GEOCHEMISTRY AND ISOTOPES OF FLUIDS FROM SULPHUR SPRINGS, VALLES CALDERA, NEW MEXICO

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ABSTRACT

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Detailed geochemistry supported by geologic mapping has been used to investigate Sulphur Springs, an acid-sulfate hot spring system that issues from the western flank of the resurgent dome inside Valles Caldera. The most intense activity occurs at the intersection of faults offsetting caldera-fill deposits and post-caldera rhyolites. Three geothermal wells in the area have encountered pressures <1 MPa and temperatures of 200°C at depths of 600 to 1000 m. Hot spring and fumarole fluids may discharge at boiling temperatures with pH $\cong$ 1.0 and SO_4 $\leqslant$8000 mg/l. These conditions cause argillic alterations throughout a large area.

Non-condensible gases consist of roughly 99% CO_2 with minor amounts of H_2S, H_2, and CH_4. Empirical gas geothermometry suggests a deep reservoir temperature of 215 to 280°C. Comparison of ^{13}C and ^{18}O between $CaCO_3$ from well cuttings and CO_2 from fumarole steam indicates a fractionation temperature between 200 and 300°C by decarbonation of hydrothermally altered Paleozoic limestone and vein calcite in the reservoir rocks. Tritium concentrations obtained from steam condensed in a mudpot and deep reservoir fluids (Baca #13, ~278°C) are 2.1 and 1.0 T.U. respectively, suggesting the steam originates from a reservoir whose water is mostly >50 yrs old. Deuterium contents of fumarole steam, deep reservoir fluid, and local meteoric water are practically identical even though ^{18}O contents range through $4\%_{00}$, thus, precipitation on the resurgent dome of the caldera could recharge the hydrothermal system by slow percolation. From analysis of D and ^{18}O values between fumarol steam and deep reservoir fluid, steam reaches the surface either (1) by vaporizing relatively shallow groundwater at 200°C or (2) by means of a two-stage boiling process through an intermediate level reservoir at roughly 200°C.

Although many characteristics of known vapor-dominated geothermal systems are found at Sulphur Springs, fundamental differences exist in temperature and pressure of our postulated vapor-zone. We propose that the reservoir beneath Sulphur Springs is too small or too poorly confined to sustain a "true" vapor-dominated system and that the Sulphur Springs system may be a "dying" vapor-dominated system that has practically boiled itself dry.

INTRODUCTION

Valles Caldera, New Mexico has been a target for geothermal exploration for the last 20 years due to its Quaternary volcanic features and abundant hot springs (Fig. 1). The caldera formed 1.1 Ma ago during catastrophic eruptions of the upper member of the Bandelier Tuff (Smith and Bailey, 1966; Doell et al., 1968) and represents the culminating episode of over 10 Ma of volcanic evolution of the Jemez Mountains volcanic field (Smith et al., 1970). Reviews of the geothermal systems within Valles Caldera have been recently published by Laughlin (1981) and Goff and Grigsby (1982).
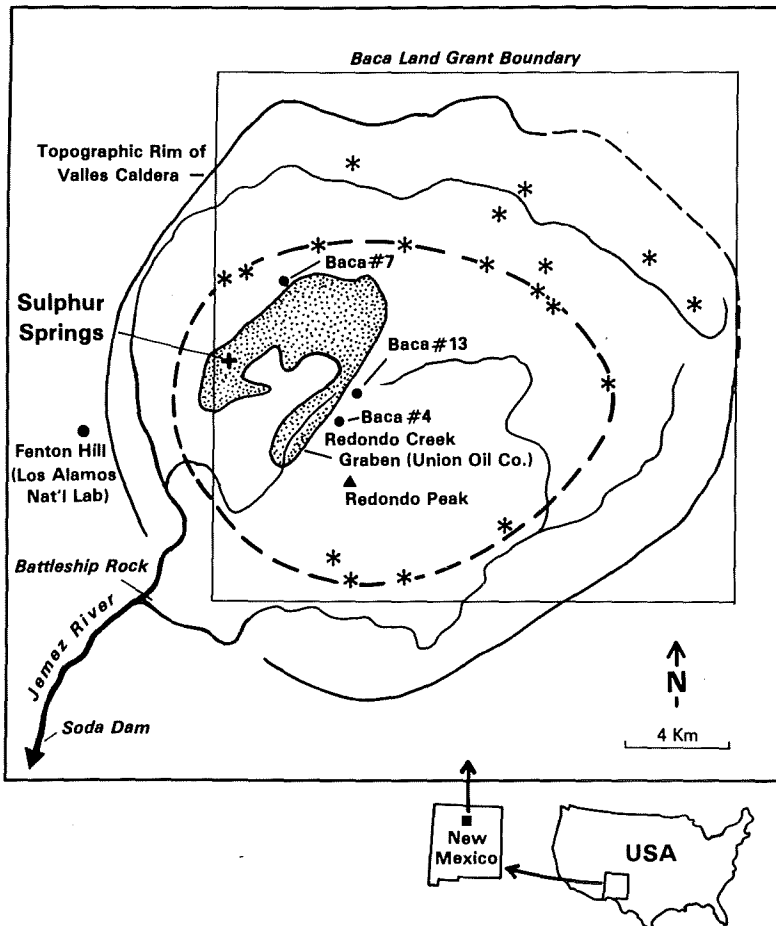

Fig. 1. Sketch map of Valles Caldera in the Jemez Mountains of northern New Mexico showing locations described in text and positions of some outlying geothermal wells. Stars indicate post-caldera rhyolite vents of the ring-fracture system. Dotted pattern outlines zone of most intense intracauldron hydrothermal alteration (modified from Dondanville, 1978).

Sulphur Springs is the hottest, most active zone of thermal manifestations within the caldera. It was once mined for the sublimed sulfur deposited around the springs and later became a resort until the 1960's (Summers, 1976). Because of its acid springs, both Renner et al. (1975) and Goff and Grigsby (1982) suggested that Sulphur Springs may be the surface expression of a small vapor-dominated reservoir. Although early geothermal wells drilled nearby have been very hot, they are subcommercial due to low steam production rates.

Union Oil Company has since drilled about 20 deep wells into the resurgent dome of Valles Caldera, 5 km east of Sulphur Springs, and has defined a neutral-chloride geothermal reservoir varying from 260 to 330°C (Dondanville, 1978). Some wells are very productive and hot, but the volume of this reservoir has recently proved to be too small to justify construction of a 50 MW(e) geothermal power plant (Kerr, 1982).

In light of the production problems encountered to the east, the Sulphur Springs area is being reevaluated by Union Oil Co. and other companies as a geothermal target. In addition, Valles Caldera is a possible choice by the Continental Scientific Drilling Program for deep drilling into a Quaternary magma-hydrothermal system (Luth and Hardee, 1980). During the last four years, Los Alamos National Laboratory has been conducting geologic and geochemical investigations at Sulphur Springs to determine the structural control of fluids and characteristics of the thermal features. The object of this paper is to discuss in detail chemical and isotopic data that bear on the temperature of the reservoir beneath Sulphur Springs and the source of the fluids. These data are then used to build a model of the Sulphur Springs geothermal system and speculate about a possible vapor-dominated origin.

GEOLOGIC SUMMARY

Goff and Gardner (1980) published a 1:5000 scale geologic map of about 6 km² around the Sulphur Springs area to serve as a base map for geothermal investigations. The Sulphur Springs area (Fig. 2) occupies a 1.5-km-wide graben-like structure bounded primarily by north- and northeast-trending faults such as the Sulphur Creek, Short Canyon and Freelove Canyon Faults. Sulphur Springs proper, where the most vigorous hot springs and fumaroles issue, lies at the intersection of the Sulphur Creek Fault and three northwest-trending cross faults. The most important of these is herein named the Bathhouse Fault. Other areas of fumaroles and gaseous cold springs occur northeast of Sulphur Springs in Short Canyon along the Short Canyon Fault and along the west segment of the Alamo Canyon Fault.

