

GEOCHEMISTRY

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INTRODUCTION

A number of important exploration and reservoir production questions can be answered from studies of the chemistry of geothermal fluids and reservoir rocks, and so geochemistry plays a relatively important role in geothermal exploration and development (Henley and Ellis, 1983). Geochemical reconnaissance involves sampling and analyzing waters and gases from hot springs and other geothermal manifestations in the area under investigation. The data obtained are then used to help locate a geothermal system, to determine whether the geothermal system is hot-water or vapor-dominated, to estimate the minimum temperature expected at depth, to predict the homogeneity of the water supply, to infer the chemical character of the waters at depth, and to determine the source of recharge water. Geochemical principles can also be applied to interpretation of chemical data from producing wells and may yield information on formation of scale in pipes or a gradual chemical change in the geothermal fluids that could indicate an impending change in production temperature.

OVERVIEW OF GEOTHERMAL GEOCHEMISTRY

Geothermal fluids contain a wide variety and concentration of dissolved constituents. The simplest chemical parameters often quoted to characterize geothermal fluids are:

1. Total dissolved solids (TDS) in parts per million (ppm) or milligrams per liter (mg/L). This gives a measure of the amount of chemical salts dissolved in the waters.
2. pH. The pH of a fluid is a measure of the acidity or alkalinity of the fluid. Neutral fluids have $\text{pH} = 7$ at room temperature. Acid fluids have pH values < 7 and alkaline fluids have pH values > 7 .

These two parameters can be measured in the field by use of a conductivity meter and a pH meter. The conductivity meter measures the TDS of a fluid by measuring its electrical conductivity. The more dissolved salts, the higher the electrical conductivity.

The amount and nature of dissolved chemical species in geothermal fluids are functions of temperature and of the local geology (see Table 1). Lower-temperature resources usually have a smaller amount of dissolved solids than do higher temperature resources, although there are exceptions to this rule. TDS values range from a few hundred to more than 300,000 mg/L. Many of the high-temperature resources in the west contain 6,000 to 10,000 mg/L TDS; whereas, a portion of

the Imperial Valley, California resources are essentially saturated with salts at 300,000 mg/L. The pH of geothermal resources ranges from moderately alkaline (8.5) to moderately acid (5.5). The dissolved solids are usually composed mainly of sodium (Na), calcium (Ca), potassium (K), chlorine (Cl), silica (SiO_2), sulfate (SO_4), and bicarbonate (HCO_3). Minor constituents include a wide range of elements with mercury (Hg), fluorine (F), boron (B) and arsenic (As) being toxic in high enough concentrations and therefore, are of environmental concern. In general, each state has regulations governing the use and disposal of waters that contain toxic or otherwise harmful constituents, and local regulations should always be consulted in planning the use of any geothermal resource. Dissolved gases usually include carbon dioxide (CO_2), hydrogen sulfide (H_2S), ammonia (NH_3) and methane (CH_4). Hydrogen sulfide (H_2S) is a safety hazard because of its toxicity to animals, including humans. Effective means have been and are still being developed to handle the scaling, corrosion, and environmental problems caused by dissolved constituents in geothermal fluids.

As geothermal fluids move through rocks, they react chemically with the rocks, which themselves are usually chemically complex. Certain minerals in the reservoir rocks may be selectively dissolved by the fluids while other minerals may be precipitated from solution or certain chemical elements from the fluid may substitute for certain other elements within a mineral. These chemical/mineralogical changes in the reservoir rocks may or may not cause volume changes, i.e., may or may not affect the permeability and porosity of the rocks. Obviously, if the mineral volume increases, it must be at the expense of open space in the rock, which caused a decrease in permeability. In locations where pressure, temperature, or rock chemistry change abruptly, minerals may be precipitated into the open spaces. This results in plugging of the plumbing system.

