LA-UR -84-1208
CONF-840809--8

LA-UR--84-1208

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SUBMITTED TO: Geothermal Resources Council 1984 Annual Meeting, Reno, Nevada, August 26-29, 1984.

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FORM NO. 836 R4
ST. NO. 2629 5/81

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HYDROGEOCHEMISTRY OF THE QUALIBOU CALDERA GEOTHERMAL SYSTEM, ST. LUCIA, WEST INDIES

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ABSTRACT

Interpretation of hydrogeochemical data and supporting geologic and electrical resistivity data have been used to define the basic structure of the Qualibou Caldera geothermal system and propose a model of hydrologic flow. The geothermal system at Sulphur Springs consists of three layers: 1. an upper steam condensate zone; 2. an intermediate vapor zone, which may be restricted to the Sulphur Springs area only; and 3. a lower brine zone. Four lines of evidence suggest that temperatures of the brine layer may exceed 230°C at depths of perhaps 1 km. Outlying thermal springs along the northwest side of the caldera do not indicate derivation from underlying high-temperature sources. We suggest that the main reservoir upflows in the Belfond-Sulphur Springs area and flows laterally in the subsurface toward the northwest caldera wall.

INTRODUCTION

St. Lucia is a volcanic island within the southern part of the Lesser Antilles, Caribbean Sea that has been built by episodic volcanism from Miocene to Quaternary time. The most recent activity has occurred at Qualibou Caldera on the southwest side of the island (Fig. 1). Several hot springs discharge within Qualibou Caldera but by far the most impressive thermal features occur at Sulphur Springs, which is close to the caldera center and the youngest pyroclastic vents. The U.K. Ministry of Overseas Development financed a drilling project at Sulphur Springs in the 1970's (Williamson, 1979). Although 7 wells were drilled to depths as great as 700 m and steam was encountered at temperatures above 200°C, this project was terminated due to high CO_2 content of the vapor, difficulty in finding permeable fractures, and lack of money. Soon thereafter, the Italian consulting firm Aquater (1982) conducted a comprehensive geothermal evaluation of Qualibou Caldera and recommended additional areas for deep exploration drilling. To date, however, the only geothermal wells drilled are those mentioned at Sulphur Springs.

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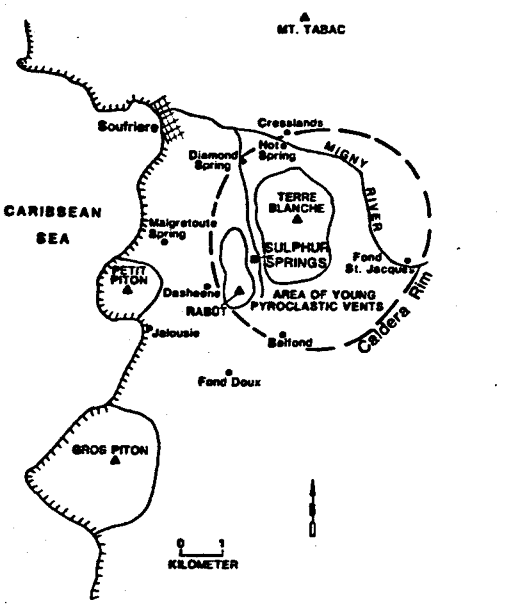

Fig. 1.
Sketch map of Qualibou Caldera showing major topographic features and sample locations.

The Qualibou Caldera geothermal system is presently being reevaluated for electrical generation. The purpose of this report is to combine previous geochemical data with new data recently acquired by the authors to outline 1. the type of geothermal system present, 2. the temperature of various geothermal horizons at depth, and 3. the possible dynamics of the geothermal reservoir.

