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Time scale of hydrothermal water–rock reactions in Yellowstone National Park based on radium isotopes and radon

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Abstract

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We have measured ^{224}Ra (3.4 d), ^{228}Ra (5.7 yr), and ^{226}Ra (1620 yr) and chloride in hot spring waters from the Norris–Mammoth Corridor, Yellowstone National Park. Two characteristic cold-water components mix with the primary hydrothermal water: one for the travertine-depositing waters related to the Mammoth Hot Springs and the other for the sinter-depositing Norris Geyser Basin springs. The Mammoth Hot Springs water is a mixture of the primary hydrothermal fluid with meteoric waters flowing through the Madison Limestone, as shown by the systematic decrease of the ($^{228}\text{Ra}/^{226}\text{Ra}$) activity ratio proceeding northward. The Norris Geyser Basin springs are mixtures of primary hydrothermal water with different amounts of cold meteoric water with no modification of the primary hydrothermal ($^{228}\text{Ra}/^{226}\text{Ra}$) activity ratio. Using a solution and recoil model for radium isotope supply to the primary hydrothermal water, a mean water–rock reaction time prior to expansion at 350°C and supply to the surface is 540 years assuming that 250 g of water are involved in the release of the radium from one gram of rock. The maximum reaction time allowed by our model is 1150 years.

Introduction

Hydrothermal activity, in the form of hot springs and geysers, is the geologic feature which most vividly characterizes Yellowstone National Park. The greatest diversity in dynamic and depositional features ascribable to this activity is found in the Norris Geyser Basin and the Norris–Mammoth Corridor (see the recent summary by White et al., 1988).

The source of heat is clearly magmatic but the exact process by which the extensive heat loss is maintained is not well understood. Fournier and Pitt (1985) and Fournier (1989) suggest that the hydrothermal system at Yellowstone is driven by the crystallization of magma

and the cooling of local hot rocks; White et al. (1988) suggest that the hot-spot refluxing of basaltic magma beneath a cover of continental rocks and acidic volcanics is the source of the heat.

The scale of the reaction time between the percolating meteoric water and the rocks in the region of the magmatic activity is controlled by the flow rate, the path length, and the rate of heating to near the critical temperature at depth (Truesdell and Fournier, 1976). The high-temperature waters are subsequently cooled by steam separation, conduction, and mixing with a cold-water reservoir during ascent; the final temperature of the hot spring is generally well below the reaction temperature.

It was the goal of our study to determine the residence time of the hot, deep water reacting with surrounding rock prior to its ascent in the hydrothermal system. To carry out our investigation, we measured the concentrations of the radium isotopes in the ^{232}Th and ^{238}U series in high-chloride, neutral-pH hot-spring waters from the Norris Geyser Basin. Each radium isotope is produced when its thorium isotope parent undergoes alpha decay: in the ^{232}Th chain, ^{228}Th to ^{224}Ra and ^{232}Th to ^{228}Ra ; in the ^{238}U chain ^{230}Th to ^{226}Ra . The half-lives of the radium isotopes (^{224}Ra , 3.4 days; ^{228}Ra , 5.7 years; ^{226}Ra 1620 years) differ by orders of magnitude and therefore provide information on processes of supply and on adsorption and desorption rates in the hydrothermal system. This study is a direct outgrowth of the earlier work at Yale on ocean ridge hydrothermal systems in the Pacific (Turekian and Cochran, 1986) and on groundwater in Connecticut (Krishnaswami et al., 1982).

Early work using bomb tritium systematics in aqueous systems of Yellowstone Park (Pearson and Truesdell, 1978) indicated that the hydrothermal waters sampled at the surface could be interpreted as being mixtures of an old (pre-bomb) primary hot-water end-member and a young cold-water component enriched in bomb tritium. The absence of bomb tritium in the hot-water end-member can only set a limit on its minimum age, 35 years. We hope, by using the radium isotope data together with the insight from the tritium data, to define the time scale of the high-temperature reaction more precisely.

Geological setting

Recently, the magmatic and volcanic history of Yellowstone National Park has been reviewed by Christiansen (1984) and Fournier (1989); the general geology of the Norris-Mammoth Corridor has been summarized by White et al. (1988). During the last two million years, the Yellowstone Plateau has experienced three explosive caldera-forming eruptions. Each

eruption laid down more than 250 km³ of rhyolitic tuffs. Between the caldera-forming events, a series of basaltic and rhyolitic flows were extruded. The total volume of these flows is much less than the total volume of the explosive tuffs. The Norris-Mammoth Corridor, which strikes north-south, is a complex subsidence structure that extends for roughly 40 km from the Norris Geyser Basin through the Mammoth Hot Springs to the La Duke-Bear Creek thermal area (see Fig. 1). The Norris Geyser Basin lies immediately outside of the caldera's northwestern rim. The western flank of the corridor is bounded by the East Gallatin fault zone, a series of north-south-striking normal faults, and the southeastern Gallatin Mountains. Similar north-south-striking faults are found to the east, though they are not as numerous. The La Duke-Bear Creek thermal area lies just outside the park boundary at the foot of the Beartooth Mountains.

The rocks which outcrop in the northern portion of the corridor are pre-Tertiary shales, carbonates, and sandstones. Included in this sequence is the Madison Limestone. Outside of the corridor, on the northern, eastern, and western flanks are Yellowstone volcanics and the same pre-Tertiary shales, carbonates, and sandstones that outcrop in the northern portion of the corridor.

