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Radium geochemistry of ground waters in Paleozoic carbonate aquifers, midcontinent, USA[†]

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Abstract

The purpose of this study was to elucidate the processes controlling the distribution and behavior of the longer-lived Ra isotopes in continuous Paleozoic carbonate aquifers of parts of Missouri, Kansas, and Oklahoma. Activities of (²²⁸Ra) and (²²⁶Ra) were analyzed in fresh and saline ground waters, brines, and rocks. The fluids have a wide salinity range (200–250,000 mg l⁻¹ total dissolved solids). The (²²⁶Ra) activity ranges from 0.66–7660 dpm kg⁻¹ and correlates with salinity and other alkaline earth element (Ca, Sr, and Ba) concentrations. The range of (²²⁸Ra:²²⁶Ra) ratios in the fluids (0.06–1.48) is similar to that in the aquifer rocks (0.21–1.53). The relatively low mean fluid (²²⁸Ra:²²⁶Ra) ratio (0.30) reflects the low Th:U ratio of the predominant carbonate aquifer rock. Radium occurs mostly (≥77%) as Ra²⁺ species in the fluids. Salinity-dependent sorption–desorption processes (with log K values from 10⁰–10⁴ and negatively correlated with salinity), involving Th-enriched surface coatings on aquifer flow channels, can explain the rapid solid–fluid transfer of Ra isotopes in the system and the correlation of Ra with salinity. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

The distribution and behavior of Ra isotopes in ground water are subjects of both practical and scientific importance. The practical importance stems from the human health risks associated with both the ingestion of Ra (NAS/NRC, 1988) and the inhalation of

Rn and its daughter products (NAS/NRC, 1988, 1998). These risks have prompted recommendations concerning the maximum Ra activity in public water supplies [total (²²⁶Ra) plus (²²⁸Ra) not to exceed 5 pCi l⁻¹ = 11.1 dpm l⁻¹] and the maximum Rn activity in household air (USEPA, 1991). The scientific importance derives largely from the potential applications of Ra isotopes in tracing the mechanisms and rates of water–rock interaction and element transport in aquifers (Dickson, 1990; Ivanovich et al., 1992; Ku et al., 1992). The information from such scientific studies can lead to an improved understanding of the factors controlling water quality and can be useful in establishing better strategies for the use and protection of underground water resources.

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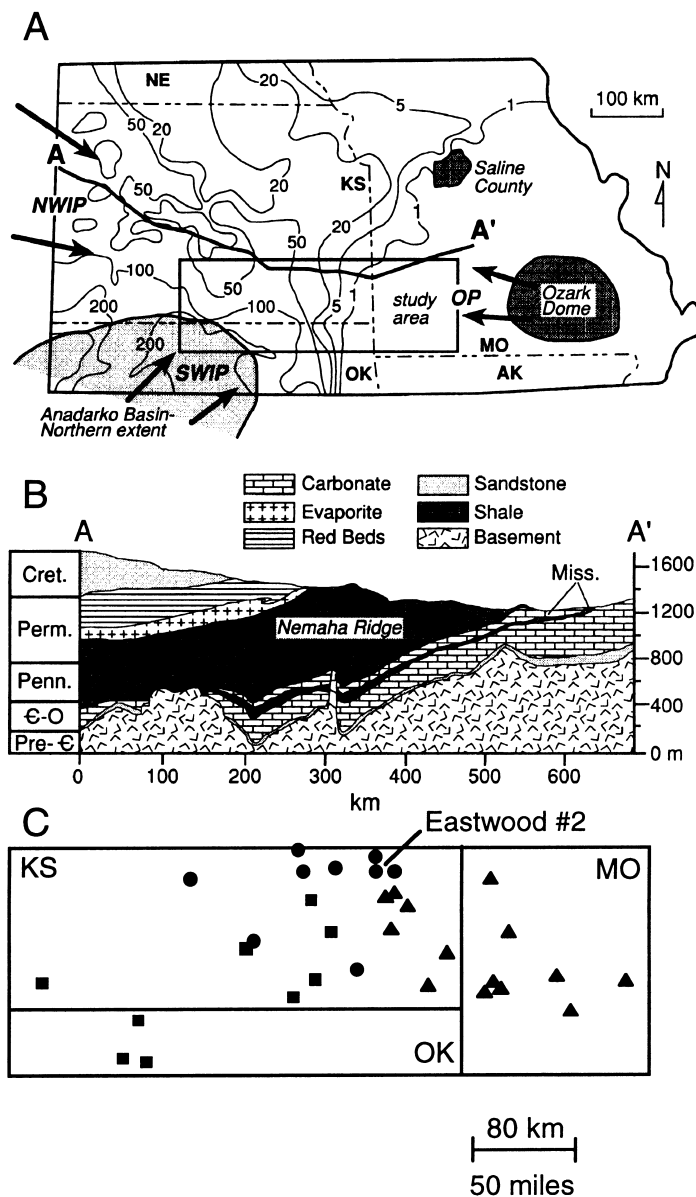


Fig. 1. (A) Map showing location of study area in southwestern Missouri, southeastern Kansas, and northeastern Oklahoma (also shown is area in Saline County, Missouri, from which four samples are included in this study). Contours of regional distribution of ground water salinities in Cambrian-Ordovician rocks expressed in g l^{-1} of total dissolved solids. Prevailing flow directions of regional ground water in the northern western interior plains aquifer (NWIP), the southern western interior plains aquifer (SWIP), and the Ozark Plateaus aquifer (OP) shown by arrows. (B) West-east geologic cross-section showing schematic stratigraphy. (C) Enlargement of study area from Fig. 1(A) showing fluid sampling localities [symbols based on geographic-geochemical correlations of Musgrove and Banner (1993) as summarized in Table 1: triangles, group 1; circles, group 2; squares, group 3]. This figure is adapted from Musgrove and Banner (1993).

Ground water from aquifers in Paleozoic sedimentary rock formations is a primary source for municipal, industrial, and agricultural water supplies throughout the midcontinent region of North America. In some areas, oil and gas are produced from these formations along with saline waters and brines. The activities of Ra isotopes in these ground waters are of considerable interest from a public health viewpoint, because of the risks associated with both their use and their disposal. High Ra activities occur in ground waters from lower Paleozoic aquifers of northern Illinois, Iowa, and eastern Wisconsin (Gilkeson et al., 1983; Lucas, 1985; Siegel, 1989) and in the Tri-State area of southeastern Kansas, southwestern Missouri, and northeastern Oklahoma (Bloch and Craig, 1981; Cowart, 1981; Macfarlane and Hathaway, 1987).

The authors measured the activities of (^{226}Ra) and (^{228}Ra) of representative ground waters, brines, and rock cores during a comprehensive chemical and isotopic study of a regional ground water mixing zone in southeastern Kansas, western Missouri, and northern Oklahoma (Banner et al., 1989, 1990; Musgrove, 1993; Musgrove and Banner, 1993) (Fig. 1(A)). Here these Ra isotope data are compared with other chemical and isotopic data for the same fluid samples (from Banner et al., 1989, 1990; Musgrove, 1993; Musgrove and Banner, 1993). Previous studies of this ground water system have (1) described the extreme range in chemical compositions of the waters, in contrast to the relatively narrow range in aquifer rock compositions, (2) documented the systematic correspondence between ground water composition and geographic location, and (3) modeled the geochemical evolution processes of the fluids including the dominant role played by regional scale mixing of three endmember fluid compositions. Thus, this data set for Ra isotopes provides an excellent opportunity to elucidate the processes controlling their behavior in this regional ground water system.

1.1. Radium geochemistry in rock–water systems

Two Ra isotopes were measured: ^{226}Ra ($t_{1/2} = 1.6 \times 10^3$ a), the daughter of ^{230}Th ($t_{1/2} = 7.52 \times 10^4$ a) in the ^{238}U decay series, and ^{228}Ra ($t_{1/2} = 5.75$ a), the daughter of ^{232}Th ($t_{1/2} = 1.39 \times 10^{10}$ a). Both of these Ra isotopes are produced by alpha decay. The shorter-lived isotopes, ^{223}Ra ($t_{1/2} = 11.68$ d) and ^{224}Ra ($t_{1/2} = 3.64$ d) were not measured, because of practical considerations and because the authors were mainly interested in elucidating processes important on longer time scales. The ratio of ^{228}Ra : ^{226}Ra in ground water is related to the Th:U concentration ratio in the aquifer rock and is a sensitive indicator of aquifer characteristics and water–rock interactions (Ku et al., 1992). Radium isotopes do not exhibit significant mass-dependent isotopic fractionation but can be geo-

chemically separated because of their widely varying half-lives. A close chemical analog for Ra is Ba (Langmuir and Riese, 1985).

