

(200)

Ref 10

Am. 16-469

USGS-OFR-76-469

UNITED STATES (DEPARTMENT OF THE INTERIOR)

GEOLOGICAL SURVEY

[Report to the
file series]

GEOCHEMICAL PREDICTION OF AQUIFER TEMPERATURES IN THE
GEOTHERMAL SYSTEM AT LONG VALLEY, CALIFORNIA

by
R. O. Fournier, M. L. Sorey, R. H. Mariner, and A. H. Truesdell

Open-file Report

76-469

This report is preliminary
and has not been edited or
reviewed for conformity with
Geological Survey standards

271203

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
MASTER

by

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

GEOCHEMICAL PREDICTION OF AQUIFER TEMPERATURES IN THE GEOTHERMAL SYSTEM
AT LONG VALLEY, CALIFORNIA

R. O. Fournier, M. L. Sorey, R. H. Mariner, and A. H. Truesdell
U.S. Geological Survey, Menlo Park, California (U.S.A.)

ABSTRACT

This paper was written to (1) illustrate a process of evaluating a geothermal energy prospect from a geochemical point of view, and (2) present a geochemical evaluation of the hydrothermal system at Long Valley, California.

Temperatures of aquifers feeding thermal springs and wells in Long Valley, California were estimated using silica and Na-K-Ca geothermometers and warm spring mixing models. The results ranged from 160° to 219°C. This information was then used to construct a diagram showing enthalpy-chloride relationships for the various thermal waters in the Long Valley region. The enthalpy-chloride information suggests that a 282°C aquifer with water containing about 375 milligrams chloride per kilogram of water is present somewhere deep in the system. That deep water would be related to 219°C Casa Diablo water by mixing with cold water, and to 201°C Hot Creek water by boiling and steam loss. Oxygen and deuterium isotopic data are consistent with this interpretation. An aquifer at 282°C with 375 mg/kg chloride allows the estimated convective heat flow in Long Valley to be increased from 4.3×10^7 to 6.6×10^7 cal/sec.

INTRODUCTION

This paper was written for two reasons: (1) to illustrate a process of evaluating a geothermal energy prospect from a geochemical point of view, and (2) to present a geochemical evaluation of the hydrothermal system at Long Valley, California.

The hydrology and geochemistry of the hydrothermal system at Long Valley, California have been described recently by Lachenbruch and others (1976), Sorey and Lewis (1976), and Mariner and Willey (1976). New information provided by M. L. Sorey, N. L. Nehring, and L. D. White (written communication, 1976) about the variation in isotopic composition of groundwater in the region and new techniques of interpreting chemical (Truesdell and Fournier, 1976a; 1976b; Fournier and others, 1976) and isotopic data (Truesdell and others, in press) from geothermal systems have prompted this reevaluation of the Long Valley hydrothermal system. The results of this reinterpretation suggest that thermal waters convecting deep in the system are hotter and slightly more saline than previously thought. However, the general model of the hydrothermal system previously proposed by Lachenbruch and Sorey (1976) and Sorey and Lewis (1976) remains unchanged. In that model the main recharge is by meteoric water that falls on the Sierra Nevada fault block at the west side of the Long Valley caldera. During deep circulation and flow toward the east and southeast, the water becomes heated. Finally the heated water mixes with and is cooled by meteoric water that falls east of the Sierra Nevada fault block. The distribution of hot springs is controlled by fractures in the caldera floor.

CHEMICAL GEOTHERMOMETERS

Chemical and isotopic data and temperatures of reservoirs feeding selected thermal springs and wells in Long Valley, estimated using the silica geothermometer of Fournier and Rowe (1966) and the Na-K-Ca geothermometer of Fournier and Truesdell (1973), are given in Table 1. The estimated reservoir temperatures are compared in Figure 1.

In Figure 1, thermal waters with the same estimated reservoir temperature from both silica and Na-K-Ca relationships will plot on the line labeled "equal temperature". It is likely either that such waters are not mixtures of higher-temperature and lower-temperature water or that the silica and Na-K-Ca reequilibrated with the wall rock after mixing. Waters which have reequilibrated are not suitable for use with warm spring mixing models (Fournier and Truesdell, 1974; Truesdell and Fournier, 1976a) to obtain information about subsurface temperature. Waters labeled d, e, and g may fall into this category. Furthermore, the low measured temperatures of those springs, 41° to 56°C, suggest that these waters have cooled by conduction while moving to the surface from reservoirs at 160° to 200°C.

The only water that plots on the high silica temperature side of the "equal temperature" line in Figure 1 is labeled c. That water was collected from a hot-pool with a large surface area and no overflow. It is likely that evaporation has caused silica to be concentrated in that water. Thus the high temperature estimated from the silica content is suspect. Because the Na-K-Ca geothermometer uses ratios of constituents it is less sensitive than the silica geothermometer to changes in absolute concentration. However, nonflowing springs generally are less suitable

than flowing springs for estimating aquifer temperatures and water c will not be considered further.

Waters labeled a, b, f, and h fall significantly below the "equal temperature" line of Figure 1. This situation may come about in various ways: (1) the emerging water may be a mixture of hot and cold water that has not equilibrated with the surrounding rock after mixing (silica-estimated temperatures generally are decreased more than Na-K-Ca-estimated temperatures by mixing); (2) silica may precipitate from cooling hot water during ascent while Na-K-Ca relationships remain unchanged; or (3) calcium may precipitate from the water during ascent (probably as calcite due to loss of CO_2), and, if Na and K do not adjust to that change through chemical reactions with clays, zeolites, or other minerals, the Na-K-Ca geothermometer will give an anomalously high estimated temperature. Water from the Casa Diablo well, labeled b, probably falls into category 3. Chemical analysis showed that that water was supersaturated with calcite after collection and it is likely that some calcite precipitated from the water before the water was filtered. Therefore, the silica temperature, 219°C , is more reliable.

Waters labeled a, f, and h probably are mixed waters and Na-K-Ca relationships give minimum probable temperatures of the hot water component. Spring a has a relatively high measured temperature (79°C) and a high rate of discharge which suggests little cooling by conduction or boiling after mixing. Therefore, spring a is suitable for application of a silica mixing model. Spring f has a relatively low rate of discharge and high silica content for its measured temperature. It is likely that this water has cooled appreciably by conduction after mixing, so it may be unsuitable for application of a silica mixing model.

Although the temperature, 90°C, of spring h is slightly below boiling for the region (94°C), it emerges near several boiling springs that have compositions similar to h. It is likely that h also may have lost some heat by boiling after mixing and, therefore, calculations based on the silica mixing model using a temperature of 90°C are likely to be in error (Fournier and Truesdell, 1974). However, the probable temperature of water h before near surface boiling occurred can be estimated when the temperatures and chloride contents of other springs at that locality are considered. Figure 2 shows a plot of chloride vs. temperature for springs emerging along Hot Creek. Sample 2 is below boiling and, with sample 1, defines a mixing or dilution line with non-thermal water, point 6. It is likely that water h in table 1 originally lay along the extension of this dilution line at a temperature of about 103°C, the rectangle labeled 8.

APPLICATION OF THE WARM SPRING MIXING MODEL

The assumptions and conditions under which the warm spring mixing model can be used are given by Fournier and Truesdell (1974). It is necessary to know the temperatures and silica contents of both a large-discharge warm spring and the cold water that mixed with the hot water component.

Measured temperatures and silica contents of groundwater at Long Valley are shown in Figure 3. Waters with temperatures less than 15°C have silica contents ranging from 16 to 77 mg/l. Although this shows that there is a wide range in possible silica values for the cold water that mixes with hot water, it is easy to evaluate what

effect different silica values for cold water have on the calculated original temperature of the hot water fraction. Truesdell and Fournier (1976a) showed that this can be done quickly and accurately using a plot of dissolved silica and water enthalpy, as shown in Figure 4. We have assumed that the cold water fraction has an enthalpy of 10 calories per gram^{1/} (cal/gm) and a silica content of 40 milligrams per kilogram (mg/kg) of water, point c_1 of Figure 4. Mixed water, h_1 , from a spring at Hot Creek has a silica content of 150 mg/kg and an enthalpy of 103 cal/gm, as estimated using Figure 2. The hot water fraction would then have a silica content, controlled by the solubility of quartz, of 270 mg/kg and an enthalpy of 205 cal/gm, point h_2 . With a cold water silica content of 20 mg/kg, point c_2 , the hot water component would have an enthalpy of 213 cal/gm, point h_3 . Increasing the cold water silica to 60 mg/kg, point c_3 , requires that the hot water component have an enthalpy of 197 cal/gm, point h_4 . Thus, using the silica mixing model, the temperature of the hot water fraction (and the temperature of the aquifer where water-rock chemical equilibration last occurred) is estimated to be $201^\circ \pm 8^\circ\text{C}$. This agrees moderately well with the temperature estimated by the Na-K-Ca method, 192°C . By a similar procedure the silica content and temperature of mixed water a yield an estimated temperature of $160 \pm 15^\circ\text{C}$ for the high temperature component of that water.

