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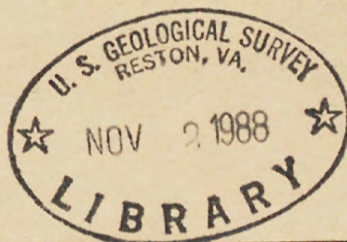
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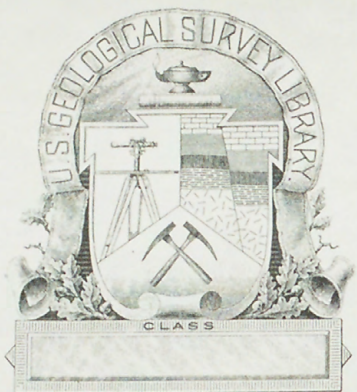
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CONDITIONS IN THE DEEPER PARTS OF THE HOT SPRING SYSTEMS OF
YELLOWSTONE NATIONAL PARK, WYOMING

Open-file Report 76-428





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UNITED STATES DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

[Reports - Open file series]

CONDITIONS IN THE DEEPER PARTS OF THE HOT SPRING SYSTEMS
OF YELLOWSTONE NATIONAL PARK, WYOMING

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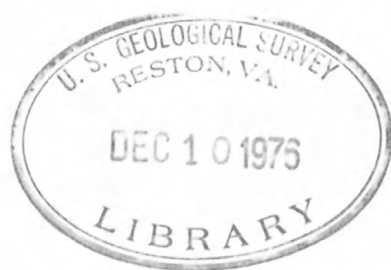
A. H. Truesdell and R. O. Fournier, 1932 -
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This report is preliminary
and has not been edited or
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Introduction

Yellowstone thermal areas are scattered over an area of nearly 50 x 60 kilometers (Fig. 1) and contain waters of diverse compositions. This has lead to the implicit assumption that Yellowstone consisted of discrete hydrothermal systems (e.g., Fournier and Truesdell, 1970). It is the purpose of this paper to suggest that these systems may be separate only near the surface and that there may exist at depth a large, relatively homogeneous body of water at 340 to 370°C containing about 1,000 ppm NaCl. This deep thermal water flows upwards losing steam into the near-surface geyser and hot spring systems where it undergoes variable amounts of dilution with cold meteoric water, reaction with rocks, and further steam loss to produce all of the hot spring waters of the Park. The evidence for these conclusions is from the application of chemical and isotopic geothermometers, from relationships between the chloride concentrations and subsurface heat contents of thermal waters, from the chemical and isotopic compositions of the waters, and from geophysical evidence.

Geology and Geophysics

As a result of an intensive program of geological, geochronological, geophysical, and geochemical studies by members of the U.S. Geological Survey, the volcanic history of Yellowstone is known in detail (Christiansen, 1976). Intense volcanism has characterized the Pleistocene history of Yellowstone Park. Three times in the past two million years volcanic activity culminating in pyroclastic eruptions has produced large volumes of ash-flow tuffs and caldera collapse. The last of these active periods was characterized by extensive rhyolitic lava flows before and

after the eruption of pyroclastic ash and caldera collapse over a 70 x 45 km area. Gravity, seismic, and magnetic studies indicate that partially molten magma underlies the entire area of this caldera at depths below 6 km and possibly extending deeper than 200 km (Eaton et al., 1975; Trimble and Smith, 1975).

Temperature gradients in lake sediments of that part of Yellowstone Lake within the caldera range from 200 to 6000°C/km, but most measurements are between 600 and 900°C/km. Heat flows calculated from these measurements average about 15 HFU (Morgan et al., 1976) and are of the same order as the average of 16 HFU for the total area within the Park east of the Continental Divide and of 43 HFU within the caldera derived from chemical measurements (Fournier et al., 1976).

The Hot Spring Systems

Hot spring and geyser basins are widely distributed within and just outside the Yellowstone caldera (Fig. 1). Thermal basins with large flows of hot water generally occupy topographic lows along surface drainages, and the few topographically elevated thermal areas are characterized by fumaroles with little water discharge. High chloride thermal waters are found along the Firehole River in Upper and Lower Geyser Basins, along the Gibbon River in Norris and Gibbon Geyser Basins, at the west end of Shoshone Lake, north of Heart Lake, and in a few isolated locations elsewhere. Thermal areas with fumaroles and acid springs are found east of the Yellowstone River, north of Norris Basin, and, to a smaller extent, in elevated areas adjacent to areas of hot water discharge. Waters of Mammoth Hot Springs to the north of the caldera precipitate travertine

(calcite) as do certain other springs within the geyser basins, although sinter (silica) precipitation is much more common.

