Proc. 5th NZ Geothermal Workshop 1983

ISOTOPE GEOCHEMISTRY OF SULPHUR SPRINGS, AN ACID-SULFATE SYSTEM IN VALLES CALDERA, NEW MEXICO

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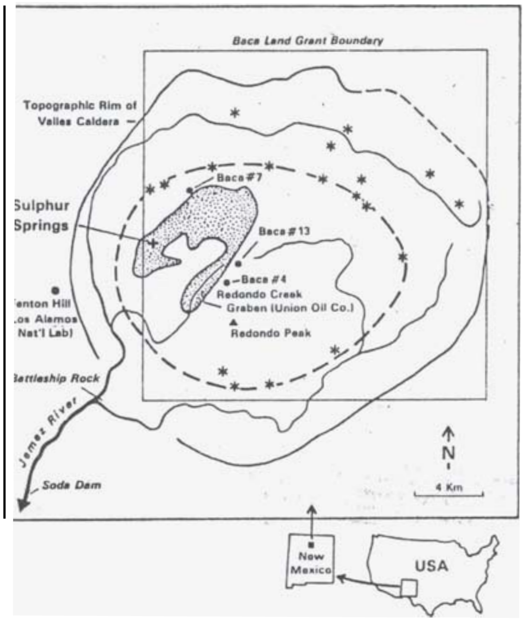
ABSTRACT

Sulphur Springs is a ¼ km^2 area of acid hot springs, mud pots, gaseous cold springs and fumaroles that issue from the western flank of the resurgent dome inside Valles Caldera, a 1.1 Myr old silicic cauldron. From assessment of the D and ^{18}O values in fumarole steam at Sulphur Springs and deep reservoir fluid in the Redondo Creek area (~300°C), we suggest that steam reaches the surface either by (1) a two-stage boiling process through an intermediate level reservoir at roughly 200°C, or (2) by vaporizing relatively shallow groundwater at 200°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.

INTRODUCTION

Valles Caldera, New Mexico, has been a target for geothermal exploration for the last 20 yeare due to its Quaternary volcanic features and abundant hot springs (Fig. 1). The caldera formed 1.1 Myr 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 Myr 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).

Sulphur Springs is the hottest, most active zone of surface manifestations within the caldera. Early geothermal bores drilled near Sulphur Springs have been very hot, but by and large they have been subcommercial due to low steam production rates. On the other hand, about 20 deep bores have penetrated the resurgent dome of Valles Caldera 5 km east of Sulphur Springs, and have defined a neutral-chloride geothermal reservoir varying from 260 to 330°C (Dondanville, 1978). Many of these wells are very productive but the volume of this reservoir has proved too small to justify construction of a 50 MW(e) power plant (Kerr, 1982). In light of this, it appears that Sulphur Springs may be re-evaluated as a gebthermal target. The object of this paper is to review recently acquired isotopic data that bears on the temperature of the resource beneath Sulphur Springs, and the sources of fluids and gas.



Pig. 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 zones of most intense intracauldron hydrothermal alteration (modified from Dondanville, 1978).

GEOLOGIC AND GEOCHEMICAL SUMMARY

The Sulphur Springs area (Fig. 2) occupies a 1.5 km wide graben-like structure bounded primarily by north and northeast-trending faults (Goff and Gardner, 1980). The stratigraphy of surface rocks consists entirely of Quaternary rhyolite and caldera-fill deposits (Smith et al., 1970). Our knowledge of the stratigraphy beneath Sulphur Springs is based on the lithology of bores Baca #2, #7, and #8. Once caldera-fill deposits are penetrated, deep bores encounter a variable thickness of Tertiary through Precambrian rocks including several hundred meters of Paleozoic limestone. Surface alteration reaches advanced argillic conditions.

