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ACTIVE HYDROTHERMAL SYSTEMS AS ANALOGUES OF FOSSIL SYSTEMS

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ABSTRACT

The physical and chemical characteristics of many diverse active hydrothermal systems have been determined from exploratory drilling and commercial production of geothermal resources. Fluid pressures and temperatures vary widely, depending on the distribution of permeable rocks and their specific permeability, the position of the water table, the source of recharge water, the salinity and gas content of the hydrothermal fluids, and the nature of the heat source. In convecting hot-water systems, the maximum temperatures attainable at given depths are given by boiling-point curves that are appropriate for hydrostatic conditions. In vapor-dominated systems, liquid water is present in pore spaces within the rock, but vapor (steam and gas) fills open fractures throughout much of the system. Temperatures and pressures vary little within vapor-dominated zones, and these systems are underpressured with respect to normal hydrostatic systems. Lithostatic fluid pressures have been encountered in deep sedimentary basins. There is reason to believe that exceptionally high fluid pressures might be encountered in other environments with temperatures higher than about 350°C. Increases in fluid pressure from hydrostatic to lithostatic can occur only where a permeability barrier prevents free movement of liquid from the high- to the low-pressure region. With increasing fluid pressures, boiling temperatures increase, or supercritical conditions might be attained. In either event, a relatively steep temperature gradient may develop across a thin impermeable barrier. Sudden rupturing of such a barrier, and the accompanying drop in confining pressure, could result in violent boiling, brecciation of the overlying rock, and simultaneous deposition of minerals.

Fluid compositions vary widely in presently active systems. Total dissolved cations adjust to the total available anions, whereas dissolved silica, cation ratios, and pH are fixed by temperature-dependent mineral-solution reactions. Most hot-spring waters at depth have pH values in the range 6-7. As these neutral to slightly acidic waters ascend they usually become more alkaline owing to loss of CO₂. The importance of contributions from magmatic

emanations to dissolved-metal concentrations in presently active systems is difficult to assess because little, if any, magmatic water appears to be present in the systems that have been well studied to date. It is possible that water evolving from crystallizing magma may become trapped in brines that underlie presently active systems at deeper levels than drilling has yet reached. Magmatic water may yet be found in some of the newly discovered acid systems associated with active or very young andesite volcanism in the South Pacific.

Evidence for underground boiling, and for mixing of waters with different compositions and temperatures, is commonly found in active systems. These processes are likely to cause deposition of minerals, such as quartz, K-feldspar, calcite, sulfides, and gold. Where ascending hot water (>100°C) flows too rapidly to be cooled entirely by conduction, the water heats the surrounding rock to the boiling temperature of the solution at the prevailing hydrostatic pressure (on the boiling-point curve), and the deposition of minerals is likely to be chemically and physically uniform (without banding). Banded mineral deposits may result from seasonal mixing of different waters, or from intermittent changes in water table that disrupt steady-state temperatures and pressures, causing massive and widespread boiling and even hydrothermal brecciation.

Hydrologic characteristics of presently active systems show great variations. Some systems discharge large amounts of hot fluid to the surface while others discharge very little. Many systems show evidence of long periods of inactivity between periods of active convective discharge. Decreased convective flow results mainly from self-sealing, but also may be influenced by changes in water table. Seismic activity, hydraulic fracturing, or a sudden decrease in water table that results in hydrothermal explosions may reopen self-sealed rock and allow convective flow to resume.

Stages in the evolution of hydrothermal activity within an intermediate to silicic volcanic system might include: (1) early venting of gas from magma directly to the surface; (2) formation of a layer of ground water (from

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condensation of steam and rain water) above the gas which increases the fluid pressure near the magma; (3) acid alteration near the base of the thickening condensate layer and formation of brine adjacent to the magma; (4) development of a relatively dilute, but chloride-rich, convecting system fed by meteoric water above the brine; (5) formation of a vapor-dominated system within rock previously heated by the convecting hot water system; and (6) final influx of cool water throughout the system as the heat source wanes.

INTRODUCTION

Investigations of fossil hydrothermal systems provide information about processes that occurred throughout the lives of those systems. Such investigations, however, seldom provide an unambiguous picture of the physical and chemical conditions throughout the system at a given time, the kind of information required to develop more than crude conceptual models. Studies of active hydrothermal systems do provide information about their physical and chemical nature at a given time, but not enough for complete understanding of the history of the system. Studies of fluid inclusions and hydrothermal alteration products, found in cores and cuttings retrieved from wells drilled in active systems, provide additional information about the previous hydrothermal history.

Fossil hydrothermal systems are of great interest because they commonly contain ores. Processes that may lead to the transport and deposition of metals in hydrothermal systems include heating and cooling, pressure changes, partitioning of volatiles between liquid and gas during boiling, mixing of different fluids, and reactions between fluids and wall rocks. Examples of all of the above processes have been found in presently active hydrothermal systems.

Relationships between hot-spring activity and ore deposition have been described and summarized in a series of papers by White (1955, 1967, 1968a, 1974, 1981). The deposition of mercury ore within the presently active hot-spring system at Sulphur Bank, California, is well documented (White and Robinson, 1962; White, 1981). Ore-grade precipitates of Au and high concentrations of Ag, Sb, Hg, and Tl have been found in sinters presently being deposited at Steamboat Springs, Nevada (White, 1955, 1981), and at Broadlands and Waiotapu, New Zealand (Weissberg, 1969; Ewers and Keays, 1977; Weissberg and others, 1979). Naboko (1974) described Hg-Sb-As mineralization and gold and polymetals being deposited from thermal waters at Uzon Caldera, Kamchatka. Ore-grade precipitates of base metals have been found in sediments beneath the Red Sea hot brine pools (Bischoff, 1969; Brewer and Spencer, 1969; Hendricks and others, 1969; Shanks and Bischoff, 1977), and precipitated from hot, deeply circulating ocean waters at oceanic spreading centers (Edmond and others, 1979; Francheteau

and others, 1979; Koski and others, 1982; Normark and others, 1982; Vidal and others, 1978). High concentrations of dissolved metals have been found in high-temperature (>300°C) brines in the Salton Sea geothermal system (White and others, 1963; White, 1968a), in low-temperature brines at Cheleken, U.S.S.R. (Lebedev, 1967, 1973, 1975), and in oil-field brines in Alberta, Canada (Billings and others, 1969) and central Mississippi (Carpenter and others, 1974). To date, however, ore-grade deposits of base metals have not been encountered in wells drilled into hot, presently active hydrothermal systems in silicic volcanic environments, although ore minerals have been reported in the vapor-dominated system at The Geysers, California (Sternfeld, 1981), in the low to moderately saline hot-water systems in New Zealand (Browne, 1969, 1971), in the highly saline system at the Salton Sea, California (McKibben, 1979), and elsewhere (summarized by Weisberg and others, 1979). This suggests that in our exploration of active hydrothermal systems we have not drilled in the right places, or deep enough, or, perhaps, at the right time to find ore-grade mineralization. Studies of fossil systems have shown that barren stages of hydrothermal activity commonly precede as well as follow ore-forming stages. In assessing the reasons why ore-grade mineralization has not been found, it should be remembered that active systems have been drilled to find hot water, not base and precious metals.

It is of practical importance to gain information about all processes that occur in active systems, and to determine whether some conditions always lead to hydrothermal alteration with ore mineralization and other conditions always lead to alteration without ore deposition; and, if so, how the alteration products differ. That sort of information might decrease the amount of exploration drilling within barren fossil hydrothermal systems, or lead to successful location of ore within a system that at first seemed unpromising. Unfortunately, the alteration products found in the cuttings and core from fruitless exploration drilling in fossil systems are seldom detailed in the literature. However, many studies of hydrothermal alteration products found in active systems have been summarized by Browne (1978). It is not the intent of this presentation to repeat that summary, but rather to focus upon the physical and chemical characteristics of the hydrothermal fluids in active systems and their possible significance in ore-forming processes.

FLUID PRESSURES AND TEMPERATURES IN ACTIVE SYSTEMS

The physical characteristics of many active hydrothermal systems in diverse geologic environments have been determined through exploratory drilling and commercial production of geothermal resources; excellent summaries are presented by Ellis and Mahon (1977), Ellis (1979), and Henley and Ellis (1983). Most geothermal wells drilled for production of

electricity are 1 to 3 km deep. Fluid pressures and temperatures vary widely, depending on the distribution of permeable rocks and their specific permeability, the position of the water table, the source of recharge water, the salinity and gas content of the hydrothermal fluids, and the nature of the heat source. In silicic volcanic environments, reservoir temperatures commonly are in the 230° to 260°C range and temperatures up to about 320°C are not unusual. A temperature of 360° to 370°C was measured in a 2000-m well drilled near Ibusuki, Japan (H. Sakai, oral communication, 1982), and a temperature above 419°C (the melting temperature of zinc) has been reported in a geothermal well near Naples, Italy (A. Ten Dam, written communication, 1982).

