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GEOCHEMICAL INDICATORS OF SUBSURFACE TEMPERATURE—
PART 2, ESTIMATION OF TEMPERATURE AND FRACTION OF
HOT WATER MIXED WITH COLD WATER

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Abstract.—The water in many warm springs with large rates of flow consists of mixtures of hot water that has come from depth and of shallow cold water. Under favorable conditions the original temperature of the hot water and the fraction of the cold water in the mixture can be estimated by using the measured temperature and silica content of the warm spring water and the temperature and silica content of nonthermal water in the region. The method has been applied with apparent success at Yellowstone National Park.

Warm ($<80°C$) springs with large rates of discharge occur in many places throughout the world. Some of these warm springs originate through deep circulation of meteoric water that is heated mainly by conductive heat transfer from the rock to the water. Other warm springs originate through mixing of high-temperature ($>100°C$) water with cold meteoric water.

As discussed in part 1 by Fournier, White, and Truesdell (companion article on p. 259 of this issue), water discharged from springs with rates of flow greater than about 100–200 l/min can be assumed to have lost little heat to the wallrock per unit mass of water during the upward movement. For nonboiling springs, if mixing has not occurred, the temperature of the spring is close to the highest temperature attained by that water. If mixing has occurred, however, water of very high temperature may be present at comparatively shallow depth. These possible differences in subsurface conditions may be differentiated in many places on chemical grounds. Specifically, the chemical composition of a water heated only to its eventual discharge temperature is likely to reflect water-rock equilibration at about that temperature, whereas the composition of a mixed water is likely to indicate marked nonequilibration between the water and rock at the spring temperature.

If the composition suggests that the warm spring water is produced by the mixing of cold meteoric water with high-temperature water, it is possible under certain conditions to calculate the temperature and fraction of the hot-water component.

TEST FOR A MIXED WATER

If several springs are present, variations in the temperature or in content of chloride, boron, or other relatively nonreactive constituents may indicate mixed water. Such water is particularly indicated where there is a regular variation in water temperature and chlorinity.

Another approach is to test whether or not the composition of a large flowing spring indicates chemical equilibration at a temperature within about $±25°C$ of the spring water. Marked nonequilibration suggests a mixed water.

The Na-K-Ca geothermometer (Fournier and Truesdell, 1973) appears to work well for testing chemical equilibration. Water composition, in molality, is related to temperature by the empirically derived equation

$$\log (Na/K) + \beta \log (\sqrt{Ca/Na}) = \frac{1647}{273 + t_{°C}} - 2.24 \qquad (1)$$

in which $\beta=1/3$ for water equilibrated above $100°C$, and $\beta=4/3$ for water equilibrated below $100°C$. First, test to see if $\beta=4/3$ yields a temperature below $100°C$; if it does not, use $\beta=1/3$ to estimate the equilibration temperature.

A more sophisticated approach is to perform a complete chemical analysis of the water and then use a computer and appropriate program (Kharaka and Barnes, 1974; Truesdell and Jones, 1973) to test various possible equilibria at the temperature of the spring and selected higher temperatures.

The silica geothermometer (Fournier and Rowe, 1966) has been the most reliable single chemical indicator of reservoir temperature in spring systems that are high in silica and are characterized by sinter deposits and boiling waters. There is an ambiguity, however, in using the silica content of a warm spring to test for water-rock equilibration at the spring temperature: a high silica content in the spring water may be due to either solution of quartz at a much higher temperature (with or without subsequent mixing of hot and cold waters) or solution of cristobalite or amorphous silica at the spring temperature. Therefore, the silica geothermometer (Fournier and Rowe, 1966) should be used with great caution to test for water-rock equilibration at the spring temperature. Although supersaturated silica solutions may occur in nature over a wide range in temperatures, they are not likely to persist for long

periods of time above about 150°C (Fournier, 1973). This is critical for the models that we present in this paper.

