Radiogenic and stable isotope studies of hot-spring deposits in Yellowstone National Park and their genetic implications

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Samples of travertine and siliceous sinter from hot-spring deposits in Yellowstone National Park of northwestern Wyoming have been analyzed for light stable (carbon and oxygen) and radiogenic (lead and strontium) isotopes. The Hillside Springs travertine contains significantly lighter $\delta^{13}\text{C}$ than the previously studied Mammoth travertine. Although this relation could indicate a component of magmatic carbon, more likely it reflects a higher temperature of precipitation for Hillside Spring travertine. Our data on Mammoth travertine shows it to have been precipitated substantially below the orifice temperature. The oxygen isotope data on the newly analyzed deposits confirm the previous studies that found the hot-spring waters to be dominated by meteoric water. The lead isotope data show that there is a sedimentary component of lead in all the hot-spring deposits analyzed, including those inside the caldera limits. Either long lateral migration of waters are involved in the recharge of the springs or there must be sediments buried at some unknown depth beneath the volcanic rocks inside the caldera because no sediments are known at the surface. The high rainfall inside the limits of the caldera would favor sediments buried at depth.

INTRODUCTION

Geothermal power has gained increasing importance in recent years (WHITE, 1969, 1971; MAHON, 1971; ELLIS, 1971). Information about sources of water and recharge areas is necessary in understanding the behavior of hydrothermal systems. In this paper we present Pb and Sr isotopic analyses of siliceous and carbonate hot-spring deposits in Yellowstone National Park, U.S.A., and similar analyses of sedimentary and volcanic rocks in that area in an attempt to trace the origin of thermal waters there. In particular, an important question is whether these waters contain a magmatic component. Such a magmatic component, if any exists, should be easier to detect in an area such as Yellowstone Park, where present-day hydrothermal activity is closely associated with voluminous rhyolitic volcanism. For this purpose, isotopic tracers (e.g., Pb and Sr) are more sensitive than chemical properties as indicators of the kinds of rocks that could have equilibrated with the thermal waters. Of course, conclusions derived from this approach have direct application only to the origin of Pb and Sr in

the hydrothermal deposits.

For some years, the U.S. Geological Survey and independent scientists have studied the Yellowstone hydrothermal systems, and considerable information is available on the (stable) isotopic and chemical compositions of thermal waters in the area and the regional geology and geophysics. Quaternary volcanism at Yellowstone comprised three main cycles of activity which culminated about 1.9, 1.2, and 0.6 m.y. ago, respectively, with eruption of enormous rhyolite ash flows and collapse of the volcanic source area to form calderas (CHRISTIANSEN and BLANK, 1972; written commun., 1976). Rhyolite flows erupted from ring fractures associated with the youngest caldera at least as recently as 70,000 years ago (EATON *et al.*, 1975). The presently active thermal systems at Yellowstone probably date from this youngest magmatic insurge. Geophysical evidence (EATON *et al.*, 1975) strongly indicated the presence of a large magma body at relatively shallow depth beneath large parts of the Yellowstone Plateau, thus the source of heat in the park's hydrothermal systems is predominantly magmatic. Current hydrothermal activity is concentrated near ring-

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Table 1. Samples analyzed in this study

Map. No.	Sample No.	Description
1	Y10-6.7	Travertine core, drill hole Y10 (WHITE <i>et al.</i> , 1975), Mammoth Terrace, Mammoth Hot Springs
1	YM-293	Travertine, New Highland Terrace, Mammoth Hot Springs
1	YM-382	Water collected at 73°C, New Highland Spring, Mammoth Hot Springs
2	YM-294	Travertine Terrace Mountain, inactive springs
3	W705-C2	Manganiferous travertine, East Black Warrior Lake, Lower Geyser Basin
4	YM-204	Manganiferous travertine, Hillside Spring, Upper Geyser Basin
4	W705-E2	Siliceous sinter, Sapphire Geyser, Upper Geyser Basin
-	6YR-158	Madison Limestone (Mississippian) (RUPPEL, 1972)
-	7YR-249	Composite sample of Mesozoic limestones of the Sawtooth, Rierdon, Swift, Morrison and Kootenai Formations (RUPPEL, 1972)

