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GEOTHERMAL RESERVOIR TEMPERATURES ESTIMATED FROM THE OXYGEN ISOTOPE COMPOSITIONS OF DISSOLVED SULFATE AND WATER FROM HOT SPRINGS AND SHALLOW DRILLHOLES

by

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ABSTRACT

The oxygen isotope compositions of dissolved sulfate and water from hot springs and shallow drillholes have been tested as a geothermometer in three areas of the western United States. Limited analyses of spring and borehole fluids and existing experimental rate studies suggest that dissolved sulfate and water are probably in isotopic equilibrium in all reservoirs of significant size with temperatures above about 140°C and that little re-equilibration occurs during ascent to the surface. The geothermometer is, however, affected by changes in $\delta^{18}O$ of water due to subsurface boiling and dilution and by addition of sulfate of near-surface origin. Methods are described to calculate the effects of boiling and dilution. The geothermometer is applied to thermal systems of Yellowstone Park, Wyoming, Long Valley, California, and Raft River, Idaho to estimate deep reservoir temperatures of 360, 240, and 142°C, respectively.

INTRODUCTION

Rafter and Mizutani [1] first attempted calculating an isotopic equilibrium temperature based on measurements of the oxygen isotope compositions of water and dissolved sulfate from geothermal boreholes at Wairakei, New Zealand and the theoretical fractionation constants of Urey et al [2]. Although the maximum measured borehole temperature was 270°C, the calculated temperature was only 140°C, suggesting either nonequilibrium conditions or uncertainties in Urey's calculated equilibrium constants. Lloyd [3] and Mizutani and Rafter [4] experimentally determined sulfate-water fractionations that differed considerably from Urey's calculations, recalculated the Wairakei bore water temperature,

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found good agreement with the maximum measured temperature. Reason-
.ole agreement between sulfate-water isotopic temperatures and measured
borehole temperatures has been demonstrated at Otake, Japan [5] and
Larderello, Italy [6]. Kusakabe [7] re-analysed the Wairakei drillhole
waters and obtained essentially the same results as the earlier work of
Mizutani and Rafter. Longinelli [8] found no temperature correlation
between the surface temperatures and the oxygen-18 compositions of
dissolved sulfate and water from warm springs in Tuscany, Italy. Because
the oxygen isotopic compositions of the dissolved sulfate and of anhydrite
from deep drillholes in the same areas were similar, Longinelli concluded
that the sulfate originated from the dissolution of evaporites encountered
during ascent to the surface and had not equilibrated isotopically.
Cortecci [6] came to a similar conclusion for dissolved sulfate in two
spring waters from the Larderello region. Mizutani and Hamasuna [9]
estimated a deep subsurface temperature of 221 to 335°C at Shimogamo,
Japan from the sulfate-water geothermometer applied to the geothermal
brines discharged from shallow drillholes (52-250 m). Sakai and Matsu-
baya [10] found that reasonable temperatures were indicated by the
sulfate-water geothermometer for volcanic waters in Japan; those calcu-
lated for Beppu were in agreement with temperatures estimated by chemical
geothermometers.

Chemical (SiO_2, Na/K, NaKCa) geothermometers [11] indicate minimum
subsurface temperatures up to 200 to 230°C, but these geothermometers
are variously affected by dilution and re-equilibration and their maxi-
mum temperature limit is below the region of greatest geothermal interest.
We wish to demonstrate here that with corrections for subsurface boiling
and dilution the sulfate geothermometer applied to surface discharges
indicates reasonable subsurface temperatures over the range of about 140
to 350°C. We describe the application of this geothermometer to the
thermal systems of Yellowstone Park, Wyoming, Long Valley, California,
and Raft River, Idaho.

OXYGEN ISOTOPE FRACTIONATION FACTORS AND RATES OF EXCHANGE FOR SO_4-H_2O

Experimental fractionation factors for the sulfate-water system
determined by Lloyd [3], by Mizutani and Rafter [4], and by Mizutani [5]
are in reasonable agreement between 100 to 200°C (fig. 1). Lloyd reported
an equilibrium fractionation between dissolved sulfate and water of

$$1000 \ln \alpha_{SO_4-H_2O} = 3.251 \ (10^6/T^2) - 5.6, \tag{1}$$

but Mizutani and Rafter found

$$1000 \ln \alpha_{SO_4-H_2O} = 2.88 \ (10^6/T^2) - 4.1 \tag{2}$$

where

$$\alpha_{SO_4-H_2O} = \frac{(^{18}O/^{16}O)SO_4}{(^{18}O/^{16}O)H_2O} = \frac{1000 + \delta^{18}O(SO_4)}{1000 + \delta^{18}O(H_2O)} \qquad (3)$$

and T is in °K. The low temperature data of Lloyd suggest nonattainment of equilibrium in his experiments but his datum at 348°C agrees with the equation of Mizutani and Rafter.