Active hydrothermal systems are now generally subdivided into two main categories, hot-water and vapor-dominated (White and others, 1971). In convecting hot-water systems, liquid fills most of the pore spaces and open fractures within the rock (Fig. 1). Although scattered

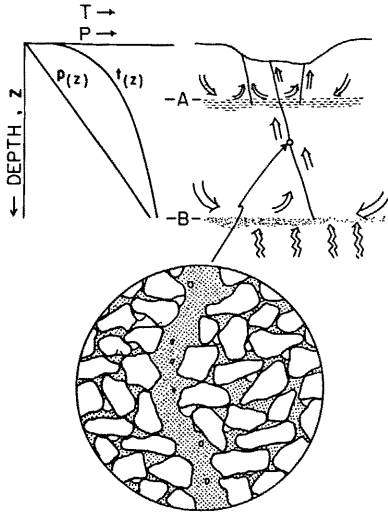


Figure 1. Schematic model of conditions in a hot-water-dominated geothermal system where boiling temperatures prevail through a steeply dipping structure filled with liquid water (from Fournier, 1981).

gas or steam bubbles may be present, liquid water is essentially the continuous phase in fractures leading from depth to the surface, and the maximum temperatures attainable at given depths are given by boiling-point curves that are appropriate for hydrostatic conditions (Figs. 1 and 4). In vapor-dominated systems, liquid water is generally present in pore spaces, but vapor (steam and gas) fills open fractures throughout much of the system (Fig. 2). Temperatures and pressures may change very little within vapor-dominated zones (generally about 240°C and 33.4 bars), and these

systems are underpressured with respect to normal hydrostatic systems through vertical

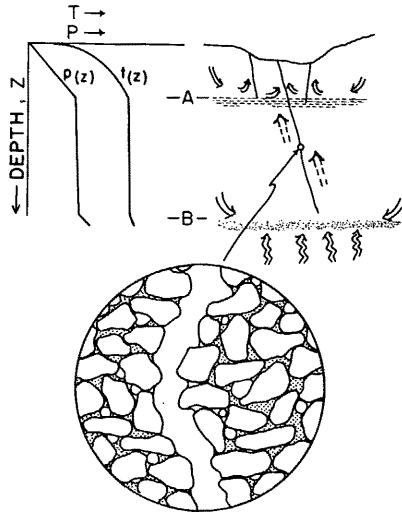


Figure 2. Schematic model of conditions in a vapor-dominated geothermal system (from Fournier, 1981).

distances of hundreds to a few thousands of meters. The existence of a hydrostatically underpressured system requires that a region of relatively low permeability surround the vapor-dominated zone that prevents the free movement of cold ground water into the system.

The buoyant force that drives convection in hot-water systems results from the greater density of relatively cold recharge water compared to hot discharging water; the "thermal-artesian" pressure of Studt (1958). Densities of pure water and aqueous NaCl solutions at the vapor pressures of the solutions are shown as functions of temperature in Fig. 3. White (1968b) constructed theoretical boiling-point curves for hydrostatic pressures controlled by the weight of an overlying column of water everywhere at its boiling temperature and showed that the maximum temperatures measured at given depths in wells drilled at Steamboat Springs, Nevada, closely agreed with that theoretical curve. Haas (1971) constructed similar boiling-point curves for water and aqueous NaCl solutions containing up to 25 weight percent salt (Fig. 4). Where partial pressures of dissolved gases are large, boiling-point curves may be significantly depressed (Sutton and McNabb, 1977; Mahon and others, 1980). A partial pressure of CO₂ of 10 bars should lower the boiling point curve of water by about 150 meters (Fig. 4).

Where maximum underground temperatures (the boiling point curve) are controlled by the weight per unit area of the overlying column of hot water, the hot outflowing part of the system must be relatively more open than the inflowing, recharge part of the system. This appears to be

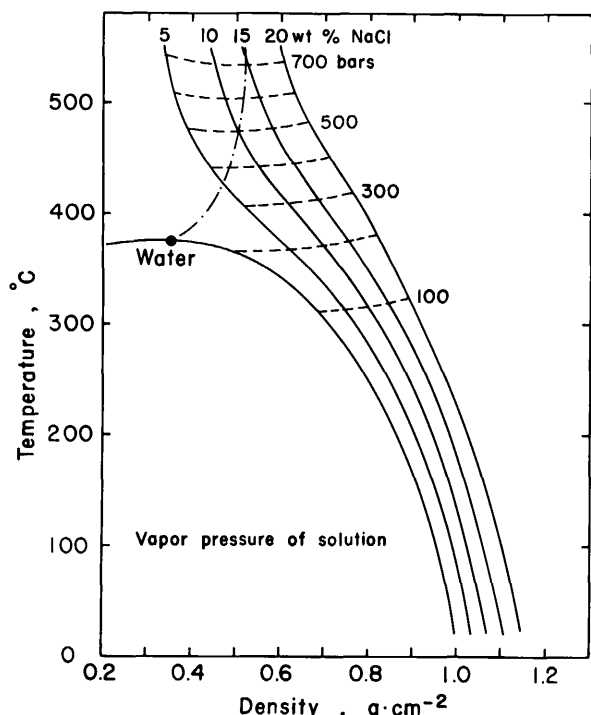


Figure 3. Density-temperature relations in the system NaCl-H₂O at the vapor pressures of the solutions. The dashed lines are isobars. The dot-dashed line is the critical curve. Densities are from an unpublished correlation of literature values by J. Tanger.

the situation in shallow parts of the hot spring system at Steamboat Springs, Nevada (White, 1968b). Where the outflow is restricted by impermeable strata, or by self-sealing resulting from mineral deposition, hydrostatic pressure may be controlled by the weight per unit area of the relatively cold recharge water. In many geyser basins at Yellowstone National Park, White and others (1975) measured fluid pressures in geothermal wells significantly above those that would be expected if the overlying hot water controlled pressure (Fig. 5). Theoretical depth-pressure curves are shown in Fig. 6 for boiling water and various boiling NaCl solutions, with pressure controlled by the weight of the overlying, freely discharging solution (Haas, 1971); for comparison, the depth-pressure curve for a cold column of water also is shown. The pressure exerted by the cold column of pure water is significantly greater at given depths than that exerted by a free-standing column of 20 weight percent aqueous NaCl everywhere at its boiling temperature; therefore, inflow of cold, dilute, meteoric water into the deep part of a hydrothermal system can cause upward convection of highly saline hot fluids, possibly with as much as 25 weight percent dissolved salts.

Boiling-point curves are calculated relative to the position of the water table that controls

hydrostatic pressure. 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 in the East Pacific (Edmond and others, 1979) are below boiling temperature because of their great depth.

Fluid pressures approaching lithostatic have been encountered in deep sedimentary basins (Kharaka and others, 1978). There is reason to believe that mineral deposition and self-sealing in deep parts of hydrothermal systems in other environments, where temperatures higher than about 350°C are attained, might allow the development of fluid pressures much greater than hydrostatic (Fournier, in press).

The consequences of the above generalizations about temperatures and pressures in presently active hydrothermal systems, relative to the deposition of ore minerals, will be discussed in following sections.

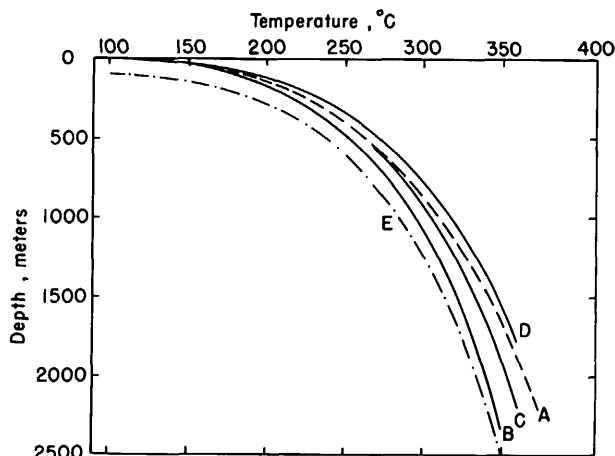


Figure 4. Depth-temperature relations for boiling solutions. Depth-pressure relations for curve A fixed by the weight per unit area of a free-standing column of cold water extending to the surface. Depth-pressure relations for curves B to E fixed by the weight of per unit area of free-standing columns of the given solutions everywhere at their boiling temperatures, and extending to the surface. Curves A and B for pure water, curve C for 10 weight percent aqueous NaCl, curve D for 20 weight percent aqueous NaCl, and curve E for water plus a partial pressure of CO₂ of 10 bars.

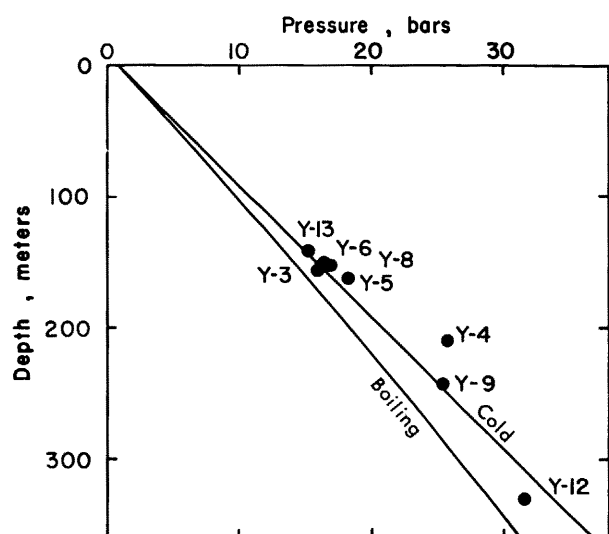


Figure 5. Depth-pressure relations for boiling and cold columns of pure water. Numbered dots show depth-pressure relations at the bottoms of shut-in wells in Yellowstone National Park, measured by White and others (1975).

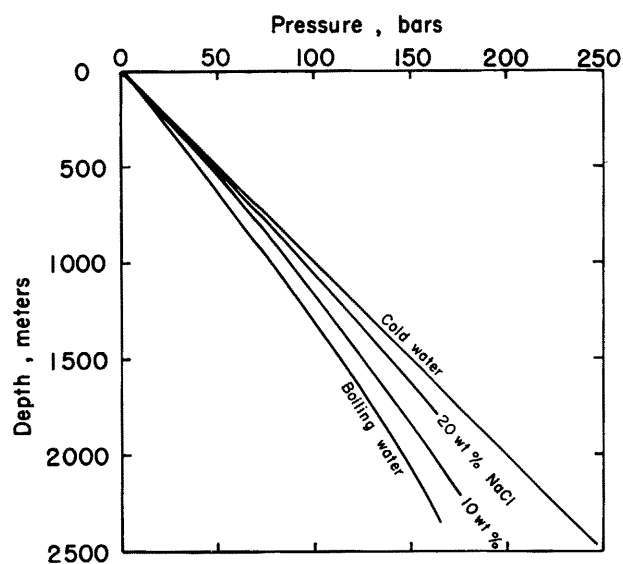


Figure 6. Depth-pressure relations for boiling and cold columns of pure water and boiling aqueous NaCl solutions.