Fig. 1. Map of Yellowstone National Park (heavy dashed boundary) showing distribution of hot spring deposits (black areas) and sample localities (numbers, see Table 1 for description) with respect to structural features of Yellowstone caldera. The caldera rim is shown by solid line (where mappable) and dotted line (where inferred). Major ring-fracture zones are shown by light dashed line and areas of resurgent rhyolite domes are shown by stippled pattern. Map is simplified from one provided by R. L. CHRISTIANSEN (written com. 1975).

fracture zones and along a linear north-south trending fault zone (the Norris-Mammoth corridor). Most thermal springs with significant discharge rates lie within the caldera formed 0.6 m.y. ago (Yellowstone caldera). A major exception to this generality is Mammoth Hot Springs, which occur at the north end of the Norris-Mammoth corridor, outside of the caldera

proper. The Mammoth springs are situated on predominantly sedimentary strata of late Paleozoic and Mesozoic age (RUPPEL, 1972), whereas springs located within the caldera issue mainly from volcanic rocks or volcanistic sediments. In this study we analyzed hot-spring deposits from both within and outside the caldera rim to determine if any differences in isotopic composition exist between waters issuing from volcanic rocks and those that come from sedimentary rocks. We reasoned that magmatic Pb or Sr would be most easily detected in waters from springs located within the caldera because these waters are most likely to interact *via* deep convective circulation with the cooling magma body beneath the park. Descriptions of the analyzed samples are given in Table 1 and their locations are shown in Fig. 1.

CHEMICAL COMPOSITIONS OF THERMAL WATERS

The wide diversity of hot spring types and water compositions found at Yellowstone National Park has led many investigators to conclude that many discrete hydrothermal systems have operated. Recently, TRUESDELL and FOURNIER (1976) have suggested that these systems are separate only near the surface and that all can be related to a single large geothermal aquifer at depth which contains dilute brine at 340° to 370°C. According to their model, this deep thermal water cools by expansion and evaporation as it ascends into near-surface geyser and hot-spring systems where it undergoes differing degrees of dilution with cold meteoric water, reaction with rocks, and further steam loss to produce the various hot-spring waters. Regardless of which view is taken, the Cl⁻-rich

Table 2. Chemical composition of the springs studied

	T(°C)	pH	ppm Si	ppm Ca	ppm Na	ppm K	ppm HCO ₃ ⁻	ppm SO ₄ ⁼	ppm Cl ⁻
Mammoth Hot Springs	69-75	6.3-6.9	46-60	209-338	122-143	42-69	526-871	477-578	161-170
Black Warrior Lake (vent)	93	7.3	199	14	89	13	150	26	52
Hillside Springs	86	6.5-7.4	175-190	8.4	124-145	6.9-8.3	246-252	12-17	66-72
Sapphire Geyser	90-95	8.1-9.2	320-355	0.3-1.6	412-445	16-20	332-406	14-55	296-308

Note: All data in this table are taken from ROWE *et al.* (1973).

acid waters of Norris Geyser Basin are believed to be most representative of deep-seated thermal waters, although even these waters probably are diluted by meteoric water. Chemical compositions of several other kinds of thermal water in the park are briefly summarized below.

