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GEOCHEMICAL INDICATORS OF SUBSURFACE TEMPERATURE—PART 1, BASIC ASSUMPTIONS

By R. O. FOURNIER, D. E. WHITE, and A. H. TRUESDELL,
Menlo Park, Calif.

Abstract.—The chemical and isotopic compositions of hot-spring water and gas are used to estimate subsurface temperatures. The basic assumptions inherent in the methods are seldom stipulated. These assumptions include (1) a temperature-dependent reaction at depth, (2) a supply of the solid phase involved in the reaction to permit saturation of the constituent used for geothermometry, (3) water-rock equilibrium at depth, (4) negligible re-equilibration as the water flows to the surface, and (5) no dilution or mixing of hot and cold water. The first three assumptions are probably good for a few reactions that occur in many places. The last two assumptions probably are not valid for many hot-spring systems; information obtained is therefore for the shallower parts of those systems, or a limiting temperature (generally a minimum) is indicated.

The recent increased interest in geothermal energy has prompted widespread exploration for this resource. As expected, the areas initially receiving the most attention are those in which fumaroles and hot springs of high temperature are found. Thermal springs are numerous in the western United States. Their temperatures range from a few degrees above mean annual temperature to boiling. In general, their relative abundance decreases with increasing temperature. From an exploration point of view, the critical question is, how did a given spring attain its observed temperature? Did the warm temperature result from water circulating deeply in a region of normal or slightly above normal geothermal gradient; that is, does the temperature of the spring represent the highest subsurface temperature deep in the system? Or, did the water come from a very high temperature environment at depth and cool on the way back to the surface? We would like to use the chemical composition of the water to answer these questions. In practice, we have found that springs with high rates of discharge are most suitable for hydrogeochemical prospecting, whereas compositions of springs with low rates of discharge are very difficult to interpret.

BASIC ASSUMPTIONS

There are many basic assumptions inherent in using geochemical indicators to estimate subsurface temperatures (White, 1974). Although these assumptions may be valid in many places, it is unlikely that they will be fulfilled everywhere. The usual assumptions are:

1. Temperature-dependent reactions occur at depth.
2. All constituents involved in a temperature-dependent reaction are sufficiently abundant (that is, supply is not a limiting factor).
3. Water-rock equilibration occurs at the reservoir temperature.
4. Little or no re-equilibration or change in composition occurs at lower temperatures as the water flows from the reservoir to the surface.
5. The hot water coming from deep in the system does not mix with cooler shallow ground water.

A schematic model of a hot-spring system (fig. 1) is useful in assessing these assumptions. Critical elements of the model include a heat source of unspecified nature at the base of the system and interconnected permeability that permits convection to occur. In response to heating, water deep in the system decreases in density and is forced up and out of the system, as at A, by pressure exerted by cold, dense water. The cold water moves down and into the system at the margins along permeable structures, possibly faults or joints such as B–B′. There are many alternative possibilities, including models in which some or all of the ascending water and gas is connate, metamorphic, or even juvenile in origin. In some places the salinity of the deep water may be high enough to counteract the effects of temperature on density. Although connate and metamorphic water is probably dominant in some hot springs (White and others, 1973), isotope data indicate that most hot-spring water is predominantly meteoric in origin.

If the maximum temperature attained by the water at depth is higher than the boiling temperature appropriate for atmospheric conditions, the water will cool by boiling (adiabatically), by conduction, or by a combination of these processes as it moves toward the surface. If, on the other hand, the maximum temperature at depth is less than the boiling temperature at atmospheric conditions, the emerging water, such as at A (fig. 1) may have approximately the maximum temperature at depth or a lower temperature, depending on whether the rate of upflow of water is very fast or slow.

