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# Summary of Section III

## Geochemical Techniques in Exploration

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### INTRODUCTION

Considerable advances have been made in the knowledge of the chemistry of geothermal fluids in the five years between the first and second United Nations Geothermal Symposia held in Pisa (1970) and San Francisco (1975). At the Pisa Symposium, Donald E. White reviewed the entire field of geothermal geochemistry. He emphasized the distinction between hot-water and vapor-dominated geothermal systems and carefully reviewed the application of quantitative and qualitative geothermometers to each type of system. Geothermal chemistry was also recently reviewed by Sigvaldason (1973), Ellis (1973, 1975), and Mahon (1973). In reporting on fluid chemistry papers from the San Francisco Symposium, I shall build on these earlier reports and include Symposium papers and abstracts with geochemical data, as well as some recent papers not submitted to the Symposium. The literature in this field is expanding so rapidly that some worthy papers were probably missed.

Geothermal fluid chemistry finds its widest application in exploration, and it is this aspect that will be stressed in this report. Recent exploration activities have resulted in new chemical data on thermal fluids from springs and wells in Afars and Issas, Canada, Chile, Columbia, Czechoslovakia, El Salvador, Ethiopia, France, Greece, Guadeloupe, Hungary, Iceland, India, Indonesia, Israel, Italy, Japan, Kenya, Mexico, New Britain, New Zealand, the Philippines, Poland, the Red Sea, Rhodesia, Swaziland, Switzerland, Taiwan, Turkey, the United States, the USSR, and Yugoslavia. New methods for estimating subsurface temperatures have been proposed based on chemical and isotopic analyses of surface and well discharges. Chemical indices based on trace constituents of spring fluids and deposits, altered rocks, soils, and soil gases have been proposed as aids to geothermal exploration. Chemical models of interaction of geothermal fluids with reservoir rocks have been constructed. Studies of alteration in geothermal systems have aided exploration and exploitation. Finally, studies of geothermal rare gases suggest that although most are atmospheric in origin, excess  $^3\text{He}$  in some systems may come from the Earth's mantle.

Although not covered in this report, chemical studies also assist in the exploitation of geothermal resources. Analyses of produced fluids indicate subsurface temperatures and production zones. Problems of scale deposition, corrosion of piping, and disposition of environmentally harmful chemical substances in geothermal fluids have been studied and

solved in some applications. Plans continue for the recovery of valuable chemicals from geothermal fluids.

### CHEMICAL COMPOSITION OF FLUIDS

Summaries of analytical data on selected thermal spring and well discharges, indicated geothermometer temperatures, and references to data sources are presented in Table 1. Most data are from papers submitted to this Symposium. The classification of geothermal system type in Table 1 is based on the assumed genesis of their anomalous heat and follows, in a general way, classifications proposed by Mahon (p. 755), Arnórsson (1974), Ivanov (1967), Kononov and Polak (p. 767), and White (1970). Volcanic systems (where the heat sources are inferred to be recent igneous intrusions) dominated by hot water or steam are distinguished from nonvolcanic systems in which the heat source is normal or elevated regional heat flow and the waters are heated by deep circulation along faults or by their position in broad downwarped sedimentary basins. There are many chemical studies of volcanic geothermal systems because these are most easily exploited with current technology; fault-related and sedimentary systems are poorly understood chemically, although these may yield large quantities of heat for non-electrical uses. Additional data on nonvolcanic geothermal systems may be found in the Proceedings of the Symposium on Water-Rock Interactions held in Prague in 1974 (Čadek, 1976). Because of their distinctive and relatively uniform chemistry, I have treated seawater systems separately and discussed them in a special section.

### Mahon's Classification

Mahon (p. 775) characterizes geothermal fluids as originating from volcanic and subvolcanic geothermal systems, which may be either water or steam systems, and from nonvolcanic geothermal systems. Volcanic water systems are usually characterized at depth by waters of the neutral sodium chloride type which may be altered during passage to the surface by addition of acid sulfate, calcium, or bicarbonate components. The concentration of chloride may range from tens to tens of thousands of ppm. The origin of the water itself is dominantly meteoric, and the concentrations of readily soluble components such as Cl, B, Br, Li, Cs, and As are related to their concentrations in the rock, to the subsurface temperature, and possibly to

contributions from deep fluids related to the volcanic heat source. Other less soluble constituents such as  $\text{SiO}_2$ , Ca, Mg, Rb, K, Na,  $\text{SO}_4$ ,  $\text{HCO}_3$ , and  $\text{CO}_3$  are controlled by subsurface temperature, mineral solubility, mineral equilibria, and pH. Gases in these systems normally include  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2$ , and inert gases, with  $\text{CO}_2$  predominant, and constitute 0 to 5% by weight of the deep fluid.

The near-surface fluids of volcanic steam (vapor-dominated) systems are low in chloride (except for fundamentally unrelated high-temperature volcanic fumaroles with HCl). They contain only elements soluble in some form in low-pressure steam ( $\text{SO}_4$  as  $\text{H}_2\text{S}$ ,  $\text{HCO}_3$  as  $\text{CO}_2$ , B as  $\text{HBO}_2$ , Hg,  $\text{NH}_3$ ). The gases are similar to those in volcanic water systems. Because of their relative rarity and because vapor rather than liquid is produced (although liquid may predominate at depth), the geochemistry of these systems is not well understood.

Nonvolcanic geothermal systems have a wide range of water compositions and concentrations, from dilute meteoric waters to connate waters, metamorphic waters, and oil field brines. The controls on their compositions are less well known than those of volcanic waters.

### Arnórsson's Classification

Arnórsson (1974) classifies Icelandic thermal fluids as related to (1) temperature, (2) rock type, and (3) influx of seawater. Low-temperature waters ( $<150^\circ\text{C}$ ) are the result of deep circulation in regions dominated by conductive heat flow (up to 4 to 5 hfu, which is above average for most of the world) and are characterized by low dissolved solids contents (200 to 400 ppm) and gases dominated by nitrogen. Higher temperature waters ( $>200^\circ\text{C}$ ) result from intrusions of igneous rocks and are characterized by higher dissolved solids contents (700 to 1400 ppm) and by gases with large amounts of  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_2$ . Fluids in silicic rocks tend to be higher in Cl and other dissolved solids than fluids of the same temperature in basaltic rocks if seawater is not involved.

### Classifications of Ivanov and Kononov and Polak

Ivanov (1967) proposed a classification of thermal fluids based on gas contents, which has been expanded by Kononov and Polak (p. 767). Fluids directly related to volcanic processes are characterized either by  $\text{H}_2\text{S}$ - $\text{CO}_2$  gases and acid sulfate or acid sulfate-chloride waters in the oxidizing zone, or by  $\text{N}_2$ - $\text{CO}_2$  gases and alkaline sodium chloride waters in the reducing zone. Fluids related to thermometamorphic processes have high  $\text{CO}_2$  gases and carbonated waters, which may in part be connate. Fluids of deep circulation but outside of volcanic and thermometamorphic zones have  $\text{N}_2$  gases and dilute sodium chloride-sulfate waters. Kononov and Polak further divide volcanic fluids into "geyseric" with  $\text{H}_2$ - $\text{CO}_2$  gases and "riftogenic" with  $\text{H}_2$  gases, which occur in spreading centers and characterize the highest temperature ( $>300^\circ\text{C}$ ) geothermal systems. It is only in "riftogenic" fluids that anomalous contents of  $^3\text{He}$  and  $\text{H}_2\text{S}$  with  $\delta^{34}\text{S}$  near zero are expected. Parts of this classification are applied in detail to Icelandic thermal fluids by Arnórsson, Kononov, and Polak (1974).

Although this classification may need modification based on the chemistry of fluids in drilled systems, it has the advantage of focusing attention on geothermal gases, which

deserve more study. The occurrence of excess  $^3\text{He}$  in the hydrothermal fluids of Kamchatka (Gutsalo, p. 745), Lassen, and Hawaii (Craig, 1976) and of Yellowstone  $\delta^{34}\text{S}$  values near zero (Schoen and Rye, 1970) suggests these fluids are "riftogenic" when, in fact, they are far from present spreading centers.

### Classifications of White

Reviews by D. E. White of mineral and thermal water chemistry (1957a, b, 1968, 1970, 1974) have greatly influenced most workers in this field. Space does not allow adequate description of his water classification schemes, which have evolved as more chemical and isotopic data became available. In brief, *meteoric* waters dominate shallow crustal circulation and mix with more saline deep waters of all types. Meteoric waters may also circulate deeply under the influence of magmatic heat and receive additions of NaCl,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and other substances from rock leaching, thermal metamorphism, and possibly magmatic fluids. These moderately saline sodium chloride deep waters of *volcanic* association undergo near-surface rock reactions and atmospheric oxidation to form the range of observed surface volcanic waters. *Oceanic* water is incorporated in marine sediments and, by extended low-temperature reactions, becomes *evolved-connate* water. Deep burial and higher-temperature reactions cause expulsion of highly altered *metamorphic* waters from rocks undergoing regional metamorphism. *Magmatic* water has been dissolved in magma but may have various ultimate origins. The existence of *juvenile* water new to the hydrologic cycle is certain, but its recognition is doubtful. Recent work by White and his coworkers has elaborated the chemical distinctions between hot-water and vapor-dominated systems (White, Truesdell, and Muffler, 1971; Truesdell and White, 1973) and demonstrated the existence of thermal water of nonmeteoric origin in the California Coast Ranges (White, Barnes, and O'Neil, 1973).

## VOLCANIC HOT-WATER SYSTEMS

### Deep Fluids

Hot-water geothermal systems with volcanic heat sources have been very thoroughly studied. The deep fluids of these systems are, in general, waters of dominantly meteoric origin with chloride contents of 50 to 3000 ppm, unless seawater, connate water, or evaporites are involved. Components of these fluids, such as Na, K, Ca, Mg, and  $\text{SiO}_2$ , that are present in major amounts in most volcanic reservoir rocks almost certainly originate from rock-water reactions. Other fluid components, such as Cl, F, B,  $\text{CO}_2$ , and  $\text{H}_2\text{S}$ , are present in these rocks only in trace quantities and have been explained as magmatic contributions (Allen and Day, 1935; White, 1957a). Experimental rock-leaching studies (Ellis and Mahon, 1964, 1967) have shown, however, that these soluble components may be extracted from most rocks at moderate temperatures (200 to  $300^\circ\text{C}$ ), and isotope studies (see below) have failed to detect magmatic water in geothermal systems. Rock leaching as a sole source of chloride has been criticized by White (1970) because it appears to require unreasonable rock volumes or unreasonable original rock chloride contents to maintain the chloride flux of old geothermal systems, such as Steamboat Springs, Nevada (age 1 to 3 m.y.; Silberman and White, 1975), or Wairakei,

New Zealand (age 500 000 years; Banwell, 1963; Healy, p. 415, suggests half this figure).

Recent isotope studies of fresh and altered Wairakei rocks suggest that the apparent water:rock mass ratio of drilled parts of this system is at least 4.3:1 (Clayton and Steiner, 1975). Since the Cl contents of possible rocks at depth in this system are less than 1000 ppm (Ellis and Mahon, 1964), a mechanism other than simple leaching would appear necessary to produce the 1400-ppm-Cl Wairakei deep water. More probably, however, the rock leached of chloride was at much deeper levels as in the deep reservoir hypothesized by Hochstein (Abstract I-16) and at those levels the water:rock ratio was much lower. However, a lower water:rock ratio requires a larger volume of rock which, if the predrilling flux of chloride ( $2.5 \times 10^{10}$  g/year; Ellis and Wilson, 1955) has been maintained over the life of the system, requires more than  $5 \times 10^3$  km<sup>3</sup> of leached rock; this is more than ten times the possible volume of the system estimated by Hochstein (Abstract I-16). To resolve this problem, Wilson (1966) and Ellis (1966) suggested that flow in geothermal systems is intermittent and that present activity is much greater than that of the past. Ellis (1970) suggests this cycle might have a period of  $10^5$  years with the active part of the cycle complete in  $10^3$  years. Experimental and model studies of nonuniformly heated fluid in porous media by Horne and O'Sullivan (1974) produced intermittent flow, which may support this suggestion. However, the numerous dormant geothermal systems (99% of the total) required by this model would be easily recognizable by fossil sinter deposits and have not been found.

The efficacy of rock leaching as a source of dissolved constituents in geothermal waters must depend on the availability of fresh rock surfaces. Heat transfer and leaching from established fractures should be rapid, and solute concentrations and temperatures would be expected to decrease rapidly. This may not occur because the growth of thermal stress fractures (Harlow and Pracht, 1972; Smith et al., 1973; Lister, Abstract II-27) would provide fresh rock surfaces and heat transfer at the same rate so that the chemical and thermal properties of convecting fluids would be uniform in time. Studies of fluid inclusions from Broadlands, New Zealand, suggest that changes of fluid concentration and temperature may have been small over the  $10^5$ -year life of this system (Browne, Roedder, and Wodzicki, 1976). Careful chemical and physical modeling is needed to further test the rock-leaching hypothesis.

The opposite hypothesis, that small quantities of magmatic fluids of high salinity supply a significant part of geothermal solutes, has been defended by White (1957a, 1970). Recent fluid inclusion and isotopic studies (reviewed by White, 1974; see also later issues of *Economic Geology*) indicate that two fluids were involved in the generation of many ore deposits. Initial fluids of porphyry copper, epithermal base metal, and other ore deposits were probably magmatic in origin, and later fluids were local meteoric waters. However, magmatic waters have not yet been positively identified in epithermal gold-silver deposits, which are most closely related to active geothermal systems. The presence of mantle-derived <sup>3</sup>He in geothermal fluids (Kononov and Polak, p. 767; Gutsalo, p. 745; and Craig, 1976) may not indicate direct contribution of other juvenile or even magmatic components because of the possibility that helium may migrate independently of other fluids or may be contained in some volcanic rocks (Lupton and Craig, 1975)

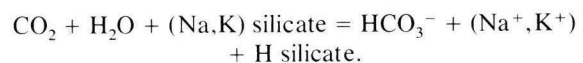
and enter geothermal fluids from rock leaching.

