GAS ANALYSES OF THERMAL WATERS IN NEW MEXICO

BY

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ABSTRACT

Nitrogen, neon, argon, krypton, helium, carbon dioxide, hydrogen sulfide, methane, oxygen, hydrogen, ammonia, and nitrogen oxide were measured in water from fifty-one thermal wells and springs in New Mexico. The gas composition of the waters was compared with silica and alkali geothermometers. Sixteen wells were sampled from the Lightning Dock Known Geothermal Resource Area.

The concentration of nitrogen, neon, and argon in most New Mexico thermal waters is close to the concentration expected for air saturation. The concentration of helium is in excess of air saturation, and is attributed to leaching of radiogenic helium by thermal waters. High concentrations of helium are associated with thermal waters near the boundaries of the northern Rio Grande rift. The concentration of carbon dioxide increases with subsurface temperature calculated from the Na-K-Ca geothermometer and probably is controlled by temperature-dependent aluminium-silicate equilibria. The concentation of hydrogen sulfide does not appear to be controlled by any water-rock equilibria. Methane in New Mexico thermal waters appears not to be controlled by any one reaction. Hydrogen was detected in only the Animas Valley hot well. Ammonia can not be explained by gas equilibria. The concentration of nitrogen oxide is in excess of air saturation.

The oxygen fugacities calculated from the carbon dioxide/methane ratios measured in New Mexico thermal waters

fall between the hematite-magnetite and nickel-nickel oxide oxygen-fugacity buffers between 37°C and 298°C.

Gases measured in the Animas Valley hot well were depleted due to subsuface boiling. The gases in the non-thermal waters in the Animas Valley showed a zonation around the hot wells similar to that found by previous chemical studies of the area.

Several gas geothermometers were applied to gas analyses of well and spring discharges from the Baca geothermal reservoir, Valles Caldera, New Mexico. Gas geothermometers based on the New Zealand geothermal system and the empirical carbon dioxide/methane geothermometer gave the best agreement with measured temperatures.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

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INTRODUCTION

STATEMENT OF PURPOSE

This study assesses the use of gases in the exploration of geothermal waters. A survey of the gas composition of fifty-one thermal wells and springs was made in New Mexico; samples were collected between March and August, 1981 (Fig. 1). The gas data were compared with geothermometers to determine which gases or gas ratios indicate high geothermal potential and whether gases in thermal waters could be used in the regional exploration of geothermal resources. Data were compared with mineral equilibria and regional geology to determine the controls of the gas chemistry of the thermal waters.

Sixteen well samples from the Animas Valley, in the Lightning Dock Known Geothermal Resource Area, were examined to test the application of gases to geothermal exploration in a known geothermal area (Fig. 2). The gas data were compared to previous geochemical and geological studies of the area to see if the data could give useful information about the chemistry, geology, and hydrology as guides for further exploration.

PREVIOUS WORK

Most studies have been of gases in high temperature reservoirs and have been used to develop geochemical models and to develop gas geothermometers (Craig, 1953, 1963; D´Amore, 1977; D´Amore and Nuti, 1977; D´Amore and Panichi,

Figure 1. Location of thermal wells and springs sampled in this study:

1. Mamby Hot Spring
2. Ponce del Leon Hot Spring
3. Statue Spring
4. Ojo Caliente
5. San Antonio Hot Spring
6. Spence Hot Spring
7. Soda Dam Hot Spring
8. Jemez Hot Spring
9. San Ysidro Hot Spring
10. Kaseman Well # 2 (Warm Springs)
11. Montezuma Hot Spring
12. Blue Canyon Well
13. Socorro Spring

14-16. Bosque Del Apache - Wells #9, 13, 20
17-19. Truth or Consequences - Yucca Bath, Sierra Grande, Artesian Bath
20-21. Radium Springs - Bath House, Well #2
22-23. Las Cruses - Las Alturas Estates - Geothermal Well #1, Presidents Well, and Golf Coarse Well.

24. Hillsboro Warm Spring.
25. Mimbres Hot Spring.
26. Faywood Hot Spring.
27. Kennecott Warm Spring Well #3.
28. Riverside Well.
29. Telephone Company Well (Cliff).

30-32. Gila Hot Springs.

33. Middle fork Gila Hot Spring.
34. Lower Frisco Hot Spring.
35. Upper Frisco Hot Spring.

36-51. Animas Valley Wells - Lightning Dock Geothermal Area

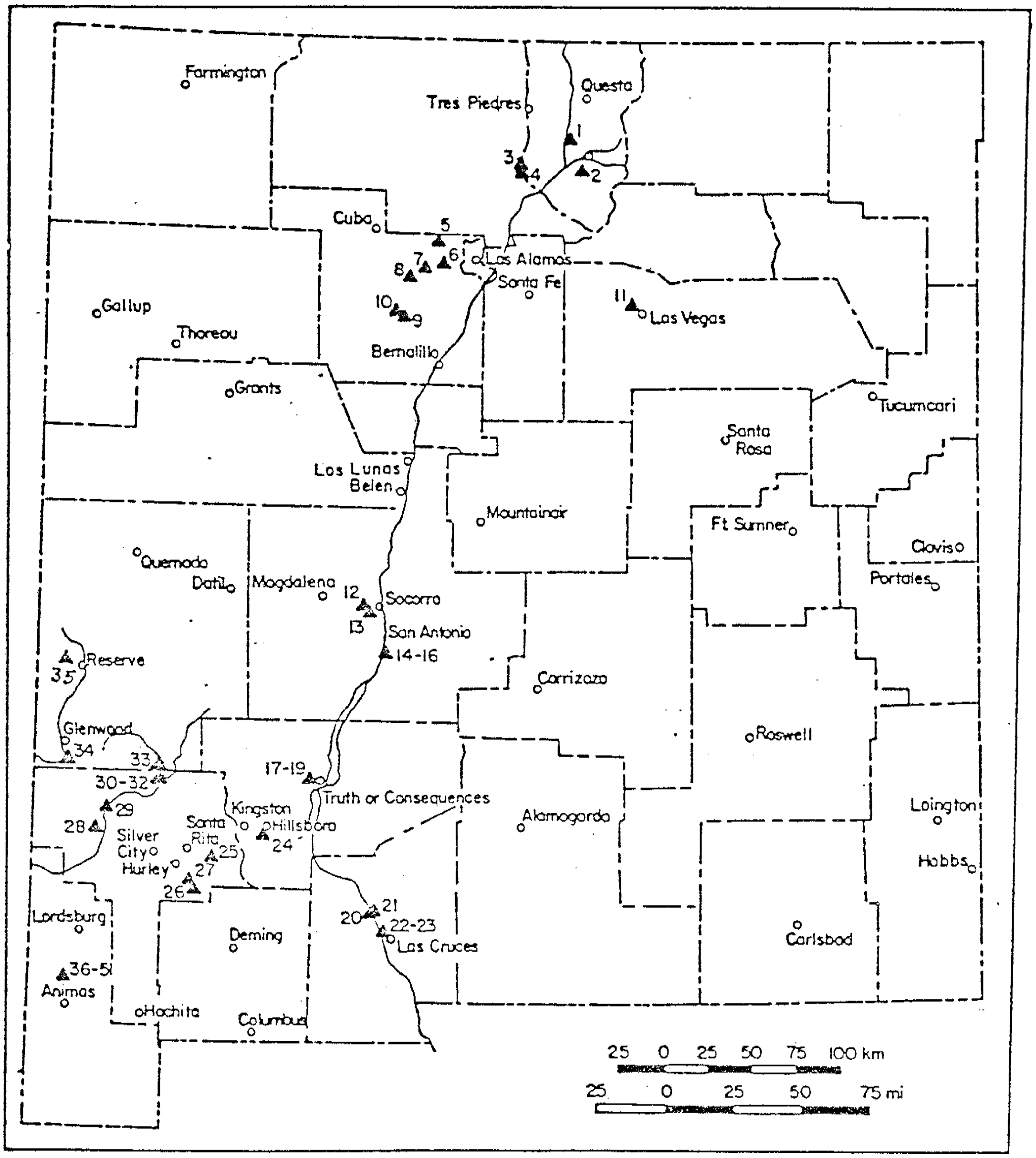
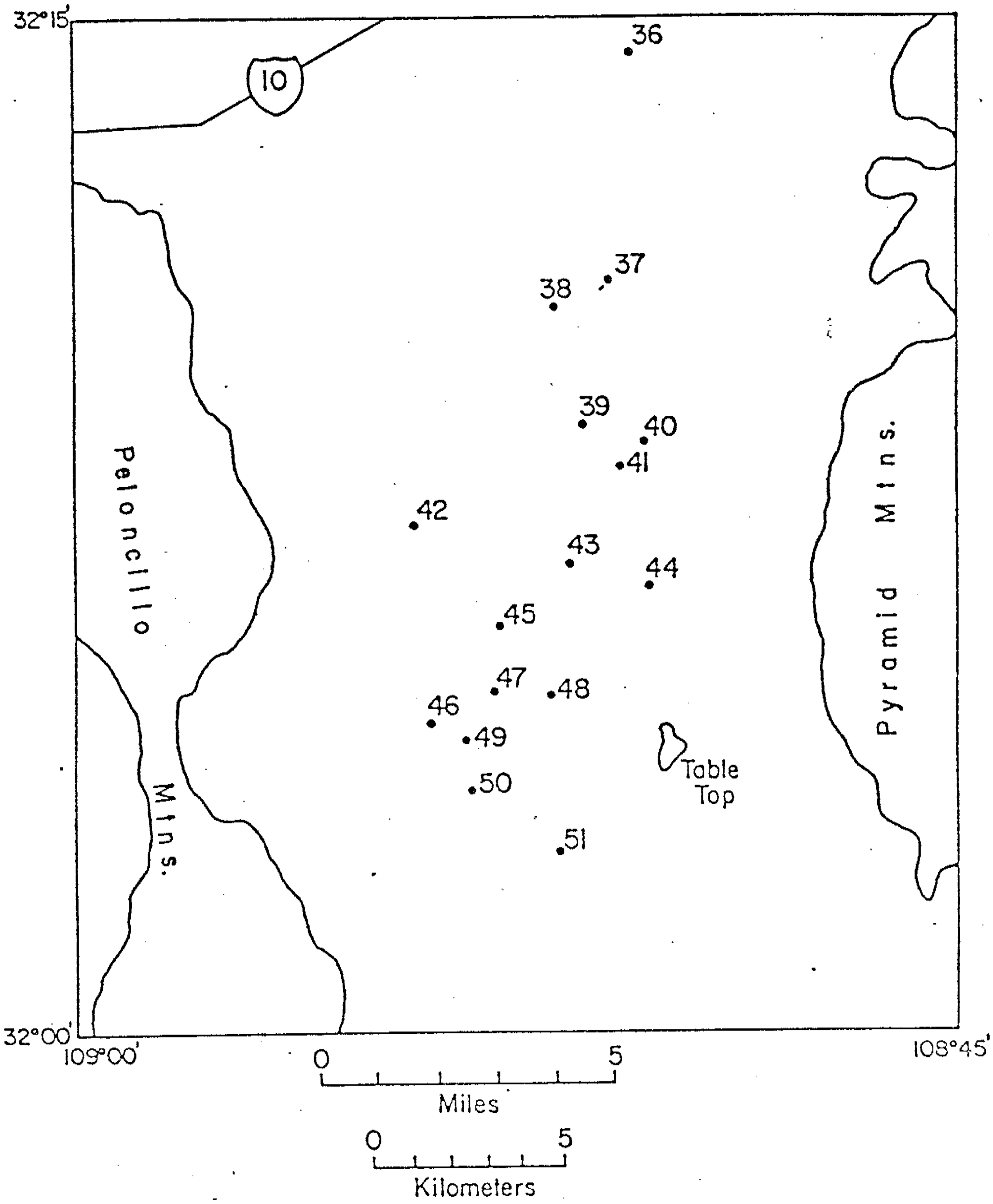

Farmington
Tres Piedres
Questa
1
2
3
4
Cuba
5
6
7
8
Los Alamos
Santa Fe
10
9
11
Las Vegas
Gallup
Thoreau
Bernalillo
Grants
Tucumcari
Santa Rosa
Los Lunas
Belen
Mountainair
Ft Sumner
Clovis
Portales
Quemado
Datil
Magdalena
12
Socorro
13
San Antonio
14-16
Reserve
35
Carrizozo
Glenwood
34
33
30-32
29
28
17-19
Truth or Consequences
Roswell
Kingston
Hillsboro
24
Santa Rita
25
Silver City
Hurley
27
26
Alamogordo
Loington
Hobbs
Lordsburg
20
21
22-23
Las Cruces
Deming
Carlsbad
36-51
Animas
Hachita
Columbus
25 0 25 50 75 100 km
25 0 25 50 75 mi

Figure 2. Location of wells sampled in the Animas Valley, Lightning Dock Known Geothermal Resource Area, New Mexico.


32°15'
32°00'
109°00'
108°45'
10
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
Peloncillo Mtns.
Pyramid Mtns.
Table Top
0
5
Miles
0
5
Kilometers

1980; Ellis, 1957; Giggenbach, 1980, 1981; Glover, 1970, Hulston and McCabe, 1962; Lyon, 1974; Nehring and D'Amore, 1981; Seward, 1974). A few studies have been made of gases in low temperature waters. Gas geothermometers were applied to gases from spring discharges for Wilbur Springs, California (Thompson, 1979). The gas chemistry of spring waters from the Shoshone Basin, Yellowstone, Wyoming was used to understand the hydrology and structure of the geothermal system (Truesdell, 1976). Helium in spring waters has been used to trace geothermal systems and to locate structures related to geothermal activity (Kahler, 1981; Mazor et al, 1973). Noble gases in thermal springs have been used to detect subsurface boiling (Mazor, 1975, 1977; Potter and Mazor, 1977).

The data and results of the present study has been published as the New Mexico Energy Institute Report "Assessment of Geothermal Reservoirs by Analysis of Gases in Thermal Waters" by Norman and Bernhardt (1982).

GEOTHERMOMETERS

A goal of the present study is to assess the use of gases as indicators of geothermal potential. Therefore, the gas data were compared with chemical geothermometers, the geothermometers being an estimate of subsurface temperature.

The concentration of silica in thermal waters has been used as a geothermometer, based on temperature-dependent solublities of quartz and other silica phases (Fournier and Rowe, 1966)). The quartz geothermometer can be expressed as:

$$T(°C) = \{1309/(5.19-\log(c))\} - 273.15,$$

where c is the concentration of silica in mg/kg (Fournier, 1980). The quartz geothermometer works best for waters with subsurface temperatures between 150°C and 250°C (Fournier, 1980). At lower temperatures chalcedony, amorphous silica, or other silica phases may control the concentration of silica in a thermal water. The geothermometer is easily effected by dilution, giving lower temperatures.

The Na/K ratio can be used as a geothermometer and is based on observed variations with temperature of the concentrations Na and K in thermal waters (Fournier and Truesdell, 1973). The geothermometer is based on a model reaction:

$$K^+ + \text{Na-feldspar} = Na^+ + \text{K-feldspar}.$$

Taking the activities of the solid phases to be unity, the equilibrium constant for the reaction is:

$$\mathrm{Log}(K1) = \mathrm{Log}(Na^+/K^+),$$

where Na+/K+ is the ratio between the activities of Na and K in the thermal water. Most thermal waters can be considered as dilute solutions, and the ratio of the activities can be approximated by the ratio of the molarities. The ratio can also be expressed in mass concentrations by the conversion:

mg/liter = molarity X molecular weight/1000.

The temperature dependence of the equilibrium constant is given by the Gibbs-Helmholtz equation:

$$d\text{Log}(Kp)/dT = H/(2.303*R*T),$$

where T is the temperature in K, R is the gas constant, H is the enthalpy change at T, and Kp is the equilibrium constant of the reaction. A geothermometer was calculated using field, theoretical, and experimental data:

$$T(^\circ C) = \{1217/(\text{Log}(Na+/K+) + 1.483)\} - 273.15,$$

where the concentration of Na amd K are in mg/kg (Fournier, 1979). The geothermometer generally gives good results for waters with subsurface temperatures greater than 150°C, but gives anomalously high temperatures for high-calcium and low-temperature waters.

Fournier and Truesdell (1973) proposed a empirical geothermometer that takes in to consideration the effects of calcium on the aluminium silicate exchange reactions. The model exchange reaction can be written as:

Ca-plagioclase + Na+ = Na-Plagioclase + 1/2 Ca++,

where $\text{Log}(K2) = 0.5 * \text{Log}(Ca{+}{+}) - \text{Log}(Na+)$, and Ca++ and

Na+ are the activities of calcium and sodium repectively. The Na-K and Na-Ca exchange reactions can be combined, and the combined equilibrium constant expressed as:

$$\mathrm{Log}(K) = \mathrm{Log}(K1) + B * \mathrm{Log}(K2),$$

where B is dependent upon the stoichiometry of the reaction (Fournier and Truesdell, 1973). An empirical geothermometer was derived using chemical data from both thermal and oil field waters:

$$T = \{1647/\mathrm{Log}(K1) + B * \{\mathrm{Log}(K2) + 2.06\} + 2.47)\} - 273.15,$$

where the concentrations of Na+, K+, and Ca++ are in mg/kg Fournier and Truesdell, 1973). Fournier and Truesdell (1973) found that B=1/3 gave the best results for waters with suburface temperatures greater than 100°C, while B=4/3 gave the best results for waters with temperatures less than 100°C.

The Na-K and Na-K-Ca geothermometers are relatively insensitive to dilution if the thermal water is more saline than the non-thermal water mixing with it. Boiling may cause precipition of calcium carbonate resulting in temperatures calculated from the Na-K-Ca geothermometer to be too high.

Paĉes (1975) suggested that high pressures of carbon dioxide result in anomalously high temperatures calculated from the Na-K-Ca geothermometer for thermal waters less than 75°C. An empirical pCO2 correction to the Na-K-Ca geothermometer was proposed. Application of Paĉes correction to thermal waters in Iceland and in the Geysers-Clear Lake region, California, gave negative results (Arnorsson, 1979; Goff and Donnelly, 1978). Norman and Bernhardt (1982) found a relationship between carbon dioxide and Na-K-Ca temperature in New Mexico thermal waters similar to that of Paĉes, but attributed it to high CO2 being indicative of high subsurface temperatures.

METHODS OF INVESTIGATION

SAMPLING

Sampling Gases

The sampling apparatus consists of a 200 milliliter sample bypass and a 33 milliliter pyrex sample container (Fig. 3). The sample container is evacuated to $1X10^{-4}$ torr before sampling.

Figure 4 is a schematic diagram of the apparatus used to sample springs. The funnel is placed over the main zone of upwelling water and gas to obtain the most representative sample. A hand vacuum pump is used to maintain a vacuum on a two gallon polyethylene carboy, the vacuum drawing water from the spring through the sample bypass. Water is circulated through the bypass for several minutes to minimize air contamination. The valve between the bypass and the sample container (V2) is then opened, and a sample is drawn into the evacuated sample cylinder. Water and gas are allowed to flow through the sample container by opening valve 3. After several minutes, the valves are closed, and the sample container is refrigerated until it is analyzed.

Two methods were used to sample wells (Fig. 5). If there is a fitting or a sampling duct on the well discharge pipe, then the sample bypass is connected directly to it via a section of 1/2 inch o.d. nalgene tubing. Water flows

Figure 3. Schematic diagram of gas sampling apparatus. Sampling apparatus is made of pyrex and glass-body, high vacuum glass stopcocks used throughout.