MIXING MODELS

Two mixing models that allow calculation of the temperature and fraction of the hot water component are shown schematically in figure 1. In model 1, figure 1A, hot water ascends from depth along a permeable channel, possibly a fault or joint. Depending on the initial temperature, the water may boil (cool adiabatically) as it rises. In this event, the water and newly forming steam rise together. At some point, M in figure 1A, the hot water encounters cold water from a permeable stratum. At the depth of mixing the weight of a column of cold water extending up to the surface is greater than the weight of the warm mixed water. Thus, the pressure relations are such that cold water enters the hot-water channel and the mixture flows to the surface and is discharged as a warm spring. Depending on the proportion of hot to cold water and the initial enthalpies of each, the spring may have a temperature ranging from very low to boiling.

In model 2, figure 1B we assume that boiling occurs in the rising hot water and that some or all of the resulting steam escapes from that water (point S) before the hot water mixes with cold water. We show a fumarole where the steam emerges and a warm spring where the hot water mixed with cold water emerges. Alternatively, the separated steam might possibly condense and combine with shallow ground water and give rise to other warm springs that are not amenable to the methods suggested in this report.

If the channel above S is filled with steam, boiling at S will be at atmospheric pressure, provided there are few constrictions in the channel or impediments to the escape of steam (no throttling occurs). If throttling of the steam occurs, or if the channel is partly or completely filled with water, boiling and escape of steam at S will be at greater than atmospheric pressure.

In both models of figure 1 the calculations depend upon ones knowing the temperatures and silica content of the cold water before mixing[1] and those of the warm spring water after mixing. In addition, it must be assumed that the initial silica content of the deep hot water is controlled by the solubility of quartz and that no further solution or deposition of silica occurs before or after mixing. Numerous observations have shown that natural water deep in hot-spring systems generally is just saturated with quartz (Mahon, 1966; Fournier and Truesdell, 1970; Ellis, 1970; Fournier, 1973). Furthermore,
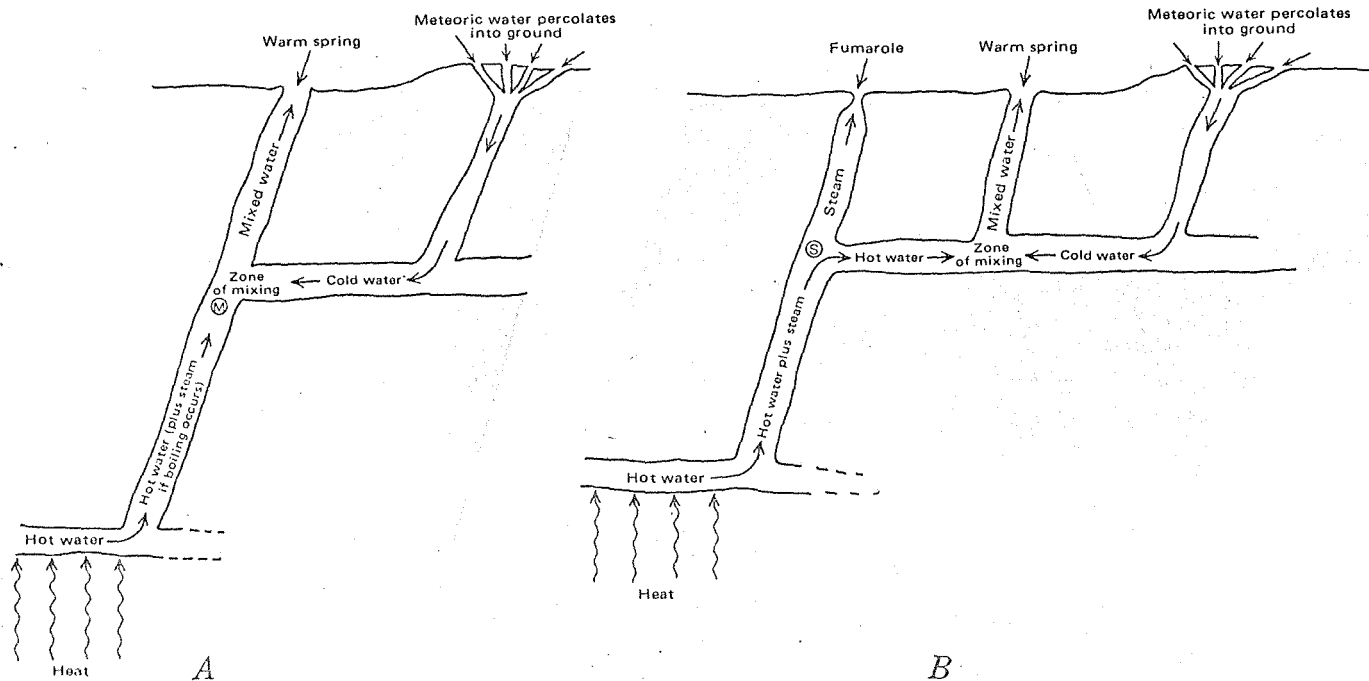

