

# Geochemistry and subsurface temperatures calculated from the Na/K/Ca Geothermometer of some hot springs Associated with the Tertiary-Quaternary volcanism of Southwestern Colombia

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## RESUMEN

Las concentraciones de sodio, potasio y calcio de 33 fuentes termales asociadas con los volcanes Puracé, Sotará, Azufral, Cumbal y Chiles, que forman parte de la zona volcánica Terciaria - Cuaternaria del Suroeste de Colombia han sido utilizadas para calcular temperaturas subterráneas. Estas fuentes termales tienen temperaturas variables que van de 17°C a 73°C y su caudal varía de 1 l/s. a 10-15 l/s; su pH generalmente es de 2.2, con la excepción de las fuentes termales de la mina de azufre "El Vinagre" con un pH de 2 a 2.2.

El geotermómetro Na/K/Ca sugiere temperaturas subterráneas mínimas de 48°C-86°C en cercanías del volcán Cumbal, y hasta 215°C-242°C en el área de los volcanes Puracé - Sotará.

Todas las fuentes termales estudiadas muestran una diferencia generalmente de 150°C-180°C entre la temperatura medida en superficie y la temperatura subterránea calculada. La variedad de aguas termales en un área particular se puede explicar como el resultado de la mezcla de un componente caliente y profundo con un componente somero más frío.

## ABSTRACT

The Na, K and Ca concentrations of 33 hot springs associated with the volcanoes Puracé, Sotará, Azufral, Cumbal and Chiles of the Tertiary - Quaternary volcanic zone of southwestern Colombia, have been used to calculate subsurface temperatures. These hot springs have temperatures ranging from 17° to 73°C and yields ranging from about 1 l/s to about 10-15 l/s. Their pH generally is 3-7 with the exception of springs from the sulphur mine "El Vinagre" which have a pH of 2.0 - 2.1.

The Na, K, Ca geothermometer suggests minimum subsurface temperatures ranging from 48°C-86°C close to the Cumbal volcano to 215°C-242°C in the area Puracé - Sotará volcanoes.

All the hot springs studied, show a difference of generally 150-180°C between spring temperature and calculated subsurface temperature. This suggests that the various thermal springs in a particular area result from a mixing of a deep hot component with a cooler shallower component.

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## INTRODUCTION TO PRINCIPLES OF CHEMICAL GEOTHERMOMETERS

For the estimation of surface temperatures in areas of elevated geothermal gradients water chemistry has proved to be a valuable tool. From the sodium, potassium and calcium concentration on the one hand, and from the concentrations of dissolved silica on the other hand, the temperature at which the thermal fluid has been in equilibrium with the reservoir rocks, is estimated. MAHON (1970), FOURNIER & ROWE (1966), WHITE (1970) and FOURNIER & TRUESDELL (1973) provided various techniques for this approach. The most promising and widespread applied temperature indicators have shown to be:

- 1) The variation in solubility of quartz and chalcedony as a function of temperature (Silica Thermometer).
- 2) The temperature dependent partitioning reactions (base exchange) of alkalis between solutions and solid-phase like:

K-feldspars and Na-feldspars with a correction applied for the Ca content of water (Na / K / Ca Thermometer).

There is some uncertainty in both methods, and decisions about the applicability of either thermometer varies for any particular region. Information on subsurface temperature conditions in a specific area may be necessary or can help considerably to choose the right method and estimate its accuracy.

Silica for example may be precipitated rapidly enough from water with temperatures higher than 180°C and thus gives erroneously low results in the temperature estimation (WHITE, 1970).

ARNORSSON (1975) points out that mixing of the hot water with cooler water also affects equilibrium with quartz and may establish equilibrium with chalcedony resulting in a supersaturation with respect to quartz if the hot water had a temperature of 150°C or more before mixing. He also states that the pH also can influence the validity of the silica thermometer in the sense that low pH values (7-8 at 20°C) may result from near surface chemical reactions or mixing with cold groundwater.

The Na/K/Ca thermometer may be in error either because of continued reaction of the water with the rocks at temperatures below the highest subsurface temperature calculated, or because of calcite precipitation. Continued reaction may yield low calculated temperatures due to increase in calcium content (FOURNIER & TRUESDELL, 1973). Calcite precipitation may field erroneously high subsurface temperatures because of decreases in Ca-content of the water (FOURNIER & TRUESDELL, 1970). Generally speaking, geothermometers of this kind should be applied to thermal water only under the following conditions:

- 1) Temperature dependent partitioning reactions occur in the reservoir, and the elements involved in the reactions are present at a sufficient concentration.
- 2) Equilibrium is attained between the water and host rock in the reservoir and no re-equilibration takes place during ascent of the water to the surface.

