

*Geochemistry of Thermal/Mineral Waters
in the Clear Lake Region, California,
and Implications for Hot Dry Rock
Geothermal Development*

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ABSTRACT

Thermal/mineral waters of the Clear Lake region are broadly classified as thermal meteoric and connate types based on chemical and isotopic criteria. Ratios of conservative components such as B/Cl are extremely different among all thermal/mineral waters of the Clear Lake region except for clusters of waters emerging from specific areas such as the Wilbur Springs district and the Agricultural Park area south of Mt. Konocti. In contrast, ratios of conservative components in large, homogeneous geothermal reservoirs are constant. Stable isotope values of Clear Lake region waters show a mixing trend between thermal meteoric and connate end-members. The latter end-member has enriched δD as well as enriched $d^{18}O$, very different from typical high-temperature geothermal reservoir waters. Tritium data and modeling of ages indicate most Clear Lake region waters are 500 to > 10,000 yr., although mixing of old and young components is implied by the data. The age of end-member connate water is probably > 10,000 yr. Subsurface equilibration temperature of most thermal/mineral waters of the Clear Lake region is $\leq 150^{\circ}C$ based on chemical geothermometers but it is recognized that Clear Lake region waters are not typical geothermal fluids and that they violate rules of application of many geothermometers. The combined data indicate that no large geothermal reservoir underlies the Clear Lake region and that small localized reservoirs have equilibration temperatures $\leq 150^{\circ}C$ (except for Sulphur Bank Mine). Hot dry rock technologies are the best way to commercially exploit the known high temperatures existing beneath the Clear Lake region, particularly within the main Clear Lake volcanic field.

I. Introduction

The Geysers–Clear Lake geothermal province is the most complex magma-hydrothermal system in the United States and contains the largest commercial geothermal field in the world (Goff and Waters, 1980; McLaughlin and Donnelly-Nolan, 1981). The province can be divided into two large geothermal regions: a vapor-dominated region in The Geysers and a region of localized, liquid-dominated reservoirs near Clear Lake. These geothermal regions are separated from each other by the northwest-trending Collayomi fault zone (Goff et al., 1977), which displays evidence of considerable late Quaternary movement (Hearn et al., 1981, p. 27). Although abundant thermal manifestations and Quaternary silicic volcanic rocks occur within the Clear Lake region, drilling of many deep wells has not found a producible geothermal reservoir (Thompson et al., in press). In fact, most wells have encountered relatively impermeable conditions at temperatures $\geq 200^{\circ}\text{C}$ and depths ≥ 2 km. Because of these results, Goff and Decker (1983) concluded that the Clear Lake region has great potential for hot dry rock (HDR) geothermal development. Burns (1991) has discussed developmental requirements for the Clear Lake HDR resource.

The object of this report is to discuss the puzzling geochemistry of thermal waters and gases in the Clear Lake region and to demonstrate that no large liquid-dominated reservoir underlies the region. The geochemical results support conclusions gained from drilling and earlier exploration: The Clear Lake region is a large hot dry rock resource and does not have large liquid-dominated reservoirs capable of generating electricity. Volcanological and heat transport issues have been discussed in a companion report (Stimac et al., 1992).

II. Fluid Geochemistry

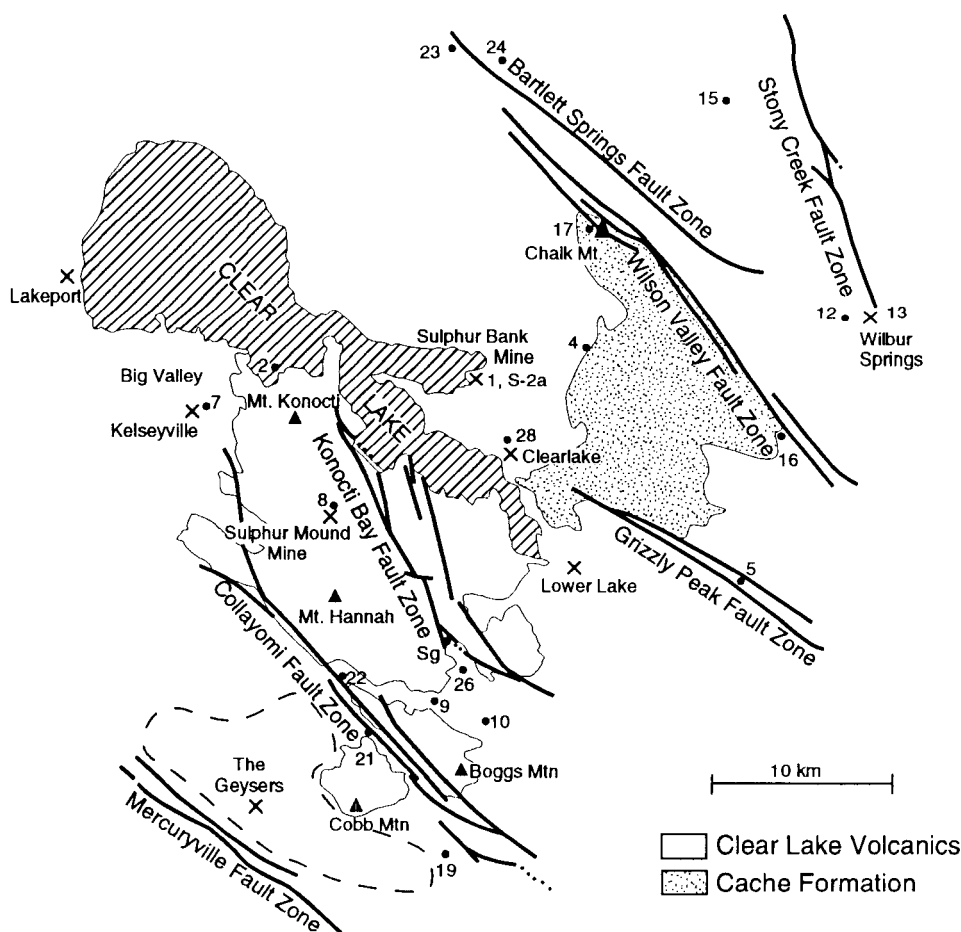
The Clear Lake region contains a very diverse suite of thermal/mineral waters that have been previously studied for various reasons (e.g., Waring, 1915; Barnes et al., 1973; White et al., 1973; Goff et al., 1977; Peters, 1991; Fehn et al., 1992). No boiling springs occur in the Clear Lake region although a few occur in The Geysers region. In addition, no springs outside of The Geysers deposit silica sinter, a characteristic of hot springs derived from reservoirs with temperatures $> 150^{\circ}\text{C}$. Instead, springs in the Clear Lake region deposit carbonate travertine, a reflection of high concentrations of HCO_3 and divalent cations (Ca, Mg, Sr) and lower temperatures of equilibration.

Thermal/mineral waters of the Clear Lake region commonly issue from fault zones containing serpentine and silica carbonate rock. As a result, Clear Lake waters often contain unusually high Mg contents (with $\text{Mg} > \text{Ca}$) and SiO_2 concentrations in near-equilibrium with amorphous silica (low-temperature silica phase) (Thompson et al., in press). High CO_2 contents (as HCO_3) make Clear Lake region waters very reactive

to rocks, particularly to relatively unstable rocks such as serpentine (Barnes et al., 1973) but do not imply that the waters are equilibrated at high temperatures ($> 150^{\circ}\text{C}$). Similar CO_2 -rich thermal fluids occur in the Central Massif of France (Fouillac, 1983) and the CO_2 is believed to come from deep tectonic/magmatic sources.

The diversity of waters in the Clear Lake region has resulted in several classification schemes that describe their origin and setting (White, 1957; Donnelly-Nolan, 1983; and above references in opening paragraph). For the present investigation, 16 thermal/mineral waters and 14 gas features (Fig. 1) ranging from 10 to 68°C were sampled across the Clear Lake HDR prospect region to show variations in chemical and isotopic compositions (Tables I, II, and III). Because the ambient temperature in the region is about 13°C , waters are considered thermal if their temperatures exceed 20°C . We divide the waters into three geothermal water types based on chemical and isotope criteria. For purposes of comparison, in this report, all chemical components are evaluated on a weight basis (mg/kg).

Fig. 1. Simplified geologic map (modified from Goff and Decker, 1983) of the Clear Lake region, California, showing locations of springs and wells appearing in Tables I to V. White areas on map consist of rocks of the Franciscan assemblage and Great Valley sequence.



Steam Condensate Waters

Steam condensate waters form by condensation of steam and other volatiles from an underlying geothermal reservoir into near-surface groundwater. During this process, H_2S is oxidized to SO_4 , and CO_2 and NH_3 are converted into HCO_3 and NH_4 , respectively. Steam condensate waters are near-neutral in pH, have $HCO_3 + SO_4 > Cl$, have $Ca + Mg > Na + K$, and have low concentrations of trace elements usually enhanced in high temperature or deeply circulating fluids (As, B, Br, Li).