Figure 1.—Schematic model (A) for obtaining a mixed-water warm spring in which both the enthalpy and silica content of the hot-water conter are the same as in the original deep water (model 1) and schematic model (B) in which the hot-water component has lost steam before mixin with cold water (model 2). (See text for discussion.)

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[1] If the average temperature and silica content of nonthermal groun water in the region are not known, we suggest estimating the mea annual temperature and using 25 mg/l of silica as a first approximatio

our observations in Yellowstone National Park (Fournier and Truesdell, 1970) and elsewhere (White, 1974) suggest that ascending boiling water generally does not dissolve or precipitate silica if the rate of upflow is fast.

In the calculations that follow, model 1 gives a probable maximum subsurface temperature attained by the hot-water component, and model 2, a probable minimum subsurface temperature. On the basis of the total chemical and physical character of the warm spring, its relation to other hot springs and fumaroles, and its geologic environment, it may be possible to choose the temperature that is more likely to be correct. Even where this is not possible, information on the range of possible subsurface temperatures will be of great interest.

CALCULATIONS

Model 1

In this model the enthalpy of the hot water plus steam that heats the cold water is the same as the initial enthalpy of the deep hot water. Two equations can be written to solve for the two unknowns—the temperature of the hot water and the proportions of the hot and cold water—because the silica content and temperature of the warm spring are different functions of the original temperature of the hot-water component. The first equation relates the heat contents or enthalpies of the hot water, H_{hot}; cold water, H_{cold}; and spring water, H_{spg}; and the fractions of cold water, X, and of hot water, $1-X$, as follows:

$$(H_{cold})(X) + (H_{hot})(1-X) = H_{spg}. \qquad (2)$$

Below 100°C the enthalpy of liquid water coexisting with steam (saturated water) in calories per gram is essentially equivalent in magnitude to the temperature of the water in degrees Celsius. Above 100°C the relation of temperature and enthalpy of saturated water can be found in steam tables (Keenan and Keyes, 1936; Keenan and others, 1969). Selected values are given in table 1.

In a similar manner the second equation relates the silica contents of hot water, Si_{hot}; cold water, Si_{cold}; and spring water, Si_{spg}:

$$(Si_{cold})(X) + (Si_{hot})(1-X) = Si_{spg}. \qquad (3)$$

The relation of dissolved silica to the temperature of the aquifer supplying the hot-water component is given by the solubility of quartz at the vapor pressure of the solution (Morey and others, 1962; Fournier, unpub. data, 1974). Selected values are given in table 1.

We use a computer program (Truesdell and others, 1973) to solve equations 2 and 3 and obtain the temperature of the hot water and the fraction of cold water in the mixture, using measurements of the spring temperature and silica content, measurements or estimates of the lowest temperature and average silica content of cold springs in the area, and tabular values of heat content of liquid water and quartz solubilities. Alternatively, a graphical solution can be obtained as follows:
1. Assume a series of values of enthalpy of hot water for the temperatures listed in table 1 and calculate X_t for each, as follows:

$$X_t = \frac{(\text{Enthalpy of hot water}) - (\text{Temperature of warm spring})}{(\text{Enthalpy of hot water}) - (\text{Temperature of cold spring})}.$$

2. Plot the calculated values of X_t in relation to the temperatures from which the assumed hot-water enthalpy values were derived (see fig. 2, curve A).