The Lava Creek Tuff which underlies the central and southern portions of the corridor was deposited during the third caldera-forming eruption, 600,000 years B.P. The Lava Creek Tuff is rhyolitic in composition. During the middle Pleistocene, volcanism was once again active in the corridor; the Plateau Rhyolites, composed of rhyolitic flows and domes, were emplaced in the central and northern parts of the corridor. The youngest, the Crystal Spring Flow member, formed 80,000 years B.P.

Methods

Eleven hot springs and one cold spring were sampled from the Norris-Mammoth corridor

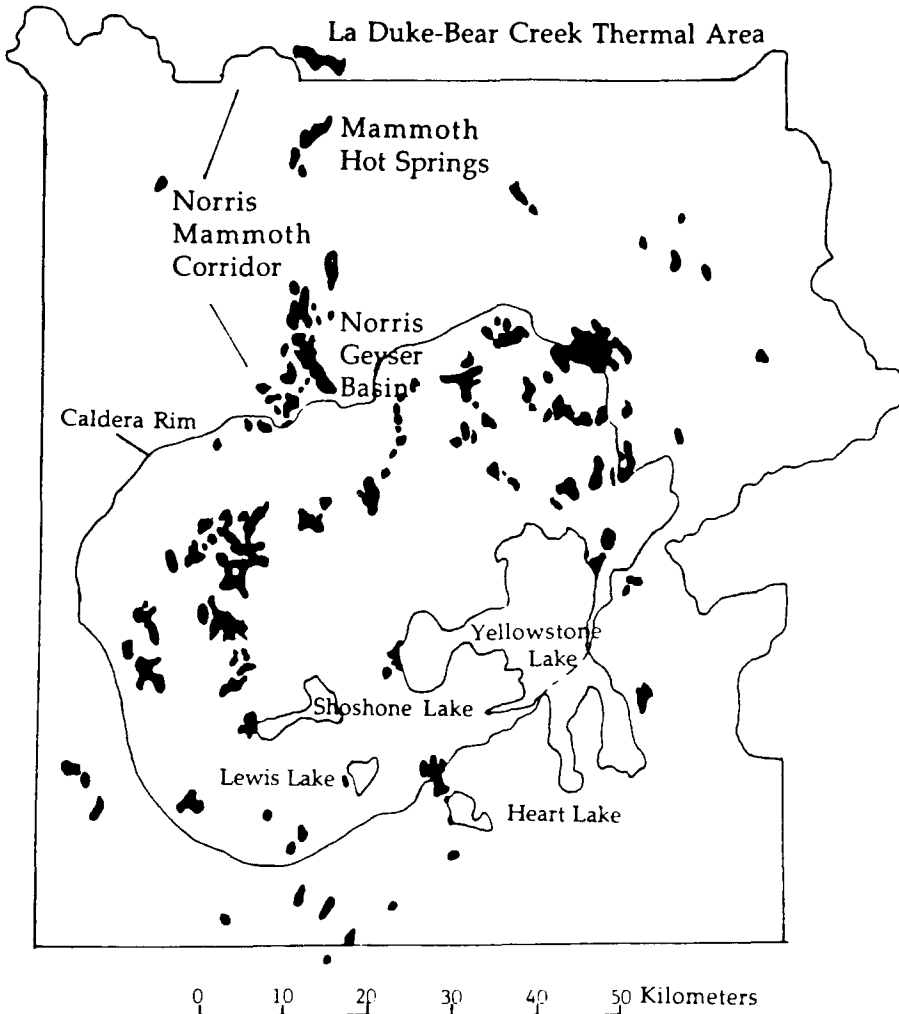


Fig. 1. Location of the Norris-Mammoth Corridor and of hydrothermal features (black areas) in Yellowstone National Park.

during July of 1987 (Fig. 2). Three criteria were used to choose the springs to be sampled: (1) geographical location in the corridor; (2) accessibility; and (3) relationship to park roads and paths (National Park Service rules discourage sampling in the view of public areas). The springs sampled are listed in Table 1 together with information on temperature and pH.

The spring water was collected in a bucket and passed through Whatman 52 hardened filter paper into a 200-liter container. The filters were changed periodically during the collection process as the flow rate decreased. Sample sizes

were generally greater than 100 liters through some were as small as 35 liters. Nitric acid was added to the spring water until a pH of around 2 was obtained. Roughly 10 grams of ferric chloride and 15 grams of calcium chloride were added to the acidified water. The water was then stirred vigorously until the calcium and ferric chlorides had fully dissolved. Once dissolved, the pH was raised to around 5 with sodium hydroxide. About 50 grams of sodium bicarbonate were added together with enough sodium hydroxide to obtain a pH of 10. After a brisk stirring, the sample was left to stand. Calcium carbonate and ferric hydroxide coprecipitated and

