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UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

CHEMISTRY OF THERMAL WATERS IN LONG VALLEY,
MONO COUNTY, CALIFORNIA

By

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RESEARCH INSTITUTE
EARTH SCIENCE LAB.

CONTENTS

	Page
Abstract-----	3
Introduction-----	3
Methods and procedures-----	5
Results-----	8

TABLES

Table 1. Conditions for atomic absorption analyses-----	9
2. Isotopic analyses of ground waters, Long Valley area, California-----	11
3. Chemical analyses of ground waters, Long Valley area, California-----	13
4. Trace constituents of ground waters, Long Valley area, California-----	14
5. Compositions of gases discharging from springs-----	15
6. Subsurface temperatures computed with SOLMNEQ from chemical data-----	16

FIGURE

Figure 1. Location map of waters sampled, Long Valley area, California-----	10
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ABSTRACT

Exploration for geothermal energy in the Long Valley area of Mono County, California, the site of a major collapse caldera, began in 1959. Since then the area has been the subject of intensive studies to determine its potential for geothermal power. In 1972, ground waters were sampled to study the hydrogeochemistry of the area, utilizing the most advanced techniques available to insure accurate chemical analyses. The waters are either a sodium bicarbonate or sodium chloride bicarbonate type. Relatively high values for chloride indicate that the thermal waters probably are part of a hot-water rather than a vapor-dominated hydrothermal system. Subsurface temperatures were calculated using six different geochemical methods.

INTRODUCTION

Exploration for geothermal power in the Long Valley area, Mono County, California, was begun in 1959 by the Magma Power Company and affiliates. To preclude the threat of pollution by geothermal waste waters, the Lahontan Regional Water Quality Control Board (No. 6) prescribed waste discharge requirements for the geothermal

wells at Casa Diablo Hot Springs (Resolution No. 61-23, December 15, 1961, amended September 27, 1962, and Resolution No. 63-10, March 22, 1963). Because the developers of geothermal energy could not meet these waste discharge requirements exploration was curtailed in late 1962.

The State of California Department of Water Resources then made a study of the natural water quality conditions in the area and the potential influence of wastes from geothermal wells on the chemical quality of the water resources of the area. They evaluated all the available water quality information, including historic data, and also collected new water samples for chemical analysis. Their report (Calif. Dept. of Water Resources, 1967) showed that wastes from geothermal wells would significantly increase the concentration of arsenic, fluoride, and boron in Lake Crowley and recommended that the policy of precluding geothermal waste discharges be continued and extended throughout the Long Valley area.

Continued interest in geothermal areas has led to further investigation of the thermal waters found in the Long Valley area. In May 1972 9 samples of spring and well waters were collected in the Long Valley area as part of the U.S. Geological Survey's program in geothermal studies. Another sample was collected in August 1973 when a new hot spring complex formed near Hot Creek. These samples were analyzed for major and minor chemical constituents, and deuterium and oxygen 18. Estimates of subsurface temperature were made on the basis of these analyses.

METHODS AND PROCEDURES

Water samples were collected at points as close to the orifices of the springs or wells as possible. The Casa Diablo geothermal well, Magma Ritchie #5, was sampled as follows: The well was fully opened and allowed to flow at maximum rate for 4 hours previous to sampling. The well was then closed and aluminum tubing 1/4 inch I.D. and 25 feet long was attached to the sampling valve on the well head and coiled inside a 30-gallon oil drum which was filled with crushed ice. The well was then reopened and the steam and hot water issuing from it was then cooled to 2°C with this device and the resulting liquid collected in a 12-liter pressure vessel. All other steps were the same as for the other waters sampled. Water was collected in a 12-liter stainless steel pressure vessel and immediately pressure filtered through a 0.45 μ (micrometer) effective pore diameter membrane filter using a cylinder containing compressed nitrogen as a pressure source. The filtered water samples were collected and stored in plastic bottles which had been acid washed to remove contaminants prior to use. Samples for metal analyses were immediately acidified with concentrated nitric acid to a pH of 2 or less to insure that the metals would remain in solution. Ten milliliters of filtered sample were diluted to 100 ml (milliliters) with distilled deionized water to slow the polymerization of silica. Three samples of unfiltered untreated water were collected in 125-ml glass bottles with polyseal caps for stable isotope analysis. Samples for aluminum analysis were obtained by refiltering about 2 liters of filtered sample through a 0.1 μ membrane

filter. Samples of any gases escaping from the spring were collected in disposable plastic syringes and these placed in a bottle of the native water for shipment back to the laboratory.

