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ABSTRACT

Twenty-seven thermal springs in Arizona, New Mexico, and Utah were sampled for detailed chemical and isotopic analysis. Sampling in New Mexico and Utah was confined to known geothermal resource areas as designated by the U.S. Geological Survey. By contrast, as many of the major thermal springs of Arizona were sampled as time allowed. The springs issue sodium chloride, sodium bicarbonate, or sodium mixed-anion waters of near neutral (6.2) to alkaline (9.2) pH. High concentrations of fluoride, more than 8 milligrams per liter, occur in Arizona in waters from Gillard Hot Springs, Castle Hot Springs, and an unnamed spring on Eagle Creek, and in New Mexico from springs along the Gila River. Deuterium compositions of the thermal waters cover the same range as those expected for meteoric waters in the respective areas. More than 50 percent of the gas escaping from Verde Hot Springs, Ariz., Thermo Hot Springs and Monroe Hot Springs, Utah, and the unnamed springs near San Ysidro, N. Mex., is carbon dioxide. Crater and Joseph hot springs in Utah discharge gas containing 20 to 25 percent carbon dioxide. Nitrogen is the principal gas discharged by the other thermal springs.

The chemical compositions of the thermal waters are interpreted to indicate that Thermo Hot Springs in Utah and Gillard Hot Springs in Arizona represent hydrothermal systems which are at temperatures higher than 125°C. Estimates of subsurface temperature based on the quartz and Na-K-Ca geothermometer differ by as much as 60°C for Monroe, Joseph, Red Hill, and Crater hot springs in Utah. Similar conflicting estimates of aquifer temperature occur for Verde Hot Springs, the springs near Clifton and Coolidge Dam, in Arizona; and the warm springs near San Ysidro, Radium Hot Springs, and San Francisco Hot Springs, in New Mexico. Such disparities could result from mixing, precipitation of calcium carbonate, or perhaps appreciable concentrations of magnesium. Mixing generally reduces the temperature estimated from the silica geothermometer, whereas precipitation of calcium carbonate or magnesium concentrations of more than 30 mg/L increase the temperature estimated from the Na-K-Ca geothermometer. The other springs and wells sampled in Arizona and New Mexico have inferred reservoir temperatures of less than 100°C.

INTRODUCTION

Dependable chemical analyses for the hot springs in Utah are available in Mundorff (1970). A study of the hot springs of New Mexico (Summers, 1976) contains a collection of chemical analyses of variable quality. A brief summary of geothermal prospects in New Mexico has also been presented by Summers (1970). Chemical analyses are generally not available for the hot springs in Arizona. A paper by Tellier (1973) on the composition of hot springs in Arizona contains many analyses in which the totals of silica, sodium, and potassium exceed the total dissolved solids determined by evaporation. Analyses of water from Indian Hot Springs, Radium Hot Springs, Quitobaquito Springs, and Agua Caliente are available in Knechtel (1935), Wilson (1933), Bryan (1925), and Ross (1920), respectively. Hem (1950) and Feth and Hem (1963) present chemical data on springs in Graham and Greenlee Counties, as well as Verde Hot Springs in Yavapai County. Dellechaie (1975) reported on a geothermal test well drilled to a depth of 2440 meters west of Florence in Pinal County. Maximum temperatures of 120°C, encountered in the well, were explained by deep circulation of meteoric water in an area of normal geothermal gradient (35°C/km). A hydrologic study by Reeder (1957) contains chemical data from warm irrigation wells in the Lightning Dock KGRA (Known Geothermal Resource Area (Godwin and others, 1971)), New Mexico. Analyses of gases escaping from the springs and isotopic compositions of the waters (δD and $\delta^{18}O$) are not available in the literature.

Our sampling program was designed to provide detailed chemical, isotope, and gas-composition data for springs in designated KGRA's in Arizona, New Mexico, and Utah. Additional sampling of thermal springs was carried out in Arizona to explore the possibility of high-temperature systems in the remainder of the State.

Clifton and Gillard hot springs are the only designated KGRA's in Arizona. Clifton Hot Springs (reported as 71°C) and Gillard Hot Springs (83°C) have the highest surface temperatures. Waring (1965) lists 21 thermal springs in Arizona and Haigler (1969) lists 23 thermal springs and 9 thermal wells. Seven of the springs in Haigler (1969) are not included in Waring (1965). Where accessible, springs with reported temperatures of more than 40°C were sampled. Agua Caliente and Radium Hot Springs in the southwestern part of the State were dry when visited during January 1975.

Our sampling in Utah was restricted to the following designated KGRA's: Crater Springs, Thermo Hot Springs, and Monroe-Joseph. Thermal springs in the Monroe-Joseph KGRA include Red Hill Hot Spring, Monroe Hot Springs, and Joseph Hot Springs. No thermal springs issue in the Cove Fort-Sulphurdale KGRA.

Samples were collected from the following KGRA's in New Mexico: Radium Springs, San Ysidro, Lower Frisco Hot Springs (San Francisco Hot Springs), and Gila Hot Springs. No samples were collected from the

Kilbourne Hole, Baca Location No. 1, or Lightning Dock KGRA's. Kilbourne Hole does not contain any thermal springs.

LOCATION

The location and a brief description of the sampled springs are given in table 1. The locations of the thermal springs (figs. 1a, 1b, and 1c) are controlled by the general structural setting. Areas of undisturbed sedimentary rock such as the Colorado Plateau, which occupies northeastern Arizona, southeastern Utah, and northwestern New Mexico, are generally devoid of thermal springs. The largest concentrations of thermal springs are in areas of faulted strata associated with relatively young volcanic rocks. Almost all thermal springs in Arizona issue along the Gila River in the southern half of the State or in a thin band along the western edge. Thermal springs in New Mexico are concentrated along the headwaters of the Gila River in the southwestern part of the State and in or near the Rio Grande rift. Thermal springs occur along major faults in the western and central part of Utah (Mundorff, 1970).

METHODS AND PROCEDURES

Water was collected in a 4-liter stainless steel pressure vessel at points as close to the orifice of the springs or wells as possible and was immediately pressure-filtered through a 0.1-μm (micrometer) membrane filter using compressed nitrogen as the pressure source. Filtered water samples were stored in plastic bottles which had been acid-washed to remove contaminants prior to use. Samples for heavy-metal analyses were immediately acidified with concentrated nitric acid to pH 2 or less to insure that the metals would remain in solution. Samples collected for magnesium and calcium were acidified with concentrated hydrochloric acid to pH 2. Ten milliliters of filtered sample were diluted to 100 mL (milliliters) with distilled, deionized water to slow the polymerization of silica. Three samples of unfiltered water were collected in 125-mL glass bottles with polyseal caps for analysis of deuterium and oxygen-18. Samples of gases escaping from the springs were collected in gas-tight glass syringes which were placed in a bottle of native water for transport to the laboratory.

Field determinations were made of water temperature, pH, alkalinity, ammonia, and sulfide. Extraction of aluminum and preservation of mercury were also performed in the field. Detailed descriptions of the sampling techniques used are given by Presser and Barnes (1974). Water temperatures were determined with a thermistor probe and a maximum reading mercury-in-glass thermometer. The pH was measured directly in the spring using the method of Barnes (1964). An alkalinity titration was performed immediately after the sample was withdrawn from the spring. Sulfide was precipitated as zinc sulfide from the hot sample and titrated by the

Table 1.--Location and description of sampled springs and wells

Spring	Location	Comments
Cochise County, Arizona		
1. Hookers Hot Springs	NE¼sec. 6, T. 13 S., R. 21 E.	Flow approximately 800 L/min; water used locally.
Gila County, Arizona		
1. Unnamed warm spring (Coolidge Dam)	Unsurveyed, (33°10' N. by 110°32' W.)	Springs no longer active; water from shallow well.
Graham County, Arizona		
1. Indian Hot Springs	SE¼NE¼sec. 17, T. 5 S., R. 24 E.	Aggregate flow 1,000 L/min; inactive resort.
2. Mt. Graham hot mineral well	NW¼sec. 1, T. 7 S., R. 25 E.	Pumped well; mineral baths.
Greenlee County, Arizona		
1. Clifton Hot Springs	NE¼SW¼sec. 30, T. 4 S., R. 30 E.	Springs issue through gravel in the west edge of the San Francisco River.
2. Unnamed hot spring (north of Clifton)	SW¼sec. 18, T. 4 S., R. 30 E.	Springs issue through gravel in the edge of the San Francisco River.
3. Gillard Hot Springs	NE¼NE¼sec. 27, T. 5 S., R. 29 E.	Springs issue for 50 meters along the north bank of the Gila River.
4. Unnamed warm springs (Eagle Creek)	NE¼sec. 35, T. 4 S., R. 28 E.	Springs issue in small adits and pits; low flow rates.
Maricopa County, Arizona		
1. Hot well (Tonopah)	NE¼sec. 26, T. 2 N., R. 7 W.	Pumped well; mineral baths.
Mohave County, Arizona		
1. Pakoon Springs	sec. 24, T. 35 N., R. 16 W.	Small springs issue in ranch tanks and ponds; some gas.
Pima County, Arizona		
1. Quitobaquito Springs	Unsurveyed, (31°57' N. by 113°1' W.)	Numerous small seep springs; aggregate flow more than 100 L/min.
Yavapai County, Arizona		
1. Verde Hot Springs	Unsurveyed, (31°57' N. by 113°1' W.)	200 L/min; springs issue from gravel or in concrete enclosures; abandoned resort.
2. Castle Hot Springs	SW¼sec. 34, T. 8 N., R. 1 W.	Flow rate approximately 1,200 L/min; active resort.

Table 1.--Location and description of sampled springs and wells--Continued

Spring	Location	Comments
Catron County, New Mexico		
1. Unnamed hot spring (Gila Wilderness)-------	Unsurveyed, 33°14' N. by 108°14' W.	Spring issues from alluvium on the ~~east~~ side of the river at the wilderness boundary; tuff-breccia bedrock, sporadic gas.
2. San Francisco Hot Springs------------------ (Lower Frisco Hot Springs)	E½sec. 23, T. 12 S., R. 20 W.	Small springs and seeps; aggregate flow less than 50 L/min; scattered for two km along the San Francisco River.
Doña Ana County, New Mexico		
1. Radium Hot Springs(well)-------------------	NW¼NE¼sec. 10, T. 21 S., R. 1 W.	Resort; original springs are dry; water is from a pumped well used by the resort.
Grant County, New Mexico		
1. Gila Hot Springs---------------------------	NW¼NE¼sec. 5, T. 13 S., R. 13 W.	Springs extensively modified as a water supply; some gas.
2. Unnamed hot spring (Gila River)------------	Unsurveyed, 33°10' N. by 108°11' W.	Seep spring; tuff-breccia bedrock.
3. Unnamed hot spring (E. Fork Gila River)----	Unsurveyed, 33°11½' N. by 108°11' W.	Springs issue from alluvium along the south side of the river just downstream from Lyons Lodge.
Sandoval County, New Mexico		
1. Unnamed mineral spring(San Ysidro)---------	NW¼SW¼sec. 16, T. 15 N., R. 1 E.	Seep spring; issues from the side of a large travertine mound; inaccessible spring in the mound releases a great deal of gas.
2. Unnamed warm spring (San Ysidro)-----------	NW¼NW¼sec. 16, T. 15 N., R. 1 E.	Small springs issuing from travertine mounds on the south side of the Salado River; considerable gas.
3. Unnamed warm spring (San Ysidro)-----------	NW¼SW¼sec. 10, T. 15 N., R. 1 E.	Small gassy spring issuing from a thin travertine mound; north side of Salado River.
Beaver County, Utah		
1. Thermo Hot Springs-------------------------	sec. 28, T. 30 S., R. 12 W.	Numerous small springs and seeps issue near the top of two parallel north-south trending ridges; sampled spring at south end of western ridge; aggregate flow 500 L/min.
Juab County, Utah		
1. Crater Hot Springs (A)--------------------- (B)---------------------	sec. 10, T. 14 S., R. 8 W. sec. 10, T. 14 S., R. 8 W.	Extensive travertine mound with numerous small springs and seeps; sample A is from a flowing well near the foundation of the abandoned resort; sample B is from a small spring at the top of the travertine mound.