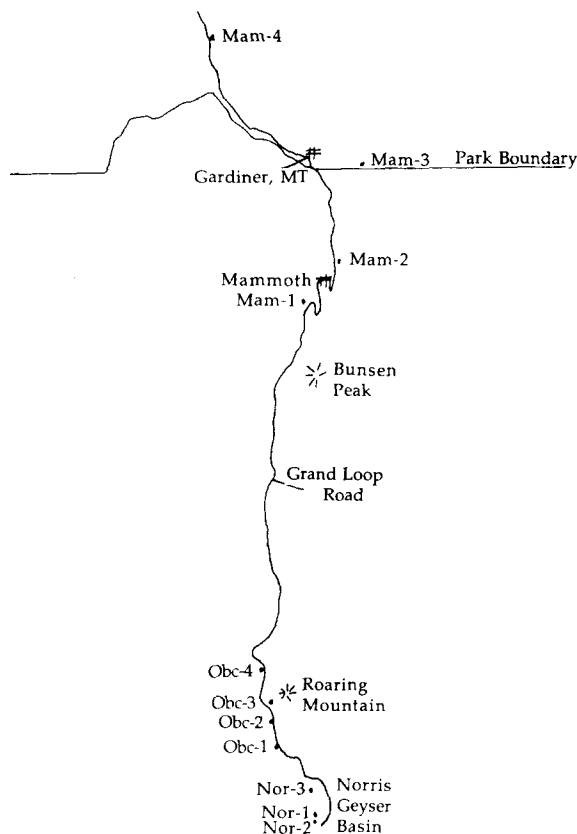


Fig. 2. The location of sampled springs and of Roaring Mountain in the Norris-Mammoth Corridor, Yellowstone National Park.

settled together in approximate 20 minutes. After decanting, the precipitate remaining in about 10 liters was then collected by filtering through a Whatman 52 filter paper. The total sampling and separation time at each spring was about five hours. The precipitate was dried overnight in an oven at 100°C . The next morning it was sealed in an aluminum can and sent, via express courier, to Yale in order to count the short-lived ^{224}Ra .

In addition to the precipitate, two liter samples of filtered acidified and unacidified water were collected in bottles and brought back to Yale for future analysis for ^{226}Ra and stable nuclides.

A coaxial intrinsic germanium gamma detector coupled to a multichannel analyzer was used

to determine the radium isotope activities in the precipitate. Typically, two days after sampling, the ^{224}Ra activity was determined from the ^{212}Pb count rate. During a second counting, which occurred more than 20 days after sealing the can (to prevent ^{222}Rn loss), ^{228}Ra and ^{226}Ra activities were determined from the ^{228}Ac and ^{214}Pb count rates, respectively. The chemical yields were determined by measuring the absolute ^{226}Ra concentration (via its daughter ^{222}Rn) in the acidified water that was brought back to the laboratory. About one liter of water was transferred to an air-tight glass vessel and purged of ^{222}Rn by bubbling helium through it for 25 minutes after which the bottle was sealed for 10 to 20 days to allow for the production of ^{222}Rn from ^{226}Ra . This ^{222}Rn , once it had effectively reached secular equilibrium with ^{226}Ra , was then extracted and counted as a measure of the absolute ^{226}Ra concentration. Chloride was measured in the non-acidified water using a Mohr-Knudsen titration.

Results

The radiochemical and chemical results are presented in Table 1. The ^{224}Ra and ^{228}Ra counting errors (1σ) are generally between 5% and 15%, and for ^{226}Ra they are generally less than 7%. However, the errors for a few springs are larger. The chemical yields of the sinter-depositing springs and the travertine-depositing springs differed. While the chemical yields of the seven sinter-depositing springs were between 25% and 40%, the yields of the four travertine-depositing springs were generally around 80%. Unlike the sinter-depositing springs, the travertine-depositing springs each yielded sufficient precipitate to fill more than one can prepared for counting. The high apparent yields of Obc-1 and Obc-3 are probably the result of particles bypassing the filter paper during the initial filtration.

The data cluster into two groups: the northern springs, Obc-4, Mam-1, Mam-2, Mam-3, and Mam-4 and the southern springs Nor-1,

TABLE 1

Radiochemical and chemical results of the Norris-Mammoth Corridor springs

Spring name	Sam- ple Vol. (l)	T (°C)	pH	(Ra-224) (dpm l ⁻¹)	(Ra-228) (dpm l ⁻¹)	(Ra-226) (dpm l ⁻¹)	$\left(\frac{\text{Ra-224}}{\text{Ra-228}}\right)$	$\left(\frac{\text{Ra-228}}{\text{Ra-226}}\right)$	Cl ⁻ (ppm)	(Rn- 222*) (dpm l ⁻¹)	
<i>Southern Springs</i>											
Nor-1	Hydrophane Springs	182	89	7	0.78 ± 0.16	0.65 ± 0.13	0.26 ± 0.02	1.20 ± 0.20	2.50 ± 0.49	629	218
Nor-2	Medusa Spring	150	84	7	7.87 ± 0.56	5.25 ± 0.41	1.35 ± 0.03	1.50 ± 0.07	3.89 ± 0.29	555	471
Nor-3	Opalescent Spring	180	84	7	1.89 ± 0.32	0.89 ± 0.16	0.20 ± 0.01	2.13 ± 0.16	4.43 ± 0.70	596	
Obc-1	Nymph Lake	60	70	7	0.43 ± 0.18	0.26 ± 0.12	0.11 ± 0.00	1.61 ± 0.36	2.40 ± 1.06	334	384
Obc-2	Bijah Spring	180	82	7	1.26 ± 0.09	1.24 ± 0.09	0.42 ± 0.02	1.02 ± 0.05	2.95 ± 0.17	135	211
Obc-3	Roaring Mountain [†]	100	55	2	29.98 ± 2.55	2.48 ± 0.23	0.50 ± 0.03	12.10 ± 0.47	4.95 ± 0.39	34	
<i>Northern Springs</i>											
Obc-4	Obsidian Creek [†]	180	93	7	2.53 ± 0.11	1.32 ± 0.09	1.37 ± 0.03	1.92 ± 0.12	0.96 ± 0.06	435	331
Mam-1	Narrow Gauge	165	71	7	17.49 ± 0.49	15.16 ± 0.50	24.77 ± 0.25	1.15 ± 0.04	0.61 ± 0.02	257	
Mam-2	Boiling River	100	100	7	4.84 ± 0.36	4.68 ± 0.33	9.96 ± 0.14	1.03 ± 0.10	0.47 ± 0.03	193	2648
Mam-3	Bear Creek	55	55	7		1.07 ± 0.23	2.90 ± 0.05		0.37 ± 0.08	46	12961
Mam-4	La Duke	35	67	7		6.07 ± 0.73	21.49 ± 0.17		0.28 ± 0.03	53	2100
<i>Apollinaris Cold Spring</i>											
Cold-1	Apollinaris	182	10	5	0.23 ± 0.07	0.32 ± 0.11	0.18 ± 0.01	0.71 ± 0.21	1.75 ± 0.61		2555
Cold-2	Apollinaris	180	10	5		0.47 ± 0.08	0.18 ± 0.01		2.63 ± 0.43		2555

