



CONCEPTUAL MODELS OF BRINE EVOLUTION IN MAGMATIC-HYDROTHERMAL SYSTEMS

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ABSTRACT

The depth of intrusion of a magmatic body is important in regard to brine evolution and to the type and intensity of hydrothermal alteration that is likely to be associated with that intrusion. At a depth of intrusion of 6–7 km, and in the absence of evaporite deposits somewhere in the section, nonmagmatic water is not likely to be converted to brine unless there are special circumstances, such as repeated magmatic intrusions and repeated fracturing of very hot rock. In contrast, brine is very likely to form from nonmagmatic water where the depth of intrusion comes within about 3–4 km of the surface, and dilute water is heated to above about 400–450 °C.

When pore-fluid pressures are controlled by hydrostatic conditions, magmatic waters will evolve to highly saline brines at depths less than about 10–12 km, irrespective of the initial concentrations of salt and water dissolved in the magma. Dilute hydrothermal fluids of meteoric origin and mixtures of meteoric water and condensed magmatic gas (steam) are likely to form convection systems that float upon the more saline and probably hotter magmatic fluid. Double-diffusive convection is likely to result from the temperature and salinity gradients.

Quasi-plastic flow and mineral deposition generally prevent flow of water at hydrostatic pressure through rock at temperatures above 350–450 °C. However, where there are steep thermal gradients and a relatively rapid rate of change of stress, such as where magma is rapidly injected from a deep environment into a more shallow environment, brittle deformation of rocks may occur at temperatures in excess of 450 °C. Ground water at hydrostatic pressure may flow into and through these fractures and become heated to very high temperatures, possibly flashing in great part to steam with the simultaneous development of a small mass of brine. This situation should persist for only a relatively short time before quasi-plastic flow and mineral deposition limit additional fluid circulation to temperatures below 350–450 °C.

A generalized model is presented for the evolution of a hydrothermal system within an oceanic volcano, such as at Hawaii, in which a slowly rising magma reservoir maintains a depth of about 3–4 km beneath the summit as the volcanic edifice builds upon the sea floor. Significant amounts of highly saline brine are likely to be generated from sea water when the magma reservoir rises to within about 4–5 km of sea level. After a volcanic island forms, fresh water may enter the top of the hydrothermal system and float upon the brine. Sulfides are likely to deposit below sea level within the chloride-rich brine portion of the system, but these deposits are not likely to be exposed during subsequent erosion. With continued growth of the volcano above sea level, temperatures and pressures within the hydrothermal system become appropriate for complete evaporation of pore waters adjacent to the rising magma chamber. Sodium sulfate- and sodium carbonate-rich brines form

above sea level where steam condenses and sulfur- and carbon-rich gases react with the country rock.

What is generally thought of as supercritical behavior of a fluid (no phase change upon heating or cooling) occurs only at pressures greater than the hypercritical pressure, a pressure great enough to ensure that the gas phase will retain all the salt that was initially dissolved in the liquid phase at a lower temperature. At hydrostatic conditions the hypercritical point for a dilute water containing about 2,000 mg/kg total dissolved solids would be at about 700 °C at a depth of 4.6 km, and for sea water it would be at about 900 °C at a depth of 12.9 km.

INTRODUCTION

Studies of fluid inclusions in minerals from fossil hydrothermal systems (Roedder, 1979) show that brines commonly occurred at different times and in different parts of those systems. Descriptions of brine-rich fluid inclusions that formed in hydrothermal systems associated with shallow intrusive rocks are presented in many articles, including Roedder (1971), Nash (1976), Eastoe (1978), Bodnar and Bean (1980), and Reynolds and Bean (1985). Brines may originate in many ways. Connate brines are encountered in many deep sedimentary basins (White, 1965), and the formation of brines by evaporation of closed basin lakes (Langbein, 1961; Hardie and Eugster, 1970; Eugster and Jones, 1979) and the interaction of meteoric water with evaporite deposits (White, 1968) are well documented. Relatively little attention, however, has been given to highly saline brines formed by the interaction of ordinary waters with hot rocks that do not contain evaporites (Bischoff and Pitzer, 1985; Fournier, 1985a). This paper stresses the importance of including information about brine evolution from dilute water, sea water, and magmatic gases in our conceptual models in order to approximate what may happen in natural magmatic-hydrothermal systems. Particular attention will be focused on the important effect that depth of magmatic intrusion has on the generation of highly saline brine from relatively dilute water of meteoric origin and from magmatic gases, and a generalized model will be presented for the evolution of a hydrothermal system within an oceanic volcano, such as at Hawaii.

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of their manuscripts dealing with experimental and theoretical aspects of the solubility of NaCl in steam. The information that they provided was of great value in deciding which data sets to use in those instances when the experimental data reported by different researchers were in conflict.

FLUID CIRCULATION AND HEAT TRANSFER IN MAGMATIC-HYDROTHERMAL SYSTEMS

It will be shown subsequently that the attainment of temperatures in excess of about 400 °C is generally a prerequisite for producing brines from dilute to moderately saline waters within convecting hydrothermal systems. Therefore, attention will be focused on the factors that are likely to limit the maximum temperature that is attained by a convecting fluid at hydrostatic pressure.

Models for fluid flow and heat transfer in hydrothermal systems have been discussed by many investigators, including Elder (1965), Bodvarsson and Lowell (1972), Lister (1974, 1980, 1983), Ribando and others (1976), Cheng and Minkowycz (1977), Cathles (1977, 1980, 1983), Norton and Knapp (1977), Norton and Knight (1977), Norton (1978, 1984), Parmentier and Spooner (1978), Torrance and Sheu (1978), Fehn and Cathles (1979), Norton and Taylor (1979), Hartline and Lister (1981), Knapp and Norton (1981), Hardee (1982), and Sleep (1983). One of the most important parameters in these models is permeability, which is generally assumed to have a constant value, or to change uniformly in response to a variable, such as time or temperature. In natural hydrothermal systems permeability is likely to change nonuniformly and even to fluctuate during the life of the system. Processes that tend to increase permeability are faulting (brittle fracture), thermal cracking upon cooling, hydrofracturing, and dissolution of minerals. Processes that tend to decrease permeability are quasi-plastic flow, precipitation of minerals, and thermal expansion of rock. All of these processes must be taken into account in our models.

Several factors influence whether a rock deforms by brittle fracture or quasi-plastic flow, including the inherent strength of the rock, depth of burial (confining pressure), temperature, state of stress, and the rate of loading (rate of change of stress). Brittle, stiff materials are able to accommodate increasingly large stress differences until their strength is exceeded and they fail by fracture. Relatively plastic, compliant materials are unable to accommodate large stresses because they deform in response to relatively small increases in stress difference. As rocks are heated and subjected to greater confining pressure, they tend to exhibit a more ductile response to increased stress difference. The situation is complicated, however, because at a given temperature some materials deform by quasi-plastic flow when the rate of loading is slow and by brittle fracture when the rate of loading is rapid (Lama and Vutukuri, 1978). Thus, a relatively fast rate of change of stress may result in brittle fracture and increased permeability, whereas, at the same temperature, a relatively slow rate of change of stress may lead to quasi-plastic deformation and a decrease in porosity and (or) increase in pore-fluid pressure.

The maximum depths of earthquake foci probably give a good indication of the depth at which quasi-plastic flow limits the downward penetration of ground water above relatively shallow magmatic bodies that are still hot. At Yellowstone National Park, information is available about earthquake focal depths and the maximum temperature likely to be attained by the hydrothermal system that convects to the surface (Fournier and Pitt, 1985). Well-located earthquakes seldom exceed about 4 km depth beneath the Yellowstone caldera but are much deeper outside the caldera. Chemical geothermometers, mixing models, and phase relations in the system NaCl-H₂O, indicate that the maximum temperature likely to be attained by the hydrothermal system is 350–430 °C (Fournier and Pitt, 1985). Based on temperature profiles calculated from heat-flow data for several localities in the Western United States and earthquake focal depths at those same locations, Smith and Bruhn (1984) conclude that the temperature at which deformation changes from frictional (brittle fracture) to quasi-plastic flow commonly ranges from about 300–450 °C. Also, self-sealing by precipitation of quartz and other minerals is likely to occur in the temperature range 350–500 °C when solutions are heated at constant pressure (Fournier, 1977, 1983a, 1983b; Sleep, 1983). Thus, permeability reduction by physical and chemical processes becomes increasingly important at temperatures above about 350 °C.

Those rocks situated at depth and in close proximity to a magma probably are at too great a temperature to sustain the large stress differences necessary to induce significant fracturing and faulting. Where fracturing has occurred in rocks at temperatures above about 350–450 °C, quasi-plastic deformation is likely to close those fractures within a relatively short time. Therefore, in most magmatic-hydrothermal systems convecting thermal waters at hydrostatic pressure probably are separated from magma by a region of hot rock that deforms quasi-plastically.

The above considerations lead to a model of a magmatic-hydrothermal system in which thermal energy is transferred mainly by conduction from very hot rock or magma to hydrostatically pressured circulating water. Minor additional heat is transferred by flow of fluids evolved from the crystallizing magma. The schematic depth-temperature profile shown in figure 55.1 represents a situation in which most of the fluid flow is restricted to a few relatively permeable channels, and the base of the convecting hydrothermal system (point B) is above the magmatic body (a simplified representation of real magmatic-hydrothermal systems in which convective flow of heated fluid is likely to occur at the sides as well as the tops of hot intrusive bodies). The temperature gradient for conductive heat flow from magma or hot impermeable rock is shown by line MB. Upward-flowing fluid in the convection system transfers heat relatively efficiently, and eventually temperatures along the flow path may approach an adiabatic profile (from B to A). If the temperature at point B is less than the critical temperature, point C, the adiabatic profile is nearly isothermal (line BA). The upper limit of the nearly isothermal region is set by the boiling-point curve. The position of the boiling-point curve is determined mainly by the location of the water table and the salinity and gas content of the particular fluid in the system.

In summary, quasi-plastic flow and mineral deposition generally prevent flow of water at hydrostatic pressure through rock at temperatures above 350–450 °C. However, where there are steep thermal gradients and a relatively rapid rate of change of stress, such as where magma is rapidly injected from a deep environment into a more shallow environment, brittle deformation of rock may occur at temperatures in excess of about 450 °C. Ground water at hydrostatic pressure may flow into and through these fractures and become heated to very high temperatures, possibly flashing in great part to steam. However, this situation should persist for only a very short time before quasi-plastic flow and mineral deposition limit additional fluid circulation to temperatures below about 450 °C.

BEHAVIOR OF CHLORIDE-RICH SALINE SOLUTIONS IN HYDROTHERMAL SYSTEMS

The following discussion is based on the experimentally determined behavior at hydrothermal conditions of the system NaCl-H₂O (Keevil, 1942; Ölander and Liander, 1950; Copeland and others, 1952; Sourirajan and Kennedy, 1962; Khaibullin and Borisov, 1966; Hilbert, 1979; Galobardes and others, 1981; Parisod and Plattner, 1981; Gunter and others, 1983; Bodnar and others, 1985; Bischoff and others, in press), NaCl-KCl-H₂O

(Ravich and Borovia, 1949), and sea water (Bischoff and Rosenbauer, 1984, 1985; Bischoff and Pitzer, 1985). In related articles (Fournier, 1983b; 1985a), the pressure-temperature-composition relations in the system NaCl-H₂O given by Sourirajan and Kennedy (1962) were used as a basis for constructing a model for the behavior of saline solutions in hydrothermal systems. Results of recent experimental studies (Bischoff and Rosenbauer, 1984, 1985; Bodner and others, 1985; Bischoff and others, in press) and theoretical modeling of the thermodynamics of the behavior of NaCl in steam (Pitzer, 1983; Pitzer and Li, 1984; Pitzer and Pabalan, in press) and in mixtures of H₂O and CO₂ (Bowers and Helgeson, 1983) show that the Sourirajan and Kennedy (1962) results for the solubility of NaCl in steam are probably considerably in error at temperatures above 400 °C. For example, the isopleth of 0.4 weight percent NaCl dissolved in steam in pressure-temperature space according to the data of Sourirajan and Kennedy (1962) is compared in figure 55.2 to the same isopleth using the model of Pitzer and Pabalan (in press). Experimental data of Ölander and Liander (1950) are compatible with either isopleth, but the results reported by Bodner and others (1985) clearly favor the Pitzer and Pabalan model. In the remainder of this paper results of the Pitzer and Pabalan (in press) model for the solubility of NaCl in steam will be used.

At a given depth and hydrostatic load (a given pressure) more saline solutions will boil at higher temperatures than less saline solutions, and the critical points of more saline solutions are encountered at higher temperatures and higher pressures (greater depths) than those of less saline solutions. Approximate boiling-point curves, extending to the critical points, for pure water and 10 and 25 weight percent NaCl solutions are shown in figure 55.3. Haas (1971) calculated boiling-point curves for water and various salt solutions of as much as 25 weight percent with an upper temperature limit of 330 °C. His results are slightly different from those shown in figure 55.3 because he assumed that hydrostatic pressure is controlled by the weight of the overlying column of boiling solution, thus correcting for changing density. The boiling-point curves shown in figure 55.3 were calculated with the assumption that the pressure-controlling column of solution has a constant density of 1. This assumption appears to be valid in some presently active hydrothermal systems (Fournier, 1983b). The physical reality appears to be that at given depths, fluid pressures within the hot part of the system are the same as fluid pressures in the surrounding cold part of the system. Lithostatic depths in figure 55.3 and subsequent figures were calculated using an average rock density of 2.5 kg/m³.

Boiling-point curves for hydrostatic conditions are calculated relative to the position of the water table. In many places that water table is far below the Earth's surface. In other places, artesian systems are present in which the pressure-controlling water table is elevated in distant hills or mountains. In still other places, hot springs discharge onto the floors of lakes or the ocean, and boiling-point curves adjust to the overlying column of lake or ocean water. Thus, the 350 °C hot-spring waters discharging on the ocean floor at 21° N. on the East Pacific Rise (Edmond and others, 1979) are below boiling temperature because of their great depth.