ENTHALPY-CHLORIDE RELATIONSHIPS

Truesdell and Fournier (1976b) and Fournier and others (1976) have described the use of enthalpy-chloride diagrams for estimating aquifer

^{1/} International Table calories per gram are used throughout this paper.
1 I.T. calorie = 4.1868 joules.

temperatures deeper in geothermal systems than can be estimated using conventional chemical geothermometers and the silica mixing model. Figure 5 shows the enthalpy-chloride relationships for waters from Long Valley. In Figure 5, of the many points representing calculated aquifer conditions (triangles), points \underline{a}_2 , \underline{h}_2 and \underline{b}_2 are considered to be most reliable. Point \underline{a}_2 was obtained by extending a line from the cold-water point through \underline{a}_1 (the measured temperature plotted as enthalpy and chloride content of water \underline{a} , Table 1) to the enthalpy of the hot water component calculated using the silica mixing model shown in Figure 4. Point \underline{h}_2 was obtained in a similar manner using the measured chloride content and estimated temperature before near surface boiling, 103°C, of \underline{h}_1 . The error bars around points \underline{a}_2 and \underline{h}_2 in Figure 5 show the effect of assuming 20 and 60 mg/kg respectively instead of 40 mg/kg for the silica content of the cold water fraction in Figure 4.

In Figure 5, point \underline{b}_2 plots directly above \underline{b}_1 because no steam was lost from the water at the time of sampling. The total flow of water and steam coming from a well at Casa Diablo was condensed in aluminum tubing submerged in an ice bath before the water sample was collected for analysis. The enthalpy of \underline{b}_2 was estimated using the silica geothermometer (Fournier and Rowe, 1966) assuming conductive cooling.

If there is a common parent water for \underline{a}_2 , \underline{b}_2 and \underline{h}_2 , it would have to be within the stippled area bounded by the extension of the lines \underline{b}_2x and \underline{h}_2x . The common parent water with the lowest possible

enthalpy is x, which is related to b₂ entirely by mixing with cold, dilute water and is related to h₂ entirely by boiling and loss of steam. Point x has a chloride content of 375 mg/kg and an enthalpy of 298 ± 10 cal/gm (water temperature of 282° ± 10°C). It will be shown later that oxygen and hydrogen isotopic data also are consistent with the existence of a water reservoir at 282°C.

If waters d, e, and g are not mixed waters, they must have cooled in great part conductively from temperatures equal to or higher than those predicted using the silica and Na-K-Ca geothermometers. The predicted aquifer temperatures, using the Na-K-Ca geothermometer, were converted to enthalpies and plotted in Figure 5 as triangles d₂, e₂, and g₂ respectively. The relationship, if any, of these waters to other waters in Long Valley is not clear. Speculation about possible relationships will come after a discussion of the oxygen and hydrogen isotopic data for Long Valley waters.

OXYGEN AND HYDROGEN ISOTOPIC RELATIONSHIPS

Figure 6 is a plot of isotopic data for deuterium and oxygen given in standard δ values, parts per mil (‰) relative to SMOW, for thermal and fresh waters from Long Valley. At the time that Mariner and Willey (1976) interpreted the geochemistry of these water samples, i was the isotopically-heaviest fresh water and they assumed that water similar to i was typical of the recharge for the geothermal system. It is generally assumed that, as meteoric water percolates deep underground and becomes heated, the oxygen isotopes will react with the oxygen in the rocks while the hydrogen isotopes remain almost unchanged. Thus, the isotopic

composition of the recharge water would shift toward b. Water b was interpreted by Mariner and Willey (1976) to be a sample of the hottest water in the system: an end-member water which mixed with cold water isotopically-similar to j yielding the other thermal waters in the region. Isotopic analyses of additional fresh water samples collected by M. L. Sorey, however, combined with the hydrologic model developed by Lachenbruch and others (1976), indicate that the recharge water should be similar in $\delta^{18}\text{O}$ to points p, r, and t of Figure 6. If this is so, water b is a mixed water rather than an end-member. This is consistent with the model developed in Figure 5. Furthermore, it will be shown that water in a 282°C aquifer would have an isotopic composition that plots at point x in Figure 6: a position that also fits in nicely with the isotopic trend shown by the thermal waters in the area.

If one looks only at the oxygen and hydrogen isotopic data there appears to be a simple mixing relationship among the waters. However, when silica, chloride, and heat content are considered, the situation appears more complex. Relationships between δD and chloride are shown in Figure 7 and between $\delta^{18}\text{O}$ and chloride in Figure 8. According to the relationships shown in Figure 5, water b is a mixture of cold water (assumed to be similar to j) and hot water at 282°C with Cl = 375 mg/kg. In Figures 7 and 8, point b₂ is derived by extending a straight line from point j through b, to a chloride content of 375 mg/kg. This fixes the δD value of point b₂ in Figure 7 at -111.1, and the $\delta^{18}\text{O}$ in Figure 8 at -13.2. In a similar fashion, points a₂ and h₂ are derived in Figures 7 and 8 by extending

lines from j through a and h to chloride contents of 437 and 472 mg/kg respectively; giving $\delta D = -112.3$ for a₂ and -110.9 for h₂, and $\delta^{18}O = -13.30$ for a₂ and -12.55 for h₂. In the discussion that follows, the isotopic composition of water at point x of Figure 5 is fixed based on enthalpy and chloride considerations involving water b from the well at Casa Diablo. The calculated isotopic compositions of a₂ and h₂ will then be checked to see if they are compatible with a model in which h₂ is derived from x by boiling and h₁ is a mixture of h₂ and j water; water a₂ is derived from h₂ by additional boiling (or conductive cooling) followed by mixing with j water and equilibration at about 160°C after mixing. After equilibration additional mixing with j water brings the composition to a₁.

Truesdell and others (in press) have calculated the variations in δD and $\delta^{18}O$ due to continuous and "single stage" steam separation from ascending thermal waters at Yellowstone National Park. In a continuous steam loss process the evolving steam moves away from the remaining liquid water as soon as it (the steam) forms. Once formed, the steam does not reequilibrate with the parent water at a lower temperature. In single stage steam separation the water may boil over a range of temperatures and pressures, but the water and steam continuously reequilibrate isotopically until the steam physically separates at a given temperature. Using equations and tables from Truesdell and others (in press), we have made similar calculations for the Long Valley waters. The results are shown in Figures 9 and 10, where curve A is for continuous steam separation and curve B is for single stage steam separation.

In Figure 9, point x was determined by extending a straight line from j through b₂ to the chloride content of x shown in Figure 5. Similarly, points a₂ and h₂ were determined by extending straight lines from j through points a₁ and h₁ to the chloride contents of a₂ and h₂ shown in Figure 5. The deuterium contents of a₂ and h₂ were also previously determined from the relationships shown in Figure 7. The steam separation curves, A and B, showing the enthalpy and δD of liquid water in equilibrium with steam after steam separates, were constructed so that they would pass through point x, the calculated 282°C parent water. Points along curves A and B to the right of point x show the isotopic effect that would be obtained when boiling starts at any given temperature above 282°C up to 360°C and the final steam separation takes place at 282°C. In that temperature range, it makes little difference whether steam separates continuously or by a single step process. Points along curves A and B to the left of point x show the isotopic effect that would be obtained by boiling at successively lower pressures from 282°C to any given lower temperature down to 90°C.

Curve C shows the hydrogen isotopic compositions of steam, in equilibrium with liquid water, that separate at any given temperature from the water of curve A. If all the steam that separates by a continuous steam separation process (curve A) condenses in one place, the bulk isotopic composition of that steam is shown by curve E. Curve D shows the isotopic composition of steam in equilibrium with water at given temperatures along curve B. Figure 10 shows oxygen isotopic data presented in the same manner as the hydrogen isotopic data of Figure 9.

According to the model presented in Figure 5, water \underline{h}_2 is derived from a 282°C water by boiling and then it mixes with water \underline{j} to give water \underline{h}_1 . The isotopic data presented in Figures 9 and 10 are in complete accord with that model; point \underline{h}_2 falls between curves A and B in Figure 9 and close to curve A in Figure 10. The position of \underline{a}_2 in Figures 9 and 10 is appropriate for continued boiling of \underline{h}_2 dropping the temperature about 20°C and then mixing with \underline{j} water.

The origin and history of waters \underline{d} , \underline{e} , and \underline{g} are difficult to establish, and it will be shown subsequently that little confidence can be placed upon conclusions drawn from their temperatures and chemical compositions. They are discussed in detail to illustrate that the interpretation of hot spring water compositions is not always straightforward. Their relatively low chloride contents suggest that they are mixed waters. Furthermore, the near agreement of the silica and Na-K-Ca geothermometers suggests that these waters equilibrated with the surrounding rock after mixing and that the temperatures of equilibration are therefore given by the geothermometers. Assuming these conditions, points \underline{d}_2 , \underline{e}_2 , and \underline{g}_2 were plotted in Figures 5, 9, and 10.

In Figure 5, if water \underline{d}_2 is a mixture of cold water, \underline{j} , and a hot water component common to \underline{b}_2 and \underline{h}_2 , the hot water must have an enthalpy of at least 377 cal/gm and a temperature of 338°C. This is not consistent with the deuterium and oxygen isotope data, however. Figures 9 and 10 show that a 338°C water would have to mix with a cold water having $\delta D = -138.0$ and $\delta^{18}O = -18.75$ (point \underline{Y}_3 in Figs. 9 and 10). There is no indication of cold water isotopically that light in the Long Valley region.

An alternative possibility is that waters d_2 , e_2 , and g_2 result from mixing of 282°C water with a relatively high enthalpy cold water component (normal cold groundwater heated by steam). If the "cold" water has 3 mg/l chloride, its enthalpy would have to be about 125 cal/gm with corresponding $\delta D = -133.4$ and $\delta^{18}O = -18.0$ (point Y_4 in Figs. 5, 9, and 10. This also is a water isotopically too light for the Long Valley region.