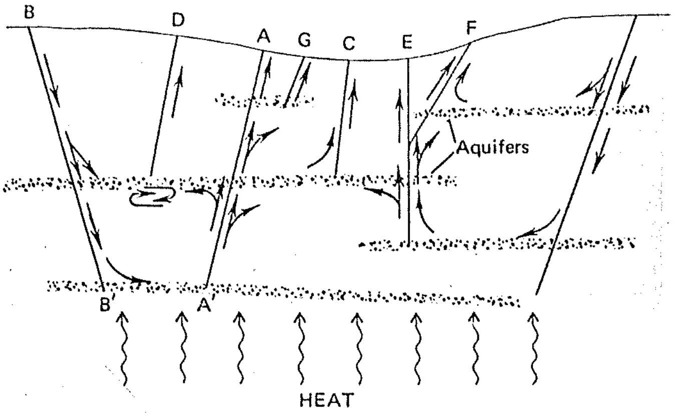

Figure 1.–Schematic model of a hot-spring system having a heat source of unspecified nature and interconnected permeability.

Solubilities

Solubilities of minerals generally change as functions of temperature and water pressure. Therefore, under some circumstances absolute quantities of dissolved constituents are useful indicators of subsurface temperature. However, the dissolving solid phase must be specified and its presence must be assumed at depth. An example is the silica geothermometer, which depends on the solubility of quartz controlling aqueous silica (Fournier and Rowe, 1966; Mahon, 1966).

In general, the solubilities of the common silicates increase with increasing temperature and pressure. As cold subsurface water is heated, it dissolves more and more silicate constituents, reaching a maximum at the hottest (and generally deepest) part of the system. Deposition of silicates may then occur as the water moves back toward the surface and cools, particularly if the cooling is adiabatic. This may result in the self-sealing of the geothermal system, as discussed by Bodvarsson (1964), Facca and Tonani (1967), and White, Muffler, and Truesdell (1971).

The common carbonates have retrograde solubilities (Holland, 1967). Other things being constant, minimum solubilities are attained at the hottest and deepest parts of the system. Generally "other things" are not constant, however. Carbonate solubilities are greatly affected by variations in pH and partial pressure of CO_2. Unfortunately, subsurface pH and P_{CO_2} are not easily estimated from the composition of hot-spring water and gas collected at the surface.

The common sulfates also have retrograde solubilities. Like the carbonates, their usefulness in geothermometry is restricted to systems in which the solid phase is present at depth. One cannot safely assume this unless sulfates have been found in cuttings or cores from holes drilled at the locality in question. In other words, there may be an inadequate supply of the "indicator" constituent in the reservoir, so that the solution at depth is unsaturated with respect to a particular phase; for example, $CaSO_4$ or $BaSO_4$.

Exchange reactions

Equilibrium constants for exchange and alteration reacti also are temperature dependent. In such reactions the ratios dissolved constituents change with changing temperature equilibration. Both chemical and isotopic reactions co under this category. Examples are Na:K ratios of chlori solutions equilibrated with alkali feldspars (Orville, 19 Hemley, 1967), Na:K ratios in natural waters (Ellis, 197 White, 1965), and Na-K-Ca relations in natural wat (Fournier and Truesdell, 1973). Again, as in the solubili method of geothermometry, the identity of the reactants a products in the high-temperature environment at depth mu be assumed. If the assumed phases are not present, t geothermometer yields anomalous results (Fournier a Truesdell, 1970, 1973).

Equilibration at depth

In order to use a geochemical method of estimati subsurface temperature, one must assume equilibrium or least an approach to equilibrium at depth for a specif "indicator" reaction. At low temperatures, this is a tenuo assumption. Metastable conditions also are likely to occu However, the assumption of attainment of equilibrium in high-temperature environment at depth is probably good f many reactions. This assumption is particularly good whe the residence time for water in a reservoir at a relative uniform temperature is long and there is effective mixing homogenization of introduced water with stored water.

When an increment of water, chemically equilibrated depth, finally does enter a channel that allows dire movement back to the surface, such as A–A′ in figure 1, th time of upward travel may be very short (minutes or hours compared with the residence time in the reservoi Consequently, even though the temperature of the water ma decrease markedly, little chemical reaction may occur durin upward flow, and the composition of the emerging water ma reflect the conditions present in the deep reservoir. Howeve reservoirs at different depths and temperatures may be presen within a given geothermal system. Hot springs located at C E, and G in figure 1 show various possibilities for wate re-equilibrating in shallow reservoirs, so that some or all of th chemical geothermometers will yield estimated subsurfac temperatures lower than the maximum temperature deep i the system.