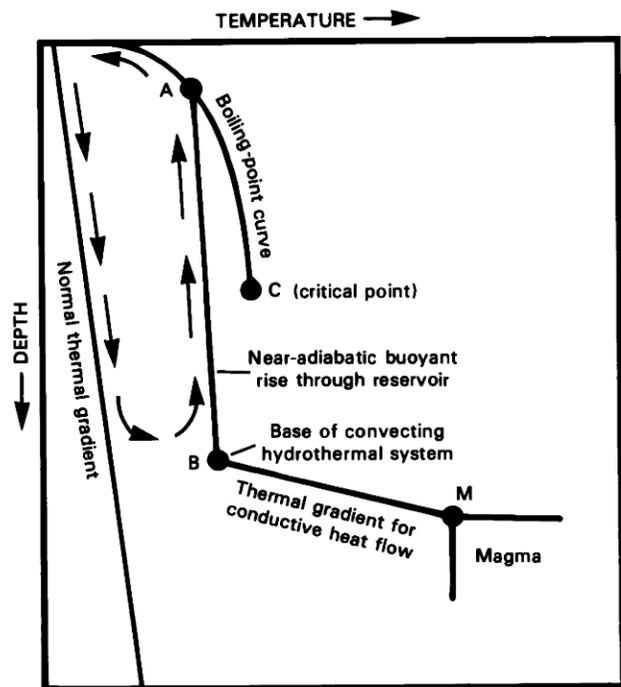


FIGURE 55.1.—Schematic depth-temperature profile for fluid flow (shown by arrows) restricted mainly to a few relatively permeable channels above magmatic heat source. Lettered points are discussed in text.

The boiling-point curves in figure 55.3 show temperature-depth conditions at which liquids of given salinity will first start to boil. Upflowing solutions start to boil as a result of decompression when the boiling-point curve appropriate for the composition of the particular fluid is first attained. However, as soon as boiling starts, a slight departure from the initial boiling-point curve occurs because of the increase in salinity of the residual solution as boiling progresses. Adiabatic cooling that results from decompression of a relatively dilute solution, starting at temperatures less than the critical temperature, can result in a moderate increase in salinity, but will not result in the generation of a brine. For example, adiabatic decompressional boiling of a dilute solution that results in cooling from 370–100 °C will be accompanied by the conversion of about 64.9 percent of the initial liquid to steam (calculated from data in steam tables of Keenan and others, 1969), and the final residual solution at 100 °C will be about 2.85 times more concentrated in nonvolatile elements than the initial solution.

Isopleths of the solubility of NaCl in aqueous liquids in 10 weight percent increments from 0 to 90 weight percent projected onto a temperature-pressure diagram are shown in figure 55.4. These isopleths are boiling-point curves, but the depth axis is very uncertain because of the previously discussed limitations and the incorporation of significant amounts of salts other than NaCl into natural brines. A liquid-saturation curve (or a total evaporation

curve) separates a field of gas plus solid salt (at lower pressures) from a field of gas plus liquid (at higher pressures). For the system NaCl-H₂O, the position of this liquid-saturation curve is fixed in temperature-pressure space and is independent of the initial proportion of NaCl and H₂O. For aqueous solutions containing mixed salts, the position of the liquid saturation curve in temperature-pressure space will depend on the nature of the salts that are present, and precipitation of some salts will likely take place within the gas plus liquid (brine) field. The short-dashed line in figure 55.4 shows the approximate position of the boundary separating fields of gas plus liquid and gas plus solid when the fluid contains a mixture of NaCl and KCl and the Na/K ratio in that fluid is appropriate for coexisting albite and K-feldspar (Orville, 1963). The salinity of the liquid phases steadily increases with increasing temperature along the liquid saturation curve (the gas + solid + liquid curve), whereas the salinity of the gas phase increases with increasing pressure. At salinities greater than about 30 weight percent the isopleths showing solubilities in the liquid phase originate at the liquid-saturation curve (the three-phase boundary that separates the field of gas plus solid salt from the field of gas plus liquid) and terminate at critical points (shown as dots for solutions with as much as 30 weight percent NaCl). The double-dot-dashed line (fig. 55.4) is the critical curve for the system NaCl-H₂O. The positions of all these curves move in temperature-pressure space as other salts are added to the system.

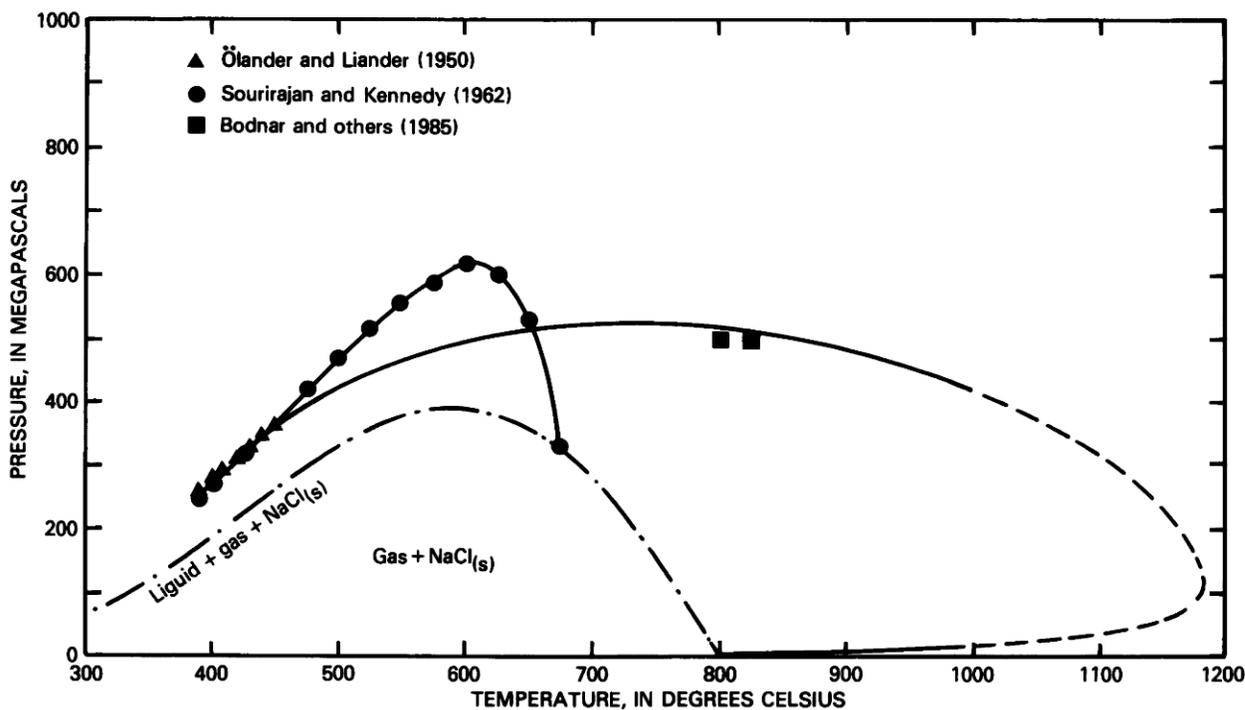


FIGURE 55.2.—Isoplethal pressure-temperature diagram for a vapor-phase composition of 0.4 weight percent NaCl in vapor+liquid region for NaCl-H₂O system. Isopleth is drawn through Sourirajan and Kennedy (1962) data, and a contrasting position for that isopleth is shown using calculated solubilities according to Pitzer and Pabalan model (in press) for temperatures above 600 °C and connected smoothly to experimental data at lower temperatures. Dashed line is projected schematically beyond range of Pitzer and Pabalan model (redrafted from Pitzer and Pabalan, in press).

Boiling-point curves and critical points of solutions show only part of the important information that must be taken into account when modeling magmatic-hydrothermal systems. General phase relations exhibited by any chloride-rich solution of given salinity in temperature-depth space are shown in figure 55.5A. The solid line is a boiling-point curve for a solution of given salinity, ending at the critical point, C. Extending to greater depth (higher pressure) and higher temperature from the critical point is what may be thought of as a condensation-point curve for a gas that contains the same concentration of dissolved salt (an isopleth) that the initial liquid contained at subcritical temperatures and pressures. Along the condensation-point curve the gas is in equilibrium with a liquid that is much more saline than the gas, and the salinity of this liquid increases steadily and dramatically going from the critical point, C, through point H to point E. In this discussion, point H is called a "hypercritical" point (Fournier, 1985a). It marks the temperature and pressure at which a fluid of given salinity behaves according to what we normally think of as supercritical behavior; at greater pressures the fluid will not boil or condense upon heating or cooling. To the left of the dotted line that passes through point H the salinity

of the gas phase decreases as temperature is increased at constant pressure. In contrast, the salinity of the gas phase increases with increasing temperature at constant pressure to the right of the dotted line.

Boiling-point and condensation-point curves are schematically shown in figure 55.5B for three compositions of fluid, equivalent to X, Y, and Z weight percent NaCl, such that $X < Y < Z$. The three boiling-point curves end at their respective critical points, C_x , C_y , and C_z . Gas of composition X is in equilibrium with liquid Y at point m, and liquid Z at point n. At point p gas of composition Y is in equilibrium with liquid Z. In actual water-salt systems, very large increases in salinity are generally required to increase the boiling point a few degrees at constant pressure, as shown in figure 55.4 for solutions up to about 30–40 weight percent dissolved NaCl. Isopleths of solubility of NaCl in steam (condensation-point curves) for salinities as great as 20 weight percent are shown in red in figure 55.6, and in figure 55.7 these isopleths are shown in red superimposed on figure 55.4. As previously noted, a rising fluid that intersects a boiling-point curve would become moderately more saline as a result of decompressional boiling with separation of steam, such as the fluid that follows path A in figure 55.5A. In contrast, hot rising fluids that follow a cooling path that is to the high-temperature side of the critical point so that the condensation-point curve is intersected, such as path B in figure 55.5A, will undergo a large increase in salinity. This will be discussed more fully later.

In summary, more saline solutions have boiling-point curves at higher temperatures and generally have critical points at much greater depths than less saline solutions. For a solution of given initial salinity, a condensation-point curve extending from the critical point to higher temperatures passes through a pressure maximum (the hypercritical point) and then loops back to intersect the liquid saturation curve at about the melting point of the pure salt (figs. 55.5A, 55.5B, 55.6, 55.7). The hypercritical point marks the temperature and pressure at which a fluid of given salinity will not boil or condense upon heating or cooling. The depths and temperatures at which these curves would be intersected in natural systems will vary greatly depending upon various hydrologic parameters and the nature of the dissolved salts and partial pressures of dissolved gases.

GENERATION OF BRINES FROM DILUTE SOLUTIONS

Adiabatic decompression of a liquid, which causes its path in depth-temperature space to intersect the boiling-point curve at a temperature below the critical temperature, is likely to result in only a moderate salinity increase. However, if the cooling path of an ascending fluid brings it into the gas plus liquid field at a temperature greater than the critical temperature, a highly saline solution (brine) will condense from that ascending fluid. The NaCl concentrations of liquids (brines) that will condense from two fluids, one containing 0.2 weight percent NaCl and the other 3.2 weight percent NaCl, that intersect condensation-point curves at various temperatures as a result of decompression are shown in figure 55.8.

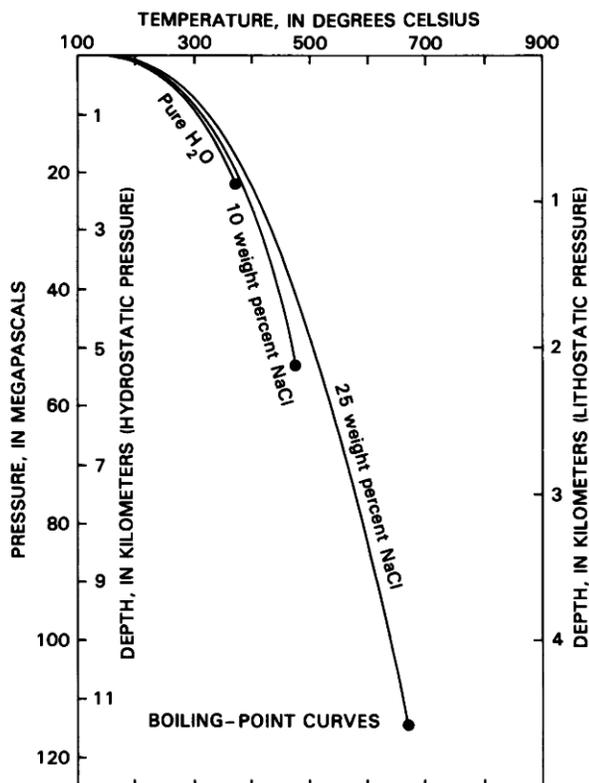


FIGURE 55.3.—Depth-temperature diagram showing approximate positions of boiling-point curves and critical points (dots) for pure water and 10 and 25 weight percent NaCl solutions.