Perhaps the most persuasive evidence for the participation of at least small amounts of magmatic components in geothermal fluids is the close temporal and spatial relation and analogous geochemical behavior of certain volcanic and geothermal systems. The volcanic zone in Taupo, New Zealand, with numerous geothermal systems, has the active volcanoes of White Island at its north end and Ruapehu and Ngauruhoe at its south end. Chemical studies of White Island have shown that fumarole discharges alternate between typical high-temperature (to 800°C) volcanic emanations with high sulfur:carbon ratios when flows of volcanic gases are not impeded, and nearly typical geothermal steam at temperatures below 300°C with low sulfur:carbon ratios when the gases are forced to pass through surface waters (Giggenbach, 1976). Some fluids of geothermal systems associated with near-active volcanoes of the Tatun Shan, Taiwan (Chen and Chern, written commun., 1975) and of Tamagawa (Iwasaki et al., 1963) and Hakone (Noguchi et al., 1970), Japan, may be similar to the drowned volcanic emanations of White Island. Hydrolysis of sulfur or near-surface oxidation of H<sub>2</sub>S cannot produce the HCl acidity proven at Hakone and Tamagawa and indicated at Tatun (analysis Ta 1, Table 1, from New Zealand Dept. Sci. Ind. Res., quoted by Chen and Chern) which must originate from high-temperature, probably magmatic, processes (White and Truesdell, 1972; R. O. Fournier and J. M. Thompson, unpub. data). Magmatic fluid contributions to these geothermal systems appear probable, but proof is lacking. More work is needed on this problem, possibly through more extensive isotopic studies of elements dissolved in geothermal waters. However, fractionation during crystallization and re-solution of trace constituents is expected to be small, so leached material may be indistinguishable from direct magmatic contributions.

### Near-surface Alteration of Hot Waters

Near-surface processes producing the varied compositions of geothermal waters of volcanic systems include steam separation during adiabatic cooling, mixture with cold shallow meteoric waters, and chemical reactions involving rock minerals, dissolved gases, dissolved constituents of diluting waters, and atmospheric gases. Many indicators of subsurface flow (see below) depend on the effects of these processes on ascending geothermal fluids. Fluid component ratios that are not affected by these processes, such as Cl:B, are useful in indicating the homogeneity of subsurface fluids and thus the continuity and size of geothermal systems (Stefánsson and Arnórsson, p. 1207; Cusicanqui, Mahon, and Ellis, p. 703).

Subsurface reactions with dissolved gases and rock minerals control the contents in the water of most components present in excess in the rock or in the dissolved gas. Most of the bicarbonate and part of the sodium and potassium are produced by reaction of dissolved CO<sub>2</sub> with the rocks to produce mica or clay minerals and bicarbonate and alkali ions (Fournier and Truesdell, 1970),

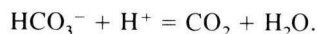


The coupled increase in HCO<sub>3</sub>:Cl and decrease in CO<sub>2</sub>:other gases during lateral flow through a near-surface aquifer has

been demonstrated for Shoshone Geyser Basin, Yellowstone (analysis US30), where near-surface rocks are glacial sediments composed of rhyolitic glass (Truesdell, 1976a). Crystallized rhyolite and ash flow tuff are not as reactive as glassy rocks, so  $\text{CO}_2$  is converted to  $\text{HCO}_3^-$  less rapidly, as at Norris Geyser Basin, Yellowstone, where waters flowing in devitrified ash flow tuff are low in  $\text{HCO}_3^-$  (analysis US34).

Mixture of deep hot water with cold meteoric waters produces variations in the concentrations (but not the ratios) of Cl, B, and other components not involved in lower-temperature rock reactions. The resulting temperatures in subsurface aquifers where mixture takes place (Truesdell and Fournier, p. 837) affect all temperature-sensitive equilibria such as quartz solution and exchange of dissolved cations with aluminosilicate minerals. With sufficient dilution, subsurface boiling may be prevented and a high partial pressure of  $\text{CO}_2$  retained in waters at temperatures well below  $200^\circ\text{C}$ . Under these conditions, the solubility of calcite is relatively high (Holland, 1967) and calcium can be leached from volcanic rocks. When these dilute high  $P_{\text{CO}_2}$ -high Ca solutions emerge at the surface, they lose  $\text{CO}_2$  and deposit travertine as well as silica.

Steam separation produces changes in water chemistry because most salts are nearly insoluble in low-pressure steam (Krauskopf, 1964) and remain entirely in the liquid phase, while gases partition strongly into the vapor (Ellis and Golding, 1963; Kozintseva, 1964). The result of these processes is an increase in nonvolatile salts and a decrease in dissolved gases (principally  $\text{CO}_2$  and  $\text{H}_2\text{S}$ ) in the liquid phase. The loss of gas produces an increase in pH from about 6 at depth to near 9 at the surface (Ellis, 1967; Truesdell and Singers, 1971) through the reaction



The effect of  $\text{CO}_2$  loss is greatest in waters with large contents of bicarbonate such as those from Shoshone Geyser Basin, Yellowstone (analysis US30) or Orakeikorako, New Zealand (analysis NZ7), so these waters become very alkaline whereas waters with little bicarbonate (for example Norris waters, analysis US34) remain near neutral.

Sulfate can originate from oxidation of  $\text{H}_2\text{S}$  by atmospheric oxygen dissolved in meteoric water of deep or shallow circulation. The amount of sulfate ion that can be formed in this manner is 22 ppm from rain water percolating underground after equilibrating with air at  $0^\circ\text{C}$  (Truesdell, 1976). This is close to the observed sulfate contents in water not affected by near-surface oxidation of  $\text{H}_2\text{S}$  in volcanic rocks with low sulfate contents, such as those in the Yellowstone caldera (analyses US29-34) and the Taupo volcanic zone (analyses NZ1-10). Higher contents of sulfate in volcanic hot water probably originate from leaching of sulfate contained in some volcanic rocks. Sulfate in low-temperature waters in basalts probably has this source (analyses Ic 1-3). In high-temperature areas the self oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{S}$  and  $\text{SO}_4$  must also be considered. The sulfate contents of thermal waters in sedimentary aquifers are usually much higher as a result of solution of sedimentary sulfate from the rock (for example Kızıldere, Turkey, analyses T1-2).

Acid waters with very high sulfate contents are produced by direct superficial atmospheric oxidation of  $\text{H}_2\text{S}$  to sulfuric acid in areas of drowned fumaroles or steaming ground

(White, 1957b). The acid-sulfate-chloride waters at Waimangu, New Zealand, and Norris, Yellowstone, probably result from percolation of this acid sulfate water into near-surface reservoirs where it mixes with chloride water from below. The change from deep, slightly acid chloride waters, to neutral  $\text{Cl-HCO}_3^-\text{SO}_4$  waters, to acid sulfate waters with decreasing depth in the Onikobe caldera has been described by Yamada (p. 665).

## Roots of Volcanic Hot Water Systems

Knowledge of the deepest parts of geothermal systems must come chiefly from refined geophysical studies and from fossil geothermal systems exposed by erosion; but experimental studies of the thermodynamic chemistry of water and rock minerals provide important constraints for modeling.

From chemical and isotopic compositions of surface fluids and the phase chemistry of water and silica, Truesdell et al. (Abstract III-87) have proposed that a 3- to 6-km-deep reservoir of dilute (1000 ppm NaCl) water at  $340$  to  $370^\circ\text{C}$  underlies much of Yellowstone. This reservoir may correspond to the deep (also 3 to 6 km) reservoir proposed by Hochstein (Abstract I-16) on geophysical evidence to underlie the Taupo volcanic zone, New Zealand. Fournier, White, and Truesdell (p. 731) proposed that the solubility maximum of quartz (at  $340^\circ\text{C}$  for dilute steam-saturated water; increasing with salinity and, to a lesser extent, pressure) acts as a thermostatic mechanism for deep waters because circulation to higher temperatures would cause rapid quartz deposition and permeability decrease. Circulation of fluids through the zone of quartz solubility maximum should produce additional porosity by solution.

## STEAM (VAPOR-DOMINATED) SYSTEMS

Certain geothermal systems (Larderello and Monte Amiata, Italy; The Geysers, California; Matsukawa, Japan; Mud Volcano, Yellowstone; and others) are characterized by production of saturated or slightly superheated steam without liquid water. Despite intensive search, few examples of this type of system have been found. Two new discoveries, the Kawah Kamojang and Salak fields of Indonesia, have been reported to this Symposium and another likely candidate has been identified in Mt. Lassen National Park, California (Renner, White, and Williams, 1975).

Although known systems have been intensively drilled, the character of the reservoir fluid, the mechanism of steam production, and the origin of these systems have been highly controversial and at least seven major models have been proposed. The latest of these models (White, Muffler, and Truesdell, 1971) has utilized the chemistry of superficial fluids and deep pressure and temperature measurements to conclude that both steam and water are present in these reservoirs. The model was elaborated and the mechanism of superheated steam production explained in a later paper (Truesdell and White, 1973).

New data on the Kawah Kamojang, Indonesia, field (Hochstein, p. 1049; Kartokusumo, Mahon, and Seal, p. 757) indicate that it is vapor dominated. Drillholes to 600 m showed the reservoir temperature below 550 m (390 m below the water table) to be  $238^\circ\text{C}$ , close to that of steam of maximum enthalpy ( $236^\circ\text{C}$ ), as predicted for these systems (James, 1968). Production initially was a steam-water mixture

that changed to saturated steam and finally superheated steam. Surface drainage and borehole fluids are nearly chloride-free (<2 ppm in hot waters; 3 to 6 ppm in drainage waters), as expected in a system with only steam flow from depth. The resistivity to 500-m depth is 2 to 5 ohm·meters, indicating a near-surface water-saturated zone above the reservoir. Deeper resistivity is >10 ohm·meters, probably indicating the presence of steam. This resistivity structure is similar to that found in the vapor-dominated Mud Volcano, Yellowstone, geothermal system (Zohdy, Anderson, and Muffler, 1973). Deeper drilling is needed at Kawah Kamojang to confirm the presence of the predicted low "vapostatic" pressure gradient. The Salak, Indonesia, field is also considered to be vapor dominated, as indicated by surface fluid chemistry (Kartokusumo and Seal, Abstract III-49).

Isotope chemistry of Larderello, Italy, steam has shown that increased production has drawn fluids from recent inflow at the sides of the reservoir and from deeper levels in the center (Celati et al., 1973; Panichi et al., 1974). Marginal inflow was also indicated by a hydrologic balance (Petracco and Squarci, p. 521). Steam from the central area has been shown to carry up to 60 ppm chloride associated with ammonia and boron (F. D'Amore, oral commun., 1975), which may indicate boiling from a high-chloride brine water table. Reassessment of original pressures of this system has indicated that, in general, they conform to the vapor-dominated model (Celati et al., p. 1583).

## NONVOLCANIC HOT-WATER SYSTEMS

Earth temperatures increase generally with depth, and although most normal thermal gradients average 25°C/km, there are broad regions where thermal gradients are 40 to 75°C/km or higher (White, 1973). In these regions, hot water may be exploited by drilling in sedimentary basins or along fault zones where deep circulation occurs. Chemical data on these waters are sparse, but thermal water in sedimentary basins appears similar to nonthermal waters in similar geologic situations. The fault-controlled waters are similar to, but more dilute than, volcanic waters. The recent review of the chemistry of subsurface water by Barnes and Hem (1973) may be useful.

Examples of thermal systems that are considered nonvolcanic in Czechoslovakia, France, Iceland, India, Israel, Japan, Switzerland, Turkey, the United States, and Yugoslavia are given in Table 1. The waters of the Pannonian and related sedimentary basins of Czechoslovakia, Hungary, and Yugoslavia appear to be crudely zoned, with bicarbonate predominating near the top of the aquifer and chloride at greater depths (for example analysis Cz1; Franko and Mucha, p. 979; Boldizsár and Korim, p. 297; Petrović, p. 531). Waters in carbonate aquifers (analysis H1, Y2?) have relatively high contents of bicarbonate, calcium, and magnesium as might be expected, and gases appear to contain more CO<sub>2</sub> than in sandstone aquifers, which have more nitrogen. Methane is also present. Sedimentary basins in Russia are reported to yield water at 40 to 105°C with 1 to 10 g/l salinity at depths of 2500 to 3000 m without further chemical data (Mavritsky and Khelkvist, p. 179). More studies are needed on thermal waters of sedimentary basins.

Waters heated by deep circulation along faults may be very dilute with only atmospheric dissolved gases if their temperatures are low (analysis US4) and become much more concentrated with more CO<sub>2</sub> and H<sub>2</sub>S as their subsurface

temperatures approach those of volcanic systems (analysis US26 for example). The water source is meteoric and salts are probably leached from rock, although evaporites may be associated with some fault-heated waters. Wollenberg (p. 1283) suggests that uranium may accumulate at depth in some of these systems owing to reducing conditions.

## SEAWATER GEOTHERMAL SYSTEMS

Many geothermal systems in coastal areas have remarkably similar thermal fluids which are mixtures of local meteoric waters and thermally altered seawater. The effect on seawater of high temperature reaction with rock is marked increase in calcium and smaller increase in potassium and occasionally chloride, with marked decreases in magnesium, sulfate, and bicarbonate, and often a smaller decrease in sodium. These changes are apparently due to formation of montmorillonite, chlorite, and albite from calcic feldspars, which releases calcium and causes consequent precipitation of anhydrite and calcite (Mizutani and Hamasuna, 1972; Bischoff and Dickson, 1975). The salinity is affected by dilution and subsurface boiling. Chemical and isotopic studies have shown the presence of altered seawater in coastal thermal areas of Fiji (Healy, 1960), Greece (analyses G1-7; Dominco and Papastamatoki, p. 109; Stahl, Aust, and Dounas, 1974), Guadeloupe (analysis Gu1; Demians d'Archimbaud and Munier-Jolain, p. 101), Iceland (analyses Ic7-10; Björnsson, Arnórsson, and Tómasson, 1972; Arnórsson, 1974; Arnórsson et al., p. 853), Israel (analysis Is1; Eckstein, p. 713), Italy (analyses It1-2; Baldi, Ferrara, and Panichi, p. 687), Japan (analyses J1-2; Mizutani and Hamasuna, 1972; Matsubaya et al., 1973; Sakai and Matsubaya, 1974), New Britain (analysis NB1; Ferguson and Lambert, 1972), New Zealand (Crafar, 1974; Skinner, 1974), and Turkey (analyses T3 and T6; Kurtman and Şamilgil, p. 447). The composition of normal seawater is given in Table 1 for comparison (analysis SW1).