Table 1.--Location and description of sampled springs and wells--Continued

Spring	Location	Comments
	Sevier County, Utah	
1. Monroe Hot Springs (A)	NW¼sec. 15, T. 25 S. R. 3 W.	Numerous small springs and seeps issuing from travertine terrace; extensive trenching to "increase" water flow has destroyed much of the terrace; aggregate flow at least 500 L/min.
(B)	do	
2. Red Hill Hot Spring	SW¼sec. 11, T. 25 S., R. 3 W.	Springs issue from a travertine terrace approximately 0.8 kilometers north of Monroe Hot Springs; both springs issue from a range-front fault.
3. Joseph Hot Springs	sec. 23, T. 25 S., R. 4 W.	Numerous small springs and seeps; most of the small springs release considerable gas; low flow rate (<100 L/min).

ARIZONA

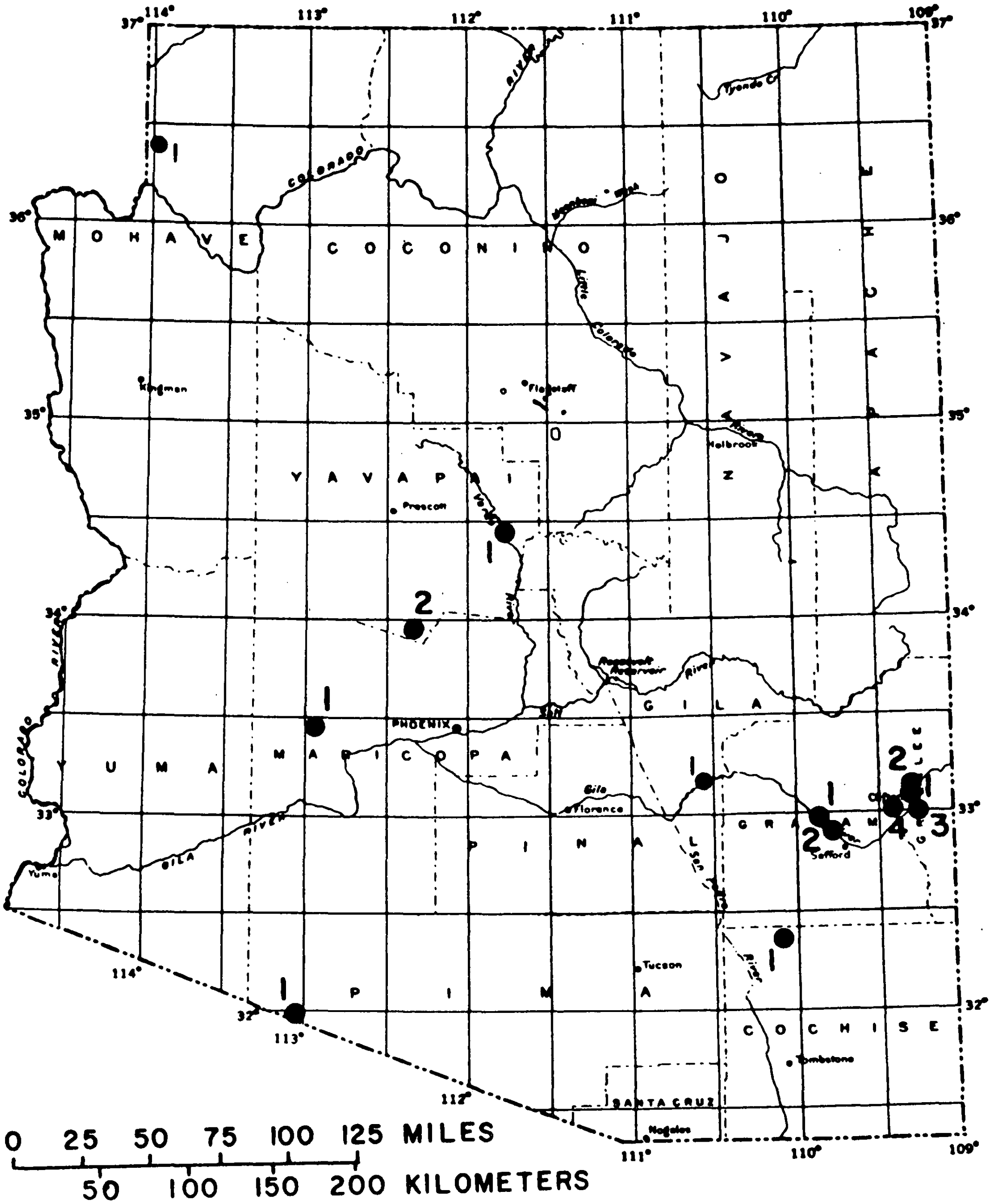

FIGURE 1a.--Location of sampled springs and wells in Arizona. Samples are numbered to correspond to their place in table 1: Cochise County, 1-Hookers Hot Springs; Gila County, 1-Unnamed warm spring (Coolidge Dam); Graham County, 1-Indian Hot Springs, 2-Mt. Graham hot mineral well; Greenlee County, 1-Clifton Hot Springs, 2-Unnamed hot spring (north of Clifton), 3-Gillard Hot Springs, 4-Unnamed warm springs (Eagle Creek); Maricopa County, 1-Hot well (Tonopah); Mohave County, 1-Pakoon Springs; Pima County, 1-Quitobaquito Springs; and Yavapai County, 1-Verde Hot Springs, 2-Castle Hot Springs.

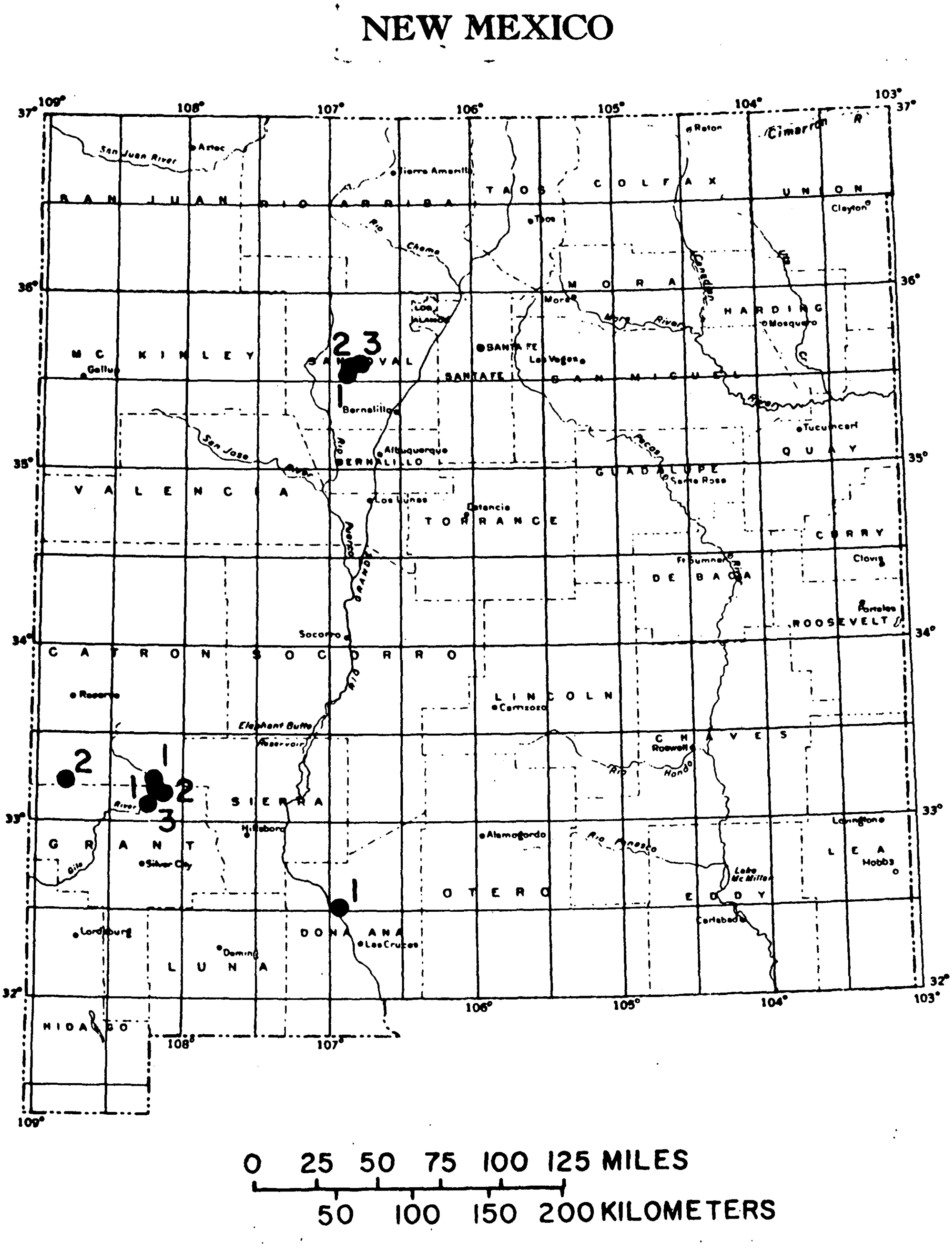

FIGURE 1b.--Location of sampled springs and wells in New Mexico. Samples are numbered to correspond to their place in table 1: Catron County, 1-Unnamed hot spring (Gila Wilderness), 2-San Francisco Hot Springs; Doña Ana County, 1-Radium Hot Springs (well); Grant County, 1-Gila Hot Springs, 2-Unnamed hot spring (Gila River), 3-Unnamed hot spring (E. Fork Gila River); and Sandoval County, 1-Unnamed mineral spring (San Ysidro), 2-Unnamed warm spring (San Ysidro), 3-Unnamed warm spring (San Ysidro).