No experimental data exist in the geothermally interesting temperature range between 200 and 350°C. Extrapolation of data taken at 100 to 200°C to a single value at 350°C probably results in some errors in calculating sulfate isotope temperatures above 200°C.

Exchange of oxygen isotopes between dissolved sulfate and water is exceedingly slow in neutral and alkaline solutions below 200°C. Lloyd [3] showed that the rates are strongly dependent on pH, with

$$\log t_{1/2} = 2.54 \ (10^3/T) + b \qquad (4)$$

where $t_{1/2}$ is the half time of the exchange in hours, T is the absolute temperature and b is 0.28 at pH 9, -1.17 at pH 7 and -2.07 at pH 3.8.

The pH of deep geothermal waters is usually near neutral [12]. If the pH is 7, and assuming a first-order reaction, the time for 99.9% isotopic exchange to equilibrium is 2 years at 300°C and 18 years at 200°C. Residence times of water in geothermal reservoirs are poorly known but appear to be long. At Steamboat Springs, Nevada, most of the water has an estimated age of at least 50 years [13]. In general, reservoir residence times for geothermal waters are probably sufficient to insure isotopic equilibrium at depth. Exchange reactions in samples stored at room temperatures after collection are negligible ($t_{3\%}$ at 25°C and pH = 7 is about 110 years).

OXYGEN-18 COMPOSITIONS OF DEEP GEOTHERMAL RESERVOIR WATER AND THE CALCULATION OF RESERVOIR TEMPERATURES

In order to apply the sulfate-water geothermometer to the estimation of geothermal reservoir temperatures, it is necessary to know the $\delta^{18}O$ value of the water with which the dissolved sulfate was in equilibrium. Water collected from a hot spring does not necessarily have the same isotopic composition as the deep hot water. The changes in oxygen isotope composition of geothermal waters between a deep reservoir and the surface may be caused by steam loss (boiling) or by dilution with near surface waters with different oxygen isotope compositions.

Deep thermal waters may be distinguished from shallow diluting waters by their chemical and isotopic compositions. Most deep thermal

waters are meteoric in origin but have been enriched in [18]O by high temperature exchange with silicates and carbonates [14] and have high chloride because of rock leaching [15] or magmatic contributions [16].

As deep geothermal water rises to the surface, it may lose temperature by conduction, steam separation or mixture with cooler water. Where steam separation occurs, [18]O and chloride are enriched in the condensed phase relative to the vapor. Dilution tends to produce water depleted in oxygen-18 and chloride relative to deep water. Therefore, in estimating the oxygen-18 composition of deep geothermal water, two factors must be considered: (1) steam loss and (2) dilution by waters above the deep reservoir.

The effects of conduction and steam separation on the oxygen isotope compositon of ascending geothermal waters may be calculated for three end-member models. Actual cooling may occur by a combination of processes which should be estimated for each case. The cooling processes considered are conduction, single-step boiling at the surface, or continuous steam loss on the way to the surface.

Case I. Conductive heat loss

In the case of isolated springs with low flows and little or no accompanying steam, cooling may have occurred by conduction [17]. If conductive cooling occurs, the oxygen isotope composition of the water will be unchanged during cooling and the oxygen isotope difference between the dissolved sulfate and the water may be compared directly with the experimental fractionation factors to determine the apparent temperature of last equilibration (eqn 2). If the equilibration time is much longer than the upflow time but much shorter than the aquifer residence time, the indicated temperature may closely approximate the aquifer temperature. The upflow and aquifer residence times must therefore be estimated for each use.