The stratigraphy of surface rocks around Sulphur Springs consists entirely of Quaternary rhyolites and caldera-fill deposits (Smith et al., 1970). Rhyolites display abundant flow-breccia within and at the base of flows
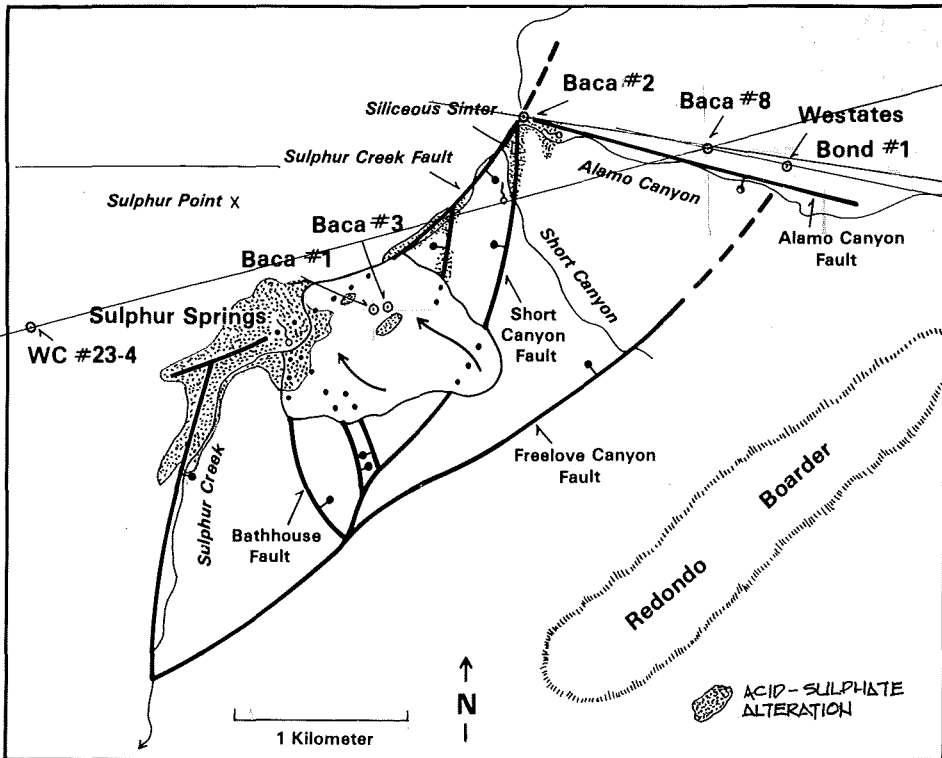
Fig. 2. Fault map of Sulphur Springs area, New Mexico (Goff and Gardner, 1980) show-ing positions of thermal areas and nearby geothermal wells. Redondo Boarder denotes the crest of the west segment of the central resurgent dome. Old silica sinter was dis-covered near the intersection of the Sulphur Creek and Short Canyon Faults.

as well as typical flow banded rock. Laminated volcaniclastic lake sedi-ments crop out at Sulphur Springs and occur in scattered patches between the contacts of caldera-fill units and overlying rhyolites. The caldera-fill as defined here is composed of unsorted rock debris of pre-Valles Caldera age and intracaldera Bandelier Tuff. Megabreccias occur within this unit containing lithic fragments of all sizes and blocks, 1 m in diameter of Mio-cene—Pliocene volcanics, Tertiary sandstones, Permian red-beds, and Penn-sylvanian limestone. Some of the breccias appear to be landslide masses from the original caldera walls. The youngest unit in the area is a large landslide complex that heads along the Short Canyon Fault and invades the Sulphur Springs area to the west.

The stratigraphy beneath the Sulphur Springs area (Fig. 3) is based on the lithology of wells Baca #2, #7, and #8. Note that once caldera-fill deposits are penetrated, deep wells encounter a variable thickness of Tertiary through Precambrian rocks including several hundred meters of Paleozoic limestone. This sequence comprises the basement rocks throughout the

western Valles Caldera region. The depth to the top of this sequence inside the caldera increases eastwards due to the combined effects of caldera collapse and down-faulting into the Rio Grande rift (Segar, 1974; Goff and Grigsby, 1982; Heiken and Goff, 1983).

Spectacular exposures of hydrothermally altered fault-breccia can be examined along the entire length of the Sulphur Creek Fault and along sections of the other faults. Severely altered zones are up to 150 m wide, particularly near fault intersections. Alteration decreases in intensity away from present sources of hydrothermal fluids. Even the least altered rocks, however, are silicified displaying replacement of some phenocrysts by microcrystalline adularia, albite, silica, and Fe-oxides. As alteration in-
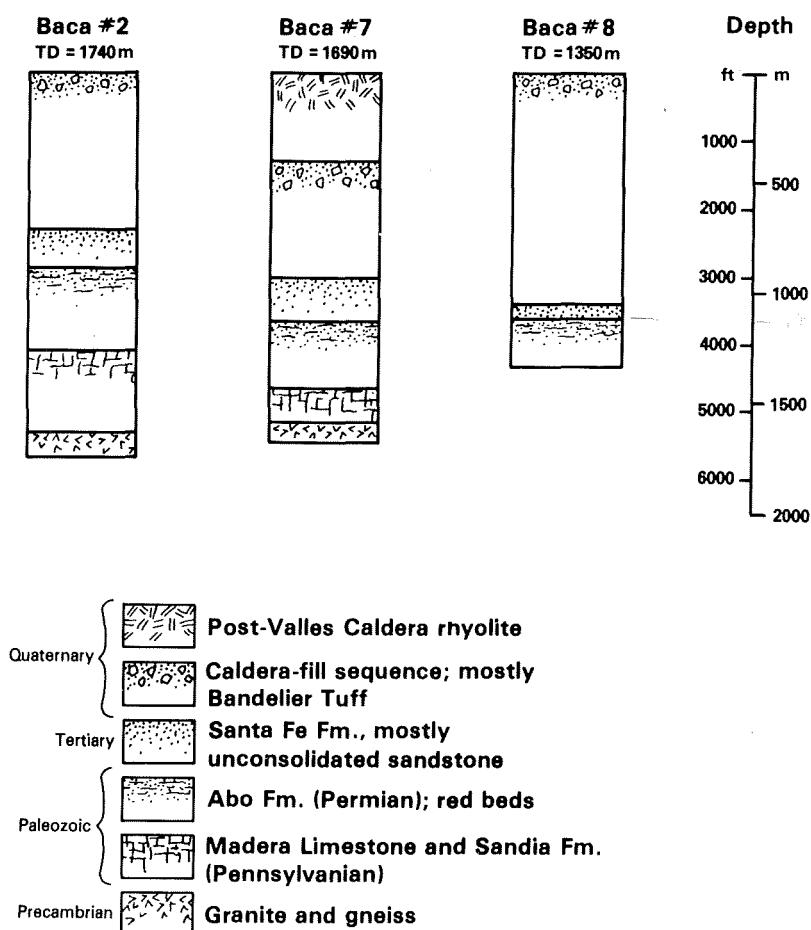

Fig. 3. Stratigraphy in the vicinity of Sulphur Springs, New Mexico (from Dondanville, 1971 and Lambert and Epstein, 1980).

creases, montmorillinite appears in the host rocks and these are cut by later veinlets of alunite-kaolinite. Advanced argillic alteration occurs in the vicinity of active hot springs and fumaroles with formation of kaolinite, alunogen, and halotrichite (Charles and Vidale, 1982). Some of the rhyolitic host rocks in these areas are leached to a porous, low-density siliceous residue superficially resembling pumice while sulfur, gypsum, pyrite, ammonium sulfate, silica minerals, and amorphous silica form next to the thermal features.

One small eroded mound of silica sinter from an extinct hot spring system was found along the Short Canyon Fault perched 50 m above the canyon bottom (Fig. 2). The sinter resembles one side of a mushroom in cross-section and sits on post-caldera rhyolite. We do not know the precise age of the deposit except that it is <1 Myr. Silica sinter of this type is usually deposited from neutral chloride springs whose reservoir temperatures exceed 180°C (White et al., 1971), thus, we speculate that the sinter precipitated from ancient geothermal fluids possibly resembling those deep inside the caldera today. The water table of the deep system has merely descended since the sinter was laid down. Similar old silica sinters are described from the Mud Volcano acid-sulfate system in Yellowstone that White et al. (1971) also believe were deposited from precursor neutral-chloride fluids.

GEOTHERMAL DRILLING

Early geothermal wells in the Sulphur Springs area (Fig. 2) were drilled prior to 1970 and are discussed briefly by Dondanville (1971). The data listed in Table 1 are significant because they verify that high-temperature, low-pressure conditions exist in the subsurface throughout an area of at least 2 km². Most wells struck some hot water but Baca #1 and #3 which were drilled less than 1 km east of Sulphur Springs, flowed considerable steam suggesting they tapped the margin of a saturated steam zone. According to the data of Table 1, a vapor-zone roughly 550 m deep overlies a deeper zone in which fractures are filled with predominately liquid water. Additional drilling to confirm the existence of a vapor-dominated reservoir beneath Sulphur Springs (as defined by White et al., 1971) has never been attempted. The existing wells encountered low permeability or had severe drilling problems, thus, none of them are capable of commercial production.

Baca #4 was drilled about 5 km southeast of Sulphur Springs in the Redondo Creek graben. This well, the discovery well of the high-temperature water-dominated reservoir beneath Redondo Creek, is listed in Table 1 for comparison with wells near Sulphur Springs because it taps a zone of higher formation pressure. Baca #13, from which we have good chemical and isotopic data, is drilled in this same zone. Both these wells are capable of commercial production.