One sigma errors reported.

*Chloride concentrations of the northern springs are 20% to 30% greater than most published results (personal communication, R. Fournier).

*Rn-222 concentrations determined by Elizabeth Colvard.

†Spring name used is not an official park name. Obc-4 is one of the Clearwater Springs.

Nor-2, Nor-3, Obc-1, Obc-2, and Obc-3. (The prefixes "Nor", "Mam", and "Obc" refer, respectively, to Norris, Mammoth and Obsidian Creek, the geographical locations of the springs). Of the eleven springs, travertine is precipitating from only the four Mammoth springs; sinter is precipitating from the other seven. While the (²²⁴Ra/²²⁸Ra) activity ratio is relatively constant for the springs measured (1.50 ± 0.60), the (²²⁸Ra/²²⁶Ra) activity ratio falls into two groups. For the northern springs, the ratio is always less than 1 and for the southern springs it is always greater than 1 (see Table 1). (The convention of using parentheses to indicate activity or activity ratios is used).

Possible aquifer rock samples were collected and analyzed for their ²³⁸U and ²³²Th contents. The (²³²Th/²³⁸U) activity ratio found in two different members of the Yellowstone group, the

Lava Creek tuff and the Obsidian Cliff member of the Plateau Rhyolites, were roughly the same, 1.3. A piece of Madison Limestone was also analyzed. While its ²³⁸U count rate was substantially above background, the ²³²Th count rate was not (see Table 2).

TABLE 2

U-238 and Th-232 concentrations of aquifer rocks from the Norris-Mammoth Corridor

	(Th-232) (dpm g ⁻¹)	(U-238) (dpm g ⁻¹)	$\left(\frac{\text{Th-232}}{\text{U-238}}\right)$
Lava Creek Tuff	7.67 ± 0.26	5.97 ± 0.13	1.28 ± 0.05
Plateau Rhyolite	7.27 ± 0.20	5.36 ± 0.10	1.36 ± 0.04
Madison Limestone	0.00	1.45 ± 0.03	

Discussion

A. Trajectories and mixing curves of thermal water of the Norris-Mammoth Corridor

Studies of the Yellowstone hydrothermal system (Truesdell and Fournier, 1976; Truesdell et al., 1977; Mazar and Thompson, 1982; and Fournier, 1988) have suggested that the thermal water from the various basins originates from the same deep reservoir. This conclusion is based on the similar maximum temperatures determined at depth, similar isotopic composition of the source water, and similar chemistries for certain diagnostic elements of the spring waters. Local variations result from differing amounts of vapor loss, dilution, and water-rock interactions that occur as the water rises to the surface. Truesdell and Fournier (1976) and Fournier (1989) have suggested that the reservoir is located beneath the caldera at a depth of 3–5 km. Truesdell et al. (1977) believe that the primary water has a chloride concentration of 310 ppm. Oxygen and hydrogen isotopes have shown that the majority of the thermal water which surfaces in Yellowstone is of meteoric origin (see Craig, 1963, and Truesdell et al., 1977). Based on these data Truesdell et al. (1977) suggest that the recharge water is either residual from a colder time (last glacial maximum) or from the Gallatin mountains which lie to the west and the northwest.

We have found that the thermal waters north of Roaring Mountain look different, chemically, from those to the south (see Table 1). The northern springs tend to contain less chloride and more ^{226}Ra with $(^{228}\text{Ra}/^{226}\text{Ra})$ less than one. The southern springs on the other hand have $(^{228}\text{Ra}/^{226}\text{Ra})$ greater than one. All but the southernmost of the five northern springs are travertine-depositing whereas all of the southern springs are sinter-depositing.

Two alternative models have been suggested for the flow of thermal water in the Norris-Mammoth Corridor. Truesdell and Fournier (1976) have suggested that the Mammoth water

rises at Norris and flows north through a series of faults. Along the way it mixes with meteoric water, dissolves carbonate rocks, and cools. White et al. (1988) have suggested that the corridor water originates from a reservoir within the Lava Creek tuff beneath Roaring Mountain. In their model, thermal waters flow both north to Mammoth and south to Norris from Roaring Mountain. Along the way the thermal water rise and is mixed with cold meteoric waters resulting in the many springs which lie in the central portions of the corridor.

When the chloride concentration of the sampled springs is plotted as a function of distance from Roaring Mountain (Fig. 3) two trajectories are discerned. North of Roaring Mountain, the chloride concentration of the springs decrease northward suggesting that more mixing with meteoric water or less boiling has occurred in each successive spring. To the south of Roaring Mountain, the chloride concentrations increase toward the Norris Geyser Basin. This implies that although the source of the primary hydrothermal water maybe from a reservoir below Roaring Mountain, the circulation southward provides water that is progressively less influenced by meteoric water or is more affected by vapor loss or both.