Steam condensate waters occur near the tops and margins of vapor-dominated geothermal systems and near upflow zones of high-temperature ($\geq 200^\circ C$) liquid-dominated systems (White et al., 1971; Goff et al., 1985). They are often closely associated with acid-sulfate waters which differ chemically from the former by having a low pH and, therefore, lacking HCO_3 . Acid-sulfate waters occur in the central sector of The Geysers steam field.

The only steam condensate water listed in Tables I–III is Anderson Hot Spring, which issues from the extreme southeast margin of The Geysers steam field, just west of the Collayomi fault zone (see also Goff et al., 1977). This spring was sampled to provide contrasting data to other fluid types that dominate in the Clear Lake region. Besides having characteristics similar to typical steam condensate waters described above, Anderson Hot Spring water has extremely low B and Cl contents when compared with other thermal waters; these contents are too low to plot on Fig. 2. In addition, Anderson Hot Spring water isotopically resembles local meteoric water (Fig. 3) and contains high amounts of tritium (4.6 T.U.) indicating that the water is relatively young, has not equilibrated at high temperature, and is not deeply circulating.

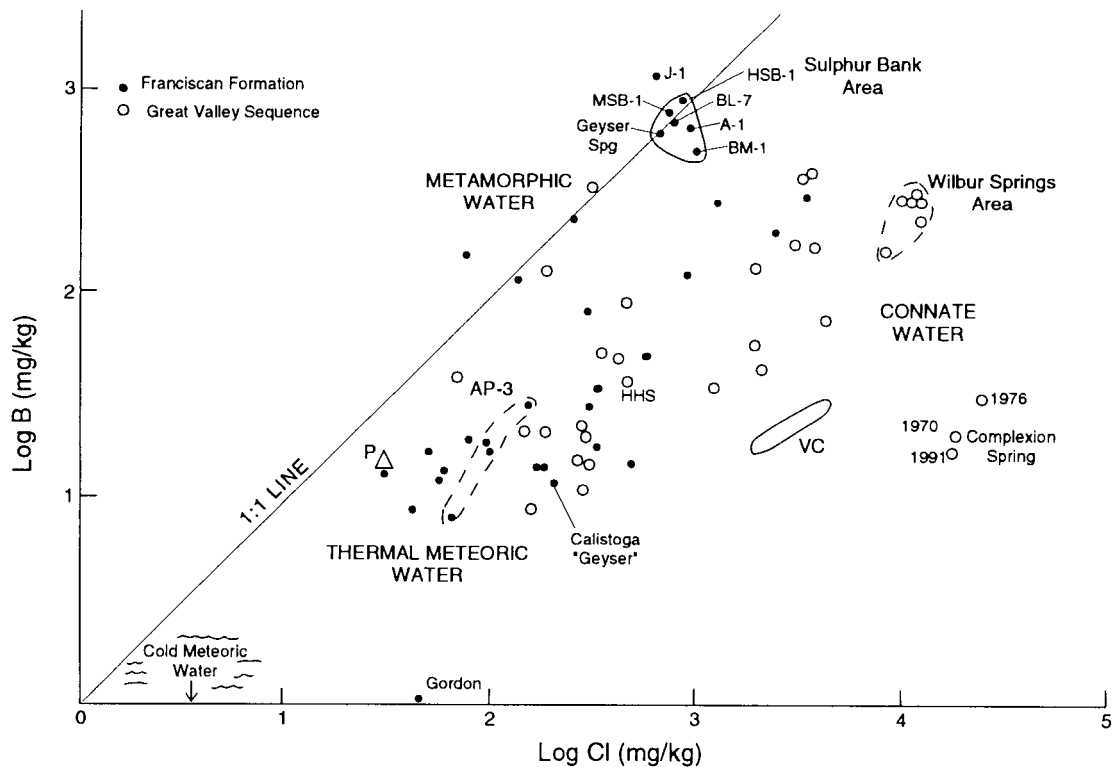


Fig. 2. Plot of log B versus log Cl for thermal/mineral waters of the Clear Lake region, California, and selected geothermal waters from Valles Caldera, New Mexico, and Platanares, Honduras: AP-3 = Agricultural Park #3 well (associated dashed line encloses points representing other well waters nearby); HHS = Howard Hot Spring water; P = deep well waters at Platanares geothermal field, Honduras; VC = deep well waters at Valles caldera geothermal field, New Mexico; Sulphur Bank area: A-1 = Audrey #1 well; BM-1 = Bradley Mining #1 well; BL-7 = Borax Lake #7 well; HSB-1 = Hawaii Sulphur Bank #1 well; J-1 = Jorgenson #1 well; MSB-1 = Magma Sulphur Bank #1 well. Data obtained from White et al. (1973), Barnes et al. (1973), Barnes et al. (1972), Thompson et al. (1981), Peters (1991), Donnelly-Nolan et al. (in preparation), and this report.

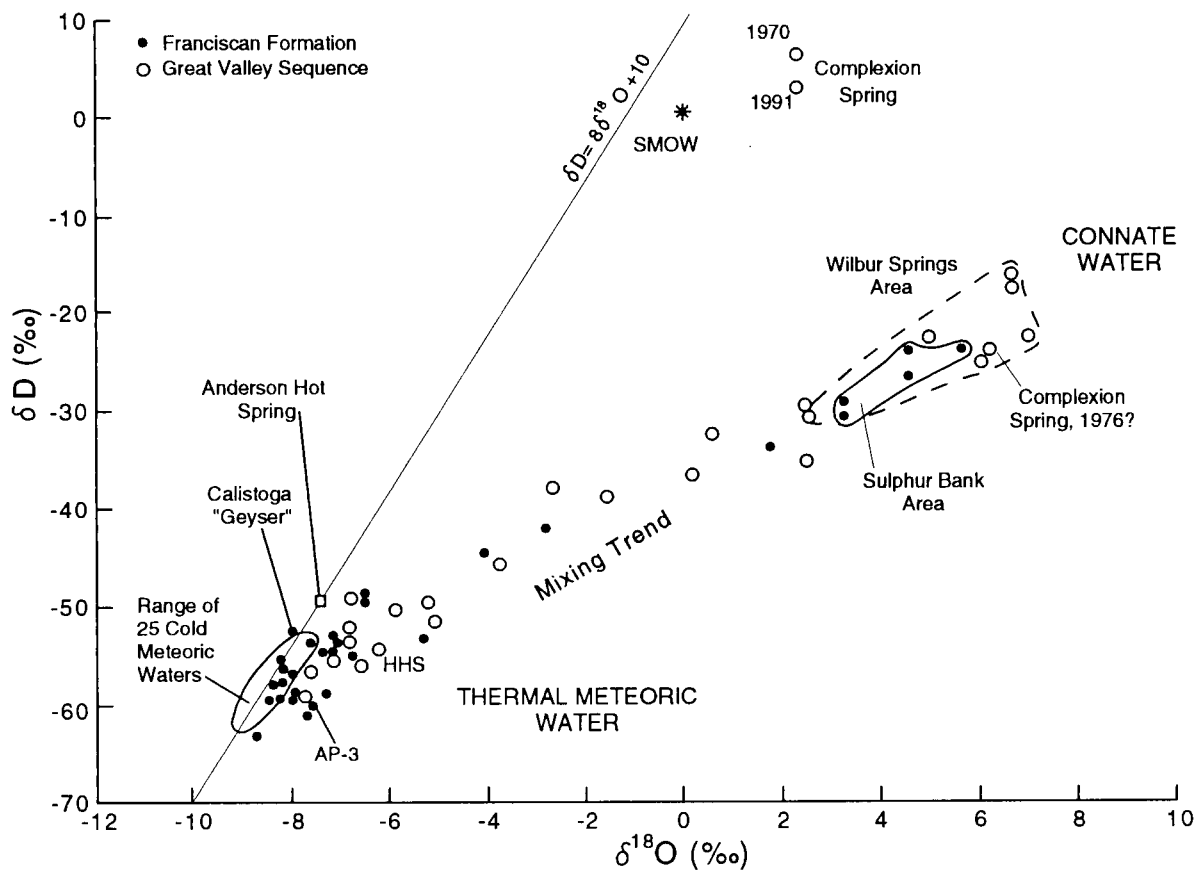


Fig. 3. Plot of δD versus $d^{18}O$ for thermal/mineral waters of the Clear Lake region, California; symbols same as Fig. 2; data sources same as Fig. 2; SMOW = standard mean ocean water.