Field determinations were made of barometric pressure, air temperature, water temperature, spring discharge, conductivity, pH, alkalinity, sulfide, mercury, ammonia, nitrate, and nitrite. Water temperatures were determined with a thermistor probe and a maximum reading mercury in glass thermometer. Conductivity was measured in the spring, using a conductivity bridge with a temperature compensator. The pH was measured directly in the spring (using the method of Barnes, 1964). Alkalinity was measured by the method of Barnes immediately after the sample was withdrawn from the spring. Sulfide (total sulfides measured as H_2S) was determined by the iodometric titration method described by Brown and others (1970, p. 154-155). Mercury was determined by a flameless atomic absorption technique (Environmental Protection Agency, 1971).

Ammonia was determined by allowing the thermal spring sample to cool to room temperature, adding NaOH to raise the pH to about 12 and measuring the NH_3 thus released with an ammonia specific ion electrode (Electrode Model 95-10, Orion Research, Inc.).^{1/}

Nitrite was determined colorimetrically by the diazotization method described by Rainwater and Thatcher (1960) except that samples were visually compared to permanent color standards rather than

^{1/} Use of trade names or commercial products in this report is for identification only and does not constitute endorsement by the U.S. Geological Survey.

measured with a spectrophotometer which is too delicate to carry in the field. Nitrate was reduced to nitrite by the cadmium-reduction method (American Public Health Association, 1971).

Oxygen isotope analysis was by the CO_2 -equilibration method of Cohn and Urey (1938) and deuterium analysis by reaction with uranium at 800°C (Bigeleisen and others, 1952). $\text{O}^{18}/\text{O}^{16}$ and D/H measurements were made mass spectrometrically.

Gases were analyzed as soon as possible after returning to the laboratory by gas chromatography. Linde Molecular Sieve 13X was used to separate and quantitate H_2 , ($\text{O}_2 + \text{Ar}$), N_2 , CO , CH_4 , and C_2H_6 , and Porapak Q was used for H_2 , (O_2 , Ar , N_2 , CO), CH_4 , CO_2 , and C_2H_6 . The columns were run at room temperature. The gases were detected by thermal conductivity. The carrier gas was helium.

Antimony, cadmium, cesium, cobalt, copper, gold, iron, lead, lithium, manganese, nickel, rubidium, silver, and zinc were determined by direct aspiration on an Instrumentation Laboratory Model 353 dual channel double beam Atomic Absorption/Emission Spectrophotometer (A.A.). Determinations of silica also were made with this instrument. A high solids burner head was used for the analysis of cesium, lithium and rubidium to allow the addition of sodium to the samples to minimize flame ionization effects. Silica required a nitrous oxide-acetylene flame and its corresponding burner head. A premixed laminar flow (Boling) burner head was used for all other elements. To minimize

corrosion of the metallic parts of the nebulizer system an iridium-platinum coated capillary tip was used. Conditions used in these analyses are given in table 1.

Water samples for aluminum were buffered at pH 8.3 and the aluminum-oxime (8-hydroxy quinolate) complex was extracted into methyl iso-butyl ketone. The organic extract was analyzed in the laboratory by A.A. at the 309 nanometer wave length. A sensitivity of 0.008 mg/l (milligrams per liter) and a detection limit of 0.003 mg/l were obtained (R. B. Barnes, unpub. data, 1973).

Samples were sent to the Geological Survey's laboratory, Salt Lake City, Utah, for routine analyses of beryllium, arsenic, calcium, magnesium, strontium, barium, sodium, potassium, sulfate, chloride, bromide, iodide, phosphate, selenium, specific conductance, and dissolved solids (residue from drying at 180°C). Boron was determined in the Menlo Park laboratory by either the Dianthrime method or the Carmine method (Brown and others, 1970, p. 54-58), depending on the concentration range. Fluoride was determined in our laboratory by specific ion electrode using the method of R. B. Barnes (written commun., 1973).

