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Geothermal Exploration in the Cordón Caulle Region, Southern Chile

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ABSTRACT

The Cordón Caulle region (40.5°S) hosts a 15 km long, NW-trending volcanic depression made up of Holocene and historic silicic lavas and pumice deposits overlying Late-Pleistocene basaltic flows. Fumaroles occur at the top of the system (~1500 m.a.s.l.), spatially associated with the edges of the depression. Fumaroles from the northeastern edge (areas of Las Sopas and Los Venados) are interpreted to arise from deeply-convected air-saturated groundwater (N_2/Ar ratios of ~ 40), whereas fumaroles from the southwestern edge (area of El Azufral) are believed to be dilute volcanic fumaroles (N_2/Ar ratios of ~ 400-500). Deep mixing between the sources of gases of Las Sopas-Los Venados and El Azufral is inferred from the relatively oxidizing conditions prevailing at Las Sopas-Los Venados (R_H factor = fH_2/fH_2O = -3.2), in comparison with the usual and expected redox state of a mature, rock-buffered system (R_H = -2.8). Boiling springs occur at the northwest tip of the Cordón Caulle area (~1000 m.a.s.l.) in close spatial relationship with collapse structures of a 10 km wide, Late-Pleistocene caldera. Boiling springs total an outflow of ~100 l/s and have intriguing chemistry: TDS < 700 mg/l, pH ~ 9, Cl/HCO_3 ratios of 0.2 (Cl <30 mg/l), Cl/B ratios of 1, lower Mg (<0.06 mg/l) relative to local meteoric waters (~ 5 mg/l), silica up to 400 mg/l (and widespread silica sinter), and δ^{18}O-δD values slightly shifted relative to the GMWL. Na-K and pH-corrected silica temperatures in the range of 150-180°C are interpreted to reflect subsurface temperatures of a secondary steam-heated aquifer overlying a main vapor-dominated system. By means of gas geothermometry (H_2-Ar, CO-CO_2 and CH_4-CO_2), temperatures greater than 260°C and up to 330°C are estimated for the deep reservoir.

1. INTRODUCTION

Chile represents one of the largest undeveloped geothermal provinces of the world. Geothermal areas in Chile are closely related to Quaternary volcanism. The volcanic-geothermal activity is primarily controlled by the convergence of the Nazca and South-American plates. Active volcanism splits into two main margin-parallel volcanic belts, namely, the Northern Volcanic Zone (NVZ: 17°-28°S) and the Southern Volcanic Zone (SVZ: 33°-46°S).

Detailed geothermal investigations in Chile, including drilling and feasibility studies, date back to the mid 1970's. At that time, a CORFO-UNDP geothermal program explored northern Chile leading to the identification of several geothermal prospects such as El Tatio, Surire and Puchuldiza (Lahsen and Trujillo, 1975; Lahsen, 1976; Lahsen, 2005, this congress). By the mid 90's, geothermal exploration was resumed by ENAP (National Oil Company) both in northern and southern Chile. In the SVZ, investigations were focused on the geothermal prospects of Calabozos (35.5°S; Grunder at al., 1987) and Nevados de Chillán (Dixon et al., 1999; Fig. 1). In 1994, a 270 m deep gradient well was drilled in the Nevados de Chillán area encountering wet steam with temperatures of 198°C (Salgado and Raasch, 2002). Later on, a compilation of geochemical data from all the thermal areas of Chile was conducted by the National Geological Survey of Chile (Hauser, 1997; Pérez, 1999), but a thorough interpretation of the structure of the geothermal systems of the SVZ was lacking. The University of Chile initiated a geothermal research program aimed at assessing geothermal resources of southern Chile, giving emphasis to the areas of Nevados de Chillán (36.9°S; Sepúlveda and Lahsen, 2003) and Puyehue-Cordón Caulle (40.5°S; Sepúlveda et al., 2004a). Only in Puyehue-Cordón Caulle and Nevados de Chillán, more than 40 MWt and 100 MWt, respectively, have been reported in association with the surface manifestations (Sepúlveda and Lahsen, 2003; Sepúlveda et al., 2004a). The presence of vigorous fumaroles and large outflows of low-chloride springs was found to be a common feature of Nevados de Chillán and Puyehue-Cordón Caulle. This is distinct from northern Chile were chloride springs are common (e.g. El Tatio, Surire and Puchuldiza; Lahsen, 1976, 1988).

Sepúlveda et al. (2004a) presented a conceptual model for the Puyehue-Cordón Caulle geothermal system, distinguishing two main upflows separated by more than 15 km. The northernmost upflow (i.e. Cordón Caulle) was interpreted to be related to a vapor-dominated system overlain by a secondary steam-heated aquifer, with the surface expression of the latter being an outflow of 100 l/s of low-chloride bicarbonate boiling springs. Na-K and silica geothermometers suggested subsurface temperatures of the steam-heated aquifer of about 170-180°C. Equilibration temperatures of the main reservoir, however, remained unconstrained. The southernmost upflow, expressed at surface through a number of hot springs collectively referred to as Puyehue-Aguas Calientes, was found to have a high degree of dilution, hampering a confident application of aqueous geothemometers.

In this study, gas chemistry data obtained from fumaroles and hot springs are used to provide a better understanding of the Cordón Caulle geothermal system.

2. GEOLOGICAL SETTING

The deep stratigraphy of the Cordón Caulle geothermal system can be inferred from rocks exposures found within and around the perimeter of the geothermal area. Quaternary volcanic rocks are the most widespread, followed by Miocene intrusions, which are found as prominent islands inside neighboring lakes, to the east along regional, intra-arc faults systems, and as accessory fragments of strombolian deposits, which are widely recognized north and south of the Cordón Caulle area, accounting for the existence of these intrusions beneath (Sepúlveda et al., 2004a). Minor Tertiary sediments and ignimbrites are also found to the north of the study area (Aguirre and Levi, 1964).