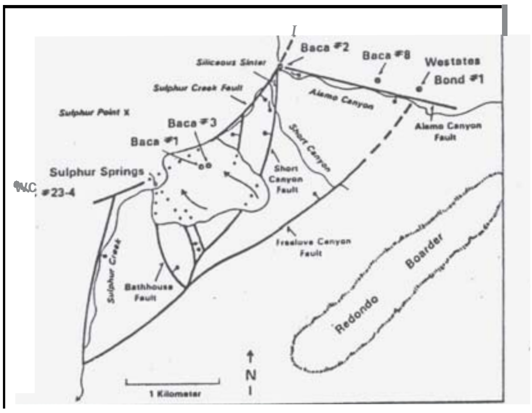


Fig.2: Fault map of Sulphur Springs area, New Mexico (Goff and Gardner, 1980) showing positions of thermal areas and nearby geothermal wells. Redondo Boarder denotes the crest of the west segment of the central resurgent dome.

Chemistry of Sulphur Springs fluids has been briefly described by Trainer (1974) and Goff and Grigsby (1982). All thermal features display traits associated with those at vapor-dominated systems, that is, they are composed of condensed steam, oxidized H_2S, and near surface groundwater in varying amounts. Trace element concentrations are low. On the other hand, samples of the deep fluids show them to be neutral-chloride in character and to have anomalous concentrations of Li, B, and As. Some wells have encountered stacked aquifers that show increasing chloride concentrations with depth (Dondanville, 1971).

ISOTOPES OF WATER

Deuterium and oxygen-18 isotopes from various fluids in the Sulphur Springs area are plotted 'on Fig. 3. 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 et al., 1956) as a broad but distinct trend. However, duplicate samples collected in different years indicate that individual thermal features retain fairly constant isotopic composition through time (Fig. 3). 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.

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 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 et al., 1956). 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 boiled from thermal fluids of meteoric composition, and some fumarole steam at Wairakei, New Zealand, which originates from steamheated groundwater (Giggenbach and Stewart, 1982).

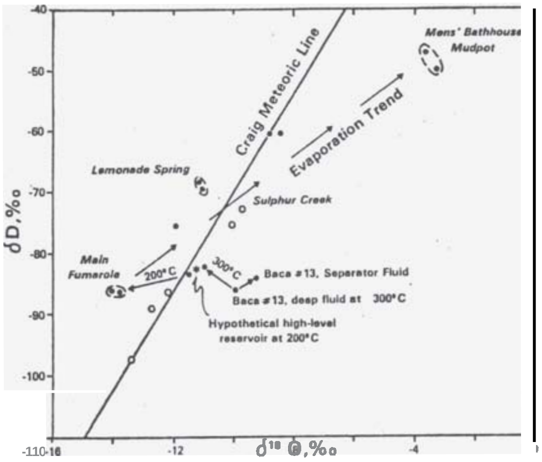


Fig. 3: Plot of deuterium versus oxygen-18 from geothermal and surface meteoric waters, Sulphur Springs, New Mexico; open circles denote meteoric fluids, dots denote thermal fluids and star represents a hypothetical. high-level reservoir at 200°C beneath Sulphur Springs.

To properly assess whether or not fumarole steam at Sulphur Springs is fractionating from deep reservoir fluids similar to Baca 113, we must first obtain values of the isotopic composition for the deep fluid, corrected for steam loss. Using wellhead data from Baca #13, the temperature of the fluid based on the calculated enthalpy of the well is 278°C, but for this assessment we shall assume the deep reservoir is about 300°C. The isotopic composition of the deep fluid from Baca #13 at about 300°C is shown in Fig. 3.

We note first that the corrected isotopic composition of Baca P13 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. 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, Hew 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.

Using isotope fractionation equations we can evaluate the isotopic composition of steam that boils 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. These hypothetical compositions were calculated at temperatures of 200 and 300°C and plotted on Fig. 3. Several conclusions can be drawn from analysis of these calculations:.