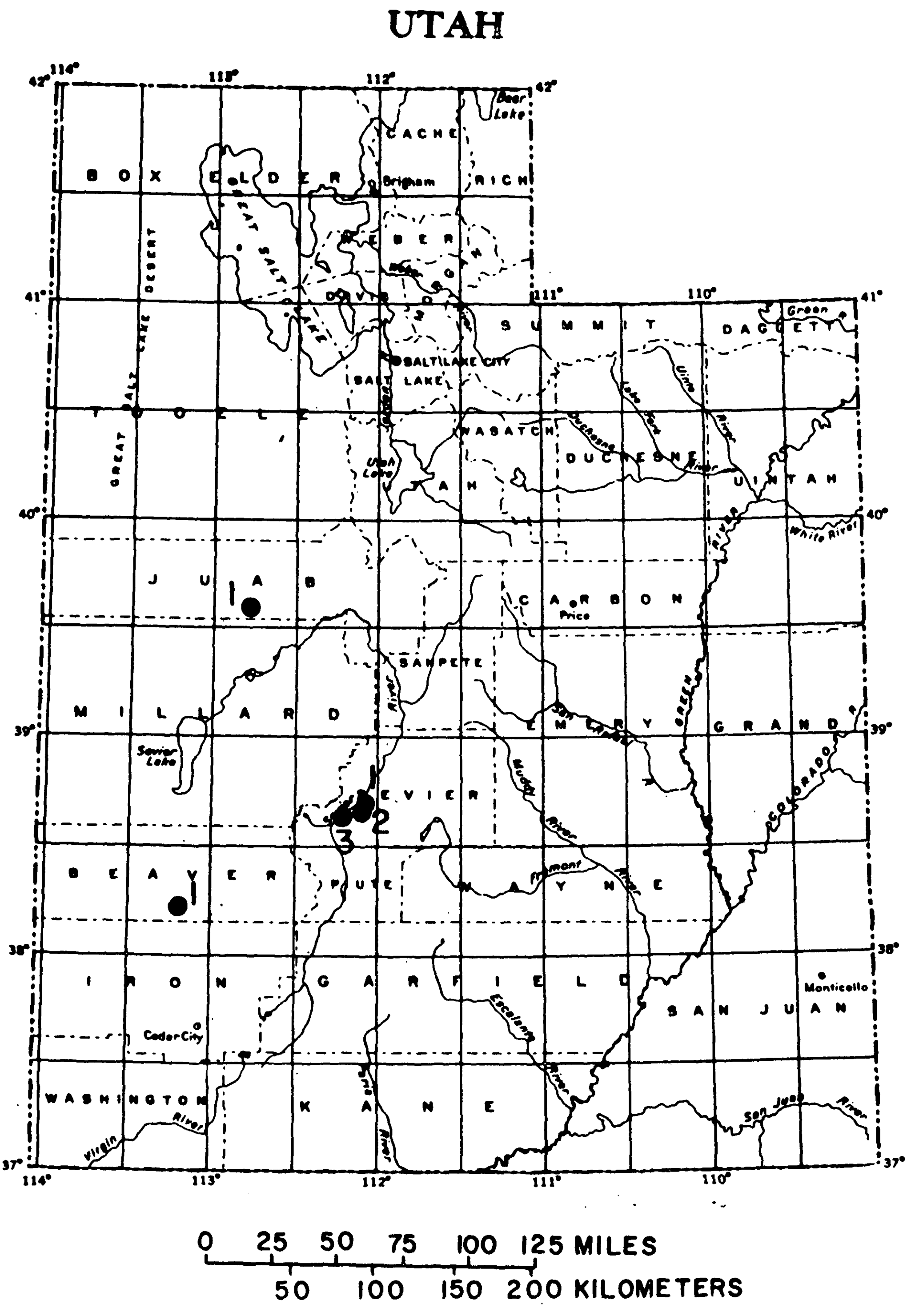

FIGURE 1c.--Location of sampled springs in Utah. Samples are numbered to correspond to their place in table 1: Beaver County, 1-Thermo Hot Springs; Juab County, 1-Crater Hot Springs; and Sevier County, 1-Monroe Hot Springs, 2-Red Hill Hot Springs, 3-Joseph Hot Springs.

iodometric method described by Brown, Skougstad, and Fishman (1970). Mercury was stabilized for analysis in the laboratory by addition of 2:1 H_2SO_4:HNO_3, 5-percent $KMnO_4$(w/v), and 5-percent $K_2S_2O_8$(w/v). Dissolved ammonia was determined by allowing the sample to cool to ambient temperature, adding sodium hydroxide to raise the pH to approximately 12, and measuring the dissolved ammonia with a dissolved ammonia specific-ion electrode. Water samples for aluminum determination were complexed with 8-hydroxyquinoline, buffered at pH 8.3, and extracted with methyl isobutyl ketone in the field as described by Barnes (1975).

Silica, sodium, potassium, lithium, rubidium, cesium, calcium, magnesium, cadmium, cobalt, copper, iron, nickel, lead, manganese, and zinc were determined in the laboratory by direct aspiration on a double-beam atomic-absorption spectrophotometer. Detection limits for the heavy metals in micrograms per liter (μg/L) are: cadmium (10), cobalt (50), copper (10), iron (20), nickel (20), lead (100), manganese (20), and zinc (10). Boron, depending on the concentration range, was determined by either the Dianthrimide or the Carmine method (Brown and others, 1970). Fluoride was determined by specific-ion electrode using the method of R. B. Barnes (U.S. Geological Survey, written commun., 1973). The colorimetric ferric thiocyanate method (American Society for Testing and Materials, 1974) was used for samples containing less than 10 mg/L (milligrams per liter) chloride. Higher chloride concentrations were titrated by the Mohr method (Brown and others, 1970). Sulfate was titrated by the Thorin method (Brown and others, 1970). Mercury was determined by a flameless atomic-absorption technique (U.S. Environmental Protection Agency, 1971). The organic extract containing the aluminum complex was analyzed by atomic absorption.

The CO_2-equilibrium method of Cohn and Urey (1938) and the uranium technique of Bigeleisen, Perlman, and Prosser (1952) were used in the analysis for oxygen and deuterium isotope ratios. Isotopic ratios of $^{18}O/^{16}O$ and D/H in the water samples were measured on a modified Nier double-collecting 6-in 60°-sector mass spectrometer.

Gases were analyzed by gas chromatography as soon as possible after returning to the laboratory, always within two weeks of collection. Linde molecular sieve 13X was used to separate and quantify (O_2 + Ar), N_2, and CH_4, while Porapak Q was used for CH_4 and CO_2.1/ The gas-chromatography columns were operated at room temperature with helium as the carrier gas. Gases were detected by thermal conductivity.

1/ The use of the brand name in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

WATER COMPOSITION

The chemical compositions of the thermal-spring waters are listed in table 2 by county and state. In Arizona, 15 water samples were collected from 13 thermal-spring areas. Six are fresh waters as defined by Robinove, Langford, and Brookhart (1958). In this classification fresh waters contain less than 1000 mg/L dissolved solids; slightly saline waters range from 1000 to 3000 mg/L; moderately saline waters from 3000 to 10,000 mg/L; and very saline waters from 10,000 to 35,000 mg/L. The fresh waters are of various types: Hookers Hot Springs, $Na-HCO_3$; unnamed hot spring on Eagle Creek, Na-Cl; hot well at Tonopah, Na-Cl; Pakoon Springs, $Ca-Mg-Na-HCO_3$; Quitobaquito Springs, $Na-SO_4$ and Castle Hot Springs, $Na-SO_4-Cl$. All of the slightly saline waters, which include the unnamed hot spring at Coolidge Dam, Indian Hot Springs, and Gillard Hot Springs, are Na-Cl waters. Clifton Hot Springs, the unnamed hot spring near Clifton, and the Mt. Graham hot mineral well issue Na-Cl waters of moderate salinity. The other moderately saline water is a $Na-HCO_3-Cl$ water from Verde Hot Springs.

The four springs sampled in the Gila Mountains of New Mexico issue fresh water of the $Na-HCO_3-Cl$ type. San Francisco Hot Springs issue slightly saline Na-Cl water. Radium Hot Springs also issue Na-Cl water but it is of moderate salinity. Springs in the San Ysidro KGRA issue moderately saline to very saline $Na-Cl-SO_4-HCO_3$ or $Na-SO_4-Cl$ waters at relatively low temperatures (11° to 25°C).

Thermo, Monroe, and Red Hill hot springs in Utah issue slightly saline waters. Thermo Hot Springs issue a $Na-SO_4-Cl-HCO_3$ water, whereas the more concentrated waters from Monroe and Red Hill hot springs are $Na-SO_4-Cl$ waters. Crater and Joseph hot springs issue moderately saline Na-Cl waters.

Generally, as salinity increases chloride becomes the major anion and the pH decreases from alkaline to near neutral. High fluoride concentrations (6 to 11 mg/L) are found in several of the fresh and slightly saline thermal waters in all three States. The ratio F/Cl decreases from 0.1 in fresh waters to 0.003 in the very saline waters. In contrast, high concentrations of boron are found only in moderately saline water (Verde Hot Springs, 8.9 mg/L B) or very saline waters (unnamed springs near San Ysidro, 7-11 mg/L B). Relatively high concentrations of magnesium (>30 mg/L) occur in slightly saline to very saline waters from Monroe Hot Springs, Joseph Hot Springs, Red Hill Hot Springs, Crater Hot Springs, Verde Hot Springs, the unnamed springs near San Ysidro and near Coolidge Dam. The springs near Clifton also contain appreciable magnesium (20 to 21 mg/L).

Minor and trace-element compositions are given in table 3. Dissolved ammonia concentrations exceed 0.1 mg/L only in waters issuing from springs associated with sedimentary rocks. Generally, lithium, rubidium, and cesium concentrations change in a manner similar to that of the sodium and potassium concentrations.

Table 2.--Major element chemical composition of thermal springs and wells

[Concentrations are in milligrams per liter]

Spring name	Temperature (°C)	pH	Silica (SiO_2)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Lithium (Li)	Alkalinity (as HCO_3)[1]	Sulfate (SO_4)	Chloride (Cl)	Fluoride (F)	Boron (B)	Dissolved constituents[2]
Cochise County, Arizona														
Hookers Hot Springs------------------------	51½	9.03	46	1.0	<0.1	68	0.5	0.11	170	3	4.0	2.0	0.03	294
Gila County, Arizona														
Unnamed warm spring (Coolidge Dam)---------	36	6.81	45	140	33	720	25	1.6	326	420	980	3.3	1.0	2,687
Graham County, Arizona														
Indian Hot Springs(A)----------------------	48	7.55	40	76	9.1	865	13	1.2	88	350	1,200	3.4	.57	2,630
(B)----------------------	45	7.51	39	78	8.1	1,000	12	1.3	89	380	1,400	3.7	.62	3,014
Mt. Graham hot mineral well----------------	42	7.58	55	110	10	2,600	11	1.9	103	680	[3] 3,800	6.4	1.4	7,436
Greenlee County, Arizona														
Clifton Hot Springs------------------------	39	7.00	55	430	16	1,500	82	2.6	163	72	[3] 3,150	2.3	.64	5,526
Unnamed hot spring (Clifton A)-------------	44	6.58	94	790	21	2,700	170	4.1	146	62	5,700	2.7	1.4	9,696
(Clifton B)-------------	59	7.07	95	740	20	2,600	170	4.0	145	68	5,500	2.8	1.2	9,352
Gillard Hot Springs------------------------	82	7.35	95	22	.8	450	14	.87	216	180	490	11	.41	1,483
Unnamed warm springs (Eagle Creek)---------	35	8.24	64	16	2.1	190	7.8	.39	283	45	120	10	.12	731
Maricopa County, Arizona														
Hot well (Tonopah)-------------------------	50½	8.24	24	14	.6	220	2.1	.24	83	87	260	5.7	.85	701
Mohave County, Arizona														
Pakoon Springs-----------------------------	30	7.82	17	48	17	20	8.2	.03	197	73	5.0	.19	.09	38

Table 2.--Major element chemical composition of thermal springs and wells--Continued