Significant differences in chemical composition are found between the thermal waters from Mammoth Hot Springs and those from within the caldera (ROWE *et al.*, 1973). Partial chemical analyses of waters from the springs studied in this paper are given in Table 2. Aquifer temperatures inferred from dissolved silica content and direct drilling range from about 170° to 250°C for intracaldera springs having large discharge rates, as compared to about 72°C for Mammoth (FOURNIER and ROWE, 1966; FOURNIER and TRUESDELL, 1971; and WHITE *et al.*, 1975). The latter figure agrees closely with orifice temperatures measured at Mammoth (FRIEDMAN, 1970; ROWE *et al.*, 1973). Na/K ratios in Mammoth spring waters are significantly lower than those in intracaldera thermal waters. This difference may result from equilibration of thermal waters in the two areas with different mineral buffers in their respective aquifers. Other important differences between waters at Mammoth and those in the caldera, such as comparatively high SO₄⁼, Ca, and HCO₃⁻ in the Mammoth water, may result from equilibration of the Mammoth water with marine evaporites and limestones. In addition, mixture of cold meteoric water with thermal water may have contributed to increased solubility of calcite at Mammoth (TRUESDELL and FOURNIER, 1976). Waters of Black Warrior Lake (vent) differ from most intracaldera thermal waters in having lower Na/K and Cl⁻. Because the Black Warrior springs have extremely large discharge rates, FOURNIER and TRUESDELL (1971) suggested that the low present-day Na/K ratios have resulted from previous leaching of Na-bearing minerals from the aquifer. ROWE *et al.* (1973) consider Black Warrior water typical of hot-spring waters that have been diluted by meteoric water at shallow

depth. Hillside Spring water closely resembles that at Black Warrior Lake. Sapphire Geyser water is typical of dilute thermal water that is high in HCO₃⁻ as the result of extensive near-surface water-CO₂-rock reaction (TRUESDELL and FOURNIER, 1976).

STABLE ISOTOPE STUDIES

CRAIG (1963) has shown that CO₃⁼-rich thermal waters at Mammoth Hot Springs have δD and δ¹⁸O values close to those of local streams and precipitation, and that deviations from these values (most pronounced in acid, boiling pools) follow an evaporation trend. Thus, acid, SO₄-rich waters, such as those in Upper Geyser Basin, are probably derived by evaporation of mixed groundwater and deep-seated water, with oxidation of H₂S to H₂SO₄. CRAIG concluded mainly from studies of other geothermal systems that most (> 95%) of the discharge volume of such thermal waters is of direct meteoric origin (CRAIG *et al.*, 1956). MAZOR and WASSERBURG (1965) found a scarcity of ⁴⁰Ar and other rare gases in Yellowstone Park thermal waters, also providing evidence against the presence of a significant amount of magmatic gas component. CRAIG (1963) also noted that δ¹³C values (in HCO₃⁻, CaCO₃, and CO₂) in Yellowstone Park hot springs were closely similar to those in marine limestones, and he suggested that C in the hydrothermal systems is principally derived from limestone or exchanged with C in limestone to such an extent that another source cannot be recognized.

It Table 3, we present new C and O isotopic analyses of two travertines from the Mammoth area and one from Hillside Springs. The Mammoth area travertines have δ¹³C and δ¹⁸O values in the range of those reported by FRIEDMAN (1970), and the Hillside travertine is significantly lighter in δ¹³C, but all values are near the range for marine carbonates. The temperature dependence of C and O isotopic fractionations between thermal waters and pre-

Table 3. Carbon and oxygen isotopic compositions

Sample	$\delta^{13}\text{C}^a$ ‰	$\delta^{18}\text{O}^a$ ‰
Y10-6.7 ^b	2.7	4.12
Mammoth travertine		
YM-294 ^b	4.83	9.34
Terrace Mtn. travertine		
YM-204 ^b	-0.98	1.54
Hillside Springs travertine		
Values for Yellowstone Park hot springs (CRAIG, 1963; FRIEDMAN, 1970)		
CaCO ₃	+2 to +5	+2 ^c
HCO ₃ ⁻	-3 to +1	-
CO ₂	-5 to -2	-
Marine limestone (FRIEDMAN, 1970)	-2.3 to +3.3	+17.7 to +25.6
Magmatic (FUEX and BAKER, 1973; DEINES and GOLD, 1973; TAYLOR, 1968)	-9 to -5	+6 to +9

^aNote: all carbon and oxygen analyses are referred to the PDB and SMOW standards, respectively.