The isotope and heat content relationships can be made compatible by mixing cold, j -type water with steam that separates at about 180°C from a_2 -type water. The resulting water, which must attain about 175°C (Y_5 in Figs. 9 and 10), would in turn mix with 282°C water to give the d_2 , e_2 , and g_2 waters. In this event, however, it would be necessary that cold water initially have an appreciable amount of chloride in it because the mixture of cold water and steam must have about 110 mg/l chloride to satisfy the relationships shown in Figure 5. Although the above scenario is possible, it seems improbable.

One water obtained from a shallow heat ^{flow} hole drilled in the eastern part of Long Valley (sample 35/29 E-4J1 reported by Lewis, 1974) had a temperature of 10°C and 260 mg/l chloride. If isotopically-light, nonthermal groundwater in the vicinity of springs d , e , and g has an appreciable chloride content, it may be possible that the thermal waters result simply from the condensation of steam in the cold groundwater. The high bicarbonate content relative to chloride supports this idea, but the relatively low sulfate does not. Also water 35/29 E-4J1 has a Cl/B molar ratio of 107. Springs d , e , and g have Cl/B ratios of about 6, similar to other thermal waters in Long Valley.

In view of the many inconsistencies in the chemical and isotopic data for waters d, e, and g, it is possible that, in spite of the agreement between the silica and Na-K-Ca geothermometers, these springs are mixed waters that have not equilibrated after mixing. If so, the relatively high dissolved silica and low temperatures of these waters require that they have cooled appreciably by conduction after mixing and/or dissolved additional silica by reactions with cristobalite or glassy rock after mixing.

SULFATE ISOTOPE GEOTHERMOMETRY

The dissolved sulfate-water isotope geothermometer has been applied to Long Valley waters by McKenzie and Truesdell (in press). Sulfate in Long Valley appears to be almost entirely contained in the deep thermal water component of the spring waters. This is suggested by the near constant atomic ratio of Cl/SO_4 of 5.6 to 6.9 reported by Mariner and Willey (1976). If sulfate were produced by surface atmospheric oxidation of H_2S , then the amount of sulfate would depend on the temperature of the spring and on the amount of H_2S introduced into the spring pool. If sulfate were produced by mixture of oxygenated diluting waters with H_2S -rich thermal waters in near-surface aquifers, as occurs at Yellowstone Park, Wyoming, then the amount of sulfate would depend on the amount of oxygen in the diluting water and would be nearly constant and independent of chloride contents. Apparently, little sulfate is produced in the chloride-rich waters at Long Valley by either of these processes, possibly because of a lack of H_2S in the thermal water.

The $\delta^{18}\text{O}$ contents of sulfate in Long Valley thermal waters have been measured for six waters and range from -7.2‰ to -7.8‰ SMOW. Three of these analyses are quoted from McKenzie and Truesdell (in press). As discussed in that paper, the $\delta^{18}\text{O}$ values of sulfate are nearly constant but the $\delta^{18}\text{O}$ values of water vary widely due to mixing. Because of this, the geothermometer temperatures indicated by these waters are minimum values. The constancy of $\delta^{18}\text{O}$ values of sulfate agrees with the deep origin of sulfate suggested by the Cl/SO_4 ratio. Although the waters are mixed, the $\delta^{18}\text{O}(\text{SO}_4)$ values may be averaged and combined with the $\delta^{18}\text{O}(\text{H}_2\text{O})$ value calculated above from isotope mixing models. The average $\delta^{18}\text{O}(\text{SO}_4)$ value is $-7.52 \pm .22\text{‰}$ and the calculated $\delta^{18}\text{O}(\text{H}_2\text{O})$ value is -13.2‰ . From the experimental data of Mizutani and Rafter (1969) and Mizutani (1972) and the high temperature experimental point of Lloyd (1968), the temperature dependence of the fractionation between dissolved sulfate and water is

$$10^3 \ln \alpha = 2.88 (10^6 / T^2) - 4.1$$

$$\text{where } \alpha = \frac{1000 + \delta^{18}\text{O}(\text{SO}_4)}{1000 + \delta^{18}\text{O}(\text{H}_2\text{O})}$$

From this equation the analyzed and calculated isotope compositions of sulfate and deep thermal waters at Long Valley indicate 269°C . If the $\delta^{18}\text{O}$ content of sulfate in water from the well at Casa Diablo is used, the calculated temperature of the deep water is 273°C . These temperatures may be somewhat low due to reequilibration of sulfate oxygen at lower temperatures during passage to the surface, but they support the temperature of 282°C calculated from mixing models.

CONVECTIVE HEAT DISCHARGE

Sorey and Lewis (1976) used measured spring discharges and aquifer temperatures based on chemical geothermometers and mixing models to estimate the heat discharged by the hot spring system in Long Valley. Their figures showed a total hot water discharge of 248 l/sec contributed by the hydrothermal system. The hot water deep in the system was assumed to be at 210°C and have an average chloride content of 280 mg/l (measured cold). From these figures a total convective heat discharge of 4.3×10^7 cal/sec was calculated based on individual hot spring measurements. An even higher heat flux of 5.4×10^7 cal/sec was calculated by Sorey and Lewis (1976) based on the rate of discharge of boron into Lake Crowley.

The new estimate of the temperature, 282°C, and chloride content, 375 mg/kg, of thermal water deep in the Long Valley hot spring system reported here requires a revision in the estimated total convective heat flow.

The total flux of chloride in the thermal waters would not be changed by the results reported here, and can be calculated using hot water discharge and average chloride concentration figures given by Sorey and Lewis (1976). That flux is

$$248 \text{ l/sec} \times 280 \text{ mg Cl/l} \approx 6.9 \times 10^4 \text{ mg Cl/sec.}$$

Each 0.376 mg chloride is associated with 298 calories (the enthalpy of liquid water in equilibrium with steam at 282°C) of heat. Therefore, the total convective heat flux above the mean annual temperature, 10°C, is

$$\frac{(6.9 \times 10^4 \text{ mg Cl/sec}) (298 \text{ cal} - 10 \text{ cal})}{(3.76 \times 10^{-1} \text{ mg Cl})} = 5.3 \times 10^7 \text{ cal/sec.}$$

A corresponding estimate based on the measured flux of boron of 3.5×10^3 mg B/sec from Sorey and Lewis (1976) and a calculated concentration of 18.8 mg B/kg in the 282°C water also yields 5.3×10^7 cal/sec for the convective heat flow.

As discussed by Sorey and Lewis (1976), a somewhat higher estimate for the convective heat flux is obtained from the measured rate of boron discharge in Lake Crowley. The average discharge for the period 1960-1973 from the Long Valley hydrothermal system is 136 metric tons/year, or 4.3×10^3 mg B/sec. Using the same .0188 mg boron association with 298 calories of heat, the convective heat flux would be

$$\frac{(4.3 \times 10^3 \text{ mg B/sec}) (298 \text{ cal} - 10 \text{ cal})}{(.0188 \text{ mg B})} = 6.6 \times 10^7 \text{ cal/sec.}$$

This estimate is about 25% greater than estimates based on boron and chloride measurements in individual springs. The difference is most likely due to unmeasured subsurface discharge of hot water. The required rate of hot water discharge at 282°C to supply 6.6×10^7 cal/sec of heat is 229 kg/sec or 306 l/sec.

CONCLUSIONS

The most reliable information about temperatures of aquifers feeding thermal springs and wells at Long Valley comes from interpretation of the chemical and isotopic compositions of waters from hot springs at Hot Creek, Little Hot Creek and a well at Casa Diablo. Interpretations of data from other thermal waters in the Long Valley area are difficult because of uncertainty about the amount of cooling by conduction and boiling, and

ambiguities and inconsistencies in mixing relationships. The Hot Creek Spring water appears to be a mixture of normal nonthermal groundwater and water equilibrated in an aquifer at about 201°C. The Little Hot Creek Spring water appears to have a high temperature component that equilibrated at about 160°C. If there is a common parent water deep in the hydrothermal system, feeding the springs at Hot Creek and Little Hot Creek and the well at Casa Diablo, that water is probably at 282°C. It would be related to the 219°C Casa Diablo water (b) by simple mixing with cold water and to the 201°C high-temperature component in the hot spring at Hot Creek by boiling and steam loss. This model is compatible with the variations in δD and $\delta^{18}O$ observed in the waters. An aquifer with water at 282°C and a chloride content of 375 mg/kg allows the previous (Sorey and Lewis, 1976) estimates of convective heat flow to be increased from a maximum of 5.4×10^7 cal/sec to 6.6×10^7 cal/sec.

REFERENCES

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. Sci.*, v. 264, p. 685-697.

Fournier, R. O., and Truesdell, A. H., 1970, Chemical indicators of subsurface temperature applied to hot spring waters of Yellowstone National Park, Wyoming, U.S.A., in *United Nations Symposium on Development and Utilization of Geothermal Resources*, Pisa, 1970: *Geothermics Spec. Issue 2*, v. 2, pt. 1, p. 525-535.

1973, An empirical Na-K-Ca geothermometer for natural waters: *Geochim. et Cosmochim. Acta*, v. 37, p. 1255-1275.

1974, Geochemical indicators of subsurface temperature - Part 2, Estimation of temperature and fraction of hot water mixed with cold water: *U.S. Geol. Survey Jour. Research*, v. 2, no. 3, p. 263-270.

Fournier, R. O., White, D. E., and Truesdell, A. H., 1976, Convective heat flow in Yellowstone National Park: *Proc. United Nations Symposium on Development and Use of Geothermal Resources*, San Francisco, 1975, v. 1, p. 731-739.

Lachenbruch, A. H., Sorey, M. L., Lewis, R. E., and Sass, J. H., 1976, The near-surface hydrothermal regime of Long Valley Caldera: *Jour. Geophys. Research*, v. 81, p. 763-768.

