the timing of these water–rock exchange and/or fluid-mixing processes in this system to the range of < 600 years. This potential interrelationship between radionuclide sorption and mineral-solution equilibria can be best examined by U-Th isotope studies in aquifers in which (1) water–rock interaction or fluid mixing has been recently active ($T < 350$ kyr), and (2) both pore fluids and recent mineral precipitates are accessible.

6. Conclusions

Groundwaters from central Missouri have a wide range in salinity (4.7–26‰), ^{238}U concentrations (50–200 pg/g), $^{234}U/^{238}U$ activity ratios (2.15–16.0), ^{232}Th concentrations (0.10–33 pg/g) and $^{230}Th/^{232}Th$ ratios (0.80×10^{-5} to 9.6×10^{-5}). Precise isotopic measurements are made on small volume samples of 0.1–4 l, and on-site filtration and chemical processing is accomplished with minimal contamination. The handling and analytical techniques can be extended to ml-size samples for ^{234}U-^{238}U studies of pore fluids. The filtration results demonstrate the predominant occurrence of ^{234}U and ^{238}U as dissolved species, ^{230}Th being mostly in solution, and the association of ^{232}Th with particulates in the groundwaters.

The groundwaters have a wide range of correlated stable isotope compositions, indicating that mixing occurs between two end-member meteoric waters with distinctly different salinities, origins and flow paths. The low U/Ca ratios and high $^{234}U/^{238}U$ activity ratios of the end-member waters likely reflect the effects of α-recoil processes within a reduced aquifer. Correlations between U/Ca and $^{234}U/^{238}U$ and between other geochemical parameters in the suite of water samples can be accounted for by a quantitative model of isotopic and elemental exchange that simulates (1) saline-dilute fluid mixing, and (2) limited extents of interaction between carbonate minerals in the aquifer and the groundwaters. The pronounced U isotopic differences between the groundwaters and their aquifer minerals make this isotopic system a potentially sensitive indicator of water–rock interaction processes. The operation of such processes, even at limited degrees, has significant implications for the use of U-series disequilibria for dating groundwaters and for predicting the mobility of actinide elements in the shallow subsurface.

The filtration results are used to estimate the concentration of ^{230}Th that would be supplied to solution from particulates via desorption or dissolution. Measured ^{230}Th concentrations in the waters are in excess of these estimated concentrations, and two to three orders of magnitude below activity levels for ^{230}Th-^{234}U equilibrium in the waters. A model involving the balance of ^{230}Th in solution through the additional supply from the *in situ* decay of ^{234}U in the waters and removal by episodic adsorption indicates a time scale of 10–10^3 years for these processes.

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