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UNITED STATES GOVERNMENT

Memorandum

TO : Geothermal Sample Collectors

DATE: October 14, 1977

FROM : A. H. Truesdell, USGS

SUBJECT: Reprints

I have collected reprints describing methods of collection and analysis of hot spring waters and geothermal well fluids. These papers are far from complete but will help to get you into the subject. In addition to these I recommend you read the following articles in the UN Geothermal Symposia Volumes (Pisa (Geothermics Special issue 2, 1970).

F. Tonani	Geochemical methods of exploration, p.492
A.J. Ellis	Quantitative interpretation of chemical characteristics of hydrothermal systems, p.516
R.O. Fournier & A.H. Truesdell	Chemical indicators of subsurfact temperature ... applied to Yellowstone waters, p.529
S.Arnorsson	Underground temperatures in Iceland ... from the silica content of water, p.536
W.A.J. Mahon	Chemistry in exploration and exploitation, p.1310
S.H. Wilson	Statistical interpretation of chemical results..., p.1323
J.B. Findlayson	The collection and analysis of ... gases, p.1344
R.B. Glower	Interpretation of gas compositions from Wairakei...,p.1355
Russell James	[papers on physics of 2 phase water-steam mixtures] p. 1502 and p.1581

San Francisco (U.S. Govt. Print Office, 1976)

Marshall Reed	Geology and metamorphism in Cerro Prieto, p.539
Plinio Baldi, et al.	...Chemical and isotopic studies of fluids of the Campi Flegrei (Italy), p.687
Herman Cusicanqui, et al.	The geochemistry of El Tatio (Chile), p.703
W. Kartokusumo, et al	The geochemistry of Kawah Kamojang (Java), p.757
V.I. Kononov and B.G. Polak	Indicators of heat rechargs ..., p.767
W.A.J. Mahon	Review of hydrogeochemistry of geothermal ..., p.775
E. Mazor	Noble gases in thermal waters ..., p.793.

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UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

SELECTING AND COLLECTING THERMAL SPRINGS FOR CHEMICAL ANALYSIS: A METHOD FOR FIELD PERSONNEL

By

J. M. Thompson

Open-file Report
75-68

This report is preliminary and has not been edited or reviewed for conformity with Geological Survey standards and nomenclature.

INTRODUCTION

Water samples of hot springs can be collected and analyzed to obtain data for estimating subsurface aquifer temperatures. Unfortunately, there are very few published guidelines to assist a field geologist in selecting and sampling a thermal spring (see, for instance, Ellis et al., 1968). This paper is an attempt to fill that void.

Presser and Barnes (1974) have described methods of analysis for numerous chemical parameters that should be determined in the field in order to produce a complete, high quality chemical analysis. Major and trace element ions are determined in the laboratory. This type of detailed analysis is mandatory if the data are used to determine the mineral (or rock)-water equilibrium. However, this type of detailed analysis is not essential for hydrogeothermometry; another type of analysis, a major ion analysis, showing a complete range in temperatures, salinities, and discharge rates is sufficient (a major ion analysis allows for a cation-anion balance check to insure that all major constituents have been determined). For the purpose here, a major ion analysis should include the cations (sodium, potassium, lithium, calcium, and magnesium), the anions (carbonate, bicarbonate, sulfate, chloride, and fluoride), plus boron, silica, and pH. A major ion analysis does not yield as accurate or complete an analysis as the first, but since the methods of both types of analysis are the same, the precision of the individual component analyses should also be the same.

EQUIPMENT

The equipment needed for collection of a thermal spring and its intended purpose is shown in Table I. (If time and space allow, a sample for water isotopes may aid interpretation. This is indicated, therefore, as optional equipment.) Note that two pH measurements are required: one to determine the spring pH and one to insure that the pH of the filtered-acidified sample is below pH 2.

SELECTION

Before selecting which spring or springs in a given area should be sampled, a reconnaissance of the ranges of hot spring activity is useful. This should include estimating the spring discharge, measuring the spring temperature, and obtaining an estimate of spring pH and chloride content from pH strip and Quantab chloride indicators. Items to be considered in selecting springs for sampling include the rate of water discharge, spring temperature, gas evolution, pH, Quantab chloride, ease of accessing the main orifice, and the number and physical character of immediately adjacent springs. Cold, warm, and hot springs of highest discharge should always be considered for sampling. If only one sample can be collected, sample the hottest discharging spring in a group of springs. If only two samples can be collected, sample the hottest and coldest discharging springs. However, if it is possible, sample springs with various temperatures and chloride concentrations in order to obtain information concerning water movement and possible subsurface mixing (Truesdell, 1974a). If possible, always sample flowing springs, the

larger the rate of discharge the better. Non-flowing pools (with or without discharging gas) yield data that are difficult to interpret. Large pools of low discharge may also be concentrating the constituent in the water by evaporation or minerals may be precipitating so that the chemical analysis is not representative of the upflowing subsurface water. Normally, springs having surface inflow from other springs should not be sampled. However, if the rate of discharge from the spring is much greater than the rate of surface inflow, the spring may be nearly representative of the subsurface upflow. Presence or absence of gas is not a critical parameter, but it should be noted (this is an important parameter if the area is considered for more extensive sampling). If possible, sample springs with a neutral to alkaline pH (pH 6 to 9). Mud pots, mud volcanoes, and turbid acid springs are usually quite difficult to filter and chemical analyses of their "major" ions as discussed here yield no useful geothermometry information. These thermal features generally have water compositions which are controlled, at least in part, by the acid leaching of the surrounding rocks.

SAMPLING PROCEDURE

Three bottles of water should normally be collected at each spring or sampling site: one filtered acidified, one filtered only, and one diluted for SiO_2. The procedure is initiated by thoroughly rinsing the syringe with spring water and then filling the syringe. The Swinnex filter unit is attached and approximately 15 ml of sample is filtered to rinse the Swinnex filter unit. The remaining volume is filtered and used

to rinse the sample bottles and caps. The filter unit is removed and the syringe is refilled. The filter unit is then replaced and the sample filtered into a 60 ml sample bottle. When the bottle is nearly full, the sample is acidified to pH <2 (six drops of acid should be sufficient; confirm with the pHydrion pH paper). This sample is for cation analysis.

This first sample is filtered and then acidified to prevent suspended solids and colloidal material from dissolving and contributing to the cation concentrations. Filtration prevents clogging of the aspirator on an atomic absorption spectrometer (AAS) and removes suspended solids and organic material that may clog pipettes and disturb spectrophotometer readings. Acidification also prevents reactions which may precipitate calcium carbonate, calcium sulfate, and magnesium carbonate after sample collection.

The above procedure is repeated to fill the 250 ml bottle. This second sample must not be acidified and is for anion analysis. This sample is filtered to prohibit algae growth in the bottle. A 0.45 μm filter is usually sufficient to remove most Protista.

A silica sample is taken by pipetting 10 ml of spring water into the bottle containing 50 ml of silica-free water (distilled-deionized or deionized-distilled water is suggested). It is imperative that the cap on this sample not leak. Diluting the sample water insures a silica concentration sufficiently low so that polymerization of silica is prevented. Suspended silicate solids dissolve slowly in natural water (pH 6 to 9) at low temperature, so that filtration is not required. Suspended colloidal amorphous SiO_2 may dissolve. This is actually

desirable since the silica concentration determined will be closer to the true silica concentration and will indicate a geothermometer temperature closer to the actual aquifer temperature.

After laboratory analysis, the investigator may refer to Table II (modified from Truesdell, 1974b) which is a summary of information obtained by chemical analysis of hydrothermal systems. In general, the data may also be used as indicators of subsurface temperature (e.g. Fournier and Rowe, 1966; Fournier and Truesdell, 1970; Mahon, 1970; Truesdell, 1974a). Should any samples indicate a geothermally interesting area, additional comprehensive sampling should be done by specialists more familiar with field collection and analysis techniques for trace element analysis, for gas analysis, and for non-radioactive isotope studies.

ACKNOWLEDGMENTS

Discussion and comments from R. O. Fournier, L. P. J. Muffler, A. H. Truesdell, and D. E. White are sincerely appreciated.

Table I

Equipment	Purpose
1. Maximum reading mercury in glass thermometer for hot and warm springs	To ascertain spring temperature
2. Conventional mercury in glass thermometer for cold springs	To ascertain spring temperature
3. A box of high quality, non-bleeding, pH indicating strips that respond in low ionic strength solutions (e.g. E. Merck Spezialindikator) or a pH meter and pH 7 buffer	To determine spring pH
4. A device to submerge a bottle in a boiling or very hot spring (e.g. a pair of tongs or a clamp)	To prevent scalding fingers and hands
5. Empty plastic sample bottles, 60 and 250 ml volume with appropriate tight sealing cap (e.g. polyseal caps)	To contain water sample and prevent spilling loss
6. A 60 ml plastic bottle containing 50 ml of silica-free water	To dilute silica sample so that polymerization does not occur
7. Plastic 10 ml pipette	To obtain silica sample
8. Large plastic syringe, 50-60 ml capacity, with Luer lock	To collect and filter water sample
9. A plastic Swinnex filter unit with either 0.22 or 0.45 μm pore size with extra filters	To filter water samples
10. A roll of pH paper (e.g. pHydrion paper 1-5.5)	To check pH of filtered-acidified sample
11. Bottle of 1:1 HCl with dropper	To acidify water sample
12. Bottle of Quantab chloride indicators (#1175)	To test for chloride
13. A dozen 50 ml or smaller plastic beakers	To hold spring sample for Quantab chloride indicator
14. A 60 or 125 ml glass bottle (optional but useful)	To collect an isotope sample

Table II.--Importance of individual components of water and gases in chemical study of geothermal system

Cl	Not affected by water-rock reaction in near surface; critical for differentiating hot-water and vapor-dominated systems; critical for determining subsurface dilution. Mixing is generally indicated if the Cl concentration difference between the highest and lowest exceeds 10-15%.
B	Not affected by water-rock reaction in near surface; relatively high in thermal water, especially those from sedimentary rocks. Can often be substituted for Cl in mixing calculations.
Cl/B	Usually distinctive for each mass of thermal water; can indicate deep interconnections and mixture of water masses. Consistency of ratio indicates a homogeneous source for the most soluble constituents.
Na, K, Ca	Strongly affected by temperature-dependent water-rock reactions (especially K and Ca); used as a geothermometer.*
SiO_2	Strongly dependent on subsurface reaction with silica minerals and silicates; used as a geothermometer.*
$Cl/(HCO_3-CO_3)$	Strongly dependent on CO_2-water-reactions that depend on temperature, CO_2 pressure, and reactive reservoir rocks; useful as an index to subsurface flow; change by a factor of 8 observed in a single system.

Table II.--Importance of individual components of water and gases in chemical study of geothermal system--Cont.

Na/Li	Qualitative index to geothermal quality; ratio is between 60 and 80 in high temperature systems; up to 1500 in normal waters.*
Mg	Qualitative index to geothermal quality; very low in high temperature systems of low salinity.*
SO_4	Of both deep and near surface origin (from oxidation of H_2S), high SO_4/Cl commonly indicates steam fed springs.
pH	Usually low in steam fed springs if H_2S is available for oxidation to SO_4 (in one case the pH is 1); field measurement allows calculation of HCO_3 - CO_3 distribution.
Temperature	Valuable for calculation of heat flow and subsurface mixture and for estimation of subsurface flow pattern.*
Discharge	Valuable for evaluating significance of temperature; also for indicating if much heat is lost by conduction. Important to estimate discharge of individually sampled springs as well as the surface discharge of each system. Valuable in estimating heat flows.

*/ From Truesdell (1974b)

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A reliable determination of the chemical composition of geothermal fluids may require special sampling and preservation techniques. A sample collected without pretreatment is usually adequate for the analysis of sodium, potassium, and chloride. Other constituents may require further treatment or even analysis in the field, depending on the data requirements. The collection and preservation methods described permit accurate results for 31 chemical variables, including major and minor chemical constituents.

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SPECIAL TECHNIQUES FOR

DETERMINING CHEMICAL PROPERTIES

OF GEOTHERMAL WATER

By T. S. Presser and Ivan Barnes

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations 22-74

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INTRODUCTION

The purpose of sampling and analysis of a natural fluid is to determine the properties of the fluid itself in its natural state. Some constituents in natural fluids are unstable and change with time. The changes result from the difference in conditions within the natural environment before sampling compared to those within the sample container in storage. Changes in temperature and partial pressures of gases, especially oxygen, carbon dioxide, and hydrogen sulfide are particularly likely to occur. Experience has shown that plastic bottles are permeable to oxygen as shown by continued oxidation of iron from ferrous to ferric in tightly closed plastic sample bottles. Plastic sample bottles are also permeable to hydrogen sulfide, as shown by the odor in storage cabinets containing tightly capped plastic bottles of samples of water containing hydrogen sulfide. Some constituents, such as sodium, potassium, and chloride, are usually stable and show no change upon storage. Sulfate is also stable in dilute samples in the absence of hydrogen sulfide.

Depending upon the purpose and nature of the study, changes in constituents upon collection and storage of samples may or may not be a problem. No one sample collection procedure will be satisfactory for all purposes. The information needed for a particular study and the desired accuracy should be established first; then appropriate sampling techniques should be selected. This paper suggests sample treatment and field analysis techniques appropriate for minimizing errors that may result from changes in water samples between time of collection and time of analysis. Methods for analysis of the samples in the laboratory are given in standard reference publications (Brown and others, 1970, and American Public Health Association, 1971).

STABILITY OF CONSTITUENTS

The most commonly observed changes in untreated samples are in pH, iron, manganese, bicarbonate, ammonia, hydrogen sulfide, calcium, and sulfate. Silica concentrations in excess of 100 mg/l (milligrams per liter) may lead to difficulties owing to precipitation and polymerization. Polymeric silica is not reactive in the ammonium molybdate method that is often used for laboratory determination of silica.

The changes in sample composition result from loss of carbon dioxide to the air space, oxidation and precipitation of iron and manganese, oxidation of hydrogen sulfide to sulfate, oxidation of ammonia, loss of calcium ion as calcium carbonate precipitates, and precipitation of silica. Waters inoculated with diatoms may also lose silica. Once a precipitate forms, there is no accurate way to restore

the initial composition of the solution. Constituents that will probably be unaffected by storage include sulfate (if no hydrogen sulfide was originally present), lithium, sodium, potassium, magnesium, fluoride, chloride, bromide, iodide, and boron.

SAMPLE TREATMENT AND FIELD ANALYSIS

Samples for determination of stable constituents require no pretreatment. A sample of adequate size, usually 2 liters, is collected in a carefully cleaned bottle, generally of glass or polyethylene. The bottle should be rinsed with the source water and then filled, leaving an air space for expansion, tightly stoppered, and designated Ru (raw, untreated).

Samples for determination of iron, manganese, calcium, and magnesium should be filtered and acidified at the time of collection, preferably with hydrochloric acid. Nitric acid and sulfuric acid cause interferences in analyses. Iron may be present as fine particles of ferric hydroxide, some of which pass 0.45μm (micrometer) filters but not 0.1μm filters. To maximize the probability (although not to make certain) of obtaining only the iron in solution, 0.1μm or finer filters should be used. Lightweight filter kits using air pressure have been found useful for field filtration. The filtration rarely takes as much as 15 minutes. A volume of 200 ml (milliliters) of filtrate acidified to pH 2 as indicated by pH paper is adequate for determining these cations by direct aspiration in the atomic absorption spectrophotometer.

If results of a high degree of accuracy are required, several precautions must be taken in the field to insure an adequately preserved sample for laboratory analysis. Polyethylene bottles with polyseal caps are recommended as sample containers. The bottles prior to use should be rinsed first with 10 percent nitric acid and second with several washings of distilled deionized water. A filtering apparatus using compressed nitrogen and a 0.1μm or 0.45μm membrane filter is preferred. The apparatus should be rinsed with distilled deionized water immediately prior to use. The first liter of filtered sample is used to rinse the collection bottles and is discarded. One liter of sample is then filtered, collected, and designated Fu (filtered, untreated) for anion analysis. One liter of sample is also filtered, collected, and acidified with high purity acid to a pH of approximately 1.5 as indicated either by pH paper or a pH meter and designated Fa (filtered, acidified) for cation analysis. Complete information on sample sizes recommended for various constituents is given in the table at the end of the paper. For trace element analysis in the part per billion range a set of more rigorous procedures is needed and will not be covered here.

The choice of acid for the acidification step is very important because several of the analyses performed in the laboratory are subject to interferences from these acids. Hydrochloric acid interferes with the analysis of silver and lead because insoluble chlorides may be formed. Hydrochloric acid free from metal contaminants is not readily available. Sulfuric acid interferes with the analysis of calcium and magnesium and some of the heavy metals. Nitric acid interferes with the analysis of strontium and calcium. However, nitric acid is the acid of choice for the heavy metal analyses because it is readily available at high purity, all metal nitrates are soluble, and it is an oxidizing acid. It is recommended that the sample for calcium and strontium analysis be acidified with hydrochloric acid and the sample for heavy metal analysis be acidified with nitric acid. Therefore, if a 1-liter sample is filtered and acidified with nitric acid for heavy metals, an additional 100 ml sample should be filtered and acidified with hydrochloric acid. If only iron, manganese, calcium, and magnesium are needed, filter and acidify two 100 ml bottles, one with hydrochloric acid and one with nitric acid. Each bottle should be labeled with the type of acid used for acidification.

If the water is expected to contain a high concentration of silica, a 1:10 dilution made in the field is desirable, as polymers may form in the concentrated sample. Ninety ml of deionized water is measured accurately and placed in a 125 ml plastic bottle prior to going into the field. At the sample site 10 ml of the sample is pipetted into the prepared bottle.

Field determination of pH and alkalinity

To obtain reliable values, pH and bicarbonate must be determined in the field (Barnes, 1964). For normal waters, two pH buffers are put in the cup of a combination electrode, or other suitable container, each is brought to the temperature of the water source, and the meter is calibrated. The stepwise procedure is:

1. Put pH 7 buffer in cup and immerse cup electrode in water source.

2. When pH reading is steady, use calibrate knob to adjust meter to pH 7.00.

3. Rinse cup, add pH 4 buffer and immerse cup electrode in water source.

4. When reading is constant, use temperature knob on pH meter to adjust meter to pH 4.00. The meter is now direct reading at temperatures near 25°C. In any event, record the observed pH of the pH 4 buffer so true pH values may be calculated later.

5. Rinse electrode and immerse in water source.

6. Record pH when reading is steady. The indicated pH of the 4 and 7 buffers and the pH of the water and the temperature are all needed for calculation of the true pH.

7. Fill buret with standard acid (usually 0.05 N H_2SO_4) for bicarbonate titration.

8. While pH electrode is immersed in water, pipet an aliquot (usually 100 ml) of water into a beaker. Add three drops methyl purple.

9. Transfer electrode to beaker. The pH of the aliquot will almost always be different from the pH of the water source owing to trivial losses of carbon dioxide. This will <u>not</u> affect the titration of bicarbonate significantly.

10. Run acid into beaker while stirring until indicator changes to gray (pH = 5.1).

11. Record at least three pairs of acid volumes and pH readings from the color change through the range to 1 full pH unit below the color change.

Bicarbonate and carbonate will be computed from a titration curve using the data pairs, the temperature, and the pH of the buffers and the water.

For hot springs there should be two pH calibrations, one in the spring (pH of water and two buffers) and one at ambient temperature (pH of water and two buffers, and titration data). The pH of the spring is computed from the high temperature data and the bicarbonate and carbonate from the low temperature data.

Field determination of ammonia

Ammonia can be determined in the field, using a millivolt meter or pIon meter with specific ion electrodes. Additional equipment and reagents needed include 1, 10, and 100 mg/l NH_3 standards (100 ml each), a small bottle of 10 N NaOH, and four graduated plastic beakers. The procedure is:

1. Put a measured volume of unknown into a beaker (usually 25 ml).

2. Add 10 N NaOH to sample, at the rate of 1 ml NaOH/100 ml sample (one drop $\sim$ 0.05 ml).

3. Immediately place electrode in the solution. Set meter to determine millivolts. Measure sample, recording millivolts.

4. Repeat the above steps with standards, measuring millivolts of the most dilute standard first.

5. Read mg/l ammonia of sample from calibration curve prepared from standards.

Direct reading ammonia scales are not recommended because the required amplification makes the meter unstable under field conditions.

Extraction of aluminum

Aluminum must be extracted from samples in the field. The authors know of no way to store water samples and get reliable aluminum-in-solution results. Data on aluminum in solution are required for studies of the reactions of aluminosilicates.

Filter each sample immediately after collection through a 0.1μm membrane filter to remove coarse particulate matter. Extract aluminum immediately upon filtration if only monomeric or readily reactive polymeric forms are to be determined. For total aluminum in the filtered sample acidify to pH 2 and allow to stand about 2 weeks to convert the larger polynuclear aluminum species to a more reactive form.

Prepare a series of standards containing 0, 5, 10, and 20μg (micrograms) Al^{+3} in 400 ml distilled, deionized water. Carry standards through the entire procedure. Detection limit is approximately 2 μg/l (0.002 mg/l). Transfer 400 ml of a sample containing less than 20 μg Al^{+3} and less than 0.4 mg Fe to a 500 ml separatory funnel. Add 10 to 15 drops of phenol red indicator and 2 ml of 5 percent 8-hydroxyquinoline. Swirl to mix. Raise the pH to about 8 by adding ammonium hydroxide dropwise, while swirling to mix, until the solution turns red. Immediately add 5 ml buffer solution and 15 ml methyl isobutyl ketone (MIBK). Shake vigorously for at least 10 seconds but no more than 30 seconds if only dissolved and readily reactive species of aluminum are to be determined. Allow the phases to separate. Drain off the aqueous phase and discard. Collect the MIBK extract, stopper tightly, refrigerate, and save for the atomic absorption measurement of aluminum.

If a greenish-black precipitate forms with 8-hydroxyquinoline as the pH is raised, the sample probably contains a large amount of iron. Discard the sample and start with a new 400 ml aliquot. Add 5 ml of 20 percent hydroxylamine hydrochloride, 5 ml of 1 percent 1,10-phenanthroline, adjust the pH to about 4, and swirl to mix. Allow the sample with added reagents to stand at least 30 minutes to reduce the iron from

ferric to ferrous and continue with the procedure beginning with the addition of the ammonium hydroxide indicator. If the orange-red color of the ferrous phenanthroline complex tends to mask the red end point of the phenol red indicator, a pH meter equipped with a combination electrode may be used to monitor the pH during the addition of the ammonium hydroxide.

Preservation of sulfide

Sulfide should be determined in the field, but for those who find this impossible, the following procedure may be used for preservation of the sulfide for periods of less than 24 hours.

Reagents:

∿0.8 N zinc acetate: Dissolve 17.6 g $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in deionized water and dilute to 100 ml with deionized water. Place in dropping bottle (20 drops = 1 ml).

∿1 N sodium hydroxide: Dissolve 4 g NaOH in deionized water and dilute to 100 ml with deionized water. Place in dropping bottle (20 drops = 1 ml).

Collect two 100 ml portions of filtered untreated sample in separate containers. To each container immediately add 1 ml 0.8 N $Zn(C_2H_3O_2)_2$ solution followed by 1 ml 1 N NaOH solution. Swirl the bottles and wait for a precipitate to form. The solution must be analyzed within the next 24 hours. One ml of 0.8 N Zn $(C_2H_3O_2)_2$ will preserve as much as 270 mg/l H_2S.

Field determination of sulfide

Reagents:

∿0.8 N zinc acetate

∿1 N sodium hydroxide

Hydrochloric acid, concentrated

0.01 N iodine (standardized against thiosulfate)

0.01 N sodium thiosulfate, standard solution of known normality (standardized against potassium iodide)

Starch solution: Dissolve 1 g soluble starch in 2 ml hot deionized water and dilute to 100 ml with hot deionized water. Add 1 ml chloroform as a preservative.

Procedure:

Prepare a blank of 100 ml deionized water and carry it through the determination with the sample. Pipet a volume of filtered, untreated sample (100 ml maximum) into a 250 ml disposable plastic beaker and adjust the volume to approximately 100 ml with deionized water. Immediately add 1 ml 0.8 N $Zn(C_2H_3O_2)_2$ and then 1 ml 1 N NaOH solution. Swirl the beaker and wait for a precipitate to form. The solution may be kept at this point and run within the next 24 hours. If the temperature of the sample is higher than 25°C, let the sample cool in the open beaker until 25°C is reached (a cold water bath may be used) before continuing the determination. Add 10 ml concentrated HCl followed immediately by 10.0 ml 0.01 N I_2. Place the beaker on the magnetic stirrer and titrate the excess iodine (yellow color) with 0.01 N $Na_2S_2O_3$, adding approximately 1 ml of starch when the color has decreased to a pale yellow color. Continue titrating until the blue starch color has disappeared (this color will return upon standing owing to air oxidation). If no iodine is liberated from the acidified sample (no yellow color), prepare a smaller sample volume or a dilution of the sample. For calculation of mg/l hydrogen sulfide, record the number of milliliters of sodium thiosulfate used for the sample and for the blank and the normality of the sodium thiosulfate solution.

Calculations:

Mg/l H_2S =

$$\frac{1{,}000}{\text{ml of sample taken}} \times 17.04 \times N\ Na_2S_2O_3 \times \left(\begin{matrix}\text{ml blank}\\ \text{titrant}\end{matrix} - \begin{matrix}\text{ml sample}\\ \text{titrant}\end{matrix}\right).$$

Size of sample required

Sample sizes cannot be arbitrarily specified. The volumes listed in table 1 are only an approximate guide. If the sample is highly concentrated much smaller volumes may suffice for some determinations depending on the necessity for dilutions. If the sample is relatively dilute, larger volumes will be needed, never smaller.

Table 1.--Guidelines for analyses performed in the laboratory

Constituent	Volume[1/]	Detection limit using only this volume	Method
pH	20 ml Ru or Fu	-	Meter
Specific conductance. .	25 ml Ru or Fu	0.1 µmho	Meter
Alkalinity as HCO_3. . . .	50 ml Ru or Fu	1 mg/l	Automatic titration
H_2S	200 ml Ru or Fu	.5 mg/l	Titration (Iodine-thiosulfate)
NH_4(N)	25 ml Ru or Fu	.1 mg/l	Specific ion electrode
SiO_2	25 ml Fu	10 mg/l	Atomic absorption
SiO_2	50 ml Fu	.1 mg/l	Colorimetric (molybdate blue)
Na	25 ml Fa or Ru or Fu	.1 mg/l	Atomic absorption
K	25 ml Fa or Ru or Fu	.1 mg/l	Do.
Ca	25 ml Fa	.1 mg/l	Do.
Mg	25 ml Fa	.1 mg/l	Do.
Cl	200 ml Fu	1.0 mg/l	Specific ion electrode titration
Cl	150 ml Fu	10 mg/l	Mohr titration
SO_4	100 ml Fu	1.0 mg/l	Colorimetric (thorin)
F.	20 ml Fu	.1 mg/l	Specific ion electrode
B	25 ml Fu or Fa or Ru	.02 mg/l	Colorimetric
Sr	25 ml Fa	.1 mg/l	Atomic absorption
Li	20 ml Fa or Fu or Ru	.01 mg/l	Do.

Table 1.--Guidelines for analyses perfomed in the laboratory--Continued

Constituent	Volume[1/]	Detection limit using only this volume	Method
Cs	20 ml Fa or Fu or Ru	0.1 mg/l	Atomic absorption
Rb	20 ml Fa or Fu or Ru	.01 mg/l	Do.
As	20 ml Fa or Fu or Ru	5 mg/l	Do.
Sb	20 ml Fa or Fu or Ru	.1 mg/l	Do.
Heavy metals			
Ag	20 ml Fa	.02 mg/l	Atomic absorption
Au	20 ml Fa	.1 mg/l	Do.
Cd	20 ml Fa	.01 mg/l	Do.
Co	20 ml Fa	.05 mg/l	Do.
Cu	20 ml Fa	.02 mg/l	Do.
Fe	20 ml Fa	.05 mg/l	Do.
Mn	20 ml Fa	.01 mg/l	Do.
Ni	20 ml Fa	.05 mg/l	Do.
Pb	20 ml Fa	.1 mg/l	Do.
Zn	20 ml Fa	.01 mg/l	Do.

1/ Ru = raw untreated

Ra = raw acidified

Fu = filtered untreated

Fa = filtered acidified

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GEOCHEMICAL INDICATORS OF SUBSURFACE TEMPERATURE—PART 1, BASIC ASSUMPTIONS

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Abstract.—The chemical and isotopic compositions of hot-spring water and gas are used to estimate subsurface temperatures. The basic assumptions inherent in the methods are seldom stipulated. These assumptions include (1) a temperature-dependent reaction at depth, (2) a supply of the solid phase involved in the reaction to permit saturation of the constituent used for geothermometry, (3) water-rock equilibrium at depth, (4) negligible re-equilibration as the water flows to the surface, and (5) no dilution or mixing of hot and cold water. The first three assumptions are probably good for a few reactions that occur in many places. The last two assumptions probably are not valid for many hot-spring systems; information obtained is therefore for the shallower parts of those systems, or a limiting temperature (generally a minimum) is indicated.

The recent increased interest in geothermal energy has prompted widespread exploration for this resource. As expected, the areas initially receiving the most attention are those in which fumaroles and hot springs of high temperature are found. Thermal springs are numerous in the western United States. Their temperatures range from a few degrees above mean annual temperature to boiling. In general, their relative abundance decreases with increasing temperature. From an exploration point of view, the critical question is, how did a given spring attain its observed temperature? Did the warm temperature result from water circulating deeply in a region of normal or slightly above normal geothermal gradient; that is, does the temperature of the spring represent the highest subsurface temperature deep in the system? Or, did the water come from a very high temperature environment at depth and cool on the way back to the surface? We would like to use the chemical composition of the water to answer these questions. In practice, we have found that springs with high rates of discharge are most suitable for hydrogeochemical prospecting, whereas compositions of springs with low rates of discharge are very difficult to interpret.

BASIC ASSUMPTIONS

There are many basic assumptions inherent in using geochemical indicators to estimate subsurface temperatures (White, 1974). Although these assumptions may be valid in many places, it is unlikely that they will be fulfilled everywhere. The usual assumptions are:

1. Temperature-dependent reactions occur at depth.
2. All constituents involved in a temperature-dependent reaction are sufficiently abundant (that is, supply is not a limiting factor).
3. Water-rock equilibration occurs at the reservoir temperature.
4. Little or no re-equilibration or change in composition occurs at lower temperatures as the water flows from the reservoir to the surface.
5. The hot water coming from deep in the system does not mix with cooler shallow ground water.

A schematic model of a hot-spring system (fig. 1) is useful in assessing these assumptions. Critical elements of the model include a heat source of unspecified nature at the base of the system and interconnected permeability that permits convection to occur. In response to heating, water deep in the system decreases in density and is forced up and out of the system, as at A, by pressure exerted by cold, dense water. The cold water moves down and into the system at the margins along permeable structures, possibly faults or joints such as B—B′. There are many alternative possibilities, including models in which some or all of the ascending water and gas is connate, metamorphic, or even juvenile in origin. In some places the salinity of the deep water may be high enough to counteract the effects of temperature on density. Although connate and metamorphic water is probably dominant in some hot springs (White and others, 1973), isotope data indicate that most hot-spring water is predominantly meteoric in origin.

If the maximum temperature attained by the water at depth is higher than the boiling temperature appropriate for atmospheric conditions, the water will cool by boiling (adiabatically), by conduction, or by a combination of these processes as it moves toward the surface. If, on the other hand, the maximum temperature at depth is less than the boiling temperature at atmospheric conditions, the emerging water, such as at A (fig. 1) may have approximately the maximum temperature at depth or a lower temperature, depending on whether the rate of upflow of water is very fast or slow.

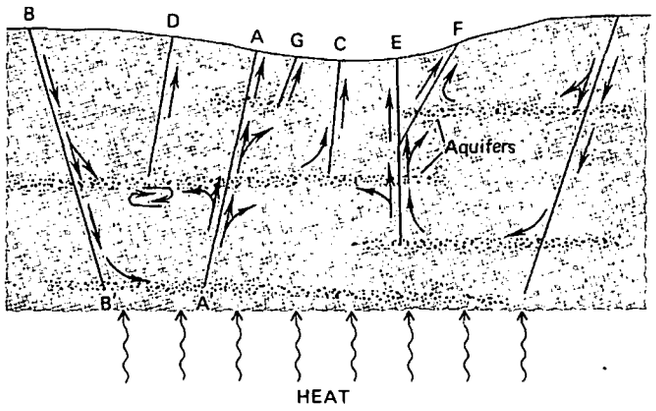

Figure 1.—Schematic model of a hot-spring system having a heat source of unspecified nature and interconnected permeability.

Solubilities

Solubilities of minerals generally change as functions of temperature and water pressure. Therefore, under some circumstances absolute quantities of dissolved constituents are useful indicators of subsurface temperature. However, the dissolving solid phase must be specified and its presence must be assumed at depth. An example is the silica geothermometer, which depends on the solubility of quartz controlling aqueous silica (Fournier and Rowe, 1966; Mahon, 1966).

In general, the solubilities of the common silicates increase with increasing temperature and pressure. As cold subsurface water is heated, it dissolves more and more silicate constituents, reaching a maximum at the hottest (and generally deepest) part of the system. Deposition of silicates may then occur as the water moves back toward the surface and cools, particularly if the cooling is adiabatic. This may result in the self-sealing of the geothermal system, as discussed by Bodvarsson (1964), Facca and Tonani (1967), and White, Muffler, and Truesdell (1971).

The common carbonates have retrograde solubilities (Holland, 1967). Other things being constant, minimum solubilities are attained at the hottest and deepest parts of the system. Generally "other things" are not constant, however. Carbonate solubilities are greatly affected by variations in pH and partial pressure of CO_2. Unfortunately, subsurface pH and P_{CO_2} are not easily estimated from the composition of hot-spring water and gas collected at the surface.

The common sulfates also have retrograde solubilities. Like the carbonates, their usefulness in geothermometry is restricted to systems in which the solid phase is present at depth. One cannot safely assume this unless sulfates have been found in cuttings or cores from holes drilled at the locality in question. In other words, there may be an inadequate supply of the "indicator" constituent in the reservoir, so that the solution at depth is unsaturated with respect to a particular phase; for example, $CaSO_4$ or $BaSO_4$.

Exchange reactions

Equilibrium constants for exchange and alteration reactions also are temperature dependent. In such reactions the ratios of dissolved constituents change with changing temperature of equilibration. Both chemical and isotopic reactions come under this category. Examples are Na:K ratios of chloride solutions equilibrated with alkali feldspars (Orville, 1963; Hemley, 1967), Na:K ratios in natural waters (Ellis, 1970; White, 1965), and Na-K-Ca relations in natural waters (Fournier and Truesdell, 1973). Again, as in the solubility method of geothermometry, the identity of the reactants and products in the high-temperature environment at depth must be assumed. If the assumed phases are not present, the geothermometer yields anomalous results (Fournier and Truesdell, 1970, 1973).

Equilibration at depth

In order to use a geochemical method of estimating subsurface temperature, one must assume equilibrium or at least an approach to equilibrium at depth for a specific "indicator" reaction. At low temperatures, this is a tenuous assumption. Metastable conditions also are likely to occur. However, the assumption of attainment of equilibrium in a high-temperature environment at depth is probably good for many reactions. This assumption is particularly good where the residence time for water in a reservoir at a relatively uniform temperature is long and there is effective mixing or homogenization of introduced water with stored water.

When an increment of water, chemically equilibrated at depth, finally does enter a channel that allows direct movement back to the surface, such as A–A′ in figure 1, the time of upward travel may be very short (minutes or hours) compared with the residence time in the reservoir. Consequently, even though the temperature of the water may decrease markedly, little chemical reaction may occur during upward flow, and the composition of the emerging water may reflect the conditions present in the deep reservoir. However, reservoirs at different depths and temperatures may be present within a given geothermal system. Hot springs located at C, E, and G in figure 1 show various possibilities for water re-equilibrating in shallow reservoirs, so that some or all of the chemical geothermometers will yield estimated subsurface temperatures lower than the maximum temperature deep in the system.

A re-equilibrated water, such as that emerging at G (fig. 1), may give a good indication of the salinity of the deep water. More commonly, deep water entering shallow reservoirs will mix with relatively dilute, shallow water, so that neither the temperature nor salinity of the deepest reservoir is indicated by the spring water that eventually emerges at the surface, as at D and F. If the residence times of both the hot- and cold-water components are long in the shallow aquifer and mixing is thorough, the composition of emerging spring water

as at D, may be indicative of the temperature of that shallow reservoir. In contrast, if the residence time in the shallow reservoir of one or both of the mixing waters is short, the composition of the emerging water (spring F) may give little or no information about that shallow reservoir. Under special circumstances, however, it may be possible to estimate the temperature and proportion of the hot-water component of a mixed water such as that emerging at F. This is discussed elsewhere (Fournier and Truesdell, 1974).

In the discussion to this point, we have assumed essentially no chemical reaction in the channels connecting different reservoirs or reservoirs with springs. Advantageous conditions that minimize reactions within channels are rapid rates of upflow, low temperature, and nonreactive wallrock. Where continued chemical reactions do occur in the channelways leading to the surface, different geochemical indicators yield different apparent temperatures, reflecting varying amounts of re-equilibration at intermediate temperatures.

Enrichment of volatiles

Tonani (1970) emphasizes the relative enrichments in spring waters and fumaroles of comparatively volatile components, particularly NH_3, B, Hg, CO_2, and sulfur compounds, that may indicate subsurface boiling. He generally assumes that steam separates from deep boiling water and that it carries other volatile constituents toward the surface. At shallow depth the steam condenses and mixes with the local ground water. Springs fed by this water are enriched in volatiles relative to chloride.

Tonani's model probably works very well for vapor-dominated systems, as described by White, Muffler, and Truesdell (1971). It has yet to be demonstrated that volatile constituents are enriched relative to chloride in neutral to alkaline hot springs above hot-water-dominated systems, even where boiling temperatures are attained at depth. Enrichment of volatile constituents in spring water may result from processes other than high-temperature boiling. Gases such as CO_2 and CH_4, if sufficiently abundant, may separate from relatively cold water deep underground and escape to the surface. If this gas later encounters shallow ground water, that ground water may become enriched in volatile constituents.

RECOMMENDED PROCEDURE

For estimating subsurface temperatures we set forth the following guidelines despite misgivings that they will be interpreted as hard-and-fast rules for always reflecting subsurface conditions. The intent is simply to suggest starting assumptions where little information is available about hydrologic conditions. As more information is obtained for a specific area, other assumptions may become more reasonable.

The recommended procedures are based upon the temperature and rate of flow of the spring water, as outlined below:

1. Boiling spring:
   (a) Small rate of flow: Assume mostly conductive cooling. Apply chemical indicators assuming little or no steam loss.
   (b) Large rate of flow: Assume adiabatic cooling. Apply chemical indicators assuming maximum steam loss.
2. Spring below boiling:
   (a) Small rate of flow: Likely to have no clear-cut interpretation. May be a water that has never been very hot, a mixed water from sources of different temperatures, or a hot water cooled entirely by conduction. Try geothermometers that assume conductive cooling; indicated temperatures are likely to be minima.
   (b) Large rate of flow: Assume no conductive cooling. Test to see if geothermometers (particularly the Na-K-Ca geothermometers (Fournier and Truesdell, 1973)) suggest chemical equilibration at the temperature (±25°C) of the water. If a higher temperature is indicated, treat as a mixed water according to the method of Fournier and Truesdell (1974).

We have not specified what large and small rates of flow are. Our intent is to distinguish between waters that cool by conduction during their ascent and those that either cool mainly by boiling or do not cool at all. This depends in part on the rate of upflow, the depth of the aquifer supplying the water, and whether a spring is isolated or is part of a larger upflowing system. For preliminary evaluation, an arbitrary cutoff at 200 l/min is suggested for a single isolated spring, and 20 l/min for single springs of larger groups.

CONCLUSIONS

Chemical analyses of hot-spring water and gas may be of great use in an exploration program for geothermal energy. Like all exploration methods, a great many assumptions must be made in order to interpret the data. We urge that these assumptions be kept in mind during the evaluation processes.

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Collection of Chemical, Isotope, and Gas Samples from Geothermal Wells

by

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ABSTRACT

Reconstruction of the downhole composition in a geothermal well requires field measurements of total fluid enthalpy and separator pressure along with chemical, isotope, and gas analyses of separated water, steam condensate and gas phases. Analyses of each phase for components distributed between phases are necessary because the fluids may not be in equilibrium at the sampling points. Cooling after separation must be sufficient to prevent loss of volatiles and water vapor. The collection and analysis schemes presented are designed to allow complete chemical and gas analyses and isotopic analyses of major carbon, oxygen, hydrogen, and sulfur containing species.

INTRODUCTION

Steam Wells

Steam wells such as those at The Geysers do not present major collection problems in obtaining a representative sample. It is usually sufficient to collect a sample from a bypass on the wellhead, taking precautions to avoid condensation in the bypass. This can be accomplished either by flowing sufficient steam to insure the temperature of the collected steam is the same as that in the well or by insulating a large diameter bypass. A probe inserted to the center of a large diameter flowing steam line has been found to provide representative samples[1/].