Many analyses of Yellowstone thermal waters have been reported since the early studies of Gooch and Whitfield (1888). The most important compilations of analyses are Allen and Day (1935), Rowe et al. (1973), and Thompson et al. (1975). Representative water analyses selected from the last two are given in Table 1.

Subsurface Temperatures - Chemical Geothermometers and Mixing Calculations

Research drilling in 1929-1930 (Fenner, 1936) and in 1967-1968 (White et al., 1975) has allowed direct measurement of underground temperatures in parts of Yellowstone thermal areas. Unfortunately, the drilling was to shallow depths (332 m maximum), and a maximum or "leveling off" temperature in a zone of fluid upflow was found only in the low-temperature system at Mammoth. Most of our knowledge of subsurface temperatures depends, therefore, on the application of chemical and isotopic geothermometers to hot spring fluids. These geothermometers depend on the existence of temperature-dependent equilibria at depth which are in part quenched or frozen in during passage to the surface. The theory of these geothermometers has been discussed by Fournier et al. (1974). Because partial reequilibration commonly does occur during passage to the surface, these geothermometers may yield only minimum temperatures. Average and maximum subsurface temperatures indicated by the silica (Fournier and Rowe, 1966; Mahon, 1966) and Na-K-Ca (Fournier and Truesdell, 1973) geothermometers for Yellowstone thermal water analyses (compiled by Rowe et al., 1973, and Thompson et al., 1975) are given in Table 2.

If subsurface mixture with cold, dilute water occurs, temperatures and concentrations may be sufficiently reduced that reequilibration is not significant. This is the basis of mixing models for warm springs (Fournier and Truesdell, 1974) and for boiling springs (Truesdell and Fournier, 1976) which allow the calculation of the mixing fraction and temperature of the hot water component. These models have been applied to Yellowstone analyses (cited previously) and the average and maximum indicated temperatures are given in Table 2. The average indicated silica temperatures for thermal areas other than Norris are well below the theoretical maximum that can be indicated without possible near-surface precipitation of amorphous silica (White et al., 1956; Fournier, 1973; Truesdell and Fournier, 1976), but again, except for Norris, the maximum indicated temperatures are either at or only slightly above that value. These observations suggest that the indicated temperatures are real and that near-surface reequilibration occurs in defined aquifers at temperatures in the range of usefulness of the boiling spring mixing model. Higher silica temperatures are indicated at Norris, probably because of unusually rapid upflow of thermal waters.

Although maximum subsurface temperatures indicated by the mixing models are higher than those indicated by the chemical geothermometers, these temperatures are probably not the actual maximum temperatures of water feeding the basins because, in the model for boiling springs, only the temperature of the least mixed water reaching the surface can be calculated and because springs suitable for the warm spring mixing model (which does not have this limitation) are not common in Yellowstone and

have seldom been analyzed. We must look elsewhere for indications of the maximum subsurface temperature in Yellowstone.

Isotope Geothermometers

Isotopic equilibration generally occurs much more slowly than chemical equilibration and is unaffected by pressure variations. Isotope fractionations are therefore potentially very useful for the thermometry of geothermal systems. Two isotope geothermometers have been applied to Yellowstone fluids. The distribution of carbon 13 between CO_2 and CH_4 ($\Delta^{13}\text{C}[\text{CO}_2, \text{CH}_4]$) in Yellowstone gases has been measured by Craig (1953; 1963), Gunter (1968), Gunter and Musgrave (1971), and G. L. Lyon (written commun., 1971). $\Delta^{13}\text{C}(\text{CO}_2, \text{CH}_4)$ temperatures range from 244 to 390°C using fractionation factors calculated by Bottinga (1969) (Table 3). McKenzie and Truesdell (1976) have measured the oxygen isotopic compositions of spring waters and dissolved sulfates of Yellowstone and, after making corrections for the effects of dilution and steam separation on the isotope composition of the waters, calculated temperatures near 350°C.

