CHEMICAL GEOTHERMOMETERS AND MIXING MODELS FOR GEOTHERMAL SYSTEMS

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Abstract—Qualitative chemical geothermometers utilize anomalous concentrations of various "indicator" elements in groundwaters, streams, soils, and soil gases to outline favorable places to explore for geothermal energy. Some of the qualitative methods, such as the delineation of mercury and helium anomalies in soil gases, do not require the presence of hot springs or fumaroles. However, these techniques may also outline fossil thermal areas that are now cold.

Quantitative chemical geothermometers and mixing models can provide information about present probable minimum subsurface temperatures. Interpretation is easiest where several hot or warm springs are present in a given area. At this time the most widely used quantitative chemical geothermometers are silica, Na/K, and Na–K–Ca.

INTRODUCTION

Both qualitative and quantitative chemical geothermometers are used in exploration for geothermal energy. The quantitative techniques currently available require chemical analyses of thermal waters from springs or wells. In contrast, qualitative techniques may be used to look for anomalous concentrations of various "indicator" elements in a large variety of hosts, including soils, soil gases, fumaroles, hot and cold springs, and streams. It is assumed that the indicator element has dispersed away from a heat source at depth. Soil and soil gas analyses offer particularly attractive possibilities for detecting "blind" or hidden geothermal targets that have no surface expression of thermal water.

This paper is not intended to be an exhaustive review of all the chemical geothermometers that have been suggested and used. Rather, emphasis is placed on the geothermometers that have received the most use and those that seem at this time to offer the most promise of future use. The isotopic geothermometers are not discussed in this paper because they are treated elsewhere in this volume.

QUALITATIVE GEOTHERMOMETERS

Most qualitative geothermometers are based on the distribution and relative concentration of volatile elements in waters and soils or variation in soil gas composition. Anomalously high concentrations of volatile elements may accumulate above or around a relatively shallow heat source, especially if subsurface boiling occurs. However, similar anomalous concentrations of volatile elements may occur where favorable structures allow volatiles to escape from deep in the crust where metamorphic reactions are in progress. Fossil (now cold) hot springs and ore deposits also may exhibit halos of volatile elements that may be difficult to distinguish from halos due to present-day activity.

White (1970) reviewed the qualitative geothermometers that had been suggested up to 1970. Tonani (1970) suggests that enrichment of B, NH_4, HCO_3, Hg, and H_2S (which oxidizes to sulfate and lowers the pH of the water) in near-surface waters may result from boiling at depth. The volatiles are partitioned into the steam phase and are transported upward, eventually becoming incorporated into shallow, relatively cold groundwater. According to White *et al.* (1971), these are the same volatile elements most characteristic of vapour-dominated systems, and their high concentrations in shallow groundwater may be indicative of such systems.

Mahon (1970) noted that high Cl/F and Cl/SO_4 ratios in liquids of a geothermal area generally indicate high temperature in the system. He also noted that variations in CO_2/NH_3, CO_2/H_2, and CO_2/H_2S from fumaroles may indicate zones likely to be close to the deep hot water. When both high and low ratios of these gases are found, the fumaroles with the lowest ratios may be closest to the aquifer (Mahon, 1970). Sigvaldason and Cuéllar (1970) consider hydrogen in thermal gases generally to be a qualitative indicator of high temperature, and state that ". . . amounts in excess of 0·5% usually mean reservoir temperatures above 200°C".

Fournier and Truesdell (1970) noted that the mol ratio $Cl/(HCO_3+CO_3)$ is very useful in distinguishing waters from different aquifers in Yellowstone National Park; higher ratios indicate waters coming from hotter aquifers.

