The Waters of Hot Springs National Park, Arkansas—Their Nature and Origin

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GEOHYDROLOGY OF GEOTHERMAL SYSTEMS

GEOLOGICAL SURVEY PROFESSIONAL PAPER 1044–C

Prepared in cooperation with the National Park Service

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1979

UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, *Secretary*

GEOLOGICAL SURVEY

H. William Menard, *Director*

Library of Congress Cataloging in Publication Data

The Waters of Hot Springs National Park, Arkansas—their nature and origin.

(Geohydrology of geothermal systems) (Geological Survey Professional Paper 1044-C)
Bibliography: p. C32-C33.
Supt. of Docs. no.: I 19.16:1044
1. Hot springs—Arkansas—Hot Springs National Park. I. Bedinger, M. S. II. United States. National Park Service. III. Series. IV. Series: United States. Geological Survey. Professional paper ; 1044-C.
GB1198.3.A8W37 551.2'3'0976741 77-608354

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402

Stock Number 024-001-03199-0

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ABSTRACT

The 47 hot springs of Hot Springs National Park, Ark., issue from the plunging crestline of a large overturned anticline, along the southern margin of the Ouachita anticlinorium, in the Zigzag Mountains. Rocks in the vicinity of the hot springs range in age from Ordovician to Mississippian. The rocks—cherts, novaculites, sandstones, and shales—are well indurated, folded, faulted, and jointed. The springs emerge from the Hot Springs Sandstone Member of the Stanley Shale near the anticlinal axis, between the traces of two thrust faults that are parallel to the axis of the anticline.

The combined flow of the hot springs ranges from 750,000 to 950,000 gallons per day (3.29×10^{-2} to 4.16×10^{-2} cubic meters per second). The flow of the springs is highest in the winter and spring and is lowest in the summer and fall. The temperature of the combined hot-springs waters is about 62 degrees Celsius.

The radioactivity and chemical composition of the hot-water springs are similar to that of the cold-water springs and wells in the area. The dissolved-solids concentrations of the waters in the area generally range from 175 to 200 milligrams per liter. The main differences in the quality of the hot water, compared with nearby cold ground waters, are the higher temperatures and the higher silica concentrations of the hot springs. Cold waters in the area generally range from 15.0 to 26.8 degrees Celsius. The silica concentrations of cold ground waters range from 2.6 to 13.0 milligrams per liter, whereas the silica concentration of the hot springs is about 42 milligrams per liter. The high silica concentration of the hot springs is due to the increased solubility of silica in hot water. The silica concentration of the hot springs indicates that the maximum temperature reached by the hot-springs water is no more than a few degrees higher than the temperature at which the springs emerge.

The tritium and carbon-14 analyses of the water indicate that the water is a mixture of a very small amount of water less than 20 years old and a preponderance of water about 4,400 years old. The deuterium and oxygen-18 concentrations of the hot-springs waters are not significantly different from those of the cold ground waters.

The presence of radium and radon in the hot-springs waters has been established by analyses. Recent (1973) analysis showed the radium concentration to be 2.1 picocuries (10^{-12} curies) per liter. Analyses made in 1953 of the radon gas, a radioactive decay product of radium, ranged from 0.14 to 30.5 nanocuries (10^{-9} curies) per liter.

Mathematical models were employed to test various conceptual models of the hot-springs flow system. The geochemical data, flow measurements, and geologic structure of the region support the concept that virtually all the hot-springs water is of local, meteoric origin. Recharge to the hot-springs artesian-flow system is by infiltration of rainfall in the outcrop areas of the Bigfork Chert and the Arkansas Novaculite. The water moves slowly to depth where it is heated by contact with rocks of high temperature. Highly permeable zones, related to jointing or faulting, collect the heated water in the aquifer and provide avenues for the water to travel rapidly to the surface.

INTRODUCTION

PURPOSE OF THE STUDY

The thermal springs of the Hot Springs National Park, at Hot Springs, Ark. (fig. 1), have been a natural resource of international renown for many years. The springs were known to President Thomas Jefferson, who initiated the first scientific study in 1804. This study, by William Dunbar and George Hunter, marked the beginning of an era of scientific curiosity as to the origin and heat source of the springs.

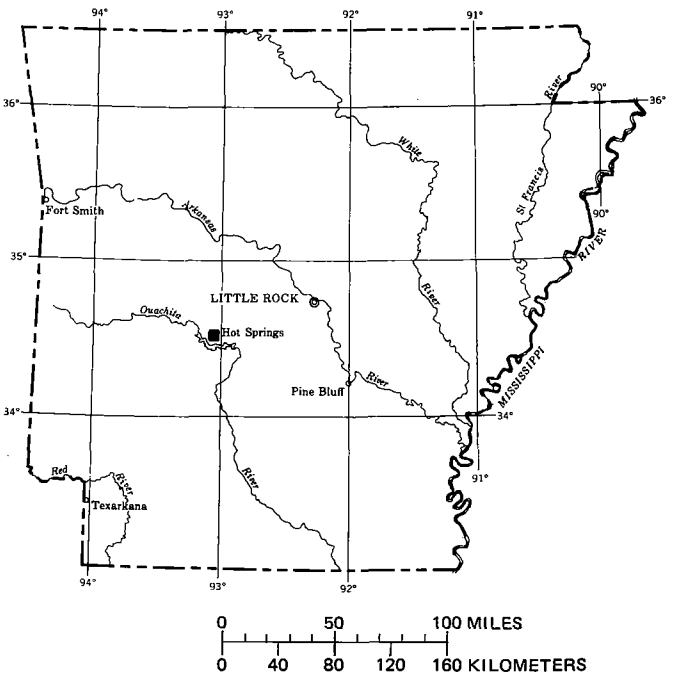


FIGURE 1.—Location of study area.

Public interest in the hot springs has been focused primarily on the therapeutic value of the waters, and, in serving such interest, this also has been the focus of Federal management since the area was established as the Hot Springs Reservation in 1832. This emphasis did not change when direct Federal supervision was implemented in 1877, nor when the area was designated as a National Park in 1921. The purpose of the park today is to preserve and protect the hot springs for present and future generations.

Long-range planning for park uses takes into consideration, however, the prospect of a shifting of emphasis from therapeutic values of the spring waters to the scientific, esthetic, and recreational values of the park as a whole. The existence of the springs and their geologic and hydrologic setting as well as their thermal characteristics play an important role in attracting visitors to the area. The purpose of this report is to describe the hot springs with reference to their flow, temperature, and chemical quality; to present information on the geologic framework of the hot springs flow system; and to define the nature of the hydrologic and geothermal flow systems as completely as possible with the data available.

METRIC UNITS

For those readers interested in using the metric system, metric equivalents of English units are given in parentheses. The English units in this report may be converted to metric units as follows:

To convert from— (English unit)	*Multiply by— (conversion factor)*	*To obtain— (metric unit)*
Inches (in)	25.4	Millimeters (mm)
Feet (ft)	3.048×10^{-1}	Meters (m)
Square miles (mi^2)	2.59×10^{6}	Square meters (m^2)
Gallons per day (gal/d)	4.38×10^{-8}	Cubic meters per second (m^3/s)
Feet per day (ft/d)	3.53×10^{-6}	Meters per second (m/s)
Curie	3.7×10^{10}	Becquerel (Bq)
Atmosphere	1.013×10^{5}	Pascal (Pa)

Chemical concentrations are given only in metric units—milligrams per liter (mg/L). For concentrations less than 7,000 mg/L, the numerical value is about the same as for concentrations in the English unit, parts per million.

The conversion from temperature in degrees Fahrenheit (°F) to temperature in degrees Celsius (°C) is expressed by: °C=(5/9)(°F−32). Kelvin=degrees Celsius+273.15.

ACKNOWLEDGMENTS

The authors are grateful for the advice, suggestions, and information given by many associates in Federal and State agencies, and for facts drawn from many published and unpublished reports. We are especially grateful to N. F. Williams, State Geologist, Arkansas Geological Commission, for his advice and interest in the study. Raymond B. Stroud, U.S. Bureau of Mines, and B. R. Haley, U.S. Geological Survey, provided advice and assistance on the geologic study. T. W. Carney, R. C. Cross, and P. A. Bailey, chemists, Arkansas Geological Commission, provided chemical analyses of rock samples. In the presentation of geothermal models, the authors especially acknowledge the assistance of M. L. Sorey of the U.S. Geological Survey. Mr. Sorey critically examined the flow models presented in the report and provided constructive criticism and technical assistance.

The authors are grateful for the cooperation and assistance of Garland Moore, Richard Ketcham, and Rock Comstock, of the National Park Service; Bernard Campbell, Superintendent, and Franklyn Hambly, Management Assistant, of the Hot Springs National Park, Ark., and Richard Rasp, Earl Adams, Lewis May, Bernie Braughton, Eugene Stringer, David Carpenter, and Alice Horner, also of the Hot Springs National Park. We also thank M. D. Bodden, J. C. Chemrys, C. T. Rightmire, and T. A. Wyerman, who provided ^{14}C, chemical, stable isotope, and tritium analyses of the samples collected in 1972.

HISTORY OF SPRING DEVELOPMENT AND SCIENTIFIC STUDY

The history of the hot-springs area has been documented in numerous publications, many of which present detailed accounts of some aspect of the springs' environment and the cultural development of the area. For the purposes of this report, therefore, and to minimize duplication, only those historic events and developmental practices that relate to the technical management of the springs are cited.

Early descriptions of the hot springs give different accounts of as many as 72 spring openings, in a belt about one-fourth mile long and a few hundred feet wide, along the southwest slope of Hot Springs Mountain. Excavation and covering of springs, to increase and concentrate flows and to protect the springs from contamination, have so altered the natural spring environment that it bears no resemblance to the original condition. Among the early investigators, Owen (1860) reported 42 springs; Glasgow (1860), 54 springs; Haywood (1902), 46 springs; and Hamilton (1932), 48 springs. In his detailed history of Hot Springs, Scully (1966, p. 139) reported 47 active springs, including 2 exhibition springs.

Prior to 1877 some of the springs were walled in and covered by masonry arches to protect them from contamination (Scully, 1966, p. 118). By the 1890's, most

of the springs were covered and a complicated piping system had evolved for supplying the bathhouses with hot water. In 1901 the springs were uncovered to give access for sampling, and chemical analyses were made by Haywood (1902). The spring enclosures were opened again in 1931 for cleaning; some of them were deepened, and the present-day (1974) collection system was constructed. The collecting system diverts the flow of 44 springs to a central reservoir, from which the water is redistributed to individual bathhouses. A map of the collection system is shown in figure 2. Since 1948 all the water delivered to the bathhouses has been metered. Excess water overflows into Hot Springs Creek when storage reservoirs are full.

Through the years (1860 to the present), at least 20 scientific investigations, directly or indirectly involving the hot springs, have been made. Although each study generally had a separate and specific objective, many of the investigators became sufficiently interested in the hot springs to try to explain the origin of the water and the source of the heat.

The chemical quality of water from the hot springs in Arkansas has been of great interest to man, probably since the hot springs were first discovered. One of the earliest scientific approaches to determine the concentration of the hot-springs waters is found in Branner's (1892) Annual Report for 1891, in which analyses of water samples collected in 1890 are tabulated in grains per gallon. At random times since 1890, analyses have been made for investigations. The purpose of many of these investigations has been to support some theraputic claim for the water or to determine whether the chemical concentration of the water has changed.

Most earlier investigators concluded that the waters discharged from the hot springs are of meteoric origin, having fallen as precipitation and recharged to the Bigfork Chert in the anticlinal valley lying just northwest, north, and northeast of Hot Springs. Some investigators have attributed some of the recharge to the outcrop of Arkansas Novaculite to the east of the hot springs. Another theory that has been regarded by some as having a degree of scientific validity is that the water may be of juvenile origin, that is, derived from the interior of the Earth and not having previously existed as atmospheric water.

Bryan (1922, p. 426) posed the question as to the meteoric, juvenile, or mixed origin of the waters discharged from the hot springs. He indicated (p. 447–448) that the juvenile theory is perhaps more satisfactory, although it rests on an insecure foundation in postulating (1) a special igneous mass that is discharging water owing to cooling and recrystallization and (2) a special fault fissure through which the water rises to the land surface. Bryan (p. 444) analyzed the merits of both the juvenile and the meteoric theories, but conceded that "a definite conclusion as to the ultimate origin of the water in the Hot Springs cannot now be reached." He pointed out (p. 443–444) that "If the water is juvenile there is presumably a constant supply, diminishing very gradually through the centuries in quantity and temperature * * * If * * * the water has a meteoric origin, it is variable in quantity, fluctuating with the seasons or with groups of years having heavy or light rainfall." Thus, Bryan recognized the critical value of precise measurements of temperature, discharge, and other parameters during a sufficient period of time to provide adequate data on which to base conclusions as to the water's origin.

Arndt and Stroud (1953) suggested a dual origin for the water. Meteoric water, they believed, entered the spring system through the lower division of the Arkansas Novaculite on Hot Springs and North Mountains. They calculated that this source of meteoric water could supply about one-sixth of the flow of the springs. The rest of the water, they considered, could be juvenile water rising from depth.

Proponents of the theory of meteoric origin of the spring waters include Weed (1902), Purdue (1910), and Purdue and Miser (1923). Purdue (1910, p. 283) described the geologic conditions supporting this view and identified the collecting area as the anticlinal valley between Sugarloaf and West Mountains. Most of the valley is underlain by the Bigfork Chert, a much-fractured formation of high permeability into which infiltrates water from precipitation. According to Purdue (p. 284), the occurrence of this formation in anticlinal valleys, with its highly inclined beds, affords the most favorable condition for the intake of water. He postulates further that the water passes through the Bigfork Chert, beneath the North Mountain syncline, and is forced upward into the Hot Springs anticline to emerge as the hot springs.

This suggested movement of water from the recharge area required geologic conditions that account for passage of the water through the Polk Creek Shale, Missouri Mountain Shale, and the Arkansas Novaculite, to discharge as it does from the Hot Springs Sandstone Member of the Stanley Shale. Such conditions would ordinarily require a fault or faults, with associated jointing and fissuring, that would provide passage through these formations. Several authors have shown such a fault (Arndt and Stroud, 1953; Fellows, 1966). Recent mapping by Haley and Stone (pl. 1) confirms the presence of a complex fault system in the area but indicates no conclusive evidence of a large fault at the hot springs. In addition to the faulting, the intensive folding and overturning of formations in the vicinity of Hot Springs are attended by intensive joint-

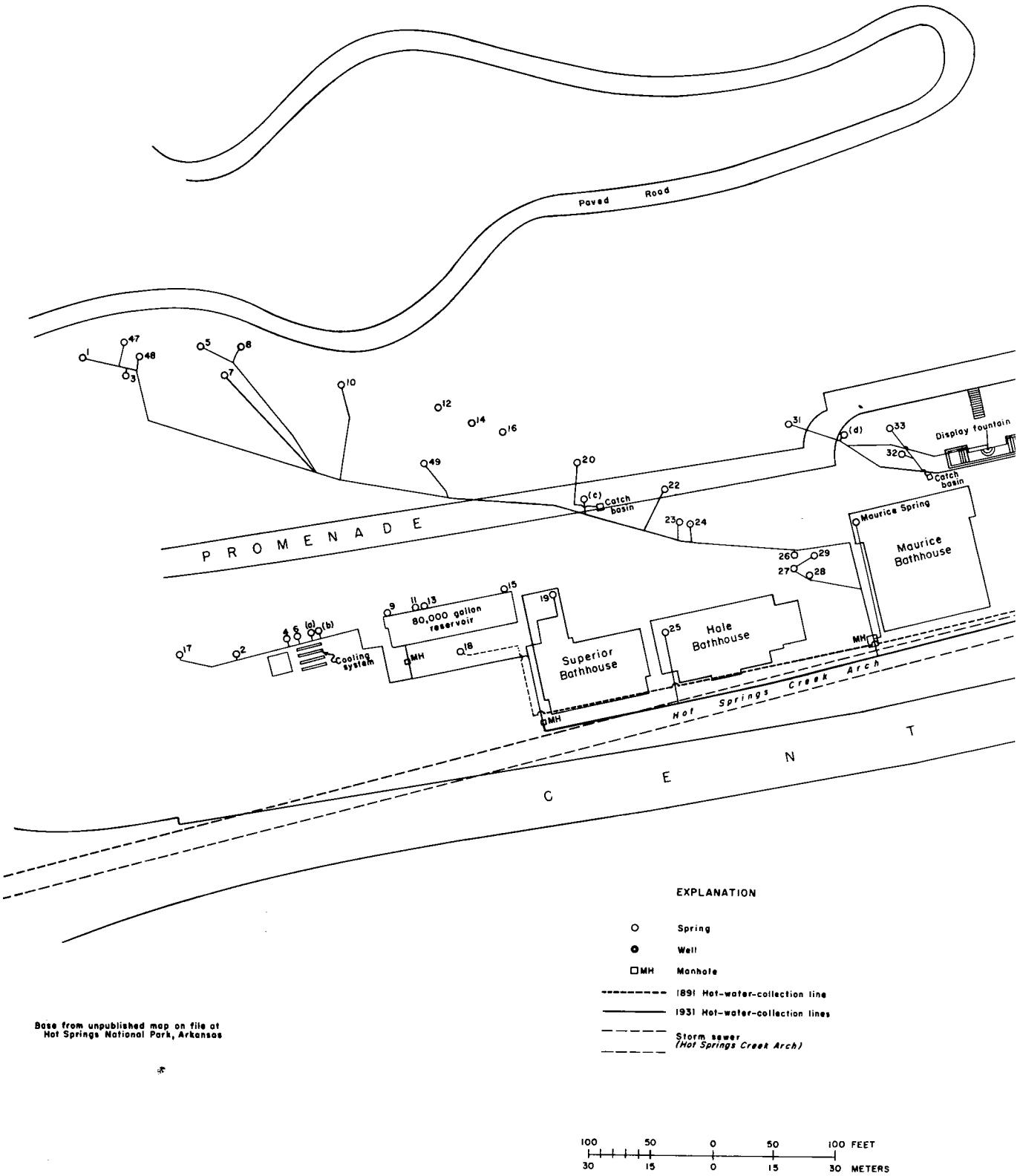
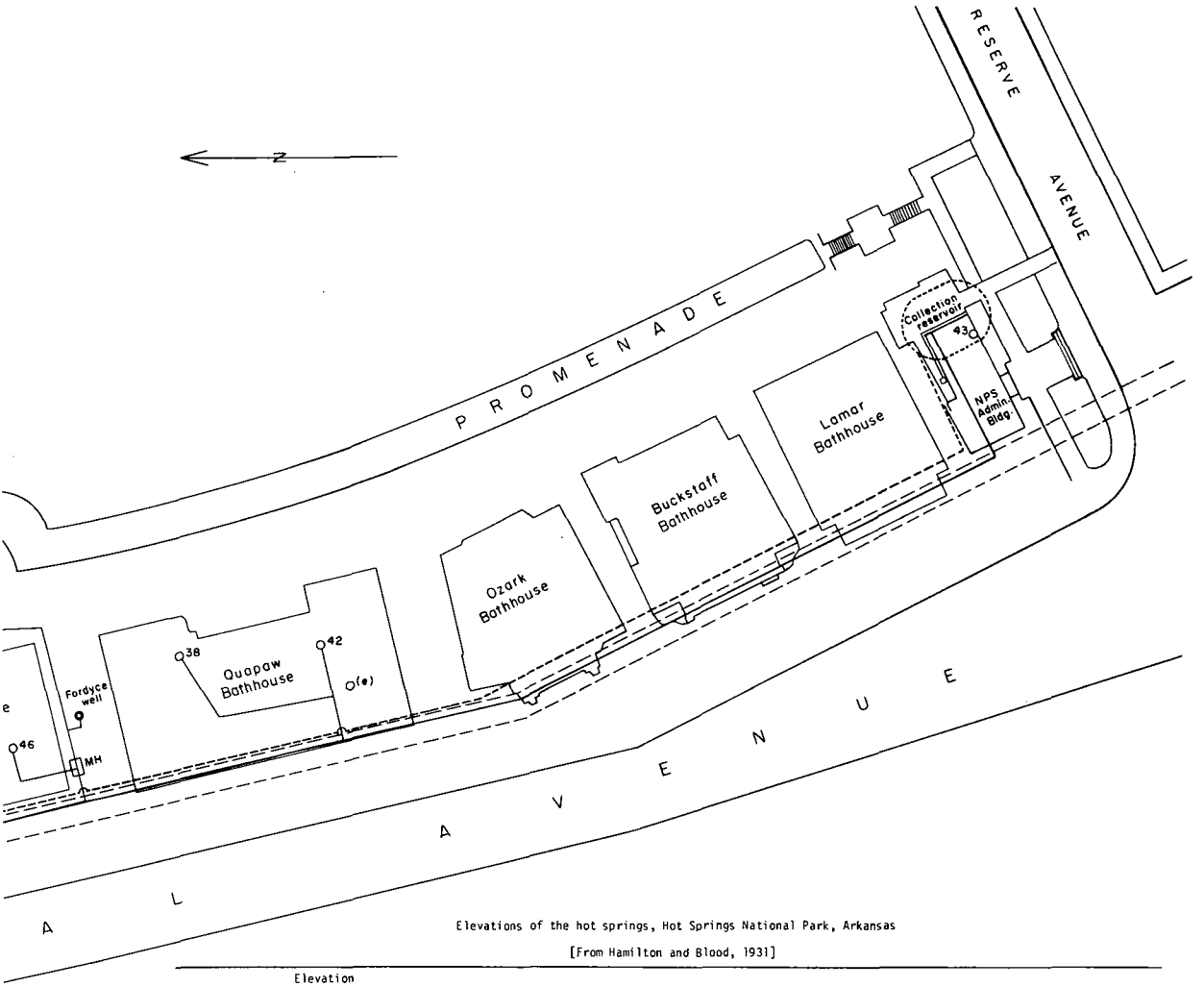