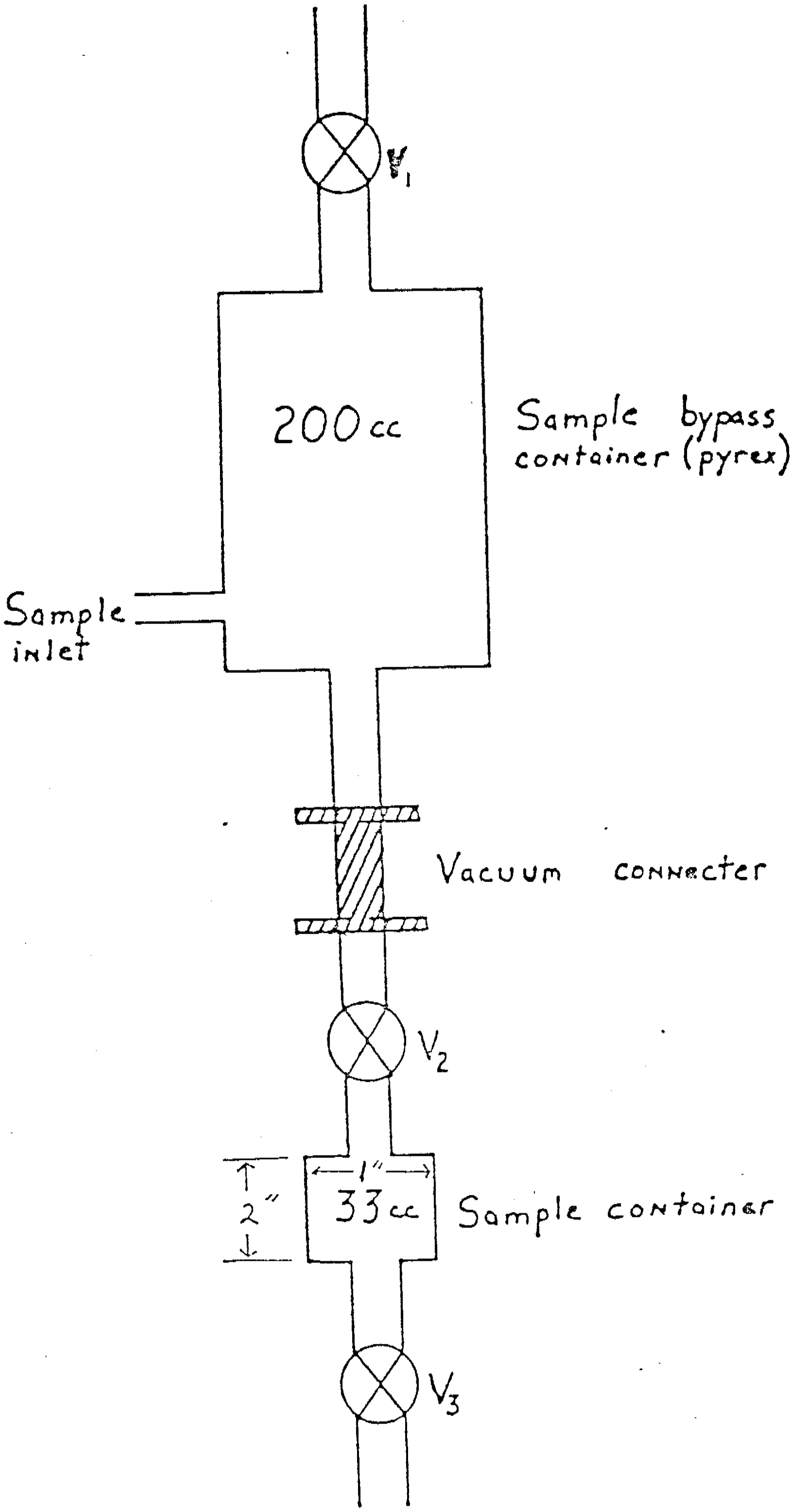
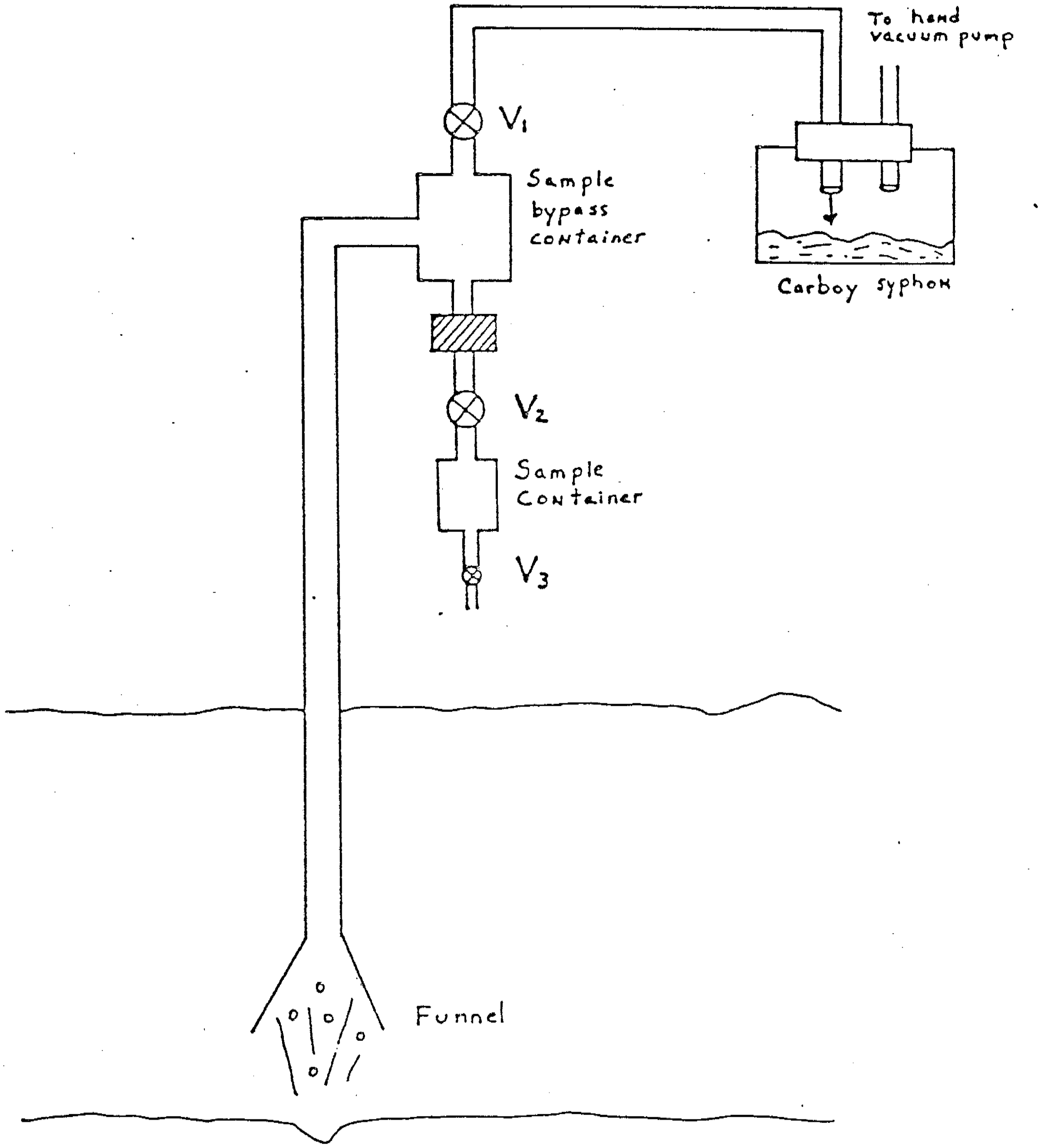

V1
200 cc
Sample bypass container (pyrex)
Sample inlet
Vacuum connecter
V2
1"
2"
33 cc
Sample container
V3

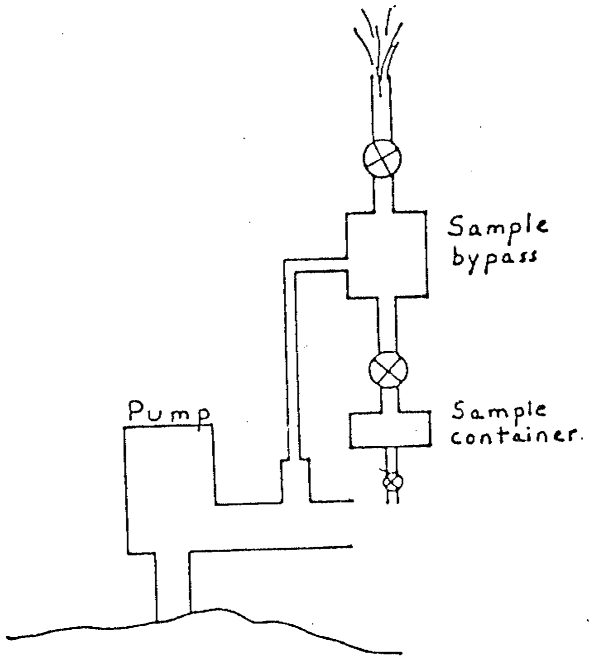
Figure 4. Sampling apparatus for springs.



Sampling a Spring

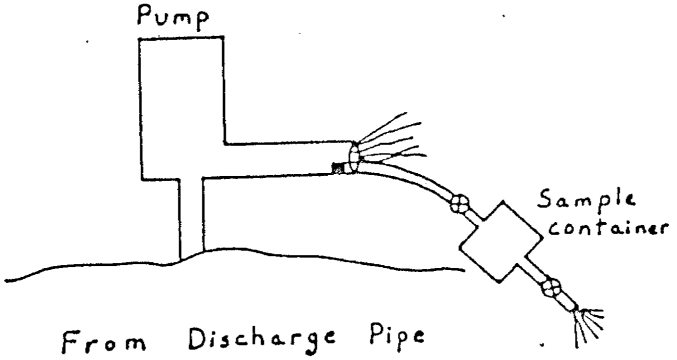
Figure 5. Sampling apparatus for wells.
a) Sampling from fitting on well discharge pipe
b) Sampling from end of well discharge pipe

Sampling Wells



From a ¼" - ½" Fitting

Fig. 5a.



From Discharge Pipe

Fig. 5b.

through the bypass, and the sample is obtained by the procedure previously discussed. If there is no fitting on the discharge pipe to obtain a sample, the sample is obtained directly from the end of the discharge pipe. Using this method, a representative sample is more difficult to obtain because the water may become air contaminated or gases may become separated from the water before the sample is taken. It is recommended that the second method be used only for wells with a temperature less than 50°C, unless the field party is protected from scalding water.

Collection of Water Sample

A 500 milliliter sample of each water was collected for cation analysis. Five milliliters of concentrated nitric acid was added to the sample to prevent precipitation of calcium, sodium, and potassium phases.

A separate 10 milliliter sample of each water was collected for silica analysis. The 10 milliliter sample was diluted with 90 milliliters of deionized distilled water to 100 milliliters to prevent the precipitation of silica.

ANALYTICAL TECHNIQUES

Analysis of Gases

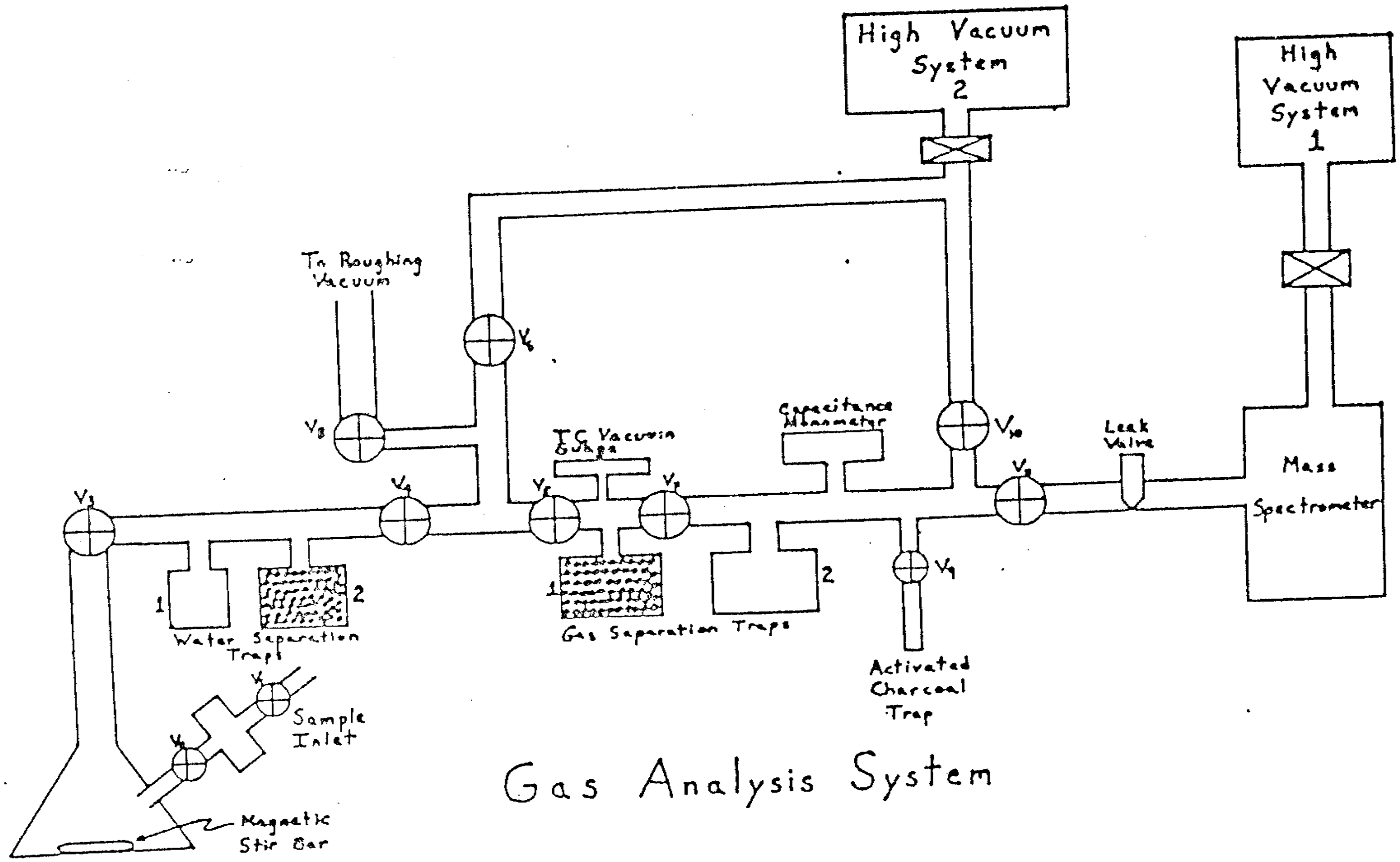
Analytical System

The analytical system consists of a sample inlet, a gas separation line, and a mass spectrometer (Fig. 6). The system is similar to the system developed by Dyck et al. (1975). The sample inlet and gas separation line are made of pyrex with high-vacuum, bellow-seal valves. Water separation trap 2 and gas separation trap 1 are filled with glass beads to provide a large surface area for condensing gases. The system is evacuated to $1X10^{-5}$ to $1X10^{-6}$ torr by an oil diffusion pump.

The pressure in the gas separation line is measured by a Baratron 221AHS absolute pressure tranducer (MKS Instruments). The instrument has a reported sensitivity of 0.5 to 1.5 pct. and a resolution of 0.001 torr.

The mass spectrometer is a Inficon IQ200 quadrupole with a electron multiplier detection system (Leybold-Heraeus). The reported sensitivity of the instrument is $1X10^{-13}$ torr. The instrument measures masses 1 to 200 over a concentration range of five orders of magnitude. The mass spectrometer was operated in the constant-delta mass mode and with an emission current of 2 ma. The electron multiplier was operated at 1200 volts. The analyzer was evacuated to a pressure of $1X10^{-8}$ to $1X10^{-9}$ torr using a oil diffusion pump. A small ion vacuum pump was used to maintain a high vacuum on the analyzer when the mass spectrometer was not in use.

Figure 6. Gas analytical system.



Gas Analysis System

Analytical Procedures

When the sample inlet and gas-separation line are evacuated to $1X10^{-5}$, the water-separation traps are cooled with a dry ice - alcohol mixture, and the gas-separation traps are cooled with liquid nitrogen. The sample is injected into the sample inlet by opening the valve between the inlet and the sample container (V3). After several minutes of boiling, the sample being agitated by a magnetic stir-bar, the sample is degassed, and the water freezes. The pressure stabilizes in twenty minutes. The analysis is carried out in three steps, summarized in Table I.

TABLE I

Outline of Analytical Steps

Step	Procedure	Fraction Analyzed	Gases Analyzed
1	Condensation of Sample in Liquid N2 trap	noncondensable	H_2, CH_4, He, Ar, Kr, N_2, O_2, NO
2	Condensation on Activated Charcoal	noncondensable	He, Ne, Ar, N_2
3	Evaporation of Liquid N_2-Condensed Gases	condensable	CO_2, H_2S, NH_3, Hydrocarbons

A sample of the noncondensable gas is introducted into the mass spectrometer by opening the leak valve. The amplitudes of the mass spectra are recorded. Then the activated charcoal trap is cooled by liquid nitrogen and is opened to the gas sample. The trap absorbs the reactive gases and the heavy noble gases, thereby increasing the relative concentration of the lighter rare gases. This is necessary to reduce the interference of the argon-20 peak on the neon-20 peak and to enhance the helium peak for low concentrations of helium. Helium, neon, argon, and nitrogen are measured in the depleted noncondensable gases. The gases are pumped away, and the liquid nitrogen traps are replaced by dry ice - alcohol traps. The condensed gases are released and measured.

The condensed gases are pumped away. The charcoal trap is heated to 80°C, releasing the absorbed gases. Infrared lamps heat the water traps, and the water condenses in the sample inlet. The sample inlet is dried. A new sample is attached to the system and is run when the pressure drops below $1X10^{-5}$ torr.

Calculation of Gas Compositions

The net mass-spectra is obtained by subtracting the background from the measured spectra. The gas composition is calculated with a computer using a least-squares matrix solution routine, developed for the system, that compares the mass spectra with the cracking outlines of known gases. The cracking outlines of the gases $H2$, $CO2$, CO, COS, $N2$, $NH3$, NO, $N2O$, $NO2$, $H2S$, $SO2$, $CL2$, $F2$, He, Ne, Ar, Kr, $CH4$, $C2H6$, $C3H8$, and $C6H12$ were determined by introducing pure, standard gases into the mass spectrometer. The sensitivities of the gases relative to nitrogen were determined by measurement of known mixtures of each gas with nitrogen. The gas compositions of each extraction step, along with the pressures and the volumes of the gas line, are used to calculate the gas composition of the total sample. The volume of water is measured and used to calculate the concentration of the gases in solution.

Analysis of Water Samples

The analytical techniques used in the analysis of water samples are summarized in Table II.

TABLE II

Analytical Techniques for Water Analysis

Element	Technique	Sensitivity*
Na	atomic absorption (Perkin Elmer Model 303)	0.015 ppm
K	atomic absorption (Perkin Elmer Model 303)	0.04 ppm
Ca	EDTA direct titration	0.1 ppm
SiO2	molybdate-yellow colorimetric method	0.1 ppm

* Na, K (Standard conditions, Perkin-Elmer); Ca, SiO2 (Smith, 1982, Personal Commun.)

SOURCES OF UNCERTAINTY

A goal of this study is to relate measured gas compositions to conditions in the subsurface. Uncertainty can come from three sources: sampling uncertainty, analytical uncertainty, and uncertainty due to processes that affect the gas composition between the geothermal rerservoir and the surface.

Sampling Uncertainty

Air contamimation of a gas sample was a problem that could not always be avoided. The sampling device was designed to minimize air contamination, but air can be added to a thermal water before a sample is taken. This was especially troublesome when the sample was taken directly from a well discharge pipe, because air in the discharge pipe can be mixed with the water by action of the well pump. Air contamination will result in an increase of the measured concentration of the atmospheric gases. The non-reactive atmospheric gases (N2, Ne, Ar, Kr) and oxygen are most affected by air contamination. Helium and carbon dioxide are found in excess of air saturation in most New Mexico thermal waters, and air contamination could result in small errors in their measured concentrations. Air contamination also can result in the oxidation of reduced gas species (e.g., hydrogen sulfide, methane). It is difficult to evaluate the errors due to air contamination because the expected values of concentration vary over a range of values, depending on the temperature and elevation of recharge into the groundwater zone. The uncertainty due to air contamination in the waters studied are given in Table III.

TABLE III

Uncertainty Due to Air Contamination

Gas	Air Sat. at 1500m, 10°C (cc(STP)/liter)*	Number of Samples in Excess of Air Sat.	Range of Error (Pct.)	Median Error (Pct.)
N_2	12	16	8 - 210	21
Ne	1.7×10^{-4}	17	6 - 188	47
Ar	0.32	12	3 - 91	19
Kr	7.5×10^{-5}	15	11 - 290	73
O_2	6.5	3	3 - 85	85

* Volumes have been recalculated at temperature = 0°C and pressure = 1 atmo. (STP). Sources of gas solubilities and atmopheric pressure with elevation: Herzberg and Mazor (1979); CRC Handbook of Chemistry and Physics, 40th ed. (1960).

The air-saturation concentration of the gases at 1500 m and 10°C is taken as an average expected for New Mexico thermal waters. Air contamination was approximately corrected by subtracting the excess nitrogen above 12 cc(STP)/liter, and subtracting the excess oxygen, helium, neon, argon, and krypton relative to their atmospheric ratios with nitrogen. The gas data used in this study were corrected for air contamination except where the uncorrected data is used to show the effects of air contamination.