The application of chemical and isotopic geothermometers to seawater thermal fluids has some unusual features. Silica geothermometers apparently behave normally, but may reequilibrate more rapidly upon cooling because of the high salinity, thus indicating lower temperatures (Fournier, 1973). Cold seawater and partly altered seawater in low-to-moderate-temperature thermal systems indicate anomalously high temperatures, near 100°C from Na:K and 170°C from Na:Ca. The sulfate-water isotope geothermometer also indicates temperatures near 180°C for cold and partially altered seawater. These high-temperature indications may be relics of partial equilibration in submarine geothermal convection systems located along spreading centers (Lister, p. 459; Williams, Abstract I-40), with the seawaters resisting reequilibration in moderate-temperature coastal geothermal systems because of insufficient rock alteration to affect their high ion contents. Seawater-rock interaction experiments now in progress (Hajash, 1974; Mottl, Corr, and Holland, 1974; Bischoff and Dickson, 1975) will provide more data on this problem and may suggest new geothermometers for these systems. Where thermal seawaters have higher chlorinities than local seawaters and there is no evidence of evaporite contribution, I have calculated the subsurface temperatures required to produce the observed concentrations by boiling (analyses G7, Ic7, NB1, and T6). The indicated subsurface temperature of the Reykjanes, Iceland, seawater geothermal system agrees with that ob-

served. Chloride leached from rocks and conductive heating would tend to increase apparent temperatures and mixing with dilute waters would tend to lower them.

## GEOOTHERMOMETERS

Where fluids from geothermal convection systems reach the surface in springs or wells, the chemical and isotopic compositions of these fluids may indicate the subsurface temperature and flow patterns, as well as the recharge source, type of reservoir rock, and other important parameters of the system. Component concentrations or ratios that can be related to subsurface temperatures are called geothermometers. Chemical geothermometers may be quantitative, so that specific subsurface temperatures may be calculated, or qualitative, so that only relative temperatures may be inferred. Important advances in the application of quantitative and qualitative geothermometers have been made since the first UN Geothermal Symposium in Pisa in 1970.

### Quantitative Chemical Geothermometers

The theory of quantitative chemical geothermometers has been discussed by Fournier, White, and Truesdell (1974). These thermometers depend on the existence of temperature-dependent equilibria at depth which are quenched or frozen during passage to the surface.

At the time of the Pisa Symposium (1970), the quartz-saturation geothermometer (Mahon, 1966; Fournier and Rowe, 1966), which depends on the near-universal equilibrium with quartz in geothermal fluids above 100 to 150°C, and on the relative reluctance of quartz to precipitate from supersaturated solutions, was widely used in exploration and in monitoring well discharges. Temperatures above 200 to 230°C are seldom indicated by this geothermometer from spring analyses because reequilibration above 200°C is relatively rapid and solutions initially saturated with quartz at higher temperatures can precipitate amorphous silica during passage to the surface (Fournier, 1973; Truesdell and Fournier, p. 837). Lower-temperature waters may be saturated with chalcedony rather than quartz (Fournier and Truesdell, 1970), with some Icelandic waters suggesting chalcedony saturation at temperatures as high as 180°C and others suggesting quartz saturation as low as 110°C (Arnórsson, 1970, 1974, 1975). Examples of many thermal waters with probable quartz or chalcedony saturation are given in Table 1, and equations (data from Fournier, 1973, 1976) for quartz saturation with conductive and adiabatic (maximum steam loss) cooling and for chalcedony saturation are given in Table 2. Adiabatic cooling is probably most common in high-temperature geothermal systems (M. Nathenson, unpub. calculations), but loss of silica from reequilibration during upward flow may make conductive quartz temperatures appear to indicate reservoir temperatures more accurately (White, 1970). Systems with both adiabatic and conductive cooling have been discussed by Fournier, White, and Truesdell (p. 731).

The other geothermometer widely used 5 years ago was the Na:K ratio. The empirical calibration of this geothermometer does not agree with experimental studies of feldspar and mica equilibria, and in 1970 there was wide divergence between calibration scales. Syntheses of available data (mostly from the Pisa Symposium) by White and Ellis (quoted in White, 1970) and by Fournier and Truesdell (1973) have

produced two slightly different scales, which are approximated by equations given in Table 2. Since the White-Ellis curve is more widely used, it has been adopted for calculations in Table 1.

Because the Na:K geothermometer fails at temperatures below 100 to 120°C and yields improbably high temperatures for solutions with high calcium contents, an empirical Na:K:Ca geothermometer was proposed by Fournier and Truesdell (1973). Na:K:Ca temperatures have been found to be closer to quartz-saturation temperatures for thermal springs of Nevada by Hebert and Bowman (p. 751), but Na:K temperatures appear to be equally accurate for 200 to 300°C low-calcium well discharges (Table 1), and may correctly indicate fluid temperatures and movement in drilled systems (Mercado, p. 487).

The cation (Na:K and Na:K:Ca) geothermometers are useful in initial evaluations of the geothermal potential of large regions because they are less affected by reequilibration and near-surface dilution than are the silica geothermometers. Cation geothermometers have been used in regional evaluations in Canada (Souther, p. 259), Iceland (Stefánsson and Arnórsson, p. 1207), India (Krishnaswamy, p. 143; Gupta, Narain, and Gaur, p. 387), Israel (Eckstein, p. 713), Italy (Fancelli and Nuti, 1974), the Philippines (Glover, 1974a, b, 1975), and the United States (Young and Mitchell, 1973; Swanberg, 1974, 1975; Mariner et al., 1974a, b; Renner, White, and Williams, 1975; Reed, 1975).

Cation geothermometers, although empirical, apparently depend on equilibria between thermal waters and aluminosilicate minerals original to the host rock or produced by alteration. If equilibrium is not achieved, or if the mineral suite is unusual, misleading temperatures may be indicated. Thus, cation geothermometers must be used with caution in geothermal systems involving seawater, because in many of these, equilibrium with rocks probably is not reached because of the resistance to chemical change of the concentrated solution; and apparent temperatures are close to those indicated by cold seawater (analysis SW 1— $t_{\text{Na:K}}$ , 100°C and  $t_{\text{Na:K:Ca}}$ , 170°C). However, in some high-temperature geothermal systems, seawater does appear to have nearly equilibrated with rock and indicated temperatures are close to those observed in drillholes (analyses Ic 7-9; analyses J1-2). Acid sulfate springs in which silica and cations are leached from surface rocks are not suitable for chemical geothermometry, although acid sulfate chloride waters of deep origin give reasonable indicated temperatures (analyses J12, Ta1-2). Cation (and silica) geothermometers may also give misleading results when applied to waters in highly reactive volcanic rocks (Fournier and Truesdell, 1970; Baldi et al., 1973; Arnórsson, 1975), especially those rocks with high contents of potassium (Calamai et al., p. 305), or to warm waters that emerge in peat-containing soils (Stefánsson and Arnórsson, p. 1207). Paces (1975) has suggested a correction factor for the Na:K:Ca geothermometer when applied to high-CO<sub>2</sub> waters.

Although many other high-temperature chemical equilibria exist, most of these equilibria are affected by subsurface conditions other than temperature, reequilibrate rapidly, or are affected by other reactions during ascent to the surface. These equilibria can, however, be used as qualitative geothermometers (see below) and, in specialized circumstances, as quantitative geothermometers.

The content of magnesium in thermal waters varies inversely with temperature, but it is also affected by CO<sub>2</sub>

pressure. Experimental calibration by Ellis (1971) allows magnesium contents to be used as a quantitative geothermometer if  $\text{CO}_2$  pressures can be otherwise calculated.

Waters with high calcium and sulfate and low bicarbonate contents, such as thermally altered seawater (see discussion above), may be saturated with anhydrite at depth and become undersaturated during ascent because of the inverse temperature dependence of anhydrite solubility (analyses *J1-2*; Sakai and Matsubaya, 1974). The contents of calcium and fluoride in geothermal waters are in part controlled by equilibrium with fluorite (Nordstrom and Jenne, Abstract III-70), but reequilibration apparently is rapid.

The reaction  $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$  may occur in geothermal reservoirs (Craig, 1953; Hulston, 1964; but see Gunter and Musgrave, 1966, 1971), and the amounts of these gases in surface discharges may indicate subsurface temperatures. Temperatures calculated from Wairakei borehole gases (analysis *NZ1*; Hulston and McCabe, 1962a; Lyon, 1974) are reasonable, but Arnórsson et al. (p. 853) have applied this method to fumarole discharges with somewhat ambiguous results.

### Mixing Models

Although mixing of thermal waters with cold near-surface waters limits the direct application of chemical geothermometers, the dilution and cooling resulting from mixing may prevent reequilibration or loss of steam and allow the calculation of deep temperatures and chemical conditions. The chloride contents and surface temperatures of springs were used to calculate minimum subsurface temperatures in early New Zealand geothermal surveys (Mahon, 1970). More recently, models have been proposed based on surface temperature and silica contents of cold and warm springs (the warm spring mixing models in: Truesdell, 1971; Fournier and Truesdell, 1974; Truesdell and Fournier, 1976), and on the temperature, chloride, and silica concentrations of mixed boiling springs and the chloride concentrations and temperatures of cold springs and nonmixed boiling springs (the boiling spring mixing model in: Truesdell and Fournier, p. 837; Fournier, White and Truesdell, p. 731). A mixing model using chloride-enthalpy relations of cold, warm, and boiling springs was proposed by Glover (1974a) for Tongonan, Philippines, geothermal waters (analysis *Ph1*). Related diagrams of chloride and enthalpy (or temperature) have been used to analyze subsurface processes in drilled systems (Giggenbach, 1971; Mahon and Finlayson, 1972; Cusicanqui, Mahon, and Ellis, p. 703).

The warm spring mixing model depends on the assumption of conservation of enthalpy and silica and on the nonlinear temperature dependence of quartz solubility. The boiling spring mixing model depends on assumed conservation of chloride and enthalpy and reequilibration with quartz after mixing. Proper application of these mixing models depends therefore on the fulfillment of a number of assumptions, the validity of which should be considered in each case. Mixing model temperatures have been calculated for appropriate spring and well analyses in Table 1. The accuracy of mixing model calculations depends to a great degree on measurement or accurate estimation of the chemistry and temperature of local cold subsurface water. For these calculations, as well as for isotope hydrology (see below), collection and analysis of cold waters should be an important part of a geochemical exploration program. The warm spring

mixing model was applied by Gupta, Saxena, and Sukhija (p. 741) to the Manikaran, India, geothermal system and by Young and Whitehead (1975a,b) to Idaho thermal waters.

Components other than silica and chloride may be used in mixing models. The temperature and salinity of a hypothetical concentrated high-temperature component have been calculated by Mazor, Kaufman, and Carmi (1973) from  $^{14}\text{C}$  contents and by Mizutani and Hamasuna (1972) from sulfate and water isotopes (analyses *Is3* and *J1*).

### Qualitative Geothermometers

Qualitative geothermometers were reviewed at the first UN Geothermal Symposium by Mahon (1970), Tonani (1970), and White (1970). These geothermometers may be applied to spring waters and gases, fumarole gases, altered rock, soils, and soil gases. Ratios and contents of dissolved hot-spring constituents and gases resulting from high-temperature reactions, but not susceptible to quantitative temperature calculation, are useful for indicating subsurface flow paths when siting wells (Mahon, p. 775).

Substances carried in steam are important in the study of systems without hot springs and may indicate subsurface flow paths more effectively than liquid water discharges, which are more subject to lateral flow (Healy, p. 415; Healy and Hochstein, 1973). Gas discharges were used by Glover (1972) to indicate upflow zones in Kenya geothermal systems, where hot water discharges were lacking or grossly contaminated with surface waters. Gas ratios were also useful at El Tatio, Chile (Cusicanqui, Mahon, and Ellis, p. 703), where extensive lateral flow of hot water occurs (see discussion below). Ammonia and boron have been used as indicators in thermal seawaters which are otherwise unresponsive to subsurface temperature (Dominco and Papastamatoki, p. 109).

New studies using sensitive analytical methods have shown that soil gases in geothermal areas have anomalous concentrations of mercury (Koga and Noda, p. 761) and helium (Roberts et al., 1975), and contain  $\text{CO}_2$  with anomalously high  $^{13}\text{C}:^{12}\text{C}$  ratios (Rightmire and Truesdell, 1974). Volatile substances dispersed from geothermal fluids may accumulate in soils and altered rocks, and patterns of soil mercury (Matlick and Buseck, p. 785) and of mercury, arsenic, and boron in altered rocks (Koga and Noda, p. 761) may indicate subsurface fluid flow, as may alteration patterns (Sumi and Takashima, p. 625).

The most important application of qualitative geothermometers is in preliminary exploration over large areas. "Blind" convection systems may exist or surface fluid flows may be inconspicuous or difficult to distinguish from non-thermal sources. In these cases, it may be possible to analyze surface fluids for distinctive "geothermal" components. Lithium in surface waters of central Italy has been tested as a geothermal indicator by Brondi, Dall'Aglio, and Vitroni (1973); and, in a study of the same area, criteria for distinguishing river sulfate of geothermal origin (from  $\text{H}_2\text{S}$  oxidation) from sulfate resulting from solution of evaporites or from oxidation of sulfide minerals have been developed by Dall'Aglio and Tonani (1973). Much anomalous boron in surface waters (other than those in closed basins) is probably of geothermal origin (Morgan, 1976), and Larderello steam has been shown to contribute large quantities of boron to surficial waters (Celati, Ferrara, and Panichi, Abstract III-11). Anomalous arsenic from natural and exploited geo-



thermal systems has been found in the Waikato River, New Zealand (Rothbaum and Anderton, p. 1417), and in the Madison River, Montana (Stauffer and Jenne, Abstract IV-14). Fish in the Waikato River appear to accumulate mercury of geothermal origin (Weissberg and Zobel, 1973), but Yellowstone fish do not (L. K. Luoma and E. A. Jenne, oral commun., 1976).