Table 1.—*Enthalpies of liquid water and quartz solubilities at selected temperatures and pressures appropriate for coexistent steam and liquid water*
[Enthalpies from Keenan and others (1969). Quartz solubilities at and below 225°C from Morey and others (1962); above 225°C from unpublished data of R. O. Fournier]

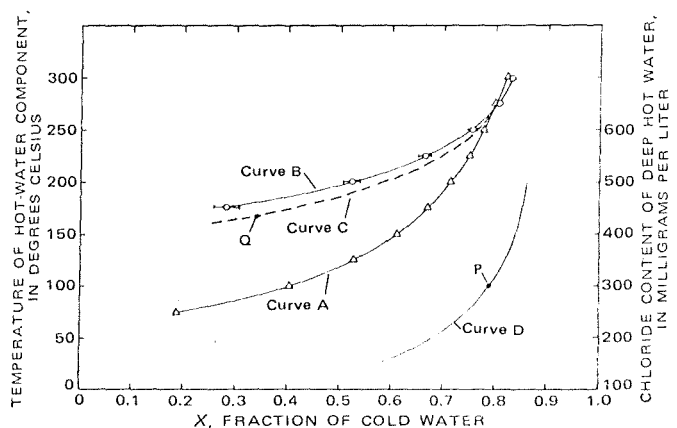| Temperature (°C)	Enthalpy (cal/g)	Silica (mg/l)	Temperature (°C)	Enthalpy (cal/g)	Silica (mg/l)
50	50.0	13.5	200	203.6	265
75	75.0	26.6	225	230.9	365
100	100.1	48	250	259.2	486
125	125.4	80	275	289.0	614
150	151.0	125	300	321.0	692
175	177.0	185			

Figure 2.—Fraction of cold water relative to temperature and chloride content of hot-water component in Terrace Spring. Triangles, X_t values listed in table 2; circles, X_{Si} values. The horizontal bars show the possible error due to uncertainty in the silica analysis of the spring water. Points P and Q discussed in text. Curve A, Fraction of cold water based on model 1 enthalpy considerations. Curve B, Fraction of cold water based on model 1 silica considerations. Curve C, Fraction of cold water based on model 2 silica considerations. Curve D, Required chloride contents of deep water.

3. Assume a series of silica contents of hot water appropriate for the temperature listed in table 1 and evaluate X_{Si} for each silica content, as follows:

$$X_{Si} = \frac{(\text{Silica in hot water}) - (\text{Silica in warm spring})}{(\text{Silica in hot water}) - (\text{Silica in cold spring})}.$$

4. On the graph previously used, plot the calculated values of X_{Si} in relation to the temperatures for which the silica contents were obtained (see fig. 2, curve B).
5. The point of intersection gives the estimated temperature of the hot-water component and the fraction of cold water.

The two curves possibly may not intersect (fig. 3) or they may intersect at an unreasonably high temperature. These situations would arise if the ascending hot water lost steam or heat before mixing with the cold water (model 2) or if the mixed water dissolved additional silica owing to contact with amorphous silica or rock containing glass. Therefore, we recommend that the mixing model described above be used with extreme caution for warm spring water that has silica contents about equal to the solubility of amorphous silica at the temperature of the spring. For temperatures below 200°C, the approximate solubility of amorphous silica can be calculated from the equation

$$-\log C = \frac{731}{T} - 4.52 \qquad (6)$$

where C is silica solubility in milligrams per liter and T is absolute temperature.
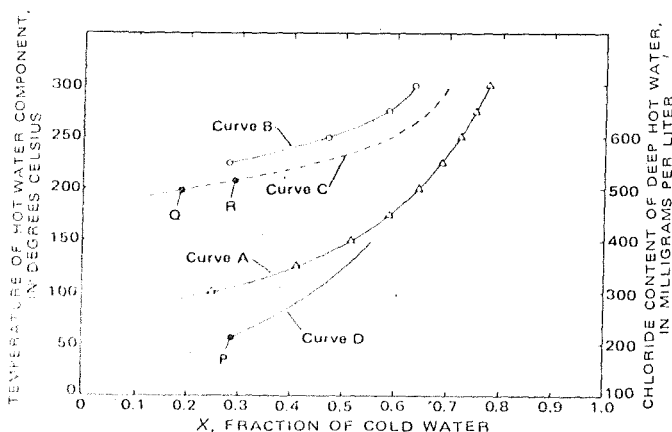

Figure 3.—Fraction of cold water relative to temperature and chloride content of hot-water component in Interchange Spring. Points P, Q, and R discussed in text. See figure 2 for explanation of symbols and curves.