These indicated gas and dissolved sulfate isotope temperatures are higher than those from chemical geothermometers because less partial reequilibration occurs in near-surface aquifers. The kinetic behavior of the gas isotope reactions is unknown, but that of the dissolved sulfate-water geothermometer has been studied by Lloyd (1968). If the subsurface pH of the Yellowstone waters is near 6, as estimated by the methods of Ellis (1970) and Truesdell and Singers (1971), the half-time for isotopic exchange between dissolved sulfate and these waters is calculated to be 25 days at 350°C, 165 days at 250°C, and 525 days at 200°C. The near-surface aquifers indicated by the mixing models and the chemical

geothermometers are at temperatures near $200 \pm 50^\circ\text{C}$, and dissolved sulfate in the Yellowstone waters seems to be little changed ($<2\%$) during passage to the surface. Therefore, the waters feeding the surface springs must rise to the near-surface aquifers very rapidly and remain in these aquifers at temperatures near 200°C no longer than a few months. If deeper, hotter aquifers exist in Yellowstone, it is doubtful that any direct chemical or isotopic evidence of their existence would reach us in surface springs. Even isotopic reactions become sufficiently rapid at 300 to 400°C that residence in any sizable aquifer at these temperatures would obliterate evidence of higher temperatures.

The Deep Aquifer

Geothermometers suggest that the deep waters feeding the geyser and hot spring systems are at temperatures above 270 to 290°C (mixing models and Na-K-Ca relations) and possibly as high as 350 or 390°C (gas and dissolved sulfate isotopes). An independent method for obtaining the temperature of a possible deep thermal water is to assume that such a water exists and use the mixing model for boiling springs (Truesdell and Fournier, 1976) to determine its temperature and chloride content (Fig. 2). This model assumes that steam loss, shown by lines radial to steam (zero chloride; enthalpy about 2780 J/g), and dilution with cold meteoric water, shown by lines radial to cold water (2 ppm Cl ; enthalpy 20 J/g), are the dominant processes determining the subsurface temperatures and chloride contents of thermal waters. The steam-loss line from the most concentrated waters of Norris Geyser Basin intersects the dilution line from Shoshone Geyser Basin at about 360°C and 300 ppm chloride. A deep thermal water at this temperature and chloride content could produce the chloride and

indicated subsurface temperatures of all the waters of the Park by the processes of adiabatic cooling (steam loss) and dilution by cold water. If only the Madison and Yellowstone River drainages are considered, it may be more reasonable to take the intersection of the (rather less well-defined) dilution line of Upper and Lower Geyser Basin waters with the Norris steam-loss line which suggests a deep parent water of 336°C and about 400 ppm chloride (Fournier et al., 1976).

If conductive heat loss occurs, water may lose heat without changing its chloride contents. The path of such a water on Figure 2 would be vertically downward. If the high chloride waters of Norris Geyser Basin were partially cooled by conduction, the calculated deep temperature would be increased; if the dilute waters of Shoshone Geyser Basin were cooled conductively, the calculated deep temperature would decrease. The large flows of the dilute Shoshone springs and the alignment of their subsurface enthalpy-chloride compositions along a well-defined dilution line (standard deviation = 5°C for area I; Truesdell and Fournier, 1976) argue against a large component of conductive cooling. It is possible that partial conductive cooling affects both high and low chloride springs to produce compensating errors in the calculated deep temperature.

This calculation is based in part on the assumptions that chloride and heat are transferred to the water deep in the system and are not modified at shallow levels except by steam loss and dilution. Additional evidence for this comes from a consideration of the isotopic composition of the waters themselves.