Hot Water Wells

Sampling hot water wells is more difficult. Small amounts of fluid must be removed from a rapidly flowing, usually two-phase, fluid in a controlled manner so the samples are representative of the whole fluid. Simply connecting a condenser to a pipe carrying a water-steam mixture does not produce the correct proportion of the two phases. It is possible to collect good samples of the water and steam phases after separation of the two-phase fluid is completed in a cyclone separator and use enthalpy measurements to calculate the total composition.

SEPARATION OF HOT WATER AND STEAM

Understanding the operation and limitations of separators is necessary before reliable samples can be collected. A centrifugal Webre separator (Fig. 1) is provided on most production wells. It consists of a vertical drum with a tangential inlet at the center, an outlet for water at the bottom, and a central outlet tube open at the top which collects the steam. The two-phase fluid enters tangentially at the center, spins rapidly around the outer wall of the drum with the water collecting on the outside and falling to the bottom and the steam moving to the inside and flowing down the central tube. The steam-water level is set by adjustment of a valve in the water flow line. Since water in the steam line to the turbines would be highly undesirable, it is usual to stabilize the water level by allowing a small flow of steam into the water line. If sampling is then done from the water line, apparent nonequilibrium fractionation of gases between steam and water will be observed. Allowing some steam in the water line also would produce slightly lower apparent enthalpy but this can be avoided by careful adjustment of separator water level during enthalpy measurements. Water samples should be taken, if possible, from a separate tap below the water outlet of the separator where the water is less likely to be contaminated with steam (Fig. 1).

If a large separator is not available, the sample can be taken with a mini cyclone separator (Figs. 2 and 3). With this separator the water and steam flows are adjusted to allow some water to issue from the steam outlet while collecting from the water outlet and vice versa. The separator and the tube from the bypass must be well insulated and the flow limited to maintain the pressure in the separator during sampling nearly equal to the pressure in the well. These measures are necessary to insure that condensation does not occur before or in the separator and that the water and steam collected from the separator have the same compositions as the phases in the well.

Enthalpy Measurements

Enthalpy measurements are routinely made on production wells by measuring the flows of steam and water from the large separator. The measurement of total enthalpy without a large separator is difficult and approximate but may be done by critical lip pressure measurements or by measuring the steam/gas ratio at two different pressures[2/]. If it is known that boiling in the formation does not occur, the bottom hole flowing temperature can be used to obtain a value for the enthalpy.

CONDENSATION AND COOLING

Steam and water exit from the separator at temperatures considerably above surface boiling and must be cooled for safe handling and to avoid the loss of volatile substances. This is most easily accomplished with a double coil condenser of ¼" stainless steel tubing connected to the separator (or bypass) by a regulating valve. Larger diameter tubing may allow inconveniently large slugs of gas and condensate to form. The first coil is immersed in water which is allowed to boil, effectively reducing the temperature of the fluid sample to 100°C or less. The second coil is held in an ice or water bath or in the air according to the desired temperature of collection. The water and steam phases can be cooled by serial passage through the same condenser but are treated differently when they emerge.

SEPARATION OF STEAM CONDENSATE AND GAS

Collection of steam condensate and gas from a steam well is the same as from a water-steam separator but the methods used may vary because of different steam/gas ratios and because it may be necessary to check for incomplete steam separation in the separator. The steam condensate and gas issue from the condenser in discontinuous slugs. The use of ¼" tubing produces relatively small, uniform slugs and the average composition of issuing fluid is uniform over the period of collection of any single sample.

A sample of gas without the steam condensate is best for gas analyses and for the study of isotopes of carbon, sulfur, and hydrogen in gas components. A steam condensate-gas separator (Fig. 4) was constructed from a graduated cylinder by attaching two tubulations at the top and one at the bottom. The flow from the condenser enters at the top (vinyl tubing is used for all connections) and the flow of condensate from the bottom is restricted with a clamp so that gas alone issues from the remaining top tubulation. The tubing on the bottom is inserted in a large bottle of steam condensate to prevent back flow of air into the separator during gas collection.

FIELD MEASUREMENTS

Steam/Gas Ratios

The steam/gas ratio may be measured by timing the alternate displacement of gas by condensate and vice versa in a bottle with one tube at each end (the least accurate method because during the condensate collection part of the volume is occupied by rising gas bubbles), by measuring the flow of water with a graduated cylinder and the flow of gas with a soap film flow-meter from the gas-water separator

(more accurate but requiring exact balancing of flows), or by allowing gas to displace condensate in a tube or separator of known volume and measuring the quantity of condensate displaced (the most accurate field method). None of these field methods measure the quantity of gas dissolved in the condensate which may be a large part of the total when the steam/gas ratio is high. More accurate steam/gas ratios may be obtained from laboratory analyses of steam condensate and gas collected in a single bottle (see below).

pH Measurements

During separation and cooling the pressure of CO_2 is above or near one atmosphere and CO_2-supercharged water or steam condensate issues from the condenser. Part of the CO_2 is rapidly lost and the pH and H_2CO_3, HCO_3 and CO_3 concentrations change until equilibrium with atmospheric CO_2 is established. For this reason pH measurements and field alkalinity titrations are not very useful. It is more useful to collect all the CO_2 by $SrCO_3$ precipitation (described later) and to measure the pH and alkalinity on air-equilibrated samples in the laboratory. This pH measurement can be related to the state of ionization of all weak acids and bases.

Pressure and Temperature Measurements

Separator pressure is needed to calculate the water/steam ratio. Temperature measurements of the water and steam condensate issuing from the condenser are needed to calculate the distribution of gases between phases and are desirable to determine if isotopic fractionation of D or ^{18}O occurred.

COLLECTION OF WATER

Figure 5 is a schematic diagram of the collection procedure discussed in the paper.

Dissolved Salts

Water samples for dissolved salts are filtered through a 0.45 μ pore membrane filter (or if suspended clay is suspected, through a 0.1 μ pore membrane) and part is acidified to pH 2 with HCl to prevent precipitation of Ca or Mg carbonates or adsorption of cations on the walls of the bottle. The dissolved salts are analysed by conventional water chemistry methods. Silica is usually present in amounts exceeding saturation with amorphous silica at room temperature so a separate sample is diluted 1:10 (or 1:20 for fluids originally over 300°C) with silica-free water to prevent precipitation and preserve monomeric silica necessary for the molybdate method. Other preservation methods are required for trace elemental analysis.

Isotopes

Water samples for isotopic analysis (^{18}O and D) are collected in glass bottle with polyseal caps without filtration (which might allow evaporation). A sample for isotopes in dissolved sulfate (^{18}O and ^{34}S) is collected in one or two liter bottles according to concentration (at least 20-30 mg SO_4 is needed for analysis) and preserved with 4 ml/ℓ of formalin solution to prevent bacterial oxidation of H_2S to SO_4. Collection of dissolved CO_2 for ^{13}C and H_2S for ^{34}S will be discussed under dissolved gases.

Dissolved Gases

Although most gas partitions into the steam phase, enough remains in the water to make analysis of dissolved gases important. The most effective way of preserving CO_2 dissolved in water (not only CO_2 but all carbonate species) is to precipitate $SrCO_3$ in a glass bottle by adding concentrated NH_4OH saturated with $SrCl_2$. The ammonia buffers the solution so that all forms of CO_2 are converted to CO_3 and precipitated. Precipitation must be done immediately because CO_2 is rapidly lost to the atmosphere. Later in the laboratory the sample is filtered, weighed, and saved for isotopic analysis.

Hydrogen sulfide is similarly precipitated as CdS with $CdCl_2$ solution. The addition of buffer is unnecessary because the natural bicarbonate - carbon dioxide buffer maintains the solution at a high enough pH (>3) to prevent loss of H_2S with an excess of Cd present.

Ammonia should be preserved in a sealed bottle, acidified if the discharge is alkaline and analysed as soon as possible. Other dissolved gases may be collected by allowing the water to almost fill a weighed, evacuated gas bottle (Fig. 6) through a vinyl tubing attachment to the condenser. The head space of this bottle is analysed for gases in equilibrium with the water.

COLLECTION OF STEAM CONDENSATE AND GAS

Dissolved Salts

Sampling of condensate may be done directly from the condenser or through the bottom tubulation of the steam condensate-gas separator and preserved as for water samples. Chemical analysis may be limited to boron, ammonia, bicarbonate and other substances that have volatile forms that may be carried in steam. On samples from a separator it is necessary to determine the completeness of the separation by analysis of the condensate for Cl, Na, or another nonvolatile substance.

Isotopes

Condensate samples for ^{18}O and D are collected as described above. Sulfate is only contained in steam condensate if produced by the oxidation of H_2S and is not collected for isotopic analysis. CO_2 and H_2S may be precipitated as described above from the condensate or separated from the caustic in the gas bottle (described later). Fractionations resulting from solution of gases in water are small and either of these separates may be analysed depending on which contains the major amount of the gas.

Tritium and carbon-14 may allow limits to be placed on the age of geothermal fluids or on the amount of dilution by near surface water. The analyses are difficult and costly and geothermal fluids contain very little of these isotopes so the collection should be carefully made to avoid contamination. A steam condensate sample should be collected for tritium, as a brine sample requires distillation to remove the salts. Dry, clean bottles should be well flushed by flowing the sample through vinyl tubing to the bottom of the bottle and allowing the bottle to overflow for some time. The bottle should then be sealed with a polyseal cap and taped with vinyl electrical tape applied in the clockwise direction.

Carbon-14 can be collected from steam condensate by precipitation of $SrCO_3$, but the amount of sample (>3 gms of carbon usually needed for analysis) requires long settling times. The collection of steam phase CO_2 from the gas-water separator into gas bubblers containing CO_2-free ammonia may be quicker and is less prone to contamination. If the steam/gas ratio is very high this method may require inconveniently long collection times, and $SrCO_3$ precipitation from steam condensate may be preferred.

Gases

The total cooled steam sample (gas and condensate) is collected into an evacuated 300 or 500 ml gas bottle (Fig. 6) containing 50 to 100 ml of 4N NaOH (prepared as carbonate-free as possible). The flow from the condenser should be reduced by regulating the valve on the separator or steam bypass. A pressure-relief valve may be used to prevent over-pressuring the gas bottle. This sample allows the most accurate measurement of steam, CO_2 and H_2S but the quantity of residual gases may be too small for some determinations. In this case a gas-only sample (without condensate) may be collected from the top of the gas-water separator. A larger quantity of caustic (100 to 150 ml) may be required because a larger quantity of CO_2 and H_2S will be collected.

The flow of gas into the bottle may at first exceed the flow into the gas-water separator and the gas flow into the bottle should be restricted by pinching the vinyl tubing until a balance is achieved. Shaking the gas bottle increases the rate of CO_2 and H_2S absorption and may be necessary at the end, although allowing the gas to bubble through the caustic produces adequate absorption during most of the collection. The CO_2 and H_2S analyses are obtained by wet chemical analysis of NaOH solution. The other gases are analysed by gas chromatography. Dissolved NH_3, CO_2, and H_2S in the steam condensate may be collected and analysed by the same methods described above for water.

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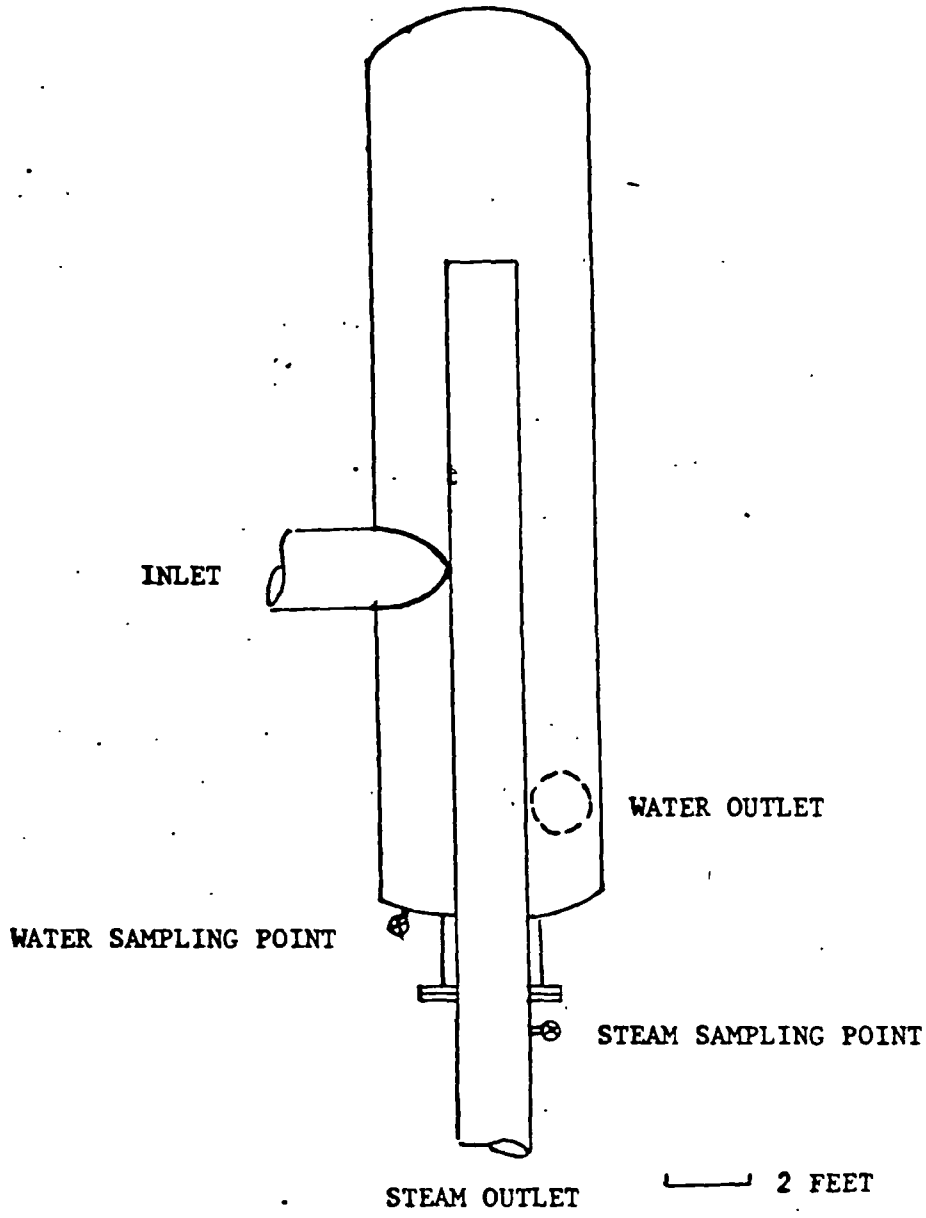

Figure 1--Cross Section of Webre Separator Showing Best Sampling Points

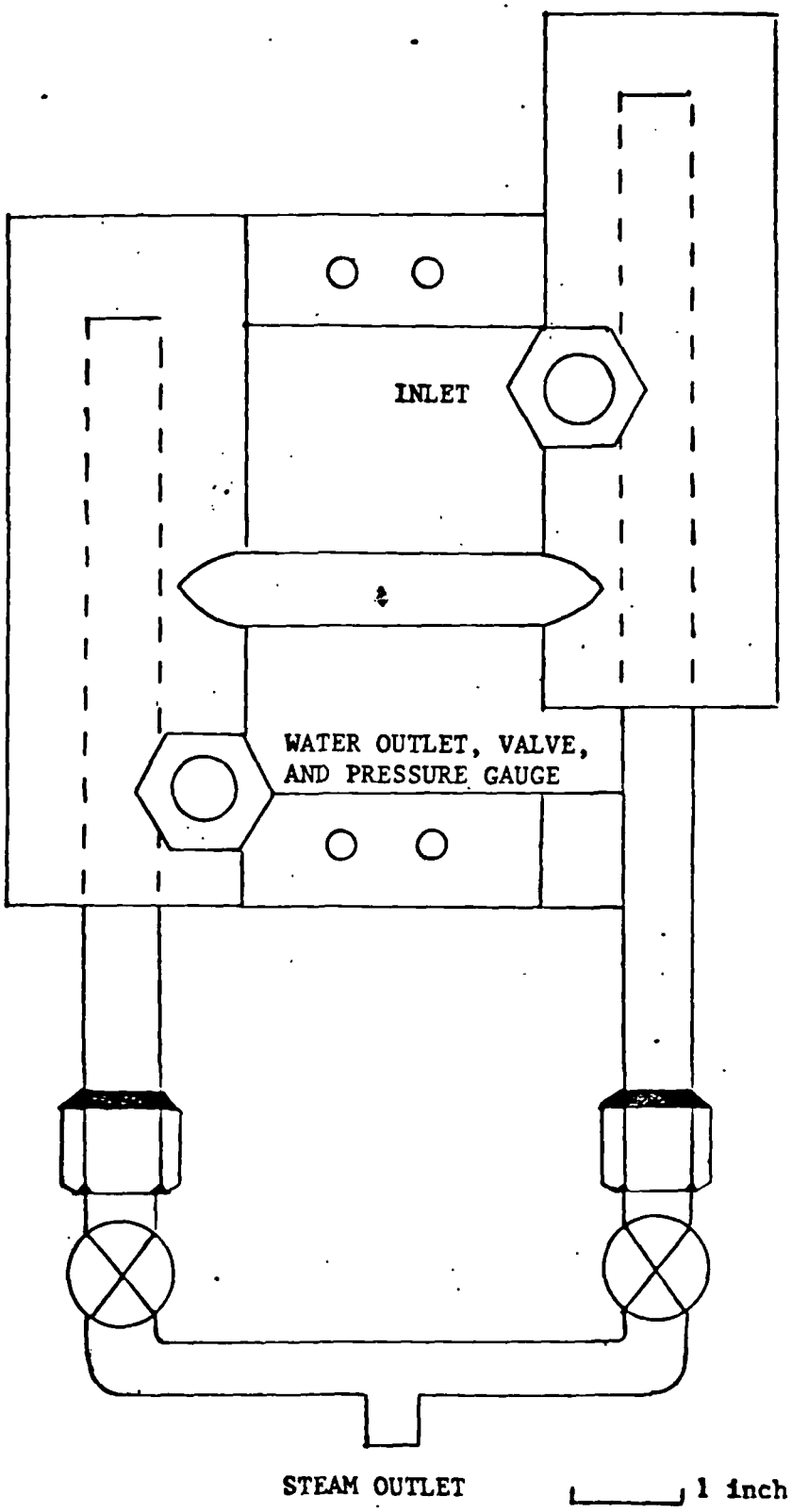

Figure 2--Mini Cyclone Separator of New Zealand Design

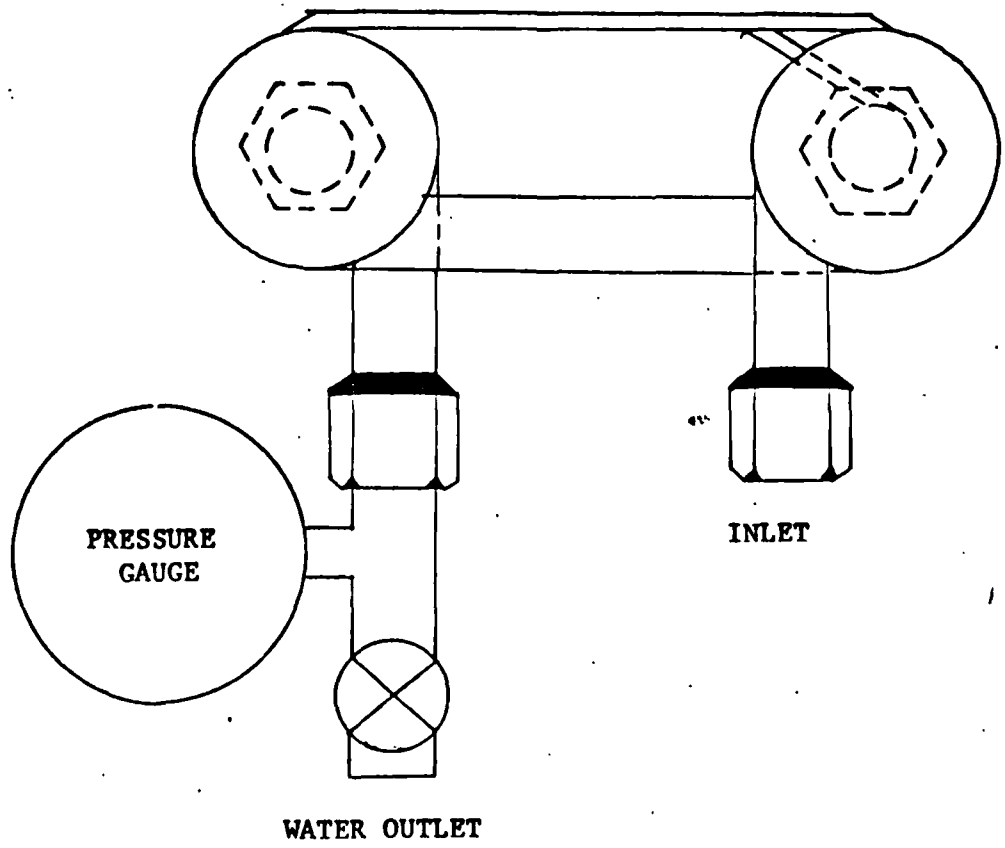

Figure 3--Top View of Mini Cyclone Separator with Pressure Gauge Attached

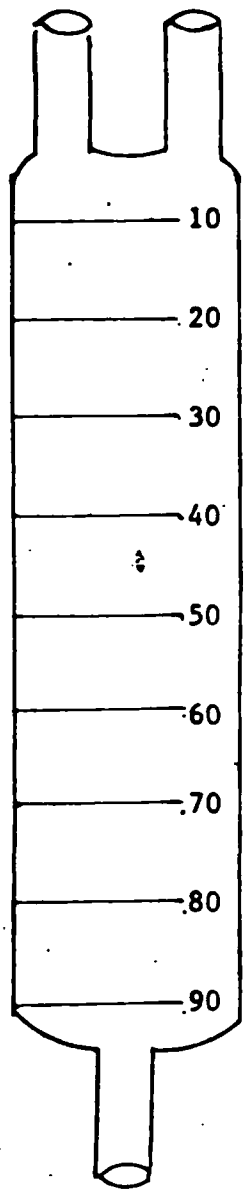

Figure 4--Steam-Gas Separator Modified
From a 100 ml Graduated Cylinder

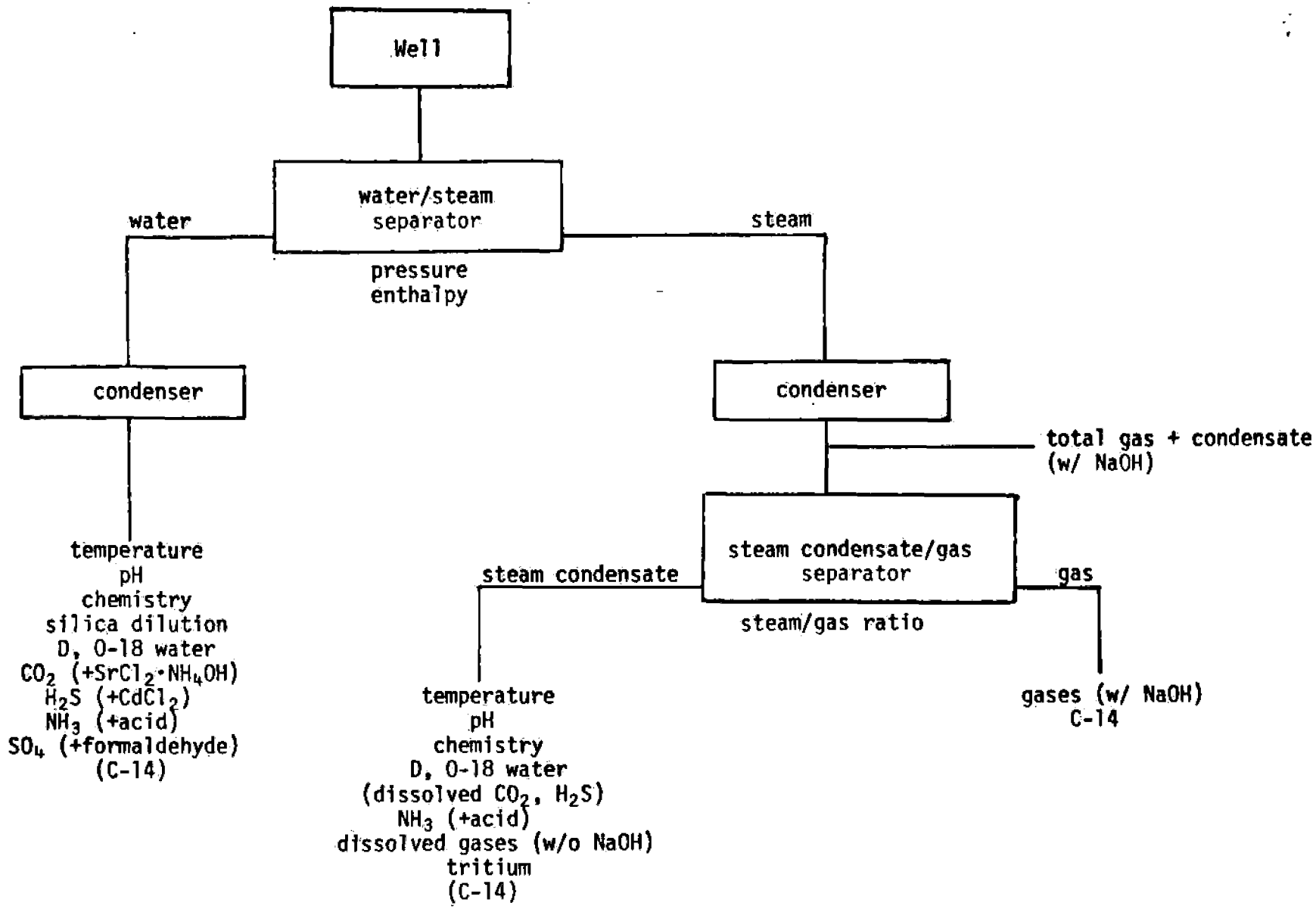

Figure 5 -- Schematic Diagram of Sampling Procedure

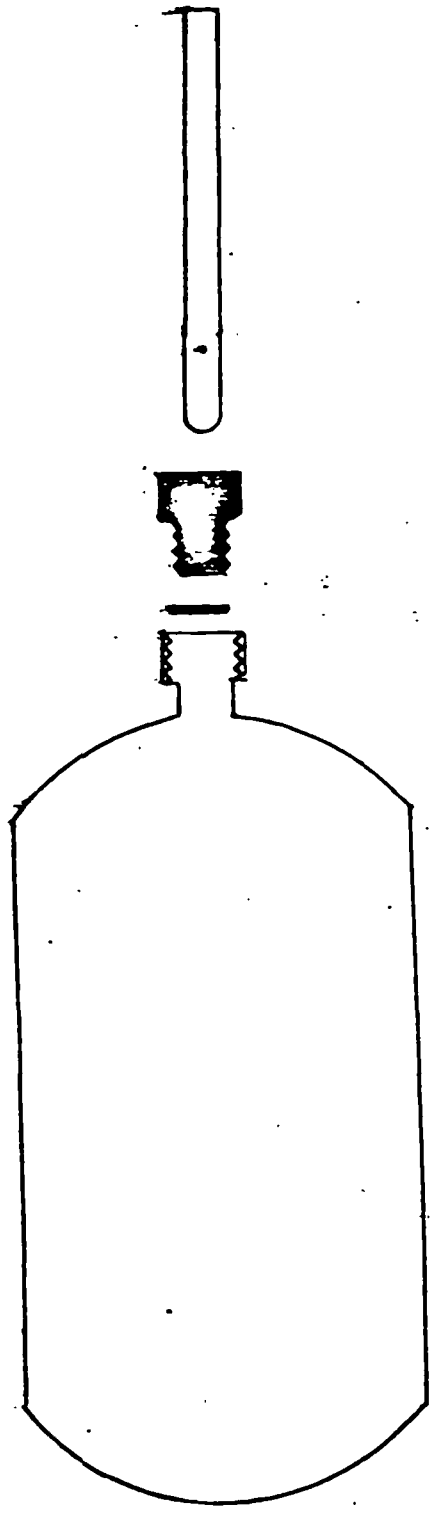

Figure 6 -- Exploded view of gas sample bottle. The bottle is opened by sliding the hole inside the o-ring. The tube may be evacuated with the bottle closed by clamping a second o-ring and washer to the top of the adapter. Gas bottles with NaOH solution are evacuated by a water aspirator with gentle boiling of the solution.

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A METHOD FOR DETERMINING THE ENTHALPY OF A STEAM/WATER MIXTURE DISCHARGED FROM A GEOTHERMAL DRILLHOLE

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(Received for publication 8 August 1966)

Summary

A chemical method is described for determining the enthalpy of steam/water mixtures discharged from geothermal drillholes in areas such as Wairakei, New Zealand. The method, which involves the measurement of the gas content of steam in the discharge at two different pressures, is rapid and simple and is capable of determining enthalpies to better than 5% in the region 400 to 500 Btu/lb.

INTRODUCTION

James (1961) reviewed a number of methods for determining the enthalpy of a steam/water mixture discharged from a geothermal drillhole. One of these methods, referred to as the "Gas Method", was investigated by the present author during the early stages of the geothermal development programme at Wairakei. During the early work many of the results obtained from the "Gas Method" were different from those obtained by the engineering methods employed by the Ministry of Works and in a number of cases were inconsistent in themselves.

The "Gas Method" for determining the enthalpy of steam/water mixtures discharged from geothermal drillholes at Wairakei arose from a suggestion by S. H. Wilson (1956—internal D.S.I.R. report) that a chemical method, either determination of gas in steam samples, or of chloride in water, could be used to determine the enthalpy of the discharge. The initial suggestion was not feasible but C. J. Banwell (1956—internal D.S.I.R. report) developed a formula for calculating the enthalpy from the gas content of two steam samples collected at two sampling points at different pressures. In 1957 R. James and A. H. Hilton, of the Chemistry Division, D.S.I.R., carried out a number of tests of the method on various bores at Wairakei with fairly satisfactory results, but it appeared that more work was required to determine suitable conditions for the accurate use of the method.

Mahon (1961) summarised the various conditions required for obtaining representative samples of steam and water for chemical analysis from drillhole discharges at Wairakei. During the work on drillhole sampling the gas enthalpy method was investigated in more detail and a set of conditions was determined for its successful application.

THEORY OF METHOD

The method is based on the fact that the deep waters in the Wairakei field contain dissolved gases (mainly carbon dioxide) (Mahon 1962; Ellis 1962). This is a fairly general situation in most hydrothermal fields.

Consider a length of pipe-line carrying an expanding steam-water mixture of enthalpy E, at points where the pressures are P_1 and P_2.

E = Enthalpy of whole discharge.
G = Concentration of gas in g/g of whole discharge.
G_1 = Concentration of gas in g/g of steam fraction at pressure P_1.
x_1 = Steam fraction in g/g of discharge mixture at P_1.
L_1 = Latent heat of vapourisation at pressure P_1.
H_1 = Heat content of liquid at pressure P_1 (in equilibrium with vapour).
R = Ratio of concentrations of gas in steam fractions at pressures P_1 and P_2.
r = Ratio of latent heats (L_1 L_2) at pressures P_1 and P_2.

then,

$$x_1 = (E - H_1)/L_1$$
$$G_1 = G/x_1 = G\ L_1/(E - H_1). \text{ Also, } G_2 = G\ L_2/(E - H_2)$$
$$R = r\ (E - H_2)/(E - H_1)$$

Rearranging gives the enthalpy E in terms of R and the known physical parameters for steam and water

$$E = (R\ H_1 - r\ H_2)/(R - r) \qquad \text{.....(1)}$$

The method assumes (a) that there is no loss of heat along the pipe due to conduction through the walls, and no appreciable effect from change of heat energy into kinetic energy: (b) that the gas is relatively insoluble in the liquid phase under the conditions of temperature and pressure. Calculations have shown the first assumption to be approximately correct.

Ellis (1962) gave a quantitative appraisal of the distribution of CO_2 H_2S, and NH_3 between the high-temperature water and steam phases in the Wairakei discharges. At the pressures present in the surface piping (<220 p.s.i.g.) practically all the CO_2 is concentrated in the steam phase. The CO_2 remaining in the water phase would not appreciably affect the enthalpy results obtained from the "Gas Method".

As originally pointed out by Banwell the use of the method depends on the extent to which the gas concentrations in the steam are affected by changes in enthalpy, pressure and pressure differences. Equation (1) shows that for a given enthalpy the greater the difference between P_1 and P_2, and consequently the greater the value of R, the more accurate the calculated enthalpy is likely to be.

EXPERIMENTAL

A. *Field Procedure*

One of the deep Wairakei drillholes, Hole 48, was made available by Ministry of Works for the experimental work. The design of the surface pipe work of the Wairakei drillholes was discussed by Smith (1958).

Fig. 1 is a diagram representing Hole 48, as arranged for the experiments.

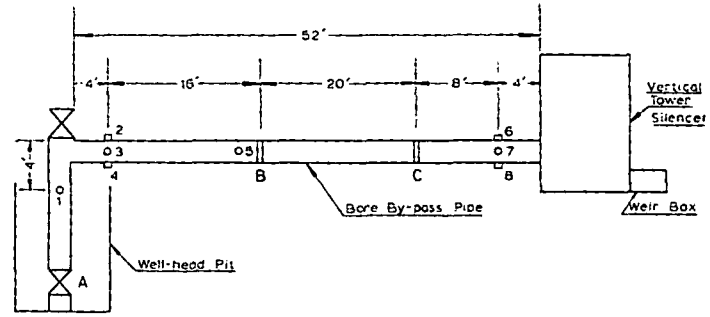

FIG. 1—Elevation diagram of surface pipes at Hole 48 as arranged for the enthalpy experiments.

A represents the master valve;

B & C represent either a throttle valve or back-pressure plate;

1, 2, 3, 4, 5, 6, 7 and 8 represent different sampling points.

The sampling points consisted of 1 in. sockets welded on to the bypass pipe. Half-inch holes were drilled through the bypass pipe and the whole assembly was closed to the atmosphere by 1 in. gate valves. At two points on the bypass, one 4 ft from the vertical wellhead pipe, the other 4 ft from the silencer, sampling points were placed on the top and bottom of the bypass as well as the side. Pressure variations along the pipe were adjusted by either a throttle valve or back-pressure plate, or both. Samples were taken through small stainless steel Webre-type separators (Pollak and Work, 1942). Three series of experiments were carried out.

1ST SERIES

In these tests a throttle valve was in position C, and position B was open. Steam condensate and gas samples were collected from the various points in the manner described by Mahon (1961):

(a) with the throttle valve wide open, i.e., with open bypass, and

(b) with the throttle valve in partly closed positions.

2ND SERIES

A back-pressure plate (4½ in. orifice) was placed in position C, and a throttle valve at position B. Steam condensate and gas samples were taken from each sampling point, using the throttle valve at B to change the pressures at the upstream sampling points.

Inset

3RD SERIES

A back-pressure plate was placed at position B and unimpeded flow conditions existed along the rest of the bypass.

During the course of the experiments Ministry of Works Measurements Group measured the discharge enthalpy for the drillhole using engineering methods (steam sampler and bottom outlet cyclone separator) (Smith 1958). The results from these tests are shown in Table 1.

TABLE 1—Enthalpy of Drillhole 48 by Physical Measurements

Date of Testing	Testing Pressure (p.s.i.g.)	Enthalpy (Btu/lb)
4/59	200	450
11/59	110	480
11/59	250	500
5/60	220	419

B. *Laboratory*

Condensate samples, collected by condensing the steam in evacuated flasks, were first shaken with sodium hydroxide to bring the carbon dioxide into solution as sodium carbonate. A given aliquot of this solution was then titrated with acid to determine the amount of carbon dioxide that was originally present in the steam.

RESULTS

Table 2 shows the gas content of steam from Hole 48 at various pressures, and the enthalpy of the discharge as derived from the gas content of the steam at two sampling pressures. To enable the gas results to be compared, the contents for the complete discharge were calculated for all experiments for a constant enthalpy value in each series. Sampling points that gave anomalously high or low gas contents in the steam were then obvious. For each pair of gas results an apparent enthalpy value was calculated, and this value depended on the positions of sampling, and the pressure difference between sampling points.

DISCUSSION

1ST SERIES

Open Bypass Conditions

The gas content of the steam at the high-pressure points 2, 3 and 4 was almost constant and, at a pressure of 60 p.s.i.g., was 55 millimoles/100 moles of steam. The gas contents of the steam at the low-pressure points 6, 7 and 8 were reasonably consistent, whilst the results from point 1 were also reliable.

With open bypass, no matter which two points were selected for an enthalpy calculation a fairly constant value was obtained. Unfortunately the most accurate values for enthalpy are obtained when the pressure difference between the two sampling points is high, and under open bypass conditions it is not possible to attain this.

Throttled by Valve at C

With the drillhole throttled by the valve at C to wellhead pressures of 133 and 153 p.s.i.g., the distribution of water in the pipe at the silencer end of the bypass was such that the Webre cyclone separator attached to point 6 at the top of the pipe became flooded, and no dry steam could be obtained. Although the enthalpies of the discharges from points 6 and 7 as measured by a calorimeter, at the above wellhead pressures, were low it was possible to obtain dry steam from point 7. At higher wellhead pressures dry steam samples could be collected from points 6, 7 and 8.

As the bypass was throttled the gas content of the steam of samples taken around the bypass at the high pressure end (points 1, 2, 3, 4 and 5) was reasonably consistent. At points 1 and 2 the gas content of the steam was slightly lower when the wellhead pressure was 193 p.s.i.g. The gas content of the steam at points 3, 4 and 5 was consistent at all wellhead pressures apart from the rather high values obtained from point 4 when the wellhead pressure was 133 p.s.i.g. At points 6, 7 and 8 the gas content varied between the points as soon as the bypass was throttled and this continued at increasing wellhead pressures. For any given wellhead pressure obtained by throttling, three values for the enthalpy of the discharge would be obtained if the relatively constant gas content of the steam taken from any of the points 1, 2, 3, 4 or 5 was combined with the gas content of the steam at points 6, 7 and 8 (top, side and bottom of pipe). The gas content of steam at point 8 appeared to be closest to the true value.

That the quantity of carbon dioxide in the water phase was negligible after steam separation was confirmed by experiments on water samples collected at different pressures along the bypass of various drillholes. Since the gas enthalpy method depends on continuous homogeneous mixing in the steam phase, i.e., of previously existing steam with the new steam formed by flashing between two given pressures, any departure from good mixing conditions would give inconsistent results. Errors in enthalpy determinations could be attributed to incomplete mixing of flashed steam with previous steam, or to loss of equilibrium between the steam and water phases whilst passing through the Webre separators. In the first case either high or low gas results would be obtained depending on what part, e.g., top or bottom, of the bypass the steam was sampled from. In most cases the second factor can be eliminated by controlling the pressure drop through the separator.

2ND SERIES

Throttled by Back Pressure Plate at C

These experiments were carried out to observe the differences, if any, that occurred when a back pressure plate was used at C instead of a throttling valve to increase the wellhead pressure and produce a relatively large pres-

sure gradient along the bypass. With a back pressure plate of given orifice size only one wellhead pressure could be obtained, but with a throttling valve also inserted in the bypass at B upstream of the plate a range of wellhead pressures was possible.

The results from the first and second series were very similar. The gas contents of the steam samples taken at high-pressure, from points 1, 2, 3 and 4, were not as constant as they were in the first test series. The gas contents of the steam taken from points 6, 7 and 8 were very variable. The highest value of gas content for any given pressure at the low pressure end of the bypass was obtained from point 8 and the lowest from point 6. The gas content of the steam from point 7 was very close to the average value obtained from points 6 and 8. However, this may only be true for a given output of the drillhole. Because of this fluctuation of gas content of steam over both the low- and high-pressure points it was not possible to determine the enthalpy of the discharge with any accuracy.

3RD SERIES

Bypass Throttled by Back Pressure at B

The results obtained during this last series of tests were not quite complete as two of the sampling points on the bypass had been damaged and could not be used.

Consistent values for the gas content of the steam were obtained from points upstream of the back pressure plate (points 2, 3 and 4). With the plate at B the gas contents of the steam sampled from points 6, 7 and 8 were also consistent as in the results from the first series under open bypass conditions. Thus irrespective of which set of high and low-pressure points the steam samples were taken, a consistent value of enthapy was obtained.

GENERAL DISCUSSION

The gas content of the steam samples collected from the various points during the third test series, when calculated as a concentration in the total discharge (i.e., the gas content existing in a single phase if steam and water were combined), using an enthalpy of 450 Btu/lb gave values of 6–7 millimoles/100 moles as compared with the value of 9·5–11 millimoles/100 moles obtained in the first series. The enthalpy of 450 Btu/lb was used because it was close to the average value obtained by Ministry of Works, during tests on the drillhole. However, it is likely that the real enthalpy of the discharge, was 400 Btu/lb during the first test series but that it changed to 450 Btu/lb during the time that elapsed between the first and second series of tests. If the gas concentrations in Table 2, 1st Series, are expressed on a total discharge basis using an enthalpy of 400 Btu/lb, values of around 7 millimoles/100 moles are obtained, which are comparable with the gas contents in total discharge shown for the second and third test series.