Gould (in Allen and Day, 1935) reported the association of mercury and thermal springs in California, and Dall'Aglio *et al.* (1966) showed that the mercury content of stream sediments defines a clear halo around the Larderello and Monte Amiata, Italy geothermal regions. Prospecting for geothermal resources using Hg anomalies is likely to become more common in the future owing to the recently developed, highly sensitive and fast method of detecting Hg in soils and soil gas (Matlick and Buseck, 1975). However, by itself, an Hg anomaly is not likely to distinguish between an active and a fossil hot spring system.

Anomalously high concentrations of nonvolatile trace elements also may be indicative of high subsurface temperature. This would be true if the element tended to be easily leached from rock at high temperature and not leached at low temperature. For instance, Brondi *et al.* (1973) report that high concentration of Li in springs and streams in Tuscany gives a good indication of high temperature at relatively shallow depths. This method of prospecting should be used with caution because variation in trace metal content may be due to factors other than high subsurface temperature, such as variations in rock type, variations in time that the water was in contact with rock, and contamination due to agricultural and industrial processes.

A relatively new prospecting method based on variations in the helium contents of soil gas (Friedman and Denton, 1976; Roberts *et al.*, 1975) may become important in the future. Roberts (1975) reported good correlation between temperature gradients and observed helium concentrations over the "blind" geothermal prospects at the Dunes, East Mesa, and Brawley geothermal areas of the Imperial Valley, California.

QUANTITATIVE GEOTHERMOMETERS

The assumptions that are usually made in using compositions of spring and well waters to estimate subsurface temperature have been discussed by White (1970) and by Fournier *et al.* (1974). These assumptions may be summarized as follows:

1.   Temperature-dependent reactions involving rock and water fix the amount or amounts of dissolved "indicator" constituents in the water.
2.   There is an adequate supply of all the reactants.
3   There is equilibrium in the reservoir or aquifer in respect to the specific indicator reaction.
4.   No reequilibration of the "indicator" constituents occurs after the water leaves the reservoir.
5.   Either no mixing of different waters occurs during movement to the surface or evaluation of the results of such mixing is possible.

The attainment of equilibrium in the reservoir will depend on a number of factors such as the kinetics of the particular reaction, the temperature of the reservoir, the reactivity of the wallrock, the concentrations of the indicator elements in the water, and the residence time of the water in the reservoir at the particular temperature. Thus, in some situations, equilibrium in the reservoir may be attained for some reactions and not for others.

Whether or not a water reequilibrates after leaving a reservoir during flow to the surface depends on similar factors: the rate of flow, the path of ascent, the type and reactivity of wallrock traversed, the initial temperature of the reservoir, and the kinetics of the various reactions that may occur. Different reactions may occur in an ascending water at different rates. Therefore, the apparent last temperature of equilibration may be different for different chemical geothermometers. The two main types of temperature dependent reactions that may be useful as quantitative geothermometers are solubility and exchange reactions. Both are discussed later.

Solubilities

Solubilities of minerals generally change as functions of temperature and pressure. However, with the notable exception of silica, solubilities of minerals have not been used extensively as geothermometers. In most natural waters dissolved silica is not influenced by common ion effects, the formation of complexes, and the loss of volatile components that make interpretations difficult for most other dissolved constituents. In addition, the assumption of an adequate supply of all the reactants is generally valid for silica but may not be valid for other reactants. For instance, a geothermometer based on the solubility of CaF_2 (fluorite) will not work if the mineral fluorite is not present where water–rock chemical equilibration takes place.
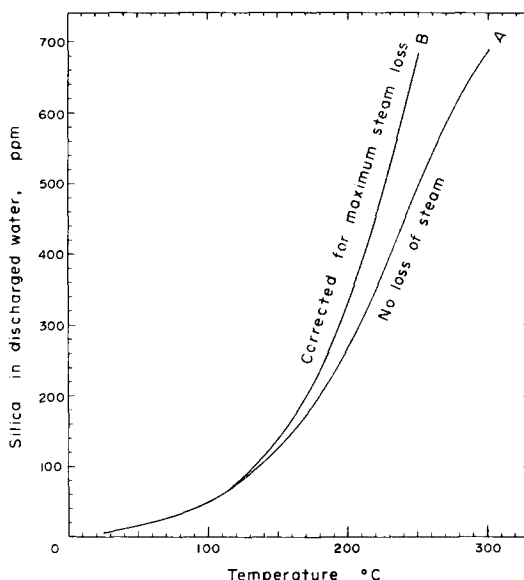