Case II. One-step steam loss

Where water travels upward in a single vertical conduit from a reservoir at a temperature above that of surface boiling, adiabatic cooling will occur with separated steam remaining in contact with water to the surface. This physical process occurs in geothermal wells discharging two phase steam-water mixtures and might occur in geyser tubes. Under these conditions, the steam remains in isotopic equilibrium with the water until it is physically separated [18] and the isotopic fractionation can be considered to occur only at the temperature of separation (in the case of springs or geysers, at surface temperature). The [18]O contents of reservoir water can be calculated from a mass balance on steam and water and from the [18]O fractionation factor at the surface temperature. This results in the equation

$$\frac{1000 + \delta^{18}0(H_2O)r}{1000 + \delta^{18}0(H_2O)s} = n + (1-n)(1/\alpha_{lv}) \simeq \alpha_{lv}^{(n-1)} \tag{5}$$

where

$\delta^{18}(H_2O)r = \delta^{18}0$ value of geothermal reservoir water

$\delta^{18}(H_2O)s = \delta^{18}0$ value of surface water

n = fraction liquid = $(Hvs - Hlr)/(Hvs - Hls)$

Hlr = enthalpy of liquid water at the reservoir temperature

Hls = enthalpy of liquid water at the spring temperature

Hvs = enthalpy of steam at the spring temperature

$\alpha_{lv} = (^{18}0/^{16}0)_{H_2O}\text{ liquid}/(^{18}0/^{16}0)_{H_2O}\text{ vapor}$

This equation was also derived by Arnason [19]. Bottinga [20] has found that experimentally determined values of α_{lv} can be expressed over the temperature range from 3 to 360°C by

$$10^3 \ln \alpha_{lv} = -3.494 + 1.2051(10^3/T) + 0.7664(10^6/T^2) \tag{6}$$

where T is in °K.

Case III. Continuous steam loss

In many geothermal areas, the existence of fumaroles and steaming ground physically separate from areas of hot springs suggests that steam that separates from ascending hot water does not remain in contact with the water and finds its own pathways to the surface. This process, in its most extreme form, would involve the continuous separation of steam from water with equilibrium fractionation of hydrogen and oxygen isotopes and immediate physical separation of the steam from the water. In an integral form, this process can be represented [17] by

$$\ln \frac{1000 + \delta^{18}0(H_2O)r}{1000 + \delta^{18}0(H_2O)s} = - \int_{Hls}^{Hlr} (1-1/\alpha_{lv}) \frac{dH}{Hvs - H} \tag{7}$$

It is apparent that when using equations 2, 5, 6 and 7, only the temperature of the reservoir is not known. Both Hlr and αSO_4-H_2O are dependent on the reservoir temperature which is then calculated by iteration. Temperatures calculated from equations 2, 5, 6, and 7 are shown in table I for spring temperatures of 80, 90 and 100°C as a function of α for sulfate and water as measured for the spring sample.

Dilution of deeply circulating thermal water by cold near-surface meteoric water commonly occurs in hot spring systems, and may obscure the calculation of the $\delta^{18}O$ value of the reservoir water. In many cases, however, the fraction of deep hot water can be calculated [11], and, with measurements of the ^{18}O contents of the cold water and of the spring water the ^{18}O contents of the deep thermal water before dilution can be calculated. An additional effect of dilution is to decrease the amount of cooling by steam separation. These effects are best considered separately.

If the hot spring issues from the surface at a temperature below boiling, and has a large flow and a cation geothermometer temperature considerably above its orifice temperature, then it is probably a mixed spring and its hot water fraction, x, can be calculated from the warm spring mixing model [21]. The ^{18}O content of the hot component can then be calculated from

$$\delta^{18}O \text{ hot} = \frac{\delta^{18}O \text{ spring} - \delta^{18}O \text{ cold} (1-x)}{x} \qquad (8)$$

In the warm spring mixing model, it is assumed that no steam loss occurs before or after mixing so no isotopic correction for steam loss should be applied and temperature calculations for case I should be followed.