The actual temperature and silica content of the "cold" component at the point of mixing can seldom if ever be known with certainty. If either the temperature or silica content of the cold water were higher than the assumed value, the resulting estimated temperature of the hot-water component would be too high.

Model 2

The enthalpy of the hot water in the zone of mixing is less than the enthalpy of the hot water at depth owing to escape of steam during ascent. The silica content of the hot-water component, however, is fixed by quartz solubility at depth and subsequent enrichment in the liquid water fraction as steam separates. At the point where steam escapes from the ascending hot water and steam mixture, S in figure 1B, the residual silica concentration in the hot water increases and is given by the equation

$$\text{Residual silica} = \frac{\text{Original silica}}{1-y} \qquad (7)$$

where y is the fraction of steam formed during movement of water from depth to S.

If one assumes a temperature, t_s, at which steam escapes, it is possible to calculate the residual silica for that condition and, using that information, estimate the original hot-water temperature before steam separates. In general, we set t_s equal to the boiling temperature imposed by local atmospheric conditions. This requires that escape of steam at point S of figure 1B occurs at atmospheric pressure, and our calculation yields a minimum probable temperature for the hot-water aquifer. The calculation is carried out as follows:

1. Use the atmospheric boiling temperature for the value of H_{hot} in equation 2 and calculate the corresponding value of X.
2. Use that value of X in equation 3 to estimate the residual silica content of the hot water at t_s.
3. Use the calculated residual silica content and curve A of Fournier and Rowe (1966, fig. 5) to estimate the original subsurface temperature before separation of steam. Curve A of Fournier and Rowe is roughly approximated by the equation

$$-\log C = \frac{1522}{t°C + 273} - 5.75. \qquad (8)$$

If superheated steam emerges from nearby fumaroles or if there are other reasons for believing that steam escapes at greater than atmospheric pressure, an alternate procedure should be used:

1. Assume a value of t_s appropriate for the pressure at which steam is thought to escape at point S of figure 1B.
2. Use steam tables (or table 1) to determine the heat content of liquid water in calories per gram at t_s and substitute

that value in equation 2 to estimate a corresponding value of X.

3. Use that value of X in equation 3 to estimate the residual silica content of the hot water at t_s.

4. Estimate the silica content, C, that would have been present in the hot-water component if steam had escaped at atmospheric pressure using the relation

$$C = \frac{\text{Residual silica}}{1 - \frac{x}{1-y}} \qquad (9)$$

where X is the fraction of steam that would be formed in going from t_s to the boiling temperature at atmospheric pressure (see fig. 4) and y is the fraction of steam formed in going from the original temperature to t_s. Both y and C are unknown in equation 8. However, the value of y will generally range from 0 to about 0.3, and as a first approximation it can be set equal to 0.1.

5. Use the value of C and Curve A of Fournier and Rowe (1966, fig. 5) or equation 8 to estimate the original subsurface temperature before separation of steam.