The two trajectories are further distinguished by their $(^{228}\text{Ra}/^{226}\text{Ra})$ signature. For the southern springs, the $(^{228}\text{Ra}/^{226}\text{Ra})$ is constant suggesting that with respect to radium, the primary hydrothermal water has undergone

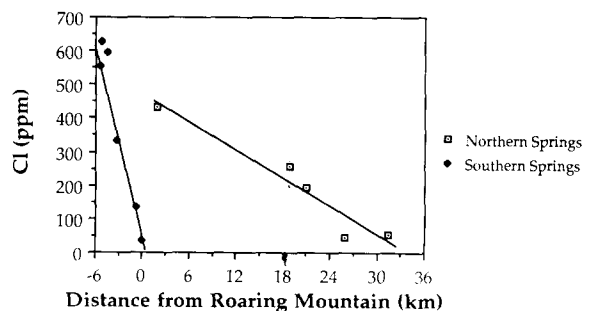


Fig. 3. Chloride concentrations of sampled springs plotted as a function of north-south distance from Roaring Mountain. North is in the positive direction.

differing amounts of boiling or mixing with a ^{228}Ra and ^{226}Ra free meteoric source or both (see Fig. 4a). For the northern springs, the ($^{228}\text{Ra}/^{226}\text{Ra}$) decreases with decreasing chloride concentration (Fig. 4b), indicating that, proceeding northward, either ^{228}Ra is being lost by radioactive decay or ^{226}Ra is being added. Clearly, the northern flowing thermal water mixes with meteoric water that has been in contact with the Madison Limestone which has a ($^{232}\text{Th}/^{238}\text{U}$) of about zero (Table 2). This dissolution of the limestone should result in increased concentration of calcium and ^{226}Ra but not ^{228}Ra . The addition of ^{226}Ra together with the decay of unsupported ^{228}Ra would explain the decrease in the ($^{228}\text{Ra}/^{226}\text{Ra}$) proceeding northward. The addition of calcium and bicarbonate by the solution of the limestone, of course, is compatible with the travertine deposition in the Mammoth springs. Figures 4a and 4b therefore support the flow patterns envisaged by White

et al. (1988) for the Norris–Mammoth Corridor. The large variations in both the ^{226}Ra and ^{228}Ra concentrations are compatible with different imprints on the primary thermal water as is evident from the high-chloride waters of the southern springs. It is not possible, therefore, to extract information on the relative importance of the radioactive decay loss of ^{228}Ra and of mixing with ^{228}Ra -free water along the northward flowing trajectory.

B. Mean water-rock reaction time of source waters

The path of the water which eventually emerges in the Yellowstone hot spring basins can be broken into three parts: (1) meteoric water enters the ground, presumably in the Gallatin Mountains; (2) the water passes into hot rock and heats to near critical temperatures; and (3) the hot water rises, cools by steam separation and mixing, and surfaces in the hot spring basins. Associated with each path is a flow time. The radium isotopes provide information only on the timescale of reaction in the thermal reservoir prior to expansion. Krishnaswami et al. (1982) found that radium is primarily delivered by recoil to groundwaters in the varied geologic terrains of Connecticut and is strongly adsorbed in the aquifer. Assuming that the chemical conditions of the “cold-water” path are similar to those of the Connecticut terrains, the concentrations of the radium isotopes in groundwater entering the thermal region will be very low. We therefore believe that time zero for our radium clock will be when the cold groundwater enters the hot rock and thus the clock provides us with an estimate of the length of time the water spends in reacting with and altering the rock. We assume that heating to a near supercritical state releases the water virtually instantaneously to the surface, freezing in the Ra isotope imprint acquired during the time of high-temperature water–rock interaction. The adsorption and desorption of Ra by reaction products such as zeolites (Sturchio et

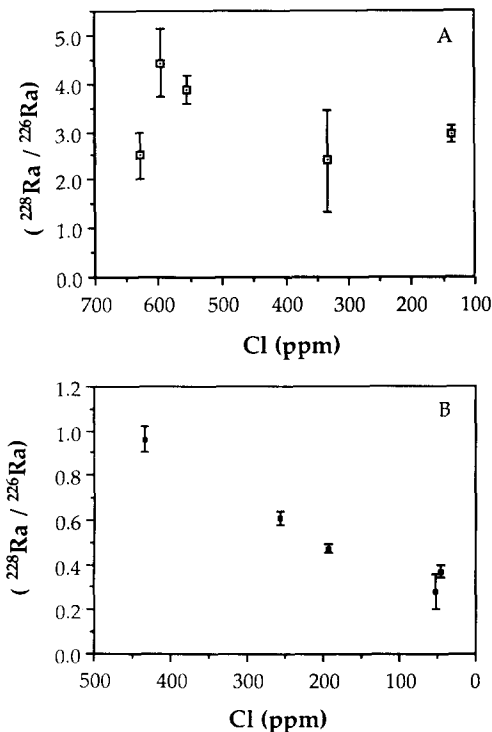


Fig. 4. $^{228}\text{Ra}/^{226}\text{Ra}$ plotted as a function of chloride concentration for (A) the southern springs and (B) the northern springs.

al., 1989) maintains the ($^{228}\text{Ra}/^{226}\text{Ra}$) of the water during the reaction time and this ratio is subject only to production and radioactive decay in the manner discussed below.