A re-equilibrated water, such as that emerging at G (fig. 1) may give a good indication of the salinity of the deep water More commonly, deep water entering shallow reservoirs wil mix with relatively dilute, shallow water, so that neither th temperature nor salinity of the deepest reservoir is indicated by the spring water that eventually emerges at the surface, a at D and F. If the residence times of both the hot- and cold-water components are long in the shallow aquifer and mixing is thorough, the composition of emerging spring water as at D, may be indicative of the temperature of that shallow reservoir. In contrast, if the residence time in the shallow reservoir of one or both of the mixing waters is short, the composition of the emerging water (spring F) may give little or no information about that shallow reservoir. Under special circumstances, however, it may be possible to estimate the temperature and proportion of the hot-water component of a mixed water such as that emerging at F. This is discussed elsewhere (Fournier and Truesdell, 1974).

In the discussion to this point, we have assumed essentially no chemical reaction in the channels connecting different reservoirs or reservoirs with springs. Advantageous conditions that minimize reactions within channels are rapid rates of upflow, low temperature, and nonreactive wallrock. Where continued chemical reactions do occur in the channelways leading to the surface, different geochemical indicators yield different apparent temperatures, reflecting varying amounts of re-equilibration at intermediate temperatures.

Enrichment of volatiles

Tonani (1970) emphasizes the relative enrichments in spring waters and fumaroles of comparatively volatile components, particularly NH_3, B, Hg, CO_2, and sulfur compounds, that may indicate subsurface boiling. He generally assumes that steam separates from deep boiling water and that it carries other volatile constituents toward the surface. At shallow depth the steam condenses and mixes with the local ground water. Springs fed by this water are enriched in volatiles relative to chloride.

Tonani's model probably works very well for vapor-dominated systems, as described by White, Muffler, and Truesdell (1971). It has yet to be demonstrated that volatile constituents are enriched relative to chloride in neutral to alkaline hot springs above hot-water-dominated systems, even where boiling temperatures are attained at depth. Enrichment of volatile constituents in spring water may result from processes other than high-temperature boiling. Gases such as CO_2 and CH_4, if sufficiently abundant, may separate from relatively cold water deep underground and escape to the surface. If this gas later encounters shallow ground water, that ground water may become enriched in volatile constituents.

RECOMMENDED PROCEDURE

For estimating subsurface temperatures we set forth the following guidelines despite misgivings that they will be interpreted as hard-and-fast rules for always reflecting subsurface conditions. The intent is simply to suggest starting assumptions where little information is available about hydrologic conditions. As more information is obtained for a specific area, other assumptions may become more reasonable.

The recommended procedures are based upon the temperature and rate of flow of the spring water, as outlined below:

1. Boiling spring:
   (a) Small rate of flow: Assume mostly conductive cooling. Apply chemical indicators assuming little or no steam loss.
   (b) Large rate of flow: Assume adiabatic cooling. Apply chemical indicators assuming maximum steam loss.
2. Spring below boiling:
   (a) Small rate of flow: Likely to have no clear-cut interpretation. May be a water that has never been very hot, a mixed water from sources of different temperatures, or a hot water cooled entirely by conduction. Try geothermometers that assume conductive cooling; indicated temperatures are likely to be minima.
   (b) Large rate of flow: Assume no conductive cooling. Test to see if geothermometers (particularly the Na-K-Ca geothermometers (Fournier and Truesdell, 1973)) suggest chemical equilibration at the temperature (±25°C) of the water. If a higher temperature is indicated, treat as a mixed water according to the method of Fournier and Truesdell (1974).

We have not specified what large and small rates of flow are. Our intent is to distinguish between waters that cool by conduction during their ascent and those that either cool mainly by boiling or do not cool at all. This depends in part on the rate of upflow, the depth of the aquifer supplying the water, and whether a spring is isolated or is part of a larger upflowing system. For preliminary evaluation, an arbitrary cutoff at 200 l/min is suggested for a single isolated spring, and 20 l/min for single springs of larger groups.

CONCLUSIONS

Chemical analyses of hot-spring water and gas may be of great use in an exploration program for geothermal energy. Like all exploration methods, a great many assumptions must be made in order to interpret the data. We urge that these assumptions be kept in mind during the evaluation processes.

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