GEOCHEMISTRY IN GEOTHERMAL EXPLORATION AND PRODUCTION

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ABSTRACT

Geochemistry has many uses in a geothermal resources development program. It can provide information about reservoir conditions before and during production, the source of recharge, and directions of fluid flow. It has important applications in regard to corrosion, scaling, and waste-disposal problems. When properly used, chemical geothermometers and mixing models applied to hot-spring waters can give accurate information about underground reservoir temperatures and salinities. However, when interpreting chemical data, attention should be given to geologic and hydrologic information. Also, chemical models must be consistent with isotopic data; plots of enthalpy versus chloride, δD, and $\delta^{18}O$ are useful for determining that consistency.

Equations expressing the solubility of quartz in water at the vapor pressure of the solution as (1) a function of temperature and (2) a function of enthalpy permit calculation of silica geothermometer temperatures for dilute solutions up to 330°C, with or without steam separation at any temperature. The solubility of quartz in NaCl solutions (expressed in mg/kg) is similar to that in pure water at temperatures below about 260°C. At higher temperatures quartz solubility in salt solution is greatly increased compared to pure water; this has great importance for determining conditions at which silica scaling is likely to occur.

INTRODUCTION

Compositions of geothermal fluids are controlled by a complex interplay of hydrologic, chemical, and physical processes. These include leaching of country rocks by migrating fluids, boiling with partitioning of volatiles between liquid and vapor phases, mixing of waters of different salinities and temperatures, and gas-water-rock reactions at widely ranging temperatures and pressures. Interpreting the chemical and isotopic compositions of naturally occurring liquids, gases, and solids in relation to these processes is what hydrothermal geochemistry is all about.

In a sense hydrothermal geochemistry is striking out in all directions at once; it is a veritable explosion of hydrothermal information and ideas. This burst of activity has come about for many reasons: (1) technological advances in instrumentation and in techniques for obtaining chemical and isotopic data, (2) exploration drilling and production of new geothermal fields, and publication of downhole information obtained from diverse geologic environments, (3) greater use of computers and the development of programs to model chemical and isotope systems, and to store, retrieve, and manipulate data, and (4) the need to solve various chemical problems related to production and waste disposal.

To summarize the many excellent and diverse geochemical papers that have been published recently would be impossible here. I shall briefly touch upon some of the ways that geochemistry can be used to aid in geothermal energy exploration and production and highlight a few geochemical matters that are of particular interest to me at this time. I shall go into detail only in regard to two aspects of geochemistry with which I have been directly involved: (1) development of geochemical tools and techniques to explore and evaluate geothermal prospects, and (2) determination of the solubility of quartz in hydrothermal solutions and its practical application.

THE MANY USES OF GEOCHEMISTRY

Geochemistry can and should be used in all phases of a geothermal resources development program, from regional exploration through specific site evaluation to production. When properly used, chemical and isotopic geothermometers (Ellis and Mahon, 1977; Fournier, 1977, 1981; Truesdell, 1976a; Truesdell and Hulston, 1980; D'Amore and Panichi, 1980) and mixing models (Fournier, 1977, 1979a; Truesdell and Fournier, 1977) can provide excellent information about underground reservoir temperatures. Isotopic data may give an indication of the source, age, and amount of water that has flowed through a geothermal reservoir (Truesdell and Hulston, 1980; Ellis and Mahon, 1977). Inert gas concentrations may give information about the initial temperature of the recharge water and whether subsurface boiling occurred before discharge at the surface (Mazor, 1977). Variations in composition of soil gases may give indications of subsurface boiling and locations of otherwise hidden faults (Tonani, 1970; Kahler, 1981; Roberts et al., 1975; Koga and Tetsuro, 1976). Helium isotopes in hot springs can be used to show mass transport from subcrustal regions (Craig et al., 1978).