TABLE 1

Some geothermal wells of the Sulphur Springs and Redondo Creek areas, Valles Caldera, New Mexico; locations on Figs. 1 and 2. Data obtained from Dondanville (1971), Lambert and Epstein (1980), and Union Oil Company open file data

Well	Depth (m)	Formation pressure (MPa)	Maximum temperature (°C)	Comments
Sulphur Springs area				
Westates-Bond #1	1130	0.76	199 @ 740 m	Permeable zones filled with liquid water
Baca #1	790	0.52	157 @ 446 m	Well encounters steam zones @ 450 m with <5% liquid water
Baca #2	1740	2.14	220 @ 430 m	Well contains liquid water; no steam zones
Baca #3	680	0.76	199 @ 555 m	Well initially flowed 89% water from zones below 585 m; 50% water 1 day later
Baca #7	1687	9.7	240 @ 1675 m	Well contains liquid water; low permeability
Baca #8	1350	7.9	283 @ 1290 m	Well contains liquid water; low permeability; pressure = 0.76 MPa @ 300 m
Redondo Creek area				
Baca #4	1553	6.9	278 @ 1485 m	Well contains mostly liquid water
Baca #13	2515	~16	310 @ 2515 m	Well contains liquid water

FLUID AND ISOTOPE GEOCHEMISTRY

Sampling and analytical methods

Samples of surface water and condensed steam were collected and analyzed according to methods outlined in Goff et al. (1982). Temperature was recorded with mercury thermometers, field pH was determined using an analog pH meter, Eh was measured by standardizing the pH meter with Quinhydrone (Kodak #217) mixed in pH4 and pH9 buffer solutions, conductivity was recorded in the laboratory, and discharge was estimated by eye or with a bucket and stop watch. Baca #13 water was obtained from a condenser, made of stainless steel tubing coiled inside a bucket, that was attached to the water side of a portable steam separator on the wellhead.

All field parameters for this fluid were measured at about 25°C (see foot-notes in Table 2).

Water samples were filtered through 0.45 μm paper into polyethylene bottles with polyseal caps. Filtered unacidified water was collected for anions, filtered acidified water was collected for cations and trace metals (pH $\leqslant$ 2 with HNO_3), and filtered water diluted 1:10 with deionized water was collected for SiO_2. Analyses (Table 2) were carried out at the Fenton Hill (Hot Dry Rock) chemistry laboratory of Los Alamos National Laboratory according to methods described in Goff et al. (1982).

Duplicate samples of gas were collected from Men's Bathhouse Mudpot according to the methods of Evans et al. (1981) by inverting a 0.25-m-wide funnel into the bubbling muck, running tygon tubing from the funnel to a U-tube immersed in an ethanol-dry ice slush, and connecting the cold trap to a T-fitting with syringe and an 125-ml evacuated gas bottle. Because this mudpot bubbles violently and is very hot and acid, some air is present in both samples in spite of precautions to flush the air away with the syringe and valves. The object of the cold trap is to condense water vapor that might react with H_2S.

Gas samples from two other springs were collected by inverting a small funnel connected directly to an evacuated gas bottle in the spring and sucking entrapped air out of the funnel with a syringe fastened to a long slender tubing. These samples contain virtually no air.

Gases were analyzed by the US Geological Survey, Menlo Park according to procedures described by Evans et al. (1981). Gas compositions are listed in Table 3 and isotopic compositions of CO_2 appear in Table 5.

Water and condensed steam samples taken for stable isotope and tritium analyses were collected in 125- and 500-ml glass bottles respectively and sealed with polyseal caps. Stable isotope ratios and tritium concentrations were determined in commercial laboratories by standard methods (Table 4). Two samples of fossiliferous Pennsylvanian limestone (Madera Limestone) were collected from points in the canyon of the Jemez River southwest of Valles Caldera (Fig. 1) where hydrothermal alteration from geothermal systems could not affect isotopic composition. Carbon-13 and oxygen-18 isotopes were determined on the carbonates by standard methods at yet another commercial laboratory (Table 5).

Hot spring chemistry

The acid springs and fumaroles at Sulphur Springs have changed in appearance somewhat since the resort days in the 1960's due to a combination of neglect and natural activity (see Summers, 1976). The hottest emanations occur just east of the Sulphur Creek Fault along the Bathhouse and adjacent cross-faults but exact structural relations are obscure because of intense argillic alteration, encroachment by landslide debris mentioned above, and human excavations.

The spring chemistry (Table 2) is briefly described by White et al. (1963, p. F46), Trainer (1974), Goff and Grigsby (1982), and Goff et al. (1982). Hot springs and mudpots at Sulphur Springs display all the traits of springs associated with vapor-dominated systems (White et al., 1971), that is, they are composed of condensed steam, sulfuric acid from oxidized H_2S, and various amounts of near surface groundwater. Chemically, they are high in SO_4, have low concentrations of Cl and have high concentrations of Al, Fe, Mn, Ca, and Mg relative to Na and K. In fact, K often exceeds Na reflecting the argillic alterations occurring in the rhyolitic host rocks. Because of the acid conditions, HCO_3 cannot exist and large amounts of silica are dissolved in the fluid. Trace-element concentrations such as Li, As, B, and most heavy metals are relatively low although they are higher than background concentrations in cold water (i.e. Sulphur Creek).

A sample of condensed steam taken from the main fumarole at Sulphur Springs is composed of dilute ammonium sulfate solution. Where steam has an opportunity to condense in a restricted depression, such as the concrete cribs at the Men's Bathhouse Mudpot, sulfuric acid and NH_4 are the main ionic species in solution. Flowing springs contain proportionately less NH_4 but additional SO_4 comes from groundwater dissolving copious sulfate salts that permeate the altered host rocks (i.e. Lemonade Spring, Table 2).

Because the composition of the springs is dependent on condensation of steam, oxidation of H_2S, and mixture with groundwater, spring chemistry changes seasonally. For example, two analyses of Men's Bathhouse Mudpot collected during winter and summer conditions show tremendous variations in pH, SO_4, and conductivity due to these seasonal differences (Table 2). The Jemez Mountains receive most precipitation in winter from snow and summer from thunderstorms, thus, the hot springs are in a state of constant chemical fluctuation.

A second type of spring that occurs mainly in Alamo and Short Canyons, consists of lower temperature gas bubbling through flowing surface water, usually a creek or adjacent pool (Table 2). Although these waters are also acid, they are considerably less concentrated than the hot springs by virtue of cooler temperatures and a lower proportion of condensed steam and acid gases. Sulphur Creek water collected just upstream of Sulphur Springs proper, is neutral in pH and actually contains some HCO_3 but also contains substantial SO_4 and Fe from sources upstream.

In striking contrast to these acid waters, geothermal fluids from the deep reservoir (i.e. Baca #13, Table 2) are neutral in pH, relatively high in Cl and low in SO_4. Contents of Na and K are much greater than Al, Fe, Mn, Ca, and Mg. Trace elements Li, As, Br, and B are also high. At the top of the deeper reservoir, neutral-chloride fluids have been encountered whose total concentration is roughly 1/3 to 1/4 the amount of the deep fluids (i.e. Baca #4 at 500 m; Dondanville, 1971). A partial chemical analysis of this more dilute fluid shows about 630 mg/l of Na, 530 mg/l of Cl and

TABLE 2

Selected chemical analyses of acid springs, condensed steam, gaseous cold springs, Sulphur Creek, and Baca #13 (uncorrected for steam loss), Valles Caldera, New Mexico; analyses by P. Trujillo, D. Counce, and G. Bayhurst, Los Alamos National Laboratory; in mg/l (except where noted)

	Men's Bathhouse Mudpot		Footbath[a] Spring	Women's Bathhouse Spring	Lemonade Spring	Steam, Main Fumarole	Gaseous Spring Short Cnyn.	Bubbling Pool Alamo Cnyn.	Sulphur Creek	Baca #13[b]
Sample:	VA-13	S-7-81	S-4-80	S-6-80	S-10-81	VA-80	S-8-81	VA-22	S-11-81	BA-1
Date:	1/79	8/81	9/80	9/80	8/81	3/82	8/81	3/79	8/81	6/82
Temp., °C	78	82	33	90	57	88	15	0.5	16	278
Flow, l/min	0	0	0	1/4	1/2	—	1	8	120	—
Field pH	2.52	0.62	1.10	1.40	2.03	4.30	2.48	4.5	6.61	7.30
Field Eh, mV	—	5	60	130	—10	—	—45	—	—85	75
Lab Conduc., μS/cm	4050	10500	30200	13400	6700	30	1990	280	690	8500
SiO_2	221	240	214	168	229	<1	70	44	44	640
Al	—	9.6	31	—	6.4	—	6.4	—	0.04	0.003
Fe	13	16	468	490	28	—	7.85	1.37	1.36	0.07
Mn	0.01	0.12	4.65	8.10	1.57	—	0.37	0.30	10.6	<0.01
Ca	2.1	7.7	56	131	160	<1	58	14.1	95	3.5
Mg	1.25	4.6	26.5	50.0	40.7	<0.01	7.85	2.75	12.8	0.01
Na	2.1	6.0	10.8	18.9	8.0	0.08	8.0	5.8	20.0	1550
K	8.2	34	94	72	7.6	<0.01	7.6	4.5	13.2	255
Li	0.02	0.02	0.10	0.17	0.05	—	0.04	0.02	0.06	22.6
NH_4	—	100.6	—	—	9.3	2.57	<0.1	—	<0.1	2.0
HCO_3	0	0	0	0	0	0	0	0	47.6	221
SO_4	786	1890	7900	6400	2370	4.5	517	109	238	49
Cl	2.48	8.5	<1	<1	3.5	<0.5	7.8	4.9	9.6	2500
F	6.36	0.18	10.6	5.2	0.20	<0.02	0.31	0.23	<0.10	9.4
Br	—	<0.1	<0.4	<0.4	<0.1	<0.02	<0.1	—	<0.1	7.00
NO_3	—	<0.1	<0.2	<0.2	<0.1	<0.02	<0.1	—	<0.1	<0.1
PO_4	—	<0.1	<0.4	<0.4	<0.1	<0.02	<0.1	—	<0.1	<1.0
H_2S (dissolved)	—	0.70	7.39	—	4.89	—	—	—	<0.05	0.21
B	<0.1	0.03	0.2	0.2	<0.1	<0.01	<0.01	<0.01	<0.01	19.6
Ba	<0.12	0.08	0.03	0.05	<0.01	—	0.04	<0.12	0.05	0.02
Cu	0.63	0.11	—	—	0.04	—	<0.01	<0.04	<0.01	0.02
Ni	<0.05	0.14	—	0.44	0.04	—	0.03	<0.05	<0.01	0.03
Pb	<0.14	0.09	—	—	<0.01	—	<0.01	<0.14	<0.01	0.05
Sr	0.03	0.15	0.10	0.07	0.02	—	0.26	0.40	0.30	0.21
Zn	0.16	0.36	—	—	0.23	—	0.07	<0.01	0.04	<0.01
As	—	<0.16	—	—	<0.16	—	<0.16	—	<0.13	1.52
Hg	—	<0.13	—	—	<0.17	—	<0.13	—	<0.17	<0.15