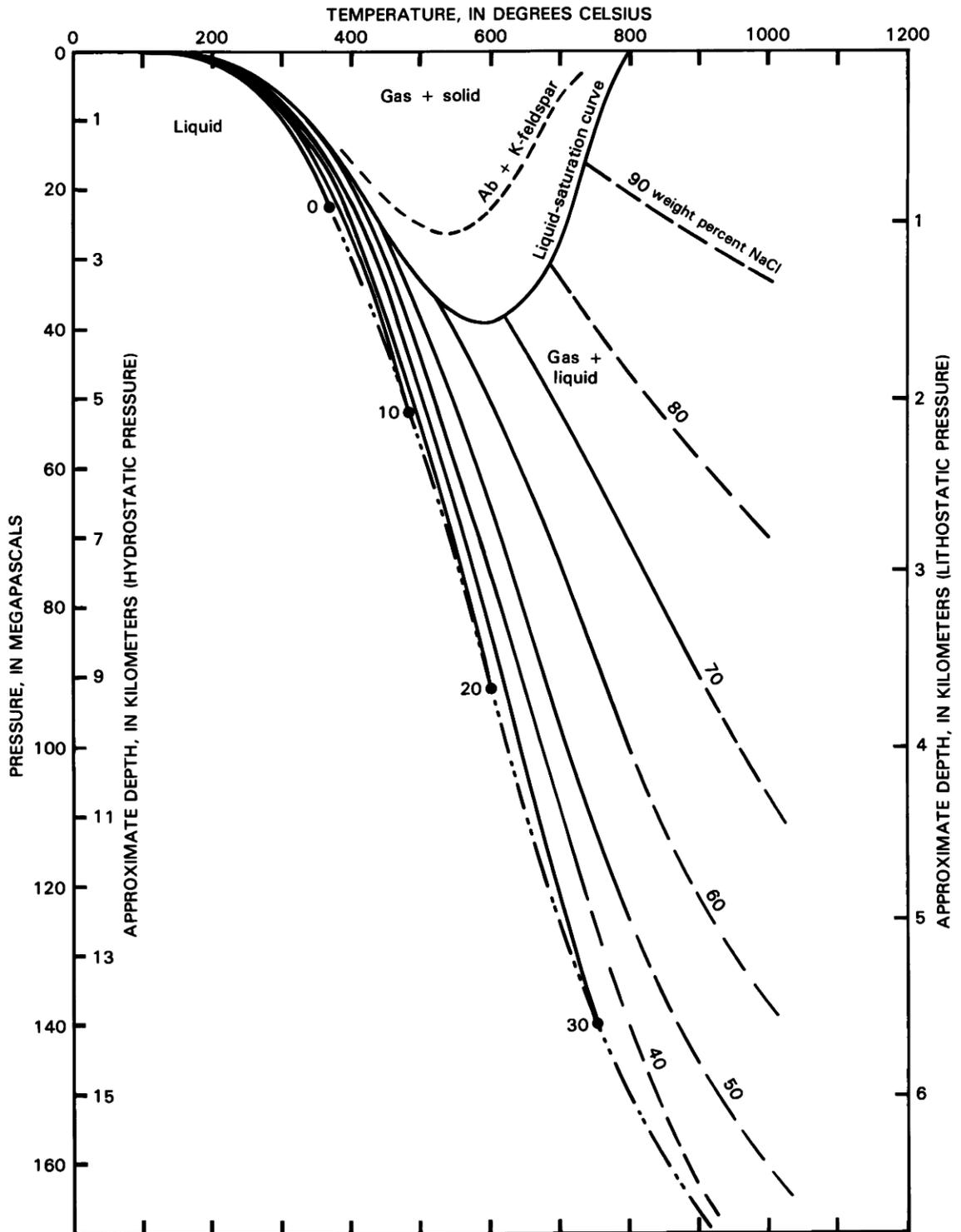


FIGURE 55.4.—Isopleths of solubility of NaCl in water in 10 weight percent increments (boiling-point curves with approximate depths for hydrostatic pressure (fluid density = 1) and lithostatic pressure (rock density = 2.5)). Double-dot-dashed line is critical curve. Liquid saturation curve is 3-phase boundary for the system NaCl-H₂O, and short-dashed line shows approximate position of liquid saturation curve for system NaCl-KCl-H₂O with Na/K ratios in liquid fixed by base exchange between albite and K-feldspar. Long dashes indicate inferred positions of curves.

A brine containing about 10 weight percent NaCl will condense from the 0.2 weight percent NaCl fluid when the condensation-point curve is intersected at a temperature of about 390 °C, and a 20 weight percent NaCl brine is generated when the condensation-point curve is intersected at about 410 °C (fig. 55.8). However, the mass of brine that forms will be small relative to the mass of coevolving, relatively dilute vapor. Because the brine has a much higher density than that of the initial fluid, the brine might counter-flow downward and accumulate in pockets or near the bottom of the hydrothermal system. Therefore, with prolonged circulation of hot fluid through the system, brine may come to fill the few fractures that are present at the base of the hot part of the convection system, bounded by hot, dilute fluid above and relatively cold water and (or) hot impermeable rock at the sides.

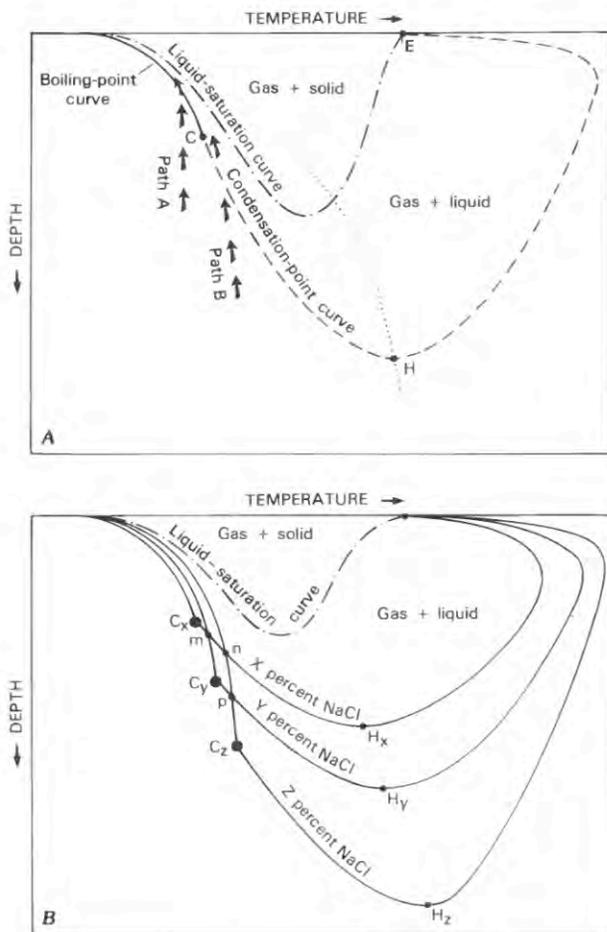


FIGURE 55.5.—Depth-temperature diagrams showing generalized phase relations. **A**, Chloride-rich aqueous solutions at constant composition. **B**, Three different compositions, X, Y, and Z, with $X < Y < Z$. Critical points for respective solutions are at C, C_x, C_y, and C_z, and hypercritical points are at H, H_x, H_y, and H_z. Dotted line and other points are discussed in text.

At given temperatures, less saline brines are generated when sea water intersects the condensation-point curve (fig. 55.8), and the intersection occurs at greater depths than for more dilute solutions. But, a larger proportion of brine is generated from sea water than from the same initial mass of a more dilute solution. The generation of brine by adiabatic decompression of sea water at temperatures above the critical point is nicely shown by Bischoff and Pitzer (1985).

In the above models brines form as a result of decompression, utilizing thermal energy contained in rising, relatively dilute fluids. Dilute fluids also may be converted to brines by prolonged boiling, utilizing thermal energy stored in hot rock to evaporate the waters. One way to accomplish this conversion is to quickly lower the hydrostatic pressure so that the boiling-point curve appropriate for the salinity of the local ground water is shifted to lower temperatures at given depths. This process might occur as a result of sudden draining of a lake or an explosive volcanic eruption. With decreasing hydrostatic pressure at any given depth, as would occur with a drop in the local ground-water table (from L1 to L2 in fig. 55.9), the boiling-point curve would shift (from A to B). Waters that were initially on or to the left of the boiling-point curve A (point C, fig. 55.9) will move into the field of gas (steam). In response to the decrease in hydrostatic pressure, the water will boil vigorously, either to dryness or until the surrounding rock temperature decreases and the salinity of the solution increases to the extent that the ground water (point D, fig. 55.9) lies on a new boiling-point curve (curve E) appropriate for the new pressure, temperature, and salinity. Small amounts of brine that form in this manner could become trapped in fluid inclusions that would give a false impression of the presence of a large convecting brine system. If the permeability of the rock is relatively low, so that the newly formed steam cannot expand and push pore fluids from the rock fast enough to prevent a large pressure increase, and if the resulting steam pressure is greater than the confining pressure, a hydrothermal explosion may occur (Muffer and others, 1971).

In volcanic environments, magma may be injected into wet rocks, causing vigorous boiling and pore-pressure buildup (Delaney, 1982). Boiling, utilizing heat stored in rock, also may occur where newly formed fractures allow water to come into contact with previously hot, dry rock. However, the quantity of brine that forms in this manner may be relatively small, either because little fluid flows through a system with low initial or rapidly decreasing permeability or because a rapid rate of flow of fluid through the system decreases the temperature of the fluid-rock interface to a value that is too low for brine to form. A decrease in temperature at the fluid-rock interface is expected because the formation of steam is likely to consume thermal energy faster than thermal energy can be transferred through rock by conduction. Thermal cracking, however, may cause new fractures to form, allowing the solution to again come into contact with rock hot enough to cause vigorous boiling.

In summary, large amounts of brine are likely to form from dilute solutions only where prolonged circulation occurs through very hot rock. This circulation is likely to occur mainly where there have been multiple injections of magma into already hot rock at moderate to shallow depths (about 2–7 km). The process of generation of

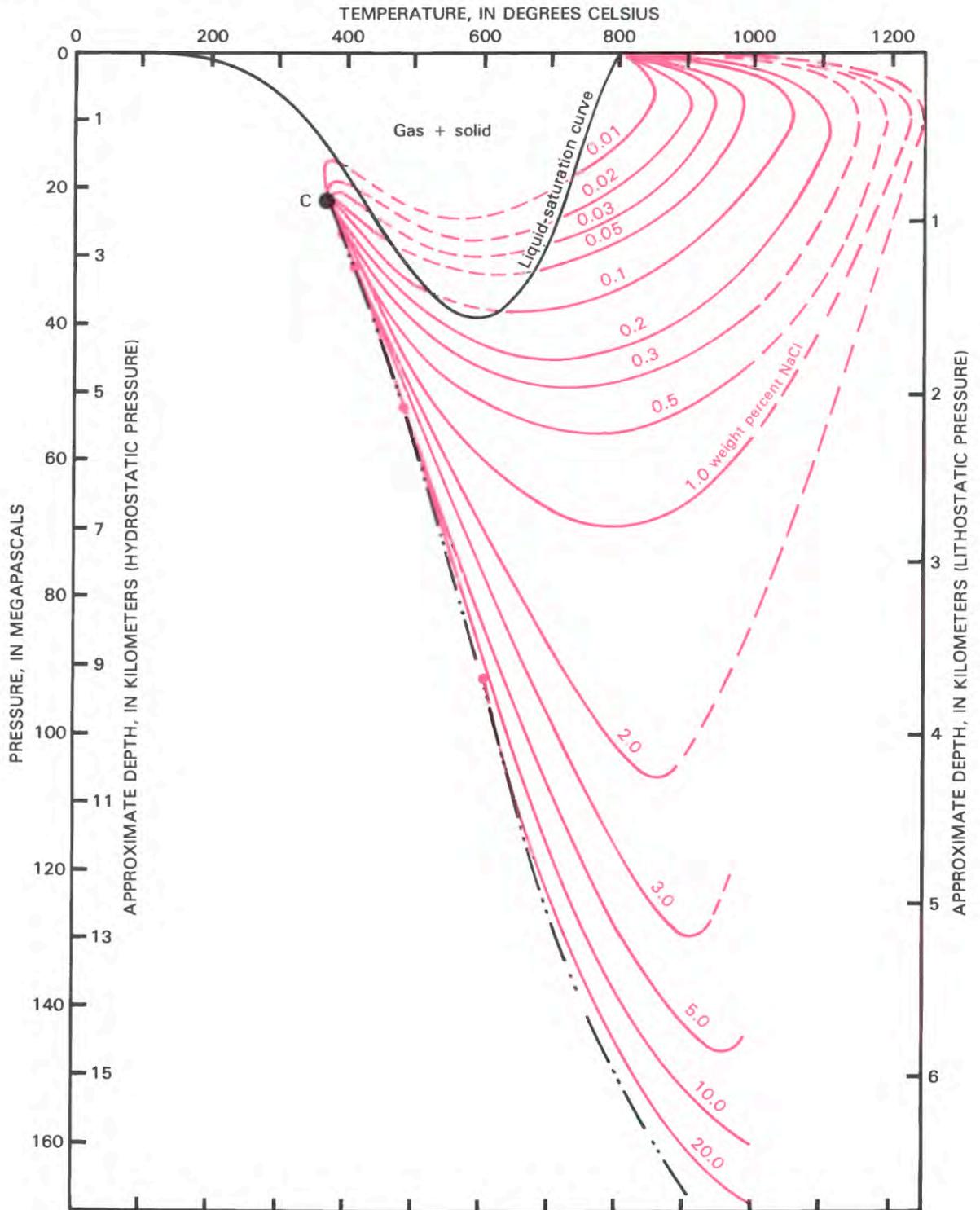


FIGURE 55.6.—Isopleths of solubility of NaCl in steam (red lines) with approximate depths for hydrostatic pressure (fluid density = 1) and for lithostatic pressure (rock density = 2.5). Double-dot-dashed line (black) is critical curve with origin at critical point of pure water (black dot). Critical points of selected salt solutions, red dots. Liquid-saturation curve (black) is 3-phase boundary for system NaCl-H₂O.