Radium may enter ground water by a number of processes including decay of dissolved parent isotopes, alpha-recoil, desorption from aquifer surfaces, dissolution of aquifer solids, ion exchange, and leaching from radiation-damaged crystals (Dickson, 1990; Krishnaswami et al., 1982; Ku et al., 1992). Input from decay of dissolved parent isotopes is generally negligible for Ra because Th isotopes are nearly insoluble in ground water (Langmuir and Herman, 1980), but Ra input from Th decay on aquifer surface coatings can be significant (Davidson and Dickson, 1986; Krishnaswami et al., 1982). Input of Ra into pore fluid by alpha-recoil depends on the activity and location of the parent isotope relative to the solid–fluid interface. The range of a recoiled nucleus is in the order of 0.02–0.05 μm within most mineral lattices (Fleischer et al., 1975), thus Ra atoms may be ejected from solids into pore fluids where parent Th atoms are located within 0.02–0.05 μm of mineral–fluid interfaces. In addition, recoil-induced lattice damage may enhance the leaching of Ra from solid phases (Fleischer, 1980). Radium can be removed from solution by radioactive decay, adsorption or ion exchange, complexation with other adsorbed species, and coprecipitation in minerals that include Ra as a trace constituent.

2. Hydrogeologic setting and ground water geochemistry

The fluids analyzed for this study were sampled from regionally extensive Paleozoic carbonate rocks of the Ozark Plateaus and Western Interior Plains aquifer systems in Missouri, Kansas, and Oklahoma (Signor and Imes, 1989) (Fig. 1(A)). Ground water in southern Missouri flows outward from the Ozark Dome through the Ozark Plateaus aquifer system; the resulting flow is westward in southwestern Missouri into southeastern Kansas (Imes and Emmett, 1994). Ground water in Kansas flows to the southeast and east through the Western Interior Plains aquifer system (Jorgensen et al., 1989). Discharge occurs through natural springs in Cambrian-Ordovician and Mississippian carbonate rocks in central and southern Missouri, and to the Missouri and Mississippi Rivers (Signor and Imes, 1989). In the southern part of the Western Interior Plains system, fluid flow is to the northeast and may originate from the Anadarko Basin (Jorgensen et al., 1989; Larson, 1971). These 3 regional flow components converge in the study area (Fig. 1(A)). The principal aquifers are within Cambrian-Ordovician and Mississippian stratigraphic units including mainly marine carbonates and minor interbedded sandstones and siltstones (Fig. 1(B)). Regional hydraulic gradients are

similar for both stratigraphic units, and the two units are hydraulically connected (Carr et al., 1986; Macfarlane and Hathaway, 1987). Thus, they are considered here as one regional hydrostratigraphic unit. Porosity and permeability vary considerably within the carbonate aquifer rocks because of the abundance of spatially heterogeneous solution channels and fractures.

The subsurface fluids in the study area have a wide range in chemical and isotopic compositions (Banner et al., 1989, 1990; Macfarlane and Hathaway, 1987; Musgrove and Banner, 1993). Salinity ranges from 200–250,000 mg l⁻¹ total dissolved solids (TDS); δD and $\delta^{18}O$ values range from -108 to -5‰ and -14.6 to +2.8‰, respectively (Table 1). Temperature ranges from 15.3 to 51.6°C, and field pH ranges from 5.84 to 8.05. Three compositional groups have been identified for these fluids (Table 1), and their geographic distribution corresponds closely with the geochemical and hydrogeologic constraints (Banner et al., 1989; Musgrove, 1993; Musgrove and Banner, 1993). These results indicate the fundamental control that fluid mixing processes have on the chemical evolution of ground water in this regional flow system. Compositions of fluid mixing endmembers were identified by Musgrove and Banner (1993). Endmember 1 is Ca-Mg-HCO₃ type water that occurs in southwestern Missouri. It has low salinity (200–800 mg l⁻¹ TDS), and δD and $\delta^{18}O$ values that reflect local meteoric recharge water of the Ozark Plateaus aquifer system. Endmember 2 is saline Na-Ca-Cl type water that occurs in southeastern Kansas. It has salinity in the range of 22,000–35,000 mg l⁻¹ TDS, δD values of -108 to -98‰, and $\delta^{18}O$ values of -14.6 to -12.4‰. These low δD and $\delta^{18}O$ values are close to those of modern meteoric precipitation in the Front Range of Colorado (Banner et al., 1989). The salinity of endmember 2 water is thought to have been acquired primarily by subsurface dissolution of Permian evaporites in central Kansas (Banner et al., 1989; Chauduri et al., 1987). Endmember 3 is Na-Ca-Cl type brine that occurs in northern Oklahoma. It has salinities of 230,000–250,000 mg l⁻¹ TDS and δD and $\delta^{18}O$ values close to modern seawater. Values of ⁸⁷Sr:⁸⁶Sr for this brine range from 0.7091–0.7099, which overlap and exceed the estimated range in ⁸⁷Sr:⁸⁶Sr ratios for both Paleozoic seawater (Burke et

al., 1982) and Paleozoic carbonate rocks in the mid-continent (Banner et al., 1988; Chauduri et al., 1987). Endmember 3 brine may have been derived from the modification of evaporated Paleozoic seawater (Musgrove and Banner, 1993).

3. Sampling and analytical methods

Of the 39 wells sampled by Musgrove (1993) and Musgrove and Banner (1993), 32 were sampled in this study and their locations are indicated in Fig. 1(C). Four of the five sites sampled by Banner et al. (1989) were also sampled in this study and are from within Saline County in central Missouri (Fig. 1(A)). Fluid samples for Ra isotope analysis (4–20 kg) were collected from pumped wells simultaneously with samples for other chemical and isotopic analyses (Musgrove, 1993; Musgrove and Banner, 1993), except for the 4 samples from saline springs and artesian wells in central Missouri (Banner et al., 1989). Samples were passed through 0.45 μm millipore-type cellulose acetate filters into acid-cleaned high-density polyethylene containers that had been pre-rinsed with the filtered sample fluid, and acidified to pH 2 immediately after collection. Some samples from municipal water supplies were not filtered. Comparison of filtered and unfiltered samples from many municipal water supplies in the midwestern US has shown negligible differences in their Ra isotope activities (Gilkeson et al., 1983; Lucas, 1985). The waters considered in this study (Table 2) showed no difference in Sr concentration or isotope ratio between filtered and unfiltered samples (Banner et al., 1989; Musgrove, 1993).

Samples having field conductivity values less than ~20,000 $\mu mhos/cm$ were processed within hours to days of collection to concentrate Ra on a Ra-selective resin prior to gamma spectrometry (Lucas and Markun, 1991; Sturchio et al., 1993). The resin was sealed into metal cans, then aged for at least one month prior to acquisition of gamma spectra. Samples having conductivity values greater than ~20,000 $\mu mhos/cm$ were sealed directly into metal cans that were filled (approximately 200 ml volume) and then aged for at least 1 month prior to gamma spectrometry. Comparison of

Table 1
Compositional characteristics of ground waters and brines^a

Group	TDS mg l ⁻¹	δD (‰)	(²²⁶ Ra) dpm kg ⁻¹	(²²⁸ Ra/ ²²⁶ Ra)
1	200–14,100	-44 to -36	0.7–186	0.12–0.74
2	6300–63,200	-108 to -50	113–1520	0.08–0.80
3	62,300–250,000	-58 to -5	431–7660	0.057–1.48

^a Data for TDS and δD from Musgrove and Banner (1993); data for (²²⁶Ra) and (²²⁸Ra/²²⁶Ra) from this study.

