Geothermal Systems Ancient and Modern: A Geochemical Review

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ABSTRACT

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Geothermal systems occur in a range of crustal settings. The emphasis of this review is on those occurring in regions of active or recently active volcanism, where magmatic heat at depths up to 8 km leads to convection of groundwater in the upper crust. Hot water (and steam) flows are controlled by the permeability of the crust and recent data have emphasised the dominance of secondary permeability, especially fractures. Drilling to depths of up to 3 km in these systems encounters near-neutral pH alkali chloride waters with temperatures up to about 350°C and chloride contents generally in the range 500 to 15,000 mg kg^{-1} although much higher salinities are encountered in some systems such as in the Imperial Valley, California. Stable isotope studies indicate the predominance of a meteoric source in the majority of geothermal systems although seawater predominates in some regions, such as Reykjanes, Iceland. Mixing of waters from both sources also occurs in some systems and some magmatic fluid may also be present.

The major element geochemistry of geothermal fluids is determined by a set of temperature-dependent mineral-fluid equilibria although chloride and rare gas contents appear to be independent variables reflecting the sources of these components (sedimentary or volcanic rocks, seawater, magmatic fluids, etc).

Boiling in the upper portion of geothermal systems is accompanied by the transfer of acidic gases (CO_2 and H_2S) to the resultant steam which may penetrate the surface as fumarolic activity or become condensed into shallow groundwaters giving rise, with oxidation, to distinctive low pH sulphate bicarbonate water.

Fluid inclusion, stable isotope and mineral alteration studies have led to the recognition in many Tertiary hydrothermal ore deposits of physical and chemical environments analogous to those encountered in the present-day systems. The vein-type gold-silver, Carlin-type gold and porphyry-type copper-molybdenum deposits of the western United States are particularly well studied examples. Sub-ocean floor equivalents of the terrestrial geothermal systems have been recognized in ocean floor spreading centres such as the East Pacific Rise and deep-sea submersible vehicles have allowed visual observation of sea floor hot springs actively depositing metal sulphides. These environments may parallel those of the Cyprus-type massive sulphide depositing systems, while sub-sea floor systems of the type responsible for Kuroko-type massive sulphide deposits may eventually be encountered in island arc settings.

INTRODUCTION

Geothermal systems occur most frequently in regions of active or recently active volcanism such as the Pacific margin. Many such systems are under-

going intensive exploration for energy utilization (e.g., Kenya, Philippines, Japan, Iceland, Indonesia, Mexico, Central and South America and New Zealand) and a number of systems are already exploited for electricity genera-

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tion or directly for industrial energy. In these volcanic geothermal systems temperatures may reach ~350°C at exploitable depths (<2.5 km). Recent deep-ocean exploration has located superficially similar sub-sea floor systems in sites of active ocean spreading such as the Mid-Atlantic Ridge, The East Pacific Rise and Galapagos Spreading Centre (Green et al., 1981, and see p. 37). Hot springs are well known also in active tectonic zones associated with plate convergence, as exemplified by the European Alps, Rocky Mountains, Himalaya and the New Zealand Southern Alps (Barnes et al., 1978a). Here meteoric waters penetrate into rocks, so rapidly uplifted and eroded that their deep heat contents have not been dissipated by conduction to the surface (Allis et al., 1979; Allis, 1981a). In more stable continental environments, in deep sedimentary basins such as in Hungary or Western Siberia, hot water occurs at temperatures reflecting normal crustal geothermal gradients. High pressure ('geopressured') reservoirs have been found associated with thick sedimentary wedges at continental margins such as in the Gulf of Mexico (Kharaka et al., 1978). Because of the wide range of environments, rock types, temperatures and degree of exploration, *we restrict this review to the high temperature systems associated with volcanism*. Evidence for the existence of geothermal systems in the past and their characteristics as metal-ore forming systems are briefly reviewed in relation to present-day systems.

The emphasis in this review is on the deep system rather than on the properties of natural surface discharges where complex mixing and steam losses occur (e.g., Fournier, 1979a). No comprehensive attempt is made to review the continuing development of stable isotope techniques in geothermal investigations as this was covered by Truesdell and Hulston (1979). Ellis and Mahon (1977) gave an extensive general review of geothermal geochemistry and Rybach and Muffler (1981) have compiled a useful set of source papers covering a number of aspects of geothermal resource assessment and development.

PHYSICAL CHARACTERISTICS OF GEOTHERMAL SYSTEMS

In regions of anomalously high heat flow, thermal convection dominates the behaviour of groundwater in permeable crust (Elder, 1966, 1981) and generates geothermal systems where hot upflow waters approach the surface. Stable isotope studies and analyses of rare gases in geothermal discharges (Mazor, 1975) have shown that the waters in these convective terrestrial geothermal systems are largely derived from air-saturated meteoric water which has penetrated the crust to the level occupied by cooling magmatic systems. Electrical resistivity soundings have shown that these hot water systems extend to depths in excess of 5 km. Fig. 1 shows the general features of a hypothetical geothermal system. Analogous seawater-fed systems are now recognised in submarine environments as well as hybrid seawater—meteoric-water systems in oceanic islands and coastal regions, e.g., Matupi Harbour, New Britain (Green et al., 1978).

Meteoric water

Steaming ground

Acid Sulphate & bicarbonate Hot Springs

Near neutral pH Chloride boiling Spring

Dilute Chloride Springs

River

Water table

Approx Scale

Sea level

-1 km

Young Volcanics and Sediments

Cold Groundwater Recharge

200°

250°

300°

0   1 km

HEAT AND MASS (NaCl, CO₂, SO₂, H₂O ...) TRANSFER FROM MAGMA SYSTEMS.

KEY

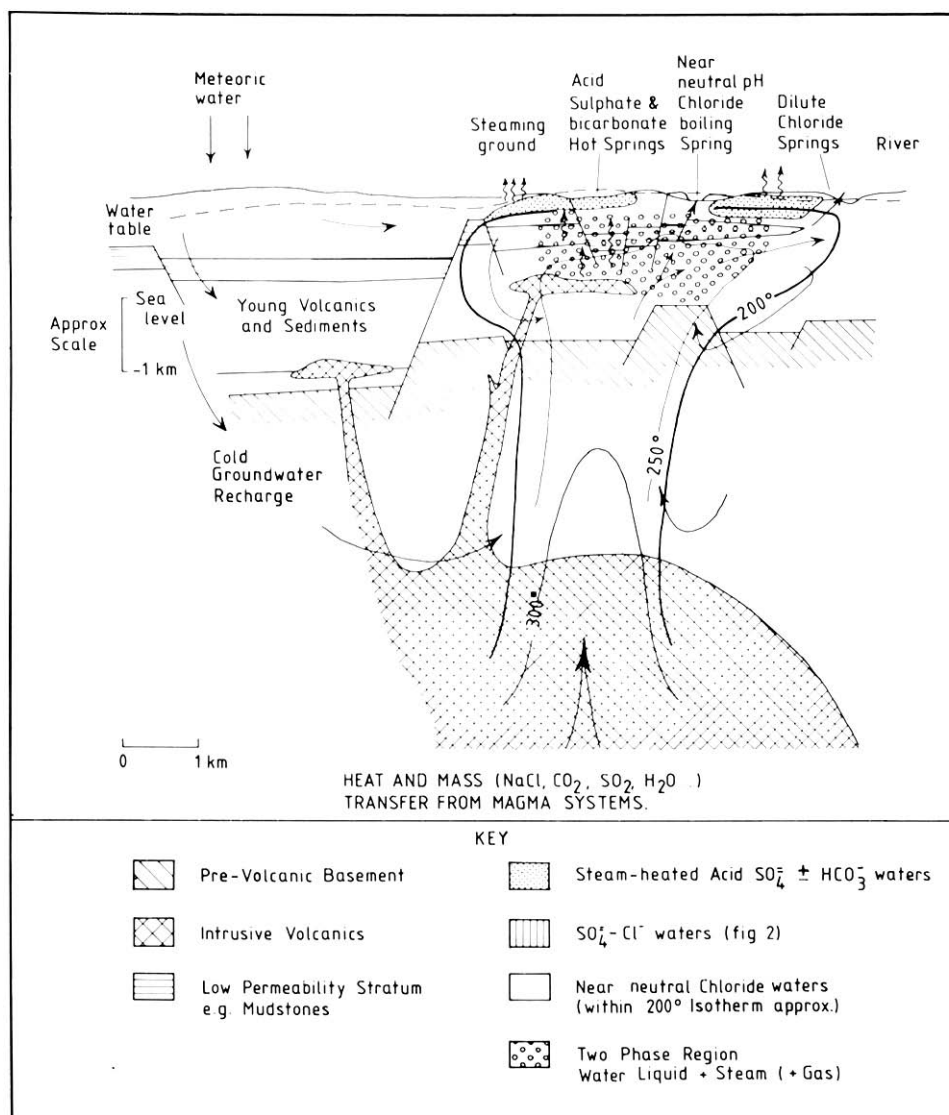|	
Pre-Volcanic Basement	Steam-heated Acid $SO_4^=$ ± HCO_3^- waters
Intrusive Volcanics	$SO_4^=$ – Cl^- waters (fig 2)
Low Permeability Stratum e.g. Mudstones	Near neutral Chloride waters (within 200° Isotherm approx.)
	Two Phase Region Water Liquid + Steam (+ Gas)

Fig. 1. Schema of the main features of a geothermal system typical of those in silicic volcanic terrane. Water recharge is provided by meteoric groundwaters and heat supplied, together with some gases, chloride, water and other solutes, by a deeply buried magmatic system leading to a convective column of near-neutral pH chloride water. Two-phase conditions occur in the upper level of the system. Steam separation processes give rise to fumaroles and steam adsorption by groundwater, with oxidation of H₂S at the water table, gives rise to steam-heated acid sulphate — bicarbonate waters. Mixing may occur between deep near-neutral pH and steam-heated waters to give relatively oxidising Cl—SO₄ waters. Outflows from the deep system occur either directly as boiling alkaline pH boiling springs generally associated with the formation of silica sinter or after dilution as near-neutral pH chloride springs.

In these geothermal systems, continuous intrusive activity or cooling of large plutons within the upper 10 km of the crust provides the thermal energy.[*1] Little direct evidence exists concerning the composition of these rocks or their mechanism of heat loss, but the recent eruption of basalt scoria from geothermal wells at Krafla, Iceland leaves little doubt about the volcanic heat source in this area (Larsen et al., 1979). Mineral alteration and devitrification reactions (10—300 kJ kg^{-1}) and the decay of radioactive nuclides (6 · 10^{-14} kJ kg^{-1} sec^{-1}, Fenn et al., 1978) may contribute a minor fraction of the total heat flow of the systems. Stratigraphic evidence suggests that the duration of geothermal activity is in the range 10^5 to 10^6 years (Browne, 1979) while the heat flow, for example, of the undisturbed Wairakei system, 4.2 · 10^5 kJ sec^{-1} (420 MW) is equivalent to the solidification of about 0.1 m^3 sec^{-1} of basalt, or for a 300,000 year life-span, about 700 km^3 basalt. The examination of deeply eroded fossil geothermal systems such as porphyry copper or epithermal ore deposits can be instructive in considering the deep thermal structure of terrestrial geothermal systems and this is discussed later.

Steady-state thermal convection dominates conductive heat flow in water-saturated crust where the dimensionless Rayleigh Number (R_a) for the system exceeds a critical value (1 to 40) which depends on the criteria adopted for the variation of fluid characteristics within the system (Horne and O'Sullivan, 1977a; Sorey, 1978; Straus and Schubert, 1977a):

$$R_a = \frac{K\beta g\Delta\theta H}{\kappa\gamma}$$

where K is the permeability of the system, β, the thermal expansivity of the fluid (about 10^3 cm^3 ^{0}C^{-1}), g acceleration due to gravity (10^3 cm sec^{-2}), κ, thermal diffusivity of fluid saturated crust (about 3 × 10^{-3} cm^2 sec^{-1}), γ, kinematic viscosity of fluid (about 12 · 10^{-4} cm^2); H, depth of system (about 8 · 10^5 cm) and $\Delta\theta$ is the vertical temperature difference across the system (500°C). The Rayleigh Number is strongly dependent on the large-scale permeability of the system so that, for the values inserted above, conductive heat transfer dominates below permeabilities of about 10^{-17} m^2 (0.01 millidarcy). Inserting typical values of K (10^{-14} — 10^{-15} m^2) found in explored geothermal systems shows that the Rayleigh Number (500 to 5000) greatly exceeds the critical value and vigorous convection is to be expected (Elder, 1966).