[a] Al and dissolved H_2S analyzed from samples collected 8/81.
[b] Sample collected by H. Crecraft, Union Oil Co. who analyzed pH, NH_4 and H_2S in field; Eh determined in lab; temperature calculated from enthalpy of well (see text); sample obtained from fluid line of steam separator on well head; steam fraction is 23.76% of total flow.

420 mg/l of HCO_3. No hot springs of identical composition to the deep fluids discharge in the Jemez Mountains although two sets of hot springs issue along the Jemez fault zone southwest of Valles Caldera with chemical and isotopic characteristics that appear to be derived from the deep fluid (Trainer, 1975; Goff et al., 1981).

Surface acid springs do not yield reliable estimates of subsurface reservoir temperatures using chemical geothermometers because the waters are composed primarily of surface groundwater and steam which contains few solutes from the boiling source below. On the other hand, Baca #13 water (corrected for steam loss) yields estimated reservoir temperatures of 249°C (quartz; Fournier and Rowe, 1966), 282°C (Na-K-Ca; Fournier and Truesdell, 1973), and 316°C (Na-Li; Fouillac, 1981), approximately the range of 260 to 330°C reported by Union Oil Co. for the reservoir. Possibly, the lower quartz temperature indicates boiling occurring in the reservoir, which precipitates SiO_2.

Gas chemistry

Although some air is present in 3 of 4 samples, Table 3 shows that the hot gases at Sulphur Springs are composed of roughly 99% CO_2 and 1% H_2S with only minor amounts of H_2 and CH_4. A small but unknown amount of NH_3 also occurs in the gas as mentioned above. Small variations occur between different springs and fumaroles. Small amounts of N_2, O_2, and Ar are probably dissolved in surface groundwaters that mix with the rising vapors but their concentration in the deep gas is virtually nil (i.e. VA-98, Footbath Spring).

The composition of the gases superficially resembles gases from other high temperature geothermal systems around the world which typically contain >90% CO_2 (D'Amore and Panichi, 1980, Table 3). However, Sulphur Springs gas is unusually rich in CO_2, resembling only a few of the examples listed by D'Amore and Panichi such as Larderello and Pozzuoli. Although the geothermal systems at Larderello and Valles Caldera are driven by magmatic processes, both systems are underlain by ancient carbonate strata; Upper Triassic at Larderello (Celati et al., 1973) and Pennsylvanian at Valles Caldera. Thus, it is possible that the CO_2 originates from thermal breakdown of carbonates rather than from deep magmatic sources. This subject will be treated further in the section on carbon isotopes.

Paleozoic rocks in the Valles region do not contain abundant organic remains in contrast, for example, to the geothermal system at Cerro Prieto, Mexico, that circulates in Plio-Pleistocene deltaic sediments of the Colorado River (Nehring and D'Amore, 1982). Whereas Cerro Prieto gases are relatively rich in H_2S, H_2, and CH_4, Sulphur Springs gases are not. Because temperatures at both Cerro Prieto and Valles Caldera exceed 300°C, we believe the differences in gas compositions reflect primary differences in the organic contents of the deeper reservoir rocks.

TABLE 3

Compositions of hot spring and fumarole gases in volume percent, Sulphur Springs, Valles Caldera, New Mexico; analyses by W. Evans, U.S. Geological Survey, Menlo Park. Analytical error is ±1%

| | Men's Bathhouse Mudpot | | | Women's Bathhouse | Footbath Spring | Fresh[a] air, |
Sample:	VA-75a	VA-75b	Normalized average, air free	VA-97	VA-98	2600 m
Date	1/82	1/82		5/82	5/82	
CO_2	26.34	88.24	98.93	96.93	99.28	0.032
H_2S	0.22	0.78	0.85	1.25	0.60	<0.0005
H_2	0.05	0.195	0.204	0.180	0.300	<0.005
He	<0.005	0.005	0.006	<0.005	<0.005	<0.005
N_2	57.66	8.45	—	1.41	0.14	78.3
O_2	15.3	2.05	—	0.16	<0.01	21.0
Ar	0.70	0.10	—	0.02	<0.01	0.93
CH_4	0.005	0.020	0.021	0.020	0.030	<0.0002
C_2H_6	<0.01	<0.01	—	<0.01	<0.01	<0.01
Total	100.28	99.84	100.01	99.97	100.35	100.26
Empirical gas geothermometers						
CO_2-H_2S-CH_4-H_2[b]			213	215	215	
CO_2-CH_4[c]			286	287	273	

[a] Average of several analyses (Evans et al., 1981)
[b] D'Amore and Panichi (1980)
[c] Norman and Bernhardt (1981)

The small amount of H_2 present at Sulphur Springs could result from high temperature reaction of water with ferrous oxides and silicates in the reservoir rocks (Matsuo, 1960; Truesdell and Nehring, 1979). H_2S and CH_4 could then form by hydrogen reduction of pyrite and CO_2 respectively (Giggenbach, 1980). Pyrite, although not overwhelmingly abundant, is known to occur throughout a zone exceeding 1000 m in well cuttings from the deep hydrothermal system (Dondanville, 1971). Pyrite is also found in surface hydrothermally altered rocks around the caldera.

Chemical compositions of Sulphur Springs gases were used to calculate subsurface reservoir temperatures by means of empirical gas geothermometers (Table 3). Unlike most gas geothermometers which demand knowledge of the gas to steam ratio (i.e. Giggenbach, 1980), empirical geothermometers do not require this ratio and can thus be applied to surface hot spring and fumarole gases. The geothermometer of D'Amore and Panichi (1980) relates gas concentrations of CO_2, H_2S, H_2, and CH_4 to measured reservoir temperatures using a data base of many explored geothermal fields. In contrast, the geothermometer of Norman and Bernhardt (1981) compares CO_2/CH_4 to the empirical Na-K-Ca temperature of spring and well waters.

The data base consists primarily of low-temperature geothermal fluids throughout the state of New Mexico. As seen in Table 3, estimated subsurface reservoir temperatures beneath Sulphur Springs average 215 and 280°C by the two thermometers respectively. The geothermometer of D'Amore and Panichi probably gives a better temperature estimate of the reservoir immediately supplying gases to Sulphur Springs because of its higher temperature data base. This is verified by bottom-hole temperatures observed in nearby wells (Table 1). The geothermometer of Norman and Bernhardt may be indicating equilibrium temperatures at greater depths in the geothermal system.

Isotopes of water

Tritium, which has a half-life of 12.3 years, is an excellent tracer for shallow groundwater flow. Pre-nuclear test average tritium from precipitation is estimated to be about 6 T.U. (Mazor and Verhagen, 1976). Due to nuclear tests in the atmosphere after 1954, this average climbed to a peak of about 3800 T.U. in 1963 for the southwest USA (F. Vuataz, Los Alamos National Laboratory, Unpubl. data, 1982). This level has been decaying since 1963. The tritium content of 1981 rainwater in Albuquerque, New Mexico, the nearest tritium station to Valles Caldera, ranges from 12 to 75 T.U. depending on the season (T. Wyerman, USGS, pers. commun., 1982).