Silica and calcium (CaCO_3) are the principal minerals usually involved. The solubility of SiO_2 decreases with a decrease in temperature, with pressure changes having very little effect. SiO_2 can be precipitated into open spaces such as fractures or pores in the rock in regions where the subsurface temperature changes abruptly and at the subsurface where hot springs discharge. Calcite (calcium carbonate) has a retrograde solubility, i.e., it is more soluble at low temperatures than at high temperatures. Other carbonate species such as dolomite (MgCO_3), as well as sulfate species such as anhydrite (CaSO_4), show similar retrograde solubility relationships with temperature. In addition, the solubility of carbonate minerals

Table 1. Representative Analyses of Geothermal Fluids

Sample	Temp. (°C)	pH (ppm)	SiO ₂ (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Li (ppm)	HCO (ppm)	SO (ppm)	Cl (ppm)	F (ppm)	B (ppm)	As (ppm)
1	42	—	52	257	17	570	—	0.5	—	932	625	2.8	2.6	—
2	89	7.9	293	5	0.8	633	71	0.7	305	—	885	1.8	4.9	2.7
3	225	8.4	690	17	0.03	1320	255	14.2	—	36	2260	1.3	—	4.8
4	<250	—	563	8	<2	2320	461	25.3	232	72	3860	6.8	—	4.3
5	292	—	705	592	0.6	6382	1951	14.5	28	<3.5	11918	—	13.4	—
6	316	—	400	28000	54	50400	17500	215	7150	5	155000	16	390	12

Sample Descriptions

1. Hot Spring, Monroa, UT.
2. Hot Springs, Steamboat, NV.
3. Well 44, Wairakei, New Zealand.
4. Brine discharge from Well 54-3, Roosevelt Hot Springs, UT.
5. Analyses calculated from flashed brine, Well M-26, Cierro Prieto, NM.
6. Brine discharge from Well 11D, Salton Sea Geothermal Field, CA.

decreases rapidly with a decrease in the partial pressure of carbon dioxide. Thus, as fluids that are saturated with carbonate approach the surface, carbonate minerals such as calcite are deposited as a result of the loss of CO₂, which evolves from the solution with the decrease in hydrostatic pressure.

The chemically complex hydrothermal system is dynamic through time. That is, for any given volume element in the reservoir, the fluid composition varies slowly with time, bringing about variation in the rock composition, porosity and permeability. However, because the rate of fluid circulation is perhaps only a few centimeters per year, in most hydrothermal systems a state of chemical equilibrium or near-equilibrium is observed to exist between reservoir fluid and reservoir rocks (Capuano and Cole, 1981; Helgeson, 1968). The assumption of chemical equilibrium is made in the application of several of the geochemical techniques discussed below. Lack of equilibrium could be evidence for rapid movement of fluid through the reservoir.

CHEMISTRY OF GEOTHERMAL FLUIDS

By taking appropriate samples of fluids from surface springs and from well discharges, a great deal can be learned about presence or absence of a geothermal resource and about the resource itself. The most important information can probably be obtained in the following topic areas:

1. Reservoir Fluid Types: Various fluid types evolve from typical geothermal systems, and identification of the fluid type can have important implications on the existence of other fluid types in the vicinity and, thus, on exploration.
2. Geothermometry: Chemical data can be used to estimate the maximum subsurface fluid temperatures to be expected in a given area.
3. Reservoir Processes: The extent of mixing of thermal and non-thermal waters and boiling in the subsurface can be determined.

4. Production Monitoring: In a producing geothermal resource, monitoring of the concentrations of chemical species over time can lead to information of the nature of the recharge to the system and to the prediction of adverse temperature changes in advance of their manifestation in the well.

GEOTHERMAL FLUID TYPES

Normal groundwaters are usually near neutral in pH and slightly bicarbonate in character. When they are heated in a geothermal system, they tend to become more sodium chloride in character, with dissolved salt contents that can range from a few hundred mg/L to more than 300,000 mg/L. If the fluid boils at depth, gases (e.g., CO₂, H₂S) are partitioned into the steam phase and migrate independently toward the surface. The gas-rich steam phase may encounter cool groundwater, which is heated. Oxidation of H₂S produces acid-sulfate waters that react with the rocks to produce characteristic advanced argillic alteration assemblages. Bicarbonate-rich geothermal waters are produced where groundwater dissolves CO₂, rising with steam from the deeper geothermal system. Any of these water types may be diluted with low salinity groundwater before being sampled from a thermal spring or by a drill hole. By study of the chemistry of the various waters found in a geothermal area, the nature of the (independent) geothermal reservoirs can be determined.