As a guide to minimum crustal permeabilities, Norton and Knapp (1977) examined the 'flow' or interconnected porosities of various rock types, which were in the range 10^{-3} to 10^{-5} compared to total porosities of 10^{-1} to

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[*1] White and Guffanti (1979) and Simkin (1979) have reviewed recent geophysical data, especially teleseismic P-wave delays, which are beginning to outline molten magma chambers beneath the active Yellowstone, Geysers-Clear Lake, Long Valley, Coso and Krafla geothermal areas.

10^{-2}. Their analysis suggested that permeabilities of the order of 10^{-18} m^2 may characterise large regions of the earth's crust. The higher values of K in geothermal areas reflect the dominance of fractures on fluid flow: e.g., K values of $10^{-14} - 10^{-15}$ m^2 may be accounted for by a single crack about 0.04 mm wide, cutting each cubic metre of rock in the system.

Early fluorescein injection and more recent isotope tracer studies (Barry et al., 1979) at Wairakei have confirmed the dominance of high permeability paths such as fracture networks through the field. Grindley and Browne (1975) noted the dominance of such secondary permeability as open fault zones in the Broadlands field, and James (1975) examined fissure flow to geothermal wells at Cerro Prieto and El Tatio. Batzle and Simmons (1976) carefully documented the history of fracturing and sealing in the Dunes and Raft River systems. McNabb and Henley (1979) examined the interaction of fluids flowing in fractures with fluid contained in lower permeability wall rocks and suggested that chemical and thermal exchanges occur by diffusion between the two fluid regimes. They also pointed out that because heat diffuses some 15—30 times faster than ions in solution, changes in the temperature and in the chemistry of solutions within a porous rock will occur at different rates when a cross-cutting fracture is invaded by a fluid which is out of thermal and chemical equilibrium with the wall rock.

Donaldson (1962), Norton and Knight (1977), Cathles (1977), and Horne and O'Sullivan (1977b) used computational and laboratory methods to model the patterns of fluid flow and temperature due to large-scale convection systems. These models each require certain boundary conditions and assumptions concerning the homogeneity of the systems and nature of the heat source, but they readily confirm the ability of the convective cooling of plutons to maintain large crustal volumes (20—50 km^3) at temperatures up to 500°C for around 10^5 years. The convective models of Donaldson (1962) and Horne and O'Sullivan (1977b) adopt a constant-temperature heat source such as might occur through repetitive intrusion, convective overturn of magma or, as advocated by Lister (1974, 1975), a process of steady state cracking of the pluton during cooling which greatly enhances the surface area for heat transfer from the pluton to the fluid. In contrast Norton and Knight (1977) and Cathles (1977) introduced a rate-limiting step on the convective system by considering that the pluton itself cooled conductively as is certainly the case at the end of a magmatic episode.

Geothermal systems are often associated with caldera structures, e.g., systems in the Rotorua and Okataina Calderas, New Zealand, Yellowstone Valley, Long Valley, Coso, U.S.A. and Krafla, Iceland. Many fossil ore-forming hydrothermal systems are similarly associated, e.g., McDermitt Caldera, Nevada, Creede and Silverton, Colorado and Vatukoula, Fiji. It may be that deep penetration of meteoric fluids for the establishment of geothermal activity is related to an extensive period of deep crustal fracturing related to caldera formation.

Just as the nature of the heat source at depth in a geothermal system is

imprecisely known, so too is the character of fluids at temperatures $> 350°C$ below explored depths.

Wooding (1963) and Henley and McNabb (1978), in discussing convection in porous media, have emphasised the role of dispersive mixing of cool and hot fluids on the margin of upward moving convective plumes. The magnitude of the dispersion is related to the degree of fracturing in the medium so that, in very permeable systems, the isotope and chemical compositions of near surface geothermal waters may be dominated by the diluting groundwaters rather than the deeper geothermal fluids.

Griffiths (1978) has discussed the possibility, raised by McNabb (1975) that geothermal systems arise from diffusive heat and mass transfer above a denser brine 'layer' at depth. Both these approaches suggest that brines of salinity higher than near-surface geothermal waters may exist in the roots of geothermal systems and be derived from a magmatic source or from deep connate-metamorphic waters such as postulated in a number of ore-genesis studies. In either case, dilution by lower-salinity waters during upflow progressively obliterates the chemical or isotope signature of the possible deep fluid. Truesdell and Hulston (1979) stress the absence of isotope evidence for contribution of magmatic water but note both evidence for magmatic gas contributions and for non-magmatic origins of some other solutes.

Henley and McNabb (1978) in correlating the hydrothermal environments of porphyry copper and geothermal systems, suggested that magmatic fluid [1] may be injected from a cooling pluton in the depths of the system, although the ultimate source of the water may be complex. A contribution of up to 10% magmatic fluid (originally at about 2 wt.% NaCl) could account for all the chloride and up to 30% of the heat budget for a system like Wairakei. Assuming that Wairakei discharged chloride water at the present natural rate for the last 300,000 years requires the availability of $4 \cdot 10^{15}$ g Cl^-. Ellis and Mahon (1964, 1967) showed that 800 ppm Cl^- was available from rock by leaching, so that some 2000 km^3 of rock would be required to be totally leached to supply this component during the system lifetime. Even if a steady state is not assumed (Ellis, 1970, Healy, 1975), about 70 km^3 would be required during the 10^4 year heating period of the system during *each* phase of its intermittent activity, a volume roughly equivalent to the present extent of the system. As complete chloride extraction from the local system rocks is unlikely, an additional deep or widespread source of components seems necessary. Sigvaldason (1979) has also commented on evidence for a magmatic input of chloride. In high-salinity systems such as the Salton Sea, seawater or evaporite sources of chloride dominate any contributory leach or magmatic sources.

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[1] We use the term 'magmatic fluid' to indicate a fluid which has evolved through chemical and isotope equilibrium with a silicate melt, regardless of the previous history of its component water.

Early exploration well data from Wairakei and Broadlands showed that temperatures in the unexploited system lay close to the boiling point with depth curve for water (Haas, 1971), although the physical behaviour of water in such a two-phase convective upflow zone is not well understood. Well discharges from the Broadlands system are characterised by carbon dioxide contents an order of magnitude larger than at Wairakei. In this and similar cases such as Ngawha (Giggenbach and Lyon, 1978) the boiling-point depth function is unique to the initial CO_2 content and enthalpy of the single-phase deep fluid (Sutton and McNabb, 1977; Mahon et al., 1980a).

In some fields low porosity combined with high heat flow may cause a steam zone to develop near the surface of a system either naturally (White et al., 1971; Ellis and Mahon, 1977; Truesdell and White, 1973) or following extensive well production (James, 1968; Weres et al., 1977). Principal examples are the Geysers, California and Lardarello, Italy. D'Amore and Truesdell (1979) discussed the complex interplay between 'reservoir' steam, steam evaporating from the deep system and steam regenerated from condensate during the exploitation of such systems and Allis (1981b) has related changes in seismicity to the cumulative effects of steam withdrawal from the Geysers field. Allis (1979a, b) and Henley (1979) described the generation of such artificial steam-dominant zones in the Wairakei and adjacent Tauhara geothermal systems consequent on the large-scale exploitation of Wairakei.

Steam or steam and gas escaping from deep hot-water systems may appear at the surface as fumarolic activity or may be absorbed by superficial groundwaters, perhaps perched above a low permeability cap-rock, to form distinctive sulphate—bicarbonate thermal waters with low chloride contents or low pH sulphate waters (Fig. 1). At Broadlands and Kawah Kamojang, Mahon et al., (1980b) have recognized the occurrence of sodium bicarbonate waters where steam and CO_2 derived from deep boiling is adsorbed into unmineralised groundwater. Each of the types of water mentioned may interact with each other to produce hybrid waters such as the sulphate—chloride water of the Frying Pan Lake, Waimangu and the chloride—bicarbonate waters encountered in some shallow Broadlands wells. Where steam flows are focussed into low flow groundwater zones or pools of condensate, steady state evaporation may lead to concentration of components and stable isotope enrichment (Giggenbach, 1978; Henley and Stewart, 1982).

In volcanic regions of high topographic relief, extensive lateral flows of hot water may occur for up to 20 km from the centre of the geothermal field, as at El Tatio, Chile and Ahuachapan, El Salvador (Healy and Hochstein, 1973; Healy, 1975) (Fig. 2). Chloride springs may consequently be a considerable distance from the exploitable geothermal reservoir, the locality of which may be identified by fumarole activity or the presence of steam-heated sulphate—bicarbonate waters higher on the volcanic slopes. Geothermal activity associated with the Hakone Volcano, Japan (Oki and Hirano, 1970), and the Kamojang system, Indonesia (Kartokusumo et al., 1975) is expressed in this way.
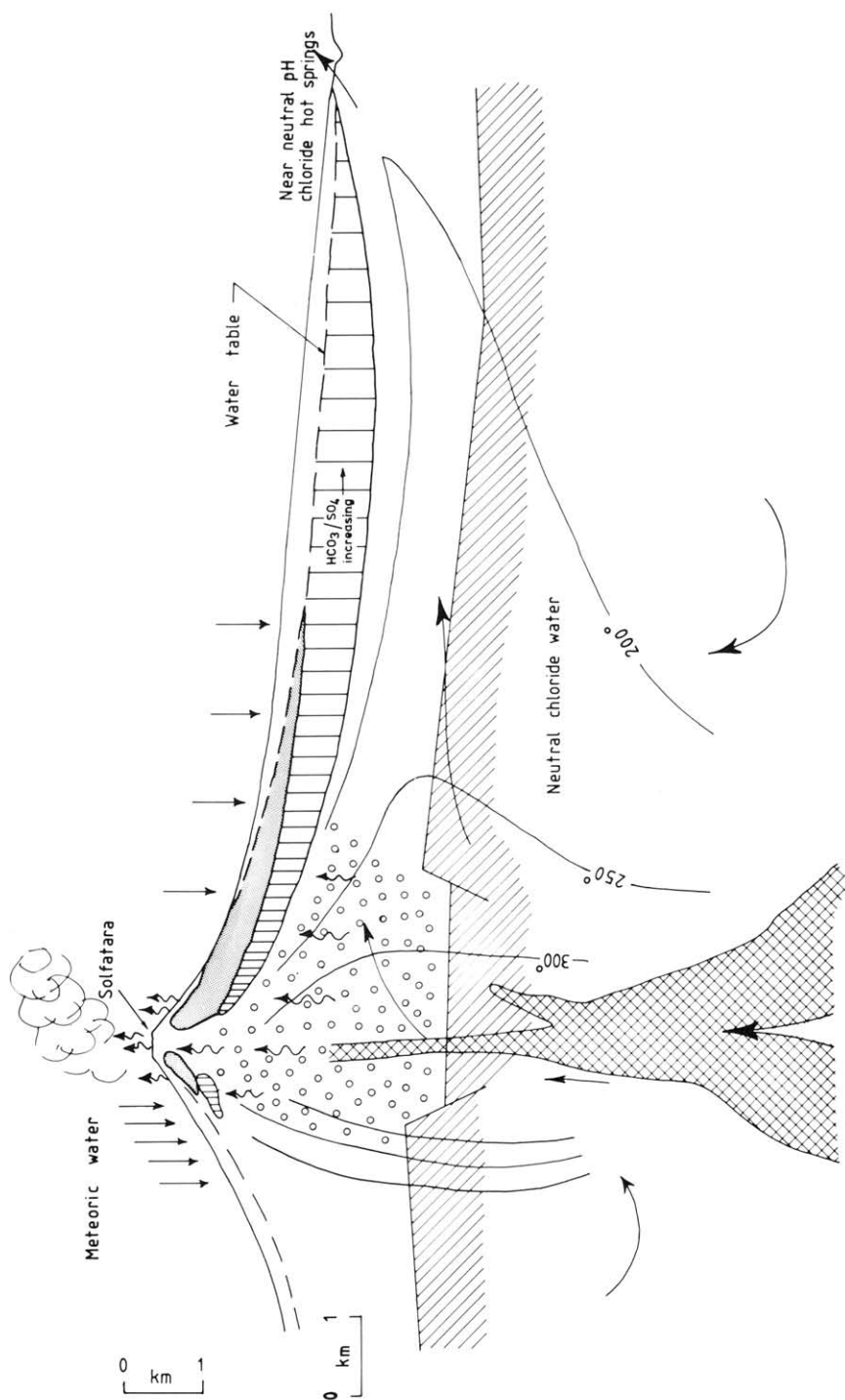
Fig. 2. Schema for a sub-horizontal flow-type geothermal system typical of active island-arc volcanoes. Lower permanent water tables in tropical regions and high relief of the volcanic structures result in a scarcity of chloride water discharges. The upflow part of the system is revealed by fumaroles, rock alteration and steam-heated, often perched, aquifers (symbols as for Fig. 1). The temperature pattern of individual systems reflects their total heat and mass flow budget.