Fig. 1. Solubility of quartz as a function of temperature. Curve A shows the solubility in liquid water in equilibrium with saturated steam. Curve B shows the amount of silica that would be left in the residual liquid after maximum loss of steam upon adiabatic cooling to 100°C and one bar pressure. Taken from Fournier and Rowe (1966).

The silica geothermometer of Fournier and Rowe (1966) is based on the solubility of quartz and is widely used to estimate subsurface temperatures in hot spring systems. The silica content of water from a hot spring or well can be correlated with the last temperature of equilibration with quartz, using Fig. 1. If the water sample is likely to have cooled mainly adiabatically (by boiling) before sampling, use curve B which corrects for the maximum possible steam loss. If the sample probably cooled mainly by conduction, use curve A. The quartz geothermometer probably works best in the temperature range 150–225°C. At higher temperatures silica is likely to deposit during ascent of the water. At lower temperatures other silica species such as chalcedony, cristobalite, or amorphous silica may control dissolved silica (Fournier and Rowe, 1966; Fournier, 1970; Fournier and Rowe, 1962; Arnorsson, 1970; Arnorsson, 1975).

Equations relating the solubility, C, in mg SiO_2 per kg water to temperature in the range 0–250°C of various pure silica minerals are as follows:

Amorphous silica
$$t_{°C} = \frac{731}{4.52 - \log C} - 273.15$$

β Cristobalite
$$t_{°C} = \frac{781}{4.51 - \log C} - 273.15$$

α Cristobalite
$$t_{°C} = \frac{1000}{4.78 - \log C} - 273.15$$

Chalcedony
$$t_{°C} = \frac{1032}{4.69 - \log C} - 273.15$$

Quartz
$$t_{°C} = \frac{1309}{5.19 - \log C} - 273.15$$

Quartz (after steam loss)
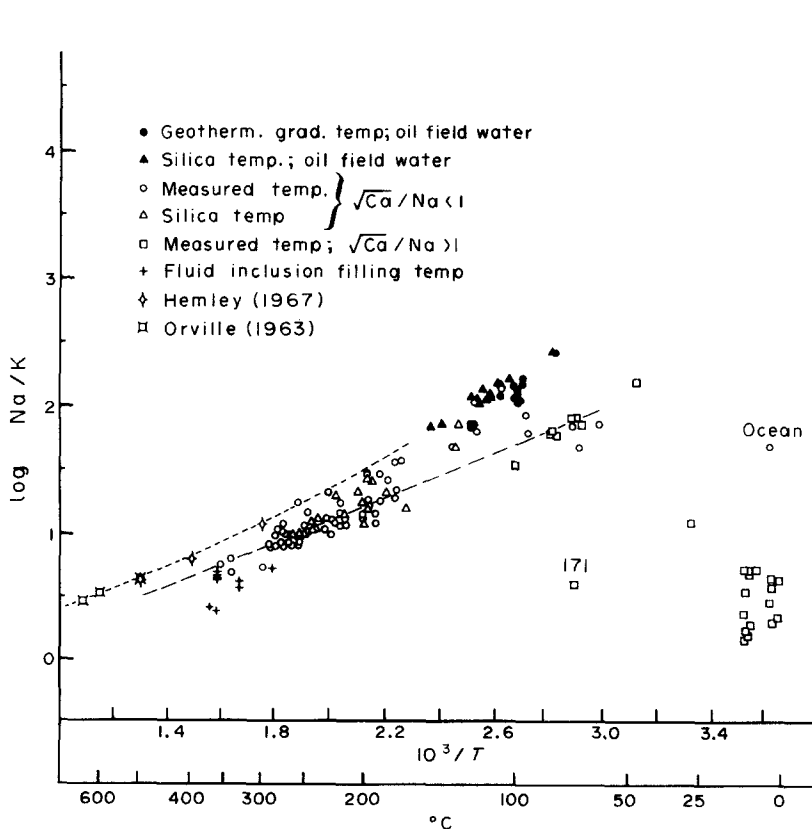$$t_{°C} = \frac{1522}{5.75 - \log C} - 273.15$$