Lacking analytical results for silica subsurface temperatures have been calculated using Na-Ca-K concentrations. The equation for temperatures above 100°C is:

$$\log_{10}(m_{Na^+}/m_{K^+}) + \beta \log_{10}(\sqrt{m_{Ca^{2+}}}/m_{Na^+}) = 1,647/T - 2,240$$

and for temperatures below 100°C the equation becomes:

$$\log_{10}(m_{Na^+}/m_{K^+}) + 4/3 \log_{10}(\sqrt{m_{Ca^{2+}}}/m_{Na^+}) = 1,647/T - 2,240$$

$$\beta = 4/3 \text{ for } Ca/Na > 1 \text{ and } t < 100^\circ C, \beta = 1/3 \text{ for } Ca/Na < \text{ or } t_{4/3} > 100^\circ C$$

Where T = Temperature in kelvin degrees

$m_{Na^+}$  = Molality of sodium ions

$m_{K^+}$  = Molality of potassium ions

$m_{Ca^{2+}}$  = Molality of calcium ions

### GEOLOGICAL SETTING OF THE HOT SPRINGS STUDIED

Hot springs located in the areas of the stratovolcanoes Puracé and Sotará (fig. 1) are related to the rock sequence termed Popayán Formation. According to ROSAS (1976)



this formation consists of Plio-Pleistocene conglomerates, agglomerates, volcanic tuffs and some lava flows of andesitic to dacitic composition, accumulated between the Central and Western Cordilleras.

The Tertiary - Quaternary Chiles, Cumbal, Azufral volcanoes (fig. 1) located in the southwestern corner of Colombia, constitute a belt of stratovolcanoes built up predominantly of andesitic and dacitic lava flows intercalated with pyroclastic material (bombs, lapilli, ashes and breccias).

Younger basaltic lava flows showing typical columnar jointing have been observed in the Chiles-Cumbal area. Some hot springs are related to a typical radial fracture pattern.

### SAMPLING AND ANALYTICAL PROCEDURES

Water samples were collected as close as possible to the opening of the hot-springs, usually showing the highest water temperature. In some areas like San Juan geothermal field and the geothermal field "Río Verde", samples were