FIGURE 2.—Locations of the hot



Elevations of the hot springs, Hot Springs National Park, Arkansas

[From Hamilton and Blood, 1931]

Spring	Elevation (feet above mean sea level)	Point of elevation if other than spring orifice	Remarks
1	682	----------	
2	616	At connection with 4-inch collector.	
3	680	----------	
4	614	At connection with 4-inch collector.	
5	683	----------	
6	613	At connection with 4-inch collector.	
7	673	----------	
8	672	----------	
9	609	Overflow elevation of 80,000-callon reservoir.	
10	679	----------	
11	609	Overflow elevation of 80,000-gallon reservoir.	
12	----------	----------	Dry, not connected to collector line.
13	609	Overflow elevation of 80,000-gallon reservoir.	
14	----------	----------	Dry, not connected to collector line.
15	609	Overflow elevation of 80,000-gallon reservoir.	
16	----------	----------	Dry, not connected to collector line.
17	621	At connection with 4-inch collector.	
18	----------	----------	
19	606	80 feet from spring, at connection with 8-inch collector.	
20	654	----------	Not connected to collector line.
22	645	----------	
23	635	----------	
24	655	----------	
25	603	----------	
26	632	----------	
27	597	90 feet from spring's collecting basin at connection of 6-inch line with 12-inch collecting main.	
28	597	---do----------	
29	597	---do----------	
31	631	----------	
32	617	At former point of connection with 3-inch collector, 40 feet from spring.	
33	617	---do----------	
38	----------	----------	
42	----------	----------	
43	576	Bottom of reservoir.	Discharges into central-collecting reservoir.
46	----------	----------	
47	683	----------	
48	681	----------	
49	----------	----------	
Unnumbered (a)	613	At connection with 4-inch collector.	
Unnumbered (b)	612	---do----------	
Unnumbered (c)	----------	----------	
Unnumbered (d)	627	At connection with collector line.	
Unnumbered (e)	----------	----------	Elevation too low to feed by gravity into collection lines.
Maurice	----------	----------	
Fordyce well	600	At connection with 3-inch collector, 20 feet from well.	

springs and hot-water-collection lines.

ing and fissuring of the sandstone, chert, slate, shale, and novaculite. It is concluded from the present study that the faults and the associated joints and fissures provide conduits for the water.

Prof. D. D. Owen, in his report of 1860 on the hot springs, said the following:

"When we reflect on the boundless and never-ceasing flow of thermal waters that must have bathed the sides of Hot Springs Ridge for countless ages * * * and however inexplicable such wonderful phenomena and changes may at first appear, yet, when the chemical principles become properly understood, disclosed by the enlightened and accurate chemical analyses, these obscure geological transformations [and the origin of the water and operation of the springs] can be satisfactorily and clearly explained."

GEOLOGIC SETTING

The rocks cropping out in the vicinity of the hot springs are sedimentary rocks, although intruded igneous rocks are exposed in the region (Purdue and Miser, 1923). The sedimentary rocks are relatively old (Paleozoic) and consist of shale, chert, novaculite, and sandstone. The names of the geologic formations, their geologic ages, and positions in the geologic column are given in table 1.

Though no significant igneous rocks are exposed in the immediate vicinity of the hot springs, their nearby occurrence has been frequently cited in literature as possible sources for the heat of the springs. The igneous rocks were intruded into the sedimentary rocks during the early Late Cretaceous time (about 90 million years ago). The larger igneous intrusions in the hot-springs region are exposed in two small areas, about 6 miles southeast of the hot springs. Elsewhere in the region, igneous intrusions occur as very small dikes and sills.

The sedimentary rocks in the vicinity of the hot springs were originally laid down on a sea bottom of nearly horizontal beds. At present the beds are generally steeply inclined, because of tremendous and complex mountain-building forces in late Paleozoic time. The rocks have been subjected to at least three episodes of structural deformations—two episodes of compression from the south, producing imbricating thrust faults and, third, forces from the north which produced overturning and folding of beds and fault planes and further faulting. The geologic map (pl. 1) shows the edges of the inclined strata where they intersect the land surface. When the formations are crossed from northwest to southeast, they are seen in cross section (pl. 1) to lie in a series of very complexly folded anticlines and synclines, with some associated thrust faults.

The hot springs emerge from the plunging crestline of a large overturned anticline along the southern margins of the Ouachita anticlinorium in the Zigzag Mountains. The Zigzag Mountains basically owe their presence to the resistant exposures of the Arkansas Novaculite. The zigzag pattern of the strata is mostly due to tightly compressed folds which plunge southwestward into the Mazarn Basin. The Mazarn Basin is a structural and topographic basin lying south of the Zigzag Mountains. The Stanley Shale, a formation much less resistant to erosion than the Arkansas Novaculite, crops out at the surface of the Mazarn Basin. The structural setting is illustrated by figure 6 in Purdue and Miser (1923).

The formations, composed predominantly of shale,

TABLE 1.—*Generalized section of sedimentary rocks in the vicinity of the hot springs*
[Modified from Purdue and Miser, 1923]

System	Formation	Maximum thickness in Hot Springs area (ft)	Lithologic description	Topography
Mississippian	Stanley Shale ridges	8,500	Greenish-black and black shale, gray sandstone, and traces of thin chert and tuff.	Broad valleys with low and hills.
	Hot Springs Sand-	150	Hard, gray quartzitic sandstone, conglomerate, and thin interbedded black shale.	Steep slopes, or narrow, sharp-crested ridges.
	Arkansas Novaculite	650	Massive- to thin-bedded novaculite, interbedded with black clay, siliceous shale, and tripoli.	High ridges and steep slopes.
Devonian				
Silurian	Missouri Mountain Shale, Blaylock, Sandstone, and Polk Creek Shale, undifferentiated.	195	Green to black shale, a few thin sandstones, and traces of conglomerate.	Steep slopes or narrow valleys.
Ordovician	Bigfork Chert	700	Thin-bedded chert, highly fractured and interbedded thin siliceous shale.	Steep-sided low ridges and round knobs.
	Womble Shale	1,500	Black shale, thin interbedded lenses of linestone, and very thin sandstones.	

include the Womble, Missouri Mountain, Polk Creek, and Stanley Shales. The shales have low permeability, but, locally, limestones in the Womble yield water to springs. Shales generally impede ground-water movement, except where open joints and fractures are present. Wells in shales generally yield meager quantities of water; recharge to shales is also small.

The Bigfork Chert typically is highly permeable, exhibiting intergranular and fracture permeability. The Bigfork Chert is composed of silt-sized, generally poorly cemented siliceous particles in thin beds ½ to 4 in (13 to 130 mm) thick, which have been weathered, leaving a friable material, interbedded with layers of dense chert 4 to 12 in (130 to 450 mm) thick. The dense chert beds were rendered permeable by fracturing, which accompanied the intense folding of the beds, whereas the decalcified silt-sized material has significant intergranular permeability near the ground surface.

Wells that yield the largest quantities of water in the region tap the Bigfork Chert. At Belvedere Country Club, northeast of Hot Springs, the Bigfork, tested by Albin (1965), was found to have a transmissivity of 2.67×10^3 ft/d ($9.42\times10-^3$ m/s). Many of the springs in the area issue from the Bigfork Chert, and many of the cold-spring emergences are controlled by contact of the Bigfork with adjacent, less permeable formations. This association of cold springs with the Bigfork Chert was noted by Purdue and Miser (1923).

The Arkansas Novaculite is composed of three divisions—an upper and a lower division of novaculite, and a middle division of chert. Locally, the upper part of the formation is composed of silt-sized siliceous particles and possesses intergranular permeability. The lower division is generally massive and dense, but is very closely fractured. The middle division is composed mostly of black shale and thin chert beds. The Arkansas Novaculite is not as permeable as the Bigfork Chert, but is locally intensely jointed. Some cold springs issue from, and many water wells tap, the Arkansas Novaculite.

The Hot Springs Sandstone Member of the Stanley Shale is a massive, quartzitic sandstone. Fairly large joints and fractures, as in the novaculite, create some highly permeable conditions, such as at the hot springs.

The hot springs emerge from the Hot Springs Sandstone Member near the axis, on the northwest limb, of a southwestward-plunging anticline. The springs emerge between the traces of two thrust faults that are parallel to the axis of the anticline (pl. 1). The locations of the hot springs, shown in figure 2, generally lie along several northeast-trending lines. According to Bryan (1924), these lineaments were inferred to be the traces of fissures by R. R. Stevens, who first noted their alinement in 1890. Jointing is common in the few exposures of the Hot Springs Sandstone Member in the hot-springs-discharge area. Thus, the hot springs are associated with thrust faults, and with normal faults and joints, on the plunging crestline of the anticline. Upward movement of the hot waters from depth is probably along the permeable fault zones. These fault zones probably carry water to near the surface, where the water follows permeable joints to the spring outlets.

Geologic sections in plate 1 show the geologic structure in the vicinity of the hot springs.

CHARACTER OF THE SPRING AND WELL WATERS IN THE HOT-SPRINGS AREA

PHYSICAL QUALITY

FLOW OF THE HOT SPRINGS

Flow of the hot springs has been measured at infrequent intervals by several investigators. The first to attempt measurements was William Dunbar, of the Dunbar and Hunter expedition, in 1803, who measured only the largest springs. In 1860, Glasgow determined the hot-springs flow to be 450,480 gal/d ($1.97\times10^{-2}m^3/s$). Probably the first accurate measurement of the total spring flow was made by Weed (1902). Weed, after measuring or estimating the flow of each spring, found the total flow to be 850,000 gal/d ($3.72\times10^{-2}m^3/s$). The flow of all but a few of the hot springs is piped into a central collecting reservoir. Hamilton, in Hamilton and Blood (1931), calculated the maximum rate of filling of the central collecting reservoir to be 960,000 gal/d ($4.21\times10^{-2}m^3/s$). Park Superintendent Libbey, in 1945, recorded that the central collecting reservoir filled with 15 ft (4.57 m) of water in 7 hours, which represents an average flow of 800,000 gal/d ($3.50\times10^{-2}m^3/s$).

The volume of the reservoir per unit change in depth is known and provides a means for periodic calculation of spring flow. One large spring emerges at the bottom of the reservoir. The flow of this spring decreases as the depth of water in the reservoir increases. Also, at depths greater than 16 ft (4.88 m), overflow occurs. Flow calculations are thus made during the filling cycle at depths less than 16 ft (4.88 m). In addition, to avoid variable effect of depth in the reservoir on the flow of springs in the reservoir, the flow calculations are adjusted to a depth of 15 ft (4.57 m) by means of a depth-versus-flow rating curve.

A hydrograph of the average of calculations of monthly flow since September 1970 is shown in figure 3. Spring discharge has ranged from 750,000 gal/d

($3.29\times10^{-2}m^3/s$) to about 950,000 gal/d ($4.16\times10^{-2}m^3/s$). Fluctuations of spring discharge follow a seasonal cycle during the year; discharge is high in the winter and spring and is low in the summer and fall. One would expect the flow of an individual spring to fluctuate seasonally, as does the total spring flow. The flow of the lower display spring (number 32) is shown by hydrograph in figure 3.

In addition to seasonal changes in flow, individual springs show long-term changes in flow. Some springs have ceased to flow and new springs have emerged during the last 170 years. These long-term changes in spring flow have not been systematically documented; many changes have doubtlessly passed, unrecorded. Measurements of Weed (1902), Hamilton (1932), and the present study afford samples for comparisons of long-term variations.

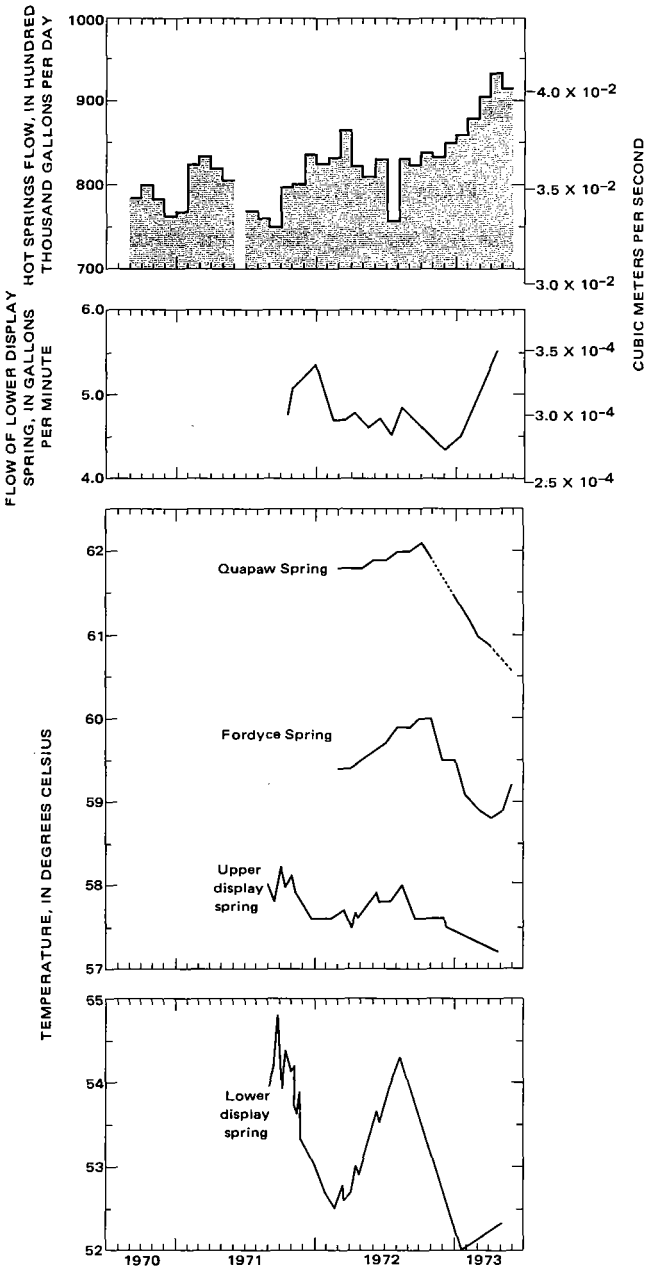


FIGURE 3.—Temperatures and flows of the hot springs.

Many changes in individual spring flow occurred between 1901 and 1931 because of excavation and construction at spring outlets, opening new springs, and drilling the Fordyce well (fig. 2). Hamilton noted that the flow of springs in group 1, which includes those at higher elevations, declined in flow from 168,000 gal/d ($736\times10^{-3}m^3/s$), in 1901, to 124,000 gal/d ($5.43\times10^{-3}m^3/s$), in 1931 (table 2).

Another group of springs, at lower elevations along the base of a tufa cliff, showed practically no change in flows from 1901 to 1931. These springs (numbers 2, 4, 6, 9, 11, 13, 15, 17, 19, and two unnumbered springs) discharged 313,500 gal/d ($1.37\times10^{-2}m^2/s$) in 1901 and 315,00 gal/d ($1.38\times10^{-2}m^3/s$) in 1931.

Thirteen springs that were measured by Weed in 1901 were not included in the 1931 collection system described by Hamilton (1932). Two of these springs are on the Arkansas Rehabilitation Center, one of which, number 39, is used for supplying hot water to the Rehabilitation Center. Four springs measured in 1901 were not flowing in 1931. Locations of six springs were unknown in 1931. Presumably, these six springs were nonexistent or had insignificant flows in 1931.

Hamilton lists five springs in his 1931 collection system that were nonexistent in 1901. Two of these (47 and 48) have declined in flows since 1931, and one (49) is now one of the larger springs in the system.

The collection system has not changed since 1931, and no springs have been excavated nor have hot-water wells been drilled, resulting in a relatively sta-

TABLE 2.—*Flows of the hot springs in group 1 in 1901 and 1931*
[From Hamilton, 1932]

Spring number	Flow, in gallons per day	
	1901	1931
11	28,800	9,600
3, 5, and 8	39,218	21,800
7	18,516	1,760
10	18,514	14,400
22	1,723	2,460
23 and 24	10,800	5,000
26	25,847	10,950
27, 28, and 29	24,418	(1)
47 and 48	Nonexistent	13,500
49	do.	(1)
Maurice Spring	do.	(1)
New	do.	2,400
Total	167,836	~124,000

[1]Not measured individually.

ble period of spring locations. However, changes in flow rates since 1931 have been noted.

Flows of several springs were measured or estimated in 1972 after the springs were uncovered for sampling in January. These measurements showed a general decline of flow in the springs located at higher elevations. In 1972 spring number 1 had a very small or no flow—a decline from 28,800 gal/d ($1.26\times10^{-3}m^3/s$) in 1901 and 9,600 gal/d ($4.21\times10^{-4}m^3/s$) in 1931. Spring numbers 47 and 48 declined from 13,500 gal/d ($5.91\times10^{-4}m^3/s$) in 1931 to 8,600 gal/d ($3.77\times10^{-4}m^3/s$) in 1972. However, spring number 7 declined from 18,516 gal/d ($8.11\times10^{-4}m^3/s$) in 1901 to 1,760 gal/d ($7.71\times10^{-5}m^3/s$) in 1931, but rose to 2,800 gal/d ($1.23\times10^{-4}m^3/s$) in 1972. Spring number 49, which was nonexistent in 1901, had a flow of 58,000 gal/d ($2.54\times10^{-3}m^3/s$) in 1972.

TEMPERATURES OF THE HOT-SPRINGS WATER

Temperature measurements were the first scientific data collected at the hot springs. William Dunbar and George Hunter, in 1804, recorded 67.8°C (Celsius) (154.0°F) for the hottest spring (Weed, 1902). In 1860, the highest temperature measured by Owen (1860) was 64.4°C (147.9°F).Glascow (1860) recorded a maximum of 65.6°C (150.1°F). The maximum temperature measured by the Geological Survey, in 1972, was 61.8°C (143.2°F).

Measurements of temperatures of individual springs by several investigators from 1890 to 1953 (table 3) show maximum temperatures of 63.9°C (147.0°F) in 1901, 64.4°C (147.9°F) in 1931, and 63.3°C (145.9°F) in 1952. Thirteen of the same hot springs were measured by Haywood (1902), Hamilton (1932), and Kuroda (1953). The average temperatures of these hot springs when measured in 1901, 1931, and 1952 were 58.2°C (136.8°F), 57.3°C (135.1°F), and 58.9°C (138.0°F), respectively.

These particular data indicate that there has been a slight decline in maximum water temperatures with time (0.6°F in 10 years). These data are not conclusive evidence of a general decline in temperatures, because of differences in samplings points, variations in temperatures with flow rates of individual springs, and temperature fluctuations in spring flows due to air temperature.