Lewis, R. E., 1974, Data on wells, springs, and thermal springs in Long Valley, Mono County, California: *U.S. Geol. Survey Open-file Report*, 52 p.

Lloyd, R. M., 1968, Oxygen isotope behavior in the sulfate-water system: *Jour. Geophys. Research*, v. 73, p. 6099-6110.

Mariner, R. H., and Willey, L. M., 1976, Geochemistry of thermal waters in Long Valley, Mono County, California: *Jour. Geophys. Research*, v. 81, p. 792-800.

McKenzie, W. F., and Truesdell, A. H., 1976, Geothermal reservoir temperatures estimated from the oxygen isotope compositions of dissolved sulfate and water from hot springs and shallow drillholes, in *Proc. Int. Atomic Energy Agency Advisory Group on the Application of Nuclear Techniques to Geothermal Studies, Pisa, 1975: Geothermics Spec. Issue (in press)*.

Mizutani, Y., 1972, Isotopic composition and underground temperature of the Otake geothermal water, Kyushu, Japan: *Geochem. Jour.*, v. 6, p. 67-73.

_____, and Rafter, T. A., 1969, Oxygen isotopic composition of sulphates. Part 3 - Oxygen isotopic fractionation in the bisulphate ion-water system: *N.Z. Jour. Sci.*, v. 12, p. 54-59.

Sorey, M. L., and Lewis, R. E., 1976, Convective heat flow from hot springs in Long Valley Caldera, Mono County, California: *Jour. Geophys. Research*, v. 81, p. 785-791.

Truesdell, A. H., and Fournier, R. O., 1976a, Procedure for estimating the temperature of a hot water component in a mixed water using a plot of dissolved silica vs enthalpy: *U.S. Geol. Survey Jour. Research*, v. 4, no. 6.

_____, 1976b, Calculation of deep temperatures in geothermal systems from the chemistry of boiling spring waters of mixed origin: *Proc. United Nations Symposium on Development and Use of Geothermal Resources, San Francisco, 1975*, v. 1, p.

Truesdell, A. H., Nathenson, Manuel, and Rye, R. O., 1976, The effects
of subsurface boiling and dilution on the isotopic compositions of
geothermal waters: Jour. Geophys. Research (in press).

FIGURE CAPTIONS

Figure 1. Comparison of reservoir temperatures estimated from the silica contents and Na-K-Ca contents of thermal waters from Long Valley, California. Letters refer to springs and wells listed in Table 1.

Figure 2. Plot of measured temperature versus chloride content for springs at Hot Creek. Points 1, 2 and 3 from Lewis (1974), point 4 unpublished data for a hot spring collected by Lewis and analyzed by J. M. Thompson, point 5 from Mariner and Willy (1976) and point 7 is the assumed temperature and chloride content of shallow nonthermal water that dilutes the thermal water. The rectangle at 8 shows the calculated range in temperatures and chloride contents expected of hot spring 5 before nearsurface boiling and/or conductive cooling.

Figure 3. Measured temperatures and silica contents of groundwaters in Long Valley, California. Letters and solid circles refer to waters listed in Table 1. Other points are shown by open circles which are plotted from data tabulated by Lewis (1974).

Figure 4. Plot for determining the dissolved silica and enthalpy values of hot- and cold-water fractions that mix underground and produce warm spring water with intermediate enthalpy and silica content (after Truesdell and Fournier, 1976a). Point h_1 is water h listed in Table 1 from a spring at Hot Creek. Points c_1 , c_2 , and c_3 show the range in silica contents likely to be present in the cold water fraction. Points h_2 , h_3 , and h_4 give the corresponding enthalpies of the hot water fraction. See text for additional discussion.

Figure 5. Enthalpy-chloride relationships for waters from Long Valley, California. Waters related by mixing with dilute, meteoric water lie along dot-dashed lines radial to the point labeled "cold water", the assumed dilute nonthermal groundwater in the region. Waters related by underground boiling processes lie along dashed curves extending away from the enthalpy of steam, which generally contains very little chloride. Circles show the enthalpies and chloride contents of the waters listed in Table 1 as directly measured. Triangles show the estimated temperatures of the aquifers where water-rock equilibration has occurred. See text for additional discussion.

Figure 6. Plot of δD versus $\delta^{18}O$ for thermal springs and fresh waters in Long Valley, California. Letters refer to waters tabulated in Table 1. Data included in the Mariner and Willey (1976) paper are shown as circles. New data for fresh waters collected by M. L. Sorey are shown as triangles. Calculated isotopic composition of water at 282°C is labeled x and shown as a square.

Figure 7. Plot of δD versus chloride for thermal springs and fresh waters in Long Valley. Circles show measured δD and chloride values. Triangles show calculated values based on the relationships shown in Figure 4. See text for additional discussion.

Figure 8. Plot of $\delta^{18}O$ versus chloride for thermal springs and fresh waters in Long Valley. Symbols are the same as those in Figure 7.

Figure 9. Plot of δD versus enthalpy showing expected variations for liquid water and steam as boiling progresses. Small dots show 10°C temperature intervals along the steam separation curves. Circles show measured enthalpies and δD values, and triangles show the corresponding calculated values at high temperatures. Letters refer to the waters listed in Table 1. See text for further explanation.

Figure 10 Plot of $\delta^{18}\text{O}$ versus enthalpy showing expected variations for liquid water and steam as boiling progresses. Small dots show 10°C temperature intervals along the steam separation curves. Circles show measured enthalpies and $\delta^{18}\text{O}$ values, and triangles show the corresponding calculated values at high temperatures. Letters refer to the waters listed in Table 1. See text for further explanation.