Isotopic Compositions of Waters and the Origin of Deep Chloride

It has been shown that most geothermal waters are dominated by meteoric water that circulates deeply and acquires heat and dissolved salts in the process (Craig *et al.*, 1956; White *et al.*, 1963; Craig, 1963). This deeply circulating meteoric water also becomes enriched in the heavy isotope of oxygen as a result of isotope exchange with rock minerals, and it returns to the surface distinctly different isotopically from meteoric water of shallower circulation. This provides an independent test of mixing processes. In Figure 3, the oxygen isotope ratio (expressed as per mil (δ) deviation from SMOW) is shown to be linearly related to the chloride content for the thermal waters of Upper, Midway, and Lower Geyser Basins, for most of Norris Geyser Basin, and for Terrace, Mammoth, and Beryl hot spring areas. The isotope-chloride relations for West Thumb are poorly understood, but may indicate inflow of partly evaporated Yellowstone Lake water. Both linear trends suggest a deep water component with the composition -12‰ $\delta^{18}\text{O}$ and 800 ppm Cl after flashing to surface pressure. These data, taken in conjunction with the isotope temperatures, strongly suggest that geothermal waters do not acquire significant amounts of additional chloride or undergo significant oxygen isotope exchange with rock at temperatures much below 300°C . There would be little acquisition of chloride above the base of circulation if its source is magmatic (White, 1957) or if its source is a deep brine that formed during the early high-temperature phase of hydrothermal activity. If a brine is involved, it must convect deep in the system at near-magmatic temperatures and be overlain by a dilute convecting hot spring system with transfer of both chloride and heat at the interface.

Evidently additional chloride is not acquired as the dilute water ascends from depth, either because the water follows well-defined passages where the original rock chloride already has been leached or because chloride is not effectively leached from rock at temperatures below 300°C. Ellis and Mahon (1964) found that the amount of chloride leached from rhyolitic rocks was thirty times greater at 350°C than at 250°C. Similarly, the exchange of oxygen isotopes between coarse grained silicates and water proceeds exceedingly slowly at temperatures below 300°C (J. R. O'Neil, personal commun., 1975).

Diverse Compositions of Yellowstone Thermal Waters

If Yellowstone thermal waters are derived from a single parent water, as suggested in the previous sections, then this water must be considerably modified during passage to the surface to produce the observed diversity of water types. Representative analyses of Yellowstone waters in Table 1 are taken from compilations of Rowe et al. (1973) and Thompson et al. (1975).

The western part of Norris Basin has the most concentrated waters, consisting of $\text{Na}^{1/}$, Cl, and SiO_2 , with only minor contents of HCO_3 , and with surface pH values near neutral (Table 1, analysis 1). Less concentrated acid waters with pH values from 2 to 4 and higher SO_4 values are also found at Norris in major amounts (analysis 2). The Firehole Basins (Upper, Midway, and Lower Basins) are characterized by more alkaline (surface pH 8 to 9.5) waters with lower Cl and SiO_2 contents and variable higher contents of HCO_3 and CO_3 . Waters with the highest Cl

^{1/}Valence is omitted from dissolved species unless required for clarity.

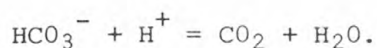
contents in these basins occur on Geyser Hill in the SE part of Upper Basin (analysis 3); waters from the western parts of Upper Basin, from Midway, and from Lower Basin have lower Cl contents and higher HCO_3 contents (analyses 4-8). Waters of Heart Lake Geyser Basin are similar to those of Lower Basin (analyses 9 and 10), but waters of Shoshone Geyser Basin are lower in Cl (analyses 11 and 12). Other thermal waters of special interest are those of Terrace, Firehole Lake, and Hillside Springs, where moderate amounts of both travertine and sinter are deposited (analyses 13-15), and those depositing copious travertine at Mammoth Hot Springs (analysis 16). Finally, in vapor-dominated systems (White et al., 1971) and at higher elevations throughout the Park, acid waters occur with high sulfate and low chloride (analysis 17).

The Differentiation of Yellowstone Thermal Waters

The major near-surface processes producing the varied compositions of thermal waters at Yellowstone include steam separation during adiabatic cooling, mixture with cold shallow meteoric waters, and chemical reactions involving rock minerals, dissolved gases, dissolved components of diluting waters, and atmospheric gases. These processes are summarized in Table 4. The differentiation of thermal waters has also been discussed by Allen and Day (1935), White (1957), and Ellis (1970).