Geothermal waters of meteoric origin may exchange oxygen isotopes with rock during deep circulation, and this "oxygen shift" has been used as a positive or negative qualitative geothermometer (Fancelli, Nuti, and Noto, Abstract III-23; Fouillac et al., p. 721).

Although sampling is difficult, gases and solids can also be used in regional exploration. In a reconnaissance study of much of central and southern Italy, Panichi and Tongiorgi (p. 815) found carbon isotopes in  $\text{CO}_2$ , and travertine associated with known and prospective geothermal areas, to be distinctly heavy compared with those from other sources. The use of other isotopes in regional exploration ( $^{34}\text{S}$  in air gases for instance) should be investigated. Mercury vapor has been found in the atmosphere of the Beppu, Japan, geothermal system (Koga and Noda, p. 761) and might be detectable in a regional survey.

## ISOTOPE HYDROLOGY AND THERMOMETRY

Isotope compositions and rare gas contents of geothermal fluids have been used to indicate sources of recharge, time of circulation, fluid mixing, and subsurface temperatures. Geothermal isotope and nuclear studies have been the subject of symposia at Spoleto, Italy (Tongiorgi, 1963), Dallas, Texas (Hall, 1974), and Pisa, Italy (Gonfiantini and Tongiorgi, 1976), and were extensively reviewed by White (1970, 1974). Many papers on nuclear hydrology with application to geothermal studies were recently presented at Vienna (International Atomic Energy Agency, 1974).

### Hydrology

A major discovery resulting from early measurements of the oxygen-18, deuterium, and tritium contents of thermal fluids was that local meteoric water overwhelmingly dominates recharge of most geothermal systems (Craig, Boato, and White, 1956; Craig, 1963; Begemann, 1963). More recent studies (reviewed by White, 1970) agree with the early data with a few exceptions. New  $^{18}\text{O}$ , deuterium and tritium measurements of cold and thermal fluids of Larderello, Italy, demonstrate local meteoric recharge with both long and short circulation times (Celati et al., 1973; Panichi et al., 1974). Meteoric water dominance has also been demonstrated for thermal fluids of El Tatio, Chile (Cusicanqui, Mahon, and Ellis, p. 703), Kawah Kamojang, Indonesia (Kartokusumo, Mahon, and Seal, p. 757), the Massif Central, France (Fouillac et al., p. 721), Iceland (Arnason, 1976; Tómasson, Fridleifsson, and Stefánsson, p. 643), Lake Assal, Afars and Issas (Bosch et al., 1976), Broadlands, New Zealand (Giggenbach, 1971), Yellowstone, Wyoming (Truesdell et al., Abstract III-87), Long Valley, California (Mariner and Willey, 1976), and southwestern Idaho (Rightmire, Young, and Whitehead, 1976). In most of these systems (El Tatio, Yellowstone, Iceland, Idaho, and Long Valley), hot-spring waters are a mixture of a local cold meteoric component and a hot thermal water component, also of meteoric origin but from higher elevation and somewhat distant from the hot-spring area.

Mixing of local cold water with hot seawater has been demonstrated by  $^{18}\text{O}$  and deuterium studies of coastal geothermal systems of Greece (Stahl, Aust, and Dounas, 1974), Italy (Baldi, Ferrara, and Panichi, p. 687), and Japan (Mizutani and Hamasuna, 1972; Matsubaya et al., 1973; Sakai and Matsubaya, 1974). Thermal connate and metamorphic waters were shown to mix with meteoric water in the California Coast Ranges by White, Barnes, and O'Neil (1973). Meteoric thermal waters are interpreted to mix with cold saline lake waters at Lake Assal, Afars and Issas, by Bosch et al. (1976), although the high salinity of borehole waters from this area (Gringarten and Stieltjes, 1976) suggests a more complicated system.

Tritium measurements have been used to demonstrate mixing with young near-surface waters. Gupta, Saxena, and Sukhija (p. 741), using this approach, calculate hot-water fractions for spring waters of Manikaran, India, that agree with those calculated from the warm-spring mixing model.

In general, radioactive isotopes have not been successful in indicating the circulation times of geothermal systems. This results from the generally long circulation times involved (except for some Larderello steam discussed above), which are usually beyond the range of tritium dating; from the large quantities of metamorphically produced old  $\text{CO}_2$ , which prevent use of  $^{14}\text{C}$  measurements; and from the common admixture of young near-surface waters with old deep waters in surface thermal discharges. Recent improvements in low-level tritium analysis may improve the situation. The radioactive  $^{39}\text{Ar}$  isotope has a half-life of 269 years, which allows a dating range of 50 to 1000 years, and has been used successfully to estimate a <70-year age for water in a Swiss thermal spring (Oeschger et al., 1974). This analysis, although difficult, should also be possible for drilled high-temperature geothermal systems.

### Geothermometry

Certain isotope geothermometers equilibrate more slowly than chemical geothermometers and are capable of indicating temperatures in the deeper parts of geothermal systems. By considering a number of chemical and isotopic geothermometers with various rates of equilibration, it may be possible to calculate the temperature history of a thermal water. This calculation would depend on the existence of considerably more rate data than are now available.

At the time of the first UN Geothermal Symposium, only the distribution of carbon isotopes between  $\text{CO}_2$  and  $\text{CH}_4$ , ( $\Delta^{13}\text{C}[\text{CO}_2, \text{CH}_4]$ ), had been tested as a geothermometer. Analyses of well discharges of Larderello (analysis It8; Ferrara, Ferrara, and Gonfiantini, 1963) and Wairakei (analysis NZ1; Hulston and McCabe, 1962b) indicated temperatures in good agreement with measured reservoir temperatures. These indicated temperatures were based on fractionation factors calculated by Craig (1953) which have been shown to be somewhat in error by Bottinga (1969). Using the corrected fractionation factors, indicated temperatures are increased by 50 to 75°C and the new temperatures are higher than those found in the reservoir. Experimental work is needed on this geothermometer to confirm the new fractionation factors, but the indicated temperatures may be real and exist in these systems below drilled depths.  $\text{CO}_2\text{-CH}_4$  temperatures at Broadlands, New Zealand (analysis NZ3), range from 385 to 425°C (Lyon, 1974) considerably above the reservoir temperatures (~270°C), although tem-

peratures in a deep Broadlands drillhole reached 307°C. New measurements at Larderello (C. Panichi, oral commun., 1975) indicate subsurface temperatures that vary with, but are higher than, observed reservoir temperatures. Temperatures for  $\Delta^{13}\text{C}(\text{CO}_2, \text{CH}_4)$  have also been calculated for geothermal fluids from Indonesia (analysis Ids 1), Kenya (analyses K1-3), and the United States (analyses US5 and US36).

Hydrogen isotope geothermometers,  $\Delta\text{D}(\text{H}_2, \text{CH}_4)$  and  $\Delta\text{D}(\text{H}_2, \text{H}_2\text{O})$ , have been tested in a few systems in Kenya; New Zealand; the Imperial Valley, California; and Yellowstone; but appear to reequilibrate rapidly and in most cases, indicate temperatures that approximate those of collection (analyses K2, NZ3, US5 and US36). Recently, Horibe and Craig (*in* Craig, 1976) have experimentally calibrated the  $\text{H}_2\text{-CH}_4$  geothermometer, which should encourage more isotopic analyses of these gases.

Although gas isotope geothermometers are the only ones available for vapor-dominated systems, they leave much to be desired as practical exploration tools for hot-water systems. Equilibrium may be achieved only below drillable depths ( $\text{CO}_2\text{-CH}_4$ ) or continue up to the sampling point ( $\text{H}_2\text{-CH}_4$ ,  $\text{H}_2\text{-H}_2\text{O}$ ), and most geothermal gases (especially from hot springs) are so low in methane that collection and separation are difficult.

For hot-water systems the most useful proven isotope geothermometer may be the fractionation of oxygen isotopes between water and its dissolved sulfate, which appears to equilibrate in geothermal reservoirs at temperatures as low as 95°C, and to reequilibrate so slowly during fluid ascent to the surface that evidence of temperatures above 300°C is preserved in some hot-spring waters. Experimental equilibrium and kinetic data have been measured by Lloyd (1968), Mizutani and Rafter (1969), and Mizutani (1972). Equilibrium has been demonstrated between dissolved sulfate and borehole water from Wairakei (analysis NZ1; Mizutani and Rafter, 1969; Kusakabe, 1974), Otake, Japan (analysis J6; Mizutani, 1972), Larderello (analysis It8; Cortecchi, 1974), and Raft River and Bruneau-Grandview, Idaho (analyses US15 and US17; Truesdell et al., unpub. data, 1975). The application of this geothermometer to boiling springs of Yellowstone, correcting for the effect of steam loss on  $^{18}\text{O}$  content of the water, was made by McKenzie and Truesdell (Abstract III-65), and unpublished measurements have been made on several other United States spring systems (analyses US7, US10, US18, US24, US26-27). Estimates of subsurface temperatures in Japanese geothermal systems without deep drillholes and uncorrected for steam loss appear reasonable (analyses J1-5; Mizutani and Hamasuna, 1972; Sakai and Matsubaya, 1974).

Two other geothermometers need more testing. The first,  $\Delta^{34}\text{S}(\text{SO}_4, \text{H}_2\text{S})$ , which has recently been calibrated experimentally by Robinson (1973), indicated unreasonably high temperatures for Wairakei bore fluids (analysis NZ2, Kusakabe, 1974) and for Mammoth, Yellowstone, water (analysis US35; Schoen and Rye, 1970). The second,  $\Delta^{13}\text{C}(\text{CO}_2, \text{HCO}_3)$  may indicate the temperature of bicarbonate formation at Steamboat Springs, Nevada, and Yellowstone (analyses US24, US30, and US32), but experimental data in this system need reevaluation (O'Neil et al., Abstract III-71).

In the rather special circumstances where water and steam phases may be separately analyzed, or steam analyzed and water isotopes estimated from other samples, the liquid-vapor fractionation of deuterium or  $^{18}\text{O}$  may be used to estimate temperatures of phase separation. This has been

done at Wairakei (Giggenbach, 1971), Campi Flegrei, Italy (Baldi, Ferrara, and Panichi, p. 687), Kawah Kamojang, Indonesia (Kartokusumo, Mahon, and Seal, p. 757), and White Island, New Zealand (Stewart and Hulston, 1976).

### Rare Gas Studies

Rare gases (He, Ne, Ar, Kr, and Xe) have been analyzed in geothermal fluids and shown to indicate the source of water recharge and, less certainly, the mechanism of steam loss (Mazor, p. 793). Ne,  $^{36}\text{Ar}$ , Kr, and Xe are not produced in rocks and do not undergo chemical reactions. However, they are affected by phase changes and their distribution between liquid and vapor is temperature dependent. For this reason, their contents in geothermal waters that have not boiled indicate that recharge waters are meteoric and allow calculation of temperatures of last equilibration with the atmosphere. In systems with subsurface boiling, the water phase is depleted in gases and their concentration patterns may indicate dilution and boiling mechanisms.

Other rare gases ( $^4\text{He}$  and  $^{40}\text{Ar}$ ) are produced from radioactive decay of rock materials and their concentrations may indicate rate of water movement through the system (Mazor, Verhagen, and Negreanv, 1974). High-temperature thermal waters in young volcanic rocks of Yellowstone and New Zealand apparently do not contain anomalous  $^{40}\text{Ar}$  (Mazor and Fournier, 1973; Hulston and McCabe, 1962b), although young volcanic rocks that have not lost volatile elements have high  $^{40}\text{Ar}$  contents (for example, Dalrymple and Moore, 1968). The origin and fate of  $^{40}\text{Ar}$  in geothermal systems needs much closer study.

Several recent studies have been made of excess  $^3\text{He}$  in ocean water (Craig, Clarke, and Beg, 1975), volcanic rocks (Lupton and Craig, 1975), and geothermal fluids of Iceland (Kononov and Polak, p. 767), Kamchatka (Gutsalo, p. 745), and Imperial Valley, Lassen, and Kilauea in the United States (Craig, unpub. data, 1975).  $^3\text{He}$  has been depleted from the atmosphere and crust because it is lost into space at a greater rate than  $^4\text{He}$ , and its enrichment in waters and rocks associated with spreading centers indicates contributions from the mantle. As noted earlier, mantle contribution of this isotope does not necessarily indicate that other mantle-derived components are present in geothermal fluids.

## CHEMICAL MODELING AND METHODOLOGY

### Modeling

Geothermal systems are chemically very active. Deep minerals are altered in response to the prevailing pressure, temperature, and chemical conditions, and ascending fluids change their physical and chemical properties rapidly over relatively short distances and effect profound mineralogical changes in rocks traversed. Mineralogical changes in these processes were reported by Bird and Elders (p. 285) and Reed (p. 539). It would appear both challenging and rewarding to model these changes, but disappointingly few attempts have been made.

Pampura, Karpov, and Kazmin (p. 809) report a chemical model for the changing compositions of ascending fluids of the Puzhetsk geothermal system. Many of the changes described earlier as occurring during the near-surface alteration of volcanic waters are successfully modeled, but the

absence of potassium in the fluids and of aluminosilicate minerals is a severe limitation. A relatively simple model for computing the downhole character of geothermal fluids (Truesdell and Singers, 1971) has been used to calculate deep pH values.

Using established models for solution and mineral equilibria, mineral alteration has been related to deep fluid chemistry for Broadlands, New Zealand, by Browne and Ellis (1970) and for Cerro Prieto, Mexico, by Reed (p. 539). In both these systems, deep waters are in near equilibrium with rock minerals and produced their observed metamorphism. Mass transfers in the Dunes, Imperial Valley, geothermal system were deduced from mineralogical changes by Bird and Elders (p. 285).

## Methodology and Data

The geochemical investigations described in this report depend both on the accurate chemical and isotopic analysis of natural fluids and on laboratory measurements of the properties of chemical substances over a range of temperature and pressure. Because analyses of many samples from a geothermal system allow a more complete reconstruction of chemical processes and deep conditions, analytical methods that are rapid and inexpensive or that can be automated are useful. Bowman et al. (p. 699) and Hebert and Bowman (p. 751) describe automated instrumental methods of water analysis that appear to be rapid and accurate and can provide analyses for trace constituents not normally measured. Some of these traces may provide geothermometers when their behavior is better understood.

