

Geochemistry of Thermal Waters in Long Valley, Mono County, California

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Thermal springs and wells in Long Valley, California, issue sodium bicarbonate-chloride waters containing 1000–1420 mg/l of dissolved solids. Thermal waters of sodium bicarbonate-chloride composition are usually associated with hot-water reservoirs. Chloride concentrations and stable isotope data indicate that the thermal waters have had varied histories. All of the thermal springs issue a mixture of fluid from the thermal reservoir and less saline, cooler water from one or more shallow aquifers. The composition of springs in Hot Creek Gorge may have been further altered by minor subsurface boiling. Thermal springs between Hot Creek and Lake Crowley issue mixtures of fresh and thermal waters which have lost heat by conductive cooling and changed composition by reaction with rock in the shallow aquifer. The silica content of water from Magma Richie 5 and mixing calculations based on the concentrations of silica in thermal waters collected from springs in Hot Creek Gorge and along Little Hot Creek indicate a temperature of at least 200°C in the thermal reservoir. The sodium-potassium-calcium geothermometer yields a reservoir temperature estimate near 200°C for most of the thermal springs. If geothermal energy is developed in Long Valley, the high concentrations of arsenic (up to 2.2 mg/l), boron (up to 15 mg/l), and total dissolved solids in the thermal fluids will make it necessary to isolate the effluent of production wells from the freshwater system.

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INTRODUCTION

The chemical composition of water from thermal springs and wells provides an indication of the temperature of the fluid in the reservoir and of the type of thermal system. The distinctive physical and chemical characteristics of hot-water and vapor-dominated systems have been discussed by *White et al.* [1971]. Hot-water systems occur in permeable rock, whereas vapor-dominated systems occur in impermeable rock. Springs associated with hot-water systems discharge chloride-rich water at an aggregate rate of several hundred to several thousand liters per minute. Individual springs associated with the hot-water system, however, may discharge as little as a few liters per minute, and low chloride, acid sulfate springs formed by steam separation may occur with the chloride-rich springs. Springs associated with vapor-dominated systems usually discharge acid sulfate waters at rates of less than 100 l/min. Some near-neutral sodium bicarbonate springs with less than 20 mg/l of chloride may also be associated with vapor-dominated systems. Although qualitative indicators of temperature in the thermal reservoir have been suggested by *Ellis* [1970], *Mahon* [1970], *Tonani* [1970], and *Fournier and Truesdell* [1970], only two quantitative geothermometers have been demonstrated to have widespread application. These quantitative geothermometers are based on silica concentration [*Fournier and Rowe*, 1966; *Mahon*, 1966] and the proportions of sodium, potassium, and calcium in the thermal fluid [*Fournier and Truesdell*, 1973]. Another quantitative geothermometer, based on the ratio of sodium to potassium [*Ellis*, 1970; *White*, 1965], has been largely superseded by the Na-K-Ca geothermometer. Qualitative chemical indices such as $Cl/(HCO_3 + CO_3)$ are, however, useful in delineating subsurface flow direction in thermal systems [*Fournier and Truesdell*, 1970; *Truesdell*, 1975].

Dilution of thermal water by fresh water (mixing) has been demonstrated in several ways. A proportional relationship between chloride concentration and spring temperature may

be an indication of mixing [*Fournier and Truesdell*, 1974]. *Fournier et al.* [1974] have stated that springs of large flow rate, more than 100 l/min, should be considered to be issuing mixed water if the Na-K-Ca geothermometer indicates a reservoir temperature more than 25°C above the measured spring temperature. *Giggenbach* [1971] has demonstrated linear relationships between chloride concentrations and the isotope ratios of hydrogen and oxygen in the mixed waters of the Broadlands geothermal field.

The first detailed chemical sampling for water quality in Long Valley was carried out by the *California Department of Water Resources* [1967] to determine the effect of geothermal development on water quality in Long Valley and indirectly the impact of such development on the water supply for Los Angeles. The state report noted that (1) the fresh waters outside the caldera are calcium bicarbonate in character and have very low total dissolved solids; (2) the hot springs issue sodium bicarbonate to sodium bicarbonate-chloride waters, high in total dissolved solids, bicarbonate, chloride, and the trace elements boron, arsenic, and fluoride; (3) the alkali lakes contain sodium bicarbonate to sodium carbonate waters; and (4) the warm springs and shallow groundwater are intermediate between fresh and hot spring water in chemical characteristics. In the state report it was concluded that discharge of geothermal waste waters rich in arsenic, fluoride, and boron to Lake Crowley and its tributaries could cause serious degradation of the water quality and constitute a threat of pollution to the water supply of the Los Angeles–Owen River Aqueduct as well as the local water resources. Magma Power Company and its affiliates drilled some 20 exploratory wells to as much as 300-m depth in the vicinity of Casa Diablo Hot Springs during the period extending from 1959 to 1962. Temperatures up to 177°C were encountered in some of the wells.

The general water quality of Long Valley is described in the state report. However, no special care was taken in preparing water samples for silica, calcium, or bicarbonate. Recent sampling by *Willey et al.* [1974], which forms the basis for this report, was concentrated on the geothermally important constituents of silica, principal cations, gas composition, and isotope ratios of oxygen and hydrogen in the major hot springs.

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Lewis [1974] has compiled the available chemical and hydrologic data for Long Valley.

METHODS AND PROCEDURES

Water samples were collected at points as close as possible to the orifice of the thermal springs or wells. If several springs issued in the same area, the spring with the highest temperature, specific conductance, and flow rate was sampled. Water was collected in a 12-l stainless steel pressure vessel and immediately pressure-filtered through a membrane filter of 0.45- μm effective pore diameter using nitrogen as a pressure source. The filtered water samples were collected and stored in plastic bottles which had been washed with acid prior to use. Ten milliliters of filtered sample were diluted to 100 ml with distilled deionized water to prevent the polymerization of silica. Samples for isotopic analyses were collected in glass bottles with polyseal caps.