GEOLOGIC AND GEOPHYSICAL BACKGROUND

The geology of St. Lucia consists of several distinct volcanic sequences interstratified with minor marine sedimentary rocks. In general, volcanism was initiated in the north around 10 Myr ago and migrated southwards. Rock compositions have evolved from basaltic to andesitic to dacitic types through time but andesites dominate volumetrically. The pre-caldera rocks surrounding Qualibou Caldera are composed primarily of andesites in the 2.5 Myr range. Later dacite eruptions produced the edifices of Petit and Gros Pitons (0.25 Myr). The exact age of formation of Qualibou Caldera is not known but recent geologic work by K. Wohletz and G. Heiken (in prep.) indicates that the caldera post-dates the Pitons. Following caldera collapse, a large central dacite dome named Terre Blanche was extruded inside the caldera. The most recent volcanism has centered around Belfond in the southern part of the caldera with creation of up to 10 phreato-magmatic vents of rhyodacitic composition. One of these is dated at 39 $\pm$ 1.5 Kyr by ^{14}C techniques on organic remains in the ash deposit (Tomblin, 1965). The well preserved cones testify that these vents are very young. Because Sulphur Springs lies a scant 1 km northwest of these vents, it is assumed that the shallow magma chamber producing the silicic pyroclasts is the heat source driving surface hydrothermal activity.

Electrical resistivity measurements (Williamson, 1979; Aquater, 1982) indicate that conductive zones $\leq$30 ohm-m occur to depths of 700 m in the Sulphur Springs area, correlating well with the known presence of 200°C steam and near-surface acid alteration. Each of the above authors implies that the conductive zones extend well beyond Sulphur Springs to north and south. A more recent resistivity investigation by Ander (in prep.) indicates that large zones $\leq$10 ohm-m occur at depths $\geq$1 km beneath the Belfond and northwest caldera areas.

The presence of at least some neutral chloride hot waters at depth is verified by drilling (Williamson, 1979). Large quantities of concentrated geothermal fluid whose Cl concentration ranged from 10,000 to 70,000 mg/l were discharged from well #4 at Sulphur Springs during wet/dry cycling. Because of the cyclic discharge, samples of unevaporated deep fluids were never obtained (Bath, 1977).

GEOCHEMISTRY

The first comprehensive hydrogeochemical studies of Qualibou Caldera were performed by Bath (1976; 1977) and Aquater (1982) during the British and Italian geothermal projects, respectively. For the purposes herein, the geochemistry in following sections is discussed by area because information on the temperature of the resource comes from Sulphur Springs while additional concepts on the dymanics of the resource come from the outlying springs.

Sulphur Springs

Sulphur Springs is one of the most impressive areas of acid springs and fumaroles ever seen by the authors. The most common thermal features are 10 to 15 pools up to 10 m across filled with fountaining black water. Of the many fumaroles, two are superheated including an awesome fumarole discharging at 171°C (185°C during a period in the 1970's; Williamson, 1979). The original dacites surrounding Sulphur Springs have been converted to kaolinite-natroalunite-cristobalite-quartz bearing rocks. Sulfur, gypsum, and pyrite are concentrated near fumaroles and steaming ground. Iron oxides form orange and red stains in dry spots and around the margin of the active area.

Most spring waters at Sulphur Springs such as the drowned fumarole (Table 1), display chemical compositions that are characteristic of acid-sulfate systems (White et al., 1971). They have relatively low pH, high SO_4, and low Cl. The condensed acid waters may or may not mix with near surface groundwater to produce hybrid compositions. Partial chemical analysis of fumarole steam associated with the acid-sulfate springs also shows high SO_4 and low Cl. Most interesting, however, is the extremely high B/Cl ratio in the superheated vents, a characteristic noted by Bath (1976) and Aquater (1982). High

TABLE 1: Chemistry of some geothermal fluids, Qualibou Caldera, St. Lucia (values in mg/l)

	Temp, °C	pH	SiO_2	Na	K	NH_4	Ca	Mg	HCO_3	SO_4	Cl	F	B	Br
Sulphur Springs														
Steam Condensate Zone, Flowing Spring	93	6.2	197	49	6.8	16.6	61.5	10.3	309	35.6	39.7	0.11	10.9	<0.1
Vapor Zone, Drowned Fumarole	100	1.6	360	6	6.7	2.4	220	72	0	6750	5.0	0.02	22.9	<1.0
Superheated Fumarole	103	8.2	<1	-	-	-	-	-	-	121	1.3	0.03	95	<0.2
Brine Zone, Well #4[a]	~200	5.1	212	5900	293	-	11600	100	-	1195	37000	-	3500	~0.5
Outlying Thermal Springs														
Diamond Warm Spring	43	6.45	171	129	11.0	0.24	69.2	42.3	686	21.8	40.0	0.15	11.1	<0.1
Cresslands Hot Spring[b]	56	6.55	110	257	16.5	0.01	163	56.5	1215	0.77	153	2.60	15.0	0.5
Malgrétoute Hot Spring[b]	57	6.4	101	267	15.4	<0.01	23.1	20.3	648	105	74	0.16	8.9	0.1