Geothermometer components are necessarily not in equilibrium under surface conditions, and special care must be taken to preserve them for analysis by dilution ( $\text{SiO}_2$ ) or filtration and acidification (Ca). Thompson (1975) and Presser and Barnes (1974) report methods for collection and preservation or field analysis of geothermal waters. Akeno (1973) describes methods for preservation and analysis of geothermal gases. Downhole samplers for geothermal wells have been described by Fournier and Morganstern (1971) and Klyen (1973). Collection of geothermal fluids was the subject of a recent workshop (Gilmore, 1976).

Potter (p. 827) and Potter, Shaw, and Haas (1975) have compiled and assessed the status of studies on the density and other volumetric properties of geothermal brine components, and, using critically evaluated data, Haas (1971) has calculated boiling point-to-depth curves for sodium chloride solutions. Compilations of geochemical data are also being made by the Lawrence Berkeley Laboratory (Henderson, Phillips, and Trippe, Abstract I-15).

It is impossible to review here the many experimental studies of solution chemistry at high temperatures and pressures that are directly applicable to geothermal systems. These studies have been recently reviewed by Ellis (1967, 1970), Franck (1973), Helgeson (1969), Helgeson and Kirkham (1974), and Marshall (1968, 1972). When sophisticated chemical models are constructed for geothermal systems in their natural and disturbed states, these experimental studies will provide vital data.

## AN EXAMPLE OF EXPLORATION GEOCHEMISTRY

The role of chemistry in geothermal exploration is well illustrated by investigations at El Tatio, Chile, reported by

Cusicanqui, Mahon, and Ellis (p. 703), Lahsen and Trujillo (p. 157), and Armbrust et al. (1974), that were made in conjunction with geological and geophysical studies (Healy and Hochstein, 1973; Hochstein, Abstract III-39; Healy, p. 415) by New Zealand and Chilean scientists with United Nations support. El Tatio lies at an altitude of 4250 m in the high Andes. There are over 200 hot springs, most of which boil (at 85.5°C at this altitude) and deposit sinter and halite. Many of these springs were analyzed for major and minor components and some, along with cold springs and snow samples, were analyzed for  $^{18}\text{O}$  and deuterium. Fumaroles were analyzed for gases.

The analyzed spring waters showed narrow ranges of Cl:B and Na:Li ratios, indicating homogeneous thermal water at depth. Waters of the northernmost spring group were rather uniform in composition, with  $8000 \pm 200$  ppm chloride,  $\text{SiO}_2$  contents of  $260 \pm$  ppm, and Na:K weight ratios near 8.2. To the south and west, spring waters have lower  $\text{SiO}_2$  contents, higher Na:K ratios, and Cl contents of about 4000 to 6000 ppm, indicating mixing with near-surface waters.

Direct application of chemical geothermometers to high-chloride spring waters indicated minimum subsurface temperatures averaging 160°C from quartz saturation, 167°C from Na:K ratios, and 205°C from Na:K:Ca relations. Maximum indicated temperatures were 189°C (quartz saturation), 210°C (Na:K), and 231°C (Na:K:Ca). The boiling-spring mixing model of Truesdell and Fournier (p. 837), not yet developed at the time of the original investigations, can be applied to these spring waters assuming that those to the north were not diluted and that those to the south and west were mixtures with cold dilute water ( $t = 4^\circ\text{C}$ ,  $\text{Cl} = 2$  ppm). Average calculated subsurface temperatures are 208°C, but the maximum indicated temperature of 274°C is considered to be a better indication of the maximum aquifer temperature. Some of the high-chloride El Tatio springs issue at temperatures below boiling, and warm-spring mixing calculations, assuming cold waters of 4°C and 25 ppm  $\text{SiO}_2$ , indicate an average subsurface temperature of 269°C (standard deviation 13°C).

The patterns of Cl contents,  $\text{SiO}_2$  contents, Na:K ratios, and Na:Ca ratios were interpreted to indicate that cold near-surface drainage from the east was entering a shallow aquifer in the western and southern areas, and diluting high-chloride water rising from greater depths.

Deuterium analyses of the thermal waters agreed with the general picture of near-surface mixing, but suggested that the deep recharge was from higher elevation precipitation with lower deuterium values. Cold-water samples from the higher mountains to the east also tended to have lower deuterium values than local precipitation and were considered possible recharge waters.

Fumarole gas analyses also suggested movement from east to west, but at shallower depths. Eastern fumaroles had much higher contents of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  than other gases, and higher ratios of  $\text{H}_2\text{S}:\text{CO}_2$ . Quantitative interpretation of gas concentrations is difficult because of the effects of rock reaction and fractional separation into steam. In general, gases tend to decrease in  $\text{CO}_2$  and  $\text{H}_2\text{S}$  content and in  $\text{H}_2\text{S}:\text{CO}_2$  ratio with lateral flow (Mahon, 1970; Truesdell, 1976a). In retrospect, more weight should have been given to the fumarole chemistry in siting exploratory wells.

On the basis of resistivity surveys and spring chemistry, six slim holes were drilled to about 600-m depth. In the west and northwest, holes 1, 2, and 4 encountered maximum

temperatures of 212 to 230°C, with temperature inversions toward the bottoms of the wells. In wells 3 and 6, in the southwest, temperature inversions were not found and 254°C was measured in well 3. Seven production wells were located near No. 3, and the best of these (No. 7) tapped fluids of 263°C. A shallow (about 170-m) aquifer at 160°C was encountered in the Trucle dacite, which is probably where mixing with near-surface water occurs to produce the lower chloride waters of the western and southern springs. Deeper aquifers in the Puripicar ignimbrite (500 to 600 m) and the Penaliri (Salado) tuffs and breccias (700 to 900 m) were at about 230 and 200 to 260°C, respectively.

Comparison of drillhole and spring analyses indicates that the most concentrated spring waters are undiluted samples of the deep thermal fluids. The quartz saturation, Na:K, and NaKCa geothermometer temperatures are low, indicating considerable subsurface reequilibration. The mixing calculation temperatures are, however, surprisingly accurate.

Lateral subsurface flow from east to west, indicated by water isotopes and fumarole gases, was confirmed by drillhole measurements. Tritium contents of drillhole fluids suggested that the subsurface transit time was 15 years (unusually short for geothermal waters), but small additions of young near-surface water would also explain the results. The early resistivity survey did not indicate lateral flow, and a resurvey was made after the exploratory holes were

drilled. This showed a much larger anomaly that could be interpreted as due to deep lateral flow.

Two chloride inventories were made to estimate the total heat flow from the heat:chloride ratio of the thermal waters, which was established from drillhole fluid temperatures and chloride contents. These were not very accurate because of salt accumulation at the surface, but indicated a heat flow of 30 to 50 × 10<sup>6</sup> cal/sec.

El Tatio is very favorable for the application of geochemical methods because there are a large number of springs with rapid flow from the thermal aquifer, and the surface chemistry indicated subsurface conditions with reasonable accuracy. Gas and isotope analyses correctly suggested subsurface flow patterns, and chemical geothermometers and mixing models predicted temperatures at increasing depths in the system.

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Table 1. Chemical summaries and geothermometer temperatures for selected thermal fluids. (See end of table for explanatory notes.)

Area	System Type	Sample Type	Sampling Temp °C	Analyses	Water Type	TDS	Gases	t <sub>SiO<sub>2</sub>adia</sub> °C	t <sub>SiO<sub>2</sub>cond</sub> °C	t <sub>Na/K</sub> °C	t <sub>Na/KCa</sub> °C	Other Geothermometers °C	Observed Temp °C (depth)	References	
Afars and Issas															
Af1	Lake Assal, Spr 6	VW	s	83	w,i	Na>Ca>>K>>Mg Cl>>SO <sub>4</sub> >>HCO <sub>3</sub>	66000	156	166	174	202	165 Na-Ca-SiO <sub>2</sub> 272 WSMM	253 (1050 m) TDS = 190000	Bosch et al. (1976); Gringarten and Stieltjes (1976)	
Canada															
British Columbia															
Ca1	Tawah Creek (#40)	VW	s	43	w	Na>Mg>K>Ca HCO <sub>3</sub> >>Cl>>SO <sub>4</sub>	2400	162	177	210	227			Souther (p. 259); Nevin and Stauder (p. 1161)	
Ca2	Meager Creek (#52)	VW	s	55	w	Na>K>Ca>Mg Cl>HCO <sub>3</sub> >SO <sub>4</sub>	2000	171	187	197	211		69 (347 m)		
Ca3	Hot Springs Isl. (#57)	VW	s	76	pw	Na>Ca>>K		138	145	161	190	205 WSMM			
Chile															
El Tatio															
Ch1	Spr 181	VW	s	84.5	w, tr, i	Na>>K>Ca>>>Mg Cl>>>HCO <sub>3</sub> >>SO <sub>4</sub>	7060	142	149	195	211	229 BSMM		Cusicanqui, Mahon and Ellis (p. 703); Lahsen and Trujillo (p. 157); Armbrust et al. (1974)	
Ch2	Spr 226		s	83	w	Na>K>Ca Cl>>SO <sub>4</sub> >HCO <sub>3</sub>	14000	184	199	210	230				
Ch3	Well 7		w	85.5	w, g	Na>>K>>Ca>>>Mg Cl>>>HCO <sub>3</sub> >SO <sub>4</sub>	15600	CO <sub>2</sub> >>>H <sub>2</sub> S	257		261	261	262 BSMM	263 (800 m)	
Ch4	Average of 26 springs with standard deviation (σ) and maximum		s	52-85.5				160 ave 15 σ 189 max			205 ave 20 σ 231 max	208 ave BSMM, 269 ave WSMM 27 σ, 13 σ 274 max, 283 max	140-170, 190-235, 236-263	Truesdell and Fournier (p. 837)	
Columbia															
Co1	Ruiz, Spr A1	VW	s	90	pw, i	Na>>K>>Ca>>Mg Cl>>HCO <sub>3</sub> >SO <sub>4</sub>	1570	CO <sub>2</sub> , H <sub>2</sub> S		255	234			Arango et al. (1970)	
Czechoslovakia															
Cz1	Danube lowland	NVS	w			inc depth HCO <sub>3</sub> -Na <1000 HCO <sub>3</sub> -Cl-Na ≤5000 Cl-HCO <sub>3</sub> -Na ≤10000							38 1000 m gradient	Franko and Mucha (p. 979)	
Cz2	Stranka	NVF	w		pw					36	115	20 Na-K-Ca-CO <sub>2</sub> 73 Chalc	40 (1005 m)	Pačes and Čermák (p. 803)	
Cz3	Karlovy Vary	NVF	w	72	pw					154	188	44 Na-K-Ca-CO <sub>2</sub> 91 Chalc	72 (6 m)		
Cz4	Jachymov	NVF	w		pw					137	92	21 Na-K-Ca-CO <sub>2</sub> 66 Chalc	30 (493 m)		
Central depression (Danube lowland)															
Cz5	Chorvotský Grob	NVS	w	46		Cl-HCO <sub>3</sub> -Na	1800						46 (970-1210m)	Franko and Račický (p. 131)	
Cz6	Topolniky	NVS	w	90		HCO <sub>3</sub> -Cl-Na	3900						90(2040-2490m)		
Cz7	Levice block, Podhájska	NVS	w	80		Cl-Na	19600						80(1160-1900m)		
Cz8	Liptov depression, Besenova	NVS	w	34		SO <sub>4</sub> -HCO <sub>3</sub> -Ca-Mg	3200						34 (420±m)		
El Salvador															
Ahuachapán															
ES1	Salitre	VW	s	63	w, tr, g, i	Na>>Ca>K>>>Mg Cl>>>SO <sub>4</sub>	1330	CO <sub>2</sub> >>>N <sub>2</sub> >>>CH <sub>4</sub>	162	175	230	207		Sigvaldason and Cuéllar (1970); Glover and Cuéllar (1970); Cataldi et al. (II-43)	
ES2	Ah-1		w	~96	w	Na>>K>Ca>>>Mg Cl>>>SO <sub>4</sub>	19300		249		259	256	231		