Analytical Errors

Extraction of Gases

The close agreement between measured concentrations of the atmospheric gases (N2, Ne, Ar, Kr) and those expected for air saturation suggests that the technique used in this study to extract gases from water is nearly 100 pct. efficient. Studies by Dyck et al.(1976) demonstrated that the extraction of gases is nearly 100 pct. using this technique.

Measurement of Pressures

Pressures of the noncondensable fraction of gases typically range from 0.15 - 0.35 torr. Using the sensitivity of the capacitance manometer, the error in the pressure measurements is less than 1 pct.. The pressure of the depleted noncondensable fraction is typically 0.005 torr, giving a error of 20 pct.. Pressure of the condensible fraction typically ranges from 0.2 to 10 torr, and has an error of less than 5 pct..

Calculation of Gas Composition

Five analyses of Socorro tap water are given in Table IV.

TABLE IV

Analyses of Gases Dissolved in Socorro Tap water

Gas	Mean ± std. dev. (cc(STP)/liter)	Precision (Pct.)	Theoretical Value (cc(STP)/liter) at 1500m, 20°C
N2	11 ± 0.3	2.4	10
O2	5.8 ± 0.8	13	5.3
NO	0.045 ± 0.014	40	$1.8X10^{-4}$
CO2	1.2 ± 0.3	25	0.23
He	$(3.5 \pm 1.3)X10^{-5}$	36	$3.8X10^{-5}$
Ne	$(1.7 \pm 0.2)X10^{-4}$	11	$1.6X10^{-4}$
Ar	0.35 ± 0.04	11	0.27
Kr	$(7.0 \pm 1.1)X10^{-5}$	15	$6.0X10^{-5}$

The precision of the analysis for gases of high to moderate concentrations (N2, O2, Ar) ranges from 2.4 to 13 pct., and for gases of low concentrations (He, Ne, Kr, NO) from 11 to 40 pct. The precision of carbon dioxide and helium is 25 pct. and 36 pct. respectively, but most thermal waters in New Mexico have higher carbon dioxide and helium concentrations and the precision is expected to be higher.

Uncertainty Due to Subsurface or Near Surface Processes

As a thermal water comes in contact with the atmosphere, gases may be lost because the gases are no longer in equilibrium with the atmosphere. This is a major problem in sampling thermal spring waters. The reasons for this will be discussed in more detail in the section on the origin of gases. The uncertainty due to loss of gases in New Mexico thermal waters are summarized in Table V.

TABLE V

Uncertainty Due to Loss of Gases

Gas	Air Sat at 1500 m, 30°C. (cc(STP)/liter)	Number of Samples Below Air Sat.	Range of Uncertainty (Pct.)	Median Uncertainty (Pct.)
N2	8.3	14	4 - 100	31
Ne	1.5×10^{-4}	22	7 - 61	33
Ar	0.23	15	4 - 73	17
Kr	4.8×10^{-5}	24	2 - 91	54

As a thermal water flows toward the surface, a gas phase may separate from the aqueous phase. The gas phase, being less dense, will ascend faster than the aqueous phase enriching the near surface waters. Four samples, all from bubbling springs, had extremely high gas concentrations. It was assumed that the high gas concentrations were due to this process. The excess gas ranges from 240 pct. to 620 pct. of the air saturation values with a median of 420 pct.. A gas-enrichment factor was calculated by dividing the measured concentration of nitrogen by 12 cc(STP)/liter. The other gases were corrected by dividing their concentration by this factor. This method gives reasonable results: the corrected concentration of the non-reactive atmospheric gases (Ne, Ar, Kr) are near their expected air-saturation values. The data used in this study have been corrected for the excess gas.

Boiling of a thermal water will result in a decrease in the concentration of gases in the residual thermal water and an enrichment of gases in steam. The concentrations of nitrogen, neon, argon, and krypton in the Animas Valley hot well were 0.001 to 0.005 of their expected air saturated concentrations; the low gas concentrations are attributed to loss of the gases during subsurface boiling.

Uncertainty in Chemical Analysis

The uncertainty in the analyses of Na, K, Ca, and SiO2 are given in Table VI.

TABLE VI

Uncertainty in Chemical Analyses

Element	Detection Limit	Uncertainty
Na	0.015 ppm	Less than 1 pct.
K	0.04 ppm	Less than 5 pct.
Ca	0.1 ppm	Less than 5 pct.
SiO2	0.1 ppm	Less than 5 pct.

The chemical geothermometers are relatively insensitive to errors in the chemical analyses because the geothermometers use the log of the concentrations. Assuming a worst-possible case of an error of 25 pct. will result in a difference of 10°C to 15°C in the temperature calculated from the geothermometers over the range of 50°C - 250°C.

RESULTS

The ranges of gas concentrations measured in New Mexico thermal waters are given in Table VII. The data is not normally distributed, and the median and mid-range spread are used instead of the mean and standard deviation to give better point estimates of the central tendency and variance.

TABLE VII

SUMMARY OF MEASURED GAS CONCENTRATIONS IN NEW MEXICO THERMAL WATERS

Gas	Number of Measurements	Range (Uncorrected)
N2	53	$5.8\text{X}10^{-3}$ - 86
O2	52	0 - 21
He	53	$1.7\text{X}10^{-5}$ - 0.67
Ne	48	$5.4\text{X}10^{-6}$ - $1.0\text{X}10^{-3}$
Ar	53	$3.4\text{X}10^{-5}$ - 1.7
Kr	48	$2.4\text{X}10^{-7}$ - $3.3\text{X}10^{-4}$
H2	1	
H2S	12	0 - 1.8
CO2	53	0.063 - 1500
CH4	51	$2.0\text{X}10^{-5}$ - 9.8
NH3	11	0 - 0.17
NO	49	$3.3\text{X}10^{-3}$ - 0.18

All concentrations in cc(STP)/liter

* Mid-Range Spread = 75% Quartile - 25% Quartile

TABLE VII

Range[1] (Corrected)	Median	Mid-Range Spread*
5.[illegible]X10^{-3} - 17	12	4.0
0 - 6	2.2	4.0
1.[illegible]X10^{-5} - 0.1	8.0X10^{-4}	2.9X10^{-3}
5.[illegible]X10^{-6} - 1.7X10^{-4}	1.6X10^{-4}	1.5X10^{-4}
3.[illegible]X10^{-5} - 0.32	0.27	0.11
2.[illegible]X10^{-7} - 7.5X10^{-5}	5.7X10^{-5}	5.1X10^{-5}
	0.013	
0 - 1.8	0.10	0.28
0.063 - 1500	4.6	13.4
2.[illegible]X10^{-5} - 9.8	0.29	0.35
0 - 0.17	9.3	44.5
3.[illegible]X10^{-3} - 0.07	1.4X10^{-2}	1.8X10^{-2}

1. Corrected for air contamination and gas enrichment.

THE ORIGIN OF GASES

Introduction

The Atmosphere-Water-Rock System

The gas composition of a water reflects its history in the hydrologic cycle and is a result of a variety of chemical reactions and physical processes occuring in the atmosphere-water-rock system (Fig. 7).

In applying thermodynamic models to natural water systems, the assumption is made that the system is in chemical equilibrium. Natural water systems are flow systems, and the system may or may not be described by equilibrium. The time invariant state of a flow system is defined as the steady state (Stumm and Morgan, 1970). Steady state conditions can be approximated by equilibrium when the flow rates of the system are small relative to the rates of chemical reaction. This condition is likely to prevail in groundwater systems (Stumm and Morgan, 1970), and equilibrium models have been applied successfully to the gas chemistry of geothermal systems (Ellis, 1957; Giggenbach, 1980, 1981; Nehring and D´Amore, 1981; Nuti et al., 1980; Seward, 1974).

A thermodynamic model can be developed for the atmosphere-water-rock system similar to that of Stumm and Morgan (1970) (Fig. 8). The thermodynamic model consists of a gas phase, a aqueous solution phase, and one or more solid

Figure 7. Hydrologic cycle in a hypothetical geothermal system (After Freeze and Cherry, 1979; White, 1968). Small errows represent flow path of water in the hydrologic system.

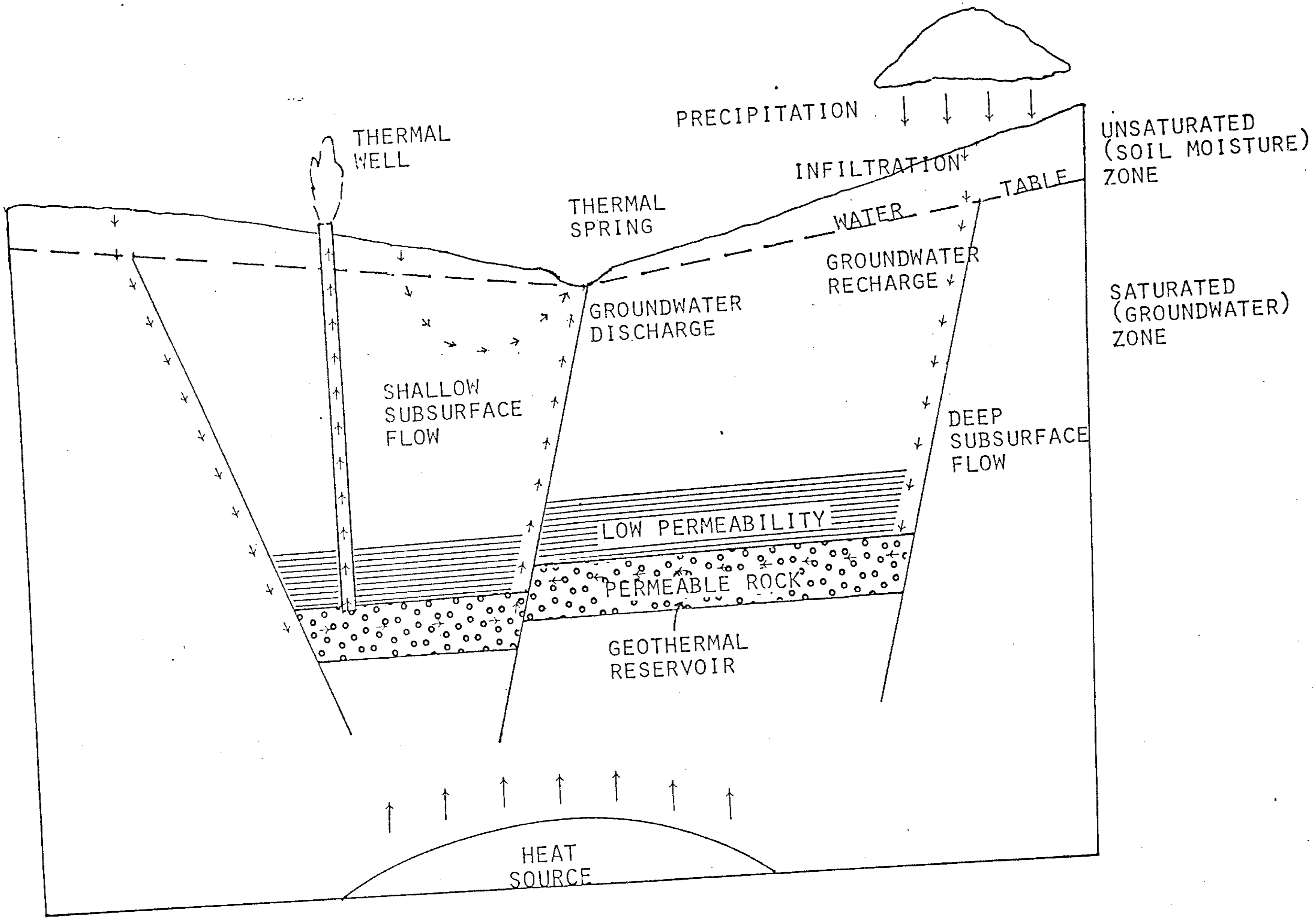
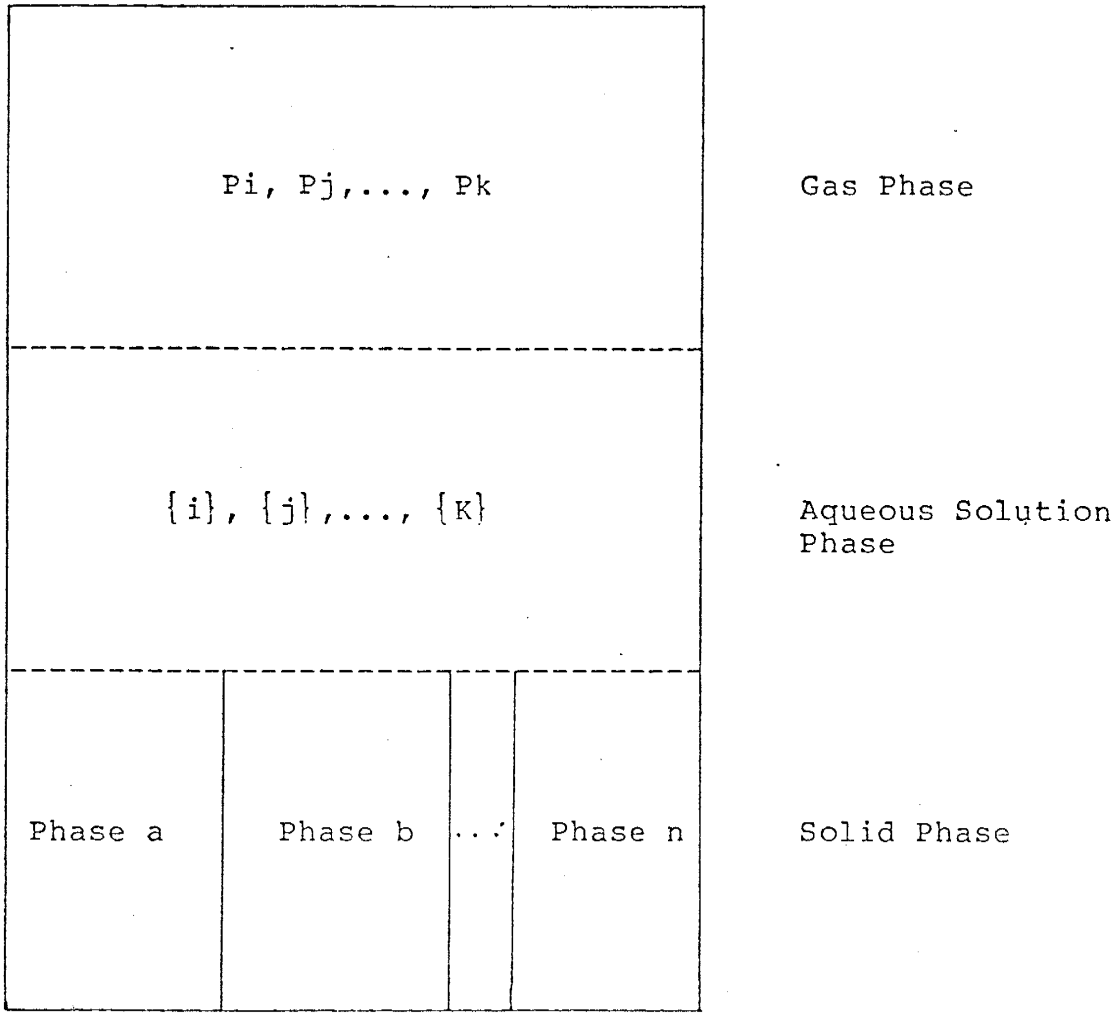

PRECIPITATION
THERMAL
WELL
INFILTRATION
THERMAL
SPRING
WATER
TABLE
UNSATURATED
(SOIL MOISTURE)
ZONE
GROUNDWATER
RECHARGE
SATURATED
(GROUNDWATER)
ZONE
GROUNDWATER
DISCHARGE
SHALLOW
SUBSURFACE
FLOW
DEEP
SUBSURFACE
FLOW
LOW PERMEABILITY
PERMEABLE ROCK
GEOTHERMAL
RESERVOIR
HEAT
SOURCE

Figure 8. Generalized thermodynamic model of a natural water system (After Stumm and Morgan, 1970).

Pi is the partial pressure of the ith component in the gas phase; The sum of Pi is equal to the total pressure of the gas phase.

{i} is the activity of the ith component in the aqueous phase; the sum of {i) is equal to the total concentration of components in the aqueous phase.

Phase a is the ath solid component of the solid phase; the sum of the component defines the composition of the solid phase.


Pi, Pj,..., Pk
Gas Phase
{i}, {j},..., {K}
Aqueous Solution Phase
Phase a
Phase b
...
Phase n
Solid Phase

phases. The gas phase is defined by the partial pressure of the gases in the gas phase. The aqueous solution phase is defined by the activity of the consituents in the aqueous solution phase. In dilute solutions, the activity of the consituents can be approximated by concentration of the consituents in solution. The solid phase is defined by the mineral composition of the solid phase and the activities of components in the mineral phases.

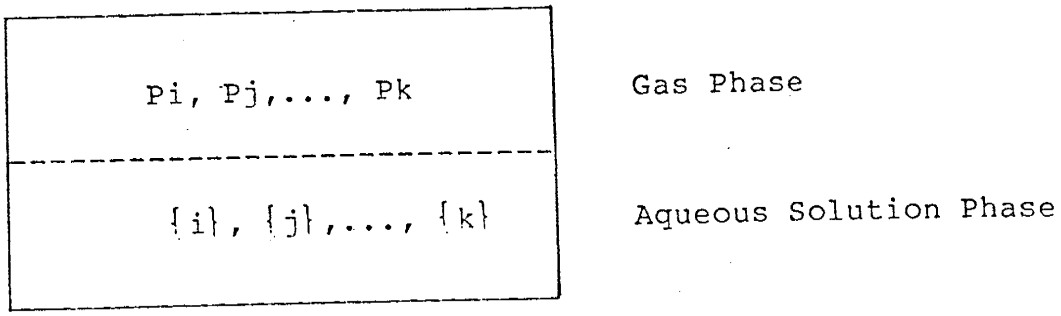
It is possible to isolate subsystems of this thermal dynamic model when considering particular parts of the hydrologic cycle to describe the interactions within the atmosphere-water-rock system (Fig. 9). In considering gases dissolved in groundwaters, the simplest system consists of a gas phase and an aqueous solution phase (Fig. 9a). This subsystem can be used to describe the portion of the hydrologic cycle where equilibrium exists at the atmosphere - water interface. Surface water is open to exchange of gas with the atmosphere. The concentration of a gas in solution depends on the temperature of the water and the partial pressure of the gas in the atmosphere. The concentration of a gas in water and the partial pressure of the gas in the atmosphere are related by Henry's Law:

$$\{gas\} = K * P,$$

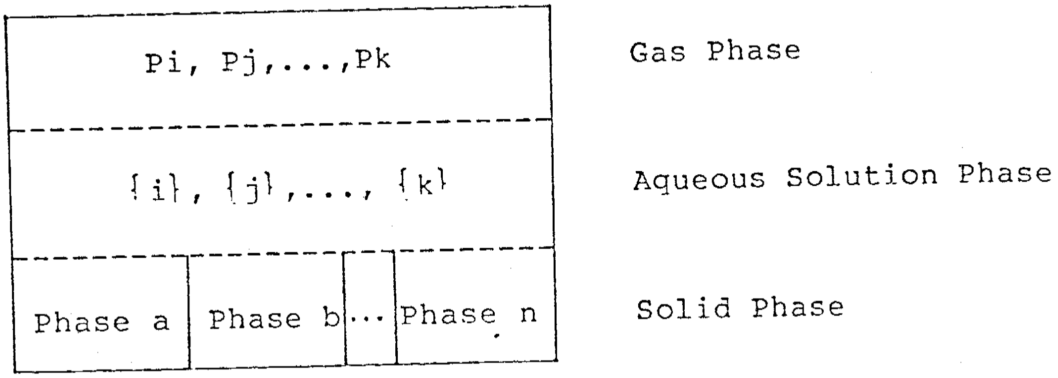
where {gas} is the concentration of a gas in aqueous solution, K is the Henry's Law coefficient at the

Figure 9. Subsystems of the general thermodynamic model of a natural water sysem (After Stumm and Morgan, 1970). Symbols are defined in Fig. 8.