Thermal Meteoric Waters

Thermal meteoric waters of the Clear Lake region are near-neutral in pH, have $Cl > SO_4$, and have moderate concentrations of some trace elements (B, Br, Li). Because $Ca + Mg$ is roughly equivalent to $Na + K$, thermal meteoric waters are either mixtures of a higher-temperature geothermal component and a cooler, near surface component or are geothermal fluids that have equilibrated at temperatures $< 150^\circ C$.

Thermal meteoric waters have higher B and Cl contents than steam condensate waters (Fig. 2), but are less concentrated than other thermal/mineral waters in the Clear Lake region. Thermal meteoric waters are isotopically similar to local meteoric water. Some show oxygen-18 shifts of up to +2%, suggesting possible high-temperature isotopic exchange between

water and rock. Thermal meteoric waters contain moderate to very low tritium (0 to 4.0 T.U.) indicating that some waters of this type are relatively old and deeply circulating.

Most thermal meteoric waters issue from Franciscan Formation bedrock or from Clear Lake volcanic rocks that appear to be underlain by Franciscan rocks (Goff et al., 1977). Thermal meteoric waters are also most common near the main mass of the volcanic field (Fig. 1). The relatively high CO_2 content of thermal meteoric waters (as HCO_3) suggests that high subsurface temperatures, associated with subsurface magma reservoirs, produce anomalous CO_2 .

Connate Waters

Connate waters, as defined by White (1957) and White et al., (1973), contain a component of fossil sea water. Connate waters of the Clear Lake region have near-neutral pH, have $\text{Cl} > \text{SO}_4$, have $\text{Na} + \text{K} > \text{Ca} + \text{Mg}$, and have high concentrations of As, B, Br, and Li. They also contain substantial CO_2 (as HCO_3) except for Complexion Spring, which has $\text{pH} > 10$ and is geochemically unusual in other respects (Barnes et al., 1972).

Although $\text{Na} + \text{K}$ contents are relatively high, the ratio of Na/K is generally > 10 , suggesting that the fluids have not equilibrated at temperatures above 150°C . Connate waters have very high B and Cl content (Fig. 2). They also are unusual isotopically because they are exceptionally enriched in deuterium as well as oxygen-18 (Fig. 3). Connate waters contain low to very low tritium content (0 to 1.4 T.U.) indicating that most of them are relatively old and deeply circulating.

Connate waters are most common in the eastern Clear Lake region and typically issue from rocks of the Great Valley sequence (Goff et al., 1977; Fehn et al., 1992) but there are important exceptions such as Newman Spring and others near the Bartlett Springs fault zone (Fig. 1). High HCO_3 contents also indicate that connate waters contain CO_2 from magmatic/tectonic processes occurring in the greater Clear Lake region.

An important subclass of connate waters is the metamorphic waters of White et al. (1973), which are thought to be produced by "progressive metamorphism of marine sediments, perhaps after compaction and loss of most of the chloride of the original marine pore waters." Metamorphic waters in the Clear Lake area are distinct chemically because they contain nearly equal B and Cl contents (Fig. 2). They are best exemplified by thermal springs and deep well waters in the Sulphur Bank mine area and by fluids produced from deep wells nearby, where subsurface temperatures are known to exceed 200°C (Beall, 1985). However, metamorphic waters are not distinct from connate waters isotopically (Fig. 3).

Metamorphic waters typically issue from rocks of the Franciscan Formation near the main Clear Lake volcanic field. Because Franciscan rocks have been subjected to significant low temperature metamor-

phism through subduction and burial beneath the Coast Range Thrust whereas Great Valley rocks have not, resulting thermal fluids emerging from Franciscan rocks are lower in Cl relative to B. Thus, two factors contribute to creation of metamorphic waters as opposed to connate waters: differences in the original character of the host marine bedrock units, including depth of burial, and differences in temperature caused by proximity to the main Clear Lake volcanic field and/or temperature of the source reservoir fluid.

Figure 3 also shows that there is a continuous isotopic gradation between connate waters of all types and thermal meteoric waters. This trend is a mixing trend between two isotopic types of water although no such mixing trend is apparent chemically (i.e. Fig. 2). Connate waters consist partially of (fossil?) pore waters existing in marine rocks whereas thermal meteoric waters are composed of locally derived meteoric waters. Some springs, such as Grizzly Spring and Chalk Mountain Spring, are obvious mixtures of both types of water.

Comparison to High-Temperature Geothermal Reservoir Waters

Thermal/mineral waters of the Clear Lake region do not have chemical characteristics indicating they have originated from a single, high-temperature reservoir. Waters that originate from a single reservoir generally have constant ratios of chemically conservative components such as B/Cl , Li/Cl , and Br/Cl (Figs. 4 and 5). For example, the geothermal reservoir of Valles Caldera, New Mexico (210 to 300°C) circulates primarily in Plio-Pleistocene volcanic rocks and displays constant ratios of conservative components. Hot springs derived from this reservoir display the same chemical ratios even though spring temperatures are significantly less than reservoir temperatures and the springs issue from Paleozoic sedimentary rocks outside of the caldera depression (Goff et al., 1988). The geothermal system of Platanares, Honduras ($>165^\circ\text{C}$) is not associated with Quaternary volcanism and circulates in weakly metamorphosed Cretaceous to Eocene sedimentary rocks but also has constant ratios of conservative components (e.g., Fig. 5 reproduced from Janik et al., 1991). Large, liquid-dominated reservoirs that do not have constant ratios of these conservative components are somewhat rare. Such reservoirs are poorly connected and have highly variable productivity (i.e., Zunil geothermal field, Guatemala; Adams et al., 1990).

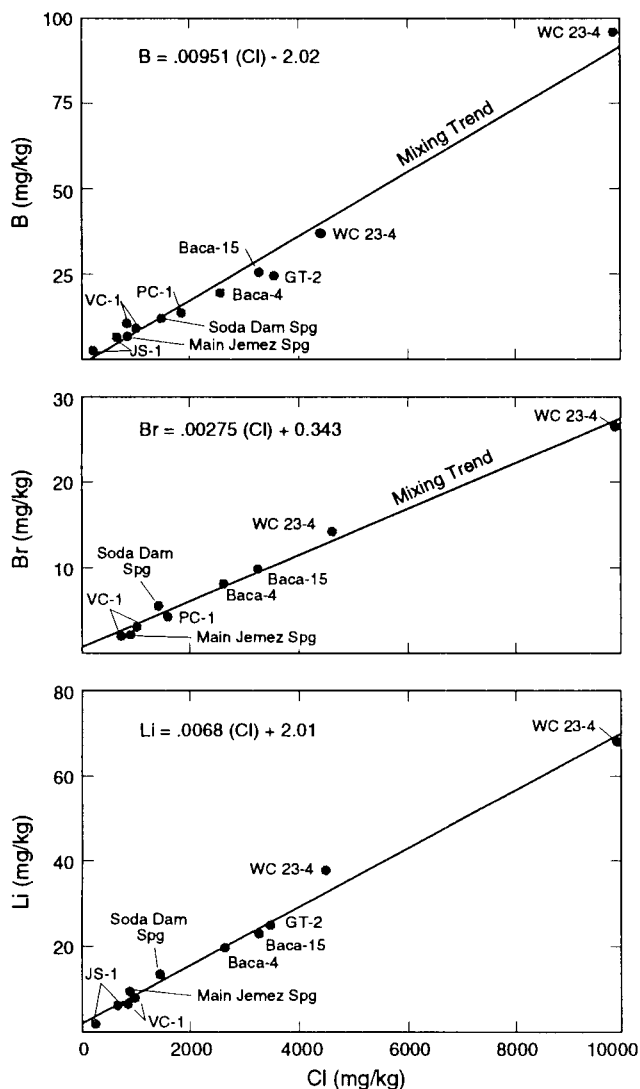


Fig. 4. Plots of B, Br, Li versus Cl for hot springs and wells of the Valles caldera geothermal system, New Mexico (from Goff et al., 1988); Valles waters display linear trends (mixing trends) on such plots of conservative components while Clear Lake region waters do not (Fig. 2).

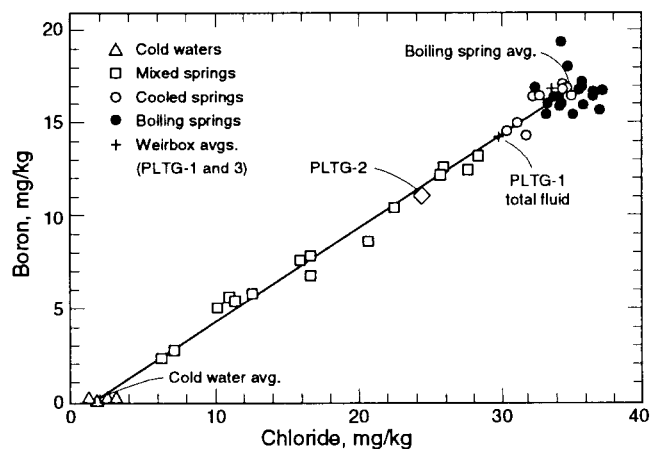


Fig. 5. Plot of B versus Cl for hot springs and wells of the Platanares geothermal system, Honduras (from Janik et al., 1991); waters of this field also show mixing and interconnection within a single reservoir unlike waters of the Clear Lake region (Fig. 2).