COMPOSITIONS OF FLUIDS IN ACTIVE HYDROTHERMAL SYSTEMS

Fluids in explored parts of presently active hydrothermal systems are dominated by meteoric

or ocean water that has changed composition during underground movement in response to changing temperature, pressure, and rock type, as well as mixing of different waters. Wooding (1963) and Henley and McNabb (1978) emphasized the importance of mixing of cool and hot fluids on the margins of upward moving convection plumes. Meteoric water is identified by isotopic evidence (Craig, 1963; White, 1968a; Truesdell and Hulston, 1980) and ocean water by isotopes, salinity, and ratios of dissolved constituents, such as Cl/Br (White, 1965). Connate and metamorphic waters have been identified by isotopic methods in thermal waters at Wilbur Springs and Sulphur Bank, California, respectively (White and others, 1973). Magmatic water has not yet been recognized in presently active systems, although some water must evolve from magmas as they crystallize. Present isotopic techniques cannot detect less than about 5 percent magmatic water in a hydrothermal fluid. Therefore, the presence of a small proportion of magmatic water and other "magmatic" constituents, such as chloride, sulfur, and metals, in presently active systems cannot be ruled out. According to Ohmoto and Rye (1974), isotopic data show that up to 25 weight percent of magmatic water could have been involved in the formation of Kuroko deposits. Evolving magmatic water might be incorporated or trapped in highly saline brines (>30 weight percent dissolved salt) that form at high temperatures and at moderate depths around crystallizing magmas. Convective circulation of these brines to shallow levels, as part of a hydrothermal system recharged by meteoric water, might not be possible because of their high densities. In order for mixing of dilute and highly saline water to occur at a rate faster than by diffusion, the two fluids should have about the same density or the rising fluid be less dense than the overlying fluid. When cold, dilute water has about the same density as hot brine, mixing might occur by flow of the cold water into the hot brine across a nearly vertical fluid composition boundary. At 300 bars, dilute water at 150°C (point A in Fig. 7) has about the same density as a 20 weight percent NaCl solution at 305°C (point B). It is possible that very saline brines, possibly containing significant proportions of magmatic water, will be encountered when geothermal wells are drilled to greater depths and higher temperatures (McNabb, 1975; Truesdell and Fournier, 1976; Griffiths, 1978).

From a comparison of the C/S ratios of volcanic and geothermal gases, Giggenbach (1977) estimated that only about 5 percent of the sulfur entering geothermal systems from magmatic sources reaches the relatively shallow level of present exploitation; the rest is fixed as sulfides in the deeper, hotter zones. This implies that we have not drilled deep enough in presently active hydrothermal systems to find commercial-grade base-metal sulfide deposits.

Changing temperature has a major effect upon the ratios of cations in solution and the

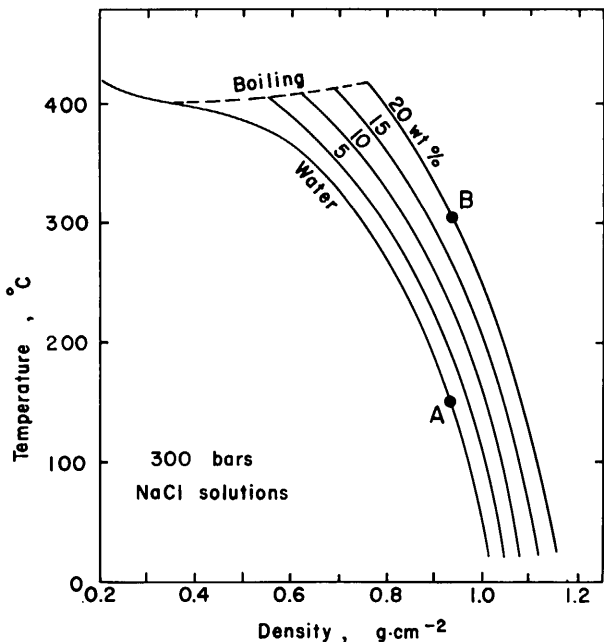


Figure 7. Density-temperature relations in the system NaCl-H₂O at 300 bars pressure. Densities are from an unpublished correlation of literature values by J. Tanger.

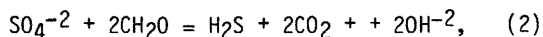
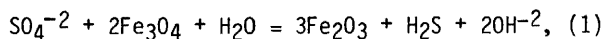
concentration of dissolved silica. The effects of pressure are more variable. For non-carbonate minerals, changing pressure at constant temperature generally has little effect on solubilities when temperatures are below about 250°C, and great effect at higher temperatures. At 400°C the solubility of quartz in water is about 1000 mg/kg at 400 bars, 500 at 300 bars, and only 50 at 100 bars (Fournier and Potter, 1982). Changing pressure is an important factor wherever decompressional boiling occurs because of evaporative concentration and partitioning of volatile components between water and steam. Where boiling takes place deep underground, volatile components, such as CO₂ and H₂S, preferentially partition into the steam phase and move with it to the upper and marginal parts of hydrothermal systems, where steam condenses. There, some CO₂ and H₂S will dissolve in cooler ground water (Ōki and Hirano, 1970; White and others, 1971; Kartokusumo and others, 1976; Mahon and others, 1980). These ground waters generally contain less chloride than do waters in the main part of the hydrothermal system because they are shallow and locally derived, or are mixtures of shallow and deeper waters. The redissolved CO₂ forms carbonic acid and attacks the wall rocks, resulting in calcium bicarbonate-rich solutions at low temperatures or sodium bicarbonate-rich solutions at temperatures above about 140°C. Calcium bicarbonate concentrations decrease at higher temperatures because of the decreasing

solubility of calcite as temperature is increased. H₂S is oxidized to H₂SO₄ in an oxygen-rich shallow environment. Therefore, the tops and margins of boiling systems become enriched in sulfate as well as bicarbonate. Where the buffer capacity of the rock is exceeded, the continued oxidation of H₂S may result in pH values less than 4 and the disappearance of bicarbonate. Thus, acid-sulfate alteration is commonly observed above boiling water tables in presently active hot-spring systems. The silicification that accompanies this acid attack is not due to influx of silica, but to strong leaching of alkalis that are flushed from the rock by condensed steam and meteoric water that percolate down to the water table.

Variations in rock type strongly influence the total salinity and particularly the chloride concentration that a hydrothermal solution is likely to attain. Geothermal waters in basaltic rocks in the interior of Iceland generally contain very low concentrations of chloride (Arnorsson and others, 1983). In contrast, geothermal waters in basalts near the seashore generally have chloride concentrations about the same as seawater. I found that geothermal waters in granites and highly metamorphosed rocks well inland from the ocean also generally contain very low concentrations of chloride. Bicarbonate is commonly the main anion in these low-chloride waters, although major amounts of sulfate may also be present. Bicarbonate concentrations are proportional to the partial pressure of CO₂. Dissolved CO₂ forms carbonic acid that reacts with the wall rock, liberating Na⁺ at high temperatures and Ca²⁺ at low temperatures, as discussed above. Geothermal waters in silicic volcanic rocks (andesites to rhyolites) commonly contain a few hundred to a few thousand mg/kg chloride (Truesdell, 1976; Ellis and Mahon, 1977), even in interior regions of Iceland (Arnorsson and others, 1983). The highest chloride concentrations are found in geothermal waters that have come in contact with sedimentary rock; particularly those containing evaporites. At Cesano, Italy, a hot (>200°C) brine, rich in sodium sulfate with over 350,000 mg/kg total dissolved solids, was encountered in a 1435-m geothermal well (Calamai and others, 1976). Evidently, magma or very hot water reacted with gypsum that is known to be present in the underlying sedimentary section at Cesano, probably producing calcium silicates and a solution rich in sulfate. The conclusion seems inescapable that the compositions of waters in the relatively shallow parts of presently active hydrothermal systems are controlled mainly by leaching of the wall rocks by meteoric water. Experimental data also support this conclusion (Ellis and Mahon, 1964, 1967; Mahon, 1967; Kissen and Pakhomov, 1967; Ellis, 1968; Ewers, 1977).

High concentrations of dissolved metals can be obtained by reaction of chloride-rich brines with surrounding rocks (Barnes and Czamanske,

1967; Helgeson, 1967, 1968; Ellis, 1968; Carpenter and others, 1974; Bischoff and Dickson, 1975; Hajash, 1975; Seyfried and Bischoff, 1977; Hanor, 1979). However, in order for an ore deposit to form, those metals must precipitate within a relatively restricted volume of rock. Base-metal ore deposits require sulfide for their formation. Iron sulfides originally present in country rock can be transformed to Cu, Zn, and Pb sulfides through reaction with sulfide-deficient, metal-bearing brines; but the formation of large sulfide vein deposits is difficult to explain by this mechanism. Sulfides can be leached from rocks by saline solutions (Mottl and others, 1979), but it is questionable whether large enough quantities can be obtained this way to explain most observed ore deposits. A plausible mechanism for generating dissolved sulfide involves leaching of sulfate and later reduction of that sulfate by bacterial activity, ferrous iron (Mottl and others, 1979) or buried organic material. It has generally been assumed that reduction by bacteria activity could occur only at temperatures below 100°C. New data showing bacterial growth at temperatures of at least 250°C at high fluid pressure (Baross and Deming, 1983) suggest that reduction by bacteria activity might take place at high temperatures deep in hydrothermal systems. This has great implications for the interpretation of gas ratios and isotopic fractionation patterns of C, O, S, and H. Reduction of sulfate to sulfide should produce an alkaline solution,



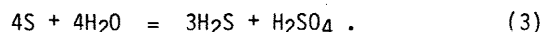
while alteration associated with sulfide mineralization usually indicates acid conditions. Deposition of calcite and albitization (as a solution is heated) or K-feldspathization (as a solution is cooled) could be a consequence of reduction of sulfate to sulfide. However, a volcanic or magmatic source of sulfide would appear to be a very favorable circumstance for precipitation of base-metal ores.