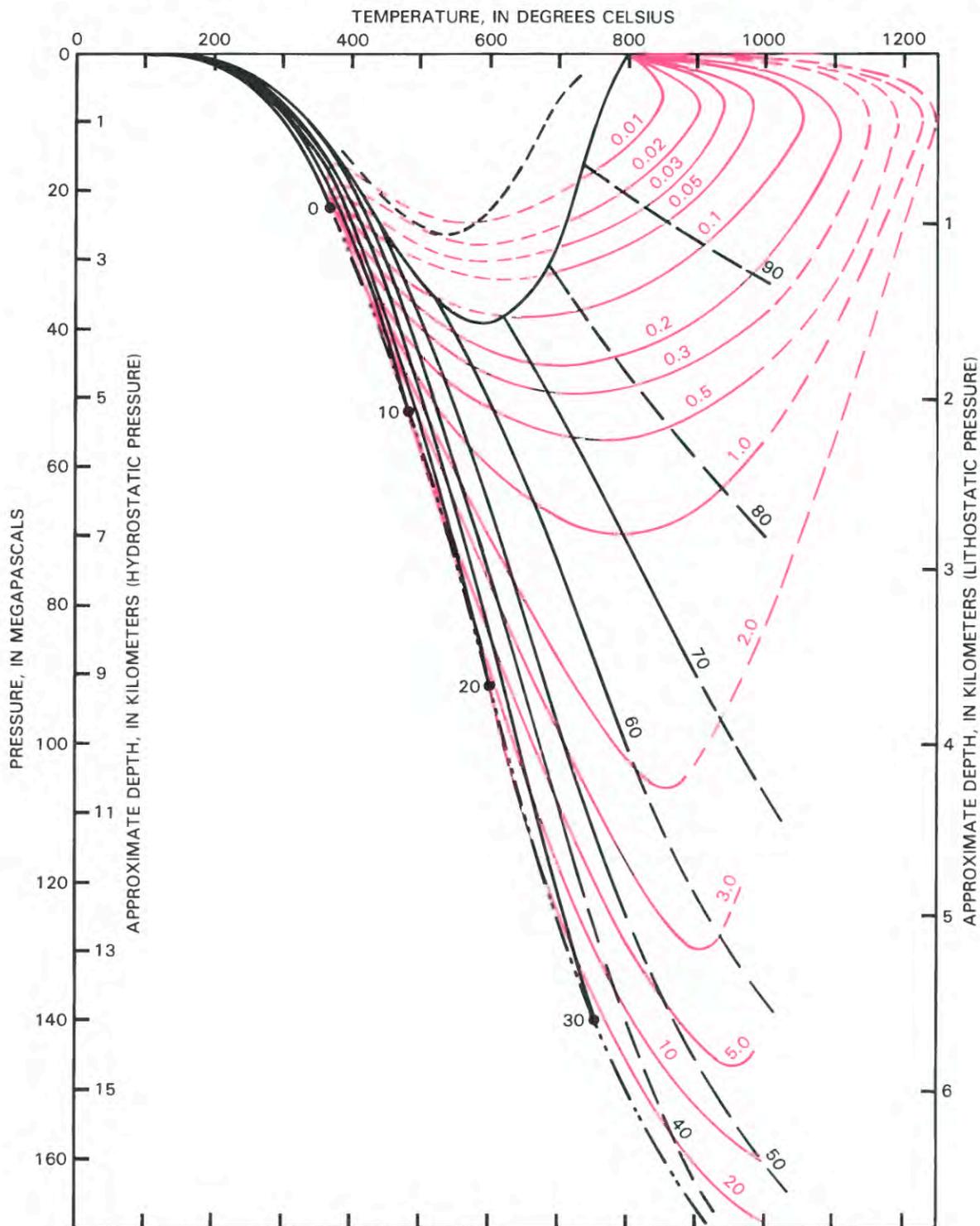


FIGURE 55.7.—Isopleths of solubility of NaCl in steam (red lines, see fig. 55.6) superimposed on isopleths of solubility of NaCl in water (black lines, see fig. 55.4).

hypersaline brines is greatly aided when the initial solution is moderately saline, such as sea water, because a given amount of a fluid that has a greater initial salinity will produce a larger mass ratio of brine to gas than will a less saline fluid.

BRINE EVOLUTION AND HYDROTHERMAL ALTERATION RELATED TO DEPTH OF MAGMATIC INTRUSION

The depth of intrusion of a magmatic body and the salinity of the ground water that enters the hydrothermal system are important in regard to brine evolution and the type and intensity of hydrothermal alteration that is likely to be associated with that intrusion. These depth-temperature-phase relations will be illustrated by comparing and contrasting a relatively dilute, chloride-rich solution containing 2,000 mg/kg total dissolved solids (TDS) to sea water. Sea water can be modeled by a 3.2 weight percent NaCl solution at high temperatures because most of the sulfate and magnesium precipitate upon heating (Bischoff and Rosenbauer, 1985).

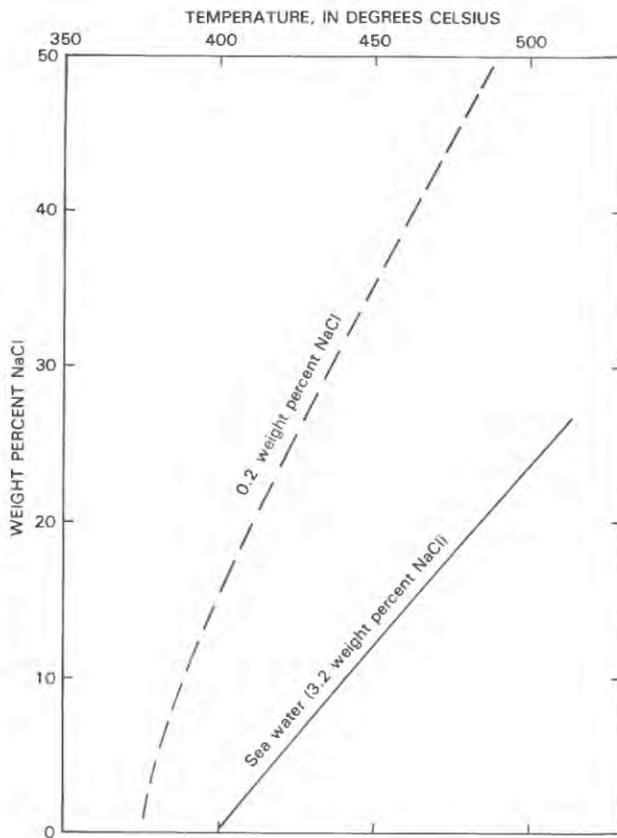


FIGURE 55.8.—Concentrations of NaCl in liquids that will condense from 0.2 weight percent NaCl and 3.2 weight percent NaCl when condensation-point curves are intersected at various temperatures as a result of decompression.

Approximate positions in depth-temperature space of the boiling-point curves, condensation-point curves, critical points (C_2 and C_3), and hypercritical points (H_2 and H_3) for the 2,000 mg/kg TDS solution and sea water, respectively, are shown in figure 55.10. The 2,000 mg/kg NaCl solution has a critical point near 375 °C at about 23 MPa and a hypercritical point at about 700 °C at 46 MPa. In contrast, the sea water has a critical point near 405 °C at about 30 MPa and a hypercritical point at about 900 °C at 129 MPa. The dashed parts of the condensation-point curves are beyond the range of experimental data and the Pitzer and Pabalan (in press) model. The position of the saturation curve in figure 55.10 is poorly constrained and is greatly dependent on the relative proportions of cations in the solution. The liquid saturation curve for the binary system NaCl-H₂O is shown by the dot-dashed line, and

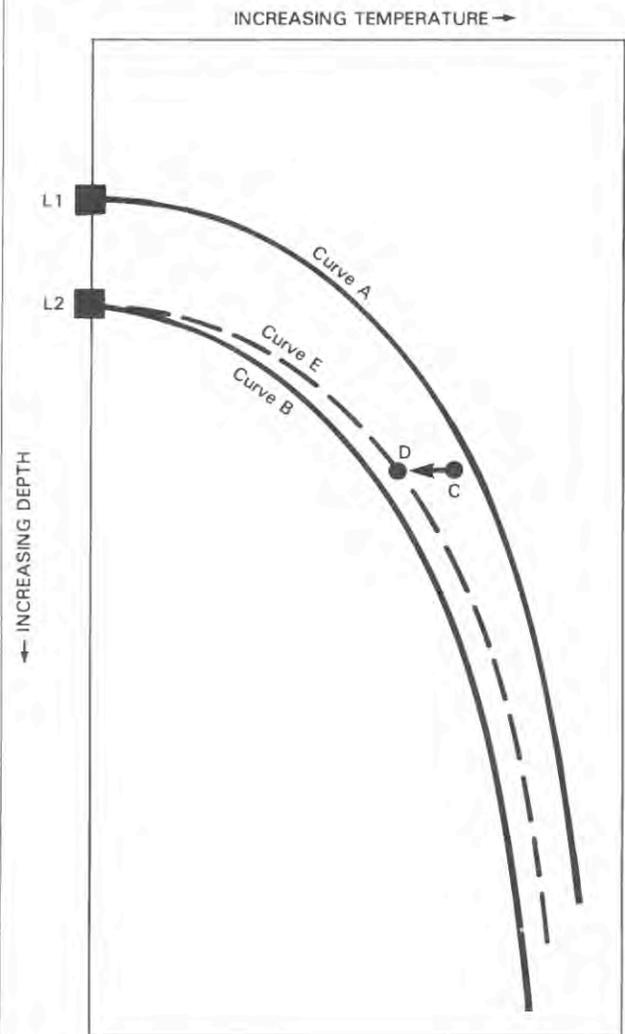


FIGURE 55.9.—Boiling-point curves related to elevation of water table. Lettered points and curves are discussed in text.

the double-dot-dashed line shows the saturation curve for the ternary system NaCl-KCl-H₂O with the Na/K ratio fixed by base exchange between albite and K-feldspar, calculated using the data of Ravich and Borovia (1949) and Orville (1963).

The schematic depth-temperature relations for a relatively early stage of development of a hydrothermal system associated with a body of magma that has been intruded to a depth of 6 km are shown in figure 55.11. The heat source has a temperature of about 800 °C (appropriate for a silicic system). A basaltic heat source could have a temperature well above 1,000 °C. Fluid flow at hydrostatic pressure (shown schematically by arrows in fig. 55.11) is assumed to be controlled by a few well-developed fractures, and temperatures in the convecting hydrothermal system are assumed to be representative of those in the fractures where the maximum rate of fluid flow occurs. The temperature gradient from the heat source to the convecting hydrothermal system is very steep (there has been insufficient time to heat much surrounding rock by conduction), and the hydrothermal system is not well developed. Because the surrounding rock was relatively cool (at a normal or slightly above normal geothermal gradient) prior to the intrusion of the magma, the convecting fluid is in the process of heating the rock adjacent to the channels that control fluid flow, and the rock, in turn, is conducting heat away from the fluid. The maximum fluid temperature of 450 °C, (fig.

55.11) is appropriate for a steady-state situation in which mineral deposition and quasi-plastic deformation have closed off permeability in rocks at higher temperatures. The sudden opening of new fractures adjacent to magma could allow fluid to move into those fractures and become heated to temperatures significantly above 450 °C, resulting in marked fluid expansion. If the expansion of the fluid does not lead to further rupturing of the rock (possibly explosively) and a decrease in fluid pressure thereafter, the expanded 2,000 mg/kg fluid would not undergo a phase change because the pressure at a depth of 5–6 km is greater than the hypercritical pressure; the gas plus brine field would not be entered. In contrast, if flow into new fractures at a depth of 5–6 km allowed sea water to be heated at hydrostatic pressure to temperatures above 450 °C, brine and gas would form as soon as the temperature exceeded about 480 °C (fig. 55.11), and the first brine generated would contain about 19 weight percent NaCl (fig. 55.8).

Given time, a larger portion of rock adjacent to the intrusive becomes heated conductively while the intrusive crystallizes and cools (fig. 55.12). The hydrothermal system heats the rock adjacent to the channels of main fluid flow to the point where the ascending fluids cool mainly by adiabatic decompression, while the fluids in less open channels cool by conduction. The maximum temperature attained by the convecting fluid in figure 55.12 is shown to be less than that in figure 55.11 because mineral deposition and quasi-plastic deformation are assumed to have slowly excluded fluid flow

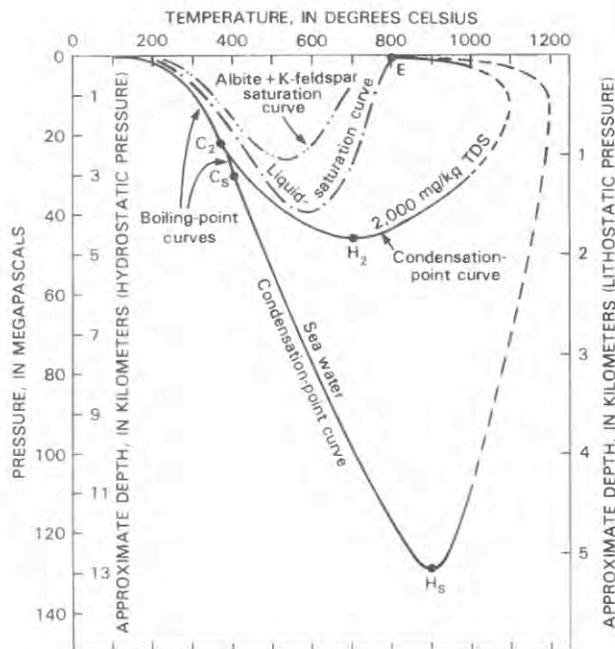


FIGURE 55.10.—Approximate positions in depth-temperature space of boiling-point and condensation-point curves for chloride-rich solution containing 2,000 mg/kg salt (about 0.2 weight percent NaCl) and sea water (about equivalent to 3.2 weight percent NaCl) at high temperatures). Critical points are at C₂ and C₅ and hypercritical points are at H₂ and H_s, respectively. Liquid-saturation curve and curve labeled Albite + K-feldspar are same as in figure 55.4.

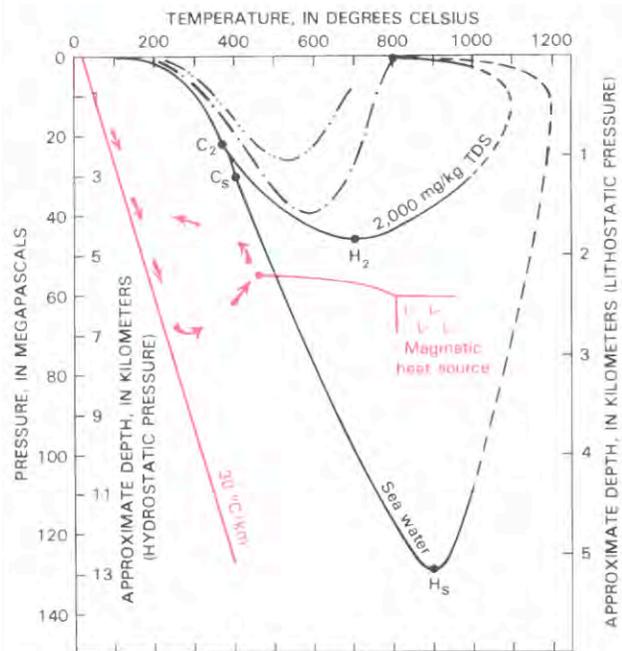


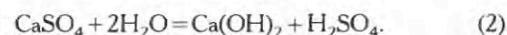
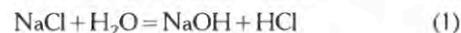
FIGURE 55.11.—Schematic depth-temperature relations (shown in red) for relatively early stage of development of hydrothermal system associated with body of magma that has been intruded to depth of 6 km below water table, superimposed on figure 55.10 (shown in black).

from portions of rock where flow had previously occurred at higher temperatures. In contrast to the situation shown in figure 55.11, renewed fracturing within hot, previously impermeable portions of rock will not result in the formation of brine during inflow of sea water because temperatures are too low for the gas plus brine field to be encountered (figs. 55.8, 55.12).