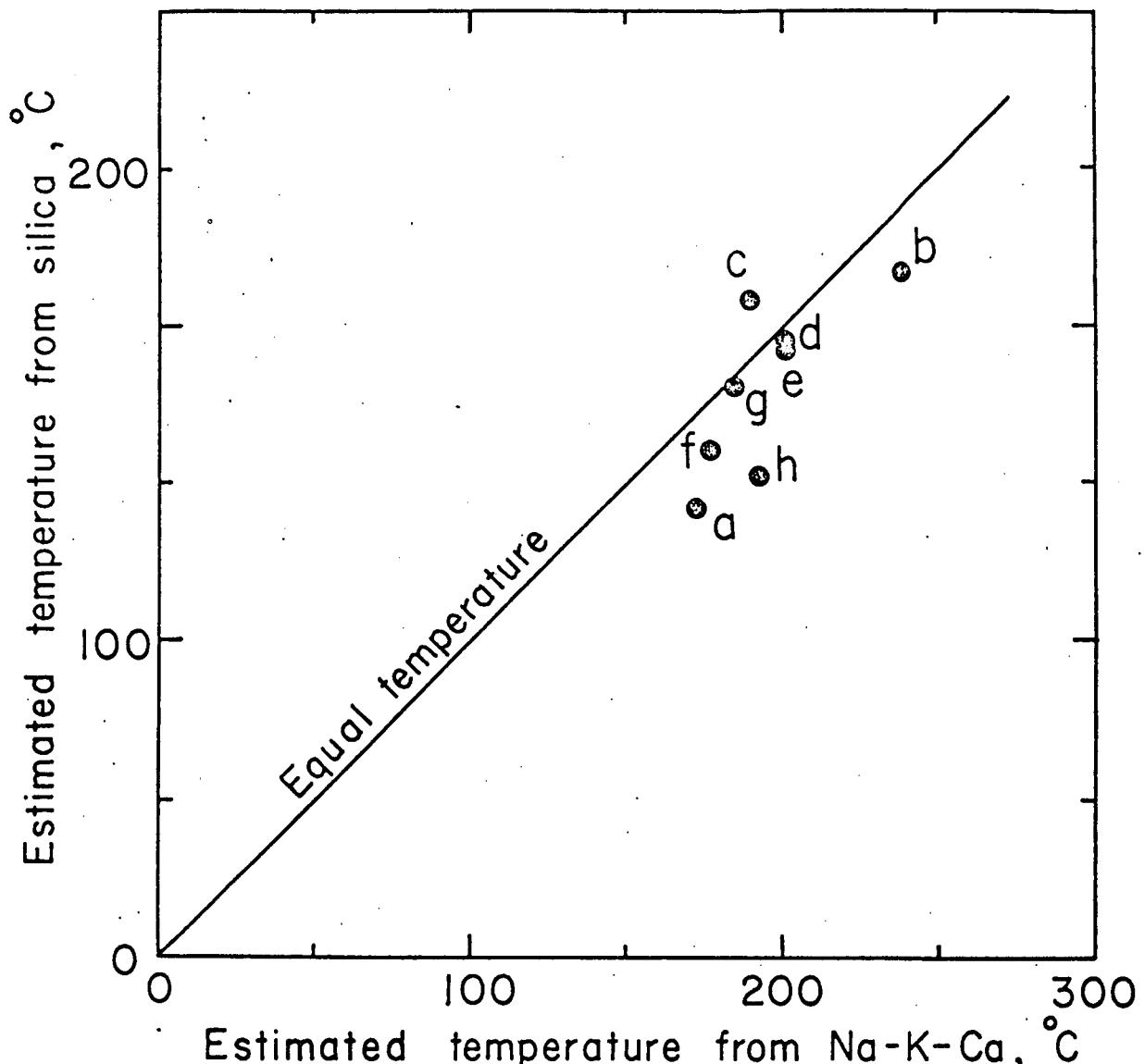


Fig. 1

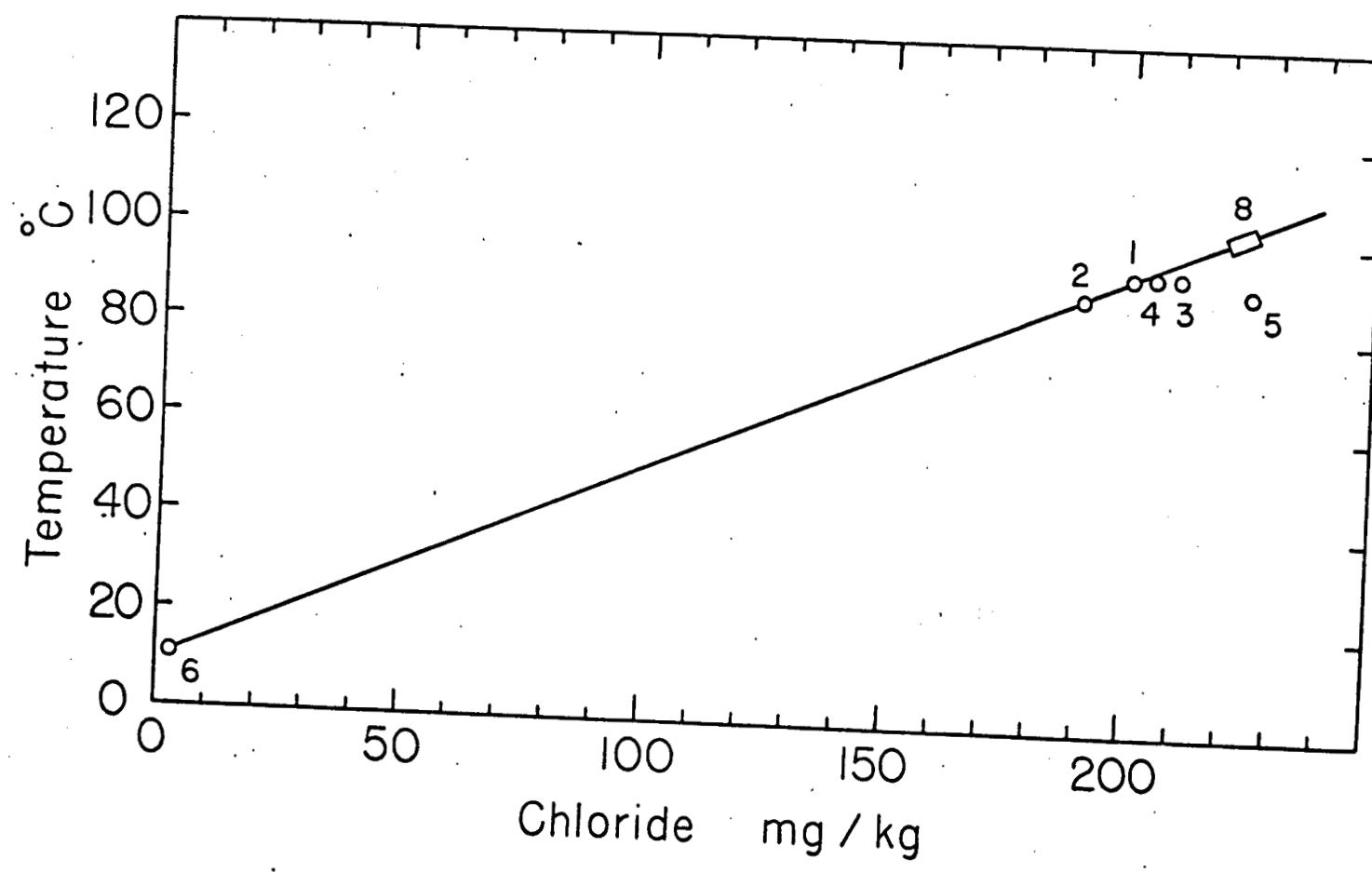


Fig. 2