Temperature fluctuations of individual springs exhibit an annual cycle that seems to be in response to the annual cycle in air temperature. Graphs of the temperatures of four springs are shown in figure 3. For some springs, short-term fluctuations corresponding to the annual cycle are evident from detailed temperature records. The short-time fluctuations are due to external environmental factors. The Fordyce Spring (Spring No. 46, fig. 2) temperature, for example, responds to such factors as heat-load changes, caused by opening the air-tight seals on the chamber enclosing the spring, and effects of mixing of the hot-springs water with seepage from nearby rainfall.

It would be expected that spring temperature increases with increase in spring flow. This relation has been examined by scatter diagrams drawn between flow and temperature for the display springs. A direct relationship is obscured because the effect of ambient air temperature varies seasonally and the high seasonal air temperature occurs during the period of low spring flow.

SILICA CONCENTRATION AS A TEMPERATURE INDICATOR

The solubilities of silica minerals increase with increase in temperature. Silica minerals dissolve until the solution is saturated many times faster than they precipitate from an oversaturated solution. Thus, a thermal water will dissolve silica minerals as its temperature rises, but as the water cools it will not rapidly lose silica. The silica concentration of water can be

TABLE 3.—*Temperatures, in degrees Celsius, of the hot springs*

Spring	Date of measurement					
	1890 (from Branner, 1892)	1900 (from Haywood, 1902)	1901 (from Haywood, 1902)	1931 (from Hamilton, 1932)	1952 (from Kuroda, 1953)	1972 (from (present study)
1	62.6	61.9	61.7	----------	62.0	54.6
2	----------	51.9	53.9	54.5	----------	----------
3	----------	61.7	61.3	60.0	62.2	52.2
4	----------	55.9	52.4	57.2	----------	----------
5	----------	61.4	61.9	61.1	61.7	----------
6	----------	57.5	58.3	57.2	58.6	----------
7	----------	60.1	60.8	----------	62.2	59.3
8	----------	35.2	36.2	61.1	----------	----------
9	59.6	61.1	62.4	62.2	61.2	----------
10	----------	57.4	57.2	60.0	----------	----------
11	----------	----------	56.8	64.4	61.2	----------
12	----------	36.2	36.2	----------	----------	----------
13	----------	----------	56.3	----------	61.2	----------
14	59.6	60.9	62.8	----------	----------	----------
15	63.6	63.9	63.9	64.4	61.2	----------
16	----------	60.8	60.9	----------	----------	----------
17	----------	55.4	56.4	55.6	56.9	56.0
18	----------	57.3	57.3	52.8	59.6	----------
19	----------	56.4	56.1	----------	----------	----------
20	----------	46.3	44.5	44.7	----------	----------
21	46.6	43.3	46.0	----------	----------	----------
22	----------	57.1	56.5	56.1	----------	----------
23	----------	62.0	62.4	50.0	59.6	56.2
24	----------	62.3	60.3	57.8	54.3	----------
25	61.6	62.7	62.9	----------	63.3	----------
26	----------	63.4	61.4	63.3	----------	----------
27	----------	----------	51.9	----------	59.2	----------
28	----------	----------	59.8	----------	60.0	----------
29	----------	57.1	57.8	----------	61.1	----------
30	----------	53.9	51.9	----------	----------	----------
31	----------	51.4	51.4	54.4	54.0	----------
32	----------	46.0	46.5	45.0	52.5	52.5
33	----------	48.3	49.2	----------	----------	57.6
34	----------	47.9	47.3	----------	57.5	----------
35	----------	39.0	43.0	----------	----------	----------
36	----------	48.9	48.8	----------	----------	----------
37	----------	52.9	52.6	----------	----------	----------
38	----------	58.8	59.8	----------	60.3	----------
39	----------	61.4	61.4	----------	----------	----------
40	----------	48.9	48.9	----------	----------	----------
41	----------	46.8	48.3	----------	----------	----------
42	51.6	----------	58.3	60.6	60.8	61.3
43	----------	46.1	----------	50.0	----------	----------
44	----------	8.0	----------	----------	----------	----------
45	----------	13.0	----------	----------	----------	----------
46	----------	51.5	----------	57.2	----------	58.3
47	----------	----------	----------	58.6	61.7	----------
48	----------	----------	----------	----------	62.2	60.0
49	----------	----------	----------	58.9	61.0	61.8
50	----------	----------	----------	62.8	----------	----------
Maurice	----------	----------	----------	----------	----------	53.3

used as a measure of the maximum temperature reached by the water (Fournier and Rowe, 1966).

The actual silica concentration of water depends on the particular silica mineral to which the water is exposed, as well as to the temperature and the rate of dissolution. In the hot-springs system, the main sources of silica are the Bigfork Chert and the Arkansas Novaculite. Chert and novaculite are both composed of chalcedony, a cryptocrystalline quartz, and microcrystalline quartz. The solubilities of chalcedony and quartz (R. O. Fournier, oral commun., 1972) are shown in figure 4.

The analyzed silica concentrations of the samples collected for this study are also shown in figure 4. The cold springs and wells are oversaturated with respect to quartz, but are undersaturated with respect to chalcedony. Though it is likely that complex silica-bearing clays or other minerals influence the silica concentration of these waters, it is also possible that, because of their low temperatures, these waters have not had sufficient time to reach saturation with the chalcedony.

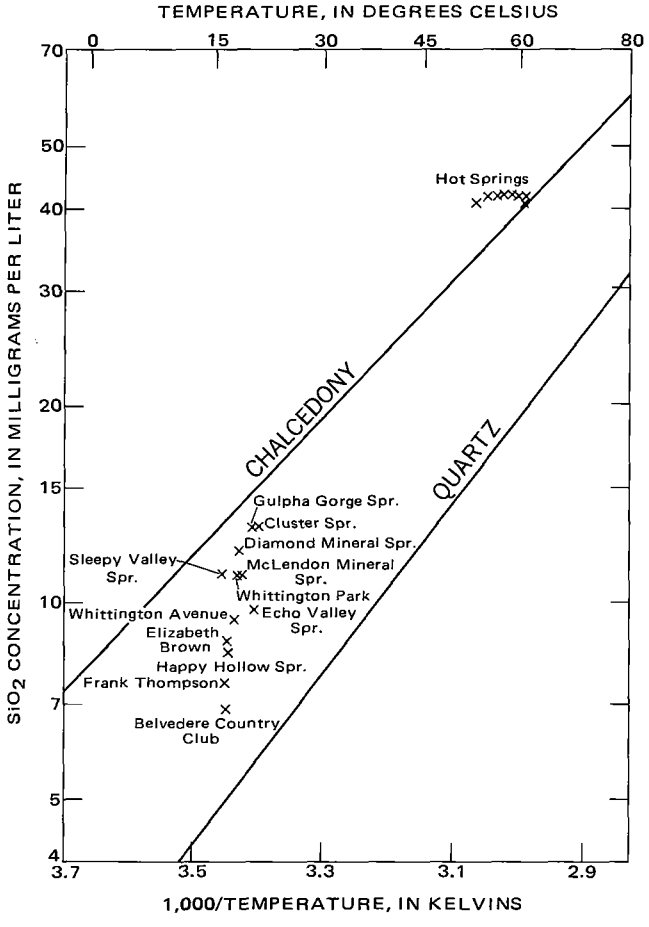


FIGURE 4.—Variation of dissolved-silica concentration with temperature.

The hot-springs waters have a uniform silica concentration (41–42 mg/L). They are oversaturated with respect to chalcedony at their temperature when collected, but the higher temperature springs approach saturation. The constant silica concentration of the springs, together with the similarities in their other chemical properties, strongly suggests that all the hot springs emanate from a single source having a uniform geothermal environment. From the silica concentration (41.5± 0.5 mg/L), the temperature of the source can be calculated as 63.2± 0.5°C (145.8± 0.9°F). The differences in temperatures of the individual springs are presumably a result of differing flow paths and rates of approach to the surface from their common source.

Silica analyses were made on groups of samples collected in 1901, 1952, and for the present study in 1972. These analyses provide a firmer base from which to judge temperature trends with time. The silica analyses of springs in a given group show less variation than overall spring temperatures. As an indicator of maximum temperature, the silica-computed temperature is not affected by external factors such as air temperature and flow of the springs.

Silica concentrations and maximum temperatures calculated from the silica concentrations (Fournier and Rowe, 1966), as well as maximum temperatures recorded at various times, are shown in the following table.

Year	Maximum temperature measured (°C)	Average SiO_2 concentration (mg/L)	Number of springs sampled	Temperature calculated from SiO_2 concentration
1804	67.8	----	--	----
1860	64.4	----	--	----
1860	65.6	----	--	----
1901	63.9	46.6	40	68.5
1931	64.4	----	--	----
1952	63.3	42.7	11	64.3
1972	61.8	41.7	9	63.2

These results are shown graphically in figure 5. According to the silica data, the spring-source temperature has been decreasing at an average rate of about 0.077°C (0.14°F) per year since 1901, although data from 1804 to 1931 indicate a lower rate of decline. Also, measured maximum temperatures from 1931 to 1972—a period in which the springs were undisturbed—have decreased at about the same rate (0.073°C, or 0.13°F per year) as the spring-source temperature decline from 1931 to 1972. This coincidence may be a fortuitous circumstance of sample timing and distribution. In addition to reflecting the change in the

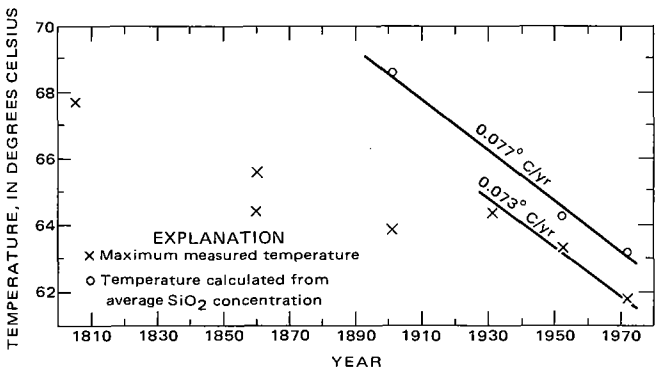


FIGURE 5.—Maximum measured and calculated temperatures of the hot springs.

source temperature, variations in measured temperatures reflect the sampling distribution, seasonal changes in temperature, and changes in temperature because of changes in flow distribution that are due to natural changes in flow distribution or due to man's efforts to enclose and control the springs. Thus, although the temperature observations may be subject to sampling bias, the silica-concentration trend of the hot springs indicates a decline in temperature.

TEMPERATURES OF THE COLD SPRINGS AND WELLS

The temperatures of ground water in wells in the vicinity of Hot Springs, other than the hot springs themselves, range from 12.0°C (53.6°F) to 52.8°C (127.0°F) (tables 4, 5; fig. 6). The warmer of these temperatures is the temperature of ground water in the immediate vicinity of the hot springs. The well on the grounds of the Arkansas Rehabilitation Center has a temperature of 52.8°C (127.0°F); the water from a well on the Arlington Hotel lawn, used to supply water to the cooling plant, has a temperature of 32.2°C (90.0°F; the temperature of the water from the well at the Arlington Hotel is reported to be 22.8°C (73.0°F)). The high temperatures are associated with the abnormally high geothermal gradient caused by heat conveyed to the surface by the waters of the hot springs.

The temperatures of ground waters in and near areas considered as potential for recharge to the hot-springs system (outcrop area of Bigfork Chert and Arkansas Novaculite) range from 15.0°C (59.0°F) to 26.8°C (80.2°F). These temperatures, considered in relation to the average annual air temperature of 17.7°C (63.9°F), indicate that some of the waters in and near the recharge area are heated by geothermal processes. Ground-water temperatures, in the range of 15.0°C (59.0°F) to 16.7°C (62.1°F), indicate a minimum of geothermal heating and reflect the fact that most recharge occurs during the cooler seasons of the year. These temperatures indicate that there is a rapid rate of movement of water downward from the surface and proximity to the recharge-source area.

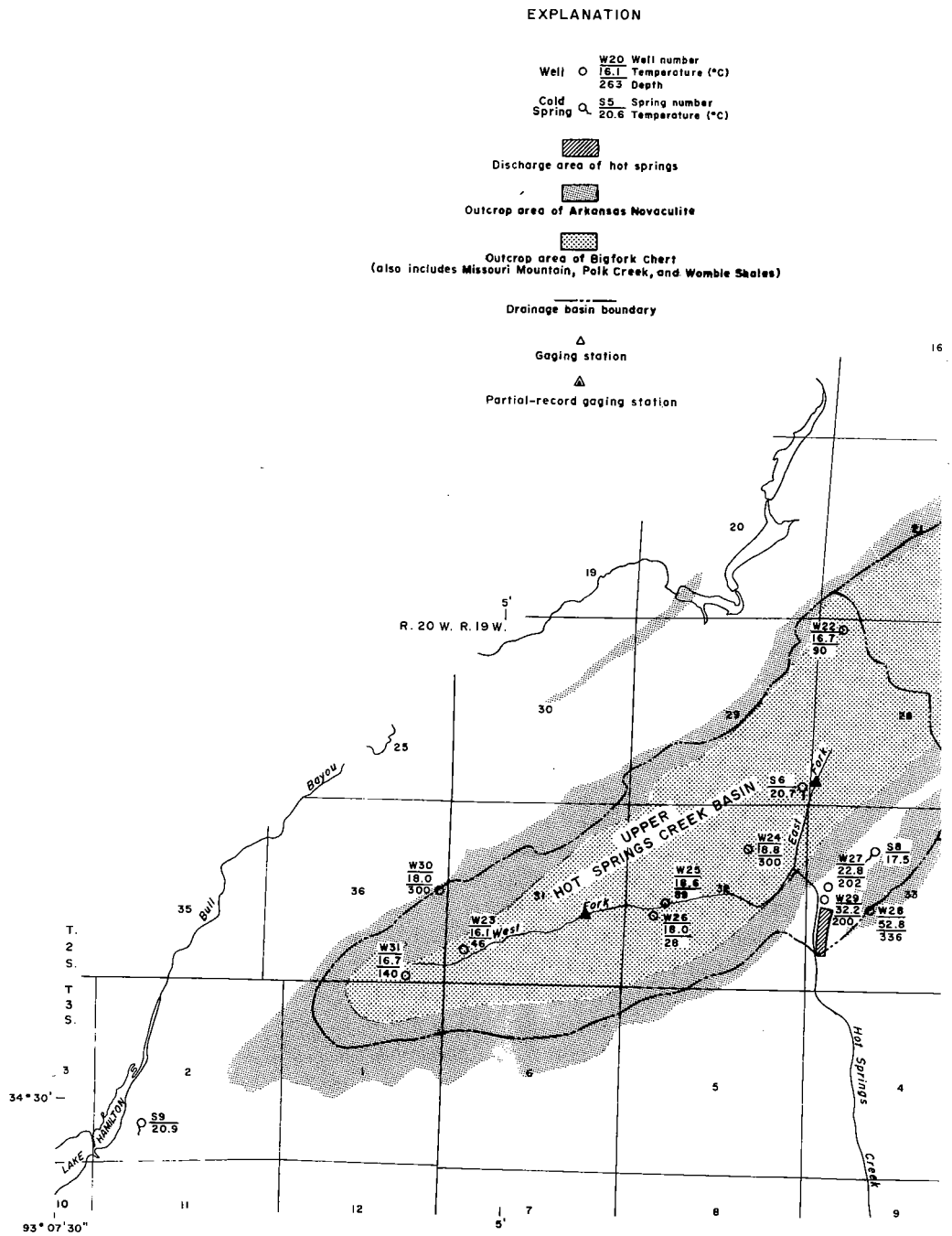
Low ground-water temperatures, lower than the average air temperature, occur in the area northeast of the springs and in the outcrop of the Bigfork Chert and the Arkansas Novaculite. Water temperatures from

TABLE 4.—*Temperatures of the cold springs*

Spring No. (fig. 6)	Name	Temperature (°C)	Date of measurement	Geologic formation
S1	Ozark Lithia	19.6	6–29–72	Bigfork Chert.
S2	J. L. Bryant (owner)	15.6	6–29–72	Do.
S3	Arbordale	26.8	6– 7–72	Do.
S4	Burton Sargo (owner)	17.8	9–12–72	Do.
S5	Echo Valley	20.5	1–27–72	Do.
S6	Ar-Scenic	20.7	11–2–71	Do.
S7	Cluster	20.8	1–26–72	Arkansas Novaculite.
S8	Happy Hollow	17.5	1–24–72	Do.
S9	Music Mountain	20.9	9–27–72	Stanley Shale.
S10	Sleepy Valley	12.0	1–28–72	Bigfork Chert.
S11	McLendon	18.6	9–27–72	Hot Springs Sandstone Member of the Stanley Shale.

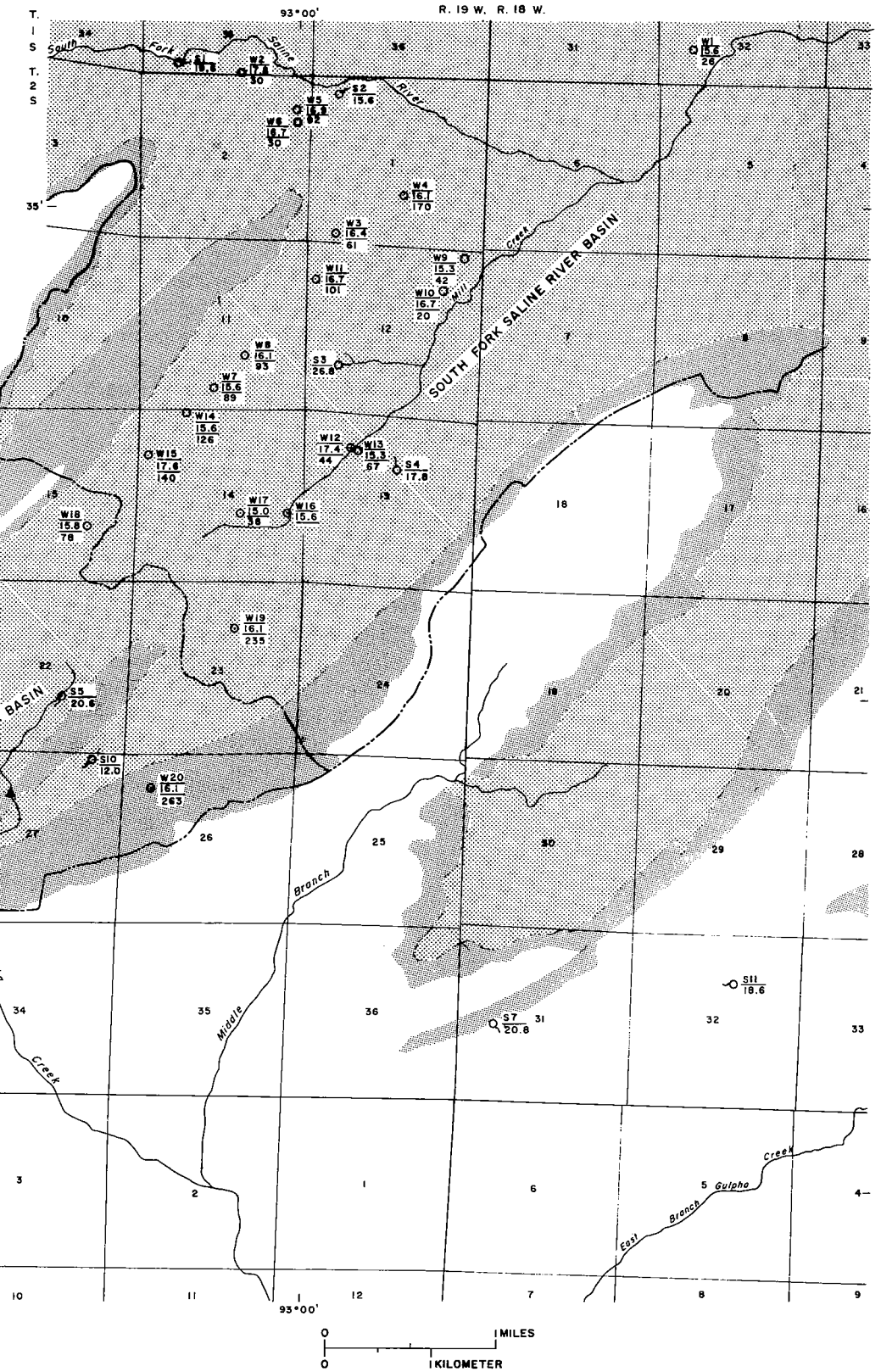
TABLE 5.—*Temperatures of water in the wells*
[Thermal gradient = (temp. (°C)−15)/depth of well (ft)]

Well No. (fig. 6)		Temperature (°C)	Date of measurement	Depth of well (ft)	Thermal gradient (°C/ft)	Geologic formation
W1	----	15.6	6–29–72	26	0.023	Bigfork Chert.
W2	----	17.8	9–13–72	30	.093	Do.
W3	----	16.4	6– 6–72	61	.023	Do.
W4	----	16.1	7–14–72	170	.065	Do.
W5	----	16.9	7–14–72	92	.021	Do.
W6	----	16.7	7–14–72	30	.057	Do.
W7	----	15.6	6– 6–72	89	.0067	Do.
W8	----	16.1	6– 6–72	93	.012	Do.
W9	----	15.3	6– 7–72	42	.0071	Do.
W10	----	16.7	6– 7–72	20	.085	Do.
W11	----	16.7	6– 6–72	101	.017	Do.
W12	----	17.4	9–25–72	44	.054	Do.
W13	----	15.3	9–12–72	67	.0045	Do.
W14	----	15.6	6– 7–72	126	.0048	Do.
W15	----	17.6	9–25–72	140	.019	Do.
W16	----	15.6	6– 2–72	----	--------	Do.
W17	----	15.0	6– 2–72	38	.0	Do.
W18	----	15.8	6– 6–72	78	.010	Do.
W19	----	16.1	6– 2–72	235	.0047	Do.
W20	----	16.1	6– 2–72	263	.0042	Arkansas Novaculite.
W21	----	20.4	9–27–72	120	.045	Do.
W22	----	16.7	11–2–71	90	.019	Bigfork Chert.
W23	----	16.1	11–2–71	46	.024	Do.
W24	----	18.8	1–22–72	300	.063	Do.
W25	----	18.6	1–28–72	89	.040	Do.
W26	----	18.0	1–24–72	28	.11	Do.
W27	----	22.8	3– 8–70	202	.039	Hot Springs Sandstone Member of the Stanley Shale.
W28	----	52.8	8– 8–72	336	.11	Do.
W29	----	32.2	3– 4–70	200	.086	Do.
W30	----	18.0	9–22–72	300	.010	Arkansas Novaculite.
W31	----	16.7	9–22–72	140	.012	Bigfork Chert.