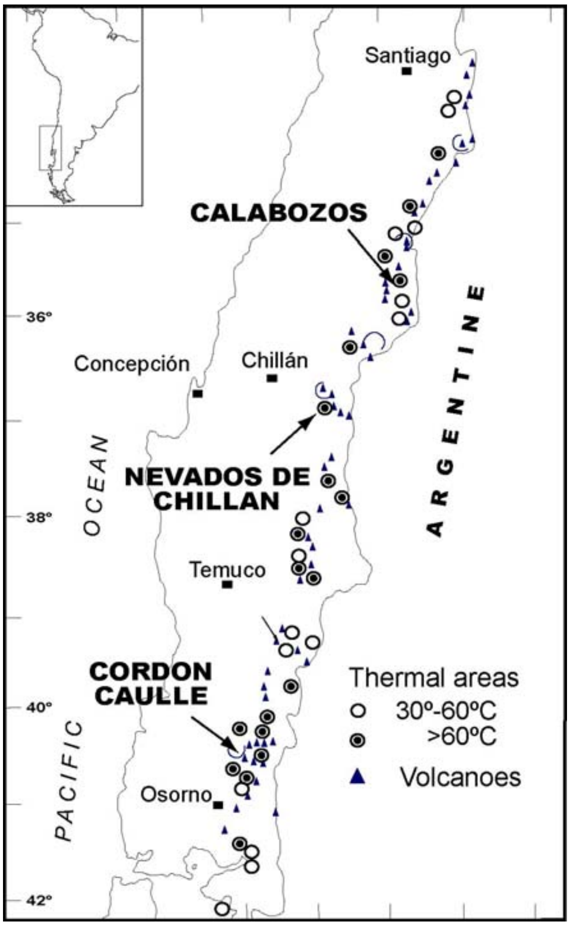

Figure 1: Some of the largest geothermal prospects of the SVZ, including the Puyehue-Cordón Caulle region.

Quaternary volcanic rocks can be grouped into the following units, from north to south: Cordillera Nevada, Cordón Caulle, Puyehue and Casablanca-Antillanca (Moreno, 1977; Fig. 2).

Cordillera Nevada consists of a 10 km wide caldera, which represents the remnant of a collapsed stratovolcano with pre-caldera sequences older than 100 ka. Late Pleistocene volcanic rocks are dominantly basaltic in composition, covering vast areas to the north and northwest of the Puyehue-Cordón Caulle geothermal area. Vigorous boiling springs, referred to as Trahuilco springs, occur at an elevation of 1000 m in association with collapse structures of Cordillera Nevada, totalizing an outflow of about 100 l/s. On a local scale, permeability controlling discharge is linked to sub-parallel jointing (up to ~100 fractures/m) of lavas cropping out nearby. Most thermal vents correspond to circular, steep-sided craters made up of silica sinter, some of which display concentric breccia aprons, pointing to the episodic occurrence of hydrothermal eruptions.

The Cordón Caulle volcanic group consists of a 13 km long, 6 km wide flat-topped volcano-tectonic depression bordered by NW-trending fractures. Late-Pleistocene volcanic rocks are dominantly basaltic in composition (younger than 300 ka; Sepúlveda et al., 2004b), being overlain by a post-glacial pumice coverage and a number of monogenetic cinder cones, lavas and lava-domes of dacite-rhyolite composition. The southwestern edge of the depression of Cordón Caulle records two historic fissure eruptions (1921-1922 and 1960). Fumaroles, solfatares, steaming-ground and acid-sulfate alteration dominate at the top of the Cordón Caulle depression at elevations from 1500 to 1700 m, being particularly well developed in the areas of Las Sopas and Los Venados, and within and around the cinder cone of El Azufral. This cone formed during the 1960 eruption and hosts to date fumaroles and solfatara (Fig. 3). Exceptionally, hot springs of bicarbonate type with small flowrate (< 10 l/s) and temperatures in the range of 30°-71°C occur over 1400 m, such as in the areas of Los Baños and Los Venados (Fig. 3), in association with perched aquifers (Sepúlveda et al., 2004). Extensive steam condensing and rock dissolution in Las Sopas give rise to numerous mud pools. Steam exhalations of Morro Solfataras (Fig. 3) occur in the form of steaming ground.

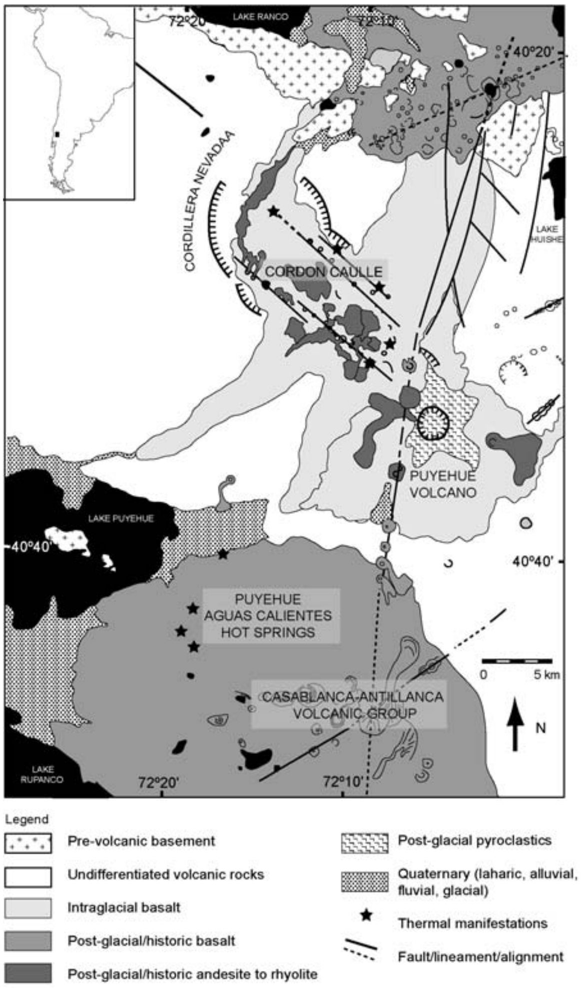

Figure 2: Geological map of the Puyehue-Cordón Caulle region (after Moreno, 1977).