[a] Analysis from Bath (1976); Br analysis from another sample and is, therefore, only approximate.

[b] Temperature and pH from Aquater (1982).

B/Cl ratios in steam generally indicate the steam originates by deep boiling of high-temperature brine (Tonani, 1970; Ellis and Mahon, 1977).

In contrast to the above, a cluster of about five springs that are near neutral in pH and contain HCO_3 as the major anion issue only from high ground around the southwest margin of Sulphur Springs. These steam condensate springs are noteworthy because they deposit $CaCO_3$ travertine, which is unstable in acid environments. Waters of this type issue from higher levels at many vapor-dominated (steam) geothermal systems. According to Mahon et al. (1980), HCO_3-rich steam condensate waters commonly form a cap or carapice to many deep neutral-chloride systems in excess of 200°C (i.e. Broadlands, New Zealand and Kamojang, Indonesia).

Acid-sulfate waters do not necessarily indicate that a vapor-dominated system lies at depth. The available drilling data reported by Williamson (1979) indicates variable conditions in the vapor zone beneath Sulphur Springs. Temperatures approach 220°C and pressure are <32 bars. "True" vapor-dominated systems ideally display temperatures of 240°C and pressures of 32 bars, thus conditions at Sulphur Springs are highly suggestive of a vapor-dominated zone of as yet unknown size.

British well #4, drilled about 100 m south of Sulphur Springs in a flat area adjacent to Terre Blanche is unusual in that it produced geothermal brine during wet/dry cycling. The temperature of this brine at a depth of 600 m was 203°C (Bath, 1977). Partial chemical analyses of the brine show tremendous chemical variation but display rather constant molar ratios of Na, K, Ca, and Mg to Cl as documented by Bath (1977, Table 2). Because of this, the variations are thought to be due to steam loss from liquid in a fracture system of limited volume. The brine chemistry is extremely unusual because Ca is roughly twice Na by weight. It is impossible to say what the exact composition of the reservoir brine is because of the variable discharge of the well.

$CaCl_2$-rich geothermal brines are very unusual compared with most geothermal fluids. They occur only in settings near the ocean such as the Salton Sea, California, the Reykjanes field in Iceland, or along oceanic spreading centers like the Atlantic II Deep (Hardie, 1983). Even these geothermal brines, however, contain more Na than Ca making the Sulphur Springs brine truly remarkable.

Hardie (1983) argues convincingly that $CaCl_2$-rich geothermal brines are generated by reacting sea water with basaltic rocks at temperatures above 250°C. The original basalts are transformed into albite-epidote-chlorite rocks accompanied by deposition of quartz, calcite, and anhydrite. Circumstantial evidence suggests the Sulphur Springs brines may have formed in this manner because the area lies a mere 3 to 4 km east of the ocean where a thick

TABLE 2: Chemistry of some geothermal gases, Qualibou Caldera, St. Lucia (values in vol-%)

	Sulphur Springs		Outlying Springs[a]		
	Superheated Fumarole	Drowned Fumarole	Diamond Spring	Cresslands Spring	Malgrétoute Spring
Temp, °C	171	100	43	56	57
He	<0.005	<0.005	tr	tr	0.0008
H_2	5.63	4.89	0.0006	0.0005	0.001
Ar	0.03	<0.003	-	-	-
O_2	0.54	0.02	13.84	0.76	0.12
N_2	2.51	1.06	78.53	8.25	35.43
CH_4	0.69	0.63	0.17	0.20	0.47
CO_2	89.59	92.07	7.46	90.8	63.98
C_2H_6	<0.01	<0.01	-	-	-
H_2S	1.09	1.84	-	-	-
CO	0.006	0.006	-	-	-
Total	100.09	100.52	100.0	100.0	100.0
Empirical Gas Geothermometer °C[b]					
CO_2-H_2S-H_2-CH_4	280	284	-	-	-