Most waters in presently active hydrothermal systems are neutral or only slightly acid because pH is controlled by silicate hydrolysis reactions involving feldspars and micas or clays (Hemley and Jones, 1964; Meyer and Hemley, 1967; Ellis, 1970, 1979; Ellis and Mahon, 1977). Yet, as mentioned above, acid alteration commonly accompanies the formation of hydrothermal ores. Until very recently, drilling for production of geothermal energy in active hydrothermal systems had encountered extremely acid conditions at depth at only a few localities in zones of active volcanism, such as Matsao in Taiwan (Chen, 1970, 1975) and Onikobe (Yamada, 1976) and Matsukawa (Nakamura and others, 1970) in Japan. It now appears that there is deep, acid-chloride thermal water

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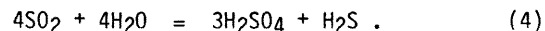
and/or deep acid alteration (pyrophyllite plus quartz) in many active hydrothermal systems associated with active or relatively young andesitic volcanism. These include Biliran (Lawless and Gonzales, 1982), Nasuji-Sogonon (Seastres, 1982), Palimpinon (Leach and Bogie, 1982), and Baslay-Dauin (Harper and Arevalo, 1982) in the Philippines, and Suretimeat (Heming and others, 1982) in the New Hebrides. In these systems it is likely that much of the acidity comes from reactions with volcanic gases, including SO_2 , H_2S , and HCl .

At Matsao and Onikobe, acid-chloride waters with pH values less than 2 were found at depths greater than 1000 meters at temperatures exceeding 275°C. The reservoir at Matsao is in quartzite, and at Onikobe it is in andesite altered to pyrophyllite and quartz. Waters collected at intermediate depths, and alteration products found in cuttings from wells, show that these deep, acidic waters are neutralized by mixing with shallow ground water and by reaction with overlying volcanic rocks as they rise toward the surface. Therefore, the acidity does not appear to be the result of downward movement of waters that had become acid by surface oxidation. Ellis (1977) attributed the deep acidity at Matsao to the reaction of water with deeply buried native sulfur deposits, producing sulfuric acid and hydrogen sulfide,



However, as mentioned above, some or all of the acidity could result from interaction of water with gases evolved from a crystallizing magma at depth, or from hydrolysis reactions between salt and water that occur at high temperatures and low pressures.

Iwasaki and Ozawa (1960) and Saki and Matsubaya (1977) present evidence for the generation of acidity by the reaction,



Relatively oxidized, sulfur-rich gases also may be evolved where gypsum or anhydrite are involved in hydrolysis reactions. For example, the 1982 eruption of El Chichon Volcano in Mexico contributed far more sulfuric acid to the atmosphere and stratosphere than is usual for comparably sized eruptions of other volcanoes, such as Mount St. Helens (B. Toon, oral communication, 1982). Gypsum beds occur in the sedimentary section beneath El Chichon, but are not present beneath Mount St. Helens. The isotopic composition of sulfur should be different in sulfate derived from gypsum compared to sulfate derived from volcanic SO_2 .

The importance of HCl as a cause of acidity in hydrothermal systems should not be overlooked. Over 7000 mg/kg Cl as HCl was found in dry steam coming from a shallow well drilled at Hakone volcano in Japan (Kimio Noguchi, oral communication, 1970). Some or all of that HCl

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may have been generated by hydrolysis of NaCl at moderate to high temperatures and low pressures:



Many investigators have found HCl in condensate after circulating dry steam over solid NaCl (Briner and Roth, 1948; Martynova and Samoilov, 1957; Galobardes and others, 1981). In experiments at 600°C I have found that significant amounts of HCl are generated by reaction 5 at pressures below about 350 bars, with more HCl produced at lower pressures. Addition of quartz to the system greatly increases the yield of HCl. This occurs because NaOH is removed from the solution by reaction with quartz, with precipitated sodium silicates as products. Solubilities of sodium silicates decrease with increasing temperature (Rowe and others, 1967). In natural systems, where aluminum is available in plagioclase and other minerals, albitization is likely to result from the hydrolysis of NaCl.

In some places acidity deep within a hydrothermal system does appear to result from downward movement of water that has become acid by oxidation of H₂S at and near the water table, as discussed previously. To the southeast of the Norris Geyser Basin in Yellowstone National Park, acid-sulfate waters are generated high on a hillside where the rocks have been extensively altered by fumarolic activity. Some of that acid water appears to percolate hundreds of meters underground where it mixes with high-temperature (~270°C) neutral water that is rich in chloride. The resulting "acid-chloride-sulfate" waters that issue as hot springs and geysers in Norris Geyser Basin have been extensively analyzed (Gooch and Whitfield, 1888; Allen and Day, 1935; Rowe and others, 1973), and exhibit widely ranging chloride and sulfate concentrations. However, the compositions of some individual "mixed-water" springs, such as Echinus, have remained remarkably constant since they were first analyzed in the late 1880's.

Truesdell (1976), Ellis and Mahon (1977), Ellis (1979) and Henley and Ellis (1983) summarize information about compositions of geothermal waters, and provide comprehensive reference lists.

MODELS OF HYDROTHERMAL SYSTEMS IN SHALLOW MAGMATIC ENVIRONMENTS

White (1973) published a schematic model of a convecting hydrothermal system within what appears to be a volcanic caldera (Fig. 8). That model shows an end-member situation in which the total convective flow is discharged at the surface; White (1973) described several other subtypes of hot-water systems, including ones with little or no surface discharge. In many hydrothermal systems it is likely that some or all of the fluid, after becoming cooled near the surface, recycles back downward in large convection cells, as shown in computer

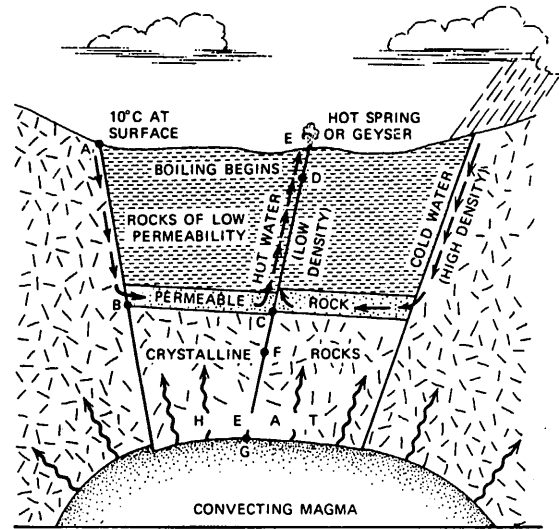


Figure 8. Schematic model of convective flow in a hydrothermal system showing effect of variations in permeability of the region on the flow, and with surface discharge of the total flow (from White, 1973).

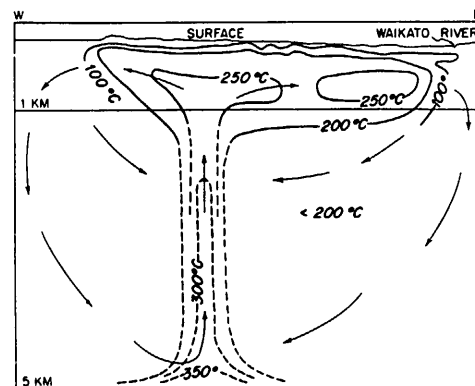


Figure 9. Cross section through the geothermal system at Wairakei, New Zealand (from Elder, 1965). The solid lines show isotherms derived by projecting measured temperatures onto the section, and dashed lines show estimated isotherms to a depth of 5 km. The approximate flow lines of meteoric water are shown by arrows.

simulations (Cathles, 1977; Norton and Cathles, 1979). Figure 9 is a cross section showing temperatures measured in wells at Wairakei, New Zealand. Note the mushroom shape of the thermal anomaly, indicating a lateral movement of hot water at shallow levels toward the

topographically low Waikato River, and a postulated counter-flow of colder water beneath it. Ellis and Wilson (1955) calculated the natural discharge of chloride and heat from the Wairakei system into the Waikato River at 460 g Cl/sec and 82,000 kcal/sec. Using their data, the calculated natural discharge of thermal water and steam was 228 kg/sec. These figures do not include discharges from geothermal wells that were produced at the same time: 340 g Cl/sec, 62,000 kcal/sec, and 169 kg water/sec. For comparison, the calculated natural discharges at Yellowstone National Park are 1,319 g Cl/sec, 1,213,000 kcal/sec, and 3,200 kg water/sec (Fournier and others, 1976).

Lateral flow of thermal water appears to occur in many systems (Healy and Hochstein, 1973; Healy, 1976). The geothermal system at El Tatio, Chile (Fig. 10) is an excellent example

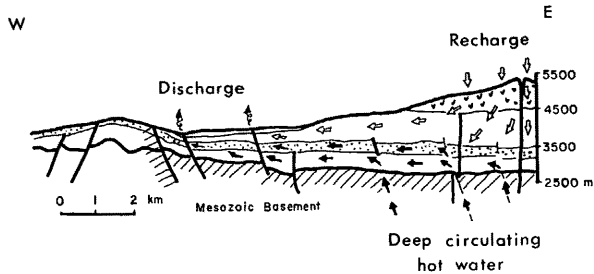


Figure 10. East-west cross section showing movement of geothermal fluids in the El Tatio system (from Lahsen and Trujillo, 1976).

of one with major lateral flow (Lahsen and Trujillo, 1976; Ellis and Mahon, 1977). Based on isotopic data, recharge for the El Tatio geothermal field comes from the high Andes Mountains at least 10 km to the east. The heat source probably also lies beneath volcanoes to the east. Hot water produced from geothermal wells at El Tatio is drawn from a reservoir at 260–265°C. The water in the reservoir contains about 5,000 mg/kg chloride and measurable tritium. In one deep well, a brine saturated with salt and at a lower temperature (180–200°C) was found underlying the high-temperature reservoir (Ellis and Mahon, 1977; W. A. J. Mahon, oral communication, 1982). From the above observations, it appears that little or none of the hot (5,600 mg/kg chloride) water flowing from east to west is recycled back into the system.

In many active hydrothermal systems that are associated with andesitic volcanoes, there appears to be underground flow of chloride-rich water laterally away from the volcanic edifice while gases rise more directly upward to the surface (Oki and Hirano, 1970; Heming and others, 1982; Harper and Arevalo, 1982; Muffler and others, 1982; Henley and Ellis, 1983).