ROCK–WATER INTERACTIONS IN GEOTHERMAL SYSTEMS

Hydrothermal alteration

Hydrothermal alteration is a general term embracing the mineralogical, textural and chemical response of rocks to a changing thermal and chemical environment in the presence of hot water, steam or gas. The limitations of the term are poorly defined so that a complete transition exists through to burial metamorphism (Zen, 1974). The criteria of distinction may well be those discussed above, i.e., the extent of heat and mass transfer within the system, so that low-grade burial metamorphic terrain would be characterised by isochemical metamorphism and lower water/rock ratios than in geothermal systems.

Water/rock ratios

Sheppard et al. (1969, 1971), Taylor (1974), Magaritz and Taylor (1975) and Criss (1981) showed that extensive oxygen isotope exchanges have occurred on a large scale, implying the activity of extensive hydrothermal systems in and adjacent to cooling batholiths (e.g., Idaho Batholith, Coast Range Batholith, British Columbia), as well as during the formation of porphyry-copper deposits and a range of other ore-depositing systems.

In British Columbia, for example, meteoric waters appear to have affected a huge volume of rock extending 300 km eastward from the quartz diorite batholith. From an oxygen isotope balance calculated water/rock (w/r) volume ratios ranged from about 0.001–0.003 for the batholithic rocks to values of 0.1–3.0 for rocks to the east of the batholith. Reviewing data for this and similar studies of ore deposits, Taylor (1974) showed that these minimum ratios normally range up to 3 or 4. For the Wairakei and the Broadlands geothermal fields in New Zealand, from oxygen isotope measurements Stewart (1978) found overall water/rock ratios of 2, and 0.7, respectively. The difference between these two fields would agree with the higher permeability observed in the Wairakei system. The Wairakei system may, in fact, approach the maximum water/rock ratio occurring in convective geothermal systems. The ratio is similar in value to the highest figure found in the Coast Range (Magaritz and Taylor, 1975). Information of this type from drilled geothermal areas is biased toward the conditions in the most permeable part of systems and should not necessarily be taken as representative of the peripheral and deeper zones. Kendal (1976), Olson (1978), and Olson and Elders (1978) showed that the degree of exchange of rocks from the Salton Sea system reflected the primary permeability of the original lithology. Similarly, Sheppard et al. (1969) showed that there was more extensive isotope exchange in the highly fractured ore depositing system at Butte, Montana than in the Santa Rita porphyry copper deposit.

The lower limit of w/r is reached when all the free water is absorbed as hy-

drous minerals; this limiting value is about 0.04 for average conditions (Hattori and Sakai, 1979). Hydration effects are not very significant at Wairakei but may have affected the deuterium contents in the Broadlands system which are slightly enriched relative to local cold surface waters.

A parameter related to rock/water ratio is the residence time of fluids in the system which reflects the gross permeability and the relative contributions of long and short recharge paths to the system. The absence of tritium (Wilson, 1963) suggested residence times for the dominant meteoric water of >100 years in Wairakei discharge. The absence of deuterium-enriched water at Wairakei suggests an absence of interglacial waters perhaps indicative of a residence time of <12,000 years (Stewart, 1978) so that the slight enrichment of Broadlands waters may reflect a contribution of older waters.

Hydrothermal alteration occurs through phase transformation, growth of new minerals, mineral dissolution and precipitation and ion exchange reactions. Although the original rock type has an influence on secondary mineralogy, its effect is less than those due to permeability, temperature and fluid composition. Browne (1978) noted that at temperatures of 250—280° the common assemblage quartz, albite, K-feldspar, chlorite, Fe-epidote, illite, calcite, pyrite was found in basalts in Iceland, sandstones in the Imperial Valley, rhyolites in New Zealand and andesites in Indonesia.

In fields dominated by fracture permeability there may be a zoning of alteration ranging from high to low rank about a major flow zone (Steiner, 1977). Oxygen isotope ratios ($^{18}O/^{16}O$) in minerals within drill cores taken at various depths in a field enable estimates to be made of the temperature profile that existed within the country before drilling occurred. $\delta^{18}O$ measurement in vein calcite has been the main technique used. Isotopic equilibrium has been demonstrated between calcite and the water from which it is precipitated (Clayton et al., 1968; Elders et al., 1978), within fissure zones of high permeability. Particularly effective applications of this method were made at Cerro Prieto by Elders et al. (1978) and at Kawerau by Blattner (1979).

Providing that there is adequate permeability, at temperatures over about 100—150°C an exchange of oxygen isotopes occurs during the interaction between water and rock minerals, particularly the fine-grained and layered alumino-silicates, and calcite (Truesdell and Hulston, 1979). However, primary quartz is slow to exchange isotopes even at temperatures over 300° (Clayton et al., 1968). For many fine-grained minerals in permeable media, isotopic equilibrium is approached at temperatures over 230—250°C, while for secondary quartz and calcite deposited in fissures isotopic equilibrium with solution is achieved (Blattner, 1975).

Alteration assemblages

A generalised summary of the temperature ranges over which various alumino-silicate minerals have been observed in geothermal areas is given
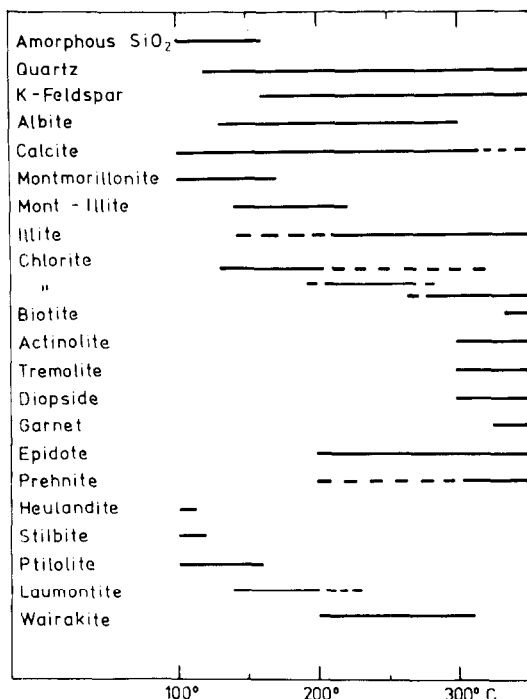
Fig. 3. Generalised summary of the temperature ranges over which alumino-silicate alteration minerals have been observed. (Solid lines give an indication of the most commonly observed temperature ranges). Temperatures of first appearance of marker minerals in the Salton Sea, Cerro Prieto and Hawaiian areas are somewhat higher than in New Zealand. Chemical controls on mineral stabilities are discussed in the text. The three chlorite stability ranges indicate the transition from swelling through mixed layer to non-swelling chlorite with increasing temperature.

in Fig. 3. The diagram gives an indication of the minerals which may be produced at different temperatures during hydrothermal alteration. The actual presence or absence of a particular mineral depends on a number of kinetic parameters as well as carbon dioxide and hydrogen sulphide activities and solution pH.

Primary minerals also vary considerably in their susceptibility to alteration. Volcanic glass is most reactive, frequently altering first to opal, smectite, calcite or zeolite and then to mixed-layer clays. The presence of such intermediate phases greatly influences local hydrogen ion and silica activities and the succeeding reaction step (e.g., Keith et al., 1978). A decreasing order of mineral susceptibility is approximately olivine, magnetite, hypersthene, horneblende, biotite = plagioclase (Steiner, 1968). Detrital quartz is frequently inert to geothermal fluids at temperatures up to $300°C$ but there is evidence from Cerro Prieto that recrystallisation occurs at higher temperatures (Hoagland and Elders, 1978).

Steiner (1968) showed how successively higher temperatures affected the formation of clay-mica group minerals following the alteration of silica-rich

volcanic glass by dilute geothermal waters. Alteration to calcium zeolites and montmorillonite occurred at temperatures of 100—120°C. With increasing temperature interstratified montmorillonite—illite occurred with the basal spacings of the mineral becoming smaller until illite appeared at 230°C. He showed a trend in calcium zeolites from mordenite (ptilolite) at temperatures of about 100°C, through laumonite from 150° to 200°C, to wairakite at higher temperatures.

At temperatures above about 180°C, mineral assemblages in geothermal systems are generally formed from solutions saturated with respect to quartz, but at lower temperatures, particularly in glassy rocks, silica activities may be higher and approximate to the solubilities of chalcedony or amorphous silica (Arnorsson, 1975). Consequently, low-temperature mineral assemblages, particularly zeolitic assemblages, are more variable (Browne, 1978), and favour the silica-rich zeolites such as mordenite.

The Reykjanes and Svartsengi, S.W. Iceland, geothermal areas provide good examples of major readjustment of inflow water compositions by high-temperature reaction with rock. These systems result from complex mixing and evaporation sequences due to the penetration of meteoric water into hot brine of seawater origin modified by fluid—basalt interactions. Sakai et al. (1980) have discussed the disequilibrium distribution of ^{34}S between sulphate and sulphide in these system waters, as well as in other Icelandic systems. With respect to seawater the Reykjanes fluid is depleted in magnesium and sulphate ions and enriched in calcium, potassium, silica and minor elements including rubidium and arsenic. A montmorillonite—zeolite—calcite alteration zone occurs to 230°C, followed by a mixed layer chlorite-montmorillonite and prehnite intermediate zone and a chlorite—epidote zone up to about 300°C. An irregular distribution of anhydrite is probably due to sulphate loss during successive incursions of seawater (Tomasson and Kristmannsdottir, 1972; Olafsson and Riley, 1978; Arnorsson, 1978a). Kristmannsdottir (1976) has carefully documented the clay mineral progression from montmorillonites to non-swelling chlorites in this system.

Hydrothermal alteration of basaltic rocks by heated seawater also occurs in oceanic spreading areas and largely has been described by reference to dredged or deep drill samples or cross-reference to ophiolite sequences (Miyashiro et al., 1971; Spooner and Fyfe, 1973; Liou and Ernst, 1979). Jehl et al. (1977) confirmed that modified seawater was the active hydrothermal phase with up to five times seawater salinity and less than 1 mole % CO_2.

The brines of the Salton Sea geothermal system and other systems in the Imperial Valley are derived from Colorado River water which has undergone partial evaporation and exchange with sandstones and shales (Truesdell et al., 1978). At Cerro Prieto, Mexico, diagenetic kaolinite—montmorillonite—dolomite—Fe-hydroxides—pyrite give way at 140° to 160°C to illite—chlorite with overgrowths of quartz and feldspar or detrital clays, together with calcite, pyrite and pyrrhotite. Above 250°C epidote appears with wairakite;

calcite being partially dissolved. Calcite is replaced entirely above 300° by prehnite—actinolite and some diopside—hedenbergite, and illite—chlorite and wairakite are almost completely lost with the incoming of biotite above 325°C (Hoagland and Elders, 1978). Kendall (1976) described a similar alteration sequence in the Magmamax wells in the Salton Sea and recognised the occurrence of garnet, talc and tremolite at temperatures higher than the biotite 'isograd'.

The general sequence of hydrothermal alteration with increasing depth in a geothermal system relates through temperature to the boiling point with depth relationship for the gas content and enthalpy of the deep single-phase inflow to the system. In the two-phase region, loss of steam with CO_2, H_2S and other dissolved gases leads to increasing pH and the development of a characteristic assemblage of calcite and alkali feldspar (Browne and Ellis, 1970), particularly in upflow zones. Elders et al. (1981) have shown how integration of isotope and alteration studies may be used to develop a useful flow model for the Cerro Prieto field.

Because of the appreciable concentrations of CO_2 in geothermal fluids and the low solubility of calcite at high temperatures, the maximum activity of calcium in solution varies from one system to another. This control, together with the variation of silica activity in some lower-temperature waters, accounts for the wide variety of calcium minerals being found in geothermal systems. For example, wairakite and epidote are common in the low carbon dioxide Wairakei system but are rare in the high CO_2 Broadlands system where calcite is abundant. Similar difference exist in the Imperial Valley with wairakite and prehnite present at Cerro Prieto but not in the Salton Sea system (Elders et al., 1978).

Distinctive alteration assemblages occur in the near-surface steam-heated zone of a geothermal system. Underground boiling, partition of dissolved gases to the steam phase and possible oxidation leads to the formation above the boiling zone of relatively acid condensate. Steiner (1977) described the acid alteration (advanced argillic) assemblages at Wairakei, characterised by kaolinite, alunite, gypsum, opal and hydrated iron oxides. In a few areas, such as Matsukawa, Japan (Nakamura et al., 1970) and Matsao, Taiwan (Chen, 1970), acid waters have been located at greater depths and at temperatures of 250—280°C. These occurrences may be due to high-temperature alteration of sulphur deposits or perhaps to an influx of acid gases (SO_2) at depth. Kaolinite, alunite, anhydrite, pyrophyllite, quartz and pyrite occur in the central zone of these fields trending outward to less acid conditions with the assemblages including montmorillonite, mica, quartz and anhydrite.