When compared with Clear Lake region waters, Platanares waters chemically resemble metamorphic water while Valles waters resemble connate water (Fig. 2). However, Clear Lake waters do not form a linear trend even on a log-log plot of B vs. Cl, indicating how different Clear Lake region waters are from location to location. Obviously, Clear Lake waters represent separate, isolated reservoirs such as Sulphur Bank Mine, the Wilbur Springs district, the Agricultural Park, near Sulphur Mound Mine, Howard Hot Springs, etc.

Clear Lake region waters are also different isotopically from typical high-temperature geothermal reservoirs (Fig. 6). For example, waters at both Valles Caldera and Platanares are very similar in deuterium to local meteoric waters of their respective regions. Both Valles and Platanares reservoir fluids display oxygen-18 enrichments of 0 to +4%, typical of high-temperature geothermal systems worldwide (Craig, 1963). In contrast, Clear Lake region waters show the unusual mixing trend between thermal meteoric and connate end-members.

High-temperature rock-water interaction of connate waters is impossible to evaluate because of this mixing trend. High-temperature rock-water interaction of thermal meteoric water can be evaluated but the results are not spectacular. For example, the thermal fluids of the Calistoga area south of the Clear Lake region show no oxygen-18 shift; thus, these fluids can not originate from a high-temperature reservoir ($>150^{\circ}\text{C}$). Fluids from the Agricultural Park reservoir near Sulphur Mound Mine show only a modest oxygen-18 shift, indicative of a possible high-temperature origin. Thermal waters of the Clear Lake region thus differ from typical geothermal reservoir fluids when evaluated by standard isotopic criteria.

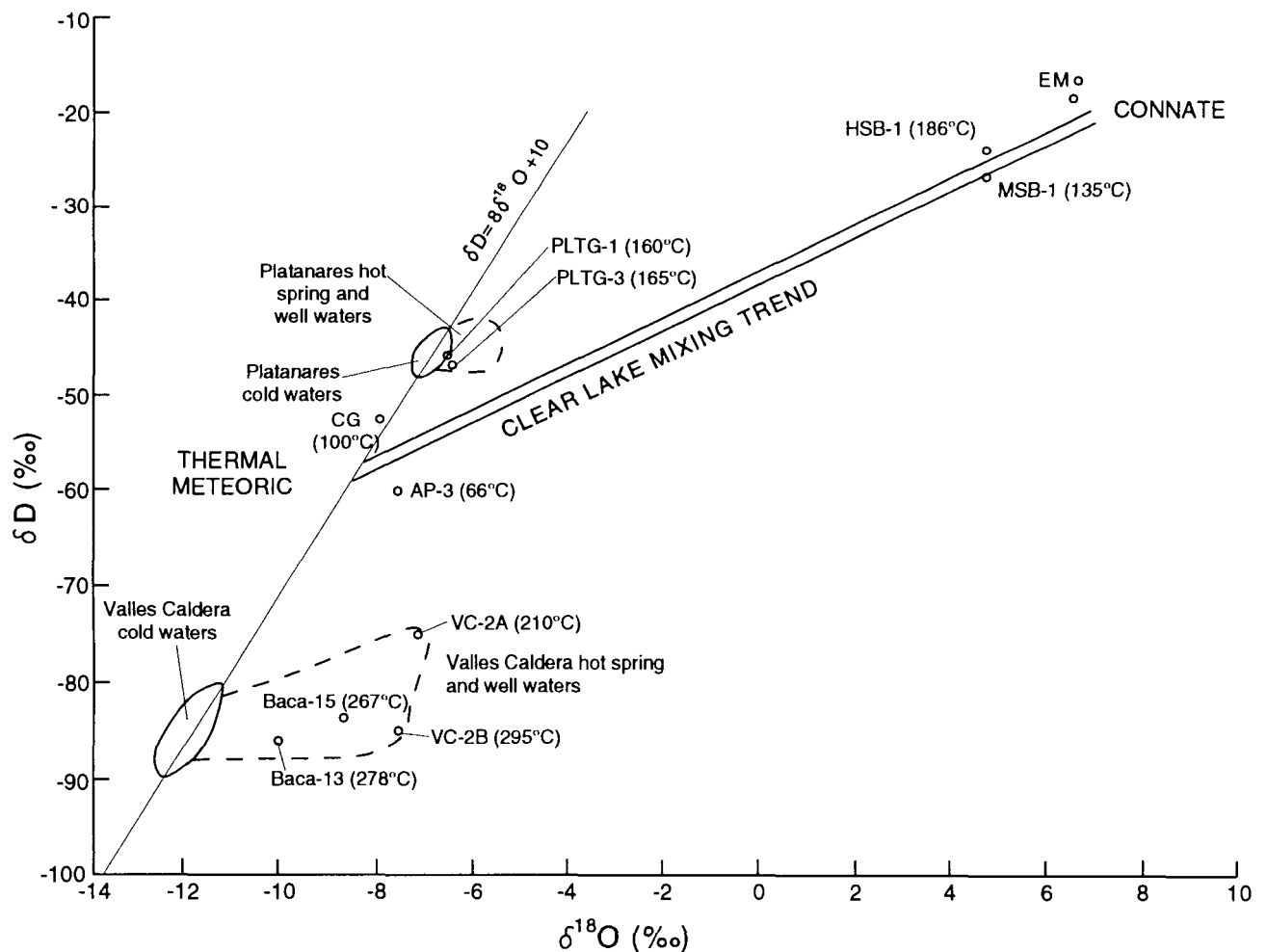


Fig. 6. Plot of δD versus $\delta^{18}\text{O}$ for thermal and nonthermal waters of the Clear Lake region, California; the Platanares geothermal system, Honduras; and the Valles caldera geothermal system, New Mexico; symbols stand for wells used in previous figures or at the Platanares and Valles caldera geothermal systems except EM = Elgin Mine hot spring and CG = Calistoga "Geyser." Connate waters of the Clear Lake region are isotopically different from high-temperature fluids in typical geothermal reservoirs (see text).

Gas Compositions

Table III lists 14 analyses of gases from within the Clear Lake region. At first inspection, many gases from the region resemble typical geothermal gases because of their high concentrations of CO_2 and weak presence of H_2S and CH_4 . However, most gases are different from gases derived from high-temperature reservoirs. Contents of H_2S are low to absent, and contents of H_2 are very low to absent. Some of the gases have N_2/Ar molar ratios close to 84, the ratio of air, indicating near-surface mixing with air. Other gases have N_2/Ar ratios close to 38, the ratio of air-saturated water, indicating mixture with near-surface groundwater. Three areas produce gases that have no obvious connection to air or air-saturated water: the Sulphur Bank Mine, Wilbur Springs, and Kelseyville areas.

Clear Lake region gases can be compared with gases from Valles caldera and Platanares in the triangular plot of Fig. 7. This plot, devised by Giggenbach and Goguel (1989) is a good means for separating gases of predominantly magmatic, crustal, and meteoric affinities. Valles Caldera gases, for example, have a distinct crustal signature even though the geothermal system is contained within a Quaternary caldera. This results from the superposition of the caldera on Paleozoic sedimentary rocks and Precambrian basement. Gases from Sulphur Bank Mine and Baker Soda Spring also have a crustal signature. Gases from Platanares, Honduras, show a significant interaction with air and air-saturated water as do gases from most Clear Lake region waters. Gases from the Wilbur Springs district and Kelseyville area are enriched in N_2 relative to He and Ar and appear to have a slight magmatic signature. More gas analyses in these two areas would be useful to further evaluate these trends.