Field determinations were made of barometric pressure, water temperature, conductivity, pH, and alkalinity. Water temperatures were determined with a thermistor probe while the conductivity was measured in the spring using a conductivity bridge with a temperature compensator. The pH was measured directly in the spring, and alkalinity was determined immediately after the sample was withdrawn from the spring [Barnes, 1964]. The water sample from Magma Richie 5 was not flashed to atmospheric pressure as are most water samples collected from 'wet' steam wells. The well was fully opened and allowed to flow for 4 hours previous to sampling. The well was then closed and 8 m of 0.64-cm-ID aluminum

tubing was attached to the sampling valve on the well head. This tubing was coiled and placed in a 30-gal. (133-l) oil drum which was filled with crushed ice. The well was then reopened, and the steam and hot water issuing from it were cooled to 2°C. The resulting fluid was collected in a 12-l pressure vessel and treated as described above.

SAMPLE LOCATIONS

Surface expressions of thermal activity in Long Valley extend from Casa Diablo Hot Springs along Hot Creek through Hot Creek Gorge. Other hot springs issue along Little Hot Creek 3.2 km north of Hot Creek Gorge, and between Hot Creek and Lake Crowley (Figure 1).

Two freshwater samples were collected from Big Spring near Lookout Mountain, northwest quadrant, section 25, T. 2S, R. 27E, and an artesian well in the northwest quadrant, section 13, T. 3S, R. 29E.

WATER COMPOSITION

Hot springs in Long Valley discharge slightly saline sodium bicarbonate-chloride water. The chemical composition of hot springs sampled for detailed chemical analysis is given in Table 1. Cool fresh waters, springs 25AS1 and the artesian well 13C1, issue nonsaline sodium bicarbonate waters (150 μmho). The fresh waters contain proportionally more calcium, more magnesium, and less chloride than the thermal spring waters (Figure 2). The *California Department of Water Resources* [1967] reported that in Long Valley the proportions of chloride and sodium increase as the total dissolved solids increase.

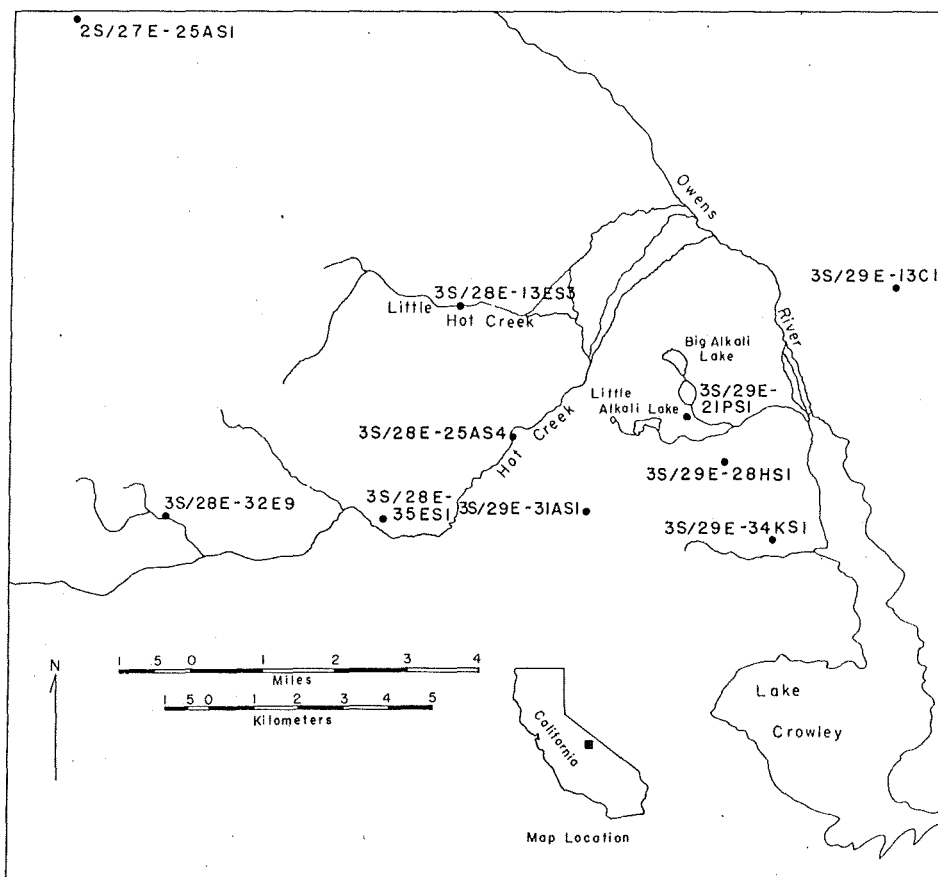


Fig. 1. Index map showing the locations of springs and wells sampled for detailed chemical analysis, Long Valley, California. The spring issuing in Hot Creek Gorge, designated 3S/28E-25AS4, was collected during August 1973. All other samples were collected during May 1972.

TABLE 1. Major Constituents of Selected Thermal and Meteoric Waters From Long Valley, California

	U.S. Public Health Water Standard Limits (Drinking Water)	3S/28E-	3S/28E-	3S/28E-	3S/28E-	3S/29E-	3S/29E-	3S/29E-	3S/28E-	2S/28E-	3S/29E-
		13ES3	32E9	35ES1	21PS1	28HS1	31AS1	34KS1	25AS4	25AS1	13C1
Sodium (Na)		410	390	380	310	400	310	320	400	23	38
Potassium (K)		30	45	25	37	43	22	28	24	4.0	1.3
Calcium (Ca)		50	0.9	3.3	25	22	15	23	1.6	5.1	5.3
Magnesium (Mg)	125	0.6	0.1	0.1	0.6	0.6	0.4	1.2	0.1	5.9	0.2
Carbonate (CO ₃)*		0.3	16.6	0.7	0.3	0.3	1.9	0.3	24.0	0	2.8
Bicarbonate (HCO ₃)*		735	416	466	828	845	516	695	549	90	111
Sulfate (SO ₄)	250	96	130	120	68	69	81	59	100	8.1	3.7
Chloride (Cl)	250	200	280	250	150	170	170	150	225	5.7	3.0
Lithium (Li)		2.8	2.8	2.5	1.5	1.7	2.0	1.6	2.3	0.04	0.14
Boron (B)		10.6	15	13	7.7	8.8	7.9	8.1	10.5	0.37	0.18
Fluoride (F)	1.7	8.4	12	11	4.6	4.8	7.5	4.6	9.6	0.5	0.6
Silica (SiO ₂)		110	340	300	250	240	150	205	150	58	64
Arsenic (As)	0.01	0.74	2.2	0.34	0.46	0.34	0.84	0.36	...	0.02	0.02
Ammonia (as N)		0.40	0.40	0.15	0.20	0.10	0.09	0.15	...	0.13	0.35
Rubidium (Rb)		0.26	0.48	0.28	0.11	0.14	0.19	0.08	...	0.01	<0.01
Sulfide, total (H ₂ S)		2.3	10	1.4	0.8	0.7	0.8	0.9	...	<0.1	3.8
pH		6.5	9.2	7.2	7.9	6.5	6.6	7.5	6.6	6.8	8.8
Temperature, °C		79	94	60	56	49	58	41	90	11	10
Specific conductance, μmho at 25°C		1950	1920	1800	1770	1790	1900	1500	1630	182	191

Analyses were L. M. Willey, J. B. Rapp, and T. S. Presser.