Temperature gradients at the margins and steam loss near surface suggest that silica deposition should occur on the boundaries of geothermal systems. Silicification is a common feature of hydrothermal rock alteration and incorporates both the addition of silica (largely as a vein mineral by fluid flow) and redistribution of the silica originally present as glass or cristobalite. Keith

et al., (1978) and White et al. (1975) described porosity reduction due to silica precipitation in rocks penetrated by drilling in Yellowstone Park and showed from pressure data between wells that there was effective self-sealing of horizontal permeability. In contrast little physical evidence for self-sealing has been obtained at Wairakei. Calcite and feldspar deposition in boiling zones may also contribute to this process of self-sealing and Oki and Hirano (1979) suggest that geothermal brines of the Hakone system are sealed against seawater intrusion by precipitated sulphate and carbonate minerals. However, sealing of vertical permeability is not well documented. Even where rocks of relatively low permeability (e.g., mudstones) cap a system chloride water and steam continue to penetrate to the surface through fracture systems. The abundance of hydrothermal explosion features containing high-chloride springs in the surface of geothermal systems (Lloyd, 1959, 1972; Muffler et al., 1971; Nairn and Wiradiradja, 1980) and hydrothermal breccias (Grindley and Browne, 1975) suggests that systems actively maintain flow paths to the surface. Build-up of gas pressure as well as seismic disturbance can initiate hydrothermal eruptions (Henley and Thornley, 1979).

Kinetics of mineral alteration reactions

Few experimental studies have been concerned specifically with the kinetics and mechanism of mineral alteration reactions. Early theoretical studies of the incongruent dissolution of feldspar (Helgeson, 1971) derived the concept that in a closed system diffusion through a growing layer of new precipitate was the rate-determining step. Subsequent studies by Lagache (1976) and Petrovic et al. (1976b) did not confirm this concept; dissolution rates appeared to be controlled by the nucleation and growth at discrete sites of intermediate phases in the sequence proposed by Helgeson (1971). Experimental studies in the system $CaO-MgO-SiO_2-H_2O-HCl$ (Sheppard, 1977) support Petrovic's model. In a steady state open system where growth sites for secondary minerals are developed, solution concentration and exposed surface area are probably the major controls on mineral alteration rates.

Henley and Harper (1979) observed relative reaction rates during the shallow reinjection of waste $95°C$ geothermal water at Broadlands. Among the transient chemical effects observed during dispersive mixing of the injected and dilute formation water the adsorptions of caesium, rubidium and potassium into clay minerals were most rapid while only partial re-equilibration occurred with respect to calcite and silica solubilities.

Composition of altered rocks

Changes in the major element composition of rocks during alteration reflect mineralogical changes, such as growth of K-feldspar and mica, or quartz deposition. Minor elements may be taken into alteration mineral lattices, or may form discrete accessory mineral phases such as oxides or sulphides difficult to detect in small amounts.

Comparing fresh and hydrothermally altered rhyolite rocks in the Waira-

kei system, Steiner (1977) showed a characteristic loss of sodium and calcium and gain of potassium and silica through all alteration zones. In the near-surface montmorillonite and intermediate micaceous clay-zeolite zones the concentrations of Al, Fe, Mn, Mg, and P were little changed, but these were depleted in the highest-rank alteration zones. The behaviour of Pb and Ag was variable, probably due to their concentration into sulphides, which occur in some of the alteration zones. Analysis of hydrothermal quartz showed lead, arsenic and silver contents of 150, 300 and 50 ppm, respectively. Koga (1967) and Ellis and Sewell (1962) showed the depletion of zinc and of boron in rocks during high-temperature alteration in the Wairakei system.

Goguel (pers. comm., 1981) confirmed the leaching of calcium and sodium from hydrothermally altered rocks of the Wairakei and Broadlands areas and showed the uptake of potassium, rubidium, caesium and lithium. Analysis of individual minerals showed the transfer of rare alkalis from the original ferromagnesian minerals and glass matrix of the volcanic rocks to particular secondary minerals; for lithium mainly into chlorite (250 ppm Li) and quartz (up to 400 ppm Li) (Barger et al. (1973) have located lepidolite in shallow altered rocks in Yellowstone); for rubidium into illite and to a lesser extent adularia; and for caesium into zeolites such as wairakite (250 ppm Cs) and to a lesser extent illite (45 ppm Cs). Lower temperatures correlated with higher caesium concentrations in wairakite from a drill-core in the El Tatio field, Chile (about 220°C). In non-zeolitic alteration zones caesium concentrations were little different from those in the original rhyolitic rocks.

From the changes in water compositions in the fields from depth to the surface and the integrated changes in rock composition during alteration, Goguel deduced water/rock mass ratios of about 100, and for constant natural water outflow rates, field life-times of 6000000–10^6 years. This again assumes that the rocks sampled by drilling were representative of overall rock alteration in the field and that constant flow and chemical conditions are maintained.

Naboko (1977) reviewed the changes in element compositions caused by the hydrothermal alteration of dacite—andesite—basalt rocks with geothermal fields in Kamchatka. During hydrothermal alteration of a similar type to the New Zealand fields, ranging from argillitic through zeolitic to quartz—feldspar, the rocks were enriched in Rb, Sc, Ga, Ge, Sr, As, Sb, Ag, Au and Sn. The elements Ti, Ba, Cu and B were depleted, while Li, Be, V, Cr, Co, Ni, Zr, Mo and Pb showed variable behaviour but on average were little changed. Zinc abundances showed a bimodal distribution suggesting leaching at some levels and deposition at others. Lithium and rubidium concentrations followed potassium, showing the general tendency to be deposited in the rocks as the water temperatures decreased.

There are still insufficient data on the chemical composition of hydrothermally altered rocks to enable statistically significant trends to be shown for many elements. The statistical method employed by Putnam (1975) for

mineralized granitic rocks may be appropriate.

Seawater composition may have been controlled through the earth's history by basalt—seawater interaction in ocean ridge geothermal systems (Wolery and Sleep, 1976; Muehlenbachs and Clayton, 1976). A number of studies have attempted to quantify the extent and sequence of reactions occurring in these systems and to examine alteration sequences preserved in ophiolite terrain. Thompson and Humphris (1977) showed that altered basalts from mid-ocean ridges had become relatively enriched in magnesium and depleted in calcium, strontium and silica. B, Li, Cu, Zn, Mn and Fe were also removed from the rock, together with some Co and Ni which were subsequently fixed in sulphide segregations. Stakes (1978) examined the alteration chemistry and mineralogy of altered gabbros from the Mid-Atlantic Ridge and East Pacific Rise as well as a metagabbro from Michigan. She suggests that the absence of smectite from the Atlantic samples implied low water—rock ratios in contrast to the occurrence of saponite in the East Pacific Rise material which, by analogy with experimental studies, (Seyfried and Mottl, 1977) was indicative of high wate—rock ratios. McGoldrick et al. (1979) showed that the thallium content of deep submarine basalts was a sensitive indicator of basalt—seawater interaction; as is the case for the Broadlands system thallium behaves in a similar way to potassium but is more highly enriched due to fixation in alteration silicates and iron-manganese hydroxides. Albarede et al. (1981) have discussed the implications for $^{87}Sr/^{86}Sr$ of seawater—basalt interaction in spreading centre hydrothermal systems.

Experimental studies

Several high-temperature experimental studies have demonstrated that appreciable concentrations of solutes such as Li, Na, K, Rb, Mg, Ca, F, Cl, B, SO_4 and NH_3 can be brought readily into solution from fresh rocks (Ellis and Mahon, 1964, 1967; Mahon, 1967; Kissen and Pakhomov, 1967; Ellis, 1968). Although the solute concentrations of dilute geothermal waters could be explicable by a simple solution mechanism, the high salinities of some waters cannot be accounted for by simple extraction from rocks in the likely range of water—rock ratios operative. These experiments also confirmed that the concentrations of silica, potassium, calcium, magnesium, iron, aluminium, manganese, fluoride, carbonate, sulphate and many heavy metals were controlled by pressure-temperature dependent equilibria between minerals and solutions. Ewers (1977) observed the ready dissolution of As, Sb, S and Se from greywackes between 100°C and 500°C. Relatively few elements (Cl, Br, B, Cs, Li, As and NH_3) are conserved in solution in deep geothermal solutions. Ratios between these components appear to reflect particular rock-types in the geothermal system.

In experiments with salt solutions, heavy metals such as iron, manganese, lead, zinc and copper are rapidly 'leached' from rocks (Ellis, 1968). With seawater reacting with basalt, Mg is first lost from solution into smectite-type

phyllosilicates, producing an acidic environment which leads to extraction from the rock of K, Ca, Mn, Fe, Cu and Zn (Bischoff and Dickson, 1975; Seyfried and Bischoff, 1977; Bischoff et al., 1981). Calcium sulphate is precipitated from solution. With low water—rock ratios (<10), after initial removal of Mg from solution, the pH slowly rises in response to hydrogen ion reaction with alumino-silicates. At high water—rock ratios (~50) there is less Mg depletion of the fluid but the pH remains low and strong leaching of the rock occurs with respect to Ca, K and Ba (Seyfried and Bischoff, 1979) and heavy-metal concentrations in solution are higher. Seawater mixed with 'altered' seawater responds by the deposition of a complex magnesium silicate. Mottl et al. (1979) showed that sulphide was readily leached from basalt as well as being formed from reduction of seawater sulphate due to ferrous iron release from the basalt. They also showed that Fe and Mn concentrations increased with increasing reaction temperature. Menzies and Seyfried (1979) showed that rock depletion in K and Rb was a function of temperature and water—rock ratio, although some altered ocean floor basalts show no such depletion, perhaps due to retrograde reactions.

Dickson (1977) demonstrated that interaction of rhyolite with saline solutions proceeded similarly but more rapidly. In these reactions anomalously high silica concentrations occurred initially (Dickson et al., 1978a) which subsequently decreased as zeolite nucleation and growth occurred (Rytuba et al., 1978; Potter and Dickson, 1980). Similar behaviour was noted for andesite as the solid reactant (Liou and Dickson, 1978).

GEOTHERMAL FLUID COMPOSITIONS

Mineral-fluid equilibria control the major element concentrations and pH of deep geothermal fluids. The development of readily applicable thermodynamic techniques for high temperature multi-component equilibria (Helgeson, 1969, 1978a) has led to a greater realisation of the large-scale rock-water equilibria controlling fluid compositions and alteration assemblages in geothermal and fossil hydrothermal systems (Arnorsson et al., 1978; Bird and Norton, 1981; Giggenbach, 1981).
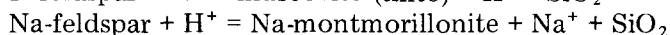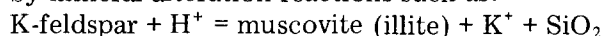
Common solutes

The total salt concentrations of geothermal fluids range from about 0.05% to 30%, but most commonly fall in the range 0.1—1%. Table I contains five relatively dilute waters from systems containing volcanic rocks (Hveragerdi, basalt; Otake, Tongonan and Ahuachapan, andesite; Wairakei and Broadlands, rhyolite). The Ngawha system contains siltstones and sandstones underlain by argillites and greywackes, and the Cerro Prieto and Salton Sea systems comprise deltaic river sediments. The Reykjanes and Hakone systems are recharged by seawater—meteoric water mixtures through basaltic rocks and the Matsao system contains highly acidic chloride—sulphate waters in an andesite—sandstone sequence. The alkali sulphate—chloride water at Cesano, Italy was derived at greater than 250°C from brecciated limestones overlain by potassic volcanics.

Features that are common to most high-temperature waters include unusually high proportions of the rare alkalis, lithium, rubidium and caesium as well as of silica, boron, arsenic, fluoride and ammonia. Except for acidic fluids, iron, magnesium, heavy metals and sulphate—chloride ratios are usually low.

Chloride ion concentration, along with temperature and local rock type, is one of the principal independent variables defining the chemistry of geothermal fluids (Ellis, 1970; Arnorsson et al., 1978). As discussed above, its possible origins are diverse and most likely, in any system, it results from mixing of two or more source fluids (White, 1974).

Since the ratios of the principal anions (K^+ and Na^+) to H^+ are determined by mineral alteration reactions such as:

K-feldspar + H^+ = muscovite (illite) + K^+ + SiO_2

Na-feldspar + H^+ = Na-montmorillonite + Na^+ + SiO_2

the pH of the geothermal system fluid is a function of the salinity of the system. For example, Salton Sea waters are much more acidic than those from Wairakei, and are noted for their corrosion potential and transport of heavy metals. At lower temperatures the pH may be controlled by other aluminosilicate mineral interactions. Arnorsson et al. (1978) suggested that up to 170°C the pH of some Icelandic waters was controlled by chlorite—smectite —water reaction.