Table 2
Compositional data for ground waters and brines^a

Sample	Date ^b	Group/type ^c	TDS (mg l ⁻¹)	Ca (mg l ⁻¹)	Sr (mg l ⁻¹)	Ba (mg l ⁻¹)	(²²⁶ Ra) dpm kg ⁻¹	(²²⁸ Ra/ ²²⁶ Ra)
Southwestern Missouri								
Lamar	910623	1/MWS	294	32	0.16	0.29	4.0 ± 0.4	0.22 ± 0.05
Webb City #7	891104	1/MWS	372	59	0.09	0.14	2.4 ± 0.4	0.18 ± 0.17
Fairview #11	910621	1/MWS	286	38	0.09	0.14	2.2 ± 0.4	0.26 ± 0.06
Miller #2	910622	1/MWS	278	36	0.04	0.01	0.8 ± 0.4	0.12 ± 0.12
Carthage #7	910622	1/MWS	568	101	0.22	0.11	4.3 ± 0.4	0.74 ± 0.04
Carthage #11	910622	1/MWS	303	39	0.09	0.14	2.4 ± 0.4	0.32 ± 0.05
Aurora #4	910625	1/MWS	328	42	0.06	0.04	0.7 ± 0.4	0.43 ± 0.22
Nevada #4	910713	1/MWS	1320	75	2.03	0.08	11.9 ± 0.4	0.20 ± 0.02
Saline County, Missouri								
Sweet Spring	891105	1/AW	4680	333	7.89	0.04	69 ± 2	0.12 ± 0.02
McCallister	891105	1/NS	6300	306	9.81	0.50	94 ± 2	0.20 ± 0.01
Blue Lick	891105	2/NS	25,500	1330	40.4	0.04	380 ± 10 397 ± 13 ^d	0.31 ± 0.01
Boone's Lick	891105	2/AW	21,600	1120	36.4	0.03	322 ± 8 315 ± 8 ^d	0.095 ± 0.005
Southeastern Kansas								
Pittsburg #10	910620	1/MWS	609	63	0.88	0.18	5.8 ± 0.4	0.24 ± 0.03
Columbus #4	910626	1/MWS	666	48	1.37	0.12	10.5 ± 0.4	0.19 ± 0.02
Elmer	910627	1/OWS	2870	19	1.10	0.15	11.5 ± 0.4	0.27 ± 0.01
Campbell #2	910621	1/OWS	6720	110	5.14	0.71	59.4 ± 0.4	0.27 ± 0.01
Nelson	891104	1/OWS	3470	77	0.03	0.16	40.2 ± 1.0	0.26 ± 0.01
McCoy	910628	1/OWS	14,100	208	15.3	1.26	186 ± 1	0.32 ± 0.01
Althouse #1	910706	2/OP	22,200	1140	43.7	0.08	1060 ± 20	0.08 ± 0.02
Koenig #2A	910707	2/OP	26,300	794	54.7	3.25	258 ± 11	0.62 ± 0.10
Perkins #2	910704	2/OP	63,200	3400	86.8	0.18	1520 ± 20	0.14 ± 0.02
Fuller #15	910623	2/OP	45,300	1635	103	4.28	783 ± 14	0.22 ± 0.03
Kimbell #1	891103	2/OP	42,900	1721	83.0	2.17	1310 ± 30 1303 ± 39 ^d	0.11 ± 0.01
Eastwood #2	891102	2/OWS	18,400	444	30.4	2.05	208 ± 5 202 ± 5 ^d	0.80 ± 0.01
Minckley A	910627	2/OWS	13,300	262	15.3	2.93	179 ± 1	0.20 ± 0.01
Love 1W	910703	2/OWS	9400	173	9.41	0.65	113 ± 1	0.17 ± 0.01
Perry	910704	2/OWS	25,300	937	27.5	3.02	331 ± 12	0.21 ± 0.07
Hyde #18	910704	3/OP	137,000	8132	1050	1.76	728 ± 14	0.12 ± 0.04
Short	910711	3/OP	114,000	5400	197	0.88	431 ± 9	0.33 ± 0.04
Clubine	910629	3/OWS	68,800	2530	124	43.5	1743 ± 4	0.105 ± 0.003
Sheik	910701	3/GP	79,200	2940	163	32.0	1260 ± 20	0.14 ± 0.02
Peck	910701	3/OP	62,300	2280	136	45.3	590 ± 13	1.48 ± 0.06
Louk 1W	910703	3/OWS	72,900	2800	137	3.31	4190 ± 30	0.096 ± 0.007
Northern Oklahoma								
Jenkins #1	910709	3/OP	249,000	25,900	1510	6.04	2150 ± 20	0.22 ± 0.01
E. McCullough	910710	3/OP	229,000	16,100	813	35.0	474 ± 13	1.14 ± 0.06
Shoffner #1	910710	3/OP	138,000	8850	283	2.16	7660 ± 50	0.057 ± 0.004

^a Data for TDS, Ca, Sr, and Ba concentrations for southwestern MO, southeastern KS, and northern OK samples from Musgrove (1993), and for central Missouri samples from Banner et al. (1989).

^b Date format is yymmdd.

^c Groups 1,2 and 3 defined in Table 1; fluid sources: MWS=municipal water supply; OWS=oilfield water supply; OP=oil production well; GP=gas production well; AW=artesian well; NS=natural spring.

^d Replicate analysis by Rn emanation method (Lucas, 1977).

data for samples analyzed using both the Ra-selective resin and the direct-counting methods showed good agreement with samples analyzed using Rn emanometry (Lucas, 1977) (Table 2).

Gamma spectra were acquired at Argonne National Laboratory (ANL) using a high-efficiency coaxial HPGe detector shielded by a Hg-filled cylindrical stainless steel sleeve within an enclosure constructed of Pb bricks. Activities of (^{228}Ra) and (^{226}Ra) in samples were calculated and decay-corrected to time of sampling, following background subtraction, from measured activities of ^{228}Ac , ^{214}Pb and ^{214}Bi relative to those of a reference material counted in the same geometry. The reference material is Ra-selective resin containing about 1 nCi (= 2220 dpm) each of (^{226}Ra) and (^{228}Ra), calibrated against the activity of (^{226}Ra) in NBS-4951. The procedural blank, determined by processing 20 l of deionized water according to the sampling procedure, was below the detection limit of the counting method. The detection limit for (^{226}Ra) was 8.1 dpm and that for (^{228}Ra) was 12.8 dpm, based on 3 σ of background counts; for Ra extracted from a 20-l sample and counted for 24 h, 0.41 dpm kg^{-1} (^{226}Ra) and 0.64 dpm kg^{-1} (^{228}Ra) could be detected. Activities are reported in units of decays per minute (dpm) per unit mass; activities and activity ratios are denoted within parentheses.

Rock samples were taken from drill core obtained by the Kansas Geological Survey. This core was taken from a drill hole in Allen County near the location of the Eastwood #2 well (Fig. 1(C)). The interval of core sampled was 35 m in length and included typical car-

bonate (limestone and dolomite) and silicate (shale and siltstone) rocks within the uppermost portion of the Mississippian strata. The rock core slices were analyzed by sealing them into metal cans and determining their (^{228}Ra : ^{226}Ra) activity ratios by gamma spectrometry after several months. Portions of these drill core slices were pulverized, dissolved in HNO_3 and HF, and analyzed at ANL for Mg, Ca, Sr, and Ba concentrations by ICP-AES and for U concentrations by alpha spectrometry (Sturchio and Binz, 1988).

4. Results

Radium isotope data for fluids are given in Table 2, along with other data for these samples from Banner et al. (1989) and Musgrove (1993). The (^{226}Ra) activities range from 0.66–7,660 dpm kg^{-1} , and the (^{228}Ra : ^{226}Ra) values range from 0.057–1.48. Data for alkaline earth elements, U, (^{234}U : ^{238}U), and (^{228}Ra : ^{226}Ra) in drill core rock samples are given in Table 3. The (^{238}U) values range from 0.31–3.11 dpm g^{-1} . The (^{234}U : ^{238}U) values range from 0.93–1.11. The (^{228}Ra : ^{226}Ra) values range from 0.21–0.80 for carbonate rocks and 1.39–1.53 for shales.

4.1. Correlations between radium and other solutes

Correlations of (^{226}Ra) activities with salinity in ground waters and brines have been recognized previously (Cadigan and Felmlee, 1977; Chung, 1981; Dickson, 1990; Gascoyne, 1989; Gilkeson et al., 1983;

Table 3
Compositional data for aquifer rocks

Sample ^a	Ca ($\mu\text{g/g}$)	Mg ($\mu\text{g/g}$)	Sr ($\mu\text{g/g}$)	Ba ($\mu\text{g/g}$)	U ($\mu\text{g/g}$)	(^{234}U : ^{238}U)	(^{228}Ra : ^{226}Ra)
Shale							
830.7	1830	6740	87	295	2.63	1.02 ± 0.04	1.53 ± 0.05
846.8	4180	3800	78	359	1.54	1.11 ± 0.06	1.39 ± 0.05
Carbonate							
926.4	331,000	2110	284	4	0.55	1.07 ± 0.05	0.52 ± 0.07
927.6	397,000	2380	338	8	0.41	0.96 ± 0.09	0.33 ± 0.08
928.6	389,000	1810	330	6	0.60	0.93 ± 0.05	0.23 ± 0.06
929.6	379,000	1920	277	7	0.70	0.93 ± 0.05	0.48 ± 0.05
930.7	402,000	1780	255	6	0.41	1.11 ± 0.06	0.80 ± 0.10
931.7	137,000	80,200	104	6	4.17	0.97 ± 0.02	0.41 ± 0.02
932.5	153,000	72,600	106	23	2.45	0.94 ± 0.03	0.39 ± 0.03
933.5	175,000	88,000	119	43	2.93	1.02 ± 0.04	0.48 ± 0.03
934.6	145,000	78,400	106	9	2.48	1.11 ± 0.05	0.41 ± 0.03
935.6	371,000	1500	184	2	1.05	1.03 ± 0.05	0.26 ± 0.06
936.9	416,000	3150	221	6	1.50	0.99 ± 0.04	0.21 ± 0.02

^a Original depth of drill-core sample in feet below surface; samples are from uppermost Mississippian strata near the Eastwood #2 water supply well (Fig. 1(C)) in Allen County, KS.