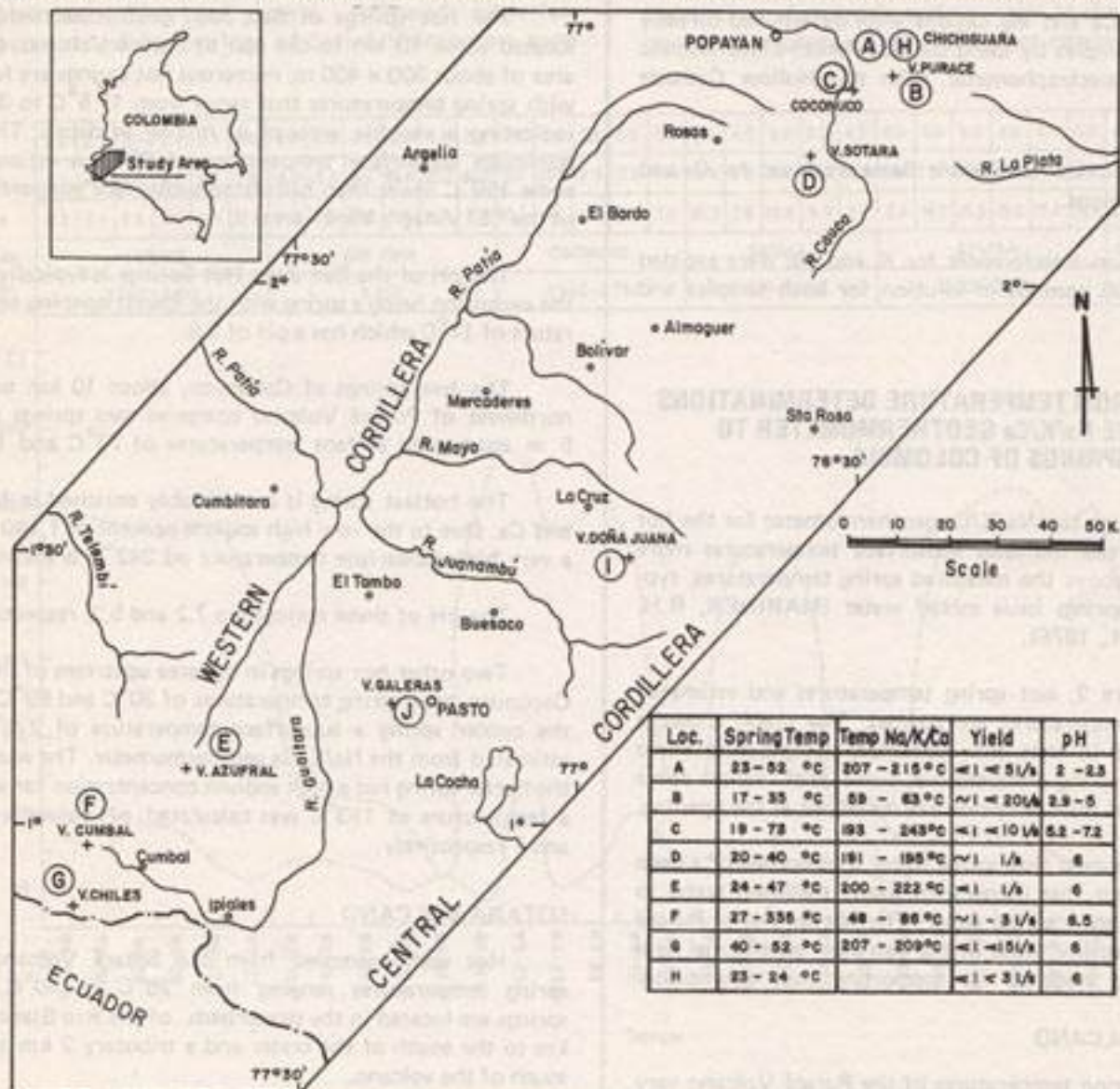


FIG. 1: Map showing sites of geothermal activity in southwestern Colombia.



recovered from several springs having different water temperatures.

Hot water was collected in 500 ml glass bottles with plastic caps. Cold water was collected and stored in 50 ml plastic bottles. The samples were not treated specifically prior to analysis. Field determinations were made of pH and water temperature, using Merck pH paper with pH range from 1-14 and a calibrated mercury thermometer of 0.1°C accuracy.

Na, K, Ca and Mg cations were determined directly from water samples by using the 306 Perkin-Elmer Atomic Absorption Spectrophotometer with the Hollow Cathode Lamp.

Nitrous oxide-acetylene flame was used for Ca and Mg determinations.

Ionization interferences for K and Na were avoided by using 1000 ppm Cs in solution for both samples and standards.

## RESULTS FROM TEMPERATURE DETERMINATIONS APPLYING THE Na/K/Ca GEOTHERMOMETER TO SOME HOT SPRINGS OF COLOMBIA

In general the Na/K/Ca geothermometer for the hot springs analyzed indicates subsurface temperatures more than 150°C above the measured spring temperatures, typical of hot springs issue mixed water (MARINER, R.H. WILLEY, L.M., 1976).

In figure 2, hot spring temperatures and estimated subsurface temperatures are plotted. The graph shows a general trend in that the subsurface temperature curve follows the spring temperature curve with values some 180°C higher than temperatures measured at the opening.

It is assumed that spring water is composed of a deep hot component that mixes with cooler shallower water to produce the hot - spring water. The hot springs of Puracé Volcano, especially those of the San Juan geothermal field show a good evidence for supporting that assumption.

### PURACE VOLCANO

Hot spring temperatures of the Puracé Volcano vary from 23°C to 52°C. The highest temperatures are recorded

from springs of the "El Vinagre" Mine. Calculated subsurface temperature indicate a very consistent temperature of 210-215°C for most of these springs, the exception is Guarquello (Chichiguara) (BK WS-27) with a temperature of 177°C resulting from a low  $\sqrt{Ca/Na}$  ratio and higher Na/K ratio. Generally the  $\sqrt{Ca/Na}$  molal ratio is very consistent and about 4.3 Na/K ratios are equally constant and close to 8.9. The pH of these springs varies from 2 - 2.1 (fig. 2, table 1).