The pH of geothermal waters collected at atmospheric pressure is usually higher than that of the original deep water due to the preferential loss of acidic gases (CO_2, H_2S) into the steam phase. For waters of near neutral pH, the change is frequently about 1—2 pH units. Arnorsson (1978b) gave a detailed discussion of this process.

The Na/K ratio of geothermal waters has been used successfully as a geothermometer in many geothermal systems, particularly for waters over about 180°C. Truesdell (1975) and Fourier (1979a) summarised empirical equations for the variation of Na/K with respect to temperature. The quotient relates to the overall reaction and exchange of Na and K between albite and K-feldspar, and decrease of Na/K with temperature reflects the net transfer of potassium from deeper hotter levels of a geothermal system to shallower levels as may be recognized from whole rock analyses. Near surface extraction of potassium into clay minerals may affect the Na/K ratio of some spring waters (Weissberg and Wilson, 1977).

Fournier and Truesdell (1973) have shown that Ca/Na and Na/K ratios reflecting a wider range of mineral-solution equilibria, may be combined into a useful Na K Ca geothermometer which they calibrated using waters from a number of geothermal fields. For waters high in magnesium, Fournier and Potter (1979) propose corrections which should be applied to the simple NaCaK ratio temperature estimate. Paces (1975) showed that calculated temperatures for some spring waters were higher than measured temperatures and suggested a correction based on the carbon dioxide content of the water. Nathenson (1981) has shown that for low flow springs from reservoirs

TABLE I

Composition of geothermal well waters; concentrations in mg/kg collected at atmospheric pressure from the discharge

Source and reference (depth)	Temperature (°C)	pH	Li	Na	K	Rb	Cs	Mg	Ca	Mn	Fe
Hveragerdi; Well G3 (a) Iceland (650 m)	216	9.6	0.3	212	27	0.04	<0.02	0.0	1.5	0.00	0.1
Otake Well 7 (b) Japan (350 m)	200	8.4	4.5	846	105	1.8	0.7	0.02	9.9	0.00	0.05
Broadlands Well 13 (d) New Zealand (1080 m)	260	8.6	12.6	980	200	2.2	1.3	0.02	2.4	–	–
Ahuachapan Well 20 (c) El Salvador (550 m)	225	–	18.5	6000	1040	7.9	6.0	0.07	450	–	–
Ngawha Well 1 (d) New Zealand (585 m)	230	7.4	12.2	950	80	0.8	0.4	–	28	0.02	0.1
Cerro Prieto Well 5 (e) Mexico (1285 m)	340	7.7	38	9062	2287	–	–	1	520	–	0.3
Salton Sea IID Well 1 (f) California *1 (1600 m)	340	4.7	215	50400	17500	135	14	54	28000	1400	2290
Reykjanes Well H8 (g) Iceland (1750 m)	275	7.1	6.6	12730	1990	5.2	–	9.8	2249	2.6	–
Matsao Well E-205 (d) Taiwan (1500 m)	245	2.4	26	5490	900	12	9.6	131	1470	40	220
Cesano Well 1 (h) Italy (1435 m)	~250	8.5	380	78930	48350	450	80	17	106	0.1	0.7
Mahiao Well 401, Tongonan, Philippines (1947 m)	324	6.7	40	7800	2110	12.5	3.5	0.28	219	–	–
Broadlands Well 6, (j) New Zealand (67 m)	50	7.9	1.3	480	48	–	0.005	91	139	–	–

Hveragerdi; Well G3 (a) Iceland (650 m)	1.9	197	0.45	61	—	0.6	480	0.1	55	7.3
Otake Well 7 (b) Japan (350 m)	3.8	1219	2.5	214	2.3	20.5	425	0.1	56	—
Broadlands Well 13 (d) New Zealand (1080 m)	4.5	1668	5.3	6.5	3.2	48	750	1.9	117	0
Ahuachapan Well 20 (c) El Salvador (550 m)	1.6	10900	46	30	12	155	556	—	23	—
Ngawha Well 1 (d) New Zealand (585 m)	0.8	1625	—	17	—	1200	460	46	61	<1
Cerro Prieto Well 5 (e) Mexico (1285 m)	2	16045	31	6	0.5	14	1250	21	56	—
Salton Sea IID Well 1 (f) California *1 (1600 m)	15	155000	120	5	12	390	400	386	7100	16
Reykjanes Well H8 (g) Iceland (1750 m)	0.14	25054	87	2.4	0.15	11.3	943	2.0	—	5
Matsao Well E-205 (d) Taiwan (1500 m)	7.0	13400	—	350	3.6	106	639	36	2	—
Cesano Well 1 (h) Italy (1435 m)	100	42850	—	163290	8.3	2650	—	82	5850	—
Mahiao Well 401, Tongonan, Philippines (1947 m)	—	14370	—	32	28	313	995	6.4	27	11.8
Broadlands Well 6, (j) New Zealand (67 m)	—	28	—	18	0.6	0.6	146	—	1290	—

(a) Ellis and Mahon (1977).
(b) Koga (1970).
(c) Choussy and Peñate (1976).
(d) Chemistry Division, D.S.I.R.
(e) Mercado (1976).
(f) Muffler and White (1969).

(g) Olafsson and Riley (1978).
(h) Calamia et al. (1975).
(i) Barnett (1979).
(j) Mahon et al. (1980b).
*1 pH and concentrations in high temperature aquifer.
*2 Total CO_2 = total carbonate species expressed as CO_2.

$<150°$ C apparent differences between the silica and alkali geothermometers may be reconciled by allowing for conductive heat loss in the spring conduits.

The rare alkalis (lithium, rubidium and caesium) are present in unusually high concentrations in high-temperature waters but this depends on local rock types. The basaltic reservoir rocks of Iceland are associated with low concentrations of rare alkalis in geothermal water, while the alkali—potassic rocks of the Cesano area contain exceptional concentrations. Fouillac and Michard (1979, 1981) suggested a general relationship between Na/Li ratio and temperature, ranging from 100—200 at 50°C to 20—70 at 300°C. Dilute waters and brines had a separate trend line.

The Na/Rb ratio in waters is of potential value as a geothermometer, particularly in revealing high temperatures at depth through the analysis of spring waters, as low-temperature hydrothermal minerals incorporate potassium in preference to rubidium (Goguel, pers. comm., 1981).

Calcium concentrations are related to the carbon dioxide content of the system and the pH defined by the dominant alumino-silicate or solution buffer system (Ellis, 1970). The controlling equilibrium is the solubility of calcite, most waters being close to saturation, so that the maximum calcium concentration is given by the following general equation:

$$a_{Ca^{2+}} = K\, a_{Na^+}^2\, m_{CO_2}^{-1}$$

where K is a temperature-dependent constant. Calcite solubility increases with falling temperature, so that highest calcium concentrations occur in waters of low temperature, high salinity and low carbon dioxide concentrations. Giggenbach (1981) showed that in the silicic volcanic terrane of the Taupo Zone systems, the dominant reaction determining fluid chemistry was the conversion of primary plagioclase by CO_2 to calcite and clay minerals, while a set of subsequent secondary mineral equilibria control relative CO_2 -$H_2 S$ concentrations.

Ellis (1971) showed that in general $a_{Mg^{2+}}/a_{H^+}^2$ ion ratios in geothermal waters reflected the conditions for coexistence of chlorite, calcite and calcium—magnesium montmorillonite.

Fluoride and sulphur are readily removed from most rock types by high temperature water (Ellis and Mahon, 1964, 1967). The maximum concentrations of sulphate and fluoride are related to calcium concentrations through the solubility equilibria for anhydrite and fluorite (Mahon, 1964; Nordstrom and Jenne, 1977; Richardson and Holland, 1979). Although anhydrite is a common alteration mineral, fluorite is not. Reviewing fluoride contents of Icelandic waters, Arnorsson et al. (1978) suggested that fluoride concentrations were limited by anion exchange with alumino-silicates containing exchangeable hydroxyl groups.

Anhydrite has a low solubility in hot water (24 ppm at 250°C, 8 ppm at 300°C) so that sulphate concentrations are low in high-temperature, near-neutral pH waters. The Cesano brine, a sodium sulphate solution, occurs in a unique chemical and redox situation. Acidic waters such as at Matsao and

near-surface steam-heated waters often contain much higher sulphate con-contrations.

Boron and arsenic are also readily released from many rock types during reaction with hot water. The Cl/B ratio in geothermal waters commonly is similar to that in the aquifer rocks (Ellis and Sewell, 1963; Mahon, 1967). Waters with exceptional boron levels, such as Ngawha, are associated with organic-rich sedimentary rocks.

Arsenic behaves as a soluble component in deep high-temperature fluids, but is depleted in near-surface waters, probably due to destabilisation of its sulphide solution complex, when H_2S is removed by boiling (Ewers and Keays, 1977; Naboko and Karpov, 1977).

The solubility of the various forms of silica increases rapidly with tem-perature and it is observed that geothermal waters are saturated with silica at the level for quartz solubility at temperatures above about 180°C but with various amorphous or unstable crystalline forms of silica at lower tempera-tures (Mahon, 1966; Fournier and Rowe, 1966; Arnorsson, 1975). Silica concentrations in waters provide an excellent geothermometer, particularly for geothermal wells where fluids reach the surface quickly and with mini-mum contact with rock surfaces at lower temperatures. Waters reaching the surface through springs, even of high flow, may lose silica through partial re-equilibration. Mixing of waters from deep levels with near-surface waters occurs in most areas, and Fournier and Truesdell (1974), Truesdell and Four-nier (1976) and Fournier (1979b) in particular have shown how 'mixing models' for geothermal areas may be constructed to allow for this type of effect.

Redox conditions

Seward (1974) reviewed the calculation of redox conditions in geothermal fields, including estimation from pH and hydrogen concentrations (either measured or calculated from ratios such as CH_4/CO_2, NH_3/N_2) and from the coexistence of redox responsive minerals such as pyrite and pyrrhotite. The hydrogen partial pressure in geothermal waters is usually in the range 0.02—0.1 bars (Ellis and Mahon, 1977), reflecting the conditions imposed by the dominant mineral buffer and alteration controlled pH. In most systems this is probably the equilibrium between pyrite and Fe-Mg/chlorite (Giggen-bach, 1980). The redox potential (f_{O_2}) also controls the concentration of sulphate (as free SO_4^{2-} or as ion pairs with sodium or potassium) and bisul-phate with respect to hydrogen sulphide and bisulphide ion. At shallow levels in geothermal systems there are marked changes in the redox environ-ment due to mineral-fluid re-equilibration following steam loss or mixing with near-surface air-saturated groundwaters or steam-heated waters. Naboko and Karpov (1977) gave examples of changing Eh and pH and mineralogy with depth in shallow wells and Pampura et al. (1975) discussed Eh-pH con-ditions in Kamchatka well waters during their cooling by steam loss from 200°C.

Minor metals

Table II gives a selection of trace metal concentrations in a range of geothermal fluids. In dilute, near-neutral pH geothermal waters typical of recent volcanic areas, the concentrations of most heavy metals are low, even for the common rock-forming elements such as manganese and iron, and usually less than the average for fresh surface water. Exceptions are those which form complex species with sulphide in high temperature solutions, such as gold, mercury, arsenic and antimony (Weissberg, 1969). Tungsten concentration may also be high locally. By contrast, in highly saline geothermal fluids heavy metal concentrations may be high to the extent that economic recovery is feasible. The Salton Sea brines discharged from exploration wells are particularly notable both for their high salinity and the abundance of sulphide scales formed in discharge pipelines (Skinner et al., 1967). McKibben (1979) has described the occurrence of hematite-dominated and sulphide-dominated mineral assemblages, as well as synsedimentary pyrite/marcasite mineralisation in the Salton Sea cores. Recrystallised early pyrite was replaced by pyrrhotite, chalcopyrite, sphalerite assemblages at greater

TABLE II

Minor element concentrations in some natural and geothermal waters

Source and temperature (°C)	pH (cold)	Cl (ppm)	Mg (ppm)	Mn (ppm)	Fe (ppm)
Fresh water		7.8	4.1	0.3—300	
Average seawater		19000	1350	0.002	0.01
Hot water, Reyholt, Iceland (98°)	9.1	90	0.03		0.006
Well 2, Broadlands, N.Z. (260°)	8.3	1180	0.01	0.009	0.23
Average Wairakei wells (250°)	8.2	1500	0.01	0.001	0.008
Aquifer, Cerro Prieto wells, Mexicali (340°)		7420—11750	6—33	0.64	0.2
Well H8, Reykjanes, Iceland (275°)	7.1	17912	7.0	1.9	
Mean, 1 and 2 I.I.D. Wells, Salton Sea (300—350°)	4.7	155000	10—54	1400	2150
Well E-205, Matsao, Taiwan (245°)	2.9	9000	88	28	148
Tamagawa Springs, Japan (98°)	1.2	3240	83	4.2	105

(a) Hawkes and Webb (1962).
(b) Krauskopf (1967).
(d) Arnorsson (1970).
(d) D.S.I.R. Chemistry Division, New Zealand.

depth. Mineralisation is present both as disseminated sulphides and as veins with a mineral abundance pattern (in decreasing order); pyrite, hematite, sphalerite, chalcopyrite, pyrrhotite, marcasite, galena.