[a] Normalized analyses of Aquater (1982)
[b] D'Amore and Panichi (1980)

sequence of pre-caldera basaltic rocks can be seen beneath overlying silicic rocks. On the other hand, Bath (1977) points out that the deuterium composition of the brines does not indicate a sea water origin because it resembles St. Lucia meteoric waters (Fig. 2). He also notes that the Br/Cl ratio of the brine is much lower than sea water. Because unexposed Tertiary carbonate strata are postulated to exist beneath the volcanic rocks, Bath (1976) suggests a possible mechanism in which HCl-rich volatiles from magmatic sources react with the carbonates to release CO_2, Ca, and Cl. Clearly, exact determination of the source of fluids must wait until a well is completed deep into the reservoir.

Subsurface Temperature of Brine Reservoir

This section discusses several lines of evidence that point to extremely high temperatures beneath Sulphur Springs and its underlying brine reservoir. Drilling to depths of 700 m encountered temperatures of 220°C (Williamson, 1979) but the following data indicate that higher temperatures exist.

1. Stable Isotopes of Water: Figure 2 shows a plot of D versus ^{18}O using samples recently collected by us and data from the British wells previously published by Bath (1976). As mentioned above, the composition of brine is essentially identical in D but considerably heavier in ^{18}O than St. Lucia surface water indicating extensive high-temperature exchange of oxygen between water and rock in the reservoir (Craig, 1961). The magnitude of the shift at Sulphur Springs is rather extreme (13°/••) rivaling the shift observed in the geothermal brines of the Salton Sea, California (14°/••). Although quite a range of values are reported for both the brine and the associated steam condensates, the isotopic compositions of the latter can be qualitatively explained by high-temperature boiling. Note that the

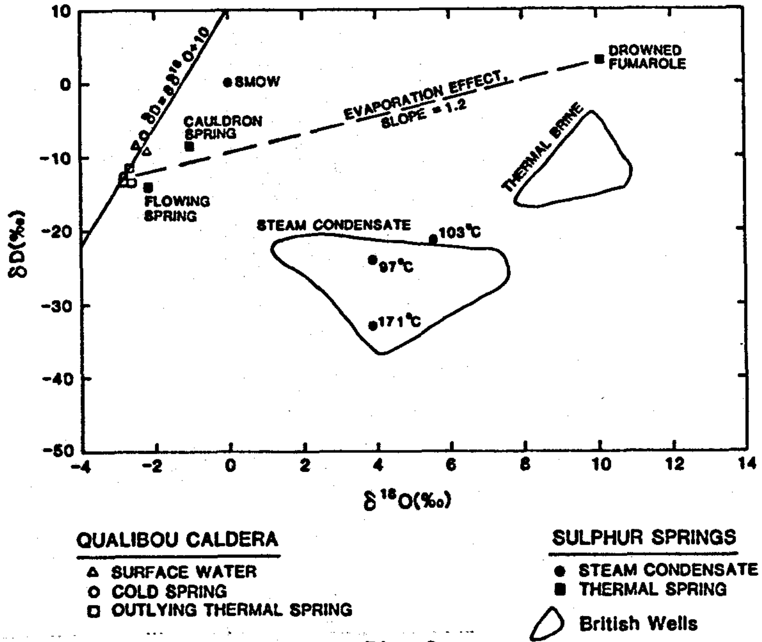

Fig. 2
Plot of deuterium versus oxygen-18 of surface waters, and geothermal fluids, Qualibou Caldera, St. Lucia; brine and steam condensate fields from Bath (1977).

compositions of fumarole steam plot on top of the field of steam condensates from the wells.