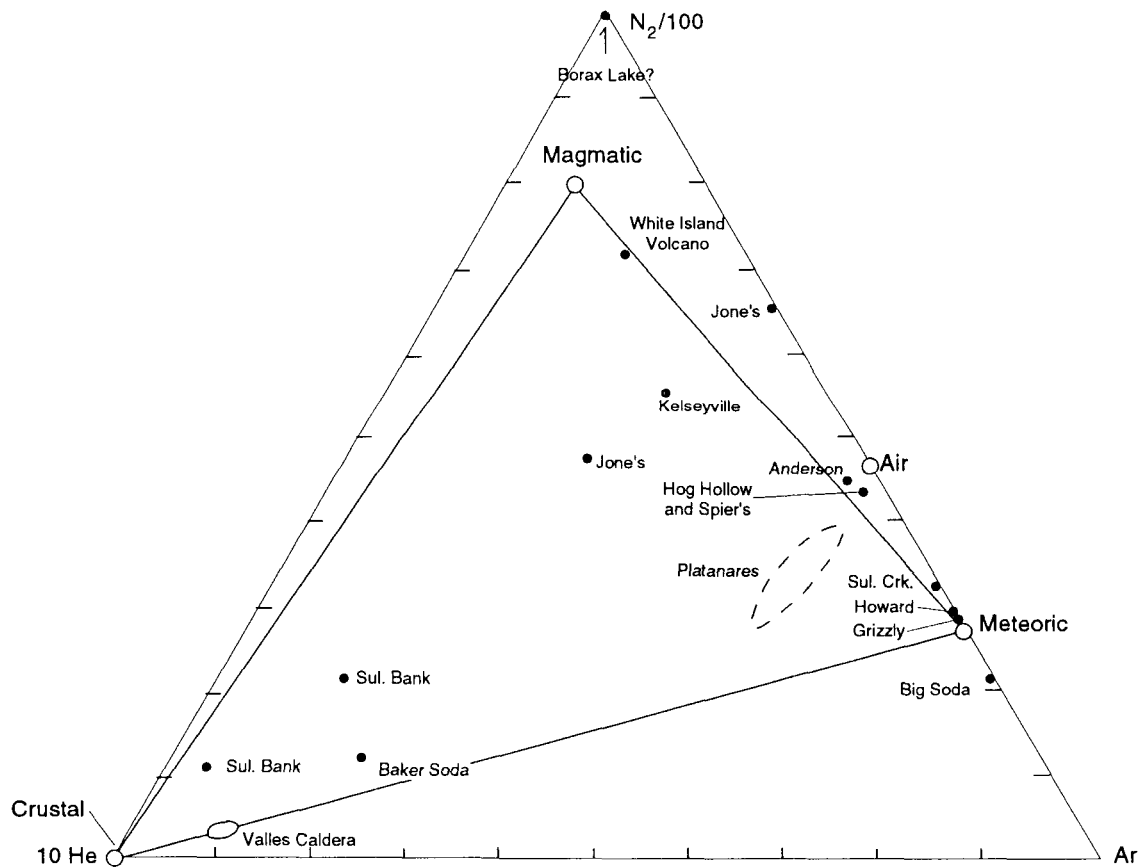


Fig. 7. Triangular plot of mol-% N_2 , He, and Ar for gases in the Clear Lake region and other gases discussed in text. Designations "Magmatic, Crustal, and Meteoric" and the point for White Island Volcano are from Giggenbach and Goguel (1989).

The apparent temperature of last equilibration of the gases can be calculated using the empirical gas thermometer of D'Amore and Panichi (1981). This geothermometer was derived from thermodynamic considerations of gas equilibria and from the compositions of gases produced at many high-temperature geothermal systems. Calculated temperatures (last column, Table III) of equilibration for Clear Lake region gases are all $\leq 135^\circ\text{C}$, even for gases at Sulphur Bank mine. A calculated temperature of 218°C is obtained for the gas at Anderson Hot Spring, a steam condensate spring on the southeast margin of The Geysers steam field. Gases in the Clear Lake region either re-equilibrate during their path to the surface or do not reflect equilibration at high temperatures.

Reservoir Residence Time

Tritium (^3H) is useful in determining the relative ages of groundwaters because it has a short half-life of 12.43 yr. and was produced in large amounts during atmospheric nuclear tests in the 1950s and 1960s (Fontes, 1980). Meteoric precipitation in the Clear Lake region is now about 4 to 7 T.U. (unpublished data). To make quantitative estimates of mean residence times of water in underground reservoirs, Goff et al. (1987, 1991) derived analytical solutions as a function of tritium content for two end-member types of reservoirs, piston-flow and well-mixed, following the methods of Pearson and Truesdell (1978). A detailed explanation of the equations and derivation of input functions for this method can be found in Shevenell (1991).

The relation between tritium input and output concentrations for the piston-flow model is expressed by

$$C_{\text{out}}(t) = C_{\text{in}}(t - \tau)e^{-\lambda\tau} \quad (1)$$

where $C_{\text{out}}(t)$ = output ^3H concentration at time t , $C_{\text{in}}(t - \tau)$ = ^3H concentration of fluid recharging the system, τ = residence time, and λ = ^3H decay constant ($5.57 \times 10^{-2} \text{ yr}^{-1}$). This equation yields a lower limit on fluid age (minimum age) in a reservoir system.

To estimate the maximum age of a reservoir fluid, the well-mixed model is utilized in which

$$\frac{dC(t)}{dt} = \frac{Q_{\text{in}}}{V} C_{\text{in}}(t) - \frac{Q_{\text{out}}}{V} C(t) - \lambda C(t) \quad (2)$$

where $C(t)$ = ^3H level in the reservoir, and at the discharge point, at time t = the year, $C_{\text{in}}(t)$ = input ^3H concentration, Q_{in} = recharge flow rate, Q_{out} = discharge flow rate, and V = the volume of fluid in the reservoir.

When little is known about the reservoir in question, steady-state conditions of flow are assumed and $Q_{\text{in}} = Q_{\text{out}}$. For the California coastal region, the tritium data from Menlo Park, California, was used to generate Tables IVa and IVb (IAEA, 1969–1986). A pre-bomb background value of 3 T.U. was assumed.

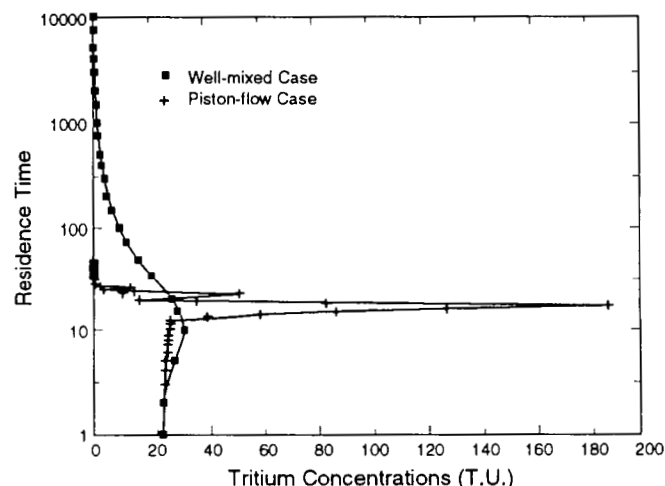


Fig. 8a. Plot of residence time (yr.) versus tritium content (T.U.) for base year 1980 for aquifers and springs in northern California; curves show piston-flow and well-mixed reservoir models. These curves are used to evaluate ages of waters collected in 1980 (see Shevenell, 1991).

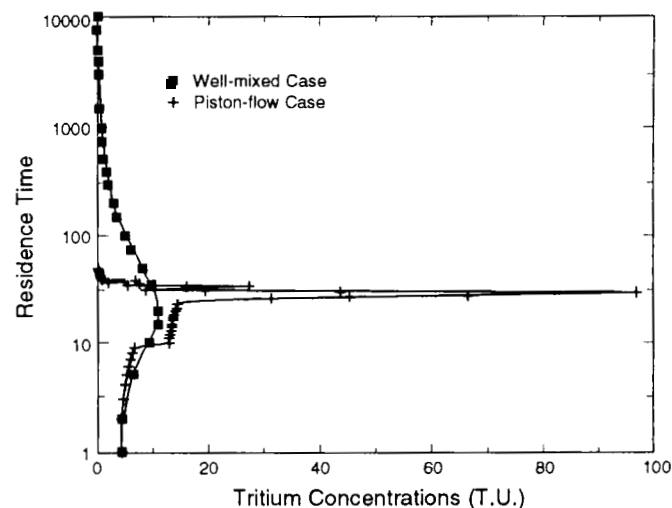


Fig. 8b. Similar plot to Fig. 8a for base year 1992.

Some thermal meteoric waters contain less ^3H than connate waters of the Clear Lake region, suggesting that many connate waters contain some relatively young, near-surface water received through mixing. For example, waters in the Wilbur Springs district contain more ^3H than the water of Big Soda Spring, which issues from a small island on the shore of Clear Lake. The oldest unmixed water is the connate fluid at Baker Soda Spring (>10,000 yr). The incredible differences in tritium content between the various waters indicate, as stated above, that they are not derived from a single reservoir.