At least in some fields the heavy metals are derived by leaching of country rock (Doe et al., 1966). Leeman et al. (1979) showed from Pb isotope compositions that lead in hot spring deposits in Yellowstone Park arose in part from a sedimentary source. Weissberg et al. (1979) reviewed occurrences of ore metals in hot spring precipitates and well discharges from a number of geothermal systems. Vidal et al. (1978) recently described the submarine occurrence off Baja California, or pyrite- and gypsum-bearing precipitates enriched with As, Hg, Sb and Tl.

Gas concentrations

The total gas content in the steam phase of geothermal well discharges ranges from about 0.01% to several tens of percent. The gases are principally CO_2 and H_2S, but include also CH_4, N_2, H_2, NH_3, and traces of the rare gases He, Ne, Ar, Kr and Xe. In liquid-dominated systems at deep

Ni (ppb)	Cu (ppb)	Pb (ppb)	Zn (ppb)	Sb (ppb)	W (ppb)	Ag (ppb)	Ref.
0.02—10	0.2—30	0.3—3	1—200			0.07—7	(a)
2	3	0.03	10	0.5		0.04	(b)
<1	<2		<2				(c)
0.1	0.6	0.8	0.6	130	87	0.5	(d)
0.7	1.3	3	1.5	70			(d)
2.2	5	4.6	6	400		4	(e)
8.6	10.4		66	0.4	0.7		(f)
	5500	91000	520000	400		1400	(g)
	35	500	8800				(d)
	10	1000	2800				(h)

(e) Mercado (1967).
(f) Olafsson and Riley (1978).
(g) White (1968).
(h) Ozawa et al. (1973).

levels the gases are dissolved in the hot water, but when steam is formed by boiling the gases pass into the steam phase.

Giggenbach (1980, 1981) showed that gases in the system C—O—H—N occur in equilibrium proportions in geothermal systems, while H_2S concentrations are related to H_2 and are controlled by the common buffer system pyrite and iron-bearing chlorite. The proportions of gases in geothermal discharges provide an excellent means of deep temperature estimation (D'Amore and Panichi, 1980; Giggenbach, 1980, 1981).

Carbon dioxide in geothermal systems may originate from decarbonation reactions from carbonate rocks or from dispersed organic matter, from solution in meteoric water or from magmatic sources. Panichi and Tongiorgi (1975) and Truesdell and Hulston (1979) summarised carbon isotope data for various geothermal areas and showed that the $^{13}C_{CO_2}$ range overlapped with, but was slightly lighter than that for carbon in marine limestones. This feature could be explained by mixing with lighter organic carbon from local sediments. The carbon isotope range from -2 to $-8°/oo$ ^{13}C is also close to that assumed for juvenile carbon, derived from magmatic systems originating in the mantle. Barnes et al. (1978b) showed that the global distribution of carbon dioxide discharges, including geothermal systems and spring waters, coincided with the major belts of crustal seismicity and concluded that CO_2 production was largely from regional or localised contact metamorphism of marine carbonate sediments.

The methane associated with high temperature geothermal areas has a ^{13}C compositional range much lighter than that of CO_2 and reflects a partial origin from organic carbon. The slow equilibration of isotopes between CO_2, CH_4, H_2 and H_2O (Sackett and Chung, 1979) allows CO_2 and CH_4 to continue to reflect their separate origins (Panichi and Gonfiantini, 1979). This makes CH_4—CO_2 carbon isotope exchange geothermometry of dubious validity.

Giggenbach (1977) showed that sulphur in geothermal gases, and fixed as sulphides within the systems, probably had a dual origin involving magmatic assimilation of crustal material containing sulphides and the subsequent evolution of a magmatic gas. By correlating the C/S ratio of volcanic and geothermal gases, he suggests that only about 5% of the sulphur entering the system with carbon dioxide may reach the exploitable zone of the system, the remainder being fixed as sulphides in the deeper hotter zones. Arnorsson (1974) correlated the sulphide concentrations and temperatures of Icelandic geothermal systems and concluded that the sulphur was of magmatic origin.

Nitrogen may originate from the atmosphere dissolved in the meteoric-water recharging geothermal systems as well as from magmatic sources, while ammonia can be liberated by rock/water reactions at high temperatures. Loss of ammonia into separated steam occurs as geothermal fluid moves toward the surface, and it may, like rubidium, be absorbed into zeolites and clays, occasionally forming distinct phases such as buddingtonite (Erd et al., 1964).

Rare gases

The ratios of the inert rare gases in many geothermal waters below the depth of boiling, suggest that they have an atmospheric origin and accompany the meteoric-water supply (Mazor and Wasserburg, 1965; Mazor, 1975). However, an excess of radiogenic argon and helium occurs in many geothermal fluids, arising from rock leaching or from magmatic-fluid contributions.

Helium concentrations in geothermal gases can exceed those in air (5.2 ppm) by up to two orders of magnitude. The isotope ratio ^{3}He/^{4}He is about $3 \cdot 10^{-5}$ for helium derived from the mantle, $3 \cdot 10^{-8}$ for the earth's crust, and $1.4 \cdot 10^{-6}$ for the atmosphere. The light isotope ^{3}He is found in excess of atmospheric proportions in gases in seawater above spreading ocean ridge centres (Jenkins et al., 1978, 1980; Lupton et al., 1977, 1979) and from oceanic basalt glasses, while helium in volcanic and geothermal gases of Kamchatka, Kurile Islands, Japan, Iceland, Hawaii, California and New Zealand also have a high ^{3}He/^{4}He ratio of about $(0.5-2) \cdot 10^{-5}$. This may arise from the leaching of recent basaltic rocks or by diffusion of helium from the mantle. There appear to be only minor contributions from crustal or atmospheric gases in these systems. The highest ^{3}He/^{4}He ratio of about $2.1 \cdot 10^{-5}$ was found in Kilauea volcanic gases (Gutsalo, 1975, 1976; Craig et al., 1978; Thomas and Kroopnick, 1978; Naughton and Thomas, 1978; Nagao et al., 1979; W.F. Giggenbach, pers. comm., 1981).

The helium isotopic ratio has the possibility of distinguishing the heat origins in geothermal systems, with the lowest ratio corresponding to crustal conductive heating situations where radiogenic ^{4}He has accumulated, and the highest ratios to areas heated by basaltic volcanism.

The ratio ^{40}Ar/^{36}Ar in the atmosphere is 295.6, but higher ratios can be expected in gases from deep levels in the earth's crust because of the production of ^{40}Ar from the radioactive decay of ^{40}K. Several geothermal areas, (e.g., Wairakei, Waiotapu and Kawerau in New Zealand, Monte Amiata (Italy), and Yellowstone Park) have an ^{40}Ar/^{36}Ar ratio in gases which differs little from that in the atmosphere, indicating a meteoric origin (Ellis and Mahon, 1977). On the other hand, in some areas of Kamchatka and of the Kurile Islands, the gases have excess ^{40}Ar present in a proportion which increases with the ratio ^{3}He/^{4}He, suggesting that radiogenic argon may accompany ^{3}He from a mantle origin (Gutsalo, 1976).

In crustal rock situations where little excess ^{3}He is present, the ratio of radiogenic to atmospheric argon in geothermal fluids may give information on the fluid residence time in the system and the permeability to local ground water inflow. For example, in Larderello steam, excess ^{40}Ar occurred, but the percentage excess decreased with time as the steam field was exploited, suggesting a shallow recharge of meteoric waters (e.g., Wairakei 10—100, Broadlands 1—19, The Geysers about 20, Larderello 40—300 nCi/kg). Radon originates from the radioactive decay of uranium-238 through the intermediates thorium-230 and radium-226, and its release into geother-

mal fluids depends on the content of parent radioactive elements in the rock, the rock mineralogy and the system-permeability, and whether liquid or gas fills the rock pores. Radon may therefore be useful as a pathfinder in geochemical exploration for geothermal energy (Wollenberg, 1975; Nielson, 1978; Cox, 1980). The short half-life of radon (3.83 days) means that measurements of its concentration can give information on the immediate history of fluid before it is discharged from wells or natural vents, and reasons for changes with time in well discharges. (D'Amore, 1975; Kruger et al., 1976; D'Amore et al., 1978; Kruger, 1978; Whitehead, 1979).

The combination of radon measurements with determinations of other rare gas isotopes, deuterium, ^{18}O, and tritium has a potential for investigating the details of geothermal reservoir fluid dynamics.

FOSSIL HYDROTHERMAL SYSTEMS

It has become clear from a host of recent geochemical studies that the majority of hydrothermal ore deposits hosted by volcanic rocks or their subjacent plutonic suites were formed within geothermal systems of similar size, chemistry and behaviour to those we see active today. Indeed no other conclusion might be expected, should uniformitarianism be accepted as the guide to geological interpretation. By the same token the study of such fossil hydrothermal systems, which have been deeply dissected by erosion, offers information on the deep characteristics of active geothermal systems which is otherwise quite unattainable.

Here we attempt to highlight aspects of those types of deposit and their environments of formation which correlate most strongly with the active geothermal systems, rather than to provide a comprehensive review of the full range of characteristics demonstrated by any particular family of hydrothermal ore deposits. Porphyry-type Cu—Mo, 'epithermal' type Au—Ag—Hg and Cyprus-type massive sulphide deposits show the strongest correlations and White (1967, 1974, 1981) has discussed the origin of these types of deposit in the context of active geothermal systems emphasizing active mercury depositing systems such as Sulfur Bank, California and Ngawha, New Zealand. The reader is referred to White's papers for full discussion of the geothermal environment of mercury ore formation. The Hg deposits and lithium-enriched tuffs of the McDermitt caldera are a particularly interesting example of a fossil geothermal system (Rytuba, 1976). Other genetic groups of hydrothermal deposits (e.g., Mississippi Valley type) may similarly find their modern analogues but these must be sought in the geothermal environments of tectonic settings other than those of the volcanic hosted systems (White, 1968).

Epithermal type gold—silver deposits occur in many Tertiary volcanic regions, in association with base metal sulphides (e.g. Tayoltita and Guanajuato, Mexico), with antimony, arsenic and mercury sulphides (Carlin, Nevada) and as telluride assemblages (Acupan, Philippines,

Vatukoula, Fiji, Thames, N.Z.). Many of these deposits are associated with active warm or hot springs, e.g., Acupan, Philippines (Sawkins et al., 1979). It was early recognised (e.g., Lindgren, 1933; White, 1955) that clear parallels exist between the near surface (<500 m) depositional environment of these deposits and that of modern hot spring systems and these have been emphasized by the results of recent exploration activity through the Western U.S.A. and Canada (e.g., McLaughlin deposit, California).

Weissberg (1969) and Weissberg et al. (1979) reviewed the occurrence of ore metals in hot spring environments such as the Champagne Pool, Waiotapu, New Zealand and the Ohaki Pool, Broadlands, New Zealand where gold and silver reach 85 and 500 ppm, respectively, in the amorphous Au—Ag—Sb —As—S precipitates. In both these geothermal systems galena, sphalerite and minor chalcopyrite occur with pyrite and pyrrhotite at depths of 200—2000 m (Browne, 1969; J.W. Hedenquist, pers. comm., 1982) in the temperature range $120°$ to $298°C$. (Browne, 1969, also recorded minor telluride in these assemblages.) These disseminated base metal sulphides occur in veins and vugs often associated with adularia and calcite, both minerals indicative of local boiling. This base metal sulphide deposition appears to be interpretable as due to the combined effects of pH increase and H_2S loss due to boiling. Ewers and Keays (1977) studied the zoning of metals within the Broadlands field using whole rock samples, sulphide concentrates and silica sinters. These data showed a crude metalliferous zoning with Sb, Au and Tl enriched near the surface and Pb, Zn, Ag, Cu, Bi, Co, Te and Se at depth. Gold in the dilute geothermal fluids of this field is transported as thiocomplexes and the deep system fluids are greatly undersaturated with respect to the metal (Seward, 1973). Its deposition in hot springs and sub-hot spring environments reflects loss of H_2S due to boiling or mixing with relatively oxidising near surface waters (see below) and T.M. Seward (pers. comm., 1982) has shown that colloidal As—Sb sulphides act as effective scavengers of gold and other metals and may be kinetically instrumental in producing the ore grade precipitates.