Early chemical characterization of reservoir fluids is essential if scaling, corrosion, and environmental problems are to be anticipated and circumvented. Spatial variation in liquid and gas compositons can give information about the size, shape, and temperature of the reservoirs, and directions of fluid flow. Relatively chloride-rich fluids tend to be found in the central upflowing zones of liquid-dominated hydrothermal systems, and relatively bicarbonate- and sulfate-rich waters in the cooler margins and tops of both liquid- and vapor-dominated systems. An exception to this generalization is in granitic and metamorphic rocks, where even the hottest upflowing waters in liquid-dominated systems may contain little chloride.

Fluids produced shortly after completion of a well *may* give an early indication of the reservoir temperature long before the well recovers thermally from the cooling effects of circulating drilling water (Fournier et al., 1980). Changing compositions of fluids (liquids and gases) produced from wells can be used to monitor changing underground temperatures, verify production from different aquifers, detect boiling in the aquifer, and monitor reservoir drawdown and influx of cold water long before cold water influx is detected by decreases in reservoir temperatures and enthalpies (Mahon, 1966; Ellis, 1977; Glover, 1970; Truesdell, 1976b; Truesdell et al., 1979; Grant et al., in press).

Relatively high concentrations of some trace elements, such as Zn, Pb, and As, and the presence of certain hydrothermal alteration products, such as K-feldspar, have been found to correspond to zones where relatively large amounts of fluid flow have occurred in the past (Browne, 1978; Christensen et al., 1980). Zones of relatively high permeability that persist in the rock up to the present are likely to be located within or near where fluid has flowed most easily in the past. Therefore, study of trace elements and hydrothermal alteration products in cuttings and core as drilling progresses may provide very useful information about how to complete a well.

Studies of hydrothermal alteration products and fluid inclusions may provide information about the thermal and chemical history of a given body of rock and the water that flowed through it. In studies of ore deposits, primary fluid inclusions are prized for the information they provide about the conditions at the time of mineral growth, while secondary fluid inclusions are generally considered a nuisance. In studies of active hydrothermal systems, however, I suggest that secondary fluid inclusions may provide the kind of information on reservoir conditions that we require, namely the range in hydrothermal temperatures and salinities to which a given body of rock has been subjected. This means that quartz, feldspar, and other minerals that formed at the time of crystallization of an igneous rock should be considered for studies of secondary fluid inclusions related to superposed hydrothermal activity.

INTERPRETATION OF HOT-SPRING WATERS

One of the most widespread uses of geochemistry by geothermal workers is to estimate reservoir temperatures from compositions of hot-spring waters. The equations for chemical geothermometry are relatively simple, and it seems that everyone with access to water analyses calculates geothermometer temperatures: unfortunately, that is the extent of many geochemical "studies." This might be acceptable practice if only one spring were available for sampling in a given region or if all the waters were identical in composition. However, this is generally not the case, and we can and should do better than that with our interpretations.

Good interpretative practice starts with good sampling procedures. This includes both the wise selection of water for analyses and the proper preservation of samples between the time of collection and analyses (Ellis and Mahon, 1977; Shannon et al., 1978). Where many hot springs are available for sampling, all too frequently only the boiling or hottest spring waters are collected while the cool and cold springs are ignored. Collecting only the hottest waters makes it very difficult to assess conductive and adiabatic cooling processes and to apply mixing models, which all require knowledge of cold, non-thermal ground-water compositions. The best sampling strategy is to collect every available ground-water, hot and cold. If for some reason there is a limitation on the number of samples that can be collected, one should try to obtain a suite of samples with a great diversity in temperatures and compositions. A conductivity meter or chloride test papers can be used to check relative salinities of various waters before deciding which ones to sample.

At the time of sampling, temperatures and measured or estimated mass flow rates for each spring and well should be recorded, whether sampled or not, and the total mass flow from the area estimated. In areas of distinct rainy and dry seasons, springs should be sampled at different times of the year to determine if there are seasonal changes in temperature, composition, and mass flow rates. In areas of few or no flowing springs and no pre-existing water or irrigation wells, one should consider drilling a few shallow wells specifically to obtain ground-water samples for chemical analysis and to determine hydrologic gradients.