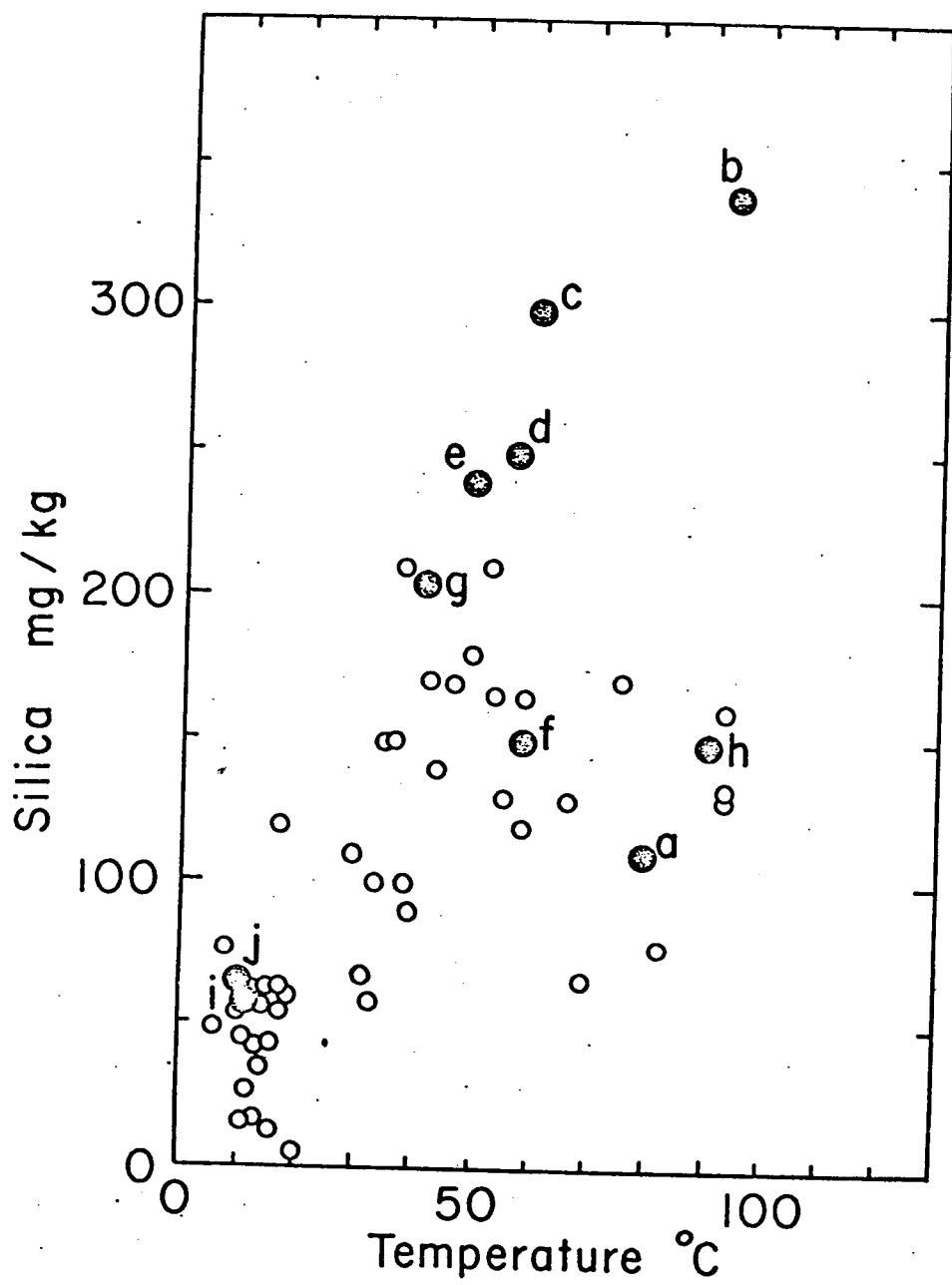


Fig. 3

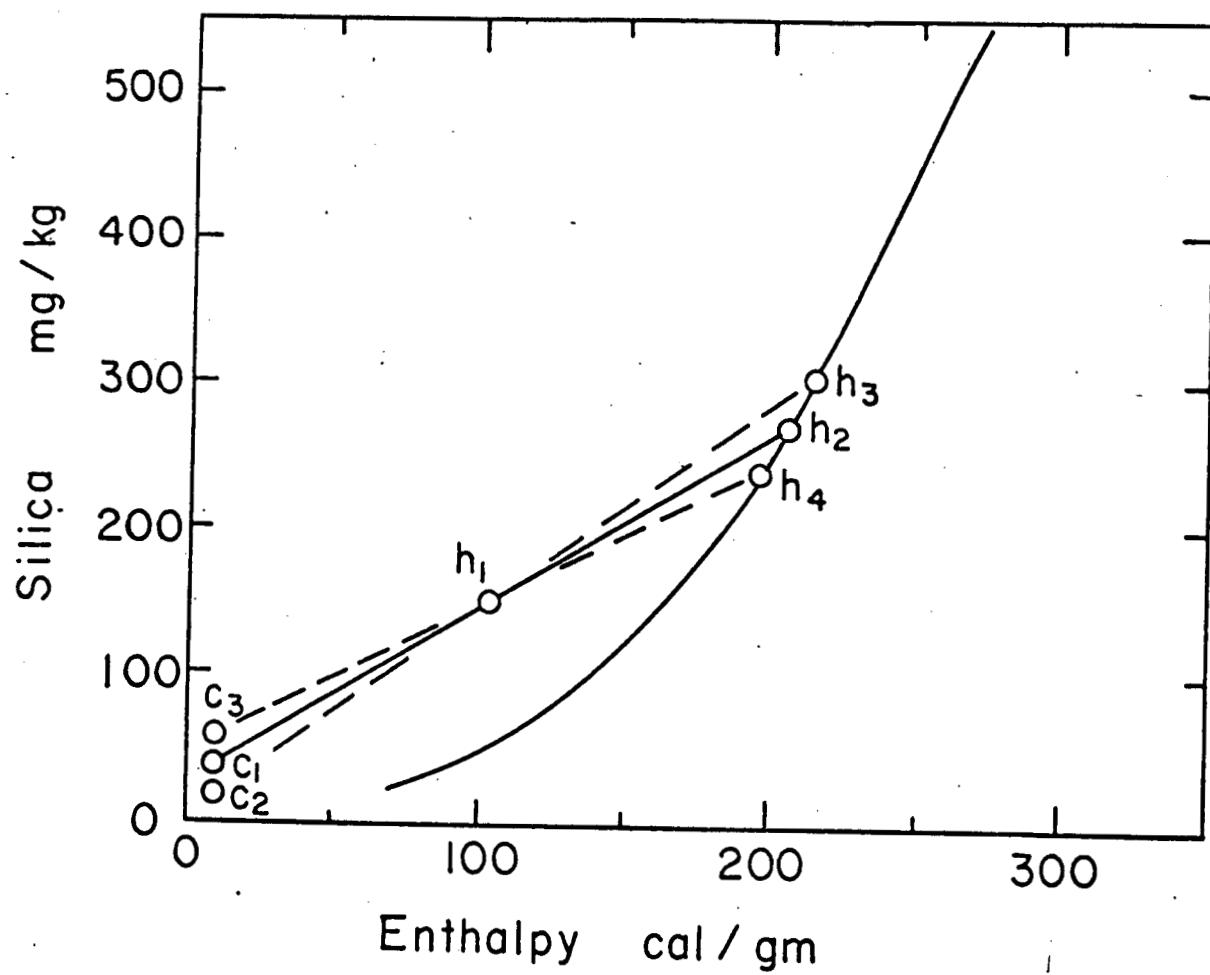
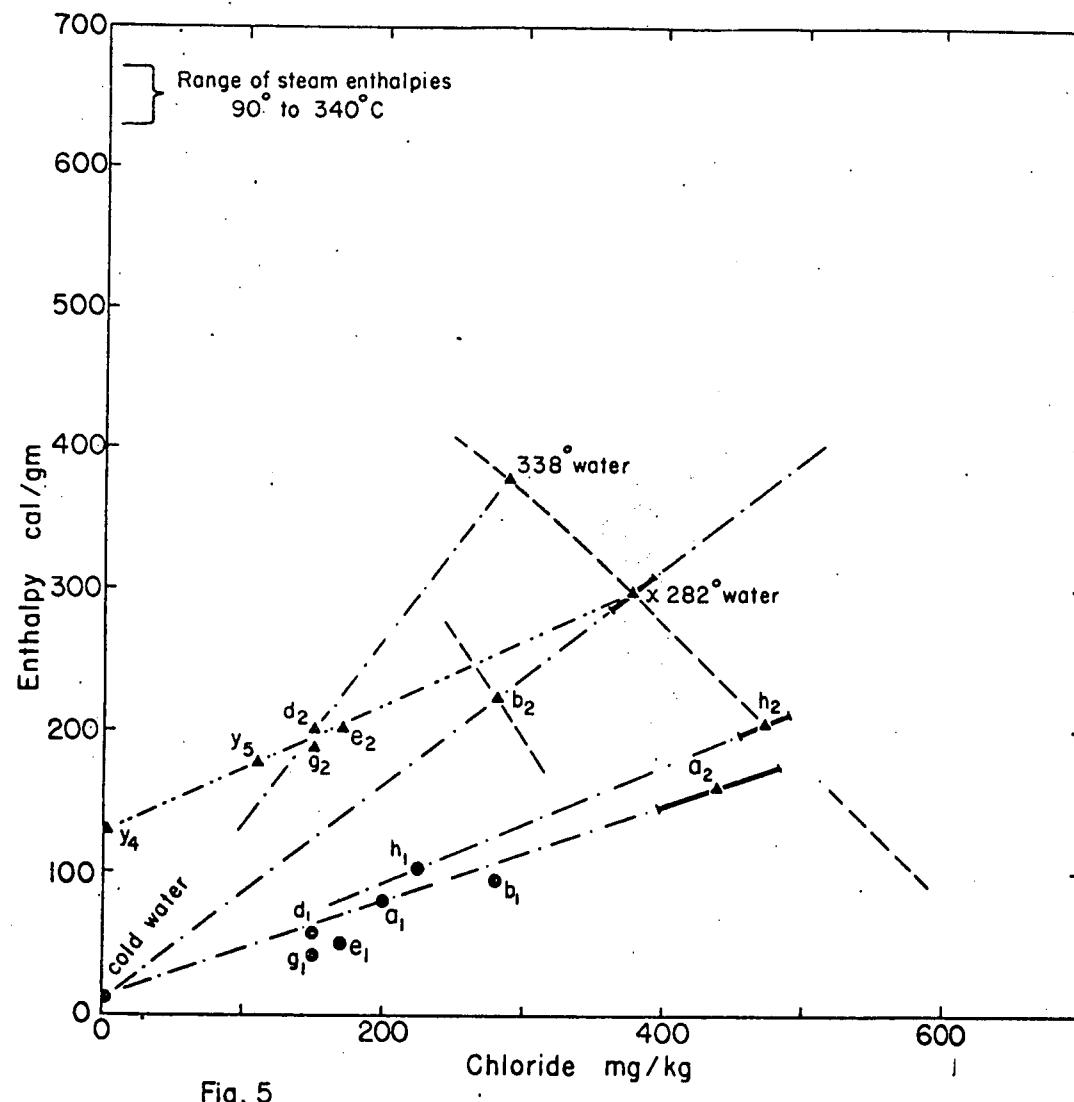