Fig. 2. Na/K values for natural waters relative to assumed equilibrium temperature. The lower dashed line combines empirical curves of Ellis (1970) and White (1965). The upper dashed line combines experimentally derived curves of Orville (1963) and Hemley (1967). The data points are tabulated in Fournier and Truesdell (1973) and this illustration is taken from that paper.

Using experimental data of Marshall and Slusher (1968), which give the solubility product of anhydrite from 100 to 200°C at various ionic strengths, Sakai and Matsubaya (1974) used the concentration product of Ca^{2+} and SO_4^{2-} to estimate subsurface temperatures in hot–spring systems. Those estimated temperatures were in accord with temperatures estimated from the oxygen isotope fractionation between sulfate and water. This anhydrite geothermometer probably works best for thermal waters with relatively low concentrations of Ca^{2+} and HCO_3^- (that is, waters in which the Ca^{2+} concentration is not controlled by the solution and precipitation of carbonate).

Exchange reactions

Equilibrium constants for exchange and alteration reactions are temperature dependent. In such reactions, the ratios of dissolved constituents change with changing temperature of equilibration. There are many possible constituents and reactions that may be useful. Examples are Na/K ratios of alkali chloride solutions equilibrated with alkali feldspars (Orville, 1963, Hemley, 1967), Na/K ratios in natural waters (White, 1970; Fournier and Truesdell, 1970; Ellis, 1970; Mercado, 1970; White, 1965), and Na–K–Ca relations in natural waters (Fournier and Truesdell, 1973).

Figure 2 shows Na/K ratios in geothermal well waters plotted as a function of the temperature of the aquifer supplying the water. The Na/K ratio generally works well for estimating temperatures of waters above 200°C. However, anomalously high estimated temperatures are obtained if the water temperature is below 100°C. The Na–K–Ca geothermometer (Fournier and Truesdell, 1973) is proving to be more reliable than the Na/K geothermometer for low temperature waters, as shown in Fig. 3. The equation for the solid line drawn in Fig. 3 is

$$\log(Na/K) + \beta \log (\sqrt{Ca}/Na) = \frac{1647}{273 + t°C} - 2\cdot24 \qquad (1)$$
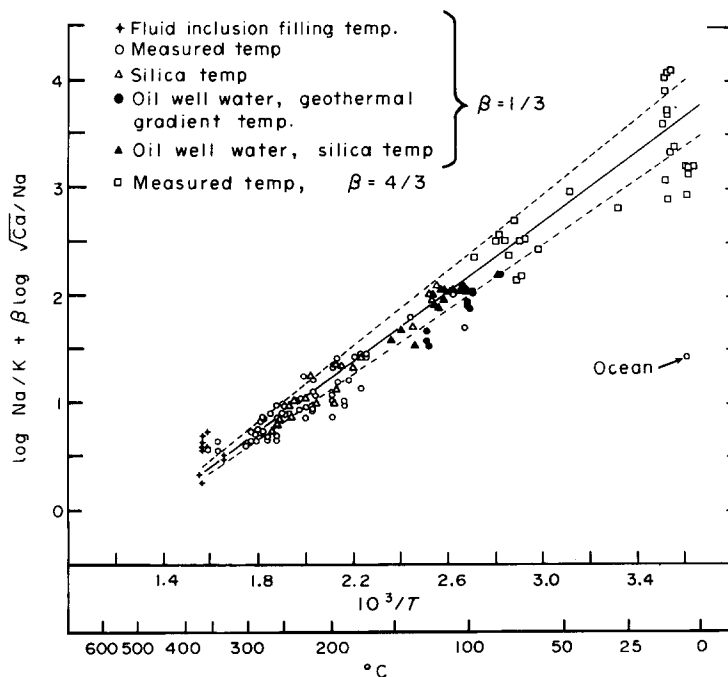