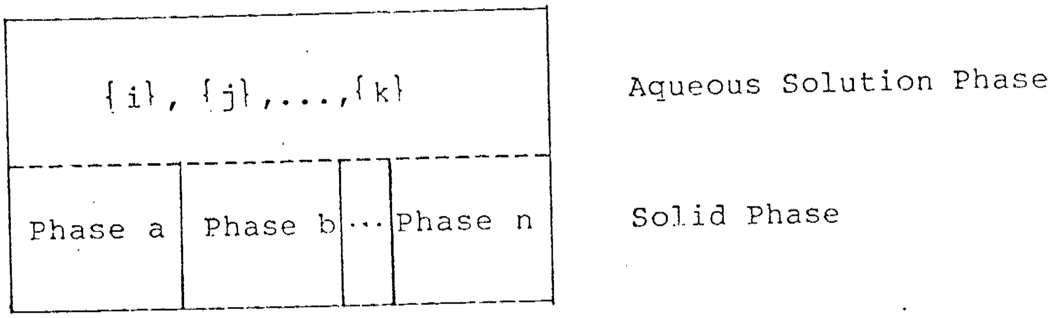
(a)


Pi, Pj,..., Pk
Gas Phase
{i}, {j},..., {k}
Aqueous Solution Phase

(b)


Pi, Pj,...,Pk
Gas Phase
{i}, {j},..., {k}
Aqueous Solution Phase
Phase a
Phase b
...
Phase n
Solid Phase

(c)


{i}, {j},...,{k}
Aqueous Solution Phase
Phase a
Phase b
...
Phase n
Solid Phase

temperature of the water, and P is the partial pressure of the gas in the atmosphere. The concentrations of gases in the atmosphere and in water in equilibrium with the atmosphere are given in Table VIII.

As water infiltrates into the soil zone and encounters the water table, the water is still in contact with the atmosphere through the gases in the pore spaces of the soil. This part of the atmosphere-water-rock system can be represented by subsystem b (Fig. 9b). The aqueous phase reacts with the solid phase and gases can be added to or removed from the aqueous phase, but the gas composition of the aqueous phase is still fixed by the composition of the atmosphere.

When water circulates below the water table into the saturated groundwater zone, it is no longer open to exchanges of gas with the atmosphere. This part of the system can be represented by subsystem c (Fig. 9c). The changes in the gas composition will depend upon whether a gas is inert or reactive and whether there are radiogenic or juvenile inputs of the gas into the system.

The concentrations of the inert gases, such as nitrogen, neon, argon, and krypton, are fixed by the partial pressures of these gases in the atmosphere, and should not change as the water circulates in a geothermal system. The composition of these gases, when sampled, should reflect the the temperature and composition of the atmosphere where the

TABLE VIII

CONCENTRATION OF ATMOSPHERIC GASES IN WATER

Gas	Concentration in Air*	Concentration in Water+			
		1000 m. Elevation		3000 m. Elevation	
		10°C	30°C	10°C	30°C
N2	0.79	12	8.2	10	6.9
O2	0.21	6.4	4.3	5.4	3.7
He	5.2×10^{-6}	3.9×10^{-5}	3.5×10^{-5}	3.2×10^{-5}	3.0×10^{-5}
Ne	1.8×10^{-5}	1.7×10^{-5}	1.5×10^{-5}	1.4×10^{-4}	1.2×10^{-4}
Ar	9.3×10^{-3}	0.33	0.21	0.27	0.18
Kr	1.1×10^{-6}	7.4×10^{-5}	4.6×10^{-5}	6.2×10^{-5}	3.9×10^{-5}
CO2	3.3×10^{-4}	0.33	0.18	0.28	0.15
CH4	2.0×10^{-6}	6.0×10^{-6}	4.6×10^{-6}	5.0×10^{-6}	3.9×10^{-6}
NO	5.0×10^{-7}	2.4×10^{-5}	1.6×10^{-5}	2.0×10^{-5}	1.4×10^{-5}

* Concentration in mole fraction, Source: CRC Hanbook of Chemistry and Physics, 58th ed.

\+ Concentration in cc(STP)/liter, Source of gas solubities and atmospheric pressures with elevation: Herzberg and Mazor (1979); CRC Handbook of Chemistry and Physics, 40th ed.

water infiltrated the groundwater zone.

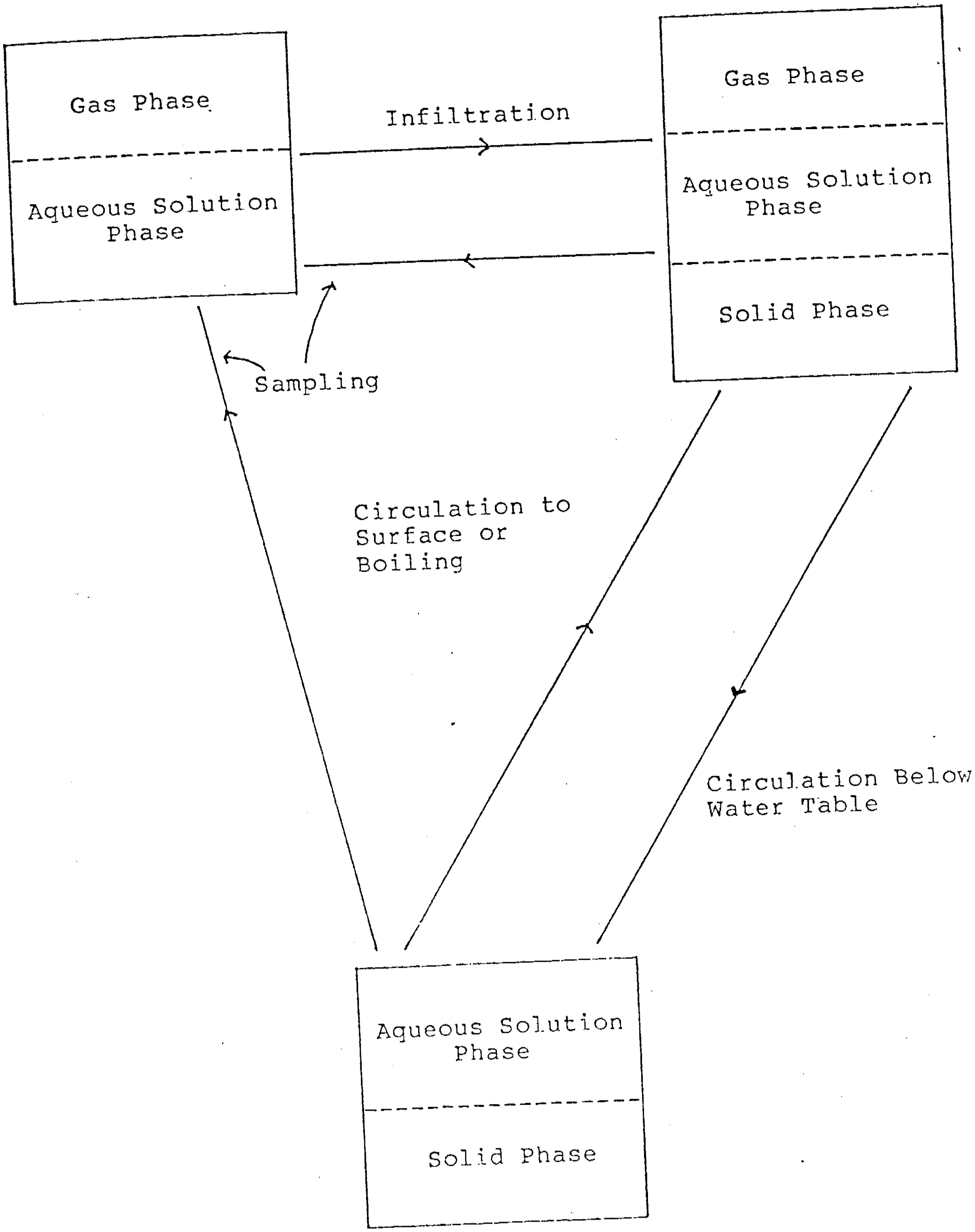
The concentration of reactive gases, such as carbon dioxide, methane, hydrogen, hydrogen sulfide, and ammonia, depends on the chemistry, temperature, and flow rate of the aqueous phase, the water-rock reactions that occur, and whether or not chemical equilibrium is obtained. Several model water-rock reactions and the gas concentration expected for chemical equilibrium are given in Table IX.

Boiling of the water will result in the formation of a gas phase (Fig. 9b). The composition of the residual aqueous phase will depend on the temperature of boiling, the amount of water vapor formed, and the partitioning of the gases between the aqueous and vapor phases.

When a groundwater disharges to the surface, it is again in contact with the atmosphere, and transfer of gases between the aqueous phase and the atmosphere can occur if the gases are no longer in equilibrium with the atmosphere. (Fig. 9b).

In summary, the gas composition of a water will depend upon the path through these various subsystems that is traveled within the hydrologic cycle (Fig. 10). In geothermal exploration, the chemistry of a thermal spring or a shallow thermal well is used to estimate the conditions of a geothermal reservoir at depth. It is assumed that the chemistry of these waters is representative of chemical equilibrium or near equilibrium conditions in the geothermal

Figure 10. Paths between the various subsystems of the general thermodynamic model of a natural water system.



Gas Phase
Aqueous Solution Phase
Infiltration
Gas Phase
Aqueous Solution Phase
Solid Phase
Sampling
Circulation to Surface or Boiling
Circulation Below Water Table
Aqueous Solution Phase
Solid Phase

TABLE IX

EQUILIBRIUM CONCENTRATIONS FOR GASES INVOLVED IN VARIOUS MODEL REACTIONS

Reaction

1 6montmor. + CO_2 + $8H_2O$ = calcite + 7kaolinite + 8qtz.

2 chlorite + 5calcite + $5CO_2$ = kaol. + qtz + dolomite + $2H_2O$

3 clinozoisite + $2CO_2$ + $2.5H_2O$ = 1.5kaolinite + 2calcite

4 plag. + CO_2 = clay + calcite

5 calcite + $2H^+$ = Ca^{++} + H_2O + CO_2 *

6 $H_2O = H_2 + 1/2O_2$

7 $FeS_2 + H_2 = FeS + H_2S$

8 $3FeS_2 + 2H_2 + 4H_2O = Fe_3O_4 + 6H_2S$

9 FeS_2 + H_2 + Al-silicate(H_2O) = Fe-Al-silicate + $2H_2S$

10 $FeS + 4H_2O = H_2 + 3H_2S$

11 $8Fe_3O_4 + SO_4^{=} + 2H^+ = 12Fe_2O_3 + H_2S$ **

12 $C + 2H_2 = CH_4$

13 $2C + 2H_2O = CO_2 + CH_4$ ***

14 $CH_4 + 4H_2 = CO_2 + 2H_2O$ ***

15 $N_2 + 3H_2 = 2NH_3$ ****

* pH = neutral + 0.5 pH
$Ca^{++} = 1X10^{-3}$ m

** pH = neutral ± 0.5 pH
$SO_4^{--} = 1X10^{-3}$ m

*** CO_2 buffered by reaction 2

**** N_2 = 10 cc(STP)/liter

All reactions involving hydrogen are buffered by reaction 6

TABLE IX

Gas	Concentrations (cc(STP)/liter)			
	50°C	100°C	200°C	300°C
CO2	0.1	3860	-	-
CO2	0.17	2.7	215	7225
CO2	3.0X10^{-3}	0.13	108	12850
CO2	-	4.0x10^{-4}	8.4	11990
CO2	7.2	23	78	69
H2	4.0X10^{-4}	6.4X10^{-3}	0.66	32
H2S	-	4.0X10^{-3}	1.0	272
H2S	2.0X10^{-3}	7.9X10^{-2}	2.0	143
H2S	1.0	2.6	20	164
H2S	0.013	0.17	3.4	73
H2S	1.4X10^{-3}	2.1X10^{-4}	1.2X10^{-4}	2.6X10^{-4}
CH4	1.9	6.0	85	-
CH4	50	9.5	2.0	1.7
CH4	3.0X10^{-3}	1.8X10^{-2}	0.45	8.2
NH3	7.0X10^{-3}	0.07	0.9	0.1

Sources of Data: Reactions 7,8,9,10,12,13,14,15 (Giggenbach, 1980); Reactions 1,2,3,4 (Giggenbach, 1981); Reaction 6 (Giggenbach, 1982), Reactions 5,11 (Helgeson, 1969) reservoir. The reaction rates of the constituents in solution must be slow relative to the time of upflow from the geothermal reservoir to the surface. The assumptions in applying chemistry of spring waters to the estimation of subsurface temperature are summarized by Fournier et al. (1974) and Ellis (1979).

Classification of the Gases

The gases measured in this study can be divided into four principle groups: 1) gases whose source is primarily the atmosphere (N2, Ne, Ar, Kr); 2) gases whose sources include the atmosphere and radiogenic decay (He, Ar); 3) gases whose sources include the atmosphere and water-rock interaction (CO2, NO); and 4) gases whose source is primarily water-rock interaction (H2S, SO2, H2, CH4, NH3).

NITROGEN, NEON, ARGON, AND KRYPTON

Data

The ranges of nitrogen, neon, argon, and krypton measured in New Mexico thermal waters are given in Table X.

Nitrogen, argon, and krypton in thermal well waters show a slight decrease in concentration at the 5 pct. level of significance with increasing subsurface temperatures calculated by the Na-K-Ca geothermometer (Norman and Bernhardt, 1982). The is no relation between these gases and temperature in the thermal spring waters.

TABLE X

MEASURED CONCENTRATIONS OF NITROGEN, NEON, ARGON, AND KRYPTON IN NEW MEXICO THERMAL WATERS *

Gas	Range	Median	Mid-Range Spread
Nitrogen	$5.8X10^{-3}$ - 37	12	5.0
Neon	$5.4X10^{-6}$ - $4.9X10^{-4}$	$2.2X10^{-4}$	$1.4X10^{-4}$
Argon	$3.4X10^{-5}$ - 0.61	0.27	0.11
Krypton	$2.4X10^{-7}$ - $2.9X10^{-5}$	$4.3X10^{-5}$	$6.7X10^{-5}$

* The concentrations are not corrected for air contamination; All concentrations in cc(STP)/liter.

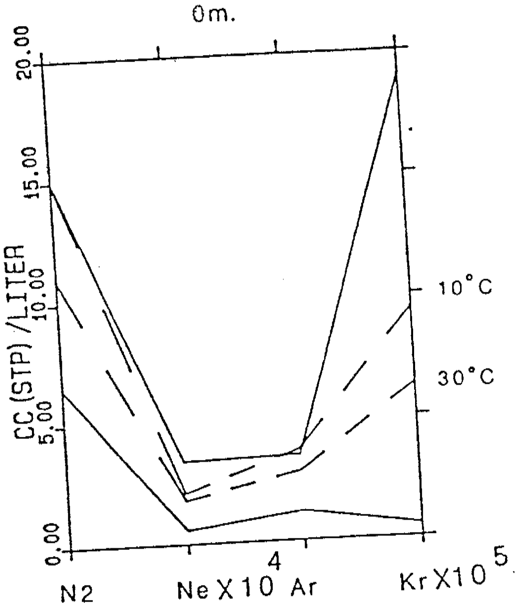
Discussion

Most of the analyses for nitrogen, neon, and argon in New Mexico thermal waters fall within or near the range expected for air-saturated waters (Figure 11). This is in agreement with other studies that have shown that the concentration of nitrogen and the noble gases is due to their solubility in water (Gunter, 1973; Herzberg and Mazor, 1979; Mazor, 1977, 1978; Mazor et al, 1973, 1974; Mazor and Wesserberg, 1965). Because the concentration of krypton is near the detection limit of the analytical system, the wide range of the krypton analyses is probably not significant.

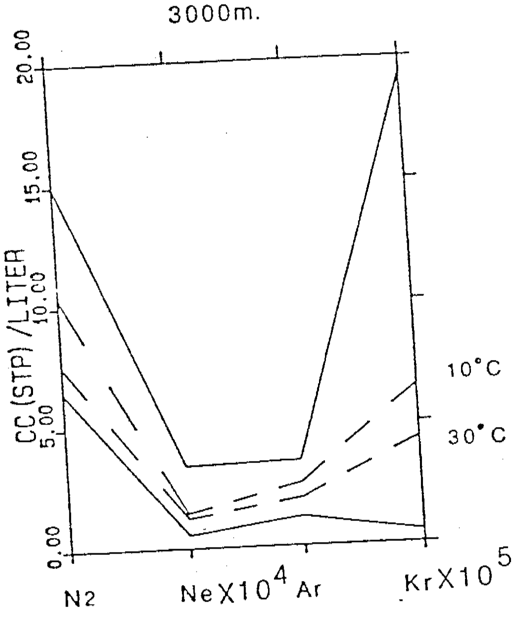
Several of the analyses of nitrogen, neon, argon, and krypton are below the air-saturation values. The loss of the gases can be explained either by boiling or by loss of gases due to a decreasing gas solubility with increasing

Figure 11. Range of Nitrogen, Neon, Argon, and Krypton measured in New Mexico thermal waters. The data not corrected for air contamination is used. The solid line enclose the range of gas analyses for most New Mexico Thermal Waters. A few extremme values were omitted to show the range of the majority of the waters. Dashed lines are the air saturation concentrations at 10°C and 30°C at sea level (a) and at 3000 meters (b).

a)


0m.
20.00
15.00
10.00
5.00
0.00
CC(STP)/LITER
10°C
30°C
N2
NeX10^4
Ar
KrX10^5

b)


3000m.
20.00
15.00
10.00
5.00
0.00
CC(STP)/LITER
10°C
30°C
N2
NeX10^4
Ar
KrX10^5

temperature.

The decrease in nitrogen, neon, and argon concentrations with the Na-K-Ca temperature is too slight to be attributed to subsurface boiling. The high Na-K-Ca temperature waters may be mixtures of boiled, gas-depleted water with non-depleted water.

When water, that was once in equilibrium with the atmosphere is heated in a geothermal system, the solublity of nitrogen, neon, argon, and krypton will decrease. The gases can be lost from a thermal water to the atmosphere when the thermal water discharges to the surface, because the gases are no longer in equilibrium with the atmosphere.

Many nitrogen, neon, argon, and krypton analyses are higher than expected from air saturation for reasonable recharge elevations. The excess gases can be attributted to air contamination of the gas sample (Phillips, 1982, personal communication). The trends due to air contamination can be calculated from techniques developed by Phillips (1981).

Application to Exploration

There is no application for nitrogen, neon, argon, and krypton in regional exploration for geothermal resources because the concentrations of these gases have little temperature dependence and because several processes may effect their concentration. The gases may be useful in studying a known geothermal resource, because the gas concentrations may be able to identify boiling in the system and to distinguish waters from different recharge areas. For example, noble gases have been used to calculate the temperature of boiling and deduce flow direction at the Larderello geothermal system, Italy (Mazor, 1978/79; Potter and Mazor, 1977) and to detect subsurface boiling in the Geysers - Clear Lake geothermal area and Lassen geothermal area, Northern California (Mazor, 1975, 1977; Potter and Mazor, 1977).