The hot springs of San Juan geothermal field are located some 10 km to the east of Puracé Volcano. In an area of about 300 x 400 m, numerous hot springs are found with spring temperatures that range from 17.5°C to 35°C, indicating a variable amount of mixing at depth. Thus a minimum subsurface temperature of 63°C is estimated, some 150°C lower than calculated subsurface temperatures of the "El Vinagre Mine" area.

The pH of the San Juan Hot Springs is typically 4.9, the exception being a spring with the lowest opening temperature of 17°C which has a pH of 2.9.

The hot springs of Coconuco, about 10 km to the northwest of Puracé Volcano comprise two springs some 5 m apart with surface temperatures of 73°C and 19°C.

The hottest spring is considerably enriched in Na, K and Ca. Due to the very high sodium content of 1,140 mg/l a very high subsurface temperature of 242°C is estimated.

The pH of these springs are 7.2 and 5.2, respectively.

Two other hot springs in the area upstream of the río Coconuco have spring temperatures of 30°C and 59°C. For the cooler spring a subsurface temperature of 215°C is estimated from the Na/K/Ca geothermometer. The water of the hotter spring has a high sodium concentration for which a temperature of 193°C was calculated; pH values are 6.5 and 7 respectively.

### SOTARA VOLCANO

Hot water sampled from the Sotará Volcano has spring temperatures ranging from 25°C to 40°C. The springs are located in the streambeds of the Río Blanco 1.8 km to the south of the crater and a tributary 2 km to the south of the volcano.

The hot spring in the streambed of the Río Blanco



has a temperature of 30°C at the opening. From the Na/K/Ca thermometer a subsurface temperature of 72°C is calculated. The low temperature suggests a considerable admixture of cold water underground.

In the streambed of a tributary to the Río Blanco several hot springs were found close together. Their temperatures varied from 25°C to 40°C. Subsurface temperatures of 68 – 76°C are calculated for the cooler springs and 191-195°C for the springs with higher spring temperatures. Thus in general, estimated subsurface temperatures of hot springs of Sotará Volcano are some

130°C lower than those of Puracé Volcano. The pH of the hot springs is 6.

### AZUFRAL VOLCANO

One hot springs is found within the caldera of Azufral Volcano. It emerges from the bottom of a wide creek at the northern end of the crater lake "Laguna Verde". Its water is clear and has a temperature of 43°C, its pH being 6. Concentrations of Na, K and Ca are very low and only slightly higher than of meteoric surface water in the area. For this reason an erroneously low subsurface temperature of 42°C