Since the gas enthalpy method depends on representative steam and gas collection at different positions on a drillholes bypass, a summary of the conditions of flow in the bypass pipe is made.

TABLE 2—Enthalpy and Gas Content of Hole 48 Discharge at Various Pressures

W.H.P. (p.s.i.g.)	Point No.	Pressure Range (p.s.i.g.)	Enthalpy Btu/lb from Gas Results E	Gas Content at Sampling Pressure (millimoles/100 moles) High Pressure	Gas Content at Sampling Pressure (millimoles/100 moles) Low Pressure	Gas Content in Total Discharge from an assumed E of 450 Btu/lb (millimoles/100 moles) High Pressure	Gas Content in Total Discharge from an assumed E of 450 Btu/lb (millimoles/100 moles) Low Pressure
1ST SERIES							
Open Bypass, No Throttle							
110	3 & 7	60–33	407	55·6	46·2	10·6	10·1
110	2 & 6	60–33	433	55·2	48·6	10·5	10·6
110	4 & 8	60–33	392	55·4	45·2	10·6	9·9
110	1 & 5	90–55	392	65·0	50·1	10·8	9·8
110	2 & 6	60–33	450	55·0	48·0	10·5	10·5
110	1 & 5	90–55	419	63·3	53·3	10·6	10·4
Bypass, Throttled							
133	2 & 6	103–40	—	flooding of separators at 6			
133	3 & 7	103–35	361	64·4	30·3	10·2	6·6
133	4 & 8	102–38	392	80·3	49·6	12·7	10·6
133	1 & 5	124–94	410	71·3	59·3	10·3	9·7
153	2 & 6	128–?	—	flooding of separators at 6			
153	3 & 7	132–35	398	72·5	35·3	10·2	7·6
153	4 & 8	128–39	438	73·1	47·2	10·4	10·0
153	1 & 7	145–38	390	74·0	31·5	9·8	6·7
153	1 & 5	146–123	575	74·5	71·5	9·8	10·4
193	2 & 6	173–33·5	505	76·6	50·3	9·0	11·0
190	3 & 7	173–30	424	90·8	40·5	10·7	9·0
193	4 & 8	175–33	447	88·3	46·5	10·3	10·2
193	1 & 5	186–168	443	84·5	78·2	9·4	9·4
193	1 & 7	187–31	422	84·8	35·0	9·4	7·7
2ND SERIES							
Bypass, Throttled							
187	3 & 7	175–24·0	462 & 466	54·8	29·7	6·4	6·9
187	2 & 6	175–26·0	496 & 513	64·7	40·5	7·6	9·2
187	4 & 8	175–26·0	370 & 370	91·5	14·7	10·7	3·4
187	1 & 7	187–25·0	468 & 465	55·8	29·4	6·2	6·7
187	1 & 8	187–26·0	393 & 390	55·4	14·0	6·1	3·2
198	3 & 7	184–24·0	450 & 446	52·2	25·2	5·8	5·8
198	2 & 6	184–26·0	489 & 495	63·0	38·0	7·1	8·7
198	4 & 8	184–26·0	403 & 410	56·1	18·7	6·3	4·3
198	1 & 7	198–24·0	458 & 453	56·0	26·6	5·9	6·1
3RD SERIES							
Bypass, Throttled							
195	3 & 7	180–29·0	441	62·9	29·2	7·2	6·5
195	2 & 6	180–29·0	441	62·9	29·2	7·2	6·5
195	4 & 8	180–28·0	441	62·9	29·2	7·2	6·5
205	2 & 6	190–30·0	436	63·9	28·6	7·0	6·4
205	2 & 7	190–28·0	439	61·5	27·9	6·8	6·3

As hot water from the deep aquifer flows up the drillhole a point is reached with lowering pressure when the water boils. By the time atmospheric pressure is reached the steam makes up about 28% by weight of the total discharge for a discharge enthalpy of 450 Btu/lb. With open bypass conditions equilibrium appeared to be maintained within the steam phase and representative steam samples could be collected at any point. When the drillhole was throttled, conditions of flow were changed. Upstream of the constriction the fluid velocities were slow, whilst downstream the velocities became very high. An agitated condition of the phases was produced upstream of the valve or back-pressure plate for a distance of at least 8 ft and possibly to a distance of up to 28 ft. The gas content of the steam in samples taken from any part of the bypass upstream of the constriction was approximately correct but rather more erratic than under open bypass conditions. Small fluctuations in the gas content of steam samples taken just downstream of the wellhead junction but over 8 ft upstream of the constriction, could be accounted for by the slight throttling action produced by the right-angled bend between wellhead and bypass.

At sampling points 8 ft downstream of the constriction, the gas content of steam samples was variable. According to A.S.T.M. Standards (Manual on Industrial Water 1953, p. 152, *Point of Sampling*) equilibrium should be attained in the phases 10 pipe diameters downstream of a constriction. This does not appear to be valid for the Wairakei discharges. At a distance of 8 ft or 12 pipe diameters downstream the steam present before the constriction and the flashed steam formed by the pressure drop through the constriction were not in equilibrium. Eight feet below the constriction, depending on the sampling position, the gas content in the steam was either higher or lower than the gas content expected in the steam at the sampling pressure. At a distance of 28 ft, or about 40 pipe diameters, downstream of the constriction the steam phases were in equilibrium, and steam samples taken from any position on the bypass (top, bottom or side) showed a constant gas content at a given pressure. The minimum distance, after a constriction at which equilibrium is attained is between 8 and 28 ft.

From the experimental results four recommendations can be made.

(1) The most accurate enthalpy results are obtained when the difference is greatest between the two pressures at which steam samples are collected.
(2) The throttling constriction used to create the pressure difference should be close to the wellhead.
(3) A representative high-pressure steam sample can be taken from a sampling point on the side of the bypass 4 ft downstream of the wellhead junction.
(4) A representative low-pressure steam sample can be taken from a sampling point on the side of the bypass 28 ft downstream of a constriction.

It should be noted that although representative samples of steam can be taken at high pressures it is not possible to calculate the gas content of the complete discharge with any precision unless the enthalpy of the discharge is known accurately. For example, the percentage of steam in the discharge at 200 p.s.i.g. is 16·5% if the enthalpy is 500 Btu/lb, but only 10·6% for an enthalpy of 450 Btu/lb. Single steam samples will give a more accurate measure of the gas content of the total discharge, if the enthalpy is not known accurately, when they are taken at low pressure.

Tests on Hole 207

It became possible later to carry out confirmatory tests on the method at Hole 207. From output measurements carried out by Ministry of Works using a Bottom Outlet Cyclone Separator (Hunt, 1961), just before the gas-enthalpy experiments, the discharge enthalpy was estimated to be 500 Btu/lb, up to a wellhead pressure of approximately 300 p.s.i.g. For the gas method experiments the bypass pipe of Hole 207 was arranged according to conditions (1) to (4) above, and the enthalpies obtained for two different wellhead pressures (Table 3) agreed to within 10 Btu/lb or 2% of the Ministry of Works figure.

TABLE 3—Results from Hole 207

W.H.P. (p.s.i.g.)	Point No.	Pressure Range (p.s.i.g.)	Enthalpy Btu/lb from Gas Results E	Gas Content at Sampling Pressure (millimoles/100 moles) High Pressure	Gas Content at Sampling Pressure (millimoles/100 moles) Low Pressure	Gas Content in Total Discharge from an assumed E of 500 Btu/lb (millimoles/100 moles) High Pressure	Gas Content in Total Discharge from an assumed E of 500 Btu/lb (millimoles/100 moles) Low Pressure
160	—	155–24	497	120	78	22·3	22·2
160	—	,,	505	116	77	21·5	22·0
160	—	,,	495	121	78	22·5	22·2
160	—	,,	497	120	78	22·3	22·2
215	—	210–26	497	138	78	22·2	22·0
215	—	,,	515	131	79	21·1	22·2
215	—	,,	500	136·5	78	22·0	22·0
215	—	,,	509	134	79	21·6	22·2

Advantages of Gas Method for Enthalpy

The gas method offers certain advantages over the three engineering methods used by Ministry of Works.

(a) The method requires only inexpensive and simple equipment.
(b) The method is fast. The enthalpy of a drillhole's discharge over a range of 5 to 6 different wellhead pressures could be determined in three or four hours, assuming that the drillhole rapidly attains stability at each wellhead pressure.
(c) The steam sampling can be carried out by unskilled personnel.
(d) Vertical discharge is necessary with the Steam Sampler method (Hunt, 1961), the fastest of the three engineering methods, and this produces unpleasant wet conditions around the drillhole.

(e) It is the only convenient method so far available by which a chemist can determine the enthalpy at the time samples of the discharge are taken for analysis. This is of importance for calculating the concentrations of constituents in the complete discharge from individual analyses of steam and water phases.

Some of the variables involved in the method have been examined in this paper, and encouraging results obtained. However, further detailed testing would be desirable before confident recommendations on its use could be made.

ACKNOWLEDGMENTS

The author would like to express his gratitude to Mr S. H. Wilson (Institute of Nuclear Sciences, D.S.I.R.) and the Project Engineer and personnel of the Ministry of Works, Wairakei, for their help and cooperation during this work.

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A DEVICE FOR COLLECTING DOWN-HOLE WATER AND GAS SAMPLES IN GEOTHERMAL WELLS

By ROBERT O. FOURNIER and JOSEPH C. MORGENSTERN,
Menlo Park, Calif.

Abstract.—A sampling device with an internal volume of about 500 ml has been designed to collect liquid and gas samples in wells where both steam and water are present at temperatures up to about 280°C. A long flexible stainless steel tube serves as the support cable. The sample device is lowered in the open position and fluid flows through it during its descent. Closure is accomplished by nitrogen gas pressure applied from the surface through the flexible tube to a piston and plunger within the sample chamber. Continued application of nitrogen gas pressure during withdrawal of the device prevents leakage caused by changing conditions of temperature and pressure. The sampling device has been used successfully to collect water and gas samples from research holes drilled in hot-springs areas of Yellowstone National Park, Wyo.

A variety of sampling devices have been used to obtain down-hole water samples from given depths within wells and drilled holes. Closure mechanisms have included electrically operated valves and spring-loaded valves actuated by preset timing devices or by "messengers" sent down the supporting cable. Most sampling devices that work well at low temperatures are ineffective in geothermal wells where boiling conditions are encountered. A sampling device that is closed and sealed deep in a geothermal well may leak owing to differential contraction of materials as the device is cooled during withdrawal. Leakages occur because pressures within sampling devices generally differ from external pressures as the devices are pulled from geothermal wells. Where the temperature is abnormally high in the upper part of a well, pressure within the sample chamber may become very high relative to the external pressure, with the result that gas and water leak from the sample chamber. In contrast, where deep temperatures are very high and shallow temperatures are low, cooling and contraction of the liquid sample and condensation of steam as the container is raised may cause a partial vacuum to form so that unwanted water from shallow depths is sucked into the sample chamber.

The sample device described here has an internal volume of about 500 ml and is designed to collect liquid and gas samples where both steam and water are present. Closure is accomplished by nitrogen gas pressure applied from the surface to a piston and plunger within the sample chamber. Continued application of this gas pressure during withdrawal of the device prevents leakage caused by changing conditions of temperature and pressure. The piston prevents mixing of the nitrogen "closure gas" with water and gas trapped in the sample chamber.

FABRICATION

A working drawing of the sampling device is shown in figure 1. All materials are stainless steel, except for one Teflon O-ring, two Viton O-rings, and parts *g* and *m* which are Teflon. The circular plate, *r*, can be manufactured from brass, aluminum, or other metal. The main body of the sampling device, parts *a* and *b*, is fabricated from 2-inch OD stainless-steel pipe. The connecting rod, part *d*, is fabricated from ½-inch OD pipe. The holes drilled along the length of *d* permit escape of air and mixing of water inside *d* with water in the main sample chamber. The number and spacing of these holes is not critical. Alternatively, a solid rod may be substituted for the ½-inch pipe, thus increasing strength and eliminating all possibility of insufficient mixing of water within *d* with water in the main sample chamber. However, a solid connecting rod would increase the weight of the device and decrease the size of the fluid sample obtained.

The internal diameter of the threaded section of part *b* above the ⅛-inch groove should be about 0.01 inch greater than the internal diameter of part *b* above the shoulder and below the ⅛-inch groove in order to facilitate the removal of gasket *g* and part *h*. The design for the closure at the bottom of part *a* is identical with that at the top of part *b*, except for the differences indicated in parts *h* and *o*.

The dimensions of the sample device that we fabricated are shown in figure 1. Larger samplers may be constructed to fulfill specific needs. If different dimensions are used, care should be exercised to insure that the connecting rod, *d*, is the proper length to allow the piston (parts *j* and *k*) to close the exit ports when the plunger, *m*, is seated in part *o*. In the closed position the Teflon O-ring rests below the exit port

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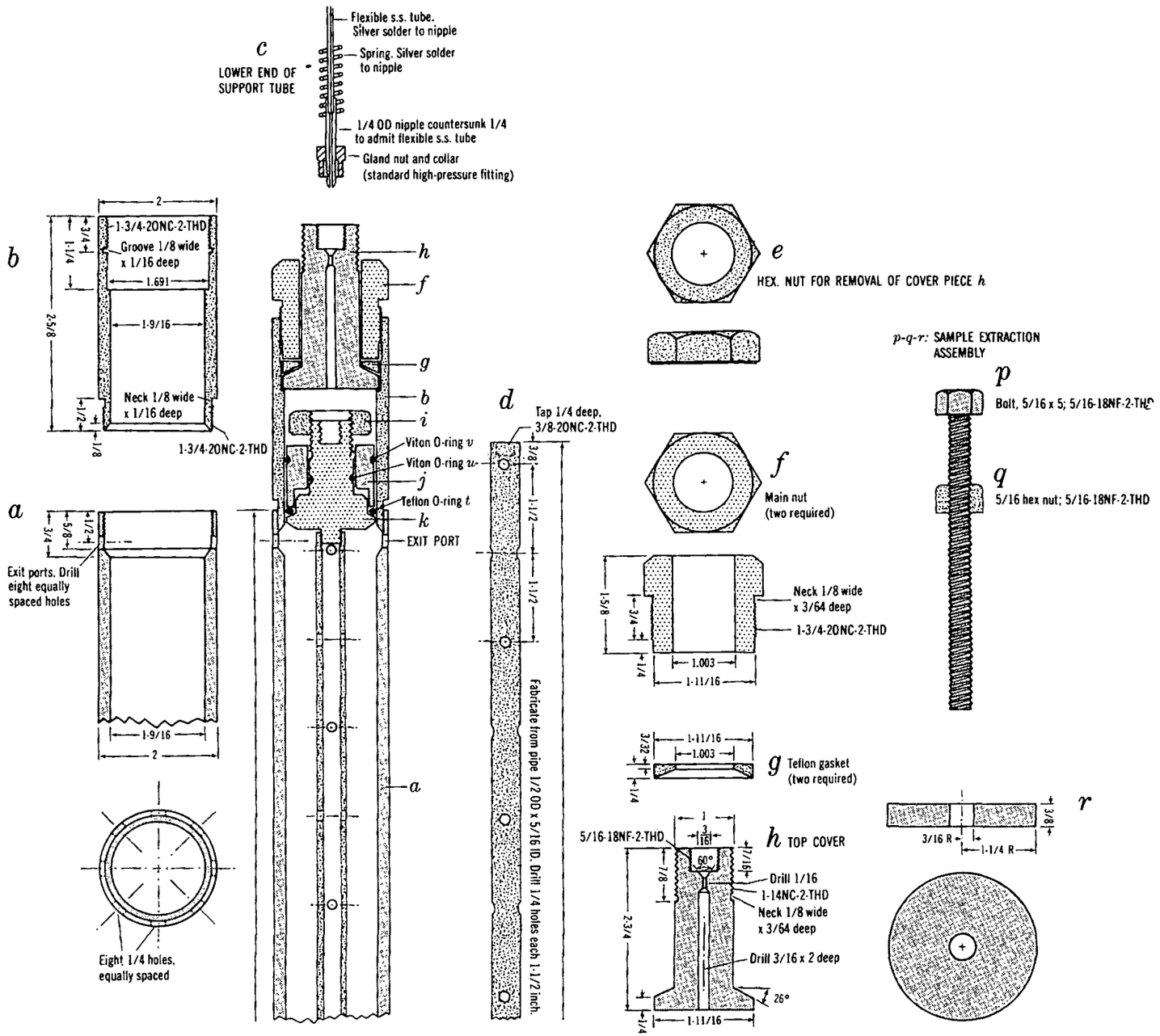
c
LOWER END OF SUPPORT TUBE
Flexible s.s. tube. Silver solder to nipple
Spring. Silver solder to nipple
1/4 OD nipple countersunk 1/4 to admit flexible s.s. tube
Gland nut and collar (standard high-pressure fitting)
b
1-3/4-20NC-2-THD
Groove 1/8 wide x 1/16 deep
Neck 1/8 wide x 1/16 deep
1-3/4-20NC-2-THD
a
Exit ports. Drill eight equally spaced holes
Eight 1/4 holes, equally spaced
h
f
g
b
i
Viton O-ring v
Viton O-ring u
j
Teflon O-ring t
k
EXIT PORT
a
d
Tap 1/4 deep, 3/8-20NC-2-THD
Fabricate from pipe 1/2 OD x 5/16 ID. Drill 1/4 holes each 1-1/2 inch.
e
HEX. NUT FOR REMOVAL OF COVER PIECE h
f
Main nut (two required)
Neck 1/8 wide x 3/64 deep
1-3/4-20NC-2-THD
g Teflon gasket (two required)
h TOP COVER
5/16-18NF-2-THD
Drill 1/16
1-14NC-2-THD
Neck 1/8 wide x 3/64 deep
Drill 3/16 x 2 deep
p-q-r: SAMPLE EXTRACTION ASSEMBLY
p
Bolt, 5/16 x 5; 5/16-18NF-2-THD
q
5/16 hex nut; 5/16-18NF-2-THD
r

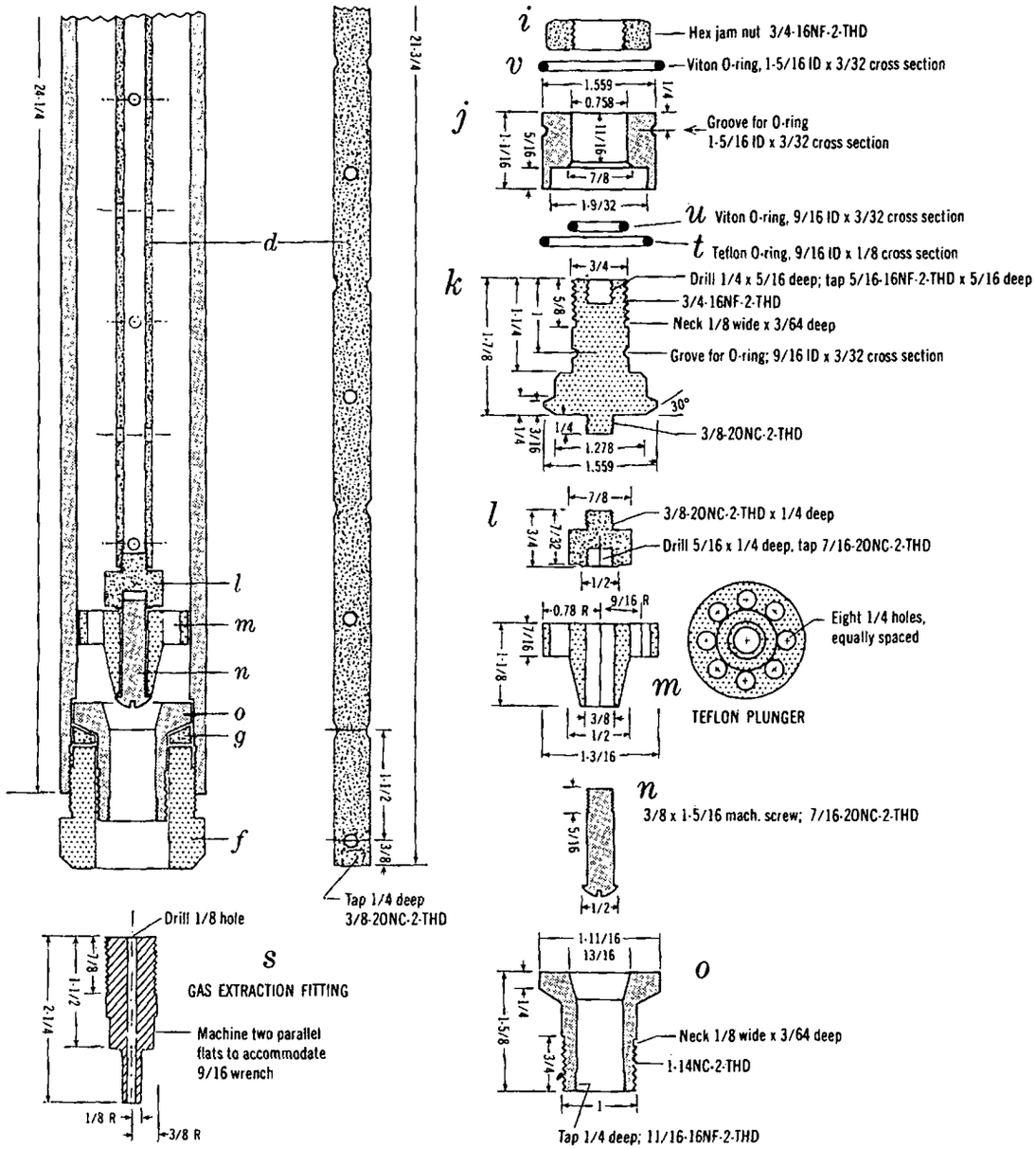

Figure 1.—Working drawing of device for collecting down-hole samples of water and gas in geothermal wells. All dimensions in inches.

groove, and the upper Viton O-ring rests above that groove. The exit port groove is formed by parts *a* and *b* when they are attached together. This groove is necessary to prevent damage to the Teflon O-ring as it moves past the exit ports.

SAMPLING PROCEDURE

The sample device is assembled as follows: The bottom cover, part *o*, Teflon gasket *g* (one of two), and main nut *f* (one of two) are assembled into the bottom of the main body, *a*, and tightened in place with the aid of a pipe wrench and adjustable wrench. The connecting rod, plunger, and part of the piston, parts *d*, *k*, *l*, *m* and *n*, are assembled finger tight. The piston is completed by placing the Teflon O-ring, *t*, $^9/_{16}$-inch ID Viton O-ring, *u*, and part *j* on part *k*. Jamnut *i* is then screwed tightly on to *k* so that the Teflon O-ring is slightly deformed. The $1^5/_{16}$-inch ID Viton O-ring, *v*, is then placed on part *j* and the piston and plunger assembly is inserted into part *a*. Part *b* is then attached to part *a* and, using the bolt *p*, the piston assembly is drawn up onto *b* until part *k* is clear of the eight ¼-inch exit ports. Bolt *p* is removed, and pieces *h*, *g*, and *f* are assembled into *b* and tightened in place with wrenches. Nut *e* is used only to extract parts *g* and *h* from part *b* after a fluid sample has been collected. The sample device is then attached to a long flexible stainless-steel tube (assembly *c*) that serves as a support cable and is ready to be used. The spring shown in assembly *c* prevents undue bending of the flexible tube at the point of connection with the nipple.

The flexible stainless-steel tube and other supporting equipment are described elsewhere (Fournier and Truesdell, 1971) (p. C146–C150, this chapter). In brief, the flexible steel tube is wound upon a reel, and a valve and pressure gage are attached to the upper end of the tube and also mounted on the reel. The flexible steel tube is placed over a sheave or pully at the top of the geothermal bore or well, and the attached sampling apparatus is placed in a pressure chamber mounted above the main valve of the well. The flexible tubing passes through a packing gland at the top of the pressure chamber. The main valve is opened and the apparatus is lowered to the desired depth, as indicated by a counter on the sheave.

As the sampler is lowered, water flows into it through the large opening at the bottom (part *o*), up through the eight holes in the Teflon plunger, part *m*, and out the eight exit ports just below the piston, *k*. As the sampler is lowered, the valve at the surface end of the flexible steel tube should be at the open position so that heated air in the small chamber of *b* will not reach pressures large enough to close the sampler prematurely. However, premature closure is very unlikely in wells filled with water because hydrostatic pressure holds the piston in an open position.

When it is desired to close and seal the sample apparatus, a cylinder of nitrogen gas[1] is connected to the upper end of the flexible steel tube. A nitrogen gas pressure of 10–20 atmospheres in excess of the calculated hydrostatic pressure for the sample depth is then applied to the top of the piston through the flexible steel tube. This forces the piston down and seats the Teflon plunger, *m*, in part *o*, sealing the bottom of the sample chamber. Simultaneously, the Teflon O-ring held between parts *j* and *k* is moved to a position below the exit ports and effectively seals the upper end of the sample chamber. An important aspect of the design of the piston assembly is that part *j* is free to move and exert continued pressure upon the Teflon O-ring after parts *m* and *k* have come to rest. Thus, a very tight seal is formed at the upper end of the chamber after the lower seal is formed and after the Teflon O-ring slides past the exit-port groove. Before detaching the gas cylinder, the valve at the top end of the flexible tube is closed so that nitrogen gas pressure is maintained in the chamber of part *b* while the sampler is removed from the well. Thus, tight seals are maintained in spite of changing conditions of temperature and pressure.

Upon removal from a hot well, the sampler is cooled, and any residual steam is condensed by suspending the sampler in a specially fabricated deep cylindrical container of water. The sample apparatus is then dried, the nitrogen gas pressure is released by opening the valve at the upper end of the flexible steel tube, and the tube, assembly *c*, is disconnected. The release of externally applied gas pressure does not open the device because equal internal pressure is exerted down on part *m* and up on part *k*. To extract the fluid sample from the container, the top cover piece, *h*, must first be removed. Using a pipe wrench and adjustable wrench, the top main nut, *f*, is unscrewed about five or six revolutions. Then nut *e* is attached to part *h* and tightened against the main nut, *f*. This pulls part *h* and gasket *g* out of the sealed position in *b* so that further unscrewing of the main nut, *f*, removes the entire closure assembly. Nut *q* and plate *r* are then placed high up on bolt *p* and the end of bolt *p* is screwed into the top of part *k* (still within part *b*). The bottom end of the sample apparatus is placed over a bottle or beaker and, while holding bolt *p* steady with one wrench, nut *q* is turned with a second wrench so that it moves down bolt *p* and against plate *r*. This pulls the piston assembly and plunger *m* upward and opens the bottom of the container so that the liquid sample may run out.

To collect a gas sample or to exclude air from the system, fitting *s* is first attached to part *o* before pulling open the device. Teflon tape is used on the threads of fitting *s* to secure a gas-tight seal. A hose, a 3-way valve, and an appropriate container are attached to fitting *s*, and these are evacuated or filled with an inert gas before opening the sampling apparatus. Note that the bottom seal of the sample device, at *m*–*o*, opens before the top seal so that there is no contamination of air leaking into the container at the top exit ports. If both liquid and gas are present in the sample chamber after cooling, a portion of the gas may be sampled by turning the apparatus upside down before opening the chamber. The gas may then be extracted into a syringe or other evacuated chamber or

[1] We used nitrogen gas because it is inert, relatively inexpensive, and easy to obtain. Other gases could be used in place of nitrogen to close the sampler.

allowed to mix with a given amount of inert "carrier" gas. The bottom of the sampler is then lowered and the liquid portion allowed to drain from the chamber.

We have found that the Teflon plunger, *m*, works well in repeated usage, even after undergoing considerable permanent deformation. However, spare Teflon parts should be kept available and used frequently. New O-rings should be installed after each run where subsurface temperatures in excess of 200°C are encountered.

APPLICATION

The sampling device has been used successfully to collect down-hole water and gas samples from research holes drilled by the U.S. Geological Survey in hot-spring areas of Yellowstone National Park (White and others, 1968). The deepest and hottest sample was collected at a depth of 1,088 feet and temperature of 240°C in the Y12 drill hole at Norris Geyser Basin. Other samples were obtained from cooler holes, but under more adverse conditions. In one hole, Y9 at Norris Geyser Basin, a sample of liquid water was collected from beneath a region of superheated steam that filled the top of the hole. When the sampling apparatus was removed from the hole, the temperature of the water sample filling the container was 180°C. In spite of an internal pressure of about 10 atm within the sample apparatus and only 1 atm pressure external to it, no leakage occurred. In another well, Y7 at Biscuit Basin, dirty water was encountered and a few sand-sized grains became caught between the Teflon plunger, *m*, and part *o* when gas pressure was applied to close the container. The Teflon flowed around the sand grains and made a perfect seal in spite of the impurities.

The sample device can be used at temperatures up to about 280°C. Above this temperature the Teflon becomes very soft, and it melts at about 300°. Substitution of other materials for the Teflon may extend the temperature range of application. For instance, copper or other easily deformable metal may be used for gaskets *g* and plunger *m*. Substitution of other materials for the O-rings presents a more difficult problem, but new plastics and silicon rubbers just appearing on the commercial market may be usable at temperatures about 280°C.

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Jour. Research U.S. Geol. Survey
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THE CALCULATION OF AQUIFER CHEMISTRY IN HOT-WATER GEOTHERMAL SYSTEMS

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Abstract.—The temperature and chemical conditions (pH, gas pressure, and ion-activities) in a geothermal aquifer supplying a producing bore can be calculated from the enthalpy of the total fluid (liquid + vapor) produced and chemical analyses of water and steam separated and collected at known pressures. Alternatively, if a single water phase exists in the aquifer, the complete analysis (including gases) of a sample collected from the aquifer by a downhole sampler is sufficient to determine the aquifer chemistry without a measured value of the enthalpy. The assumptions made are that the fluid is produced from a single aquifer and is homogeneous in enthalpy and chemical composition. These calculations of aquifer chemistry involving large amounts of ancillary information and many iterations require computer methods. A computer program in PL-1 to perform these calculations is available from the National Technical Information Service as document PB-219 376.

In active hydrothermal systems that have been drilled, mineral alteration and deposition can be related to observed temperatures and fluid compositions. Chemical analyses of water and steam produced from many types of geothermal systems are now available. However, analyses of fluids collected at the surface do not describe the chemistry of fluids as they occur at depth. The chemical differences between the fluids at the surface and in the deep aquifer are due to the decrease of pressure and temperature during production. Adiabatic expansion during passage up the drill hole may result in steam separation, cooling, and an increase in the concentration of the solutes in the water phase. Loss of dissolved CO_2 and H_2S from the water to the vapor increases the pH value of the water. The increase in pH and solute concentration and the decrease in temperature may cause the water to become supersaturated with calcite or silica minerals and may result in scaling of well casings. The continued production of a geothermal system is likely to decrease the reservoir pressures enough to form steam in the aquifer (Mahon, 1970). The resulting decrease in gas pressures, increase in aquifer pH, and temperature lowering may cause increased calcite deposition in the casing and possibly in the aquifer. Potential mineral deposition may be calculated if the chemistry of aquifer fluids is known.

Underground water temperatures may be calculated from known mineral solubility or ion exchange reactions that control water compositions; for example, quartz solubility (Fournier and Rowe, 1966; Mahon, 1966), Na:K ratios (White, 1965; Ellis, 1970), or Na:K:Ca ratios (Fournier and Truesdell, 1973). The assumptions underlying these calculations have been discussed by White (1970).

Thus, for practical reasons as well as to increase our knowledge of natural systems, it is of interest to calculate the chemical properties of geothermal fluids before they are changed during production. This is the purpose of the computer program described here.

ACKNOWLEDGMENTS

The computer program is a further development of the method of Ellis (1967, 1970) and was partly written in the laboratories of the Chemistry Division, Department of Scientific and Industrial Research (D.S.I.R.), New Zealand, while the author was on a training grant from the U.S. Geological Survey. The calculations have been discussed with A. J. Ellis, W. A. J. Mahon, Werner Giggenbach, and R. B. Glover of the D.S.I.R., New Zealand, and Ivan Barnes, L. J. P. Muffler, R. O. Fournier, and D. E. White of the U.S. Geological Survey. The program was initially written in Elliot-Algol.

ASSUMPTIONS

These calculations assume that fluid from a geothermal well (1) is produced from a single aquifer, (2) does not gain or lose significant heat or matter during passage up the well and through surface pipes to sampling points, and (3) maintains chemical equilibrium at each point of steam-water separation.

The first assumption that the fluid is produced from a single aquifer must be judged in each situation. In general, wells in which discharge enthalpy and silica contents indicate the same aquifer temperature are most probably from a single aquifer and existed in that aquifer as a single liquid phase. Two or more aquifers may, however, contribute fluids to a producing bore. This circumstance can be deduced from the drilling log, the ratios of gaseous components in the steam (Glover, 1970), or a comparison of the water composition with that of other wells in the field (Mahon, 1970).

The second assumption is most probably true for the well-studied and long-producing Wairakei, New Zealand, geothermal system in which the composition of produced fluids has been nearly constant over a decade of observation and in

which the mass of scale deposited is negligible (Mahon, 1970; Grindley, 1965, p. 58). Here also the conductive heat flow is small compared with the heat delivered to the surface in the fluid (Dawson and Dickinson, 1970; Grindley, 1965). This assumption is probably true also for many but not all other hot-water geothermal systems.

The assumption of chemical equilibrium is more difficult to justify. It has been observed that, in the aquifer, saturation with quartz is exactly maintained (Mahon, 1970), and most equilibria involving species dissolved in the aquifer water phase should be more rapid than saturation equilibria with a solid phase. However, during passage up the well and through the separator, CO_2 may not maintain an equilibrium distribution between the steam and water, as shown by Glover (1970), who found at Wairakei that the distribution coefficient for CO_2 between vapor and liquid water was about 70 rather than the equilibrium value of 460 (Ellis and Golding, 1963). The calculated total CO_2, based on analyses of the separated steam may be low by 2 percent or less. This would not significantly change the calculated CO_2 pressures or aquifer pH.

The difference between the actual total pressure in the aquifer and the saturated water-vapor pressure at the aquifer temperature is assumed to have a negligible effect on the equilibrium constants. The constants used in the program all refer to saturated water-vapor pressure conditions.

CHEMICAL AND PHYSICAL CHANGES ON PRODUCTION

The calculations performed in the program can be best illustrated by following the chemical and physical changes in the fluid produced from a representative aquifer. Analyses of water and gas samples from well 20 of the Wairakei, New Zealand, geothermal field are used as an example. The changes are discussed in the order that they occur; that is, from inaccessible conditions to the separated water and steam as analyzed. The program works backwards along the line of these changes and reconstructs the inaccessible states.

The calculated conditions prior to entering the bore are given in table 1. Note that the pH of 6.34 is nearly the neutral pH at the temperature 246°C and that virtually all boric and silicic acids and nearly all carbonic acid and hydrogen sulfide are undissociated. A substantial proportion of total sulfate exists as bisulfate ion, fluoride as neutral hydrogen fluoride; and ammonia as ammonium ion. Ion pairs such as NaCl, KCl, $NaSO_4^-$ and $CaSO_4^0$ are more stable than at low temperatures (see tables 4 and 5) and are present in moderate amounts. The enthalpy (enthalpy refers to specific enthalpy throughout) of the fluid is slightly less than that of water in equilibrium with steam (table 1), and a gas phase is probably not present.

The aquifer fluid flows toward and into the well along a gradient of decreasing pressure resulting from the lower density of the two-phase steam-water mixture in the well. The decrease in pressure causes steam separation and a decrease in temperature. These processes continue in the well and in the steam-water separator, which was operated at a pressure of 16.3 bars absolute and a temperature of 202°C. With the decrease of pressure and temperature, the fluid separates into 10.1 percent steam with an enthalpy of 667.4 cal/g and 89.9 percent water with an enthalpy of 206.1 cal/g. (1 cal=4.184 abs J.) The total enthalpy remains 252.8 cal/g (0.101×667.4+0.899×206.1) because no significant amount of heat has been lost in the passage up the well. The gases originally dissolved in the water have largely exsolved into the gas phase (experimental distribution coefficients for CO_2 and H_2S, tables 4 and 5, greatly favor the gas phase, particularly near 200°C). From the separator, the steam is collected and analyzed for CO_2 and H_2S. Collection and analysis methods

Table 1.—*Aquifer fluid adjacent to hole 20, Wairakei, New Zealand*
[1 cal = 4.184 abs J.]

Temperature	°C	246
Pressure	bars abs	37.6
Enthalpy[1]	cal/g	252.8
pH[2]		6.34
CO_2 partial pressure	bars	9.79
H_2S partial pressure	do	0.0093

Dissolved constituents	*Concentrations in mmol/1,000 g H_2O*
Li^+	1.5
Na^+	38.3
K^+	4.1
Rb^+	.025
Cs^+	.014
Ca^{+2}	.43
Mg^{+2}	.0
F^-	.29
Cl^-	42.9
Br^-	.05
I^-	.002
SO_4^{-2}	.079
H_3BO_3	1.74
$H_2BO_3^-$	.002
$H_2CO_3^0+CO_{2aq}$	7.89
HCO_3^-	.35
CO_3^{-2}	.00001
$H_4SiO_4^0$	7.85
$H_3SiO_4^-$	.006
$H_2SiO_4^{-2}$	.00001
NH_4^+	.002
NH_{3aq}	.011
H_2S_{aq}	.25
HS^-	.022
HF^0	.050
HSO_4^-	.0023
HCl^0	.00006
$NaCl^0$	1.27
KCl^0	.097
$MgSO_4^0$	.0
$CaSO_4^0$	.025
KSO_4^-	.015
$NaSO_4^-$	.15
$CaCO_3^0$	.0002
$MgOH^+$	.0

[1] Saturated-water enthalpy is 254.6 cal/g.
[2] Neutral pH is 5.6 at 246°C.

Table 2.—*Analysis as reported on water and steam from well 20, Wairakei, New Zealand*

Temperature of steam separation	°C	202
Temperature of water separation	°C	99 and 202[a]
CO_2 in high pressure steam	mmol/100 mol H_2O	142
H_2S in high pressure steam	mmol/100 mol H_2O	4.5
Water pH measured at 20°C		8.0

Dissolved constituents	*Concentrations in water as analyzed at 20°C in mg/kg*	*Dissolved constituents*	*Concentrations in water as analyzed at 20°C in mg/kg*
Li	14.8	Br	5.4
Na	1,260	I	.4
K	228	SO_4	35
Rb	3.0	B	26
Cs	2.5	HCO_3	7.7
Ca	25	CO_3	0
Mg	0	SiO_2	650
F	8.8	NH_3	.3
Cl	2,164	H_2S	0

for steam and water are given in Ellis, Mahon, and Ritchie (1968). The gas analysis is given in table 2. The steam and water leave the separator in separate lines, and the water enters a silencer, which discharges to the atmosphere. In the silencer an additional 20 percent of the original water is flashed to steam, and the remaining water flows out the weir box where it is sampled. The proportions of steam and water at each separation point are calculated from an enthalpy balance with the assumption of constant enthalpy. The water sample in a capped polyethylene bottle is cooled and taken to the laboratory where it is analyzed and the pH is measured. The amount of CO_2 and H_2S dissolved in the water after separation is negligible relative to that which partitions into the gas phase and is not analyzed. The enthalpy of the whole fluid is calculated from measurements of the flows of steam and water under controlled conditions.

The properties of the water as analyzed are given in table 2. The steam and water analyses were made by the staff of the Chemistry Division, D.S.I.R., New Zealand. The water analysis has been recalculated in table 3 to show what species were present in the analyzed solution at 20°C. The water composition differs substantially from the composition of the aquifer fluid. The separation of steam has increased the concentration of mineral constituents that are insoluble in steam (compare Li^+ in the tables). The separation of CO_2 and H_2S into the steam phase has increased the pH by 1.7 units.

The pH increase and temperature decrease have increased the ionization of weak acids, particularly boric acid, silicic acid, and carbonic acid. Ion pairs are generally less stable at lower temperatures (tables 4 and 5) and are thus less in evidence. The most important change is the partition of acid gases (CO_2, H_2S) into the steam with the resultant increase in pH. The aquifer pH, the activity coefficient of H^+, and the potassium contents can be combined to calculate a K/H concentration ratio of $10^{3.63}$ which is similar to the extrapolated, pressure-corrected experimental value of $10^{3.62}$ for water in equilibrium with K-mica, K-feldspar, and quartz near 250°C (Hemley, 1959; R. O. Fournier, oral. commun., 1972; Ellis and McFadden, 1972). This similarity suggests that mineralogical buffer systems are the major control on the pH of this aquifer fluid.