^bAnalyst: J. WHELAN.

^cValue taken for travertine deposited at 73°C at spring orifice, Mammoth Hot Springs; coexisting water had $\delta^{18}\text{O} = +18.11$ ‰.

Fig. 2. Relations between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in travertines from Yellowstone National Park. Analyses from this paper are shown as triangles; open circles represent orifice travertine from Mammoth Hot Springs (MHS); stippled equilibrium and disequilibrium trends are shown for two springs at MHS (FRIEDMAN, 1970); open squares represent Phanerozoic limestones from the Gardiner area (FRIEDMAN, 1970). Carbonates in altered rocks from Wairakei, New Zealand (CLAYTON and STEINER, 1975) and Salton Sea, California (CLAYTON *et al.*, 1968), hydrothermal systems are shown for reference.

cipitated travertines is clearly demonstrated in FRIEDMAN's (1970) study of Mammoth Hot Springs (see Fig. 2). The results of that study

suggest that our samples of Mammoth travertine precipitated at temperatures substantially below that of the present-day orifice (about 73°C). In fact, the Terrace Mountain travertine probably formed slowly in a cold proglacial lake.

FRIEDMAN (1970) showed that Mammoth waters presently discharge with $\delta^{18}\text{O}$ values of about -18.1 permil at their orifice temperature. If it is assumed that Hillside Spring travertine precipitates at a similar temperature ($T = 86^\circ\text{C}$ for issuing water, Table 2), $\delta^{18}\text{O}$ in the equilibrium water would be about -18.5 permil. In neither of these hot springs does the thermal water reflect equilibration with marine carbonates, with fresh volcanic rock like the local rhyolites (FRIEDMAN *et al.*, 1974; FRIEDMAN, pers. com. 1975) or altered rocks like those in the Salton Sea (CLAYTON *et al.*, 1958) or Wairakei (CLAYTON and STEINER, 1975) hydrothermal systems (see Fig. 2). Oxygen in the Yellowstone thermal waters probably is buffered by oxygen in the large volumes of meteoric water circulating in that hydrothermal system, and exchange with reservoir rocks probably is comparatively insignificant.

SCHOEN and RYE (1970) found a small range of $\delta^{34}\text{S}$ values in H_2S (+0.7 to +2.6 permil) and native S (-1.7 to +1.4 permil, relative to coexisting H_2S) for springs within the caldera or close to the ring fracture zone (including Norris Geyser Basin). They concluded that most of the H_2S rising to the surface in these areas comes either from a body of degassing magma or from igneous rocks containing unfractionated

sulfur. In contrast, respective $\delta^{34}\text{S}$ values for H_2S and S at Mammoth are -3.0 and -8.4 permil. The depletions in ^{34}S indicated by these values were tentatively attributed to the presence of a sedimentary component (H_2S baked out of underlying sediments) and bacterial oxidation of H_2S to form light S. Water at Mammoth Hot Springs contained very heavy SO_4^{2-} ($\delta^{34}\text{S} = +20.5$ permil), compared with SO_4^{2-} from other areas ($\delta^{34}\text{S}$ ranged from $+1.8$ to 3.3 permil), suggesting that sulfur in the Mammoth water was derived largely from marine evaporites.

LEAD AND STRONTIUM ISOTOPIC TRACER STUDIES

Radiogenic isotopes are potentially useful in elucidating the origin of thermal waters if representative end-member components can be analyzed, and if variations in isotopic composition in these materials are sufficiently large compared with analytical uncertainties. Pb and Sr isotopic ratios measured for hot spring deposits can confidently be considered representative of those ratios in the associated thermal waters because, unlike constituents or light stable isotopes, the heavy nuclides are not significantly fractionated during chemical reactions. Variations in Pb and Sr isotopic composition in hot-spring deposits may result from mixing in variable proportions of Pb and Sr derived from two or more reservoirs. At Yellowstone National Park we are concerned with two major reservoirs: rhyolitic lavas and tuffs (these are considered representative of a rhyolitic magma body at depth), and sedimentary rocks exposed outside of Yellowstone caldera. Because the Pb and Sr contents of meteoric waters are generally quite low (WEDEPOHL, 1974; TUREKIAN, in press), isotopic compositions of these elements probably will be dominated by Pb and Sr in the rocks in contact with such waters.