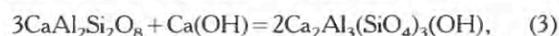
A situation in which a later magmatic body intrudes an older, partly cooled magmatic body at a depth of about 6 km is shown in figure 55.13. The younger magma injects into rock that was preheated by the previous intrusion, and the hydrothermal system in the vicinity was already well established. Also, in the intrusive process, new fractures are likely to form, allowing fluid to re-enter rock that had previously become essentially impermeable through mineral deposition and slow quasi-plastic deformation. In this situation, as the fluids convect upward there is a good chance that both the dilute solution and sea water would enter the gas plus brine field to the right of their respective critical points (points C_2 and C_3). In that event, highly saline brines would form by condensation (disproportionation of the initial fluid into a small volume of highly saline liquid and a much larger volume of less saline gas), as previously discussed and shown in figure 55.8. If the relatively dense brine that forms by condensation accumulates in pockets or at the base of the hydrothermal system, important consequences in regard to ore deposition would occur because the chloride-rich brine would scavenge metals from the surrounding rock, and these metals would

then be localized and available to combine with sulfur that is released by still-crystallizing magma (Fournier, 1983b).

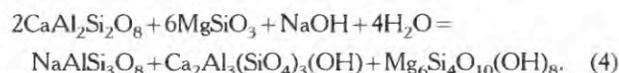
Intrusions that penetrate to less than about 3–4 km and that attain temperatures above about 400 °C are likely to have associated hydrothermal systems that extend into the field of gas plus liquid, and possibly into the field of gas plus solid salt (fig. 55.14). Within the gas plus solid salt field, acid gases are likely to be generated by the hydrolysis of salts (Fournier, 1985a, 1985b),



The hydroxides react with silicates to form a variety of alteration products, including epidote, albite, and chlorite,



and



The hydrolysis of salts, yielding acidic gases, becomes increasingly important at lower pressures. Therefore, acid alteration is likely to be far more abundant in and around shallow intrusive igneous rocks than deeper intrusive igneous rocks.

Most potassic alteration probably is the result of decreasing temperature that favors the exchange of dissolved K for Na in

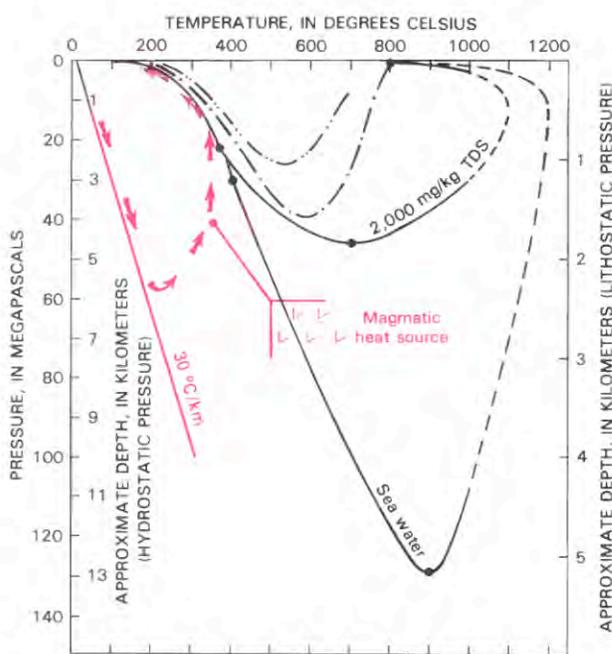


FIGURE 55.12.—Schematic depth-temperature relations (shown in red) for a relatively late stage of development of hydrothermal system associated with body of magma that has been intruded to depth of 6 km below water table, superimposed on figure 55.10 (shown in black).

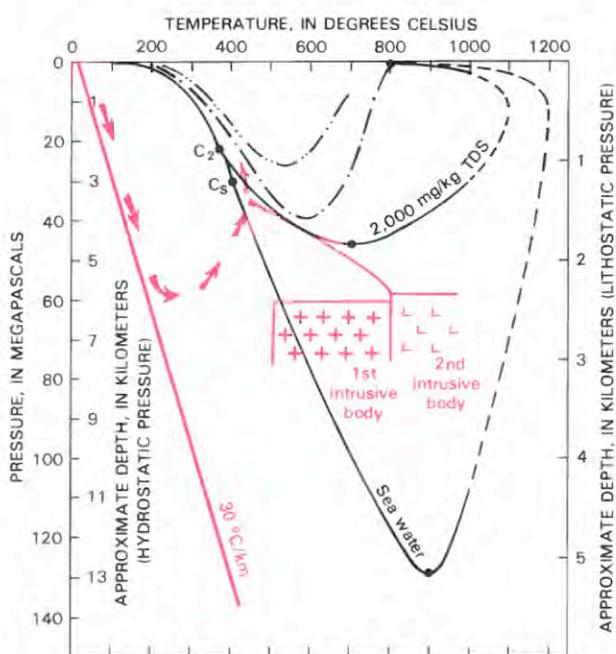


FIGURE 55.13.—Schematic depth-temperature relations (shown in red) for hydrothermal system where there have been multiple injections of magma to depth of about 6 km below water table, superimposed on figure 55.10 (shown in black).

feldspars and micas, so that as the rocks become more potassic, the solution becomes more sodic. However, under some circumstances potassic alteration also may result from a decrease in pressure (Fournier, 1976, 1983b). Within the field of gas plus brine, with decreasing pressure NaCl precipitates from solution before KCl, causing K exchange for Na in albite to maintain the required Na/K ratio in the aqueous solution for chemical equilibrium with the coexisting feldspars. After all the available albite is converted to K-feldspar by base exchange, the solution can become richer in potassium relative to sodium (by continued precipitation of NaCl with decreasing pressure), and the boundary of the gas plus solid region shifts toward lower pressures. Where there is no boiling of liquids or condensation of gas, the hydrothermal alteration products at temperatures of 300–500 °C are likely to be predominantly quartz, albite, K-feldspar, epidote, chlorite, and amphibole, with minimal acid and potassic alteration.

In summary, at a depth of intrusion of 6–7 km, brines are not likely to form by boiling of dilute ground water or by condensation of relatively saline gas unless there are special circumstances, such as repeated magmatic intrusions that preheat the surrounding rock and repeated fracturing of very hot rock that allows convecting water to become heated to temperatures above 450–500 °C. In contrast, brines are very likely to form by boiling of dilute ground water or by condensation of relatively saline gas where the depth of intrusion comes to within about 3 or 4 km of the surface, because the gas plus brine field is entered at a temperature less than 450 °C (fig. 55.14).

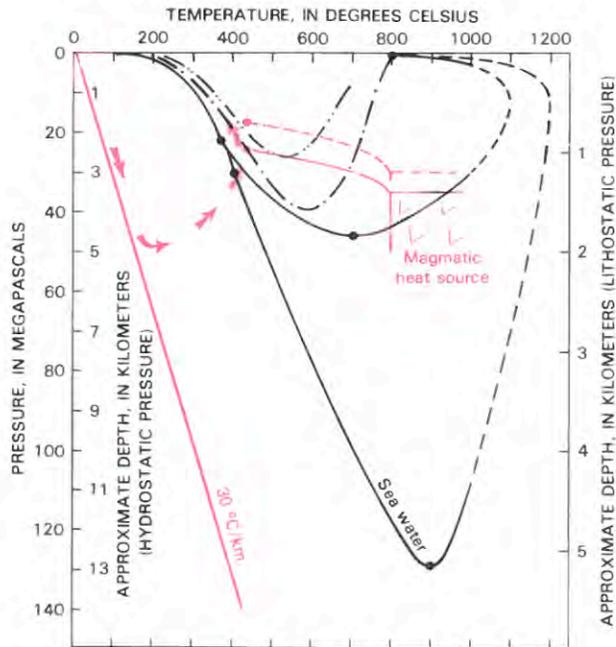


FIGURE 55.14.—Schematic depth-temperature relations (shown in red) for hydrothermal systems where depth of intrusion is within about 3–3.5 km below top of water table, superimposed on figure 55.10 (shown in black). See text for discussion.

The above-mentioned depth ranges are very approximate because of variations of hydrostatic pressure that result from different elevations of the water table, different densities of the fluids, different partial pressures of dissolved gases, different positions of the phase boundaries (shown in figures 55.10–55.14) because of variations in composition of the dissolved salts, and the possible formation of vapor-dominated regions (White and others, 1971) within parts of some hydrothermal systems. Little increase in fluid pressure or temperature is expected from the top to the bottom of a vapor-dominated region, so the relations shown in figures 55.10–55.14 will be displaced downward by the thickness of any vapor-dominated zone. In oceanic volcanic systems that have not formed islands, the depth of intrusion is the depth below sea level and not the depth below the ocean floor.

HYDROTHERMAL ACTIVITY ASSOCIATED WITH OCEANIC VOLCANOES

Several differences exist between the hydrothermal systems that are likely to develop in and around a continental volcanic center and an oceanic volcanic center. One difference is in the composition and amount of magmatic water that separates from a crystallizing silicic magma compared to a basaltic magma (silicic magmas are richer in water and chloride as shown by their hydrous minerals and quenched glass compositions). More important differences are the greater hydrostatic pressure that will prevail during the early stages of formation of an oceanic hydrothermal system and the fact that the oceanic systems are recharged by an abundant supply of sea water. In contrast, the abundance and composition of recharge water in continental systems is extremely variable.

The hydrothermal systems that develop within volcanic edifices that are built upon the sea floor, such as the Hawaiian Islands, are likely to have complex histories. The old sea floor is about 5 km below sea level near Hawaii. Therefore, extrusion of lava at a new volcanic center on that sea floor brings magma into contact with sea water at a pressure such that brine (equivalent to about 20 weight percent NaCl) plus vapor forms only at temperatures above about 480 °C (figs. 55.8 and 55.10). However, that hot brine is likely to have a density less than about 0.7 kg/m³, which is considerably less than that of the surrounding cold sea water, so both the vapor and the brine will rise and mix with the overlying cold water. Rapid chilling of the surface of the magma and a relatively slow transfer of heat by conduction to the interface with convecting sea water is likely to restrict brine formation to a very short time. Compositionally stratified layers of brine may develop by double-diffusive convection (Huppert and Turner, 1981; Huppert and Sparks, 1984; Vitagliano and others, 1984) in the ocean water above the heat source, but these brine layers are likely to be very transient.

Beneath the sea floor, heating of pore water to temperatures greater than 500–650 °C may occur over a significant period of time where magma is repeatedly injected to relatively shallow levels. Heating sea water to above 500 °C will cause a brine with more than 20 weight percent dissolved salt plus relatively dilute gas to form at a depth of about 0.5 km beneath the sea floor (about 5.5 km beneath the ocean surface, fig. 55.10). At a depth of 4 km beneath the sea

floor (9 km beneath the ocean surface) temperatures in excess of 650 °C are required to form highly saline brine from sea water. The gas component may convect all the way up to the sea floor, cooling, condensing, and mixing with pore water as it rises. The pore water may be sea water or previously condensed gas that contains low to moderate chloride and is rich in carbonate and sulfate, owing to water-rock reactions involving CO₂, SO₂, and H₂S. The brine component will first rise, but then as it cools its density will increase to the point that buoyant upflow will stop. Double-diffusion convection may result in compositionally stratified zones of water above and to the sides of the magmatic heat source. In response to double-diffusion convection, the densities of the hot, saline fluids will adjust and become essentially the same as the densities of the cold, surrounding pore fluids (sea water) at the same depths.

The above scenario assumes that the permeability is great enough that fluid expansion caused by heating of pore water can be accommodated by convective flow of fluid away from the hot part of the system without a hydrothermal explosion (Delaney, 1982), yet low enough that the magma-fluid interface will not be quickly quenched to below 500–650 °C by convecting water. The major factors that limit the amount of brine (greater than 3.2 weight percent NaCl equivalent) that forms are the size, depth, shape, and temperature of the heat source and the total amount and rate of movement of sea water through the system. The rate of movement is likely to slow with time because permeability is decreased by the formation of hydrous alteration products after volcanic glass, by precipitation of sulfate from sea water as it is heated at the inflow part of the system, by precipitation of silica, sulfides, and other minerals at the outflow part of the system, and by quasi-plastic flow of rock at high temperatures.

Decker (chapter 42) noted that the shallow magma chambers beneath Kilauea and Mauna Loa Volcanoes are both at a depth of about 3 km below the respective summits. He concluded that "The long term process of evolution of Hawaiian volcanoes apparently involves progressively upward remelting, stoping, and (or) shoving aside of the rocks which overlie the shallow magma reservoir systems." With the assumption that a 3-km depth to the top of a shallow magma reservoir is approximately maintained from the time a Hawaiian-type volcanic edifice starts to build on the sea floor through the period of island growth, some generalities can be made about the probable associated hydrothermal system.