In the usual reconnaissance application, water samples are taken for analysis from springs and wells in the vicinity of the prospect. For detailed reservoir studies, fluid samples can also be taken from producing wells or from wells recently drilled but not yet producing. Great care must be taken to ensure that the samples contain only pristine reservoir, well, or spring fluid. In the case of a recently drilled well, the well must be flowed until all traces of the drilling fluid have been removed. Sampling of fluids should be repeated at intervals of hours. When the analysis of these samples becomes constant, the fluid is assumed to represent reservoir fluid. Proper sampling technique is very important and should be entrusted only to someone with experience. The samples must be

filtered and properly acidified for preservation until analysis. The sampler should help design the sampling program with a chemist at the laboratory where the analyses will be performed. At each sample location, pH and temperature are measured at the time of collection.

Various systems have been devised to diagram water chemistry for better visual presentation (Hem, 1970). One of the most popular in geothermal work is a plotting method given by Piper (1944). This method is based on the relative amounts of Na + K, Mg, Ca, Cl + F, SO₄, and HCO₃ + CO₃ in a fluid. These components are the major ions in thermal and non-thermal waters, and classifications based on them agree well with observations on the formation of various geothermal water types. To construct a Piper plot, also called a "tri-linear plot", the concentrations of the cations and anions are transformed from units of ppm or mg/L into the units of milli-equivalents and the percentages of the cation and anion combinations as given above are plotted on a diagram similar to that shown in Figure 1. Any water analysis will contain

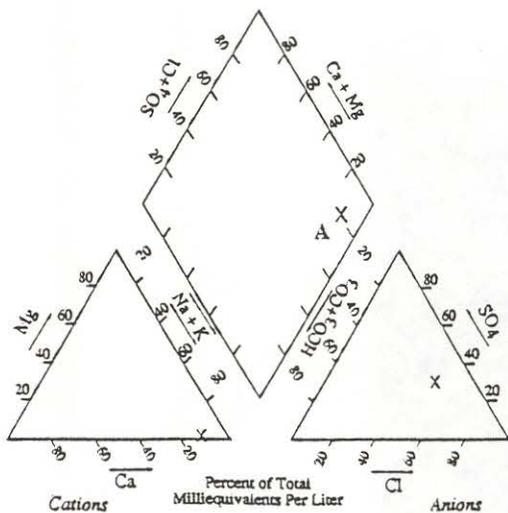


Figure 1. Illustrative tri-linear plot.

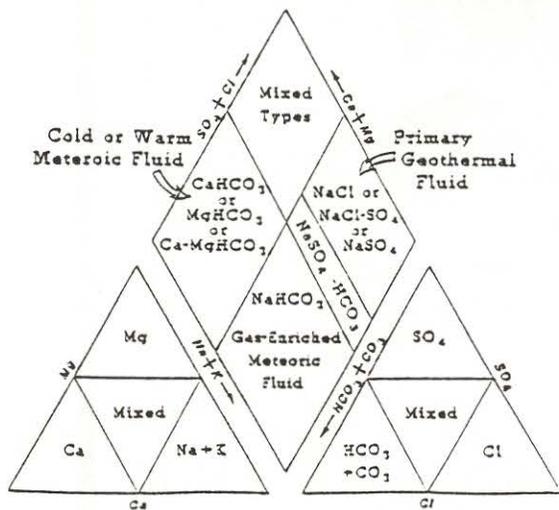


Figure 2. Tri-linear water classification.

cations that yield one point on the lower left portion of the diagram and anions that yield one point of the lower right portion. The cation and anion percentages are combined by projecting them onto the central rhombohedron, as illustrated with the water analysis shown as point A in Figure 1. The diagram can be used to plot all of the waters from a prospecting area, and classification of water types can then be developed by comparing the result to the general classification diagram shown in Figure 2.

Figure 3 shows a classification of water types found at the Meager Creek geothermal area in southwestern British Columbia (Adams and Moore, 1987). In this study, the authors showed that the several water types were chemically independent, i.e., that they had not evolved from a common water type nor had one evolved from any other. This result implies that there is no through-going permeability in the part of the Meager Creek area explored, and that the several waters originate in unconnected probable small reservoirs. Murray (1985) shows a Piper plot of waters from the Calistoga geothermal area in the Napa Valley of California (Figure 4.). Their results suggest that thermal water rises along a central fault in the valley. The thermal water is progressively diluted with non-thermal groundwater, gradually becoming enriched

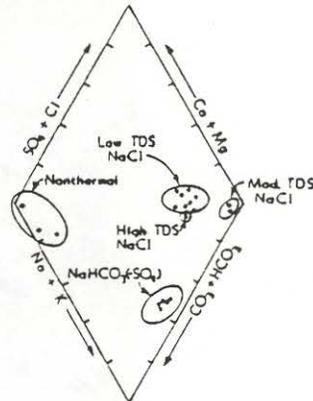


Figure 3. Tri-linear diagram, Meager Creek, B.C.