HELIUM

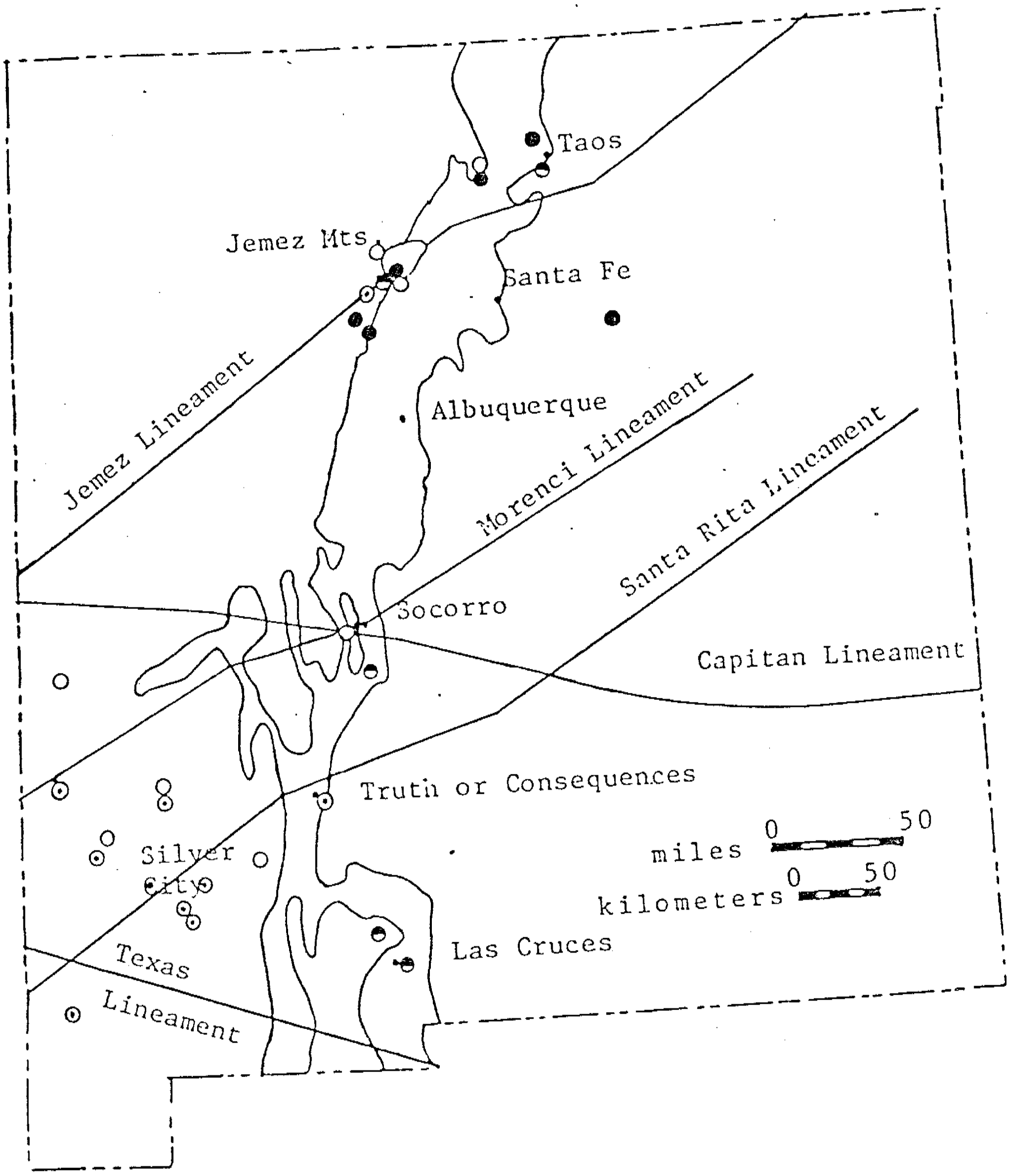
Data

The concentration of helium measured in New Mexico thermal waters ranges from $1.7\text{X}10^{-5}$ to 0.1 cc(STP)/liter, with a median of $8.0\text{X}10^{-4}$ cc(STP)/liter.

Thermal waters associated with the Rio Grande rift tend to have higher helium concentrations than thermal waters located off the rift (Fig. 12). The highest helium concentrations were found in thermal waters near the intersection of the Jemez Lineament with the boundaries of the Rio Grande rift.

At the 1 pct. level of significance, the concentration of helium in thermal well waters increases with increasing subsurface temperature calculated by the Na-K-Ca geothermometer (Norman and Bernhardt, 1982). There is no

Figure 12. Generalized map of the Rio Grande rift and major crustal lineaments (After Chapin et al., 1978). Data points are helium concentration of New Mexico thermal waters in cc(STP)/liter.



Helium Concentration

cc(STP)/Liter X 1000

> 10 ●

5 -10 ◒

1 - 5 ⊙

< 1 ○

correlation between helium concentration and the Na-K-Ca geothermometer in thermal spring waters (Norman and Bernhardt, 1982).

Discussion

Helium is found in excess of air saturation in all thermal waters sampled except for the Animas Valley hot well. The range of helium measured in New Mexico thermal waters is within the range observed in other thermal waters. (Mazor and Wasserburg, 1965; Craig et al, 1978; Mazor, 1972; Mazor et al, 1973; Mazor et al., 1974; Mazor, 1978/79; Wehlan et al., 1979). The excess helium in thermal waters is attributed to the leaching of radiogenically produced helium from country rock (Kahler, 1981). High temperatures enhance the leaching of helium from minerals and increase the mobility of helium (Mazor, 1977).

The time required to accumulate helium in groundwaters by radiogenic decay of uranium and thorium to the concentration observed in New Mexico thermal waters is summarized in Table XI. The ages are calculated assuming that all the helium produced goes into the water. Thus, these ages should be considered minimium values.

The ages of many geothermal systems are estimated to be on the order of 1,000 to 100,000 years (Ellis, 1979). White (1974) estimates th age of the Steamboat Springs, Nevada geothermal system to be on the order of 100,000 to

TABLE XI

TIME REQUIRED FOR ACCUMULATION OF HELIUM IN PORE WATERS IN THE RANGE OF HELIUM CONCENTRATIONS OF NEW MEXICO THERMAL WATERS

Helium Concentration (cc(STP)/liter)	Accumulation Time (years)	
	Average Granite*	"Hot" Granite+
$1.0X10^{-4}$	22,000	7,400
$1.0X10^{-3}$	360,000	120,000
$1.0X10^{-2}$	3,700,000	1,200,000
$1.0X10^{-1}$	37,000,000	12,000,000

Times for helium accumulation calculated from
$\text{He(cc/liter)} = d \text{ X } t(1.19X10^{-13} \text{ X } U + 2.88X10^{-14} \text{ X } Th)$
(Andrews and Lee, 1980)

d = density (g/cm3) of source rock
t = time (years)

* Average Granite: U = 5 ppm, Th = 20 ppm: Krauskopf (1967)

\+ Conway Granite, New Hampshire: U = 15 ppm, Th = 60 ppm: Rogers and Gathan (1965)

1,000,000 years. Logsdon (1981) estimates the age of the thermal waters in the Animas Valley, New Mexico to be on the order of 100,000 years. The Valles Caldera, New Mexico formed 1.1 million years ago (Goff and Grisby, 1982), and the caldera thermal waters would be younger than 1.1 million years. These ages are too short a period to explain helium concentrations in New Mexico thermal waters greater than 0.01 cc(STP)/liter.

It is possible that the helium-rich thermal waters in the Rio Grande rift are due to a locally high concentration of uranium in the crust. However, production rates of radiogenic helium calculated for a granite high in uranium and thorium are too low to account for the high helium concentrations (Table XI). The helium rich waters are associated with areas of high heat flow, which has been attributed to recent magmatic and tectonic activity and not to high radioactivity in the crust (Edwards et al., 1978). Therefore, it is unlikely that the high helium concentrations can be explained by high uranium and thorium concentrations.

Some of the helium in the thermal waters may result from circulation of the thermal waters in uranium rich sediments. None of the thermal waters studied, with the exception of the thermal waters in the Bosque Del Apache Game Refuge, are in the vicinity of known uranium mineralization. In general, most sedimentary rocks have uranium and thorium concentrations less than the Conway Granite (Table XI). However, it is not possible to determine the contribution of helium from this source to the waters studied.

Helium from geothermal reservoirs can migrate toward the surface along permeable faults and fractures (Kahler, 1981). Transport of helium may be three orders of magnitude more effective along faults then through surrounding country rock (Reimer et al, 1976). High helium has been detected over deep faults (Bulashevich and Bashorin, 1973; Datta, et al, 1980; Hinkle and Kilburn, 1980). Deep faults can transport helium derived from radiogenic decay from a large volume rock (Datta et al., 1980).

High 3He/4He raios were found in thermal waters from the Valles Caldera, Jemez Mountains (Craig, 1982, personal commun.). High 3He/4He ratios have been observed in other thermal waters and along deep faults (Bulashevich and Bashorin, 1973; Hinkle and Kilburn, 1980), and it is believed that the high ratios are characteristic of magmatic or mantle-derived helium (Craig et al., 1978, 1979; Gutsalo, 1975; Welhan et al, 1979; Barnes et al., 1981). It is possible that the high helium associated with other thermal waters located near the intersection of the Jemez Lineament and the Rio Grande rift could be due to input of mantle-derived helium.

The boundary faults of the Rio Grande rift could act as a conduit for deep, radiogenically derived helium and may explain the generally higher concentrations of helium observed in the rift thermal waters relative to the non-rift thermal waters. The intersection of the boundary faults of the Rio Grande and the Jemez Lineament may be especially favorable for the transport of crustal and possibly mantle helium.

Application to Exploration

Helium concentrations cannot be used directly to estimate temperatures of a geothermal reservoir because helium concentrations are controlled by other factors besides temperature. Helium in thermal waters is associated with deep faults and areas of high heat flow and may be used to locate areas favorable for geothermal resources.

CARBON DIOXIDE

Data

The concentration of carbon dioxide measured in New Mexico thermal waters ranges from 0.063 to 1500 cc(STP)/liter, with a median of 4.6 cc(STP)/liter.

In general, thermal waters along the Rio Grande Rift have higher concentrations of carbon dioxide than waters outside the rift.

At the 1 pct. level of significance, the concentration of carbon dioxide in thermal well waters was found to increase with subsurface temperatures calculated by the

Na-K-Ca geothermometer (Norman and Bernhardt, 1982). No correlation was observed between carbon dioxide concentrations in thermal spring waters and temperature (Norman and Bernhardt, 1982).

Discussion

Water in equilibrium with the atmosphere at 20°C can dissolve 0.27 cc(STP)/liter of carbon dioxide. All waters sampled, with the exception of the Upper Frisco Spring and the Animas Valley hot well, have carbon dioxide greater than the air-saturation value.

The excess carbon dioxide could come from several sources:

1) calcite - aluminum-silicate equilibria;
2) dissolution of carbonates;
3) breakdown of organic matterial; and
4) magma degassing.

The range of carbon dioxide measured in New Mexico thermal waters falls within the range expected for various calcite - aluminum-silicate equilibria (Table IX). The calculated carbon dioxide partial pressures for New Mexico thermal well waters with Na-K-Ca temperatures greater than 60 C are plotted on a mineral stablity diagram for calcium-aluminium-silicates (Fig. 13). The pCO2 of the waters was calculated using the Henry's Law coefficient at the Na-K-Ca temperature of the water, assuming the concentration of carbon dioxide measured in the thermal

Figure 13. Stability diagrams for calcium-aluminum-silicate (a) and feldspar-mica (b) (After Giggenbach (1981)). Data points from New Mexico thermal well discharges with Na-K-Ca temperatures greater than 60°C, pCO2, in atmospheres, was calculated at the Na-K-Ca temperature. Squares are data from Baca geothermal reservoir, Valles Caldera, New Mexico released by Union Geothermal (1981), octagons are data from New Mexico thermal waters sampled. The following reactions are considered in Figure 13a.

1 6montmorill. + CO_2 + $8H_2O$ = calcite + 7kaolinite + 8quartz

2 chlorite + 5calcite + $5CO_2$= kaolinite + qtz + dolomite +$2H_2O$

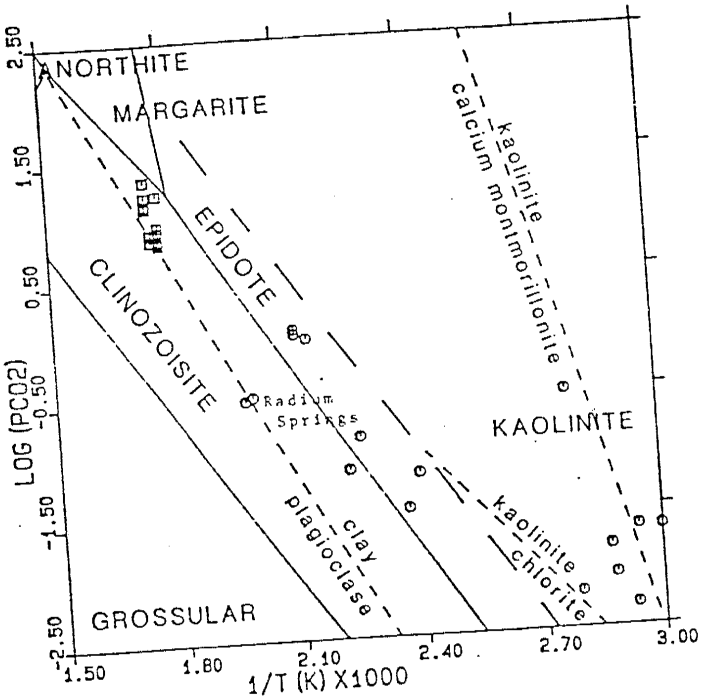
3 clinozoisite + $2CO_2$ + $2.5H_2O$ = 1.5kaolinite + 2calcite

4 3grossular + $5CO_2$ + H_2O = 2clinozoisite + 5calcite + 3quartz

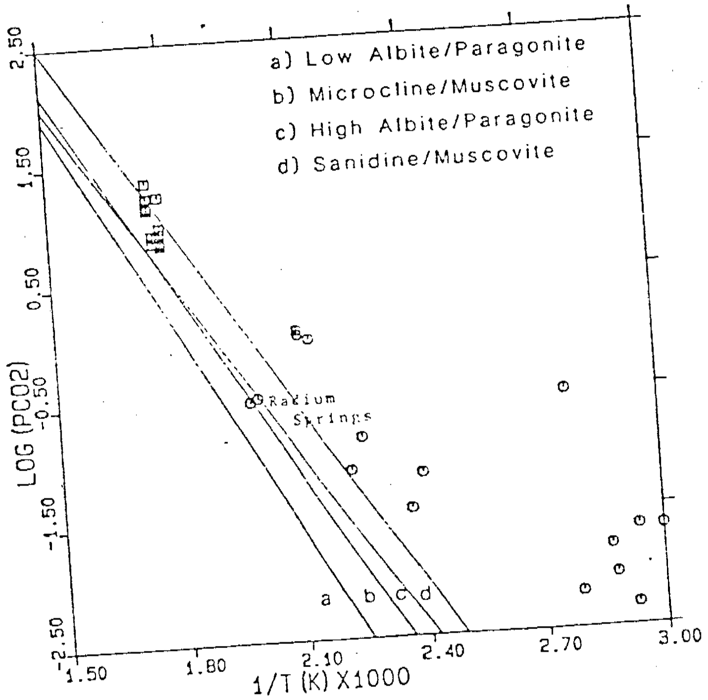
5 Plagioclase. + CO_2 = clay + calcite

Reactions 1 and 2 are from Helgeson (1969);
Reactions 3, 4, 5 are from Giggenbach (1981).

a)


ANORTHITE
MARGARITE
EPIDOTE
CLINOZOISITE
GROSSULAR
KAOLINITE
kaolinite
calcium montmorillonite
clay
plagioclase
kaolinite
chlorite
Radium Springs
LOG (PCO2)
2.50
1.50
0.50
-0.50
-1.50
-2.50
1.50
1.80
2.10
2.40
2.70
3.00
1/T (K) X1000

b)


a) Low Albite/Paragonite
b) Microcline/Muscovite
c) High Albite/Paragonite
d) Sanidine/Muscovite
a
b
c
d
Radium Springs
LOG (PCO2)
2.50
1.50
0.50
-0.50
-1.50
-2.50
1.50
1.80
2.10
2.40
2.70
3.00
1/T (K) X1000

waters is representative of the geothermal reservoir. The data points fall in two mineral fields: waters with Na-K-Ca temperatures greater than 140°C fall in the epidote field; waters with Na-K-Ca temperatures less than 140°C fall in the kaolinite field.

In the kaolinite field, the reaction boundaries between kaolinite-calcium montmorillonite and kaolinite-chlorite are plotted (Fig. 13a). The data from thermal waters with Na-K-Ca less than 70°C and log(pCO2) greater than -1.7 fall in the kaolinite stability field. The data from waters with Na-K-Ca temperatures greater than 70°C fall in the calcium montmorillonite stablity field.

The carbon dioxide data fall along the trend of alteration mineralogy with increasing temperature observed in many geothermal systems. Epidote is an important alteration mineral in high temperature waters and is found in the deeper and hotter parts of many geotheral systems (Browne, 1978; Ellis and Mahon, 1977; Giggenbach, 1981; Muffler and White, 1968; Rose and Burt, 1979). In the shallower and cooler portions of geothermal system, zeolites, montmorillonite clays, and kaolinite are major alteration minerals (Ellis and Mahon, 1977; Rose and Burt, 1979; Steiner, 1977). Kaolinite is most common in near surface alteration associated with acidic conditions (Rose and Burt, 1979; Steiner, 1977). The results of this study are consistant with studies of many other geothermal systems

orsson, 1979; Elders et al, 1979; Muffler and White,
68; Truesdell 1976).

The data from the Baca reservoir and from the Radium
rings area fall near Giggenbach's (1981) semiempirical
lagioclase/clay line (figure 13a) and feldspar-mica reaction
ines (Figure 13b). The data from New Zealand thermal waters
all near these lines, and Giggenbach (1981) suggested that
he plagioclase reaction is the most important mineral
uffer controlling carbon dioxide in the high temperature
New Zealand geothermal systems.

Therefore it is reasonable that the main control of
carbon dioxide in New Mexico thermal waters is by
temperature dependent calcite - silicate reactions, the
specific reaction depending on temperature.

Significant carbon dioxide can be added to a thermal
water by the hydrolysis of calcite (Table IX). The
concentration of carbon dioxide in thermal waters in the Las
Cruces area and in the Jemez Mts. is too high to be
accounted for by this reaction. Only thermal waters in the
Truth or Consequences area could have been derived from a
carbonate source.

Carbon dioxide from the breakdown of organic material
or from biologic processes may be added to some New Mexico
thermal waters. Without carbon isotope data, it is not
possible to distinguish organic from inorganic carbon
dioxide in the New Mexico thermal waters.

Application to Geothermal Exploration

Carbon dioxide is the best gas for use in geothermal exploration. Carbon dioxide is controlled by temperature dependent equilibria and may be used to estimate subsurface temperature. Carbon dioxide can be used to model the alteration mineralogy of a geothermal system , possibly giving information about the properties of the reservoir. The pCO2 of a geothermal reservoir can be estimated by using the Henry´s Law coefficient at the temperatures indicated by geothermometers, giving information about the physical and chemical properties of geothermal reservoir fluids.

HYDROGEN SULFIDE

Data

Hydrogen sulfide was detected in nine thermal waters. The concentration of hydrogen sulfide ranged from 0.016 to 1.8 cc(STP)/liter with a median of 0.1 cc(STP)/liter. The occurrence of hydrogen sulfide is restricted to thermal waters located within the Rio Grande Rift.

There was no correlation observed between hydrogen sulfide concentrations and geothermometers (Norman and Bernhardt, 1982).

Discussion

Hydrogen sulfide is not a component of the atmosphere and must be added to the thermal waters by water-rock interaction. One can postulate several sources for hydrogen sulfide in New Mexico thermal waters:

1) mineral equilibria;
2) reduction of sulfate;
3) breakdown of organic matterials; and
4) magma degassing.

The concentration of hydrogen sulfide measured in New Mexico thermal waters is within the range expected from various hydrogen sulfide-iron mineral reactions (table IX). The concentration of hydrogen sulfide in thermal waters from the Valles Caldera Reservoir, New Mexico, can be explained by mineral equilibria, but this doesn´t seem the case in thermal waters studied.

The concentration of hydrogen sulfide is difficult to interpret. Chemical reactions involving hydrogen sulfide reequilibrate rapidly with changes in temperature (Nehring and D´Amore, 1981; Truesdell, 1976). Also, hydrogen sulfide is readily oxidized to sulfate in oxygenated waters. Therefore, the concentrations of hydrogen sulfide in the waters studied are probably not equilibrium values, and it may not be possible to relate the measured concentrations of hydrogen sulfide to reservoir conditions.

Only small amounts of hydrogen sulfide can be produced from the reduction of sulfate by magnetite (Table IX). High sulfate concentrations or low pH and large amounts of magnetite are required to produce enough hydrogen sulfide to be within the range measured in New Mexico thermal waters. Sulfate does not reduce directly to hydrogen sulfide but goes through a series of intermediate oxidation steps.

Some hydrogen sulfide in New Mexico thermal waters may be derived from the breakdown of organic material or by the reduction of sulfate by organic matterial, but only trace amounts of organics, with the exception of methane, are detected in New Mexico thermal waters.

In summary, it is not possible to deduce the controls of hydrogen sulfide in the thermal waters studied.

Application to Exploration

Hydrogen sulfide concentrations could not be used to calculate temperatures, but in New Mexico thermal waters the presence of hydrogen sulfide may indicate temperatures greater than 100°C. Hydrogen sulfide appears not to be controlled by mineral or gas equilibria in low temperature (less than 100°C) geothermal systems and temperatures calculated from equilibria based on hydrogen sulfide would be suspect.

METHANE

Data

The concentration of methane in New Mexico thermal waters ranges from 2.0E-5 to 9.8 cc(STP)/liter, with an median of 0.29 cc(STP)/liter.

At the 5 pct. level of significance, the concentration of methane in thermal well waters decreases slighty with increasing temperature calculated from the the Na-K-Ca geothermometer (Norman and Bernhardt, 1982). There is no correlation between the concentration of methane in spring waters and the Na-K-Ca geothermometer (Norman and Bernhardt, 1982).