A more precise estimate is possible if an iterative process is used in which the value of y is adjusted to reflect successive estimates of the original temperature. In general, we do not believe that the overall accuracy of the method warrants this additional effort.
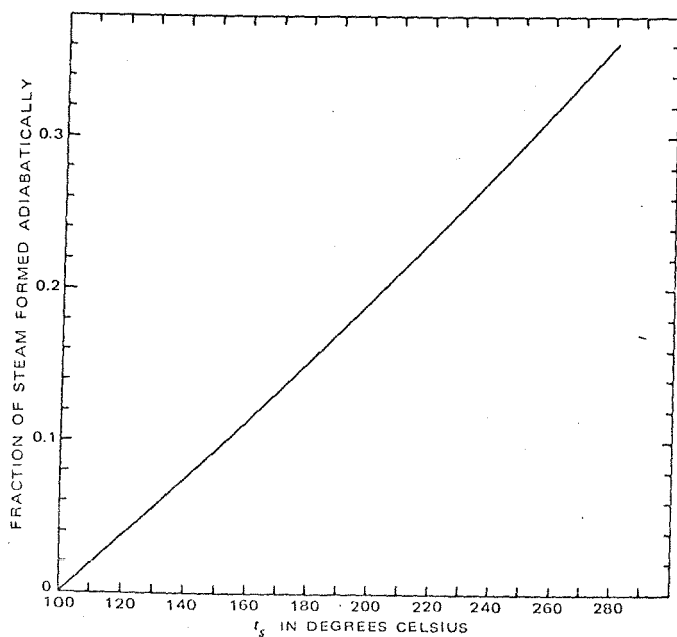

Figure 4.—Fraction of steam that would form by adiabatic cooling from t_s to $100°C$.

EXAMPLES OF APPLICATION

These mixing models proposed have been applied to a few large-flowing warm springs in Yellowstone National Park. The results are geologically reasonable but have been substantiated by shallow drilling in the proximity of only one (Interchange Spring) of the springs in question.

The average silica content of the nonthermal ground water in the park was found to be 25 ± 2 mg/l and the temperature of the coldest spring was $5°C$, in good agreement with the mean annual temperature of $4°C$.

Terrace Spring near Madison Junction flows at about 5,500 l/min, the water temperature is $62°C$, and silica content is 140 mg/l (Allen and Day, 1935, p. 353–354). The sodium, potassium, and calcium contents of the water yield an estimated aquifer temperature of $200°C$, using the method of Fournier and Truesdell (1973). As this temperature is far greater than the spring temperature of $62°C$, the spring is assumed to be a mixed-water type.

Calculated fractions of cold water, assuming various temperatures of hot water and using model 1 and equations 4 and 5, are listed in table 2, column 1, and are plotted in figure 2, curves A and B. The curves intersect at $265°C$ and a cold water fraction of 0.79. This is a very high estimated aquifer temperature and can be thought of as the maximum probable temperature of the hot-water component.

Although there are no nearby fumaroles, boiling pools, or other physical evidence that points to model 2 as a reasonable possibility, we have applied that model to Terrace Spring in order to establish a lower limit to the probable maximum subsurface temperature at that locality.

Curve C of figure 2 was generated by assuming various values of t_s and using equations 7 and 9 and other relations as discussed in the section on calculations. If steam escaped at atmospheric pressure from an ascending boiling water, the hot-water component would have been at about $92°C$ at the time of mixing with cold water, and the original temperature of that hot water would have been $165°C$ (point Q, fig. 2). This is the minimum probable temperature of the aquifer supplying the hot-water component. If higher pressures are assumed for escape of steam, larger fractions of cold water are required and higher estimated aquifer temperatures result, as shown by curve C, figure 2. Again, the probable upper temperature limit is about $265°C$ where curves A, B, and C intersect at a common point.

For Terrace Spring the aquifer supplying the hot water is probably closer to $265°$ than $165°C$. The spring is located between Lower Geyser Basin (9 km to the south) and Norris Geyser Basin (14.5 km to the northeast) at a relatively low topographic position along the bounding fault of a large caldera (Keefer, 1971; Christiansen and Blank, 1972). Recent drilling by the U.S. Geological Survey has shown that subsurface temperatures beneath parts of Lower Geyser Basin exceed $205°C$; those beneath Norris Geyser Basin exceed $240°C$ (White and others, 1968). Silica and Na-K-Ca geo-

Table 2.—Values of X_t and X_{Si} at different assumed temperatures of the hot-water component for warm springs in Yellowstone National Park
[See text for details]