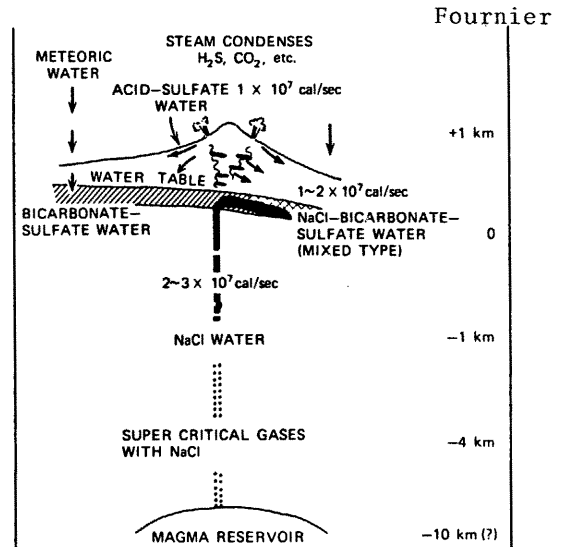


Figure 11. Schematic model for the geochemical development of fluids in the Hakone geothermal system (from Oki and Hirano, 1970).

Figures 11 and 12 show conceptual models of volcanic hydrothermal systems at Hakone, Japan (Oki and Hirano, 1970), and Lassen, California (Muffler and others, 1982), respectively. In Fig. 11 upward flow of hot and supercritical gas is shown above (and presumably from) a magma reservoir, and acidic fumaroles and springs emerge high on the slopes of the volcano. Acid-sulfate and bicarbonate-rich waters form in condensate zones and percolate downward and outward, mixing with deeper chloride-rich waters, as discussed previously. Henley and McNabb (1978) and Henley and Ellis (1983) showed how these models might be related to ore deposition. Beneath Lassen volcano, Muffler and others (1982) showed a relatively shallow vapor-dominated reservoir, underlain by 240°C water that is rich in chloride (Fig. 12). There, gases feeding the fumaroles and acid-sulfate springs on the summit and slopes of the volcano are thought to have been dissolved in upflowing chloride-rich (~2,300 mg/kg) water that boils at about 240°C. White and others (1971) suggested that mercury deposits may form above vapor-dominated systems and porphyry copper mineralization may occur in the zone of boiling brine below the vapor-dominated systems.

Many important variables govern the character and evolution of hydrothermal systems, and the time and place of ore deposition. These include the initial water, chloride, metal, and sulfur contents and oxidation state of the magma, the depth, size, shape and composition of the magma, the degree of "conditioning" of the overlying rocks by previous intrusions and extrusions that heated, fractured and altered those rocks, the position of the water table, the magnitude and distribution of porosity throughout the system, the pore pressures that are attained, and the compositions of the surrounding rocks. The evolution of water from

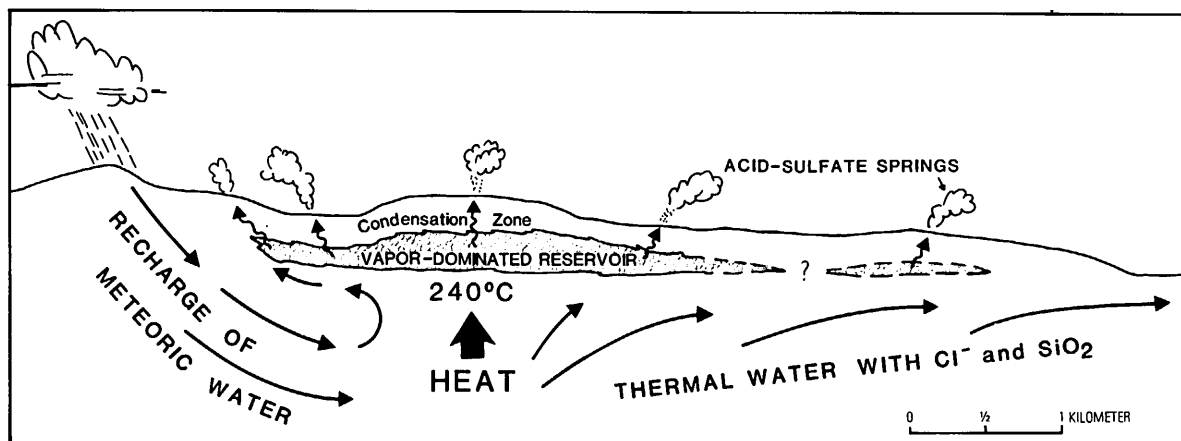


Figure 12. Schematic cross section of the Lassen geothermal system (from Muffler and others, 1982).

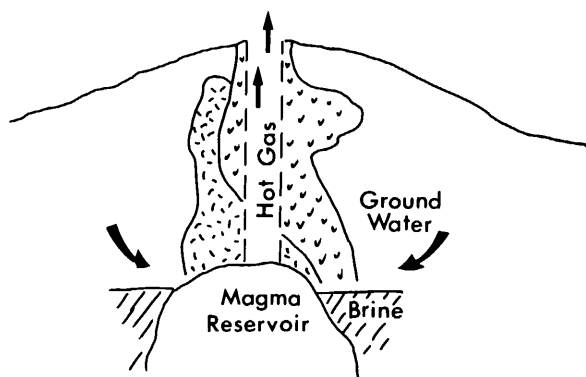


Figure 13. Schematic cross section of a volcanic system venting gas to the surface from a magma reservoir at moderate depth. See text for discussion.

magmas has been discussed by many authors, including Morey (1922), Goranson (1931), Bowen (1933), Burnham (1967, 1979), Fournier (1968), and Whitney (1975), and the generation of chloride-rich gases and brines has been discussed by Sourirajan and Kennedy (1962), Ryabchikov and Hamilton (1971), Fournier (1972), Holland (1972), Kilinc and Burnham (1972), Carmichael and others (1973), Cunningham (1978), Henley and McNabb (1978), Burnham (1979), and Cloke and Kesler (1979).

Figure 13 shows a schematic cross section illustrating a situation in which very hot (500°–800°C) volcanic gases vent directly to the surface. Such gases usually are rich in H₂O, SO₂, H₂S, CO₂, and HCl, and may carry significant quantities of metals (Fenner, 1933; White and Waring, 1963; Menyailov and Nikitina, 1974; Tkachenko and Zotov, 1974; Gerlach and Nordlie, 1975; Graeber and others, 1982). Usually the parent magmas are visible, or thought to be very close to the surface within

the volcanic edifice. Gases evolved from magmas a few to several kilometers deep are likely to cool appreciably by conduction, adiabatic expansion, and condensation of water as they rise. However, conductive cooling of upward streaming gas might not be significant where prior eruptions and intrusions of magma within the conduit zone have heated the surrounding rock to high temperatures. The heat stored in the surrounding rock could provide extra energy to the rising gas, counteracting cooling by adiabatic expansion. Volcanic necks and dikes which are still hot, but solidified and thoroughly cracked by shrinkage during solidification and cooling, would make excellent conduits to bring very hot gases to the surface from considerable depth.

From the bottom to the top of the conduit leading from the magma to the surface there may be steady or abrupt decreases in pressure. Decreasing pressure greatly decreases the ability of a water-rich gas to transport dissolved substances, such as silica and salts, as shown in Figs. 14–16. It is likely that precious metals, sulfides, and other minerals also would precipitate as a result of decreasing pressure and expansion of a gas, particularly where throttling occurs (Barton and others, 1961; Toulmin and Clark, 1967). Therefore, venting of magmatic gases (and of non-magmatic water and other volatiles heated to near magmatic temperatures) directly to the surface, as depicted in Fig. 13, is likely to be relatively short-lived, particularly where the magma is more than 1 or 2 km deep. Mineral deposition, either high in the system or very close to the magma could terminate this venting.

An estimate of the ability of hot, water-rich gases to transport dissolved salt can be obtained from the experimental results of Sourirajan and Kennedy (1962) in the system H₂O–NaCl. Figure 15 shows compositions of coexisting gas plus solid salt and gas plus brine at 700°C and at various depths, with

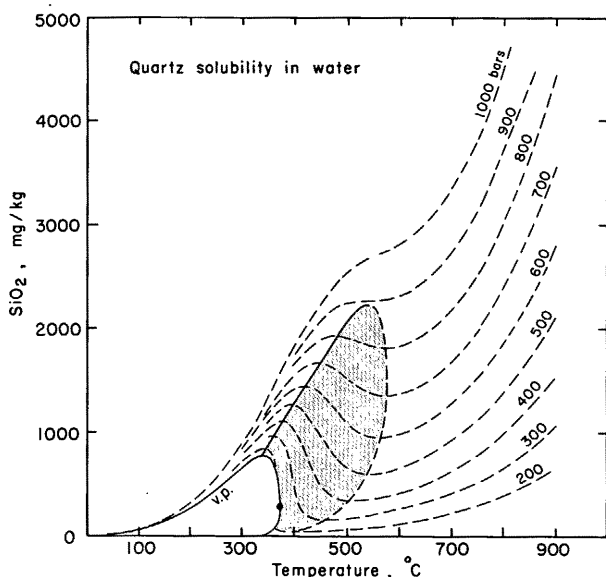


Figure 14. Solubilities of quartz in water up to 900°C at the indicated pressures, calculated using the equation of Fournier and Potter (1982). The shaded area emphasizes a region of retrograde solubility.

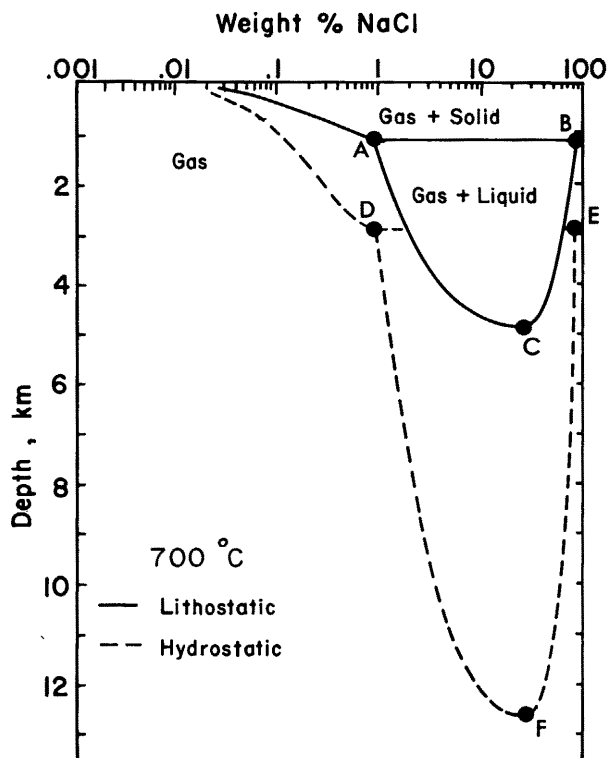


Figure 15. Compositions within the system NaCl-H₂O of coexisting gas plus solid salt and gas plus brine at 700°C and at various depths, with results for lithostatic fluid pressures contrasted with hydrostatic pressures (assuming hydrostatic pressure controlled by a cold column of dilute water).