Large low-grade disseminated gold deposits of the Carlin-type occur within the altered and silicified argillaceous, carbonaceous limestone of the Roberts Mountain Formation, Nevada. Pyrite is abundant and the gold occurs in stratiform bodies as part of an arsenic, antimony, thallium, mercury assemblage, consisting of sulphates and sulfosalts and abundant organic matter. The gold occurs as submicroscopic particles, mostly in pyrite and arsenopyrite, and ranges in grade from 15 g tonne^{-1} in the Cortez deposit to 29 g tonne^{-1} in the Carlin deposit (Wells and Mullens, 1973). Carlin itself has produced over 10^8 g of gold. Dickson et al. (1978b, 1979) showed that the ore fluids were dominantly meteoric in origin and that temperatures for the gold—pyrite phase of deposition were in the range $160—180°C$, while later vein temperatures ranged from $235°$ to $300°C$. Dickson et al. (1979) and Radtke et al. (1980) consider that these deposits were formed as part of the evolution of a geothermal system in which heat was derived from Ter-

tiary sub-volcanic intrusives, and ore and gangue components from deep rock—water interactions at temperatures in excess of 350°C. They suggested that ore formation was a response to a rapid change of temperature, perhaps due to a sudden release of pressure or increase in vertical permeability.

Casadevall and Ohmoto (1977) discussed ore-forming conditions in the Sunnyside Mine, Eureka District, Colorado where gold—silver—copper—lead —zinc—cadmium veins occur to depths of about 600 m. These formed 13—16.6 million years ago during resurgent volcanism within the 28 m.y. old San Juan—Uncompahgue caldera complex. Stable isotope data showed that the ore-forming fluid was dominantly meteoric in origin and they concluded that the main stages of base metal ore deposition occurred at 250—320°C, at fluid pressures of 110—220 bars. Carbon dioxide, ranged from 0.01 to 0.2 molal (0.04—0.9 wt.%), the higher values being dominant. Redox (P_{O_2} = 10^{-30} — 10^{-32} bars) and pH (4.3—5.9) conditions were estimated from mineral assemblages and thermochemical data.

In the majority of geothermal systems deep system waters are buffered with respect to f_{O_2} by pyrite-reduced iron assemblages (such as pyrite—pyrrhotite, pyrite—chlorite; see p. 23) at a value far below that inferred for ore deposition at Sunnyside. Here, as well as for a number of other epithermal deposits (e.g., Tonopah, Nevada, Pueblo Viejo, Dominican Republic) (Kesler et al., 1981) the relatively high oxygen fugacity of the ore deposition environment (where HSO_4 > H_2S) and low pH with respect to deep system waters is most likely the result of mixing with steam-heated acid sulphate waters generated above the boiling zone of the system. Such interactions are common in volcanic geothermal systems; e.g., at Matsao, Taiwan acid sulphate waters occur with alunite in sandstone at depths of over 500 m, above a normal chloride water zone at temperatures of around 250°C (Chen, 1975; Lan et al., 1980). At Matsukawa, Japan, acid sulphate waters with low chloride content are associated with kaolinite—alunite—pyrophyllite to depths of 700 m (Nakamura et al., 1970).

In Fig. 4 the solubility of gold as thiocomplexes has been recalculated as a function of pH, f_{O_2} and ΣS from the data of Seward (1973). These data show that the gold content of deep system waters at Sunnyside could not have been more than 50 ppm and by analogy with Broadlands may have been considerably undersaturated. Up to 300°C the solubility of gold as chloride complexes is imprecisely known but based on the data of Henley (1973) is unlikely to exceed 5 ppb under the depositional conditions at Sunnyside and thiocomplexing dominates the transport of gold in the deep system (extrapolation of lower temperature data suggests far lower solubilities in the region $5 \cdot 10^{-6}$ ppm). Mixing of relatively oxidised acid sulphate waters with deep system H_2S dominant waters would result in an intermediate redox environment of the type shown by the Sunnyside data. Under these conditions the solubility of gold is a factor of at least 10^3 less than in the deep system waters. The precipitous drop in solubility close to the HSO_4 : H_2S species boundary may lead to rapid bonanza-style deposition of
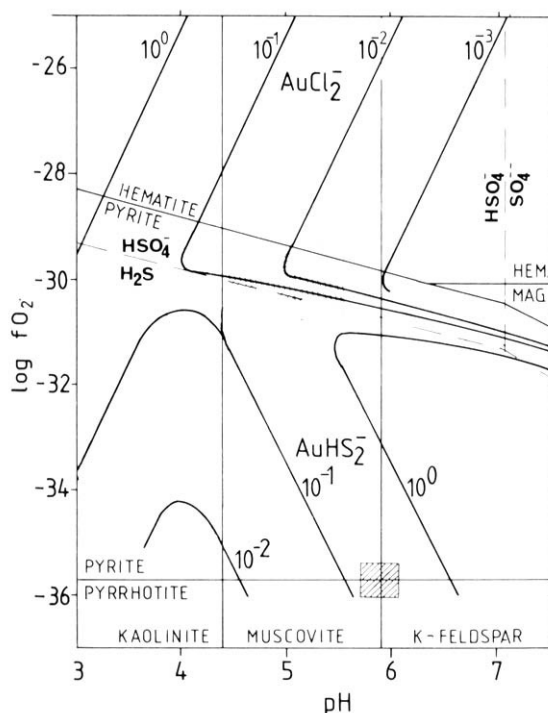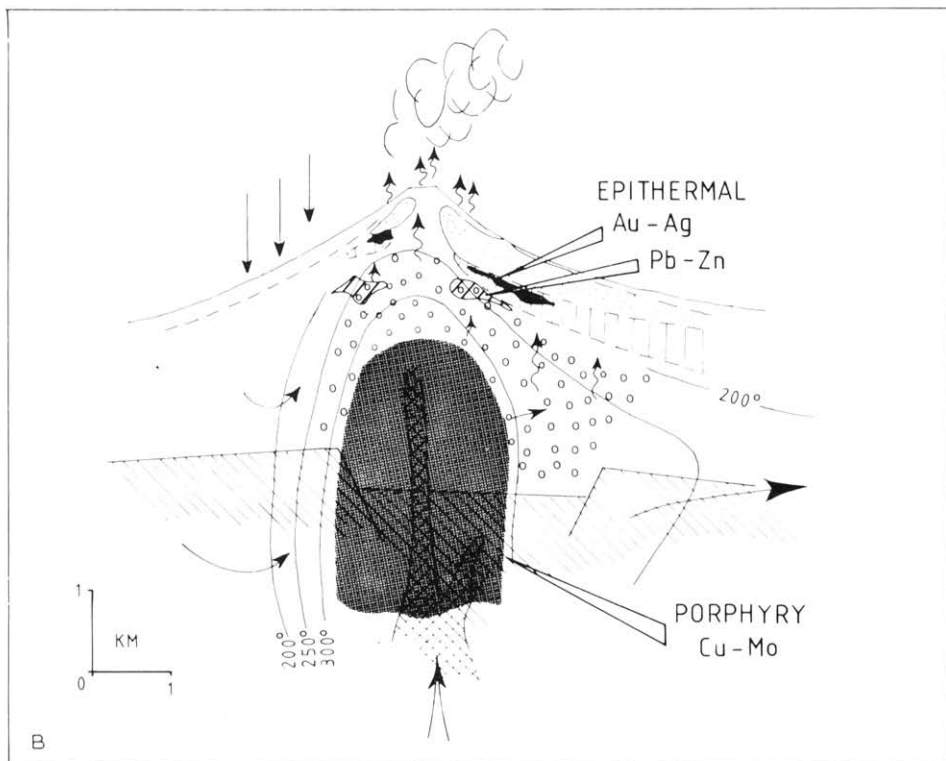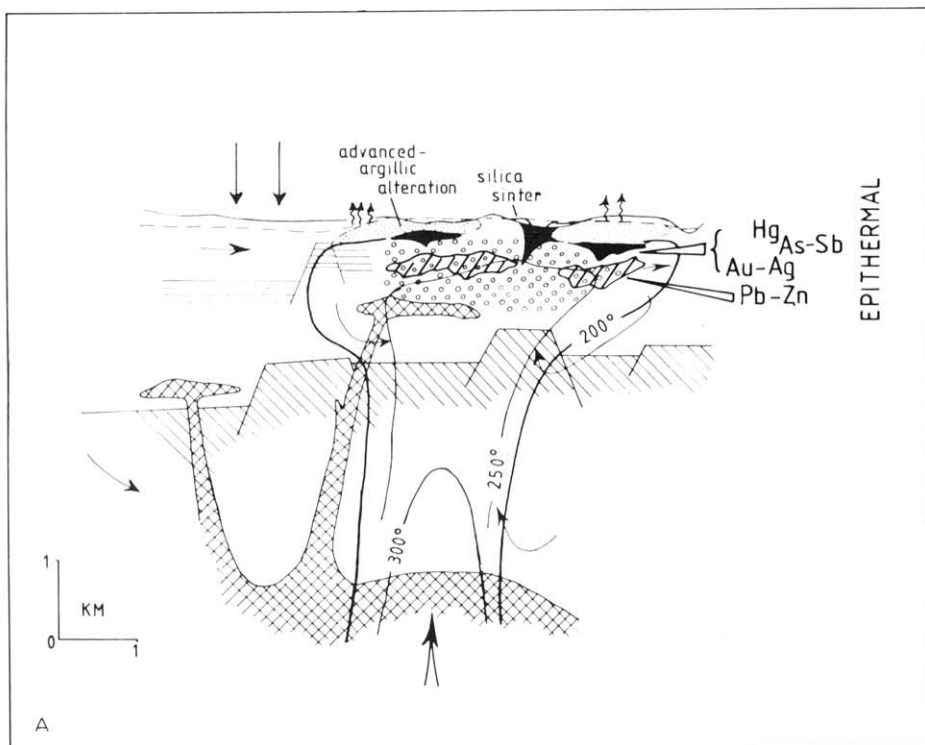
Fig. 4. Gold solubility contours for $AuCl_2^-$ and $Au(HS)_2^-$ in ppm as a function of oxygen fugacity and pH at 300°C in relation to the stability fields of pyrite, pyrrhotite, magnetite, hematite, kaolinite, muscovite, K-feldspar. The additional contribution of $Au(HS)^0$ species has been omitted ($m_K^+ = 0.02$; $m_{Cl}^- = 0.08$; $m_{H_2S} = 0.05$; data sources: Helgeson, 1969; Seward, 1973; Henley, 1973). The stippled region is the depositional environment deduced for the Sunnyside mine by Casadevall and Ohmoto (1977) and cross-hatched area the chemical environment of a typical geothermal system in which f_{O_2} is buffered close to the pyrite—pyrrhotite phase boundary: evidence from Broadlands suggests that such fluids are generally well undersaturated with respect to gold. The low pH and relatively high f_{O_2} for Sunnyside suggest that mixing of acid sulphate type steam-heated waters and deep near-neutral chloride waters may have led to ore deposition; gas loss due to boiling results in temperature decrease and relative increase of pH and f_{O_2}, and may contribute to ore deposition. (Use of Helgeson's data for the $AuCl_2^-$ reaction in preference to the experimental data gives solubilities 100 × less than those shown in the HSO_4^- field, inferring an even greater solubility hiatus in the vicinity of the H_2S—HSO_4^- boundary.)

some 90% of the gold in the mixing zone. As well as increasing pH, loss of H_2S by boiling of deep system fluid also affects a reduction in gold solubility but for waters initially well below saturation the removal of 50% of the H_2S by boiling from 325° to 300°C may only render the solution just supersaturated with effective deposition of no more than a few percent of the transported gold.

Barton et al. (1977), Bethke and Rye (1979) and Wetlaufer et al. (1979) have described the ore forming environment of the silver—PbS—ZnS deposits at Creede, Colorado in relation to present day geothermal systems. Redox conditions in the vein assemblage are similar to Sunnyside, again sug-

A

advanced-
argillic
alteration   silica
                    sinter

Hg As-Sb
Au-Ag
Pb-Zn

EPITHERMAL

200°

250°

300°

1

KM

0   1

B

EPITHERMAL
Au-Ag
Pb-Zn

200°

200°
250°
300°

PORPHYRY
Cu-Mo

1

KM

0   1

gesting that mixing as well as boiling may have played a significant role in ore deposition in this near-surface environment. Base metal sulphides (galena, sphalerite ...) occur in and below Au—Ag ore zones at Tayoltita and Guanajuato in Mexico. At Tayoltita over 283 tonnes of gold and 14000 tonnes of silver have been produced. Deposition occurred over a 300 m vertical interval at an inferred depth of 500—600 m, temperatures were in the range 260—290°C and salinities were up to 8.4 wt.% NaCl equiv. (Clarke and Albinson, pers. comm., 1980). At Guanajuato deposition temperatures were around 230°C, fluid salinities were of the order 3 wt.% NaCl equiv. and the formation depth was about 340 m (Buchanan, 1980). In both deposits deposition occurred from boiling fluids, that at Guanajuato perhaps being higher in dissolved CO_2 leading to calcite dominance over epidote in the ore assemblage (Browne and Ellis, 1970). The depositional environments of these deposits are clearly analogous to those at Broadlands and Waiotapu with lead and zinc and perhaps some gold deposited directly due to boiling. *Apparent* salinities of the Broadlands fluids determined by fluid inclusion measurements are higher than those measured directly for reservoir fluids through the presence of up to 3 wt.% CO_2 in solution (Browne et al., 1974). The presence of dissolved gas may at least in part accounts for the *apparent* salinity difference between ore-forming fluids and those actually present in the majority of present-day geothermal systems.