When analytical data are available for several water samples, interpretation should start with a general assessment of how each of the samples relates to the others. Relations involving chloride are particularly important because chloride is more likely to be conservative in a hydrothermal system than most other dissolved components; that is, the chloride concentration in thermal water rising from a reservoir is not likely to change significantly by interaction with the surrounding rock, unless the water traverses evaporites containing halite. Changes in chloride concentration are most likely the result of boiling (evaporation) and mixing processes, while concentrations of most other components can also change as a result of continued water-rock reactions. I recommend the following interpretive procedure:

1. Look for indications of conductive cooling, mixing, and adiabatic processes using graphs of Cl vs. t°C (measured temperature at point of collection), δD vs. $\delta^{18}O$, δD vs. Cl, and $\delta^{18}O$ vs. Cl.
2. Look for indications of water-rock reactions at intermediate temperatures using graphs of Cl vs. SiO_2, Cl vs. cation (Na, K, Li, Ca, and Mg), and Cl vs. HCO_3 (computed from total equivalents HCO_3 and CO_3).
3. Look for groups of waters that are compositionally similar in some respects but different from other waters. Possible ways to subdivide are by Na/K, K/Li, Cl/B, Cl/(HCO_3 and CO_3) in equivalents, and by salinity range.
4. Within groups of similar waters determine the best samples or best chemical data to use for calculating geothermometer temperatures.
5. Determine if the silica mixing model is applicable using criteria discussed by Fournier and Truesdell (1974), Truesdell and Fournier (1977), and Fournier (1981).
6. Display the interpreted subsurface conditions on an enthalpy vs. chloride plot.
7. Check to see if tritium and stable-isotope data are consistent with the relations shown in the enthalpy vs. chloride plot. I do this with graphs of enthalpy vs. isotopes and chloride vs. isotopes.

When steam has separated from a water before that water was collected (a boiling spring or flashed well water), the isotopic composition of that water must be corrected for the partitioning of isotopes between the liquid and gas phases. Truesdell et al. (1977) showed that the final isotopic composition of a water that flashed from a given initial temperature and pressure to a final temperature will depend upon whether the steam remained with the boiling water until it separated all at once at a given pressure (single-stage steam separation), or whether the steam underwent either continuous or multi-stage removal from the residual liquid at a succession of specific decreasing pressures and temperatures. Truesdell et al. (1977) give equations and graphs for determining the isotopic compositions of waters that result from single-stage and continuous steam separation. I find it instructive to construct enthalpy vs. δD and enthalpy vs. $\delta^{18}O$ diagrams using fractionation factors listed in that paper. For example in Fig. 1, point GF28 shows the enthalpy and δD values of water in a boiling spring (410 J/g) after an unknown amount of steam separation. The silica concentration in that water indicates an initial reservoir temperature of about 260°C (1134 J/g), if the water cooled entirely by conduction, or 230°C (990 J/g) if it cooled nearly adiabatically. Point A shows the initial condition of the reservoir water if cooled conductively, point B1 the initial condition if the water cooled adiabatically with single-stage steam separation at atmospheric pressure, and point B2 the initial condition if the water cooled by boiling owing to decompression with continuous separation of steam. Because spring GF28 had only a moderate flow rate of 15 to 25 L/min at the time of collection and was not vigorously boiling, the water most likely cooled partly by conduction and partly by boiling. The stippled area in Fig. 1 shows the range of initial reservoir conditions for all combinations of conductive and adiabatic cooling. Point S1 gives the isotopic compositions of all of the steam that would separate in a single-stage process, and point S2 shows the isotopic composition of the first steam that separates at 230°C with continuous steam separation. The line S2-S1 shows how the isotopic composition of the evolved steam would change as the water temperature decreased along the curve B2-GF28. A plot of enthalpy vs. $\delta^{18}O$ for sample GF28 would be similar to Fig. 1.