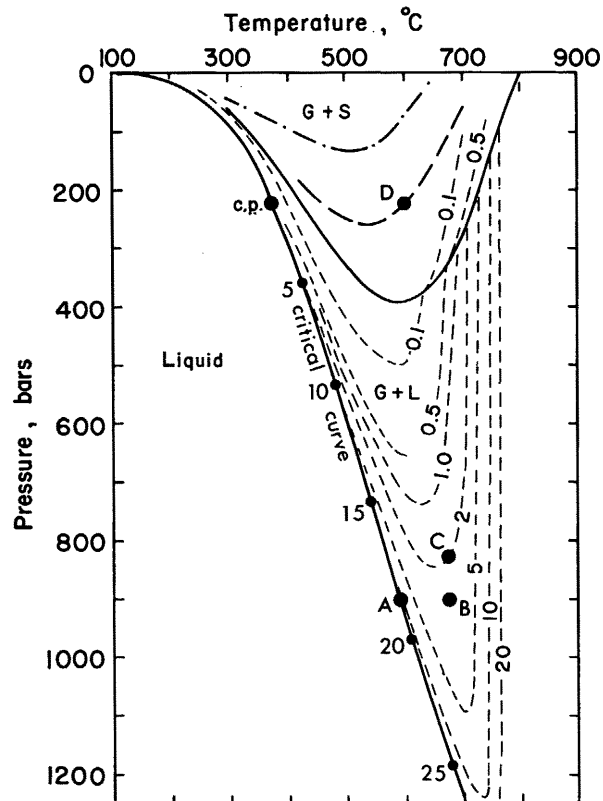


Figure 16. Some phase relations in the systems NaCl-H₂O and NaCl-KCl-H₂O projected onto a pressure-temperature diagram. The solid lines outline phase boundaries in the system NaCl-H₂O and short dashed lines show isopleths of NaCl solubility in steam. See text for discussion.

results for lithostatic fluid pressures contrasted with hydrostatic pressures (assuming hydrostatic pressure controlled by a cold column of dilute water). It is assumed in Fig. 15 that the partial pressure of water is equal to the total pressure. At 700°C a true NaCl brine may not exist at a pressure less than about 287 bars. Adding other salts to the system, such as KCl and CaCl₂, will allow brine to exist at significantly lower pressures, and will slightly increase the total amount of salt that can dissolve in the gas. Gas (steam) will dissolve increasing amounts of salt as pressure is increased (going to greater depths) from near atmospheric to about 287 bars. At a depth where 287 bars fluid pressure is reached, the solid salt will melt and that melt will dissolve a small amount of water, point B for lithostatic fluid pressures and point E for hydrostatic pressures. This melt may be called a brine, but this terminology can lead to confusion because at high temperatures and high pressures the gas phase too may dissolve enough salt to be called a brine. Liquid B would be in equilibrium with

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gas at point A and liquid E with gas at point D. With further increase in pressure at greater depths, the gas can dissolve more salt and the coexisting liquid will dissolve more water (become more dilute) until the critical pressure is attained, point C for lithostatic fluid pressures and point F for hydrostatic pressures. Composition–depth diagrams at other temperatures would look similar to Fig. 15. Solubilities of salt in the gas phase and critical pressures both decrease with decreasing temperature, and the pressure of the gas plus solid field reaches a maximum at about 600°C.

In Fig. 16 the gas-plus-solid and gas-plus-liquid fields are projected onto a temperature–pressure diagram. Figure 16 was drawn with the pressure coordinate increasing downward to emphasize changing conditions with depth. A depth scale is not given in Fig. 16 because factors other than depth may influence fluid pressure. Fluid pressures may range from less than hydrostatic to greater than lithostatic at the same place at different times. A portrayal of more than one of the many plausible depth–temperature conditions in one diagram would result in a confusing jumble of lines. In Fig. 16 the boiling–point curve for pure water is shown, ending at the critical point, c.p., and a critical curve for increasing NaCl concentrations extends downward from that point. Boiling–point curves appropriate for increasing salinities would be displaced slightly to the right of the pure water curve and terminate at appropriate points on the critical curve. Termination points for 5, 10, 15, 20, and 25 weight percent NaCl are indicated. For a solution of given salinity, critical conditions can exist at only one temperature and pressure, such as point A in Fig. 16. To the left of the critical curve, and at pressures greater than the critical pressure, solutions are supercritical; but the fluids act more like liquids than gases in their ability to dissolve minerals, such as quartz. To the right of the critical curve is a field of liquid plus gas. The short dashed lines show isopleths of NaCl solubility in a gas phase that is in equilibrium with a liquid of specific composition (not shown), or solid salt (see Sourirajan and Kennedy (1962) for compositions of coexisting gas and liquid, and Fig. 15 for relations at 700°C). The critical point for an aqueous solution containing 2 weight percent NaCl is close to 395°C and 275 bars. A fluid containing 2 weight percent NaCl at 700°C and 900 bars (point B in Fig. 16) might be called a supercritical gas by many people. From a different point of view, however, that fluid is a gas that is unsaturated with salt. Decreasing the pressure to below 825 bars (point C) would cause the gas to become supersaturated, and it would separate into brine plus gas containing less dissolved NaCl, as discussed by Henley and McNabb (1978). Decreasing the temperature of a 2 weight percent NaCl solution from point B (675°C) to less than 595°C (point A) would cause the solution to become supercritical in the strict sense, until the temperature fell below

395°C. Note in Fig. 16 that at temperatures above about 700°C very high concentrations of dissolved salt may exist in the gas phase, but this gas could be in equilibrium with a much more concentrated brine.

At moderate to low pressures a field of gas plus solid salt is encountered, in which brine is unstable, and the gas phase can dissolve little "non-volatile" material, such as silica and NaCl. Adding KCl to the system contracts the gas-plus-solid field to lower pressures (Ravich and Borovia, 1949). The heavy dashed line (Fig. 16) shows the approximate limit of the gas-plus-solid salt field when NaCl/KCl ratios in the fluids are fixed by base exchange of Na and K between coexisting albite and K-feldspar (Orville, 1963; Fournier, 1976). The dot-dashed curve outlines the gas-plus-solid field when NaCl/KCl ratios in the fluids are given by ternary eutectic conditions in the system NaCl-KCl-H₂O (Ravich and Borovia, 1949), more potassic conditions than are likely to be found in most hydrothermal solutions. At 600°C and 220 bars two alkali feldspars can coexist with liquid plus gas of appropriate Na/K composition (point D in Fig. 16). Because the compositions of most natural waters are rich in NaCl compared to KCl, a decrease in pressure would cause NaCl to precipitate preferentially, and the liquid to become richer in potassium (Fournier, 1976; Cloke and Kesler, 1979). This increase in potassium in the liquid would promote base exchange, resulting in the conversion of albite to K-feldspar (or muscovite) until all the albite was used up. Thereafter, with continued decrease in pressure the liquid and feldspar would become more potassic as NaCl continued to precipitate (Fournier, 1976). This mechanism may account for much of the high-temperature potassic alteration found in porphyry-copper and porphyry-molybdenum deposits.

Where magmas are more than 1 or 2 km deep, or where a conduit has cooled appreciably before the current magmatic event, condensation of ascending high-temperature, water-rich gas is likely to occur within the vent. Acids carried in the gas at high temperatures are mainly associated complexes. Where condensation occurs, these acids will dissolve in the liquid, dissociate with decreasing temperature, and cause acid alteration of the surrounding rock. A neutral, chloride-rich solution, of moderate salinity and dominated by meteoric water, is likely to evolve above and at the sides of the acid-altered rock and hot gas region. This is essentially the model of Oki and Hirano (1970), depicted in Fig. 11. In that figure a highly saline brine might be shown accumulating at the sides of the magma reservoir. Also, a small vapor-dominated system, similar to the one postulated at Lassen Volcano by Muffler and others (1982), could be incorporated into Fig. 11.

Figure 17 shows a schematic section through a hydrothermal system in which a self-sealed

envelope has developed in the country rock close to a magmatic intrusion. In some systems the self-sealed envelope might be totally within the chilled part of the intrusive body. Fluid at about lithostatic pressure fills the fractures between the impermeable barrier and the magma. This fluid is likely to be highly saline liquid (>50 weight percent salt), but, depending on the temperature, pressure, origin, and prior history of the fluid, it could be a gas of moderate to low salinity, or a brine capped by a gas. At a depth between 4 and 5 km the confined fluid pressure resulting from lithostatic load could approach 1000 bars, and a gas at 650°C could contain over 5 weight percent dissolved salt.

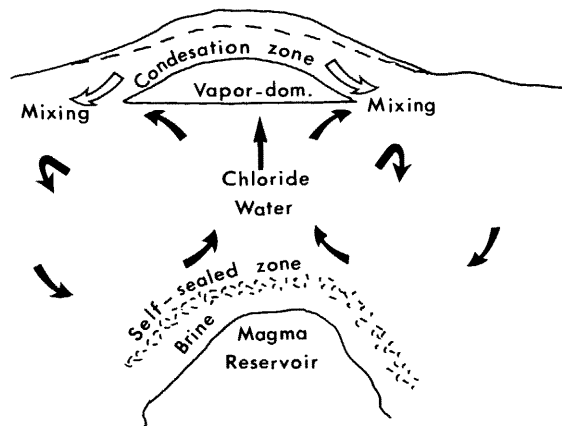


Figure 17. Schematic cross section of a hydrothermal system with a self-sealed envelope separating geopressured fluid from a hydrostatically pressured convecting fluid. See text for discussion.