Discussion

The concentration of methane in New Mexico thermal waters is within the range expected from several reactions involving methane (Table IX), but the methane data does not fit any one of these reactions alone. The slight decrease in the concentration of methane may be due to methane being controlled by some temperature-dependent reaction, but methane from organic or biological sources is possible.

The origin of methane in New Mexico thermal waters can not be determined from the availible data. Carbon isotopic data may be helpful in distinguishing methane from organic verse inorganic sources.

OTHER GASES

Oxygen

The concentration of oxygen measured in New Mexico thermal waters ranges from 0 to 6.5 cc(STP)/liter with a median of 2.2 cc(STP)/liter. The high concentration of oxygen in many New Mexico thermal waters is not easily explained. The concentration of oxygen in groundwaters is generally low because the bulk of the oxygen in recharge water is consumed by both soil microbial activity and by water-rock reactions occuring below the water table (Freeze and Cherry, 1979). Oxygen can be added to a thermal water by mixing of the thermal water with near surface groundwater, reequilibration with the atmosphere as the thermal water discharges to the surface, or by air contamination of the thermal water during sampling.

Hydrogen

Hydrogen was detected only in the Animas Valley hot well, at a concentration of 0.013 cc(STP)/liter. Using the dissociation of water and the empirical oxygen fugacity buffer for geothermal gases of D´Amore and Panichi (1980), a temperature of 114°C is calculated. This is in fairly close agreement with the 96°C discharge temperature of the hot well, suggesting that the hydrogen may be controlled by the dissociation of water.

Only concentrations of hydrogen greater than 10^{-3} cc(STP)/liter can be detected in the analytical system used. The use of hydrogen in geothermal exploration will depend on detection limits for hydrogen in the analytical system used.

Ammonia

Ammonia was detected in only eleven thermal waters. The concentration of ammonia ranged from 1.1×10^{-3} to 0.17 cc(STP)/liter, with a median of 9.3×10^{-3} cc(STP)/liter. There was no correlation observed between the Na-K-Ca geothermometer and either ammonia concentration or the nitrogen/ammonia ratio (Norman and Bernhardt, 1982).

Ammonia can be controlled by the reaction:

$$N_2 + 3H_2 = 2NH_3$$

in geothermal waters (D´Amore and Nuti, 1977; Giggenbach, 1980). However, the lack of correlation of ammonia with temperature suggests that ammonia may not be controlled by a temperature-dependent reaction in the waters studied.

Ammonia can be formed by the breakdown of nitrogen-rich organics, such as proteins (Barnes, 1970; D´Amore and Nuti, 1977; Brook, 1981). Possible sources of ammonia in the waters of this study is from the breakdown of organic material or from biological processes.

Nitrogen Oxides

Nitrogen oxides were measured in all thermal waters sampled. The various nitrogen oxides were not differentiated from each other and were reported as NO. Nitrogen oxides in New Mexico thermal waters range from 3.3×10^{-3} to 6.7×10^{-2} cc(STP)/liter with a median of 1.4×10^{-2} cc(STP)/liter. There is a slight decrease in the concentration of nitrogen oxide at the 5 pct. level of significance with Na-K-Ca temperature (Norman and Bernhardt, 1982).

Water in equilibrium with the atmosphere at 20°C can dissolve 2.5×10^{-5} cc(STP)/liter NO, which is too low to explain the concentration of nitrogen oxide observed in New Mexico thermal waters. Nitrogen oxides can be derived from denitrification reactions of nitrate or nitrite by bacterial activity and from the oxidation of ammonia (Schlegel, 1974; Manahan, 1979). It is possible that the nitrogen oxides in New Mexico thermal waters are due to biological activity.

THE GEOCHEMICAL SIGNIFICANCE OF THE CARBON DIOXIDE/METHANE GEOTHERMOMETER

An empirical geothermometer based on a correlation between carbon dioxide/methane ratios in New Mexico thermal well waters and the Na-K-Ca geothermometer was proposed by Norman and Bernhardt (1982). It was assumed that the relationship was due to carbon dioxide and methane being controlled by some temperature-dependent reaction.

Chemical equilibrium between carbon dioixde and methane can be represented by the reaction:

$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$

Because hydrogen was not detected in most waters sampled, it is not possible to directly evaluate this reaction. However, hydrogen can be controlled by the dissociation of water:

$$2H_2O = 2H_2 + O_2,$$

and the reaction between carbon dioxide and methane can be rewritten as:

$$CO_2 + 2H_2O = CH_4 + 2O_2.$$

The oxygen fugacity of the thermal waters was calculated from the CH_4/CO_2 ratios; the oxygen fugacities fall between the hematite-magnetite and Ni-NiO oxygen fugacity buffers and near the empirical geothermal gas-oxygen fugacity buffer of D´Amore and Panichi (1981)

(Fig. 14). The oxygen buffering in the system Fe-O-S was not considered because hydrogen sulfide was detected in only a few waters.

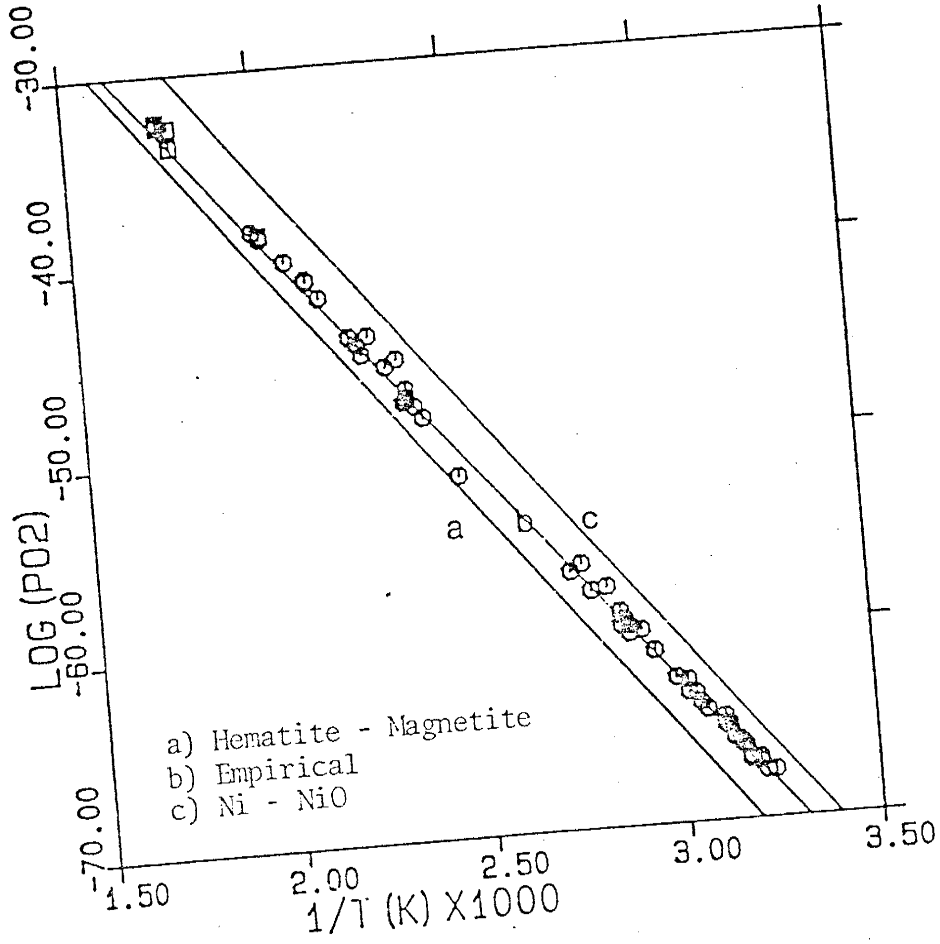
This result is consistant with other geochemical data; the oxygen fugacity for most rock systems fall between the hematite-magnetite and hematite-quartz-faylite (close to the Ni-NiO) buffers (Carmichael et al., 1974). The oxygen fugacity of the thermal waters appears to principally governed by the presence of iron and can be represented by the reaction:

$$Fe^{++} = Fe^{+++} + e^{-}.$$

Studies of redox equilibria in the Broadlands geothermal system (Seward, 1974) show that the gas and water chemistry are in equlibrium with the pyrite-pyrrhotite system and that Fe++ is the main iron species in solution. Therefore it is reasonable that the carbon dioxide/methane ratios in geothermal waters would fall between the hematite-magnetite and Ni-NiO oxygen buffering systems.

The correlation of CO_2/CH_4 ratios with temperature and the calculation of reasonable oxygen fugacities from these ratios suggest that the assumption of equilibrium between carbon dioxide and methane in the New Mexico thermal waters may be reasonable. Early studies of carbon dioxide and methane in geothermal systems showed good agreement between measured well bore-hole temperatures and temperatures calculated from isotopic and chemical equilibria (Craig, igure 14. Log(fO2) calculated from CO2/CH4 ratios measured in New Mexico thermal waters. Squares are data from Baca geothermomal reservoir, New Mexico released by Union Geothermal (1981); octagons are data from New Mexico thermal waters sampled in this study. Several oxygen fugacity buffers are plotted for reference:

(a) Hematite - magnetite;
(b) Empirical oxygen figacity buffer based on gas equilibria (D´Amore and Panichi, 1981);
(C) Nickel - Nickel Oxide.


-30.00
-40.00
-50.00
-60.00
-70.00
LOG (PO2)
1.50
2.00
2.50
3.00
3.50
1/T (K) X1000
a
b
c
a) Hematite - Magnetite
b) Empirical
c) Ni - NiO

; Hulston and McCabe, 1962). Studies of chemical librium of geothermal gases have shown that carbon xide and methane are in equilibrium in many geothermal tems (D´Amore, 1976; D´Amore and Nuti, 1977; Truesdell Nehring, 1978/79; Giggenbach, 1980, 1981). Furthermore, othermometers have been used based on the carbon oxide-methane equilibria (D´Amore and Panichi, 1980; hring and D´Amore, 1981; Giggenbach, 1980).

An alterative explaination is that carbon dioxide and ethane are not in equilibrium. The correlation between the O2/CH4 ratio and Na-K-Ca geothermometry may represent the orrelation of carbon dioxide with geothermometry discussed earlier. Gunter and Musgrave (1971) and Gunter (1978) used the recalculated carbon-13 exchange equilibria of Bottinga (1969) and found that temperatures calculated for the isotopic equilibria were higher than chemical equilibria and measured temperatures. They concluded that carbon dioxide and methane are not in equilibrium and were derived from different sources. Hulston (1977), Lyon and Hulston (1980), and Giggenbach (1982) attribute the higher isotopic temperatures to the slower kinetics of the isotopic exchange reaction relative to chemical equilibrium. The higher temperatures would represent hotter temperatures deeper in the geothermal system. Carbon dioxide and methane from different sources may come to chemical equilibrium without ever reaching isotopic equilibrium.

The problem of equilibrium between carbon dioxide and methane in geothermal systems has not been resolved, and further research is needed to clarify the problem. At this time neither hypothesis proposed here is preferred.

GAS CHEMISTRY OF THE LIGHTNING DOCK KNOWN GEOTHERMAL RESOURCE AREA, ANIMAS VALLEY, NEW MEXICO

INTRODUCTION

Sixteen wells were sampled at the Lightning Dock Known Geothermal Area in the Animas Valley, New Mexico. The area was studied to asses the applicability of gas chemistry in understanding a relatively simple geothermal system. The gas data were compared with previous geologic, geophysical, and geochemical studies of the area.

The Animas Valley is a graben located in the Basin and Range province in southwestern New Mexico. Thermal wells originally produced 101°C water from altered rhyolite at 27m depth (Summers, 1976); but in 1981, the measured discharge temerature was 96°C. The Pyramid Mountains, to the east of Animas Valley, are part of the mid-Tertiary volcanic complex of the Muir cauldron (Elston and Deal, 1978). The thermal water is localized by the intersection of the ring fracture zone and a north trending Basin and Range fault along the eastern edge of Animas Valley (Logsdon, 1981). The Lightning Dock thermal anomaly is believed to be a relict from period of larger hydrothermal activity (Landis and Logsdon, 1981).

A 165°C reservoir temperature was calculated from the silica and Na-K-Ca geothermometers (Landis et al., 1976). Stable isotopic and mixing-model studies suggest that the thermal water is condensate from steam from a deep 250°C reservoir (Landis and Logsdon, 1980; Logsdon and Landis, 1981). Regular chemical patterns in the non-thermal waters in the vicinity of the hot well suggest that thermal waters from the deep reservoir seep along a fault trending to the southwest of the hot wells, and are dispersed northward by the shallow non-thermal waters (Landis and Logsdon, 1980).

GAS CHEMISTRY OF THERMAL WATER

Data

The gas composition of the thermal and non-thermal waters in the Animas Valley is summarized in Table XII.

Table XII

Analyses of Gases in the Thermal and Non-thermal Waters in the Animas Valley

Gas	Hot Well (cc(STP)/liter)	Aver. Non-thermal Well (cc(STP)/liter)
N2	$5.8X10^{-3}$	12
O2	$6.0X10^{-5}$	4.6
He	$1.7X10^{-5}$	$3.4X10^{-4}$
Ne	$5.4X10^{-7}$	$1.7X10^{-4}$
Ar	$3.4X10^{-5}$	0.29
Kr	$2.4X10^{-8}$	$6.2X10^{-5}$
CO2	0.26	4.0
CH4	$2.0X10^{-5}$	0.62
NO	$1.5X10^{-7}$	$2.1X10^{-2}$

Discussion

The total gas concentration in the hot wells is low relative to the non-thermal water in the Animas Valley. Nitrogen, argon, and krypton were far lower than expected for meteoric groundwaters. The water produced from the hot well was boiling at 96°C, it is believed that the low gas content of the hot well waters was due to vapor-loss during subsurface boiling.

Therefore, it is unlikely that the gas composition of the water sampled is representative of the gases in the geothermal reservoir. The gas composition of the thermal water will change with vapor loss because of differences between the vapor/liquid partitioning coefficents for the various gases. Attempts to restore the gas analyses to their preboiled concentration by a Rayleigh distillation model were unsuccessful.

A temperature of 170°C was calculated from the gas composition of the hot well using the reaction:

$$\mathrm{CO2 + 2H2O = CH4 + 4H2},$$

and a temperature of 240°C was calculated using the empirical $\mathrm{CO2/CH4}$ geothermometer (Norman and Bernhardt, 1982). These temperatures agree well with the shallow reservoir and deep reservoir temperature, respectively, calculated by Logsdon (1981) using the Na-K-Ca and silica geothermometers and mixing models.

The agreement between temperatures calculated from gas geothermometers and temperatures calculated from the Na-K-Ca and silica geothermometers is surprising. Boiling will cause the carbon dioxide/methane ratio to increase because the vapor/liquid partition coefficent for carbon dioxide is lower than the coefficient for methane, resulting in a high temperature to be calculated from the empirical CO2/CH4 geothermometer. Because the gas composition of the hot well water is not representative of the reservoir water, the agreement of the gas geothermometers with the temperatures calculated by Landis and Logsdon (1980) is probably coincidental.

Helium and nitrogen have the same vapor/liquid partitioning coefficient at 100°C. Boiling will not significantly change this ratio, and the helium/nitrogen ratio of the depleted water would be representative of the ratio in the preboiled thermal water. The He/N2 ratio measured in the hot well water is $2.0X10^{-4}$. Assuming an reasonable initial nitrogen concentration of the shallow thermal water to be 10 cc(STP)/liter, the helium concentration would be $2.0X10^{-3}$ cc(STP)/liter.

Logsdon (1981) estimates that the shallow geothermal reservoir contains 0.25 deep thermal water and 0.75 shallow non-thermal water. Using thses mixing proportions, a helium concentration of 7.7×10^{-3} CC(STP)/LITER was calculated for the deep 250 C reservoir water.

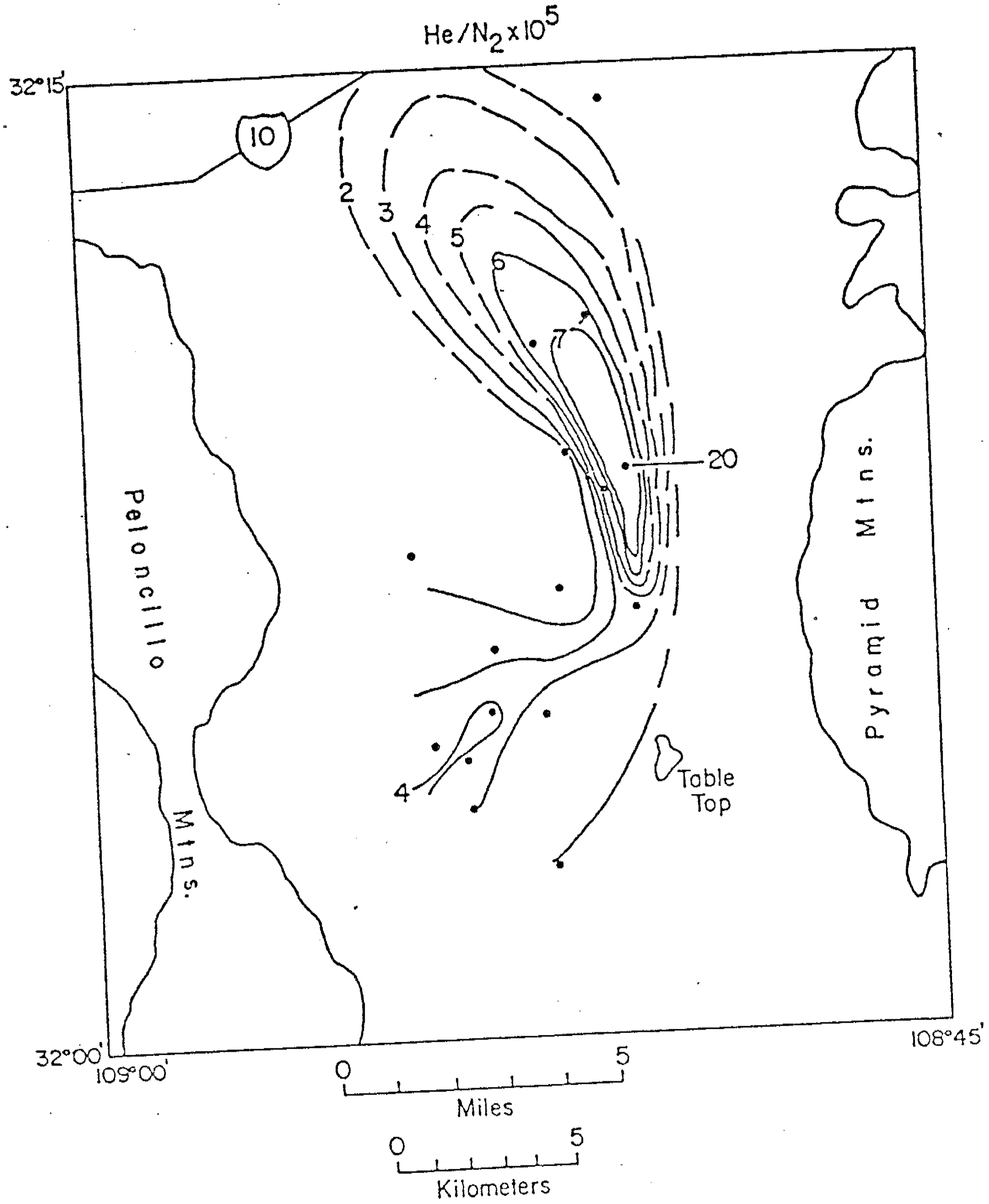
A log(pCO2) of 0.35 atm. was calculated for the deep geothermal reservoir from mass transfer considerations (Logsdon, 1982, personal communication). Utilizing the relationship between carbon dioxide and Na-K-Ca temperature observed in New Mexico thermal waters (Fig. 7, Norman and Bernhardt, 1982), and the Henry's Law coefficient at the Na-K-Ca temperature of the thermal waters, a log(pCO2) = 0.37 atm. is calculated at 250°C for the deep geothermal reservoir, in close agreement with Logsdon's calculations.

ZONATION OF GASES IN NON-THERMAL GROUNDWATERS

A regular zonation of carbon dioxide and helium was observed in the near surface non-thermal groundwaters in the Animas Valley. The zonation for helium/nitrogen is given in Fig. 15; the pattern for CO2 is very similar. High carbon dioxide and helium is found where thermal waters rise along faults and mix with the non-thermal groundwaters and disperse northward. The highest carbon dioxide and helium is found around the hot wells, where the main upflow of thermal water occurs.