The Puyehue volcanic group corresponds to a 2236 m high stratovolcano with a 2.5 km wide crater. The bulk of the Puyehue volcano is made up of intra-glacial basaltic lavas dating back to about 200 ka (e.g. Gerlach et al., 1987). An explosive stage commenced in the post-glacial lapse resulting in extensive pumice deposits and the current collapsed morphology of the volcano. More effusive andesite and dacite flank eruptions represent the latest activity of Puyehue. Local steaming ground occurs over the northwestern flank of Puyehue close to the summit (2000 m).

The Casablanca-Antillanca volcanic complex comprises a basaltic stratovolcano and a cluster of basaltic scoria cones. Most of the Puyehue-Aguas Calientes springs emerge from glacial-fluvial deposits along stream valleys, at elevations between 200-490 m, and locally, from fractured lahars of the Casablanca-Antillanca group (Fig. 3).

In this study, Las Sopas, Morro-Solfataras, Los Venados and Trahuilco, are collectively referred to as the Cordón Caulle geothermal system. Most of the thermal manifestations of Cordón Caulle are spatially associated with the northeastern edge of the depression. Acid-sulfate alteration and silica sinters are largely restricted to active thermal vents, suggesting that Cordón Caulle is a relatively young geothermal system (<10,000 years). The abrupt transition from basaltic to felsic volcanism in the post-glacial lapse, observed both in the Puyehue volcano and over Cordón Caulle, is believed to be associated with the onset of geothermal activity (Sepúlveda et al., 2004a).

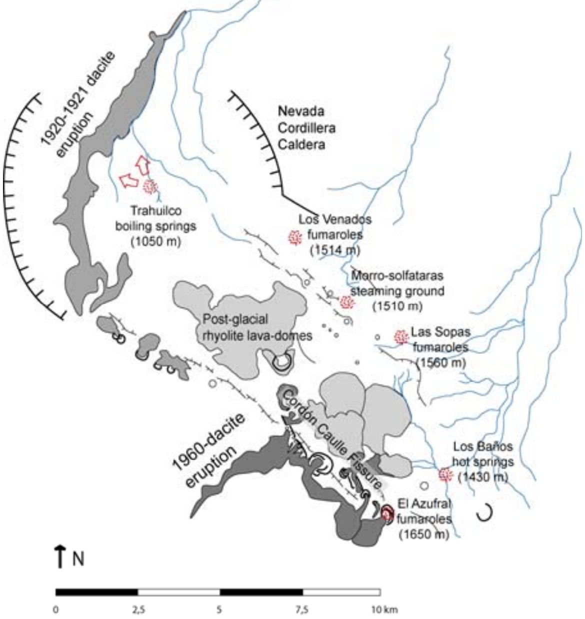

Figure 3: Localization of thermal manifestations of Cordón Caulle.

3. GEOCHEMICAL BACKGROUND

Sepulveda et al. (2004a) presented chemical and isotopic data from several thermal discharges of Cordón Caulle and Puyehue-Aguas Calientes. They proposed that Cordón Caulle was hosting the largest geothermal system, with the major outflow concentrated in the locality of Trahuilco (>100 l/s). Trahuilco springs were characterized by high dissolved silica (up to 400 mg/l) and concomitant silica sinter, lower Mg (<0.06 mg/l) and higher B/Cl ratios (= 1) relative to the local meteoric waters (Mg 2-5 mg/l), and a slight δ^{18}O shift relative to the local meteoric composition (Fig. 6). In contrast, Puyehue-Aguas Calientes spring were found to be highly diluted for a confident application of aqueous geothermometers. Evidence supporting strong dilution in the Puyehue-Aguas Calientes springs included the overall low TDS (< 350 mg/l), the high Mg content relative to Na and K, and the δ^{18}O-δD signature resembling the local meteoric composition (Fig. 5). In addition, both Cl/HCO_3 ratios of 2 (Cl > 100 mg/l) and Cl/B ratios of 250 obtained for Puyehue-Aguas Calientes greatly differed from those of Cordón Caulle (Fig. 4), pointing to a separate upflow.

Trahuilco springs were relatively diluted (TDS < 700 mg/l) and particularly low in chloride (Cl <30 mg/l; Cl/HCO3 ratios of 0.2) compared to typical springs from high-temperature, liquid-dominated geothermal systems, such as those of northern Chile (Cl > 1000 ppm in El Tatio; Lahsen, 1988). In addition, isotopic data from Trahuilco strongly invoked a mixing trend between groundwater (melting water) and steam (fumarole condensates), in favor of a steam-heated origin for Trahuilco (Fig. 5). Furthermore, Na-K and pH-corrected silica temperatures fell within the range of 160-180°C. Based on this evidence, Sepúlveda et al (2004a) hypothesized about the existence of a secondary steam-heated aquifer overlying a main vapor-dominated system.

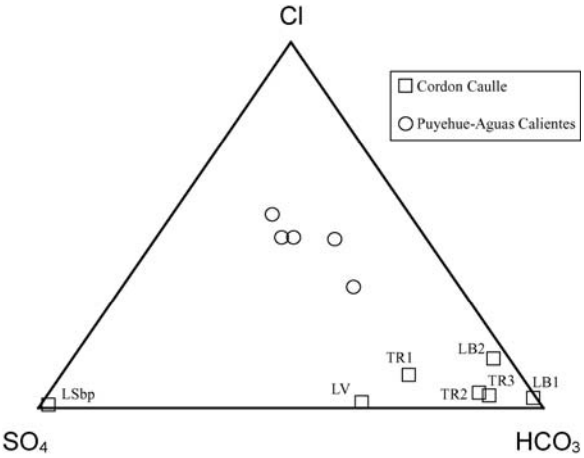

Figure 4: Cl-SO_4-HCO_3 ternary diagram (Sepúlveda et al., 2004a). TR = Trahuilco hot spring; LV = Los Venados hot spring; LB = Los Baños hot spring; LSbp = Las Sopas boiling pool (see Figure 3 for location).