We have analyzed numerous samples of rhyolite lava and tuff, a sample of Mississippian Madison Limestone, and a composite sample of Mesozoic sedimentary rocks from the area near Mammoth Hot Springs. Our sampling of rhyolitic rocks covers the entire chronological and spatial distribution of rhyolites at Yellowstone, and is therefore considered representative of the range in isotopic composition of these rocks. Such variations as occur are relatively small in magnitude and are briefly described below. Our sampling of the sedimentary column

is admittedly minimal, but because the analyses are similar to those of other limestones of similar age (see below), we consider them at least indicative.

Pb isotopic analyses were carried out using either the PbS method (DOE *et al.*, 1967) or the silica gel- H_3PO_4 method (CAMERON *et al.*, 1969), and a 12-inch-radius NBS mass spectrometer. Samples were dissolved in dilute HCl (carbonates) or in HF-HClO_4 (silicates), and Pb was extracted using dithizone (only for samples analyzed by the PbS method), anodic electrodeposition or HBr cation exchange. Blanks were about 50 ng/g sample during early stages of this work and were reduced to about 10 ng/g sample during later stages when samples with very low Pb contents were processed. All isotopic ratios were corrected for mass fractionation in the spectrometer *via* intercomparison with the NBS common lead standard and BCR-1 reference sample. Isotopic ratios reported relative to ^{204}Pb are believed accurate to $\pm 0.15\%$, or better in the case of the silica gel analyses. Sr isotopic analyses were carried out on a 6-inch-radius mass spectrometer with digital recording of data. Normalized $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are adjusted to a value of 0.7080 for the E & A SrCO_3 reference standard, and are believed accurate to ± 0.0003 . All concentration data for Pb, U, Th, Rb, and Sr were determined by isotope dilution and are believed accurate to $\pm 5\%$ or better.

Strontium isotopic ratios and Rb and Sr contents of travertines, thermal water from Mammoth, sedimentary rocks, and several rhyolites are given in Table 4. Three travertines from the Mammoth area have essentially the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.710) as the water collected there, whereas travertine from Black Warrior Lake, within the caldera, has a slightly higher value. These variations are not large and may not be geologically significant. The two limestones differ greatly: the Madison Limestone has about the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as the travertines, and the leach (carbonate) fraction of the Mesozoic limestone has a much lower value. The residue (clastic) fraction of Mesozoic limestone contains rather radiogenic Sr, which is consistent with a detrital provenance having an apparent middle to late Paleozoic age. Present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Yellowstone Park rhyolites are also fairly radiogenic, increasing with increasing Rb/Sr. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios corrected for *in situ* decay of ^{87}Rb since the rocks crystallized, or such ratios measured in

Table 4. Strontium isotopic compositions and contents of rubidium and strontium in selected travertines, sediments and volcanic rocks

Sample		ppm Rb	ppm Sr	$\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$	Rb/Sr
<i>Travertines</i>					
1	Y10-617 leach	0.13	1610.	0.7106	0.00008
2	YM-294 leach	—	—	0.7103	
3	YM-293 leach	—	—	0.7103	
4	W-705-C2 leach	—	—	0.7111	
<i>Water, Mammoth Hot Springs</i>					
4	YM-382	0.30	1.7	0.7103	0.177
<i>Sedimentary carbonates</i>					
6	6YR-158 leach	0.50	40.7	0.7109	0.0123
7	7YR-249 leach	1.73	356.	0.7074	0.00486
8	7YR-249 residue	34.9	59.	0.7186	0.592
9	7YR-249 whole rock (calc)	11.	273.	0.7081	0.0403
<i>Rhyolites</i>					
10	6YC-138	221.	18.	0.7121	12.3
11	YR-3	289.	2.4	0.7276	120.
12	YR-5	181.	20.5	0.7130	8.82
13	YR-6	165.	36.9	0.7115	4.47