A hydrostatically pressured hydrothermal system of low to moderate salinity, dominated by meteoric water, circulates at the sides and above the self-sealed envelope. The maximum temperature attained within this "meteoric" system is likely to be about 350° to 450°C (Fournier, 1977; in press). Both pressure and temperature gradients across the self-sealed zone of rock are likely to be large, and a small amount of brine and gas may leak at slow rates into the hydrostatic system. Deposition of sulfides is likely to occur where hot brine and cooler dilute water mix.

In the volcanic systems discussed above, magma reservoirs were shown directly beneath volcanoes, and hydrothermal activity of greatest intensity was located above the tops of the magma chambers. However, conduits from deep magma chambers to volcanoes may be inclined. They may also tap elongate bodies of magma, rather than the spherical bodies that are commonly shown. Movement of water at great depth is likely to be controlled mostly by

faults and joints, and hydrothermal systems may develop by deep circulation at the sides of a magmatic bodies, rather than above the tops. In the silicic caldera system at Yellowstone National Park, centers of hydrothermal activity are concentrated along the caldera ring fracture, at intersections of faults resulting from resurgent doming, and along radial faults extending away from the caldera.

Evidence of hydrothermal conditions that change with time has been found in several active systems. On the basis of observed self-sealing, chemical balance, and isotopic evidence, Ellis (1979) concluded that brief periods (of the order of 10^3 years) of major flow of hot water from active systems commonly alternate with long periods (10^4 – 10^5 years) of conductive water heating and minor outflow. Ellis (1979) also concluded that periods of major flow may be triggered by tectonic activity or by hydrothermal explosions. Fluid-inclusion data show that there have been major changes in temperature–depth profiles within the Kirishima geothermal field in southern Kyushu, Japan (Hayashi and others, 1981), and at Yellowstone National Park (K. E. Bargar, oral communication, 1983). The changes in temperature at both localities can be correlated with changing water tables. At The Geysers, California, fluid inclusion data and the high-temperature character of the coexisting mineral assemblage indicate that the present vapor-dominated system (240°C) has evolved from an earlier and hotter (350°C) hot-water system (Sternfeld, 1981; McLaughlin et al., 1983).

BOILING AND BRECCIATION

Enthalpy–chloride relations found in different parts of presently active hydrothermal systems (Fournier, 1979) show that boiling occurs deep in these systems as well as near the surface. Boiling will change the composition of a hydrothermal fluid by increasing the concentrations of dissolved constituents that remain in the residual liquid and by removing dissolved gases that strongly partition into the steam phase (Ellis, 1967). This partitioning of volatiles, in turn, may significantly change the pH of the system. All these factors are likely to contribute to the deposition of ore minerals.

Where ascending hot water (>100°C) flows too rapidly to be cooled entirely by conduction, the water heats the surrounding rock to temperatures appropriate for boiling at the prevailing hydrostatic pressure (the boiling-point curve). With steady rates of fluid flow, the deposition of minerals from solutions that are cooled adiabatically is likely to be chemically and physically uniform (without banding). Locally intermittent geyser activity may temporarily disrupt the steady-state temperature, pressure, and chemical composition of the water, causing deposition of compositionally banded minerals as conditions oscillate from "normal" to "geyser".

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Possibly more important but less widely recognized periodic boiling may result from seasonal changes in the water table. Where ascending hot water has heated the adjacent rock to a boiling-point curve appropriate for a high water table, a rapid drop in the water table will result in lower hydrostatic pressure at given depths throughout the system. Consequently, heat stored in the rock will cause vigorous and widespread boiling until the system boils dry or until rock and water temperatures decrease enough to correspond to a new boiling-point curve appropriate for the lower water table. Similarly, intermittent boiling might also occur within hot-spring systems that discharge into lakes or shallow oceanic environments, triggered by sudden changes in lake level (Muffler and others, 1971), or unusually low tides. In some convection systems, self-sealing at the outflow causes hydrostatic pressure to increase to the weight of the cold column of recharge water, as discussed previously. Intermittent seismic activity or hydraulic fracturing, induced by local excess gas pressure or heating of confined fluids, may break the sealed cap. This may allow hot water to flow freely with a drop in pressure throughout the hot-water column until mineral deposition reseals the outflow conduit, or the water supply is exhausted. This process may operate at time intervals from months to thousands of years.

Self-sealing within shallow, outflow channels of hydrothermal systems, followed by increased temperatures and pressures, and subsequently by sudden rupturing of the seal with explosive force, has been evoked as a mechanism to explain hydrothermal brecciation in many presently active systems (Lloyd, 1959, 1972, 1976; Skinner, 1966; Muffler and others, 1971; Grindley and Brown, 1976; Henley and McNabb, 1978; Keith and Muffler, 1978; Ellis, 1979; Henley and Thornley, 1979; Nairn and Wiradiradja, 1980). At Yellowstone National Park Muffler and others (1971) attributed the formation of hydrothermal eruption craters up to 0.6 km in diameter to decreased hydrostatic pressures resulting from sudden draining of glacial lakes.

Self-sealing may also occur deep in a hydrothermal system. Figure 14 shows that at constant pressure and increasing temperature, quartz has a solubility maximum (first reported by Kennedy, 1950) that extends from about 340°C at the vapor pressure of solution to 520°C close to 900 bars. The stippled area in Figure 14 shows a region of retrograde solubility in P-T space. Where water is heated at constant pressure less than about 900 bars, it will dissolve silica until either the solution starts to boil (at pressures below about 165 bars) or the solubility maximum is reached. With further heating that water will precipitate quartz. The precipitation of quartz in deep parts of a hydrothermal system may decrease the permeability to such an extent that convecting meteoric water can no longer attain temperatures much greater than

those shown by the quartz solubility maximum in Figure 14. Therefore, the time interval over which meteoric water may interact directly with a shallow intruded body of magma (or very hot solidified magma) may be limited to the early stage of development of the hydrothermal system, or may occur episodically thereafter with creation of new fractures by tectonic activity or thermal or hydraulic cracking (Phillips, 1973; Henley and McNabb, 1978; Ellis, 1979).

Deep hydrothermal explosion activity is a possible consequence of the deposition of an impermeable quartz seal (Henley and McNabb, 1978). Large and steep temperature and pore-pressure gradients are likely to evolve where an impermeable zone becomes established around a heat source. Although convective flow of meteoric water is cut off from the outside, the pore spaces within the zone between the quartz-sealed barrier and the remaining very hot rock are likely to contain gas or brine. This fluid may be entirely or partly meteoric or connate water, remaining from before the silica sealing became complete. However, some or all of that fluid could be volatiles evolved from a crystallizing magma. If volatiles do continue to be evolved from a crystallizing magma, it is easy to envision a situation in which the fluid pressure on the high-temperature side of the quartz seal becomes very large, (Phillips, 1973); sufficiently large to cause formation of a breccia pipe or even a conduit for a volcanic eruption (Morey, 1922).

Hydraulic fracturing will occur when the pore fluid pressure exceeds the confining pressure (the least principle stress) by an amount equal to the tensile strength of the rock. The confining pressure may range from less than normal hydrostatic to lithostatic, depending on whether open fissures are present, the nature of the fluid in those fissures, and permeability relations. Propagation of either a hydraulic or tectonic fracture through impermeable rock from a region of high fluid pressure into a region of lower fluid pressure may cause a significant decompression of the high-pressure fluid. If the thermal energy in the decompressing liquid and surrounding rock is large, massive flashing of water to steam may result. The expanding steam may explosively propel rock fragments into the air, where flashing occurs at relatively shallow levels, and into cavities and open fissures at deeper levels. Even without a magmatic contribution to the trapped fluids, pore pressures of those fluids could increase sufficiently to rupture the enclosing rock as a result of conductive heating.

Many of the conclusions in the above discussion are based on the solubility behavior of quartz in pure water. The effects of added salts can be modeled using NaCl solutions. Calculated solubilities of quartz in aqueous NaCl, using the method of Fournier (1983), show that adding dissolved salts should change the position of the quartz solubility maximum toward

higher temperatures, and thus the extent of the field of retrograde quartz solubility shown in Fig. 14. However, the conclusion that quartz deposition may cause an impermeable barrier to form, preventing fluids at hydrostatic pressure from interacting directly with very hot rock or magma, is not changed by adding salt to the system (Fournier, in press).

Because the initial permeability several kilometers deep in a hydrothermal system is likely to be limited to a few widely spaced fractures or fractured zones of rock, an impermeable zone resulting from quartz deposition in those few fractures may go unrecognized as a significant feature. Also, in fossil hydrothermal systems where estimated temperatures at the time of vein formation are $>340^{\circ}\text{C}$, it may be difficult to determine whether a given quartz vein was deposited as a result of increasing or decreasing temperature. If there is other hydrothermal alteration associated with the quartz deposition, that alteration may give an indication of the thermal history: for example, where a solution is heating, albite is likely to form in veins and after K-feldspar, and where a solution is cooling, K-feldspar or muscovite is likely to be deposited in veins and after plagioclase (Hemley et al., 1971).

Ores have been found in brecciated rocks and breccia pipes in too many deposits to enumerate here. Horikoshi (1969) and Henley and Thornley (1979) suggested that hydrothermal eruptions have initiated ore deposition in many Miocene Kuroko deposits. Hydrothermal explosive activity may affect ore deposition for various reasons, both physical and chemical. Brecciation greatly increases the permeability, providing easy access for later hydrothermal fluids that may deposit ores. The sudden and massive conversion of water to steam (boiling) may cause deposition of ore minerals for the reasons discussed above. Deposition of quartz and, to a lesser extent, K-feldspar is likely to occur wherever there is a sudden drop in pore pressure when initial temperatures exceed about 340°C . Also, the K-feldspar that forms as a result of a sudden drop in pressure is likely to be more potassium-rich than that which was in equilibrium with the fluid prior to the drop in pressure (Fournier, 1976). Therefore, hydrothermally brecciated rubbles that formed at very high temperatures are likely to be cemented by quartz, very potassium-rich feldspar, and a variety of other minerals, including sulfides. However, these minerals may also cement breccias that form at lower temperatures; quartz, adularia, and generally pyrite are the phases observed in the hydrothermal breccias that formed at Wairakei and Broadlands at about $200^{\circ}\text{--}300^{\circ}\text{C}$ (Grindley and Browne, 1976). Where exceptionally high degrees of silica supersaturation occur, particularly at lower temperatures, amorphous silica may precipitate and later alter to chalcedonic silica or quartz.