Table 3.—*Calculated composition at 20°C of separated well water from well 20, Wairakei, New Zealand*

[Water pH measured at 20° C is 8.0]

Dissolved constituents	*Concentrations in mmol/1,000 g H_2O*	*Dissolved constituents*	*Concentrations in mmol/1,000 g H_2O*
Li^+	2.1	$H_3SiO_4^-$	.25
Na^+	54.9	$H_2SiO_4^{-2}$	.00009
K^+	5.85	NH_4^+	.017
Rb^+	.035	NH_3^0	.0006
Cs^+	.019	H_2S	.0
Ca^{+2}	.62	HS^-	.0
Mg^{+2}	.0	HF^0	<.000005
F^-	.47	HSO_4^-	<.000005
Cl^-	61.3	HCl^0	<.000005
Br^-	.068	$NaCl^0$	.05
I^-	.003	KCl^0	.005
SO_4^{-2}	.315	$MgSO_4^0$	.0
H_3BO^3	2.26	$CaSO_4^0$	.007
$H_2BO_3^-$	.15	KSO_4^-	.005
$H_2CO_3^0+CO_{2aq}$	.003	$NaSO_4^-$	.04
HCO_3^-	.126	$CaCO_3^0$	.0002
CO_3^{-2}	.001	$MgOH^+$	.0
$H_4SiO_4^0$	10.6		

DATA REQUIRED

Data necessary to the calculation of aquifer chemistry consist of (1) a chemical analysis of the water separated from the water-steam mixture produced from the well, (2) the content of carbon dioxide and hydrogen sulfide in the separated steam, (3) the pressures of water and steam separation and the atmospheric pressure, and (4) the enthalpy of the whole fluid. The water analysis must include the pH, the temperature of pH measurement, and concentrations of all major dissolved constituents, particularly those that form weak acids or bases at low or high temperatures (HCO_3^-, SO_4^{-2}, BO_3^-, F^-, SiO_2, and so forth. A silica analysis is essential because the temperature of the aquifer is calculated by assuming that the aquifer water phase is saturated with quartz (Mahon, 1966).

The CO_2 and H_2S contents of separated steam must be known because both of these gases dissolve in water to form weak acids and their separation from water raises the pH. The pressure of steam separation is introduced because the separation and collection of steam for gas analysis is most efficiently done at high pressure (to achieve a maximum gas to H_2O ratio) and the collection of water is usually from the silencer at atmospheric pressure (Ellis, Mahon and Ritchie, 1968). If the sample is from a downhole sampler, the water analysis and the CO_2 and H_2S contents are sufficient to

calculate the aquifer chemistry, provided that the fluid sampled was a single liquid phase.

AQUIFER TEMPERATURE CALCULATION

The temperature of an aquifer feeding a geothermal well is measured infrequently, and the measurements when made are uncertain. It has been shown (Fournier and Rowe, 1966; Mahon, 1966, 1970) to be preferable to calculate the aquifer *temperature from the silica content of the discharge, assuming* equilibrium with quartz in the aquifer, rather than to measure the temperature directly. The original silica content in the deep water must be calculated from analytical data allowing for concentration from steam separation and for the presence of steam in the aquifer. The calculation of the aquifer temperature requires enthalpy values of saturated steam and water at that temperature, and therefore an iteration procedure is necessary.

If the pH of the aquifer fluid is greater than about 7, some silica is present as silicate ions, and the indicated temperature from total silica will be too high. In this instance, concentrations of ionic silica species are calculated and subtracted from total silica concentrations because the silica concentration used for the temperature estimate is specifically $SiO_2(aq)$.

CALCULATION OF THE EFFECTS OF STEAM SEPARATION AND EXCESS ENTHALPY

The enthalpies of the total fluid and of water and steam at the pressure and temperature of the aquifer and at each point of separation are necessary for calculating the proportion of water and steam separated and the degree of concentration of the dissolved mineral constituents in the water and of the dissolved gases in the stream. For these calculations, the program uses thermodynamic data for pure water from Keenan, Keyes, Hill, and Moore (1969). The effect of the low mineral contents (<0.3 wt percent NaCl) of most geothermal waters on the thermodynamic properties of water is negligible (J. L. Haas, written commun., 1971). The content of dissolved gases in steam from most geothermal discharges is low (<2 wt percent), and their effect on the thermodynamic properties has been neglected.

With the assumption of constant total enthalpy, the fraction of water or steam in the fluid can be calculated for any temperature (t) from the equations,

$$\text{fraction water} = \frac{\text{enthalpy of steam at } t - \text{fluid enthalpy}}{\text{enthalpy of vaporization at } t}$$

and

$$\text{fraction steam} = \frac{\text{fluid enthalpy} - \text{enthalpy of water at } t}{\text{enthalpy of vaporization at } t}.$$

If the enthalpy of the fluid is the same or lower than that of water saturated with steam at the aquifer temperature, then no steam is present in the aquifer, and the concentrations of mineral constituents owing to later steam separation are calculated from the following:

Original concentration = concentration in complete discharge = (analyzed concentration in water) X (fraction of water in separator 1) X (fraction of water in separator 2) X (fraction of water in silencer).

If, however, the enthalpy of the fluid is higher than that of steam-saturated water at the aquifer temperature, the presence of steam in the aquifer is indicated. The presence of steam causes the mineral constituents in the original waters as calculated above to be too low, so that the following correction factor is applied:

$$\text{Concentration in original water} = \frac{\text{concentration in complete discharge}}{\text{fraction of water in the aquifer}}.$$

The presence of steam is often the result of lowered pressure owing to extensive production. Because CO_2 and H_2S are strongly partitioned into the steam phase, the development of steam in the aquifer may result in a decrease in gas pressures and an increase in aquifer pH with the possibility of carbonate scale deposition in the aquifer and in the well casing.

Because of instrumental inaccuracies, measurement of the enthalpy of drillhole discharges is necessarily somewhat approximate; therefore, samples with fluid enthalpies within ±28 cal/g (50 Btu/lb) of the enthalpy of water in equilibrium with steam at the aquifer temperatures are recalculated assuming exact equilibrium.

GAS PARTIAL PRESSURES

If the gas (CO_2, H_2S) contents of the sampled steam and the fraction of steam in the fluid at the sampling point are known, the total gas contents of the aquifer fluids may be calculated. If a single liquid phase exists in the aquifer, the gas partial pressures may be calculated directly from experimental data on the solubility of gas in water at high temperatures (Ellis and Golding, 1963; Kozintseva, 1964). If both steam and water exist in the aquifer, a large fraction of the gas partitions into the aquifer steam phase, and the partial pressure of the gas is a quadratic function of the total gas content.

CHEMICAL MODEL

The calculation of the chemistry of the aquifer fluids requires knowledge of the total content of all solution components and of the dissociation constants of all weak acids and bases and all ion pairs. The total contents of components other than gases and hydrogen ions are easily calculated from the water analysis with allowance for the effects of steam separation and of steam in the aquifer as described earlier. The contents of dissolved gases in the water may be calculated from their solubilities, their contents in the separated steam, the steam fraction, and if there is excess enthalpy, from the fractions of steam and water in the aquifer. For the calculation

of the total content of hydrogen ion, the state of ionization of all weak acids and bases under the conditions of analysis must first be ascertained. This is done through the calculations of a chemical model (Garrels and Thompson, 1962; Ellis, 1967).

SOLUTION OF MASS ACTION AND MASS BALANCE EQUATIONS

In the chemical model for the water as analyzed, the analytical concentrations, experimental dissociation constants, mass balances, and the measured pH are used to calculate the distribution of weak acid species and experimental dissociation constants, and mass balance equations are used to calculate that of ion pairs. Weak acids dissociate to form hydrogen ions by equations such as those for silicic acid as follows:

$$H_4SiO_4 = H^+ + H_3SiO_4^-,$$

and

$$H_3SiO_4^- = H^+ + H_2SiO_4^{-2}.$$

The concentration of each species is determined by the total concentration, the pH, the activity coefficients of the species, and the equilibrium constants for distribution of species at chemical equilibrium. For the preceding reactions we can write the equilibrium equations as follows:

$$K_1 = \frac{m_{H_3SiO_4^-}\,\gamma_{H_3SiO_4^-}\,10^{-pH}}{m_{H_4SiO_4}\,\gamma_{H_4SiO_4}},$$

$$K_2 = \frac{m_{H_2SiO_4^{-2}}\,\gamma_{H_2SiO_4^{-2}}\,10^{-pH}}{m_{H_3SiO_4^-}\,\gamma_{H_3SiO_4^-}}.$$

The mass balance equation for total silica (silicic acid and silicate ions) is

$$m_{Si\ total} = m_{H_4SiO_4} + m_{H_3SiO_4^-} + m_{H_2SiO_4^{-2}}.$$

The mass action equations can be combined with the mass balance equation to solve for $m_{H_4SiO_4}$.

$$m_{H_4SiO_4} = \frac{m_{Si\ total}}{1 + \gamma_{H_4SiO_4}\left(\frac{K_1\ 10^{pH}}{\gamma_{H_3SiO_4^-}} + \frac{K_1\ K_2\ 10^{2pH}}{\gamma_{H_2SiO_4^{-2}}}\right)}.$$

The value of $m_{H_4SiO_4}$ is then substituted into the mass action equations to solve for $m_{H_3SiO_4^-}$ and $m_{H_2SiO_4^{-2}}$. Activity coefficients are calculated from the extended Debye-Huckel equation as described later, and the ionic strength is calculated by iteration. Calculation of the concentration of ion pairs is accomplished by a slightly different procedure, which is illustrated by the calculation of the calcium ion species. The mass action expressions,

$$K_1 = \frac{m_{Ca^{+2}}\,\gamma_{Ca^{+2}}\,m_{SO_4^{-2}}\,\gamma_{SO_4^{-2}}}{m_{CaSO_4}\,\gamma_{CaSO_4}},$$

and

$$K_2 = \frac{m_{Ca^{+2}}\,\gamma_{Ca^{+2}}\,m_{CO_3^{-2}}\,\gamma_{CO_3^{-2}}}{m_{CaCO_3}\,\gamma_{CaCO_3}},$$

are combined with the mass balance expression,

$$m_{Ca\ total} = m_{Ca^{+2}} + m_{CaSO_4} + m_{CaCO_3},$$

to produce an expression for free (uncomplexed) Ca^{+2} ion,

$$m_{Ca^{+2}} = \frac{m_{Ca\ total}}{1 + \gamma_{Ca^{+2}}\left(\frac{m_{SO_4^{-2}}\,\gamma_{SO_4^{-2}}}{K_1\,\gamma_{CaSO_4}} + \frac{m_{CO_3^{-2}}\,\gamma_{CO_3^{-2}}}{K_2\,\gamma_{CaCO_3}}\right)}$$

The value of $m_{Ca^{+2}}$ may be substituted into the mass action expressions to solve for the ion pairs. In these equations Ca total is from the analysis, the dissociation constants depend only on temperature, and the activity coefficients are calculated from the ionic strength, which changes slowly during iteration. The molalities of the anions (SO_4^{-2}, CO_3^{-2}) are corrected in each iteration loop by summing the calculated species (for example, $m_{SO_4^{-2}} = m_{HSO_4^-} + m_{KSO_4^-} + \ldots$) and comparing the sum with the analytical concentration of total anion. If the sum calculated differs from the analytical concentration by more than 0.1 percent, the free anion concentration is corrected by an amount depending on the difference. When all anions have been checked (and corrected if necessary), the program iterates if corrections have been made to any of them. *Thus, the program leaves the loop when the concentrations of* all species satisfy the mass balances to 0.1 percent.

TOTAL IONIZABLE HYDROGEN ION CONTENT

The total content of hydrogen ions in an aqueous solution includes not only free ions but also those in combination in weak acids and in water itself. Only part of these can be ionized under the range of conditions found in natural waters.

This part, the total "ionizable" hydrogen ion content, is calculated by summing the contents of H^+ ion and of all the undissociated and partly dissociated weak acids—HCO_3^-, HBO_2, H_2S, NH_4^+, HSO_4^-, HF, HCl, $H_3SiO_4^-$, $H_4SiO_4^-$, (two times), and H_2CO_3 (two times). When the total ionizable hydrogen ion content has been corrected for electrolyte concentration changes due to steam separation and the presence of aquifer steam as discussed earlier, the H_2S and CO_2 originally dissolved in the water are added (the CO_2 two times as H_2CO_3).

AQUIFER CHEMICAL MODEL

The aquifer chemical model is calculated using the analysis corrected for steam separation and aquifer steam contents, values of dissociation constants at the aquifer temperature and saturated water vapor pressure, and the total ionizable hydrogen ion content. The method of calculation of the chemical model is the same as before except that the pH is now a dependent rather than an independent variable. Because almost all of the hydrogen ion occurs in complexes, changes in the calculated pH cause relatively large changes in the anion *mass balances, and the program converges very slowly.* A change in the criteria of convergence from 1 percent to 0.1 percent of the anion mass balances doubles the number of iterations and changes the final calculated pH by 0.1 to 0.15 units.

The correctness of the calculated model is dependent on the existence and validity of high-temperature quartz solubility values, gas solubility constants, and dissociation constants for the weak acids and bases and ion pairs present in the water. The data used in the program are given in tables 4 and 5 with their sources. They are of uneven quality, and as better data become available, the program can be easily updated. Tabular data are interpolated by a program written by P. C. Doherty of the U.S. Geological Survey. Single-ion activity coefficients have been calculated from the extended Debye-Hückel equation, with a small hydration coefficient (the "B." of Helgeson, 1969) assumed constant with temperature. This equation differs little from that suggested by Davies (1962). The ionic strength (I) of most geothermal waters is moderate (<0.08m), and the ionic activity coefficients are not very sensitive to the *ion size ($\mathring{a}$) and hydration parameters chosen.* The equation used is:

$$\log \gamma_i = \frac{-A z_i^2 I^{1/2}}{1 + \mathring{a}_i B I^{1/2}} + 0.04\,I.$$

The constants A and B are from a tabulation by Helgeson (1967) and are for molal units. Values of $\mathring{a}$ are taken from Kielland (1937).

Table 4.—*Solubility constants and dissociation constants in* KA(I) *and* KT(I) *arrays, analytical expressions.*

Reaction	Analytical expression if used (T in K, t in °C)	Log K 25°	Log K 250°	Note	Reference
1 .... H_2CO_3 app$=H^++HCO_3^-$	Log K= -2382.3/T+8.153-0.02194T	-6.38	-7.88	(1)	Ryzhenko (1963).
2 .... $H_2S=H^++HS^-$	Log K= -3279.0/T+11.17-0.02386T	-6.94	-7.6		D'yachkova and Khodakovskiy (1968).
3 .... $HBO_2+OH^-=H_2BO_3^-$	Log K=1573.21/T+28.6059+0.012078T -13.2258 log T	+4.76	+1.98	(2)	Mesmer, Baes, and Sweeton (1972).
4 .... $H_4SiO_4=H^++H_3SiO_4^-$	See table 5	-9.63	-9.63	(4)	Cobble (1964); Ryzhenko (1967).
5 .... $HF=H^++F^-$	....do	-3.18	-5.80	(3)	Ellis (1963).
6 .... $HSO_4^-=H^++SO_4^{-2}$	Log K= -557.2461/T+5.3505-0.01834127T	-1.99	-5.31		Lietzke, Stoughton, and Young (1961).
7 .... $H_2O=H^++OH^-$	Log K= -4470.99/T+6.0875-0.01706T	-13.995	-11.38		Harned and Owen (1958, p. 645).
8 .... $NH_3(H_2O)=NH_4^++OH^-$	See table 5	-4.75	-6.00		Wright, Lindsay, and Druga (1961).
9 .... $HCl=H^++Cl^-$	....do	-6.10	-.67		Helgeson (1969).
10 .... $NaCl=Na^++Cl^-$	....do	+1.60	-.25	(5)	Pearson, Copeland, and Benson (1963); Dunn and Marshall (1969); Hanna, Pethybridge, and Prue (1971).
11 .... $KCl=K^++Cl^-$	....do	+1.59	-.1		Helgeson (1969); Hanna, Pethybridge, and Prue (1971).
12 .... $MgSO_4=Mg^{+2}+SO_4^{-2}$	....do	-2.25	-5.7	(3)	Do.
13 .... $CaSO_4=Ca^{+2}+SO_4^{-2}$	....do	-2.30	-4.1	(3)	Do.
14 .... $KSO_4^-=K^++SO_4^{-2}$	....do	-.83	-2.35	(3)	Quist and others (1963); Truesdell and Hostetler (1968).
15 .... $NaSO_4^-=Na^++SO_4^{-2}$	....do	-.83	-2.35	(6)	
16 .... $CaCO_3=Ca^{+2}+CO_3^{-2}$	....do	-2.30	-5.90	(3)	Helgeson (1969).
17 .... $MgOH^+=Mg^{+2}+OH^-$	....do	-2.60	-4.65	(3)	Do.
18 .... $H_3SiO_4^-=H^++H_2SiO_4^{-2}$	Log K= -3450/T+6.34-0.0216T	-11.7	-11.5		Naymov, Ryzhenko, and Kodakovskii (1971).
19 .... $HCO_3^-=H^++CO_3^{-2}$	Log K=-2730.7/T+5.388-0.02199T	-9.12	-11.34		Ryzhenko (1963).
KS ...... H_2S gas $= H_2S$ aq	K=357+15.688t-0.038253t^2	+2.86	+3.28		Kozintseva (1964).
K .... CO_2 gas$+H_2O=H_2CO_3$ app	See table 5	+3.21	+3.72	(1)	Ellis and Golding (1963).

[1] H_2CO_3 apparent includes H_2CO_3 and CO_2 aqueous.
[2] H_2BO_3 given in print out as BO_2. Reaction written by Mesmer, Baes, and Sweeton (1972) as $B(OH)_3+OH^-=B(OH)_4^-$.
[3] Extrapolated above 200°C.
[4] Extrapolated above 200°C. Agrees with Ryzhenko (1965) to 200°C.
[5] Extrapolated below 100°.
[6] Assumed identical to K KSO_4.

Table 5.—*Log* K(pK), *and* CO_2 *and quartz solubility, data in tabular form interpolated by look-up subroutine*
[For reaction equations and source of data, see table 4]

°C	(4) H_4SiO_4°	(5) HF°	(8) $NH_3(H_2O)$°	(9) HCl°	(10) NaCl°	(11) KCl°	(12) $MgSO_4$°	(13) $CaSO_4$°	(14) KSO_4^-	(16) $CaCO_3$°	(17) $MgOH^+$	CO_2 solubility	Quartz solubility[1] (p/m)
0	10.2	2.96	4.87	-7.5	-1.65	-1.65	2.05	2.3	0.65	3.0	2.58	700	2.4
10	9.94	3.00	4.80	-6.8	-1.63	-1.62	2.10	2.3	.71	3.05	2.58	1000	3.6
25	9.63	3.18	4.75	-6.1	-1.60	-1.59	2.25	2.3	.83	3.20	2.60	1630	6.6
35	9.48	3.25	4.70	-5.7	-1.40	-1.50	2.35	2.35	.90	3.27	2.63	2100	8.6
50	9.30	3.40	4.70	-5.0	-1.20	-1.40	2.60	2.40	1.00	3.40	2.7	2900	13.5
75	9.11	3.64	4.75	-3.8	-.90	-1.20	2.90	2.55	1.15	3.65	2.9	4000	27
100	9.03	3.85	4.85	-2.9	-.55	-1.00	3.20	2.7	1.30	3.90	3.1	5200	48
125	9.03	4.09	4.97	-2.0	-.55	-.90	3.55	2.9	1.45	4.15	3.33	6000	80
150	9.10	4.34	5.10	-1.23	-.45	-.75	3.90	3.1	1.60	4.50	3.6	6600	125
175	9.23	4.59	5.33	-.60	-.30	-.60	4.40	3.35	1.78	4.85	3.85	6800	190
200	9.36	4.89	5.53	-.07	-.15	-.40	4.80	3.6	1.93	5.20	4.1	6400	265
225	9.48	5.3	5.73	.30	.05	-.20	5.25	3.8	2.10	5.55	4.35	5900	367
250	9.63	5.8	6.0	.67	.25	.10	5.7	4.1	2.35	5.90	4.65	5300	490
275	9.83	6.2	6.3	.95	.60	.30	6.1	4.3	2.55	6.20	4.9	4600	615
300	10.2	6.8	6.75	1.2	.95	.6	6.4	4.5	2.75	6.45	5.15	3900	680
325	10.5	7.1	7.25	1.6	1.35	1.0	6.7	4.75	2.9	6.65	5.45	3100	720
350	11.0	7.4	8.0	2.5	2.0	1.7	7.0	5.0	3.1	7.0	5.7	2100	(750)

[1] Quartz solubility in water at saturated water vapor pressure. 0°–240°C from Morey, Fournier, and Rowe (1962); 260°–325°C from Kennedy (1950). An incorrect 350° value is included because the look-up subroutine requires a monotonic function.

The algol version of this program (Truesdell and Singers, 1973) has just been published.

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Vapor-Dominated Hydrothermal Systems Compared with Hot-Water Systems[1]

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Abstract

Vapor-dominated ("dry-steam") geothermal systems are uncommon and poorly understood compared with hot-water systems. Critical physical data on both types were obtained from U. S. Geological Survey research in Yellowstone Park. Vapor-dominated systems require relatively potent heat supplies and low initial permeability. After an early hot-water stage, a system becomes vapor dominated when net discharge starts to exceed recharge. Steam then boils from a declining water table; some steam escapes to the atmosphere, but most condenses below the surface, where its heat of vaporization can be conducted upward. The main vapor-dominated reservoir actually is a two-phase heat-transfer system. Vapor boiled from the deep (brine?) water table flows upward; most liquid condensate flows down to the water table, but some may be swept out with steam in channels of principal upflow. Liquid water favors small pores and channels because of its high surface tension relative to that of steam. Steam is largely excluded from smaller spaces but greatly dominates the larger channels and discharge from wells. With time, permeability of water-recharge channels, initially low, becomes still lower because of deposition of carbonates and $CaSO_4$, which decrease in solubility with temperature. The "lid" on the system consists in part of argillized rocks and CO_2-saturated condensate.

Our model of vapor-dominated systems and the thermodynamic properties of steam provide the keys for understanding why the major reservoirs of The Geysers, California, and Larderello, Italy, have rather uniform reservoir temperatures near 240° C and pressures near 34 kg/cm² (absolute; gases other than H_2O increase the pressures). Local supply of pore liquid and great stored heat of solid phases account for the physical characteristics and the high productivity of steam wells.

We suggest that vapor-dominated systems provide a good mechanism for separating volatile mercury from all other metals of lower volatility. Mercury is likely to be enriched in the vapor of these systems; the zone of condensation that surrounds the uniform reservoir is attractive for precipitating HgS.

A more speculative suggestion is that porphyry copper deposits form below the deep water tables hypothesized for the vapor-dominated systems. Some enigmatic characteristics of these copper deposits are consistent with such a relationship, and warrant consideration and testing.

Introduction

ALTHOUGH hot springs throughout the world have been studied for centuries, direct knowledge of their subsurface relationships was lacking until commercial and research drilling was initiated in the 20th Century. With a few notable exceptions (Allen and Day, 1927; Fenner, 1936) little significant scientific data were available prior to 1950.

Efforts to produce electricity from natural steam were first successful in the Larderello region of Italy, starting about 1904. Drilling from 1920 to 1925 showed that large quantities of natural steam could also be obtained at The Geysers in California, but economic development was not feasible until 1955. At both The Geysers and Larderello, wells deeper than a hundred meters or so[2] and near centers of surface activity were found to yield slightly superheated steam (Burgassi, 1964). Some wells on the borders of the active systems[3] produced hot water

[1] Publication authorized by the Director, U. S. Geological Survey.

[2] The metric system is used throughout this paper. Some readers may find useful the following conversion factors:

Length:	1 m = 3.281 ft; 1 km = 3,281 ft = 0.6214 mi.
Temperature:	(°C × 9/5) + 32 = °F.
Pressure:	1 kg/cm² = 0.9678 atm = 0.9807 bars = 14.22 psi. All pressures absolute, with 0.78 kg/cm² added to gage pressure for Yellowstone Park, and 1.03 kg/cm² added to gage pressure at sea level and geothermal areas at low altitudes.
Heat:	1 cal = 3.9685 × 10^{-3} BTU; 1 cal/gm = 1.80 BTU/lb.

[3] A geothermal system includes a source of heat within the earth's crust (regional heat flow or local igneous intrusion) and the rocks and water affected by that heat. When geothermal systems involve circulating waters, they are also

and steam in noncommercial quantities and pressures (Allen and Day, 1927, p. 82); the characteristics of such wells have not yet been adequately described.

From 1946 to 1970 approximately 100 geothermal systems throughout the world were explored at depth by drilling. Initially, the objective of this search was to discover areas yielding dry steam, as at Larderello and The Geysers. This effort, however, soon revealed that most hot-spring systems yield fluids that are dominated by hot water rather than by steam.

New Zealand first demonstrated that a source of dry steam was not essential for the generation of geothermal power. At Wairakei, subsurface hot water at temperatures up to 260° C is erupted through wells to the surface; some of the water flashes to steam as temperature and pressure decrease to the operating pressure, commonly from 3 to 6 kg/cm². This steam, generally 10 to 20 percent of the total mass flow, is separated from the residual water and directed through turbines to generate electricity. The high energy potential of subsurface water has also been demonstrated in Mexico, Iceland, Japan, USSR, El Salvador, the Philippines, and the United States.

A few systems, other than Larderello and The Geysers, yield vapor with little or no associated liquid water. These include the Bagnore and Piancastagnaio fields near Monte Amiata southeast of Larderello (Burgassi, 1964; Cataldi, 1967), and probably the Matsukawa area of northern Honshu, Japan, (Saito, 1964; Hayakawa, 1969; Baba, 1968), the Silica Pit area of Steamboat Springs, Nevada (White, 1968b), and the Mud Volcano area of Yellowstone National Park, considered in this report.

Hot-water systems have attracted nearly all of the research drilling in natural hydrothermal areas. The first two research holes in the world were drilled by the Geophysical Laboratory of the Carnegie Institution of Washington in the hot water systems of Yellowstone Park in 1929–30 (Fenner, 1936), and seven of the eight research holes drilled at Steamboat Springs, Nevada, in 1950–51 (White, 1968b) were in a hot-water system. The eighth was in the small vapor-dominated Silica Pit system, subsidiary to the larger water-dominated area.

Although research drilling by the U. S. Geological Survey in Yellowstone National Park during 1967 and 1968 was aimed mainly at a better understanding of the hot-water systems of the major geyser basins, a specific effort was made to find and drill a vapor-dominated system. The Mud Volcano area was found to be such a system and is described here.

In spite of long and extensive commercial development at Larderello and The Geysers, the origin and nature of the systems that yield dry or superheated steam, and why they differ from the abundant hot-water systems, are not nearly so well understood. Facca and Tonani (1964), for example, seem to deny that Larderello and The Geysers differ significantly from Wairakei, New Zealand, and the other water-dominated areas. Marinelli (1969) states that Larderello is a hot-water area. James (1968) and in less detail Elder (1965) and Craig (1966) have instead proposed that the reservoirs are filled with steam maintained by boiling from a deep water table.

We submit, in agreement with James (1968), that fundamental differences do exist between two main types of natural hydrothermal systems; each type is recognizable by geologic, physical, and geochemical criteria. However, in contrast with James (1968) and others, we consider that steam and water must coexist in the reservoirs of these systems that yield dry steam at the surface.

Acknowledgments

We are much indebted to our associates, R. O. Fournier, John Haas, Warren Nokleberg, and J. T. Nash, for their helpful suggestions and review of this manuscript. Gunnar Bodvarsson has been especially helpful in clarifying the properties of coexisting liquid and vapor and in pointing out important differences in specific resistance to flow of liquid water and steam.

Summary of Characteristics of Hot-water Systems

Hot-water systems are usually found in permeable sedimentary or volcanic rocks and in competent rocks such as granite that can maintain open channels along faults or fractures. Total discharge from typical systems ranges from several hundred to several thousand liters per minute (lpm), with individual springs commonly discharging a few lpm to several hundreds of lpm. Where near-surface rocks are permeable and the surrounding water table is relatively low, much or all of the circulating hot water escapes below the ground surface, and little or none is discharged from local surface springs. For example, nearly 95 percent of the water at Steamboat Springs, Nevada, escapes in such a way (White, 1968b). On the other hand, where spring outlets are at or below the level of the surrounding water table, all hot water of the system is likely to be discharged in local visible springs.

The spring systems that discharge at low to moderate temperatures are commonly similar chemically

called hydrothermal systems. The hot part of each hydrothermal system is commonly emphasized, but in its broader meaning the marginal parts involve convective downflow of cold water, and are also included. A hot spring area is the surface expression of a geothermal system and contains hot springs, fumaroles, and other obvious hydrothermal phenomena.

to nearby ground waters, but the near-boiling hot waters of moderate to high discharge are nearly always characterized by relatively high contents of alkali chlorides, SiO_2, B, and As (table 1, anals. 4, 8, and 10; White and others, 1963, Tables 17 and 18). In confusing contrast, some gassy springs of low discharge may differ greatly from these chloride-rich waters in physical and chemical characteristics. Surrounding ground is commonly bleached and hydrothermally altered to a porous siliceous residue that may be mistaken for hot-spring sinter. The bleached ground may contain native sulfur, white, yellow, and orange sulfate minerals, and clay minerals, especially kaolinite; vegetation is generally sparse or absent. Chemical analyses of such springs (table 1, anal. 9; White and others, 1963, table 20) contrast strikingly with those of higher discharge; chloride is generally less than 20 ppm, sulfate is the dominant anion, pH is usually between 2.5 and 5, and Fe, Al, Ca, and Mg are abundant relative to Na and K.

Where these two contrasting types of springs coexist in the same general area, topographic relationships and results of shallow drilling and augering indicate that the nearly neutral to alkaline chloride springs are from the main water body, occurring where the water table intersects the ground surface. Where the water table is low, acid springs may result from boiling at this water table. Some steam condenses in cooler ground and in pools of rain water, perched ground, and previously condensed steam.

H_2S that evolves with the steam reacts near the surface with atmospheric oxygen to form sulfuric acid, thus accounting for the high sulfate contents and the low pH's characteristic of these waters. Bacterial oxidation of intermediate forms of sulfur may be involved (Schoen and Ehrlich, 1968). The acid dissolves available cations from the surrounding rocks, which are adequate sources for the reported constituents (White and others, 1963, table 20).

The geochemistry of chloride is critical in understanding the differences between the coexisting neutral-chloride and acid-sulfate waters, as well as the differences between vapor-dominated systems and hot-water systems. Most metal chlorides are highly soluble in liquid water, and the low content of Cl in most rocks can be selectively dissolved in water at high temperatures (Ellis and Mahon, 1964, 1967). The common metal chlorides, however, have negligible volatility and solubility in low-pressure steam (Sourirajan and Kennedy, 1962; Krauskopf, 1964). The only chlorides with sufficient volatility to account for significant transfer of Cl in steam at low temperatures and pressures are HCl and NH_4Cl, both of which are minor constituents of most hot-spring systems. The very low Cl content of the perched acid springs associated with some hot-water systems is thus consistent with near-surface attainment of acidity from oxidation of H_2S, rather than by vapor transfer of HCl from initially acid sources.

The temperatures of many explored hot-water systems increase with depth to a "base" temperature (Bodvarsson, 1964a, 1970) that differs with each system that has been drilled deep enough. Temperatures at Wairakei, New Zealand, rise to a maximum of 260° C near 450 m of depth but increase little if any more at further explored depths (Banwell and others, 1957, p. 52–56), and at Steamboat Springs, Nevada, the temperatures in six drill holes were near 170° C at depths close to 100 m, but deeper drilling found no higher temperatures even though major channels were intersected below 150 m (White, 1968b). In such an area, meteoric water (Craig, 1963; White, 1968b) evidently penetrates to considerable depths along permeable channels of a huge convection system; the water is heated to its base temperature by rock conduction, perhaps augmented slightly by magmatic steam. It then rises in the core of the spring system, losing only a little heat because of its relatively high rate of upflow through wallrocks of low thermal conductivity. As the hot water rises the hydrostatic pressure decreases, and eventually a level is attained where pressure is low enough for boiling to begin.

Of about one hundred hot-water systems throughout the world that have now been explored by drilling, fewer than 30 are known to exceed 200° C in temperature and only about 10 demonstrably exceed 250° C. The liquid of the two reservoirs known to exceed 300° C is brine rather than relatively dilute water. The Salton Sea system has about 250,000 ppm of dissolved salts and a maximum temperature of about 360° C (Helgeson, 1968). The Cerro Prieto system, about 90 km to the south in Baja California, Mexico, has a salinity of about 17,000 ppm and temperatures as high as 388° C (Mercado, 1969).

Hot-water systems have a high potential for self-sealing (Bodvarsson, 1964b; Facca and Tonani, 1967) by means of deposition of minerals in outlet channels. SiO_2 is the most important constituent for the self-sealing of high-temperature systems because quartz is so abundant and its solubility increases so much with temperature (Fournier and Rowe, 1966). Quartz dissolves rather rapidly at high temperatures; when quartz-saturated waters are cooled, quartz precipitates rather readily down to about 180° C but with increasing sluggishness at lower temperatures. The SiO_2 content of many waters, after cooling, greatly exceeds the solubility of quartz and may even exceed the solubility of amorphous SiO_2. Near the surface where temperatures are near or below

Table 1.—Chemical analyses of waters associated with vapor-dominated and hot-water geothermal systems

Name	1/ The Geysers	2/ The Geysers	3/ GS-7	4/ Spring 8	5/ Mud Volcano	6/ Mud Volcano	7/ Y-11, Mud Volcano
Location	Calif.	Calif.	Steamboat, Nev.	Steamboat, Nev.	Yellowstone, Wyo.	Yellowstone, Wyo.	Yellowstone, Wyo.
Water type	HCO_3-SO_4	Acid-sulfate	HCO_3-SO_4	Cl-HCO_3	Acid-sulfate	HCO_3-SO_4	HCO_3-SO_4
System type	Vapor-dom.	Vapor-dom.	Vapor-dom.	Hot water	Vapor-dom.	Vapor-dom.	Vapor-dom.
SiO_2	66	225	14	293	540	215	
Al		14		0.5	146		
Fe		63		0.05	17		
Mn		1.4		0.05			
As				2.7			
Ca	58	47	6.3	5.0	14	28.7	28
Mg	108	281	0	0.8	11	16.4	0.47
Na	18	12	9.3	653	16	74.3	105
K	6	5	4.5	71	17	47.5	12.6
Li			0	7.6		.20	.18
NH_4	111	1,400		<1	26	.18	3.2
N		9.5			43		
HCO_3	176	0	21	305		298	258
CO_3	—	—	—	—	—	—	
SO_4	766	5,710	24	100	3,149	65.3	74
Cl	1.5	0.5	0.5	865	Tr.	13.5	9.6
F			0	1.8	1	2.0	
Br				0.2			
NO_3			Tr.	—			0.2
B	15	3.1	1.3	49		.6	0.1
H_2S	0	—	2.4	4.7	0		
Total reported	1,330	7,770	83	2,360	3,980	761.7	491.4
pH	.neutral	1.8±	6.5	7.9	Strong acid	7	8.5(?)
Temperature °C	100	Boiling?	161	89.2	65	58.5	131.7

1/ Witches Cauldron, White and others, 1963, p. F47, modified from Allen and Day, 1927.

2/ Devils Kitchen, White and others, 1963, p. F46, modified from Allen and Day, 1927.

3/ White and others, 1963, p. F47. Condensate in apor-filled hole.

4/ . . . Do . . . . . .p. F40.

5/ Allen and Day, 1935, p. 427; described as "Big Sulphur Pool" 0.3 km N of Mud Volcano; location indicates Old Sulphur Cauldron of fig. 4, 60 m SSW of Y-11 drill hole.

6/ Spring discharging from sinter, E. bank of Yellowstone River 0.5 km SE of Y-11 drill hole; has deposited sinter in recent past, if not now. Analyzed by Mrs. Roberta Barnes.

7/ Erupted from Y-11 drill hole Sept. 22, 1969 after hole had caved to 28 m depth (table 1); collected by R. O. Fournier, analysis by Mrs. Roberta Barnes. pH not representative of in-hole environment because of CO_2 loss, storage in plastic with clays.

Note: The word apor should read vapor in footnote 3.
Reference to Table 1 in footnote 7 should read Table 4.

100° C, the excess silica in such waters may precipitate as chalcedony, opal, and cristobalite (White and others, 1956). Self-sealing by silica minerals is likely to be slight in hot-water systems that do not exceed 150° C, but as maximum temperatures increase above this value, the potential for self-sealing increases greatly.

Calcite, zeolites, and some other hydrothermal

Table 1.--Chemical analyses of waters associated with vapor-dominated and hot-water geothermal systems (continued)

Name	8/ Morris Basin	9/ Morris Basin	10/ Well 4	11/ Well 5	12/ Carboli A.	13/ Well MR-1
Location	Yellowstone, Wyo.	Yellowstone, Wyo.	Wairakei, N.Z.	Wairakei, N.Z.	Italy	Matsukawa, Japan
Water type	$Cl(HCO_3)$	Acid sulfate	Cl	HCO_3 SO_4	SO_4 $HCO_3(Cl)$	$SO_4(HCO_3)$
System type	Hot water	Hot water	Hot water	Vapor-dom.(?)	Hot water	Vapor-dom.(?)
SiO_2	529	109	386	191		635
Al		2.4			Trace	29
Fe		0.8			Trace	508
Mn						
As	3.1					
Ca	5.8	2.2	26	12		
Mg	0.2	0	<0.1	1.7	5.0	8.7
Na	439	2.0	1,130	230	56.6	264
K	74	3.0	146	17	32.0	144
Li	8.4		12	1.2		
NH_4	0.1	30	0.9	0.2	19.0	
H		14				
HCO_3	27	--	35	670	89.7	37
CO_3	--	—	0(?)			
SO_4	38	758	35	11	137.4	1,780
Cl	744	15	1,930	2.7	42.6	.12
F	4.9		6.2	3.7		
Br	0.1					
NO_3	—					
B	12	6.9	26	0.5	13.9	61.2
H_2S	.0		1.1	0		Trace
Total reported	1,890	943	3,750	1,140	396.2	3,478.9
pH	7.5	1.97	8.6	6.7		4.9
Temperature °C	84.5	90	228+	High	~300	~240

8/ Dr. Morey's Porkchop, 60 m southwest of Pearl Geyser (White and others, 1963, p. F40).

9/ Locomotive Spring, 55 m WSW of Morris Basin drill hole of Fenner (1936); seeping discharge (White and others, 1963, p. F46).

10/ Typical of shallow Wairakei system; 375 m deep with maximum temperature of 245°C (Banwell and others, 1957). Analysis by Wilson; also contains 11 ppm free CO_2 (Wilson, 1955; quoted in White and others, 1963, p. F40).

11/ Western part of Wairakei field (Wilson, 1955, quoted in White and others, 1963, p. F47). Similar to some waters of vapor-dominated systems; 467 m deep, maximum 217°C at 271 m.

12/ Deepest well of hot-water field on So. border Larderello steam fields (Cataldi and others, 1969). Orig. anal. in ppm, supplied by R. Cataldi, 1970.

13/ Well 945 m deep, produced steam, some water for 1 year before drying; this anal. while still wet; condensate of steam 50 ppm H_2S and 6.2 ppm S (Nakamura and Sumi, 1967; Hayakawa, 1969).

minerals are also effective in producing self-sealed margins of some hot-water systems, but generally less so than the silica minerals. Self-sealing is likely to be most extensive where temperatures decrease most rapidly. These marginal parts are of secondary interest for production drilling, and they have not been

Table 2.—Analyses of gases associated with vapor-dominated and hot-water geothermal systems, in volume percent

	Total vapor, including H_2O		Gases, excluding H_2O					
	1/ The Geysers, California	2/ Larderello, Italy	3/ The Geysers, California (1), recalc.	4/ Larderello Italy (2), recalc.	5/ Y-11 Mud Volcano, Yellowstone	6/ Mud Volcano Yellowstone	7/ Y-9, Morris, Yellowstone	8/ Spring Morris Yellowstone
H_2O	98.045	98.08						
CO_2	1.242	1.786	63.5	93.02	98.4	98.90	91.5	97.40
H_2	0.287	-0.037	14.7	} 1.92	<0.01	0.00	0.9	0.00
CH_4	0.299		15.3		Tr.	0.10	0.1	0.20
C_2H_6					0.0		0.0	
N_2	} 0.069	0.0105	} 3.5	0.54	0.8	} 1.00	5.1	} 1.60
A					0.013		0.08	
H_2S	0.033	0.049	1.7	2.55	0	0.10	1.4	0.75
NH_3	0.025	0.033	1.3	1.72				
H_3BO_3	0.0018	0.0075	0.09	0.39				
O_2					0.2	0.00	1.0	0.05?
Total	100.002	100.003	100.09	100.14	99.42	100.10	100.08	100.00

1/ Well 1, The Geysers (Allen and Day, 1927, p. 76).

2/ Average vapor from producing wells (Burgassi, 1964), recalculated from analysis in gm per kgm; 2,850,000 kg produced per hour; also contains 1 cm^3 total rare gases per kg.

3/ Recalculated from 1/, without H_2O.

4/ Recalculated from 2/, without H_2O.

5/ Collected July 10, 1968, by R. O. Fournier, when hole was still open to 316 ft (table 3).

6/ Gas from same spring as anal. 5 of table 1 (Allen and Day, 1935, p. 86).

7/ Collected by R. O. Fournier, Sept. 18, 1969, and analyzed by D. Byrd, U.S. Geol. Survey; gas separated from water; nearest drill hole to springs of anal. 8 and 9, table 1.

8/ Gas from unnamed acid-sulfate spring "near Congress Pool," perhaps Locomotive (table 1, anal. 9). Allen and Day, 1935, p. 86, 469.