If the mixed spring is boiling at the surface, then the boiling spring mixing model [22] and the silica geothermometer [11] may allow calculation of the fraction of the hot component and of the enthalpy, Hm, after mixing but before steam is lost during passage to the surface. In this mixing model it is assumed that although no steam is lost before mixing, there is steam lost after mixing. This steam may all be lost at the surface (case II) or continuously from the depth where it starts to boil (case III). The $\delta^{18}O$ value of the deep component is derived by first calculating the effect of boiling after mixing (substituting Hm from the mixing model for Hlr in equation 5 or 7) then calculating the effect of mixing from equation 8. If the highest chloride spring is itself mixed, the calculated fraction of the hot water will be too high and its calculated $\delta^{18}O$ value will be too small. This will result in too low a calculated temperature. The amount of steam loss will be underestimated and this will partially compensate by producing a somewhat higher calculated temperature.

If the steam loss occurs before mixing, the mixing model cannot be applied. The erroneous application will produce the same result as if the spring with the highest chloride content were actually a mixed water and the calculated temperature will be a minimum value.

MIXING EFFECTS ON OXYGEN ISOTOPES OF SULPHATE

In sampling a thermal area, care must be taken to avoid springs that contain sulfate of near surface origin. In most cases this may be

accomplished by choosing springs with minimum sulfate contents and minimum sulfate to chloride ratios. If many springs have the same minimum sulfate to chloride ratio and differing chloride (and sulfate) concentrations, this indicates that dilution is occurring without production of sulfate from oxidation of hydrogen sulfide by oxygen dissolved in the diluting water. If on the other hand, many springs have the same minimum sulfate contents irrespective of the chloride contents, the presence of sulfate produced during dilution by oxidation of hydrogen sulfide is indicated. The spring(s) with the lowest sulfate to chloride ratios contain the smallest amount of this sulfate and should produce the best estimates of the deep temperature of the system.

SAMPLE COLLECTION AND ANALYSIS

In this study water samples were collected in polyethylene bottles from what was considered the vent or the hottest part of each spring pool. Some of the samples were treated with zinc acetate and potassium hydroxide to precipitate hydrogen sulfide which might produce sulfate by oxidation. Sulfate from some samples was separated by ion exchange in the field (see later) with the same object. In neither case was the amount or oxygen isotope composition of the sulfate significantly different from those of samples that were carried untreated to the laboratory. The possibility remains that in some waters with high hydrogen sulfide and low sulfate contents, oxidation may occur possibly through the agency of sulfur oxidizing bacteria. It is recommended for these waters that field ion exchange, zinc treatment, or removal of bacteria in the field by filtering through a membrane filter with 0.45 μ pore diameter be done as a precaution.

A measured volume of each water sample was passed through a column containing an anion exchange resin (Bio-Rad AG1-8x, 50-100 mesh, chloride form, 0.7 x 4 cm column) as suggested by Mizutani and Rafter [23]. Sulfate was eluted from the resin with 100 ml of 0.5 M sodium chloride, precipitated by standard gravimetric methods, dried, and weighed. This procedure removes cations other than sodium that may co-precipitate with barium sulfate. Impure barium sulfate produces traces of sulfur dioxide during the reduction which interferes with mass spectrometric analysis. The ion exchange procedure also concentrates samples of low sulfate concentration.

The barium sulfate was converted to carbon dioxide for mass spectrometric analysis by the graphite reduction method of Rafter [24] modified for internal resistance heating [25]. The oxygen isotope ratios of water were determined by the carbon dioxide-equilibration method with a precision of $\pm 0.1°/_{oo}$. All results are reported relative to SMOW. Repeated analyses of a barium sulfate standard prepared from reagent sodium sulfate produced a mean $\delta^{18}O$ value of $+4.77°/_{oo}$ with a standard deviation of $.17°/_{oo}$ (34 determinations). Fewer analyses of a second standard prepared from reagent sulfuric acid produced a mean of $11.40°/_{oo}$ and a standard deviation of $0.13°/_{oo}$ (7 determinations). Alternation of standards showed no memory effect. Analyses of New Zealand Institute of

Nuclear Sciences standards R2998 and R4595 gave $\delta^{18}O$ values of +11.5 and 10.2°/$_{oo}$, close to their accepted values of +11.6 and +10.3°/$_{oo}$ [26].

APPLICATION TO GEOTHERMAL SYSTEMS

Yellowstone Park, Wyoming

Table II lists spring temperatures, chloride and sulfate concentrations, and $\delta^{18}O$ values of spring waters and dissolved sulfate for springs sampled at Yellowstone Park, Wyoming. Calculated temperatures based on the distribution of ^{18}O between sulfate and water assuming either conductive heat loss (case I), single-stage steam loss at the surface temperature (case II), or continuous steam loss (case III) from the deep reservoir to the surface with no correction for dilution are also tabulated. Spring locations and complete chemical analyses of the waters are reported elsewhere [27,28].