Spring name	Temperature (°C)	pH	Silica (SiO_2)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Lithium (Li)	Alkalinity (as HCO_3)[1]	Sulfate (SO_4)	Chloride (Cl)	Fluoride (F)	Boron (B)	Dissolved constituents[2]
Pima County, Arizona														
Quitobaquito Springs------------------------	23	7.90	42	34	10	190	4.4	0.11	298	93	140	4.4	0.67	820
Yavapai County, Arizona														
Verde Hot Springs--------------------------	36	6.51	69	110	39	950	35	1.2	1,570	560	550	1.4	8.9	3,931
Castle Hot Springs-------------------------	46	7.45	58	33	2.4	200	4.7	.29	125	210	140	8.4	.90	789
Catron County, New Mexico														
Unnamed hot spring (Gila Wilderness)-------	66	7.78	85	14	.1	150	3.1	.36	135	79	105	9.5	.11	587
San Francisco Hot Springs------------------	37	7.35	84	46	6.2	270	15	.43	121	39	430	1.4	.26	1,015
Dona Ana County, New Mexico														
Radium Hot Springs (well)------------------	52	7.13	78	120	15	1,100	160	1.2	414	260	[3]1,650	4.8	.68	3,857
Grant County, New Mexico														
Gila Hot Springs---------------------------	68	8.13	74	9.9	<.1	125	3.0	.23	101	45	105	9.1	.10	468
Unnamed hot spring (Gila River)------------	43	7.88	72	16	.7	145	2.7	.25	130	67	120	8.9	.14	558
Unnamed hot spring (E. Fork Gila River)----	[4]36	8.27	62	9.7	.6	100	1.5	.17	89	27	92	6.1	.12	385
Sandoval County, New Mexico														
Unnamed mineral spring (San Ysidro)--------	11	7.27	18	220	110	3,800	140	6.3	2,265	3,700	2,700	2.0	8.0	13,002
Unnamed warm spring (San Ysidro)-----------	25	6.25	15	390	65	3,000	91	5.2	1,855	2,600	[3]2,400	4.0	6.9	10,465
Unnamed warm spring (San Ysidro)-----------	15	6.33	20	300	68	2,000	83	6.1	2,005	1,200	1,900	3.4	11	7,653

Table 2.--Major element chemical composition of thermal springs and wells--Continued

Spring name	Temperature (°C)	pH	Silica (SiO_2)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Lithium (Li)	Alkalinity (as HCO_3)[1]	Sulfate (SO_4)	Chloride (Cl)	Fluoride (F)	Boron (B)	Dissolved constituents[2]
Beaver County, Utah														
Thermo Hot Springs	89½	7.98	113	71	10	380	52	1.3	360	480	225	6.6	0.93	1,700
Juab County, Utah														
Crater Hot Springs (A)	84	6.48	69	340	52	830	57	1.0	156	680	1,500	2.5	.86	3,692
(B)	82	6.84	69	340	54	840	59	1.0	158	680	1,500	2.6	.80	3,748
Sevier County, Utah														
Monroe Hot Springs (A)	70	6.20	59	300	36	530	55	.63	447	880	620	2.7	3.0	2,948
(B)	61	[5]7.0	59	300	38	580	52	.64	405	900	650	2.6	2.9	3,004
Red Hill Hot Spring	76½	6.25	58	290	34	590	60	.72	416	890	660	2.8	2.8	3,019
Joseph Hot Springs	63	6.51	90	260	44	1,450	50	1.9	408	1,200	1,700	3.0	4.9	5,230

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[1] Total alkalinity as bicarbonate.

[2] Dissolved constituents is the sum of the analyzed major constituents.

[3] Bromide: San Ysidro (7.9 mg/L), Radium Hot Spring (1.2 mg/L), Clifton Hot Springs (2.5 mg/L) and Mt. Graham hot mineral well (2.5 mg/L); Iodide: San Ysidro (0.3 mg/L), Radium Hot Springs (<0.1 mg/L), Clifton Hot Springs (0.1 mg/L), and Mt. Graham hot mineral well (0.3 mg/L).

[4] Temperature taken after collection, thermistor malfunction at spring did not allow an in-spring temperature to be determined.

[5] pH approximate due to meter instability.

Table 3.--Minor and trace element chemical composition of thermal springs and wells[1/]

[Concentrations are in milligrams per liter; dashes indicate the absence of data]

Spring name	Aluminum (Al)	Rubidium (Rb)	Ammonia (as N)	Cesium (Cs)	Manganese (Mn)	Copper (Cu)	Nickel (Ni)	Mercury (Hg)	Zinc (Zn)	Iron (Fe)
Cochise County, Arizona										
Hookers Hot Springs------------------------	0.035	<0.02	0.1	<0.1	<0.02	<0.01	<0.02	<0.0001	<0.01	<0.02
Gila County, Arizona										
Unnamed warm spring (Coolidge Dam)----------	<.001	.24	<.1	.1	<.02	<.01	<.02	---	<.01	<.02
Graham County, Arizona										
Indian Hot Springs (A)----------------------	<.001	.09	.1	<.1	<.02	<.01	<.02	.0001	.01	<.02
(B)----------------------	---	.07	<.1	<.1	<.02	<.01	<.02	.0004	<.01	<.02
Mt. Graham hot mineral well-----------------	.002	.07	.1	<.1	.09	<.01	.04	.0003	<.01	<.02
Greenlee County, Arizona										
Clifton Hot Springs------------------------	.001	.55	<.1	.3	.32	.02	.04	.0003	.02	<.02
Unnamed hot spring (Clifton A)--------------	<.001	1.2	.1	.5	1.0	.02	.06	.0001	.03	<.02
(Clifton B)--------------	---	1.2	---	.5	---	---	---	---	---	---
Gillard Hot Springs------------------------	.009	<.02	<.1	<.1	<.02	<.01	<.02	.0002	<.01	<.02
Unnamed warm springs (Eagle Creek)----------	<.001	.08	---	<.1	<.02	<.01	<.02	---	<.01	<.02
Maricopa County, Arizona										
Hot well (Tonopah)--------------------------	---	<.02	---	<.1	<.02	<.01	<.02	---	.01	.03
Mohave County, Arizona										
Pakoon Springs------------------------------	<.001	<.02	<.1	<.1	<.02	<.01	<.02	<.0001	<.01	<.02

Table 3.--Minor and trace element chemical composition of thermal springs and wells[1/]--Continued

Spring name	Aluminum (Al)	Rubidium (Rb)	Ammonia (as N)	Cesium (Cs)	Manganese (Mn)	Copper (Cu)	Nickel (Ni)	Mercury (Hg)	Zinc (Zn)	Iron (Fe)
Pima County, Arizona										
Quitobaquito Springs-------------------------	0.002	<0.02	---	<0.1	<0.02	<0.01	<0.02	---	<0.01	<0.02
Yavapai County, Arizona										
Verde Hot Springs---------------------------	.002	.10	<.1	<.1	.06	.01	.02	.0002	.04	.02
Castle Hot Springs--------------------------	---	.02	---	<.1	<.02	<.01	<.02	<.0001	<.01	<.02
Catron County, New Mexico										
Unnamed hot spring (Gila Wilderness)--------	.004	.03	---	<.1	<.02	<.01	<.02	---	<.01	<.02
San Francisco Hot Springs-------------------	---	.08	---	<.1	.03	<.01	<.02	---	<.01	<.02
Dona Ana County, New Mexico										
Radium Hot Springs (well)-------------------	<.002	1.3	<.1	.1	<.02	<.01	.02	<.0001	.08	<.02
Grant County, New Mexico										
Gila Hot Springs----------------------------	.005	.02	<.1	<.1	<.02	<.01	<.02	<.0001	<.01	<.02
Unnamed hot spring (Gila River)-------------	---	.02	---	<.1	<.02	<.01	<.02	<.0001	<.01	<.02
Unnamed hot spring (E. Fork Gila River)-----	---	<.02	---	<.1	<.02	<.01	<.02	---	<.01	<.02
Sandoval County, New Mexico										
Unnamed mineral spring (San Ysidro)---------	---	.64	---	.3	.05	.01	.04	---	.05	<.02
Unnamed warm spring (San Ysidro)------------	.007	.48	.12	.4	.30	.02	.04	<.0001	.06	.42
Unnamed warm spring (San Ysidro)------------	---	.49	---	.4	.57	.01	.03	<.0001	.02	.14

Table 3.--Minor and trace element chemical composition of thermal springs and wells[1/]--Continued

Spring name	Aluminum (Al)	Rubidium (Rb)	Ammonia (as N)	Cesium (Cs)	Manganese (Mn)	Copper (Cu)	Nickel (Ni)	Mercury (Hg)	Zinc (Zn)	Iron (Fe)
Beaver County, Utah										
Thermo Hot Springs----------------------------	0.003	0.50	0.10	0.2	0.02	<0.01	<0.02	<0.0001	<0.01	0.02
Juab County, Utah										
Crater Hot Springs (A)----------------------	.002	.26	.12	<.1	.25	.03	.02	<.0001	.06	.26
(B)----------------------	---	.24	---	<.1	.25	.01	<.02	---	.02	<.02
Sevier County, Utah										
Monroe Hot Springs (A)----------------------	.002	.22	.26	.1	.09	.01	<.02	.0002	.04	.90
(B)----------------------	---	.20	---	<.1	.11	<.01	<.02	---	.01	<.02
Red Hill Hot Spring------------------------	.005	.26	.42	.1	.07	.01	<.02	.0002	.03	.86
Joseph Hot Springs--------------------------	<.002	.24	.20	.1	.19	.01	.02	<.0001	.03	.27

[1/] Detectable concentrations of cadmium, cobalt, and lead were not found in any of the hot spring waters. Detection limits for the direct aspiration of solutions containing these elements on our A.A. are 0.01, 0.05, and 0.10 mg/L, respectively.

GAS COMPOSITION

Compositions of gases from 10 springs are given in table 4. Ellis (1970) has shown that springs associated with higher temperature thermal reservoirs (>200°C) discharge gas containing a large percentage of carbon dioxide. Springs associated with lower temperature thermal systems release principally nitrogen (Bodvarsson, 1964). Hookers Hot Springs, Indian Hot Springs, Pakoon Springs, and the unnamed hot spring on the Gila River discharge nitrogen-rich gas at very sporadic rates. The unnamed springs at San Ysidro and Monroe, Crater, Joseph, Thermo, and Verde hot springs discharge mixtures of carbon dioxide and nitrogen intermittently.

SOLUTION-MINERAL EQUILIBRIUM

Solution-mineral equilibrium calculations indicate that the concentrations of some of the chemical constituents may be altered by reequilibration with minerals at the spring orifice. Calculated free energies for the formation of carbonates, silicates, and fluorite from the spring waters are given in table 5. The silicate values are important because equilibration of the spring water with silica phases at the spring orifice would result in erroneous estimates of the temperature in the aquifer. Similarly, equilibrium or supersaturation with respect to calcium carbonate may indicate that calcium has been lost from the thermal fluid between the aquifer at depth and the surface.

Based on thermodynamic calculations, silica phases other than quartz could be controlling the silica concentration at some of the spring orifices, that is, amorphous silica at San Francisco Hot Springs; alpha-cristobalite at Gila Hot Springs, the unnamed springs at San Ysidro, Thermo Hot Springs, and Monroe Hot Spring; chalcedony at Hookers Hot Springs, Crater Hot Springs, and Red Hill Hot Springs. Calcium carbonate could be in equilibrium with waters in Clifton Hot Springs, Gillard Hot Springs, the hot well at Tonopah, Verde Hot Springs, Gila Hot Springs, the unnamed springs near San Ysidro, the well at Radium Springs, and all the springs sampled in Utah.

Equilibrium of fluorite (CaF_2) with the spring water is not important in controlling the calcium concentrations in the springs listed; calcium concentrations are a function of pH rather than fluoride concentrations. Fluorite is significantly unsaturated (arbitrarily more than 1 kcal1/) at Verde, San Francisco, Hookers, the unnamed hot springs near Clifton, and Pakoon Springs.

1/ To convert kilocalories to joules, multiply by 4.184×10^3.

Table 4.--Compositions of gases escaping from thermal springs
[Composition is in volume percent]

Spring name	Oxygen (O_2) and argon (Ar)	Nitrogen (N_2)	Methane (CH_4)	Carbon dioxide (CO_2)
Cochise County, Arizona				
Hookers Hot Springs------------------	5.8	92	<0.1	<0.1
Graham County, Arizona				
Indian Hot Springs(A)----------------	5.8	95	<.1	<.1
Mohave County, Arizona				
Pakoon Springs-----------------------	21	77	<.1	1.4
Yavapai County, Arizona				
Verde Hot Springs--------------------	1.6	20	<.1	73
Grant County, New Mexico				
Gila Hot Spring----------------------	7.5	86	<.1	1/
Sandoval County, New Mexico				
#2 Unnamed spring near San Ysidro----	1.1	32	<.1	61
Beaver County, Utah				
Thermo Hot Springs-------------------	1.5	4.8	<.1	84
Juab County, Utah				
Crater Hot Springs-------------------	3.6	76	.6	21
Sevier County, Utah				
Monroe Hot Springs-------------------	3.0	39	.3	57
Joseph Hot Springs-------------------	2.2	73	.1	26

---

[1] No data due to breakage of syringe during analysis.