2. Gas Geothermometry: Samples of gas were collected from various thermal features including the two superheated fumaroles (Table 2). When air contamination is corrected, all samples are virtually identical. Several samples contain minute but detectable quantities of CO which is produced only in very high-temperature systems (Evans et al., 1981). Using the empirical gas geothermometer of D'Amore and Panichi (1980), Sulphur Springs gases indicate a consistent subsurface reservoir temperature of 280°C.

3. Enthalpy of Superheated Fumaroles: Muffler et al. (1982) discuss the thermodynamic significance of the superheated fumaroles at Lassen, California in some detail. According to these authors, superheated fumaroles discharge steam from subsurface reservoirs by means of an adiabatic rather than isothermal process. If we plot the measured temperature of the 171°C steam vent on Fig. 3 (which shows the relationship between saturated steam and the isothermal decompression paths of superheated steam for pure water) we note that an isoenthalpic (vertical) line lies to the right of the maximum enthalpy of saturated steam, approximately 236°C at 31 bars. The curve surrounding saturated steam would be shifted to the right if the system consists of brine instead of pure water. The temperature of maximum enthalpy of steam is also increased in a brine system. Thus, if the steam discharging from this vent originates from isoenthalpic decompression in the reservoir, the deep brine temperature must be in the neighborhood of 260°C.

4. High-temperature Behavior of Boric Acid: Tonani (1970) and Ellis and Mahon (1977) discuss the behavior of volatile boric acid in high-temperature geothermal systems and the use of B in geothermal exploration. If we use Fig. 4 reproduced from Ellis and Mahon and calculate the value of $-\log K_d$ (where K_d = concentration of B in vapor/concentration of B in brine) using B concentrations of steam and brine in Table 1, a rough estimate of the temperature of the brine reservoir is 230°C. We note here that the apparent B concentration of the brine reported by Bath (1976) is amazingly high, about three times higher than values reported from such high-B areas as Ngawha, New Zealand and The Geysers - Clear Lake region, California.

Interestingly, the estimated temperature of the brine reservoir using the brine chemistry and chemical geothermometers (Fournier, 1981, Table 4.1) is much lower than either the temperatures measured in the British drill holes or the inferred temperatures discussed above. Using the analysis in Table 1 as an example, T(Qtz, maximum steam loss) = 172°C, T(Na-K-Ca) = 151°C, and T(Na-K) = 163°C.

Outlying Thermal Springs and Cold Waters

Three areas occur west and north of Sulphur Springs where other hot springs emerge: Diamond, Cresslands, and Malgrétoute (Fig. 1). The striking fact about the chemistry of this group (Table 1) is their general resemblance to steam condensate waters at Sulphur Springs suggesting that they have a similar origin. They contain high HCO_3, high B, variable SO_4, and relatively low Cl. Although Na is the dominant cation, Ca+Mg may be relatively high. Trace

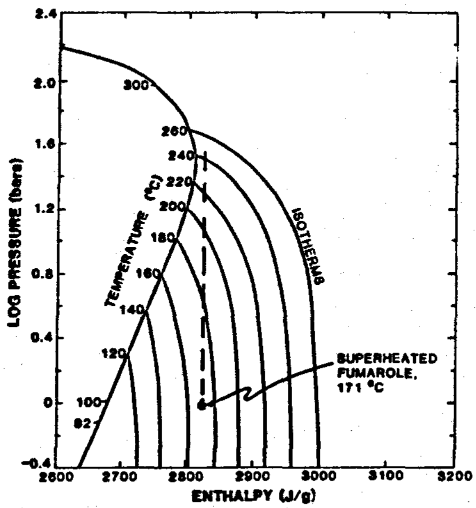

Fig. 3.
Plot of log pressure versus enthalpy showing the relations between saturated steam, the isothermal decompression paths of superheated steam, and the surface enthalpy, temperature and pressure of a superheated fumarole, Sulphur Springs, St. Lucia. The vertical dashed line is an isoenthalpic line (adapted from Muffler et al., 1982).