As shown in the previous section, the southern springs of the Norris–Mammoth Corridor are composed of two components, the primary hydrothermal source water and effectively Ra-free meteoric water. The former carries the chemical and radiochemical imprint diluted or concentrated but otherwise unmodified by the meteoric component and the effects of boiling. The virtual constancy of the ($^{228}\text{Ra}/^{226}\text{Ra}$) is compatible with this view.

We can therefore use the ($^{228}\text{Ra}/^{226}\text{Ra}$) of these southern springs to determine the water–rock reaction time prior to expansion and supply to the surface. In order to do this we make three fundamental assumptions: (1) the chemical and radiochemical properties of the reacting rock is comparable to the two rocks analyzed for U and Th, namely the Lava Creek tuff and the Plateau rhyolite; (2) the waters charging the reaction area are virtually pure meteoric water with little dissolved material derived from the low temperature alteration of the country rock during its descent to the high temperature reaction zone; and (3) the rate of supply of the expanded hydrothermal fluid to the surface occurs rapidly — a matter of days at the most — after expansion occurs. Under these conditions ($^{228}\text{Ra}/^{226}\text{Ra}$) in the water can provide the mean water–rock reaction time in the thermal source-region (see Turekian and Cochran, 1986; Kadko and Moore, 1988).

The general equations for the evolution of ^{228}Ra or ^{226}Ra in an aquifer are given by:

Solution phase

$$\frac{dC}{dt} = P - \lambda C - k_1 C + k_2 \bar{C} \quad (1)$$

Adsorbed phase

$$\frac{d\bar{C}}{dt} = k_1 C - \lambda \bar{C} - k_2 \bar{C} \quad (2)$$

where, for either isotope:

C = concentration in solution (atoms l^{-1})

\bar{C} = concentration in adsorbed phase referred to the solution (atoms l^{-1})

P = production rate in solution (atoms $\text{min}^{-1} l^{-1}$)

k_1 = adsorption coefficient (min^{-1})

k_2 = desorption coefficient (min^{-1})

λ = decay constant (min^{-1}).

Using the equations above, Krishnaswami et al. (1982) determined the adsorption and desorption rate constants, k_1 and k_2 , for radium in Connecticut groundwaters by assuming that the steady state ($dC/dt=0$) had been achieved for the shorter-lived radium isotopes, ^{224}Ra and ^{228}Ra , and that the production of these isotopes could be estimated by the ^{222}Rn activity in the water. Equilibrium should be achieved for ^{224}Ra after two weeks and for ^{228}Ra after 30 years (five half lives of each Ra isotope). Thus, assuming that the water is older than 30 years, k_1 and k_2 can be estimated with the above equations using the values for the southern springs in Table 1: k_1 is roughly $50,000 \text{ yr}^{-1}$ and k_2 is roughly 200 yr^{-1} (see Krishnaswami et al., 1982, for the details of the calculation). Knowledge of k_1 and k_2 , constants which are characteristic of all Ra isotopes, will allow us to simplify equation (1). Assuming steady state has been achieved between the adsorbed and desorbed state, equation (2) can be rewritten as:

$$K_D = \frac{\bar{C}}{C} = \frac{k_1}{k_2 + \lambda} \quad (3)$$

In the case where $\lambda \ll k_2$, the equation can be simplified to:

$$k_1 C \approx k_2 \bar{C} \quad (4)$$

We believe that in the case of the ^{228}Ra and ^{226}Ra the above approximation is valid. λ_8 and λ_6 , the decay constants, are respectively 0.12 yr^{-1} and 0.00043 yr^{-1} , much less than k_2 . Because the adsorption-desorption rate constants are large compared with the decay constants, we feel that equilibrium between the adsorbed and desorbed states for ^{228}Ra and ^{226}Ra can be assumed and equation (1) simplifies to:

$$\frac{dC}{dt} = P - \lambda C \quad (5)$$

The solution of this equation depends on the nature of P . The three modes of production of radium in the aqueous phase are in situ decay of the dissolved parent thorium isotope, recoil from the aquifer rock, and aquifer rock dissolution. Because thorium is virtually totally adsorbed at the neutral pH of the springs studied, we assume that production of the radium isotopes in the water due to dissolved thorium is negligible. Supply of the radium isotopes to the water is dominated by recoil during alpha decay of the parent Th isotopes in and adsorbed on the aquifer rock and to a lesser degree by the dissolution of aquifer rock. The recoil flux of the radium isotopes is proportional to the ^{222}Rn flux to the groundwater (Krishnaswami et al., 1982). ^{222}Rn is short-lived (3.8 day half-life) and a noble gas; it is not likely to adsorb on surfaces and thus its activity in the water represents the recoil of radon and by inference all other nuclides in the U and Th decay chains produced by alpha decay. The recoil productions of the U and Th chain nuclides are related to the ^{222}Rn flux by ϵ , the theoretically calculated recoil supply efficiencies relative to ^{222}Rn . For the ^{232}Th series nuclides, the recoil flux is determined by multiplying the radon flux by the ($^{232}\text{Th}/^{230}\text{Th}$) of the aquifer rock and the appropriate value of ϵ .

For recoil production alone, the solutions to equation (5) for each radium isotope are:

$$\begin{aligned} (^{228}\text{Ra})_{\text{recoil}} &= \epsilon_8 \left(\frac{^{232}\text{Th}}{^{230}\text{Th}} \right)^* (^{222}\text{Rn}) (1 - e^{-\lambda_8 t}) \quad (6) \end{aligned}$$

and

$$(^{226}\text{Ra})_{\text{recoil}} = \epsilon_6 (^{222}\text{Rn}) (1 - e^{-\lambda_6 t}) \quad (7)$$

where ϵ_6 and ϵ_8 are the recoil supply efficiencies relative to ^{222}Rn and λ_6 and λ_8 are the decay constants for ^{226}Ra and ^{228}Ra respectively and

the asterisk (*) indicates that the value refers to the rock.