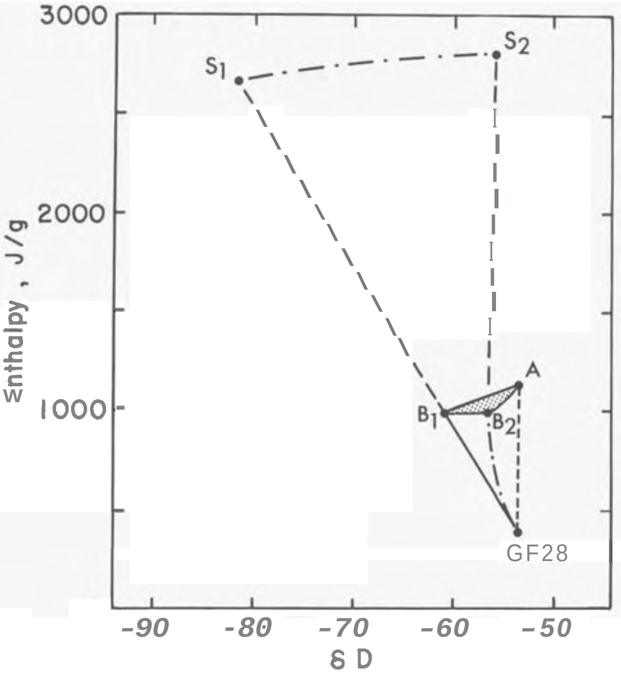

Fig. 1. Graph of enthalpy versus δD showing the ranges in possible initial reservoir conditions and separated steam for different cooling mechanisms that result in a hot spring water represented by point GF28. See text for discussions.

A consistent picture should emerge when the same waters that have been plotted on an enthalpy vs. chloride diagram are plotted on enthalpy vs. δD and enthalpy vs. $\delta^{18}O$ diagrams. If not, deficiencies are present in the model or in the data.

In some situations tritium analyses can be very helpful in a geothermal exploration program. When applying geochemical geothermometers, waters that have been underground for a long time, as shown by low tritium values, are more likely to have attained water-rock chemical equilibrium than those that have been underground only a short time (high tritium). When assessing the hydrologic significance of mixing of high- and low-temperature waters it is of value to know if the low-temperature component is from a shallow, local source, or a deeper, cold aquifer. Where hot springs (or well waters) contain different amounts of chloride and tritium as a result of different amounts of mixing of hot and cold waters, extrapolation to zero tritium gives the maximum chloride in the deep component. Repeat analyses of tritium and chloride over a protracted period of time can be used to confirm that the deep component has zero tritium. Information about the chloride concentration in the deep, high-temperature component can, in turn be used in an enthalpy-chloride mixing model to estimate the temperature of that hot-water component.

When interpreting chemical geothermometers, keep in mind the effects that different hydrologic conditions may have upon hot-spring compositions. The reliability or faith that one places upon particular geothermometer results should depend upon the number of thermal waters that were analyzed and the mass flow rates and measured temperatures of those waters.

If the silica, Na-K-Ca, and Na/K geothermometers all give temperatures in excess of 150°C and Mg^{+2} concentrations are relatively low, chances are good that a deep reservoir temperature will be as great or greater than that indicated by the geothermometers. If the silica temperature is much less (<25°C) than the Na-K-Ca, Na-K-Ca-Mg, and Na/K temperatures, then either silica may have precipitated from solution after leaving the reservoir or the water is a mixed water that did not re-equilibrate after mixing. If the silica (chalcedony) and Na-K-Ca geothermometers give temperatures below 100°C and Na/K gives a temperature greatly above 100°C, the Na/K temperature probably is in error. If a water contains little Mg and the Na-K-Ca temperature is several degrees above the Na/K temperature, the Na-K-Ca temperature may be too high because $CaCO_3$ precipitated from solution before the water was collected (or after collection if the sample was not acidified). The precipitation of $CaCO_3$ is likely to have influenced the calculated Na-K-Ca temperature if the solution was saturated in respect to calcite at the time and place of sampling. However, even though the solution may be unsaturated with respect to calcite at the time and place of collection, $CaCO_3$ may have precipitated from a boiling solution underground, with the solution subsequently becoming unsaturated with $CaCO_3$ during subsequent cooling.