Note: Reference to Table 3 in footnote 5 should read Table 4.

cored and studied in much detail except in research drilling in Yellowstone Park (unpublished data).

For similar geochemical reasons, most hot-water systems with subsurface temperatures of 180° C or higher (White, 1967a) have hot springs or geysers that deposit sinter (amorphous silica precipitated on the ground surface by flowing hot water). Waters that deposit sinter nearly always have SiO_2 contents of at least 240 ppm, equivalent to a quartz-equilibration temperature of 180° C. Because the solubility of amorphous SiO_2 is so much higher than that of quartz, a quartz-saturated water at 180° C must cool to about 70° C in order to precipitate amorphous silica. If the water becomes sufficiently concentrated in SiO_2 by evaporation, as on the borders of pools and in erupted geyser water, precipitation can occur at somewhat higher temperatures.

The existence of sinter, as distinct from travertine ($CaCO_3$) and siliceous residues from acid leaching, is evidence for a hot-water system with present or past subsurface temperatures of more than 180° C.

Summary of Characteristics of Vapor-dominated ("Dry-steam") Systems

The near-surface rocks of Larderello, Italy, and The Geysers, California, are relatively tight and incompetent, and evidently do not permit large quantities of meteoric water to penetrate deep into their systems (White, 1964). Even in these areas, however, isotopic data indicate that most of the water is of surface origin (Craig and others, 1956; Craig, 1963).

Surface springs at The Geysers[4] typically have

[4] "The Geysers" is an unfortunate misnomer. The area has never had true geysers, which are restricted to the hot-water systems (White, 1967a).

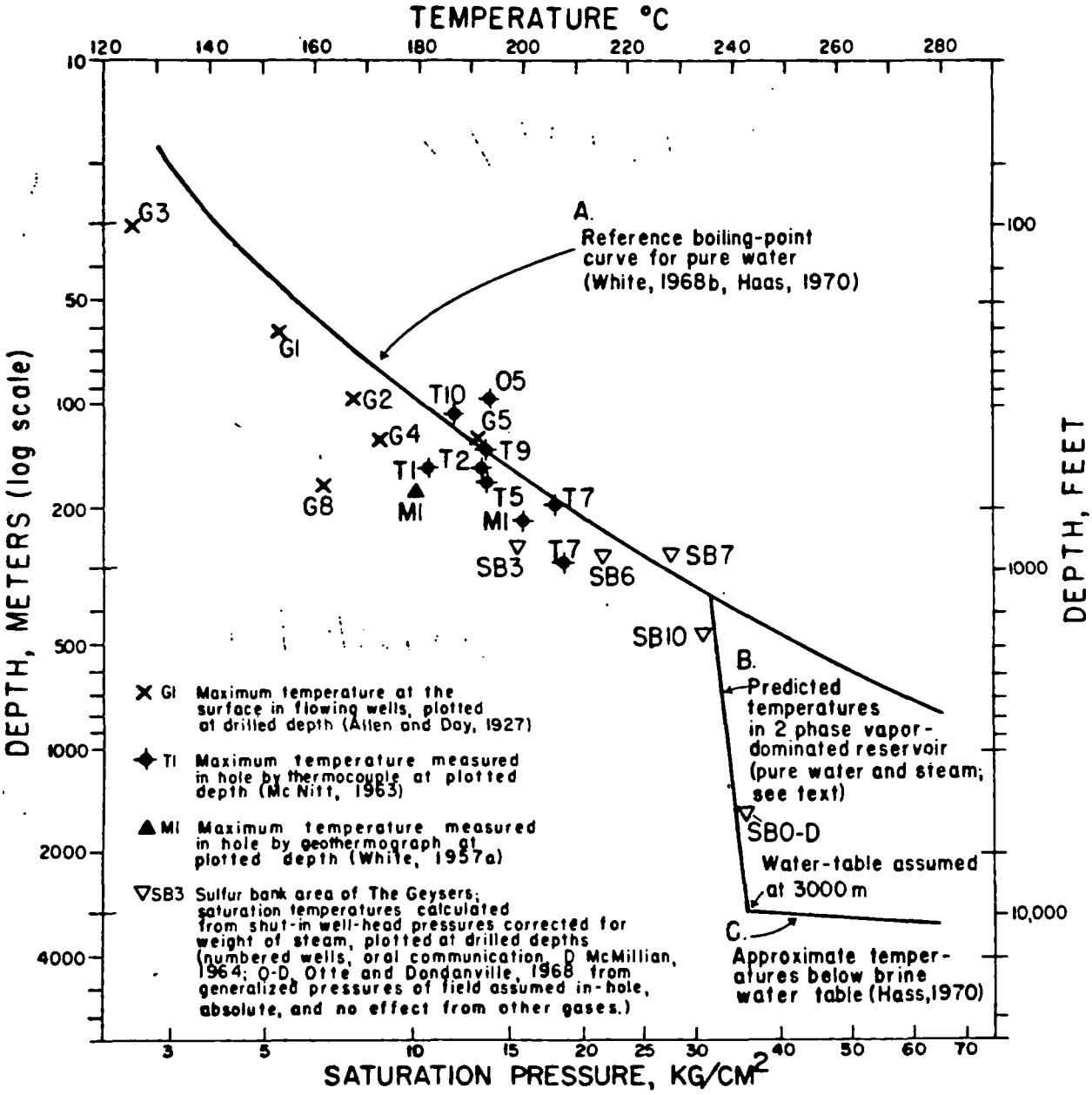

FIG. 1. Measured and calculated temperatures from The Geysers, Calif., with some theoretical curves. The reference boiling-point curve for pure water, curve A, differs in shape from its usual representation because of the logarithmic scale for depth. Note that curves B and C are *temperature-deficient* and *pressure-deficient* relative to curve A.

very low discharge, totaling little more than 100 lpm (Allen and Day, 1927). Most of the springs are strongly acidic (pH from 2 to 3). The few neutral springs (Table 1, anal. 1) have chloride contents of less than 2 ppm, similar to local rain water. A careful search of the creek that flows through the area was made on the chance that undetected chloride springs might be seeping into the creek (White, 1957a, p. 1651). However, throughout an area of at least 30 square miles surrounding The Geysers, the surface and ground waters are no higher in chloride than normal cold streams.

Chloride contents have not been included in reports on natural springs associated with the original vapor-dominated Larderello fields, but available descriptions of spring activity, dominated by mud pots and fumaroles, suggest the presence of sulfate waters low in chloride. However, present springs are not low in pH (R. Cataldi, written commun., 1970), perhaps because of the neutralizing action of abun-

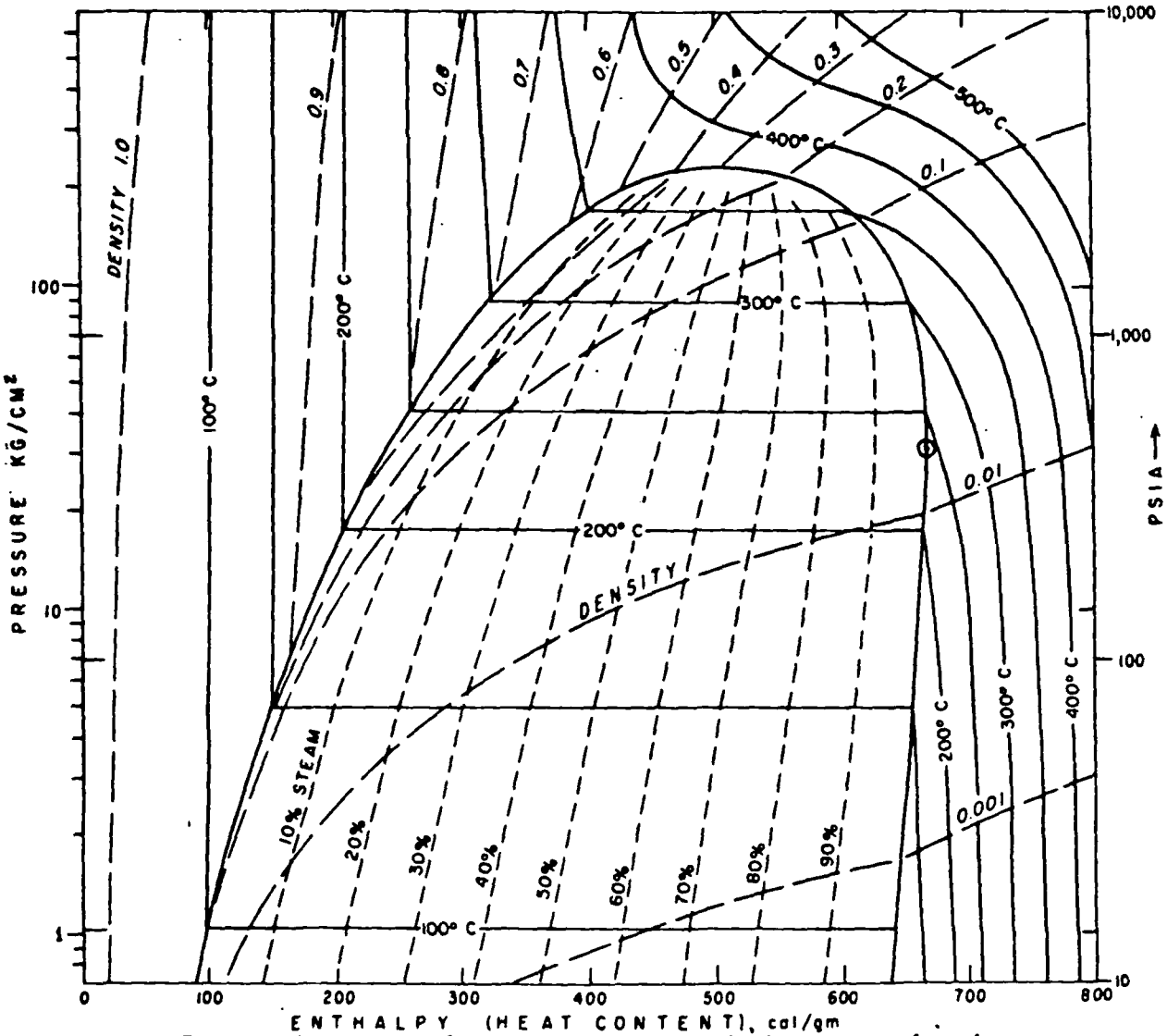

FIG. 2. Pressure-enthalpy diagram for pure water and vapor, showing contours of equal temperature, density, and mass proportions of steam to water (computed from Keenan and Keyes, 1936). Open circle indicates maximum enthalpy of saturated steam, 670 cal/gm at 236° C and 31.8 kg/cm².

dant NH_3 absorbed from the gases. Some springs and wells of the Carboli area just south of the vapor-dominated fields (Cataldi and others, 1969) contain some chloride (42.6 ppm, Table 1). Although this Cl content is not notably high, it is consistent with the abundant water and old travertine which suggest that Carboli is a hot-water system.

In general where surface springs are all low in chloride and subsurface thermal waters are similarly low (< 20 ppm) a vapor-dominated system is indicated. The Cl content of steam is normally less than 1 ppm, but near-surface waters involved in condensation of the steam commonly contain a few ppm of Cl because, with little or no discharge, Cl can be selectively concentrated.

Typical wells at Larderello (Burgassi, 1964) produce dry or slightly superheated steam with 1 to 5 percent of CO_2 and other gases (Table 2, anal. 2). Liquid water evidently occurs in some noncommercial wells on the borders of the fields. Shut-in wellhead pressures in typical steam wells tend to increase with depth up to a maximum of about 32 kg/cm² (Penta, 1959; Burgassi, 1964). Increased productivity reported at greater depths evidently is not due to significantly higher initial pressures. Ferrara and others (1963) list the temperatures of two Larderello wells as 251° C, but all other cited wells are 240° C or lower (depths not given).

Typical wells at The Geysers also produce dry or superheated steam containing gases similar to those

in the Larderello field (Table 2, anal. 1). Pressures up to about 35 kg/cm² were measured in the deeper wells (500 psi, Otte and Dondanville, 1968), but whether pressures were at the well-head or in-hole, and gage or absolute were not specified.

Figure 1 shows the maximum temperatures measured or calculated for individual shallow wells in The Geysers field. For a variety of reasons each point is individually unreliable and is probably not identical with the original ground temperature at its plotted depth. Nevertheless, temperatures of shallow wells (< 350 m) do show a rather close relationship to curve A, the reference boiling-point curve for hydrostatic pressure of pure water. A few points plot above this curve, indicating pressures above hydrostatic but below lithostatic.

All of the early shallow wells at The Geysers were drilled in or near fumaroles, hot springs, and hydrothermally altered ground that provided evidence of surface discharge of thermal fluids. Figure 1 suggests, and our model (to be discussed) assumes, that liquid water condensed from rising steam fills much of the pore spaces; this condensed water provides a major buffering control over temperatures and pressures in the zone of upflowing fluids. McNitt (1963) concluded from other data that a near-surface zone is water saturated; we support his general conclusions but disagree on the nature of the evidence.

Although available data are scanty, temperatures at The Geysers increase irregularly with depth, probably along or near the hydrostatic boiling-point curve, until temperatures near 236° C (and pressures near 32 kg/cm²) are attained, with only slight additional increases approximately along curve B of figure 1 to explored depths. In the Sulphur Bank area of The Geysers (Otte and Dondanville, 1968), about 1½ km west-northwest of the original field, wells range from 450 m to more than 2,000 m in depth and are remarkably uniform in temperature (close to 240° C) and in pressure (about 35 kg/cm²), as shown in Figure 1. Otte and Dondanville state that "the fluid exists in the reservoir as superheated steam," but the reported temperatures and pressures indicate approximate saturation. No specific data for individual wells are available.

No data have been published to indicate that wells in the central parts of any vapor-dominated field have penetrated a deep water-saturated zone or a water table. In such a penetration, in-hole pressures should increase downward through the water-filled parts of shut-in wells instead of remaining near 32 kg/cm². This evidently does occur in parts of the Italian fields (R. Cataldi, written commun., 1970), but detailed relationships are not yet available. The expected temperature-depth relationships below the deep water table are shown in Figure 1, curve C. This curve has an increasing slope with depth and all points on it are also deficient in pressure with respect to external water pressures, probably to depths of 2,000 m or more below the water table.

Table 3.—Pressures and temperatures in a two-phase reservoir in which steam is the continuous phase. Top of reservoir assumed to be 236°C 31.8 kg/cm², and 360 m deep (from hydrostatic boiling-point curve).

Depth meters	Pressure, kg/cm² (bottom hole)	Temperature °C
360	31.8	236.0
500	32.0	236.1
1,000	33.5	239.0
1,500	34.3	240.3
2,000	35.1	241.6

Note: Second line of column 3 should read 236.3.

James (1968) noted that initial temperatures and pressures of the Larderello steam fields were close to the temperature (236° C) and pressure (31.8 kg/cm²) of saturated steam of maximum enthalpy (670 cal/gm; indicated on Fig. 2). James reasoned that enthalpies up to this maximum can be obtained in undisturbed steam reservoirs by evaporation at a subsurface water table. Higher temperatures (and pressures) can exist below but not *at* the water table. He reasoned that if saturated steam at 350° C and 68.7 kg/cm², for example, with an enthalpy of only 612 cal/gm (Fig. 2), formed deep in a system and rose up to levels of lower hydrostatic pressure, part of the steam would increase in enthalpy as it continued to rise while the rest would condense to liquid water and remain behind. For a pure water system, this separation of liquid from vapor continues until the pressure at maximum enthalpy is attained.

The enthalpy of saturated steam near its maximum, however, is not very sensitive to changes in temperature and pressure (Fig. 2). James suggested that the top of a natural vapor-dominated reservoir is likely to have a temperature near 236° C and a pressure near 31.8 kg/cm² but that, because of the weight of steam in a deep reservoir, the temperature near a boiling water table may be as much as 240° C at a pressure near 34 kg/cm². Table 3 shows expected depth-related variations in temperature and pressure of a pure water system in a homogeneous, vapor-dominated reservoir.

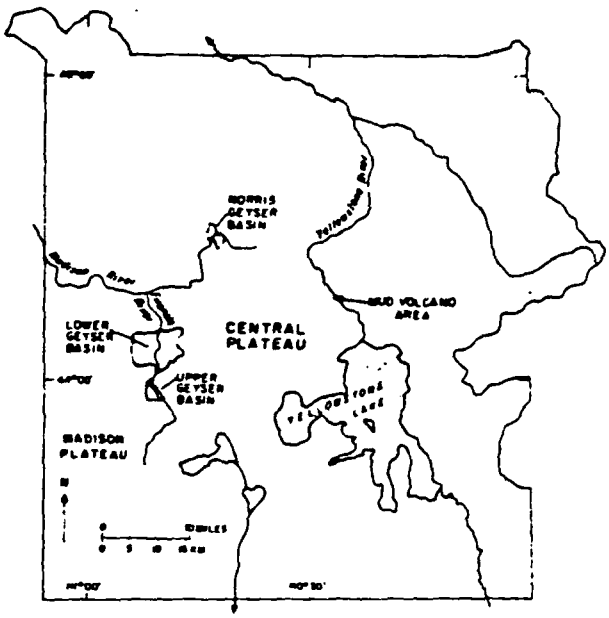

FIG. 3. Index map of Yellowstone National Park, Wyoming, showing location of Mud Volcano area and the major geyser basins.

The scanty available data suggest that temperatures and pressures may exceed the limits suggested by James because of the effects of dissolved salts and the partial pressures of other gases. In addition, although the maximum enthalpy of steam does seem to buffer these systems at temperatures near 236° to 240° C and pressures near 32 to 34 kg/cm², we see no fundamental reason why the available heat supply may not form somewhat more steam than can escape at these pressures through available channels. In this paper we shall assume James' suggested range in temperatures and pressures as the most probable, but we emphasize that more precise data are essential in understanding the detailed characteristics of these systems.

Recorded temperatures of the vapor-dominated reservoirs are significantly lower than in some hot-water fields, which range up to 388° C (Mercado, 1969). The Carboli field on the southern edge of the Larderello steam fields is notable in being the only described field in the Larderello region that produces more water than steam by mass and thus is a hot-water system. Its maximum temperature is about 300° C (Cataldi and others, 1969), which clearly exceeds all temperatures reported from the vapor-dominated areas.

The Mud Volcano Area, Yellowstone Park

General Setting.—The Mud Volcano area is located along the Yellowstone River about 8 km north of Yellowstone Lake (Fig. 3). Bedrock of the area is rhyolitic ash-flow tuffs erupted approximately 600,000 years ago (R. L. Christiansen and J. D. Obradovich, 1969, written commun.). Glacial gravels and sands of Pinedale age (about 25,000 to 12,000 years B.P.) mantle the bedrock except near the center of the area.

Thermal activity in the Mud Volcano area consists almost entirely of vigorously bubbling mud pots, acid-sulfate springs, and steam vents concentrated on north-northeast lineaments. Total discharge is only about 80 lpm (Allen and Day, 1935, p. 58) from an area of 2½ km². There are no chloride-rich springs like those of the major geyser basins, even along the Yellowstone River, which is the local base level for the water table of the area. Instead, acid-sulfate and nearly neutral bicarbonate-sulfate springs occur along the river (anals. 5 and 6, Table 1). A little silica is being deposited by evaporation from algal mats at two of these nearly neutral springs, and opal-cemented Holocene alluvium is common along the riverbanks. Although none of the present springs has enough silica to deposit hard sinter from flowing water on the surface (generally requiring at least 240 ppm SiO_2), three small areas of old sinter occur as much as 3 m above river level. This indicates that sometime in the past 12,000 years silica-rich water, presumably also rich in chloride, discharged at the surface in the Mud Volcano area.

Acid-sulfate springs similar in discharge and chemistry to the Mud Volcano springs occur locally where H_2S is abundant in high ground of the major Yellowstone geyser areas (anal. 9, Table 1). However, in contrast to drill hole Y-11 in the Mud Volcano area (anal. 7, Table 1), all drill holes in the geyser basins tapped water rich in chloride and similar to waters from the geysers and the principal flowing springs (anal. 8, Table 1).

Y-11 was drilled by the U. S. Geological Survey at the north end of the Mud Volcano area, 75 m north-northeast of Old Sulphur Cauldron. Figure 4 shows the locations of the hole and the "tree line," inside of which trees do not grow because temperatures are too high. Also shown are two heat-flow contours mapped by snowfall calorimetry (White, 1969). The 900 μcal/cm² sec (microcalories per sq cm per second) contour is probably within 20 percent of the existing total conductive and convective heat flow. This heat flow is about 600 times the world-wide average conductive heat flow of the earth (Lee and Uyeda, 1965). The 5,000 μcal contour is less precisely located, but total heat flow obviously increases rapidly southeast from Y-11 drill hole.

Near-surface Ground Temperatures.—Relationships between heat flow, depth, and temperature determined in shallow auger holes near Y-11 clarify some principles of major significance to the vapor-

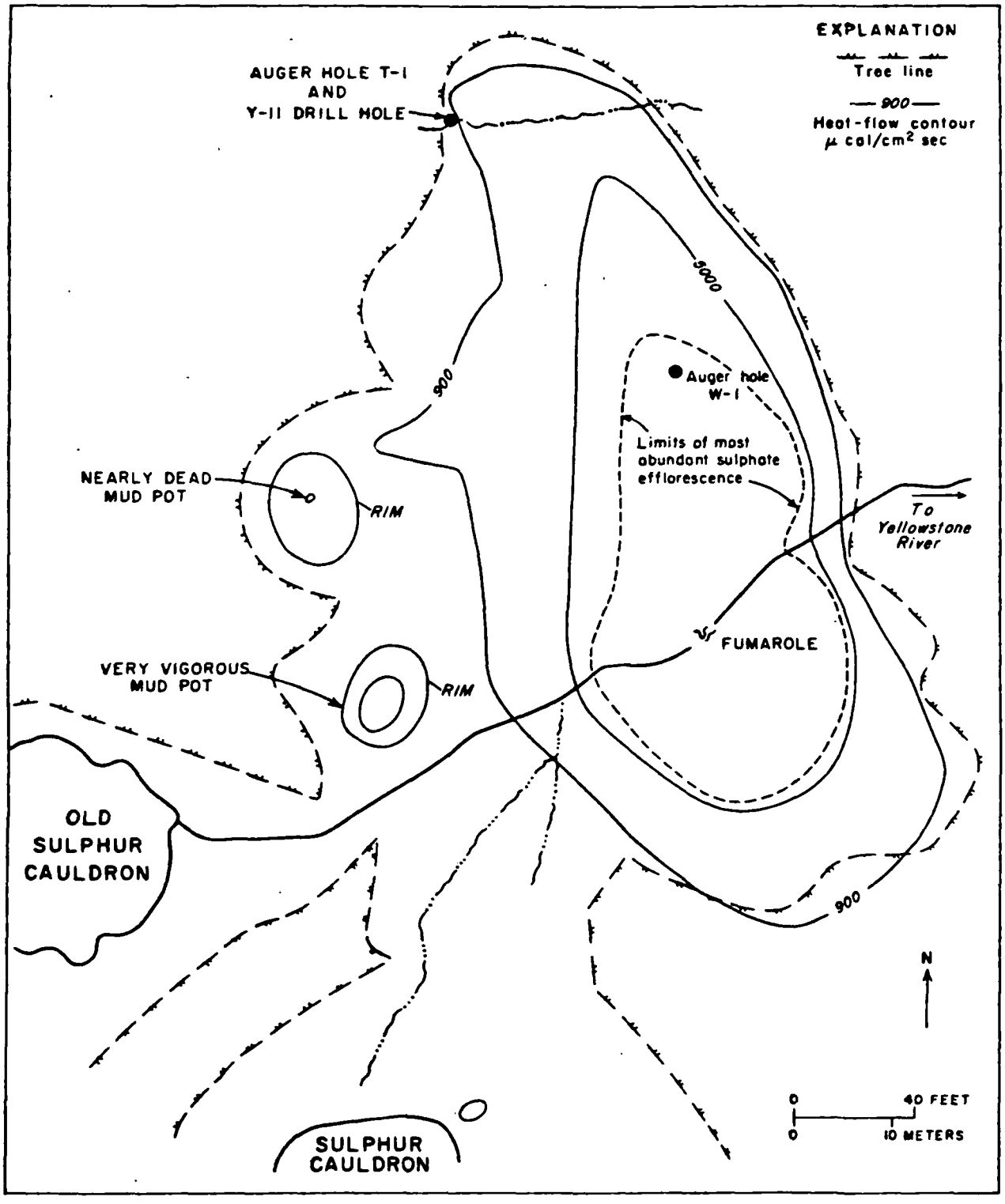

FIG. 4. Sulphur Cauldron area, north end of Mud Volcano area, showing location of Y-11 drill hole relative to heat flow and other features.

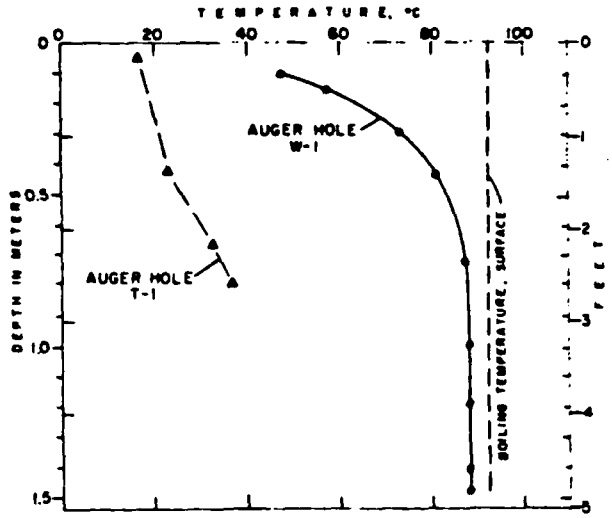

FIG. 5. Temperature-depth curves in shallow auger holes in ground with dispersed upflow of steam and other gases.

dominated systems. Hole T-1 (Fig. 5) was augered on the Y-11 site just prior to drilling, and hole W-1 was augered 35 m to the southeast (Fig. 4). The near-surface temperature at any given depth increases abruptly to the southeast, correlating with increasing heat flow.

Temperatures in W-1 increased rapidly with depth to about ¾ m, where they leveled off at 88.2° C. From 1.0 to 1.55 m there was no temperature change. Consequently, heat cannot be transferred by conduction through this interval, and *all* heat that flows out at the surface must be transferred in steam and other gases through the no-gradient zone. Total heat flow at the surface of W-1 auger hole has not been measured by snowfall calorimetry, but extrapolation of data on Figure 4 suggests a heat flow of perhaps 10,000 μcal/cm^2 sec.

The leveling off of temperatures in W-1 at 4.1° C below the boiling temperature of pure water (92.3° C at this altitude) is due to the high content of CO_2, H_2S, and other gases in the rising vapor. The vapor pressure of water at 88.2° C is 491 mm of Hg, but the atmospheric pressure averages about 572 mm of Hg. Thus 14 percent of the total vapor pressure results from the partial pressures of other gases. At a depth where the temperature is 85° C, 25 percent of the total pressure is due to residual gases (143 mm of 572 mm of total Hg pressure); similarly, 50 percent consists of other gases at 75° C, 90 percent at 40° C, and 97.7 percent at 15° C.

The depth at which the temperatures level off is dependent on the heat flux from below, the thermal conductivity of the soil, the air-ground interface temperature, and the amount and nature of precipitation of the preceding few days or weeks. If the rate of upflow of steam increases sufficiently, a surface fumarole is produced. If, in contrast, the rate of upflow decreases, complete condensation occurs at a greater depth appropriate to the thermal conductivity heat flow, and surface temperature.

In the steam-gas mixture in W-1 auger hole, no steam condenses between a depth of 1.0 m and the bottom of the hole because of the absence of a tem-

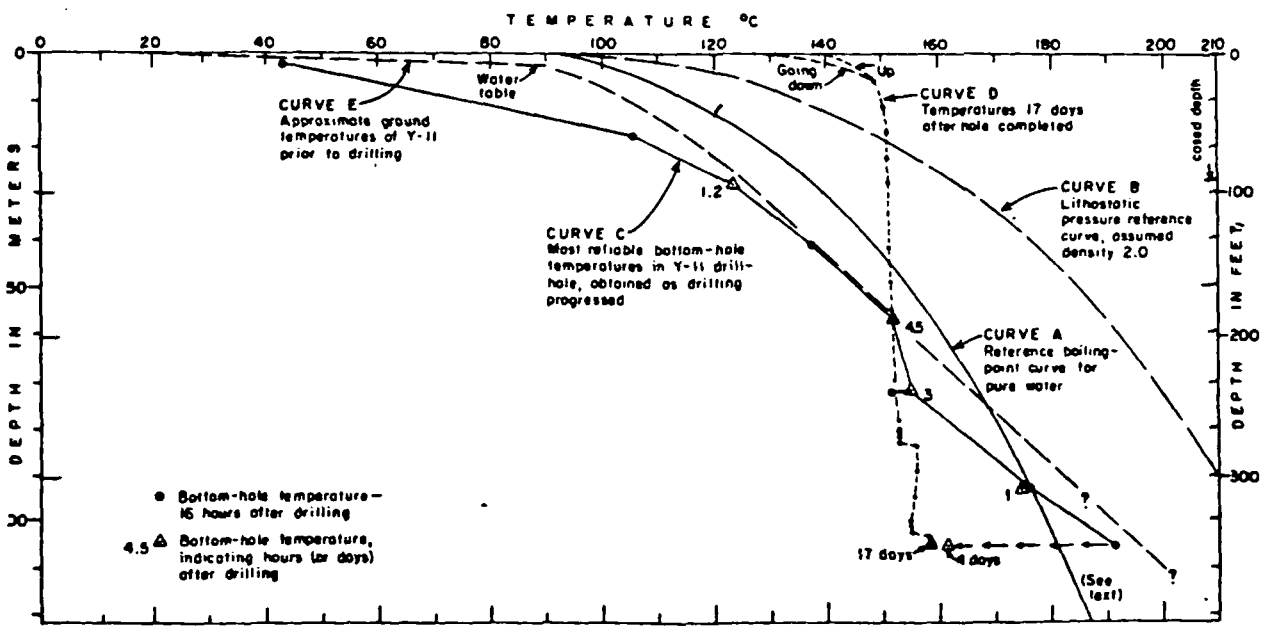

FIG. 6. Temperatures in Y-11 (Sulphur Cauldron) drill hole, Mud Volcano area, Yellowstone Park, Wyoming.

Table 4.—Temperatures, pressures, and other data from V-11 (Sulphur Cauldron) drill hole, Mud Volcano area, Yellowstone National Park, Wyoming

Underlined data considered most reliable

Date and time 1968		Observation depth, m	Temperature, °C	Depth to water m	Total pressure kg/cm²	Comments
May 15	8:35A	2.0	43.0 ?			Drilled to 6.1 m, set 4 in. casing, and cemented on May 14; on cement at 2.0 m, temp. probably minimum.
	12:10	8.3	(36.0)	2.3		80 min. after circulation ceased; good water level 1 hr. after circulation ceased.
	3:25	18.1	87.0		0.85	Drilled 18.3 m; pressure all gas.
16	8:15A	17.3	104.4 } 105.4	2.3	1.17	Do.
	8:23		106.4		1.08	Gas only; 91°C at water level.
	1:25P	27.7	123.3		2.05	1.2 hrs. since circulation; could have erupted; drilled, set 27.4 m 3 in. casing and cemented.
17	8:00A	13.7	73.0			On cement; temperature probably minimum.
	4:45P	(41.8)	(116.1)	5.2		Drilled 41.8 m; lost circulation 37.2-41.8 m.
18	7:50A	41.4	137.0 } 137.1	4.9		Gas pressure from outside rods, 1.56 kg/cm²; temperature at water level inside rods 73°C.
	8:08A		137.2			
	1:00P	(57.0)	(120.3)	4.7		Lost circulation 41.8-57.0 m; temp. 1-1/2 hrs. after circulation.
19	10:40A	56.9	152.4 } 151.9	4.6		23 hrs. after circulation.
	11:05		151.4			
20	7:56A	57.0	151.4 } 151.9			45 hrs. after circulation.
	8:05	57.0	153.4			
	8:12		150.9			
	8:22		151.9	0.3		Water level fluctuating.
	2:00P	72.2	156.5		0.8	3 hrs. after circulation, pressure fluctuating; water discharged outside of rods; drilled 72.3 m.
21	7:45A	72.2	151.1 } 151.6		3.5-3.6	Gas pressure; note temp. decrease since May 20. Drilled to 93.6 m; erupted after pulling core; nearly all steam after much initial water.
	7:57		152.0			
	12:20P	93.4	174.3		5.8 then to 4.1	Temp. 40 min. after eruption; some water with steam at 4.1 kg/cm².
	3:45P		174.7		7.8 down to 5.9	Leaking steam at 7.8 kg/cm², then down to 5.9 kg/cm², some water.
	3:50				4.4	Pressure on side valve, outside drill rods.
22	8:00A	93.6	175.7 } 175.9		10.1 down to 8.0	Leaking vapor only.
	8:12		176.1			Vapor and a little water; drilling increasingly difficult >100 m. Violent eruption at 105.7 m, initially much water (drill water?), then mostly steam.
23	8:15A		191.6 } 191.4		12.7 to 11.2	Leaking vapor only. Drill rods in hole a few feet off bottom; exact depth not noted.
	8:30A	105.7	191.1			
	~11:00A				5.5	Rods pulled, pumping cold water down outside rods throughout; pressure with open hole >27.4 m. Hang up at about 33.6 m, erupted to clear--powerful steam eruption but little water.
27	Not noted	105.5	161.1 } 161.3		5.3	Note major permanent changes in temperature and pressure after rods out of hole.
			161.4		5.4	
June 19	10:00A	~105	158.6		5.3 to 5.4	Thermistor temperature series plotted on fig. 6. Temperature generally steady and reproducible down to 84.1 m, fluctuating somewhat at greater depths, up to 4°C at bottom (maximum is plotted).
10		96.3			5.0	R. O. Fournier attempted to sample; filled with vapor to existing bottom.
28		39.0			4.6	Blocked; no access to greater depths; no water to 39.0 m.
Sept. 1969 21		28.0	131.7		3.2 to 3.5	Attempting thermistor series; initial temperature at top 75°C, increasing to 107°C with leakage of gas. Hole filled with gas to cave at 28.0 m just below casing; thermistor wedged and lost. Erupted gas, mud, and water, and collected water sample.
						Pumped in 5 sacks of cement at pressures up to 11.3 kg/cm².

perature gradient. As steam rises above a depth of 1 m, however, a little starts to condense as a temperature gradient first becomes evident. The gradient increases upward as the surface is approached, so more water vapor can condense. The residual gases are progressively concentrated upward as H_2O

is condensed, the velocity of upflow consequently decreases, and a correspondingly smaller proportion of the total heat is transported by water vapor. Convective transport of heat at the air-ground interface must be largely in the residual gases, but water vapor, even though a minor constituent, is still a significant transporter of heat because of its high heat of vaporization (588 cal/gm at 15° C), relative to heat content of other gases.

The water vapor that condenses between 1.0 m and the surface at W-1 percolates downward against the flow of steam. The ground is unsaturated with liquid at the bottom of the auger hole and probably to the local water table (2.3 m in Y-11 drill hole). Below the water table at W-1, pressures must exceed atmospheric, and temperatures probably rise along or near the hydrostatic boiling point curve of Figure 6.

The near-surface temperature gradient in auger hole W-1 of Figure 5 is much higher than in T-1, as we should expect from the heat-flow contours of Figure 4. Projection of the T-1 gradient downward to the water table at 2.3 m suggests that temperatures were slightly below boiling at this depth. It appears that only a little water vapor and other gases were rising at the Y-11 site prior to drilling, and most heat was being transferred from the water table to the ground surface by conduction.

Physical Measurements Made During Drilling of Y-11.—Data from Y-11 are summarized in Table 4, and bottom-hole temperatures are plotted in Figure 6. The bottom-hole temperatures considered to be most reliable are connected by a solid line. Much effort was made to obtain reliable data from Y-11 as drilling progressed, in part because of the paucity of such data from the large commercial vapor-dominated systems. Because of the high cost of drilling and other factors, available data from the commercial systems are entirely restricted to completed wells, and almost no data are obtained at shallow and intermediate depths as drilling progresses.

In the recent holes drilled in Yellowstone National Park, temperatures measured at each temporary bottom, just before resumption of drilling (generally after overnight shut-down of about 16 hours), provided reasonable approximations of pre-drilling ground temperatures; they are far superior to temperature profiles measured in completed holes (White, Fournier, Muffler, and Truesdell, unpublished data). Measured bottom-hole temperatures in Y-11, however, are less reliable than in the other holes but are considered to be within a few degrees of original ground temperature. At depths less than 27.4 m, rapid drilling plus the setting of two strings of casing prevented acquisition of reliable data. From 37.2 to 79.3 m, all drill water was lost into the ground, and at greater depths only about 50 percent returned to the surface. Despite the apparent high permeability and loss of drill water, however, the temperature of 151.9° C at 57.0 m depth is probably reliable because it was repeated on successive days with no disturbance by drilling.

A temperature profile made in the open hole 17 days after completion is shown on Figure 6 (curve D). It differs greatly from the temperature profile obtained as drilling progressed. The temperatures from 12.2 to 83.5 m were almost constant, rising only 2° or so, to 153° C at 83.5 m. At greater depths, rapid fluctuations of 1° to 5° were observed. These fluctuations were not due to instrumental defects and were far too large and too rapid to be caused by only a vapor phase; coexistence of steam and water is thus indicated from 83.5 to 103.7 m. The pressure of saturated steam at 153° C is 5.3 kg/cm^2, which is very close to the measured well-head pressure, 5.4 kg/cm^2. The temperature of 158.2° C at 103.7 m, however, is not consistent with the well-head pressure, unless liquid water was present near the bottom of the hole. From drill records, we conclude that water was probably entering the hole from depths as shallow as 58 m or less, while an upward flow of steam dominated the central part of the casing. Detailed relationships that existed during the thermistor measurements between 83.5 and 103.7 m cannot be deciphered completely. Evidently some steam was flowing in near 84.2 and 103.7 m. Water seeping down from higher levels did not accumulate extensively but was either forced out into permeable walls or was evaporated by the higher temperature steam. At shallow depths in the hole, horizontal and vertical temperature gradients were so high that most water vapor condensed and residual gases were concentrated, as in auger hole W-1. The condensed water trickled down the walls of the casing.

On several occasions during the drilling of Y-11, we were unable to prevent the hole from erupting for short intervals. The eruptions differed notably, however, from those in holes in the hot-water systems of the geyser basins. In drill holes in permeable rocks, with adequate water supply, and a temperature of 160° C, for example, only 11 percent of the total liquid water vaporizes to steam when erupted (at constant enthalpy) to atmospheric pressure (Fig. 2). The remaining 89 percent of the erupted mass is liquid; the large content of liquid water produces effects that are similar to those of the early stages of geyser eruptions. During an eruption of Y-11, however, the local supply of liquid water was soon nearly exhausted and steam became completely dominant. We estimated that the steam was associated with less than 10 percent of liquid water

by weight. Although at no time did the hole discharge dry steam free of liquid water, we are confident that a dry discharge would have occurred if the eruption had been permitted to continue or if the hole had been cased a little deeper. (The hole was uncased below 27.4 m, and the bottom-hole temperatures indicate an original dominance of liquid water in pore spaces to depths of about 73 m; curves C and E, Fig. 6.)

The pressure of 12.7 kg/cm² measured in the drill rods on May 23 at the greatest drilled depth represents the approximate total pressure at the drill bit, assuming vapor-filled drill rods raised the usual 3 to 4½ m above bottom (1 to 1½ lengths of drill rods), and neglecting the weight of the vapor. If 3.7 m off bottom is assumed, with liquid water filling the hole below the rods, the calculated bottom-hole pressure was about 13.1 kg/cm² (with a possible range from about 12.8 to 13.6 kg/cm²). The pressure at the bottom of an open hole 105.8 m deep and filled with water everywhere just at boiling should be 10.5 kg/cm². Thus, the excess pressure above hydrostatic was about 2.6 kg/cm² or 25 percent. The fact that temperatures and pressures are higher than those of a simple hydrostatic control is important and must be consistent with any satisfactory general model of the vapor-dominated systems.

Liquid-dominated and Vapor-dominated Parts of the System.—In Y-11 drill hole, water-saturated ground evidently extended from the water table at 2.3 m down to a depth of about 73 m. At 72.2 m, the bottom-hole temperature measured 3 hours after drilling ceased was 154.5° C; 18 hours later it had dropped 3° C. We believe that this change was due to the cooling effect of drill water continuing to drain down the hole and into channels that had formerly been dominated by vapor. The pre-drilling ground temperature probably was not attained at this drilled depth and was probably about 165° C (Fig. 6, curve E); flow of water down the hole prevented a normal temperature recovery.

The hole was definitely in vapor-dominated ground at a depth of 93.4 m. At this depth an unanticipated eruption through the drill rods first discharged abundant drill water and then changed rapidly to wet steam with only traces of liquid water. Such a change in behavior is not particularly significant in tight rocks of a hot-water system when the water available for immediate eruption is exhausted; the behavior is similar to that of a geyser as it changes from its main eruptive phase to a steam phase (White, 1967a). However, permeability was so high at all depths below 37 m in Y-11 that little or no drill water returned to the surface. Lack of permeability clearly does not explain the observed eruptive behavior; a limited supply of *available liquid water* provides the only reasonable alternative. If all lost drill water had remained in nearby permeable ground, the eruption likewise could not have been so nearly dry. The drill water must have percolated down former vapor-filled channels to become unavailable in supporting the eruption.