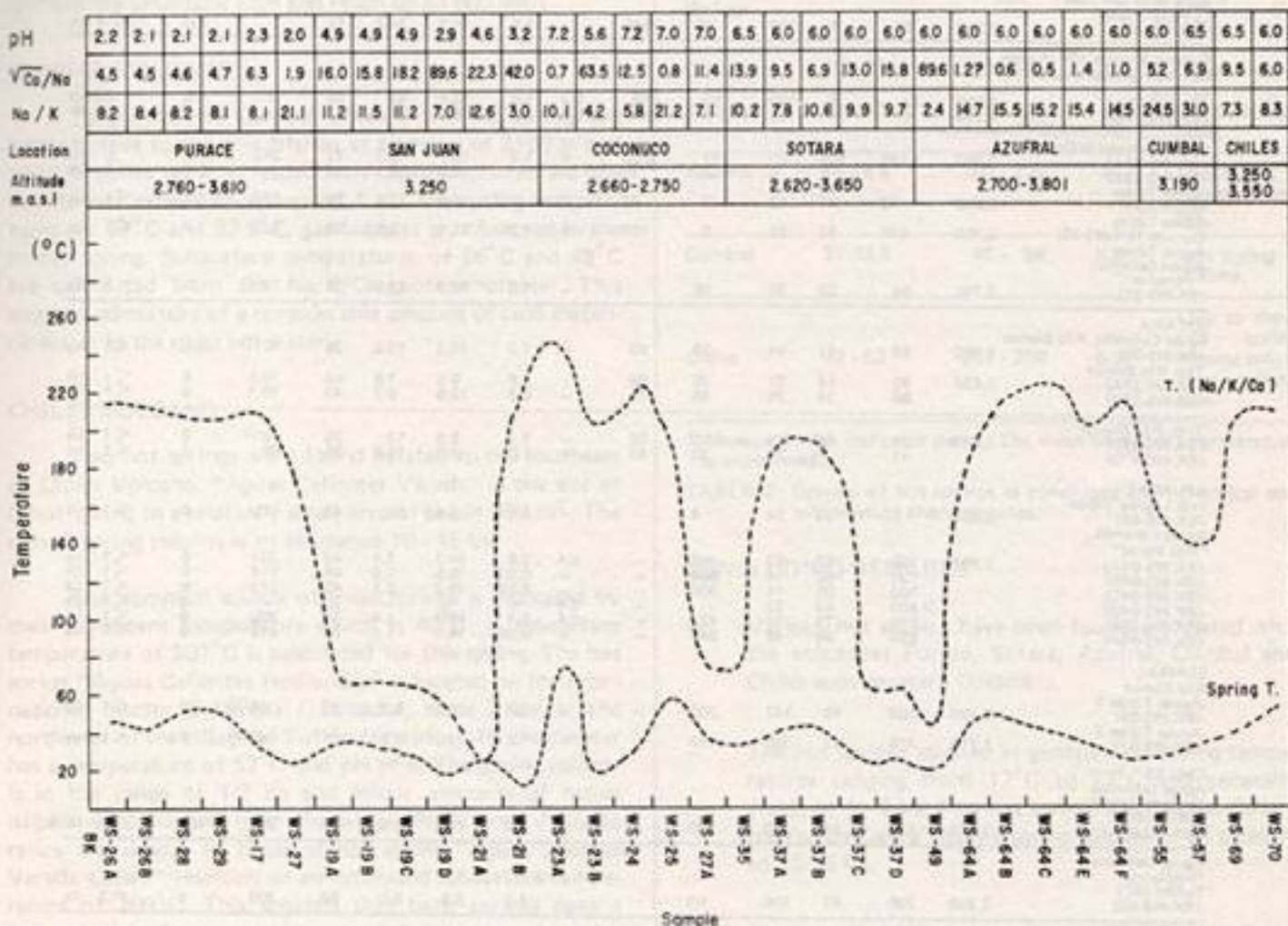


FIG. 2: Temperatures of some hot springs of southwestern Colombia compared to subsurface temperatures calculated from the Na / K / Ca geothermometer.