The application of an Mg^{+2} correction to the Na-K-Ca geothermometer may be essential if a water really comes from a low-temperature (<100°C) underground environment. However, if a water comes from a high-temperature environment and picks up Mg^{+2} on the way to the surface, the Mg^{+2} correction will lead to estimated temperatures that are too low. At this time there is no easy way to determine when to apply and when to ignore the Mg^{+2} correction.

Agreement between the $\Delta^{18}O$ ($H_2O-HSO_4^-$) isotope geothermometer and other geothermometers suggests that the water had a comparatively long residence time in an underground reservoir at about the indicated temperature. In some places, such as Yellowstone National Park, Wyoming (McKenzie and Truesdell, 1977), and Long Valley, California (Fournier et al., 1976), the $\Delta^{18}O$ ($H_2O-HSO_4^-$), geothermometer gives temperatures much higher than those indicated by the silica and cation methods, but is in agreement with mixing model temperatures. When the $\Delta^{18}O$ ($H_2O-HSO_4^-$) temperature is higher than other geothermometer temperatures, it suggests that intermediate temperature reservoirs are present and that water moves through them with residence times of a few weeks to a few months.

AN UPDATE ON THE SOLUBILITY OF QUARTZ AND PRACTICAL APPLICATIONS

Over the past several years there has been an accumulation of experimental results by various workers for the solubility of quartz in water at and near the vapor pressure of the solution (Fournier and Potter, 1982). The data suggest that the solubility of quartz at 250°C is slightly less than that given by Fournier and Rowe (1966). A revised equation for the solubility of quartz in water along the vapor-pressure curve for the temperature range 25° to 330° is given by Fournier and Potter (in press) as

$$t = C_1 + C_2S + C_3S^2 + C_4S^3 + C_5\log S, \qquad (1)$$

where t is temperature in degrees Celsius, S is silica concentration in mg/kg, and C_1 through C_5 are constants given in Table 1.

Other vapor-pressure quartz-solubility curves have been suggested (Walther and Helgeson, 1977; Fleming and Crerar, 1982) that are significantly below the Fournier and Potter (in press) curve. I believe that the calculated values of Walther and Helgeson (1977) are low because they assumed that solubilities of quartz at 1013 bars reported by Morey et al. (1962) were correct. It now appears that at 1013 bars and temperatures below 200°C Morey et al. (1962) measured the solubility of chalcedony rather than quartz. The position of the Fleming and Crerar (1982) curve is strongly influenced by results of experiments by Crerar and Anderson (1971). Fournier (1979b) and Fournier and Potter (1982) concluded that the experimental technique employed by Crerar and Anderson (1971) was likely to have produced quartz-solubility values that were too low. If the Fournier and Potter (in press) quartz-solubility curve is correct, then the excellent discussion by Fleming and Crerar (1982) of pH effects on quartz solubility and applications to geothermal fluid processing should be modified, using

$$\log K_C = D_1 + D_2T + D_3T^{-1} + D_4T^{-2} + D_5T^{-3} \qquad (2)$$

where K_C is the neutral pH molal solubility of quartz, T is absolute temperature, and D_1-D_5 are constants given in Table 1.

In the silica geothermometer description by Fournier and Rowe (1966), two reference curves were drawn; one showed dissolved silica with conductive cooling and the other dissolved silica after adiabatic cooling to 100°C at constant enthalpy. However, where boiling springs occur at high elevations, adiabatic cooling continues to temperatures significantly lower than 100°C. Also, well waters are commonly sampled after steam separation at temperatures above 100°C. Fournier and Potter (in press) use a plot of dissolved silica vs enthalpy (Fig. 2) as a simple method of correcting for steam separation at any temperature. The enthalpy of liquid water at the collection temperature (or collection pressure) can be determined from steam tables (Keenan et al., 1969). Points C and E in Fig. 2 represent two samples collected after steam loss at different temperatures, and the line *AB* shows the solubility of quartz at the vapor pressure of the solution as a function of enthalpy. Points G_C and G_E show the enthalpy of steam in equilibrium with points C and E respectively. The intersections of the lines drawn from G_C to C and C_E to E with curve AB (points F and D respectively) give the initial enthalpies of the reservoir fluids before adiabatic cooling. Fournier and Potter (in press) give the equation of line AB as