Table 5.--States of reactions with respect to calcite, aragonite, chalcedony, alpha-cristobalite, and fluorite

Spring name	ΔG (kcal)[1]				
	Calcite	Aragonite	Chalcedony	Alpha-cristobalite	Fluorite
	Cochise County, Arizona				
Hookers Hot Spring	-0.13	-0.20	-0.06	-0.35	-3.45
	Gila County, Arizona				
Unnamed warm spring (Coolidge Dam)	-.31	-.37	+.42	+.16	+.03
	Graham County, Arizona				
Indian Hot Springs (A)	-.16	-.23	+.19	-.09	-.35
(B)	-.28	-.35	+.22	+.06	-.22
Mt. Graham Hot mineral well	-.12	-.19	+.49	-.22	+.48
	Greenlee County, Arizona				
Clifton Hot Springs	+.18	+.12	+.54	+.27	+.18
Unnamed hot spring (Clifton A)	-.17	-.24	+.83	+.55	+.55
(Clifton B)	+.77	+.68	+.65	+.36	-1.81
Gillard Hot Springs	+.12	0.00	+.31	.00	+.34
Unnamed warm spring (Eagle Creek)	+.55	+.48	+.62	+.36	+.33
	Maricopa County, Arizona				
Hot well (Tonopah)	+.02	-.05	-.22	-.51	-.46
	Mohave County, Arizona				
Pakoon Springs	+.36	+.31	-.09	-.35	-2.47
	Pima County, Arizona				
Quitobaquito Springs	+.28	+.23	+.56	+.30	+.05
	Yavapai County, Arizona				
Verde Hot Springs	-.08	-.14	+.71	+.44	-1.01
Castle Hot Springs	-.45	-.51	+.45	+.17	+.55

Table 5.--States of reactions with respect to calcite, aragonite, chalcedony, alpha-cristobalite, and fluorite--Continued

Spring name	ΔG (kcal)[1/]				
	Calcite	Aragonite	Chalcedony	Alpha-cristobalite	Fluorite
		Catron County, New Mexico			
Unnamed hot spring (Gila Wilderness)-----	+0.04	-0.05	+0.43	+0.14	+0.17
San Francisco Hot Springs-----------------	-.54	-.60	+.80	+.53	-1.35
		Dona Ana County, New Mexico			
Radium Hot Springs (well)-----------------	+.51	+.43	+.58	+.30	+.24
		Grant County, New Mexico			
Gila Hot Springs--------------------------	+.21	+.11	+.28	-.02	-.07
Unnamed hot spring (Gila River)-----------	-.21	-.28	+.61	+.34	-.32
Unnamed hot spring (E. Fork Gila River)---	-.33	-.40	+.59	+.32	-.31
		Sandoval County, New Mexico			
Unnamed mineral spring (San Ysidro)-------	+.74	+.70	+.30	+.04	-.43
Unnamed warm spring (San Ysidro)----------	-.04	-.10	-.04	-.30	-.55
Unnamed warm spring (San Ysidro)----------	-.11	-.15	+.28	+.02	+.50
		Beaver County, Utah			
Thermo Hot Springs------------------------	+2.21	+2.08	+.28	-.03	+.20
		Juab County, Utah			
Crater Hot Springs (A)--------------------	+.04	-.08	+.10	-.21	-.26
(B)--------------------	+.65	+.53	+.12	-.18	-.12
		Sevier County, Utah			
Monroe Hot Spring (A)---------------------	-.03	-.13	+.18	-.13	-.14
(B)---------------------	+1.50	+1.41	+.28	-.01	-.13
Red Hill Hot Springs----------------------	+.10	-.02	+.07	-.23	-.15
Joseph Hot Springs------------------------	+.10	+.01	+.52	+.22	-.18

[1/] Magnitude of ΔG is the departure from theoretical equilibrium in kilocalories; (+) values indicate supersaturation, (-) values unsaturation. Calculations were carried out using the computer program SOLMNEQ (Kharaka and Barnes, 1973). To convert from kilocalories to joules multiply by 4.184×10^3.

ISOTOPES

The isotopic compositions of the hot spring waters are listed in table 6. The data are expressed in the δ-notation

$$\delta_x = \frac{R_x - R_{std}}{R_{std}} 10^3\text{, where } R_x = (D/H)_x \text{ or } (^{18}O/^{16}O)_x \text{ of the sample}$$

and R_{std} is the corresponding ratio for Standard Mean Ocean Water (SMOW). Deuterium compositions are approximately those expected for meteoric water in the respective areas. Oxygen shifts, relative to the meteoric water line established by Craig (1961), are all relatively small (table 6). These minor shifts may result from such factors as rapid circulation of water through the system or low reservoir temperatures, either of which allow relatively little reaction between water and country rock. Other possibilities include dilution of geothermal fluids with fresh water, or association with old geothermal systems in which isotopic equilibrium between water and rock has been established by replacing the heavy oxygen atoms originally present in the rock with lighter oxygen atoms from the water.

Deuterium compositions of water from San Francisco Hot Springs and the adjacent river are sufficiently different, 8 parts per mil, that large-scale dilution by river water does not appear likely, nor is the river the likely recharge source for the spring. By contrast, the thermal well at Radium Springs (δD = -74.6‰) and the adjacent Rio Grande (δD = -72.5‰) are similar in deuterium composition. Therefore, water from the river may be mixing with the thermal water or may be the recharge source for the well. Deuterium compositions of thermal springs in the San Ysidro KGRA (δD = -86.5‰) and the upper Cañon de San Diego adjacent to Valles Caldera are similar (δD = -86.8‰; F. W. Trainer, U.S. Geological Survey, oral commun., 1977), indicating that the springs may be part of the same thermal system or, at least, the springs have recharge water of similar isotopic composition.

Mixing of thermal and fresh water can be conclusively demonstrated from the relationship of the deuterium composition and the chloride concentration (Giggenbach, 1971). In the simplest case, a fresh water containing a low chloride concentration dilutes a high-chloride thermal water to produce thermal waters of intermediate chloride composition. If the fresh and thermal waters have different deuterium compositions then the springs issuing water of intermediate chloride composition will also have intermediate deuterium compositions. A plot of δD versus chloride concentration for these waters would be a straight line. These plots (fig. 2) may be interpreted to suggest dilution in the springs near Clifton, Arizona. Mixing does not appear to be affecting the composition of most of the sampled springs in the Gila Mountains, New Mexico. Dilution may have occurred in the unnamed hot spring on the east fork of the Gila River; however, some dilution was expected as this spring issues

Table 6.--Thermal water δD and $\delta^{18}O$ in parts per mil (‰)
[Delta values are reported relative to SMOW]

Spring name	δD	$\delta^{18}O$	Oxygen shift[1]
Cochise County, Arizona			
Hookers Hot Springs	-83.7	-11.77	-0.06
Gila County, Arizona			
Unnamed warm spring (Coolidge Dam)	-79.3	-10.75	+0.41
Graham County, Arizona			
Indian Hot Springs (A)	-85.8	-11.42	+0.56
(B)	-86.4	-11.42	+0.63
Mt. Graham hot mineral well	-83.4	-11.03	+0.65
Greenlee County, Arizona			
Clifton Hot Springs	-76.2	- 9.73	+1.05
Unnamed hot spring (Clifton A)	-84.0	-10.95	+0.80
Gillard Hot Springs	-86.5	-10.87	+1.19
Unnamed warm springs (Eagle Creek)	-89.0	-12.01	+0.37
Maricopa County, Arizona			
Hot well (Tonopah)	-75.3	- 9.89	+0.77
Mohave County, Arizona			
Pakoon Springs	-103.9	-13.85	+0.39
Pima County, Arizona			
Quitobaquito Springs	-61.7	- 8.28	+0.68
Yavapai County, Arizona			
Verde Hot Springs (A)	-85.2	-11.65	+0.25
Castle Hot Springs	-83.2	-11.38	+0.27

Table 6.--Thermal water δD and $\delta^{18}O$ in parts per mil (‰)--Continued

Spring name	δD	$\delta^{18}O$	Oxygen shift[1]
Catron County, New Mexico			
Unnamed hot spring (Gila Wilderness)	-83.6	-11.03	+0.67
San Francisco Hot Springs	-78.6	-10.44	+0.64
Dona Ana County, New Mexico			
Radium Hot Springs (well)	-74.6	- 9.06	+1.52
Grant County, New Mexico			
Gila Hot Springs	-82.8	-11.03	+0.57
Unnamed hot spring (Gila River)	-81.2	-10.87	+0.53
Unnamed hot spring (E. Fork Gila River)	-80.5	-10.75	+0.56
Sandoval County, New Mexico			
Unnamed mineral spring (San Ysidro)	-85.6	-10.01	+1.94
Unnamed warm spring (San Ysidro)	-90.1	-11.22	+1.29
Unnamed warm spring (San Ysidro)	-86.5	-10.12	+1.94
Beaver County, Utah			
Thermo Hot Springs	-118.3	-14.32	+1.72
Juab County, Utah			
Crater Hot Springs (A)	-126.3	-16.09	+0.95
(B)	-126.6	-15.81	+1.27
Sevier County, Utah			
Monroe Hot Springs (A)	-128.3	-16.95	+0.34
(B)	-127.3	-16.68	+0.48
Red Hill Hot Spring	-127.3	-16.95	+0.21
Joseph Hot Springs	-133.4	-17.32	+0.60

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[1] Shift in $\delta^{18}O$ relative to the meteoric water line, $\delta D = 8\delta^{18}O + 10$.