With the start of volcanic activity the shallow magma chamber would be about 8 km below sea level, and sea water is converted to highly saline brine and gas only at temperatures above about 625 °C at that depth. Very little sea water is likely to become heated to that temperature. As the volcanic pile gets larger and the magma chamber rises, the temperature at which sea water in the vicinity of the magma chamber is converted to highly saline brine and gas decreases, and the likelihood of sea water attaining that temperature increases. The shallowest depth below sea level at which brine will condense from fluid of sea-water salinity is about 3 km at a temperature of about 405 °C (the critical point for a 3.2 weight percent NaCl solution, fig. 55.10). At lower temperatures and pressures the sea water will boil when heated. When the top of the

volcanic pile comes close to sea level, the top of the shallow magma chamber may be close enough to the surface (about 3–3.5 km) for portions of the associated hydrothermal system to be heated to the point of complete evaporation (enter the gas plus solid region at temperatures above about 400–450 °C, as shown in fig. 55.14). The evolving gas (steam) will be very rich in acids (chloride as well as sulfur species), but will carry only minor dissolved salt.

The hydrologic situation changes somewhat after a volcanic island emerges from the sea, because meteoric water becomes available to enter the hydrothermal system. Rain water percolates through permeable lava into the ground and, by the Ghyben-Herzberg principle (Bates and Jackson, 1980), forms a lens of fresh water that floats upon saline water (fig. 55.15). In the Hawaiian Islands the head of fresh water above sea level generally increases at a rate of about 0.2 m/km (1 ft/mi) from the shore (Peterson, 1981). However, on the Island of Hawaii, to the east of Kilauea and south of Hilo, the head of fresh water rises at a rate of about 0.8 m/km (Davis and Yamanaga, 1973). When steady-state conditions exist (and volcanic heat is not a factor) the head of fresh water above sea level is balanced by a thickness of fresh water below sea level about 40 times as great (Peterson, 1981). Where volcanic heat is a factor, the position of the fresh water-saline water interface is likely to be considerably different from that predicted on the basis of normal thermal gradients, because the densities of dilute water, sea water,

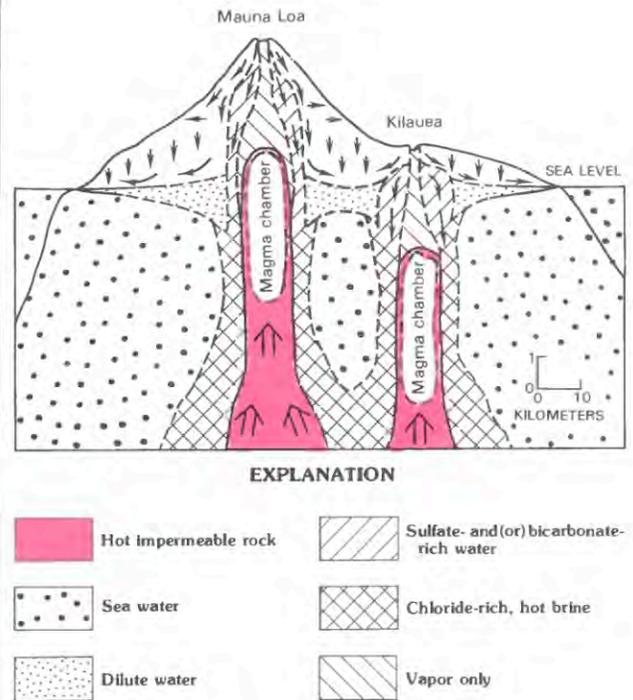


FIGURE 55.15.—Schematic diagram with vertical exaggeration showing shallow magma reservoirs and associated hydrothermal systems beneath Mauna Loa and Kilauea Volcanoes, Hawaii.

and highly saline brine decrease at different rates when heated. Also, hydrothermal alteration that decreases permeability occurs where ground water is heated and cooled. Therefore, the usual assumptions about densities and permeabilities that are made when calculating the elevation and thickness of the Ghyben-Herzberg lens will not be valid. In addition, ground water above shallow magma chambers will likely become rich in sodium sulfate (possibly also rich in bicarbonate) as a result of reactions involving volcanic gases and oxidation of sulfides in the rock. The boundaries between dilute water, sea water, sodium sulfate-rich water, steam, and chloride-rich brine are likely to be complex and transient, changing in response to heating when pulses of magma are injected into shallow reservoirs and when volcanic eruptions occur. Double-diffusive convection (Huppert and Turner, 1981) is likely to occur at these boundaries as a result of sharp thermal and salinity gradients.

Thin and discontinuous bodies of perched water are found within the volcanic edifice above the Ghyben-Herzberg lens, and perched streams flow through lava tubes. For simplicity, discontinuous bodies of perched water are not shown in figure 55.15. In the vicinities of volcanic eruptive centers, bodies of perched ground water may be fed in part from downward percolation of meteoric water and in part from condensation of steam rising from below.

The top of the shallow magma reservoir beneath Kilauea is about 2 km below sea level, and sea water (chemically changed in response to water-rock reactions at high temperatures, and about equivalent in salinity to a 3.2 weight percent NaCl solution) should be present within the volcanic edifice at that depth (fig. 55.15). The depth-temperature range is such that sea water will start to boil at a temperature of about 365 °C in the immediate vicinity of the top of the magma chamber and may even evaporate to dryness (figs. 55.14, 55.15). Within large volcanic edifices gravitational slumping (Fiske and Jackson, 1972) produces tensional stresses that may result in fracturing of rocks at very high temperatures where quasi-plastic flow would normally occur. Therefore, for relatively short, but significant, periods the maximum temperature attained by the convecting hydrothermal system may be considerably above 400–500 °C. Much of the steam that forms by reaction of the hydrothermal system with very hot rock probably will condense above the magma chamber, and the accompanying gases will react with rock, creating a saline solution that is rich in sodium sulfate (and bicarbonate, depending on pH), as previously discussed.

The temperature profile in a well drilled beneath the summit of Kilauea Volcano (Keller and others, 1979) indicates that a water table was encountered 488 m deep (about 600 m above sea level). Whether this is perched water or part of a large, continuous hydrothermal system that underlies the volcano is not known.

The top of the shallow magma reservoir beneath Mauna Loa is about 1 km above sea level, and that reservoir extends above the level of the Ghyben-Herzberg lens of dilute water (fig. 55.15). A hot sodium sulfate-rich brine probably is present between the colder dilute water and the magma reservoir. A vapor-only zone may be present in the upper part of the system where temperatures are too high and pore-fluid pressures are too low for liquid of any composition to exist.

The rift zones on the Island of Hawaii are kept heated by repeated injections of magma that flow laterally from the summit regions (Fiske and Jackson, 1972). The Ghyben-Herzberg lens pinches out near the shoreline, so sea water may come into contact with very hot rock along the rift zone at a relatively low pressure. If the sea water is heated to much higher temperatures than the dilute water in the overlying Ghyben-Herzberg lens, the interface between the two may be depressed considerably below the normal level, and mixing by double-diffusive convection is likely to occur.

In summary, in oceanic volcanic systems, such as at Hawaii, the shallow magma reservoir feeding the eruptions maintains about a 3–4 km depth beneath the summit as the volcanic edifice builds upon the sea floor. The pore spaces in the rocks surrounding the magma reservoir are filled with chemically altered sea water (most of its Mg and SO₄ lost by precipitation) that is converted to highly saline brine plus gas when the condensation-point curve is intersected, either by heating or decompression, at temperatures above about 405 °C at depths greater than about 3 km below sea level. At lower temperatures and pressures sea water boils as a result of heating or decompression, but this boiling may progress to dryness in rock that has been heated to a high temperature by magma that has been injected to a relatively shallow level. In the Hawaiian systems the transformation of sea water to highly saline brine may start when the heat source attains a depth of about 12–13 km below sea level, provided (1) hydrostatic pore pressures prevail, (2) the partial pressures of noncondensable gases, such as CO₂, are small relative to the total fluid pressure, and (3) the sea water comes in contact with rock that is at a temperature greater than about 800–900 °C (fig. 55.10). These conditions, if attained, are likely to be short lived at 12–13 km. The depth at which sea water may be converted to highly saline brine plus gas by heating is decreased where pore pressures are greater than hydrostatic, and increased by high partial pressures of noncondensable gases. When volcanic activity first appears upon the sea floor, the shallow magma reservoir is likely to be about 8–9 km below sea level, and temperatures in the 600–700 °C range are required to convert sea water to highly saline brine and gas. As the volcanic edifice grows, and the shallow magma reservoir rises, sea water converts to highly saline brine and gas at still lower temperatures. A significant amount of chloride-rich brine may accumulate adjacent to the magma reservoir, especially where repeated episodes of magma injection fracture the adjacent rocks and allow sea water access to very hot rock. Double-diffusive convection occurs at the contacts with colder and less saline waters. Sulfides are likely to deposit within the chloride-rich brine portion of the system below sea level, but these deposits are not likely to be exposed during subsequent erosion because they will always remain below sea level. After the volcano rises above the sea, fresh water enters the top of the hydrothermal system and prevents the buoyant upflow of heated sea water to elevations above sea level. Continuously or episodically thereafter, temperatures may become high enough, and pore pressures low enough to completely evaporate all pore waters near the top of the magma reservoir. Sodium sulfate- and sodium carbonate-rich brines form where steam condenses and sulfur- and carbon-rich gases react with the country rock.

EVOLUTION OF MAGMATIC FLUIDS

Many investigators have discussed the evolution of aqueous fluids from crystallizing magma, including Morey (1922), Bowen (1933), Emmons (1933), Fenner (1933), Lindgren (1937), Neuman (1948), Burnham (1967, 1979), Fournier (1968, 1972), Holland (1972), Phillips (1973), Norton and Cathles (1973, 1979), Whitney (1975), Cunningham (1978), Henley and McNabb (1978), Eastoe (1982), and Henley and Ellis (1983). Most investigators have assumed that the aqueous phase evolved from crystallizing magma is either a gas or supercritical fluid. Whether this is true or not depends both on the salinity of the magmatic fluid and on the pore pressure of the fluid in the rocks adjacent to the magma. If the permeability of the surrounding rocks is relatively low, the pore-fluid pressure in those rocks may be affected by the thermal effects of the magmatic intrusion (Delaney, 1982) and the rate at which aqueous fluid is expelled from the magma. Therefore, the pore-fluid pressure in the adjacent rocks may range from hydrostatic (or less if a vapor-dominated system is present) to the pressure that will cause hydrofracturing of the rock (a maximum pressure about equal to lithostatic pressure plus the tensile strength of the rock). The adjacent rocks may be outer parts of the magma that have already crystallized.

Chloride is likely to be the dominant anion in most aqueous fluids that evolve from solidifying magmas, although fluoride and boron species may be very important in some places. The total dissolved cations adjust to the available anions so that charges are balanced, and cation ratios are fixed by fluid-rock base exchange reactions. Carbon and sulfur compounds will be present mainly as gaseous species, CO_2 , SO_2 , and H_2S , at magmatic temperatures and have little influence on the cation-anion balance. Therefore, the salinity of an aqueous fluid that separates from a crystallizing magma depends mainly on the initial concentrations of chloride and water dissolved in the magma, and on how much of that chloride and water are incorporated within minerals that form during the solidification process. Magmas that form by partial fusion of crustal rocks that contain evaporite deposits are likely to have relatively large concentrations of chloride, carbon, and sulfur, and magmas that form by partial fusion of rocks that contain large quantities of hydrous minerals (such as shales) are likely to be relatively rich in water. The average shale contains about 0.15 weight percent chloride (Billings and Williams, 1967) and about 5 weight percent water (Clarke, 1924). Noble and others (1967) analyzed many obsidian glasses that had not been leached by water after solidification and found a maximum concentration of about 0.75 weight percent chloride. It seems reasonable to assume that silicic magmas that form by partial fusion of sediments might contain about 0.1–0.8 weight percent chloride and about 1–5 weight percent water. Then, for magmas initially containing 1 weight percent water that is evolved as a magmatic fluid (little water is tied up in hydrous minerals), the chloride concentration in that fluid could range from about 10–44 weight percent (equivalent to about 16–72 weight percent NaCl). For magmas initially containing 5 weight percent water, the chloride concentration in an evolved aqueous magmatic fluid could range from

about 2–14 weight percent (equivalent to about 3–23 weight percent NaCl) if no water were incorporated in hydrous minerals.

The critical curve for the system $\text{NaCl-H}_2\text{O}$ is shown in relation to the granite minimum melting curve (Tuttle and Bowen, 1958) in figure 55.16. Two situations are represented in that figure: water pressure equal to lithostatic pressure (in red) and hydrostatic pressure (in black). Where pore-fluid pressures in the adjacent rock are about equal to the lithostatic pressure, aqueous fluids that evolve from silicic magmas that are crystallizing along the granite minimum melting curve should retain their initial salt/water ratios as they cool at depths greater than about 5 km. Where pore-fluid pressures in the adjacent rock are about equal to the hydrostatic pressure, initial salt/water ratios in magmatic fluids are likely to be maintained only at depths greater than about 13 km. A decrease in pore-fluid pressure from lithostatic to hydrostatic would likely cause a magma on the granite minimum melting curve to become supercooled by about 75 °C, with the simultaneous evolution of a highly saline brine and moderately saline to dilute gas.