1. It is impossible to obtain 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 obtain steam observed at Sulphur Springs by a two stage boiling process from Baca #13 at 300°C and a second higher level reservoir at 200°C (other multi-stage boiling processes could also be postulated);

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

Because we do not have samples of fluid at depth directly below Sulphur Springs it is impossible to know whether process 2 or 3 is at work (or perhaps yet another process), but we can at least comment on them. If conclusion (2) is correct it fits our knowledge of the deep reservoir beneath Redondo Creek, where superimposed reservoirs of water are known to exist at least locally. However, the two areas are far enough apart that the deep reservoirs may be quite different chemically and isotopically. If conclusion (3) is correct, we are somewhat surprized that the low-tritium steam at Sulphur Springs (2.0 T.U.) has not undergone more enrichment of oxygen-18 than it displays.

CARBON-13 AND OXYGEN-18

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‰ and an average $\delta^{18}O$ = 12.4‰ (Table 1). 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‰ and $\delta^{18}O$ = 24.3‰. 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‰ 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.

Table 1 : 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.

	Sample	$\delta^{13}C$, ‰ (PDB)	$\delta^{18}O$, ‰ (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-91	-3.61	91.111
CO_2, Footbath Spring	VI-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	24.1
Average Madera Limestone		-4.4±1.2	24.3±0.4
Average Carboniferous Marine Limestone*		~-2.0	~24.0
Reservoir Carbonate, Baca #7†			
Carbonate, altered tuff, 115 m	07-29	-5.5	-0.7
Carbonate, tuffaceous SS, 1050 m	B7-30	-6.0	1.9
Madera Limestone, 1475 m	01-44	-3.1	2.3
Madera Limestone, 1515 m	B7-45	-1.1	-1.5
	B7-45	-0.5	-4.3
Calculated Hypothetical Parent Calcite of Surface CO_2			
$CaCO_3$ at 200°C		-4.1	1.3
$CaCO_3$ at 300°C		-6.9	2.7

* Data obtained from Hoefs (1973, pp. 26 and 91).

† Data obtained from Lambert and Epstein (1980, Table 1).

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 isotope fractionation equations, 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 1). Because epidote is reported as a hydrothermal alteration product in the deep reservoir from Baca #2 and #4, we propose the following decarbonation reaction as the source of CO_2:

$$CaCO_3 + SiO_2 \xrightarrow{200\text{ to }300°C} CO_2\uparrow + \text{Ca-Al silicate} \quad (1)$$
$$\text{(epidote?)}$$

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 described as follows. 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. If the deep fluid beneath Sulphur Springs can be represented by Baca #13, our isotopic assessment suggests that underlying superimposed reservoirs could supply steam to the surface by a two-stage boiling process. Thus, a deeper reservoir at about 300°C boils steam that condenses at an intermediate level, and this upper reservoir boils steam to the surface at 200°C. This model assumes, however, that the Redondo Creek Reservoir is more extensive in size than drilling has proved it to be.

A second model is possible in which local meteoric water circulates rapidly to depths where reservoir temperatures of 200°C exist and then delivers steam to the surface in a simple single-stage boiling process. However, we feel this model suffers from one problem: Tritium data indicate the fumarole steam originates from water at least 50 years old and, if so, the groundwater should be isotopically enriched in oxygen-18 (like Baca #13), yielding isotopically heavier steam. Instead, the steam is depleted in oxygen-18 with respect to meteoric water.

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 C02 and carbona'tites (Taylor et al., 1967; Evans et al., 1981); thus, a magmatic source for most of the CO_2 at Sulphur Springs is unlikely.

ACKNOWLEDGEMENTS

The authors thank Baca Land and Cattle Co., Abilene, Texas, Bill Mondt, Albuquerque, New Mexico, and Union Oil Co., Santa Rosa, California, for access to the Sulphur Springs area. Many people at both the U.S. Geological Survey and Los Alamos National Laboratory provided field or analytical support. The first author is particularly grateful to the Geothermal Institute at the University of Auckland, New Zealand, for making this contribution possible. Funding came primarily from the U.S. Department of Energy, Office of Basic Energy Science.

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