Analysts: W. T. HENDERSON and R. A. HILDRETH (Nos. 1-10), W. I. MANTON (Nos. 11-13, pers. com. 1970).

feldspar separates having low Rb/Sr, (DOE, CHRISTIANSEN, HEDGE and LEEMAN, unpublished data), are less radiogenic and much more uniform, averaging about 0.710. These values might be more representative of the isotopic composition of Sr in the magma chamber beneath the park.

Although material balance models can be made to account for the isotopic composition of Sr in the park's thermal waters, such calculations give no unique result because the analyzed reservoir rocks are so similar in $^{87}\text{Sr}/^{86}\text{Sr}$ to the travertines. Sr in the thermal waters could be derived from (1) a cooling rhyolitic magma body, (2) limestone like the Madison, or (3) a combination of nonradiogenic Mesozoic limestone and rhyolitic lavas and tuffs. Although the travertines have high Sr contents, the waters from which they precipitate contain little Sr (about 2ppm). Thus any or all of the potential Sr reservoir rocks we analyzed may be important in the overall Sr budget, with the exception of the low-Sr rhyolites. Basalts in Yellowstone Park typically contain about 300ppm Sr, and have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios close to 0.706. However, basaltic rocks are present only in small volumes and are not considered as significant reservoir rocks.

Lead isotopic ratios and Pb, U, and Th contents are given in Table 5 for rhyolites (only

our silica gel analyses are given), and Table 6 for hot spring deposits and sediments at Yellowstone. We do not intend to discuss here the petrogenetic significance of these data, but it is of interest that Yellowstone Park basalts (DOE, CHRISTIANSEN, HEDGE and LEEMAN, unpublished data) have lead isotopic compositions in the same range as the rhyolites. Leads in Yellowstone Park rhyolites can be distinguished into three main compositional groups: (1) the extensive ash flows and the voluminous rhyolite flows which preceded them, which have $^{206}\text{Pb}/^{204}\text{Pb}$ ratios between 16.88 and 17.30; (2) intracaldera flows with $^{206}\text{Pb}/^{204}\text{Pb}$ ratios ranging from 17.55 to 17.63; and (3) flows outside the caldera with values less than 16.9. Both (2) and (3) apply to rhyolites less than 0.6m.y. old. Possibly the post-caldera rhyolites which erupted outside the ring fracture zone (group 3) are more representative of lower crustal lead, whereas the late-stage intracaldera rhyolites (group 2) reacted with earlier emplaced granitic bodies contaminated with upper crust and through which the intracaldera rhyolites ascended. We also reanalyzed by the silica gel method two andesites from the Absaroka Volcanic Supergroup. PETERMAN *et al.* (1970) presented PbS analyses of these and other volcanic rocks. The Pb isotopic composition of Absaroka rhyolites and shoshonites overlaps