Tritium concentrations from thermal features at Sulphur Springs, Sulphur Creek and Baca #13 reservoir fluid are listed in Table 4. Sulphur Creek has a value of 39 T.U. or roughly the average value of tritium in recent rainwater. Thus, Sulphur Creek appears to derive most of its flow from meteoric precipitation. The tritium value of Baca #13 is only 1.0 T.U. indicating it is comprised of deeply circulating water >50 years old. Likewise, tritium at Men's Bathhouse Mudpot contains only 2.1 T.U. suggesting it is composed primarily of condensed steam rising from a deep reservoir mixed with a small amount of surface groundwater. The flowing hot springs, on the other hand, possess tritium levels between 10 and 20 T.U. verifying that they are mixtures of condensed steam and shallow groundwater. The mixing relationship between condensed steam and surface groundwater is demonstrated in plots of tritium versus Mg and Na concentration, assuming that these species come primarily from groundwater (Fig. 4). Because most cations originate in the shallow groundwater, other cations besides Mg and Na could be used in this plot although these show the mixing relationship best.

Deuterium and oxygen-18 isotopes from various fluids in the Sulphur Springs area are plotted on Fig. 5. The fumarole steam and acid springs display tremendous isotopic variation due to evaporation effects from high temperatures and vigorous discharge of CO_2 gas through the fluids. These samples cross the Craig meteoric water line (Craig, 1961) as a broad but distinct trend. However, duplicate samples collected in different years in-

dicate that individual thermal features retain fairly constant isotopic composition through time (Table 4).

Gaseous cold springs and Sulphur Creek water also display a surprising range of isotope concentrations due, we believe, to the combined effects of elevation and evaporation. The three gaseous springs having the lightest bulk isotope compositions plot very close to the Craig meteoric line and are composed primarily of flowing water. Their isotope variations are probably due to different recharge elevations on the resurgent dome (elevation in Valles Caldera ranges from 2600 to 3450 m). Sulphur Creek and the gaseous spring of similar isotopic composition are isotopically heavier and fall to the right of the Craig line because of evaporation.

Because of the known high temperatures beneath the Sulphur Springs area, it is easy to assume that fumarole steam is fractionating from a high-temperature reservoir at depth. Surprisingly, the isotopic composition of
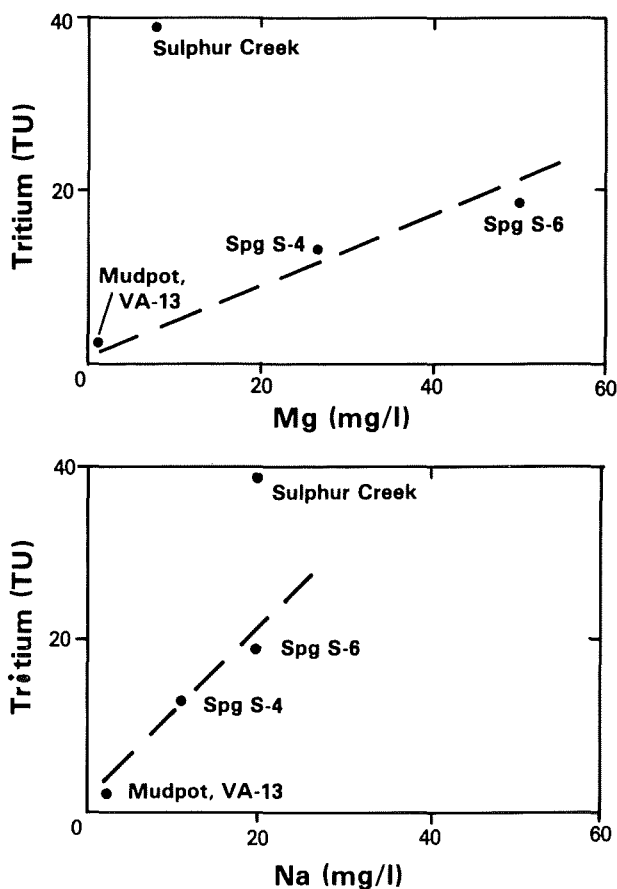
Fig. 4. Plot of tritium versus magnesium and sodium from geothermal fluids and Sulphur Creek, Sulphur Springs, New Mexico.
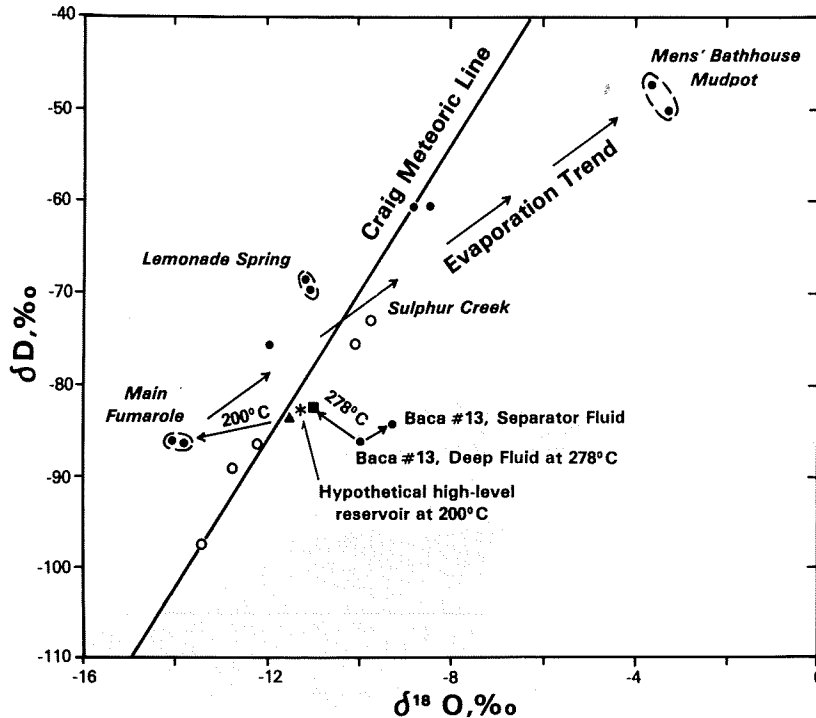
Fig. 5. Plot of deuterium versus oxygen-18 from geothermal and surface meteoric waters, Sulphur Springs, New Mexico; open circles denote meteoric fluids, dots denote thermal fluids, square represents composition of steam produced by single-stage boiling of Baca #13 at 278°C, triangle represents composition of parent water that produces fumarole steam by single-stage boiling at 200°C, and star represents a hypothetical high-level reservoir at 200°C beneath Sulphur Springs.

fumarole steam is lighter in oxygen-18 than local meteoric water whereas fluids (including steam) from most high-temperature geothermal systems are heavier in oxygen-18 due to rock-water isotope exchange (Craig, 1961). In this regard, condensed steam at Sulphur Springs isotopically resembles fumarole steam from systems like Mokai—Atiamuri, New Zealand (Hulston et al., 1981) which has fractionated from thermal fluids of meteoric composition and some fumarole steam at Wairakei, New Zealand, which originates from steam heated groundwater (Giggenbach and Stewart, 1982).

To properly assess whether or not fumarole steam at Sulphur Springs is fractionating from deep reservoir fluids similar to Baca #13, we must first obtain values of enthalpy and isotopic composition for the deep fluid corrected for steam loss. Using the method of enthalpy and isotope balances described by Truesdell and Henley (1982, p. C5):

$$Hw_{deep} = yHs_{sep} + (1 - y) Hw_{sep} \tag{1}$$

TABLE 4

Analyses of oxygen-18, deuterium, and tritium from waters and condensed steam, Sulphur Springs area, Valles Caldera, New Mexico; tritium analyses by Teledyne Isotopes, Patterson, New Jersey; stable isotopes by L. Merlivat, Saclay, France relative to SMOW; precision is ±0.15 in ^{18}O and ±0.5 in ^{2}H

	Sample	Date	Temp., °C	δ^{18}O, ‰	δ^2H, ‰	^{3}H, T.U.
Sulphur Springs						
Footbath Spring	S-4-81	8/81	39	−20.40?	−82.1	
	VA-77	1/82	18			13.2 ± 1.7
Electric Spring	S-5-81	8/81	32	−11.90	−75.8	
Women's Bathhouse Spring	S-6-81	8/81	86	−8.45	−60.8	
	VA-76	1/82	89			18.6 ± 2.2
	VA-13	1/79	78	−3.75	−50.2	
Men's Bathhouse Mudpot	S-7-81	8/81	82	−3.65	−47.1	
	VA-75	1/82	72			2.1 ± 0.5
Unnamed Hot Spring	VA-14	1/79	63	−8.80	−60.7	
Lemonade Spring	S-10-80	9/80	58	−11.05	−69.7	
	S-10-81	8/81	57	−11.10	−68.7	
Main Fumarole,	VA-23/2	3/79	94	−14.05	−86.0	
Condensed Steam	S-12-80	9/80	94	−13.8	−86.4	
Unnamed Spring	S-17-81	8/81	19	−10.05	−75.4	
Sulphur Creek	S-11-81	8/81	16	−9.75	−72.9	
	VA-78	1/82	0.5			39.0 ± 4.3
Alamo Canyon						
Bubbling Pool	VA-22	3/79	0.5	−13.45	−97.3	
Short Canyon						
Gaseous Spring	S-8-80	9/80	8	−12.20	−86.4	
	S-8-81	8/81	15	−12.75	−89.2	
Deep Geothermal Fluid, Redondo Creek						
Baca #13[a]	BA-1	6/82	278	−9.25	−84.3	1.0 ± 0.4