RESULTS

Figure 1 shows the locations and designations of the springs and wells sampled. Table 2 lists the springs and wells sampled by the designation given in the State of California report (Calif. Dept. of Water Resources, 1967), gives the name and location, and the results of the isotope analysis of the water. The isotope analyses are reported

Table 1.--Conditions for atomic absorption analyses

Element	Wavelength mm	Sensitivity ^{1/} mg/l	Detection limit mg/l	Other
Sb	217.6	0.5	0.1	
Cd	228.8	0.01	0.005	
Cs ^{2/3/}	852.1	0.1	0.05	R406 photomultiplier
Co	240.7	0.06	0.02	
Cu	324.7	0.03	0.01	
Au	242.8	0.1	0.06	
Fe	248.3	0.05	0.02	
Pb	217.0	0.1	0.04	R106 photomultiplier
Li ^{2/}	670.7	0.03	Not determined	
Mn	279.5	0.02	0.08	
Ni	232.0	0.05	0.02	
Rb ^{2/3/}	780.0	0.03	0.01	R406 photomultiplier
SiO ₂ ^{4/}	251.6	5	Not determined	NO ₂ -C ₂ H ₆ flame
Ag	328.1	0.04	0.03 ^{5/}	
Zn	213.9	0.01	0.005	R106 photomultiplier

1/ Sensitivity is defined as the concentration, mg/l, which gives 1 percent absorption (4.4 milliabsorbances).

2/ Ionization of alkali metals in the air-acetylene flame causes significant losses of observed signal in A.A. analysis. All samples and standards were adjusted to 1000-2000 mg Na/l to minimize these ionization effects.

3/ Greater sensitivity could be obtained using flame emission but matrix effects precluded the use of this method.

4/ Rapid clogging of the nitrous-oxide burner head with carbon caused many problems. A high solids nitrous oxide burner head would have been desirable for this analysis.

5/ Some interference from the sodium 330.2 nanometer line was observed. Using a slit width of 40 micrometers 10,000 mg Na/l gave a false silver value of 0.03 mg/l.

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MT. MORRISON QUADRANGLE
CALIFORNIA
15 MINUTE SERIES (TOPOGRAPHIC)