Base from U. S. Geological Survey
Hot Springs North 1:24,000, 1966
Hot Springs South 1:24,000, 1966
Lonsdale SW unedited advance print 1:24,000, 1972
and Malvern 1:62,500, 1948

FIGURE 6.—Locations of



the cold springs and wells.

several wells in the area are higher than the average air temperature. The higher temperatures indicate geothermal heating due to a long residence time of the water in the aquifer. Of the five wells sampled having temperatures higher than the average air temperature, four are flowing artesian wells.

The cold-water springs in the area are generally warmer than the well waters. The spring temperatures range from 15.6°C (60.1°F) to 26.8°C (80.2°F). The designation of "cold-water" to these springs is for the purpose of distinguishing them from the hot springs of Hot Springs National Park. The warmer springs in this cold-water group could be correctly classified as thermal springs.

CHEMICAL QUALITY

The ground water of the hot springs contains a variety of chemical species in solution. Knowledge of the chemical types and concentrations is useful in interpreting patterns of ground-water movement, source of the water, and in determining whether there has been a change in the chemical concentration of the water through the years. Chemical analyses may also hold clues to the longevity of the hot springs.

There has been little change in the chemical quality of the hot-springs waters during the period of record from 1890 to 1970. A small change in the silica concentration is indicated, and its significance has been discussed. Minor variations in other constituents are consistent with normal variations in most ground water.

As part of this study, samples for chemical and isotope analyses were collected in 1972 from 15 cold wells and springs in the Hot Springs region and from 9 hot springs. Table 6 gives the results of the chemical analyses made for this study. The concentration of certain dissolved constituents may change between the time of field collection and the time of laboratory analysis owing to loss of gases, temperature changes, and precipitation of solids. To insure that the analyses would represent the natural chemistry of the water as closely as possible, certain analyses were made in the field, and parts of the samples were treated before being sent to the laboratory, to prevent changes before analysis.

Temperature was measured at the collection site using thermometers readable to 0.1°C (0.18°F). Alkalinity, pH, and dissolved oxygen (DO) were also measured as part of the sample collection procedure because they are liable to change by exchange with atmospheric CO_2 or O_2 gas when a water sample is shipped or stored. The precautions mentioned by Barnes (1964) were observed in the pH and alkalinity measurements. The pH values are considered accurate to ±0.02 units. The dissolved oxygen analytical procedure was that described by Brown, Skougstad, and Fishman (1970, p. 126). A separate bottle of each sam-

TABLE 6.—*Chemical analyses of water*

[Results in milligrams per

Well or spring number[1] (fig. 6)	Name of well or spring	Date of collection	Water temperature (°C)	Silica (SiO_2)	Aluminum (Al)	Total iron (Fe)	Total manganese (Mn)	Zinc (Zn)	Calcium (Ca)	Magnesium (Mg)
S8	Happy Hollow Spring	1-24-72	17.5	8.4	0.00	0.00	0.00	0.03	0.2	0.3
W19	Belvedere Country Club well	9-25-72	16.8	6.9	.05	.98	.02	.04	.1	.1
W20	Frank Thompson's house well	9-24-72	16.8	7.5	.04	.02	.00	.02	.2	.1
S10	Sleepy Valley Spring	1-28-72	12.0	11	.40	2.1	.13	.10	3.7	1.0
W17	Bill Sargo's well	9-24-72	18.1	8.1	.20	2.0	.03	.02	.8	.5
W16	R. B. Yates' well	9-25-72	21.2	7.9	.04	.04	.10	.06	5.9	1.5
S9	Music Mountain Spring	9-27-72	20.9	2.6	.08	.04	.00	.00	11	1.4
S7	Cluster Spring	9-26-72	20.8	13	.00	.66	.25	.01	42	2.5
S11	McLendon Mineral Spring	9-27-72	18.6	11	.00	1.0	.75	.06	40	1.4
W21	Gulpha Gorge Well	9-27-72	20.4	13	.00	1.2	.13	.02	46	2.8
W12	Elizabeth Brown well	9-24-72	17.4	8.7	.00	2.1	.33	.17	55	1.9
W26	Whittington Avenue Spring	1-24-72	18.0	9.4	.0	.79	.08	.10	50	2.3
W25	Whittington Park well	1-28-72	18.6	11	.0	1.6	.11	.12	63	3.4
S5	Echo Valley Spring	1-27-72	20.5	9.7	.0	1.3	.15	.08	67	2.9
W24	Diamond Mineral Spring	1-22-72	18.8	12	.0	.37	.12	.06	66	3.6
	Maurice Hot Spring	1-20-72	53.3	42	.0	.00	.10	.05	45	4.8
	Hot Spring No. 17	1-25-72	55.4	41	.0	.00	.00	.05	44	4.6
	Hot Spring No. 23	1-26-72	56.2	41	.0	.00	.09	.03	44	4.6
	Hot Spring No. 33	1-26-72	57.6	42	.0	.04	.27	.08	45	4.8
	Hot Spring No. 46	1-18-72	58.3	42	.0	.33	.25	.07	45	4.8
	Hot Spring No. 48	1-25-72	60.0	42	.0	.02	.18	.06	45	4.7
	80,000-gallon reservoir	1-27-72	61.0	42	.0	.00	.20	.04	45	4.8
	Hot Spring No. 42	1-19-72	61.3	42	.0	.01	.23	.02	45	4.8
	Hot Spring No. 49	1-21-72	61.8	41	.0	.06	.25	.06	44	4.8

[1]U.S. Geological Survey station numbers of wells and springs are given in table 7.
[2]Laboratory analysis.
[3]Contains trace of hydrogen sulfide (H_2S).

NOTE.—Differences in implied accuracy of analyses for aluminum due to differences in types of equipment used.

ple was acidified at the time of collection and taken to the laboratory for analyses for aluminum (Al), iron (Fe), manganese (Mn), zinc (Zn), calcium (Ca), magnesium (Mg), and strontium (Sr). Analyses for these seven ions, as well as for sodium (Na) and potassium (K), were made by atomic absorption spectroscopy. All determinations were made by using methods standard in U.S. Geological Survey laboratories (Brown and others, 1970). The analyses of aluminum for samples collected in September 1972 were made from a larger aliquot than was used for the analyses of the samples collected earlier. Thus the precision reported in table 6 is greater for the samples collected in September 1972. The precision of all analyses is estimated to be plus or minus one-half of the last reported digit. That is, a reported 2.1 mg/L implies a concentration of between 2.05 and 2.15 mg/L. A reported 0.00 mg/L means that analysis was made for that constituent but the constituent was not found in concentrations greater than 0.005 mg/L.

The chemical analyses given in table 6 are arranged approximately in order of increasing total dissolved-solids concentration. U.S. Geological Survey station numbers of the sampling points are given in table 7. Two, or possibly three, of the analyses given in table 6 are not of particular use in describing the chemical history of the hot-springs-area ground waters. Music Mountain Spring issues from Stanley Shale, and its chemical characteristics, particularly its silica and chloride concentrations, are unlike those of waters in the hot-springs-flow system. The R. B. Yates' well, although in the geographic and geologic area of interest, is very shallow, and the water has a high concentration of nitrate (NO_3=8.3 mg/L) and chloride (Cl=6.4 mg/L). This chemistry and the location of the well suggest that the water is influenced by man's activity and does

TABLE 7.—*Station numbers of wells and springs given in table 6*

Station number	*Name of well or spring*
343110093025301	Happy Hollow Spring
343252091002301	Belvedere Country Club well
343204093005501	Frank Thompson's house well
343211093011501	Sleepy Valley Spring
343227093002201	Bill Sargo's well
343327093000401	R. B. Yates' well
342954093070101	Music Mountain Spring
343033092584901	Cluster Spring
343105092572001	McLendon Mineral Spring
343130093020801	Gulpha Gorge well
343347092594201	Elizabeth Brown well
343052093040802	Whittington Avenue Spring
343056093040601	Whittington Park well
343231093012801	Echo Valley Spring (Big Chalybeate)
343112093033601	Diamond Mineral Spring (Lithox)
343051093031101	Maurice Hot Spring
343057093031301	Hot Spring No. 17
343053093031101	Hot spring No. 23
343051093030901	Hot Spring No. 33 (Upper Display)
343049093031101	Hot Spring No. 46
343058093030803	Hot Spring No. 48
343055093031201	80,000-gallon reservoir
343047093031001	Hot Spring No. 42 (Health Services)
343035093031001	Hot Spring No. 49

from the hot springs, cold springs, and wells

liter, except as indicated]

Stron	Sodiu	Potas	Amm	Bicarbo (field)	Sulfa	Chlo	Fluo	Nitra	Orth	Orga	Dissolved solids: Resid at 180°C	Dissolved solids: Sum ue	Speci µm	pH (	Diss
0.00	1.3	0.2	----	[2]1	1.4	2.3	0.1	0.0	0.03	----	14	11	22	4.58	6.3
.00	1.0	.2	0.04	5	1.6	1.4	.0	.3	.04	0.08	12	15	15	5.20	.6
.00	.7	.3	.04	[2]0	1.6	.9	.0	.2	.00	.04	12	18	36	4.70	10.2
.01	1.3	.8	----	[2]2	14	2.1	.2	.1	.35	----	36	41	47	[2]4.82	3.3
.00	2.8	1.4	.00	[2]0	7.4	3.6	.1	1.7	.06	.10	26	36	44	4.62	1.8
.00	5.4	1.4	.02	9	10	6.4	.1	8.3	.02	.01	51	54	77	5.32	4.8
.01	2.4	1.0	----	[2]29	8.6	4.7	.1	.7	.01	----	47	60	104	[2]7.12	----
.10	4.6	1.7	.08	147	11	2.7	.2	.1	.12	.04	146	149	219	6.72	.0
.07	1.7	1.0	.06	145	7.2	1.6	.2	.1	.39	.01	131	141	232	7.15	.0
.08	2.9	1.5	.02	157	10	2.3	.2	.1	.07	.08	152	165	247	7.10	.0
.24	1.6	.7	.06	183	7.0	2.0	.1	.1	.31	.05	164	173	274	6.92	.0
.20	1.5	.9	----	157	14	2.1	.2	.1	.12	----	157	164	276	6.69	.0
.26	1.6	1.4	----	227	9.8	1.9	.2	.1	.00	----	193	200	331	7.6	([3])
.11	1.3	.6	----	219	7.2	2.0	.2	.1	.06	----	196	202	339	7.25	.0
.11	1.9	1.8	----	211	12	2.0	.3	.1	.00	----	204	212	354	7.08	.0
.11	4.0	1.5	----	156	9.0	1.9	.2	.0	.04	----	189	191	269	7.03	2.0
.11	3.9	1.5	----	[2]160	7.8	1.8	.2	.0	.00	----	184	187	266	[2]7.70	3.6
.11	3.9	1.5	----	159	8.2	1.9	.2	.2	.09	----	185	188	269	7.52	3.9
.11	4.0	1.5	----	164	8.2	1.9	.2	.0	.02	----	188	193	269	7.13	1.1
.11	4.0	1.5	----	164	7.8	1.9	.2	.0	.04	----	187	195	269	7.01	.6
.12	4.0	1.5	----	165	8.6	1.9	.2	.1	.00	----	189	196	276	7.27	2.4
.12	4.0	1.5	----	165	8.0	1.8	.2	.0	.00	----	188	191	275	7.36	3.3
.11	4.0	1.5	----	159	8.6	1.9	.2	.0	.04	----	188	191	272	6.93	.0
.11	3.8	1.5	----	155	8.2	1.9	.2	.0	.06	----	184	191	268	6.95	.4

not represent the natural conditions of interest in this report. The water from Bill Sargo's well, too, has slightly high chloride and nitrate concentrations (3.6 and 1.7 mg/L, respectively) and may not be completely representative of natural conditions.

The water from the hot springs is distinctive chiefly by its relatively low mineral concentration (table 6). The mineral concentration of the water probably is low because the rocks associated with the hot springs are made up of only a few minerals, each of which has a low solubility. Most ground water in Arkansas contains from two to to three times more dissolved minerals than the hot-springs water.

GEOCHEMISTRY OF HYDROGEN AND OXYGEN ISOTOPES

The elements hydrogen and oxygen have several naturally occurring isotopes. Hydrogen has stable isotopes of mass 1, common hydrogen or protium (H or ^{1}H), and of mass 2, deuterium (D or ^{2}H). A radioactive isotope of hydrogen, tritium (^{3}H), also occurs in the environment and is discussed below. Common oxygen has a mass of 16 ($^{16}0$), but oxygen of mass 17 ($^{17}0$) and mass 18 ($^{18}0$) also occur.

As absolute isotopic abundances or ratios are difficult to analyze with precision, it is customary to measure and express isotopic variations as deviations from an arbitrary standard. These deviations are expressed in delta notation where

$$\delta = \left(\frac{R \text{ sample}}{R \text{ standard}} - 1 \right) \times 1{,}000.$$

Here, R is the isotopic ratio (D/H; $^{18}0/^{16}0$), and δ is in parts per thousand, or per mil ($^{0}/_{00}$) The delta notation is less difficult to use than it seems.

The standard to which natural-water isotopic measurements are referred is Standard Mean Ocean Water (SMOW) (Craig, 1961a). The concentrations of the various isotopic molecular species in this standard are $H_2{}^{18}O \cong 2{,}000$ mg/L, $H_2{}^{17}O \cong 420$ mg/L, and $HD^{16}O \cong 316$ mg/L. $H_2{}^{16}O$ makes up the remainder, and all other species total less than 1 mg/L. Knowledge of the ^{17}O concentration of a sample provides no more information than knowledge of the ^{18}O concentration; therefore, the ^{17}O concentration is generally not reported. The stable isotopic chemistry of water is thus expressed in terms of δD and $\delta^{18}O$.

Natural waters are generally depleted in D and ^{18}O relative to SMOW—that is, their δD and $\delta^{18}O$ values are negative. This depletion occurs because the vapor pressure of water molecules containing the heavier isotopes is slightly less than that of common water, $H_2{}^{16}O$. During evaporation and condensation in the hydrologic cycle, molecules containing heavier isotopes are concentrated in the liquid phase. As water evaporates from the ocean, the vapor is depleted in D and ^{18}O and the amount of depletion becomes greater as the temperature of evaporation decreases. Further isotopic fractionation takes place as water is condensed and reevaporated during atmospheric transport, and the amount of fractionation is inversely proportional to temperature.

The D and ^{18}O concentration of meteoric water—that is, water of recent atmospheric origin—varies regularly over the land surface of the Earth. A great number of measurements show that for meteoric water not subject to much evaporation, δD and $\delta^{18}O$ are related by the expression by Craig (1961b):

$$\delta D = 8\delta^{18}O + 10. \qquad (1)$$

The amount of depletion also increases with altitude, latitude, and distance from the ocean. The general pattern of isotopic distribution in North America has been mapped (Sheppard and others, 1969).

Figure 7 shows the variation of δD and $\delta^{18}O$ from several hydrothermal localities and the trend line for meteoric waters, equation 1. The meteoric waters from the localities shown illustrate the tendency for increasing depletion from the oceanic isotopic composition with latitude, altitude, and distance.

Figure 7 illustrates that the ^{18}O content of many thermal waters is enriched relative to normal meteoric waters of the same D content. An explanation for this shift might be that the hot waters represent mixing between meteoric water and water emanating from hot or molten rock at great depths within the earth—that is, magmatic water, the isotopic composition of which is not precisely known but which may well be in the range shown in the figure. Were this explanation correct, there should be a shift in δD, as well as in $\delta^{18}O$ toward whatever isotopic composition may be typical of magmatic water. As is particularly well illustrated by the Nevada and Yellowstone Park series, such a deuterium shift does not occur. Because a deuterium shift is absent and because of the existence of another process to explain the ^{18}O shift, magmatic waters are probably not significant contributors to hydrothermal systems.

The process bringing about the ^{18}O shift is probably an isotopic-exchange reaction between the water and rock in a system. Such a reaction for a silica mineral can be written as

$$Si^{16}O^{18}O \div H_2{}^{16}O \rightarrow Si^{16}\,O^{2} + H_2{}^{18}O.$$

Because ^{18}O in most igneous minerals is enriched relative to SMOW, the effect of this reaction is to drive the $\delta^{18}O$ in exchanging waters toward positive values. Also, because of the low hydrogen concentration of most of the rock, the δD of waters is relatively unchanged.

Isotopic-exchange reactions, as in all chemical reactions, proceed faster at high temperatures, and their

effects are generally detected only in systems in which the water temperature approaches or is higher than 100°C (212°F). Because of the utility of stable isotopes in pervious interpretative work in such systems, D and ^{18}O measurements were made on several samples from the hot-springs system.

Isotopic analytical results are given in table 8 and shown in figure 7. Deuterium in the cold waters has an average $\delta D = -228.6‰$, whereas the average of the hot springs is insignificantly different at $-28.3‰$. These values agree with previous estimates (Sheppard and others, 1969) that deuterium in meteoric water in the central Arkansas region should be within a few per mil of -30. The coincidence of values for the hot- and cold-water sampling points is strong evidence that there is no detectable source of meteoric water contributed to the hot springs from outside the region.

The average $\delta^{18}O$ of the hot springs is $-5.2‰$, and the average of the cold springs is $-5.1‰$. The lack of oxygen shift shows that there is no oxygen-isotope exchange between the hot springs and oxygen-bearing minerals in the aquifer. This lack of oxygen-isotope exchange could be true only if (1) the maximum temperature within the hot-springs system is not much higher than the springs' surface temperatures and (or) (2) the flow rate of the waters through the hottest part of the system is relatively high, so that there is little time for exchange.

In summary, the deuterium and ^{18}O data suggest that the concept given elsewhere in this report concerning the hydrology of the Arkansas hot springs is reasonable and that (1) virtually all the water in the hot springs is of local, meteoric origin—any theories implying long-distance (that is, many tens or hundreds of miles) water movement, or the presence of juvenile or magmatic water in the springs, must be disregarded—and that (2) the maximum temperature reached by most of the hot-springs water cannot be many tens of degrees higher than the springs' surface temperature; also (3), the resident time of the hot-springs waters in the heated part of the system is a relatively short time, that is, not more than perhaps a few hundred years. The silica concentration of the hot-springs water, discussed in a previous section, and the ^{14}C concentration, discussed in the following, refine these conclusions further.