Concentrations are in milligrams per liter.

*Total alkalinity distributed as carbonate (CO₃) and bicarbonate (HCO₃).

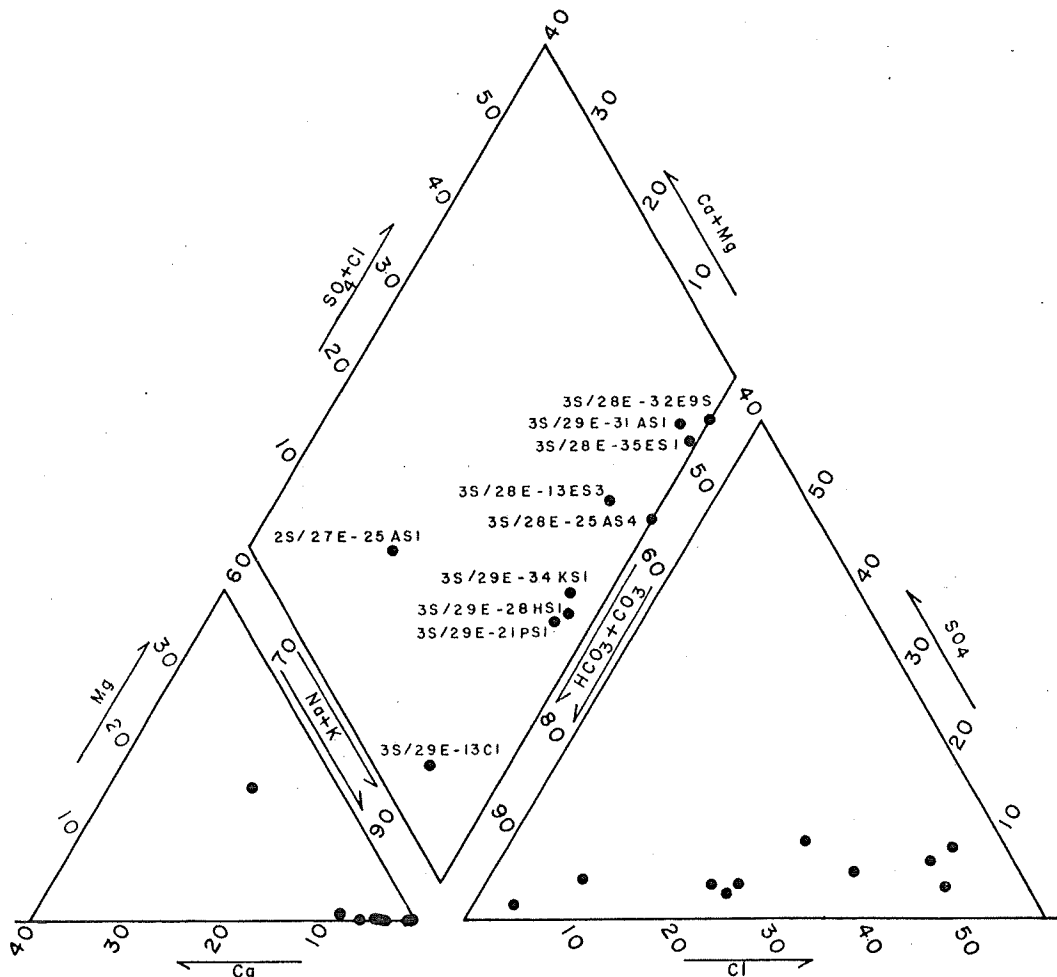
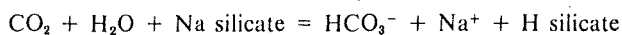


Fig. 2. Modified trilinear plot of waters collected for detailed analysis, Long Valley, California.

Progressing from the fresh waters to thermal waters, a marked decrease occurs in the proportion of the divalent cations, especially calcium, relative to the monovalent cations sodium and potassium.

Ratios of elements which may be useful in determining flow direction and extents of solution-rock interaction have varying patterns of distribution (Table 2). The high ratios of Cl/Ca and Cl/Mg in thermal waters from along Hot Creek are probably due to the loss of carbon dioxide and the precipitation of calcium carbonate at depth. The $(Ca^{1/2})/Na$ ratios for these springs are less than 1 for the same reason. Springs with higher ratios of Cl/Ca and Cl/Mg generally have lower Ca/Mg ratios, perhaps indicating precipitation of magnesian calcite. Cl/(HCO₃ + CO₃) ratios decrease as spring temperature decreases. Truesdell [1975] attributed a similar change in Shoshone Geyser Basin, Yellowstone Park, Wyoming, to the reaction



That is, as hot water cools in contact with alkali aluminosilicate (or silicate) minerals at constant activity of the alkali ions, the pH increases [Hemley, 1959] and more dissolved carbon dioxide is converted to bicarbonate with simultaneous introduction of alkali ions. If this reaction is controlling the Cl/(HCO₃ + CO₃) ratio, then the Cl/Na ratio should change in a similar manner, and the ratio of Na/(Cl + HCO₃ + CO₃) should remain approximately constant. The Cl/Na ratios generally follow the Cl/(HCO₃ + CO₃) ratios, although the Na/(Cl + CO₃ + HCO₃) ratios range from 0.81 to 1.05. Thermal springs along Hot Creek and Little Hot Creek have constant ratios of Na/(Cl + CO₃ + HCO₃), 0.98–1.01, indicating that solution of sodium feldspar and precipitation of clay may be controlling the ratio in this area. However, lower ratios of Na/(Cl + CO₃ + HCO₃) and higher Cl/K ratios in the area between Hot Creek and Lake Crowley may indicate solution of something other than sodium feldspar or the precipitation of some sodium-potassium phases.