Forty-six days after completion of the hole, measurements made by an in-hole sampling device (Fournier and Truesdell, 1970) demonstrated that the hole was filled with vapor to 96.4 m, where caving had occurred. Presumably all drill water was then exhausted and all inflowing pore water from higher levels either evaporated completely or escaped downward through former vapor-filled channels.

From these data we can conclude that vapor pressure in the hot core of the system below about 76 m is now significantly above hydrostatic pressure (Fig. 6). Some vapor is being forced upward and outward into the cooler walls. The excess driving pressure above hydrostatic presumably is dispersed in overcoming the frictional resistance to flow of vapor along narrow channelways, which become increasingly clogged upward and outward with liquid water condensed from steam; some of the gases other than steam dissolve in this liquid condensate. If many large free-flowing channels vented to the surface as fumaroles and mud volcanoes, the high vapor pressures in excess of hydrostatic obviously could not be maintained.

Another factor that may be of major importance in impeding the escape of vapor is the formation of montmorillonite and kaolinite, which are the dominant alteration products in rocks and fracture fillings of Y-11 drill core from about 15 to 58 m. Montmorillonite and kaolinite also occur sporadically at greater depths but are generally less abundant than other hydrothermal minerals and unaltered rock silicates. The condensed steam is saturated with CO_2 and other gases from the rising vapor. This carbonated water, represented by analyses 6 and 7 of Table 1, is highly effective in altering feldspars and other silicates to clay minerals, and in leaching cations from the rocks. Pyrite is also relatively abundant through the same general interval, from 18 to 61 m, but is sporadic at greater depths. Much sulfide from the rising H_2S evidently dissolves in the condensate and becomes fixed, combining with Fe of the rocks.

The hot vapor-dominated core of the system evidently is not sharply separated by a single fluid interface from the cooler liquid-dominated walls. We conclude that, in the core of the system, the largest fractures and open spaces are mostly or entirely filled with vapor but open spaces of similar dimensions in the margins of the system are largely filled with liquid water, except for dispersed clays

and vapor bubbles that sporadically rise through the water.

General Model of Vapor-dominated Geothermal Systems

A vapor-dominated geothermal system must normally develop from water-saturated rocks. This statement may be unconvincing for young volcanic rocks (how do we *know* that such rocks were ever water-saturated?) but is irrefutable for old marine sediments that are now far below the regional water table, as in Tuscany and The Geysers. A new regime is initiated with the introduction of a local potent source of heat at depth (probably a body of magma). Much heat is transferred via conduction and circulating water into surrounding rocks that have some permeability. Because of thermal expansion and resulting decrease in density of the heated water, a *hot-water* convection system is then initiated. Most rocks seem to be sufficiently permeable to persist as hosts for hot-water systems; the rate of flow of water remains high enough and the supply of conducted heat below the circulation system remains low enough for most of the water flowing through the system to remain liquid. Near-surface temperatures in the hotter systems, however, are high enough for some boiling to occur as the water rises to intersect the boiling point curve (A of Fig. 6). The depth where boiling first occurs in the rising water depends mainly on the temperature of the water.

Many hot-water systems are to a major extent self-regulating. With more heat flow, the upflowing

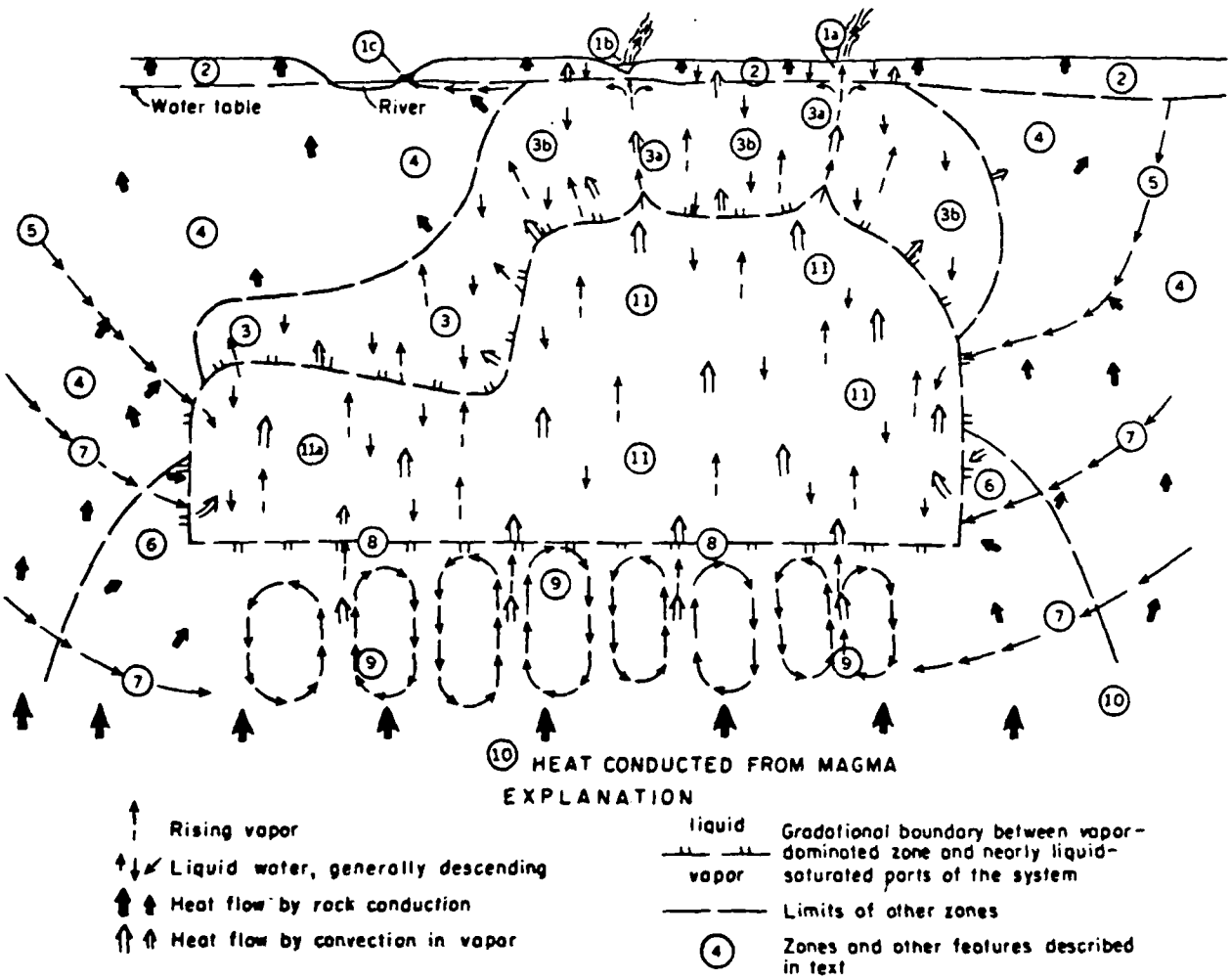

FIG. 7. Model of dynamic vapor-dominated geothermal reservoir surrounded by water-saturated ground. The most significant parts of the model, inward and downward by number, are: 4) zone of conductive heat flow; 3) zone of condensation of steam (conductive and convective heat flow equally important); 11) main vapor-dominated reservoir, with convective upflow of heat in steam in larger channels, and downflow of condensate in small pores and fractures (surface tension effects); 9) deep zone of convective heat transfer, probably in brine; 10) deep zone of conductive heat flow (too hot for open fractures to be maintained). Other features are discussed in text.

water becomes hotter and lower in density and viscosity; the pressure drive for recharge increases, and the increased rate of through-flow removes most of the additional heat. This self-regulation, however, may be limited by insufficient permeability.

With sufficiently potent heat supply or, for any reason, a decreasing rate of recharge of water, a hot-water system of limited permeability may start to boil off more water than can be replaced by inflow. A *vapor-dominated system* then starts to form. Direct evidence for the assumed initial dominance of liquid water is lacking for the major vapor-dominated systems. Hot-spring sinter constitutes the clearest evidence, and is so interpreted for the Mud Volcano system. However, sinter is deposited only from very hot water that flows so rapidly to the surface that little SiO_2 precipitates en route. In addition, the early hot-water stage of these systems of high heat flow and low permeability is likely to have been brief and their thin sinter deposits (if any) are likely to be destroyed by erosion.

Figure 7 is our tentative general model of a well-developed vapor-dominated system. Different parts, discussed below, are keyed by number on the figure.

(1) Fluids that discharge at the surface provide much of the evidence for a vapor-dominated system. Fumaroles (1a) are generally at temperatures near surface boiling or somewhat lower. High-chloride springs are completely absent; associated springs and mud pots are generally acid, high in sulfate, and low in discharge (such as 1b of Fig. 7, and anals. 2 and 5, Table 1), and they deposit little if any sinter. Surrounding ground may be bleached and lacking in vegetation. Some springs not so strongly influenced by oxidation of H_2S (or containing enough NH_3 absorbed from gases) are nearly neutral in pH and are dominated by bicarbonate and sulfate without much chloride (1c, Fig. 7, and anals. 1 and 6, Table 1).

(2) Zone 2 lies between the ground surface and the water table.[5] Where hot enough, steam and other gases rise above the water table, as in auger hole W-1 of Figure 5. At the water table heat transfer is nearly all convective, but as the temperature gradient increases upward and water vapor condenses, near-surface heat transfer becomes largely conductive.

(3) Zone 3 inhibits the free escape of rising vapor. The zone is nearly saturated with liquid water derived largely from condensing steam rich in CO_2. Montmorillonite and kaolinite form by reaction of this CO_2-saturated condensate with rock silicates. Clay minerals and condensed water clog most pore spaces and channels, impeding but in many places not prohibiting the escape of residual uncondensed gases. Temperatures in this zone may be similar to those along the hydrostatic reference curve A of Figure 6. Near major channels of upflowing steam (3a, Fig. 7), temperatures and pressures are somewhat above hydrostatic, and conductive heat flow and condensation of steam are consequently high; at least part of the condensate is swept upward to the water table or to surface springs, mud pots, and mud volcanoes. A crude steady-state rate of upflow is determined by pressure gradients, dimensions of the channels, strength of wallrocks, and impedance provided by condensate and suspended clays. Other parts of zone 3 (3b, Fig. 7) are dominated by downflowing condensate and some surface water, with temperatures that are likely to be somewhat lower than those along reference curve A of Figure 6. As temperature gradients in general increase outward and upward through zone 3, more of the heat of vaporization in the rising steam can be transferred by conduction, so water vapor is continuously condensing and the rate of mass flow of vapor therefore decreases upward. A part of the heat in rising vapor is transferred through local horizontal gradients to heat the downward-percolating condensate, which must absorb heat as it descends into hotter ground. The dashed line bounding the outer part of zone 3 marks the gradation in mode of heat transfer from dominantly convective to dominantly conductive.

The lower limit or "pinch-out" of zone 3 is at a depth where the hydrostatic pressure of water in the reservoir margins exceeds the total vapor pressure of steam and gases in the reservoir. Below this depth, vapor can no longer effectively penetrate the reservoir margin.

Wells drilled into parts of zone 3 may produce liquid dominantly, but if drilled and cased into deeper parts they probably yield wet steam and some water when first produced (as in Y-11 drill hole). If an uncased section of hole intercepts channels of upflowing steam and zones of cooler downflowing condensate, the temperature and pressure of the steam will commonly dominate the hole. This occurred in Y-11 below 72 m.

(4) Zone 4 is characterized mainly by conductive heat flow, with heat being supplied from condensing steam within zone 3. Wells bottomed in zone 4 may fill with water, and may erupt hot water and some steam, but discharge rates are likely to be low and the wells noncommercial.

(5) Representative channels of intermediate-level recharge are deep enough at points of entry for hydrostatic pressure to exceed the vapor pressure of

[5] In sands and gravels the water table is easily recognized. In clays, however, the water table is poorly defined, but we consider it to be the level at which water is maintained in a shallow open hole. The zone of saturation can rise as much as 10 m above this level, owing to surface tension in the clays. Hydrostatic pressure increases downward only below the water table as defined in the open hole.

about 31 to 35 kg/cm² in the main reservoir (zone 11).

Channels of inflow tend to be enlarged by solution of SiO_2 as the inflowing water is heated by conduction (indicated by heat-flow arrows in Fig. 7). Channels are diminished, however, by deposition of $CaCO_3$ and $CaSO_4$, which are rather unusual in *decreasing* in solubility with increasing temperature (see, for example, Holland, 1967). In all rocks with recharge waters relatively high in $CaCO_3$ and $CaSO_4$, channel permeabilities are especially likely to *decrease* rather than increase with time. These considerations may be important in understanding Larderello, which involves anhydrite-bearing limestone and shales, and The Geysers, where mafic lavas and serpentine are associated with graywacke and shale.

(6) Zone 6 consists of reservoir margins where temperatures decrease *toward* the reservoir. The depth of the top of zone 6 is not easily predicted. If there were no convective heat flow, the depth would be near that of the 240° C isotherm of the original conductive gradient from the surface to the magma chamber. If 600° C is assumed at 4 km, for example, and the rocks are homogeneous, 240° C would be at 1.6 km depth. The development and downward penetration of the main vapor-dominated reservoir as excess pore water is vaporized result in extensive convective modifications of temperature that greatly change the relationships. Convective cooling from downflowing meteoric water increases this depth, and a shallower intrusion at higher temperature decreases it. These reservoir margins contain channels of inflowing water at pressures that are close to hydrostatic and much greater than ~33 kg/cm² of the reservoir. Sharp pressure and temperature gradients decreasing toward the reservoir must therefore exist in zone 6. In contrast to zone 3, heat is transmitted through zone 6 by conduction (and inflowing H_2O) to the reservoir. The temperatures of zone 6 grade downward into, and are maintained by conduction from zone 10.

(7) Channels of inflowing water are narrowed by precipitation of calcite and anhydrite as zone 6 is approached; clogging of channels by these minerals of decreasing solubility may be offset entirely or in part by solution of quartz, which increases in solubility as long as the liquid water continues to rise in temperature. At the outer edge of zone 6, however, pressures and temperatures in the recharge channels attain their maxima; with further flow toward the reservoir, boiling commences and *temperature declines* as the pressure drops to that of the reservoir. The fluid in these channels is now a two-phase mixture of steam and water. Specific resistance to flow (resistance per unit of *mass*) of steam is much greater than that of liquid water, and specific flow resistance of a two-phase mixture is greater than a linear combination would indicate (I. G. Donaldson and Gunnar Bodvarsson, oral commun., 1970). Because of evaporative concentration by boiling and because of decreasing temperature, quartz and other minerals are now deposited, further impeding the flow of the two-phase mixture. The result of all of these processes is to decrease the rate of recharge through the deeper channels.

(8) The deep subsurface water table recedes as long as the heat supply is sufficient for net loss of liquid water and vapor from the system to exceed net inflow (water table shown in Fig. 7 is horizontal, but it may be very irregular in detail). As mentioned above, recharge tends to decrease with time as resistance to flow of H_2O through individual channels increases. As the water table recedes and liquid water in the reservoir is largely replaced by vapor at nearly constant pressure throughout the reservoir, the driving pressure on the deeper channels of inflow increases, offsetting in part the increasing impedances. A crude steady state may be attained in some systems, especially as rate of heat flow eventually starts to decline.

(9) With time, if not initially, the water boiling below the deep water table becomes a brine as recharging water boils off and as dissolved substances of low volatility are residually concentrated. Vapor from brine is superheated with respect to pure water at the same pressure. Steam boiling from 25 percent NaCl brine at 35 kg/cm², for example, is superheated by about 12° C with respect to saturated steam and pure water (254° vs 242° C, Haas, 1970). The critical temperature of a salt solution increases above that of pure water (374° C) as salinity increases: that of a 1 percent NaCl solution is about 384° C (Sourirajan and Kennedy, 1962, p. 134); that of a 10 percent solution is about 480° C; and that of a 25 percent solution is about 675° C. Thus, brine can be a very effective agent for convectve transfer of heat and dissolved matter at temperatures much above 374° C. Note that Figure 7 has no vertical scale; the depth of zone 9 may be 1,000 m or more, and through all or most of this depth, pressures are *lower* than hydrostatic pressures outside the system (Fig. 1, curve C, increases downward in slope).

(10) Conductive heat flow from the magma predominates deep under the reservoir where rock plasticity due to increasing temperature prevents the maintenance of open channels. On the outer margins of zone 10 where convective disturbance is not so severe, conductive heat flow predominates to higher levels than under zone 9, grading upward without distinct boundaries into zones 6 and 4. The amount of convective circulation may eventually de-

crease beneath the vapor-dominated reservoir by decreased permeability from deposition of minerals, and possibly as a stable salinity gradient becomes established.

11) The main vapor-dominated reservoir contains *liquid water and vapor coexisting,* except possibly in major channels of steam discharge and locally just above the brine water table. Steam and other gases rise in the largest channels where resistance to flow is lowest. Steam starts to condense on the outer borders of the reservoir and continues to condense from all vapor escaping into zone 3, where temperatures decrease outward and provide a thermal gradient for conductive transfer of the heat of vaporization of steam. The condensate from zone 3 percolates down into the reservoir, favoring narrow channels and pore spaces between mineral grains because of surface tension and the lower specific resistance to flow of liquid water relative to steam.

Edwin Roedder (personal commun., 1970) has suggested that our model for vapor-dominated systems is similar in many respects to recently-developed remarkable devices that have been called "heat pipes" (Eastman, 1968). These devices may be "several thousands of times more efficient in transporting heat than the best metallic conductors." They consist of a closed chamber with inside walls lined by a capillary structure or wick, and saturated with a volatile fluid. Heat is transferred by vapor from the hotter to the cooler end, where the vapor condenses. The liquid condensate returns by capillary action to the evaporator section; temperature gradients in the pipe may be extremely low. The top end may be the hotter, with capillary return of liquid (to some limited height) being opposed by gravity. Our natural "heat pipes" are not completely closed systems, and their depth has no theoretical limit because gravity assists rather than opposes the return flow of condensate.

Parts of the subsurface reservoir such as 11a of Figure 7 may be isolated from direct outflow of vapor and may be representative of parts of the Larderello and The Geysers systems that have no apparent direct discharge in fumaroles. Pressures throughout the reservoir are controlled primarily by the total vapor pressure at the boiling water table, modified by frictional resistance to the upward flow of vapor and by the weight of the vapor. Near the top of the reservoir the vapor may be greatly enriched in CO_2, H_2S, and other gases that are not flushed out of the system as actively as near the top of the main reservoir (11). Much water vapor condenses below the boundary of the vapor-dominated reservoir near 11a. In contrast to the flushed part of the main reservoir, significant thermal gradients exist in the poorly flushed parts. Consequently, some steam can condense and other gases are residually concentrated. Pressure of the remaining water vapor requires lower saturation temperatures, as shown in Table 5. This table suggests that temperatures in isolated parts of the reservoir differ little from 236° C until the residual gases are enriched above 5 percent. With higher residual gas contents, temperature gradients and conductive heat flow increase.

Table 5.--Saturation temperatures of water calculated for ideal steam-gas mixtures at constant vapor pressure, 31.8 kg/cm^2.

Percent steam	Percent other gases	Pressure, kg/cm^2	Saturation temp., °C
100	0	31.8	236
99	1	31.5	235.5
98	2	31.2	234.9
95	5	30.2	233.1
90	10	28.6	230.1
80	20	25.4	223.7
70	30	22.3	216.9
50	50	15.9	200.1
30	70	9.5	176.8
10	90	3.2	134.7
5	95	1.6	113.0
1	99	0.3	68.0

The above-described relationships may explain the relatively high pressures and low temperatures of the vapor-dominated fields of Bagnore and Piancastagnaio near Monte Amiata (Burgassi and others, 1965; Cataldi, 1967). Initial pressures were 22 to 40 kg/cm^2 and gas contents of the vapor were as high as 96 percent, but reported temperatures did not exceed about 150° C (Burgassi, 1964; Burgassi and others, 1965; Cataldi, 1967). Pressures and gas contents of the vapor decreased rapidly with production.

Similar reasoning indicates that high contents of gas in vapor coexisting with liquid water at a temperature near that of the maximum enthalpy of steam can result in total vapor pressure significantly above 31.8 kg/cm^2 at 236° C (Table 6). These data indicate that, as contents of other gases increase in the vapor phase at constant temperature of liquid and vapor, total pressures must increase. The least

Table 6.--Total vapor pressures of steam-gas mixtures coexisting with liquid water at 236°C

Vol. percent gas in vapor	H_2O pressure kg/cm²	Pressure other gases, kg/cm²	Total pressure, kg/cm²
0	31.8	0	31.8
1	31.8	0.3	32.1
2	31.8	0.7	32.4
5	31.8	1.7	33.5
10	31.8	3.5	35.3
20	31.8	7.9	39.8
50	31.8	31.8	63.6

Note: Pressures 32.4 and 39.8 in column 4 should read 32.5 and 39.7 respectively.

actively flushed extensions of The Geysers field that have recently been discovered are likely to have higher gas contents and initial pressures than the original field.

Table 6 also suggests a possible triggering mechanism for some hydrothermal explosions and phreatic eruptions (Muffler and other, 1970) in gas-rich hot-spring and volcanic systems where escape of vapor and flushing of residual gases are inhibited by barriers of low permeability. Local accumulatons of gas-rich vapor can attain pressures that exceed hydrostatic and perhaps even lithostatic, finally resulting in rupture and explosive eruption.

The tentative model described above has additional support from thermodynamic calculations and comparison of actual production data with production predicted on the basis of our model (manuscript in preparation). We are hopeful that the model will prove to be of value in predicting the behavior of individual wells, in detecting interference between wells, in detecting inhomogeneities within the reservoir, in calculating reserves of steam in the original vapor-dominated reservoir, and in detecting a major influence by increased boiling below the water table as a result of declining reservoir pressures.

Speculations Relating Vapor-dominated Systems and Ore Deposits

Some mercury deposits may have formed in the upper parts of vapor-dominated systems. We also suggest, more tentatively, that porphyry copper deposits may have formed in the deep brine zones hypothesized to underlie vapor-dominated reservoirs.

Mercury Deposits.—Many mercury deposits appear to have formed near the surface in relatively recent time. Furthermore, mercury deposits occur on the periphery of two active vapor-dominated geothermal systems: The Geysers in California and Monte Amiata in Italy (White, 1967b; Dickson and Tunell, 1968). Recent geothermal exploration for extensions of The Geysers field disclosed dry steam 2½ km to the west under the Buckman mercury mines. Other wells yield dry steam near Anderson Springs, only 1½ km from the Big Chief and Big Injun mercury mines (White, 1967b), which are 10 km southeast of the original steam field. A number of other mercury mines in the district are within 3 km of steam wells.

Vapor-dominated systems of high gas content, previously discussed, have recently been discovered from 3 to 10 km south and southwest of the major Monte Amiata mercury mine (Burgassi and others, 1965; Cataldi, 1967), the largest Italian mercury deposit. No vapor-dominated reservoir has been found to prove a genetic relation to the mercury deposits, although abnormally high temperatures (63° C at 440 m depth) and notable concentrations of CO_2 and H_2S characterize these Italian deposits (White, 1967b). Dall'Aglio and others (1966) have shown that mercury occurs in anomalous amounts (> 1 ppm) in stream sediments in and around the Larderello-Monte Amiata fields. The anomalies in some stream drainages may be related to specific mercury deposits, but many clearly are not. These widespread anomalies instead seem more directly related to the geothermal fields and their broad anomalies in temperature gradient (Burgassi and others, 1965, Fig. 7).

Krauskopf (1964) has emphasized the high volatility of mercury, which provides an attractive mechanism for separating this metal from most others. The vapor-dominated geothermal systems, as we now understand them, provide a mechanism for shallow, moderately high temperature vapor-phase separation of mercury from other metals. Mercury is known to occur in vapor from The Geysers steam field (White, 1967b, p. 590, and unpub. data), and large mercury anomalies have been found in Yellowstone Park in mudpots of the Mud Volcano area and elsewhere, that are maintained by steam flow and condensation (W. W. Vaughn, U. S. Geol. Survey, written commun., 1969). Especially attractive is the possibility that Hg and H_2S dissolve in the steam condensate of zone 3 of our model (Fig. 7), precipitating as HgS as temperature decreases and as the pH of the condensate increases from reaction with silicates.

We do not claim that *all* mercury deposits form in this way. The Sulphur Bank and Abbott mines east of The Geysers, for example, are associated with discharging thermal chloride waters that may be, respectively, metamorphic and connate waters being forced out of their source rocks by lithostatic pressure (White, 1957b, 1967b). During peak mineralization at high temperatures, similar water was almost certainly being discharged, perhaps with more abundant vapor than now.

Porphyry Copper Deposits.—The possibility that porphyry copper deposits may be forming in the zone of boiling brine below vapor-dominated systems (zone 9 of Fig. 7) should be tested in these systems by looking for copper minerals in core and cuttings from the deepest drill holes. The model provides attractive possibilities for explaining many aspects of these deposits:

1. Recent isotope studies (Sheppard, Nielsen, and Taylor, 1969) demonstrate that water of meteoric origin probably is dominant over water of other origins during mineralization stages.

2. Temperatures of filling of fluid inclusions are most commonly above 250° C and exceptionally range up to 725° C (Edwin Roedder, oral and written commun.). The salinities of many inclusions are exceedingly high, probably ranging up to 60 percent of total fluid by weight. However, many inclusions are largely vapor, probably indicating boiling of the saline fluid at the time of entrapment.

3. Fluid relationships and the geologic setting of Copper Canyon, Nevada, are considered to be generally similar to porphyry copper deposits (J. T. Nash, written commun., 1970). Extensive fluid-inclusions studies by Nash and Theodore (1970) demonstrate that a) temperatures are most commonly in the range of 315° to 375° C; b) salinities of the ore fluids are commonly in the order of 40 percent (or higher, if $CaCl_2$ is abundant), with highest salinities in and near the porphyry intrusion and with lower salinities (2 to 15 percent) in peripheral gold-bearing deposits; c) vapor bubbles were trapped in many inclusions, demonstrating the prevalence of boiling or near-boiling conditions. The copper deposits are largely dispersed in the intruded rocks adjacent to the porphyry, and thus are within the spectrum of deposits that have been called porphyry copper deposits (Lowell and Guilbert, 1970).

4. High-salinity brines can develop from residual concentration of dilute (or saline) recharge water, providing a satisfactory system for transferring heat, metals, sulfur and CO_2 from the large magma body that presumably underlies the small multiple porphyry intrusions of most deposits. The critical temperature of water increases with salinity; with sufficient contents of alkali and calcium chlorides, water can remain liquid at temperatures as high as those of the magma body. Copper and other metals could be derived from the local porphyries, a larger underlying magma chamber, and from surrounding rocks.

5. The return flow of condensate through the vapor-dominated reservoir is relatively dilute, but is normally saturated in SiO_2 (with respect to quartz, 440 ppm at 240° C, Fournier and Rowe, 1966). Reevaporation of this water may account for much of the abundant hydrothermal quartz of porphyry copper deposits.

6. Condensate from the discharge areas of vapor-dominated systems is high in sulfate. Some and perhaps much of this condensate may drain downward to the deep water table and account for the abundant anhydrite of many porphyry copper deposits.

7. The most commonly quoted range in depth for the tops of porphyry copper deposits is from 1,000 to 3,000 meters (Lowell and Guilbert, 1970). The shallower depths seem too low for attaining the indicated temperatures and salinities, but may be possible in a brine below a shallow vapor-dominated reservoir (Fig. 1, curve C, can be at shallower as well as greater than plotted depth).

8. If porphyry copper deposits were indeed formed at depths of 1,000 to 3,000 meters, if most of the water of the ore fluids is of surface origin, as indicated by isotopes, and if near-magmatic temperatures and excess heat flow were maintained close to the surface for thousands of years, some type of hydrothermal activity *must* have characterized the then-existing ground surface. Hot-water systems are numerically far more abundant than vapor-dominated systems, and may be the surface expression of some kinds of ore generation (White, 1967b, 1968a), but dissolved salts are *dispersed* by discharging water, and extreme salinities are not ordinarily attained. The highest salinity yet known in active hot-water systems is about 25 percent, characterizing both the Salton Sea and the Red Sea geothermal brines (White, 1968a). Chemical evidence indicates strongly that the high salinities of these two systems result from the solution of NaCl-rich evaporites. We doubt that evaporites are also involved in the generation of all porphyry copper deposits; some other mechanism for attaining extreme salinity is indicated. Our proposed mechanism for residual concentration of salts by boiling below vapor-dominated systems is a feasible and attractive possibility.

9. The postulated water below a vapor-dominated reservoir may be characterized by high positive temperature and salinity gradients extending downward from the deep water table (Fig. 1), thereby providing a favorable environment for upward transport and

deposition of copper sulfides and pyrite. Temperatures in the water-dominated zone must increase toward the source of heat, presumably an igneous intrusion; actual gradients are highly dependent on the extent of convection in this zone. Formation of vapor bubbles probably occurs largely near the base of penetration of water of the system, where temperatures are highest relative to pressure. Salinity is thereby increased by residual concentration near the base, where permeability is low enough to inhibit convection. On the other hand at higher levels near the deep water table, dissolved salts are being diluted by three processes: (a) *condensation* of dilute water from steam bubbles rising in the brine, as pressures decrease to about 34 kg/cm², as discussed above; (b) downward percolation of *condensate* of steam from the upper margins of the vapor-dominated reservoir; and (c) entry of *new water* recharging the system; this water is likely to be considerably more dilute than the average deep water.

Porphyry copper deposits should be reexamined with consideration of these speculations on temperatures and salinities. If temperatures and salinities do increase sharply downward, our model may provide a new understanding of mode of transport and deposition of the ore minerals. Both decreasing temperature and decreasing salinity upward should favor precipitation of copper sulfides because of the decreasing stability of copper chloride complexes. Introduction of the ore metals may normally occur during a late stage in the total activity after very high salinities have been attained from residual concentration by boiling, and perhaps after the deepest permeable fractures (zone 9 of Fig. 7) have extended downward into a partly cooled major magma chamber.

Porphyry copper deposits should also be examined to determine whether the primary deposits were limited in upward development by a subsurface water table (8 of Fig. 7). Copper and other base metals have low volatilities and could not be transferred into the vapor-dominated reservoir. Pyrite and cinnabar are likely to be characteristic of the zone of condensation (zone 3), and pyrite can also form within the reservoir (zone 11) by reactions involving H_2S and Fe of the rocks. However, pyrite is likely to be much more abundant below the brine water table. Thus, where the original upper limit of copper mineralization and the level of the former brine water table are exposed in the present topography, the water table may be indicated by an anomalous upward *decrease* in supergene oxidation, where pyrite was initially so scarce.

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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}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 nonelectrical 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 SiO_2, Ca, Mg, Rb, K, Na, SO_4, HCO_3, and CO_3 are controlled by subsurface temperature, mineral solubility, mineral equilibria, and pH. Gases in these systems normally include CO_2, H_2S, H_2, CH_4, N_2, and inert gases, with 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 (SO_4 as H_2S, HCO_3 as CO_2, B as HBO_2, Hg, 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°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°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 CO_2, H_2S, and 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 H_2S-CO_2 gases and acid sulfate or acid sulfate-chloride waters in the oxidizing zone, or by N_2-CO_2 gases and alkaline sodium chloride waters in the reducing zone. Fluids related to thermometamorphic processes have high CO_2 gases and carbonated waters, which may in part be connate. Fluids of deep circulation but outside of volcanic and thermometamorphic zones have N_2 gases and dilute sodium chloride-sulfate waters. Kononov and Polak further divide volcanic fluids into "geyseric" with H_2-CO_2 gases and "riftogenic" with H_2 gases, which occur in spreading centers and characterize the highest temperature (>300°C) geothermal systems. It is only in "riftogenic" fluids that anomalous contents of ^3He and H_2S with $\delta^{34}S$ 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 ^3He in the hydrothermal fluids of Kamchatka (Gutsalo, p. 745), Lassen, and Hawaii (Craig, 1976) and of Yellowstone $\delta^{34}S$ 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, CO_2, H_2S, 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 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, CO_2, and H_2S, 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°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 or rock which, if the predrilling flux of chloride (2.5×10^{10} g/year; Ellis and Wilson, 1955) has been maintained over the life of the system, requires more than 5×10^3 km^3 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 ^{3}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_2S 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_2 with the rocks to produce mica or clay minerals and bicarbonate and alkali ions (Fournier and Truesdell, 1970),

$$CO_2 + H_2O + (Na,K)\ \text{silicate} = HCO_3^- + (Na^+,K^+) + H\ \text{silicate}.$$

The coupled increase in HCO_3:Cl and decrease in CO_2:other gases during lateral flow through a near-surface aquifer has

been demonstrated for Shoshone Geyser Basin, Yellowstone (analysis US*30*), 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 CO_2 is converted to HCO_3 less rapidly, as at Norris Geyser Basin, Yellowstone, where waters flowing in devitrified ash flow tuff are low in HCO_3 (analysis US*34*).

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 CO_2 retained in waters at temperatures well below 200°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_{CO2}-high Ca solutions emerge at the surface, they lose 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 CO_2 and H_2S) 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

$$HCO_3^- + H^+ = CO_2 + H_2O.$$

The effect of CO_2 loss is greatest in waters with large contents of bicarbonate such as those from Shoshone Geyser Basin, Yellowstone (analysis US*30*) or Orakeikorako, New Zealand (analysis NZ7), so these waters become very alkaline whereas waters with little bicarbonate (for example Norris waters, analysis US*34*) remain near neutral.

Sulfate can originate from oxidation of H_2S 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°C (Truesdell, 1976). This is close to the observed sulfate contents in water not affected by near-surface oxidation of H_2S in volcanic rocks with low sulfate contents, such as those in the Yellowstone caldera (analyses US*29-34*) and the Taupo volcanic zone (analyses NZ*1-10*). 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 SO_2 to H_2S and 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 T*1-2*).

Acid waters with very high sulfate contents are produced by direct superficial atmospheric oxidation of H_2S 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 Cl-HCO_3-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°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°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°C, close to that of steam of maximum enthalpy (236°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 borehold 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 Cz*1*; Franko and Mucha, p. 979; Boldizsár and Korim, p. 297; Petrović, p. 531). Waters in carbonate aquifers (analysis H*1*, Y*2*?) have relatively high contents of bicarbonate, calcium, and magnesium as might be expected, and gases appear to contain more CO_2 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 US*4*) and become much more concentrated with more CO_2 and H_2S as their subsurface temperatures approach those of volcanic systems (analysis US*26* 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 G*1-7*; Dominco and Papastamatoki, p. 109; Stahl, Aust, and Dounas, 1974), Guadeloupe (analysis Gu*1*; Demians d'Archimbaud and Munier-Jolain, p. 101), Iceland (analyses Ic*7-10*; Björnsson, Arnórsson, and Tómasson, 1972; Arnórsson, 1974; Arnórsson et al., p. 853), Israel (analysis Is*1*; Eckstein, p. 713), Italy (analyses It*1-2*; Baldi, Ferrara, and Panichi, p. 687), Japan (analyses J*1-2*; Mizutani and Hamasuna, 1972; Matsubaya et al., 1973; Sakai and Matsubaya, 1974), New Britain (analysis NB*1*; Ferguson and Lambert, 1972), New Zealand (Crafar, 1974; Skinner, 1974), and Turkey (analyses T*3* and T6; Kurtman and Şâmilgil, p. 447). The composition of normal seawater is given in Table 1 for comparison (analysis SW*1*).

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 NaKCa. 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, NB*1*, 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.

GEOTHERMOMETERS

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 NaKCa geothermometer was proposed by Fournier and Truesdell (1973). NaKCa 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 NaKCa) 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*—$t_{Na:K}$, 100°C and t_{NaKCa}, 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 J *1-2*). 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 J *12*, Ta *1-2*). 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 NaKCa geothermometer when applied to high-CO_2 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_2

pressure. Experimental calibration by Ellis (1971) allows magnesium contents to be used as a quantitative geothermometer if 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 *JI-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 $CO_2 + 4H_2 = CH_4 + 2H_2O$ 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 NZ*I*; 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 Ph*I*). 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}C contents and by Mizutani and Hamasuna (1972) from sulfate and water isotopes (analyses Is*3* and *JI*).

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 CO_2 with anomalously high ^{13}C:^{12}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 nonthermal 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 Vitrani (1973); and, in a study of the same area, criteria for distinguishing river sulfate of geothermal origin (from H_2S 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 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}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}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}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 CO_2, which prevent use of ^{14}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}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 CO_2 and CH_4, ($\Delta^{13}C[CO_2,CH_4]$), had been tested as a geothermometer. Analyses of well discharges of Larderello (analysis *It8*; Ferrara, Ferrara, and Gonfiantini, 1963) and Wairakei (analysis NZ*1*; 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. CO_2-CH_4 temperatures at Broadlands, New Zealand (analysis NZ*3*), 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 $\Delta^{13}C(CO_2,CH_4)$ have also been calculated for geothermal fluids from Indonesia (analysis Ids *1*), Kenya (analyses K*1-3*), and the United States (analyses US*5* and US*36*).

Hydrogen isotope geothermometers, $\Delta D(H_2,CH_4)$ and $\Delta D(H_2,H_2O)$, 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 K*2*, NZ*3*, US*5* and US*36*). Recently, Horibe and Craig (*in* Craig, 1976) have experimentally calibrated the H_2-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 (CO_2-CH_4) or continue up to the sampling point (H_2-CH_4, H_2-H_2O), 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 NZ*1*; Mizuntani and Rafter, 1969; Kusakabe, 1974), Otake, Japan (analysis J*6*; Mizutani, 1972), Larderello (analysis It*8*; Cortecci, 1974), and Raft River and Bruneau-Grandview, Idaho (analyses US*15* and US*17*; 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}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 US*7*, US*10*, US*18*, US*24*, US*26-27*). Estimates of subsurface temperatures in Japanese geothermal systems without deep drillholes and uncorrected for steam loss appear reasonable (analyses J*1-5*; Mizutani and Hamasuna, 1972; Sakai and Matsubaya, 1974).

Two other geothermometers need more testing. The first, $\Delta^{34}S(SO_4,H_2S)$, which has recently been calibrated experimentally by Robinson (1973), indicated unreasonably high temperatures for Wairakei bore fluids (analysis NZ*2*, Kusakabe, 1974) and for Mammoth, Yellowstone, water (analysis US*35*; Schoen and Rye, 1970). The second, $\Delta^{13}C(CO_2,HCO_3)$ may indicate the temperature of bicarbonate formation at Steamboat Springs, Nevada, and Yellowstone (analyses US*24*, US*30*, and US*32*), 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}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}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 (^4He and ^{40}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}Ar (Mazor and Fournier, 1973; Hulston and McCabe, 1962b), although young volcanic rocks that have not lost volatile elements have high ^{40}Ar contents (for example, Dalrymple and Moore, 1968). The origin and fate of ^{40}Ar in geothermal systems needs much closer study.

Several recent studies have been made of excess ^3He 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). ^3He has been depleted from the atmosphere and crust because it is lost into space at a greater rate than ^4He, 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 Pauzhetsk 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 (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}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 ±200 ppm chloride, SiO_2 contents of 260± ppm, and Na:K weight ratios near 8.2. To the south and west, spring waters have lower 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 NaKCa relations. Maximum indicated temperatures were 189°C (quartz saturation), 210°C (Na:K), and 231°C (NaKCa). 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°C, 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 SiO_2, indicate an average subsurface temperature of 269°C (standard deviation 13°C).