For aquifer rock dissolution, we have assumed that the whole rock dissolves uniformly to yield an average dissolution rate, S . Under these conditions, the solutions to equation (5) are:

$$(^{228}\text{Ra})_{\text{sol}} = \frac{(^{228}\text{Ra})^*}{\lambda_8} S (1 - e^{-\lambda_8 t}) \quad (8)$$

and

$$(^{226}\text{Ra})_{\text{sol}} = \frac{(^{226}\text{Ra})^*}{\lambda_6} S (1 - e^{-\lambda_6 t}) \quad (9)$$

Where S is the rock reaction rate per unit mass of water ($\text{g l}^{-1} \text{yr}^{-1}$ or equivalent).

The general solution to equation (5) for both recoil and dissolution is the linear contribution of the equations above. The ratio of ($^{228}\text{Ra}/^{226}\text{Ra}$) in the water therefore has the complete expression:

$$\begin{aligned} \left(\frac{^{228}\text{Ra}}{^{226}\text{Ra}} \right) &= \quad (10) \\ \frac{\left\{ \epsilon_8 \left[\frac{^{232}\text{Th}}{^{238}\text{U}} \right]^* (^{222}\text{Rn}) + \frac{(^{228}\text{Ra})^*}{\lambda_8} S \right\} (1 - e^{-\lambda_8 t})}{\left[\epsilon_6 (^{222}\text{Rn}) + \frac{(^{226}\text{Ra})^*}{\lambda_6} S \right] (1 - e^{-\lambda_6 t})} \end{aligned}$$

This can be resolved to the form used by Kadko and Moore (1988) by the substitution of Wt for S^{-1} where W is the amount of water (in grams) needed to dissolve one gram of rock. We further assume that in the rock ^{228}Ra is in equilibrium with the ^{232}Th and ^{226}Ra is in equilibrium with ^{238}U .

Therefore, the final equation becomes:

$$\begin{aligned} \left(\frac{^{228}\text{Ra}}{^{226}\text{Ra}} \right) &= \quad (11) \\ \frac{\left[\epsilon_8 \left(\frac{^{232}\text{Th}}{^{238}\text{U}} \right)^* (^{222}\text{Rn}) + \frac{(^{232}\text{Th})^*}{1000\lambda_8 Wt} \right] (1 - e^{-\lambda_8 t})}{\left[\epsilon_6 (^{222}\text{Rn}) + \frac{(^{238}\text{U})^*}{1000\lambda_6 Wt} \right] (1 - e^{-\lambda_6 t})} \end{aligned}$$

Assuming that thorium is strongly adsorbed on surfaces of the aquifer, values of ϵ for ^{228}Ra and ^{226}Ra are, respectively, $\epsilon_8=0.769$ and $\epsilon_6=0.961$ (Krishnaswami et al., 1982). The (^{222}Rn) was obtained from measurements made by Elizabeth Colvard of the National Park Service (Table 1). In our calculations we use an average value of 300 dpm l^{-1} . (This number may be as high as 500 dpm l^{-1} , W.B. Hamilton, pers. commun., 1988). We assume that the radon concentration in the water is not seriously affected during vapor loss.

The value of W (the amount of water needed to release radium from one gram of rock) is difficult to obtain directly. We have chosen to use the chloride concentration in the hydrothermal end member as an approach to the problem. We balance the chloride with the major cations found in the hydrothermal fluid (sodium, potassium, and calcium) and assume the cations originated from the dissolution of an average Yellowstone volcanic group rock which also released the radium. The difference between the relative abundances of the cations in solution and in the rock we attributed to ion exchange reactions.

The amount of water needed to dissolve one gram of rock can be estimated if congruent dissolution is assumed, no precipitation of the chloride occurs and the chloride and cation concentrations are known in the fluid and aquifer rock respectively. Hamilton (1963) measured the concentrations of the major elements in the Yellowstone group volcanics. For the ash tuff deposits he reports calcium concentrations between 0.16 wt.% and 0.24 wt.%, sodium between 2.45 wt.% and 2.67 wt.%, and potassium between 3.82 wt.% and 4.14 wt.%. For the purposes of this study, we have assumed a calcium concentration of 0.21 wt.%, sodium of 2.5 wt.%, and potassium of 4.0 wt.% for the rock and a hydrothermal water chloride concentration of 310 ppm, which is the value that Truesdell et al. (1977) calculated for the primary thermal water prior to vapor loss. The W calculated with

these values for the average Norris Geyser Basin water is roughly 250.

Figure 5 is a plot of equation (11), assuming a mean (^{222}Rn) of 300 dpm l^{-1} , for the Norris Geyser Basin springs, the aquifer rock U and Th concentrations of Table 2, the ϵ values given above, and W 's of ∞ , 250 and 70. $W=\infty$, the recoil end member, yields the maximum age; and, 70 is the minimum W permissible since any lower value yields ($^{228}\text{Ra}/^{226}\text{Ra}$) less than the mean value of about 3.5, the average for Norris Geyser Basin springs. The water-to-rock ratio of 70 yields a unique solution for a ($^{228}\text{Ra}/^{226}\text{Ra}$) = 3.5. All higher values of water-to-rock ratio yield two solutions. One solution is for recoil-dominated production ($T > T_{\text{max}}$) and the other is for dissolution-dominated production ($T < T_{\text{max}}$), where T_{max} is defined to be the time at which the ($^{228}\text{Ra}/^{226}\text{Ra}$) activity ratio is at its maximum. T_{max} values in the three cases shown in Figure 5 are each about 25 years.