The position of the granite minimum melting curve is shown in figure 55.17 as it relates to the isopleths of solubility of NaCl in steam and liquid water (fig. 55.7). Point y on the granite minimum melting curve indicates the lowest pressure (with water pressure equal to total pressure) at which the magma can retain 4 weight percent dissolved water (Tuttle and Bowen, 1958). A further

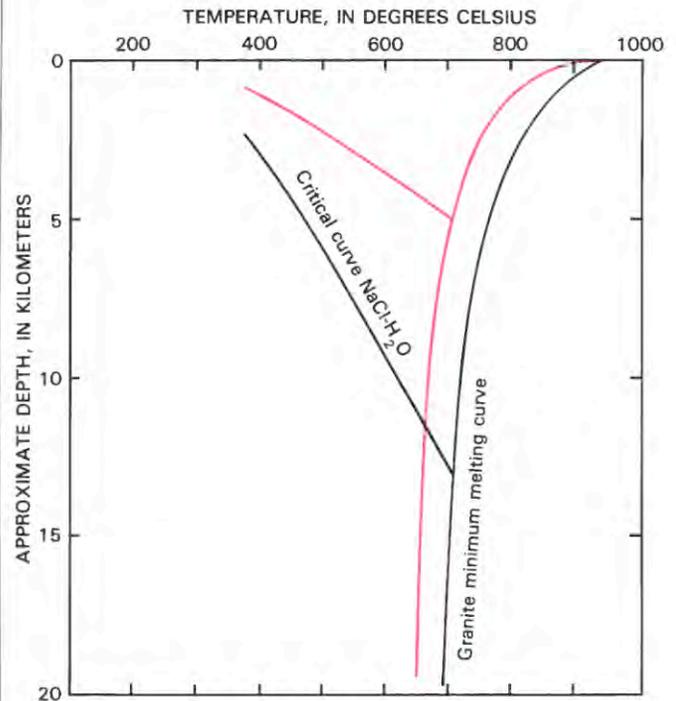


FIGURE 55.16.—Approximate positions of critical curve for system $\text{NaCl-H}_2\text{O}$ and of granite minimum melting curve (Tuttle and Bowen, 1958). Red lines, water pressure equal to lithostatic pressure; black lines, hydrostatic pressure.

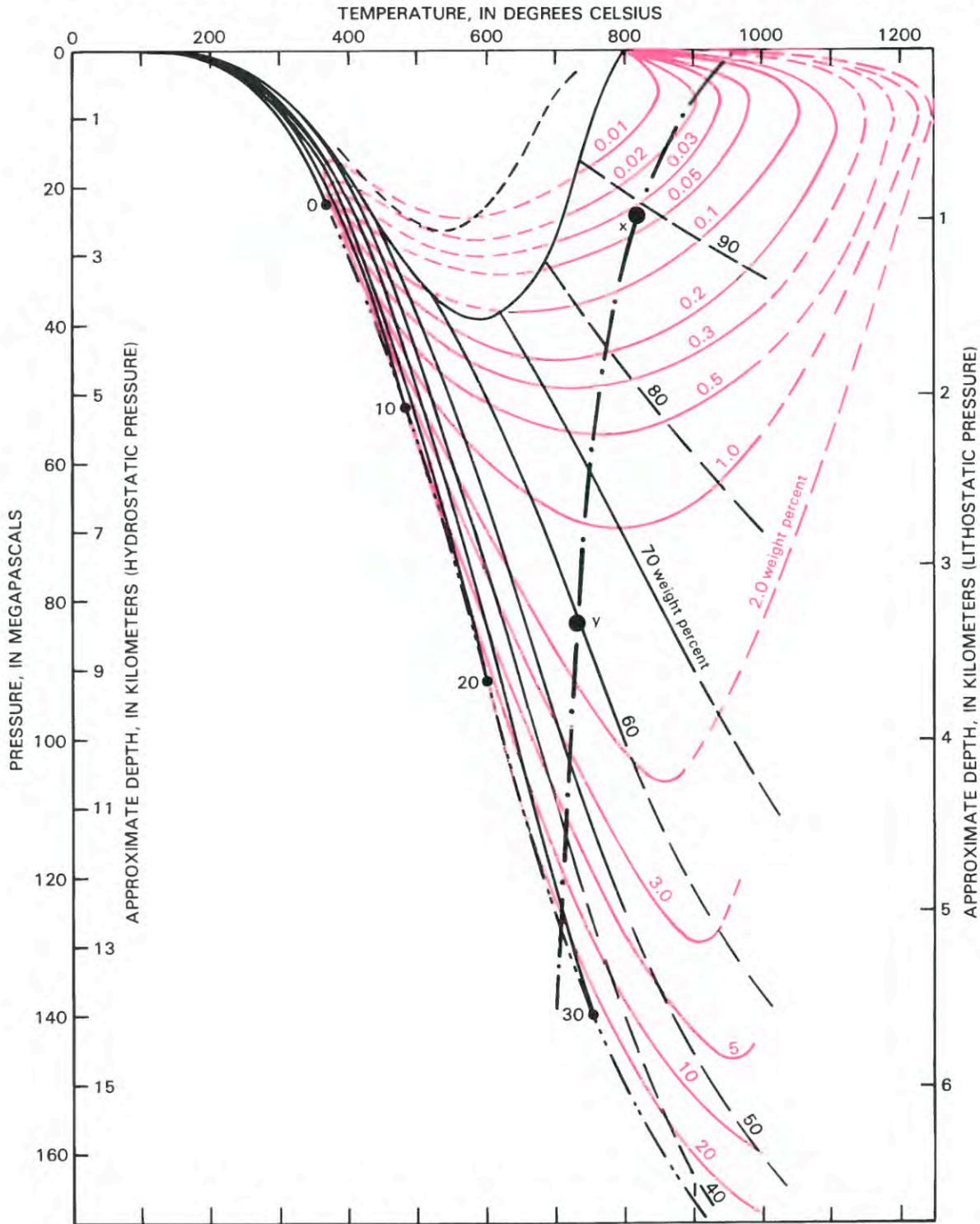


FIGURE 55.17.—Granite minimum melting curve (Tuttle and Bowen, 1958) shown by dot-dashed line, superimposed on figure 55.7. Lettered points are discussed in text.

decrease in pressure would result in evolution of water and an immediate crystallization of the magma. Chloride initially dissolved in the magma will partition strongly into the aqueous phase (Kilinc and Burnham, 1972), and the maximum salt (as NaCl) that the aqueous gas phase can carry is 1–2 weight percent. Point x on the granite minimum melting curve indicates the lowest pressure at which the magma can retain 2 weight percent dissolved water, and the maximum salt that the aqueous gas phase can carry is only about 0.05 weight percent. A much greater solubility of salt in the gas phase at point x would be estimated using the results reported by Sourirajan and Kennedy (1962).

From the foregoing discussion it appears that when pore-fluid pressures are controlled by hydrostatic conditions, magmatic waters are likely to evolve to highly saline brines at depths less than about 10–12 km, irrespective of the initial concentrations of salt and water dissolved in the magma. Dilute hydrothermal fluids of meteoric origin and mixtures of meteoric water and condensed magmatic gas (steam) are likely to form convection systems that float upon the more saline and probably hotter magmatic fluid. Double-diffusive convection is likely to result from the temperature and salinity gradients.

CONCLUSIONS

Our present knowledge of hydrothermal mineral deposits and active geothermal systems demonstrates the importance of interaction of shallow dilute meteoric water and deeper brines. The highly concentrated brines thus far encountered in active hydrothermal systems are all in environments in which the waters may have interacted with evaporites. Experimental data, however, indicate that highly saline as well as moderately concentrated brines may evolve from a crystallizing magma, depending on the initial water and chloride contents and on the depth of crystallization. Brines may also develop from dilute meteoric water as a result of heating. Heating a solution of given composition to above its critical temperature at a pressure a little above its critical pressure results in its disproportionation into a more concentrated liquid (brine) and a gas. What is generally thought of as supercritical behavior of a fluid occurs only at pressures great enough to ensure that the gas phase will retain all the salt that was initially dissolved in the liquid phase at a lower temperature. As a result of boiling and gas disproportionation, highly saline brines are likely to evolve in and around shallow magmatic intrusions, particularly at depths less than 3 to 4 km. However, a relatively large amount of dilute water must be heated to a very high temperature to produce a small amount of brine. The injection of dilute water into very hot rock is an inefficient way to produce brine because the rock at the liquid interface is chilled rapidly by the colder water and because relatively little water is likely to be involved. Adiabatic decompression of a dilute to moderately saline solution (such as sea water) that is part of a large convection system appears to be a more promising method of producing significant amounts of brine. In a large convecting system heat may be extracted from a large volume of rock, and highly saline brines will form if the decompression path of the fluid brings it into the field of gas plus brine at a temperature a few degrees above the critical temperature. By gravitational settling this brine may accumulate at

the base of hydrothermal convection in the few fractures that are present in otherwise impermeable rock. The brines formed by heating and adiabatic decompression of dilute to moderately saline water of meteoric origin (including sea water) will augment brines that result from crystallization and degassing of the magmatic heat source. These hot brines will scavenge metals from the surrounding rock, and the base metals in turn will react with much of the sulfur that is liberated from crystallizing magma. Thus, a base metal ore deposit may form in the brine portion of the system, while the dilute hydrothermal system remains relatively unmineralized with respect to base metals.

REFERENCES

- Bates, R.L., and Jackson, J.A., 1980, Glossary of geology (2d ed.): Falls Church, Va., American Geological Institute, 749 p.
- Billings, G.K., and Williams, H.H., 1967, Distribution of chlorine in terrestrial rocks (a discussion): *Geochimica et Cosmochimica Acta*, v. 31, p. 2247.
- Bischoff, J.L., and Pitzer, K.S., 1985, Phase relations and adiabats in boiling seafloor geothermal systems: *Earth and Planetary Science Letters*, v. 75, p. 327–338.
- Bischoff, J.L., and Rosenbauer, R.J., 1984, The critical point and two-phase boundary of seawater, 200°–500°C: *Earth and Planetary Science Letters*, v. 68, p. 172–180.
- , 1985, An empirical equation of state for hydrothermal seawater (3.2% NaCl): *American Journal of Science*, v. 285, p. 725–763.
- Bischoff, J.L., Rosenbauer, R.J., and Pitzer, K.S., in press, A note on the system NaCl-H₂O: Relations of vapor-liquid near the critical temperature of water and of vapor-liquid-halite from 300° to 500°C: *Geochimica et Cosmochimica Acta*.
- Bodnar, R.J., and Bean, R.E., 1980, Temporal and spatial variations in hydrothermal fluid characteristics during vein filling in preore cover overlying deeply buried porphyry copper-type mineralization at Red Mountain, Arizona: *Economic Geology*, v. 75, p. 876–893.
- Bodnar, R.J., Burnham, C.W., and Sterner, S.M., 1985, Synthetic fluid inclusions in natural quartz III: Determination of phase equilibrium properties in the system H₂O-NaCl to 1000°C and 1500 bars: *Geochimica et Cosmochimica Acta*, v. 49, p. 1861–1873.
- Bodvarsson, G., and Lowell, R.P., 1972, Ocean floor heat flow and circulation of interstitial waters: *Journal of Geophysical Research*, v. 77, p. 4472–4475.
- Bowen, N.L., 1933, The broader story of magmatic differentiation, briefly told, in *Ore deposits of the western states (Lindgren volume)*: New York, American Institute of Mining and Metallurgical Engineers, p. 106–128.
- Bowers, T.S., and Helgeson, H.C., 1983, Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system H₂O-CO₂-NaCl on phase relations in geologic systems: Equation of state for H₂O-CO₂-NaCl fluids at high pressures and temperatures: *Geochimica et Cosmochimica Acta*, v. 47, p. 1247–1275.
- Burnham, C.W., 1967, Hydrothermal fluids at the magmatic stage, in Barnes, H.L., ed., *Geochemistry of hydrothermal ore deposits*: New York, Holt, Rinehart and Winston, p. 34–76.
- , 1979, Magmas and hydrothermal fluids, in Barnes, H.L., ed., *Geochemistry of hydrothermal ore deposits (2d ed.)*: New York, John Wiley, p. 17–136.
- Cathles, L.M., 1977, An analysis of the cooling of intrusives by ground-water convection which includes boiling: *Economic Geology*, v. 72, no. 5, p. 804–826.
- , 1980, Fluid flow and genesis of hydrothermal ore deposits: *Economic Geology*, 75th Anniversary Volume, p. 424–457.
- , 1983, An analysis of the hydrothermal system responsible for massive sulfide deposition in the Hokuroku Basin of Japan, in Ohmoto, H., and Skinner, B.J., eds., *The Kuroko and related volcanogenic massive sulfide deposits*: *Economic Geology*, Monograph 5, p. 439–487.