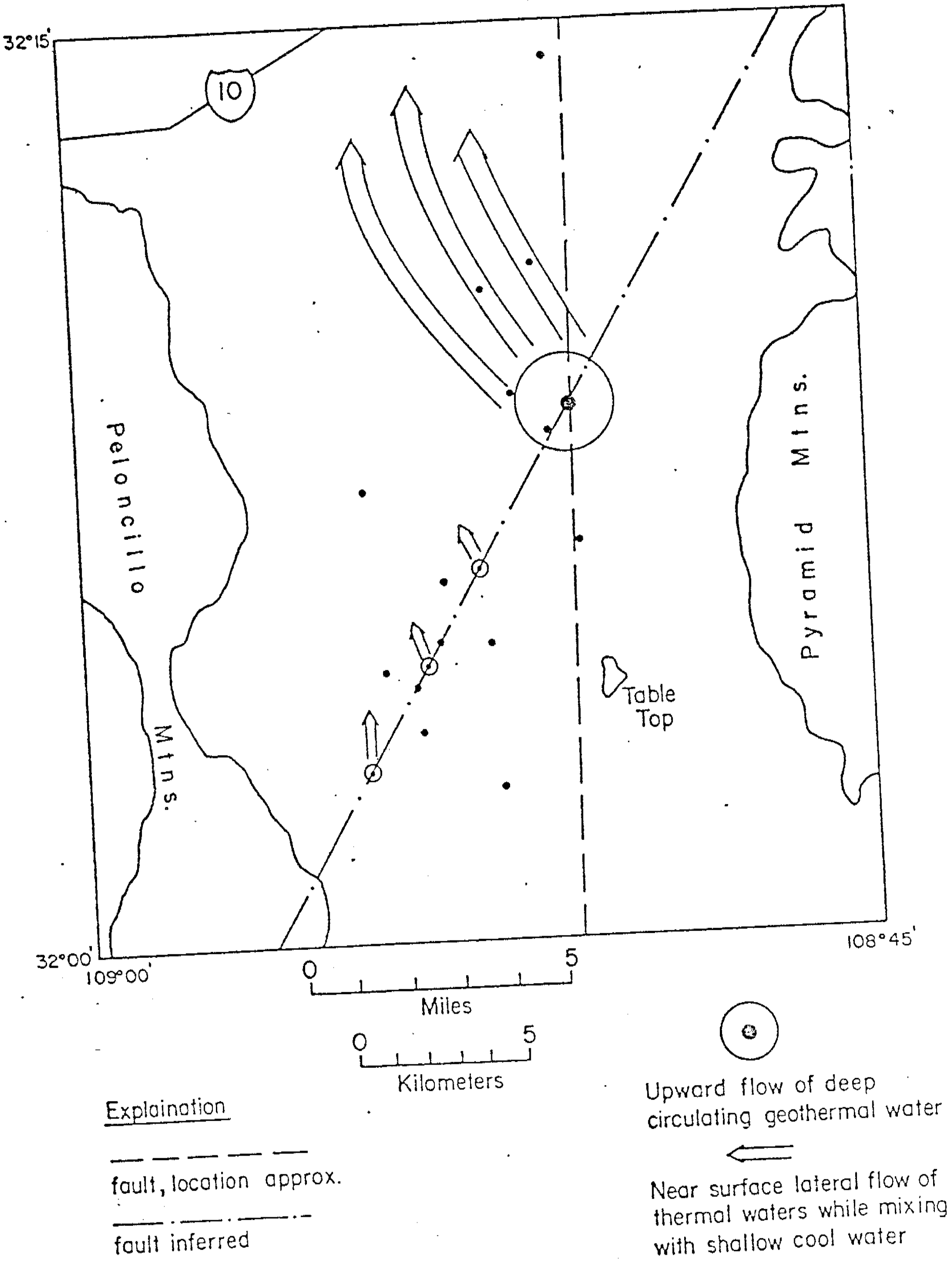
The gas data is consistant with Logsdon's model for the Lightning Dock geothermal area. Thermal waters flow along the southwest trending fault from a reservoir to the southwest of the hot wells. Small amounts of geothermal

Figure 15. Isopleths of He/N2 molar ratios in Animas Valley groundwaters (Figure 19, Norman and Bernhardt, 1982).


He / N_2 x 10^5
32°15'
10
2
3
4
5
6
7
20
4
Peloncillo Mtns.
Pyramid Mtns.
Table Top
32°00'
109°00'
108°45'
0
5
Miles
0
5
Kilometers

water leak up the fault and mix with near-surface, non-thermal waters. Major upflow of thermal water into the non-thermal water occurs at the intersection of the fault with a north-trending basin and range fault bordering the eastern side of the Animas Valley. The thermal waters are dispersed by northwest-flowing nonthermal groundwaters. The model is summarized in Figure 16.

Figure 16. Hydrological-geothermal model of the Animas Valley (After Logsdon, 1981; Figure 22, Norman and Bernhardt, 1982).


32°15'
10
Peloncillo Mtns.
Pyramid Mtns.
Table Top
32°00'
109°00'
108°45'
0
5
Miles
0
5
Kilometers
Explaination
fault, location approx.
fault inferred
Upward flow of deep circulating geothermal water
Near surface lateral flow of thermal waters while mixing with shallow cool water

COMPARISION OF GAS GEOTHERMOMETRS USING GAS ANALYSES FROM THE BACA GEOTHERMAL RESRVOIR, VALLES CALDERA, NEW MEXICO

Baca Geothermeral Site

The Baca geothermal site is located in the Valles Caldera, Jemez Mountians, New Mexico. Geothermal fluids with temperatures between 260°C to 300°C are produced from a liquid dominated reservoir from the Bandelier tuff in a graben structure in the resurgent dome near the center of the Valles caldera (Slodowski, 1977; Dondanville, 1978; Goff and Grigsby, 1982). A vapor-dominated reservoir occurs near the surface, accompanied by modern hot springs, fumerolic activity, and hydrothermal alteration.

Gas Composition of Thermal Waters

Gas analyses of steam from production wells have been released by Union Geothermal (1981). Selected gas analyses are presented in Table I, Appendix III.

The gas composition of the geothermal waters was estimated by calculating the mass balance between separated steam and water, assuming that the gases were partitioned totally into the steam phase. This is similar to the method used by Nehring and D´Amore (1981) in calculating the gas composition of the Cerro Prieto thermal waters. The estimated gas composition of the Baca reservoir fluids from analysis of steam is given in Table II, Appendix III.

Comparision of Gas Geothermometers

The gas analyses were used to calculate temperatures from several gas geothermometers. The reservoir temperatures for the individual wells are estimated using silica and alkali geothermometers. The temperatures are compared in Table XIII.

The temperatures calculated from the empirical CO2/CH4 geothermometer (Norman and Bernhardt, 1982) and from geothermometers based on gas and mineral equilibria in the New Zealand geothermal systems (Giggenbach, 1982, 1981) gave the best agreement with reported temperatures in the Baca reservoir. Temperatures calculated from gas geothermometers assuming equilibrium with anhydrite, graphite, or pyrrhotite did not agree with the measured temperatures.

Temperatures calculated from different gas analyses from the same well do not always agree. The variation in gas chemistry may be due to differences in reservoir or well production conditions.

Temperatures calculated for wells from quartz, Na-K, and Na-K-Ca geothermometers are in good agreement with each other and with the measured reservoir temperature. The temperatures calculated from different chemical analyses from the same well agreed within a few degrees. The different chemical geothermometers give a wide range of temperatures for Sulfur Springs.

TABLE XIII

Comparision of chemical and gas geothermometers for the Baca wells and springs, Jemez Mts., N.M.

	Baca #4	Baca #11		Baca #13		Sulfur Spring
T quartz	189	283	298	292	298	186
T Na-K	297	312	309	279	279	300
T Na-K-Ca	296	298	296	289	289	227
T CO_2-CH_4-H_2[1]	274	314	348	260	269	498
T CO_2-CH_4-H_2-H_2S[1]	325	297	317	311	280	271
T NH_3[1]	-	240	-	-	-	-
T H_2S-CO_2-H_2[1]	410	528	535	673	659	-
T CO_2-H_2S[2]	225	281	283	251	267	-
T CO_2[2]	280	291	292	283	298	-
T H_2[3]	212	245	269	194	194	-
T CO_2-CH_4-H_2-H_2S[4]	135	135	146	140	90	-
T CO_2-CH_4-H_2[4]	307	370	396	286	297	-
T CO_2-H_2[5]	234	265	290	219	226	-
T CO_2-H_2S[5]	151	175	200	145	156	-
T CO_2/CH_4[6]	288	297	313	314	349	230

1. Giggenbach (1980)
2. Giggenbach (1981)
3. Giggenbach (1982)
4. D´Amore and Panichi (1980)
5. Nehring and D´Amore (1981)
6. This study

All temperatures in celsius

Application of Gas Geothermometers to Geothermal Exploration

The application of gas geothermometers to thermal spring discharges assumes that the chemistry of the thermal spring is representative of equilibrium at depth and that processes such as boiling or degassing have not significantly changed the gas composition.

Most gas geothermometers require the partial pressure of the gases of interest. The concentration of gases in thermal springs may not be representative of the gas pressures in the geothermal reservoir (Truesdell, 1975). Giggenbach (1980) developed geothermometers that required no knowledge of gas pressures, but he cautions against using these geothermometers for anything but well discharges.

The application of gas geothermometers that are based on hydrogen or hydrogen sulfide equilibria to thermal springs is limited. Hydrogen concentration in thermal waters below boiling is generally low and would be difficult to detect, depending on the analytical system used. Hydrogen sulfide reequilibrates and is oxidized rapidly as thermal waters cool and discharge to the surface. The hydrogen sulfide concentration probably would not be representative of conditions at depth.

In applying gas geothermometers to unknown areas, it is necessary to have some knownledge of the mineralogy of the geothermal system, because different gas geothermometers are based on equilibrium with different mineralogies. Only the CO2-CH4-H2 geothermometers of Giggenback (1980) and Nehring and D´Amore (1981), The NH3-N2-H2 geothermometer of Giggenbach (1980), and the CO2/CH4 geothermometer of Norman and Bernhardt (1982) do not assume any gas-mineral reaction.

Temperatures calculated from gas geothermometers applied to thermal spring discharges from the the Valles Caldera, New Mexico, and to the Wilbur Springs area, California are in good agreement with with subsurface temperatures (Goff, 1982, personal communication; Thompson, 1979).

CONCLUSIONS

The concentration of nitrogen, neon, and argon in most New Mexico thermal waters is close to that expected for air saturation at reasonable recharge elevations and temperatures. Deviations from the air-saturation concentration can be attributed to air contamination, gas enrichment by separation of a gas and water phase, or loss of gases from a thermal water to the atmosphere.

The concentration of helium in New Mexico thermal waters, with the exception of the Animas Valley hot well, is in excess of air saturation, and is attributed to the leaching of radiogenically produced helium by thermal waters. The concentration of helium in some thermal waters, especially those associated with the boundary faults of the northern Rio Grande rift, is too high to be accounted for by the age of the waters alone. The faults may transport deep radiogenic and possibily mantle helium to the surface.

The concentration of carbon dioxide in New Mexico thermal waters increases with Na-K-Ca temperature, and can be explained by carbon dioxde being controlled by temperature-dependent aluminium-silicate reaction. Carbon dioxide appears to be the best gas for use in geothermal exploration.

The concentration of hydrogen sulfide does not appear to be controlled by water rock equilibria. The hydrogen sulfide may have reequilibrated as the thermal waters cooled or may have been oxidized by mixing of thermal water with oxygenated near-surface groundwaters.

The concentration of methane does not appear to be controlled by any one reaction. The oxygen fugacities calculated from the CO2/CH4 ratios measured in New Mexico thermal waters fall between the hematite-magnetite and nickel-nickel oxide oxygen fugacity buffers, suggesting equilibrium may be possible. However, at this time, neither the hypothesis of equilibrium or of non-equilibrium between methane and carbon dioxide is preferred.

Hydrogen was detected in only the Animas Valley hot well. The concentration of hydrogen is close to that expected from the dissociation of water at the measured temperature of the well.

Ammonia appears not to be controlled by chemical equilibria in the waters studied and probably has an organic or biologic source.

The concentration of nitrogen oxide is in excess of that expected from air saturation and probably has a biologic source.

The gases in the Animas Valley hot well were depleted due to subsurface boiling. The helium/nitrogen ratio of the depleted water is probably representative of the water in the geothermal reservoir. The p(CO2) calculated from the carbon dioxide data from New Mexico thermal waters is in close agreement with previous studies. The zonation of gases in the non-thermal groundwaters is consistent with previous chemical studies by Logsdon (1981) and can be interpreted as due to seepage of thermal waters along a southwest-trending fault and dispersion of the gases by northwest-flowing, near-surface groundwaters.

Several gas geothermometers were applied to gas analyses of well and spring discharges from the Baca geothermal reservoir. Gas geothermometers based on the New Zealand geothermal system and the empirical CO_2/CH_4 geothermometer gave the best results.

APPENDIX I

Gas and Chemical Analyses of New Mexico Thermal Waters

The location of the thermal waters sampled is summarized in Table I. Gas and chemical analyses of the thermal waters sampled are summarized in Tables II and III, respectively. The reservoir temperature was calculated using the following geothermometers:

TQ = quartz geothermometer (Fournier and Rowe, 1966);
Tch = chalcedony geothermometer (Fournier and Rowe, 1966);
TNa-K = Na-K geothermometer (Fournier, 1979);
TNa-K-Ca = Na-K-Ca geothermometer (Fournier and Truesdell, 1973);

TNa/Li = Na-Li geothermometer (Fouillac and Michard, 1981)
TCO2/CH4 = CO2/CH4 geothermometer (Norman and Bernhardt, 1982).

The results are summarized in Table IV

Table I - Location of Samples

Sample Name	Location #	County:Location	Description	Temp.
Mamby Hot Spring	1	Taos: 26N.11E.1.120	spring	38 C
Ponce del Leon Spr.	2	Taos: 24N.13E.7.000	spring	34 C
Statue Spring	3	Taos: 24N.8E.26.400	spring	29 C
Ojo Caliente	4	Taos: 24N.8E.24.110	spring	43 C
San Antonio Hot Spr.	5	Sandoval: 20N.3E.29.120	spring	42 C
Spence Spring	6	Sandoval: 19N.3E.28.310	spring	42 C
Soda Dam Spring	7	Sandoval: 18N.2E.14.000	spring	45 C
Jemez Spring	8	Sandoval: 18N.2E.23.000	spring	53 C
San Ysidro Spring	9	Sandoval: 15N.1E.10.200	spring	24 C
Kaseman Well#2	10	Sandoval: 16N.1W.1.410	spring	54 C
Montezuma Hot Spr.	11	San Miguel: 17N.15E.36.440	spring	49 C
Blue Canyon Well	12	Socorro: 3S.1W.16.323	well	33 C
Socorro Spring	13	Socorro: 3S.1W.21.111	spring	32 C
Bosque del Apache #9	14	Socorro: 5S.1E.30.241	well	17 C
Bosque del Apache #20	15	Socorro: 6S.1E.12.231	well	24 C
Bosque del Apache #13	16	Socorro: 6S.1E.17.213	well	33 C
Yucca Bath Spring	17	Sierra: 13S.4W.33.000	spring	43 C
Sierra Grande	18	Sierra: 13S.4W.33.000	well	44 C
Artesian Bath	19	Sierra: 13S.4W.33.000	well	45 C
Radium Springs Bath	20	Dona Ana: 21S.1W.10.213	well	53 C
Radium Springs #2	21	Dona Ana: 21S.1W.10.213	well	53 C
NMSU Geothermal #1	22	Dona Ana: 23S.2E.34.000	well	61 C
NMSU Presidents Well	23a	Dona Ana: 23S.2E.34.000	well	59 C
Golf Course Well	23b	Dona Ana: 23S.2E.34.000	well	30 C
Hillsboro Warm Spr.	24	Sierra: 31 57.2´ 107 34.9´	spring	34 C
Mimbres Spring	25	Grant: 18S.10W.13.110	spring	58 C

Table I - continued

Sample Name	Location #	County:Location	Description	Temp.
Faywood Spring	26	Grant: 20S.11W.20.243	spring	55 C
Warm Spring Well #3	27	Grant: 20S.11W.18.324	well	34 C
Riverside Well	28	Grant: 6S.17.W.424	well	38 C
Telephone Co. Well	29	Grant: 5S.17W.27.240	well	25 C
Gila Hot Springs	30	Grant: 3S.13W.5.120	well	62 C
Gila Hot Springs	31	Grant: 3S.13W.5.120	spring	59 C
Gila Hot Springs	32	Grant: 3S.13W.5.120	well	65 C
Mid. Fork Gila River	33	Grant: 2S.14W.24.442	spring	65 C
Lower Frisco Spring	34	Catron: 12S.20W.23.120	spring	49 C
Upper Frisco Spring	35	Catron: 5S.19W.35.100	spring	39 C
Animas Valley 6-30-12	36	Hidalgo: 24S.20W.1.440	well	19 C
Animas Valley 3-28-4	37	Hidalgo: 24S.20W.25.421	well	20 C
Animas Valley 3-28-3	38	Hidalgo: 24S.20W.35.124	well	20 C
Animas Valley 3-28-2	39	Hidalgo: 25S.20W.12.213	well	8 C
Animas Valley 6-19-7	40	Hidalgo: 25S.19W.7.134	well	96 C
Animas Valley 3-28-1	41	Hidalgo: 25S.20W.13.120	well	19 C
Animas Valley 7-6-13	42	Hidalgo: 25S.20W.16.333	well	26 C
Animas Valley 7-6-15	43	Hidalgo: 25S.20W.25.323	well	19 C
Animas Valley 6-23-10	44	Hidalgo: 25S.20W.25.411	well	23 C
Animas Valley 6-23-11	45	Hidalgo: 25S.20W.27.411	well	20 C
Animas Valley 6-23-8	46	Hidalgo: 26S.20W.5.411	well	19 C
Animas Valley 6-23-5	47	Hidalgo: 25S.20W.34.444	well	21 C
Animas Valley 6-19-6	48	Hidalgo: 25S.20W.35.443	well	24 C
Animas Valley 6-23-9	49	Hidalgo: 26S.20W.4.344	well	21 C
Animas Valley 7-6-16	50	Hidalgo: 26S.20W.9.344	well	20 C
Animas Valley 7-6-14	51	Hidalgo: 26S.20W.14.334	well	22 C

Table IIa - Composition of Gases Dissolved in Thermal Waters+

SAMPLE NUMBER	TEMP.	N2	O2	HE X1000	NE X10000	AR	KR X100000
1	38°C	86	21	250	5.1	1.7	n.d.
1*		12	2.5	36	0.71	0.24	n.d.
2	34°C	12	0.77	10.1	1.5	0.17	2.5
3	29°C	2.5	1.6	1.6	3.0	0.10	0.95
4	43°C	2.4	0.22	42	0.73	0.053	0.42
5	42°C	5.5	3.1	0.13	1.9	0.18	2.0
6	42°C	5.6	3.8	0.17	1.2	0.21	17
7a	45°C	6.3	0.77	9.6	n.d.	0.10	n.d.
7b	45°C	21	6.7	9.0	n.d.	0.16	n.d.
8	53°C	4.8	1.6	2.3	0.68	0.13	0.86
9	24°C	14	0.054	36	2.6	0.61	18
10	54°C	77	0.3	660	10	1.5	13
10*		12	0.05	100	1.6	0.23	2.0
12	33 C	8.5	5.4	0.29	1.1	0.34	14
13	32 C	11	0.53	0.42	4.5	0.22	1.7
14	17 C	13	tr.	0.40	2.3	0.23	0.82
15	24 C	15	0.29	0.90	2.1	0.30	29
16	33 C	14	tr.	5.0	1.8	0.28	8.4
17	43 C	7.6	2.0	0.41	0.64	0.20	2.4
18	44 C	11	2.4	1.8	2.1	0.31	4.8
19	45 C	11	2.2	1.9	2.8	0.32	2.7
20	53 C	6.5	0.58	4.3	n.d.	0.20	n.d.
21	53 C	6.0	0.32	3.5	1.1	0.12	0.56
22a	61 C	8.6	.026	6.7	1.0	0.21	5.7
22b	61 C	13	0.026	6.2	0.58	0.30	1.2
23a	59 C	7.6	0.013	3.6	0.68	0.18	1.9
23b	30 C	8.0	0.008	3.3	1.1	0.19	3.9
24	34 C	9.2	3.1	0.80	·3.8	0.29	24
25	58 C	48	16	6.3	10	1.3	33
25*		12	4	1.2	2.5	0.33	8.3
26	55 C	12	2.2	1.1	1.2	0.29	6.7
27	34 C	25	5.2	1.3	n.d.	0.37	6.0
27*		12		1.3	n.d.	0.22	6.0
28	38 C	17	0.21	2.8	1.4	0.39	6.7
29	25 C	11	0.29	0.36	1.0	0.29	2.9
30	62 C	11	0.99	0.64	1.2	0.31	19
31	59 C	13	0.77	1.8	0.85	0.27	3.4
32	65 C	15	1.0	2.5	0.75	0.35	6.1
33	65 C	41	0.52	2.3	4.7	0.89	13
33*		12	0.15	0.67	1.3	0.26	4.4
34	49 C	16	4.3	1.4	4.9	0.36	12
35	39 C	4.8	4.4	0.32	1.8	0.61	14
36	19 C	14	5.8	0.16	1.8	0.29	4.1
37	20 C	8.6	2.2	0.58	2.3	0.20	2.7
38	20 C	7.7	3.6	0.52	1.7	0.25	4.3
39	8 C	12	5.4	0.18	1.7	0.54	1.7
40	96 C	.0058	0.00006	0.017	0.0054	0.000034	0.0024