Temperature (assumed) of hot water (°C)	1		2		3		4	
	X_t (t=62°C)	X_{Si} (SiO$_2$=140 mg/l)	X_t (t=49°C)	X_{Si} (SiO$_2$=100 mg/l)	X_t (t=61°C)	X_{Si} (SiO$_2$=122 mg/l)	X_t (t=76°C)	X_{Si} (SiO$_2$=270 mg/l)
50	....	.....	0.022	.....	.....	.....	.....	.....
75	0.186	.....	.371	.....	0.200	.....	.....	.....
100	.401	.....	.537	.....	.410	.....	0.253	.....
125	.527	.....	.635	.....	.534	.....	.410	.....
150	.610	.....	.699	0.250	.616	0.030	.514	.....
175	.669	0.280	.744	.531	.674	.394	.587	.....
200	.713	.521	.778	.688	.718	.596	.642	.....
225	.748	.662	.805	.779	.792	.715	.686	0.279
250	.776	.751	.827	.837	.780	.790	.721	.469
275	.799	.805	.845	.873	.803	.835	.750	.584
300	.820	.828	.861	.888	.823	.855	.775	.633

1. Terrace Spring near Madison Junction. Flow approximately 5,550 l/min. Data from Allen and Day (1935).
2. Spring 1.4 km N. of Biscuite Basin, about 8 m E. of road. Flow about 190 l/min.
3. Spring 2.25 km N. of Biscuite Basin, about 60 m E. of road. Flow about 100 l/min.
4. Interchange Spring, Black Sand Basin. Flow about 2,300 l/min.

thermometers applied to boiling hot-spring water at Norris suggest subsurface temperatures of 250° to 270°C.

The chloride content of Terrace Spring, 64 mg/l is consistent with the higher aquifer temperature and correspondingly large calculated fraction of cold water. Given the chloride concentration in the spring and the average chloride in nonthermal water in the region (<1 mg/l), the chloride content of the deep hot water can be calculated, assuming any given proportion of hot and cold water. Curve D, figure 2, shows the results of that calculation. For a cold-water fraction of 0.79, the chloride content of the hot-water fraction would be about 300 mg/l (point P, fig. 2). This is close to the chloride content of thermal water (before steam loss) found at Lower Geyser Basin.

The second example is one in which mixing model 1 fails, but model 2 gives excellent results. Interchange Spring in Black Sand Basin came into being as a result of an excavation for a highway interchange for diverting traffic around the Old Faithful area. The spring had a temperature of 76°C, a silica content of 270 mg/l, and a flow rate of about 2,000 l/min. The Na-K-Ca content suggests a temperature of 205°C. The calculated fractions of cold water at given temperatures of the hot-water component are listed in table 2, column 4, and plotted in figure 3.

The most notable feature of figure 3 is that curve A, based on enthalpy considerations, and curve B, based on model 1 silica considerations, do not intersect. Evidently either steam escaped from the hot-water component before mixing or the warm spring water dissolved extra silica after mixing occurred. The warm water may be picking up extra silica, for it emerges from sands and gravels composed mostly of fresh obsidian. The obsidian glass could dissolve and raise aqueous silica to saturation with respect to amorphous silica. At 76°C the solubility of amorphous silica is 266 mg/l, which is within the analytical error of the 270 mg/l silica found in the spring water.

We favor the first alternative because the large rate of flow makes equilibration with amorphous silica unlikely and because model 2 gives results in close agreement with what is known about subsurface temperatures near Interchange Spring.

The variation of original hot water temperature relative to the fraction of cold water in the warm spring, curve C, figure 3, is based on model 2 silica considerations. If steam escaped at atmospheric pressure before mixing of hot and cold water, the remaining hot water would have been at 92°C (boiling temperature at the altitude of the spring) and its original temperature would have been about 200°C (point Q, fig. 3).

About the same temperature is estimated from chloride considerations. The chloride content of Interchange Spring is 224 mg/l, the calculated chloride contents of the hot-water component, assuming various fractions of mixed cold water, are shown by curve D, figure 3. The highest concentration of chloride found in discharging boiling springs and geysers in Black Sand Basin was 315 mg/l. Presumably this is the residual chloride concentration attained after maximum separation of steam owing to adiabatic cooling of the ascending water. Therefore, the maximum chloride content of the hot-water component in Interchange Spring is likely to have been 315 mg/l; the corresponding maximum fraction of cold water, 0.285 (point P, fig. 3). This requires that the hot-water component have a temperature of 110°C or less at the time of mixing. For a cold water fraction of 0.285, curve C of figure 3 shows an original hot-water temperature of about 208°C (point R).