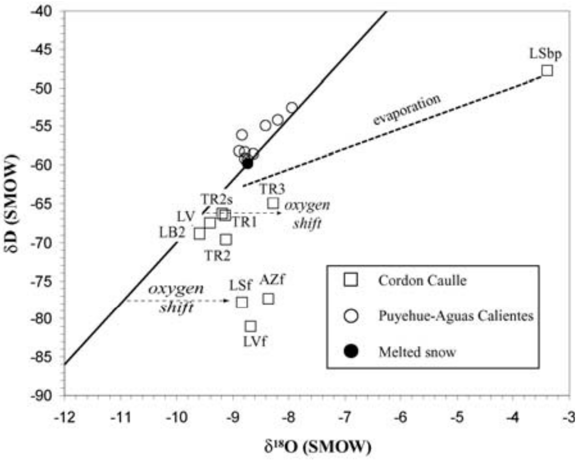

Figure 5: δD-δ^{18}O plot applied to Puyehue-Aguas Calientes and Cordón Caulle. LSf, AZf and LVf = fumarole condensates (after Sepúlveda et al., 2004a).

4. METHODS

New water samples from the locality of Trahuilco and gas samples from the areas of Las Sopas, Los Venados and El Azufral are used here to refine the existing conceptual model of Cordón Caulle. Water samples were collected from three thermal vents referred to as A, B and C. Rivers, cold springs and lakes were also sampled to get an average local meteoric composition. Water samples were analyzed in three different laboratories (Sernageomin, Chile; Thermochem, USA; and the University Ludwig Maximilians of Munich, Germany). Gas samples were collected into partially-evacuated gas bottles, containing 4 to 6 N NaOH for the absorption of alkali soluble gases (CO_2 and NH_3), and 1 N $CdCl_2$ for absorption of H_2S. The latter was aimed at measuring air contamination by keeping O_2 free from reacting with H_2S to form sulfate. Gas samples for CO determination were taken without NaOH. Sample collection was carried out in duplicate when possible. Fumaroles were sampled by inserting a titanium tube into the vent. For diffuse gas exhalations a funnel was put and buried with clays to minimize air inflow. Gas samples from hot springs were collected by immersing a funnel up-side down into the water discharge. CO_2, H_2S and NH_3 were determined by analysis of the gas absorbent reagent (infrared acid evolution analysis for CO_2; Iodine titration for H_2S and flow injection analysis for NH_3). Non-condensable gases CH_4, N_2, Ar and H_2, were measured by gas chromatography conductivity detection.

5. RESULTS AND DISCUSSION

5.1. Water chemistry

Selected thermal vents varied in style from constant (e.g. samples A and B) to variable overflow (e.g. sample C), the latter being induced by eruptive pulses with a water column up to 5 m high. Sample *C* averaged the highest flow rate (>30 l/s), pH (about 9.2) and TDS (about 650 mg/l). Average Na, K and Ca contents of sample *C* (Na = 131 ± 9 and K = 4.6 ± 0.2; Ca = 1.1 ± 0.1) and samples *A* and *B* (Na = 90 ± 7; K = 3.4 ± 0.2; Ca =1.3 ± 0.1) allow to anticipate a more diluted character for samples *A* and *B* relative to *C*, based on comparison with the local meteoric composition (Na = 6.2; K = 0.9; Ca = 3.2). A hypothetical diluting trend is portrayed in Figures 6 and 7 showing that neither Na/K nor K/Ca ratios are absolutely immune to dilution. This is important for the interpretation of Na-K geothermometry and K-Ca geobarometry (Giggenbach, 1988).

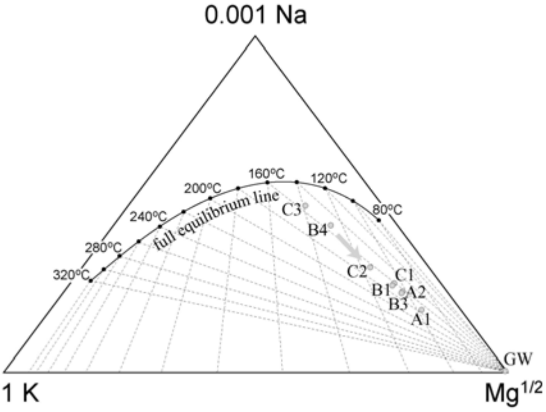

Figure 6: Na-K-Mg ternary diagram (after Giggenbach, 1988) applied to Trahuilco. The arrow portrays a diluting trend towards groundwater (GW), whose composition is derived from local meteoric water samples (*n* = 18).

Following a conceptual approach, Giggenbach (1984) obtained a general equation for calcite-Ca-Al-silicate equilibrium straddling all the temperatures of interest:

$$Logf_{CO_2} = 0.0168t - 3.78 \quad (1)$$

with *t* in °C. Below 200°C, a reaction candidate to govern CO_2 pressures is given by:

$$laumontite + K\,feldspar + CO_2 \Leftrightarrow calcite + K\,mica + 4SiO_2 + 3H_2O \quad (2)$$