SAMPLE LOCATIONS

Long Valley, California

0 1 2 3 4 Miles

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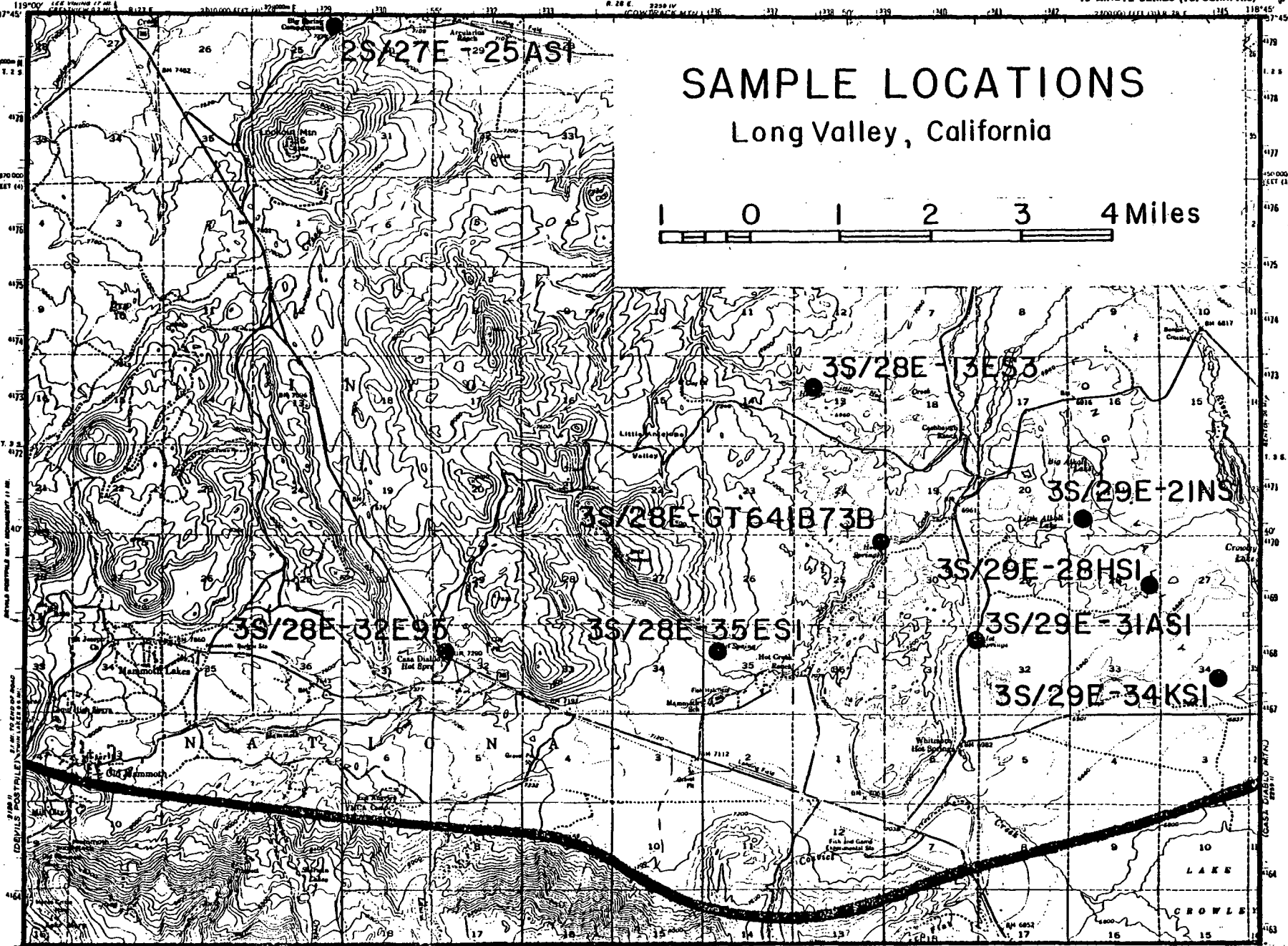


Table 2.--Isotopic analyses of ground waters, Long Valley Area, California

Designation	Name	Location	$\delta^{18}\text{O}$ (SMOW)	δD (SMOW)
2S/27E-25AS1	Big Spring Campground	NW $\frac{1}{4}$ sec.25, T. 2 S., R. 27 E.	-15.89	-115.4
3S/28E-13ES3	Hot Spring on Little Hot Creek	NW $\frac{1}{4}$ sec.13, T. 3 S., R. 28 E.	-15.34	-121.8
3S/28E-32E95	Casa Diablo Geothermal Well			
	Magma-Ritchie #5	NW $\frac{1}{4}$ sec.32, T. 3 S., R. 28 E.	-14.16	-115.8
3S/28E-35ES1	Hot Bubbling Pool	NW $\frac{1}{4}$ sec.35, T. 3 S., R. 28 E.	-12.44	-111.0
3S/28E(GT63IB73B)	Hot Creek (new hot spring)	NW $\frac{1}{4}$ sec.25, T. 3 S., R. 28 E.	Analysis not complete	
3S/29E-13C1	Artesian well	NW $\frac{1}{4}$ sec.13, T. 13 S., R. 29 E.	-17.07	-129.5
3S/29E-21NS1	Unnamed hot spring	SW $\frac{1}{4}$ sec.21, T. 3 S., R. 29 E.	-16.17	-123.9
3S/29E-28HS1	Unnamed hot spring	SE $\frac{1}{4}$ sec.28, T. 3 S., R. 29 E.	-15.85	-123.4
3S/29E-31AS1	Unnamed hot spring	NE $\frac{1}{4}$ sec.31, T. 3 S., R. 29 E.	-15.23	-121.2
3S/29E-34KS1	Unnamed hot spring	SE $\frac{1}{4}$ sec.34, T. 3 S., R. 29 E.	-16.08	-124.9

11

in the familiar δ -notation in parts per thousand relative to the SMOW standard. Table 3 gives the analyses of major chemical constituents in the waters sampled, whereas table 4 presents analyses of trace constituents. Only two hot springs in Long Valley had a significant amount of gas being discharged and table 5 lists their compositions.