+ All gases reported as cc(STP)/liter

* Corrected for air contamination or excess gas

Table IIa Continued+

H2	H2S	SO2	CO2	CH4	CnHn	NH3 X1000	NO X100	SAMPLE NUMBER
-	-	-	9.4	3.9	-	12	18	1
-	-	-	1.3	0.56	-	2.6	1.6	1*
-	-	-	0.43	0.033	-	1.1	5.1	2
-	-	-	204	0.25	-	1.9	0.63	3
-	-	-	25	0.05	-	23	1.5	4
-	-	-	0.62	0.34	-	-	1.1	5
-	-	-	0.37	0.18	-	-	0.77	6
-	0.34	-	220	9.8	-	-	-	7a
-	0.21	-	180	4.6	-	-	-	7b
-	0.84	-	180	0.17	-	-	0.74	8
-	1.8	-	1500	.062	-	170	0.33	9
-	0.55	-	462	1.5	-	720	7.2	10
-	0.086	-	72	0.23	-	79	1.1	10*
-	-	-	1.8	0.35	-	-	1.6	12
-	-	-	2.1	-	-	-	1.2	13
-	0.021	-	8.2	0.33	-	-	1.3	14
-	-	-	1.6	-	-	-	1.7	15
-	0.016	-	13	0.36	-	-	1.0	16
-	-	-	8.1	0.23	-	-	1.2	17
-	-	-	14	0.38	-	-	1.6	18
-	-	-	14	0.38	-	-	1.5	19
-	-	-	65	0.19	-	-	2.4	20
-	-	-	68	0.09	-	-	0.71	21
-	0.038	-	200	0.16	-	-	0.61	22a
-	0.092	-	220	0.25	-	-	1.4	22b
-	0.10	-	180	0.34	-	-	-	23a
-	0.28	-	78	0.24	-	-	1.7	23b
-	-	-	4.6	0.26	tr.	46	1.0	24
-	-	-	0.34	3.2	tr.	-	10	25
-	-	-	0.34	0.80	tr.	-	2.5	25*
-	-	-	15	0.29	tr.	16	0.52	26
-	-	-	15	0.19	-	-	1.4	27
-	-	-	15	0.19	-	-	1.4	27*
-	-	-	5.3	0.41	-	-	2.3	28
-	-	-	0.42	0.25	-	-	-	29
-	-	-	0.68	.062	-	-	0.49	30
-	-	-	0.27	0.11	-	-	0.66	31
-	-	-	1.7	0.27	tr.	-	1.5	32
-	-	-	1.3	0.17	tr.	-	1.2	33
-	-	-	1.3	0.052	tr.	-	0.47	33*
-	-	-	2.9	0.65	tr.	-	2.6	34
-	-	-	0.063	0.014	tr.	-	4.4	35
-	-	-	2.2	0.85	-	-	2.5	36
-	-	-	6.5	0.23	-	-	1.4	37
-	-	-	6.5	0.36	-	-	1.3	38
-	-	-	2.4	0.36	-	-	2.0	39
0.013	-	-	0.26	.00002	-	-	0.000015	40

+ All gases reported as cc(STP)/liter
* Corrected for air contamination or excess gas

Table IIa - Continued+

Sample Number	Temp.	N2	O2	He X1000	Ne X10000	Ar	Kr x100000
41	19 C	15	3.0	0.49	1.6	0.29	12
41*		12		0.49	1.6	0.25	12
42	26 C	10	3.7	0.16	0.81	0.26	9.6
43	19 C	14	7.0	0.11	0.92	0.39	3.4
43*		12		0.11	0.92	0.31	3.4
44	23 C	13	4.1	0.48	1.7	0.29	13
45	20 C	12	4.9	0.24	1.7	0.25	4.7
46	19 C	11	5.0	0.18	1.6	0.27	6.0
47	21 C	37	12	0.58	1.4	0.58	9.5
47*		12		0.58	1.4	0.28	9.5
48	24 C	12	1.7	0.42	2.8	0.27	5.7
49	21 C	12	4.6	0.38	3.0	0.34	0.52
50	20 C	12	5.7	0.36	1.4	0.29	5.5
51	22 C	12	5.5	0.23	1.6	0.29	11

+ All gases reported as cc(STP)/liter
* Corrected for air contamination of excess gas

Table IIb - Composition of Gas Bubbling from Springs+

Sample Number	Temp.	N2	O2	He	Ne	Ar	Kr
11	49 C	87	0.084	0.70	-	1.5	0.000003
24	34 C	54	18	0.000047	0.000023	1.7	0.0000014

+ All gases reported as vol. pct.

Table IIa - Continued

H2	H2S	SO2	CO2	CH4	CnHn	NH3 X1000	NO X100	SAMPLE NUMBER
-	-	-	8.4	0.68	-	-	3.0	41
-	-	-	8.4	0.68	-	-	3.0	41*
-	-	-	1.6	0.46	-	-	2.2	42
-	-	-	4.2	0.65	-	-	3.4	43
-	-	-	4.2	0.65	-	-	3.4	43*
-	-	-	6.0	0.67	-	-	2.1	44
-	-	-	8.3	0.53	-	-	2.9	45
-	-	-	3.4	0.8	-	-	0.58	46
-	-	-	2.7	1.4	tr.	1.5	2.7	47
-	-	-	2.7	1.4	tr.	1.5	2.7	47*
-	-	-	4.6	0.52	-	-	1.7	48
-	-	-	2.0	0.80	-	-	2.4	49
-	-	-	2.9	0.23	-	-	0.92	50
-	-	-	1.1	0.76	-	-	2.3	51

+ All gases reported as cc(STP)/liter
* Corrected for air contamination or excess gas

Table IIb Continued+

H2	H2S	CO2	CH4	CnHn	NH3	NO	Sample Number
-	-	0.20	2.8	-	.000104	.000210	11
-	-	27	1.5	tr.	.27	.00058	24

+ All gases reported as vol. pct.

Table III - Chemical Analyses*

Location #	Sodium	Potassium	Lithium	Calcium	SiO2	pH
1	153	8.9	0.31	28	57	7.6
2	157	4.5	0.30	2.3	49	7.4
3	187	16	0.45	135	21	7.0
4	938	40	3.5	32	65	7.8
5	23	1.8	0.05	5.0	80	7.4
6	61	1.5	0.76	17	69	7.6
7	995	211	15	187	30	7.7
8	638	78	9.1	92	91	7.2
9	1780	81	5.8	323	18	7.6
10	3700	121	5.7	341	39	6.8
11	203	6.3	0.41	11	68	7.7
12	55	3.3	0.06	27	28	7.2
13	53	3.0	0.05	18	26	7.2
14	140	8.3	-	120	40	7.7
15	96	4.4	-	24	42	7.9
16	810	8.4	1.1	120	67	7.4
17	746	65	1.2	165	41	7.2
18	853	64	1.3	152	43	7.6
19	864	65	1.3	148	42	7.6
20	1167	185	1.2	92	63	6.8
21	1120	173	1.2	120	64	6.8
22	386	54	0.51	82	73	6.8
23a	450	55	0.48	105	71	7.1
23b	240	26	0.26	680	50	6.8
24	186	14	0.28	10	135	6.8
25	111	1.3	0.13	2.4	55	7.9
26	98	7.7	0.15	47	40	8.0
27	51	4.6	0.07	53	50	6.7
28	138	1.8	0.14	21	39	6.8
29	216	0.85	0.27	4.0	44	8.2
30	142	3.5	0.26	57	71	7.6
31	135	3.4	0.26	13	68	7.4
32	148	3.7	0.24	10	71	7.6
33	165	3.9	0.45	17	73	7.6
34	296	17	0.46	51	80	7.6
35	71	0.24	0.01	0.8	49	8.1
36	375	6.8	0.19	171	56	7.1
37	491	25	0.95	104	94	7.0
38	66	2.0	0.05	30	42	7.0
39	105	3.5	0.35	61	37	7.0
40	299	22	0.74	29	106	6.8
41	408	12	0.45	233	41	6.9
42	131	2.6	0.41	27	38	7.0
43	160	4.5	0.16	102	38	7.2
44	138	5.5	0.17	72	31	7.0
45	105	2.9	0.12	60	37	7.0
46	113	3.3	0.12	74	45	6.8
47	98	4.7	0.11	20	37	7.0
48	170	6.3	0.24	37	31	7.6
49	93	2.4	0.13	37	44	7.0
50	131	2.4	0.12	41	37	7.2
51	96	2.1	0.11	30	33	7.6

* All concentrations in mg/liter

Table IV - Geothermometry*

Location Number	Meas. Temp.	Quartz	Chal.	Na-K	Na-K-Ca	Na-Li	CO2/CH4
1	38	108	79	175	92	119	12
2	34	101	71	129	74	115	73
3	29	66	34	205	80	130	58
4	43	114	86	153	161	164	205
5	42	125	97	196	58	123	20
6	42	118	89	118	39	294	7
7	45	80	48	112	152	319	92
8	53	132	105	250	212	250	232
9	24	60	28	158	157	153	346
10	54	90	60	137	152	101	188
11	49	116	88	134	131	118	-116
12	33	73	42	159	49	81	39
13	32	88	57	152	55	83	-
14	17	92	61	176	58	-	112
15	24	94	63	158	68	-	-
16	33	116	87	146	144	94	110
17	43	93	62	205	180	106	141
18	44	95	64	193	176	100	111
19	45	93	63	194	176	100	120
20	53	113	84	260	232	78	192
21	53	114	85	257	226	80	220
22	61	120	92	247	202	92	238
23a	59	119	90	234	194	130	207
23b	30	102	72	80	88	-.14	190
24	34	155	130	193	173	100	85
25	58	107	77	82	78	85	-50
26	55	92	62	197	71	101	123
27	34	102	72	208	48	94	138
28	38	90	59	87	48	77	73
29	25	96	65	40	62	89	0
30	62	119	90	120	48	112	67
31	59	117	88	122	76	115	13
32	65	119	90	121	85	104	47
33	65	120	92	118	77	140	97
34	49	125	97	174	154	101	35
35	39	101	71	34	46	-4	35
36	19	108	78	104	55	44	15
37	20	133	106	164	149	115	101
38	20	94	63	132	37	63	85
39	8	89	58	138	44	155	49
40	96	140	114	190	170	132	290
41	19	93	63	131	67	81	70
42	26	89	59	109	53	80	26
43	19	89	59	128	45	77	48
44	23	81	49	149	56	88	60
45	20	88	58	128	40	83	78
46	19	97	66	84	40	80	32
47	21	89	58	161	74	83	4
48	24	80	49	144	76	96	59
49	21	96	66	123	42	95	13
50	20	88	57	105	43	72	73
51	22	83	52	114	42	84	-7

* All temperaures in celsius

APPENDIX II

CORRELATION COEFFICIENTS

Correlation Coefficients were calculated between gas data and the chemical geothermometers (quartz, chalcedony, Na-K, Na-K-Ca, Na-Li) and between gas data and the measured discharge temperature. The critical correlation coefficients at the 5 pct. and tha 1 pct. levels of significance are summarized in Table I. Correlation coefficiences calculated for the gas data that are below the critical values are considered not significant. The correlation coefficients for the total data, the well data, and the spring data are summarized in Tables II, III, IV respectively.

Table I

Critical Correlation Coefficients at the 5 pct. and 1 pct. Levels of Significance*

Sample Type	Number of Samples	Correlation Coefficients	
		5 pct.	1 pct.
Total	51	0.27	0.35
Wells	31	0.36	0.46
Springs	20	0.44	0.56

* From Table XI, Romano (1977)

TABLE II Correlation coefficients for all data.

	TOTAL					
	T_Q	T_{ch}	T_{Na-K}	$T_{Na-K-Ca}$	$T_{Na/Li}$	T_m
N_2	-.17	-.16	-.25	-.19	-.04	-.07
He	-.03	-.02	-.02	.24	.11	.18
Ne	-.16	-.16	-.03	-.13	-.20	-.32
Ar	-.27	-.27	-.36	-.32	-.32	-.18
Kr	.03	.02	-.20	-.27	-.15	-.10
H_2S	-.21	-.21	.10	.28	.31	.02
CO_2	-.29	-.29	.15	.29	.23	.01
CH_4	-.25	-.25	-.18	.09	.59	.03
NH_3	-.39	-.39	.12	.05	.10	-.12
NO	-.17	-.16	-.26	-.33	-.42	-.34
He/N_2	-.12	-.11	.05	.18	.15	-.02
He/Ne	.04	.05	.02	.25	.16	.17
He/Ar	.06	.07	-.01	.24	.17	.09
He/Kr	.11	.11	.17	.31	.17	.17
CO_2/N_2	-.30	-.29	.27	.32	.30	.05
CO_2/Ne	-.07	-.06	.37	.49	.27	.24
CO_2/Ar	-.26	-.25	.28	.44	.51	.17
CO_2/Kr	-.10	-.10	.35	.50	.58	.28
CO_2/CH_4	-.27	-.27	.07	.18	.11	.08
log (CO_2/CH_4)	.06	.06	.51	.61	.08	.38
CO_2/H_2S	.12	.12	.37	.43	.09	.35
N_2/NH_3	.02	.04	-.01	-.07	.03	.002
$CO_2 \cdot$He	-.31	-.31	.02	.17	.13	-.08
CO_2/Ar·He/Ar	-.33	-.33	-.01	.3	.49	.14
T_Q	1	1	.29	.41	.02	.40
T_{ch}		1	.30	.42	.01	.40
T_{Na-K}			1	.68	.11	.32
$T_{Na-K-Ca}$				1	.26	.49
$T_{Na/Li}$					1	.24
T_m						1

TABLE III Correlation coefficients for samples from springs

	T_Q	T_{ch}	T_{Na-K}	$T_{Na-K-Ca}$	$T_{Na/Li}$	T_m
N_2	-.10	.09	-.2	.07	.03	.24
He	-.17	-.15	-.01	.24	-.06	.04
Ne	-.13	-.13	-.01	-.19	-.34	-.35
Ar	-.19	-.19	-.42	-.23	-.46	-.05
Kr	.25	.24	-.22	-.10	-.18	-.1
H_2S	-.36	-.35	.16	.39	.29	-.23
CO_2	-.51	-.5	.06	.26	.18	-.36
CH_4	-.31	-.31	-.24	.21	.65	.09
NH_3	-.56	-.56	.21	.01	-.01	-.46
NO	.04	.053	-.39	-.31	-.45	-.13
He/N_2	-.25	-.24	.06	.16	-.02	-.36
He/Ne	-.09	-.08	.07	.23	-.02	-.05
He/Ar	-.05	-.02	-.08	.27	.03	-.12
He/Kr	-.03	-.04	-.01	.24	.07	-.19
CO_2/N_2	-.57	-.56	.24	.24	.24	-.28
CO_2/Ne	-.42	-.42	.19	.39	.31	-.26
CO_2/Ar	-.59	-.59	.15	.36	.53	-.28
CO_2/Kr	-.43	-.43	.19	.39	.66	-.1
CO_2/CH_4	-.41	-.40	.05	.20	.64	-.36
log (CO_2/CH_4)	-.4	-.40	.25	.43	.25	-.19
CO_2/H_2S	-.53	-.53	-.15	.41	.49	.001
N_2/NH_3	-.03	-.01	-.02	-.21	-.11	-.19
$CO_2\cdot$He	-.43	-.45	.01	.22	.05	-.34
CO_2/Ar·He/Ar	-.56	-.57	-.17	.32	.45	-.07
T_Q	1	1	.21	.19	-.15	.15
T_{ch}		1	.22	.20	-.16	.14
T_{Na-K}			1	.22	.06	-.21
$T_{Na-K-Ca}$				1	.28	-.14
$T_{Na/Li}$					1	.08
T_m						1

TABLE IV Correlation coefficients for samples from wells

	T_Q	T_{ch}	T_{Na-K}	$T_{Na-K-Ca}$	$T_{Na/Li}$	T_m
N_2	-.22	-.23	-.36	-.45	.09	-.24
He	.62	.62	.61	.79	.07	.74
Ne	-.27	-.27	-.06	-.11	.06	-.42
Ar	-.38	-.38	-.37	-.44	.42	-.25
Kr	-.26	-.26	-.18	-.38	-.12	-.10
H_2S	.23	.23	.01	.21	-.49	.20
CO_2	.53	.53	.63	.69	.06	.63
CH_4	-.41	-.41	-.31	-.37	-.03	-.48
NH_3	-.13	-.13	.03	-.05	.02	-.13
NO	-.45	-.44	-.16	-.33	-.19	-.45
He/N_2	.60	.60	.68	.84	-.04	.72
He/Ne	.59	.59	.58	.68	.06	.72
He/Ar	.62	.63	.67	.83	-.02	.70
He/Kr	.28	.28	.32	.33	.29	.33
CO_2/N_2	.54	.54	.65	.72	.05	.64
CO_2/Ne	.48	.49	.56	.60	.12	.58
CO_2/Ar	.54	.54	.65	.72	.05	.63
CO_2/Kr	.47	.48	.63	.66	.09	.57
CO_2/CH_4	.52	.53	.67	.71	.02	.62
log (CO_2/CH_4)	.64	.65	.70	.77	-.05	.71
CO_2/H_2S	.44	.44	.49	.50	.14	.49
N_2/NH_3	-.01	.01	-.33	.16	.46	.13
$CO_2 \cdot He$	.39	.40	.55	.55	.07	.48
$CO_2/Ar \cdot He/Ar$	.52	.53	.65	.70	.07	.62
T_Q	1	1	.41	.62	.18	.61
T_{ch}		1	.42	.63	.18	.62
T_{Na-K}			1	.80	.27	.56
$T_{Na-K-Ca}$				1	.19	.68
$T_{Na/Li}$					1	.21
T_S						1

APPENDIX III

GAS DATA FROM BACA GEOTHERMAL RESERVOIR WELLS AND SPRINGS, VALLES CALDERA, NEW MEXICO

Selected gas analyses of Baca reservoir fluids, released by Union Geothermal (1981), are summarized in (Table I). The gas composition of geothermal wells was estimated by calculating the the mass balance between steam and water by assuming that the gases were partitioned totally into the steam phase. The results are summarized in Table II.

TABLE I

Gas Data from Baca Geothermal Reservoir Production Wells and Springs, Valles Caldera, Jemez Mountains, New Mexico

Gas	Baca Well #4 (ppm volume)	Baca Well # 11 (ppm volume)		Baca Well #13 (ppm volume)		Sulfur Spring (mole %)
		Two analyses		Two analyses		
CH4	2.5	2.9	1.7	1.4	1.3	0.1
H2S	79	257	229	49	92	0.4
CO2	12,430	17,780	16,750	14,140	34,570	97.9
H2	12.5	23.3	37.6	5.7	6.0	0.03
N2	n.r.	245	70	79	122	1.0
NH3	3.3	3.1	n.r	n.r	n.r.	n.r.
He	n.r.	n.r.	0.63	0.77	0.17	n.r.

n.r. = none reported

Gas Data Released by Union Geothermal (1981)

TABLE II

Estimated Gas Composition of Baca Geothermal Fluids

	Baca #4 (ppm volume)	Baca #11 (ppm volume)		Baca #13 (ppm volume)	
CH4	0.69	1.0	0.7	0.42	0.36
H2S	22	92.5	93.9	14.7	25.8
CO2	3418	6400	6868	4242	9680
H2	3.4	8.4	15.4	1.7	1.7
N2	-	88.4	28.7	23.7	34.2
NH3	0.91	1.1	-	-	-
He	-	-	0.26	0.23	0.17
Steam Fraction	0.28	0.36	0.41	0.30	0.2

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