Steam separation produces changes in water chemistry because salts are essentially insoluble in low pressure steam (Krauskopf, 1964) and remain entirely in the liquid phase, while gases partition strongly into the vapor (Ellis and Golding, 1963; Kozintseva, 1964). The result of these processes is an increase in nonvolatile salts and a decrease in dissolved gases (principally CO_2 and H_2S) in the liquid phase. The loss of gas

produces an increase in pH from about 6 at depth to near 9 at the surface (Ellis, 1970; Truesdell and Singers, 1971) through the reaction

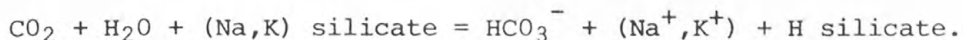


The effect of CO_2 loss is greatest in waters with large contents of HCO_3 such as those from Upper and Lower Geyser Basins (analyses 3-8, Table 1), so these waters become very alkaline whereas Norris waters, with very little HCO_3 , remain near neutral (analysis 1).

Mixture with cold meteoric waters produces the main variations in the concentrations (but not the ratios) of chloride, boron, and other components not involved in lower temperature rock reactions. Mixture with cold water also controls the temperatures in subsurface aquifers where mixture takes place (Truesdell, 1976; Truesdell and Fournier, 1976) and thus affects temperature-sensitive equilibria such as quartz solution and ion exchange with feldspars. If temperatures are sufficiently reduced, steam separation is prevented and a high partial pressure of CO_2 may be maintained in waters at temperatures near surface boiling. Under these conditions, the solubility of calcite is relatively large (Holland, 1967) and calcium can be leached from the rock. When these dilute, high P_{CO_2} -high Ca solutions emerge at the surface, they lose CO_2 and deposit travertine as well as silica. This is the origin of the Firehole Lake, Hillside, and Terrace Springs (analyses 13-15), as well as of isolated springs elsewhere (e.g., analysis 12).

Most of the bicarbonate and part of the sodium and potassium in hot spring waters is produced by reaction of dissolved CO_2 with volcanic glass and feldspar to produce mica or clay minerals and bicarbonate and alkali

ions (Fournier and Truesdell, 1970),



The coupled increase in HCO_3/Cl ratios and decrease in CO_2 /other gas ratios during lateral flow through a near-surface aquifer has been demonstrated for Shoshone Geyser Basin (Truesdell, 1976). The effect of this reaction (and of dilution) can be seen by comparing analyses 3 and 4, 5, 6, 7 and 8, 9 and 10, and 11 and 12. Norris waters and, to a lesser extent, Geyser Hill (Upper Basin) waters rise rapidly through crystalline rock which is not as reactive as the glacial sediments containing volcanic glass found in other areas, so little CO_2 is converted to bicarbonate.

Sulfate in Yellowstone waters originates in large part from oxidation of H_2S by atmospheric oxygen dissolved in meteoric water of deep or shallow circulation (Truesdell, 1976). The theoretical amount of SO_4 ion that can be formed in this manner is 22 ppm from rain water percolating underground after equilibrating with air at 0°C . This is close to the observed contents in the waters of Upper, Midway, and Lower Geyser Basins and of neutral Norris waters (analyses 1 and 3-8). Areas outside the caldera may more easily leach sulfate from sedimentary rocks, as is shown by the high sulfate contents of Mammoth and Heart Lake waters (analyses 9, 10, and 16).

Acid waters with extremely high SO_4 contents (analysis 17) are produced by direct superficial atmospheric oxidation of H_2S to sulfuric acid in areas of drowned fumaroles or steaming ground (White, 1957). The acid-chloride waters at Norris (analysis 2) probably result from

percolation of this acid sulfate water into near-surface reservoirs where it mixes with chloride water from below. The high partial pressure of CO₂ and large Ca contents of Mammoth Hot Springs (analysis 16) may result from Norris acid chloride waters moving northward along a fault zone and reacting with sediments consisting in part of limestone. The waters are also considerably diluted with cold meteoric water in the process (Fig. 2).

The Location of the Deep Reservoir

The depth to Yellowstone's deep geothermal reservoir is estimated to be more than 2 or 3 kilometers and less than 5 kilometers. The maximum temperatures indicated by the enthalpy-chloride relations and the isotope geothermometers are in the range 340 to 390°C. The minimum depth at which hot water can remain liquid is determined by the pressure of an overlying column of vapor-saturated water. For these temperatures, this minimum depth is 2 to 3 kilometers (Haas, 1971; Manuel Nathenson, written commun., 1974). The existence of overpressure in Yellowstone systems of up to 6.2 bars (White et al., 1975) would only decrease this depth by about 100 meters. If the water is not saturated with steam throughout, the depth to the reservoir will be greater.