(Giggenbach, 1984). By using the SUPCRT software package (Johnson et al., 1992), we obtain:

$$Logf_{CO_2} = 0.0180T - 4.73 \quad (3)$$

On the other hand, Arnórsson (1985) found that CO_2 partial pressures from a number of geothermal worldwide followed invariably the expression:

$$LogP_{CO_2} = -2.81 - 5012.7/T - 0.00919T + 6.464LogT \quad (4)$$

CO_2 partial pressures of the parent fluid of Trahuilco are estimated by use of the K^2/Ca-geobarometer (Giggenbach, 1988), based on the assumption of equilibrium according to:

$$3K\,feldspar + CO_2 + Ca^{2+} + H_2O \Leftrightarrow calcite + K\,mica + 6SiO_2 + 2K^+ \quad (5)$$

from which the following expression is derived:

$$Log\frac{K^2}{Ca} - Logf_{CO_2} = 3.0 \quad (6)$$

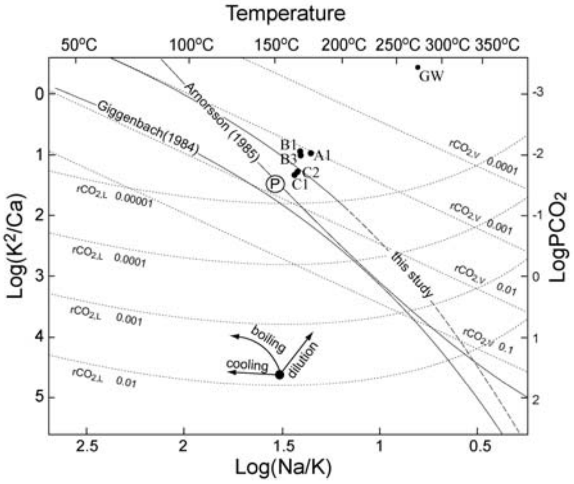

Figure 7: Na-K-Ca geoindicator applied to Trahuilco springs (after Giggenbach, 1988).

There is a reasonable agreement between theoretical, rock-buffered (eqs. 1 and 3) and empirical CO_2 partial pressures (eq. 4), as shown in the Log(Na/K) vs. Log(K^2/Ca) plot (Fig. 7). By use of equation 6, K^2/Ca ratios of Trahuilco lead to the following equilibrium scenarios: (1) CO_2 partial pressures of $10^{-1.7}$ bars (eq. 6) and reservoir temperatures of about 170°C (eq. 3), for calcite-laumontite equilibrium and negligible dilution so that samples *C1* and *C2* are representative of the deep environment; and (2) CO_2 partial pressures of $10^{-1.5}$ bars and reservoir temperatures of about 150°C (eq. 4), for a partially diluted parent fluid following a behavior close to empirical (e.g. point *P* in Figure 7). Full equilibrium CO_2 pressures in the range of $10^{-1.5}$ to $10^{-1.7}$ bars and reservoir temperatures of 150°-170° are consistent with the silica and Na-K temperatures obtained by Sepúlveda et al. (2004a).

5.2. Gas chemistry

In the following discussion, all concentrations are in mol % on a water-free basis. A first classification of gases from Cordón Caulle is made on the basis of the most abundant gas species CO_2 and H_2S, normalized to CH_4 (Fig. 8). Fumaroles of Las Sopas and Los Venados show relatively homogeneous contents of CO_2 and H_2S, with CO_2 ranging from 90 to 94 % and H_2S varying from 4.7 to 6.9 %. El Azufral shows lower CO_2 (82-83 %) and higher H_2S (13 %) relative to Las Sopas-Los Venados, a first hint on two separate sources for these gases, preliminary referred to as “volcanic” (El Azufral) and “geothermal” (Las Sopas-Los Venados). Gas samples from Trahuilco springs have higher CH_4 (15 %) compared to fumarolic gases (< 0.05 %). Note also that Las Sopas is more enriched in NH_3 (> 0.2 %; Fig. 9) compared to Los Venados. Given the relatively high solubility of NH_3, selective removal of this gas will take place in close proportion to steam condensing, suggesting a more peripheral character for Los Venados.

A second approach to classify gases is made up on the basis of N_2/Ar ratios normalized to CO_2 (e.g. Giggenbach and Goguel, 1989; Fig. 10). N_2/Ar ratios allow an estimation of the degree to which gas samples are a mixture of magmatic and atmospheric components. N_2/Ar ratios are about 84 in air, 38 in air-saturated groundwater (ASW), and 800 or higher in magmatic gases (Giggenbach and Goguel, 1989). Las Sopas and Los Venados show N_2/Ar ratios close to the ASW composition, suggesting deep convection of ASW into the geothermal system. Conversely, El Azufral shows N_2/Ar ratios in the range of ~340-550, pointing to a greater proximity to a magmatic source (Fig. 10). Gases from Trahuilco are a mixture of ASW and air components, as indicated by the N_2/Ar ratio of about 50). The higher CH_4 (15.4 %) relative to CO_2 (7.9 %) of Trahuilco can be interpreted in terms of temperature-dependent equilibrium, as we will discuss below.

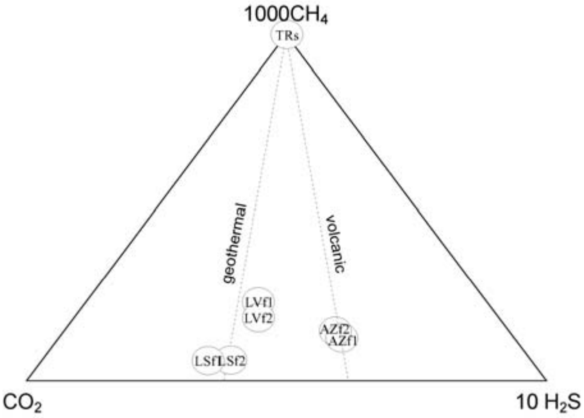

Figure 8: CH_4-CO_2-H_2S ternary diagram. Fumarolic gases from: AZ = El Azufral; LS = Las Sopas; LV = Los Venados; hot spring sample from TR = Trahuilco.