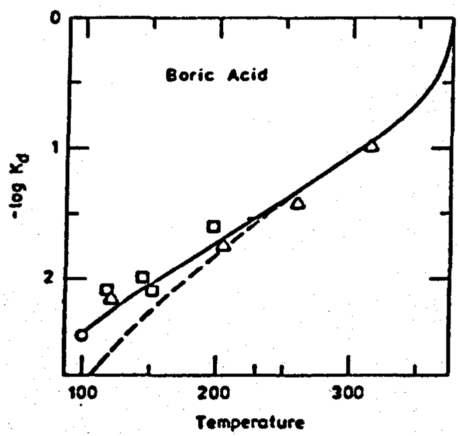

Fig. 4.
Plot of $-\log K_d$ versus temperature (from Ellis and Mahon, 1977).

element concentrations other than B are low. Because the solubility of Ca+Mg decreases with increasing temperature in any fluid that has appreciable HCO_3, these waters do not indicate equilibration at temperatures above 100°C. Stable isotope analyzes of these springs (Fig. 2) fall on the meteoric water line, again suggesting equilibration at lower temperatures.

Gas Chemistry, Outlying Springs

Aquater (1982) obtained gas analyses on the dissolved gases in the outlying springs discussed herein and their data appear in Table 2. Several facts suggest these gases are not derived directly from a high-temperature resource at depth or that the main condensation zone is laterally displaced from the springs: 1. The gases contain no measurable H_2S, 2. their concentrations of H_2 are exceptionally low, and 3. their concentrations of N_2 (presumably from air) are very high. Because there is so little H_2S at Diamond and Malgrétoute springs (even though the waters resemble steam condensate waters at Sulphur Springs), it could be postulated that H_2S has been lost during lateral flow from a main zone of condensation near Sulphur Springs. If this is not the case, it suggests that the geothermal fluids beneath Diamond and Malgrétoute are cooler in temperature and/or the zone of condensation is so thick it strips H_2S from the gas.

CONCLUSION: MODEL OF GEOTHERMAL RESERVOIR, QUALIBOU CALDERA

Using the history of previous drilling, recent resistivity data (Ander, in prep.), our concept of lateral flow in geothermal systems (Healy and Hochstein, 1973; Goff et al., 1981), and our interpretations of the geochemical data presented above, we postulate that the main Qualibou Caldera geothermal system rises beneath the Belfond-Sulfur Springs area and flows laterally toward the northwest caldera wall. The geothermal system at Sulphur Springs consists of three layers: an upper condensation zone; an intermediate vapor zone, which may be vapor-dominated; and a lower brine zone. The vapor zone reaches ground surface only at Sulphur Springs due, no doubt, to localized faulting and fracture permeability. The thickness of the vapor zone is conjectural because of the highly variable discharge characteristics of the deep wells at Sulphur Springs; a rough estimate is 600 m but it may be greater. The shape of the vapor-zone is even more conjectural; it apparently does not extend 700 m north of Sulphur Springs to British well #1 where a temperature of only 66°C was recorded at 450 m (Williamson 1979). The extent of the vapor zone in other directions is completely unknown and it may be that the vapor zone is merely a vapor conduit existing only at Sulphur Springs. In that case, the zone of condensation would surround the vapor zone.

We know even less about the brine zone except that it exists in some form beneath Sulphur Springs. Electrical resistivity data (Ander, in prep.) suggests that it occurs primarily in two deep regimes beneath the northwest caldera and the Belfond area. Several lines of evidence indicate the deep brine exists at temperatures ≥230°C. It is not clear, however, whether it upflows beneath Sulphur Springs or beneath the Belfond area where the youngest volcanism is.

Evidence for existence of a separate high-temperature system in the northwest collapse zone is not convincing because there are no high-temperature springs or gas discharges.

ACKNOWLEDGMENTS

The authors wish to thank the people of Qualibou Caldera, St. Lucia for their cooperation on this project. Chemical analyses were provided by P. Trujillo, Jr. and D. Counce, Los Alamos National Laboratory. Gases were analyzed by B. Evans, U.S.G.S., Menlo Park, California. Stable isotope analyses were obtained from C. Janik, U.S.G.S., Menlo Park and the Centre d'Etudes Nucléaires de Saclay, France. The published and unpublished work of A. H. Bath is greatly appreciated. This work was funded by the U.S. State Department, Agency for International Development.

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