The isotope of hydrogen is tritium (H^3 or T), which has an atomic mass of 3 and is radioactive, with a half-life of about 12¼ years. Tritium is formed continuously by cosmic rays impinging on the upper atmosphere. This natural tritium is present in precipitation at levels of from 1 to 10 T atoms per 10^{18} H atoms.

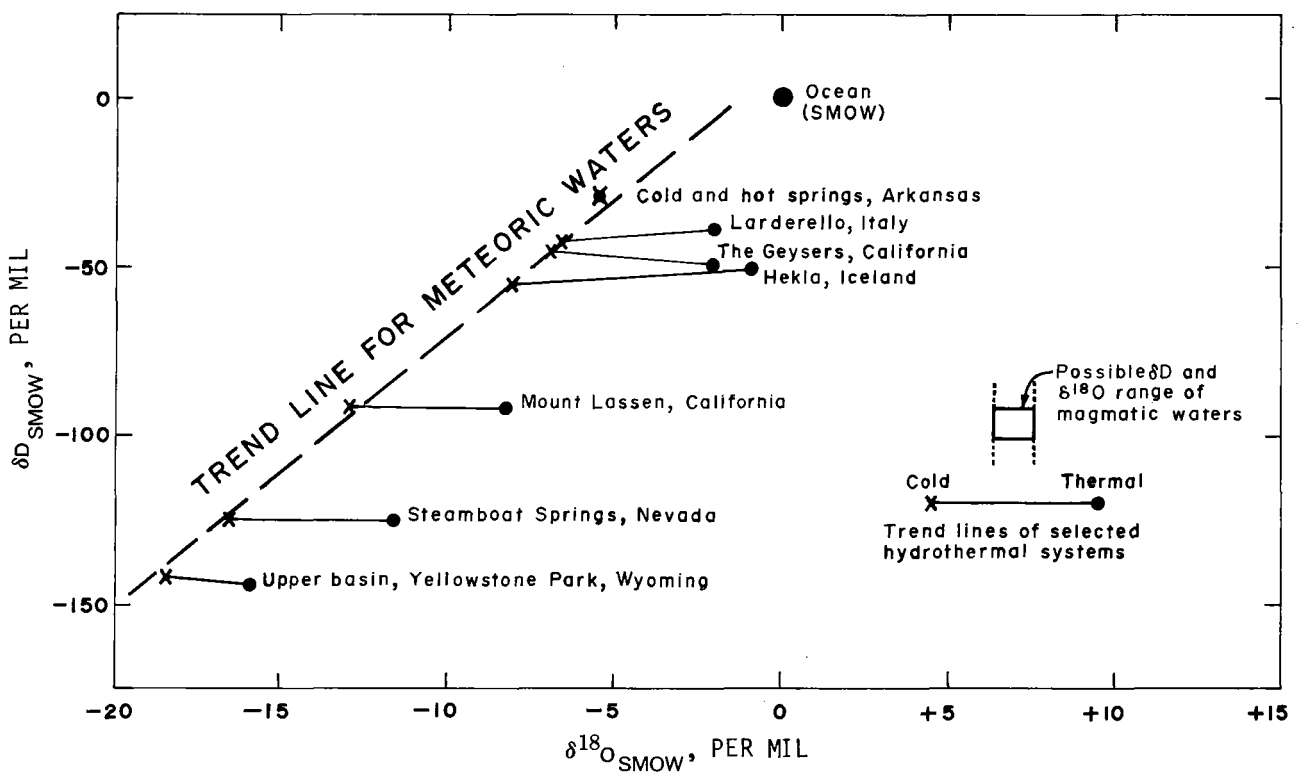


FIGURE 7.—Comparison of isotopic composition of waters from the cold and hot springs of Arkansas and of hydrothermal waters elsewhere (after White and others, 1973, fig. 1).

Tritium is measured by analyzing its rate of radioactive decay in a water sample, and the results are expressed as tritium units (Tu), one of which is equal to a T/H ratio of 10^{18}. Thus, natural tritium is present in the range of from 1 to 10 Tu.

Large quantities of tritium are produced by nuclear devices, and the atmospheric testing of such devices—particularly fusion devices (hydrogen bombs)—from the early 1950's through 1962 raised the level of tritium in precipitation to many times its natural level of from 1 to 10 Tu. Peak tritium levels occurred in the spring of 1963, when precipitation at St. Louis, for example, reached levels of more than 2,500 Tu. Since then, tritium levels have been decreasing at about 30 percent per year. During the 1950's, tritium levels were in the range of several hundred tritium units, also well above natural levels.

The tritium concentrations of samples collected from the hot springs are given in table 8.

Results of radioisotope measurements of tritium and also ^{14}C, that are discussed below, are expressed with a statistical-error term corresponding to one standard deviation (1σ). There is a probability of two in three that the true value of a quantity is within the 1σ range. For Diamond Mineral Spring (table 8), with tritium shown as 1.5 ± 0.4 Tu, there is a 67-percent probability that the true tritium concentration is between 1.1 and 1.9 Tu, and a 95-percent (2σ) chance that it is between 0.7 and 2.3 Tu.

TABLE 8.—*Hydrogen- and oxygen-isotope concentration of waters in the hot-springs area*

Well or spring No.[1] (fig. 6)	Name	Date of collection in 1972	δD SMOW ‰	$\delta^{18}O$ SMOW ‰	Tritium (TU±1σ
S8	Happy Hollow Spring	Jan. 24	-30	-5.8	1.1±0.6
W19	Belvedere Country Club Well	Sept. 25	-23	(2)	41.8±2.0
W20	Frank Thompson's house well	Sept. 24	-28	(2)	85.3±1.6
S10	Sleepy Valley Spring	Sept. 28	-30	-5.5	34.1±2.1
W17	Bill Sargo's well	Sept. 24	-30	(2)	91.8±4.7
W16	R. B. Yates' well	Sept. 25	-28	(2)	27.7±1.6
S11	McLendon Mineral Spring	Sept. 27	-29	(2)	1.5±0.8
W21	Gulpha Gorge well	Sept. 27	-30	(2)	1.3±0.4
S7	Cluster Spring	Sept. 26	-30	(2)	.7±0.6
W26	Whittington Avenue Spring	Jan. 24	-26	-4.1	2.8±0.5
W25	Whittington Park well	Jan. 28	-29	-5.3	1.2±0.8
S5	Echo Valley Spring	Jan. 27	-30	-5.1	3.1±0.6
W12	Elizabeth Brown well	Sept. 24	-29	(2)	.9±0.5
W24	Diamond Mineral Spring	Jan. 22	-29	-4.9	1.5±0.4
	Maurice Hot Spring	Jan. 20	-27	-3.9	1.2±0.3
	Hot Spring No. 17	Jan. 25	-30	-5.4	3.0±0.5
	Hot Spring No. 23	Jan. 26	-28	--	.7±0.8
	Hot Spring No. 33	Jan. 26	-28	-5.4	.9±0.6
	Hot Spring No. 46	Jan. 18	-29	-5.5	3.1±0.6
	Hot Spring No. 48	Jan. 25	-28	-5.7	.7±0.4
	80,000-gallon reservoir	Jan. 27	-29	-4.9	1.0±0.7
	Hot Spring No. 42	Jan. 19	-28	-5.4	2.7±0.3
	Hot Spring No. 49	Jan. 21	-28	-5.6	9±0.4

[1]U.S. Geological Survey numbers of wells and springs are given in table 7.

[2]Not analyzed.

Of the nine hot springs, four have tritium levels that are so low that they may, within a 95-percent confidence limit, contain no tritium; that is, the 2σ range of their analyses includes zero. The rest of the hot springs contain tritium, but not more than 3 Tu. A sample that contained 3 Tu could be water that fell as rain in the 1940's that had an initial tritium concentration of about 10 Tu. This explanation is unlikely, though, because evidence discussed below suggests that the hot-springs waters have ages of thousands of years, and there is another explanation for the 3-Tu level which also accounts for the different tritium concentrations of the several springs.

It is possible that some of the hot springs include a small proportion of water of very recent origin which mixes with the main flow of heated water near the springs' outlets. Such water could contain water from the 1960's that has tritium levels of several hundred or more tritium units. An admixture of less than 1 percent of such water would raise the tritium level to that measured, and such an amount would be too small to measurably affect any other characteristics of the sample. Thus, the tritium level suggests that there is no significant amount of water less than several decades old in any of the hot springs.

Of the 14 cold wells and springs, 5 have tritium levels higher than 25 Tu and the rest have levels lower than 3 Tu. Those with little tritium, such as the hot springs, contain no significant amounts of recently recharged water, whereas those with high tritium concentrations contain significant quantities of water recharged within the past 15 years. Their high tritium concentration reinforces the preceding conclusion that the chemistry of Belvedere Country Club well and Frank Thompson's house well is that of recharge to the system and that Bill Sargo's well and R. B. Yates' well could be influenced by man's activity. The fact that Happy Hollow Spring, although chemically identical with the high-tritium Belvedere Country Club well and Frank Thompson's house well, contains only 1.1 ± 0.6 Tu is somewhat puzzling. A possible explanation is that the water in this spring fell as rain at, say, 5 Tu in the prebomb era (pre-1953) and has no component of post-1953 water. Sleepy Valley Spring shows only slight effects of mineral-water reactions, and its high tritium concentration is therefore not unexpected.

CARBONATE GEOCHEMISTRY

The most common inorganic, carbon-bearing chemical species are carbon dioxide (CO_2), a gas which readily dissolves in water, bicarbonate (HCO_3^-), the predominant carbon species in most waters in nature, and carbonate (CO_3^{-2}), found in such minerals as calcite ($CaCO_3$) but also present in low concentrations in solu-

tion. The prevalent species in a given solution depend on the hydrogen-ion (H^+) concentration of the solution. The pH of a solution is a measure of its H^+ activity (pH $= -\log a_{H+}$). A solution having a low pH has a relatively high H^+ activity, or is acidic; one having a high pH represents an alkaline solution, one having a relatively low H^+ activity.

The interreactions among the three carbonate species are:

$$CO_2(gas) + H_2O \rightarrow H_2CO_3, \quad (2)$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^-, \quad (3)$$

and

$$HCO_3^- \rightarrow H^+ + CO_3^{-2}. \quad (4)$$

Water in contact with a gas phase containing CO_2 will dissolve CO_2, according to reaction 2, in an amount proportional to the partial pressure of CO_2 in the gas (P_{CO2}). Some of the H_2CO_3 so formed will dissociate, by reaction 3, to bicarbonate and hydrogen ion, which will lower the pH of the solution. If an alkaline substance is present, the H^{+so} formed will be removed from solution, permitting more HCO_3^- to form. Carbonate minerals are common alkaline substances and are dissolved by H^+ by the reaction

$$CaCO_{3(solid)} + H^+ \rightarrow Ca^{+2} + HCO_3^-. \quad (5)$$

If a water originally charged with CO_2 is brought into contact with a carbonate mineral, the reaction

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{+2} + 2HCO_3^- \quad (6)$$

will occur. This reaction is the most important in controlling the chemical character of waters in the hot-springs area, and together with the solution of silica, discussed previously, also controls the chemistry of the hot springs themselves.

In discussing the carbonate chemistry of these waters, the term "total dissolved carbonate" is often used. This term refers to the molar sum of the dissolved carbonate species H_2CO_3, HCO_3^-, and CO_3^{-2}. This is not an analyzed value, but is calculated from the HCO_3^- and pH values given in table 2, and the equilibrium-constant expressions corresponding to reactions 2, 3, and 4. These calculations were made using the computer program WATEQ (Truesdell and Jones, 1974). The total dissolved-carbonate concentrations so calculated for the waters sampled are given in table 9.

Some of the wells and springs were sampled for analyses of their dissolved-gas concentration. Figure 8 shows the relation between the analyzed partial pressure of CO_2 (PCO_2), with the PCO_2 calculated from the values of pH and HCO_3^- given in table 6. Some of the analyzed values are larger than the calculated values, but most agree within 25 percent. Although this may appear a large error, it introduces very little error into the much larger calculated total dissolved-carbonate concentration, which is the parameter of interest.

Water entering a ground-water system is exposed to gases from the Earth's atmosphere and from the gas phase in the soil zone. The soil air is the last gas phase

TABLE 9.—*Carbon-isotope date for waters in the hot-springs area*

Well or spring No.[1] (fig. 6)	Name	Total dissolved carbonate (millimoles per liter)	Measured $\delta^{13}C$ PDB (‰)	Proportion plant carbonate	Calculated $\delta^{13}C$ PDB (‰)	Measured ^{14}C (percentage modern $\pm 1\sigma$)	Adjusted ^{14}C (percentage modern)	Adjusted age (years)
S8	Happy Hollow Spring	1.13	(2)	1.000	−24.0	(2)	Recharge.	
W19	Belvedere Country Club well	1.44	−22.5			101.7±1.6		
W20	Frank Thompson's house well	0.88	−23.7			98.9±1.5		
S10	Sleepy Valley Spring	1.41	−22.6	.904	−21.7	(2)	------	------
W17	Bill Sargo's well	[2]1.02	−24.1	------	------	(2)	------	------
W16	R. B. Yates' well	1.85	−23.6	------	------	[3]111.8±1.3	------	------
S11	McLendon Mineral Spring	2.78	−13.8	.620	−14.9	39.5±0.8	63.7	3,730
W21	Gulpha Gorge well	3.05	−14.4	.585	−14.0	35.5±0.5	60.7	4,130
S7	Cluster Spring	3.49	−15.8	.670	−16.1	37.3±0.4	55.7	4,840
W26	Whittington Avenue Spring	3.85	−14.3	.650	−15.6	31.2±0.5	48.0	6,070
W25	Whittington Park well	3.94	−13.8	.565	−13.6	23.7±0.3	41.9	7,180
S5	Echo Valley Spring	4.06	−14.9	.558	−13.4	22.2±0.3	39.8	7,620
W12	Elizabeth Brown well	3.88	−15.5	.625	−15.0	21.2±0.4	33.9	8,940
W24	Diamond Mineral Spring	4.15	−13.3	.566	−13.6	19.4±0.3	34.3	8,850
	Maurice Hot Spring	3.00	−14.7	------	------	(2)	------	------
	Hot Spring No. 17	2.70	*−14.1	------	------	*36.9±0.5	------	------
	Hot Spring No. 23	2.74	*−14.2	------	------	*35.1±0.6	------	------
	Hot Spring No. 33	3.06	−14.6	------	------	(2)	------	------
	Hot Spring No. 46	3.18	*−14.8	------	------	*35.6±0.7	------	------
	Hot Spring No. 48	2.97	*−14.3	------	------	*38.7±0.7	------	------
	80,000-gallon reservoir	2.97	*−14.4	------	------	*30.4±0.6	------	------
	Hot Spring No. 42	3.18	(2)	------	------	(4.6±1.2)	------	------
	Hot Spring No. 49	3.07	*−16.1	------	------	*36.8±0.9	------	------
	Average of samples indicated by (*)	------	−14.6	.608	------	35.6±	58.5	4,430

[1] U.S. Geological Survey numbers of wells and springs are given in table 7.
[2] Not analyzed.
[3] Man influenced; not representative.

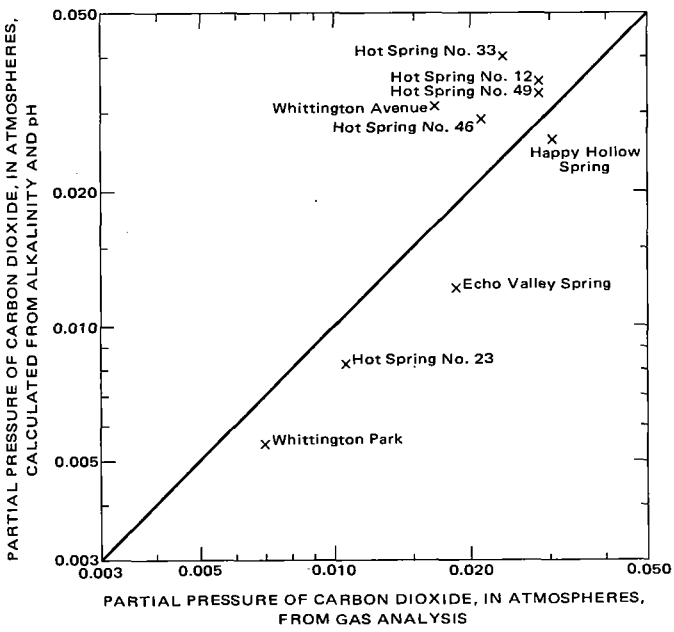


FIGURE 8.—Relation between analyzed and calculated partial pressures of CO_2.

to which the water is exposed before it enters the water-saturated zone, so the composition of the soil air controls the type and amount of gases initially dissolved in ground water. The main difference between the open atmosphere and soil air is that the soil air contains considerably more CO_2. In the open atmosphere, the partial pressure of CO_2 (PCO_2) is about 3×10^{-4} atm (atmospheres). Water in contact with this PCO_2 at 17°C (62.6°F) contains about 1.3×10^{-2} millimoles per liter (mmol/L) H_2CO_3, or about 0.8 mg/L. In soils, though, much of the CO_2 is produced by plant-root respiration and by decay of plant debris, so the PCO_2 in soil air is one or more orders of magnitude higher than that in the open atmosphere.

Because of differences in soil and plant types, the soil air PCO_2 may differ from place to place, but should be reasonably constant within a given area. An analysis of the composition of the gas dissolved in Happy Hollow Spring, one of the waters containing dissolved material which, except for silica, is probably derived mainly from atmospheric precipitation, showed its PCO_2 to be 3×10^{-2} atm, equivalent to an H_2CO_3 concentration of about 1.4 mmol/L, or 87 mg/L. Gas analyses were not made for the other two most dilute samples—from Frank Thompson's well and the Belvedere Country Club well—but analyses of their HCO_3^- and H^+ (pH) concentrations were made. From these data and from the known equilibrium constants for the reactions between carbonate species (1 and 2 above), the PCO_2 of the gas in equilibrium with them can be calculated (Truesdell and Jones, 1974). For the water from Frank Thompson's well, the PCO_2 so calculated is about 2×10^{-2} atm. The average total dissolved carbonate ($H_2CO_3+HCO_3^-$) in these three samples was 1.15 mmol/L.

The chemistry of the remaining cold waters sampled differs from that of atmospheric precipitation, as represented by Happy Hollow Spring, Frank Thompson's well, and the Belvedere Country Club well, primarily in having higher alkaline-earth (Ca^{+2}, Mg^{+2}, and Sr^{+2}) and bicarbonate (HCO_3^-) concentrations. Reactions representing the solution of mineral carbonate are written in terms of an idealized $CaCO_3$ mineral. In nature, $CaCO_3$ may contain other elements of the alkaline-earth group such as magnesium (Mg^{+2}) and strontium (Sr^{+2}), replacing calcium. These substitutions have little effect on the carbonate in the ground water, and so in discussing the measured water chemistry, the total alkaline-earth concentration (Ca+Mg+Sr) is used, whereas in discussing reactions, only the idealized-Ca^{+2} form is used.

Figure 9 is a graph showing the concentrations of alkaline-earth against total dissolved-carbonate concentrations ($H_2CO_3+HCO_3^- + CO_3^{-2}$). On this graph, the point at zero alkaline-earth concentration is at the average total-carbonate concentration of the three most dilute samples (1.15 mmol/L). From this point, lines are drawn showing the trend of compositions which would result from solution of carbonates by reactions 5 and 6. Three of the samples—Sleepy Valley Spring, Cluster Spring, and Whittington Avenue Spring—fall near the line of reaction 6. In these samples, the dissolved carbonate in excess of that in the recharge water is half from solution of carbonate minerals and half from solution of further soil-zone-derived CO_2. The other samples plot between the two lines, and a greater proportion of their excess carbonate is from solution of carbonate minerals alone.

To adjust ^{14}C (radiocarbon) measurements on ground waters so that they can be used to calculate ground-water ages, it is necessary to know the proportion of total dissolved carbonate that has come from solution of soil-zone CO_2. This factor can be derived from the chemical information in figure 9, but before describing the method, a discussion of the isotopic chemistry of carbon is appropriate.