The oxygen isotope compositions of the waters, with the exception of those from West Thumb are a linear function of chlorinity (fig. 2), and, at zero chlorinity, the $\delta^{18}O$ value (-19°/$_{oo}$) agrees with the average value for local meteoric water [14]. The data suggest that deep thermal water with a high chloride content and enriched in ^{18}O relative to meteoric water is diluted by the shallow inflow of water with little or no chloride and and ^{18}O concentration equal to local meteoric water. The origin of both waters in this process is meteoric, but the former has undergone isotope exchange with rocks and addition of chloride during passage through a deep, hot reservoir. The isotopically heavy West Thumb thermal waters may result in part from mixture with water from Yellowstone Lake which has been enriched in ^{18}O due to evaporation.

Oxygen-18 concentrations of dissolved sulfate (table II) range from approximately -9 to -13°/$_{oo}$ excluding samples with obvious contributions of near-surface sulfates. This range possibly indicates some exchange in shallow reservoirs and some extraneous sulfate additon. However, the relatively small variation in $\delta^{18}O$ values of sulfate and the fact that they apparently are nearly independent of chloride content (fig. 2) does suggest that, whereas dilution occurs in the near surface zone, the sulfate in isotope equilibrium with water at depth does not reequilibrate greatly during its rather rapid rise to the surface. The very light $\delta^{18}O(SO_4)$ values are the most ^{18}O-depleted sulfates from a natural source thus far reported. The very negative values alone indicate a previous high temperature history as only by equilibration with relatively light water at high temperature can sulfates of such low $^{18}O/^{16}O$ ratios be formed.

The apparent small effect of dilution on the $\delta^{18}O$ value of the sulfate poses a problem. The relatively constant sulfate content of the springs suggests that part of the sulfate is produced during mixing but little evidence of this sulfate is found in the analyses. It appears possible that this sulfate is fortuitously similar isotopically to the deep sulfate because of production at lower temperatures in equilibrium

with water that is isotopically light because of dilution. The calculated amount of this sulfate is from 10 to 40% of the total.

At Mammoth hot springs, probable solution of gypsum from marine evaporites occurs. This is reflected both by the heavy $\delta^{18}O$ (+10.3%, table 2) and heavy $\delta^{34}S$ (+20.5°/$_{oo}$ [29]) of the dissolved sulfate which are within the range of values for marine sulfate [30] and significantly enriched in ^{34}S and ^{18}O relative to sulfate in other areas of the Park. At Norris, some spring waters (Little Whirligig, Echinus, and Horseshoe in table II) contain sulfate probably formed by the surficial oxidation of hydrogen sulfide that has mixed with deep water to produce acid-sulfate-chloride water. This sulfate produced at low temperatures possibly by kinetic processes is much heavier than the sulfate from the deep reservoir.

The oxygen isotope composition of Yellowstone waters have been affected by subsurface boiling and dilution with cold meteoric waters. The $\delta^{18}O$ value of the deep thermal water by calculations described earlier combining the boiling spring model with the steam loss models to be -15.5°/$_{oo}$ with continuous steam loss after mixing and -16.0°/$_{oo}$ with one step steam loss after mixing (the standard deviation of both calculations is 0.8°/$_{oo}$). Assuming that the deep sulfate unaffected by exchange during ascent or by contributions of sulfate of surface origin has a $\delta^{18}O$ value of -12.7 $\pm$ 0.2°/$_{oo}$ (estimated from fig. 2) the calculated temperature of the deep reservoir at Yellowstone is 340 to 380°C. The oxygen isotope composition of the deep water cannot be calculated from dilute high-carbon dioxide springs such as Terrace and Firehole lake because these appear to be isotopically light from low temperature exchange with carbon dioxide.