Low ratios of Na/K for thermal springs along Hot Creek may indicate that they are associated with a higher-temperature part of the thermal reservoir. Orville [1963] and White [1965] have shown that low Na/K ratios indicate high temperatures of equilibrium. The $(Ca^{1/2})/Na$ ratios range from 0.28 for the steam well at Casa Diablo to 2.0 for the hot spring on Little Hot Creek. Ratios of Cl/Rb, Na/Rb, and Na/Li generally increase in hydrothermal areas as the fluids react with the country rock, producing hydrothermal minerals [Ellis, 1970]. In Long Valley, Cl/Rb, Na/Rb, and Na/Li ratios are smallest for hot springs along Hot Creek, increasing as spring temperatures decrease toward Lake Crowley. Perhaps thermal spring waters issuing in the area between Hot Creek and Lake Crowley have relatively less rubidium and lithium because of more extensive reaction with the country rock. The slight increase in Cl/Li and Cl/F as the spring temperatures decrease may indicate loss of these minor elements into alteration minerals. Low NH₃/Na ratios are found in the springs which are releasing gas. Ratios of Cl/SO₄ are nearly constant, increasing slightly from northwest to southeast with the highest ratios in thermal springs south of the alkali lakes.

Thermal springs in Long Valley have Cl/B ratios in the range 6.6–5.6. Cl/B ratios for springs in and near Hot Creek Gorge may be highest (6.4–6.6) because of phase separation with loss of boron into the vapor phase. Such phase separation is not uncommon in hot-water systems; this vapor phase con-

TABLE 2. Atomic Ratios of Major and Minor Elements in Thermal and Meteoric Waters From Long Valley, California

Spring	Cl/Ca	Cl/Mg	Cl/Na	Cl/K	Cl/SO ₄	Ca/Mg	Ca ^{1/2} /Na	Na/Li	Na/K	Cl/F	Cl/B	Na/NH ₃	Cl/Li	Cl/Rb	Na/Rb	Cl/(HCO ₃ + CO ₃)	Na/(Cl + HCO ₃ + CO ₃)
3S/28E-13ES3	4.5	228	0.32	7.4	5.6	50.5	2.0	43	23	13	5.7	625	14	1890	5880	0.47	1.01
3S/28E-32E9	352	1920	0.47	6.9	5.8	5.5	0.28	42	15	15	5.7	588	20	1320	2860	1.55	1.31
3S/29E-31ASI	13	291	0.36	8.5	5.7	22.7	1.43	48	24	12	6.6	2000	17	2380	6670	0.56	1.01
3S/28E-21PSI	6.7	171	0.31	4.5	6.0	25.3	1.8	62	14	18	6.0	1000	20	4170	14,300	0.31	0.76
3S/29E-28HSI	8.7	194	0.28	4.4	6.7	22.2	1.3	71	16	19	5.9	2500	20	2380	9090	0.35	0.93
3S/29E-34KSI	7.4	86	0.30	5.9	6.9	11.6	1.7	83	20	18	5.6	1250	18	4170	14,300	0.37	0.89
3S/28E-35ESI	86	1714	0.43	11	5.6	20.0	0.55	59	26	12	5.8	1670	20	2330	5560	0.92	1.12
3S/28E-25AS4	159	2572	0.37	10	6.1	16.2	0.37	45	28	12	6.4	1250	19	2080	5880	0.62	1.04
2S/27E-25ASI	1.3	0.7	0.16	1.6	1.9	0.52	11.3	167	10	6.0	4.7	106	0.11	0.62
3S/29E-13C1	0.64	10	0.05	2.5	2.2	16.1	7.0	83	50	2.8	5.2	67	0.05	0.92
Steamboat Springs*	59	820	0.80	14	31	13.9	0.39	27	18	200	5.4	2940	3703	3.94	0.998
Broadlandst†	1127	...	0.80	8.4	30	...	0.007	35	18	111	10.1	167	28	25,000	33,300	4.79	0.911

All ratios are molar ratios except Cl/HCO₃ + CO₃ and Na/Cl + HCO₃ + CO₃, which are equivalence ratios. Ratios were calculated with the aid of the computer program SOLMNEQ [Kharaka and Barmes, 1973]. Ratios containing carbonate or bicarbonate species are calculated from carbonate alkalinity, not total alkalinity (carbonate and bicarbonate) reported in Table 1.

*Data from Mariner et al. [1974].

†Spring 1 from Browne and Ellis [1970].

denses to produce acid sulfate springs. An analyzed acid sulfate spring from the Casa Diablo area has a Cl/B ratio of 0.12 [data from Lewis, 1974].

Ellis [1970] has shown that ratios of chloride, boron, and bicarbonate may be used to distinguish aquifers within the Ohaki-Broadlands geothermal field. Waters from the same aquifer have chemical compositions with almost constant Cl/B ratios regardless of the bicarbonate concentrations. Ratios of Cl/B are 5.7 ± 0.1 for most of the hot springs in the Long Valley area. The springs in and near Hot Creek Gorge which have higher Cl/B ratios may result from boron loss due to minor subsurface boiling. If the thermal waters come from the same aquifer, then differences in chloride concentration may be a function of the extent of mixing. In simple mixing, thermal fluids rising from depth mix with fresh water near the surface. If simple mixing without boiling or conductive cooling is controlling the chloride concentration and spring temperature, a plot of the chloride concentration versus the water temperature should be a straight line. However, a linear relationship between chloride concentration and water temperature does not exist in Long Valley (Figure 3). Springs which plot above the ideal mixing composition may result from vapor loss or conductive cooling. Springs with the largest chloride concentration and highest temperatures occur in Hot Creek Gorge.