The reservoir cannot be very deep in Yellowstone because geophysical evidence for a mass of molten rock (magma) at depth suggests that this magma may be as shallow as 5 kilometers (Eaton et al., 1975; Trimble and Smith, 1975). The maximum depth of epicenters of earthquakes occurring to the WNW of Yellowstone Park changed abruptly from 15 kilometers outside the Yellowstone caldera to 5 kilometers inside in the vicinity of Norris Geyser Basin (Trimble and Smith, 1975).

Geologic studies of Yellowstone suggest that, at estimated aquifer depth of 3 ± 1 kilometers within the caldera, the rocks are ash-flow tuffs, rhyolitic flows, and sediments (R. L. Christiansen, personal commun., 1975). These units would provide a suitable reservoir for the deep hot fluid. Fractures in otherwise impermeable rocks also may create an aquifer that extends across rock types.

It is probable that the deep aquifer underlies the entire area within the Yellowstone caldera (Fig. 1). Temperature measurements in the sediments of Yellowstone Lake indicate gradients of 500 to 900°C per kilometer for the area within the caldera, and heat flows calculated from these gradients (Morgan et al., 1976) are similar to those derived from chloride-heat budgets for thermal water of the Madison and Yellowstone River drainages (Fournier et al., 1976). It is possible that the relatively impermeable lake sediments prevent the formation of the zones of intense convective upflow separated by zones of diffuse downflow characteristic of the rest of the caldera.

Thermostatic Processes in High Temperature Systems

The geothermal systems of Yellowstone obtain their heat from cooling magma which probably is at temperatures above 600°C. Deeply circulating dilute water, as discussed earlier, does not attain these temperatures but is probably heated by conduction through an unknown thickness of rock. This rock may be water-saturated and it is reasonable to ask why the convection system does not extend to magmatic temperatures. This may possibly occur for more saline waters (Taylor, 1974), but there are mechanisms which may limit maximum temperatures of dilute geothermal waters.

The solubility of quartz in pure water in equilibrium with steam has been shown to have a maximum at about 335°C (Kennedy, 1950). With increasing pressure the maximum becomes less pronounced and its temperature slowly increases. At pressures greater than 750 bars the maximum disappears. Thus, boiling waters at 335°C can dissolve a maximum amount of silica and will deposit quartz if they are either heated or cooled. The solution of silica may create permeability in deep aquifers where fractures are limited. If water circulating in an aquifer at 335°C entered a hotter region at greater depths, it would quickly deposit quartz because the rate of deposition is rapid at these temperatures; when this occurred, permeability would be decreased. If the water circulated upwards into cooler rock, deposition of quartz would also occur but the slope of the solubility curve is less and the rate of deposition is less, so the quartz would be distributed over a greater volume of rock and would not decrease permeability so abruptly. This mechanism would limit downward circulation of dilute waters to the level at which temperatures are about 335 to 380°C (depending on pressure).

Another mechanism may also contribute to limiting temperatures in high temperature geothermal systems that are near the boiling point at all depths. The specific volume of vapor-saturated liquid water (without dissolved salts or gases) increases very rapidly above 350°C. The change in specific volume from 340 to 350°C is 6 percent, that from 350 to 360°C is 9 percent, but that from 360 to 370°C is 17 percent (Keenan et al., 1969). The specific volume of compressed liquid water at pressures above those of saturation also exhibits marked but smaller

increases. Large gradients in specific volume would produce rapid convection to remove heat and limit the maximum temperature of the system.

Summary

In this paper it is suggested that beneath Yellowstone thermal systems there is a large aquifer at a depth of 2 to 4 kilometers which contains a dilute chloride water at 340 to 370°C. This aquifer may be controlled entirely or in part by solution or fracture permeability that transects rock types. Water flows upwards from the deep aquifer along available fractures, losing steam in the process, and into more shallow aquifers that in turn feed the geyser and hot spring systems. In these shallow systems, it is diluted, reacts with rocks and fluids, and loses more steam to produce the varied hot spring waters of the Park. The deposition of silica at the bottom of the system and increased convection at near-critical temperatures will limit the maximum temperatures and depth of circulation of dilute high temperature thermal waters such as those of Yellowstone.