$$S = E_1 + E_2H + E_3H^2 + E_4H^3 + E_5H^4 \qquad (3)$$

where S is silica concentration in mg/kg, H is enthalpy of liquid water in J/g, and E_1 through E_6 are constants given in Table 1. They also give a computer program in BASIC to calculate silica (quartz) geothermometer temperatures with adiabatic cooling to any temperature, with initial reservoir temperatures up to 330°C, and a computer program to calculate silica mixing model temperatures with or without steam loss before mixing.

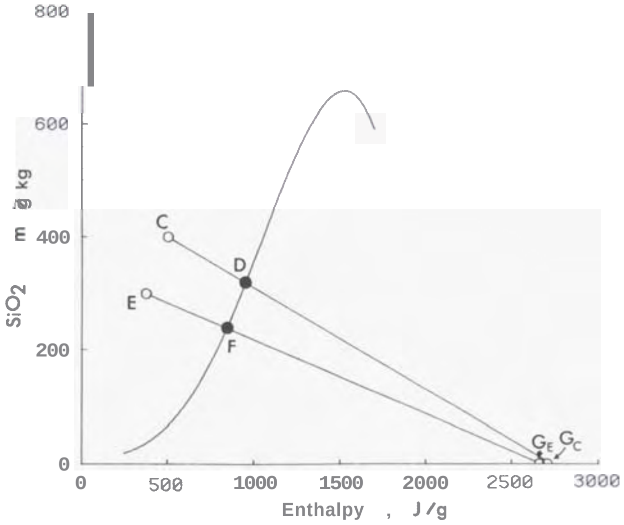

Fig. 2. Dissolved silica versus enthalpy for quartz dissolved in pure water at the vapor pressure of the solutions. See text for discussion.

Fournier and Potter (1982) found that, in logarithmic plots of dissolved silica vs. specific volume of water, the experimental data lie along smooth, nearly parallel isothermal curves, and they devised an equation that fits most of the data quite well. The Fournier and Potter (1982) equation allows the silica geothermometer, derived vapor for pressure conditions, to be corrected for pressure effects in deep reservoirs.

Up to this point silica geothermometry has been discussed for dilute solutions, but what is the effect of dissolved salt? This is of great interest from the point of view of scaling. On the basis of a small amount of data Fournier and Rowe (1966) concluded that the addition of 2 m NaCl generally does not significantly influence the solubility of quartz. That conclusion now appears valid at the vapor pressure of the solution only at temperatures below about 260°C and at high pressures (>1000 bars) below about 400°C, and when solubilities are expressed in units of mg/kg. Figure 3 shows the solubility of quartz in pure water and in 4 m NaCl at 350°C as a function of pressure. In Fig. 3, note the

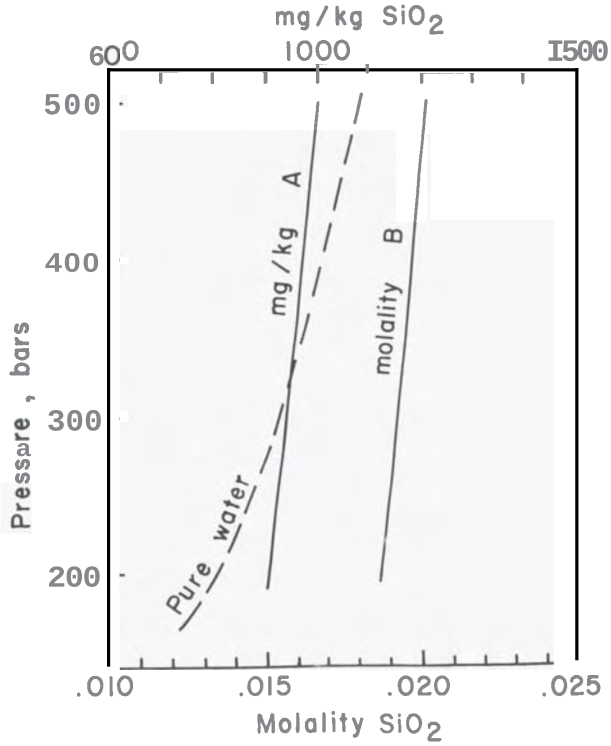

Fig. 3. Quartz dissolved in water and 4 m NaCl at 350°C.