Fehn et al. (1992) have recently studied residence times and source ages of hydrothermal fluids of the connate and mixed connate-thermal meteoric types in the eastern Clear Lake region (named by them formation- and mineral-type waters) using ^{129}I and ^{36}Cl . They found that the source of I (and, therefore, most of the Cl) in these waters was from units with ages of 60 to 80 Ma, most likely the Franciscan Assemblage and Great Valley Sequence. They also found that the residence time of end-member formation waters was probably not longer than 84,000 yr. Although the ^3H data are not capable of determining a maximum age for such old fluids, they are capable of showing the effects of mixing processes between connate fluids and relatively young near-surface waters. Thus, connate fluids in the Wilbur Springs area appear to be the oldest waters in the Clear Lake region based on their ^{129}I and ^{36}Cl relations (Fehn et al., 1992) but they contain measurable ^3H , indicating that they are mixed with younger water.

Chemical Geothermometry

Chemical geothermometer temperatures calculated from data in Table I and other sources are listed in Table V. The reader should consult Fournier (1981) for a generalized discussion of chemical geothermometers and their application. Because thermal/mineral waters of the Clear Lake region have widely different chemistries related partly to diverse bedrock compositions, it is difficult to evaluate the role of temperature on chemical composition (see also, Thompsen et al., in press).

Barnes et al. (1973) noted that the silica concentrations of many Clear Lake region waters were saturated with respect to amorphous silica at the discharge temperature of the spring. Goff et al. (1977) applied silica mixing models and postulated that the

spring waters could have originally equilibrated at 200°C. Goff and Donnelly (1978) determined that the Na-K-Ca geothermometer was positively correlated with Cl content (total salinity) and that very saline waters yielded higher estimated temperatures than more dilute thermal waters. This relation was partly correlated with bedrock type.

Several recent geothermometers have been developed since the late 1970s, of which some are very sensitive to low-temperature equilibration (e.g., K/Mg geothermometer of Giggenbach, 1986). Most geothermometers are empirical, that is, a temperature-dependent equation is determined from the chemistry and temperature of fluids produced from high-temperature geothermal reservoirs. Because good data are available only from high-temperature reservoirs (low-temperature reservoirs have no commercial value), chemical geothermometers work best and show best agreement for high-temperature waters. Because no such reservoir has been produced in the Clear Lake region and because the geothermometers are designed only for liquid-dominated reservoirs (not vapor-dominated reservoirs like The Geysers), Clear Lake waters yield extremely variable estimates of subsurface temperature.

When geothermometers sensitive to low-temperature equilibration are applied (Mg/Li, K/Mg, Na-K-Ca with Mg correction), most Clear Lake region waters (even water produced from high-temperature wells in the Sulphur Bank Mine area) appear to have equilibrated at temperatures of about 150°C or less. Apparently, the effect of Mg overcompensates the temperature corrections for some Clear Lake region waters. Possibly, high CO_2 contents and resulting reactions of water with rock at low temperatures may effect the geothermometers (Fouillac, 1983). It is our opinion that most spring waters in the Clear Lake region do not originate from reservoirs > 150°C.

Very limited data are available from fluids produced by high-temperature wells in the Clear Lake region but data from five wells at or near Sulphur Bank Mine were used in Table V. For these wells, the quartz-conductive and Na-K-Ca ($\beta = 1/3$) geothermometers yield temperatures in general agreement with maximum measured temperatures. This is a characteristic of most high-temperature waters, and further suggests that most springs in the Clear Lake region do not originate from high-temperature reservoirs ($\geq 150^\circ\text{C}$).

Table I
Selected Chemistry of the Thermal/Mineral Waters of the Clear Lake Region, California
 (values in mg/kg, except where noted) (a)

Sample No.	Name	Date	Water Type ^(b)	Temp. °C	pH (Lab)	SiO ₂	Li	Na	K	Mg	Ca	Sr	F	Cl
CL-91-2	Big Soda Spring	03/06/91	TM	31.3	6.68	133	0.45	95	11.5	110	79.8	0.58	0.32	56.8
CL-91-4	Hog Hollow Spring	03/07/91	TM	30.0	6.59	149	0.51	196	11.8	47.2	105	0.90	0.30	169
CL-91-5	Baker Soda Spring	03/07/91	C	21.3	7.34	88	6.25	2600	207	279	92.6	2.00	0.52	2985
CL-91-8	Ag. Park Well #3	03/08/91	TM	65.7	7.25	189	1.09	148	35.5	16.0	23.4	0.31	0.15	153
CL-91-9	Ettawa Spring	03/08/91	TM	21.7	6.95	104	0.61	572	10.4	228	31.6	1.25	<0.02	183
CL-91-10	Spier's Spring	03/08/91	TM	24.2	6.82	151	1.26	391	15.8	310	27.8	0.85	<0.02	448
CL-91-12	Jones Hot Spring	03/09/91	C	61.9	7.88	89	14.0	9740	513	41.0	5.6	1.10	5.15	11210
CL-91-13	Wilbur Hot Spring	03/09/91	C	55.6	7.68	199	12.1	8580	460	54.8	5.6	2.00	3.32	10710
CL-91-15	Complexion Spring	03/09/91	C	8.9	10.82	15	<0.1	11845	335	22.9	3.7	0.50	0.14	17260
CL-91-16	Grizzly Spring	03/09/91	C	19.4	7.05	90	3.80	2686	45	686	52.3	13.0	0.40	3750
CL-91-17	Chalk Mt. Spring	03/09/91	C	16.1	7.04	100	9.35	2290	242	588	89.7	4.10	0.64	3384
CL-91-19	Anderson Hot Spring	03/11/91	SC	49.4	6.42	85	0.18	39	9.5	52.4	157	1.19	0.35	2.1
CL-91-21	Gordons Hot Spring	03/11/91	TM	34.6	7.54	171	0.15	56	3.9	31.5	10.8	0.30	<0.02	45.4
CL-91-22	Sulfur Creek Spring	03/11/91	TM	21.0	6.61	141	0.98	165	14.8	156	20.8	0.50	0.05	255
CL-91-23	Newman Spring	03/12/91	C	29.5	7.25	179	22.6	2340	54.3	529	154	3.70	0.37	3181
CL-91-26	Howard Hot Spring	03/13/91	TM	46.3	7.13	156	1.30	254	21.7	297	31.6	1.00	<0.02	457

Table I (continued)

Sample No.	Name	Date	Water Type ^(b)	Temp. °C	Br	HCO ₃	SO ₄	B	As	NH ₄
CL-91-2	Big Soda Spring	03/06/91	TM	31.3	0.27	1039	0.2	12.3	<0.1	<0.05
CL-91-4	Hog Hollow Spring	03/07/91	TM	30.0	0.64	809	0.2	14.8	<0.1	11.1
CL-91-5	Baker Soda Spring	03/07/91	C	21.3	11.1	4650	0.25	171	0.7	138
CL-91-8	Ag. Park Well #3	03/08/91	TM	65.7	0.84	386	25.2	29.8	<0.05	14.6
CL-91-9	Ettawa Spring	03/08/91	TM	21.7	1.01	2572	0.3	21.0	<0.1	4.56
CL-91-10	Spier's Spring	03/08/91	TM	24.2	2.56	2096	6.3	91.0	<0.1	32.8
CL-91-2	Big Soda Spring	03/06/91	TM	31.3	0.27	1039	0.2	12.3	<0.1	<0.05
CL-91-4	Hog Hollow Spring	03/07/91	TM	30.0	0.64	809	0.2	14.8	<0.1	11.1
CL-91-5	Baker Soda Spring	03/07/91	C	21.3	11.1	4650	0.25	171	0.7	138
CL-91-8	Ag. Park Well #3	03/08/91	TM	65.7	0.84	386	25.2	29.8	<0.05	14.6
CL-91-9	Ettawa Spring	03/08/91	TM	21.7	1.01	2572	0.3	21.0	<0.1	4.56
CL-91-10	Spier's Spring	03/08/91	TM	24.2	2.56	2096	6.3	91.0	<0.1	32.8
CL-91-23	Newman Spring	03/12/91	C	29.5	11.8	4319	34.9	366	1.4	86.2
CL-91-26	Howard Hot Spring	03/13/91	TM	46.3	2.35	1680	0.1	37.4	<0.1	15.0

(a) Analyses by P. E. Trujillo and D. Counce (LANL).

(b) TM = thermal meteoric water; C = connate water; SC = steam condensate water.