[a]Sample obtained by H. Crecraft, Union Oil Co., from fluid line of steam separator at 0.908 MPa absolute pressure at 2615 m elevation and 23.76% steam; temperature calculated from enthalpy of well (see text).

and

$$\delta w_{\text{deep}} = \delta w_{\text{sep}} - y \, 10^3 \ln\alpha \qquad (2)$$

where y equals the steam fraction from the separation, Hw and Hs equal the enthalpy of water and steam, δw equals the isotopic composition of water, α equals the fractionation factor at temperature T, and subscripts "deep" and "sep" denote conditions of the deep fluid and separator fluid. The fractions of steam and separator pressure recorded when Baca #13 fluids were collected are noted in Table 4. Using steam tables eq. 1 yields a solution for Hw_{deep} of 1226 J which is equivalent to a reservoir temperature of 278°C. The fractionation temperature of 176°C is obtained from the separator pressure also using steam tables. The value of $10^3 \ln\alpha$ is approximated as a function of temperature using the graphs of Friedman and O'Neil (1977). The isotopic composition of the deep fluid at 278°C from eq. 2 is then $\delta D = -86.3‰$ and $\delta^{18}O = -9.96‰$.

The corrected isotopic composition of Baca #13 plots directly to the right of local meteoric water precipitated on the resurgent dome of the

caldera suggesting that this local source recharges the deep reservoir in Valles (Craig, 1963). Baca #13 is about 2‰ heavier in oxygen-18 than local meteoric water, a smaller isotopic shift than observed at many high-temperature geothermal systems (White, 1968). On the other hand, the oxygen-18 shift at Valles Caldera is comparable to the shift observed at Upper Geyser Basin in Yellowstone, Wyoming and greater than the shift observed at Wairakei, New Zealand. The reason for the relatively small enrichment in oxygen-18 is probably due to the extensive hydrothermal alteration that has already occurred in the caldera reservoir rocks. Lambert and Epstein (1980) observed that the oxygen-18 of Valles intracaldera tuffs (determined from cuttings in Baca #4 and #7) is as much as 7‰ lighter than fresh tuffs on the caldera flanks. Thus, isotopic exchange at high temperatures between present meteoric fluids recharging the system and hydrothermally altered reservoir rocks causes only small enrichments of oxygen-18 in the existing reservoir fluids. Even though the volume of water in the present hydrothermal system may be small, the large ^{18}O shift in the altered rocks implies that a large water to rock mass ratio has affected the reservoir rocks through time.

Using the familiar isotope fractionation equation:

$$\delta w - \delta s \cong 10^3 \ln\alpha \tag{3}$$

where δs equals the isotopic composition of steam, we can evaluate the isotopic composition of steam that fractionates from Baca #13 reservoir fluid and the composition of parent waters that could produce steam at Sulphur Springs to see if the resulting values are comparable. As an example, steam produced by single stage boiling of Baca #13 deep fluid at 278°C is shown by the solid square in Fig. 5 whereas the parent water that would produce the steam collected at the Main Fumarole by single stage boiling at 200°C is depicted by a solid triangle. Several conclusions can be drawn from analysis of these calculations:

(1) It is impossible to fractionate steam of the composition discharging at Sulphur Springs by single stage boiling of reservoir fluid compositionally like Baca #13 at known reservoir temperatures of 200 to 300°C.

(2) It is possible to fractionate steam observed at Sulphur Springs by a two stage boiling process from Baca #13 at 278°C and a second higher level reservoir at 200°C (other multi-stage boiling processes could also be postulated.

(3) It is possible to fractionate Sulphur Springs steam from local meteoric water that has circulated to depth and achieved reservoir temperatures of 200°C. This could be steam-heated groundwater of the type described by Giggenbach and Stewart (1982, fig. 1a).

It is difficult to decide which conclusion, 2 or 3, is more plausible as an explanation for the source of Sulphur Springs steam. Both conclusions have some merit when considering the data at hand. Conclusion 2 fits our knowledge of the reservoirs in the Redondo Creek area where it is docu-

mented that hot water at 200°C and relatively low salinity overlies the deep 300°C reservoir (i.e. Baca #4; Dondanville, 1971). The isotopic composition of such a hypothetical reservoir of intermediate temperature is shown by the star in Fig. 5. On the other hand, there is no reason to suppose that Sulphur Springs has such a configuration of reservoirs beneath it. Also, such a complicated model does not address how volatile and soluble components would behave.

Conclusion 3 requires that meteoric water circulate to reservoir temperatures and depths without becoming isotopically enriched in oxygen-18. However, the low tritium value obtained from the condensed steam argues that the source water is fairly old, $\geqslant 50$ years. If the water is that old, why is it not isotopically heavier in oxygen-18, unless of course, the rocks in the Sulphur Springs reservoir are so thoroughly altered that they are now extremely light in oxygen-18. Conclusion 3 is a much simpler and more intuitively reasonable explanation for the source of steam than conclusion 2.

Isotopes of CO_2 and carbonate

Carbon-13 and oxygen-18 isotope analyses were obtained to determine the source of CO_2 (magmatic or hydrothermal?) and its temperature of formation at depth. The composition of fumarole CO_2 at Sulphur Springs is relatively uniform having an average $\delta^{13}C = -3.8\%o$ and an average $\delta^{18}O = 12.4\%o$ (Table 5). On the other hand, "fresh" Madera Limestone from the Paleozoic sequence southwest of Valles Caldera was determined to have average $\delta^{13}C = -4.4\%o$ and $\delta^{18}O = 24.3\%o$. These latter values compare favorably with those reported for world average Carboniferous marine limestone (Hoefs, 1973). In striking contrast, carbonate from cuttings in Baca #7 at hydrothermal reservoir depths (>550 m), including three samples from the Madera Limestone (Lambert and Epstein, 1980), is about $20\%o$ lighter in oxygen-18 than limestone outside the caldera even though carbon-13 values are about the same. From these pronounced differences in oxygen-18 of the carbonates, we conclude that Madera Limestone inside the caldera has isotopically re-equilibrated with meteoric-hydrothermal fluids, just as the overlying tuffaceous rocks have.

If we assume that CO_2 at Sulphur Springs is produced by decarbonation of calcite, we can calculate the isotopic compositions of hypothetical parent calcites at reservoir temperatures using the appropriate form of Eq. 3 and values of $10^3 \ln\alpha$ from the graphs of Friedman and O'Neil (1977). Calculated values of $\delta^{13}C$ and $\delta^{18}O$ for these hypothetical parents at 200 and 300°C fall within the range of values determined for calcites in the deep reservoir suggesting that our initial assumption is correct (Table 5). Because epidote and zeolites are reported as hydrothermal alteration products in the deep reservoir from the Baca wells, we propose that calc-silicates are forming by decarbonation processes in which calcite reacts with hydrothermal silica at temperatures of 200 to 300°C.

TABLE 5

Analyses of carbon-13 and oxygen-18 in CO_2 and carbonate from Valles Caldera area, New Mexico; gas analyses by L.D. White, U.S. Geological Survey, Menlo Park; carbonate analyses by Geochron Laboratories, Cambridge, Massachusetts, except where noted; precision in $\pm 0.15\%_{oo}$ in both ^{13}C and ^{18}O

	Sample	$\delta^{13}C, \%_{oo}$ (PBM)	$\delta^{18}O, \%_{oo}$ (SMOW)
Fumarole gas, Sulphur Springs			
CO_2, Men's Bathhouse Mudpot	VA-75a	−4.98	11.80
	VA-75b	−4.28	12.93
CO_2, Women's Bathhouse Spring	VA-97	−3.61	27.17?
CO_2, Footbath Spring	VA-98	−2.47	12.60
Average CO_2 (excluding ^{18}O in VA-97)		−3.8 ± 0.8	12.4 ± 0.4
Pennsylvanian Limestone, southwest of Valles Caldera			
Madera Limestone, near Soda Dam	F81-182	−5.6	24.0
Madera Limestone, near Battleship Rock	F81-183	−3.1	24.7
Average Madera Limestone		−4.4 ± 1.2	24.3 ± 0.4
Average Carboniferous Marine Limestone[a]		~ −2.0	~ 24.0
Reservoir carbonate, Baca #7[b]			
Carbonate, altered tuff, 715 m	B7-29	−5.5	−0.7
Carbonate, tuffaceous SS, 1050 m	B7-30	−6.0	1.9
Madera Limestone, 1475 m	B7-44	−3.1	2.3
Madera Limestone, 1515 m	B7-45	−3.3	−1.5
	B7-45	−0.5	−4.3
Calculated hypothetical parent calcite of surface CO_2 (from eq. 3 in text)			
$CaCO_3$ at 200°C		−4.1	1.3
$CaCO_3$ at 300°C		−5.9	2.7

[a] Data obtained from Hoefs (1973, pp. 26 and 97).
[b] Data obtained from Lambert and Epstein (1980, table 1).