Acknowledgments

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Figure Captions

- Figure 1. Index map of Yellowstone Park, Wyoming. Thermal areas (stippled) and caldera outline are shown.
- Figure 2. Enthalpy-chloride relations for Yellowstone thermal waters. The surface chloride and enthalpy of the highest chloride springs in each geyser basin are indicated at the bottom of the figure, and the subsurface chloride and enthalpy are shown for all analyzed springs. Intersections of dilution lines from subsurface compositions of mixed springs and boiling lines drawn between steam and surface compositions of the highest chloride springs are indicated for each basin with the calculated temperature. Subsurface chloride and enthalpy as calculated from the warm spring mixing model are indicated by octagons.
- Figure 3. Oxygen isotope-chloride compositions for selected Yellowstone cold and thermal springs.

Table 1.--Analyses of Selected Yellowstone Thermal Waters

	NORRIS GEYSER BASIN		UPPER GEYSER BASIN		MIDWAY GEYSER BASIN	LOWER GEYSER BASIN			HEART LAKE GEYSER BASIN		SHOSHONE GEYSER BASIN		DILUTE TRAVERTINE-DEPOSITING SPRINGS			MAMMOTH HOT SPRINGS	HOT SPRINGS BASIN
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	Pork Chop Spring	Little Whirligig Geyser	Ear Spring	Sapphire Spring	Excelsior Spring	Snort Spring	Ojo Caliente Spring	Near Cleopatra Geyser	Spike Geyser	Rustic Geyser	Spring 192	Boiling Spring	Hillside (Upper)	Fire-hole Lake (Lower)	Terrace	New Highland	Perpetual Spouter
	(1)	(1)	(2)	(2)	(1)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
Temp. (°C)	71	91	95	95	76	93	95	92	93.5	91	89.5	94	84.5	93	66	73.5	89
pH	7.1(3)	3.2(4)	9.0(3)	8.5(3)	8.0(3)	9.3(4)	8.0(3)	9.0(3)	8.9(3)	8.7(3)	7.4(3)	7.0(3)	6.7(3)	6.8(3)	6.3(2)	7.3(4)	3.0(3)
SiO ₂	435 (4)	420 (4)	362 (4)	334 (4)	303 (4)	242	230	414	366	318	350	170	168	213	148	53.8	317
Al	<.1	2.1	--	--	<.1	.18	--	--	--	--	--	0.08	0.12	--	0.18	--	--
Fe	<.1	1.0	0.05	--	<.1	.01	--	0.05	--	--	--	0.05	--	--	0.15	--	--
Ca	6.4	2.5	0.6	0.3	2.5	1.6	0.9	0.5	0.9	1.2	0.3	4.1	7.9	15.1	6.7	345	37
Mg	0.5	0.5	0.01	0.01	.1	.04	0.02	0.01	0.01	0.05	0.01	.05	0.16	.05	0.8	76	3.8
Na	526	349	335	450	385	314	335	380	400	405	350	295	149	85	324	130	187
K	66	83	16.5	15.8	15	10	9.5	12.5	24.2	15.5	13	11.3	7.5	16	37	55	16
Li	7.4	5.3	5.2	2.3	2.8	4.0	4.2	2.8	6.7	5.0	1.5	1.6	0.8	0.4	0.6	1.6	0.04
NH ₄	--	--	0.4	0.2	--	0.1	0.3	3.0	0.1	0.1	0.1	--	0.1	0.1	--	--	171
HCO ₃	18	0	174	595	546	41	225	380	159	318	230	449	217	165	696	864	--
CO ₃	0	0	--	--	0	69	--	--	64	--	--	3.3	16	--	50	--	--
SO ₄	33	113	21.5	16.5	34	23	24	22	100	160	70	36	14	27	11	568	1530
Cl	860	607	417	308	270	344	331	325	363	303	323	135	72	44	69	166	0.1
F	--	3.3	26	30	24	33	31	22	38	26	21.5	15	12	10	6.7	2.5	0.8
B	15	9.2	4.3	3.2	3.4	4.1	4.1	3.5	3.6	3.3	3.7	1.7	1.1	0.5	1.1	3.7	5.0
As	--	--	--	--	2.3	--	--	--	--	--	--	--	--	--	--	--	--
H ₂ S	--	--	4.1	2.6	--	3.7	1.3	1.1	--	--	--	--	--	0.2	--	5.8	--
Cl/HCO ₃	82	--	4.1	0.89		5.3	2.5	1.5	2.8	1.6	2.4	0.5	0.5	0.5	0.2	.33	--
Cl/SO ₄	71	15	53	51		41	37	40	9.8	5.1	13	10	14	4.4	17	.79	--
Cl/B	17	20	30	29		26	25	28	31	28	27	24	18	27	19	14	--

1) Analysis from Rowe, Fournier and Morey (1973). Mg contents (by EDTA titration) are probably high.