Isotopic data for deuterium and oxygen 18 (Table 3 and Figure 4) are given in the standard δ values, parts per mil (‰). Hot springs in Long Valley range from -12.44 to -16.09 in $\delta^{18}\text{O}$ and from -111.0 to -124.9 in δD . The two fresh waters range from -15.89 to -17.07 in $\delta^{18}\text{O}$ and -115.4 to -129.5 in δD . Recharge water for the hot-spring system in Long Valley may have approximately the composition of the cold spring at Big Spring Campground ($\delta^{18}\text{O} = -15.9$, $\delta\text{D} = -115.4$). The recharge water reacts with rock in the thermal reservoir until at least $\delta^{18}\text{O} = -14.2$ is attained; then dilution by a fresh water of approximate composition $\delta^{18}\text{O} = -18.4$ and $\delta\text{D} = -135$

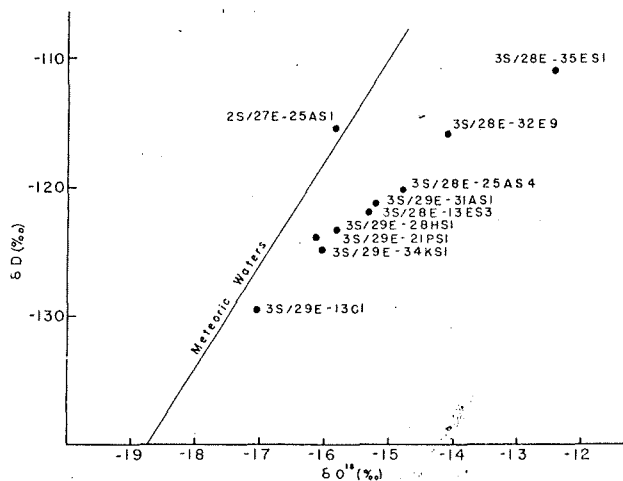


Fig. 4. Detailed plot of δD versus $\delta^{18}\text{O}$ for thermal springs and fresh waters in Long Valley, California. Fresh waters include 25AS1 and 13CI.

would produce the various thermal waters. The plots of δD -chloride and $\delta^{18}\text{O}$ -chloride (Figure 5) emphasize the mixed character of most of the hot-spring waters. Thermal-spring waters from the Hot Creek Gorge area (31ASI and 25AS4) show slight concentration of heavy isotopes. This could result from subsurface boiling, which was inferred from the Cl/B ratios. The hot pool (35ES1) located between Hot Creek Gorge and Casa Diablo Hot Springs has been strongly fractionated, probably by evaporation. The isotopic shift for thermal springs in Long Valley is less than for most other major thermal areas as shown in Figure 6 [modified from Craig, 1963]. The small $\delta^{18}\text{O}$ shift, similar to that observed at Wairakei, may indicate that the hot-spring system in Long Valley is moderately old and has isotopically well flushed conduits.

Gas escaping from thermal springs along Hot Creek and

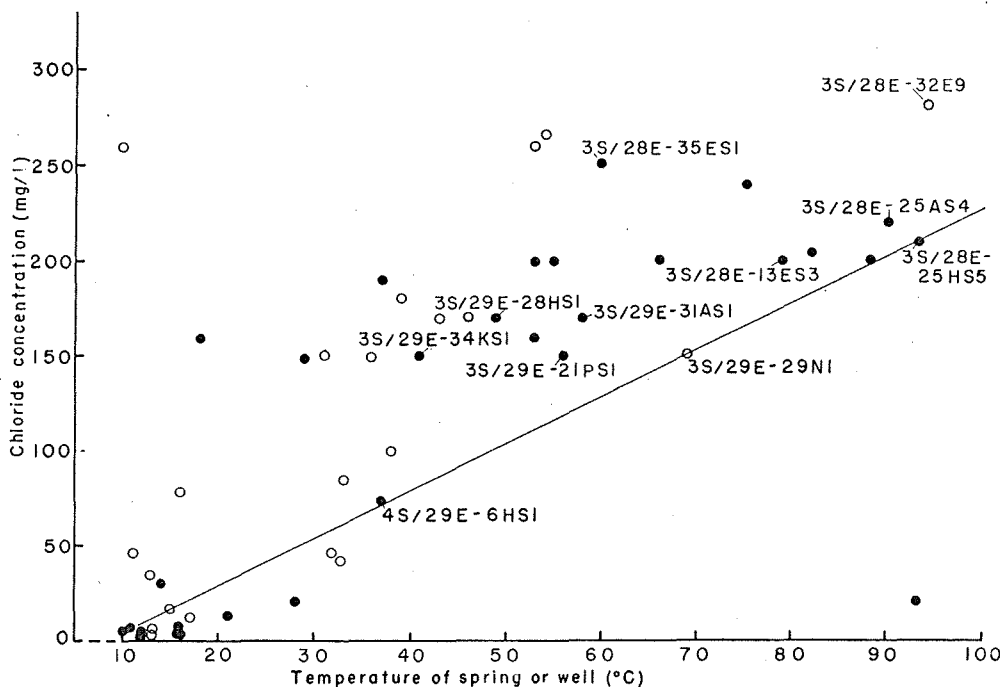


Fig. 3. Chloride concentration versus temperature of thermal springs and wells in Long Valley, California [data from Willey et al., 1974, and Lewis, 1974]. Open circles represent wells, filled circles represent springs.

TABLE 3. Isotopic Composition of Thermal and Meteoric Waters in Long Valley, California

Sample	$\delta^{18}\text{O}$	δD
2S/27E-25AS1	-15.89	-115.4
3S/28E-13ES3	-15.34	-121.8
3S/28E-32E9	-14.16	-115.8
3S/28E-35ES1	-12.44	-111.0
3S/28E-25AS4	-14.83	-120.3
3S/29E-13C1	-17.07	-129.5
3S/29E-21PS1	-16.17	-123.9
3S/29E-28HS1	-15.85	-123.4
3S/29E-31AS1	-15.23	-121.2
3S/29E-34KS1	-16.08	-124.9

Analysts were L. A. Adami and S. J. Grigg.

Little Hot Creek is 89–93% carbon dioxide (Table 4). *Browne and Ellis* [1970] reported that the noncondensable fraction of five steam wells in the Ohaki-Broadlands field contained 92–95% carbon dioxide. Noncondensable gases from Steamboat Springs, Nevada, contain an even larger percentage of carbon dioxide, 98% [*White et al.*, 1963]. The increase in the nitrogen content of gas escaping from the cooler springs in Long Valley may result from water-rock reactions. *Truesdell* [1975] has shown that in Shoshone Geyser Basin, Yellowstone Park, Wyoming, the active gases such as carbon dioxide are removed by water-rock reactions as the water temperature decreases, producing an increase in the percent of nonreactive gases. The high carbon dioxide and low methane concentrations of gases escaping from the springs in Long Valley suggest that the thermal reservoir is in igneous rocks. Springs associated with thermal reservoirs in sedimentary or low grade metamorphic rock are rich in carbon dioxide and methane [*Ellis*, 1967].