ISOTOPIC CHEMISTRY OF CARBON

The element carbon has three naturally occurring isotopes with masses of 12, 13, and 14. Carbon of masses 12 (^{12}C) and 13 (^{13}C) are stable isotopes, whereas carbon of mass 14 (^{14}C) is radioactive. In any chemical reaction such as the solution of CO_2 to form HCO_3^-, or the formation of carbohydrates from CO_2 by plants during photosynthesis, the light isotope (^{12}C) reacts faster than the heavier isotope (^{13}C). The isotope ratios of reactant and product species are different, and

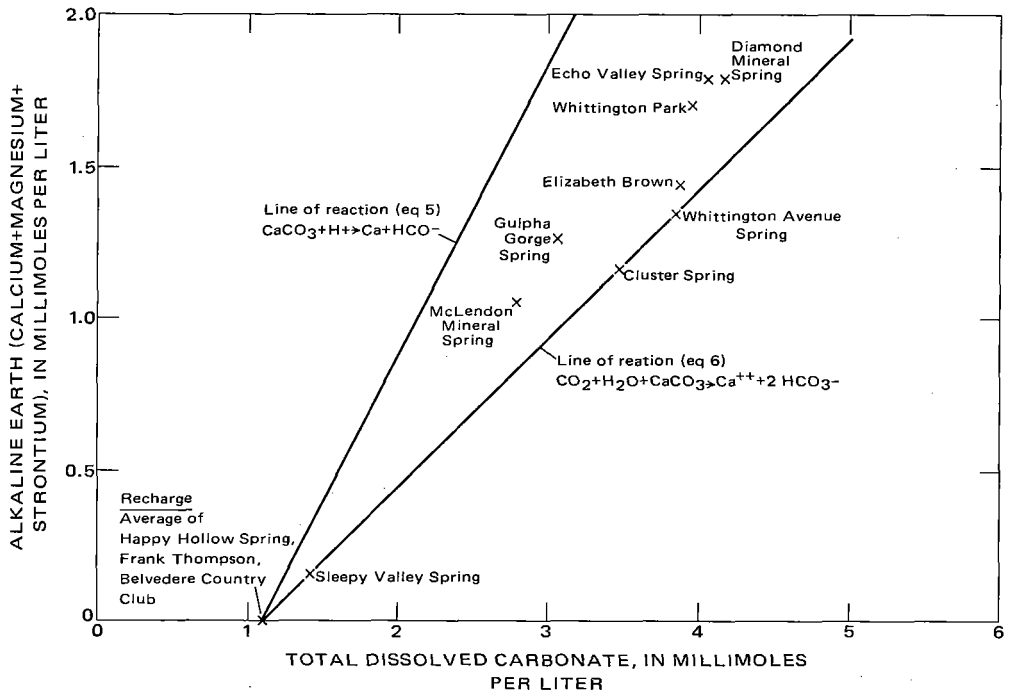


FIGURE 9.—Relation of alkaline-earth concentration to dissolved-carbonate concentration.

isotopic fractionation occurs. Carbon-isotope ratios are measured relative to an arbitrary standard, a calcite of marine origin known as PDB and expressed in the δ-notation, as are hydrogen- and oxygen-isotope ratios.

$\delta^{13}C$ values for samples from a single type of carbon-bearing material are relatively constant, but one material may have quite different $\delta^{13}C$ values from another. Marine limestones, for instance, have $\delta^{13}C$ values close to zero (because a marine carbonate is used as the standard), whereas atmospheric CO_2 and plants typical of the hot-springs region are depleted in ^{13}C and have $\delta^{13}C$ values of about $-7‰$ and $-24‰$, respectively. These large differences make $\delta^{13}C$ measurements valuable in determining the sources of dissolved-carbonate species (Pearson and Hanshaw, 1970).

The naturally occurring radioisotope of carbon (^{14}C) has a half-life of about 5,730 years. Natural ^{14}C is formed by cosmic-ray reactions in the upper atmosphere and is found at virtually a constant concentration in atmospheric CO_2. ^{14}C concentrations are measured and reported as percentages relative to a standard whose ^{14}C concentration is that of an ideal plant, grown in 1950, in the absence of any atmospheric CO_2 of industrial origin. ^{14}C is produced as a byproduct of nuclear explosions, and in the last 25 years the ^{14}C level in the atmosphere has risen considerably higher than its natural level (100-percent modern).

Plants using atmospheric CO_2 assimilate ^{14}C. When a plant dies, the amount of ^{14}C it contains decreases because of radioactive decay, and the amount remaining, relative to that of an ideal living plant, measures the time that has elapsed since its death. This is the principle on which the radiocarbon (^{14}C)-dating method is based.

The equation for radioactive decay is

$$\frac{A_{sm}}{A_{std}} = \exp(-\lambda t),$$

where A_{sm}/A_{std} is the ratio of sample to standard activity, λ is the decay constant of the isotope (1/8,266 for ^{14}C), and t is the age in years. (The half-life of an isotope is the value of t when $A_{sm}/A_{std}=0.5$; that is, $t_{1/2}=\ln 2/\lambda=5{,}730$ years for ^{14}C). For calculation, the decay equation is often written using natural logarithms (ln) as

$$t = -8{,}266 \ln \left(\frac{A_{sm}}{A_{std}} \right).$$

As discussed, the CO_2 in the soil air is a product of plant respiration and decay. Because of its plant origin, soil-air CO_2 has the same carbon-isotopic composition as plants; its $\delta^{13}C$ value is about $-24‰$, and its ^{14}C concentration is close to 100 percent (in the prebomb era). Soil CO_2 dissolved by ground water will also inherit its plant isotopic character, and if soil CO_2 were the only source of carbonate dissolved in a ground wa-

ter, its ^{14}C concentration would directly reflect the age of the ground water—that is, the time that has elapsed since the water left the soil zone.

Ground water generally contains mineral carbonate, which is commonly of marine origin and has a $\delta^{13}C$ value near 0‰. Because of its great age relative to the half-life of ^{14}C, mineral carbonate has no ^{14}C. Solution of ^{14}C-free carbonate lowers the measured-^{14}C concentration of carbonate dissolved in ground waters and gives the water a falsely old apparent age. However, if the relative amounts of soil-derived and mineral carbonate are known, this effect can be corrected.

For example, consider a water of an age of zero years, with a total dissolved carbonate of 4.00 mmol/L, of which 3.00 mmol/L is from soil CO_2 (^{14}C=100 percent) and 1.00 mmol/L from carbonate minerals (^{14}C=0 percent). The measured ^{-14}C concentration of this water will be

$$\frac{((3.0\times1.0)+(1.0\times0.0))}{4.0} = 75\text{-percent modern},$$

and its apparent age will be

$$t = -8{,}266 \ln (75/100) = 2{,}380 \text{ years},$$

instead of its real age, zero years.

By knowing the proportions of the sources of carbonate to a ground water, it is possible to adjust the measured-^{14}C concentration to its correct value and so obtain a corrected age. The adjustment factor, P, is the ratio of soil-air-derived (=plant) carbonate concentration to total dissolved-carbonate concentrations:

$$P=\frac{C_{\text{plant}}}{C_{\text{total}}}. \tag{7}$$

For this example,

$$P=\frac{3.00}{4.00} = 0.75.$$

The adjusted ^{14}C concentration is

$$^{14}C\ (\text{adjusted})=\frac{^{14}C\ (\text{measured})}{P},$$

and for this example

$$^{14}C\ (\text{adjusted}) = \frac{75\text{ percent}}{0.75} = 100\text{ percent},$$

corresponding to an age of zero, as specified.

Chemical information on ground water can often be used to determine the proportion, P, of soil-air-derived carbonate to total carbonate. A graphical representation of changes in water chemistry, such as that given in figure 9, can be useful. Consider Whittington Avenue Spring. The total carbonate concentration of this sample (3.85 mmol/L) is the sum of (1) carbonate dissolved by atmospheric precipitation in the recharge area, here taken as the average of the three very dilute samples, Happy Hollow Spring, Frank Thompson's well, and the Belvedere Country Club well shown in figure 9, or 1.15 mmol/L, and (2) additional carbonate from the reactions

$$CaCO_3+H^+\rightarrow Ca^{+2}+HCO_3^- \tag{5}$$

and

$$CO_2+H_2O+CaCO_3\rightarrow Ca^+ +2HCO_3^- \tag{6}$$

or, 2.70 mmol/L.

Note that in reaction 5 all the bicarbonate is from the solution of mineral carbonate and that an equivalent amount of alkaline earth (Ca) also appears in solution. In reaction 6, half of the bicarbonate is of mineral and half of gaseous (plant and soil-air) origin. In reaction 6, twice as much bicarbonate as alkaline earth is produced, but the amount of mineral carbonate added still equals the amount of alkaline earth, as in reaction 5.

The Whittington Avenue Spring contains 1.34 mmol/L of alkaline earth in solution, and from the preceding paragraph, this will be the amount of mineral carbonate dissolved, as well. That is, of the 2.70 mmol/L total carbonate present in excess of that in the recharge, 1.34 mmol/L is of mineral origin and 1.36 mmol/L (2.70–1.34) of plant origin.

To sum these considerations algebraically,

$$C_{\text{total}}=C_{\text{recharge}}+C_{\text{mineral}}+C_{\text{gaseous}}, \tag{8}$$

where C is the carbonate concentration from the subscript sources. C_{recharge} and C_{gaseous} are of plant (=soil-air) origin and $C_{\text{mineral}}=C_{\text{alkaline earth}}$. Equation 8 becomes

$$C_{\text{total}}=C_{\text{plant}}+C_{\text{alkaline earth}},$$

or

$$C_{\text{plant}}=C_{\text{total}}-C_{\text{alkaline earth}}. \tag{9}$$

The ^{14}C-adjustment factor, equation 7, can now be solved:

$$P=\frac{C_{\text{plant}}}{C_{\text{total}}}=\frac{C_{\text{total}}-C_{\text{alkaline earth}}}{C_{\text{total}}}=1-\left(\frac{C_{\text{alkaline earth}}}{C_{\text{total carbonate}}}\right) \tag{10}$$

For the Whittington Avenue Spring,

$$P=1-\left(\frac{1.34}{3.85}\right)=0.65.$$

The stable carbon-isotopic composition of the total carbonate dissolved in a ground water sample also reflects the proportions of the source carbon. As discussed, the $\delta^{13}C$ value for plants is about −24‰,

whereas that for marine mineral carbonate is about $0^{o}/_{oo}$. The $\delta^{13}C$ value of a sample will be in proportion to the amounts and isotopic compositions of its carbonate sources:

$$\delta^{13}C_{sample}=\delta^{13}C_{plant}\left(\frac{C_{plant}}{C_{total}}\right)+\delta^{13}C_{mineral}\left(\frac{C_{mineral}}{C_{total}}\right).$$

Because $\delta^{13}C_{mineral} = 0^{o}/_{oo}$, the last term is zero and

$$\delta^{13}C_{sample}=\delta^{13}C_{plant}\left(\frac{C_{plant}}{C_{total}}\right), \qquad (11)$$

which, on recalling equation 7 and substituting an average value for $\delta^{13}C_{plant}$, becomes

$$\delta^{13}C_{sample}=-24P. \qquad (12)$$

Carbon-isotope data and calculated total carbonate concentrations of samples in the hot-springs area are given in table 9. For each, a value for P, the proportion of plant carbonate, calculated using equation 10, is shown. Also, $\delta^{13}C$ values, calculated from equation 12, are given for comparison with the measured $\delta^{13}C$ values.

Agreement between measured and calculated $\delta^{13}C$ values is excellent, suggesting that the geochemical processes, described in the preceding paragraphs, adequately model the field situation. The average value of the differences between the calculated and measured $\delta^{13}C$ values is $0.75^{o}/_{oo}$, and the average value of the measured $\delta^{13}C$ values themselves is $16.7^{o}/_{oo}$. The error associated with the calculated values of P can be estimated as $0.75/16.7 \times 100 = 4$ percent. This is larger than the ^{14}C-analyzed errors and corresponds to an error band of ±500 years for a sample of 4,000 years and of ±1,000 years for a sample of 9,000 years.

The adjusted ages of the cold wells and springs that were sampled are consistent with inferences previously drawn from their chemical character and their tritium concentrations. The Belvedere Country Club well and Frank Thompson's well, which represent water recharging the system, have ^{14}C concentrations near 100-percent modern. The R. B. Yates' well, which on chemical criteria is suspected to include recent water showing man's influence, has both ^{14}C and tritium levels found only in the last 20 years.

The adjusted ages of the remaining cold-water samples range from 3,700 to 8,900 years and increase in age with increasing total carbonate concentration.

AGE OF THE HOT-SPRINGS WATER

As the analyses in table 6 show, the hot springs have almost identical chemical characteristics, suggesting that they have a common origin. The only detectable differences among them are in their carbonate concentrations, shown by the different HCO_3^- and pH values in table 6, and in the total carbonate concentrations calculated from these values and given in table 9.

Calculations have been made to determine whether the waters of the hot-springs system are saturated with respect to the mineral calcite ($CaCO_3$)—that is, to determine whether the calcium and carbonate concentrations of the waters are such that they will dissolve more calcite or deposit calcite from solution. The mineral calcite ($CaCO_3$) dissolves according to the reaction

$$CaCO_3 \rightarrow Ca^{+2}+CO_3^{-2}.$$

At saturation, the product of the thermodynamic activities of the dissolved materials ($a_{Ca^{+2}}, a_{CO_3^{-2}}$) equals a constant ($KT$), the value of which is a function of temperature. That is, at saturation

$$[a_{Ca^{+2}}][a_{CO_3^{-2}}]= KT.$$

It is convenient to express the degree of saturation of a water in terms of the logarithm of the ratio of the activity product (AP) to the equilibrium constant (KT). The AP of an undersaturated water is less than one, so log (AP/KT) is negative. Conversely, log (AP/KT) of an oversaturated water is positive.

In the previous general discussion of carbonate chemistry, equations 2, 3, and 4 were given showing the interreactions among the carbonate species CO_2 (gas), HCO_3^-, and CO_3^{-2}. According to these equations, a change in any one of the carbonate species will produce a change in the others. Combining equations 2, 3, and 4, for example, gives

$$2HCO_3^- \rightarrow CO_2(gas)+CO_3^{-2}+H_2O,$$

which shows that if CO_2 gas leaves water, responding to a decreasing (P_{CO_2}), the CO_3^{-2} concentration may increase. This reaction in turn will increase the AP for calcite and thus the degree of saturation of the water with respect to calcite.

Certain of the hot springs visibly evolve gas where they emerge at the Earth's surface, and because this gas is in part CO_2, the carbonate chemistry of individual springs should differ as a function of the amount of gas evolved. Measured and analyzed CO_2 partial pressures (P_{CO_2}) from some of the springs are shown in figure 8. Comparison of this figure with the total dissolved-carbonate data in table 9 shows that a spring such as number 23 that has a low P_{CO2} value, which presumably results from evolution of a significant amount of dissolved gas, has a lower total dissolved-

carbonate concentration than such springs as numbers 42 and 49 that have higher P_{CO2} values. The P_{CO2} of these waters is as high as 0.035 atm (fig. 8), whereas the $P_{CO2}$of the Earth's atmosphere to which they are exposed at the surface is only 0.0003 atm. The hot-springs waters certainly could lose CO_2 to the atmosphere as they approach the surface.

To follow the influence of CO_2 outgassing on the overall carbonate chemistry of the spring water, calculations of log (AP/KT) at various values of P_{CO2} were made for a relatively cool spring (No. 23, 56.2°C (133.2°F)) and for a hot spring (No. 49, 61.8°C (143.2°F)). The results of these calculations are shown in figure 10. The path of decreasing calcite saturation with increasing P_{CO2} for spring number 23 is slightly offset from that of number 49 because of the temperature difference between the springs. More important,

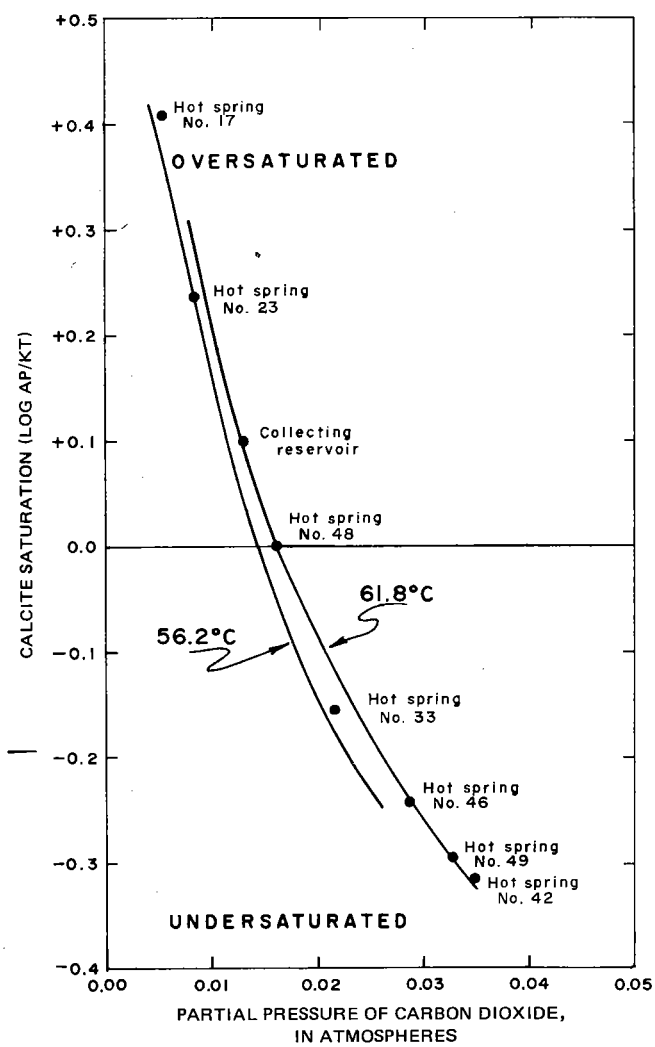


FIGURE 10.—Relation between calcite saturation and partial pressure of carbon dioxide in the hot springs.

the points corresponding to the other springs sampled lie on or between the two calculated lines. From this comparison we conclude that the differences among the hot springs in pH and HCO_3^- (table 6), in total dissolved carbonate (table 9), and in P_{CO2} (fig. 8) are superficial and due only to different amounts of outgassing in the near-surface distributary system to the springs.

Figure 10 shows that certain of the springs are oversaturated with respect to calcite. Table 6, though, shows that the calcium concentration of the springs is identical (44.5±0.5 mg/L) and that the springs that were sampled had not yet begun to deposit calcite, though they have the potential to do so. If allowed to flow freely on the surface, all the springs would continue to lose CO_2 and thus would deposit calcite. The tufa associated with the springs shows such deposition does occur.

One significant difference between the hot-springs waters and the cold wells and springs in the region is their sodium (Na) concentration. The average sodium concentration of the 12 relevant cold-water samples is 1.8 mg/L (0.08 mmol/L), whereas that of the hot springs is 4.0 mg/L (0.18 mmol/L). There is no difference between the carbonate, sulfate, or chloride concentrations of the cold and hot springs to balance the additional sodium as there would be if the sodium were a product of the solution of some mineral. Instead, the sodium must result from a reaction by which it is exchanged for some other positively charged dissolved ion. Such a reaction can be written

$$Ca^{+2}+Na_2\,X \rightleftarrows Ca\,X\,2Na^+, \qquad (13)$$

in which Ca^{+2} represents an alkaline earth and $Na_2\times$ and Ca X represent solids, perhaps clay minerals, in the aquifer system, with X the substrate on which the exchange occurs.

This exchange reaction must be considered in calculating the proportion of plant to total carbonate to adjust the measured ^{14}C concentrations of the hot springs and to determine their water ages. To calculate this proportion for the cold springs, the expression

$$P=1-\left(\frac{C_{\text{alkaline earth}}}{C_{\text{total carbonate}}}\right) \qquad (10)$$

was used. In deriving equation 10, it was assumed that only mineral carbonate solution affected the alkaline-earth concentration of the waters, and the validity of this assumption was borne out by the agreement between the calculated and measured stable carbonisotope concentration ($\delta^{13}C$) of the samples. In the hot-springs waters, the alkaline-earth concentration is dependent on exchange reaction 13, as well as on the carbonate chemistry, thus equation 10 cannot be used.