Fig. 3.   The middle line is the curve for geothermometry of natural waters using the Na–K–Ca relationship suggested by Fournier and Truesdell (1973). The two dashed lines show + 15 and − 15°C with respect to the middle curve. The data points are tabulated by Fournier and Truesdell (1973) and this illustration is taken from that paper.

in which concentration units are mol/kg and $\beta = 1/3$ for water equilibrated above 100°C, and $\beta = 4/3$ for water equilibrated below 100°C. Paces (1975) recommends that a correction factor be applied to equation (1) for waters less than 75 C with partial pressure of CO_2 in the aquifer above 10^{-4} atm. The correction factor, I, to be subtracted from the right side of equation (1) is

$$I = -1\cdot36 - 0\cdot253 \log P_{CO_2} . \qquad (2)$$

This is consistent with the conclusion of Renner *et al.* (1975) that many temperatures predicted for high CO_2 spring waters of California seem to be unreasonably high.

The ratios $\sqrt{Ca}/K$ and $\sqrt{Ca}/Na$ also may be useful for estimating temperatures (Fournier and Truesdell, 1973). According to Mahon (1970), Cusicanqui and Ellis found that springs supplied most directly from hot aquifers have the highest Na/Ca ratios. This is probably due to the retrograde solubility of calcium carbonate.

COOLING OF ASCENDING WATER

Ascending hot water may cool by boiling (adiabatically), by conduction, by mixing with shallow colder water, and by combinations of these processes. Chemical analyses of spring waters may provide information about which of these processes are occurring in a given hot spring system.

Waters that ascend quickly and directly from aquifers with little conductive cooling are likely to have chemical compositions that reflect rock–water equilibrium at the aquifer temperature. Where the aquifer is at a temperature below atmospheric boiling, the water can emerge at about the aquifer temperature. But where the aquifer is at a higher temperature than the atmospheric boiling temperature, the water will cool adiabatically, emerge as a boiling spring, and the separation of steam during the ascent must be considered.

Where waters ascend either slowly or indirectly to the surface, conductive cooling is likely to occur. Even water from a spring with a large rate of flow may cool considerably by conduction if it moves horizontally for a long distance at a shallow level. In this case, different springs along the flow path or springs with different rates of discharge could have different temperatures but similar compositions.

Where hot ascending waters cool by mixing with cooler groundwater, springs with different temperatures are likely to have different chemical compositions. For instance, variations in chloride and boron are likely to be greater among individual springs of a group than can be explained by varying steam loss. In this event, mixing models may indicate the original temperature of the hot-water component.

MIXING MODELS

The water in many hot springs consists of mixtures of deep hot water and shallow cold water. Partial or complete chemical equilibration may or may not occur after mixing. If chemical equilibrium is established after mixing, the chemical geothermometers indicate temperatures of the mixed water, not the hot water component. Accordingly, whether or not equilibrium is established after mixing, the temperature of the hot water component cannot be estimated from a solubility relation unless the mixing is taken into account. In contrast, an estimated temperature of the hot-water component based on an exchange reaction using a ratio of dissolved constituents may be little affected by mixing provided that (1) the deep hot water is relatively concentrated in the indicator elements and the shallow water is very dilute in respect to those same elements, and (2) little or no chemical reaction occurs after mixing to change the relative concentrations of the indicator elements. Dilution will have an effect upon the Na–K–Ca geothermometer because the square root of the concentration is involved in the calculation.