Data in *Lewis* [1974] indicate that the surface of the zone of saturation generally parallels the topography, sloping toward Lake Crowley. Between Hot Creek and Lake Crowley the shallow aquifer has been contaminated by thermal fluid. Contamination is evident in the chemical composition and temperatures of springs and wells between Hot Creek and Lake Crowley. Chloride concentrations (Figure 7) indicate that chloride-rich water is being introduced into the zone of saturation in the Hot Creek Gorge and perhaps into the alkali lake area. This chloride-rich water is altering the chloride concentration of the zone of saturation for 7 or 8 km east and east-southeast of Hot Creek Gorge. The concentration of chloride in the zone of saturation decreases from 200 mg/l in the Hot Creek Gorge area to 50 mg/l within 7–8 km. Temperatures in springs and wells show a similar trend (Figure 8) with temperatures decreasing from 93° to 30°C within the same distance. Therefore the best area for mixing calculations should be along Hot Creek or Little Hot Creek, areas where water in the zone of saturation has not been contaminated.

GEOOTHERMOMETERS

The qualitative and quantitative chemical geothermometers are valid only for hot-water systems. The high chloride content (200 mg/l) of the thermal springs in Long Valley indicates that they are associated with a hot-water system. Qualitative indicators suggested by *Ellis* [1970], *Fournier and Truesdell* [1970], *Mahon* [1970], and *White* [1970] are listed in Table 5. Qualitatively, these chemical indicators as well as the water temperatures indicate that the hot springs and steam well near Hot Creek (32E9, 25AS4, and 35ES1) should be associated with the hottest part of the geothermal system.

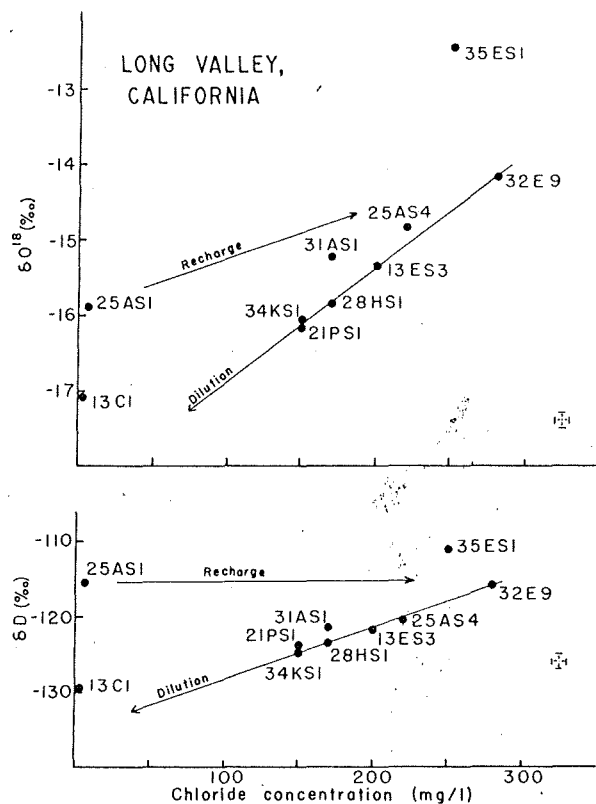


Fig. 5. Plots of δD -chloride and $\delta^{18}\text{O}$ -chloride for springs and wells. Long Valley, California.

The chemical compositions of thermal spring or well waters can be used to estimate the last temperature at which the thermal fluid was in equilibrium with the reservoir rock. However, several of the thermal waters violate basic assumptions, discussed by *Fournier et al.* [1974], which must be fulfilled before the quantitative geothermometers can be meaningful. Mixing of thermal and fresh water has been demonstrated by stable isotope and chloride-temperature relationships. Reaction of thermal fluid with country rock has been implied from the reaction parameters $\text{Cl}/(\text{HCO}_3 + \text{CO}_3)$ and $\text{Na}/(\text{Cl} + \text{HCO}_3 + \text{CO}_3)$. Thus two of the basic assumptions of quantitative geothermometry, negligible mixing of thermal fluids with other waters and negligible water-rock interaction at lower temperatures, are violated. Temperatures estimated from the concentrations of silica and the cations (sodium, potassium, and calcium) are listed in Table 6. The conductive quartz curve was utilized for all samples except the new spring in Hot Creek Gorge, 25AS4, where the adiabatic curve was used because the spring was boiling. The steam-water mixture from the 'steam' well (32E9) was condensed without any steam loss, and the other springs were not boiling. Springs issuing at temperatures below boiling may be mixed waters and/or may have cooled by conduction. If the thermal fluids mix with dilute surface waters, the silica concentrations will be sharply decreased along with the temperature estimate based on the silica con-

TABLE 4. Compositions of Gases Escaping From Thermal Springs in Long Valley, California

Spring	$\text{O}_2 + \text{Ar}$	N_2	CH_4	CO_2	Total
3S/28E-13ES3	1.8	6.3	0.1	92.7	100.9
3S/28E-35ES1	1.6	10.7	0.0	88.8	101.1
3S/28E-25AS4	3.5	8.4	0.3	88.8	101.0
3S/29E-21PS1	6.0	65.1	0.3	37.2	108.6

Analyst was J. B. Rapp. Analysis is in volume percent.