In discussing the carbonate chemistry of the cold

springs, the relationship between the stable carbon-isotope concentration ($\delta^{13}C$) of a sample and the proportion of plant to mineral carbonate,

$$\delta^{13}C_{sample}=\delta^{13}C_{plant}\left(\frac{C_{plant}}{C_{total}}\right), \quad (11)$$

was presented. This equation can be used directly to find the ^{14}C adjustment factor, P:

$$P=\left(\frac{C_{plant}}{C_{total}}\right)=\frac{\delta^{13}C_{sample}}{\delta^{13}C_{plant}}. \quad (14)$$

By using an average $\delta^{13}C_{plant}=-24^{o}/_{oo}$ as before (eq. 12), this becomes

$$P=\delta^{13}C_{sample}/-24^{o}/_{oo}.$$

Isotopic fractionation takes place between CO_3^{-2}, HCO_3^-, and CO_2 (gas) as outgassing and CO_3^{-2} production from HCO_3^- occur. However, at the temperature of these springs ($\cong$62°C) the fractionation accompanying the reaction $HCO_3^- \rightarrow H^+ \rightarrow CO_2 + H_2O$ is nearly equal to and opposite that of the reaction $HCO_3^- \rightarrow H^+ + CO_3^{-2}$ (Pearson and others, 1972). Thus isotopic fractionation will not interfere with the calculation of P by equation 14.

Because the hot springs are chemically and isotopically so similar, their average adjusted ^{14}C concentrations and ages were calculated (table 9). Only those samples for which both ^{13}C and ^{14}C data are available were used in this average. As table 9 indicates, the proportion of plant carbonate to total carbonate in them, from equation 14, is 0.608, and their adjusted ^{14}C concentration is 58.5-percent modern, corresponding to a water age of 4,430 years.

Although the total carbonate concentration of the hot-springs water before near-surface outgassing of CO_2 is not known, it certainly cannot be lower than the highest value measured—3.18 mmol/L. This value is plotted with the adjusted age on figure 11 for comparison with the ages and carbonate concentrations of the cold wells and springs. That the hot springs, cold springs, and wells are part of the same group is clear and is additional evidence that all are part of the same hydrologic system.

A hydrologically important inference can be drawn from figure 11. The hot springs are on a trend line defined by both older and younger cold-water samples. Thus, it is probable that the age of the hot-springs water is due largely to its resident time in the cold-water part of the flow system, rather than to an extended period in a zone of heating. A rapid traveltime through the heated part of the system is in keeping with earlier conclusions from oxygen-isotope (^{18}O) exchange, suggesting no prolonged period of heating. That the surface temperatures of the hot springs closely approach their probable maximum temperatures, as calculated from their silica concentrations, also implies rapid flow which prevents significant heat loss as the heated water rises to the surface.

RADIOACTIVITY OF THE WATERS IN THE HOT-SPRINGS REGION

The radioactivity of the waters of the hot springs has been studied by several investigators. The first study was by Haywood (1902), followed by Boltwood (1905), Schlundt (1935), and Kuroda, Damon, and Hyde (1953). Much of the early interest was because of the balneological use of the water. In 1953 studies by Arndt and Damon (1953) were sponsored by the U.S. Atomic Energy Commission, whose interest was the radon concentration and the source of the radioactivity.

The presence of radium in the waters of the hot springs was established by Schlundt (1935) when he determined an average value of 1.38 picograms per liter (1.35 picocuries per liter) of radium for three samples. Recent (July 1973) analyses of the waters by the U.S. Environmental Protection Agency show a radium concentration of 2.1±0.22 picocuries (10^{-12} curie) per liter. Radon, a gas that is a radioactive decay product of radium, was analyzed in the hot springs by Boltwood (1905), Schlundt (1935), and Kuroda, Damon, and

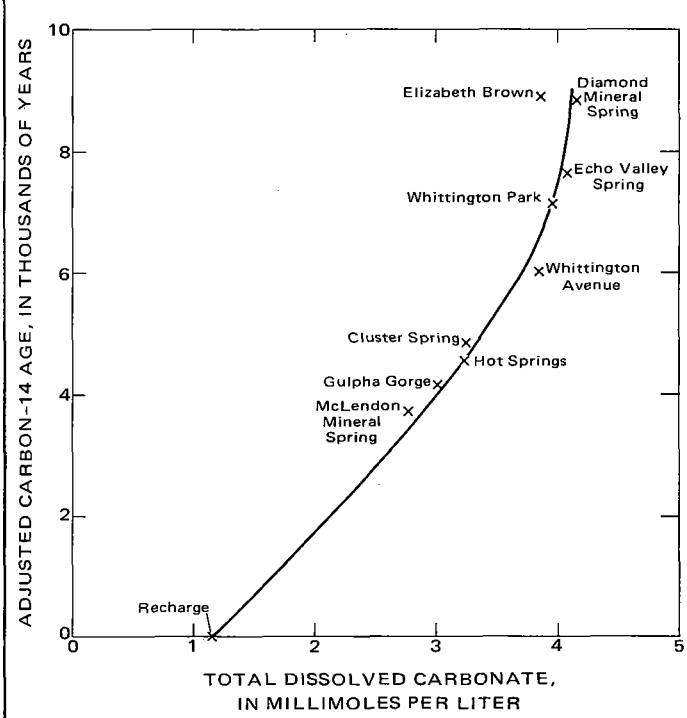


FIGURE 11.—Relation between adjusted carbon-14 age and total carbonate.

Hyde (1953). Boltwood (1905) reported the radon concentration of 45 springs, ranging from 0.017 to 9.03 nanocuries (10^{-9} curie) per liter, with modal value of 0.466 nanocurie per liter. Schlundt found the radon concentration of six hot springs to range from 0.125 to 0.46 nanocurie per liter, with a modal value of 0.32 nanocurie per liter. Kuroda, Damon, and Hyde (1953) reported the radon concentration of 25 hot springs to range from 0.14 to 30.5 nanocuries per liter, with a modal value of 0.82 nanocurie per liter.

The variations from spring to spring found by each investigator reflect the combined influence of differences in analytical methods and natural variations.

The source of radium and radon in the hot-springs waters is not definitely known, nor have the waters been analyzed for the presence of other radioactive elements. The presence of radium and radon in the region is not peculiar to the waters of the hot springs. Waters from deep wells at Hope, 68 mi (109.4 km) southwest of Hot Springs, and at Prescott, 53 mi (85.3 km) southwest of Hot Springs, ranged in radon concentration from 0.05 to 1.88 nanocuries per liter (Kuroda, 1953). Waters from the warm and cold springs near Caddo Gap, 33 mi (53.1 km) west of Hot Springs, ranged in radon concentration from 0.13 to 1.85 nanocuries per liter (Kuroda, 1953). Cold springs in the immediate vicinity of Hot Springs also contained radium and radon. The U.S. Environmental Protection Agency reported a radon concentration of Happy Hollow Spring of 1.0 ± 0.15 picocuries per liter and a radon concentration of Whittington Avenue Spring of 0.58 ± 0.12 picocuries per liter. Kuroda (1953) reported the following radon concentrations, all in nanocuries per liter: Whittington Avenue Spring, 0.36; Whittington Park well, 0.03; Happy Hollow Spring, 0.74; and Sleepy Valley Spring, 4.37 and 2.80. In addition, Kuroda (1953) reported the radioactivity of four samples of rainwater ranging from 2.72 to 6.37 nanocuries per liter. Radon concentration of spring waters issuing near the uranium-vanadium-niobium bearing depositis at Potash Sulphur Springs, 6 mi (9.65 km) southeast of Hot Springs, averaged about 15 nanocuries per liter (Arndt and Damon, 1953.)

THE HOT-SPRINGS FLOW SYSTEM

The geologic, hydrologic, and water-chemistry data and interpretations presented in previous sections of the report provide the bases from which a conceptual model of the hot-springs flow system can be formed. Digital models of the flow system provide a test of the conceptual model and a vehicle for further refinement of the conceptual model.

CONCEPTUAL MODEL

The hot-springs water is meteoric; that is, it is derived from precipitation. The water is recharged to formations in the hot-springs region (within a few tens of miles), as opposed to being recharged to formations distant (several tens or hundreds of miles) from the hot springs. The origin and proximity of recharge of the hot-springs water are revealed by the chemical constituents and isotopes in the water and the flow variations of the hot springs.

The formation or formations that form the recharge area must possess the following general characteristics:

1. The outcrop area must be relatively large and permeable, that is, from 3 to 10 mi^2 (7.77 to 25.9 km^2), assuming permeabilities that would permit average recharge rates of from 2 to 6 in (50.8 to 152.4 mm) per year.
2. The elevations of water levels in the recharge area must be high enough to provide hydraulic head for spring flow. The springs emerge at elevations ranging from 576 to 683 ft (175.6 to 208.2 m) above mean sea level.
3. The recharge formations must be hydraulically connected to the permeable zones that feed the springs.

Consideration of the lithology and structure of rocks in the area reveals two formations whose outcrops may serve as recharge areas—the Bigfork Chert and the Arkansas Novaculite. The outcrop area of the Bigfork Chert meets several of the requirements of the hot-springs recharge area—the Bigfork crops out over an area of about 36 mi^2 (93.2 km^2) north and northeast of the hot springs, in the area shown in figure 6. The Bigfork Chert generally possesses moderately high fracture and intergranular permeability. Faults and fracture zones are common. Permeable zones extending from the Bigfork Chert to the hot springs could be provided by faults (pl. 1) that connect the Bigfork Chert with permeable zones in the Arkansas Novaculite and the Hot Springs Sandstone Member of the Stanley Shale or that provide a permeable fault zone through the Missouri Mountain and the Polk Creek Shales to the hot springs.

The Arkansas Novaculite crops out in the vicinity of the hot springs in a smaller area than does the Bigfork Chert (fig. 6). Within the mapped area in figure 6, the outcrop of the Arkansas Novaculite covers about 13 mi^2 (33.7 km^2). Permeability of the Arkansas Novaculite varies greatly; in places it is moderately high. The outcrop of Arkansas Novaculite occupies the highest elevation in the vicinity of the hot springs.

The elevation of head in the recharge area required to provide hot-spring flow depends on such factors as transmissivity of the aquifer, areal extent of the recharge area, distance of the recharge area from the springs, depth of flow of water en route to the springs, and the temperature of the water in the aquifer. These factors, except for the effect of temperature on hydraulic head, are accounted for in the digital models of the aquifer. The effect of the increased temperature of water in the flow system reduces the head required in the recharge area to drive the system. The density of water above 4.0°C (39.2°F) decreases as its temperature increases. Water at 61.7°C (143.1°F) (average hot-springs temperature) is 98 percent as heavy as water at 17.7°C (63.9°F) (average temperature of recharge water). Therefore, a column of water at 17.7°C (63.9°F), 1,000 ft (304.8 m) in length, will support a 1,020-ft (310.8 m) column of water at 61.7°C (143.1°F). It would be possible for a thermal artesian system to have a lower water-level elevation in the recharge area than in the discharge area. However, under conditions of uniform areal heat flow, it would not be possible for artesian flow to be initiated without sufficient head in the recharge area to drive the system.

Water levels in the outcrop area of the Bigfork Chert range from a few feet above land surface (flowing wells) to 30 ft (9.14 m) below land surface. Water levels in the Arkansas Novaculite range from a few feet above land surface to 50 ft (15.2 m) below land surface. As an approximation of the area in which heads in the Bigfork Chert and the Arkansas Novaculite are at a minimum to sustain flow in the artesian system, the outcrop area above 700 ft (213.4 m) mean sea level was chosen. Within the area shown in figure 6, about 8.5 mi^2 (22.0×10^6 m^2) of the outcrop of Bigfork Chert is above 700 ft (213.4 m) mean sea level, and almost all the outcrop of Arkansas Novaculite is above 700 ft (213.4 m) mean sea level. However, under about 5 mi^2 (13.0×10^6 m^2) of the Arkansas Novaculite outcrop, the northwest limit of the anticline north of the hot springs, the formation dips northwestward and probably is not in a favorable structural position to supply water to the hot springs.

Analysis of streamflow provides information on the magnitude of recharge. Stream discharge and rainfall records have been collected on three small basins in the vicinity of the hot springs (Bedinger and others, 1974). The locations of the gages on East Fork and West Fork of Hot Springs Creek are shown in figure 6. The gage on Glazypeau Creek is located about 9 mi (14.5 km) north-northeast of the hot springs. Each basin is relatively small and is underlain principally by Bigfork Chert. The Arkansas Novaculite underlies the higher elevations of East Fork and West Fork of Hot Springs Creek (fig. 6).

Base flow is ground-water discharge to the stream and is derived from recharge of precipitation. A relatively large part of rainfall on the Bigfork Chert outcrop recharges the subsurface reservoir. Base flows in the East and West Forks of Hot Springs Creek are 61 and 84 percent, respectively, of precipitation (Bedinger and others, 1974). These figures are primarily a measure of the recharge to the Bigfork Chert. Also, the base-flow studies indicate that interbasin transfers of ground water occur. Such interbasin transfers of ground water, probably from several stream basins, supply the water to the hot springs.

The large surface area, the great capacity to admit recharge, and the relatively high permeability of the Bigfork suggest that the Bigfork Chert is the principal recharge source to the hot-springs artesian system. The Arkansas Novaculite has a smaller outcrop area of potential recharge, a lower capacity to admit recharge, and a generally lower permeability. However, the Arkansas Novaculite is probably a source of part of the recharge to the hot-springs system. Further analysis of the Bigfork Chert and Arkansas Novaculite as the recharge sources and principal aquifers of the flow system is made in the section on modeling.

The ^{14}C age of the hot-springs water averages 4,430 years. The greater part of the time that the water is in underground circulation the movement is very slow. That is, movement is on the order of a few feet to a few tens of feet per year and is distributed through a large volume of the aquifer. This slow movement of water continues to relatively great depths in the aquifer and probably includes lateral circulation where sufficient heat is absorbed to reach temperatures greater than 60°C. This heat is supplied by conduction through adjacent rocks of lower permeability. In the absence of fluid circulation, heat is conducted toward the land surface at rates near 1.2×10^{-6} calories per second per centimeter squared, or 1.2 heat-flow units in most of the Eastern United States. In areas of abnormally high crustal radioactivity, the geothermal heat flow may be as high as 2.2 heat-flow units (M. L. Sorey, written comm., 1976). On the basis of an assumed thermal conductivity of 0.006 calorie per second per centimeter squared and heat flow of 1.2–2.0 heat-flow units, the normal geothermal temperature gradient in the vicinity of the hot springs should be between 0.006°C/ft and 0.01°C/ft, although the available subsurface temperature information is insufficient to confirm these gradients. With these gradients and a maximum spring temperature at depth of 63°C based on silica

concentrations, the minimum depth of fluid circulation would range from 4,500 to 7,500 ft.

Highly permeable zones, probably related to jointing or thrust faulting, collect the heated water in the aquifer and provide avenues for the water to travel to the surface. Rapid movement of the water from depth to the surface is indicated by the very small decrease in temperature from the maximum temperature attained at depth to the temperature at the surface.

DIGITAL FLOW MODELS

The purpose of modeling the hot-springs flow system was to test several hypotheses regarding the nature of the flow system. Each hypothesis requires details of aquifer geometry and various combinations of hydrologic variables, such as area and depth of circulation, hydraulic conductivity, and porosity. The model analysis provides a means for estimating values of these variables that can be compared with observed data for the hot springs (such as temperature, discharge, ^{14}C concentration, and silica concentration).

The equation for the heat-flow model is

$$H=KN\left(\frac{XD}{YD}\left(\left(X_1-X_0\right)\left(\frac{MA_1+MA_0}{2}\right)+\left(X_3-X_0\right)\left(\frac{MA_3+MA_0}{2}\right)\right)+\frac{YD}{XD}\left(\left(X_2-X_0\right)\left(\frac{MA_2+MA_0}{2}\right)+\left(X_4-X_0\right)\left(\frac{MA_4+MA_0}{2}\right)\right)+(XD)(YD)\left(\frac{TTOP-X_0+DH_0}{DP_0}\right)\right)+SP\left(X_1Q_1+X_2Q_2+X_3Q_3+X_4Q_4-X_0Q_0\right)$$

The subscripts in the preceding equation refer to node location (a node is the center of a volume element); 0 refers to the nodal location being considered, 1 refers to the node above, 2 refers to the node to the right, 3 refers to the node below, and 4 refers to the node to the left. In the preceding equation, H is the heat-flow residual, in British thermal units per day; KN is the thermal conductivity, in British thermal units per day-foot-degree Fahrenheit; X is the temperature, in degrees Fahrenheit; XD is the horizontal node spacing, in feet; YD is the vertical node spacing, in feet; MA is the thickness of the aquifer (equivalent to thickness of the model), in feet; $TTOP$ is the temperature at land surface, in degrees Fahrenheit; DP is the depth to the midpoint of the aquifer (average of the depth to the top and the depth to the base), in feet; DH is the temperature gradient at the base of the aquifer, in degrees Fahrenheit per foot; SP is the volumetric specific heat of water, 62.4 British thermal units per degrees Fahrenheit-cubic foot (4.18×10^6 joules per degrees Celsius-cubic meter); $Q_{1,2,3,4}$ is the inflow of water from node 1, 2, 3, and 4, respectively, in cubic feet per day; and Q_0 is the outflow of water from the element, in cubic feet per day.

The equation for the ground-water-flow model is

$$QT=\frac{XD}{YD}\left(\left(\frac{P_1MA_1+P_0MA_0}{2}\right)\left(S_1-S_0\right)+\left(\frac{P_3MA_3+P_0MA_0}{2}\right)\left(S_3-S_0\right)\right)+\frac{YD}{XD}\left(\left(\frac{P_2MA_2+P_0MA_0}{2}\right)\left(S_2-S_0\right)+\left(\frac{P_4MA_4+P_0MA_0}{2}\right)\left(S_4-S_0\right)\right)$$

QT is the ground-water flow residual, in cubic feet per day; P is the hydraulic conductivity, in feet per day; and S is the ground-water potential (head), in feet. Other symbols and the subscripts are as explained for the heat-flow model.

DESCRIPTION OF THE HYDROTHERMAL MODEL

The heat-flow and ground-water flow models are based on the equations of continuity for heat and water, respectively. That is, the net flux of heat, or water, into an element of volume is equal to the change in heat, or water, concentration of the element. Under steady-state conditions, neither temperature nor head change with time, and the net flux of heat, or water, into any element of the model is equal to zero. The equation of continuity for heat, or water, is written for each of the elements of the model. If there are N elements in the model, the result is N linear equations in N unknown temperatures, or heads. These N linear equations are solved by (1) assuming an initial temperature, or head; (2) using the Jacobi iteration method to calculate new values for temperature, or head; and (3) calculating the residual for each element. The residual is the sum of the head, or water, inflow to each element. The residual would be zero for each element if the N temperatures, or heads, were exact solutions of the N equations. The initial values used were 18.3°C (64.9°F) for the heat-flow model and 0 ft head for the ground-water flow model. Steps 2 and 3 are repeated until the sum of all the residuals in the model is less than 0.1 percent of the total flux in the model. The total flux is equal to the total heat inflow to the heat-flow model, or to the total recharge for the ground-water flow model.

According to R. O. Fournier (oral commun., 1972), the relation between saturated silica concentration and temperature is

$$MGL = 60{,}060\left(10-\left(\frac{1{,}032}{K}+0.09\right)\right),$$

where MGL is the silica concentration at saturation with chalcedony, in milligrams per liter; and K is the temperature, in degrees Kelvin (°C+273.2). The assumptions made in the model of silica concentration are: (1) If the water is supersaturated with silica (silica concentration greater than that given by the preceding equation), the silica will remain in solution and not precipitate; (2) if the water is undersaturated with silica (silica concentration less than that indicated by the preceding equation), sufficient silica will go into solution so that the water becomes saturated with silica. The effect of these two assumptions requires that the water either be saturated or supersaturated with silica. The iterative procedure for calculating the silica distribution in the aquifer is as follows. First, the silica concentration at a node was calculated from the inflow by

$$SIL = \frac{Q_1SIL_1+Q_2SIL_2+Q_3SIL_3+Q_4SIL_4}{Q_1+Q_2+Q_3+Q_4},$$

where SIL is the silica concentration at a node as calculated from the inflow, in milligrams per liter; $SIL_{1,2,3,4}$ are silica concentrations at surrounding nodes, in milligrams per liter; and $Q_{1,2,3,4}$ are inflows (zero, if outflow) from surrounding nodes, in cubic feet per day. Subscripts are as defined in the heat-flow equation. The silica concentration at the node is chosen as the larger of SIL, given previously, or MGL, as given in the previous equation. On the first iteration, all the silica values are as given by the equation for MGL. Succeeding iterations produce silica values as weighted from inflow by the equation for SIL. An indicator is kept for the maximum change in silica from one iteration to the next. When this indicator becomes less than 0.0001, the final silica values have been computed and the iteration is stopped.