Gutsalo, 1964; Kraemer and Reid, 1984; Krishnaswami et al., 1991; Mazor, 1962; Sutcliffe and Miller, 1981; Tanner, 1964; Tokarev and Shcherbakov, 1960). The observed correlation between the (^{226}Ra) activities in the fluid samples from the present study ($0.66\text{--}7660\text{ dpm kg}^{-1}$) and their total dissolved solids concentrations ($\text{TDS} = 278\text{--}249,000\text{ mg l}^{-1}$) is shown in Fig. 2. [Based on this correlation, ground water having $\text{TDS} \geq 1360\text{ mg l}^{-1}$ will have (^{226}Ra) exceeding the EPA limit of 11.1 dpm l^{-1} . If the ($^{228}\text{Ra}:$ ^{226}Ra) ratio is 0.5, then the TDS value corresponding to the EPA limit for combined (^{226}Ra) and (^{228}Ra) is 911 mg l^{-1}]. Also shown in Fig. 2 are previously reported data from the eastern portion of the study area from Macfarlane and Hathaway (1987); these data are consistent with the correlation defined by the present data. The activity of (^{226}Ra) correlates with Ca, Sr, and Ba concentrations in the fluid samples (Fig. 3). The correlations of (^{226}Ra) with Ca and Sr are somewhat better than that with Ba. Correlation of (^{226}Ra) with Ca was also noted in ground waters from within the Stripa granite (Andrews et al., 1989).

The concentrations of ^{230}Th and ^{232}Th have been measured in only two of these fluids, those from Blue Lick and Boone's Lick springs in Saline County, Missouri (Banner et al., 1990). The values of ($^{226}\text{Ra}/^{230}\text{Th}$) and ($^{228}\text{Ra}/^{232}\text{Th}$) in these fluids are in the range of $10^4\text{--}10^6$, based on the $<0.1\text{-}\mu\text{m}$ filtered fraction data

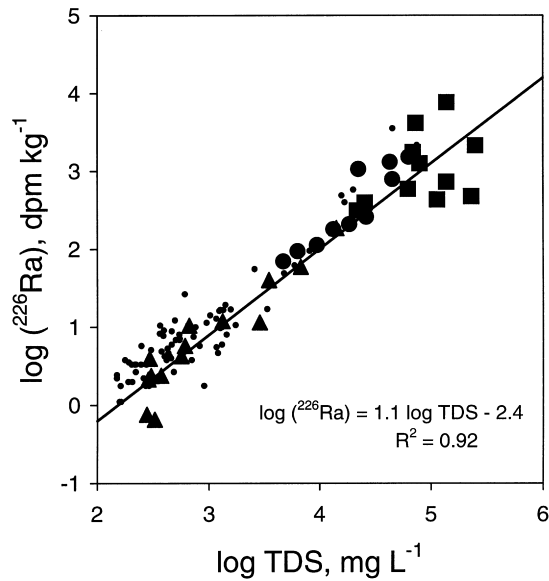


Fig. 2. Log (^{226}Ra) (dpm kg^{-1}) vs salinity (log TDS in mg l^{-1}) for ground water samples. Solid line shows positive correlation. Symbols represent ground water groups as in Fig. 1(C). Also shown (small filled circles), but not used to define the correlation line, are data from Macfarlane and Hathaway (1987).

of Banner et al. (1990) and the Ra isotope data from Table 2. Therefore, the (^{226}Ra) and (^{228}Ra) activities are essentially unsupported by dissolved Th parent isotopes. The concentrations of ^{234}U and ^{238}U have been measured in a larger number of fluid samples, mainly in the eastern portion of the study area (Cowart, 1981; Macfarlane and Hathaway, 1987) including Saline County, Missouri (Banner et al., 1990); reported values of U concentration range from 0.01 to 0.58 pg g^{-1} and those for ($^{234}\text{U}/^{238}\text{U}$) range from 1.5 to 16.0.

4.2. Relation of fluid radium isotope activities to aquifer rock composition

Rock samples and fluids have similar ranges of values of ($^{228}\text{Ra}/^{226}\text{Ra}$) (Tables 2 and 3). These values are consistent with the generally low Th:U ratios of marine carbonate rocks and with the high measured $^{230}\text{Th}:$ ^{232}Th ratios of the aquifer fluids (Banner et al., 1990). $^{230}\text{Th}:$ ^{232}Th atom ratios in the $<0.1\text{-}\mu\text{m}$ filtered fraction of central Missouri saline waters (Boone's Lick and Blue Lick springs) range from 0.8×10^{-5} to 9.6×10^{-5} (Banner et al., 1990). At secular equilibrium in the ^{232}Th - and ^{238}U -series, this range of Th isotope ratios would yield values of ($^{228}\text{Ra}:$ ^{226}Ra) ranging from 0.056–0.67; 89% of the measured fluid ($^{228}\text{Ra}:$ ^{226}Ra) values (all but the four samples having the highest values) are within this range (Table 2). If these measured $^{230}\text{Th}:$ ^{232}Th atom ratios are representative of adsorbed Th on aquifer surfaces, then this coincidence may imply a direct supply to fluid of ^{228}Ra and ^{226}Ra from aquifer surfaces by recoil and desorption without significant retardation of ^{228}Ra rela-

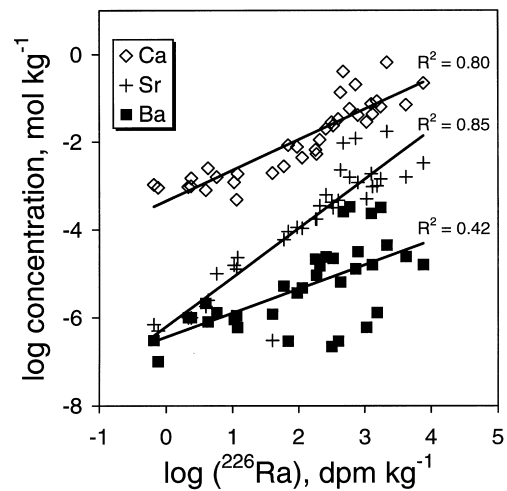


Fig. 3. Log Ca, Sr, and Ba (molar) vs log (^{226}Ra) (dpm kg^{-1}) for ground water samples, illustrating positive correlation among all elements.

tive to ^{226}Ra . The lowest fluid (^{228}Ra : ^{226}Ra) values are lower than those of the aquifer rocks, but this can be explained by the production of excess ^{226}Ra from the accumulation of excess adsorbed ^{230}Th on aquifer surfaces from the decay of the excess ^{234}U in solution.

4.3. Solubility and speciation of radium

In order to examine thermodynamic controls on Ra distribution, solubility and speciation calculations were performed. The calculations used comprehensive chemical analytical data and field parameters (T, pH) from Banner et al. (1989) and Musgrove (1993) along with the (^{226}Ra) data from this study. Solubility calculations were done using the computer programs PHREEQE (Parkhurst et al., 1980) and PHRQPITZ (Plummer et al., 1988). PHREEQE results were used for fluids having ionic strengths up to 0.1 M, and PHRQPITZ results were used for higher ionic strength fluids. The resulting saturation index values ($\text{SI} = \log \text{IAP}/K_T$) for calcite, barite, and gypsum are shown vs TDS in Fig. 4. Calcite and barite are near saturation in all samples having $\text{TDS} < 10,000 \text{ mg l}^{-1}$ ($\text{SI} = 0.0 \pm 0.5$). In samples having TDS greater than $10,000 \text{ mg l}^{-1}$, SI values for calcite and barite are also near saturation but show more scatter ($\text{SI} = 0.0 \pm 1.5$). High SI values for calcite may reflect partial CO_2 loss during

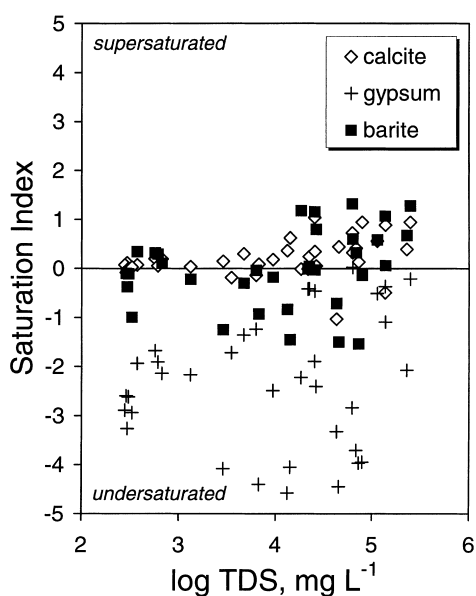


Fig. 4. Saturation index (SI) vs salinity ($\log \text{TDS}$ in mg l^{-1}) showing calcite, barite, and gypsum saturation states in ground water samples, calculated using PHREEQE (Parkhurst et al., 1980) and PHRQPITZ (Plummer et al., 1988). The fluids are generally near saturation with calcite and barite, whereas gypsum is generally undersaturated.

sampling of the deeper, warmer fluids. The large scatter in SI values for barite may reflect greater analytical uncertainty for Ba, as well as difficulty in calculating activity coefficients for high ionic strength solutions (Nordstrom and Munoz, 1986). Gypsum is significantly undersaturated in all samples, except several having high TDS values. RaSO_4 is undersaturated by 5 or more orders of magnitude, and RaCO_3 is undersaturated by 9 or more orders of magnitude.