The patterns of Cl contents, 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 CO_2 and H_2S than other gases, and higher ratios of H_2S: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 CO_2 and H_2S content and in H_2S: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 × 10^6 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_{SiO_2} adia °C	t_{SiO_2} cond °C	$t_{Na/K}$ °C	t_{NaKCa} °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_4>>HCO_3	66000		156	166	174	202	~165 Na-Ca-SiO_2 272 WSMM	253 (1050 m) TDS = 190000	Bosch et al. (1976); Gringarten and Stieltjes (1976)
	Canada														
	British Columbia														
Ca1	Tawah Creek (940)	VW	s	43	w	Na>Mg>K>Ca HCO_3>>Cl>>SO_4	2400		162	177	210	227			Souther (p. 259); Nevin and Stauder (p. 1161)
Ca2	Meager Creek (852)	VW	s	55	w	Na>K=Ca>Mg Cl>HCO_3>SO_4	2000		171	187	197	211		69 (347 m)	
Ca3	Hot Springs Isl. (857)	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_3>>SO_4	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_4>HCO_3	14000		184	199	210	230			
Ch3	Well 7		w	85.5	w,g	Na>>K>>Ca>>>Mg Cl>>>HCO_3≥SO_4	15600	CO_2>>>H_2S	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_3>SO_4	1570	CO_2,H_2S			255	234			Arango et al. (1970)
	Czechoslovakia														
Cz1	Danube lowland	NVS	w			inc depth HCO_3-Na ↓ HCO_3-Cl-Na Cl-HCO_3-Na	<1000 ≤5000 ≤10000	N_2,CH_4,CO_2						38 1000 m gradient	Franko and Mucha (p. 979)
Cz2	Stranka	NVP	w		pw						36	115	20 Na-K-Ca-CO_2 73 Chalc	40 (1005 m)	Pačes and Čermák (p. 603)
Cz3	Karlovy Vary	NVP	w	72	pw						154	188	44 Na-K-Ca-CO_2 91 Chalc	72 (6 m)	
Cz4	Jachymov	NVP	w		pw						137	92	21 Na-K-Ca-CO_2 66 Chalc	30 (493 m)	
	Central depression (Danube lowland)														
Cz5	Chorvotský Grob	NVS	w	46		Cl-HCO_3-Na	1800							46 (970-1210m)	Franko and Račický (p. 131)
Cz6	Topolniky	NVS	w	90		HCO_3-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_4-HCO_3-Ca-Mg	3200							34 (420m)	
	El Salvador														
	Ahuachapán														
ES1	Salitre	VW	s	63	w,tr,g,i	Na>>Ca>K>>>Mg Cl>>>SO_4	1330	CO_2>>>N_2>>>CH_4	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_4	19300		249		259	256		231	

	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_{NaKCa} °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_3>>SO_4>>Cl	1640		151	158	196	207	225 WSMM		UNDP (1971); Demissie and Kahsai (I-10); Gonfiantini, 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_3>Cl>SO_4	2510		159	168	158	211			
E3	Tendaho Spr 15	VW	s	100	w,tr	Na>>K>Ca>>>Mg Cl>>SO_4>>HCO_3	1950		206	224	193	204			
E4	Lake Afrera Spr 31	VW	s	57.5	w,tr	Na>Ca>>K>>Mg Cl>>>SO_4>>>HCO_3	19100		124	130	150	179	208 WSMM		
	France														
	Massif Central														
F1	Chatesuneuf, bain tempéré	NVP	s	37	pw	Na>>Ca>K			143	155	154	178	~50 Na-K-Ca-CO_2 130 Chalc		Fouillac et al. (p. 721)
F2	Chatelguyon, Alice	NVP	s	35.5	pw,i	Na>Ca>>K			139	150	198	183	~50 Na-K-Ca-CO_2 124 Chalc		
F3	Ste. Marguerite, Rive d'Allier	NVP	s	29	pw	Na>>Ca≥K			137	148	215	203	~50 Na-K-Ca-CO_2 122 Chalc		
F4	Royat, Eugénie	NVP	s	33	pw	Na>>Ca>K			126	136	215	195	~50 Na-K-Ca-CO_2 108 Chalc		
	Greece														
G1	Kamena Vorla, Gamma 9	VSw	w	47.9	w	Na>>Ca>Mg>K Cl>>SO_4>HCO_3	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_4>>HCO_3	27800		45	45	119	173	11 Chalc		
G3	Edipsos, Damaria	VSw	s	78.5	w	Na>>Ca>>K>Mg Cl>>>SO_4>HCO_3	33400		110	112	120	174	81 Chalc		
G4	Lesbos, Arginos	VSw	s	81	w	Na>>Ca>K>Mg Cl>>SO_4>>HCO_3	11800		135	141	171	191	113 Chalc 198 WSMM		
G5	Nisiros, Demotika Loutra	VSw	s	48.5	w	Na>>Ca>Mg>K Cl>>>SO_4>>HCO_3	32000		160	174	114	167			
G6	Milos, Mavros Gremos	VSw	w	45	s	Na>>Ca=K>>Mg Cl>>>SO_4≥HCO_3	33800		172	185	232	205		138 (70 m)	
G7	Sousaki, borehole	VSw	w	73	pw	Na>>K>Ca>Mg Cl>>>SO_4	45100	CO_2,H_2S			249	265	>120 boiling calc.	73 (145 m)	
	Guadeloupe														
Gu1	Bouillante 2	VSw	w	~99	pw,tr,g	Na>>Ca>K>>>Mg	>24600	CO_2>>>H_2S			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_4>HCO_3	3020		152	164	199	189	200 WSMM2		
	Hungary														
	Pannonian Basin														
H1	Triassic dolomite	NVS	w	100?	w	Na≥Ca>>Mg>K HCO_3>SO_4≥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_3>>>SO_4=Cl	1560	CH_4,CO_2,N_2		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_{SiO_2} adia °C	t_{SiO_2} cond °C	$t_{Na/K}$ °C	t_{NaKCa} °C	Other Geothermometers °C	Observed Temp °C (depth)	References
	Iceland														
Ic1	Selfoss	NVF	s	79	w,i	Na>>Ca>>K>>>Mg Cl>>SO_4>CO_2	667	N_2>>CO_2	122	126	87	120	96 Chalc	91	Arnórsson (1974); Arnason (1976); Tómasson, Fridleifsson and Steffánsson (p. 643); Björnsson, Arnórsson and Tómasson (1972); Arnórsson et al. (p. 853)
Ic2	Deildartunga	NVF	s	99	w,i	Na>>>Ca>K>>Mg SO_4>Cl>CO_2	358		145	150	86	123	124 Chalc		
Ic3	Seltjarnarnes	NVF	s	83	w,i	Na>>Ca>>K>>>Mg Cl>>SO_4>>>CO_2	1110		137	143	68	109	115 Chalc	119	
Ic4	Lýsuhóll	NVF	s	40	w,i	Na>>Ca>K≥Mg CO_2>>>Cl>>SO_4	1670	CO_2>>>N_2	160	176	162	174	153 Chalc		
Ic5	Torfajokull, Eyrarhver	VW	s	95	w,i	Na>>>K>>>Ca>>Mg Cl>>SO_4≥CO_2	1350		194	209	148	199	193 Chalc		
Ic6	Geysir	VW	s	84	w,i	Na>>K>>>Ca>>Mg CO_2≥Cl≥SO_4	1130		227	256	200	220			
Ic7	Reykjanes	VSw	s	99	w,tr,g	Na>>Ca>K>>>Mg Cl>>>SO_4>>>CO_2	48300	CO_2>>>N_2>H_2S >O_2>>CH_4	234	262	210	231	262 boiling calc.		
Ic8	Reykjanes Well 8	VSw	w	270	w,i	Na>>Ca≥K>>>Mg Cl>>>CO_2>>>SO_4	33650			270	234	240		270	
Ic9	Svartsengi Well 3	VSw	w	236	w,i	Na>>K>Ca>>>Mg Cl>>>CO_2>>SO_4	22460			241	251	245		236	
Ic10	Krisuvik Well 6	VSw?	w	258	w	Na>>>K>Ca>>>Mg Cl>>>HCO_2>SO_4	2600			257	260	234	215-240 K(CO_2+CH_4)	258 (500 m)	
Ic11	Námafjall Well 4	VW	w	258	w,g,i	Na>>K>>>Ca>>>Mg CO_2>SO_4>Cl	956	H_2>CO_2>H_2S >N_2>>CH_4		261	262	237		258	
Ic12	Hveragerdi Well 4	VW	w	198	w,g,i	Na>>>K>>Ca>>Mg CO_2>Cl>SO_4	681	CO_2>>>H_2= H_2S>>CH_4		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_3>Cl>>SO_4	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_3>Cl>>SO_4	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_3>SO_4>>Cl	1250		153	166	148	170			
Ida4	Well CGW1	VW	w	85		Na>>>K=Ca>>Mg HCO_3>SO_4>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_3>Cl>>SO_4	595		141	148	288	204	209 WSMM		
Ida6	Spr 11		s	82	w	Ca>Na>Mg>K HCO_3>>Cl>>SO_4	550		127	131	268	194	170 WSMM		
Ida7	Kasol (NW Him. II)	VW	s	42	w	Ca>Na>Mg>K HCO_3>>SO_4=Cl	531		105	111	322	195	224 WSMM		
Ida8	Tatwani (NW Him. III)	VW	s	57	w	Na>>>Ca>K>Mg Cl>HCO_3>>>SO_4	611		90	93	117	146	113 WSMM		
Ida9	Kopili, Naga-Lushai	VW?	s	57	w	Na>>>Ca>>K>Mg HCO_3=SO_4>Cl	449		116	122	108	129			
Ida10	Tural Ratnigiri, West Coast	VW?	s	61	w	Na>Ca>K>>>Mg Cl>>SO_4>HCO_3	922		119	125	279	207	203 WSMM		
Ida11	Tuwa, Cambay	NVS	s	63	w	Ca>>Na+K>>Mg Cl>>SO_4	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_3>SO_4	468		120	124	50	114			
Ida13	Dug well, Sohna	NVS?	s	42	w	Na>Ca>>Mg>K HCO_3>Cl>>SO_4	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_{NaKCa} °C	Other Geothermometers °C	Observed Temp °C (depth)	References
	Indonesia														
Id1	Kawah Komojang, Well 6	VS	w	238	w,pi,pg	Na>>K>>>Ca SO_4>>>Cl	730	CO_2>>H_2S		240	232	217	220-230 "Isotope" 260 $\delta^{13}C(CO_2,CH_4)$	238 (620 m)	Kartokusumo, Mahon and Seal (p. 757); Ellis (pers. commun., 1975)
Id2	Dieng, Pulosari Spr	VW	s	55	w	Na≥Ca>K≥Mg Cl>SO_4=HCO_3	1340		143	153	436	250	203 WSMM2	173 (139 m)	Truesdell (1971); Radja (p. 233) quoted from Danilchik (1973)
	Israel														
Is1	Hamam El Farun	MVSw?	s	72	pw	Na>>Ca>>K	>12900				93	143			Eckstein (p. 713)
Is2	Rift Valley Spr	MVF?	s		pg			rare gases							Mazor (p. 793)
Is3	Hammat Gader	MVF	s	52±	pw,i,g, ^{14}C	Na>Ca>>Mg>K Cl>HCO_3>SO_4	1490	N_2>O_2>CH_4, rare gases			175	90	68 ^{14}C mixing		Mazor, Kaufman and Carmi (1973)
	Italy														
	Campi Flegrei														
It1	Spr 6D	VSw	s	34	w,tr,i	Na>>Ca≥K>>Mg Cl>>>SO_4>HCO_3	3600		116	123	252	217	271 WSMM	>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≥K Cl>>>SO_4>>HCO_3	25500		161	171	97	167	130-190 $\delta^{18}O$-D (steam-water)		
It3	Stufe d'Merone		s								>300				Maidav and Tonani (p. 1143)
It4	Tuscany, Romana, Spr 50 (group C)	VW	s	56	w,tr,g	Ca>>Mg>>K=Na SO_4>HCO_3>>>Cl	2390	CO_2>>>N_2>>>O_2	108	113	760	260	82 Chalc 163 WSMM		Baldi et al. (1973)
It5	Cesano Well 1	VW	w		w,tr	Na>K>>>Ca>>Mg SO_4>>Cl>>HCO_3	356000		148	153	548	521		210 (1400 m)	Calamai et al. (p. 305)
It6	Tuscany Spr 12836	VW	s	38	w	Ca≥Na>Mg>>K HCO_3>>SO_4>Cl	6400		74	77	190	78			Brondi, Dell'Aglio and Vitrani (1973)
It7	Acqua Borra	VW	s	37	pw,i	Na>>>Ca>K	>10600				169	198			Fancelli and Nuti (1974)
	Larderello														
It8	Wells	VS	w		i,T								220-390 $\delta^{13}C(CO_2,CH_4)$ 152-329 $\delta^{18}O(SO_4,H_2O)$	~240	Panichi et al. (1974); Ferrara, Ferrara and Gonfiantini (1963); Cortecci (1974)
It9	B.S. Michele	VS	s	47	pw,i	Na≥Mg>Ca>>K Cl>HCO_3>SO_4	357				312	84			
	Japan														
	Coastal Waters														
J1	Shimogamo 20	VSw	w	100	pw,i, i(SO_4)	Ca≥Na>>>K>>>Mg Cl>>>SO_4>HCO_3	~18000				154	174	200 $\delta^{18}O(SO_4-H_2O)$ 150 $CaSO_4$ 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_4)	Na>>Ca>K>>Mg Cl>>>SO_4	~19000				167	200	200 $\delta^{18}O(SO_4-H_2O)$ ~200 $CaSO_4$ sat.		Sakai and Matsubaya (1974); Matsubaya et al. (1973)
	Arima Type														
J3	Yashio	MVS?	s	1	pw,i, i(SO_4)	Na>>K≥Ca>>Mg Cl>HCO_3>SO_4	~34000				183	231	170 $\delta^{18}O(SO_4-H_2O)$		
	Greentuff Type														
J4	Tottori	MVS?	s	48	pw,i, i(SO_4)	Na>>Ca>>K>Mg SO_4>Cl>HCO_3	~4700				76	130	102 $\delta^{18}O(SO_4-H_2O)$		
	Volcanic Type														
J5	Beppu	VW	s	100	pw,i, i(SO_4)	Na>>K>Ca>Mg Cl>>SO_4>>>HCO_3	~3800				232	239	193 $\delta^{18}O(SO_4-H_2O)$		
J6	Otaki 8	VW	w		w,tr,i, i(SO_4)	Na>>K>>Ca>>>Mg Cl>>SO_4>>HCO_3	3190			227	222	229	220 $\delta^{18}O(SO_4-H_2O)$	195 (500 m)	Mizutani (1972); Koga (1970)
J7	Otaki Spr		s	97	w	Na>>K>>Ca≥Mg Cl>>>SO_4>HCO_3	3680		236		210	223			Nakamura (1969)
	Matsukawa														
J8	Well MR3	VS	w	~99	w	Na>K>Ca>>>Mg SO_4>>>HCO_3>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_{NaKCa} °C	Other Geothermometers °C	Observed Temp °C (depth)	References
	Japan (continued)														
	Volcanic Type														
	Matsukawa														
J9	Akagawa		s	42	w	Na>>K=Ca>>Mg SO_4>>>Cl	800		239		358	232		250 (1100 m)	Fujii and Akeno (1970); Baba et al. (1970)
J10	Matsukawa		w		c	NH_4>>HBO_2>F>>Hg>>As	20								Koga and Noda (p. 761)
	Onikobe														
J11	Mitaki	VW	s	54.5	pw	Na>>Ca>K>>>Mg Cl>>HCO_3>>SO_4	1540				252	208			Yamada (p. 665); Hitosugi and Yonetani (1972)
J12	Katayama G0-10	VW	w		pw	Na>Ca≥K>>Mg Cl>>>SO_4>>>HCO_3	10800				361	270		295 (1300 m)	
	Kenya														
K1	Olkaria #2	VW	w			Cl>HCO_3			240		250		360 $\Delta^{13}C(CO_2,CH_4)$ >300 $K(CO_2 \rightarrow CH_4)$	286 (1300 m)	Noble and Ojiambo (p. 189); recalc. 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	w	99	w,pg	Na>>K>Ca>>>Li>>>Mg Cl>>>HCO_3>>SO_4	27600	CO_2>>H_2S	278		319	292	288 BSMM	289 (1300 m)	Reed (p. 539); Mercado (p. 487)
M2	Well M9	VW	w	99	w,pg	Na>>K>Ca>>>Li>>Mg Cl>>>HCO_3>SO_4	17500	CO_2>>H_2S	228		249	250	292 BSMM	228 (1400 m)	
	New Britain														
NB1	Matupi-Rabalankaia	VSw	s	85	pw,pg	Na>>Mg>Ca>K Cl>>SO_4	34200	CO_2>>>H_2S			143	189	>150 boiling calc.		Ferguson and Lambert (1972)
	New Zealand														
	Wairakei														
NZ1	Well 44	VW	w	~99	w,i,g	Na>>K>>>Ca>>>Mg Cl>>>SO_4>HCO_3	4600	CO_2>>>N_2>H_2 >>O_2>CH_4>Ar	248		255	259	360 $\Delta^{13}C(CO_2,CH_4)$ 200 $K(CO_2 \rightarrow CH_4)$ $^{40}Ar/^{36}Ar$=290	248	Mahon (1973); Lyon and Hulston (1970); Lyon (1974)
NZ2	Well 28		w	~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	w	~99	w,i,g,tr	Na>>K>>>Ca>>>Mg Cl>>>HCO_3>>>SO_4	4120	CO_2>>>CH_4>N_2 >>H_2>>>Ar>O_2	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 $K(CO_2 \rightarrow CH_4)$ $^{40}Ar/^{36}Ar$=270	273 (771 m) 307 (2160 m) in research well	Mahon and Finlayson (1972); Giggenbach (1971); Seward (1974); Ritchie (1973); recalc. from Lyon (1974); Macdonald (p. 1113)
NZ4	Springs		s						179 ave 11 σ 202 max			183 ave 17 σ 218 max	270 ave BSMM 23 σ 306 max	260,265,272	Truesdell and Fournier (p. 837); Mahon (1973, 1972)
	Kawerau														
NZ5	Well 8	VW	w	~99	w,g	Na>>K>>>Ca>Mg Cl>>HCO_3>>SO_4	3070	CO_2>>>H_2S ≥HC>N_2>H_2	263		265	283		260	
NZ6	Springs		s						188 ave 7 σ 199 max			227 ave 8 σ 239 max	225 ave BSMM 24 σ 267 max	185,218,235 260,265,281	

	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_{NaKCa} °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_3≥SO_4	1290		234		250	249		237±	
NZ8	Spr 179 (Area 2)		s	98.5	w	Na>>K>>>Ca HCO_3=Cl>>SO_4	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 BSMM 7 σ 252 max	232-241	
	Waiotapu														
NZ10	Well 6	VW	w	~99	w,g	Na>>K>>>Ca>>>Mg Cl>>>HCO_3≥SO_4	3370	CO_2>>H_2S>>>H_2>N_2>HC	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_3>>>SO_4	4700		220		157	193		220-225	
	Philippines														
Ph1	Tongonan 222	VW	s	85.6	w,i	Na>>K>Ca>>>Mg Cl>>>HCO_3>>SO_4	3170		154	163	224	216	243 BSMM 246 Cl-E	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_3>SO_4	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_4>>HCO_3	9540			57	18	98	75 WSMM	40.5 (1020 m)	Dowgiałło (p. 123)
P2	Zakopane	NVS	w	36	pw,i		328						37-47 $\Delta^{18}O(SO_4,H_2O)$	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_4	257000			108	62	159	210 heat balance 211 WSMM 261 $\Delta^{18}O(SO_4,H_2O)$		Schoell (p. 583); Brewer and Spencer (1969); Longinelli and Craig (1967)
	Rhodesia														
RI	Binga Spr			100	pg			rare gases					>boiling rare gas		Mazor (p. 793)
SWI	Sea Water			4-30+	w	Na>>Mg>>Ca=K Cl>>SO_4>>>HCO_3	34500			<25	101	173	180± $\Delta^{18}O(SO_4-H_2O)$		Hood (1972); Longinelli and Craig (1967)
	Swaziland														
SwaI	Mkoba Spre		s	51.5	pw,pg,i	Na>>>Ca>>K HCO_3>>Cl>>SO_4	190	rare gases			53	54			Mazor, Verhagen and Negreanv (1974)
	Switzerland														
SwiI	Lavey les Bains	NVF?	w	63				rare gases							Mazor (p. 793)
	Taiwan														
	Tatun Shan														
TaI	Hsinpeitou	VW	s	98	w	Na>K>Ca>>Mg Cl>SO_4	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_4	15000	CO_2>H_2S	251		264	246		240 (293 in E208)	
Ta3	Ilan Tuchung IT-1	VW?	w	98	w,g,i	Na>>>K HCO_3>>>SO_4>Cl	3640	CO_2>>H_2S	178	189	45	~160	187 $\Delta^{18}O(SO_4,H_2O)$	164 max 173 (240 m)	Fournier, Mehring and MRSO (unpub. data, 1976)

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_{NaKCa} °C	Other Geothermometers °C	Observed Temp °C (depth)	References
	Turkey														
	Kizildere														
T1	Demirtas	VW	s	100	w,pg	Na>>>K>>>Ca>Mg HCO_3>>SO_4>Cl	3780	CO_3>>>H_2S	156	163	177	231			Dominco and Şamilgil (1970)
T2	Well KD-16		w	99	w	Na>>>K>>>Ca>Mg HCO_3>SO_4>>Cl	4210		166	175	172	226	225 BSMM	207 (666 m)	Alpan (p. 25)
T3	Seferihisar, Cuma	VSw	s	82	w	Na>>K>Ca>>Mg Cl>>>HCO_3>SO_4	19500		175	188	223	238		137 (70 m)	Kurtman and Şamilgil (p. 447); Eşder and Şimşek (p. 349); Tan (p. 1523); Öngür (II-36)
T4	Afyon, Gecek H.	VW	w	96	w	Na>>Ca>K>>Mg Cl>HCO_3>SO_4	5490		147	153	166	187	198 WSMM	106 (905 m)	
T5	Ankara, Kizilcahamam	VW	s	55?	w	Na>>K>Ca>>Mg HCO_3>>Cl>SO_4	2480		114	120	195	201	176 WSMM		
T6	Canakkale, Tuzla	VSw?	s	102	w	Na>>Ca>K>>>Mg Cl>>>SO_4>HCO_3	58700		107	107	220	242	285 boiling calc	145 (49 m)	
T7	Aydin, Germencik	NVS		87?	w,pg	Na>>>K>Ca>>>Mg HCO_3>Cl>>>SO_4	4930	CO_2,H_2S,SO_2	178	189	158	193			
	United States														
	Alaska														
US1	Pilgrim	NVF?	s	55	w,i	Na>Ca>>K>>>Mg Cl>>>HCO_3>SO_4	5550		129	137	110	146			Miller (1973); Miller, Barnes and Patton (1975)
US2	Umnak Island	VW	s	100	w	Na>>>K>Mg>>>Ca Cl>>SO_4	1610		194	209	158	236			
	Arizona														
US3	Casa Grande	NVS?	w	82	w	Na>>Ca>>>K>>>Mg Cl>>SO_4>>>HCO_3	2600		109	112	39	66	81 Chalc	102 (2500 m)	Dellechaie (p. 339)
	Arkansas														
US4	Hot Springs Nat. Park, Spr 42	NVF	s	61.3	w,i,^{14}C	Ca>>Mg≥Na>K HCO_3>>>SO_4>>Cl	270	N_2>CO_2>O_2		63.5	394	4			Bedinger et al. (1974)
	California														
	Imperial Valley														
US5	IID #2	VW	w	211	w,i	Na>Ca>K>>>Mg Cl>>>SO_4	259000			372?	354	308	380 $\Delta^{13}C(CO_2,CH_4)$ 220 $\Delta D(H_2,H_2O)$ 255 $\Delta D(CH_4,H_2)$	300 (1110 m) 340 (IID #1)	White (1968); Craig (1976)
US6	Mesa	VW	w		pw	Na>>Ca≥K	28000±				207±	230±		200 (2400±m)	Swanberg (1974)
	Long Valley														
US7	Magma #5	VW	w	180	w,i	Na>>K>>>Ca>>Mg HCO_3>Cl>SO_4	1700			219	203	238	240 $\Delta^{18}O(SO_4,H_2O)$	180	Mariner and Willey (1976); Sorey and Lewis (1976); Truesdell (unpub. data, 1975)
US8	Little Hot Creek Spr		s	79	w,i,g	Na>>Ca>K>>>Mg HCO_3>>Cl>SO_4	1660	CO_2>>>N_2>>O_2+Ar>>>CH_4	153	143	156	171	220 BSMM		
US9	Surprise Valley, Lake City	NVF?	s	96.5	w,i	Na>>>K>Ca>>>Mg SO_4>Cl>HCO_3	1210		170	180	118	160		160	Reed (1975)
US10	Morgan Springs	VW	s	95.4	w	Na>>K>>Ca>>>Mg Cl>>>SO_4>HCO_3	4590		179	190	227	229	213 $\Delta^{18}O(SO_4,H_2O)$		White, Hem and Waring (1963); Truesdell, Bowen and Nehring (unpub. data, 1976)
	Clear Lake														
US11	Wilbur Spr	VW	s	55	w,tr,g,i	Na>>>K>NH_4>>Mg Cl>HCO_3>>>SO_4	27200	CO_2>>>CH_4	166	180	126	240	205 WSMM2		Berkstresser (1968); White, Barnes and O'Neil (1973); Barnes, Hinkle et al. (1973); Barnes, O'Neil et al. (1973); Goff, Donnelly and Thompson (unpub. data, 1976)
US12	Elgin Spr	VW	s	68.5	w,i	Na>>>K>NH_4>>Mg>>Ca Cl>HCO_3>>>SO_4	28900		179	194	132	238			
US13	Seigler Spr	VW	s	52	w,i,g	Na>Mg>>K>Ca HCO_3>>Cl	1130	CO_2>>>CH_4>N_2>O_2	160	168	211, 257	169, 215	195 WSMM2		
US14	Thermal waters							rare gases							Mazor (p. 793)

	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_{NaKCa} °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_4>HCO_3	3360	N_2>>CO_2>>O_2>>R	131	136	90	139	142 $\Delta^{18}O(SO_4,H_2O)$	RRGE1 147 (1526 m)	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_3>SO_4≥Cl	372		107	111	98	131	145 WSMM		
US17	Bruneau-Grandview, Well 5S3E-28	NVS?	w	65	w,g,i	Na>>>K>Ca HCO_3>>Cl>SO_4	324	N_2>>O_2>CH_4	129	136	40	105	115 $\Delta^{18}O(SO_4,H_2O)$ 108 Chalc		
US18	Weiser, Well 11N6W-10	NVF?	s	76	w,i	Na>>>K>Ca SO_4>HCO_3>Cl	566		149	157	95	141	228 WSMM 234 $\Delta^{18}O(SO_4,H_2O)$		
	Montana														
US19	Marysville	NVF?	w	98		Na>>>K>Ca>>>Mg HCO_3>SO_4>>Cl	690		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_3>>SO_4>Cl	975		154	161	143	173	223 WSMM		Robertson, Fournier and Strong (p. 553)
	Nevada														
US21	Beowane	NVF?	s	98	w	Na>>>K>>>Ca>>>Mg HCO_3>SO_4>Cl	1140		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_3>>SO_4>>Cl	1370		118	125	223	197	215 WSMM		
US23	Kyle	NVF?	s	77	w,tr	Na>>Ca>K>Mg Cl>HCO_3>>>SO_4	2270		152	161	234	211	257 WSMM		
US24	Steamboat	VW?	s	94	w	Na>>>K>>Ca>>>Mg Cl>HCO_3>>SO_4	2370		188	201	184	207	220± $\Delta^{18}O(SO_4,H_2O)$ 190± $\Delta^{18}C(CO_2,HCO_3)$	186 (222 m)	
	New Mexico														
US25	Jemez Mtn., Jemez Spr	VW	s	75	w	Na>>Ca>K>>>Mg Cl>HCO_3>>>SO_4	3500		122	125	215	202	165 WSMM		Trainer (1974)
	Oregon														
US26	Alvord	NVF?	s	76	w	Na>>>K>>Ca>>Mg HCO_3>Cl>>SO_4	3400		140	148		198	217 WSMM 209 $\Delta^{18}O(SO_4,H_2O)$		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_4>>Cl≥HCO_3	850		130	136	102	130	192 WSMM 196 $\Delta^{18}O(SO_4,H_2O)$		
	Utah														
US28	Roosevelt Hot Spr	VW?	s	85	w	Na>>K>>>Ca Cl>>>HCO_3>SO_4	7850		196	202	273	284		260+	Mundorff (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 BSMM 5 σ 272 max		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_3>Cl>>SO_4	1250	CO_2>>>R>>>H_2S	185	199	110	171	272 BSMM 260 $\Delta^{18}O(SO_4, H_2O)$ 190± $\Delta^{13}C(CO_2,HCO_3)$		
	Upper Basin														
US31	Springs	VW	s						195 ave 11 σ 210 max			186 ave 20 σ 221 max	230 ave BSMM 18 σ 280 max	181 (152 m)	
US32	Ear Spr		s	95	w	Na>>>K>>>Ca>>>Mg Cl>>HCO_3>>SO_4	1370		206	224	122	186	314 $\Delta^{18}O(SO_4,H_2O)$ 201 $\Delta^{13}C(CO_2,HCO_3)$		
	Norris Basin														
US33	Springs	VW	s						210 ave 22 σ 255 max			251 ave 32 σ 294 max	276 ave BSMM 32 σ 374 max	237.5 (332 m)	
US34	Porcelain Terrace		s			Na>>K>>>Ca>>>Mg Cl>>>HCO_3>SO_4	2000		250	291	289	272	309 $\Delta^{18}O(SO_4,H_2O)$		

	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_{NaKCa} °C	Other Geothermometers °C	Observed Temp °C (depth)	References
	United States (continued)														
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US16	Crank Well	NVP	w	90	w,i,g	Na>>Ca>>K>>>Mg Cl>>>SO_4>HCO_3	3360	N_2>>CO_2>>O_2>>R	131	136	90	139	142 $\Delta^{18}O(SO_4,H_2O)$	RRGE1 147 (1526 m)	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_3>SO_4≥Cl	372		107	111	98	131	145 WSMM		
US17	Bruneau-Grandview, Well 5S3E-28	NVS?	w	65	w,g,i	Na>>>K>Ca HCO_3>>Cl>SO_4	324	N_2>>O_2>CH_4	129	136	40	105	115 $\Delta^{18}O(SO_4,H_2O)$ 108 Chalc		
US18	Weiser, Well 11N6W-10	NVP?	s	76	w,i	Na>>>K>Ca SO_4>HCO_3>Cl	566		149	157	95	141	228 WSMM 234 $\Delta^{18}O(SO_4,H_2O)$		
	Montana														
US19	Marysville	NVP?	w	98		Na>>>K>Ca>>>Mg HCO_3>SO_4>>Cl	690		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_3>>SO_4>Cl	975		154	161	143	173	223 WSMM		Robertson, Fournier and Strong (p. 553)
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US22	Buffalo Valley	NVP?	s	49	w,tr	Na>>Ca>K>Mg HCO_3>>SO_4>>Cl	1370		118	125	223	197	215 WSMM		
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US24	Steamboat	VW?	s	94	w	Na>>>K>>Ca>>>Mg Cl>HCO_3>>SO_4	2370		188	201	184	207	220± $\Delta^{18}O(SO_4,H_2O)$ 190± $\Delta^{18}C(CO_2,HCO_3)$	186 (222 m)	
	New Mexico														
US25	Jemez Mtn., Jemez Spr	VW	s	75	w	Na>>Ca>K>>>Mg Cl>HCO_3>>>SO_4	3500		122	125	215	202	165 WSMM		Trainer (1974)
	Oregon														
US26	Alvord	NVP?	s	76	w	Na>>>K>>Ca>>Mg HCO_3>Cl>>SO_4	3400		140	148		198	217 WSMM 209 $\Delta^{18}O(SO_4,H_2O)$		Mariner et al. (1974b); Lund, Culver and Svanevik (p. 2147); Truesdell, Sammel, Mariner and Nehring (unpub. data, 1975)
US27	Klamath Falls, Olene Gap	NVP?	s	74	w	Na>>Ca>>K>>>Mg SO_4>>Cl≥HCO_3	850		130	136	102	130	192 WSMM 196 $\Delta^{18}O(SO_4,H_2O)$		
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US30	Spr 35		s	93	w	Na>>>K>>>Ca>Mg HCO_3>Cl>>SO_4	1250	CO_2>>>R>>>H_2S	185	199	110	171	272 BSMM 260 $\Delta^{18}O(SO_4,H_2O)$ 190± $\Delta^{13}C(CO_2,HCO_3)$		
	Upper Basin														
US31	Springs	VW	s						195 ave 11 σ 210 max			186 ave 20 σ 221 max	230 ave BSMM 18 σ 280 max	181 (152 m)	
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	Norris Basin														
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US34	Porcelain Terrace		s			Na>>K>>>Ca>>>Mg Cl>>>HCO_3>SO_4	2000		250	291	289	272	309 $\Delta^{18}O(SO_4,H_2O)$		

tr	trace water analysis
trg	trace gas analysis
g	gas analysis
i	water (^{18}O,D) or other isotopes
T,^{14}C	tritium, carbon-14

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.

$\Delta^{13}C(CO_2,CH_4)$: Temperatures indicated by the fractionation of ^{13}C between CO_2 and CH_4. The notation for this and other isotope geothermometers is self-evident (see text).

$K(CO_2 \rightarrow CH_4)$: Temperature calculated from chemical equilibrium constants for the reaction $CO_2 + 4H_2 = CH_4 + 2H_2O$.

Boiling calculation: Temperature calculated from the apparent increase in concentration of seawater due to boiling.

Na-Ca-SiO_2, isotope mixing, ^{14}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.

Table 2. Equations for geothermometers.

Silica Geothermometers (SiO_2 in ppm)*

Quartz, adiabatic cooling (± 2°C from 125–275°C)

$$t°C = \frac{1533.5}{5.768 - \log SiO_2} - 273.15$$

Quartz, conductive cooling (± 0.5°C from 125–250°C)

$$t°C = \frac{1315}{5.205 - \log SiO_2} - 273.15$$

Chalcedony, conductive cooling

$$t°C = \frac{1015.1}{4.655 - \log SiO_2} - 273.15$$

Na/K Geothermometers (Na, K in ppm)

White and Ellis (see text) (± 2°C from 100–275°C)

$$t°C = \frac{855.6}{\log(Na/K) + 0.8573} - 273.15$$

Fournier and Truesdell (1973)

$$t°C = \frac{777}{\log(Na/K) + 0.70} - 273.15$$

NaKCa Geothermometer (Na, K, Ca in moles/liter)

Fournier and Truesdell (1973, 1974)

$$t°C = \frac{1647}{\log(Na/K) + \beta \log(\sqrt{Ca}/Na) + 2.24} - 273.15$$

$\beta = 4/3$ for $\sqrt{Ca}/Na > 1$ and $t < 100°C$

$\beta = 1/3$ for $\sqrt{Ca}/NA < 1$ or $t_{4/3} > 100°C$

*Data from Fournier (written commun., 1973)

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PROCEDURE FOR ESTIMATING THE TEMPERATURE OF A HOT-WATER COMPONENT IN A MIXED WATER BY USING A PLOT OF DISSOLVED SILICA VERSUS ENTHALPY

By A. H. TRUESDELL and R. O. FOURNIER, Menlo Park, Calif.

Abstract.—A graphical method using a plot of dissolved silica versus enthalpy allows quick determination of the temperature of the hot-water component of a nonboiling thermal spring. The method is applicable to warm spring waters that either have not lost heat before mixing or have lost heat by separation of steam before mixing.

Fournier and Truesdell (1974) published graphical and analytical procedures for estimating the temperature and proportion of a hot-water component mixed with a cold water. These procedures, valid for warm springs of large flow rate, were based on heat and silica balances. This paper presents simplified graphical procedures for obtaining those results. The method makes use of the dissolved silica-versus temperature graph of Fournier and Rowe (1966, fig. 5), replotted in figure 1 as dissolved silica versus enthalpy of liquid water in equilibrium with steam. To simplify the procedure, we have chosen to plot enthalpy in International Table calories (cal_{IT}) per gram (above 0°C) rather than joules per gram because the enthalpy of liquid water is numerically approximately the same as the temperature.

In using figure 1, one may assume either that no steam or heat had been lost from the hot-water component before mixing or that steam had separated from the hot-water component at an intermediate temperature before mixing. In either event, it is necessary to assume that no loss of heat occurs after mixing, that the initial silica content of the deep hot water is controlled by the solubility of quartz, and that no further solution or deposition of silica occurs before or after mixing. These assumptions are discussed in greater detail in Fournier and Truesdell (1974).

PROCEDURE

Assuming no loss of steam or heat before mixing; then do the following:

1. Determine or estimate the temperature and silica content of nonthermal ground water in the region and plot as a point in figure 1, the silica-versus-enthalpy graph. Plot temperature in degrees Celsius as calories. This is shown as point A in figure 2.
2. Plot the temperature and silica content of the warm spring water as another point on the graph, point B in figure 2 (again plotting temperature as calories).
3. Draw a straight line through the two points and extend that line to intersect the quartz solubility curve, point C in figure 2. Point C is the enthalpy and silica content of the deep hot-water component.
4. Obtain the temperature of the hot-water component from its enthalpy by using steam tables (Keenan and others, 1969) or figure 3.
5. Determine the fraction of hot water in the warm spring by dividing the distance AB by AC.

It is possible that point B may plot at too high a silica value for the extension of line AB to intersect the quartz solubility curve. This may be due to the assumption of too low a value for the silica content of the nonthermal water, and this value may be increased if it seems reasonable. Alternately, the hot-water component may have lost heat, but not silica, before mixing. If heat was lost by separation of steam, it is possible to evaluate the situation.

Assuming steam loss from an adiabatically cooled liquid before mixing with cold water; then do the following:

1. Plot the temperature and silica contents of the warm and cold waters as in the above procedure (fig. 4, points A and D).
2. Draw a straight line between those points (A and D) and extend that line to the liquid-water enthalpy equivalent of the temperature at which

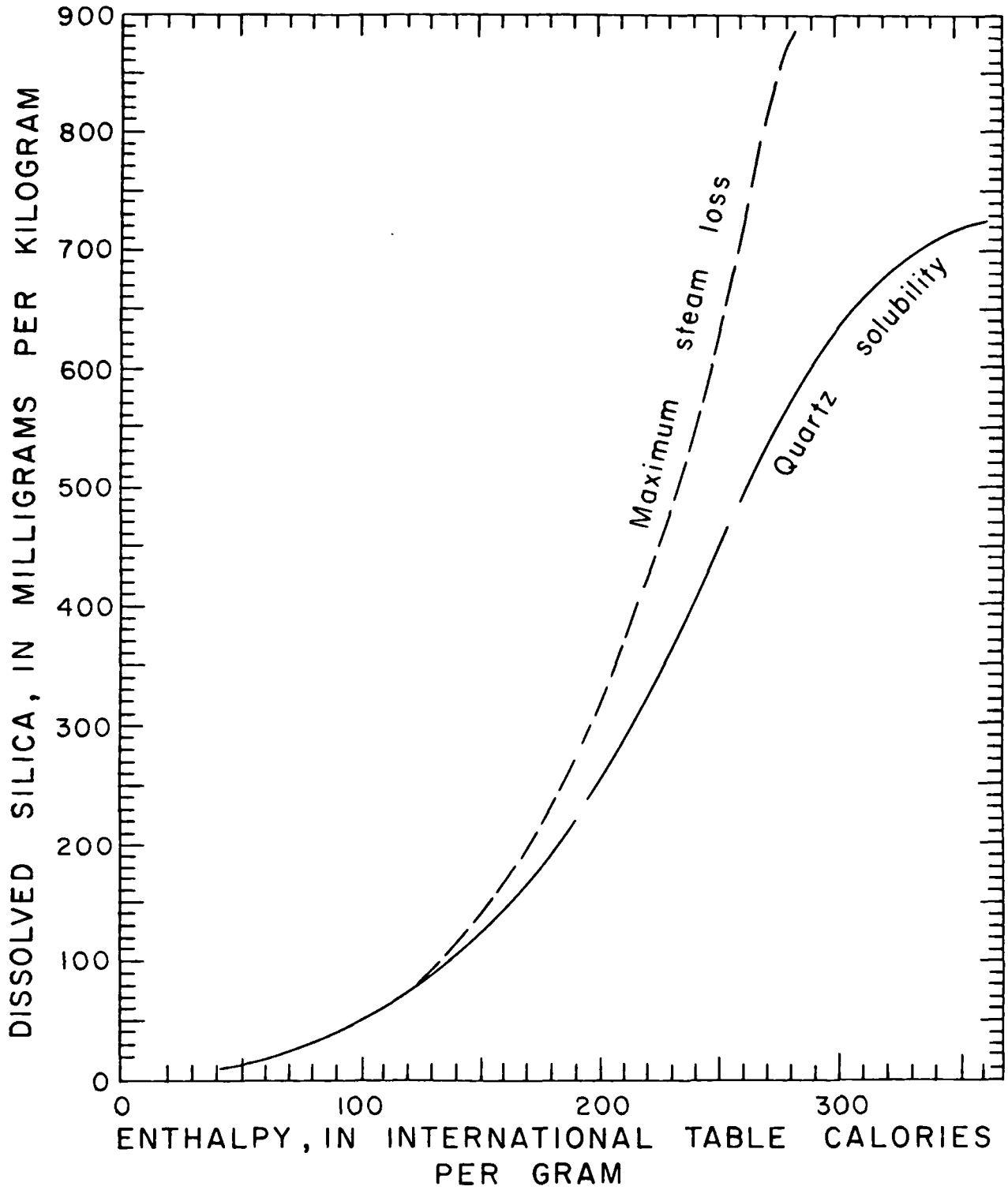

FIGURE 1.—Dissolved silica–enthalpy graph for determining temperature of a hot-water component mixed with cold water yielding warm spring water.

steam is assumed to have escaped before mixing (point E for 100°C in fig. 4).

3. Move horizontally across the diagram parallel to the abscissa until the maximum steam-loss curve is intersected (point F in fig. 4). Point F gives the enthalpy of the hot-water component before the onset of boiling, and point G gives the original silica content before loss of steam occurred.