Table 5. Lead contents and isotopic compositions of selected rhyolites

Sample	Material	ppm Pb	$\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{208}\text{Pb}}{^{204}\text{Pb}}$	Geologic Unit	
1	YG-72-5	Glass	33.5	17.549	15.568	38.329	West Yellowstone flow
2a	720-76	Glass	32.8	17.631	15.595	38.335	Nez Perce flow
2b		Sanidine	27.6	17.622	15.590	38.323	
3	OCB66-13	Sanidine	—	17.553	15.546	38.229	Dry Creek flow
4	6YR-138	Glass	31.7	16.599	15.425	38.415	Cougar Creek flow
5	6YR-137	Glass	36.5	17.137	15.538	38.289	Obsidian Cliff flow
6a	2YR-118	Sanidine	—	16.871	15.470	38.003	Rhyolite from Snake River Butte
6b				16.892	15.492	38.049	
7	690-20	Sanidine	—	17.245	15.553	38.334	Rhyolite from Osborne Butte
8	OCB-563	Sanidine	—	17.291	15.573	38.447	Lewis Canyon Rhyolite
9	OCB-601	Sanidine	—	17.253	15.559	38.279	Mount Jackson Rhyolite
10	YG70-4	Sanidine	—	17.269	15.550	38.434	Upper Falls, Uncle Tom Parkin
11	6YC-146	Glass	31.3	17.299	15.544	38.415	Lava Creed Tuff, mbr. B
12	OCB66-01	Sanidine	—	16.995	15.491	38.057	Huckleberry Ridge Tuff, mbr. 8
13	P-496	Whole rock	14.7	16.260	15.350	36.678	Andesite from the Absaroka Volcanic Supergroup, Washburn center
14	7PD-1	Whole rock	11.9	16.521	15.389	36.888	Andesite from the Absaroka Volcanic Supergroup, Sunlight center

Note: all analyses in this table are by the silica gel technique and are corrected for mass fractionation during the analysis.

Analysts: W. P. LEEMAN (Nos. 1, 2a, 2b, 6b, 8, 9, 13, 14) and M. H. DELEVAUX (Nos. 3, 4, 5, 6a, 7, 10, 11, 12).

Table 6. Lead, uranium and thorium contents and lead isotopic compositions of selected travertines and sedimentary carbonates

	ppm Pb ^c	ppm U ^c	ppm Th ^c	$\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{208}\text{Pb}}{^{204}\text{Pb}}$
Y10-6.7	Travertine core, Mammoth Hot Springs, active area ^a					
Leach	0.034	0.014	0.001	18.32	15.63	38.09
Residue	0.14	0.35	0.04	—	—	—
(0.93%)						
YM-294	Travertine, Terrace Mountain ^b					
Leach	—	0.032	0.030	17.704	15.59	38.33
	0.122	0.030	0.030	17.695	15.59	38.31
Residue	4.7	1.61	3.42	—	—	—
(0.16%)						
W705-C2	Manganiferous travertine, East Black Warrior, Lower Geyser Basin ^b					
Leach	12.7	1.6	0.2	17.726	15.67	38.55
Residue	7.5	1.95	1.6	—	—	—
Whole rock	—	—	—	17.762	15.71	38.65
W705-E2	Siliceous sinter, Sapphire Geyser, Upper Geyser Basin ^a					
Whole rock	0.3	0.4	0.1	18.017	15.600	38.379
6YR-158	Madison Limestone (Mississippian) ^a					
Leach	10.2	—	—	20.173	15.923	39.561
7YR-249	Mesozoic limestone composite ^b					
Leach	4.51	1.40	1.32	19.305	15.67	38.82
Residue	3.75	1.84	2.90	18.988	15.74	39.38
(28.3%)						

^aIsotopic composition analyzed by W. P. LEEMAN, using silica gel.

^bIsotopic composition analyzed by B. R. DOE, using PbS-NH₄OH.

^cAll concentration analyses are by DOE, except for sample 6YR-158 (LEEMAN).

that of Yellowstone Park, but the Absaroka andesites contain less radiogenic Pb that may be representative of lower crustal Pb.

Lead in the Madison Limestone and in the Mesozoic limestone composite is quite radiogenic, with $^{206}\text{Pb}/^{204}\text{Pb}$ ratios greater than 19.0. This radiogenic character is typical of leads from marine limestones (DOE, 1970), and may reflect deposition in the ocean basins of radiogenic lead derived from weathering of old continental crustal material having high U/Pb ratios. The carbonate fraction of the Mesozoic composite contains more radiogenic lead than the clastic fraction. Although our sampling of the sedimentary section is minimal, the similarity of our samples to other marine limestones (Fig. 3) suggests there is a distinct isotopic difference between leads in Yellowstone's sedimentary rocks and leads in the rhyolites.