The calculated temperatures of 360±20°C agree approximately with temperatures (244 to 390°C) estimated from $\Delta^{13}C$ [CO_2-CH_4] measurements [14,31,32,] and calculated fractionation factors [33] and with calculated temperatures of 340 to 360°C based on the enthalpy-chloride relations of waters [34,35]. Mixing model calculations suggest temperatures greater than those estimated by the chemical geothermometers, but less than temperatures based on $\Delta^{18}O$(sulfate-water) [35]. All geothermometers and mixing models indicate the highest subsurface temperatures at Norris Geyser Basin which suggests that these hot spring waters ascend most rapidly from the deep aquifer with the least dilution and re-equilibration. The data support the hypothesis [34,35] that a deep aquifer at about 360°C exists at Yellowstone Park and that the temperatures indicated by chemical geothermometers and mixing models represent conditions in shallower reservoirs.

Long Valley, California

The geochemistry of the Long Valley, California geothermal system has been described by Mariner and Willey [36]. The hot spring waters are apparently all mixtures of thermal water and dilute near-surface

meteoric water, as demonstrated by linear relations between chloride and oxygen and hydrogen isotopes [36] and by heat and material balances [37]. As in the case of Yellowstone there is no positive evidence that nonmixed thermal water issues from any spring nor has any been found in the limited geothermal drilling that has been done so far. The application of the sulfate isotope geothermometer to the available fluids of this system will thus yield minimum temperature estimates as discussed earlier.

Samples of spring and well waters collected by L. M. Willey were made available to us for sulfate oxygen isotope measurements (table II). The selection of waters for analysis is not as critical as at Yellowstone because the Long Valley thermal fluids apparently have little or no excess hydrogen sulfide and dilution occurs without the production of additional sulfate ions. This is shown by the near constancy of the sulfate to chloride ratios of springs with a wide range of chloride contents. The dissolved sulfate is therefore entirely of deep origin and would be expected to have the same oxygen isotope composition with small differences due to re-equilibration and analytical uncertainty. The data in table II show this to be approximately true.

The calculated temperatures at Long Valley range from 184 to 246°C with the highest value obtained for water from the Magma-Ritchie #5 well. This well was sampled by conductive cooling of the entire fluid from the well to ambient temperatures, so the most reasonable calculated temperature is from Case I using the measured subsurface temperature of the well.

Raft River, Idaho

At Raft River, Idaho an aquifer with a temperature of 147°C was found at a depth of about 1500 m by deep drilling [38]. This geothermal system was discovered through chemical analyses of two shallow hot wells drilled for stock watering and irrigation [39]. The temperatures (table II) calculated for conductive cooling (considered most reasonable because of the very low flow of the wells) range from 135 to 142°C. These temperatures approximate the maximum temperature measured in the deep well and indicate that isotopic equilibrium is attained between water and dissolved sulfate at this temperature.

CONCLUSIONS

The exchange of oxygen isotopes between dissolved sulfate and water in geothermal reservoirs appears to be rapid relative to residence times and isotopic equilibrium has been demonstrated in drilled systems. On the other hand exchange appears to be sufficiently slow that O^{18} contents of sulfate are little changed during ascent of thermal waters to the surface. However, ^{18}O contents of ascending thermal waters are affected by boiling and dilution but these effects can be calculated and reasonable temperatures estimated. Analyses of O^{18} in dissolved sulfate and water from hot springs and shallow wells of Yellowstone Park, Wyoming,

Long Valley, California and Raft River, Idaho indicate reservoir temperature for these systems of about 360, 240, and 142°C, respectively.

ACKNOWLEDGMENTS

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TABLE I. Subsurface temperatures calculated for conductive cooling, one-step steam loss and continuous steam loss.[a]

1000 ln α	$T_s=80°C$			$T_s=90°C$		$T_s=100°C$	
	T_I,°C	T_{II},°C	T_{III},°C	T_{II},°C	T_{III},°C	T_{II},°C	T_{III}, °C
18.99	80						
17.74	90	89	89				
16.58	100	98	98	99	99		
14.53	120	116	116	117	117	118	118
12.77	140	133	134	135	135	136	136
11.25	160	150	151	153	153	153	154
9.93	180	165	168	167	170	169	171
8.76	200	181	185	183	186	185	188
7.74	220	195	201	198	203	200	205
6.84	240	209	217	212	219	215	221
6.03	260	222	232	225	235	229	237
5.31	280	234	248	238	250	242	252
4.67	300	246	262	250	265	254	267
4.09	320	257	277	262	280	266	282
3.56	340	267	291	272	294	277	297
3.08	360	277	305	282	308	287	311
2.65	380	286	318	292	322	297	325
2.26	400	295	331	301	335	306	338
1.89	420	303	343	309	347	315	351
1.56	440	310	356	317	360	323	363
1.26	460	317	367	324	372	330	

a Symbols

$$\alpha = \frac{1000 + \delta^{18}O(SO_4)}{1000 + \delta^{18}O(H_2O)}$$

T_s = surface temperature

T_I, T_{II}, T_{III} = Subsurface temperature calculated for (I) conductive cooling, (II) one step steam loss and (III) continuous steam loss.