TABLE 1

LOCATION & SAMPLE No.	Altitude	Na	K	Ca	Mg	SO <sub>4</sub> <sup>2-</sup>	Fe	Ca/Mg	Na/K	Ca/Na	T(1)	T* NaKCa pH	Yield	
<b>PURACE</b>														
Aguas Calientes de Guarquello, (BK-WS-27)	2,760	360	29	37	44	200	0.1	1.8	21.1	1.9	23	177	2	< 1 1/2
Termas de Pilimbala, (BK-WS-17)	3,350	144	32	94	145	1800	40	0.4	7.6	7.7	32	207	2.3	~ 3 1/2
<b>La mina El Vinagre</b>														
1st. level (BK-WS-26A)	3,610	316	60	140	254	3750	67	0.3	8.9	4.3	46	211	2.1	< 1 1/2
1st. level (BK-WS-26B)	3,611	324	60	145	258	3750	73	0.3	9.1	4.3	42	210	2.1	1-3 1/2
Nacimiento (BK-WS-28)	3,590	300	58	133	250	3750	73	0.3	8.8	4.6	52	210	2.0	3-5 1/2
Bacula (BK-WS-2a)	3,570	300	58	89	246	3700	67	0.2	8.8	3.6	50	215	2.1	3-5 1/2
<b>Aguas Termales de San Juan</b>														
(BK-WS-19A)	3,250	61	9	207	60	1125	0.1	2.5	11.2	16	35	63(3)	4.9	10-15 1/2
(BK-WS-19B)		57	9	200	59	1125	0.1	2.6	11.5	16	33	63	4.9	5-10 1/2
(BK-WS-19C)		53	8	246	53	1125	0.2	2.7	11.2	16	28	59	4.9	3-5 1/2
(BK-WS-19D)		2	0	1	0	1125	-	-	-	-	17	-	2.9	< 1 1/2
<b>Agua Soda San Juan - La Plata - Road, (BK-WS-20)</b>														
	3,240	48	8	210	66	1500		1.9	10.2	34.7	17		5.0	< 1 1/2
<b>Sulphur Springs, 700 m after San Juan Spring, road to La Plata</b>														
(BK-WS-21A)	3,230	32	4	163	42	750	0.2	1.0	13.6	45	26	(21)	4.6	2-3 1/2
(BK-WS-21B)	3,230	4	1	4	1	750	8.3	2.4	6.8	57	7	-	3.2	2-3 1/2
<b>Aguas Termales de Conuco</b>														
(BK-WS-23A)	2,660	1,140	192	52	17	3000	0	1.8	10.1	0.7	73	243	7.2	< 5 1/2
(BK-WS-23B)		8	2	6	-	15	-	-	6.8	35.1	19	-	5.2	< 1 1/2
<b>Aguas Tibias</b>														
(BK-WS-24)	2,690	72	21	62	0	58	-	-	5.8	12.5	30	215	6.5	< 1 1/2
<b>Aguas Tibias Cascada (BK-WS-25)</b>														
	2,700	646	52	21	6	750	0	2.2	21.1	0.8	59	193	7	< 1 1/2
<b>Aguas Tibias "Versalles" (BK-WS-27)</b>														
	2,750	84	20	70	98		-	1.3	10.2	13.9	35	72(3)	7	~ 3 1/2
<b>SOTARA</b>														
<b>Aguas Calientes, Rio Blanco</b>														
(BK-WS-35)	3,650	66	11	64	29	83	-	1.3	10.2	13.9	35	72(3)	6.5	< 1 1/2
<b>Trib. Rio Blanco</b>														
(BK-WS-37A)	3,620	90	16	37	36	96	-	1.6	9.5	7.8	40	19.5	6	< 1 1/2
(BK-WS-37B)		89	14	28	49	75	-	0.3	10.6	6.9	40	19.1	6	< 1 1/2
<b>Trib. Rio Blanco</b>														
(BK-WS-37C)	3,620	58	10	43	20	58	-	1.3	9.9	13	25	76(3)	6	< 1 1/2
(BK-WS-37D)		41	7	32	20	40	-	1.0	9.7	15.8	25	68	6	< 1 1/2
<b>AZUFRAL</b>														
<b>Trib. Laguna Verde (BK-WS-49)</b>														
	3,802	5	3	14	4	-	-	2.1	2.4	89	43	(42)	6	< 1 1/2
<b>Aguas Calientes "Rio Verde"</b>														
(BK-WS-64A)	2,700	750	87	57	600	-	0.4	0.6	14.7	1.1	47	203	6	< 1 1/2
(BK-WS-64B)		730	80	14	600	-	-	0.01	15.5	0.6	46	218	6	< 1 1/2
(BK-WS-64C)		750	85	11	600	-	-	0.01	15.2	0.5	40	222	6	< 1 1/2
(BK-WS-64D)	> 600	87	22	-	-	-	0.4	-	-	-	36	-	6	< 1 1/2
(BK-WS-64E)		710	78	74	472	-	0.4	0.1	15.4	1.4	34	200	6	< 1 1/2
(BK-WS-64F)		620	96	48	645	-	-	0.05	14.5	1.0	24	212	6	< 1 1/2
<b>CUMBAL</b>														
<b>Rio Blanco</b>														
<b>Aguas Tibias 1 (BK-WS-55)</b>														
	3,190	260	18	142	200	-	-	0.4	24.5	5.2	27	86(3)	6	< 1 1/2
<b>Aguas Tibias 2 (BK-WS-57)</b>														
	3,210	310	17	360	115	-	-	1.8	31	6.9	34	48(3)	6	< 1 1/2
<b>CHILES</b>														
<b>Aguas Calientes "Vereda Calera"</b>														
<b>Tufiño (EC)</b>														
(BK-WS-69)	3,250	133	31	120	80	-	-	0.9	7.3	9.5	40	207	6.5	< 10-15 1/2
<b>Aguas Calientes "Hedionda"</b>														
<b>Tufiño (EC)</b>														
(BK-WS-69)	3,350	200	41	108	56	-	-	1.1	8.3	6.0	52	209	6	~ 2 1/2

T\*

N/K/Ca:

T(1):

Note:

(2):

(3):

Fournier &amp; Truesdell, 1973

Temperature at the Opening

All temperatures in centigrade (°C). All ratios are molal ratios concentrations in ppm,

Adjusted in m a.s.l.

for  $\beta = 4/3$



is calculated which is unlikely to reflect the actual temperature conditions underground. The water is interpreted as being local meteoric water percolating to shallow depths.