Isotopic compositions of lead in the hot-spring deposits vary slightly, but all have $^{206}\text{Pb}/^{204}\text{Pb}$ ratios between those of the rhyolites and the sediments, and these ratios plot close to a line between the two fields representing those rock types in a $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ plot (Fig. 3). Such linear arrays occasionally have been interpreted as secondary isochrons, but in this case the array almost certainly represents mixing of volcanic and sedimentary lead in the thermal waters. There is no consistent correlation between isotopic composition and locality of the hot springs. Leads in travertine from Mammoth Hot Springs and Terrace Mtn., both located outside the caldera, have the highest and lowest $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, respectively,

whereas lead in siliceous sinter from Sapphire Geyser has a ratio between these two values and lead in travertine from Black Warrior Lake has a composition close to that at Terrace Mtn. Systematics in the $^{208}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ diagram are not as straight forward, mainly because $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are more variable in the reservoir rocks, but the diagram is consistent with the mixing hypothesis. Without information on the partitioning of Pb between travertine or sinter and thermal waters, or more detailed study of the sediments, we cannot present a quantitative assessment of the mixing relations. Nevertheless, it appears that lead in hot springs, even within the caldera, contains a significant amount of component derived from the sedimentary section. None of the hot spring deposits seem to contain lead solely of volcanic origin.

CONCLUSIONS

Chemical and isotopic studies of hydrothermal systems in Yellowstone National Park indicate that the minor element composition of thermal waters is derived from complex interaction with two main reservoirs: (1) the volcanic rocks and/or the subjacent magma chamber, and (2) the sedimentary (and minor igneous) rocks underlying the park and in the drainage areas for meteoric waters at the park. The sedimentary reservoir is expectedly diverse in composition and has not yet been adequately sampled. On the other hand, the Yellowstone volcanic-plutonic reservoir can be characterized reasonably well on the basis of present sampling. With these limitations in mind, the thermal waters appear to contain significant amounts of components of both volcanic and sedimentary Pb and Sr. C and S (at Mammoth Hot Springs) are derived mainly from the sedimentary reservoir, and H and O are believed to be predominantly meteoric. Thus the amounts of these elements contained in the various hot springs are controlled by the dominant reservoirs for each element. It should be noted that the volcanic Pb (and Sr) detected in Yellowstone Park hot springs may be derived entirely by leaching of volcanic rocks and does not necessarily indicate a direct magmatic water component. The presence of significant amounts of sedimentary Pb in all the hot springs studied within Yellowstone caldera indicates that sedimentary rocks are present in the aquifers of these springs. Involvement of sediments also seems likely on the basis of field observations, because travertine is found within the caldera, and formation of travertine

Fig. 3. Lead isotope systematics for volcanic rocks, hot spring deposits, and limestones from Yellowstone National Park. Analyses of Paleozoic limestones from Colorado and Nevada are shown for comparison (DOE, 1976).

through leaching of silicate volcanic rocks is unlikely. The presence of the travertine and the isotopic evidence could be taken to indicate the presence of sedimentary rocks somewhere within the caldera. Although the presence of such rocks at depth cannot be precluded, the mapping of R. L. CHRISTIANSEN (written commun., 1976) indicates that they are at least scarce at the surface of the caldera. If sedimentary rocks are indeed absent within the caldera, the conclusion would be that much of the water circulating through the Yellowstone hydrothermal systems is derived from recharge areas well outside the caldera ring-fracture zone. This conclusion would also require the travertine forming components to be introduced to the area. Therefore, no unique conclusion can be reached as to the location of the sediments, but, because the major rainfall in the area occurs within the caldera, the favored interpretation is that sedimentary rocks must exist at depth within the caldera limits.

This study illustrates the utility of tracer studies of hydrothermal systems, particularly when several isotopic systems are employed. Under favorable conditions, information can be obtained regarding the nature of reservoir rocks, elemental budgets, and hydrologic characteristics of such hydrothermal systems.

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