Radium as a trace component in a mineral solid solution may control Ra activity in a coexisting fluid (Langmuir and Riese, 1985). For example, the saturation of sulfate minerals appears to control Ra activities in some deep brines from the Palo Duro Basin (Langmuir and Melchior, 1985). Similarly, Andrews et al. (1989) suggested that carbonate minerals control Ra activity in ground water circulating within the Stripa granite, on the basis of carbonate mineral saturations and the observed correlation between (^{226}Ra) and Ca. Implications of solid-solution formation for Ra behavior would depend on values for the mineral-fluid distribution coefficients of Ra. Taking the mean values of the Ra:Ca and Ra:Ba ratios of the fluids (Table 2) and rocks (Table 3), respectively, apparent distribution coefficients for Ra can be calculated relative to Ca and Ba as follows: $D_{\text{Ra}/\text{Ca}} = (\text{Ra}:\text{Ca})_{\text{rock}} / (\text{Ra}:\text{Ca})_{\text{fluid}}$ and $D_{\text{Ra}/\text{Ba}} = (\text{Ra}:\text{Ba})_{\text{rock}} / (\text{Ra}:\text{Ba})_{\text{fluid}}$. The resulting values are $D_{\text{Ra}/\text{Ca}} = 2.3$ and $D_{\text{Ra}/\text{Ba}} = 110$. Using available thermochemical data for Ra and alkaline earth correlations, Langmuir and Riese (1985) calculated a value for $D_{\text{Ra-barite}}$ of 1.8 at 25°C and 0.9 at 100°C . A value of 0.013 for $D_{\text{Ra-calcite}}$ was calculated by Gnanapragasam and Lewis (1991). These data indicate that Ra is excluded from calcite relative to Ca, but Ra is neither strongly preferred nor excluded by barite relative to Ba. The estimated $D_{\text{Ra}/\text{Ca}}$ and $D_{\text{Ra}/\text{Ba}}$ values are two orders of magnitude larger than their equilibrium values (~ 0.01 and ~ 1 , respectively) and thus inconsistent with control of fluid Ra activities by solid solution in calcite and barite. Saturation of the fluids with calcite and barite appears to inhibit Ra isotope exchange with these phases in this system. Similar bulk rock-fluid isotopic disequilibrium was demonstrated for O, Sr, Nd, and U isotopes in this system by Banner et al. (1989; 1990). Banner et al. (1989) suggested that the flow channel surfaces within the aquifer could be coated with minerals precipitated from, and in isotopic equilibrium with, the aquifer fluid. This process could also inhibit further isotopic exchange with portions of the bulk rock away from flow channels and interconnected porosity.

Equilibrium speciation calculations for Ra were performed using the Geochemist's Workbench[®] code (Bethke, 1996) and the Ra thermodynamic data of Langmuir and Riese (1985). The predicted activities are based on the *B-dot* (modified Debye-Hückel)

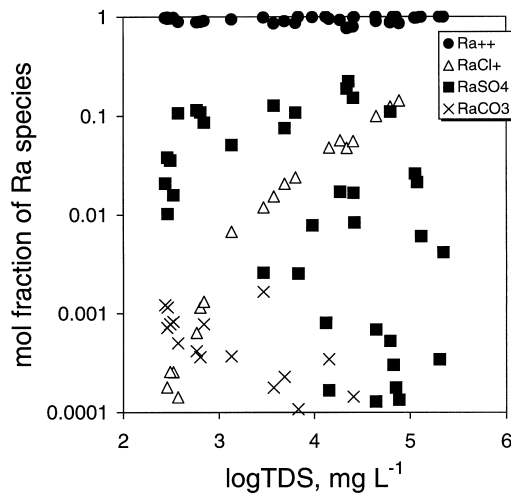


Fig. 5. Variation of Ra speciation as a function of salinity (log TDS in mg L^{-1}). The dominant Ra species in all samples is Ra^{2+} .

equation (Helgeson, 1969; Helgeson and Kirkham, 1974). These calculations show that the dominant dissolved Ra species, independent of salinity, is Ra^{2+} ; in no case is the Ra^{2+} fraction less than 77% of the total Ra in solution (Fig. 5). The next most abundant Ra species is RaCl^+ or RaSO_4 , depending on the $\Sigma\text{SO}_4/\Sigma\text{Cl}$ ratio in the solution (Fig. 6). RaCl^+ and RaSO_4 activities are correlated with ΣCl and ΣSO_4 concentrations, respectively.

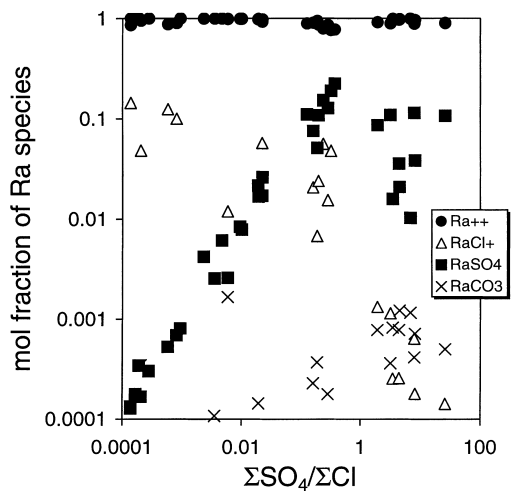


Fig. 6. Variation of Ra speciation as a function of $\Sigma\text{SO}_4/\Sigma\text{Cl}$. The second most abundant Ra species is RaCl^+ ($\Sigma\text{SO}_4/\Sigma\text{Cl} < 0.1$) or RaSO_4 ($\Sigma\text{SO}_4/\Sigma\text{Cl} > 0.1$).

5. Discussion

The Ra isotopes are produced by decay of Th isotopes, and practically all Th is associated with solids. Therefore, the location of Th isotopes within the mineral grains of the rock or on surface coating of aquifer solids is critical to the mechanism of Ra input to the ground water. The continual radioactive decay of dissolved Ra isotopes requires that, in order to maintain appreciable steady-state Ra activities in ground water, transfer of Ra from rock to water must occur on a time scale that is rapid relative to the half-lives of the Ra isotopes being considered. There is minimal evidence for dissolution of bulk aquifer rock in this system (Banner et al., 1989, 1990). If bulk rock dissolution or weathering does not replenish dissolved Ra activity, then dissolved Ra input must be generated by alpha recoil and desorption from Th parent atoms located at the surfaces of aquifer flow channels and interconnected pore spaces.

5.1. Mean path length of Ra in the aquifer

The mean path length of a Ra atom in an aquifer is limited by the mean life of the atom ($1/\lambda$), the flow rate of the fluid in the aquifer, and the interaction of the Ra with the aquifer surface. At sufficiently low flow rates, the diffusivity of an atom controls its mean path length. Flow rates in this hydrogeologic system are on the order of $\leq 1 \text{ m a}^{-1}$ (Signor and Imes, 1989), implying that the Ra isotopes in a given volume of fluid are derived from within a relatively small distance of the sampling point. For example, if the fluid velocity is 1 m a^{-1} and Ra sorption is negligible, then most of the ^{228}Ra inventory of a fluid sample must be generated from within 8.3 m upstream and most of the ^{226}Ra inventory must be generated from within 2.3 km upstream. These represent upper limits in this system. If fluid velocity is $< 1 \text{ m a}^{-1}$, and/or if Ra sorption is high, these length scales are proportionally smaller. For example, if the retardation factor (Krishnaswami et al., 1982) is 1000, then these mean free paths are reduced by a factor of 1000. This contrasts with the history of the Cl^- ions and water molecules in these fluids. The Cl^- ions may have traveled hundreds of km from Permian salt beds in western Kansas, and the water molecules may have traveled up to 1000 km from a recharge area in the Colorado Front Range (Banner et al., 1989; Musgrove and Banner, 1993).