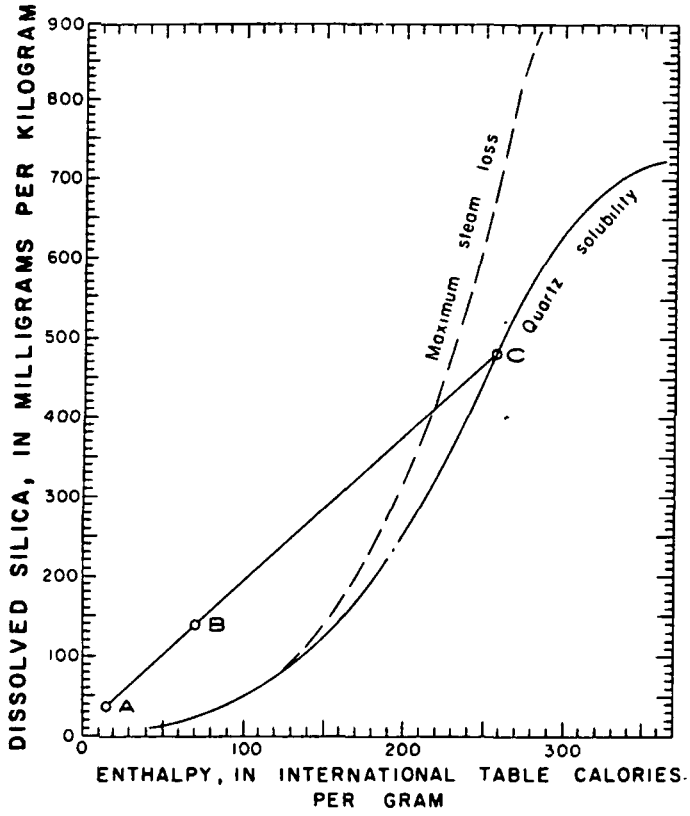

FIGURE 2.—Dissolved silica–enthalpy graph to be used when assumption is made that no steam or heat has been lost before mixing. See text for explanation.

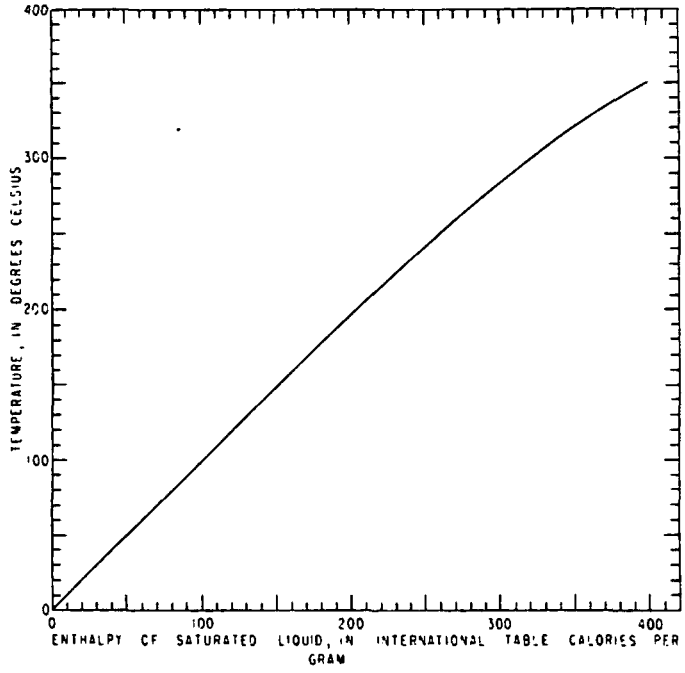

FIGURE 3.—Temperature-enthalpy relations for liquid water in equilibrium with steam.

4. Determine the fraction of hot water (after steam loss) in the warm spring by dividing the distance AD by AE. The weight fraction of original hot water lost as steam before mixing, x, is given by the formula

$$x = 1 - \frac{\text{silica value at point G}}{\text{silica value at point F}}.$$

If steam is lost at temperatures above 100°C, point F will lie on an intermediate steam loss (ISL) curve between the 100°C maximum steam loss (MSL) curve and the quartz solubility (QS) curve. The relative distance of the ISL curve from the QS and MSL curves is in the proportion $(H_{QS}-H_{ISL})/(H_{ISL}-H_{100})$ where H_{QS} is the enthalpy of liquid water at the quartz solubility curve at a given value of silica, H_{ISL} is the enthalpy of liquid water at the actual temperature of steam loss, and H_{100} is the enthalpy of liquid water at 100°C.

If steam separates at less than 1 atmospheric pressure, the enthalpy of the residual liquid water will be

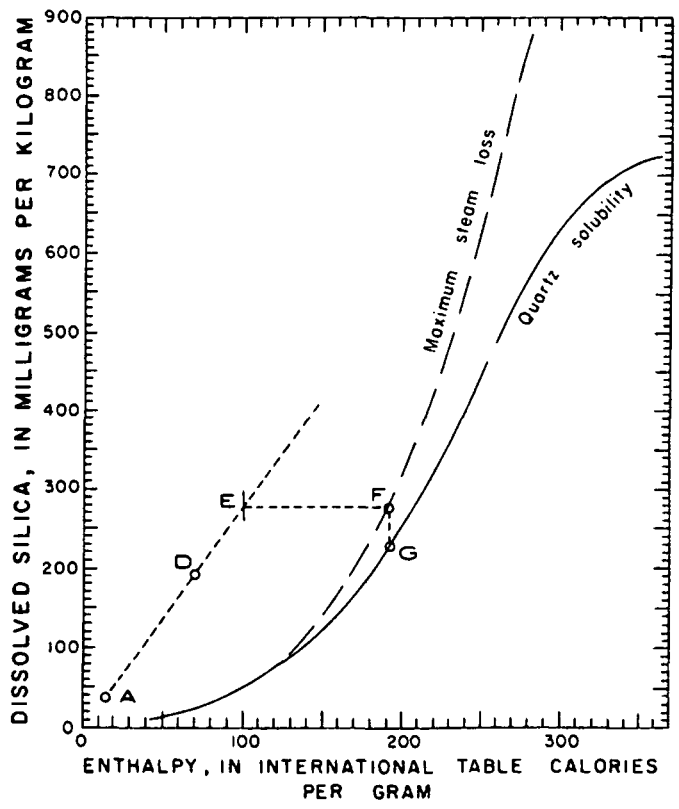

FIGURE 4.—Dissolved silica–enthalpy graph to be used when assumption is made that steam separated at 100°C from the hot-water component before mixing. See text for explanation.

less than 100 cal_{IT}/g. Point F will then be positioned on a different maximum steam-loss curve located slightly to the left of the maximum steam-loss line shown in figure 4. However, the change in position of the maximum steam loss curve as a function of the atmospheric pressure (altitude) is generally trivial.

DISCUSSION

The maximum enthalpy of the hot-water component that can be reliably determined is set by the point at which an extended line, such as AB (fig. 2), would be tangent to the quartz solubility curve. For most reasonable silica contents of nonthermal water, this will be at about 300 cal_{IT}/g (~285°C). Higher initial enthalpies of the hot-water component would cause an extended line to intersect the quartz solubility curve at two points, and the lower enthalpy point probably would be erroneously selected as the solution to the mixing problem. Although this presents a problem in interpretation, another problem inherent in dealing with very high enthalpy waters (above 275 to 300 cal_{IT}/g) is probably more serious. Quartz precipitates relatively quickly from such waters, and, therefore, temperatures derived from any relation assuming no silica precipitation are likely to be in error.

This method does allow easy evaluation of the effects of variations in assumed silica content and temperature of nonthermal water. The method also allows results obtained assuming no steam loss to be compared quickly with results obtained assuming steam loss at various intermediate temperatures. Similar graphical methods can be used to accommodate other silica phases such as chalcedony and cristobalite.

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Calculation of Deep Temperatures in Geothermal Systems from the Chemistry of Boiling Spring Waters of Mixed Origin

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ABSTRACT

Compositions of hot spring waters which result from subsurface mixture of hot and cold water components can be used to estimate the original temperature and fraction of the hot water component. Computations based on the chemistry of warm ($t < 80°C$) springs of mixed water origin were described by Fournier and Truesdell (1974). A new method has been devised to calculate the temperature and fraction of the hot water component of mixed springs that issue at boiling temperatures. The surface temperature, chloride, and silica content of the mixed spring water and the temperature and chloride content of an assumed unmixed spring water and of local cold ground water are used to calculate the temperature and fraction of the hot component of the mixture. In using the method, it is necessary to assume that (1) a sample of unmixed water is available; (2) no heat loss or gain occurs before or after mixing; (3) re-equilibration with quartz occurs after mixing; and (4) silica is not precipitated during ascent of the mixed water to the surface sampling point. If assumptions 1, 2, and 4 are not entirely true, the calculated temperature will usually be a minimum value. If assumption 3 is not true, too high a value is obtained. Results of calculations by graphic and analytical methods described here are given for selected areas in New Zealand, Chile, and Yellowstone Park.

INTRODUCTION

The maximum underground temperature of a geothermal system is critical to the evaluation of its energy potential. Under favorable conditions, determination of underground temperatures can be made from surface samples of hot spring waters by the use of chemical geothermometers (Fournier, White, and Truesdell, 1974). These geothermometers, however, do not usually indicate temperatures exceeding 200 to 230°C even though higher temperatures are found when these systems are drilled (Mahon and Finlayson, 1972). This temperature limit results from re-equilibration during passage of the water to the surface (Fournier, 1973; Fournier and Truesdell, 1973) and limits the usefulness of chemical geothermometers to lower temperature systems and to indicating temperatures of shallow aquifers in high-temperature systems. Higher subsurface temperatures may be indicated by isotope geothermometers (Hulston and McCabe, 1962; Craig, 1963; Gunter, 1968; McKenzie and Truesdell, 1975) and by calculations based on the temperature and silica content of warm springs of large flow that result from the subsurface mixture of hot and cold waters (Fournier and Truesdell, 1974). Unfortunately, the warm-spring mixing model method does not work where the mixed water emerges at boiling temperature, as is the case for many high temperature systems. A new calculation method described here, applicable to high-temperature systems with boiling springs of differing chloride content, is applied to geothermal systems in the United States, New Zealand, and Chile.

LIMITATIONS OF SILICA GEOTHERMOMETER

The geothermometer based on the assumed saturation with respect to silica minerals is by far the best understood (Fournier, 1973). Above about 150°C, geothermal waters in equilibrium with rocks containing excess normative silica are generally saturated with quartz. If these waters move rapidly to the surface from aquifers at temperatures less than about 200 to 230°C, they may retain all or very nearly all of their dissolved silica and will indicate the temperature of quartz equilibrium. This has been demonstrated for spring waters rising from shallow aquifers in Yellowstone Park (Fournier and Truesdell, 1970). (In some places where subsurface water-rock equilibration occurs at a temperature below about 140 to 150°C, dissolved silica may be controlled by the solubility of chalcedony rather than quartz.) If, however, the equilibration occurs in deeper, hotter aquifers, the content of dissolved silica will be such that the solubility of amorphous silica will be exceeded during passage of the water to the surface. When this happens, some silica is very likely to be deposited because the precipitation of amorphous silica from supersaturated solutions is rapid relative to quartz, which precipitates slowly at temperatures less than 200°C (White, Brannock, and Murata, 1956; Fournier, 1973). For systems in which quartz is present at depth, the maximum subsurface temperature that can be indicated by the silica geothermometer without possible deposition of amorphous silica depends principally on the temperature of the spring and, therefore, for boiling springs, on the atmospheric pressure. This relation is shown in Figure 1, in which the solubility curve of amorphous silica (Fournier, 1973) is combined with the silica geothermometer curves for adiabatically and conductively cooled spring waters (Fournier and Rowe, 1966; Mahon, 1966). If the surface

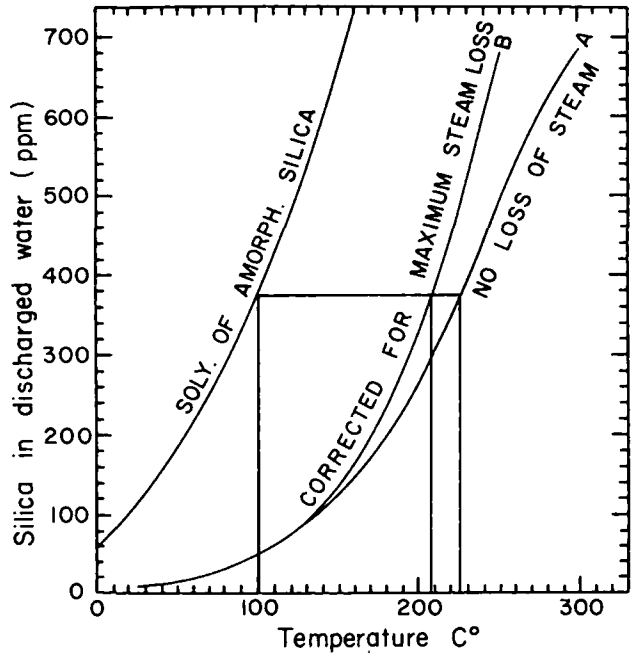

Figure 1. Solubility of amorphous silica and quartz (curve A) as a function of temperature. Curve B shows the amount of silica that would be in solution after an initially quartz-saturated solution cooled adiabatically to 100°C without any precipitation of silica. Modified from illustrations in Fournier and Rowe (1966).

boiling temperature is 100°C (for sea-level geothermal systems), saturation with amorphous silica represents about 370 ppm SiO_2, which could result from subsurface quartz saturation at 206°C with adiabatic cooling or at 226°C with conductive cooling. If quartz saturation occurs at higher temperatures, near-surface precipitation of amorphous silica may occur. At the elevation of Yellowstone Park, boiling occurs at 92°C and amorphous silica saturation represents 340 ppm SiO_2 in solution. Dissolved silica values for most Yellowstone waters other than Norris waters show an abrupt cut-off at about 370 ppm SiO_2 (Fig. 2). Some Norris waters have higher SiO_2 contents because they flow rapidly to the surface from very hot aquifers that probably exist at relatively shallow depths. The highest-altitude geothermal area for which detailed analyses are available is El Tatio, Chile, where water boils at 85.5°C (A. J. Ellis, written commun., 1975). In this system, the predicted limits are 305 ppm SiO_2 or quartz saturation temperatures of 195°C (adiabatic) with 211°C (conductive). The maximum observed silica content is 280 ppm (Ellis, written commun., 1975), which corresponds to an indicated temperature of 188°C (or 202°C), considerably below the maximum temperature (260°C) encountered in drill holes in this system (Armbrust et al., 1974).

MIXTURE CALCULATIONS

One way to estimate subsurface temperatures above the temperature limits of the silica geothermometer is to examine the chemistry of springs that result from the subsurface mixture of hot and cold waters. If this subsurface mixture produces a temperature below boiling, and if the flow is sufficiently large that this temperature is unchanged during passage to the surface, then the warm spring mixing model of Fournier and Truesdell (1974) may be applied to calculate the temperature and fraction of the hot water component. This model depends on the admixture of cold water diluting the dissolved silica sufficiently so that saturation with and precipitation of silica does not occur and that the mixture does not equilibrate with silica minerals after mixing because of the low temperature. These conditions are met in parts of Yellowstone thermal systems, where reasonable subsurface temperatures have been calculated (Fournier and Truesdell, 1974). Unfortunately, the use of this mixture calculation is limited by the scarcity of suitable springs, by the problem of steam loss before mixing (as discussed in the original paper), by its sensitivity to the silica content of the cold water, usually not accessible to direct measurement, and by its inability, for geometric reasons, to indicate temperatures above about 300°C. These disadvantages do not apply to a new mixing model suggested for systems containing boiling springs of different chloride contents resulting from the mixing of different amounts of hot and cold water.

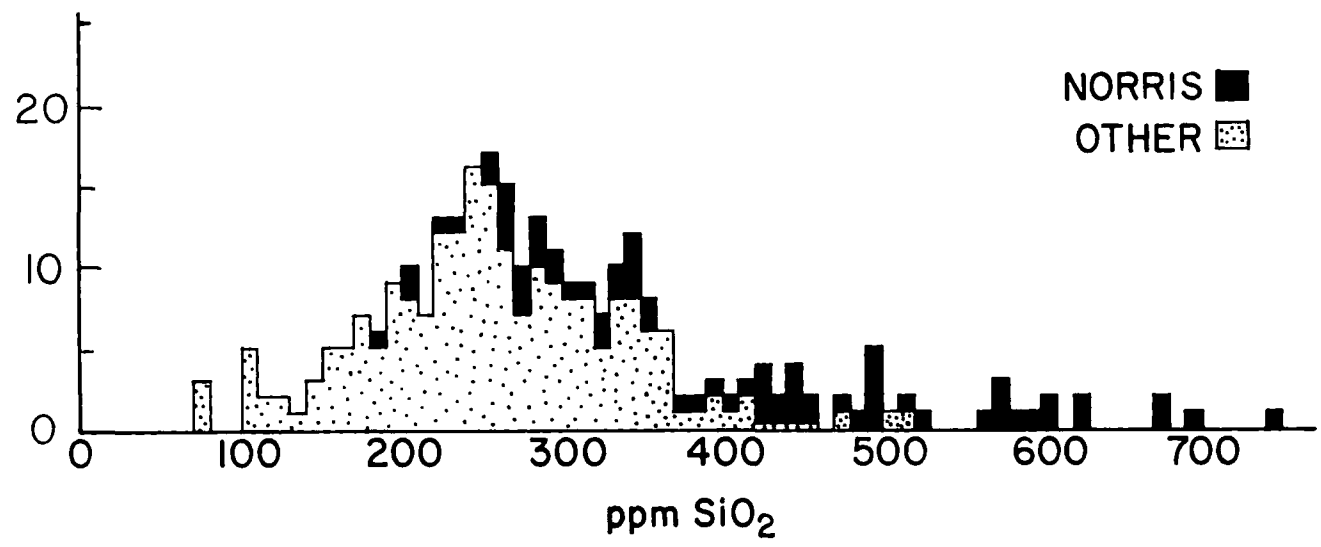

Figure 2. Frequency of silica contents dissolved in Yellowstone Park hot-spring waters.

MIXING MODEL FOR BOILING SPRINGS

If cold water at 5°C mixes with hot water at 270°C (a reasonable average for drilled high-temperature systems), hot water fractions of about 0.5 to 0.8 will produce water temperatures of 150 to 210°C. These waters can be expected to equilibrate with quartz if they remain in an aquifer at these temperatures for a relatively long time and will not deposit amorphous silica during passage to the surface. The indicated quartz saturation temperatures of boiling springs in Yellowstone (Fig. 2) and in other systems tend to be in the middle of this range, suggesting that dilution by cold water and re-equilibration with quartz in shallow aquifers may be common features of high-temperature geothermal systems.

If these processes are common and if the silica geothermometer reliably indicates temperatures resulting from mixing, then only the mixing fraction need be determined in order to calculate the temperature of the hot-water component for these high-temperature geothermal systems.

GRAPHICAL METHOD OF CALCULATION

The simplest method of calculating the temperature of the hot-water component uses a plot of water enthalpy versus chloride content (Fig. 3). On this plot, the composition of the cold water, of steam, and of all the hot spring waters issuing at surface boiling temperatures (HS_1 through HS_n) can be represented. Lines from the hot spring waters toward the average composition of the separated steam (HS_1 to steam, and so on) represent the variation in enthalpy and chloride content of the liquid water fraction caused by the process of steam separation during passage to the surface. (The enthalpy of the separated steam may vary from 2676 to 2804 joules per gram between 100 and 327°C. We recommend using an average value of 2775 joules per gram or 639 calories per gram.) The points AQ_1 through AQ_n on each of these lines are fixed from the temperature indicated by the silica geothermometer applied to the respective springs, assuming adiabatic cooling, and with water enthalpy obtained from steam tables (in Keenan et al., 1969).

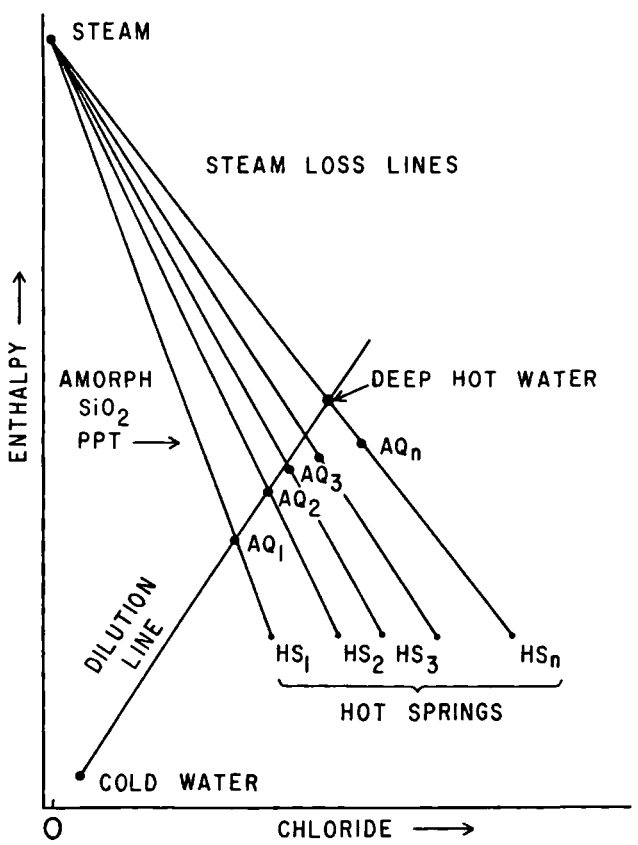

Figure 3. Hypothetical plot of enthalpy relative to chloride for various waters that result from the mixing of hot and cold waters. Enthalpies of deep waters are estimated using the silica content of hot-spring waters.

If a spring water is thought to cool mainly by conduction, a slightly higher estimated subsurface temperature and enthalpy would be obtained using the silica geothermometer, and the chloride content of the deep water would be the same as that of the emerging spring water, that is, a point AQ_x would plot directly above the point HS_x instead of along a line pointing to steam. A more complete discussion of the problem of treating data where both adiabatic and conductive cooling may have occurred is given in Fournier, White, and Truesdell (1975).

If the AQ points are aligned radial to the cold-water point (a "dilution line"), then cold-water dilution is strongly indicated as the dominant process controlling the subsurface temperatures and relative chloride contents. This is illustrated by data from Shoshone Geyser Basin, Yellowstone Park, Wyoming, and from Orakeikorako, New Zealand (Figs. 4 and 5). It is to be expected that the indicated water enthalpies of the more concentrated (higher chloride contents) springs will fall below the dilution line if the temperature of the hot-water component is above that which produces amorphous silica deposition, as discussed earlier. If only a few waters are sufficiently diluted to result in mixed temperatures below the amorphous silica deposition limit, then the dilution line may have to be forced through the cold-water point. In either case, the intersection of the dilution line with the steam separation line of the highest chloride water represents the estimated water enthalpy and chloride content of the *least diluted* water before passage to the surface. If several waters of a spring system have chloride contents near the maximum, then these waters may reasonably be taken to represent samples of the undiluted hot water, and their deep temperature, taken from the intersection of their steam separation lines with the dilution line, may be taken to be that of the undiluted hot water. The proportion of deep hot water to cold water in the mixed water, such as AQ_2 in Figure 3, is given by the relative lengths of the line segments from the cold-water point to AQ_2 and from AQ_2 to the hot-water point.

Generally, when a high-temperature water mixes with a low-temperature water the resulting solution will be supersaturated with silica in respect to the solubility of quartz. In the above discussion, it was assumed that the silica in the water re-equilibrated (precipitated quartz) after mixing and before further cooling. For situations in which dissolved silica does not re-equilibrate completely after mixing, the estimated enthalpy of the mixed water will be slightly higher than the true enthalpy and the corresponding AQ point (Fig. 3) will plot too high.

ANALYTICAL METHOD OF CALCULATION

The same results may be obtained from an analytical solution. It is possible to write heat balance and chloride

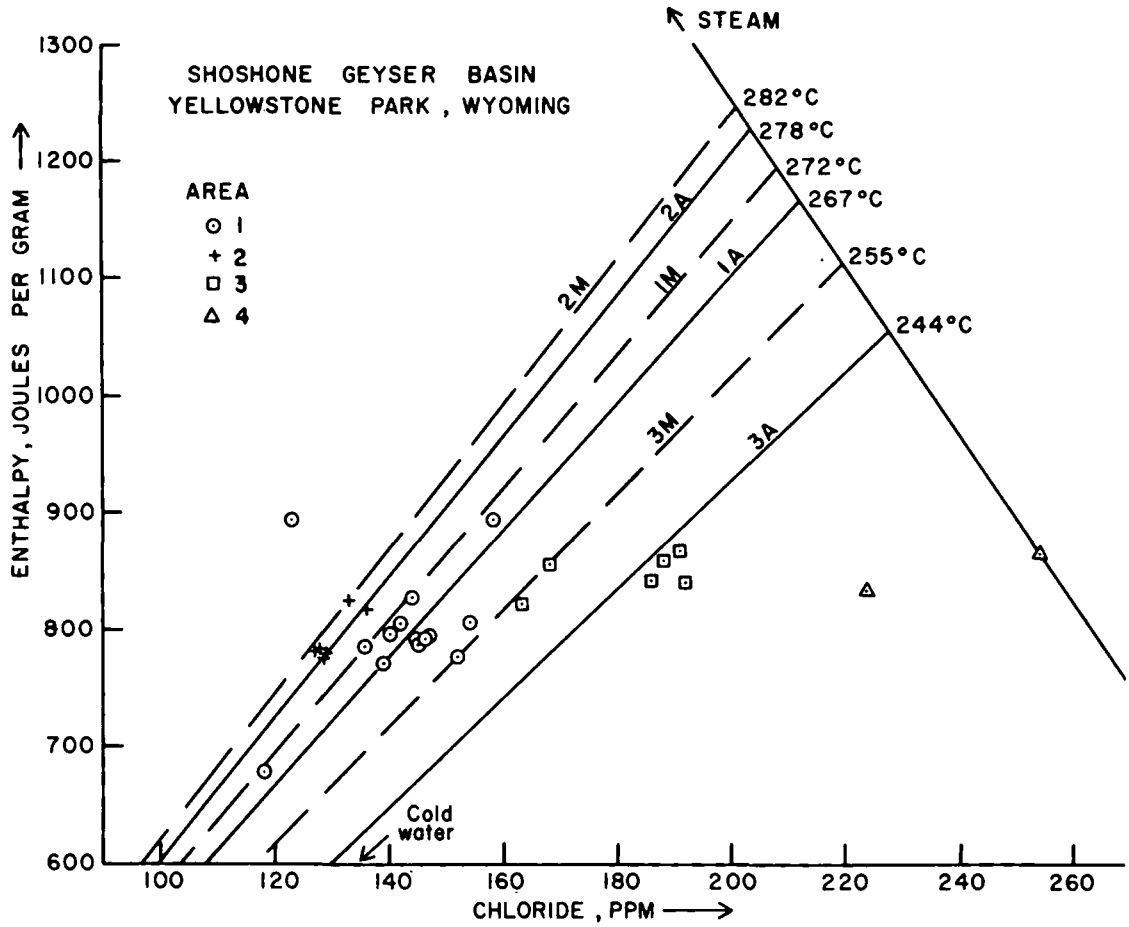

Figure 4. Enthalpy relative to chloride for waters from four geographic areas within Shoshone Geyser Basin, Yellowstone National Park. 1A and 1M respectively refer to the average and maximum lines through the data points for area 1. Similarly, 2A and 2M and 3A and 3M refer to average and maximum lines through the data points for areas 2 and 3.

balance equations for each part of the overall process. For the mixture of hot water with cold water, these equations are:

$$h_m = Xh_h + (1 - X)h_c \tag{1}$$

and

$$\mathrm{Cl}_m = X\mathrm{Cl}_h + (1 - X)\mathrm{Cl}_c \tag{2}$$

where h and Cl are specific enthalpy and chloride content, subscripts m, h, and c are mixed, hot and cold respectively, and X is the fraction of hot water. For the processes of steam separation during passage to the surface for a mixed water, the equations are:

$$h_m = Yh_m^s + (1 - Y)h_m^w \tag{3}$$

and

$$\mathrm{Cl}_m = Y\mathrm{Cl}_m^s + (1 - Y)\mathrm{Cl}_m^w, \tag{4}$$

in which the symbols are as before, with superscripts s and w referring to steam and water at surface temperature and Y the fraction of steam formed. Similar equations for an unmixed spring water which results from the passage to the surface of the undiluted hot component of the mixture are:

$$h_h = Zh_h^s + (1 - Z)h_h^w \tag{5}$$

and

$$\mathrm{Cl}_h = Z\mathrm{Cl}_h^s + (1 - Z)\mathrm{Cl}_h^w \tag{6}$$

in which Z is the resulting fraction of steam. Because the solubility of chloride in low-pressure steam is very small, Cl^s can be set equal to zero, and equations (3) and (4) and (5) and (6) may be combined as:

$$\mathrm{Cl}_m = \frac{h_m^s - h_m}{h_m^s - h_m^w}\mathrm{Cl}_m^w \tag{7}$$

and

$$\mathrm{Cl}_h = \frac{h_h^s - h_h}{h_h^s - h_h^w}\mathrm{Cl}_h^w \tag{8}$$

When equations (7) and (8) are combined with equations (1) and (2), and with $(h^s - h^w)$ written as h^e, the heat of evaporation, the final equations are:

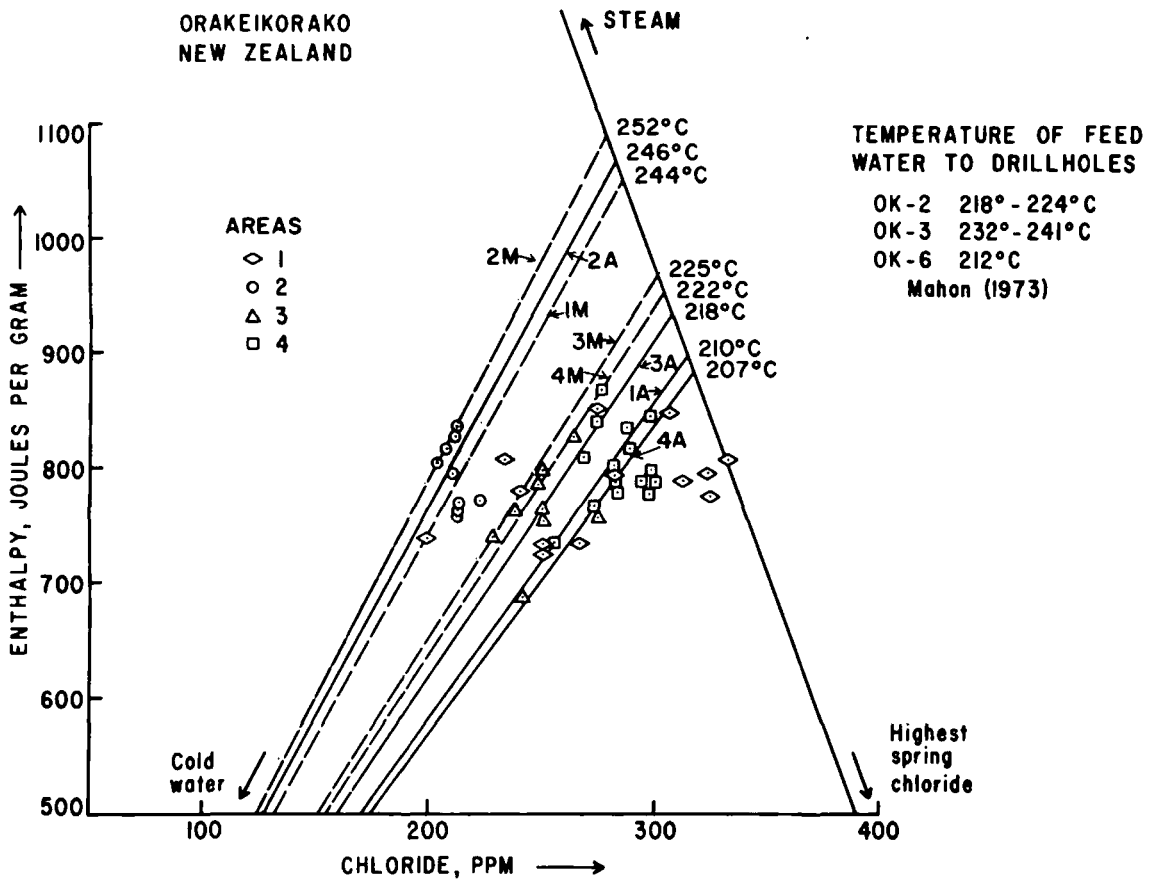

Figure 5. Enthalpy relative to chloride for waters from four geographic areas at Orakeikorako, New Zealand. 1A and 1M respectively refer to the average and maximum lines through the data points for area 1. Similarly, the A and M notation is used for the average and maximum lines through the data points for areas 2 and 3.

$$X = \frac{Cl_m^w h_h^e (h_m^s - h_m) + Cl_h^w h_m^e (h_m - h_c) - Cl_c h_m^e h_h^e}{Cl_h^w h_h^e (h_h^s - h_c) - Cl_c h_m^e h_h^e} \quad (9)$$

and

$$h_h = \frac{h_m - h_c}{X} + h_c \quad (10)$$

In these equations, h^s, h^e, and h^c are surface values of enthalpy of steam, of evaporation, and of cold water that can be found in steam tables (Keenan et al., 1969) for measured or estimated surface temperature of hot and cold springs, and Cl_m^w and Cl_h^w are the surface chloride contents of the mixed water and the presumed nonmixed water. The value of h_m is the subsurface enthalpy of the mixed water before steam separation, which can be obtained from the silica content of the water using the silica geothermometer with correction for steam loss (Mahon, 1966; Fournier and Rowe, 1966) and the steam tables. Once the hot water fraction, X, is calculated, the subsurface enthalpy of the hot water, h_h, may be calculated and its temperature derived from the steam tables.

The analytical method is not recommended as superior to the graphic method; in fact, the errors involved in the calculation may be obscured by its use. It can, however, be incorporated in computer programs along with other geothermometric methods for screening of hot spring data.

APPLICATION OF MIXING CALCULATIONS

Mixing calculations have been made for hot springs in Yellowstone Park, Wyoming, USA, in the Taupo volcanic zone, New Zealand, and at El Tatio, Chile. Two hot spring systems for which numerous modern analyses were available have been treated in detail and are shown in Figures 4 and 5. These areas are Shoshone Geyser Basin, Yellowstone (Truesdell, 1975a; Thompson et al., 1975) and Orakeikorako, New Zealand (Mahon, 1972). In each of these areas, fault control of hot spring locations is evident, and hot springs located along a single fault tend to lie along a single dilution trend on the enthalpy-chloride diagram. At Orakeikorako, aquifers are considered to exist at different temperatures and these aquifers are intersected by different faults, giving rise to chemical zonation in the spring waters (Mahon, 1972 and 1973). At Shoshone, subsurface information is lacking, and the alternative interpretation that some waters have lost silica and others gained steam is favored.

In Figure 4, the subsurface enthalpy and chloride contents of Shoshone hot spring waters, calculated by means of the computer program GEOTERM (Truesdell, 1975b), are plotted using different symbols for the spring waters of the western area (I), the central area (II), the south central area (III), and the north central area (IV). Waters from these areas form chemically distinct regions on a plot of their Cl/SO_4 ratios versus their Cl/HCO_3 ratios. Except

for one water with an anomalously high calculated enthalpy, the enthalpy-chloride points of waters of area I are reasonably well aligned along a narrow dilution trend that intersects the steam loss line of the highest chloride spring at an enthalpy corresponding to about 270°C, taken as the temperature of the hot component of the mixture. Although the average projection of these area I points indicates a hot-component temperature of 267°C, the maximum indicated temperature of 272°C is considered more likely because some of the waters may have lost silica. The area II points do not have as wide a range of chloride and enthalpy and plot to the left of the area I points, suggesting that, during or before mixing, these waters may have gained steam from subsurface boiling of other water, and that the indicated temperatures (278°C average; 282°C maximum) are therefore probably too high. The silica contents of the waters of areas III and IV are close to saturation with amorphous silica; and as they appear to have lost silica during ascent, their indicated hot-component temperatures are too low. Springs with acid waters were not included because their silica contents do not reflect subsurface equilibrium with quartz.

Only area I springs have a wide range of subsurface enthalpy and chloride and line up along a convincing dilution line (line *IM*). These springs have the greatest areal spread, and, in aggregate, discharge most of the thermal water of the basin. It is therefore probable that the thermal water entering the base of the system had a temperature of 272°C, as indicated by the maximum projection of the dilution line of area I on the steam-loss line of the most concentrated spring. It is possible, however, that this most concentrated spring is itself mixed, that it may have lost silica during ascent, and that the temperature of the hot component of the mixture may be higher.

Examination of the detailed hot spring data available for the Orakeikorako, New Zealand, geothermal system (Mahon, 1972) shows a somewhat similar picture. Three of the four areas distinguished by Mahon on geographic and chemical grounds seem to contain waters that fall along well-defined trends (lines 2-4, Fig. 5), with maximum indicated temperatures only slightly higher than average indicated temperatures. The observed aquifer temperatures from drill hole data (Mahon, 1973) are very close to the calculated temperatures. In this system, the existence of several dilution trends is probably not due to silica loss or steam gain but to the existence of several aquifer waters with different temperatures feeding hot springs through separate faults and being separately diluted. For this reason, the indicated temperatures for each of the four areas are given in Table 1.

Hot spring chemical data for other systems in Yellowstone and New Zealand for the El Tatio, Chile, system have been used to calculate geothermometer and mixing model temperatures with reasonable agreement between the latter and the observed production aquifer temperatures for drilled systems (Table 1). In order to test the method as objectively as possible, the hot spring analyses have been used without statistical weighting (except for the elimination of acid sulfate spring analyses). In an exploration program, it may be advisable to weight spring data using criteria described by Fournier, White, and Truesdell (1974), a method applied to hot springs of the Long Valley, California, geothermal system (Sorey and Lewis, 1975) and to the Upper, Lower, and Norris Geyser Basins of Yellowstone National Park (Fournier, White, and Truesdell 1975).

SUMMARY

In this paper it is demonstrated that, in high-temperature geothermal systems with boiling hot springs having a range of chloride contents, aquifer temperatures above the usual range of the silica geothermometer may be calculated from a simple mixing model. The requirements for this calculation include that: (1) no loss or gain of steam occur before mixing takes place; (2) the temperatures resulting from mixing be within the range of accuracy of the quartz-saturation geothermometer (usually 150 to 205°C); (3) no precipitation of silica occur after mixing; and (4) no conductive loss of heat occur before or after mixing. These requirements are met by numerous high-temperature geothermal systems in Yellowstone Park, USA, in the Taupo volcanic zone, New Zealand, and elsewhere. In drilled systems, calculated temperatures are close to those encountered in drilling.

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Table 1. Subsurface temperatures (°C) of geothermal systems observed in drill holes and calculated from chemical geothermometers and from the boiling spring mixing model using the computer program GEOTERM (Truesdell, 1975b).

Thermal system		Temperatures indicated from hot spring chemistry: SiO_2 Adiabatic	Na-K-Ca $\beta = 1/3$	Boiling spring mixing model	Temperatures observed in production zone or hole maximum	Reference
Yellowstone Park (Wyoming, U.S.A.)						
Shoshone	ave.	190	175	267	—	1
Basin	std. dev.	10	16	5 area I		
	max.	203	223	272		
Lower	ave.	179	162	210	170, 174, 203*	1,2,3
Basin	std. dev.	11	16	18		
	max.	213	218	303		
Upper	ave.	195	186	230	143*, 170*, 180*	1,2,3
Basin	std. dev.	11	20	18		
	max.	210	221	280		
Norris	ave.	210	251	276	196*, 238*	1,2,3
Basin	std. dev.	22	32	32		
	max.	255	294	374		
Taupo Volcanic Zone (New Zealand)						
Broadlands	ave.	179	183	270	260, 265, 272	4,5
	std. dev.	11	17	23		
	max.	202	218	306		
Kawerau	ave.	188	227	225	185†, 218†, 235†,	5,6,7
	std. dev.	7	8	24	260, 265, 281	
	max.	199	239	267		
Orakeikorako						
Area 1	ave.	183	226	210	212, 218–222,	5,8
	std. dev.	9	11	18	232–241	
	max.	204	240	244		
Area 2	ave.	188	232	246		
	std. dev.	6	7	7		
	max.	196	245	252		
Area 3	ave.	179	229	218		
	std. dev.	10	19	7		
	max.	194	264	225		
Area 4	ave.	188	221	207		
	std. dev.	7	15	8		
	max.	202	236	222		
Waiotapu	ave.	187	185	293	210, 260, 295*	5,9
	std. dev.	22	46	—		
	max.	210	236	293		
El Tatio	ave.	160	205	208	140–170, 190–235,	7,10,11
(Chile)	std. dev.	15	20	27	236–263	
	max.	189	231	274		

*Drilling was terminated before the maximum temperature was reached.
†Temperature calculated from discharge silica contents.

References: (1) Thompson et al., 1975; (2) Rowe, Fournier, and Morey, 1973; (3) White et al., 1975; (4) Mahon and Finlayson, 1972; (5) Mahon, 1973; (6) Mahon, 1962; (7) Truesdell and Singers, 1971; (8) Mahon, 1972; (9) Wilson, 1963; (10) Armbrust et al., 1974; (11) Ellis, 1975 written commun.

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