Area	System Type	Sample Type	Sampling Temp °C	Analyses	Water Type	TDS	Gases	t <sub>SiO<sub>2</sub> adia</sub> °C	t <sub>SiO<sub>2</sub> cond</sub> °C	t <sub>Na/K</sub> °C	t <sub>Na/KCa</sub> °C	Other Geothermometers °C	Observed Temp °C (depth)	References
Ethiopia														
E1	East of Awasa (Spr 6-4)	VW	s	87	w, tr	Na>>K>>Ca>Mg HCO <sub>3</sub> >>SO <sub>4</sub> >>Cl	1640	151	158	196	207	225 WSMM		UNDP (1971); Demissie and Kahsai (I-10); Gofiantini, Borsa, Ferrara and Panichi, 1973, Earth and Planetary Sci. Letters, v. 18, p. 13-21.
E2	Aluto Spr 10	VW	s	96.5	w, tr	Na>>>K>>>Ca>Mg HCO <sub>3</sub> >Cl>SO <sub>4</sub>	2510	159	168	158	211			
E3	Tendaho Spr 15	VW	s	100	w, tr	Na>>K>Ca>>>Mg Cl>>SO <sub>4</sub> >>HCO <sub>3</sub>	1950	206	224	193	204			
E4	Lake Afrera Spr 31	VW	s	57.5	w, tr	Na>Ca>>K>>Mg Cl>>>SO <sub>4</sub> >>>HCO <sub>3</sub>	19100	124	130	150	179	208 WSMM		
France														
Massif Central														
F1	Chateauneuf, bain tempéré	NVF	s	37	pw	Na>>Ca>K		143	155	154	178	~50 Na-K-Ca-CO <sub>2</sub> 130 Chalc		Fouillac et al. (p. 721)
F2	Chatelguyon, Alice	NVF	s	35.5	pw, i	Na>Ca>>K		139	150	198	183	~50 Na-K-Ca-CO <sub>2</sub> 124 Chalc		
F3	Ste. Marguerite, Rive d'Allier	NVF	s	29	pw	Na>>Ca>K		137	148	215	203	~50 Na-K-Ca-CO <sub>2</sub> 122 Chalc		
F4	Royat, Eugénie	NVF	s	33	pw	Na>>Ca>K		126	136	215	195	~50 Na-K-Ca-CO <sub>2</sub> 108 Chalc		
Greece														
G1	Kamena Vorla, Gamma 9	VSW	w	47.9	w	Na>>Ca>Mg>K Cl>>SO <sub>4</sub> >HCO <sub>3</sub>	18900	96	99	121	169	67 Chalc		Dominco and Papastamatoki (p. 109); Stahl, Aust and Dounas (1974)
G2	Thermopylae, Psoroniria	VSW	s	32.5	w, i	Na>>Ca>Mg>K Cl>>SO <sub>4</sub> >>HCO <sub>3</sub>	27800	45	45	119	173	11 Chalc		
G3	Edipsos, Damaria	VSW	s	78.5	w	Na>>Ca>>K>Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	33400	110	112	120	174	81 Chalc		
G4	Lesbos, Arginos	VSW	s	81	w	Na>>Ca>K>Mg Cl>>SO <sub>4</sub> >>HCO <sub>3</sub>	11800	135	141	171	191	113 Chalc 198 WSMM		
G5	Nisiros, Demotika Loutra	VSW	s	48.5	w	Na>>Ca>Mg>K Cl>>>SO <sub>4</sub> >>HCO <sub>3</sub>	32000	160	174	114	167			
G6	Milos, Mavros Gremos	VSW	w	45	s	Na>>Ca>K>>Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	33800	172	185	232	205		138 (70 m)	
G7	Sousaki, borehole	VSW	w	73	pw	Na>>K>Ca>Mg Cl>>>SO <sub>4</sub>	45100			249	265	>120 boiling calc.	73 (145 m)	
Guadeloupe														
Gu1	Bouillante 2	VSW	w	~99	pw, tr, g	Na>>Ca>K>>>Mg	>24600			242	232		242 (338 m)	Demians d'Archimbaud and Munier-Jolain (p. 101); Cormy, Demians d'Archimbaud and Surcin (1970)
Gu2	Spr G52.4		s	59	w	Na>Ca>>K>>Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	3020	152	164	199	189	200 WSMM2		
Hungary														
Pannonian Basin														
H1	Triassic dolomite	NVS	w	100?	w	Na>Ca>>Mg>K HCO <sub>3</sub> >SO <sub>4</sub> >Cl	1410		103	181	75		150? (950±m)	Boldizsár and Korim (p. 297)
H2	U-Plio. sandstone	NVS	w	99?	w	Na>>>K>>Ca HCO <sub>3</sub> >>>SO <sub>4</sub> =Cl	1560		107	119	164		100-150 (2250±m)	

Table 1. Chemical summaries and geothermometer temperatures for selected thermal fluids (continued).

Area	System Type	Sample Type	Sampling Temp °C	Analyses	Water Type	TDS	Gases	t <sub>SiO<sub>2</sub> adia</sub> °C	t <sub>SiO<sub>2</sub> cond</sub> °C	t <sub>Na/K</sub> °C	t <sub>NaKCa</sub> °C	Other Geothermometers °C	Observed Temp °C (depth)	References			
Iceland																	
Ic1	Selfoss	NVF	s	79	w, i		Na>>Ca>>K>>Mg Cl>>SO <sub>4</sub> >CO <sub>2</sub>	667	N <sub>2</sub> >>CO <sub>2</sub>	122	126	87	120	96 Chalc	91	Arnórsson (1974); Arnason (1976); Tómasson, Fridleifsson and Stefánsson (p. 643); Björnsson, Arnórsson and Tómasson (1972); Arnórsson et al. (p. 853)	
Ic2	Deildartunga	NVF	s	99	w, i		Na>>Ca>>K>>Mg SO <sub>4</sub> >Cl>CO <sub>2</sub>	358		145	150	86	123	124 Chalc			
Ic3	Seltjarnarnes	NVF	s	83	w, i		Na>>Ca>>K>>Mg Cl>>SO <sub>4</sub> >>>CO <sub>2</sub>	1110		137	143	68	109	115 Chalc	119		
Ic4	Lýsuhóll	NVF	s	40	w, i		Na>>Ca>>K>>Mg CO <sub>2</sub> >>>Cl>>SO <sub>4</sub>	1670	CO <sub>2</sub> >>>N <sub>2</sub>	160	176	162	174	153 Chalc			
Ic5	Torfajokull, Eyrahrver	VW	s	95	w, i		Na>>>K>>>Ca>>Mg Cl>>SO <sub>4</sub> >>CO <sub>2</sub>	1350		194	209	148	199	193 Chalc			
Ic6	Geysir	VW	s	84	w, i		Na>>K>>>Ca>>Mg CO <sub>2</sub> >Cl>SO <sub>4</sub>	1130		227	256	200	220				
Ic7	Reykjanes	VSw	s	99	w, tr, g		Na>>Ca>>K>>>Mg Cl>>>SO <sub>4</sub> >>>CO <sub>2</sub>	48300	CO <sub>2</sub> >>>N <sub>2</sub> >H <sub>2</sub> S >O <sub>2</sub> >>>CH <sub>4</sub>	234	262	210	231	262 boiling calc.			
Ic8	Reykjanes Well 8	VSw	w	270	w, i		Na>>Ca>>K>>>Mg Cl>>>CO <sub>2</sub> >>>SO <sub>4</sub>	33650			270	234	240		270		
Ic9	Svartsengi Well 3	VSw	w	236	w, i		Na>>>K>>>Ca>>>Mg Cl>>>CO <sub>2</sub> >>>SO <sub>4</sub>	22460			241	251	245		236		
Ic10	Krisuvik Well 6	VSw?	w	258	w		Na>>>>K>>>>Ca>>>>Mg Cl>>>>HCO <sub>3</sub> >>SO <sub>4</sub>	2600			257	260	234	215-240 K (CO <sub>2</sub> +CH <sub>4</sub> )	258 (500 m)		
Ic11	Námafjall Well 4	VW	w	258	w, g, i		Na>>>K>>>>Ca>>>>Mg CO <sub>2</sub> >SO <sub>4</sub> >Cl	956	H <sub>2</sub> >CO <sub>2</sub> >H <sub>2</sub> S >N <sub>2</sub> >>>CH <sub>4</sub>		261	262	237		258		
Ic12	Hveragerdi Well 4	VW	w	198	w, g, i		Na>>>>K>>>>Ca>>>>Mg CO <sub>2</sub> >Cl>SO <sub>4</sub>	681	CO <sub>2</sub> >>>>H <sub>2</sub> = H <sub>2</sub> S>>>>CH <sub>4</sub>		200	169	187	182 Chalc	198		
India																	
Puga, Ladakh (NW Himalaya subprov. I)																	
Ida1	Spr 101	VW	s	83	w		Na>>>K>>>>Ca=Mg HCO <sub>3</sub> >Cl>>SO <sub>4</sub>	2850			149	157	258	247	221 WSMM	Shanker et al. (p. 245); Chaturvedi and Raymahashay (p. 329); Gupta, Saxena and Sukhija (p. 741); Jangi et al. (p. 1085); Krishnaswamy (p. 143); Gupta, Narain and Gaur (p. 387)	
Ida2	Well GW5	VW	w	100	w		Na>>>K>>>>Ca>>>>Mg HCO <sub>3</sub> >Cl>>>SO <sub>4</sub>	2420			163	171	248	234	231 WSMM		100 (51 m) max 135 (42 m)
Chumathang, Ladakh (NW Himalaya I)																	
Ida3	Spr 40	VW	s	49	w		Na>>>K>>>>Ca>>>>Mg HCO <sub>3</sub> >SO <sub>4</sub> >>>Cl	1250			153	166	148	170			
Ida4	Well CGW1	VW	w	85	w		Na>>>>K>>>>Ca>>>>Mg HCO <sub>3</sub> >SO <sub>4</sub> >Cl	1480			161	171	151	171			102 (20 m) max 109 (30 m)
Manikaran, Himachal Pd. (NW Him. II)																	
Ida5	Spr 4	VW	s	81	w, T		Na>>>Ca>>K>>Mg HCO <sub>3</sub> >Cl>>>SO <sub>4</sub>	595			141	148	288	204	209 WSMM		
Ida6	Spr 11		s	82	w		Ca>Na>Mg>K HCO <sub>3</sub> >>>Cl>>>SO <sub>4</sub>	550			127	131	268	194	170 WSMM		
Ida7	Kasol (NW Him. II)	VW	s	42	w		Ca>Na>Mg>K HCO <sub>3</sub> >>>SO <sub>4</sub> =Cl	531			105	111	322	195	224 WSMM		
Ida8	Tatwani (NW Him. III)	VW	s	57	w		Na>>>>Ca>>K>>Mg Cl>HCO <sub>3</sub> >>>>SO <sub>4</sub>	611			90	93	117	146	113 WSMM		
Ida9	Kopili, Naga-Lushai	VW?	s	57	w		Na>>>>Ca>>>>K>>Mg HCO <sub>3</sub> =SO <sub>4</sub> >Cl	449			116	122	108	129			
Ida10	Tural Ratnigiri, West Coast	VW?	s	61	w		Na>Ca>K>>>>Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	922			119	125	279	207	203 WSMM		
Ida11	Tuwa, Cambay	NVS	s	63	w		Ca>>Na+K>>>>Mg Cl>>>SO <sub>4</sub>	3527			119	124				110-151 (2700m) 170(>3400m)	
Ida12	Bakreshwar, W. Bengal (E.I. province)	VW?	s	81	w		Na>>>>K>>>>Ca=Mg Cl=HCO <sub>3</sub> >SO <sub>4</sub>	468			120	124	50	114			
Ida13	Dug well, Sohna	NVS?	s	42	w		Na>Ca>>>>Mg>K HCO <sub>3</sub> >Cl>>>>SO <sub>4</sub>	701			94	97	192	161	165 WSMM		

Area	System Type	Sample Type	Sampling Temp °C	Analyses	Water Type	TDS	Gases	$t_{SiO_2}^{adia}$ °C	$t_{SiO_2}^{cond}$ °C	$t_{Na/K}$ °C	$t_{Na/KCa}$ °C	Other Geothermometers °C	Observed Temp °C (depth)	References	
Indonesia															
Ids1	Kawah Komolang, Well 6	VS	w	238	w, pi, pg	Na>>K>>>Ca SO <sub>4</sub> >>>Cl	730	CO <sub>2</sub> >>H <sub>2</sub> S	240	232	217	220-230 "Isotope" 260 $\Delta^{13}C$ (CO <sub>2</sub> , CH <sub>4</sub> )	238 (620 m)	Kartokusumo, Mahon and Seal (p. 757); Ellis (pers. commun., 1975)	
Ids2	Dieng, Pulosari Spr	VW	s	55	w	Na $\hat{z}$ Ca>K $\hat{z}$ Mg Cl>SO <sub>4</sub> =HCO <sub>3</sub>	1340		143	153	436	250	203 WSM2	173 (139 m)	Truesdell (1971); Radja (p. 233) quoted from Danilchik (1973)
Israel															
Is1	Hamam El Farun	NVSw?	s	72	pw	Na>>Ca>>K	>12900			93	143			Eckstein (p. 713)	
Is2	Rift Valley Spr	NVF?	s		pg			rare gases						Mazor (p. 793)	
Is3	Hammat Gader	NVF	s	52±	pw, i, g, <sup>14</sup> C	Na>Ca>>Mg>K Cl>HCO <sub>3</sub> >SO <sub>4</sub>	1490	N <sub>2</sub> >O <sub>2</sub> >CH <sub>4</sub> , rare gases		175	90	68 <sup>14</sup> C mixing		Mazor, Kaufman and Carmi (1973)	
Italy															
Campi Flegrei															
It1	Spr 6D	VSw	s	34	w, tr, i	Na>>Ca $\hat{z}$ K>>Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	3600		116	123	252	217	271 WSM	>300 (1800 m)	Baldi, Ferrara and Panichi (p. 687); Cameli et al. (p. 315)
It2	Spr 5	VSw	s	88	w, tr, i	Na>>>Ca $\hat{z}$ K Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	25500		161	171	97	167	130-190 $\Delta^{18}O$ -D (steam-water)		
It3	Stufe d'Nerone		s								>300			Meidav and Tonani (p. 1143)	
It4	Tuscany, Romana, Spr 50 (group C)	VW	s	56	w, tr, g	Ca>>Mg>>K=Na SO <sub>4</sub> >HCO <sub>3</sub> >>>Cl	2390	CO <sub>2</sub> >>>N <sub>2</sub> >>>O <sub>2</sub>	108	113	760	260	82 Chalc 163 WSM		Baldi et al. (1973)
It5	Cesano Well 1	VW	w		w, tr	Na>K>>>Ca>>Mg SO <sub>4</sub> >>Cl>>HCO <sub>3</sub>	356000		148	153	548	521		210 (1400 m)	Calamai et al. (p. 305)
It6	Tuscany Spr 12836	VW	s	38	w	Ca $\hat{z}$ Na>Mg>>K HCO <sub>3</sub> >>SO <sub>4</sub> >Cl	6400		74	77	190	78			Brondi, Dall'Aglio and Vitroni (1973)
It7	Acqua Borra Larderello	VW	s	37	pw, i	Na>>>Ca>K	>10600				169	198		Fancelli and Nuti (1974)	
It8	Wells	VS	w		i, T								220-390 $\Delta^{13}C$ (CO <sub>2</sub> , CH <sub>4</sub> ) 152-329 $\Delta^{18}O$ (SO <sub>4</sub> , H <sub>2</sub> O)	~240	Panichi et al. (1974); Ferrara, Ferrara and Gonfiantini (1963); Cortecchi (1974)
It9	B.S. Michele	VS	s	47	pw, i	Na $\hat{z}$ Mg>Ca>>K Cl>HCO <sub>3</sub> >SO <sub>4</sub>	357				312	84			
Japan															
Coastal Waters															
J1	Shimogamo 20	VSw	w	100	pw, i, i(SO <sub>4</sub> )	Ca $\hat{z}$ Na>>>K>>>Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	~18000				154	174	200 $\Delta^{18}O$ (SO <sub>4</sub> -H <sub>2</sub> O) 150 CaSO <sub>4</sub> sat. 221-335 isotope mixing	n.a. (179 m)	Mizutani and Hamasuna (1972); Sakai and Matsubaya (1974)
J2	Ibusuki 4	VSw	s	97	pw, i, i(SO <sub>4</sub> )	Na>>Ca>K>>Mg Cl>>>SO <sub>4</sub>	~19000				167	200	200 $\Delta^{18}O$ (SO <sub>4</sub> -H <sub>2</sub> O) ~200 CaSO <sub>4</sub> sat.		Sakai and Matsubaya (1974); Matsubaya et al. (1973)
Arima Type															
J3	Yashio	NVSw?	s	1	pw, i, i(SO <sub>4</sub> )	Na>>K $\hat{z}$ Ca>>Mg Cl>HCO <sub>3</sub> >SO <sub>4</sub>	~34000				183	231	170 $\Delta^{18}O$ (SO <sub>4</sub> -H <sub>2</sub> O)		
Greentuff Type															
J4	Tottori	NVSw?	s	48	pw, i, i(SO <sub>4</sub> )	Na>>Ca>>K>Mg SO <sub>4</sub> >Cl>HCO <sub>3</sub>	~4700			76	130		102 $\Delta^{18}O$ (SO <sub>4</sub> -H <sub>2</sub> O)		
Volcanic Type															
J5	Beppu	VW	s	100	pw, i, i(SO <sub>4</sub> )	Na>>K>Ca>Mg Cl>>>SO <sub>4</sub> >>>HCO <sub>3</sub>	~3800				232	239	193 $\Delta^{18}O$ (SO <sub>4</sub> -H <sub>2</sub> O)		
J6	Otaki 8	VW	w		w, tr, i, i(SO <sub>4</sub> )	Na>>K>>Ca>>>Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	3190		227	222	229		220 $\Delta^{18}O$ (SO <sub>4</sub> -H <sub>2</sub> O)	195 (500 m)	Mizutani (1972); Koga (1970)
J7	Otaki Spr		s	97	w	Na>>K>>Ca $\hat{z}$ Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	3680		236		210	223			Nakamura (1969)
Matsukawa															
J8	Well MR3	VS	w	~99	w	Na>K>Ca>>>Mg SO <sub>4</sub> >>>HCO <sub>3</sub> >Cl	2760				429	273			Sumi and Maeda (1973)