5.2. Bulk rock dissolution and Th enrichment on aquifer surfaces

The most saline fluids contain up to 6 times as much (^{226}Ra) as an equivalent mass of typical carbonate aquifer rock [based on measured ^{238}U concentrations

(Table 3) assuming secular equilibrium in the rock], indicating that the surface layers along flow channels may be enriched in ^{230}Th and ^{232}Th . Enrichment of ^{230}Th in surface layers can be supported by decay of dissolved ^{234}U followed by sorption of ^{230}Th (Banner et al., 1990), but ^{232}Th in these layers has no dissolved parent and therefore, unless there is an external source, ^{232}Th must be supplied by bulk dissolution of aquifer rock. For example, the dissolution of carbonate aquifer rocks along fluid flow channels could leave behind deposits of relatively insoluble residue, e.g. silicates, phosphates, and hydroxides enriched in ^{232}Th and ^{238}U , at the flow-channel surface. In addition to being a source for ^{228}Ra and ^{226}Ra input to the fluid, such deposits could also limit further interaction of the fluid with the bulk rock.

Bulk rock dissolution rates sufficient to redistribute ^{232}Th and ^{238}U within the aquifer over a period of millions of years can be much slower than those required to sustain activities of (^{226}Ra) and (^{228}Ra) in fluid. For example, the average apparent dissolution rate of dolomite estimated from eight flow paths in the Madison Aquifer (Montana, Wyoming, and South Dakota) is $0.24 \mu\text{mol l}^{-1} \text{a}^{-1}$ (Plummer et al., 1990). Based on this rate and the data in Tables 2 and 3, it is possible to evaluate how much (^{226}Ra) could be contributed to the fluid by the process of dedolomitization. Drill core sample 931.7 appears to consist of about 96% dolomite and 4% calcite, based on its Ca and Mg concentrations (and ignoring the minor amounts of silicates that may be present). This sample has a ^{238}U concentration of $4.17 \mu\text{g g}^{-1}$, and would contain 3.13 dpm g^{-1} of (^{226}Ra) at radioactive equilibrium; therefore, it has a (^{226}Ra):Ca ratio of 915 dpm (^{226}Ra)/mol Ca. The Ca concentrations in the fluids range from $10^{-3.3}$ to $10^{-0.2} \text{ mol l}^{-1}$, and the corresponding range of times required for release of these amounts of Ca to the fluid by dolomite dissolution at a rate of $0.24 \mu\text{mol l}^{-1} \text{a}^{-1}$ would be 2.1×10^3 to $2.6 \times 10^6 \text{ a}$. The corresponding release rate of (^{226}Ra) would be $2.2 \times 10^{-4} \text{ dpm l}^{-1} \text{a}^{-1}$, which is clearly insufficient to maintain the observed levels of (^{226}Ra) in the fluids. This is an upper limit, as it does not account for Ra incorporated in calcite that may precipitate as dolomite dissolves. The concomitant release rate of (^{230}Th) would be equal to that of (^{226}Ra) at radioactive equilibrium, however, and this would result in a cumulative ^{230}Th release far greater than the ^{230}Th concentrations measured by Banner et al. (1990) in the $<0.4 \mu\text{m}$ filtered fractions of fluids from Blue Lick and Boone's Lick, Missouri [equivalent to (^{230}Th) values of 4.6×10^{-4} to $1.2 \times 10^{-2} \text{ dpm l}^{-1}$]. Similar arguments can be made for ^{232}Th . Thus, even though Ra release by slow bulk dissolution is inadequate to maintain fluid Ra activities, cumulative Th release greatly exceeds that necessary to maintain the negligible fluid Th activities.

This slow release of Th, which is relatively insoluble in water (Langmuir and Herman, 1980), provides a mechanism by which to enrich the surfaces of aquifer flow channels and other pore space in Th isotopes that can serve to generate Ra isotopes and thereby maintain fluid Ra isotope activities.

5.3. Salinity-dependent sorption and fluid Ra activity

Reversible surface exchange processes are generally considered to be important in controlling the transport of Ra isotopes in ground water systems (e.g., Dickson, 1990; Krishnaswami et al., 1982, 1991; Ku et al., 1992). Exchange constants for these processes are strongly dependent on the type of substrate, solution composition (including Eh and pH), temperature, and time (Benes, 1990). Adsorption-desorption reactions for Ra isotopes at aquifer surfaces occur within minutes to days (Krishnaswami et al., 1982, 1991), and thus are practically instantaneous with respect to the half-lives of ^{228}Ra and ^{226}Ra . This mechanism allows efficient fluid input of Ra isotopes from Th isotopes adsorbed on aquifer surfaces. However, the supply to fluid of a shorter-lived Ra isotope (e.g., ^{228}Ra) relative to a longer-lived Ra isotope (e.g., ^{226}Ra) could be limited by transport kinetics if diffusion through a low-permeability solid layer is involved.

The observed decrease in Ra adsorption with increasing salinity (Hammond et al., 1988; Herczeg et al., 1988; Kraemer and Reid, 1984; Krishnaswami et al., 1991; Tanner, 1964; Zukin et al., 1987; this study) has been attributed to a variety of factors including: competition of cations for available adsorption sites (Kraemer and Reid, 1984; Li and Chan, 1979; Nathwani and Phillips, 1979; Tanner, 1964); an increase in mineral surface charge (Mahoney and Langmuir, 1991); the increasing stability of inorganic Ra complexes in high ionic strength solutions (Hammond et al., 1988; Herczeg et al., 1988; Zukin et al., 1987); and the formation of strong organic complexes (Dickson, 1990; Langmuir and Riese, 1985; Molinari and Snodgrass, 1990). In addition, the relatively low oxidation potentials of the saline ground waters and brines sampled in this study (-0.52 to $+0.15 \text{ V}$; Musgrove, 1993) may decrease the adsorption of Ra indirectly by inhibiting the formation of Mn-oxide and/or -hydroxide coatings on aquifer flow-channel surfaces (Herczeg et al., 1988). Such Mn coatings are known to adsorb Ra strongly (Moore and Reid, 1973). Low Eh values also reduce the stability field of sulfate minerals, allowing higher concentrations of alkaline earth elements to build up in solution (Bloch and Key, 1981; Gilkeson et al., 1983; Langmuir and Melchior, 1985).

A simple model, based on that proposed by Krishnaswami et al. (1982), can explain the observed corre-

lations between (^{226}Ra) and salinity (Fig. 2) as well as that between (^{226}Ra) and other alkaline earth element concentrations (Fig. 3). This model involves the following assumptions: (1) bulk dissolution of aquifer rock is too slow to generate a significant input of dissolved Ra isotopes (cf Banner et al., 1989; Plummer et al., 1990); (2) the concentration of dissolved Th isotopes is negligible (Banner et al., 1990; Langmuir and Herman, 1980); (3) aquifer flow channels and interconnected pore spaces have a surface coating that is enriched in Th and has a range in $^{230}\text{Th}:$ ^{232}Th ratios similar to that measured in the fluids (Banner et al., 1990); and (4) the ^{228}Ra and ^{226}Ra generated by decay of ^{232}Th and ^{230}Th in this surface coating is transferred to solution by alpha recoil and desorption. In addition, it is assumed that adsorption of Ra isotopes to the surface coating is reversible and obeys first-order kinetics, and all Ra nuclei generated in the surface coating are recoiled into the fluid or into a location from which they may be desorbed. Accordingly, at steady state, the mass balance for a given radionuclide in an aquifer is given for the dissolved portion by

$$P + k_2 C_{\text{ads}} = \lambda C + k_1 C, \quad (1)$$

and for the adsorbed portion by

$$k_1 C = \lambda C_{\text{ads}} + k_2 C_{\text{ads}}, \quad (2)$$

where P is the supply rate of the nuclide to the solution (atoms time^{-1} volume^{-1}); λ is the decay constant of the nuclide (time^{-1}); k_1 and k_2 are the first-order adsorption and desorption rate constants, respectively (time^{-1}); C_{ads} is the concentration of the nuclide adsorbed on the aquifer surface coating, expressed as equivalent concentration in fluid (atoms volume^{-1}); and C is the concentration of the nuclide dissolved in the fluid phase (atoms volume^{-1}). The dimensionless distribution coefficient, K , can be defined as

$$K = C_{\text{ads}}/C = k_1/(k_2 + \lambda). \quad (3)$$

For nuclides having $\lambda \ll k_2$, which is generally the case for Ra isotopes in ground waters (Krishnaswami et al., 1982, 1991), it follows that

$$K \cong k_1/k_2. \quad (4)$$

The observed correlation between (^{226}Ra) and TDS (Fig. 2) must be limited at the high TDS end by halite saturation, because the dominant solutes in the most saline fluids are Na and Cl (Musgrove, 1993; Musgrove and Banner, 1993). The correlation for (^{226}Ra) vs Cl^- predicts an extrapolated (^{226}Ra) value of about 4130 dpm kg^{-1} , assuming halite saturation at 50°C . This agrees well with the value of 4190 dpm kg^{-1} predicted by the correlation between (^{226}Ra) and TDS at the highest TDS value. If it is assumed that

(^{226}Ra) = $4190 \text{ dpm kg}^{-1} = C_{\text{max}}$, and that $K = 1$ at the highest TDS value ($\sim 251,000 \text{ mg l}^{-1}$) so that $C_{\text{max}} = C_{\text{ads}}$, then the K value for each sample can be calculated using Eq. (3). The resulting K values range from about 10^0 – 10^4 and are negatively correlated with TDS (Fig. 7); these K values agree with those derived independently for other shallow brines ($K = 10^0$ – 10^2 ; Krishnaswami et al., 1991) and low-salinity ($< 2500 \text{ mg l}^{-1}$ TDS) ground waters ($K = 10^3$ – 10^5 ; Krishnaswami et al., 1982).