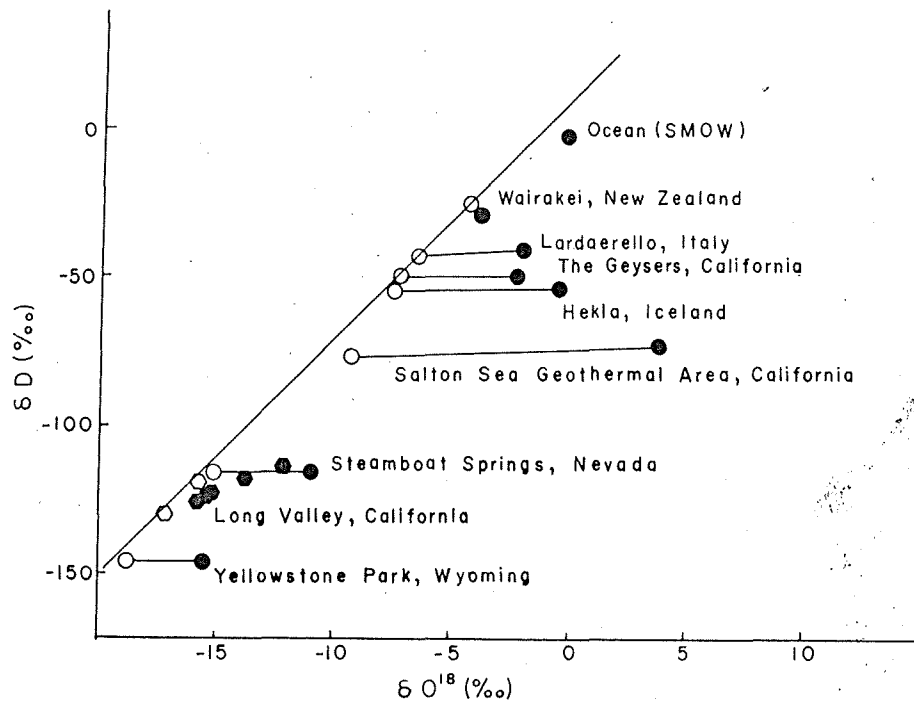


Fig. 6. Isotopic composition of some of the major thermal areas of the world as compared with that of Long Valley, California [after Craig, 1963]. Thermal springs are represented by filled symbols, fresh waters by open symbols. Waters from Long Valley are represented by hexagons, while other thermal areas are represented by circles.

centrations. However, mixing should affect the cation ratios less, and the cation geothermometer should produce an estimate nearer the true reservoir temperature. The Na-K geothermometer should not be used where the $(Ca^{1/2})/Na$ ratio is more than 1 [Fournier and Truesdell, 1973]. The $(Ca^{1/2})/Na$ ratio is greater than 1 for all the samples except the 'steam' well (32E9), the new spring (25AS4), and the hot pool (35ES1). The geothermometers are meaningless for the hot pool (35ES1)

because of evaporation and precipitation of calcite. Loss of carbon dioxide from the well and the new spring may have resulted in the loss of calcium as calcium carbonate precipitated from the thermal fluid. For these samples, neither the Na-K-Ca nor Na-K geothermometer may give an accurate estimate of the temperature in the thermal reservoir.

The Na-K-Ca geothermometer for all the thermal springs (Table 6) indicates reservoir temperatures more than 25°C

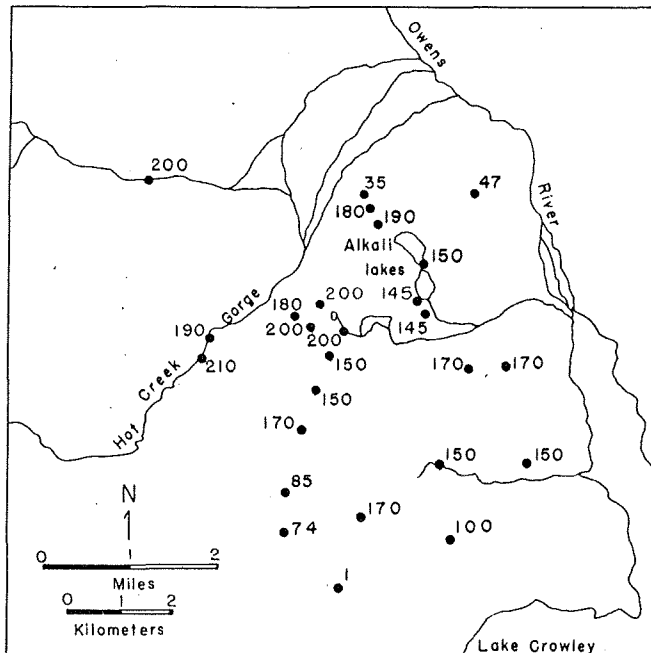


Fig. 7. Areal distribution of chloride in thermal springs and wells, Long Valley, California. Data from Willey *et al.* [1974] and Lewis [1974]. Chloride concentrations are in milligrams per liter.

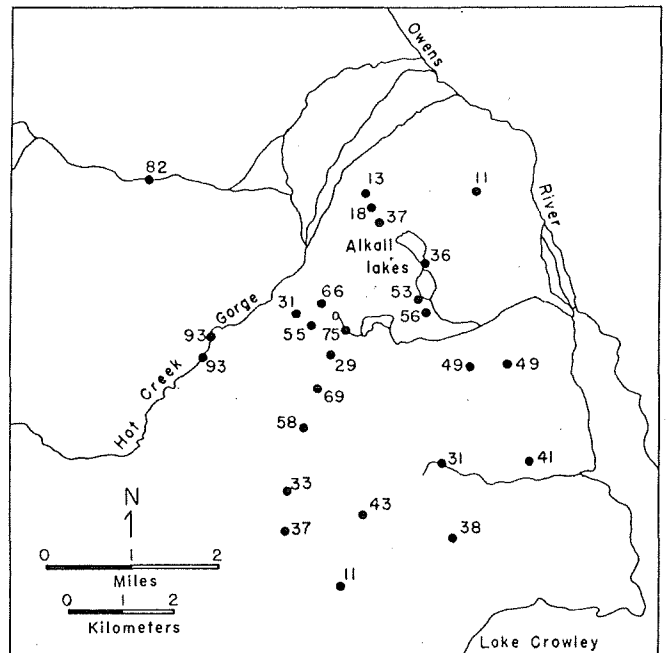


Fig. 8. Areal distribution of temperatures in thermal springs and wells, Long Valley, California. Data from Willey *et al.* [1974] and Lewis [1974]. Temperatures are °C.