Fournier and Truesdell (1974) described two mixing models that may be applied to springs with large rates of flow and temperatures below boiling. To apply either model, the silica content and temperature of the warm spring and the cold water must be known. In model 1, the enthalpy of the

hot water plus steam that mixes with and heats the cold water is the same as the initial enthalpy of the deep hot water. In other words, the deep hot water may boil before mixing, but all the steam condenses in the cold water. In model 2, the enthalpy of the hot water in the zone of mixing is less than the enthalpy of the hot water at depth owing to escape of steam during ascent. In both models it is necessary that the initial silica content of the deep hot water is controlled by the solubility of quartz and that no further solution or deposition of silica occurs before or after mixing.

The original procedure for applying these models is cumbersome. Truesdell and Fournier (1977) have devised a much simpler procedure utilizing a plot of dissolved silica versus enthalpy, as illustrated in Fig. 4. For the situation in which no steam is lost before mixing, plot the silica and heat contents (enthalpies) of the cold and warm spring waters as two points, A and B, and draw a straight line through these points to intersect the quartz solubility curve (note that below 100°C the temperature in degrees Celsius is numerically equivalent to cal/g. Point C then gives the original silica content and enthalpy of the deep hot water. The original temperature of the hot-water component is then obtained from steam tables (Keenan *et al.*, 1969).
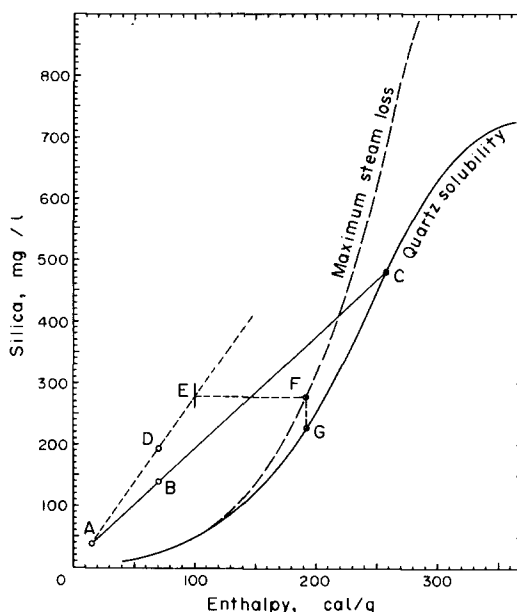

Fig. 4.   Dissolved silica–enthalpy graph for determining the temperature of a hot-water component mixed with cold water yielding warm spring water. See text for explanation. Taken from Truesdell and Fournier (1977).

For the situation in which the maximum amount of steam is lost from the hot water before mixing, plot the silica and heat contents of the cold and warm spring waters as two points, A and D, in Fig. 4. Draw a straight line through those points and extend that line to the enthalpy of the residual liquid water at the assumed temperature of separation and escape of steam, *ca.* 100°C. In this case the residual liquid water before mixing will have an enthalpy of *ca.* 100 cal/g, point E of Fig. 4. To obtain the original enthalpy of the hot-water component, move horizontally across the diagram from point E to the maximum steam loss curve, point F. The original silica content of the hot-water component is given by point G. If steam is assumed to escape from water at a temperature above 100°C, the original enthalpy of the hot water will lie at a value along a horizontal line, between the maximum steam loss curve and the quartz solubility curve (no steam

loss). The distance along the horizontal line between the two curves and away from the maximum steam loss curve will be in the proportion

$$\frac{Hx - 100}{Hq - 100}$$

where Hx is the enthalpy of liquid water in cal/g at the assumed steam separation temperature, and Hq is the enthalpy of liquid water where the horizontal line intersects the quartz solubility curve.