On the other hand, it may be that oxygen-18 in CO_2 is equilibrating with oxygen-18 in reservoir steam as gases rise from the boiling interface at depth. If we estimate an equilibration temperature between these gas phases using Eq. 3, etc. as above, we obtain a temperature of approximately 125°C. Because we know the temperature of the boiling interface is 200°C based on drilling information and gas geothermometry, it is not clear what the 125°C temperature means unless it represents an "integrated" temperature of equilibration between ground surface and depth.

The CO_2 at Sulphur Springs is slightly heavier in ^{13}C than CO_2 reported from volcanic eruptions such as Mount St. Helens, Washington (−7 to −11‰; Evans et al., 1981) or than proposed values for mantle derived carbon (−5 to −8‰; Barnes et al., 1978). Thus, if CO_2 is being released from crystallizing silicic magma bodies beneath Valles Caldera, its presence is masked at Sulphur Springs by production of CO_2 from decarbonation of reservoir carbonate.

MODEL OF SULPHUR SPRINGS SYSTEM

Our conception of the geothermal system beneath Sulphur Springs is presented in the cross-section of Fig. 6. Because of the existence of acid-sulfate waters and fumarole steam that is isotopically 2‰ lighter in oxygen-18 than local meteoric water, a vapor-zone must underlie Sulphur Springs that transfers steam to the surface from a boiling reservoir of at least 200°C. Estimates of the thickness (~550 m) and the temperature (~200°C) at the bottom of this vapor-zone are based on the sparse drilling records available for Baca #1 and Baca #3 (Table 1).

Our analysis of the stable isotopes at Sulphur Springs and from the deep fluid represented by Baca #13 suggests that local meteoric water circulates to depths where reservoir temperatures of 200°C exist and then boils steam in a simple single-stage process. It is not clear as to why the source ground-water is not isotopically enriched in oxygen-18 because tritium data indicates the water is at least 50 years old. One explanation is that the reservoir rocks beneath Sulphur Springs are so altered that they are very light in oxygen-18.
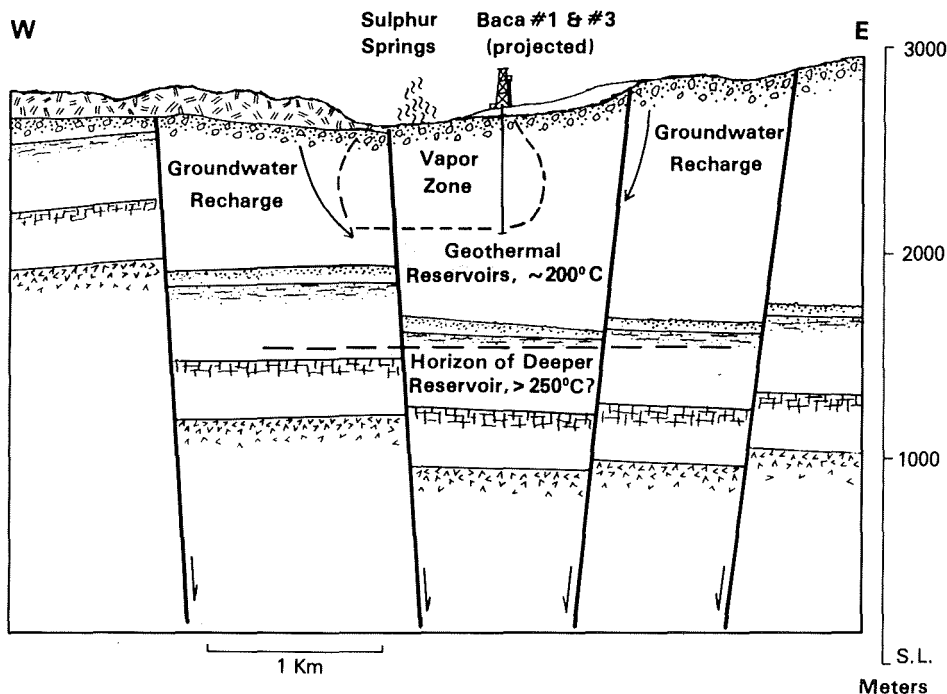
Fig. 6. Schematic cross-section of Sulphur Springs, New Mexico showing proposed model of underlying geothermal system; structure from geology of Goff and Gardner (1980), stratigraphy of Dondanville (1971) and Lambert and Epstein (1980), and gravity interpretation of Segar (1974). Lithologies same as Fig. 3 except landslide exists immediately beneath Baca #1 and #3.

We acknowledge that a second model is possible in which underlying superimposed reservoirs could supply steam to the surface by a two-stage boiling process. Thus, a deeper reservoir >250°C boils steam that condenses at an intermediate level and this upper reservoir boils steam to the surface at 200°C. From available data on Baca #4 (Dondanville, 1971), we know that superimposed reservoirs do exist in the Redondo Creek area of Valles Caldera. However, we do not favor this model because it is much more complicated and does not address how volatile and soluble components could behave.

Our notion of the horizontal dimensions and shape of the vapor zone is extremely vague due to a paucity of drilling information. We speculate that the vapor zone is restricted to a radius of 1 km or so around Sulphur Springs based on a combination of available well data, structural geology, style and extent of hydrothermal alterations, and localized discharge of hot springs and fumaroles. Probably, the vapor zone is more extensive in the fractured and faulted block east of the Sulphur Creek fault zone.

Stable isotope data, particularly deuterium, suggest that recharge to both the deep reservoir beneath Redondo Creek and the postulated reservoir beneath Sulphur Springs may originate from local precipitation on the resurgent dome of the caldera. Because the deep reservoir is now known to be of limited volume (Kerr, 1982) and to be extremely localized along fractures and adjacent permeable horizons (Hulen and Nielson, 1982), overlying meteoric sources of water are more than adequate to recharge the system even though altered and silicified caldera-fill rocks inhibit recharge.

Stable isotopes of fumarole CO_2 are compatible with its derivation by decarbonation of reservoir calcite at depths >700 m and temperatures of 200 to 300°C. This calcite occurs as vein-fillings in upper formations of the reservoir and as isotopically reconstituted Paleozoic limestone at depth. The analyzed compositions of carbon-13 and oxygen-18 in Sulphur Springs CO_2 fall outside the range of values generally reported for magmatic CO_2 and carbonatites (Taylor et al., 1967; Evans et al., 1981), thus, a magmatic source for most of the CO_2 at Sulphur Springs is unlikely.

Although several characteristics of the Sulphur Springs system resemble those described at known "vapor-dominated" geothermal systems (i.e. acid-sulfate springs, argillic alterations, precursor deposits of silica sinter, potent heat source, deep boiling reservoir, low recharge rate, impermeable reservoir rocks), fundamental differences exist in temperature and pressure (White et al., 1971). Known vapor-dominated systems have rather uniform reservoir temperatures around 240°C and pressures around 3.3 MPa which corresponds to the pressure at maximum enthalpy of steam (James, 1968). Presence of substantial quantities of other gases in the vapor besides steam raises the pressure but lowers the temperature of the reservoir. However, available data from Baca #1 and #3 immediately east of Sulphur Springs indicates the vapor zone there has lower temperature *and* lower

pressure than a well-developed vapor-dominated system as defined by White et al. (1971).

We are not sure why Sulphur Springs is not a true vapor-dominated system but we believe the reason is linked to the relatively small size and localized nature of the reservoirs inside Valles. Because of this, the volume of vapor boiling off the hot water reservoir beneath Sulphur Springs is lost to the surface through faults and fractures faster than temperature and pressure can rise to vapor-dominated conditions. In other words, there is no impermeable cap that adequately confines this system. Perhaps, Sulphur Springs represents a small vapor-dominated system that is in the waning stages of activity and has practically boiled itself dry. If so, it is possible that fluids from the deep reservoir beneath Sulphur Springs are more concentrated than the fluids encountered in the Redondo Creek area of the caldera.

REFERENCES

Barnes, I., Irwin, W.P. and White, D.E., 1978. Global distribution of carbon dioxide discharges and major zones of seismicity. U.S. Geol. Surv., Water Resour. Invest. 78-79, 12 pp.
Bodvarsson, G.S., Vonder Haar, S., Wilt, M.J. and Tsang, C.F., 1980. Preliminary estimation of the reservoir capacity and the longevity of the Baca geothermal field, New Mexico. Soc. Pet. Eng. 9273, 11 pp.

Celati, R., Noto, P., Panichi, C., Squarci, P. and Taffi, L., 1973. Interactions between the steam reservoir and surrounding aquifers in the Larderello geothermal field. Geothermics, 2: 174—182.

Charles, R.W. and Vidale, R.J., 1982. Some phase relations at Sulphur Springs, New Mexico. Trans. Am. Geophys. Union, 63: 464—465.