Table II
Selected Isotope Data and Minimum/Maximum Mean Residence Times
of Thermal/Mineral Waters of the Clear Lake Region, California^(a)

Sample No.	Name	Measured Temp. (°C)	Emergence Elev. (m)	$\delta^{18}\text{O}$ (%)	δD (%)	^3H (T.U.)	Min. Age ^(b) (yr)	Max. Age ^(b) (yr)
CL91-2	Big Soda Spring	31.3	404	-7.91	-58.6	0.09	>50	7500
CL91-4	Hog Hollow Spring	30.0	439	-7.68	-61.7	0.27	43	2500
CL91-5	Baker Soda Spring	21.3	427	-1.60	-38.9	0.04	>50	>10,000
CL91-8	Agric. Park #3 Well	65.7	622	-7.57	-60.1	0.09	>50	7500
CL91-9	Ettawa Spring	21.7	598	-7.69	-58.9	1.13	38	600
CL91-10	Spier's Spring	24.2	457	-5.86	-50.1	2.97	35	200
CL91-12	Jones Hot Spring	61.9	416	6.99	-22.6	0.49	35	1400
CL91-13	Wilbur Hot Spring	55.6	411	6.01	-25.2	0.23	46	3000
CL91-15	Complexion Spring	9.8	518	2.25	2.8	1.44	35	450
CL91-16	Grizzly Spring	19.4	390	0.14	-36.5	0.61	35	1100
CL91-17	Chalk Mountain Spring	16.1	378	-2.71	-37.7	1.05	35	650
CL91-19	Anderson Hot Spring	49.4	488	-7.35	-49.3	4.62	1	125
CL91-21	Gordon's Warm Spring	34.6	732	-7.13	-54.6	0.20	49	3500
CL91-22	Sulphur Creek Spring	21.0	756	-7.13	-55.0	3.97	35	150
CL91-23	Newman Spring	29.5	610	2.49	-35.2	0.32	40	2000
CL91-26	Howard Hot Spring	46.3	665	-6.24	-54.4	0.00 ^(c)	43	4500
S-2a	Geyser Spring, S. Bank Mine ^(d)	69.5	400	3.23	-29.4	1.10	20	350
Sg	Hot Sulfur Spring, Seigler Springs ^(e)	52.0	683	-8.14	-55.9	0.23	46	6000

(a) Deuterium and oxygen-18 analyses by M. Colucci, Southern Methodist University, except where noted; tritium analyses by H. G. Ostlund, University of Miami, except where noted.

(b) Minimum age using piston-flow model; maximum age using well-mixed model; see text and Table IV.

(c) Tritium value in 1977 was 0.27 T.U. (Forsythe, 1978); the 1977 value is used to estimate ages.

(d) Data from White et al. (1973) on sample collected in 1957.

(e) Data from White et al. (1973) on sample collected in 1954, except tritium value which is from sample collected in 1977 (Forsythe, 1978).

Table III
Selected Gas Analyses of Thermal/Mineral Features of the Clear Lake Region
(values in mol-%)

Sample No.	Description	Date Collected	Temp (°C)	CO ₂	H ₂ S	H ₂	CH ₄	N ₂	NH ₃	Ar	He	O ₂	CO	C ₂ H ₆
<u>"Caustic" Gas Samples (a)</u>														
CL91-1A	Herman Pit, Sulfur Bank Mine	03/06/91	10.1	86.62	0.0325	0.000	10.508	2.661	0.0018	0.0107	0.0200	0.0801	--	0.0000
CL91-1B	Herman Pit, Sulfur Bank Mine	03/06/91	10.1	87.12	0.0169	0.0000	9.980	2.564	0.0010	0.0153	0.0077	0.1545	--	0.0000
CL91-2	Big Soda Spring	03/06/91	31.3	99.84	0.0000	0.0000	0.146	0.014	0.0003	0.0005	0.0000	0.0029	--	0.0008
CL91-5	Baker Soda Spring	03/07/91	21.3	98.78	0.0000	0.0000	0.714	0.392	0.0002	0.0062	0.0022	0.1100	--	0.0006
CL91-12	Jones Hot Spring	03/09/91	61.9	40.65	0.3691	0.0353	51.898	6.757	0.0024	0.0353	0.0000	0.0943	--	0.1473
CL91-16	Grizzly Spring	03/09/91	19.4	98.31	0.0000	0.0000	1.112	0.289	0.0001	0.0073	0.0000	0.2919	--	0.0000
CL91-22	Sulfur Creek Spring	03/11/91	21.0	97.45	0.3833	0.0000	0.791	1.023	0.0004	0.0211	0.0000	0.0246	--	0.0017
CL91-24	Gas Spring	03/12/91	10.0	96.15	0.0000	0.0000	1.107	2.810	0.0003	0.0000	0.0000	0.0000	--	0.0000
CL91-26	Howard Hot Spring	03/13/91	46.3	99.65	0.0000	0.0011	0.058	0.204	0.0001	0.0049	0.0000	0.0778	--	0.0000
CL91-28	Borax Lake Gas Well	03/14/91	10.0	85.37	0.0064	0.0000	13.414	1.144	0.0007	0.0000	0.0000	0.0000	--	0.0000
<u>"Flow-Through" Gas Samples (b)</u>														
CL91-4	Hog Hollow Spring	03/07/91	30.0	84.65	<0.0005	<0.0002	1.23	10.81	--	0.135	0.0004	2.85	<0.001	0.0026
CL91-7	Kelseyville Methane Well	03/08/91	10.4	66.94	<0.0005	<0.0002	26.99	5.73	--	0.0293	0.0016	0.660	<0.001	0.0718
CL91-10	Spier's Spring	03/08/91	24.2	82.79	<0.0005	0.0002	0.0243	14.16	--	0.177	0.0006	3.70	<0.001	<0.0002
CL91-12	Jones Hot Spring	03/09/91	61.9	47.16	0.60	0.108	51.08	2.28	--	0.0118	0.0013	0.144	<0.001	0.103
CL91-19	Anderson Hot Spring	03/11/91	49.4	82.09	0.351	0.135	5.19	10.14	--	0.12	0.0006	1.76	<0.001	0.039
CL91-28	Borax Lake Gas Well	03/14/91	10.0	19.84	<0.0005	<0.0002	3.53	60.4	--	0.774	0.0012	16.23	<0.001	0.0022
C0181B77	Wilbur Hot Spring	?/??	-55	95.59	2.92	<0.01	3.58	0.28	--	<0.02	<0.02	0.04	--	<0.05
	Fresh Air			0.032	<0.0005	<0.0005	<0.0002	78.3	--	0.93	<0.005	21.0	--	<0.01

(a) Gas analyses by P. E. Trujillo, LANL.

(b) Gas analyses by W. C. Evans, USGS; isotope analyses by L. D. White, USGS.

(c) Temperature calculated using empirical gas geothermometer of D'Amore and Panichi (1981). Values in parentheses are calculated from adjusted analyses using at least 0.001 mol-% H₂, and 0.001 mol-% H₂S.

Table III (continued)

C ₃ H ₈	C ₄ H ₁₀	Total	N ₂ /Ar	¹³ C-CO ₂ (‰)	T-DP(c) (°C)
--	--	99.93	249	--	(96)
--	--	99.95	168	--	(105)
--	--	100.00	28.1	--	(56)
--	--	100.01	63.2	--	(50)
--	--	99.99	191	--	135
--	--	100.02	39.6	--	(48)
--	--	99.70	48.5	--	(126)
--	--	100.07	--	--	(49)
--	--	99.99	41.6	--	(60)
--	--	99.94	--	--	(84)
<0.0005	<0.0005	99.68	80.1	-12.7	(50)
<0.0006	<0.0005	100.42	196	-10.5	(16)
<0.001	<0.001	100.85	80.0	-12.8	(79)
0.0196	0.0029	101.51	193	-9.0	157
0.0171	0.007	99.85	84.5	-13.3	218
<0.0005	<0.001	100.78	78.0	-5.6	(68)
--	--	99.41	--	-9.68	--
--	--	100.26	84.2	--	--

Table IVa
Tritium Concentrations and Residence Times for Selected Base Years in Northern California,
Well-mixed Case (Menlo Park Datum)