TABLE II. Chemical and isotopic data and calculated deep reservoir temperatures for selected thermal waters of Yellowstone Park, Wyoming, Long Valley California and Raft River, Idaho

	T_s,°C	Cl,mg/l	SO_4,mg/l	$\delta^{18}(H_2O)_s$ ‰	$\delta^{18}(SO_4)$ ‰	T_I,°C	T_{II},°C	T_{III},°C
Yellowstone Park, Wyoming								
Mammoth Hot Springs Area								
New Highland	74	166	568	-18.5	+10.3	22		
Between Mammoth and Norris								
Appolinaris	8	2	7	-18.9	- 5.9	135	115	120
Norris Geyser Basin								
New Bathtub	92	580	42	-14.3	-12.9	449	321	365
Near Son of Green Dragon	94	686	na	-13.2	-10.6	381	294	323
Base of Porcelain Terrace	94	686	30	-15.6	-12.9	381	294	323
Little Whirligig	91	582	113	-14.6	- 7.7	236	210	216
Echinus	83	109	270	-17.1	- 4.0	134	129	129
Horseshoe	88	341	175	-14.3	- 4.5	181	167	169
Between Norris and Lower								
Beryl	92	540	63	-14.5	- 9.9	300	251	266
Terrace	60	65	15	-19.1	- 9.7	186	165	170
Lower Geyser Basin								
Kaleidoscope	89	300	24	-16.2	-12.0	314	258	275
Firehole Lake	94	55	25	-19.2	-11.7	223	201	206
Ojo Caliente	94	330	20	-16.6	-11.3	278	238	250
Snort	94	340	21	-16.4	-11.8	300	252	266
Excelsior	87	270	30	-16.6	-12.6	321	261	280
Upper Geyser Basin								
Ear	95	417	25	-15.7	-12.8	366	288	314
Chinaman	94	368	25	-15.6	-11.8	329	268	287
Sunset Lake	71	310	na	-15.3	-12.4	366	275	306
Gem	88	280	19	-16.8	-12.6	314	257	275
Sapphire	94	308	17	-16.6	-11.7	290	246	259
Shoshone								
Shoshone 32a	94	278	50	-16.4	-10.0	249	219	226
Shoshone 35	93	165	50	-17.1	-11.1	259	225	234
Shoshone 86	95	238	52	-16.5	-10.7	264	230	239
Shoshone 156	94	135	36	-17.5	-11.1	248	219	226
West Thumb								
Bluebell	79	304	61	-13.4	-11.0	391	290	325
Lakeside	81	301	46	-14.2	- 9.5	297	245	261
Big Cone	81	237	51	-12.9	- 9.3	337	266	289
Long Valley, California								
Casa Diablo Geothermal Well								
Magma-Ritchie #5	177	280	130	-14.2	- 7.7	246	238	239
Hot Creek (New hot spring)	90	225	100	-14.8	- 7.8	234	208	214
Unnamed hot spring (GT 31)	58	170	81	-15.2	- 7.2	213	184	191
Raft River, Idaho								
BLM hot well	90	890	61	-17.9	- 4.9	135	131	131
Crank hot well	90	1850	60	-17.2	- 4.7	142	136	137
RRGE 2 deep well	130	672	56	-17.5	- 4.7	138	137	137

na, not analysed

Legend (axis and plot labels):

$1000 \ln \alpha \; SO_4\text{-}H_2O \longrightarrow$

$10^6 \, T^{-2} (°K) \longrightarrow$

$T, °C \longleftarrow$

□ Lloyd [3]
○ Mizutani and Rafter [4]
△ Mizutani [5]
+ Wairakei bore water [1]

$1000 \ln \alpha = 2.88 \, (10^6 \, T^{-2}) - 4.1$