Craig, H., 1961. Isotopic variations in meteoric waters. Science, 133: 1702—1703.

Craig, H., 1963. The isotopic composition of water and carbon in geothermal areas. In: E. Tongiorgi (Editor), Nuclear Geology on Geothermal Areas, Spoleto, 1963. Consiglio Nazionale Della Ricerche, Lab. di Ged. Nucleare, Pisa, pp. 17—53.

D'Amore, F. and Panichi, C., 1980. Evaluation of deep temperatures of hydrothermal systems by a new gas geothermometer. Geochim. Cosmochim. Acta, 44: 549—556.

Doell, R.R., Dalrymple, G.B., Smith, R.L. and Bailey, R.A., 1968. Paleomagnetism, potassium-argon ages, and geology of rhyolites and associated rocks of the Valles Caldera, New Mexico. Geol. Soc. Am. Mem., 116: 211—248.

Dondanville, R.F., 1971. The hydrothermal geology of the Valles Caldera, Jemez Mountains, New Mexico. Union Oil Company, Santa Rosa, California, Open-file Consult. Rep., 36 pp. (with appendices).

Dondanville, R.F., 1978. Geologic characteristics of the Valles Caldera geothermal system, New Mexico. Geotherm. Resour. Counc., Trans., 2: 157—160.

Evans, W.C., Banks, N.G. and White, L.D., 1981. Analyses of gas samples from the summit crater. In: P.W. Lipman and D.R. Mullineaux (Editors), The 1980 Eruptions of Mount St. Helens, Washington. U.S. Geol. Surv., Prof. Pap., 1250: 227—231.

Fouillac, C. and Michard, G., 1981. Sodium/lithium ratio in water applied to geothermometry of geothermal reservoirs. Geothermics, 10: 55—70.

Fournier, R.O. and Rowe, J.J., 1966. Estimation of underground temperatures from the silica content of water from hot springs and wet-steam wells. Am. J. Sci., 264: 685—697.

Fournier, R.O. and Truesdell, A.H., 1973. An empirical Na-K-Ca geothermometer for natural waters. Geochim. Cosmochim. Acta, 37: 1255—1275.

Friedman, I. and O'Neil, J.R., 1977. Chapter KK. Compilation of stable isotope fractionation factors of geochemical interest. In: M. Fleischer (Editor), Data of Geochemistry, Sixth Edition. U.S. Geol. Surv., Prof. Pap. 440-KK, 10 pp. w/49 figures.

Giggenbach, W.F., 1980. Geothermal gas equilibria. Geochim. Cosmochim. Acta, 44: 2021—2032.

Giggenbach, W.F. and Stewart, M.K., 1982. Processes controlling the isotopic composition of steam and water discharges from steam vents and steam-heated pools in geothermal areas. Geothermics, 11: 71—80.

Goff, F.E. and Gardner, J.N., 1980. Geologic map of the Sulphur Springs geothermal system, Valles Caldera, New Mexico. Los Alamos Scientific Laboratory Map, LA-8634-MAP, 2 sheets.

Goff, F.E. and Grigsby, C.O., 1982. Valles Caldera geothermal systems, New Mexico, U.S.A. J. Hydrol., 56: 119—136.

Goff, F.E., Grigsby, C.O., Trujillo, P., Counce, D. and Kron, A., 1981. Geology, water geochemistry, and geothermal potential of the Jémez Springs area, Cañon de San Diego, New Mexico. J. Volcanol. Geotherm. Res., 10: 227—244.

Goff, F.E., McCormick, T., Trujillo, P.E., Counce, D. and Grigsby, C.O., 1982. Geochemical data for 95 thermal and non-thermal waters of the Valles Caldera-southern Jemez Mountains region, New Mexico. Los Alamos National Laboratory report, LA-9367-OBES, 51 pp.

Heiken, G. and Goff, F., 1983. Hot dry rock geothermal energy in the Jemez volcanic field, New Mexico. J. Volcanol. Geotherm. Res., 15: 223—246.

Hoefs, J., 1973. Stable Isotope Geochemistry. Springer-Verlag, New York, N.Y., 140 pp.

Hulen, J.B. and Nielson, D.L., 1982. Stratigraphic permeability in the Baca geothermal system, Redondo Creek area, Valles Caldera, New Mexico. Trans. Geotherm. Resour. Counc., 6: 27—31.

Hulston, J.R., Henley, R.W., Glover, R.B. and Cox, M.A., 1981. Stable isotope and geochemical reconnaissance of the Mokai geothermal system, Taupo volcanic zone. Proc. of the New Zealand Geothermal Workshop, 1981, Univ. Auckland, Auckland, N.Z., pp. 81—86.

James, R., 1968. Wairakei and Larderello; geothermal power systems compared. New Zealand J. Sci. and Tech., 11: 706—719.

Kerr, R.A., 1982. Extracting geothermal energy can be hard. Science, 218: 668—669.

Lambert, S.J. and Epstein, S., 1980. Stable isotope investigations of an active geothermal system in Valles Caldera, Jemez Mountains, New Mexico. J. Volcanol. Geotherm. Res., 8: 111—129.

Laughlin, A.W., 1981. The geothermal system of the Jemez Mountains, New Mexico, and its exploration. In: L. Rybach and L.J.P. Muffler (Editors), Geothermal Systems: Principles and Case Histories. Wiley, New York, N.Y., pp. 295—320.

Luth, W.C. and Hardee, H.C., 1980. Comparative assessment of five potential sites for hydrothermal-magma systems: Summary. U.S. Dept. Energy Rept. DOE/TIC-11303, 51 pp.

Matsuo, S., 1960. On the origin of volcanic gases. J. Earth Sci., Nagoya Univ., Japan, 8: 222—245.

Mazor, E. and Verhagen, B.Th., 1976. Hot springs of Rhodesia: their noble gases, isotopic and chemical composition. J. Hydrol., 28: 29—43.

Nehring, N.L. and D'Amore, F., 1981. Gas chemistry and thermometry of the Cerro Prieto geothermal field. Proc. 3rd Symp. on the Cerro Prieto Geothermal Field, Baja California, Mexico, March 1981, San Francisco, Lawrence Berkeley Laboratories report 11967.

Norman, D.I. and Bernhardt, C.A., 1981. Assessment of geothermal reservoirs by analysis of gases in thermal waters. Final tech. rept. New Mexico Energy Institute, New Mex. State Univ., Las Cruces, 130 pp.

Renner, J.L., White, D.E. and Williams, D.L., 1975. Hydrothermal convection systems. In: D.E. White and D.L. Williams (Editors), Assessment of Geothermal Resources of the United States — 1975. U.S. Geol. Surv., Circ., 726: 5—57.

Segar, R.L., 1974. Quantitative gravity interpretation, Valles Caldera area, Sandoval and Rio Arriba Counties, New Mexico. Consulting report for Union Oil Co., Santa Rosa, California, 11 pp. w/maps.

Smith, R.L. and Bailey, R.A., 1966. The Bandelier Tuff: a study in ashflow eruption cycles from zoned magma chambers. Bull. Volcanol., 29: 83—104.

Smith, R.L., Bailey, R.A. and Ross, C.S., 1970. Geologic map of the Jemez Mountains, New Mexico. U.S. Geol. Surv., Misc. Geol. Invest. Map I-571.

Summers, W.K., 1976. Catalog of thermal waters in New Mexico. N.M. Bur. Mines Miner. Resour., Hydrol. Rep. 4, 80 pp.

Taylor, H.P., Frechen, J. and Degens, E.T., 1967. Oxygen and carbon isotope studies of carbonatites from the Laucher See district, West Germany and the Alno district, Sweden. Geochim. Cosmochim. Acta, 31: 407—422.

Trainer, F.W., 1974. Ground water in the southwestern part of the Jemez Mountains volcanic region, New Mexico. N.M. Geol. Soc., Guidebook, 25th Field Conf., pp. 337—345.

Trainer, F.W., 1975. Mixing of thermal and nonthermal waters in the margin of the Rio Grande Rift, Jemez Mountains, New Mexico. N.M. Geol. Soc., Guidebook, 26th Field Conf., pp. 213—218.

Truesdell, A.H. and Henley, R.W., 1982. Quantitative chemistry of high-temperature geothermal fluids. Technical Training Course No. 8, Geoth. Resources Counc., Davis, California, 68 pp.

Truesdell, A.H. and Nehring, N.L., 1979. Gases and water isotopes in a geochemical section across the Larderello, Italy, geothermal field. Pure Appl. Geophys., 117: 276—289.

White, D.E., 1968. Environments of generation of base-metal ore deposits. Econ. Geol., 63: 301—335.

White, D.E., Hem, J.D. and Waring, G.A., 1963. Chemical composition of subsurface waters. In: Data of Geochemistry (6th edition). U.S. Geol. Surv., Prof. Pap., 440-F: F1—F67.

White, D.E., Muffler, L.J.P. and Truesdell, A.H., 1971. Vapor-dominated hydrothermal systems compared with hot-water systems. Econ. Geol., 66: 75—97.