The measurements of tritium in waters of the Norris Geyser Basin made by Pearson and Truesdell (1978) provide a way of choosing between two values of T resulting from the values of W between 70 and infinity. Tritium (half-life of 12.3 years), although naturally produced in the atmosphere, is today overwhelmingly the result of atmospheric thermonuclear testing between 1953 and 1963. Twenty nine of the 37 springs that Pearson and Truesdell (1978) analyzed had undetectable tritium ($< 0.5 \text{ TU}$;

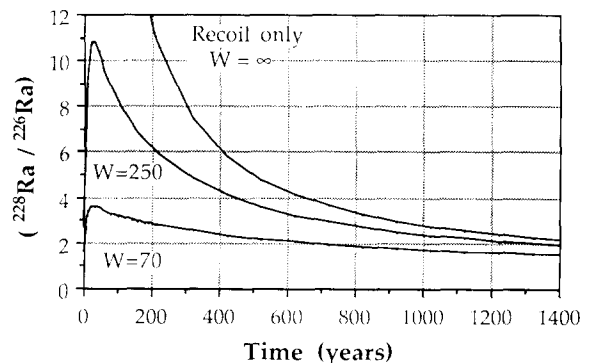


Fig. 5. Plot of equation (11) on $^{228}\text{Ra}/^{226}\text{Ra}$ versus time axes for $W = 70, 250, \text{ and } \infty$.

note that $TU = 10^{-18}$ atoms tritium per atom hydrogen); five off the springs had values between 5 and 30 TU. Pearson and Truesdell (1978) concluded that these springs are mixtures of waters derived from a cold surface reservoir with a short mean residence time carrying from a cold surface reservoir with a short mean residence time carrying the bomb tritium signature and a thermal reservoir which contains no tritium indicating water supply prior to 1953. (This would be 34 years before the time of our sampling.) Therefore, the water-rock reaction times must be greater than 34 years based on the tritium data.

The maximum reaction time based on ($^{228}\text{Ra}/^{226}\text{Ra}$) would be obtained if production of radium were entirely by recoil (i.e. $W = \infty$). The maximum age allowed is for the infinite value of W for a mean ($^{228}\text{Ra}/^{226}\text{Ra}$) of 3.5 ± 1 for the Norris Geyser Basin, is 1150 years. The high concentration of cations found in the typical chloride-neutral Norris Geyser Basin springs and the degree of alteration found in cores from the region (see Sturchio et al., 1986; White et al., 1988) indicate that rock reaction with the thermal water has occurred.

Assuming $W = 250$, based on our previous discussion, the length of time for the water-rock reaction in the hydrothermal system prior to expansion and delivery to the surface is between 350 years and 950 years (2σ error) with the most likely time being about 540 years (see Figure 6).

The size of the hot water reservoir beneath the Norris Geyser Basin can be determined from the water-rock reaction time and the flux of water out of the basin. White et al. (1988) calculated an average flux of 95 g s^{-1} during 1966–1967. Assuming a chloride concentration of 310 ppm for the parent hydrothermal water, $9.7 \times 10^9 \text{ kg}$ of hydrothermal water leaves the reaction zone each year. Using the most likely high temperature reaction time of 540 years the hot water reservoir size is $5.2 \times 10^{12} \text{ kg}$.

The Galapagos and East Pacific Rise hydrothermal vent systems have water-to-rock ratios

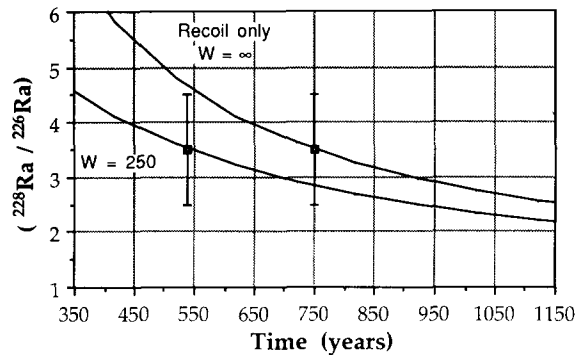


Fig. 6. Plot of equation (11) on $^{228}\text{Ra}/^{226}\text{Ra}$ versus time axes for $W = 250$ and ∞ . Plotted on the calculated curve is the average Norris Geyser Basin spring with 2σ error bars.

of about 5 and mean reaction times of about 40 years (Turekian and Cochran, 1986). These differences from Yellowstone in both water-to-rock ratio and reaction times may be due to the low pH and high salinity of the oceanic systems relative to the continental Yellowstone system and to the concentration of the heat sources: immediate in the marine hydrothermal and more diffuse in the continental system.

Conclusions

(1) The two major hot-spring types in the Norris–Mammoth Corridor are defined by ($^{228}\text{Ra}/^{226}\text{Ra}$) and conform to the chloride vs distance plots in keeping with the model of White et al. (1988).

(2) The ($^{228}\text{Ra}/^{226}\text{Ra}$) of the Norris Geyser Basin springs are effectively the same and yield a reaction time of about 540 years for the hot, primarily meteorically derived, water with the surrounding rocks in the source region of the springs. This reaction time estimate assumes that about 250 g of water are needed to alter one gram of aquifer rock.

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