Sudden decreases in pore fluid pressure may also contribute to the formation of porphyry

ores (Fournier, 1968, 1972; Henley and McNabb, 1978). Consider a fluid evolving from a small body of metal-rich magma that is crystallizing at a depth of about 1 to 4 km. If the pore pressure is near lithostatic, that fluid is likely to be a gas of moderate to high salinity that is unsaturated with salt. Metals initially in the melt will partition into the saline fluid. Slow, uniform crystallization of magma, without a drop in fluid pressure, will result in slow release of gas and most of the dissolved metals into the country rocks, where vein deposits might form if other circumstances are favorable. In contrast, a sudden drop in fluid pressure to hydrostatic or less will chill the magma by about 75°C , freeze phenocrysts in a fine-grained groundmass, and cause the gas to split into highly saline brine plus dilute gas, or gas plus solid salt. Some metals will enter the gas phase and be transported upward. However, most should precipitate as sulfides as the magma is chilled, or remain dissolved in any dense brine that forms. If the magma body is small enough to be chilled throughout its extent, and if most of its dissolved water escapes with the gas phase, there may be little further hydrothermal alteration until the rock cools enough to allow liquid at hydrostatic pressure into the system, or until there is another pulse of magmatic intrusion. Self-sealing by quartz deposition as water is heated to temperatures above $340^{\circ}\text{--}400^{\circ}\text{C}$ will tend to prevent movement of water into the system, as discussed above, but thermal cracking and tectonic movements may counteract this effect to some extent.

DISCUSSION AND CONCLUSIONS

The major- and trace- element compositions of thermal waters in explored parts of presently active hydrothermal systems appear to be controlled mainly by reaction of deeply circulating meteoric water with the surrounding rocks. There may be undetected magmatic contributions of water and other chemical constituents to these systems, particularly gases. However, the thermal energy that causes convective circulation of fluids with temperatures above about 200°C generally comes from a magmatic source within 10 km of the surface.

Mercury appears to be depositing in high enough concentration and sufficient quantity to form ore in altered rocks above some presently active systems, and mineable quantities of native sulfur have been formed by fumarole activity near the summits of many active volcanoes. Other types of epithermal ore deposits could form as a result of continued hydrothermal activity similar to that presently observed. Commercial grade concentrations of gold and silver, along with high concentrations of relatively volatile elements, such as S, Hg, Sb, As, Se, and Tl, have been found in precipitates deposited from some hot-spring waters.

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Ore-grade deposits of base metals have not yet been encountered by wells drilled in active systems for production of geothermal resources, although iron sulfides, galena, sphalerite, chalcopyrite, and other base metal minerals have been found in cores and cuttings. In many of these systems the sulfides are precipitating from relatively dilute (less than a few thousand mg/kg total dissolved solids), neutral pH, chloride waters. With favorable hydrologic conditions that restrict the flow of most of the thermal water to a few relatively open channels, base-metal and precious-metal ore deposits could form at moderate to shallow depths in a system similar to those presently being investigated. Sulfides and precious metals are particularly likely to be deposited where ascending solutions boil, either continuously or episodically. Presently active systems with deep acidity, such as many that are now being investigated in regions of active and recently active andesitic volcanism in Japan and in the South Pacific, may provide new information about ore-forming processes.

It is possible that some presently active systems are underlain by highly saline brines that transfer heat by convection from very hot rock or magma to the overlying cooler, dilute system. Significant amounts of water and other constituents derived from magma (particularly sulfur and metals) may be trapped within that brine. Ore deposits may form where sulfur-rich gases, evolved from a crystallizing magma, flow into a surrounding brine that is rich in chloride and metals. Ores might also be deposited where the convecting brine boils or at interfaces between hot brine and cooler, dilute fluid. In some systems brines with successively higher salinities may underlie each other. At very high temperatures and relatively low pressures, gas plus solid salt could underlie a brine or a dilute hydrothermal system. Hydrologically this is an unstable situation that might be maintained by self-sealing that reduces the permeability of rock between the gas and the overlying liquid.

In some volcanic systems very hot sulfur- and chloride-rich gases vent directly from visible magma to the atmosphere. In other volcanic systems the hot gases that vent at the surface have near-magmatic temperatures and are assumed to come from magmas at undetermined depth. In some volcanic or subvolcanic systems the magma may be sufficiently deep that the escaping gases must bubble through (and react with) an overlying zone saturated with water before finally venting to the surface. The water in the saturated zone may be mostly condensed "magmatic" water or mostly meteoric water. The thickness of this water saturated zone may strongly influence the pore pressure where the gases are evolved from the magma. If the pore pressures are sufficiently low (<100-300 bars), brine is not likely to form (Fig. 16), and some metals are likely to be carried off with the gas as volatile complexes. Where these gases cool and condense, acid

alteration will occur and an ore deposit may form, possibly by mechanisms discussed by Lovering (1961) or Walker (1965). If pore pressures are in the range 300-600 bars, the gas evolved from a magma will probably split into gas plus liquid (brine) upon cooling to less than 650°-700°C, and metals initially carried in the gas are likely to partition strongly into the brine. Because that brine is relatively dense it is likely to drain downward and remain near the magma, while the gas phase rises, as in the model of Henley and McNabb (1978). At still higher pressures (generally at greater depths) the gas phase that evolves is likely to be a moderately saline fluid that is unsaturated with salt; the salinity is dependent on the initial concentrations of water and salt in the magma (Kilinc and Burnham, 1972; Holland, 1972). With cooling, that gas may become a supercritical fluid (Fig. 16), or with decreasing pressure it may separate into gas plus brine and eventually into gas plus solid salt.

The geologic record (and sometimes memories of local inhabitants) shows that some hot-spring systems have undergone great reductions in surface discharge by natural processes, and subsequent drilling has shown that large reservoirs of hot water remain at relatively shallow depths. Other hot-spring systems appear to have undergone repeated periods of decline and rejuvenation. Most of these changes appear to be the result of changing water tables and changing permeabilities as a result of mineral deposition, although waxing and waning heat sources will affect all hydrothermal systems. Self-sealing is a common phenomenon that occurs at and near the tops of hydrothermal systems. Increases in fluid pressure below the self-sealed zone may result, followed by hydrothermal explosions that brecciate the overlying rocks, opening the system to renewed flow. Ore deposition may accompany or follow the explosive activity. Self-sealing may also occur deep in hydrothermal systems, particularly near very hot bodies of rock. Narrow zones of self-sealed rock may separate geopressured brine from more dilute, hydrostatically pressured water. Seismic activity or hydraulic pressure may rupture this deep seal and decrease the fluid pressure within the brine, causing it to boil. The large pressure gradient and expanding gas phase may cause brine plus gas to squirt through the fractured region into the hydrostatically pressured system. Ore deposition may take place where the fluids mix and where boiling occurs. Deposition of quartz, sulfides, and other minerals is likely to re-establish the self-seal in a relatively short time.

The following sequence of changes might occur in a hydrothermal system that forms in a volcanic environment with a magma reservoir 1 to about 5 km deep. After volcanic eruptions cease, hot gases continue to vent to the surface. These gases may be derived in part from the remaining magma and in part from ground water (containing dissolved salts that may

hydrolyze) that seeps into contact with the magma or with very hot rock (Fig. 13). In the shallowest magma systems, gas plus solid salt will be present in the hottest parts, and brine may form at slightly cooler margins where inflowing waters boil (Fig. 13). In deeper magma systems, brines may also form by dissociation of upflowing gas of moderate salinity into liquid of higher salinity plus gas of lower salinity. The liquid (brine) that forms will drain back downward, possibly interacting further with the magma or additional gas. If self-sealing keeps inflowing water away from magma and very hot rock and the outflow part of the system remains open, or if a relatively shallow layer of water does not soon become established in the path of the gas discharge, the magma may boil dry and cool at a relatively low vapor pressure. However, a shallow layer of ground water is likely to form above the gas region, derived in part from condensation of steam and in part from meteoric water. Acid alteration will occur at the base of the liquid water layer where condensation occurs. The acidity is likely to result from H_2S , SO_2 , and HCl . Neutralization of HCl by reactions with rocks contributes to the chloride content of the overlying water. As the ground water layer becomes thicker, the fluid pressures in the underlying system increase; brines as well as gas may exist in contact with the more shallow magmas, and brines already formed in the deeper systems may become more dilute.

Eventually the hot-gas region will completely disappear, being displaced by relatively dilute but chloride-rich meteoric water that flows from the sides and above. The dilute, meteoric hydrothermal system may float directly on brine or be separated by a narrow self-sealed impermeable barrier (Fig. 17). Convective flow of this dilute hydrothermal system heats a large body of the overlying rock to temperatures in the 250° – $350^{\circ}C$ range. If the permeability at the deep margins of the convecting meteoric system then becomes restricted, and the heat source remains large, a vapor-dominated system might become established above the convecting dilute hot-water system (Figs. 12, 17). This vapor-dominated system may slowly expand downward as fluid pressures drop and heat previously stored in the rock is used to convert water to steam. Boiling of the hot-water part of the system during this process may result in formation of a second brine of intermediate salinity between the vapor-dominated zone and the underlying initial brine. When the available thermal energy is finally dissipated the vapor-dominated region will be displaced by relatively cool water.

The above sequence of events may be interrupted by renewed pulses of magmatic injection or by hydrothermal explosive activity at shallow or deep levels. In many places the stage during which there is relatively low fluid pressure immediately around the magma and venting of very hot gases directly to the atmosphere may be omitted. This may happen if

the magma reservoir is relatively deep and the rocks in the vent are cool or impermeable. Fluid pressures near the magma also may remain relatively high if venting of gas or liquid occurs on the floor of the ocean or a deep lake.

It appears that different types of ore deposits may form at the same time in different parts of a hydrothermal system; for example, epithermal gold may occur in sinters and shallow veins, while base-metal sulfides may be deposited at deeper levels, possibly underlain by still deeper porphyry deposits. Ore deposition may also be episodic, occurring mostly during and shortly after events that open self-sealed systems to increased flow, or immediately after pulses of renewed igneous intrusion.

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