Table 1. Chemical summaries and geothermometer temperatures for selected thermal fluids (continued).

Area	System Type	Sample Type	Sampling Temp °C	Analyses	Water Type	TDS	Gases	$t_{SiO_2}^{adia}$ °C	$t_{SiO_2}^{cond}$ °C	$t_{Na/K}$ °C	$t_{Na/KCa}$ °C	Other Geothermometers °C	Observed Temp °C (depth)	References
Japan (continued)														
Volcanic Type														
Matsukawa														
J9	Akagawa	s	42	w	Na>>K=Ca>>Mg SO <sub>4</sub> >>Cl	800		239		358	232		250 (1100 m)	Fujii and Akeno (1970); Baba et al. (1970)
J10	Matsukawa	w		c	NH <sub>4</sub> >>HBO <sub>2</sub> >F>>Hg>>As	20								Koga and Noda (p. 761)
J11	Onikobe													
J11	Mitaki	VW	54.5	pw	Na>>Ca>K>>>Mg Cl>>HCO <sub>3</sub> >>SO <sub>4</sub>	1540				252	208			Yamada (p. 665); Hitosugi and Yonetani (1972)
J12	Katayama GO-10	VW		pw	Na>Ca>K>>Mg Cl>>>SO <sub>4</sub> >>>HCO <sub>3</sub>	10800				361	270		295 (1300 m)	
Kenya														
K1	Olkaria #2	VW		w	Cl>HCO <sub>3</sub>			240		250		360 $\Delta^{13}C(CO_2, CH_4)$ >300 K(CO <sub>2</sub> +CH <sub>4</sub> )	286 (1300 m)	Noble and Ojiambo (p. 189); recalculated from Lyon, Cox and Hulston (1973 a,b); Glover (1972, 1973)
K2	Eburru	VW?		f								490 $\Delta^{13}C(CO_2, CH_4)$ ~130 $\Delta D(H_2, CH_4)$		
K3	Hannington	VW?		s		6000-14500		170		47-68		240-500 $\Delta^{13}C(CO_2, CH_4)$		
Mexico														
Cerro Prieto														
M1	Well M5	VW	99	w, pg	Na>>K>Ca>>>Li>>>Mg Cl>>>HCO <sub>3</sub> >>SO <sub>4</sub>	27600	CO <sub>2</sub> >>H <sub>2</sub> S	278		319	292	288 BSMM	289 (1300 m)	Reed (p. 539); Mercado (p. 487)
M2	Well M9	VW	99	w, pg	Na>>K>Ca>>>Li>>Mg Cl>>>HCO <sub>3</sub> >SO <sub>4</sub>	17500	CO <sub>2</sub> >>H <sub>2</sub> S	228		249	250	292 BSMM	228 (1400 m)	
New Britain														
NB1	Matupi-Rabalankaia	VSw	85	pw, pg	Na>>Mg>Ca>K Cl>>SO <sub>4</sub>	34200	CO <sub>2</sub> >>>H <sub>2</sub> S			143	189	>150 boiling calc.		Ferguson and Lambert (1972)
New Zealand														
Wairakei														
NZ1	Well 44	VW	~99	w, i, g	Na>>K>>>Ca>>>Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	4600	CO <sub>2</sub> >>>N <sub>2</sub> >H <sub>2</sub> >>>O <sub>2</sub> >CH <sub>4</sub> >Ar	248		255	259	360 $\Delta^{13}C(CO_2, CH_4)$ 200 K(CO <sub>2</sub> +CH <sub>4</sub> ) <sup>40</sup> Ar/ <sup>36</sup> Ar=290	248	Mahon (1973); Lyon and Hulston (1970); Lyon (1974)
NZ2	Well 28		~99	i								305 $\Delta^{18}O(SO_4, H_2O)$ 400 $\Delta^{34}S(SO_4, H_2S)$		Kusakabe (1974)
Broadlands														
NZ3	Well 8	VW	~99	w, i, g, tr	Na>>K>>>Ca>>>Mg Cl>>>HCO <sub>3</sub> >>>SO <sub>4</sub>	4120	CO <sub>2</sub> >>>CH <sub>4</sub> >N <sub>2</sub> >>H <sub>2</sub> >>>Ar>O <sub>2</sub>	278		311	302	385 $\Delta^{13}C(CO_2, CH_4)$ 275 $\Delta D(CH_4, H_2)$ 265 $\Delta D(H_2, H_2O)$ 325 K(CO <sub>2</sub> +CH <sub>4</sub> ) <sup>40</sup> Ar/ <sup>36</sup> Ar=270	273 (771 m) 307 (2160 m)	Mahon and Finlayson (1972); Giggemach (1971); Seward (1974); Ritchie (1973); recalculated from Lyon (1974); Macdonald (p. 1113)
NZ4	Springs			s				179 ave 11 $\sigma$ 202 max				183 ave 17 $\sigma$ 218 max	260, 265, 272	Truesdell and Fournier (p. 837); Mahon (1973, 1972)
Kawerau														
NZ5	Well 8	VW	~99	w, g	Na>>K>>>Ca>Mg Cl>>HCO <sub>3</sub> >>SO <sub>4</sub>	3070	CO <sub>2</sub> >>>H <sub>2</sub> S ~HC>N <sub>2</sub> >H <sub>2</sub>	263		265	283		260	
NZ6	Springs			s				188 ave 7 $\sigma$ 199 max				227 ave 8 $\sigma$ 239 max	225 ave 24 $\sigma$ 267 max	185, 218, 235 260, 265, 281

Area	System Type	Sample Type	Sampling Temp °C	Analyses	Water Type	TDS	Gases	tSiO <sub>2</sub> adia °C	tSiO <sub>2</sub> cond °C	tNa/K °C	tNa/KCa °C	Other Geothermometers °C	Observed Temp °C (depth)	References	
New Zealand (continued)															
Orakeikorako															
NZ7	Well 3	VW	w	99	w	Na>>K>>>Ca>Mg Cl>>HCO <sub>3</sub> ≥SO <sub>4</sub>		1290		234	250	249	237±		
NZ8	Spr 179 (Area 2)		s	98.5	w	Na>>K>>>Ca HCO <sub>3</sub> =Cl>>SO <sub>4</sub>		1230		192	220	245	252 BSMM		
NZ9	Springs (Area 2)		s						188 ave 6 σ 197 max		232 ave 7 σ 245 max	246 ave 7 σ 252 max	232-241		
Waiotapu															
NZ10	Well 6	VW	w	99	w,g	Na>>K>>>Ca>>>Mg Cl>>>HCO <sub>3</sub> ≥SO <sub>4</sub>	CO <sub>2</sub> >>H <sub>2</sub> S>>> H <sub>2</sub> >N <sub>2</sub> >HC	3370		257	269	260	260		
NZ11	Springs		s						187 ave 22 σ 210 max		185 ave 46 σ 236 max	293 BSMM	210,260,295		
NZ12	Ngawha Well 1	VW	w	99	w	Na>>>K>Ca Cl>B>HCO <sub>3</sub> >>>SO <sub>4</sub>		4700		220	157	193	220-225		
Philippines															
Ph1	Tongonan 222	VW	s	85.6	w,i	Na>>K>Ca>>>Hg Cl>>>HCO <sub>3</sub> >>SO <sub>4</sub>		3170		154	163	224	216	196 (305 m) well TGE 4	Glover (1974a,b; 1975)
Ph2	Okoy R. PA6	VW	s	94	w,i	Na>>K>Ca>>>Mg Cl>>>HCO <sub>3</sub> >SO <sub>4</sub>		5400		171	182	190	207	198 BSMM	
Poland															
West Carpathians and Sudeties															
P1	Koszuty	NVS	w	40.5	w	Na>>>Ca>>>Mg>K Cl>>>SO <sub>4</sub> >>HCO <sub>3</sub>		9540			57	18	98	40.5 (1020 m)	Dowgiałło (p. 123)
P2	Zakopane	NVS	w	36	pw,i			328					37-47 Δ <sup>18</sup> O(SO <sub>4</sub> ,H <sub>2</sub> O)	36 (1560 m)	Cortecci and Dowgiałło (1975)
Red Sea Brine															
RS1	Atlantis II deep	VSw		56	w, tr, i	Na>>>Ca>K>Mg Cl>>>SO <sub>4</sub>		257000			108	62	159	210 heat balance 211 WSMM 261 Δ <sup>18</sup> O(SO <sub>4</sub> ,H <sub>2</sub> O)	Schoell (p. 583); Brewer and Spencer (1969); Longinelli and Craig (1967)
Rhodesia															
R1	Binga Spr			100	pg		rare gases						>boiling rare gas	Mazor (p. 793)	
SW1	Sea Water			4-30+	w	Na>>Mg>>Ca=K Cl>>SO <sub>4</sub> >>>HCO <sub>3</sub>		34500			<25	101	173	180± Δ <sup>18</sup> O(SO <sub>4</sub> -H <sub>2</sub> O)	Hood (1972); Longinelli and Craig (1967)
Swaziland															
Swa1	Mkoba Sprs		s	51.5	pw,pg,i	Na>>>Ca>K HCO <sub>3</sub> >>>Cl>>>SO <sub>4</sub>		190	rare gases		53	54		Mazor, Verhagen and Negreanv (1974)	
Switzerland															
Swi1	Lavey les Bains	NVF?	w	63			rare gases							Mazor (p. 793)	
Taiwan															
Tatun Shan															
Ta1	Hsinpeitou	VW	s	98	w	Na>K>Ca>>>Mg Cl>SO <sub>4</sub>		8180		168	177	405	278	263 WSMM	White and Truesdell (1972); Chen and Chern (written commun., 1975)
Ta2	Matsao E205		w	99	w,g	Na>>K>Ca=Mg Cl>>>SO <sub>4</sub>	CO <sub>2</sub> >H <sub>2</sub> S	15000		251	264	246	240 (293 in E208)		
Ta3	Ilan Tuchung IT-1	VW?	w	98	w,g,i	Na>>>K HCO <sub>3</sub> >>>SO <sub>4</sub> >Cl	CO <sub>2</sub> >>H <sub>2</sub> S	3640		178	189	45	~160	187 Δ <sup>18</sup> O(SO <sub>4</sub> ,H <sub>2</sub> O) 164 max 173 (240 m)	Fournier, Nehring and MRSO (unpub. data, 1976)