Two types of ground water could be distinguished in the Long Valley area. One type is low in dissolved solids and may be classed as locally derived meteoric water (Big Spring Campground and the artesian well). The other type is a thermal water high in dissolved solids. Because the two water types are of similar isotopic composition, the isotopic data cannot be used to distinguish between these two types of water.

The relatively high content of chloride suggests that the hot springs in Long Valley are part of a hot-water system rather than a vapor-dominated system (White, Muffler, and Truesdell, 1971). The subsurface temperatures of the geothermal reservoir were computed by Y. K. Kharaka using the computer program SOLMNEQ (Kharaka and Barnes, 1973). SOLMNEQ computes the temperatures of the geothermal reservoir by six geochemical methods. Table 6 lists the results of these calculations. The quartz temperatures are based on the assumption that the silica content of hot spring water is controlled by the solubility of quartz at depth (Fournier and Rowe, 1966). The conductive temperature assumes that all cooling of the water is by conduction whereas the adiabatic temperature is useful if steam is lost from the

Table 3.--Chemical analyses of ground waters, Long Valley area, California

Spring or well designation	Chemical constituents in milligrams per liter milliequivalents per liter								Chemical constituents in milligrams per liter					Temp. when sampled (°C)	pH	Specific conductance (micromhos at 25°C)	Dissolved solids (Evaporated at 180°C)
	Calcium Ca	Magnesium Mg	Sodium Na	Potassium K	Bicarbonate HCO ₃	Carbonate CO ₃	Sulfate SO ₄	Chloride Cl	Arsenic As	Boron B	Fluoride F	Lithium Li	Silica SiO ₂				
Big Spring Campground 2S/27E-25AS1, 5/21/71	5.1 .255	5.9 .486	23 1.001	4.0 .103	90 1.482	0 0	8.1 .169	5.7 .161	0.02	0.37	0.5	0.04	58	11	6.8	182	156
Hot Spring, Little Hot Creek, 3S/28E-13ES3, 5/18/72	50 2.495	.6 .050	410 17.835	30 .768	735 12.047	.3 .010	96 1.999	200 5.642	.74	10.6	8.4	2.8	110	79	6.5	1,950	1,260
Geothermal Well Magma- Ritchie 5, 3S/28E-32E95, 5/19/72	.9 .045	.1 .009	390 16.965	45 1.151	450 7.374	29.6 .987	130 2.707	280 7.899	2.2	15	12	2.8	340	94	9.2	1,920	1,420
Hot Bubbling Pool 3S/28E-35ES1, 5/24/72	3.3 .165	.1 .009	380 16.530	25 .640	466 7.636	.7 .024	120 2.499	250 7.053	.34	13	11	2.5	300	60	7.2	1,800	1,300
New Spring Hot Creek GT631B73B, 8/29/73	1.6 .080	.1 .009	400 17.268	24 .614	580 9.490	25.9 .863	100 2.082	225 6.346	--	--	--	--	150	90	7.9	1,770	--
Artesian Well 3S/29E-13G1, 5/23/72	5.3 .265	.2 .017	38 1.653	1.3 .034	111 1.825	2.8 .092	3.7 .078	3.0 .085	.02	.18	.6	.14	64	10	8.8	191	166
Hot Spring 3S/29E-21NS1, 5/22/72	25 1.248	.6 .050	310 13.485	37 .947	828 13.576	.3 .010	68 1.416	150 4.232	.46	7.7	4.6	1.5	250	56	6.5	1,790	1,260
Hot Spring 3S/29E-28HS1, 5/22/72	22 1.098	.6 .050	400 17.400	43 1.100	845 13.851	.3 .010	69 1.437	170 4.796	.34	8.8	4.8	1.7	240	49	6.6	1,900	1,340
Hot Spring 3S/29E-31AS1, 5/20/72	15 .749	.4 .033	310 13.485	22 .563	516 8.451	1.9 .063	81 1.687	170 4.796	.84	7.9	7.5	2.0	150	58	7.5	1,500	1,000
Hot Spring 3S/29E-34KS1, 5/23/72	23 1.48	1.2 .099	320 13.920	28 .716	695 11.385	.3 .010	59 1.229	150 4.232	.36	8.1	4.6	1.6	205	41	6.6	1,630	1,130