2) Analysis from Thompson, Presser, Barnes and Bird (1975)

3) Field measurement

4) Laboratory measurement

Table 2

Chemical geothermometer and mixing calculation
temperatures in °C

Geyser Basin		SiO ₂	NaKCa	Mix I	Mix II
West Thumb	ave.	188	186	220	211
	std. dev.	14	10	-	24
	max.	209	202	220	233
Heart Lake	ave.	196	188	-	221
	std. dev.	12	29	-	8
	max.	214	223	-	232
Shoshone	ave.	190	175	238	265
	std. dev.	10	16	-	21
	max.	203	223	238	316
Upper	ave.	195	186	259	230
	std. dev.	11	20	10	18
	max.	210	221	273	280
Lower + Midway	ave.	179	162	260	210
	std. dev.	11	16	16	18
	max.	213	218	283	303
Norris	ave.	210	251	262	276
	std. dev.	22	32	13	32
	max.	255	294	276	374

Table 3.--Carbon dioxide-methane isotope temperatures for Yellowstone hot spring gases

Location	$\delta C^{13}(CO_2)$	$\delta C^{13}(CH_4)$	$10^3 \ln \alpha$	calc t°C	ref.
Upper Geyser Basin					
Daisy Geyser	- 1.1	-28.4	27.7	264	1
Iron Spring	- 1.7	-27.4	26.1	283	1
Black Sand	- 2.1	-26.5	24.8	300	1
Punch Bowl	- 2.5	-22.6	20.4	372	1
Near Castle Geyser	0.0	-29.1	29.5	244	2
Artemesia Geyser	-25.5(?)	-44.8(?)	20.0	380	2
Y-8 downhole	- 1.5	-25.8	24.6	303	3
Lower Geyser Basin					
Kaleidoscope	- 2.8	-23.8	21.3	356	1
Firehole Lake	- 4.4	-26.1	22.0	344	1
Ojo Caliente	- 6.4	-20.6	14.4		1
Near Skeleton Pool	- 0.1	-25.1	25.3	293	2
Y-4 downhole	- 2.3	-22.3	20.2	376	3
Y-5 downhole	- 1.9	-25.5	23.9	314	3
Norris Geyser Basin					
Emerald Spring	- 1.3	-24.1	23.1	327	2
Y-12 downhole	- 2.9	-27.0	24.5	305	3
Washburn Springs					
Devils Inkpot	- 3.8	-23.5	20.0	380	2
East Spring	- 7.4	-26.6	19.5	390	2
Mammoth Springs					
Y-10 downhole	- 3.5	-24.7	21.5	353	3

References:

- 1) Craig (1953) and Craig (1963)
- 2) Gunter (1968) and Gunter and Musgrave (1971)
- 3) G. Lyon, written communication, 1971.

Table 4

Chemical processes in Yellowstone thermal systems

Deep aquifers

Heat gain by conduction or convection

Salts and gases from rock leaching or magma (Cl, B, Na, CO₂, H₂S and other)

Isotope exchange (H₂O - rock; CO₂ - CH₄; SO₄⁼ - H₂O)

Mineral solution (quartz = SiO₂ aq, etc.)

Shallow aquifers

Ion exchange (K⁺ + Na rock = Na⁺ + K rock)

Rock alteration (CO₂ + H₂O + Na rock = Na⁺ + HCO₃⁻ + H rock)

Boiling and volatile loss (2 HCO₃⁻ = CO₂↑ + CO₃⁼ + H₂O)

Mineral precipitation (Ca⁺⁺ + CO₃⁼ = CaCO₃, etc.)

Dilution

Fluid-fluid reactions (H₂S + 2 O₂ aq = SO₄⁼ + 2 H⁺)

Surface oxidation (Mn, Fe oxides ppt.; H₂S → sulfuric acid)

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