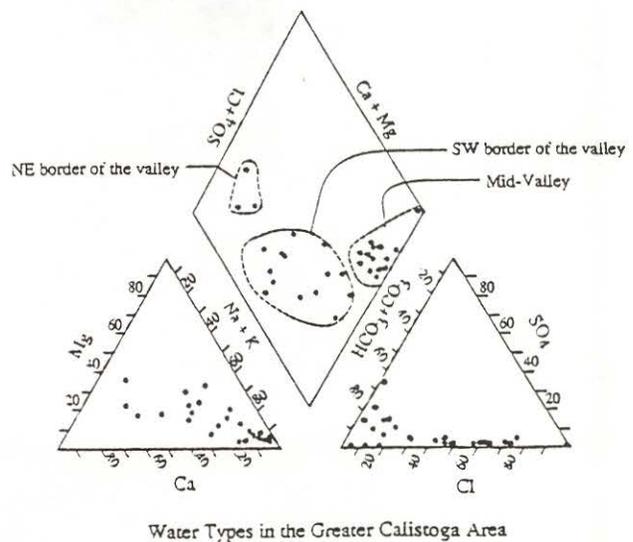


Figure 4. Tri-linear diagram, Calistoga, California.

in iron, sulfate and bicarbonate. The several water types in the valley can all be related chemically to the thermal water seeping up the central fault, and water geochemistry can be used to trace and map geothermal waters in the valley.

CHEMICAL GEOTHERMOMETRY

Chemical analyses of geothermal fluids can sometimes be used to estimate subsurface reservoir temperature. This information is of obvious interest during exploration, when information from measurements in drill holes may be unavailable; but, it is also very important during drilling because: (a) accurate temperature measurements cannot be made in a well until after thermal effects of the drilling process have been dissipated (weeks to months after drilling is finished) and (b) chemical geothermometry may indicate that temperatures higher than those found in the drill hole may be found elsewhere.

Several major-element geothermometers have been used successfully for estimating subsurface temperature, and reviews of these geothermometers were given by Fournier (1981) and by Henley (1984). In certain geothermal areas, the silica content of geothermal fluids appears to be limited above about 350°F by the solubility of the mineral quartz (SiO₂) and to be limited below 350°F by the solubility of amorphous silica. Both solubilities are temperature dependent, as shown in Figure 5, which gives a graph of the solubility of various silica phases versus temperature.

Table 2 gives some of the silica geothermometer equations as an illustration. A second system of geothermometers is based upon the equilibrium reached among sodium (Na), potassium (K) and calcium (Ca) where reservoir rocks contain abundant quartz and feldspar (Fournier and Truesdell, 1973). One common geothermometer of this class is also shown in Table 2.

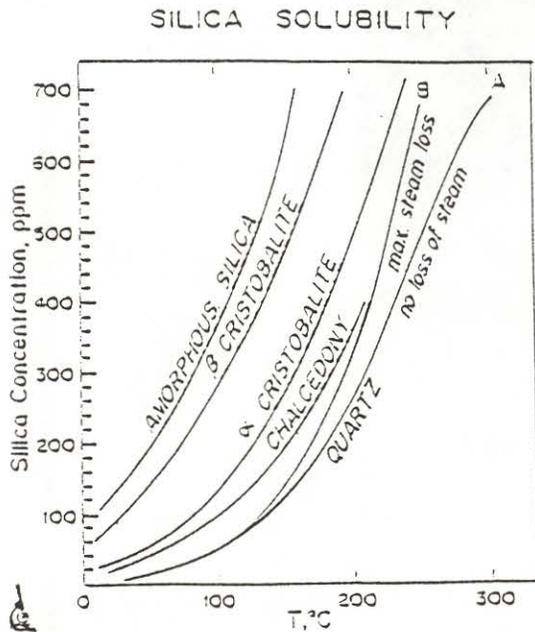


Figure 5. Solubility of silica species in hot water.