Area	System Type	Sample Type	Sampling Temp °C	Analyses	Water Type	TDS	Gases	$t_{SiO_2}$ adia °C	$t_{SiO_2}$ cond °C	$t_{Na/K}$ °C	$t_{Na/KCa}$ °C	Other Geothermometers °C	Observed Temp °C (depth)	References
United States (continued)														
Idaho														
Raft River														
US15	Crank Well	NVF	w	90	w,i,g	Na>>Ca>>K>>>Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	3360 N <sub>2</sub> >>CO <sub>2</sub> >>O <sub>2</sub> >>R	131	136	90	139	142 Δ <sup>18</sup> O(SO <sub>4</sub> ,H <sub>2</sub> O)	RRGE1 (1526 m)	147 Young and Mitchell (1973); Young and Whitehead (1975a,b); Williams et al. (p. 1273); Rightmire, Young and Whitehead (1976); Truesdell, Nehring and Thompson (unpub. data, 1975)
US16	Well 11S25E-11		w	60	w	Na>>>Ca>K>>Mg HCO <sub>3</sub> >SO <sub>4</sub> >Cl		107	111	98	131	145 WSMM		
US17	Bruneau-Grandview, Well 5S3E-28	NVS?	w	65	w,g,i	Na>>>K>Ca HCO <sub>3</sub> >>Cl>SO <sub>4</sub>	N <sub>2</sub> >>O <sub>2</sub> >CH <sub>4</sub>	129	136	40	105	115 Δ <sup>18</sup> O(SO <sub>4</sub> ,H <sub>2</sub> O) 108 ChalC		
US18	Weiser, Well 11N6W-10	NVF?	s	76	w,i	Na>>>K>Ca SO <sub>4</sub> >HCO <sub>3</sub> >Cl		149	157	95	141	228 WSMM 234 Δ <sup>18</sup> O(SO <sub>4</sub> ,H <sub>2</sub> O)		
Montana														
US19	Marysville	NVF?	w	98		Na>>>K>Ca>>>Mg HCO <sub>3</sub> >SO <sub>4</sub> >Cl		125	128	124	158	98 ChalC	98 (1000 m)	Blackwell and Morgan (p. 895); Morgan (written commun., 1976)
US20	Big Creek	?	s	93	w	Na>>>K>Ca>>>Mg HCO <sub>3</sub> >>SO <sub>4</sub> >Cl		154	161	143	173	223 WSMM		Robertson, Fournier and Strong (p. 553)
Nevada														
US21	Beowane	NVF?	s	98	w	Na>>>K>>>Ca>>>Mg HCO <sub>3</sub> >SO <sub>4</sub> >Cl		198	214	151	194		212 (400 m)	Mariner et al. (1974a); Bowman et al. (p. 699); Wollenberg (p. 1283); White (1968); Truesdell and Nehring (unpub. data, 1975)
US22	Buffalo Valley	NVF?	s	49	w,tr	Na>>>Ca>K>Mg HCO <sub>3</sub> >>SO <sub>4</sub> >>Cl		118	125	223	197	215 WSMM		
US23	Kyle	NVF?	s	77	w,tr	Na>>>Ca>K>Mg Cl>HCO <sub>3</sub> >>>SO <sub>4</sub>		152	161	234	211	257 WSMM		
US24	Steamboat	VW?	s	94	w	Na>>>K>>>Ca>>>Mg Cl>HCO <sub>3</sub> >>>SO <sub>4</sub>		188	201	184	207	220± Δ <sup>18</sup> O(SO <sub>4</sub> ,H <sub>2</sub> O) 190± Δ <sup>18</sup> C(CO <sub>2</sub> ,HCO <sub>3</sub> )	186 (222 m)	
New Mexico														
US25	Jemez Mtn., Jemez Spr	VW	s	75	w	Na>>>Ca>K>>>Mg Cl>HCO <sub>3</sub> >>>SO <sub>4</sub>		122	125	215	202	165 WSMM		Trainer (1974)
Oregon														
US26	Alvord	NVF?	s	76	w	Na>>>K>>>Ca>>>Mg HCO <sub>3</sub> >Cl>>>SO <sub>4</sub>		140	148		198	217 WSMM 209 Δ <sup>18</sup> O(SO <sub>4</sub> ,H <sub>2</sub> O)		Mariner et al. (1974b); Lund, Culver and Svanevik (p. 2147); Truesdell, Sammel, Mariner and Nehring (unpub. data, 1975)
US27	Klamath Falls, Olene Gap	NVF?	s	74	w	Na>>>Ca>>>K>>>Mg SO <sub>4</sub> >>Cl>HCO <sub>3</sub>		130	136	102	130	192 WSMM 196 Δ <sup>18</sup> O(SO <sub>4</sub> ,H <sub>2</sub> O)		
Utah														
US28	Roosevelt Hot Spr	VW?	s	85	w	Na>>>K>>>Ca Cl>>>HCO <sub>3</sub> >SO <sub>4</sub>		196	202	273	284		260+	Mundurff (1970); Swanberg (1974); Beaver County News (1976)
Wyoming														
Yellowstone Park														
Shoshone Basin														
US29	Area I Sprs	VW	s					190 ave 10 σ 203 max		175 ave 16 σ 223 max	267 ave 5 σ 272 max	BSMM		Truesdell and Fournier (p. 837, σ = std. dev.); McKenzie and Truesdell (III-65); Thompson et al. (1975); White et al. (1975); Truesdell and Fournier (1976b); Truesdell (unpub. data, 1975)
US30	Spr 35		s	93	w	Na>>>K>>>Ca>Mg HCO <sub>3</sub> >Cl>>SO <sub>4</sub>	CO <sub>2</sub> >>>R>>>H <sub>2</sub> S	185	199	110	171	272 BSMM 260 Δ <sup>18</sup> O(SO <sub>4</sub> , H <sub>2</sub> O) 190± Δ <sup>13</sup> C(CO <sub>2</sub> ,HCO <sub>3</sub> )		
Upper Basin														
US31	Springs	VW	s					195 ave 11 σ 210 max		186 ave 20 σ 221 max	230 ave 18 σ 280 max	BSMM	181 (152 m)	
US32	Ear Spr		s	95	w	Na>>>K>>>Ca>>>Mg Cl>>HCO <sub>3</sub> >>>SO <sub>4</sub>		206	224	122	186	314 Δ <sup>18</sup> O(SO <sub>4</sub> ,H <sub>2</sub> O) 201 Δ <sup>13</sup> C(CO <sub>2</sub> ,HCO <sub>3</sub> )		
Norris Basin														
US33	Springs	VW	s					210 ave 22 σ 255 max		251 ave 32 σ 294 max	276 ave 32 σ 374 max	BSMM	237.5 (332 m)	
US34	Porcelain Terrace		s			Na>>>K>>>Ca>>>Mg Cl>>>HCO <sub>3</sub> >SO <sub>4</sub>		250	291	289	272	309 Δ <sup>18</sup> O(SO <sub>4</sub> ,H <sub>2</sub> O)		

Table 1. Chemical summaries and geothermometer temperatures for selected thermal fluids (continued).

Area	System Type	Sample Type	Sampling Temp °C	Analyses	Water Type	TDS	Gases	t <sub>SiO<sub>2</sub> adia</sub> °C	t <sub>SiO<sub>2</sub> cond</sub> °C	t <sub>Na/K</sub> °C	t <sub>NaKCa</sub> °C	Other Geothermometers °C	Observed Temp °C (depth)	References	
United States (continued)															
Wyoming															
Yellowstone Park															
Mammoth															
US35	New Highland	VW	s	73.5	w, i, g	Ca>Na>K>Mg HCO <sub>3</sub> >SO <sub>4</sub> >>Cl	2270	CO <sub>2</sub> >>>H <sub>2</sub> S>>R	103	105	421	96	300 Δ <sup>34</sup> S(SO <sub>4</sub> , H <sub>2</sub> S) 74 Chalc	73 (15-113 m)	Schoen and Rye (1970); Robinson (1973)
US36	Washburn Spr	VS	f	82	w, trg, i								380 Δ <sup>13</sup> C(CO <sub>2</sub> , CH <sub>4</sub> ) 115 ΔD(H <sub>2</sub> , H <sub>2</sub> O) 70 ΔD(CH <sub>4</sub> , H <sub>2</sub> )		Recalc. from Gunter and Musgrave (1966, 1971)
US37	Research Wells	VW	w										>boiling rare gases		Mazor (p. 793)
USSR															
Kamchatka															
Panzhetka															
UR1	Well 4	VW	w	?	w	Na>>>K>Ca>>>Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	3180		193?	209	194	209		219	Vakin et al. (1970); Manukhin (II-29)
UR2	Paryaschy		s	99	w	Na>>>K>Ca>>Mg Cl>>>SO <sub>4</sub> >HCO <sub>3</sub>	3110		160	168	156	186			
Bolshe Banny															
UR3	Well 35	VW	w	?	w	Na>>>K>Ca SO <sub>4</sub> >>Cl>HCO <sub>3</sub>	1330		177?	188	161	177		171	
UR4	Spr 4		s	99	w	Na>>>K>Ca SO <sub>4</sub> >>Cl>HCO <sub>3</sub>	1200		160	168	167	183			
Yugoslavia															
Y1	Pannonian Basin	NVS		80-90		HCO <sub>3</sub> -Na, Cl-HCO <sub>3</sub> -Na, Cl-Na	<35000	N <sub>2</sub> , CH <sub>4</sub>							Petrović (p. 531)
Y2	Middle Serbia	NVS				HCO <sub>3</sub> -Na-Ca-Mg		CO <sub>2</sub>							
Y3	Crystalline and young tectonic areas	NVF?				HCO <sub>3</sub> -SO <sub>4</sub> -Na-Ca-Mg	<1000	N <sub>2</sub> , O <sub>2</sub> , ±Rn							

Note: The following abbreviations are used in Table 1.

#### System Type

VW volcanic hot water system  
 VS volcanic steam (vapor-dominated) system  
 VSw volcanic system involving seawater  
 NVSw nonvolcanic system involving seawater  
 NVS nonvolcanic sedimentary basin with thermal water  
 NVF nonvolcanic system with heat from deep circulation along faults

#### Sample Type

s spring  
 f fumarole  
 w well

**Sampling Temperature** is the surface temperature for a spring or a nonboiling well discharge, the temperature of steam separation for well discharges above boiling, or the downhole temperature if a downhole sampler was used or if the analysis was recalculated to downhole conditions.

#### Analyses

w water analysis with all major ions and SiO<sub>2</sub>  
 pw partial water analysis  
 pg partial gas analysis

t<sub>SiO<sub>2</sub> adia</sub> is the quartz saturation temperature (°C) assuming maximum steam loss during cooling (adiabatic cooling) calculated by the computer program GEOTERM (Truesdell, p. 831), along with t<sub>SiO<sub>2</sub> cond</sub>, t<sub>NaKCa</sub>, WSMM, and BSMM, which are defined below. No allowance has been made for dissociation of dissolved silica. Some spring systems have data indicated as ave. (average), max. (maximum), and σ (standard deviation).

t<sub>SiO<sub>2</sub> cond</sub> is the quartz saturation temperature assuming no steam loss during cooling (conductive cooling).

t<sub>Na/K</sub> is the temperature calculated from the ratio of Na to K using the White-Ellis curve of Table 2.

t<sub>NaKCa</sub> is the NaKCa temperature calculated using the equation of Table 2.

#### Other Geothermometers

Na-K-Ca-CO<sub>2</sub>: The NaKCa geothermometer with correction applied for high CO<sub>2</sub> contents (Paces, 1975).

Chalc: The chalcidony saturation geothermometer with conductive cooling (Table 2).

CaSO<sub>4</sub> sat.: Temperature calculated for saturation of anhydrite (see text).

WSMM: The warm spring mixing model described in the text with no steam loss before mixing. Where no other data were available, the cold water component temperature was estimated as equal to the mean annual temperature and the SiO<sub>2</sub> content was assumed to be 25 ppm.

WSMM2: The warm spring mixing model, assuming steam separation at 100°C before mixing. Same assumed cold water component as above.

BSMM: The boiling spring mixing model described in the text. The cold spring temperature was estimated as above and the Cl contents estimated (in the absence of data) as 2 to 15 ppm according to the distance from the ocean.

tr trace water analysis  
 trg trace gas analysis  
 g gas analysis  
 i water (<sup>18</sup>O,D) or other isotopes  
 T,<sup>14</sup>C tritium, carbon-14

$\Delta^{13}\text{C}(\text{CO}_2, \text{CH}_4)$ : Temperatures indicated by the fractionation of <sup>13</sup>C between CO<sub>2</sub> and CH<sub>4</sub>. The notation for this and other isotope geothermometers is self-evident (see text).  
 $K(\text{CO}_2 \rightarrow \text{CH}_4)$ : Temperature calculated from chemical equilibrium constants for the reaction  $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$ .  
 Boiling calculation: Temperature calculated from the apparent increase in concentration of seawater due to boiling.  
 Na-Ca-SiO<sub>2</sub>, isotope mixing, <sup>14</sup>C mixing, "isotope", heat balance, Cl-E: Special methods explained in the original references.

**Observed Temperature** is *aquifer* temperature rather than maximum temperature where aquifers are identified; otherwise, maximum recorded temperature.

**References** in many cases are grouped where data for a well, spring, or geothermal system are from more than one source. "recalc. from" means that temperatures were calculated from a calibration curve other than that used by the author.

**Water Type** is calculated on a *weight* basis. The symbols mean:  
 A = B A approximately equals B in concentration  
 A ≥ B A is 1 to 1.2 times the concentration of B  
 A > B A is 1.2 to 3 times the concentration of B  
 A >> B A is 3 to 10 times the concentration of B  
 A >>> B A is more than 10 times the concentration of B

**TDS** is the sum of the reported constituents of the analysis in ppm (mg/kg).  
**Gases** are in order of molar or volume abundance with the same symbols as for water type.

Table 2. Equations for geothermometers.

<i>Silica Geothermometers</i> (SiO <sub>2</sub> in ppm)*	
Quartz, adiabatic cooling (± 2°C from 125–275°C)	$t^\circ\text{C} = \frac{1533.5}{5.768 - \log \text{SiO}_2} - 273.15$
Quartz, conductive cooling (± 0.5°C from 125–250°C)	$t^\circ\text{C} = \frac{1315}{5.205 - \log \text{SiO}_2} - 273.15$
Chalcedony, conductive cooling	$t^\circ\text{C} = \frac{1015.1}{4.655 - \log \text{SiO}_2} - 273.15$
<i>Na/K Geothermometers</i> (Na, K in ppm)	
White and Ellis (see text) (± 2°C from 100–275°C)	$t^\circ\text{C} = \frac{855.6}{\log(\text{Na}/\text{K}) + 0.8573} - 273.15$
Fournier and Truesdell (1973)	$t^\circ\text{C} = \frac{777}{\log(\text{Na}/\text{K}) + 0.70} - 273.15$
<i>NaKCa Geothermometer</i> (Na, K, Ca in moles/liter)	
Fournier and Truesdell (1973, 1974)	$t^\circ\text{C} = \frac{1647}{\log(\text{Na}/\text{K}) + \beta \log(\sqrt{\text{Ca}}/\text{Na}) + 2.24} - 273.15$
$\beta = 4/3$ for $\sqrt{\text{Ca}}/\text{Na} > 1$ and $t < 100^\circ\text{C}$	
$\beta = 1/3$ for $\sqrt{\text{Ca}}/\text{Na} < 1$ or $t_{4/3} > 100^\circ\text{C}$	

\*Data from Fournier (written commun., 1973)

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