- Cheng, P., and Minkowicz, W.J., 1977, Free convection about a vertical flat plate embedded in a porous medium with application to heat transfer from a dike: *Journal of Geophysical Research*, v. 82, p. 2040-2044.
- Clarke, F.W., 1924, The data of geochemistry, 5th ed.: U.S. Geological Survey Bulletin 770, 841 p.
- Copeland, C.S., Silverman, J., and Benson, S.W., 1952, The system NaCl-H₂O at supercritical temperatures and pressures: *Journal of Chemical Physics*, v. 21, p. 12-16.
- Cunningham, C.G., 1978, Pressure gradients and boiling as mechanisms for localizing ore in porphyry systems: U.S. Geological Survey Journal of Research, v. 6, no. 6, p. 745-754.
- Davis, D.A., and Yamanaga, George, 1973, Water resources summary island of Hawaii: Hawaii Division of Water and Land Development Report R47, 42 p.
- Delaney, P.T., 1982, Rapid intrusion of magma into wet rock: Ground water flow due to pore pressure increases: *Journal of Geophysical Research*, v. 87, p. 7739-7756.
- Eastoe, C.J., 1978, A fluid inclusion study of the Panguna porphyry copper deposit, Bougainville, Papua New Guinea: *Economic Geology*, v. 73, p. 721-748.
- 1982, The physics and chemistry of the hydrothermal system in the Panguna porphyry copper deposit, Bougainville, Papua New Guinea: *Economic Geology*, v. 77, p. 127-153.
- Edmond, J.M., Craig, H., Gordon, L.I., and Holland, H.D., 1979, Chemistry of hydrothermal waters at 21°N on the East Pacific Rise [abs.]: *Eos (American Geophysical Union Transactions)*, v. 60, p. 864.
- Elder, J.W., 1965, Physical processes in geothermal areas, in *Terrestrial heat flow: American Geophysical Union Geophysical Monograph 8*, p. 211-239.
- Emmons, W.H., 1933, On the mechanism of the deposition of certain metalliferous lode systems associated with granitic batholiths, in *Ore deposits of the western states (Lindgren vol.)*: New York, American Institute of Mining and Metallurgical Engineers, p. 327-349.
- Eugster, H.P., and Jones, B.F., 1979, Behavior of major solutes during closed basin evolution: *American Journal of Science*, v. 279, p. 609-631.
- Fehn, U., and Cathles, L.M., 1979, Hydrothermal convection at slow-spreading mid-ocean ridges: *Tectonophysics*, v. 55, p. 239-260.
- Fenner, C.N., 1933, Pneumatolytic processes in the formation of minerals and ores, in *Ore deposits of the western states (Lindgren vol.)*: American Institute of Mining and Metallurgical Engineers, p. 58-106.
- Fiske, R.S., and Jackson, E.D., 1972, Orientation and growth of Hawaiian volcanic rifts: The effect of regional structure and gravitational stress: *Proceedings of the Royal Society of London*, v. 329, p. 299-326.
- Fournier, R.O., 1968, Depths of intrusion and conditions of hydrothermal alteration in porphyry copper deposits [abs.]: *Geological Society of America Abstracts with Program*, 1968 Annual Meeting, p. 101.
- 1972, The importance of depth of crystallization on the character of magmatic fluids [abs.]: *International Geological Congress, 24th, Montreal, 1972, sec. 10*, p. 214.
- 1976, Exchange of Na⁺ and K⁺ between water vapor and feldspar phases at high temperature and low vapor pressure: *Geochimica et Cosmochimica Acta*, v. 40, p. 1553-1561.
- 1977, Constraints on the circulation of meteoric water in hydrothermal systems imposed by the solubility of quartz [abs.]: *Geological Society of America Abstracts with Program*, v. 9, p. 979.
- 1983a, Self-sealing and brecciation resulting from quartz deposition within hydrothermal systems: *International Symposium on Water-Rock Interaction, 4th, Misasa, Japan, 1983, Extended Abstracts*, p. 137-140.
- 1983b, Active hydrothermal systems as analogues of fossil systems, in *Raleigh, C.B., ed., The role of heat in the development of energy and mineral resources in the Basin and Range Province: Geothermal Resources Special Report 13*, p. 263-284.
- 1985a, Continental scientific drilling to investigate brine evolution and fluid circulation in active hydrothermal systems, in *Observation of the continental crust through drilling*: New York, Springer-Verlag, p. 98-122.
- 1985b, Silica minerals as indicators of conditions during gold deposition, in *Tooker, E.W., ed., Geologic characteristics of sediment- and volcanic-hosted disseminated gold deposits—search for an occurrence model*: U.S. Geological Survey Bulletin 1646, p. 15-26.
- Fournier, R.O., and Pitt, A.M., 1985, The Yellowstone magmatic-hydrothermal system: *International Symposium on Geothermal Energy, Geothermal Resources Council, Hawaii, 1985, International Volume*, p. 319-327.
- Galobardes, J.F., Van Hare, D.R., and Rogers, L.B., 1981, Solubility of sodium chloride in dry steam: *Journal of Chemical Data*, v. 26, p. 363-366.
- Gunter, W.D., Chow, I-M, and Girsperger, S., 1983, Phase relations in the system NaCl-KCl-H₂O II: Differential thermal analysis of halite liquidus in the NaCl-H₂O binary above 450 °C: *Geochimica et Cosmochimica Acta*, v. 47, p. 863-873.
- Haas, J.L., 1971, Effect of salinity on the maximum thermal gradient of a hydrothermal system at hydrostatic pressure: *Economic Geology*, v. 66, p. 940-946.
- Hardee, H.C., 1982, Permeable convection above magma bodies: *Tectonophysics*, v. 84, p. 179-195.
- Hardie, L.A., and Eugster, H.P., 1970, The evolution of closed-basin brines: *Mineralogical Society of America Special Publication 3*, p. 273-279.
- Hartline, B.K., and Lister, C.R.B., 1981, Topographic forcing of supercritical convection in a porous medium such as the ocean crust: *Earth and Planetary Science Letters*, v. 55, p. 75-86.
- Henley, R.W., and Ellis, A.J., 1983, Geothermal systems ancient and modern: A geochemical review: *Earth-Science Reviews*, v. 19, 50 p.
- Henley, R.W., and McNabb, Alex, 1978, Magmatic vapor plumes and ground-water interaction in porphyry copper emplacement: *Economic Geology*, v. 73, 19 p.
- Hilbert, R., 1979, PVT-Daten von Wasser und von wässrigen Natriumchlorid-Lösungen bis 873 K, 4000 Bar und 25 Gewichtsprozent NaCl: Karlsruhe University, Ph.D. Dissertation, 212 p.
- Holland, H.D., 1972, Granites, solutions and base metal deposits: *Economic Geology*, v. 67, p. 281-301.
- Huppert, H.E., and Sparks, R.S.J., 1984, Double-diffusive convection due to crystallization in magmas: *Annual Review of Earth and Planetary Science*, v. 12, p. 11-37.
- Huppert, H.E., and Turner, J.S., 1981, Double-diffusion convection: *Journal of Fluid Mechanics*, v. 106, p. 299-329.
- Keenan, J.H., Keys, F.G., Hill, P.G., and Moore, J.G., 1969, Steam tables (international edition—metric units): New York, John Wiley & Sons, 162 p.
- Keevil, N.B., 1942, Vapor pressure of aqueous solutions at high temperatures: *Journal of the American Chemical Society*, v. 64, p. 841-850.
- Keller, G.V., Grose, L.T., Murray, J.C., and Skokan, C.K., 1979, Results of an experimental drill hole at the summit of Kilauea Volcano, Hawaii: *Journal of Volcanology and Geothermal Research*, v. 5, p. 345-385.
- Khaibullin, K., and Borisov, N.M., 1966, Experimental investigation of the thermal properties of aqueous and vapor solutions of sodium and potassium chloride at phase equilibrium: *Teplofizika Vysokikh Temperatur*, v. 4, p. 518-523 (English translation, p. 489-494).
- Kilinc, I.A., and Burnham, C.W., 1972, Partitioning of chloride between a silicate melt and coexisting aqueous phase from 2 to 8 kilobars: *Economic Geology*, v. 67, p. 231-235.
- Knapp, R.B., and Norton, D., 1981, Preliminary numerical analysis of processes related to magma crystallization and stress evaluation in cooling pluton environments: *American Journal of Science*, v. 281, p. 35-68.
- Lama, R.D., and Vutukuri, V.S., 1978, Handbook on mechanical properties of rocks—testing techniques and results—volume II: Clausthal, Germany, Trans Tech Publications, 484 p.
- Langbein, W.B., 1961, Salinity and hydrology of closed lakes: U.S. Geological Survey Professional Paper 412, 20 p.
- Lindgren, W., 1937, Succession of minerals and temperatures of formation in ore deposits of magmatic affiliation: *American Institute of Mining and Metallurgical Engineers Transactions*, v. 126, p. 356-376.
- Lister, C.R.B., 1974, On the penetration of water into hot rock: *Geophysical Journal of the Royal Astronomical Society*, v. 39, p. 465-509.
- 1980, Heat flow and hydrothermal circulation: *Earth and Planetary Sciences Annual Review*, v. 8, p. 95-117.

- 1983, The basic physics of water penetration into hot rock, in Rona, P.A., Bostrom, K., Laubier, L., and Smith, K.L., Jr., eds., *Hydrothermal processes at seafloor spreading centers*: New York, Plenum Press, p. 141–168.
- Morey, G.W., 1922, The development of pressure in magmas as a result of crystallization: *Washington Academy of Science Journal*, v. 12, p. 219–230.
- Muffler, L.J.P., White, D.E., and Truesdell, A.H., 1971, Hydrothermal explosion craters in Yellowstone National Park: *Geological Society of America Bulletin*, v. 82, p. 723–740.
- Nash, J.T., 1976, Fluid-inclusion petrology—data from porphyry copper deposits and applications to exploration: U.S. Geological Survey Professional Paper 907-D, 16 p.
- Neuman, H., 1948, On hydrothermal differentiation: *Economic Geology*, v. 43, p. 77–83.
- Noble, D.C., Smith, V.C., and Peck, L.C., 1967, Loss of halogens from crystallized and glassy silicic volcanic rocks: *Geochimica et Cosmochimica Acta*, v. 31, p. 215–223.
- Norton, Denis, 1978, Sourcelines, source regions, and pathlines for fluid flow in hydrothermal systems related to cooling plutons: *Economic Geology*, v. 73, p. 21–28.
- 1984, Theory of hydrothermal systems: *Annual Review of Earth and Planetary Sciences*, v. 12, p. 155–177.
- Norton, Denis, and Cathles, L.M., 1973, Breccia pipes—products of exsolved vapor from magmas: *Economic Geology*, v. 68, p. 540–546.
- 1979, Thermal aspects of ore deposition, in Barnes, H.L., ed., *Geochemistry of hydrothermal ore deposits* (2d ed.): New York, John Wiley, p. 611–631.
- Norton, Denis, and Knapp, R., 1977, Transport phenomena in hydrothermal systems: The nature of porosity: *American Journal of Science*, v. 277, p. 913–936.
- Norton, Denis, and Knight, J., 1977, Transport phenomena in hydrothermal systems: Cooling plutons: *American Journal of Science*, v. 277, p. 937–981.
- Norton, Denis, and Taylor, H.P., 1979, Quantitative simulation of the hydrothermal systems of crystallizing magmas on the basis of transport and oxygen isotope data: An analysis of the Skaergaard intrusion: *Journal of Petrology*, v. 20, p. 421–486.
- Ölander, A., and Liander, H., 1950, The phase diagram of sodium chloride in steam above the critical point: *Acta Chemica Scandinavica*, v. 4, p. 1437–1445.
- Orville, P.M., 1963, Alkali ion exchange between vapor and feldspar phases: *American Journal of Science*, v. 261, p. 201–237.
- Parisod, C.J., and Plattner, E., 1981, Vapor-liquid equilibria of the NaCl-H₂O system in the temperature range 300–440 °C: *Journal of Chemical Engineering Data*, v. 26, p. 15–20.
- Parmentier, E.M., and Spooner, E.T.C., 1978, A theoretical study of hydrothermal convection and the origin of the ophiolitic sulfide ore deposit of Cyprus: *Earth and Planetary Science Letter*, v. 40, p. 33–44.
- Peterson, F.L., 1981, Geologic and hydrologic framework: A history of development, in Fujimura, F.N., and Chang, W.B.C., eds., *Groundwater in Hawaii, a century of progress*: Manoa, University of Hawaii Press, p. 1–13.
- Phillips, W.J., 1973, Mechanical effects of retrograde boiling and its probable importance in the formation of some porphyry ore deposits: *American Institute of Mining and Metallurgical Engineers Transactions*, sec. B, v. 82, p. B90–B98.
- Pitzer, K.S., 1983, Thermodynamics of sodium chloride solutions in steam: *Journal of Physical Chemistry*, v. 87, p. 1120–1125.
- Pitzer, K.S., and Li, Y., 1984, Critical phenomena and thermodynamics of dilute aqueous sodium chloride to 823 K: *Proceedings of the National Academy of Science*, v. 81, p. 1268–1271.
- Pitzer, K.S., and Pabalan, R.T., in press, Thermodynamics of NaCl in steam: *Geochimica et Cosmochimica Acta*.
- Ravich, M.I., and Borovia, F.E., 1949, Phase equilibria in ternary water-salt systems at elevated temperatures [in Russian]: *Akademiya Nauk SSSR, Institut Obshchei i Neorganicheskoi Izvestiia, Sektor Fiziko Khimicheskogo Analiza*, v. 19, p. 69–81.
- Reynolds, T.J., and Bean, R.E., 1985, Evolution of hydrothermal fluid characteristics at the Santa Rita, New Mexico, porphyry copper deposit: *Economic Geology*, v. 80, p. 1328–1347.
- Ribando, R.J., Torrance, K.E., and Turcotte, D.L., 1976, Numeric models for hydrothermal circulation in the ocean crust: *Journal of Geophysical Research*, v. 81, p. 3007–3012.
- Roedder, Edwin, 1971, Fluid inclusion studies on the porphyry type deposit at Bingham, Utah, Butte, Montana, and Climax, Colorado: *Economic Geology*, v. 66, p. 98–120.
- 1979, Fluid inclusions as samples of ore fluids, in Barnes, H.L., ed., *Geochemistry of hydrothermal ore deposits* (2d ed.): New York, John Wiley, p. 684–737.
- Sleep, N.H., 1983, Hydrothermal convection at ridge axes, in Rona, P.R., and Lowell, R.L., eds., *Hydrothermal processes at seafloor-spreading centers*: New York, Plenum Press, p. 71–82.
- Smith, R.B., and Bruhn, R.L., 1984, Interplate extensional tectonics of the eastern Basin-Range: Inferences on structural style from seismic reflection data, regional tectonics, and thermal mechanical models of brittle-ductile deformation: *Journal of Geophysical Research*, v. 89, p. 5733–5762.
- Sourirajan, S., and Kennedy, G.C., 1962, The system H₂O-NaCl at elevated temperatures and pressures: *American Journal of Science*, v. 260, p. 115–141.
- Torrance, K.E., and Sheu, J.P., 1978, Heat transfer from plutons undergoing hydrothermal cooling and thermal cracking: *Numerical Heat Transfer*, v. 1, p. 147–161.
- Tuttle, O.F., and Bowen, N.L., 1958, Origin of granite in the light of experimental studies in the system NaAlSi₃O₈-KAlSi₃O₈-SiO₂-H₂O: *Geological Society America Memoir* 74, 153 p.
- Vitagliano, P.L., Della Volpe, C., and Vitagliano, V., 1984, Gravitational instabilities in free diffusion boundaries: *Journal of Solution Chemistry*, v. 13, p. 549–562.
- White, D.E., 1965, Saline waters of sedimentary rocks: *American Association of Petroleum Geologists Memoir* 4, p. 342–366.
- 1968, Environments of generation of some base-metal ore deposits: *Economic Geology*, v. 63, p. 301–335.
- White, D.E., Muffler, L.J.P., and Truesdell, A.H., 1971, Vapor-dominated hydrothermal systems compared to hot water systems: *Economic Geology*, v. 66, p. 75–97.
- Whitney, J.A., 1975, Vapor generation in a quartz monzonite magma: A synthetic model with application to porphyry copper deposits: *Economic Geology*, v. 70, p. 346–358.