Table 2. Chemical Geothermometer Equation.
All concentrations are in mg/kg.

SILICA

Quartz - no steam loss

$$T(^{\circ}\text{C}) = \frac{1309}{5,190 - \log \text{SiO}_2} - 273.15$$

Quartz - maximum steam loss

$$T(^{\circ}\text{C}) = \frac{1522}{5.75 - \log \text{SiO}_2} - 273.15$$

ALKALI

Na/K (Fournier)

$$T(^{\circ}\text{C}) = \frac{1217}{\log (\text{Na}/\text{K}) + 1.483} - 273.15$$

$$T(^{\circ}\text{C}) = \frac{1647}{\log (\text{Na}/\text{K}) + \beta \cdot [\log (\sqrt{\text{Ca}/\text{Na}} + 2.06) + 2.24]} - 273.15$$

* $\beta = 4/3$ for $\sqrt{\text{Ca}/\text{Na}} > 1$, $T < 100^{\circ}\text{C}$; $\beta = 1/3$ for $\sqrt{\text{Ca}/\text{Na}} < 1$, $T > 100^{\circ}\text{C}$

Other silica geothermometers are based upon equilibrium with the minerals chalcedony, α -cristobalite, or β -cristobalite, and it is obviously of importance to know which silica minerals exist in the reservoir rocks. If drill information is not available on this point, as is usually the case early in an exploration program, one must rely on geologic mapping and inference to provide this information.

Different geothermometers frequently give different results when applied to the same fluid. Use of other data may help shed light on the relative reliability of the various geothermometers in specific geologic situations. For example, silica concentration can be affected by the pH of the fluid, and temperatures calculated from the Na-K-Ca geothermometer may be in serious error if the CO₂ or magnesium concentrations are too high or if there has been addition of any of these elements through interaction of the fluid with sedimentary rocks or ion-exchanging minerals such as clays or zeolites. Mixing of the thermal reservoir waters with normal groundwater can also change concentrations of the critical elements in a geothermometer, and can result in a calculated temperature that is either too high or too low. In addition, some geothermometers do not work well where reservoir temperatures are below ~ 300°F.

Care must obviously be taken in interpretation of chemical geothermometer data, and in this matter there is no good substitute for experience. Anyone can apply the geothermometer equations to the chemical analyses; but, the interpretation of the results can be extremely involved, and is best left to appropriate experts.

AGE DATING OF GEOTHERMAL WATERS

Radioactive isotope chemistry has been used to attempt to determine the age of the water in geothermal systems, using techniques similar to those for dating of rocks. The most successful applications have used tritium, a naturally occurring radioactive isotope of hydrogen, which has a half life of 12.26 years. Minor amounts of tritium are naturally produced continually in the stratosphere by the action of cosmic radiation on hydrogen in the air. However, major amounts of tritium have been put into the atmosphere by thermonuclear weapons testing. Tritium concentration is expressed in terms of the Tritium Unit (TU), which is equivalent to a ratio of tritium to hydrogen-1 of 10^{-18} . In continental climates in the temperate zone, cosmic radiation produces about 10 TU. As many as 10,000 TU were measured in 1963 following extensive atmospheric nuclear weapons testing. Ambient tritium levels thereafter decreased until about 1968, and since then have remained fairly constant. The following generalizations can be made concerning the age of geothermal water in the absence of mixing. A tritium content of <3 TU indicates that no water younger than 25 years is present. Values of 3 to 20 TU suggest that some amount of thermonuclear tritium is present, which indicates that the fluids entered the groundwater environment in the 1954-1961 time frame. If more than 20 TUs are found, the water entered the system after 1963. Many geothermal reservoir waters are older, some much older, than 25 to 50 years of useful dating range available with tritium. Typically, convecting hydrothermal fluids move at speeds measured in feet or tens of ft/y. However, tritium dating of water can indicate rapid movement in a system.

PRODUCTION MONITORING

It is important to obtain and analyze samples from geothermal production wells on a periodic basis beginning at the start of production. By collecting a history of production chemistry data, processes and changes in the reservoir can be more easily understood and predicted. Monthly samples should be taken and analyzed from each production well in large, high-production systems, and quarterly samples should be taken in smaller systems.

These intervals are meant to be simple guidelines. The geothermal developer should obtain competent consulting help in designing and carrying out a sampling and analysis program.

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