13

Table 4.--Trace constituents of ground waters, Long Valley area, California

[micrograms per liter]

Constituent	Symbol	2S/27E 25AS1	3S/28E 13ES3	3S/28E 32E95	3S28E .35ES1	3S/28E GT631B73B	3S/29E 13C1	3S/29E 21NS1	3S/29E 28HS1	3S/29E 31AS1	3S/29E 34KS1
Aluminum	Al	2	6	--	57	60	3	2	3	6	<2
Antimony	Sb	<100	<100	200	300	--	<100	<100	<100	<100	<100
Barium	Ba	N.D.	N.D.	N.D.	N.D.	--	N.D.	20	N.D.	N.D.	--
Beryllium	Be	--	<10	<10	--	--	10	--	<10	--	--
Bromide	Br	200	800	1,100	800	--	30	500	600	600	500
Cadmium	Cd	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Cesium	Cs	<50	300	600	450	--	<50	100	50	200	100
Cobalt	Co	<60	<60	<60	<60	<60	<60	<60	<60	<60	<60
Copper	Cu	<30	70	<30	20	20	<30	40	30	<30	<30
Gold	Au	<100	<100	<100	<100	--	<100	<100	<100	<100	<100
Iodide	I	N.D.	800	400	500	--	N.D.	400	400	500	400
Iron, total	Fe	<50	150	50	<50	<50	<50	230	<50	<50	450
Lead	Pb	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Mercury	Hg	<.1	<.1	.1	.3	1.3	.1	<.1	.1	.1	<.1
Manganese	Mn	<20	240	<20	<20	<20	<20	100	80	<20	85
Nickel	Ni	<50	100	<50	<50	<50	<50	<50	<50	<50	<50
Nitrogen, ammonia	N	130	400	400	150	--	350	200	100	90	150
Nitrogen, nitrate	N	100	50	<50	50	--	50	50	50	50	50
Nitrogen, nitrite	N	<50	<50	<50	<50	--	<50	<50	<50	<50	<50
Phosphorus, ortho-phosphate	P	1,000	150	180	710	--	150	280	460	430	180
Rubidium	Rb	10	260	480	280	--	<10	110	140	190	80
Selenium	Se	N.D.	5	1	4	--	2	5	4	N.D.	--
Silver	Ag	<40	<40	<40	<40	--	<40	<40	<40	<40	<40
Strontium	Sr	70	600	140	100	--	40	200	140	280	--
Sulfides, total	H ₂ S	<100	2,300	10,000	1,400	--	3,800	800	700	800	900
Zinc	Zn	45	440	190	45	<10	<10	180	120	20	100

N.D.--Not detected, analyzed at central laboratory

Table 5. Compositions of gases discharging from springs

[All results are in volume percent. P = poropak; M = molecular sieve. H₂ and C₂H₆ were sought and not found in both samples.]

Spring	Column packing	O ₂ +Ar	N ₂	CH ₄	CO ₂	Total
Hot Spring, Little Hot Creek 3S/28E-13ES3	P	--	--	0.08	92.7	100.9
	M	1.8	6.3	.10		
Hot Bubbling Pool 3S/28E-35ES1	P	--	--	0.05	88.8	101.1
	M	1.6	10.7	0.04		

Table 6.--Subsurface temperatures computed with SOIMNEQ from chemical data

[Temperatures given in °C]