5.3. Review on gas geothermometry

Assessment of reservoir temperatures can be carried out by means of gas geothermometers. Of particular interest are gas ratio-based methods proposed by Giggenbach (1987, 1993) and Giggenbach and Goguel (1989). The most heavily used gas ratios include H_2/Ar, CO_2/Ar, CO/CO_2, and CH_4/CO_2, which can be combined in pairs into the so-called gas-ratio grids (Giggenbach and Goguel, 1989; Giggenbach, 1993). A comprehensive revision of these methods can be found in Powell (2000).

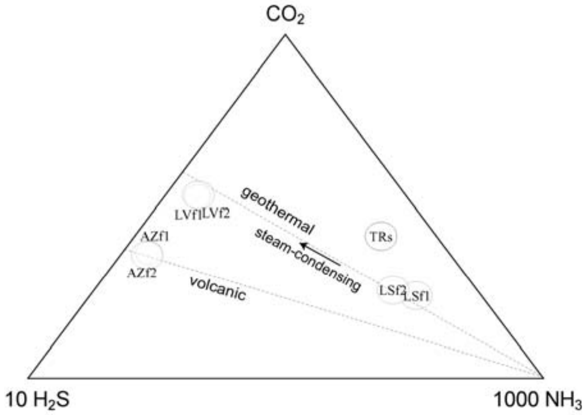

Figure 9: CO_2-H_2S-NH_3 ternary diagram for gas samples of Cordón Caulle. Caption as in Figure 8.

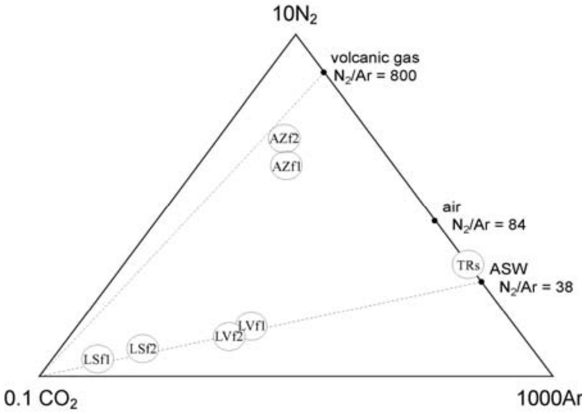

Figure 10: N_2-CO_2-Ar ternary diagram. Caption as in Figure 8.

5.3.1 The CO_2/Ar-H_2/Ar grid

H_2 is an active participant in many temperature and redox-dependent reactions. Since H_2 normally occurs under measurable concentrations, it becomes a valuable redox indicator in comparison with O_2 at geothermal conditions (< 500°C). The factor $R_H = \mathrm{Log}(fH_2/fH_2O)$ was introduced by Giggenbach (1987) to quantify the redox state, as dictated by the reaction:

$$2H_2O(g) \Leftrightarrow 2H_2(g) + O_2(g) \quad (7)$$

The expression linking R_H and oxygen fugacities is given by:

$$Logf_{O_2} + 2R_H = 5.3 - \frac{25552}{(t+273)} \quad (8)$$

with t in °C (Giggenbach, 1997). According to Giggenbach (1987), the usual and expected redox state of a mature geothermal system hosted in basaltic to andesitic rocks can be approximated to that of a rock matrix with a $FeO/FeO_{1.5}$ activity ratio of 1. Using fayalite and hematite as thermodynamic proxies (i.e. FH buffer), Giggenbach (1987) arrived at a nearly temperature-independent value of $R_{H,FH}$ = -2.8, which represents redox conditions bracketed between the rock buffers Quartz-Fayalite-Magnetite (FM) and Hematite-Magnetite (HM). Based on the SUPCRT software package (Johnson et al., 1992), we found that $R_{H,FH}$ can be fitted to the expression:

$$R_{H,FH} = -3.63 + \frac{592}{(t+273)} \qquad (9)$$

with t in °C, valid from 100° to 350°C. In the absence of detailed information regarding mineral redox buffers for intrusions cropping out in the vicinity of Cordón Caulle (likely to extend deep into the geothermal system), a semi-quantitative approach based on Fe^{+3}/Fe_{total} ratios in hornblende is used to test the validity of the FH buffer. Hornblende-bearing intrusions of Cordón Caulle have Fe^{+3}/Fe_{total} ratios of 0.20 ± 0.03 (n = 6; Sepúlveda et al., 2004b), which compared with experimental Fe^{+3}/Fe_{total} ratios in hornblende obtained under FM ($Fe^{+3}/Fe_{total} = 0.12$; Spear, 1981) and HM ($Fe^{+3}/Fe_{total} = 0.40$; Clowe et al., 1988) conditions, support indeed near FH redox conditions.

The assumption that H_2 will approach FH-redox conditions and that CO_2 is buffered by calcite-Ca-Al-silicate equilibrium, are incorporated into the H_2/Ar vs. CO_2/Ar gas ratio grid (Giggenbach and Goguel, 1989; Fig. 11). The grid also assumes that Ar is essentially meteoric in origin. Accepting that the initial concentration of Ar in ASW is in equilibrium with atmospheric gases (N_2 = 78.1%; O_2 = 21%; Ar = 0.9 %) and that the recharge of geothermal systems is mostly meteoric in origin, the initial Ar concentration in reservoir waters can be set up at $r_{Ar,L} = 0.30\text{x}10^{-6}$ (Giggenbach and Goguel, 1989), which is the Ar concentration for 10°C ASW. An advantage of the H_2/Ar geothermometer arises from the very low and similar solubilities of H_2 and Ar, predicting almost complete partition of these gases into the few percent of "first-formed" steam and great immunity of H_2/Ar ratios to secondary steam condensing. H_2 and Ar are therefore expected to reach the surface proportions representative of the deep equilibrated liquid (Giggenbach and Goguel, 1989). A potential drawback of the H_2/Ar geothermometer arises from the uncertainty in the actual argon concentrations of hydrothermal waters. For instance, Powell (2000) documented the existence of single phase liquid samples from the Tiwi field, Philippines, with about ten times more argon than in air-saturated groundwater, while also showing atmospheric N_2/Ar ratios