Fig. 4



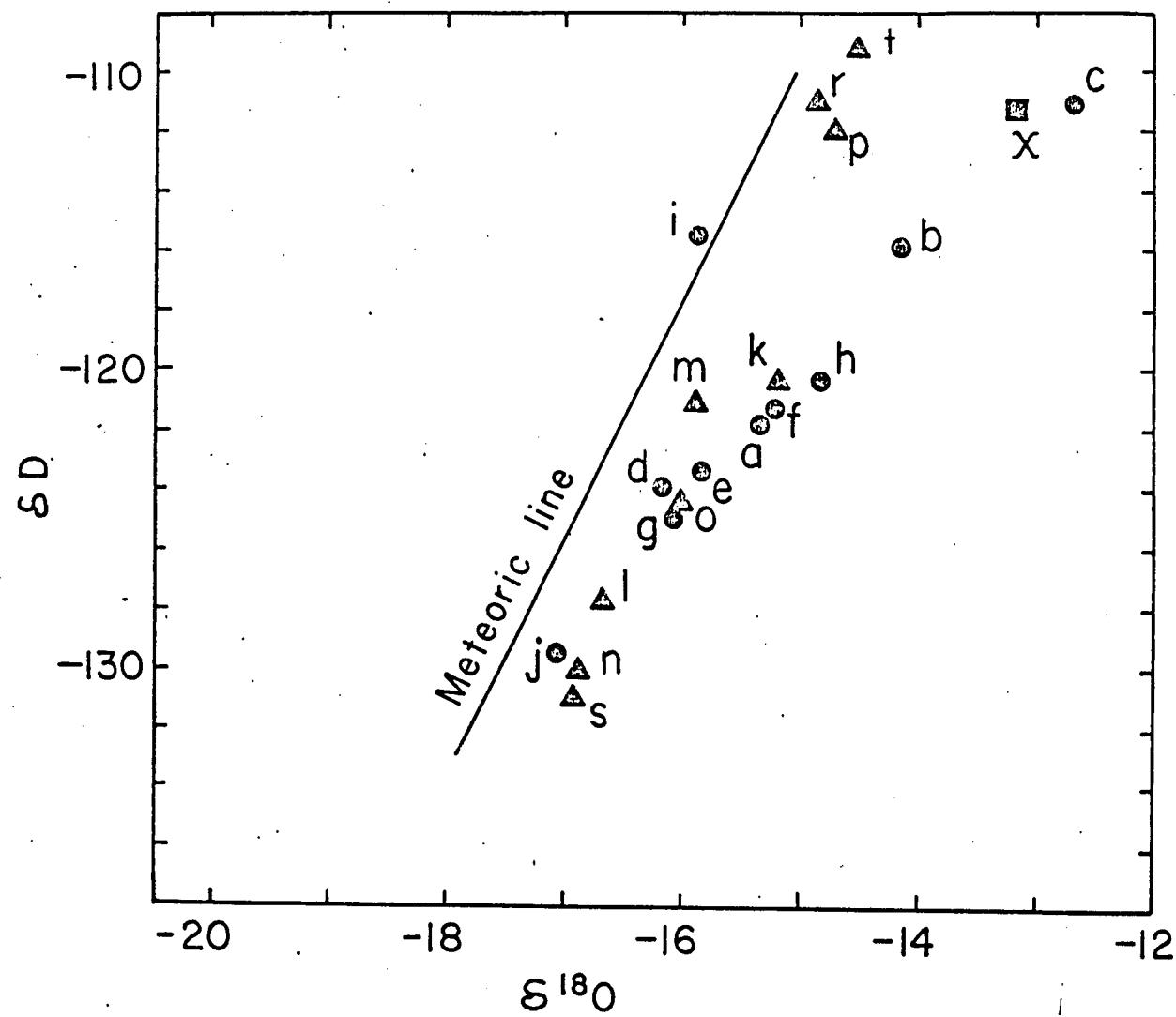


Fig. 6

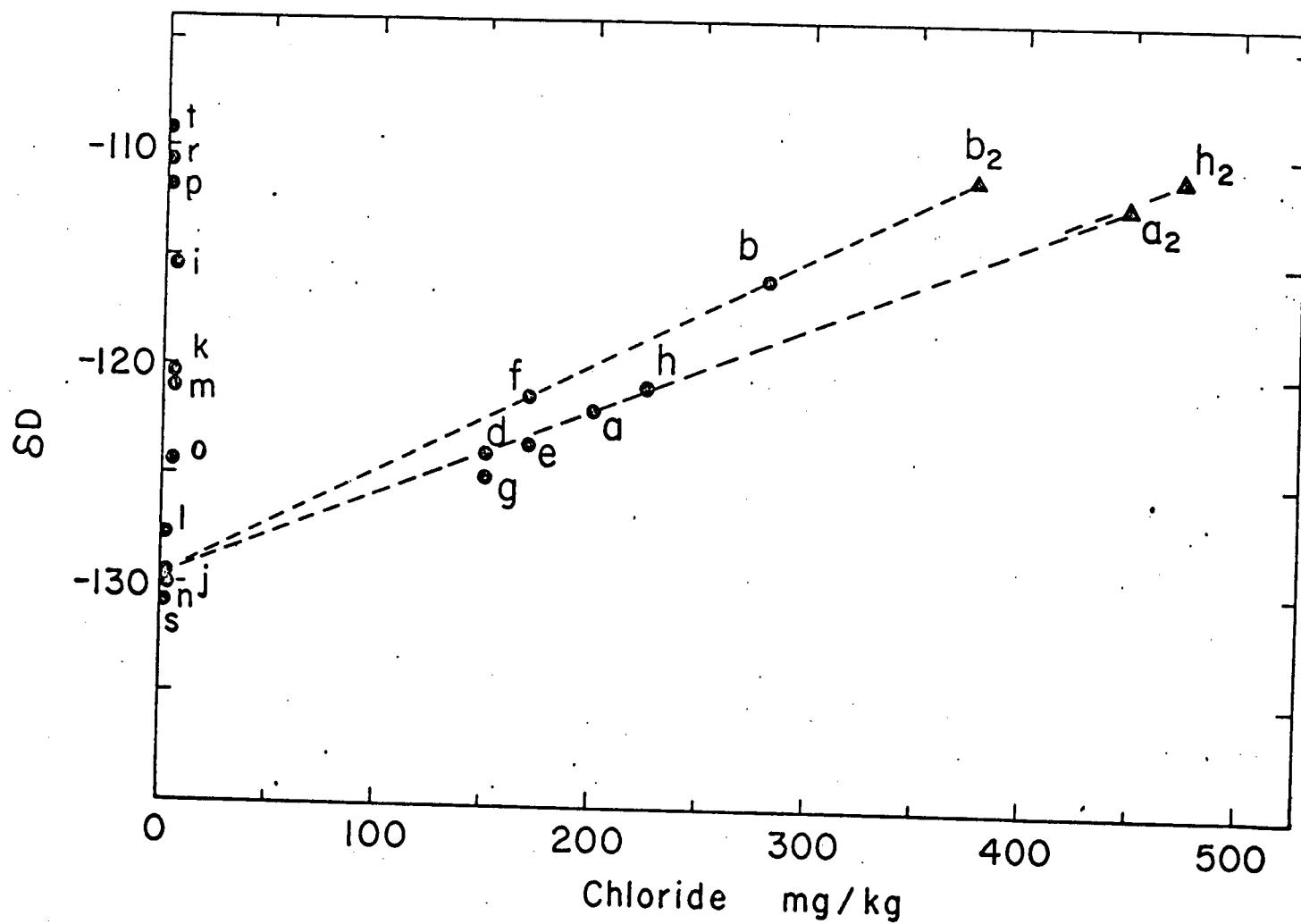


Fig. 7

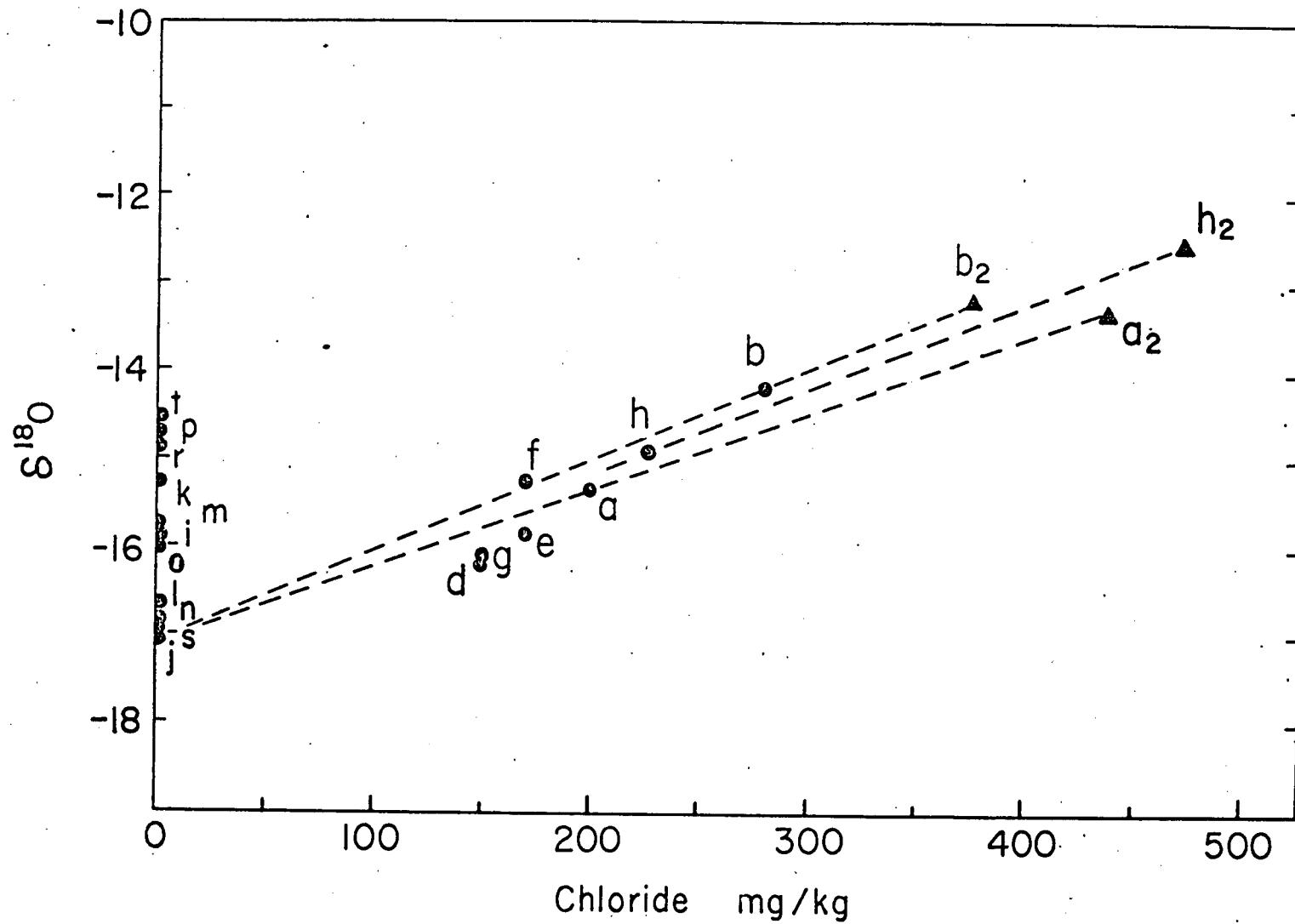


Fig. 8

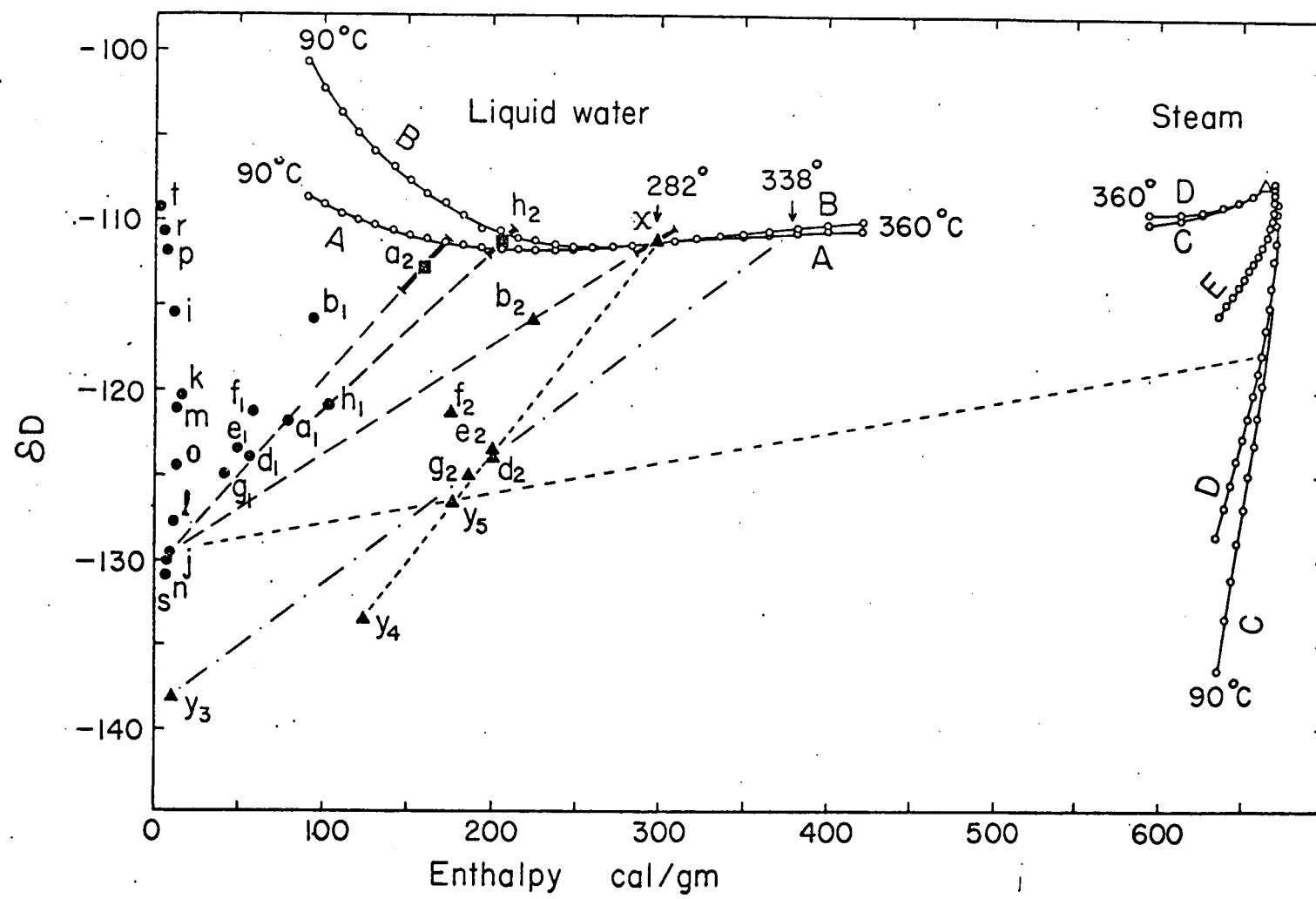


Fig. 9

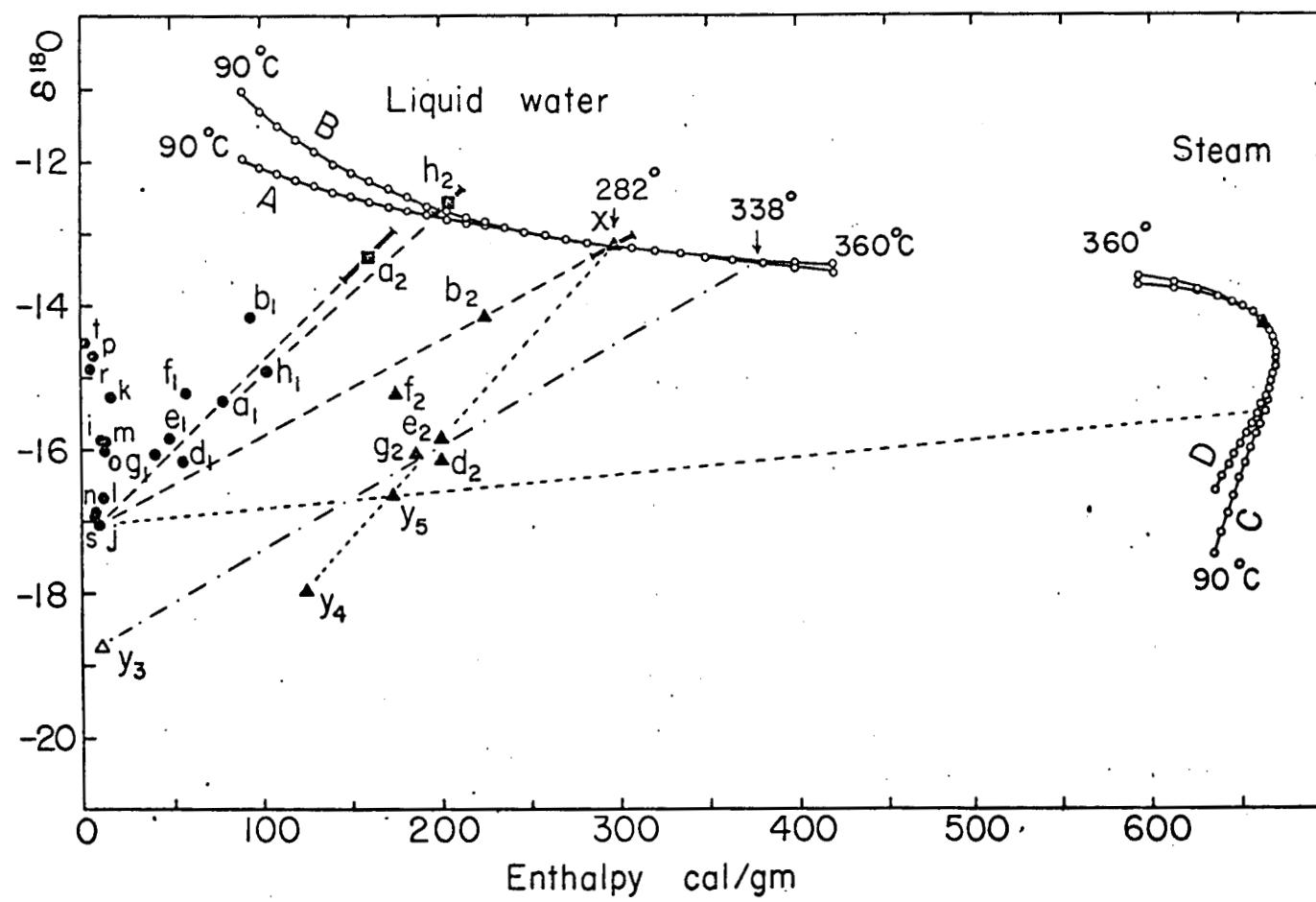


Fig. 10

Table 1. Selected chemical and isotopic constituents, physical measurements, and temperatures estimated by chemical geothermometers for thermal and meteoric waters from Long Valley, California.^{1/2/3/}

Location	Locality (springs unless otherwise noted)	SiO ₂	Na	K	Ca	Cl	HCO ₃ ^{4/}	Discharge l/min	Measured Temp.	Quartz ^{5/} Temp.	Na-K-Ca ^{6/} Temp.	δD	δ ¹⁸ O	
									°C	°C	°C			
a	3S/28E-13ES3	Little Hot Creek	88 ^{7/}	410	30	50	200	736	280	79	129	172	-121.8	-15.34
b	3S/28E-32E9	Casa Diablo Well	340	390	45	0.9	280	449		94	219	238	-115.8	-14.16
c	3S/28E-35ES1	Hot Bubbling Pool	300	380	25	3.3	250	467	0	60	209	189	-111.0	-12.44
d	3S/29E-21PS1	Near Big Alkali Lake	250	310	37	25	150	829	100	56	196	200	-123.9	-16.17
e	3S/29E-28HS1	S.E. of Big Alkali Lake	240	400	43	22	170	846	200	49	193	200	-123.4	-15.85
f	3S/29E-31AS1	N. of Whitmore H.S.	150	310	22	15	170	520	90	58	161	176	-121.2	-15.23
g	3S/29E-34KS1	W. of Lake Crowley	205	320	28	23	150	696	150	41	182	184	-124.9	-16.08
h	3S/28E-25AS4	Hot Creek	150	400	24	1.6	225	597	400	90	153	192	-120.3	-14.83
i	2S/28E-25AS1	Big Springs	58	23	4.0	5.1	5.7	90	380	11	109	83	-115.4	-15.89