The silica contents of boiling springs and geysers in the vicinity of Interchange Spring indicate an aquifer temperature of 190° to 205°C. In addition, two shallow holes drilled near-

by indicate subsurface temperatures exceeding 170° to 180°C. Both holes were terminated before a maximum or leveling-off temperature was attained. One hole is about 900 m to the southeast and had a bottom-hole temperature of 180°C (Fenner, 1936). The other is about 600 m to the west and had a bottom-hole temperature of 170°C (White and others, 1968; Honda and Muffler, 1970).

Apparently the hydrologic system supplying water to Interchange Spring is very similar to model 2. We suggest that the hot-water fraction of the mixed water in Interchange Spring comes from an aquifer at 200° to 208°C. That water cools adiabatically, forming steam as it rises toward the surface. At a shallow level, but before mixing with cold water occurs, the high-enthalpy steam fraction escapes from the remaining lower enthalpy liquid water. This low-enthalpy water at 92° to 110°C then encounters cold ground water and a mixed water at 76°C results. The separated steam fraction probably emerges 350 m northwest of Interchange Spring at the Pine Springs group, where violently boiling springs occur with little or no discharge.

Ideally, large-flow warm springs in a given locality with different temperatures and different compositions should give the same estimated hot-water temperature. Such is found for two large-flow unnamed springs located between Biscuit Basin and Midway Geyer Basin in Yellowstone National Park. The springs have temperatures of 49° and 61°C and silica contents of 100 and 122 mg/l respectively, (table 2, cols. 2 and 3). Applying model 1, the intersection of curves A and B, figure 5, indicates a cold-water fraction of 0.82 for the 49°C spring and 243°C as the maximum probable temperature of the hot-water component. The intersection of curves C and D, figure 5, gives exactly the same temperature, 243°C, for the high-temperature component of the 61°C water. As expected, the fraction of cold water, 0.77, is less in the 61°C water than in the 49°C water. Applying model 2, and assuming $t_s = 100°C$, a minimum probable temperature of 166°C is obtained for the original temperature of the hot-water component in each spring, which indicates clearly that two waters are mixing in different proportions. Unfortunately, additional data is insufficient to indicate whether the higher or lower estimated temperature of hot-water component is more nearly correct.

CONCLUSIONS

The water in both boiling and nonboiling springs may be a mixture of hot water coming from depth and of cold, near-surface meteoric water. Under favorable conditions nonboiling thermal springs with large rates of flow may yield information about the temperature or range in probable temperatures of the hot-water component and the fraction of cold water in the mixture.

The assumptions necessary for using the mixing models described in this paper probably will not be met in most places. However, even a 10-percent success rate would make
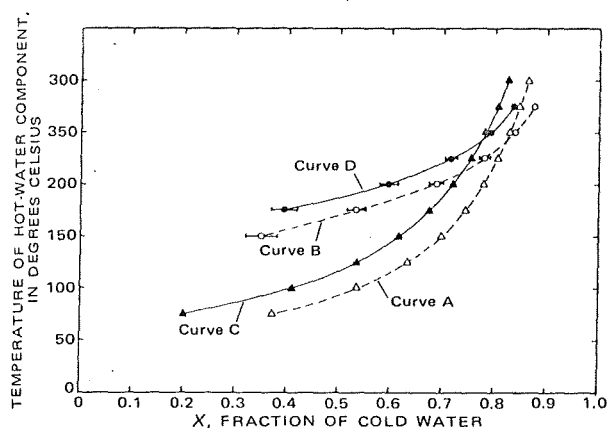

Figure 5.—Fraction of cold water relative to temperature of hot-water component in two springs located between Biscuit and Midway Basins. See figure 2 for explanation of curves and symbols; open symbols refer to the 49°C water and solid symbols to the 61°C water.

them valuable adjuncts of other methods for evaluating the geothermal potential of an area.

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