6. Summary and conclusions

The chemical compositions and activities of (^{228}Ra) and (^{226}Ra) were measured in subsurface fluids and aquifer rocks representing 3 regional flow systems in southwestern Missouri, southeastern Kansas, and northern Oklahoma. The fluids have a wide range in chemical composition, whereas the aquifer rock is relatively homogeneous. Dissolved Ra occurs mostly as the species Ra^{2+} on the basis of speciation calculations made with available thermodynamic data. The (^{226}Ra) activities and the salinities of the fluids are well correlated. The ($^{228}\text{Ra}:$ ^{226}Ra) values in the fluids are similar to those of the rocks. These fluid ($^{228}\text{Ra}:$ ^{226}Ra) values are also consistent with the measured $^{230}\text{Th}:$ ^{232}Th atom ratios of the fluids. A simple model involving reversible sorption of Ra, a salinity-dependent distribution coefficient for Ra, and a Th isotope-enriched surface layer on aquifer flow channels is consistent with the apparently rapid solid–fluid transfer of Ra isotopes and the correlation of (^{226}Ra) with salinity.

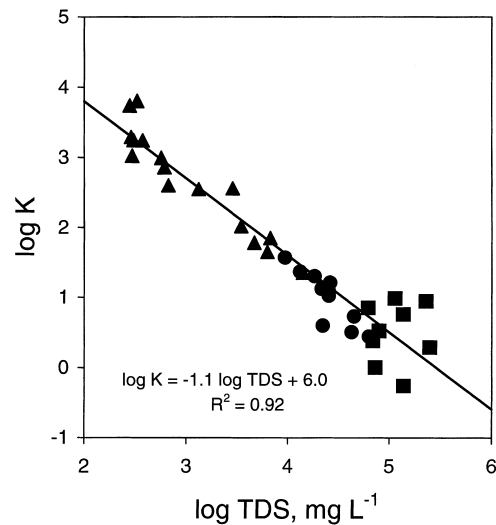


Fig. 7. Variation of $\log K$ (dimensionless) with salinity (\log TDS in mg l^{-1}).

The results of this study confirm and strengthen the conclusions of previous work. In similar aquifer systems worldwide, these data can be used to predict Ra activities and Rn emanation potential as a simple function of salinity. This study also emphasizes the need for further study of the behavior of Th in aquifer systems, particularly as it controls Ra distribution and is important as an analog for reduced Pu that may contaminate the environment in the vicinity of nuclear waste handling and storage facilities.

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References

- Andrews, J.N., Ford, D.J., Hussain, N., Trivedi, D., Youngman, M.J., 1989. Natural radioelement solution by circulating ground waters in the Stripa granite. *Geochim. Cosmochim. Acta* 53, 179–1802.
- Banner, J.L., Chen, J.H., Wasserburg, G.J., Moore, C.H., 1990. ^{234}U – ^{238}U – ^{230}Th – ^{232}Th systematics in saline ground waters from central Missouri. *Earth Planet. Sci. Lett.* 101, 296–312.
- Banner, J.L., Hanson, G.N., Meyers, W.J., 1988. Determination of initial Sr isotopic compositions of dolostones from the Burlington-Keokuk formation (Mississippian): Constraints from cathodoluminescence, glauconite paragenesis and analytical methods. *J. Sediment. Petrol.* 58, 673–687.
- Banner, J.L., Wasserburg, G.J., Dobson, P.F., Carpenter, A.B., Moore, C.H., 1989. Isotopic and trace element constraints on the origin and evolution of saline ground waters from central Missouri. *Geochim. Cosmochim. Acta* 53, 383–398.
- Benes, P., 1990. Radium in (continental) surface water. In: *The Environmental Behavior of Radium*, vol. 1. Intl. Atomic Energy Agency, Vienna, pp. 373–418 Chap. 4-3.
- Bethke, C.M., 1996. *Geochemical Reaction Modeling*. Oxford University Press, New York.
- Bloch, S., Craig, R.L., 1981. Radioactive springs in the watershed of a proposed reservoir in Sequoyah County, Oklahoma: origin and environmental effect. *Geology* 9, 195–199.
- Bloch, S., Key, R.M., 1981. Modes of formation of anomalously high radioactivity in oilfield brines. *Amer. Assoc. Petrol. Geol. Bull.* 65, 154–159.
- Burke, W.H., Denison, R.E., Hetherington, E.A., Koepnick, R.B., Nelson, H., Otto, J.B., 1982. Variation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout Phanerozoic time. *Geology* 10, 516–519.
- Cadigan, R.A., Felmlee, J.K., 1977. Radioactive springs geochemical data related to uranium exploration. *J. Geochem. Explor.* 8, 381–395.
- Carr, J.E., McGovern, H.E., Gogel, T., 1986. Geohydrology of and Potential for Fluid Disposal in the Arbuckle Aquifer in Kansas. US Geol. Surv. Open-file Rept. 86-491.
- Chauduri, S., Broedel, V., Clauer, N., 1987. Strontium isotopic evolution of oil-field waters from carbonate reservoir rocks in Bindley Field, central Kansas, USA. *Geochim. Cosmochim. Acta* 51, 45–53.
- Chung, Y., 1981. Radium-226 and radon-222 in southern California ground water: spatial variations and correlations. *Geophys. Res. Lett.* 8, 457–460.
- Cowart, J.B., 1981. Uranium isotopes and ^{226}Ra content in the deep ground waters of the Tri-State region, USA. *J. Hydrology* 54, 185–193.
- Davidson, M.R., Dickson, B.L., 1986. A porous flow model for steady-state transport of radium in ground waters. *Water. Resour. Res.* 22, 34–44.
- Dickson, B.L., 1990. Radium in ground water. In: *The Environmental Behavior of Radium*, vol. 1. Intl. Atomic Energy Agency, Vienna, pp. 335–372 Chap. 4-2.
- Fleischer, R.L., 1980. Isotopic disequilibrium of uranium: alpha-recoil damage and preferential solution effects. *Science* 207, 979–981.
- Fleischer, R.L., Price, P.B., Walker, R.M., 1975. *Nuclear Tracks in Solids*. Univ. of Calif. Press, Berkeley.
- Gascoyne, M., 1989. High levels of uranium and radium in ground waters at Canada's Underground Research Laboratory, Lac du Bonnet, Manitoba, Canada. *Appl. Geochem.* 4, 577–591.
- Gilkeson, R.H., Cartwright, K., Cowart, J.B., Holtzman, R.B., 1983. Hydrologic and Geochemical Studies of Selected Natural Radioisotopes and Barium in Ground Water in Illinois. Univ. Illinois Water Res. Center Rept. 83-0180.
- Gnanapragasam, E.K., Lewis, B.A., 1991. Elastic strain energy and the distribution coefficient of radium in solid solution with calcium salts. *Geochim. Cosmochim. Acta* 59, 5103–5111.
- Gutsalo, L.K., 1964. On the distribution of radium in the ground waters of the central part of the Dnieper-Donets basin. *Geokhimiya* 12, 1305–1312.
- Hammond, D.E., Zudin, J.G., Ku, T.L., 1988. The kinetics of radioisotope exchange between brine and rock in a geothermal system. *J. Geophys. Res.* 93, 13175–13186.
- Helgeson, H.C., 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Amer. J. Sci.* 267, 729–804.
- Helgeson, H.C., Kirkham, D.H., 1974. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures, II. Debye-Hückel parameters for activity coefficients and relative partial molal properties. *Amer. J. Sci.* 274, 1199–1261.
- Herczeg, A.L., Simpson, H.J., Anderson, R.F., Trier, R.M.,