Genetic studies on these epithermal type deposits frequently adhere to the gross convective characteristic of the Wairakei geothermal system when closer attention to the near-surface topographically controlled hot water hydrology and its interaction with the deeper system fluids may be more appropriate as an exploration guide. As in the present-day systems, fractures or hydrothermal explosion vents may focus deep system fluids into the surface depositional environments and act as effective fluid mixing environments as is the case for the Champagne Pool, Waiotapu. Fig. 5A mimics the schematic flow model of a typical geothermal system (Fig. 1) and attempts to emphasize the depositional environments of epithermal ores in relation to the near-surface hydrology of the system. Evidence for direct involvement of magnetic fluids in epithermal ore genesis through introduction of metals into the underlying geothermal systems is scant; stable isotope

Fig. 5. Environments of hydrothermal ore deposition in typical geothermal systems associated with: A. a silicic volcanic terrane; and B. a calc—alkaline stratovolcano. The systems' structure and symbols for fluid compositions are as for Fig. 1. Advanced argillic alteration corresponds to the zone of acid sulphate (steam-heated) waters and argillic through propylitic alteration to the chloride water zone. Higher alteration grades would occur in the deeper zones, closer to any 'magmatic' fluid input and may be associated with skarn type mineralisation. (The limits of the porphyry ore zone in B are schematic only; the existence of equivalent mineralisation in the subsilicic terrane is a matter of speculation.) Epithermal ores may be associated with typical near surface features such as silicification and silica sinters, and telescoping of metal zonation may occur. Ore deposits occur in close association with major flow controls such as deep fractures ('veins') or hydrothermal explosion vents.

data from Creede and from Comstock (O'Neil and Silberman, 1974) merely hint at this possibility and it is most likely that any deep system input is highly dispersed by the time the near surface environment is reached — as is the case for active geothermal system fluids. Leaching of part or all the ore metals from country rock in the system is an equally unproven alternative.

'Porphyry copper' deposits, ranging from 50 to 500 million tonnes of ore at over 0.4% copper, are abundant in the Late Cretaceous—Tertiary volcanic belts of the Circum-Pacific and Alpine zones. In the southwest United States, typified by the Bingham deposit, Utah, these large disseminated sulphide deposits are associated with felsic rocks (quartz monzonites and porphyries), but in British Columbia and the Southwest Pacific with diorites and andesite. Sillitoe (1973) recognized that these deposits were formed at depth in subvolcanic hydrothermal systems, which are perhaps most similar to those currently active in the Central and South American volcanic regions and the Philippines. Wood (1980) has described the common occurrence of chalcopyrite, with galena and sphalerite at temperatures of 300—320°C in the Mahiao—Tongonan geothermal field, Philippines. The Southern Negros geothermal system is close to an actively explored porphyry copper deposit, while porphyry prospects and deposits are found for example in Chile, Panama, Mexico and Fiji near to active geothermal systems. Particularly detailed studies of the El Salvador, Chile and Butte, Montana porphyry copper deposits are by Gustafson and Hunt (1975) and Brimhall (1979), respectively.

Lowell and Guilbert (1970) and Guilbert and Lowell (1974) have stressed the common large-scale pattern of alteration developed in porphyry systems; a potassic assemblage coincides with low-grade ore in the core of the deposit which is mantled by a higher-grade ore shell associated with a pyrite—phyllic alteration assemblage and this, in turn, by a less altered argillic—propylitic zone containing veins of gold, silver, copper, zinc and lead. Roedder (1971) and others have shown that fluid inclusions from the periphery of the deposits contain fluids of less than 6% salinity, while in the core high-salinity fluids (~50 wt.%) coexist with a lower salinity vapour phase in a boiling relationship. Homogenisation temperatures range from about 200° to 350°C in the periphery and from 500° to 700°C in the core. Sheppard et al. (1969, 1971) reported a zoning of stable isotopes in alteration minerals which they interpret as due to the presence of meteoric groundwaters in the peripheral zone and mixed meteoric—magmatic waters in the core. Estimates of depths of formation range down to about 5 km for Bingham. At El Salvador and elsewhere, late-stage advanced argillic alteration is recognised, representing acid-type near-surface water interaction.

White et al. (1971) attempted to model the ore-forming environment by analogy with that of vapour-dominated hydrothermal systems, but Sillitoe (1973) could not reconcile their model with the occurrence of highly saline solutions in porphyry copper inclusions or with the absence of the typical porphyry alteration in drilled vapour-dominated systems.

Henley and McNabb (1978) suggested that porphyry ore deposits are formed where a rising plume of high temperature magmatic fluid penetrates and mixes with low salinity groundwater or deep formation fluids. Consequent composition, redox and temperature changes lead to the concentric alteration sequence and ore deposition. They suggested that, at the pressures and temperatures deduced for the system, magmatic fluid in the system $NaCl\text{---}H_2O \pm CO_2$ (Sourirajan and Kennedy, 1962) must be evolved from the magmatic system as a low-salinity vapour which would condense to a high-salinity liquid coexisting with vapour as pressure decreased during upward buoyant flow. Dilution with low-salinity groundwaters would occur during subsequent convective ascent through the crust.

Henley and McNabb's model may offer a glimpse of the deep roots of active geothermal systems, as shown in Fig. 1. Geothermal systems in the Taupo Volcanic Zone occur in deep pyroclastic sequences overlying a greywacke basement within which active magmatic systems may be operating and evolving heat both by conductive and convective heat loss. The hidden presence of such a deep magmatic system could account for an additional supply of chloride and sulphur. An interesting facet of these fossil geothermal systems is the preservation of a record of early magmatic fluid injection into the system followed by waning stage redistribution of ore components and superimposition of lower temperature mineral assemblages. This pattern may characterise present-day geothermal systems but may not be demonstrable at the shallow levels reached by drilling. Giggenbach (1977) has suggested that more than 95% of the sulphur introduced at deep levels in a geothermal system may be fixed at depth as metal sulphide. Fig. 5B shows the geothermal environment inferred for porphyry ore formation. It is of interest to consider whether epithermal and porphyry environments are mutually exclusive or gradational. The Comstock Lode, Nevada occurs within the eroded remnant of a typical andesite stratovolcano and is regionally associated with porphyry ore environments. The epithermal ores of silicic volcanic terrane appear to show no such proximity to porphyry ores but this may relate to erosion level rather than to any fundamental difference in the nature of the geothermal system, its fluid phase or host rocks. Uplift and $\frac{1}{2}$-1 km of erosion from a stratovolcano may readily intersect both the porphyry and epithermal environment, while the equivalent erosion or dissection of silicic terrane remains essentially in the epithermal zone.

Submarine massive sulphide deposits contain a metal suite similar to that of porphyry deposits and occur in a similar volcanic environment (Hutchinson and Hodder, 1972). The deposits are best known in the Kuroko districts of Japan (Lambert and Sato, 1974; Ishihara, 1974) and the Archaean greenschist belts of Canada (Sangster, 1972). They form as massive fine-grained sulphide bodies on the contemporary sea-floor atop or adjacent to mineralised stockwork zones in altered felsic volcanics (Lambert and Sato, 1974). Solomon (1976), Andrews and Fyfe (1976) and MacGeehan (1978)

recognised that the environment of ore deposition was that of submarine discharge from sub-sea floor geothermal systems. Recent isotope studies confirm that the ore-forming fluids originate in this way although Ohmoto and Rye (1974) and Hattori and Sakai (1979) have shown that some meteoric water may be incorporated in the ore fluids in some deposits suggesting that close analogy may exist with the active Hakone geothermal system, Japan. Henley and Thornley (1979, 1981) suggest that sub-sea floor geothermal systems in these environments were supplied by sulphur and ore metals by both the leaching demonstrated by experimental studies and magmatic vapour by analogy with the porphyry ore model. Ore deposition may have been consequent on hydrothermal eruptions through the sea-floor and subsequent higher power discharge through the eruption vents until resealing occurred by mineral deposition. Examples of this sequence are at Buchans, Newfoundland and Kosaka, Japan as well as a number of deposits in the Noranda district. The possibility of magmatic fluid involvement is also suggested by recent isotope data from the Kosaka and Buchans deposits (Hattori and Muehlenbachs, 1980; Kowalik et al., 1981). Correlatives of the Kuroko environment have yet to be located; a task of some difficulty in view of the active volcanism and rapid sedimentation of their island arc submarine setting. The nearest equivalents are the metalliferous sediments off Santorini and Vulcano and those in Matupi Harbour, New Britain (for review see Cronan, 1980).

The sub-sea floor geothermal systems of the Red Sea (Degens and Ross, 1969) have attracted much attention as analogues of sea floor mineralisation, correlating *perhaps* with Precambrian stratiform base metal sulphide deposits, such as Mt. Isa, Queensland. Bignell et al. (1976) have carefully documented the chemistry and mineralogy of the metalliferous muds which occur within sea floor depresssions in contact with hot brine. Although the water itself may have a complex origin, it is generally accepted that the high salinity is due to dissolution of Miocene evaporites. Mixing of brine and Red Sea waters appears to account for the range of salinities occurring in the Atlantis II and Discovery Deeps (Danielsson et al., 1980). Shanks and Bischoff (1977) proposed that the metals (dominantly Cu, Zn, Pb) were derived by brine—basalt interaction at 150—250°C and that metal precipitation occurs largely in response to dissociation of chloride complexes during cooling; sulphur being provided by inorganic reduction of sulphate.

Cyprus-type massive sulphide deposits are characterised by a simpler sulphide assemblage (chalcopyrite, pyrite and some sphalerite) and an association with pillow basalts in the Tethyan Troodos ophiolite sequence in Cyprus and Palaeozoic Appalachian ophiolites of Newfoundland (Upadhayay and Strong, 1973). The sulphide ores are overlain by an amorphous deposit (umber) consisting of Fe, Mn oxides with silica and alumina, while the deposits themselves undergo submarine weathering to a Mn-poor, Fe-rich sediment, or 'ochre' (Constantinou, 1976). Spooner and Fyfe (1973), Spooner et al. (1974, 1977) and Chapman and Spooner (1977) showed that

the deposits formed above large-scale hydrothermal systems which operated in the oceanic lithosphere. At the same time deep drilling and dredging in the areas of ocean floor spreading of the East Pacific and North Atlantic identified the presence of such systems operating in present-day crust. These systems are characterised by metalliferous sediments over a wide area, thickened manganese encrustations (Scott et al., 1976; Natland and Rosendahl, 1979; Corliss et al., 1978; Grill et al., 1981) and abundant organic growth close to geothermal discharge points. Natland et al. (1979) suggest that the Galapagos sub-sea floor system is at least 30,000 years old and that water—rock ratios were initially low, leading to manganese poor sedimentation but subsequently increased to the stage of localised formation of the hydrothermal mounds of manganese-rich material.

The close similarity between the tectonic settings of exposed fossil ore depositing systems of Cyprus and Newfoundland and of the East Pacific, and North Atlantic spreading centres may have led to the anticipation of the discovery of actively forming Cyprus-type ore bodies and one of the most exciting recent developments in ore deposition geochemistry has been the direct observation of active sulphide-depositing vents (black 'smokers') by deep diving on the East Pacific Rise (lat. 21°N) (Franchetau et al., 1979; Hekinian et al., 1980). Water temperatures in the vents exceed 350°C. In the Galapagos Rift, vents of similar chemistry but lower discharge temperature ($\sim 10°C$) occur, perhaps indicative of greater dilution and sub-sea floor ore deposition (Corliss, 1979). Studies to date have confirmed the strong analogies between these active ore-depositing systems and the Cyprus-type ore deposits while highlighting certain important distinctions, such as the size and rate of destruction by oxidation, which may infer that the Cyprus ores owe their preservation to their scale and this in turn to relatively faster spreading rates during their formation (East Pacific Rise Study Group, 1981). Discussion also focusses on whether the ore metals are leached by convecting seawater or whether this medium actually intersects sulphide segregations in shallow magma chambers.

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