difference in relative positions of the pure water and 4 m NaCl lines when solubilities are expressed in mg/kg and in molality units.

Fournier (in press) has developed a method of calculating quartz solubilities in NaCl solutions at any temperature and pressure for which solution density data are available, and Fournier and Marshall (in press) have extended that method to amorphous silica in a large variety of saline solutions. Calculated solubilities of quartz in pure water and NaCl solutions of different molalities at the vapor pressure of the solution are shown in Fig. 4. On the basis of the information shown in Fig. 4, I conclude that as we drill to deeper reservoirs with higher temperatures and greater salinities, we may encounter brines with tremendous silica-scaling potentials, far in excess of potentials expected from the pure water data.

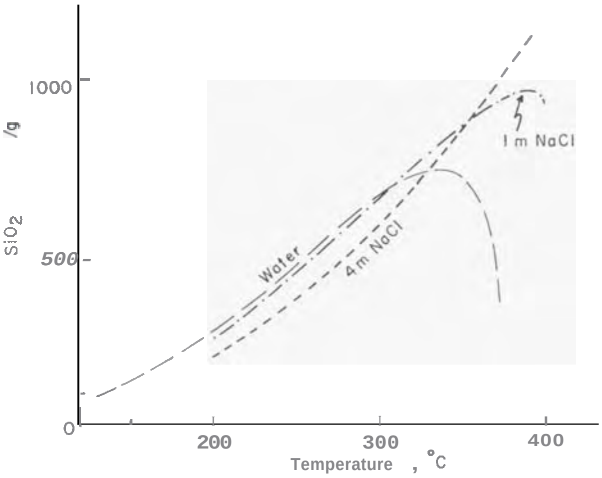

Fig. 4. Quartz dissolved in water and NaCl solutions at the vapor pressures of the solutions.

Finally, I would like to speculate briefly about what constraints the geochemical behavior of silica might impose upon hydrologic models of water circulating near very hot rock or magma. Because of the solubility maxima shown in Fig. 4, dilute water that is heated to temperatures above about 350'' to 400°C will precipitate quartz as a result of that heating. The precipitated quartz may clog the channels of flow to such an extent that an impermeable barrier would form, separating a dilute low-temperature (<350°C) system from either a high-temperature gas or a brine. If a brine fills the open space on the high-temperature side of the barrier, the thermal gradient across that barrier might be very large and the fluid pressure in the pore spaces on the high-temperature side equal to lithostatic pressure. Those who drill toward very high temperature targets should keep in mind that both temperatures and fluid pressures might suddenly increase far more rapidly than anticipated.

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Table 1--Constants for equations 1, 2, and 3

Equation 1	Equation 2	Equation 3
$C1 = -4.2198 \times 10^{1}$	$D1 = 1.3290 \times 10^{1}$	$E1 = -3.5532 \times 10^{0}$
$C2 = 2.8831 \times 10^{-1}$	$D2 = -9.4573 \times 10^{-3}$	$E2 = 1.4600 \times 10^{-1}$
$C3 = -3.6686 \times 10^{-4}$	$D3 = -7.5578 \times 10^{3}$	$E3 = -4.9270 \times 10^{4}$
$C4 = 3.1665 \times 10^{-7}$	$D4 = 1.2488 \times 10^{6}$	$E4 = 1.2305 \times 10^{-6}$
$C5 = 7.7034 \times 10^{1}$	$D5 = -8.2181 \times 10^{7}$	$E5 = -4.9421 \times 10^{-10}$