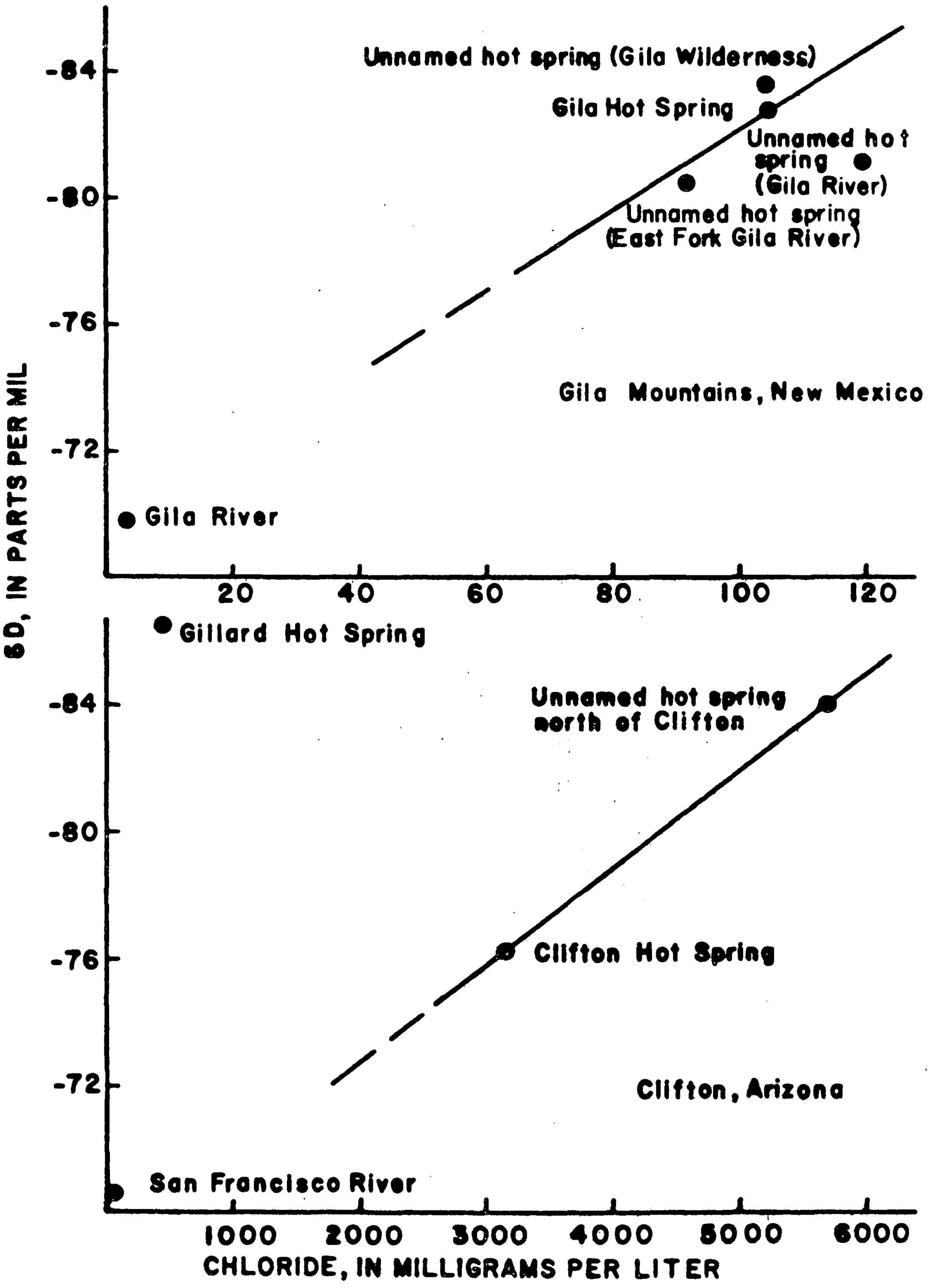

FIGURE 2.--Deuterium versus chloride plots for water collected from the Gila Mountains, N. Mex., and Clifton, Ariz.

from gravel adjacent to the river. Monroe and Red Hill hot springs in Utah may issue mixed waters but available isotopic data are inconclusive. More detailed sampling would be required to prove mixing in any of the areas.

GEOTHERMOMETRY

The chemical geothermometers, based on the concentration of silica or the proportions of sodium, potassium, and calcium in the spring waters, are relevant only if the hot spring or well is associated with a hot water system. These geothermometers are meaningless for the acid-sulfate springs associated with vapor-dominated systems such as The Geysers in California or Larderello in Italy. White, Muffler, and Truesdell (1971) have discussed the important characteristics of hot water and vapor-dominated systems. All the hot spring waters discussed in this report have either a neutral or slightly alkaline pH which is characteristic of hot water systems.

The basic assumptions (Fournier, White, and Truesdell, 1974) which must be fulfilled before the geothermometers can be meaningful are listed below:

1. Temperature-dependent reactions at depth.
2. An adequate supply of the constituents used for geothermometry.
3. Water-rock equilibrium at depth.
4. Negligible reequilibration as the water flows to the surface.
5. No dilution or mixing of hot and cold waters.

The last two assumptions are violated in some of the sampled springs.

The quartz geothermometer (Fournier and Rowe, 1966) is based on the assumption that the solubility of quartz is controlling the concentration of silica in the reservoir fluid. However, Arnórsson (1975) has demonstrated that the silica concentration in many hot springs associated with low-temperature reservoirs (less than 180°C) is controlled by the solubility of chalcedony.

The Na-K-Ca geothermometer (Fournier and Truesdell, 1973) has superseded the previously suggested Na-K geothermometer of Ellis (1970) and White (1970). In deciding which Na-K-Ca geothermometer to use (beta equals 1/3 or 4/3), the guidelines of Fournier and Truesdell (1973) were generally used. They suggested that log ($\sqrt{Ca}/Na$) be calculated. If the value is negative, then beta equal 1/3 should be used to estimate the temperature. However, if log ($\sqrt{Ca}/Na$) is positive then the temperature should be estimated with beta equal to 4/3. If the calculated temperature with beta equal to 4/3 is less than 100°C, accept it as the best temperature estimate, otherwise recalculate with beta equal to 1/3.

Most problems in interpreting the results of geothermometer calculations are due to reequilibration or mixing. Reequilibration can affect either the silica or Na-K-Ca geothermometers. The most common problem with the Na-K-Ca geothermometer is the precipitation of calcium carbonate. Loss of calcium, due to escape of carbon dioxide, causes the Na-K-Ca geothermometer to estimate excessively high temperatures. Therefore, waters which are in equilibrium or supersaturated with calcite or aragonite often give excessively high estimates of aquifer temperature. Similarly, waters in equilibrium with fluorite could contain too much or too little calcium, depending on the extent of water-rock interaction. Calcium concentrations could be excessively high if fluorite dissolution is controlling the Ca/F ratio. Conversely, calcium released by the dissolution of plagioclase could react with fluoride to precipitate fluorite. However, we have shown that in Montana equilibrium with calcium carbonate is attained before equilibrium with fluorite (Mariner and others, 1976). The proportions of Na, K, and Ca are assumed to be controlled by exchange reactions among silicates even though the absolute concentration of calcium is controlled by the solubility of carbonate (Fournier and Truesdell, 1973). Magnesium concentrations which are sufficiently large compete with the other cations in the exchange reactions and result in excessively high estimates of aquifer temperature. However, magnesium concentrations are never large in high-temperature geothermal systems (Mahon, 1970; Ellis, 1970).

The silica geothermometers are based on the temperature-dependent solubility of a silica mineral, generally quartz or chalcedony. Waters which are theoretically in equilibrium with amorphous silica are difficult to interpret because they may result from the cooling of waters originally in equilibrium with quartz or chalcedony in a higher temperature aquifer or weathering reactions at the spring temperature. Mixing of fresh water with thermal water decreases the silica concentration by dilution and results in low estimates of aquifer temperatures. Mixing diagrams (Truesdell and Fournier, 1977) can be used to determine the aquifer temperature if the mixed water has not lost heat after mixing. Conductive heat losses are particularly severe in springs of low discharge (<100 L/min). For example, if a thermal water at 125°C in which chalcedony is controlling the silica concentration is mixed with a cold water (10°C containing 50 mg/L silica), a mixed water at 75°C containing 91 mg/L silica is produced. If no heat is lost by conduction, a reservoir temperature of 125°C is determined from the mixing diagram (fig. 3). If the mixed water cools to 60°C before it issues at the surface, an aquifer temperature of 145°C is estimated. Additional cooling greatly magnifies the problem. If the water cools to 50°C before it issues at the surface, an aquifer temperature of 161°C is estimated. The argument is also valid for aquifers in which the solubility of quartz is controlling the silica concentration.

The geothermometers calculated from the water analyses are presented in table 7 with comments on problems of interpretation. The underlined numbers represent the best estimates selected on the basis of the criteria

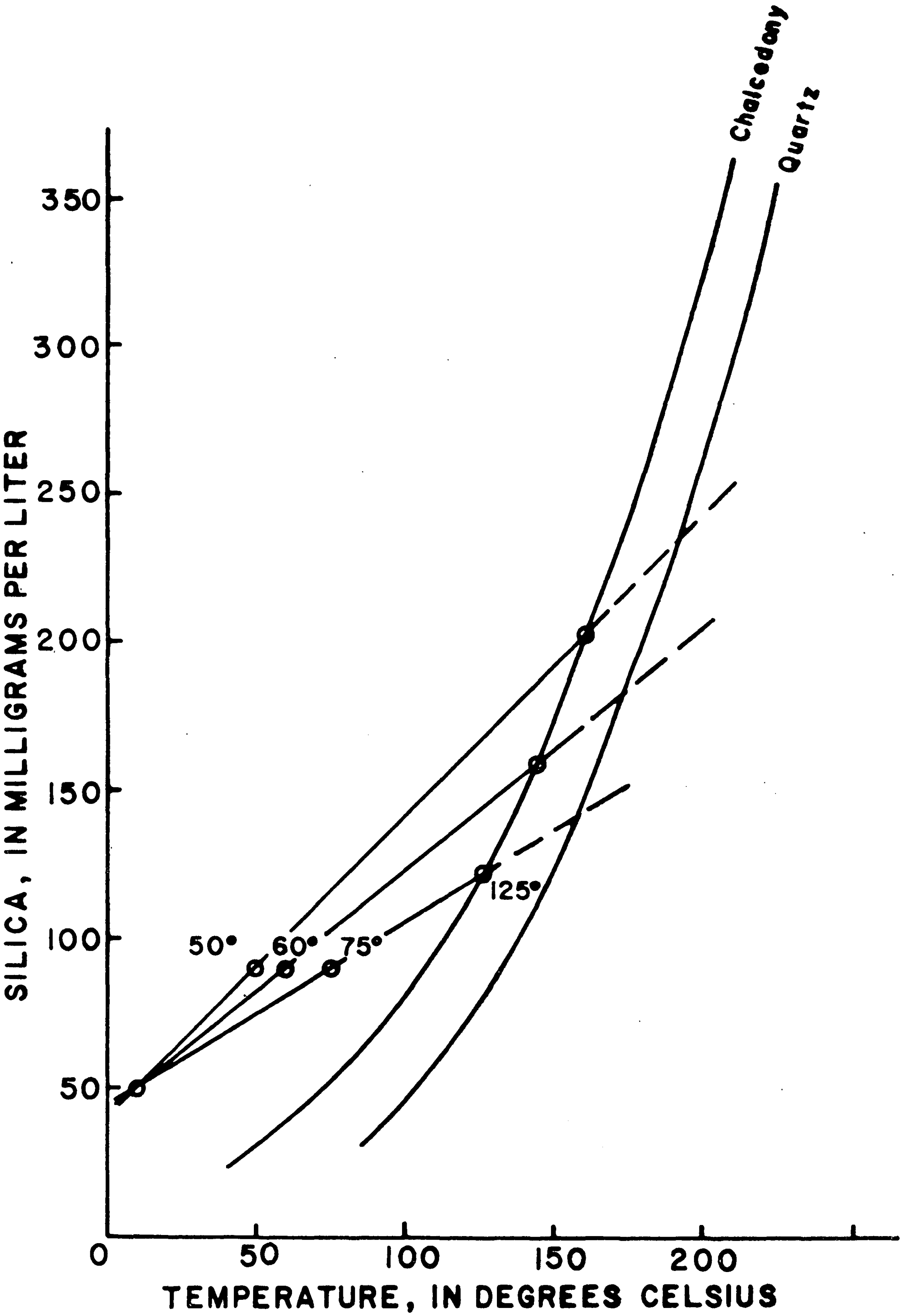

FIGURE 3.--Dissolved silica-temperature graph for determining the temperature of a hot-water component mixed with cold water to produce a warm spring water. If precise calculations are required, see Truesdell and Fournier (1977) and use enthalpy and silica concentrations in milligrams per kilogram.