j	3S/29E-13Cl	Wilfred Canyon Well	64	28	1.3	5.3	3.0	117	25	10	114	53	-129.5	-17.07
k	4S/29E-6P	Near Lv 4					<10		10	16			-120.3	-15.26
l	4S/28E-9FS1	E. of Laurel Canyon		5	1	16	1	46	250	12		11	-127.7	-16.68
m	3S/28E-35KS1	State Fish Hatchery	33	15	3	13	2.7	95	4000	13		50	-121.0	-15.89
n	2S/28E-14M	McLaughlin Creek					<10		4000	8			-130.0	-16.87
o	2S/27E-27B	Deadman Ck. at Highway 395					<10			13			-124.4	-16.01
p	3S/27E-7P	S. Tributary of Deadman Ck.					<10			7			-111.8	-14.71
r	3S/26E-36P	Near Minaret Summit					<10		100	5			-110.7	-14.87
s	2S/29E-21D	N.W. of O'Harrel Canyon					<10		400	7			-130.9	-16.91
t	4S/27E-6A	Mammoth Mountain					<10		100	2			-109.2	-14.52

^{1/}Data for features a through j from Mariner and Willey (1976).

^{2/}Features k through t collected by M. Sorey, δ¹⁸O analyzed by N. Nehring, δD analyzed by D. White, Cl analyzed by L. Tanner.

^{3/}Chemical concentrations are in milligrams per liter.

^{4/}Total alkalinity calculated as HCO₃.

^{5/}By the method of Fournier and Rowe (1966).

^{6/}By the method of Fournier and Truesdell (1973).

^{7/}The original reported silica content was 110 mg/l. Four more recent hot spring samples collected from the same locality have all contained 88 mg/l silica with only minor differences in other dissolved constituents. Therefore, it is likely that the original silica analysis was in error.