Spring or well	Surface temperature	Discharge (liters per minute)	Quartz temperature (conductive)	Quartz temperature (adiabatic)	Amorphous silica temperature	Na/K temperature	Na/K + Ca temperature
2S/27E-25AS1	10	380	108.9	108.6	-11.1	258.9	82.9
3S/28E-13ES3	79	280	142.6	137.2	19.1	150.0	171.6
3S/28E-32E95	94	--	219.2	199.7	93.8	201.0	237.7
3S/28E-35ES1	60	0	209.4	191.9	83.7	139.6	188.9
3S/28E-GT63IB73B	90	~400 variable	161.2	152.7	36.4	131.7	191.8
3S/29E-13C1	10	25	113.7	112.8	-6.9	85.5	53.0
3S/29E-21NS1	56	100	195.7	180.9	69.9	205.3	199.9
3S/29E-28HS1	49	200	192.7	178.5	67.0	192.3	200.0
3S/29E-31AS1	58	190	161.2	152.7	36.4	146.9	175.6
3S/29E-34KS1	41	150	181.6	169.5	56.1	168.7	183.7

sample during its ascent to the surface. The amorphous silica temperature is based on the assumption that the silica content of the water is controlled by the solubility of amorphous silica. This geochemical thermometer should only be considered in waters supersaturated with amorphous silica. It gives erroneous temperatures in this area because computations with SOLMNEQ showed the waters sampled to be unsaturated with respect to amorphous silica.

The Na/K temperatures are from an empirical curve of temperature versus the atomic Na/K ratio (Ellis and Mahon, 1967). The Na/K + Ca temperatures are from the empirical equation

$$\log(\text{Na/K}) + \beta \log(\sqrt{\text{Ca/Na}}) = \frac{1,656}{273.16 + t} - 2.258$$

where t is the equilibration temperature of the underground reservoir in degrees centigrade, concentrations of Na, K, and Ca are in molality, and β is one-third for waters equilibrated above 100°C and β is four-thirds for water equilibrated below 100°C (Fournier and Truesdell, 1972). The Na/K + Ca temperatures were computed with the appropriate (one-third above 100°C, four-thirds below 100°C) value of β .

REFERENCES

- American Public Health Association, 1971, Standard methods for the examination of water and wastewater, p. 458-461.
- Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geol. Survey Water-Supply Paper 1535-H.
- Bigeleisen, J., Perlman, M. L., and Prosser, H. C., 1952, Conversion of hydrogenic materials to hydrogen for isotope analysis: Anal. Chemistry, v. 24, p. 1356-1357.
- Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geol. Survey Techniques of Water-Resources Inv., book 5, chap. A-1, 160 p.
- California Department of Water Resources, 1967, Investigation of geothermal waters in the Long Valley area, Mono County, 141 p.
- Cohn, M., and Urey, H. C., 1938, Oxygen exchange reactions of organic compounds and water: Am. Chem. Soc. Jour., v. 60, p. 679.
- Ellis, A. J., and Mahon, W. A. J., 1967, Natural hydrothermal systems and experimental hot water/rock interactions (Part II): Geochim. Cosmochim. Acta, v. 31, p. 519-539.
- Environmental Protection Agency, 1971, Methods for chemical analysis of water and wastes, p. 121-130.
- Fournier, R. O., and Rowe, J. J., 1966, Estimation of underground temperatures from the silica content of water from hot springs and wet-steam wells: Am. Jour. of Science, v. 264, p. 685-697.

Fournier, R. O., and Truesdell, A. H., 1972, An empirical Na-K-Ca geothermometer for natural waters: *Geochim. Cosmochim. Acta*, v. 37, p. 1255-1275.

Kharaka, Y. K., and Barnes, Ivan, 1973, SOLMNEQ: Solution-mineral equilibrium computations: U.S. Geol. Survey Computer Contribution, PB215-899, 82 p.

Rainwater, F. H., and Thatcher, L. L., 1960, Methods for collection and analysis of water samples: U.S. Geol. Survey Water-Supply Paper 1454, p. 221-223.

White, D. E., Muffler, L. J. P., and Truesdell, A. H., 1971, Vapor-dominated hydrothermal systems compared with hot-water systems: *Economic Geology*, v. 66, p. 76-80.