The close equivalence between mole fractions $x_i = n_i/(\Sigma n_i + n_{H2O})$ and mole ratios (i.e. $r_i = n_i/n_{H2O}$), supported by the relatively low gas content in most geothermal systems (usually < 5%), is adopted in the derivation of H_2/Ar ratios equilibrated in a liquid phase:

$$Log\left(\frac{x_{H_2}}{x_{Ar}}\right)_L \cong Log\left(\frac{r_{H_2,L}}{r_{Ar,L}}\right) = R_{H,FH} - LogB_{H_2} - Logr_{Ar,L} \qquad (10)$$

(Giggenbach and Goguel, 1989). where $B_i = r_{i,V}/r_{i,L}$ is the vapor/liquid gas distribution coefficient of the gas i, with B_{H2} given by:

$$LogB_{H_2} = 6.2283 - 0.01403T \qquad (11)$$

with T in °C (Giggenbach, 1980). For gases equilibrated in a vapor phase at the same Ar concentration (i.e. $r_{Ar,V} = r_{Ar,L}$):

$$Log\left(\frac{x_{H_2}}{x_{Ar}}\right)_V \cong Log\left(\frac{r_{H_2,V}}{r_{Ar,V}}\right) = R_{H,FH} - Logr_{Ar,L} \qquad (12)$$

Based on the simplified framework given by $P_{otal} \sim P_{H2O}$ and the Raoult's law corrected for steam compressibility z:

$$P_i = \left(\frac{P_{H_2O}}{z}\right) r_{Ar,V} \qquad (13)$$

(Powell, 2000), CO_2/Ar gas ratios in equilibrated liquid and vapor can be assumed to be of the form:

$$Log\left(\frac{x_{CO_2}}{x_{Ar}}\right)_L \cong Log\left(\frac{r_{CO_2,L}}{r_{Ar,L}}\right) = LogP_{CO_2} - Log\left(\frac{P_{H_2O}}{z}\right) - LogB_{CO_2} - Logr_{Ar,L} \qquad (14)$$

and

$$Log\left(\frac{x_{CO_2}}{x_{Ar}}\right)_V \cong Log\left(\frac{r_{CO_2,V}}{r_{Ar,V}}\right) = LogP_{CO_2} - Log\left(\frac{P_{H_2O}}{z}\right) - Logr_{Ar,L} \qquad (15)$$

respectively, where $R_{H,FH}$ and CO_2 partial pressure are fitted to equation 3 and 6, respectively, and:

$$LogB_{CO_2} = 4.7593 - 0.01092t \qquad (16)$$

(Giggenbach, 1980). From tabulated steam properties (e.g. Zarrouck and Watson, 2001), it follows that:

$$Log\left(\frac{P_{H_2O}}{z}\right) = 6.13 - \frac{2306}{(t+273)} \qquad (17)$$

with t in °C, valid from 100° to 350°C. Reservoir temperatures obtained by use of the CO_2/Ar-H_2/Ar grid range from 270°C to 340°C and, in agreement with the more peripheral character anticipated for Los Venados (Fig. 8), the highest temperatures are yielded by Las Sopas. The fact that fumarolic gases of Cordón Caulle plot above the liquid equilibration line (Fig. 11) gives insight into equilibration under two phase or close-to-vapor-dominated conditions, or Ar loss induced, for instance, by multi-step boiling and re-equilibration of a residual liquid phase from a liquid-dominated system, or less probably, R_H greater (i.e. more reducing) than $R_{H,FH}$.

5.3.2 The CO/CO_2-CH_4/CO_2 grid

Theoretical H_2 pressures imposed by $R_{H,FH}$, in accordance with equation 3, reasonably agree with empirical H_2 partial pressures documented for worldwide dilute reservoir waters (< 500 ppm) below 250°C (Arnórsson, 1985). However, high-temperature, saline solutions (> 300°C or >200°C if Cl > 500 ppm) show highly scattered H_2 pressures that can be reconciled neither with $R_{H,FH}$ constant at -2.8 (Giggenbach, 1987) nor other rock buffers, giving insight into temperature-dependent equilibria other than those related to rock buffers, such as:

$$MC\text{:}\ CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2 \qquad (18)$$

$$CC\text{:}\ CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad (19)$$

According to Giggenbach (1987):

$$LogK_{MC} = Log\frac{f_{CO_2}}{f_{CH_4}} + 4R_H + 2Logf_{H_2O} = 9.67 - \frac{8821}{t+273} \quad (20)$$

$$LogK_{CC} = Log\frac{f_{CO}}{f_{CO_2}} - R_H = 2.49 - \frac{2248}{t+273} \quad (21)$$

where water fugacity is given by:

$$Logf_{H_2O} = 4.9 - \frac{1980}{(t+273)} \quad (22)$$

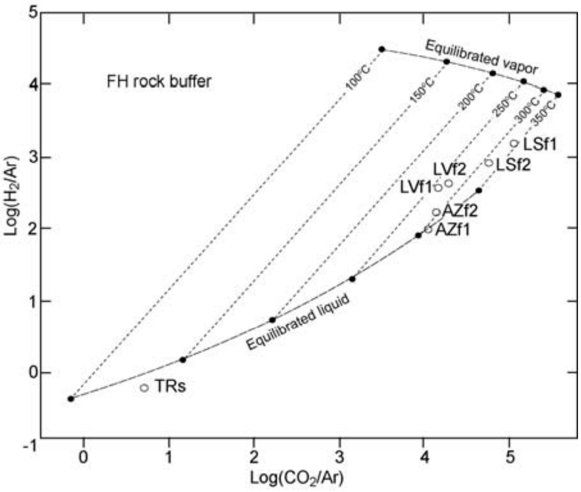

Figure 11: The CO_2/Ar-H_2/Ar grid (after Giggenbach and Goguel, 1989), with externally fixed H_2 (eq. 9) and CO_2 (Arnórsson, 1985).