Outside the caldera, some 2.8 km to the northwest of the crater a very small low-temperature geothermal field is located close to the Río Verde. The area is some 400 m<sup>2</sup> in surface and samples have been recovered from six different springs. The springs have volumes of about 0.5 - 1 l/s (at the most). In all springs gas bubbles can be observed. Spring temperatures are in the range of 24.5°C to 47°C; pH is constant and 6. From the Na/K/Ca geothermometer subsurface temperatures of 201-222°C are estimated. Mg-concentrations are unusually high and reach up to 600 mg/l.

### CUMBAL VOLCANO

To the east of Cumbal Volcano two hot springs are located close to the Río Blanco at altitudes of 3190 m and 3210 m above sea level respectively. Spring volumes are low and do not exceed an estimated 1 l/s. The spring temperatures are 27°C and 33.5°C, gas bubbles are observed in the hotter spring. Subsurface temperatures of 86°C and 48°C are calculated from the Na/K/Ca geothermometer. This suggests admixture of a considerable amount of cold meteoric water to the deep hot water.

### CHILES VOLCANO

Two hot springs were found located to the southeast of Chiles Volcano. "Aguas Calientes Vereda" is the site of 5 hot spring in a relatively small area of about 300 m<sup>2</sup>. The overall spring volume is an estimated 10 - 15 l/s.

The common source of these springs is indicated by their consistent temperature which is 40°C. A subsurface temperature of 207°C is calculated for this spring. The hot spring "Aguas Calientes Hediondas" is located on the international border Colombia / Ecuador, some 3 km to the northwest of the village of Tufiño (Ecuador). Its clear water has a temperature of 52°C and pH of 6. The spring volume is in the range of 1-2 l/s and minor amounts of native sulphur is deposited from the water. Na/K and  $\sqrt{Ca}/Na$  ratios are similar to those of hot spring "Aguas Calientes Vereda Calera" resulting in an estimated subsurface temperature of 209°C. This suggests that both springs have a common deep hot water component that mixes with cooler shallower water in slightly different proportions to produce the variation in surface water temperature.

In brief, the various hot springs of southwestern Colombia in the departments of Cauca and Nariño, can be grouped as given in Table 2.

Group	Spring Temp (°C)	Calculated Subs. Temp. (°C)	pH*	Remarks
Puracé (+Guarquesillo).	23 - 52	(177)- <u>215</u>	2.1-2.3	Low spring volume except for "Nacimientito", Sulphur deposition.
San Juan Thermal Springs	17 - 35	59 - <u>63</u>	2.9-5.0	Various hot springs with varying discharge rates.
Coconuco	19 - 73	193 - 243	5.2-7.2	Clear water
Sotará	20 - 40	191 - <u>196</u>	6	Low discharge rates.
Azufraí	24 - 47	200 - 222	6	Low spring volume with gas.
Cumbal	27-33.5	48 - 86	6.5	Low spring volume.
Chiles	40 - 52	207 - 209	6.0	Low to medium spring volume sulphur deposition.

\* Measured with indicator paper. The most consistent temperature is underlined.

TABLE 2: Groups of hot springs as concluded from chemical and temperature characteristics.

### CONCLUDING REMARKS

- Various hot springs have been found associated with the volcanoes Puracé, Sotará, Azufraí, Cumbal and Chiles southwestern Colombia.
- The hot springs studied in general have spring temperatures ranging from 17°C to 73°C and generally yields of 1 - 2 l/s. Few hot springs e.g. "Aguas Calientes Vereda Calera" have a spring volume of an estimated 10-15 l/s.
- From the Na/K/Ca geothermometer minimum subsurface temperatures ranging from 48°C to 243°C are calculated for the various geothermal areas.



- The highest consistent subsurface temperatures of 207°C and 209°C are calculated for the Puaracé area and the Chiles area. The hot springs of the other areas show wider variations in their calculated subsurface temperatures.
- A difference of 150 to 180°C between measured spring temperature and calculated subsurface temperature suggests that the hot springs result from a mixing of a deep hot component with a cooler shallower component. This can be particularly well observed for the hot springs of the springs of the San Juan geothermal field, the geothermal field north of Azufra Volcano and the Cumbal and Sotará hot springs.
- This study is far from being conclusive. Nevertheless this kind of approach with a complementary work on the silica geothermometer and isotopic analysis may prove to be useful in the preliminary evaluation of the geothermal potential of the country.

#### ACKNOWLEDGMENTS

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