Residence Time (yr)	Tritium Concentration (T.U.)													
	1960	1965	1970	1975	1980	1984	1985	1986	1987	1988	1989	1990	1991	1992
1	80.39	267.65	52.46	35.17	25.42	13.57	10.33	8.59	7.44	6.56	5.82	5.17	4.61	4.10
2	74.25	247.29	69.10	36.72	25.73	16.05	12.70	10.41	8.75	7.49	6.50	5.70	5.02	4.44
5	49.04	168.00	89.30	47.30	29.40	19.71	16.88	14.51	12.52	10.83	9.41	8.19	7.15	6.29
10	30.04	105.83	76.52	49.11	32.66	23.13	20.64	18.42	16.43	14.66	13.08	11.67	10.41	9.29
15	21.54	76.92	62.21	43.82	31.05	23.05	20.96	19.06	17.32	15.73	14.28	12.96	11.75	10.66
20	16.77	60.36	51.72	38.36	28.30	21.66	19.92	18.31	16.82	15.44	14.16	12.98	11.90	10.90
35	10.07	36.34	33.87	26.96	21.11	16.94	15.82	14.76	13.77	12.83	11.95	11.13	10.35	9.63
50	7.19	26.30	25.07	20.56	16.53	13.54	12.73	11.96	11.22	10.53	9.87	9.25	8.66	8.11
75	4.87	17.88	17.46	14.66	12.04	10.03	9.48	8.95	8.45	7.97	7.51	7.08	6.66	6.27
100	3.68	13.54	13.39	11.38	9.44	7.94	7.52	7.13	6.74	6.38	6.03	5.69	5.37	5.07
150	2.47	9.12	9.13	7.85	6.59	5.59	5.31	5.04	4.78	4.54	4.30	4.07	3.86	3.65
200	1.86	6.87	6.92	5.99	5.06	4.31	4.10	3.90	3.70	3.52	3.34	3.17	3.00	2.84
300	1.25	4.61	4.67	4.06	3.45	2.95	2.81	2.68	2.55	2.42	2.30	2.19	2.08	1.97
400	0.94	3.46	3.52	3.07	2.62	2.25	2.14	2.04	1.94	1.85	1.76	1.67	1.59	1.51
500	0.75	2.78	2.83	2.47	2.11	1.81	1.73	1.65	1.57	1.49	1.42	1.35	1.28	1.22
750	0.50	1.85	1.89	1.66	1.42	1.22	1.17	1.11	1.06	1.01	0.96	0.91	0.87	0.83
1000	0.38	1.39	1.42	1.25	1.07	0.92	0.88	0.84	0.80	0.76	0.73	0.69	0.66	0.62
1500	0.25	0.93	0.95	0.84	0.72	0.62	0.59	0.56	0.54	0.51	0.49	0.46	0.44	0.42
2000	0.19	0.70	0.71	0.63	0.54	0.46	0.44	0.42	0.40	0.38	0.37	0.35	0.33	0.32
3000	0.13	0.46	0.48	0.42	0.36	0.31	0.30	0.28	0.27	0.26	0.25	0.23	0.22	0.21
4000	0.09	0.35	0.36	0.31	0.27	0.23	0.22	0.21	0.20	0.19	0.18	0.18	0.17	0.16
5000	0.08	0.28	0.29	0.25	0.22	0.19	0.18	0.17	0.16	0.15	0.15	0.14	0.13	0.13
7500	0.05	0.19	0.19	0.17	0.14	0.12	0.12	0.11	0.11	0.10	0.10	0.09	0.09	0.08
10000	0.04	0.14	0.14	0.13	0.11	0.09	0.09	0.09	0.08	0.08	0.07	0.07	0.07	0.06

Table V
Calculated Temperatures (°C) for Selected Thermal/Mineral Waters in the Clear Lake Region, California
Using a Standard Suite of Chemical Geothermometers(a)

Sample No.	Name	Measured	Silica			Na-K-Ca		Na/K	Na/Li	Mg/Li	K/Mg	Na-K-Ca(Mg)	
		Temp. (°C)	Am	CH	QC	4/3	1/3	(WE)	(Cl<7000)			R	Mg-Corr
CL-91-2	Big Soda Spring	31.3	32	129	154	73	(168)	209	185	42	45	68	"Cool"
CL-91-4	Hog Hollow Spring	30.3	38	136	161	75	(144)	139	136	54	54	41	31
CL-91-5	Baker Soda Spring	21.3	11	102	130	(263)	205	164	130	100	102	70	"Cool"
CL-91-8	Agric. Park #3 Well	65.7	53	154	176	(154)	229	306	229	90	93	39	40
CL-91-9	Ettewa Spring	21.7	19	113	139	(112)	116	56	80	40	36	91	"Cool"
CL-91-10	Spier's Spring	24.2	39	137	162	(127)	146	107	152	54	41	93	"Cool"
CL-91-12	Jones Hot Spring	61.9	11	103	131	(710)	237	127	(97)	166	162	20	104
CL-91-13	Wilbur Hot Spring	55.6	56	158	180	(673)	235	129	(96)	153	152	27	74
CL-91-15	Complexion Spring	9.8	--	20	53	(689)	205	82	--	--	157	18	105
CL-91-16	Grizzly Spring	19.4	12	104	131	(189)	131	52	96	72	54	94	"Cool"
CL-91-17	Chalk Mountain Spring	16.1	17	110	137	(273)	220	194	172	101	96	82	"Cool"
CL-91-19	Anderson Hot Spring	49.4	9	100	128	45	(184)	309	182	30	48	35	43
CL-91-21	Gordon's Warm Spring	34.6	46	146	170	75	(149)	152	138	31	36	80	"Cool"
CL-91-22	Sulfur Creek Spring	21.0	35	133	157	(120)	174	176	206	56	46	90	"Cool"
CL-91-23	Newman Spring	29.5	49	150	173	(158)	135	70	260	133	61	83	"Cool"
CL-91-26	Howard Spring	46.3	41	140	164	(131)	175	171	192	55	48	92	"Cool"
Sg	Seigler Hot Springs ^(b)	53.3	48	148	171	(121)	186	208	190	49	50	89	"Cool"
S-2	Geyser Spring, SB Mine ^(c)	69.5	--	63	94	(172)	132	60	163	115	67	74	"Cool"
	Bradley #1 ^(d)	200	34	132	156	(358)	228	177	--	--	157	4	205
	Bradley #2 ^(d)	175	--	81	111	(250)	124	25	--	--	102	27	63
	Borax Lake 7-1 ^(d)	250	--	--	--	(203)	170	117	162	141	108	25	68
	Audry #1 ^(d)	297	95	206	220	(277)	244	249	242	168	142	13	147
	Jorgensen #1 ^(d)	275	112	226	237	(274)	206	162	--	--	140	8	159

(a) Temperatures calculated from the GATHERM code of Urbani (1986). Equations for many geothermometers are found in Fournier (1981), except where noted; AM = amorphous silica; CH = chalcedony; QC = quartz conductive; 4/3 and 1/3 refer to the beta factor of the Na-K-Ca geothermometer; Na/K (WE) = White-Ellis equation (Trudell, 1976); Na/Li (Cl<7000) = equation for dilute waters of Fouillac and Michard (1981) except values in parentheses (concentrated waters); Mg/Li = equation of Kharaka and Mariner (1989); K/Mg = equation of Giggenbach (1986); R and Mg-corr refer to the R factor and corrected value of the Na-K-Ca geothermometer of Fournier and Potter (1979). Values in parentheses violate rules of application.

(b) Temperatures calculated from chemical values of Thompson et al. (1981).

(c) Temperatures calculated from chemical values of White et al. (1973).

(d) Calculated temperatures and measured temperatures from data in Beall (1985).

III. Conclusions

Thermal/mineral waters of the Clear Lake region can be subdivided into thermal meteoric and connate types that are weakly gradational chemically and strongly gradational isotopically to each other. Although many Clear Lake waters resemble geothermal fluids at known high-temperature geothermal reservoirs, Clear Lake waters differ widely from location to location. Gas compositions also vary widely from location to location. Many gases in the Clear Lake region contain chemical signatures from air and air-saturated water suggestive of near-surface effects. Although some Clear Lake region waters contain very little tritium, most contain moderate amounts of tritium (>0.4 T.U.), suggesting that they are mixed with some younger, near-surface water. Chemical geothermometers applied to waters and gases suggest that most Clear Lake fluids equilibrated at temperatures $\leq 150^{\circ}\text{C}$.

Because of chemical and isotopic inhomogeneity, we conclude that Clear Lake waters do not originate from one large liquid-dominated reservoir. Reservoirs at Sulphur Bank Mine, Wilbur Springs district, the Agricultural Park near Sulphur Mound Mine, Howard Hot Springs, etc., are not commercially exploitable for electricity because of small size, subcommercial temperatures, and other factors. Because high temperatures ($> 200^{\circ}\text{C}$) but little or no fluids occur in most wells drilled in the Clear Lake region from the Collayomi fault zone northeast to Sulphur Bank Mine, HDR technologies have the best chance for commercial success in the region. HDR potential beneath the Wilbur Springs area, Chalk Mountain area, Bartlett Springs fault zone, and other sites beyond the main volcanic field is not promising based on temperatures measured in existing wells ($\leq 140^{\circ}\text{C}$ at 2360 m) or temperatures based on chemical geothermometers. Temperatures of 200°C at 3000 m or shallower are required for economic development of electricity by HDR (Goff and Decker, 1983) because of drilling and engineering costs and probable limitations on power plant designs.

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