- Mathieu, G.G., Deck, B.L., 1988. Uranium and radium mobility in ground waters and brines within the Delaware Basin, southeastern New Mexico. *Chem. Geol.* 72, 181–196.
- Imes, J.L., Emmett, L.F., 1994. *Geohydrology and Modeling Analysis of the Ozark Plateaus Aquifer System in Missouri, Arkansas, Oklahoma and Kansas*. US Geol. Surv. Prof. Paper 1414-F.
- Ivanovich, M., Latham, A.G., Longworth, G., Gascoyne, M., 1992. Applications to radioactive waste disposal studies. In: Ivanovich, M., Harmon, R.S. (Eds.), *Uranium-Series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences*, 2nd ed. Clarendon Press, pp. 583–630.
- Jorgensen, D.G., Helgesen, J.O., Imes, J.L., 1989. Regional Aquifers in Kansas, Nebraska, and Parts of Arkansas, Colorado, Missouri, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming — Geologic Framework. US Geol. Surv. Prof. Paper 1414-B.
- Kraemer, T.F., Reid, D.F., 1984. The occurrence and behavior of radium in saline formation water of the US Gulf Coast region. *Chem. Geol. (Isotope Geosci.)* 2, 153–174.
- Krishnaswami, S., Graustein, W.C., Turekian, K.K., Dowd, J.F., 1982. Radium, thorium, and radioactive lead isotopes in ground waters: application to the in-situ determination of adsorption rate constants and retardation factors. *Water Resour. Res.* 18, 1663–1675.
- Krishnaswami, S., Bhushan, R., Baskaran, M., 1991. Radium isotopes and ^{222}Rn in shallow brines, Kharaghoda (India). *Chem. Geol. (Isotope Geosci.)* 87, 125–136.
- Ku, T.L., Luo, S., Hammond, D., Leslie, B., 1992. Applications of decay-series disequilibria to water–rock interactions and geothermal systems. In: Ivanovich, M., Harmon, R.S. (Eds.), *Uranium-Series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences*, 2nd ed. Clarendon Press, pp. 631–668.
- Langmuir, D., Herman, J., 1980. The mobility of Th in natural waters at low temperatures. *Geochim. Cosmochim. Acta* 44, 1753–1766.
- Langmuir, D., Melchior, D., 1985. The geochemistry of Ca, Sr, Ba, and Ra sulfates in some deep brines from the Palo Duro Basin, Texas. *Geochim. Cosmochim. Acta* 49, 2423–2432.
- Langmuir, D., Riese, A.C., 1985. The thermodynamic properties of radium. *Geochim. Cosmochim. Acta* 49, 1593–1601.
- Larson, T.G., 1971. Hydrodynamic Interpretation of Mid-Continent. In: Cram, I.H. (Ed.), *Future Petroleum Provinces of the United States — Their Geology and Potential*. Am. Assoc. Petrol. Geol. Mem. 15, 1043–1046.
- Li, Y.H., Chan, L.H., 1979. Desorption of Ba and ^{226}Ra from riverborne sediments in the Hudson Estuary. *Earth Planet. Sci. Lett.* 43, 343–350.
- Lucas, H.F., 1977. Alpha scintillation radon counting. In: Harward, E.D. (Ed.), *Workshop on Methods for Measuring Radiation in and Around Uranium Mills*, vol. 3. Atomic Industrial Forum, Washington, DC, pp. 69–96.
- Lucas, H.F., 1985. ^{226}Ra and ^{228}Ra in water supplies. *J. American Water Works Assoc.* 77, 57–67.
- Lucas, H.F., Markun, F.J., 1991. The determination of ^{226}Ra and ^{228}Ra in water and solids by the least squares gamma spectrometric method. *J. Environ. Radioactivity* 15, 1–18.
- Macfarlane, P.A., Hathaway, L.R., 1987. *The Hydrogeology and Chemical Quality of Ground Waters from the Lower Paleozoic Aquifers in the Tri-State Region of Kansas, Oklahoma, and Missouri*. Kansas Geol. Surv. Ground water Ser. 9.
- Mahoney, J.J., Langmuir, D., 1991. Adsorption of Sr on kaolinite, illite, and montmorillonite at high ionic strengths. *Radiochim. Acta* 54, 139–144.
- Mazor, E., 1962. Radon and radium content of some Israeli water sources and a hypothesis on underground reservoirs of brines, oils, and gases in the Rift Valley. *Geochim. Cosmochim. Acta* 26, 765–786.
- Moore, W.S., Reid, D., 1973. Extraction of radium from natural waters using manganese-impregnated acrylic fibers. *Deep-Sea Res.* 23, 647–651.
- Molinari, J., Snodgrass, W.J., 1990. The chemistry and radiochemistry of radium and the other elements of the uranium and thorium natural decay series. *The Environmental Behavior of Radium*, Tech. Reports Series, 310, Intl. Atomic Energy Agency, Vienna, vol. 1, Chap. 1–2, 11–56.
- Musgrove, M., 1993. *Origin, Evolution, and Mixing of Saline and Dilute Ground Waters in Three Regional Flow Systems, Midcontinent, USA*. Unpubl. MA thesis, Univ. Texas, Austin.
- Musgrove, M., Banner, J.L., 1993. Regional ground-water mixing and the origin of saline fluids: midcontinent, United States. *Science* 259, 1877–1882.
- Nathwani, J.S., Phillips, C.R., 1979. Adsorption of ^{226}Ra by soils in the presence of Ca^{2+} ions. Specific adsorption (II). *Chemosphere* 5, 293–299.
- NAS/NRC, 1988. *Health Risks of Radon and Other Internally Deposited Alpha Emitters*. National Academy Press, Washington, DC.
- NAS/NRC, 1998. *Health Effects of Exposure to Radon*. National Academy Press, Washington, DC.
- Nordstrom, D.K., Munoz, J.L., 1986. *Geochemical Thermodynamics*. Blackwell Scientific Publications, Palo Alto.
- Parkhurst, D.L., Thorstenson, D.C., Plummer, L.N., 1980. PHREEQE — A Computer Program for Geochemical Calculations. US Geol. Surv. Water-Resources Inv. Rept. 80-96.
- Plummer, L.N., Busby, J.F., Lee, R.W., Hanshaw, B.B., 1990. Geochemical modeling of the Madison Aquifer in parts of Montana, Wyoming, and South Dakota. *Water Resources Res.* 26, 1981–2014.
- Plummer, L.N., Parkhurst, D.L., Fleming, G.F., Dunkle, S.A., 1988. A Computer Program Incorporating Pitzer's Equations for Calculation of Geochemical Reactions in Brines. US Geol. Surv. Water-Resources Inv. Rept. 88-4153.
- Siegel, D., 1989. *Geochemistry of the Cambrian-Ordovician Aquifer System in the Northern Midwest, United States*. US Geol. Surv. Prof. Paper 1405-D.
- Signor, D.C., Imes, J.L., 1989. Swain, L.A., Johnson, A.I. (Eds.), *Regional Aquifer Systems of the United States: Aquifers of the Midwest Region*, Monograph Series 13. American Water Resources Association, Bethesda, MD, pp. 149–163.
- Sturchio, N.C., Binz, C.M., 1988. Uranium-series age determi-

- nation of calcite veins, VC-1 drill core, Valles Caldera, New Mexico. *J. Geophys. Res.* 93, 6097–6102.
- Sturchio, N.C., Bohlke, J.K., Markun, F.J., 1993. Radium isotope geochemistry of thermal waters, Yellowstone National Park, Wyoming, USA. *Geochim. Cosmochim. Acta* 57, 1203–1214.
- Sutcliffe, H., Miller, R., 1981. Data on Ground Water Quality with Emphasis on Radionuclides. Sarasota County, Florida. US Geol. Survey Open-File Rept. 80–1223, pp. 13.
- Tanner, A.B., 1964. Physical and chemical controls on distribution of radium-226 and radon-222 in ground water near Great Salt Lake, Utah. In: *Proc. Symp. on the Natural Radiation Environment*. Univ. of Chicago Press, pp. 253–276.
- Tokarev, A.N., Shcherbakov, A.V., 1960. Radiohydrogeology (Eng. trans.). US Atomic Energy Comm. Rept. AEC-tr-4100.
- USEPA, 1991. National Primary Drinking Water Regulations: Radionuclides, 40CFR Parts 141, 142 (proposed). *Federal Register* 56-138, 33050-33127.
- Zukin, J.G., Hammond, D.E., Ku, T.L., Elders, W.A., 1987. Uranium-thorium series isotopes in brines and reservoir rocks from two deep geothermal well holes in the Salton Sea geothermal field, southeastern California. *Geochim. Cosmochim. Acta* 51, 2719–2731.