TABLE 5. Qualitative Chemical Indicators of Thermal Reservoir Temperatures

Sample Designation	Ca*	HCO ₃ *	Mg/Ca†	Na/Ca‡	Cl	
					(HCO ₃ + CO ₃)§	Cl/F
3S/28E-13ES3	50	735	0.020	14.3	0.47	12.8
3S/28E-32E9	0.9	450	0.183	754	1.55	12.5
3S/28E-35ES1	3.3	466	0.050	200	0.92	12.3
3S/28E-21PS1	25	828	0.040	21.6	0.31	17.5
3S/29E-28HS1	22	845	0.045	31.7	0.35	19.0
3S/29E-31AS1	15	516	0.044	36.0	0.56	12.2
3S/29E-34KS1	23	695	0.086	18.8	0.37	17.5
3S/28E-25AS4	1.6	580	0.113	432	0.62	12.3
2S/27E-25AS1	5.1	90	1.910	7.8	0.11	5.9
3S/29E-13C1	5.3	111	16.0	12.5	0.05	2.8

*Low concentrations of calcium (Ca) and bicarbonate (HCO₃) in near-neutral pH waters may indicate high temperatures [Ellis, 1970].

†Low ratios of magnesium to calcium (Mg/Ca) may indicate high temperatures [White, 1970].

‡High ratios of sodium to calcium (Na/Ca) may indicate high temperatures [Mahon, 1970].

§Highest ratios of chloride to total carbonate (Cl/(HCO₃ + CO₃)) in waters from the same thermal system indicate the highest temperature in the thermal aquifer [Fournier and Truesdell, 1970]. Ratios were calculated with the aid of the computer program SOLMNEQ [Kharaka and Barnes, 1973] after noncarbonate alkalinity was removed.

^{||}Highest ratios of chloride to fluoride (Cl/F) may indicate high temperatures [Mahon, 1970].

above the measured spring temperatures, typical of thermal springs which issue mixed water. Calculations based on the mixing model of Fournier and Truesdell [1974] and assuming temperatures of fresh water from 10° to 17°C with possible silica concentrations from 32 to 64 mg/l indicate reservoir temperatures between 170° and 200°C for the thermal spring on Little Hot Creek. This range of possible reservoir temperatures is due to the uncertainty of the silica concentration and temperature of the cool-water component. Similar calculations for the new spring in Hot Creek Gorge, 25AS4, indicate temperatures of 200° to 225°C. Mixing calculations on 31AS1 located south of Hot Creek Gorge indicate a minimum temperature of 275°C. However, the chloride-temperature plot (Figure 3) may indicate conductive cooling from 76° to 58°C. Assuming that the spring temperature would be 76°C if it had not lost heat by conductive cooling reduces the estimated temperature to 225°C. The estimated reservoir temperature would be further reduced for springs in the Hot Creek Gorge area if some steam separation had occurred, as is indicated by isotope and Cl/B data.

The springs sampled for detailed analysis in the alkali lake area discharge waters with a complex history. Isotopic compo-

sitions indicate mixing with a fresh water. Chloride-temperature relationships indicate that the waters are mixed and may have lost heat by conduction. Mixing calculations using a fresh water of 10°C containing 60 mg/l silica produce an unacceptable calculated temperature (500°C). A possible explanation is that the thermal spring waters are in metastable equilibrium with amorphous silica in the shallow aquifer. All three springs have silica concentrations which would be in equilibrium with amorphous silica at temperatures 10°-15°C above the temperature of the respective spring waters. Cation geothermometers for these three springs estimate temperatures near 200°C.

The best estimate of reservoir temperature may be 220°C, based on the silica concentration in the condensate from the steam well (32E9). Isotopic data and reaction indices indicate that the condensate has not been appreciably altered by dilution, vapor loss, or reaction with the country rock.

Temperatures of 200°-220°C are reasonable minimum temperatures for the thermal reservoir based on the chemical composition of the hot springs. Higher temperatures are possible. On the basis of the silica and Na-K-Ca geothermometers, thermal springs in the Broadlands area of New Zealand

TABLE 6. Estimated Reservoir Temperatures

Sample Designation	Surface Temperature, °C	Discharge, l/min	Chemical Geothermometers*		
			Quartz	Na-K	Na-K-Ca
3S/28E-13ES3	79	280	143	150	172
3S/28E-32E9	94	...	219	201	238
3S/28E-35ES1	60	0	209	140	189
3S/28E-21PS1	56	100	196	205	200
3S/29E-28HS1	49	200	193	192	200
3S/29E-31AS1	58	190	161	147	176
3S/29E-34KS1	41	150	182	169	184
3S/28E-25AS4	90	400±	153	132	192
2S/27E-25AS1	10	380	109	259	83
3S/29E-13C1	10	25	114	86	53

*Basic assumptions of quantitative geothermometry [after Fournier et al., 1974]: (1) temperature dependent reactions in the thermal reservoir must control the water composition. (2) equilibrium must exist between the fluid in the thermal reservoir and the reservoir rock. (3) minerals which supply the constituents used as a basis for the geothermometers must occur in the reservoir rock, (4) negligible re-equilibrium must exist at lower temperatures, and (5) negligible mixing with other waters must occur as the thermal fluid rises to the surface.

should have been associated with a reservoir at a temperature of at least 220°C. Wells drilled near the springs intersect aquifers containing fluid up to 285°C [Mahon and Finlayson, 1972].

SUMMARY

The chloride concentrations, spring temperatures, and isotopic compositions indicate mixing of thermal and fresh waters in the Long Valley geothermal area. Some spring temperatures may be modified by conductive cooling. The thermal spring waters have chemical compositions which indicate a hot-water system similar to the New Zealand geothermal fields. The minimum estimated temperature of the thermal reservoir is 200°C, based on the silica and cation concentrations.

Thermal springs between Hot Creek and Lake Crowley have a different history than the springs along Hot Creek or Little Hot Creek. Possibly part of the thermal fluid rising along Hot Creek enters a shallow aquifer which feeds the springs and wells between Hot Creek and Lake Crowley. Some additional thermal fluid from the deep reservoir may enter the shallow aquifer near Big Alkali Lake. Conductive cooling of mixed thermal and fresh water in this shallow aquifer may control the spring temperature more than simple mixing. Therefore the main thermal reservoir is more directly associated with the thermal springs along Hot Creek and Little Hot Creek. Mixing may also have altered the chemical composition of these springs. Springs in the Hot Creek Gorge area may have been slightly concentrated by some vapor loss during near-surface boiling.

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