The iterative procedure for calculating time of travel uses the equation

$$TT = \frac{Q_1TT_1+Q_2TT_2+Q_3TT_3+Q_4TT_4+\frac{(XD)(YD)(POR)}{730}}{Q_1+Q_2+Q_3+Q_4+(B)(XD)(YD)}$$
$$(D_1(MA_1+MA_0)+D_2(MA_2+MA_0)+D_3(MA_3+MA_0)+D_4(MA_4+MA_0)),$$

where TT is the time of travel, in years; D is one if the corresponding Q is positive and zero if the corresponding Q is zero; POR is the porosity, dimensionless; and B is the recharge rate at the node, in feet per day. Other symbols and the subscripts are as defined previously. An indicator is used that is the maximum change in time of travel from one iteration to the next. When this indicator becomes less than or equal to 0.0001, the iteration is stopped.

The model for ^{14}C is based upon the exponential decay of ^{14}C, a radioactive isotope of carbon. This decay can be expressed as

$$C14_t = C14\, e^{-(1.2097\times10^{-4})t}$$

where C14 is the initial ^{14}C content, $C14_t$ is the ^{14}C concentration after a period of time has elapsed, and t is the elapsed time, in years. The recharge area of the aquifer is not the only source for the carbon in the water, as some carbon is added by solution of aquifer material. As table 9 shows, within the bulk of the system, only 55 to 65 percent of the carbonate present is ^{14}C bearing. The ^{14}C model uses 65 percent as an initial value and decreases this value according to the exponential decay. The ^{14}C model is an iterative procedure calculating ^{14}C from the equations

$$C14 = \frac{Q_1C14_1e^{A_1}+Q_2C14_2e^{A_2}+Q_3C14_3e^{A_3}+Q_4C14_4e^{A_4}+B(XD)(YD)}{Q_1+Q_2+Q_3+Q_4+B(XD)(YD)}$$

and

$$A_i = \frac{(-1.2097\times10-^4)(XD)(YD)(POR)(MA_1+MA_0),\ i=1,2,3,4}{730\ Q_i},$$

where C14 is the ^{14}C concentration, in percent of modern as measured, and other symbols and subscript meanings are as used previously. An indicator is used whose value is the maximum change of C14 from one iteration to the next. When this indicator becomes less or equal to 0.0001, the iteration is terminated.

APPLICATION OF DIGITAL MODELS TO THE HOT-SPRINGS FLOW SYSTEM

Most of the data on the hot-springs flow system, such as water temperature, water samples for analysis, and flow measurements, have been collected from points at or near the Earth's surface. Subsurface data are from wells, the deepest of which is about 336 ft (102.4 m). Conditions at depth must be inferred by such means as projection of surface dips of rock formations and faults and changes in temperature and chemical nature of the water from the recharge area to the springs. The digital models provide a further tool with which conditions at depth can be inferred. Measured properties of the flow system and the water can be entered into the digital model. The flow model provides simultaneous solutions to the equations for each of the several properties. The design of the system at depth can be

changed experimentally within the bounds of known parameters so that the model results are compatible with all measured properties related to the system.

Following is a summary of variables that must be specified in designing a steady-state model of the flow system.

1. Thickness, porosity, hydraulic conductivity, and depth of the aquifer.
2. Thermal conductivity of the rocks and heat flow into the aquifer.
3. Recharge to the aquifer.
4. Temperature of water in the recharge area.

The initial flow models were designed from projections of surface dips of the geologic formations and from known and estimated hydrologic and thermal properties of the aquifer. Two flow models were designed and tested during the study. In one model the Bigfork Chert served as the principal aquifer. In the other model the Arkansas Novaculite served as the principal aquifer. During development of each model, the design was changed in attempting to achieve harmony between the input data and the known constraints on the system.

The Bigfork Chert was modeled as a two-dimensional plane, inclined in the subsurface to the southeast (fig. 12). The flow of water was modeled to a point in the subsurface beneath the spring discharge area. Flow upward to the surface was not modeled because the model is limited to a two-dimensional representation of the flow system. Temperature and silica data on the hot springs indicate that the flow of water from depth to the surface is relatively rapid. That the flow from depth to the surface was not modeled is not considered significant with regard to conclusions drawn from the model. Following is a summary of the input data for the Bigfork Chert model.

Thickness of aquifer ft	1,500
Porosity	0.20
Hydraulic conductivity at 18.3°C (nonuniform) ft/d	0.5–10
Thermal conductivity cal/s-cm°C	0.006
Heat flow (nonuniform) hfu	2.2–22.0
Recharge rate (nonuniform) ft/yr	0.05–0.25

The Bigfork Chert in the model is thicker than the average reconstructed stratigraphic thickness for this formation. However, the Bigfork Chert contains multiple folding, which increases the actual thickness of the water-bearing zone. Also, the underlying Womble Shale contains permeable zones of limestone and chert which effectively increase the thickness of the contiguous water-bearing zone. The hydraulic conductivity of the Bigfork Chert was modeled as 1 ft/day ($3.53\times10^{2}6$ m/s) over the outcrop area and in most of the subsurface. The higher values of hydraulic conductivity were modeled in a zone trending east-northeast from the hot springs, parallel to the trace of the thrust faults through the hot-springs area (fig. 2). The hydraulic conductivity in the model, after being adjusted by the program to reflect the temperature of the water, ranged from 1 to 25 ft/day ($3.53\times10^{2}6$ to $8.82\times10^{2}5$ m/s). The maximum depth of water circulation in the model is 6,000 ft (1,830 m). Heat was added at the lower surface of the model at rates of 2.2 hfu over most of the model area and 22.0 hfu over the area near the springs. Heat was removed from the upper surface of the model at rates calculated from the product of thermal conductivity and the temperature difference between each node and the assumed land-surface temperature of 18.3°C divided by the depth of the node. The abnormally high heat flows of 22.0 hfu near the springs and 2.2 away from the springs were necessary to achieve the observed temperature at the springs. Results of the model are summarized in table 10.

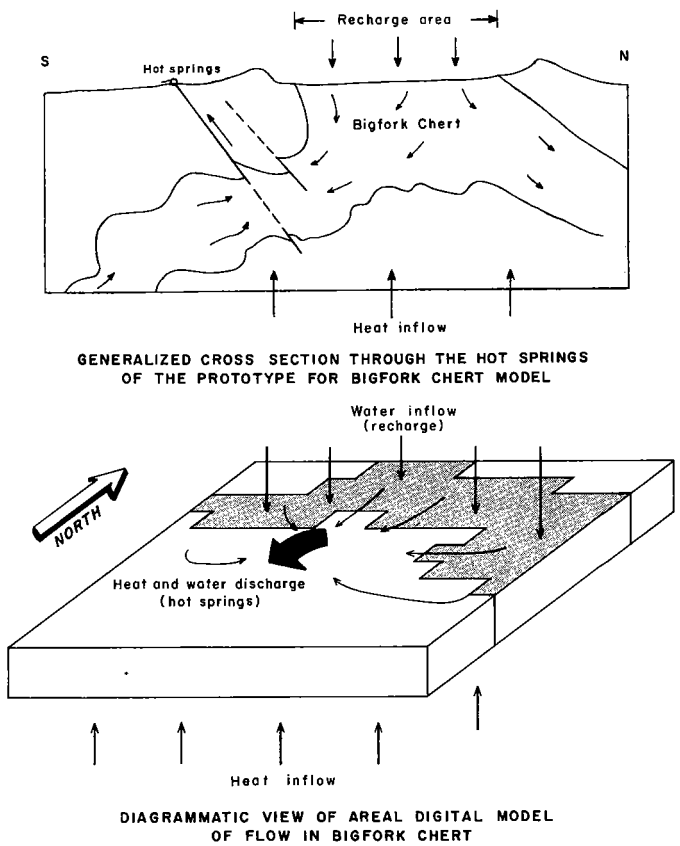


FIGURE 12.—Model of flow in the Bigfork Chert.

TABLE 10.—*Comparison of the modeled and observed data for the hot springs using the Bigfork Chert as the principal aquifer*

Parameter	Modeled	Observed
Temperature ---------- °C--	61.2	61.7
Flow ---------- ft³/d--	0.97×10^5	1.1×10^5
Silica ---------- mg/L--	40.7	41.7
Carbon-14 age ---------- yr--	5,026	4,430
Maximum head in recharge area above hot springs ---------- ft--	18	260

The results of the Bigfork Chert model indicate that the known and assumed values of the parameters are within the hydrologic constraints on the system. The model indicates that the available head difference is ample to provide the hydraulic pressure for the spring flow. An additional component of head is produced by the decreased density of the water at temperatures higher than the assumed temperature in the recharge area (18.3°C (64.9°F)). The ample head available to drive the flow system provides a leeway in several of the estimated values of parameters used in the model, such as thickness and permeability of the aquifer and rate and areal extent of the recharge. For example, a valid model could be designed using lower values for permeability and thickness of the Bigfork Chert, or a valid model could be designed using a lower recharge rate over a larger area or using a higher recharge rate over a smaller area.

The critical constraint on the Bigfork Chert model is the high heat flow needed to obtain the observed spring temperature. It was not possible to obtain the 62°C–discharge temperature using a uniform heat inflow of 2.2 hfu, which as discussed previously is the maximum known value of crustal heat flow in the Eastern United States. This heat-inflow deficiency suggests consideration of an alternative model of the Bigfork Chert in which the ground-water flow system supplying the hot springs absorbs heat throughout a larger area.

The Arkansas Novaculite was modeled as a nearly vertical two-dimensional plane inclined slightly to the southeast (fig. 13). Flow was modeled to a point in the subsurface near the springs from which flow to the surface is probably rapid and through a very permeable zone. Following is a summary of input data for a model of the Arkansas Novaculite:

Thickness of aquifer ---------- ft--	500
Porosity ----------	0.1
Hydraulic conductivity ---------- ft/d--	1.
Thermal conductivity ---------- cal/s-cm-°C--	0.0062
Heat flow ---------- hfu--	2.2
Recharge rate ---------- ft/yr--	0.63

Results of the Arkansas Novaculite model are summarized in table 11. One constraint on this model is that the required difference in head between the recharge area and the springs (1,222 ft, or 372 m) exceeds the available head by a factor of 3. This required head difference is also much larger than the head provided by the water level in the recharge area (420-ft, or 128-m, maximum) and the temperature differential (estimated to be about 160 ft, or 49 m). [1] Known values of hydraulic conductivity of the Arkansas Novaculite indicate that the average value cannot reasonably be expected to exceed 1 ft/d, 0.30 m/d, (at 18.3°C) throughout an area as large as that modeled.

[1]For $\frac{\delta\rho}{\rho_0} = 0.02$ and $L=8{,}000$ ft, $\delta H=0.02$ (8,000 ft)=160 ft, where $\delta\rho$ is the change in density, ρ_0 is the initial density of the water, L is the depth of circulation, and δH is the head provided by the temperature differential.

TABLE 11.—*Comparison of the modeled and observed data for the hot springs using the Arkansas Novaculite as the principal aquifer*

Parameter	Modeled	Observed
Temperature ---------- °C--	54.4	61.7
Flow ---------- ft³/d--	0.85×10^5	1.1×10^5
Silica ---------- mg/L--	36.0	41.7
Carbon-14 age ---------- yr--	2,760	4,430
Maximum head in recharge area above hot springs ---------- ft--	1,222	420

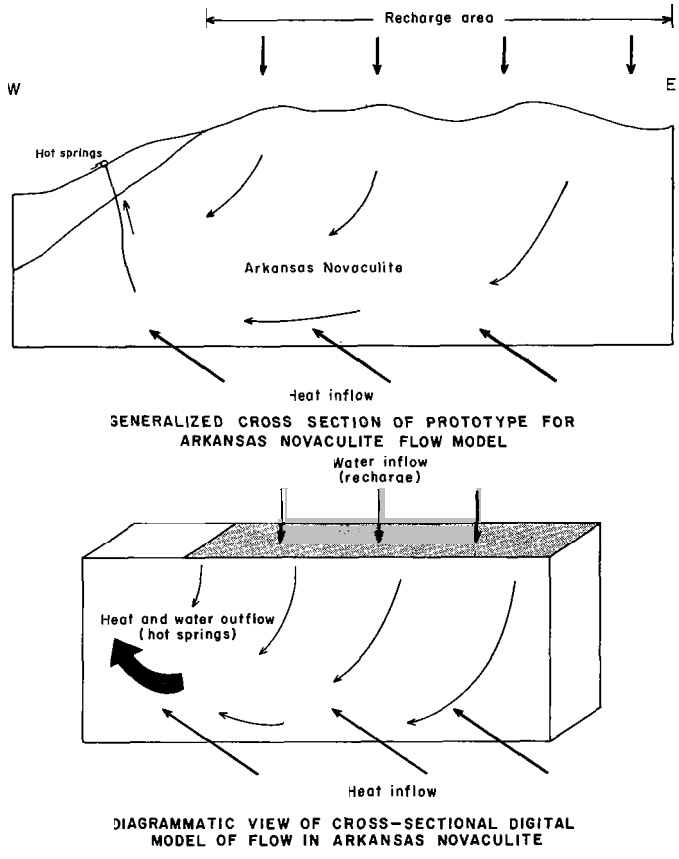


FIGURE 13.—Model of flow in the Arkansas Novaculite.

The Arkansas Novaculite model could also be rejected on structural considerations. To obtain a discharge temperature within 10 percent of the observed spring temperature, the depth of circulation in the novaculite model was 8,000 ft (2,440 m), and heat was added over the lower surface of the slightly inclined plane, 1.52 by 26 mi, or 40 mi2 (2.45 by 41.8 km, or 102.4 km2) (as indicated in fig. 13) at a uniform rate of 2.2 hfu and removed over the upper surface of the plane at rates proportional to the temperature difference between each node and the land surface. Structurally, a continuous aquifer in the Arkansas Novaculite with this lateral extent and depth is of doubtful validity.

DISCUSSION OF MODELS

Neither the Bigfork Chert model nor the Arkansas Novaculite model, previously described, is entirely satisfactory in describing the hot-springs flow systems. In terms of hydrologic and structural constraints on the model, the Arkansas Novaculite model is the least plausible, whereas the Bigfork Chert model is the most suitable. In terms of thermal considerations, both models require abnormally high heat flow to achieve the observed temperature of the hot springs.

An alternative Bigfork Chert model, which could match the observed discharge temperatures with observed heat flows in the Eastern United States, would involve lateral circulation of ground water over an area on the order of 50 mi2, which, in turn, would require that the recharge areas be distributed over a larger region than in the Bigfork Chert described previously. Recharge from distances as great as 5–10 mi would probably be sufficient. Such a flow system may be possible along the plane of the thrust fault(s) that intersects the hot springs and dips to the northwest (pl. 1). The criteria for the recharge areas along the thrust fault(s) would be that recharge occur at distances as great as 5–10 mi north and northeast of the hot springs at elevations above the spring discharge and that there be hydraulic connection with the fault plane at sufficient depth to allow water to move laterally toward the springs. Ground water movement would be relatively slow to the point where it intercepts the thrust fault plane. Movement along the fault plane would be relatively rapid to the points of spring emergence. Such a model would meet the age requirements indicated by 14C analyses.

CONCLUSIONS

The hot springs of Hot Springs National Park, Arkansas, issue from the Hot Springs Sandstone Member of the Stanley Shale of Mississippian age at the crest of a plunging overturned anticline, along the southern margin of the Ouachita anticlinorium. The combined flow of the 47 hot springs ranges from 750,000 to 950,000 gallons per day (3.28×10^{-2} to 4.16×10^{-2} cubic meters per second). The temperature of the combined hot-springs water is about 62° Celsius. Using silica concentration as an indicator, the maximum temperature of the water at depth is estimated to be not more than a few degrees Celsius higher than the temperature at the surface. Silica concentrations of the water since 1901 and maximum temperature measurements since 1804 indicate a small decline in temperature with time.

Tritium and Carbon-14 analyses of the water indicate that the water is a mixture of a very small amount of water less than 20 years old and a preponderance of water about 4,400 years old. The radioactivity and chemical concentration of the hot springs are similar to that of cold-water springs in the area. The dissolved solids concentrations range from 175 to 200 milligrams per liter. The main differences in the quality of the hot water, compared with the nearby cold ground water, are the high temperature and higher silica concentrations of the hot springs.

The geochemical data, flow measurements, and geologic structure of the region support the concept that virtually all the hot-springs water is of meteoric origin recharged locally. Recharge to the hot-springs artesian system is by infiltration of rainfall in the outcrop areas of the Big fork Chert and Arkansas Novaculite. The water moves slowly to depth where it is heated by contact with rocks of high temperature. Highly permeable zones, related to jointing or faulting, collect the heated water in the aquifer and provide avenues for the water to travel to the surface.

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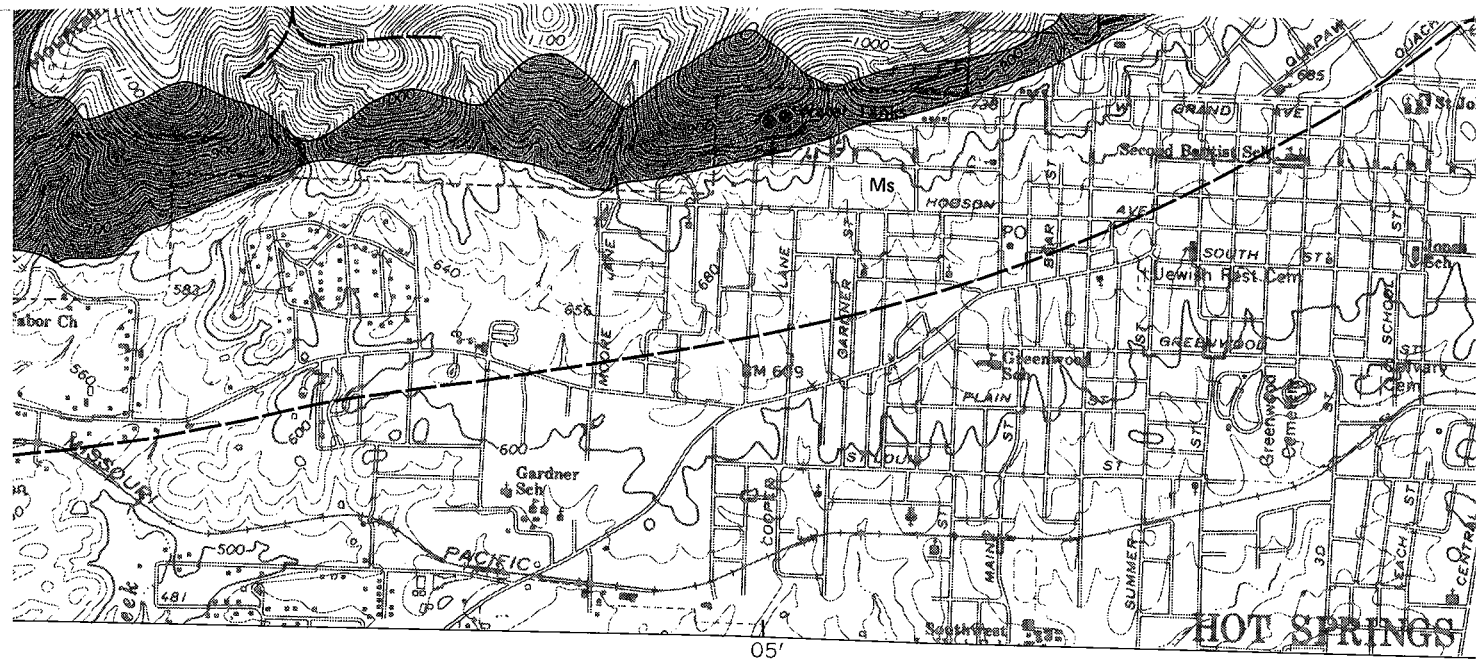

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