The above mixing models cannot be applied to boiling springs because heat is carried away in steam after mixing. Under some conditions, however, a different mixing model may be used to calculate subsurface temperatures deeper in the system than would be obtained from the usual method of applying the silica or quartz geothermometer (Truesdell and Fournier 1975; Fournier *et al.*, 1975; Fournier and Rowe, 1966). The boiling springs model makes use of a plot of enthalpy vs chloride (Fig. 5), and it works best where the initial temperature of the hot-water component is above 200°C. In using the model it is necessary to assume that (1) no heat loss or gain occurs before or after mixing; (2) re-equilibration with quartz occurs after mixing (most likely to occur > 200°C); and (3) silica is not precipitated during ascent of the mixed water to the surface sampling point.
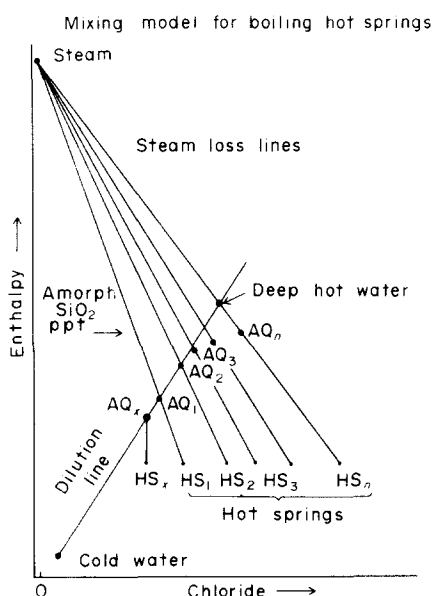

Fig 5. Hypothetical plot of enthalpy relative to chloride for various waters that result from the mixing of hot and cold waters. Enthalpies of deep waters are estimated using the silica content of hot-spring waters. Taken from Truesdell and Fournier (1975).

The construction and use of the enthalpy versus chloride plot are discussed by Truesdell and Fournier (1975). In brief, the chloride content of the cold water, of steam, and of hot-spring waters issuing at surface boiling temperature (HS$_1$ through HS$_n$ in Fig. 5) can be represented on this plot. Lines from the hot-spring waters towards the average composition and enthalpy of the separated steam (HS$_1$ to steam, etc. in Fig. 5) represent the variation in enthalpy and chloride content of the liquid water fraction caused by the process of steam separation during passage to the surface. The points AQ$_1$ and AQ$_n$ on each of these lines are fixed from the temperature indicated by the silica geothermometer applied to the respective springs, assuming adiabatic cooling and with water enthalpy obtained from steam tables (Keenan *et al.*, 1969). The dilution line shows the heat and chloride contents of waters that would result from mixing of a deep hot water with cold, dilute shallow water. Points AQ$_3$ to AQ$_n$ are shown below the dilution line because silica is likely to

precipitate from high-temperature (> 225°C) waters during movement to the surface and enthalpy is estimated from the silica content of the emerging spring water.

If a spring water is thought to cool mainly by conduction, a slightly higher estimated subsurface temperature and enthalpy would be obtained using the silica geothermometer, and the chloride content of the deep water would be the same as that of the emerging spring water (i.e. a point AQ_x would plot directly above the point HS_x instead of along a line pointing to steam). A more complete discussion of the problem of treating data where both adiabatic and conductive cooling may have occurred is given in Fournier *et al.* (1975).

CONCLUSIONS

Chemical techniques are relatively fast and inexpensive and should be a part of any geothermal energy exploration and evaluation program. Interpretation of analytical results, however, is not always easy. In some places accurate reservoir temperatures are given directly by geothermometers such as silica, Na/K and Na–K–Ca. In other places mixing models must be used to estimate temperatures of reservoirs deep in the system.

Even where leakage of thermal water to the surface is not obvious, high underground temperature may be indicated by anomalously high concentration in groundwater soil and soil gas of elements that disperse away from high-temperature environments.

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