Table 7.--Estimated thermal aquifer temperatures based on the chemical composition of the thermal spring waters

Spring name	Geothermometers (all temperatures are in degrees Celsius (°C))					Spring temperature (°C)	Comments
	Alpha-cristobalite[1]	Chalcedony[1]	Quartz	Na-K-1/3Ca	Na-K-4/3Ca		
			Cochise County, Arizona				
Hookers Hot Springs	28	[2]46	98	79	63	51½	Low-temperature reservoir; nonquartz silica control.
			Gila County, Arizona				
Unnamed warm spring (Coolidge Dam)	46	66	94	137	111	36	Low flow; probably low-temperature reservoir; large concentration of magnesium.
			Graham County, Arizona				
Indian Hot Springs (A)	40	60	92	109	104	48	Probable low temperature; calcite ppt (?); nonquartz silica control.
(B)	39	59	91	102	102	45	Probable low temperature; calcite ppt (?); nonquartz silica control.
Mt. Graham hot mineral well	55	76	106	75	102	42	Probable low temperature; calcite ppt (?); nonquartz silica control.
			Greenlee County, Arizona				
Clifton Hot Springs	56	76	106	161	139	39	Calcite ppt (?); probably a mixed water; however the spring has a very low flow rate.
Unnamed hot spring (Clifton A)	83	106	134	172	163	44	Calcite ppt (?); probably a mixed water; very low flow rate.
(Clifton B)	83	106	134	174	165	59	Calcite ppt (?); probably a mixed water; very low flow rate.
Gillard Hot Springs	83	106	134	139	131	82	Possible equilibrium with alpha-cristobalite and aragonite at spring temperature; may be a mixed water (?) from 140°C reservoir.

Table 7.--Estimated thermal aquifer temperatures based on the chemical composition of the thermal spring waters--Continued

Spring name	Geothermometers (all temperatures are in degrees Celsius (°C))					Spring temperature (°C)	Comments
	Alpha-cristobalite[1]	Chalcedony[1]	Quartz	Na-K-1/3Ca	Na-K-4/3Ca		
			Greenlee County, Arizona--Continued				
Unnamed warm spring (Eagle Creek)--------	60	82	114	142	104	35	Equilibrium with amorphous silica at spring temperature; supersaturated calcite; probable low-temperature reservoir, very low flow rate.
			Maricopa County, Arizona				
Hot well (Tonopah)----------------------	--	35	70	86	65	50½	Low-temperature reservoir.
			Mohave County, Arizona				
Pakoon Springs--------------------------	--	25	57	213	58	30	Low-temperature reservoir.
			Pima County, Arizona				
Quitobaquito Springs--------------------	43	62	94	11	68	23	Low-temperature reservoir.
			Yavapai County, Arizona				
Verde Hot Springs-----------------------	67	89	118	146	136	36	Equilibrium with calcite and amorphous silica at spring temperature? Probably a low-temperature reservoir in a basaltic aquifer.
Castle Hot Springs----------------------	58	79	109	113	71	46	Low-temperature reservoir.

Table 7.--Estimated thermal aquifer temperatures based on the chemical composition of the thermal spring waters--Continued

Spring name	Geothermometers (all temperatures are in degrees Celsius (°C))					Spring temperature (°C)	Comments
	Alpha-cristobalite[1/]	Chalcedony[1/]	Quartz	Na-K-1/3Ca	Na-K-4/3Ca		
Catron County, New Mexico							
Unnamed hot spring (Gila Wilderness)-----	77	100	129	110	73	66	Low-temperature reservoir; dilute water.
San Francisco Hot Springs----------------	77	100	129	151	107	37	Low flow rate (est. 20 L/min); no gas; approximate equilibrium with amorphous silica at the spring temperature, probably a low-temperature aquifer (<100°C).
Doña Ana County, New Mexico							
Radium Hot Springs (well)----------------	73	96	124	222	214	52	Reported bottom-well temperature 74°C; $CaCO_3$ ppt ; perhaps insufficient development prior to sampling.
Grant County, New Mexico							
Gila Hot Springs-------------------------	67	89	122	114	78	68	Low-temperature reservoir; dilute water.
Unnamed hot spring (Gila River)----------	67	89	120	104	65	43	Low-temperature reservoir; dilute water.
Unnamed hot spring (E. Fork Gila River)--	58	79	112	92	56	[3/]36	Low-temperature reservoir; dilute water.
Sandoval County, New Mexico							
Unnamed mineral spring (San Ysidro)------	10	27	60	162	206	11	Geothermometers doubtful because of water rock interaction and $CaCO_3$ ppt.
Unnamed warm spring (San Ysidro)---------	4	20	53	144	158	25	Geothermometers doubtful because of water rock interaction and $CaCO_3$ ppt.
Unnamed warm spring (San Ysidro)---------	14	31	63	155	155	15	Geothermometers doubtful because of water rock interaction and $CaCO_3$ ppt.
Beaver County, Utah							
Thermo Hot Springs-----------------------	88	112	144	200	153	89½	Possible equilibrium with alpha-cristobalite at spring temperature; low flow rate makes interpretation difficult; probably 150°C system with water chemistry modified by water-rock reaction.

Table 7.--Estimated thermal aquifer temperatures based on the chemical composition of the thermal spring waters--Continued

Spring name	Geothermometers (all temperatures are in degrees Celsius (°C))					Spring temperature (°C)	Comments
	Alpha-cristobalite[1]	Chalcedony[1]	Quartz	Na-K-1/3Ca	Na-K-4/3Ca		
			Juab County, Utah				
Crater Hot Springs (A)	68	90	119	164	123	84	High flow rate; precipitation $CaCO_3$ probable; probably a low-temperature system (<100°C).
(B)	68	90	119	164	123	82	High flow rate; precipitation $CaCO_3$ probable; probably a low-temperature system (<100°C).
			Sevier County, Utah				
Monroe Hot Springs (A)	60	81	118	179	118	70	High flow rate; precipitation $CaCO_3$ possible, could be a mixed water or 90°C system.
(B)	60	80	117	172	117	61	High flow rate; precipitation $CaCO_3$ possible, could be a mixed water or 90°C system.
Red Hill Hot Spring	--	80	110	179	124	76½	High flow rate; precipitation $CaCO_3$ possible, could be a mixed water or 90°C system.
Joseph Hot Springs	78	101	129	141	132	63	High flow rate; precipitation $CaCO_3$ possible, could be a mixed water or 100°C system.

[1] Dissociation of H_4SiO_4 taken into consideration in calculating the chalcedony and alpha-cristobalite geothermometers.

[2] Underlined numbers are the geothermometer estimates favored by the authors.

[3] Temperature not measured in spring due to thermistor malfunction.

of questionable validity because the spring waters may have lost heat conductivity and gained silica by water-rock reaction. Gillard Hot Springs also issues at a low flow rate but it does not contain appreciable magnesium. The low magnesium concentration may indicate that the springs are associated with a higher temperature aquifer.

None of the springs or wells sampled in New Mexico appear to have geothermal potential. The four thermal springs in and near the Gila KGRA all have chemical compositions which indicate probable equilibrium with a thermal aquifer only 10° to 20°C greater than the spring temperatures. Estimated reservoir temperatures based on the Na-K-Ca geothermometer range from 56° to 78°C. Similar temperatures (62° to 77°C) are calculated if the solubility of alpha-cristobalite is assumed to be controlling the silica concentrations. The nitrogen-rich gas escaping from the springs also favors a low-temperature reservoir. San Francisco Hot Springs is chemically and physically similar to springs near the Clifton KGRA in Arizona. The springs issue on the edge of a river, at low flow rates, at low temperatures (37°C), and without the release of appreciable gas. Equilibrium with amorphous silica at the spring temperature is theoretically possible. The chalcedony geothermometer indicates a temperature of 100°C. If mixing has occurred and quartz rather than amorphous silica is controlling the silica concentration, then a temperature of more than 200°C is estimated. The Na-K-1/3Ca geothermometer indicates a temperature of 151°C; however, the Na-K-4/3Ca geothermometer indicates 107°C. The magnesium concentration (6.2 mg/L) may be large enough to influence the choice between the Na-K-4/3Ca and Na-K-1/3Ca geothermometers as the Na-K-4/3Ca geothermometer indicates a temperature very near 100°C. The magnitude of the magnesium interference on the Na-K-Ca geothermometer has never been evaluated. This problem is discussed in more detail later. The lack of a gas phase and the low spring temperature make association with a high-temperature aquifer unlikely.

Similar problems occur at the Radium Hot Springs well. The water may be in equilibrium with alpha-cristobalite at the reported bottom-hole temperature (74°C) or may issue a mixed water from a reservoir at 160°C or more in which quartz is controlling the silica concentration. Precipitation of calcium carbonate and the rather large magnesium concentration (15 mg/L) may be the reason for the 220°C temperature estimated from the Na-K-Ca geothermometer. The low flow rate, low temperatures, and possible precipitation of calcium carbonate make quantitative interpretation of the geothermometers difficult in the San Ysidro KGRA. Equilibrium with chalcedony or alpha-cristobalite is possible for all three springs. Trainer (1975) has suggested that these springs may represent fluid which has leaked from the thermal system in Valles Caldera.

All the thermal springs sampled in Utah could be considered mixed waters because they issue at less than boiling temperatures and have cation geothermometer estimates markedly higher than the measured spring temperature. Calculations assuming equilibrium with quartz and dilution with a cold water at 10°C which contains 30 mg/L silica indicate a possible reservoir temperature of 130°C to 140°C for Red Hill, Monroe, and Crater hot springs. The Na-K-Ca geothermometer indicates temperatures which are 20° to 30°C higher, possibly due to precipitation of calcium carbonate as the water moves to the surface. Those waters all have relatively large magnesium concentrations (>30 mg/L). The low flow rate of Joseph Hot Springs results in considerable conductive heat loss and the estimated reservoir temperature of 150°C based on mixing calculations may be excessively high. The temperature estimated from the Na-K-Ca geothermometer (200°C) indicate that Thermo Hot Springs may be associated with a high-temperature reservoir. Mixing calculations assuming equilibrium with quartz, dilution with a cold water of 10°C containing 30 mg/L silica, and no boiling, indicate a possible reservoir temperature of 190°C. The quartz geothermometer, assuming no mixing or boiling, indicates 144°C. The sulfate-isotope geothermometer (McKenzie and Truesdell, 1975), assuming no mixing or boiling, indicates an aquifer temperature of 151°C (N. L. Nehring, U.S. Geological Survey, oral commun., 1976). A second sulfate-isotope sample collected and analyzed by A. H. Truesdell of the U.S. Geological Survey indicated an aquifer temperature of 142°C. The Na-K-Ca geothermometer probably estimates an excessively high temperature because calcium has been lost from the solution by precipitation of calcite. The agreement between the quartz and sulfate-isotope geothermometers may be fortuitous but until proof of mixing is available an aquifer temperature of 140°C to 145°C is the best estimate.

The high magnesium concentrations (>30 mg/L) at Thermo, Monroe, Joseph, Red Hill, and Crater hot springs may indicate that the cation proportions as well as silica concentrations have been altered by water-rock interaction after the fluid left the thermal aquifer. This may invalidate the Na-K-Ca and quartz or chalcedony geothermometers. Furthermore, these springs issue near basaltic rocks, alteration of which would produce chalcedony rather than quartz. Mixing calculations assuming equilibrium with chalcedony rather than quartz indicate aquifer temperatures less than 100°C except at Joseph Hot Springs. The 200°C estimate for Joseph Hot Springs may be due to conductive cooling. The high magnesium concentration and lack of evidence of mixing seem to favor a low temperature (80° to 130°C) for the aquifers associated with Monroe, Joseph, Red Hill, and Crater hot springs.