with *t* in °C (Giggenbach, 1996). By means of the CO/CO_2 vs. CH_4/CO_2 gas ratio grid (Fig. 12), simultaneous assessment of subsurface temperatures and R_H values can be performed. In using the grid, proportionality between gas ratios $r_{A,V}/r_{B,V}$ and fugacity ratios f_A/f_B is assumed (correction for steam compressibility is canceled out). The expression linking gas ratios of equilibrated liquid and vapor is:

$$Log\left(\frac{r_A}{r_B}\right)_V = Log\left(\frac{r_A}{r_B}\right)_L + Log\left(\frac{B_A}{B_B}\right) \quad (23)$$

The equations for B_{CH4} *and* B_{CO} coefficients (Giggenbach, 1980; Bertrami et al., 1985) are:

$$LogB_{CH_4} = 6.0783 - 0.01383t \quad (24)$$

$$LogB_{CO} = 6.3173 - 0.01388t \quad (25)$$

with *T* in °C. Upon the premise of full equilibrium in a two-phase environment, fumarolic gases of Cordón Caulle predict temperatures of 260°C-310°C and redox conditions given by R_H = -3.2, which is slightly more oxidizing than the expected $R_{H,FH}$ rock-buffered redox state (Fig. 12). The CO/CO_2 ratio of Trahuilco gives too high and probably unrealistic temperatures. Following the arguments in favor of a magmatic component present in El Azufral and a rock buffer near $R_{H,FH}$, deep mixing of Las Sopas-Los Venados with volcanic fluids can be invoked to explain the shift in redox conditions from the expected $R_{H,FH}$ (i.e about -2.8) to -3.2.

It follows from the CO/CO_2 vs. CH_4/CO_2 grid that, in order to meet the conditions of two-phase equilibration of fumarolic gases from Las Sopas-Los Venados and single liquid phase equilibration of gases from the hot spring of Trahuilco, variable R_H is required. By selecting R_H of -3.0 to -3.2 for Las Sopas-Venados and R_H of -2.8 for Trahuilco, a more consistent picture of redox conditions and subsurface temperatures is obtained, as shown in the H_2/Ar-CH_4/CO_2 grid (Fig. 13). Fumarolic gases are estimated to have equilibrated above 260°C, possibly in excess of 300°C, in agreement with the previous gas ratio grids. The temperature of Trahuilco, of about 160°C, is in good agreement with cation and silica geothermometry. In adjusting the H_2/Ar-CH_4/CO_2 grid to the expected equilibration conditions, no reference has been made to the kinetics of the reactions involved. This omission should be recalled given the faster kinetics of the H_2/Ar ratios compared with that of the CH_4/CO_2 ratios (Giggenbach, 1987).

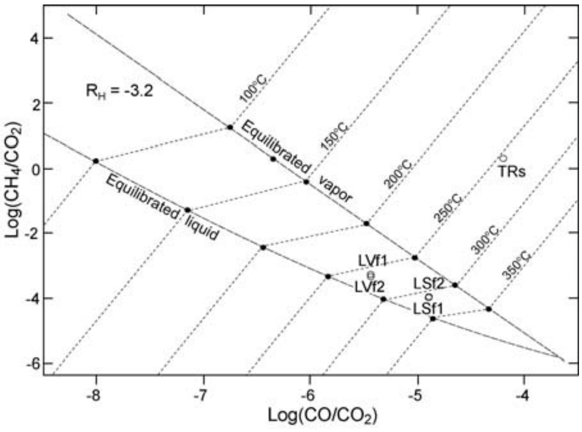

Figure 12: The CO/CO_2-CH_4/CO_2 grid for RH = -3.2.

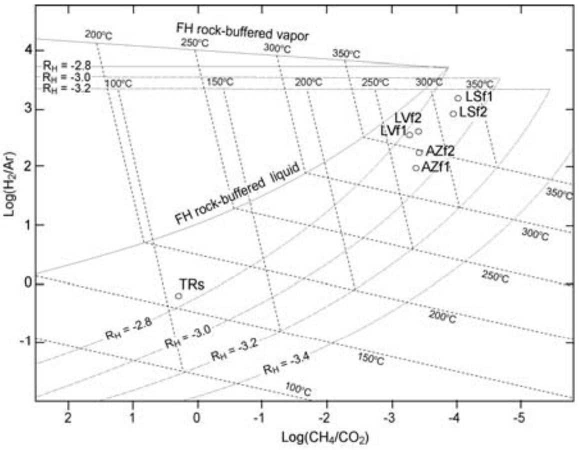

Figure 13. The CH_4/CO_2 vs. H_2/Ar grid (after Giggenbach 1993), presented at several R_H values. Expected equilibration conditions are satisfied for R_H = -3.2 to -3.0 (fumarolic gases) and R_H = -2.8 (hot spring gases).

6. SUMMARY: THE CONCEPTUAL MODEL

Geochemical exploration in the Cordón Caulle geothermal system has lead to a refined conceptual model consisting of a main vapor-dominated system at depth overlain by a secondary-steam heated aquifer. By use of Na/K, silica (quartz) and K^2/Ca geoindicators, the temperature of this steam-heated aquifer is estimated to range from 150° to 180°C. Reservoir temperatures derived from gas geothermometry range from 260° to 340°C. Gas pairs CO-CO_2, CH_4-CO_2 and H_2/Ar appear to have equilibrated under slightly more oxidizing conditions than those imposed by rock-buffered conditions. Based on the high N_2/Ar ratios (~ 400-500) and recent volcanic activity centered in the cinder cone of El Azufral, the shift to more oxidizing conditions is ascribed to incursion of acidic volcanic fluids. Las Sopas-Los Venados are interpreted to represent the geothermal counterparts of the system, with Los Venados being the most peripheral to the main upflow.

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