A relationship appears to exist between the magnesium concentration of the water and the difference between the values estimated from the Na-K-Ca and chalcedony geothermometers (fig. 4). In the limiting case, differences between the temperatures estimated from the geothermometers increase approximately 1½°C for each 1 mg/L increase in magnesium. The larger deviations from the limiting case (fig. 4) may be caused by factors which we have discussed previously, such as precipitation of calcium carbonate, dilution, equilibrium with quartz, or extensive reaction between water and the conduit walls. Precipitation of calcite is the most probable cause for a large part of the deviations from the line observed for the well at Radium Hot Springs, Thermo Hot Springs, Red Hill Hot Springs, Monroe Hot Springs, the unnamed hot springs on

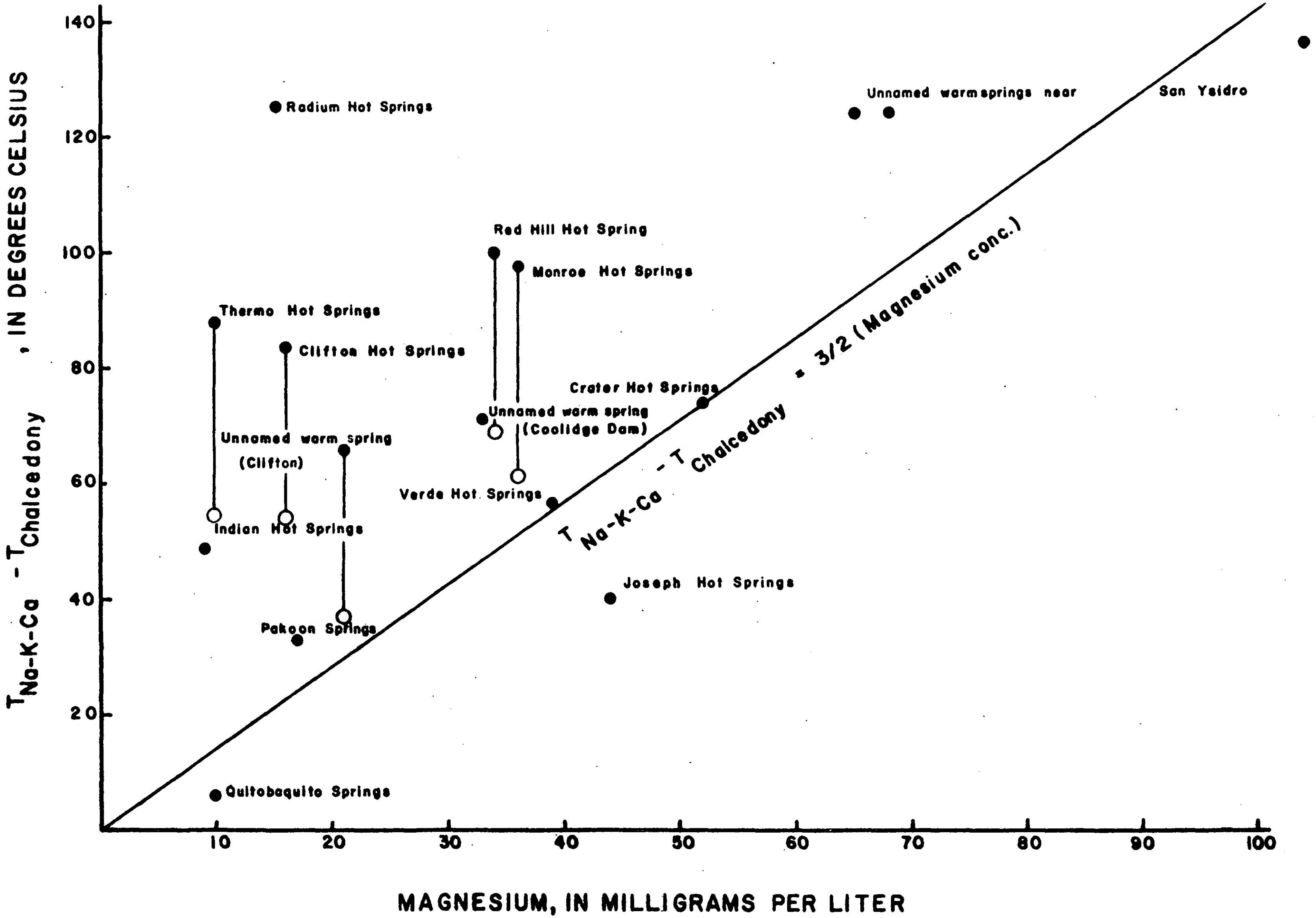

FIGURE 4.--Plot of the differences in estimated aquifer temperatures between the Na-K-Ca and chalcedony geothermometers as a function of the magnesium concentration. The assumption that quartz rather than chalcedony is controlling the silica concentration in waters which are thought to be associated with higher temperature aquifers markedly improves the trend. Points representing equilibrium with quartz are depicted as open circles.

Eagle Creek, and some of the springs in the San Ysidro KGRA. These springs are all slightly supersaturated with respect to calcite and have travertine deposits. The thermal springs in and near Clifton may deviate from the trend because of dilution or equilibrium with quartz in the thermal aquifer. Dilution may also have occurred at Indian Hot Springs, the springs near Coolidge Dam, and in any of the springs depositing calcite. Joseph Hot Springs may plot below the line because silica was released by reaction between the water and the walls of the conduit. Equilibrium with quartz rather than chalcedony is possible at Thermo Hot Springs, Red Hill Hot Springs, Monroe Hot Springs, Clifton Hot Springs, and the unnamed spring near Clifton. A much tighter group of points is achieved if this assumption is correct (points assuming equilibrium with quartz are shown as open circles, on fig. 4). This observation is approximate and no alteration of the Na-K-Ca geothermometer is suggested at this time.

Swanberg (1974) inferred that many of the hot springs in Utah are attractive geothermal prospects. However, he did not utilize all of the chemical data available in Mundorff (1970). Calculations based on the assumption that the solubility of chalcedony is controlling the silica concentration indicate that most of the springs could be in equilibrium with chalcedony at temperatures near or only slightly above the measured spring temperatures (table 8). Also, based on data in Mundorff (1970), all the springs are slightly supersaturated with respect to calcium carbonate and precipitation may be controlling the calcium concentration in many of the waters. The conclusion of Mundorff (1970) that most of these springs are deep circulation waters which have never been appreciably hotter than the spring temperature is plausible. The low P_{CO_2} for these waters, less than 0.05 atm, also favors a low-temperature system. High magnesium concentrations in these waters may account, in part, for the higher temperatures estimated using the Na-K-Ca geothermometer.

SUMMARY

The hot springs sampled in Arizona, New Mexico, and Utah have a considerable range in chemical composition. The most dilute waters contain 290 to 1,000 mg/L dissolved constituents and are sodium bicarbonate or sodium bicarbonate chloride waters of slightly alkaline pH (7.9-9.2). Fluoride is particularly abundant in these low-salinity waters. Castle Hot Springs, the unnamed spring on Eagle Creek, and springs in the Gila Mountains contain more than 8 mg/L fluoride. The more saline waters are usually sodium mixed-anion in character and have near neutral pH's (6 to 8). These more saline waters do not contain nearly as much fluoride although they are theoretically in thermodynamic equilibrium (±0.2 kcal) with fluorite at the respective spring temperatures. Deuterium compositions in all the thermal waters are those expected for meteoric waters in the respective areas. Nitrogen is the principal gas discharged by most of the thermal springs. Carbon dioxide

Table 8.--Chemical potential for the formation of calcite from spring waters, calculated P_{CO_2}, chalcedony temperatures, and Na-K-Ca temperatures for selected thermal springs in Utah [Calculated values and reported spring temperatures are based on the data of Mundorff (1970)]

Spring[1]	$\Delta G_{calcite}$ (kcal)[2]	P_{CO_2} (atm.)	$T_{chalcedony}$ (°C)	$T_{Na-K-Ca}$ (°C)	Spring temperature (°C)
Utah Hot Springs---------------	+0.81	0.02	54	234	57
Ogden Hot Springs--------------	+1.36	<.01	65	223	57
Southwest Hooper Warm Springs--	+1.02	.01	70	223	32
Meadow Hot Springs-------------	+1.39	.01	68	68	41
Hooper Hot Springs-------------	+1.39	.01	47	205	48
Castilla Hot Springs-----------	+1.26	.03	48	62	40
Crystal (Madsens) Hot Springs-	+1.90	<.01	41	188	43
Stinking Hot Springs-----------	+.92	.03	63	186	47
Fish Springs-------------------	+.12	.01	31	168	22
Laverkin (Dixie) Hot Springs---	+1.43	.04	45	191	42
Wasatch Hot Springs------------	+1.61	<.01	22	150	41
Becks Hot Springs--------------	+1.32	<.01	51	154	55
Uddy Hot Springs---------------	+.89	.02	42	165	53
Goshen Warm Springs------------	+.59	<.01	25	150	21
Blue Warm Springs--------------	+.83	<.01	--	161	27
Big Warm Spring----------------	+.13	<.01	-1	166	18
Grantsville Warm Springs-------	+.64	<.01	44	152	24
Crystal Hot Springs------------	+.88	.03	71	204	58

[1] Complete spring descriptions, locations, and chemical analyses are given in Mundorff (1970).

[2] "Plus" ΔG values indicate supersaturation and "minus" values indicate undersaturation.

makes up more than 20 percent of the gas discharging from Thermo, Monroe, Crater, Joseph, Red Hill, and Verde hot springs as well as the unnamed warm springs in the San Ysidro Known Geothermal Resource Area. Chloride-isotope relationships demonstrate that the thermal springs near Clifton issue mixed waters from a single thermal system. These same relationships show that springs along the headwaters of the Gila River in New Mexico are not part of a large system in which the waters are diluted near the surface. Insufficient data are available to demonstrate mixing in the other areas.

Based on the chemical and isotopic composition of the thermal waters and assuming no mixing, Thermo Hot Springs may be associated with a 140°C system. Mixing calculations for Crater, Monroe, and Red Hill hot springs, assuming equilibrium with quartz, produce temperature estimates near 150°C for the thermal aquifers. Similar calculations, assuming equilibrium with chalcedony, indicate temperatures of less than 100°C. The Na-K-Ca geothermometer indicates temperatures of 165°C to 180°C for these springs; however, these estimates are probably too high because of the high magnesium concentration. Thermal springs in or near the Gila KGRA in New Mexico are associated with low-temperature (<100°C) systems. Estimated temperatures for springs or wells in the Radium, San Ysidro, and San Francisco KGRA's in New Mexico are conflicting. The very low flow rates, low temperatures, and large magnesium concentration of the warm springs in the San Ysidro KGRA make the water chemistry useless for quantitative geothermal calculations. Qualitatively, the springs may be associated with a high-temperature system, but this association would have to be indirect. The combination of low flow rate, low surface temperature, and no gas discharge at San Francisco Hot Springs probably indicates association with a small, low-temperature system. Water from the well at Radium Hot Springs is supersaturated with respect to calcium carbonate and theoretically in equilibrium with alpha-cristobalite at the reported bottom-hole temperature. The chemical composition does not provide sufficient data to determine the geothermal potential of the area. Gillard Hot Springs and the thermal springs near Clifton may be associated with higher temperature (>125°C) systems. Mixing has been demonstrated only in the Clifton area. Some conductive heat loss has certainly occurred and the temperature of 165°C estimated from the quartz mixing model is probably too high. Verde Hot Springs and the spring near Coolidge Dam issue water with large magnesium concentrations (>30 mg/L). This may indicate either continued water-rock reaction after the fluid left the thermal aquifer or association with a low-temperature aquifer in "basaltic" rocks. Either possibility could cause the quartz and Na-K-Ca geothermometers to indicate excessively high temperatures. None of the other thermal springs which we sampled in Arizona have apparent geothermal potential.

The temperature differences noted between the chalcedony and Na-K-Ca geothermometers indicate that some modification of the Na-K-Ca geothermometer is desirable. At least, the present Na-K-Ca geothermometer should be used with care to estimate aquifer temperatures from water analyses in which the magnesium concentration exeeds 10 mg/L.

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