INTRODUCTION

In 1999 the Department of Geology of the University of Chile initiated a geothermal research program aimed at characterizing and assessing the geothermal resources of Central-South Chile. The Cordón Caulle thermal area (40.5°S) was one of the several promising areas identified on the basis of existing literature (Lahsen, 1978, 1986, 1988; Hauser, 1997; Pérez, 1999) and geological reconnaissance surveys. Geochemical surveys carried out in the Cordón Caulle area focused first on collection of water samples for chemical and stable isotope determination. Despite their large outflow (up to 100 l/s), thermal waters were found to be atypical, with bicarbonate as the major anion, relatively diluted (TDS <600 mg/l), with high Mg^{++} relative to Na^{+} and K^{+}, and with an isotopic signature (^2H, ^18O) close to the local meteoric water composition, unambiguously indicating a steam-heated origin. As a result, a conceptual model consisting of a vapor-dominated system overlie by a shallow steam-heated aquifer was proposed for the Cordón Caulle area. Due to the lack of chloride springs, solute geothermometers had little success in determining subsurface temperatures and geochemical surveys concentrated in gas chemistry leading to new findings discussed herein.

SAMPLING AND ANALYTICAL METHODS

Gas samples were collected in partially-evacuated bottles equipped with a stopcock valve. Reagents NaOH and CdCl₂ were added into the gas bottles in order to retain alkali soluble gases (e.g. CO₂, H₂S and NH₃) and prevent O₂ from reacting with H₂S to form sulfate, respectively. Samples for CO analysis only contained CdCl₂. In case of vigorous fumaroles, a titanium tube was put into the vent with the contact zone being buried with hydrothermal clays to minimize air inflow. Gas analysis were carried out in the Laboratories of THERMOCHEM, USA. CO₂, H₂S and NH₃ were determined by analysis of gas absorbent reagent (infrared acid evolution analysis for CO₂; iodine titration for H₂S and flow injection analysis for NH₃). Non-condensable gases CH₄, N₂, Ar and H₂, were measured by gas chromatography conductivity detection, and moles calculated by relationship of headspace volumes and pressures.

GEOLOGICAL SETTING

The Quaternary volcanic-geothermal activity of the Southern Andes of Chile (33°-46°S) is primarily controlled by the convergence of the Nazca and South-American plates (Fig. 1). Most
polygenetic volcanoes situated in the segment between 39° and 46°S, align parallel to the 1000 km long, NNE-trending Liquiñe-Ofqui Fault Zone (LOFZ), an intra-arc strike-slip fault system predating the Cretaceous (Cembrano et al., 1996, 2000; Fig. 1). Other volcanic centers, preferentially monogenetic in style, occur parallel to second-order anisotropies oblique to the arc axis, mainly NE and NW-oriented. Geothermal activity is absent along the NE-trending domains, largely represented by the alignment of post-glacial basaltic scoria cones and maars (37°-42°S). NE-trending domains are parallel to the maximum shortening direction imposed by the Quaternary dextral-transpressional stress state (Cembrano and Moreno, 1994; López-Escobar et al., 1995; Lavenu and Cembrano, 1999). Of greater interest are NW-trending domains, where felsic volcanism and geothermal activity are of common occurrence. This is the case of the Cordón Caulle geothermal area (40.5°S), a 15 km long, 5 km wide, volcanic graben bordered by NW-trending faults, where lavas, tephra and ignimbrites have accumulated since the Late Pleistocene (Moreno, 1977; Fig. 2). The Cordón Caulle area is bounded to the south-east by the Puyehue stratovolcano (2236 m) and to the north-west by the Cordillera Nevada Caldera, both being edified over a basement of Miocene intrusions and minor Paleozoic granites (Munizaga et al., 1988), Tertiary sediments and ignimbrites. The southwestern border of the graben – the so-called Cordón Caulle Fissure (Moreno, 1977) – is a major feeder of post-glacial and historic lavadomes and fissure lavas of dacite to rhyolite composition (latest events: 1921-1922 and 1960). Fumaroles and acid-sulfate waters occur at the top of the system in association with the northeastern border of the graben (~1500 m). Las Sopas and Los Venados correspond to the main fumarolic zones where intense acid-sulfate alteration consisting of elemental sulfur, kaolinite, pyrite and quartz develops. The crater El Azufral, dating from the latest eruption of the Cordón Caulle Fissure in 1960, also hosts fumaroles around which elemental sulfur deposits and acid-sulfate alteration occurs. Further north-west are vigorous boiling hot springs of alkaline bicarbonate type discharged from the rims of the Cordillera Nevada Caldera (~1000 m), with an outflow ranging from 70 to 100 l/s. Active deposition of silica sinter and geyserites – a particular variety of silica sinter consisting of amorphous silica in round shapes – takes place at the outflow zone.

Figure 1 (left-hand side). The location of the Cordón Caulle area with respect to the continental margin and tectonic plates, the Quaternary volcanic arc of Southern Chile (33-46°S) and the Liquiñe-Ofqui Fault Zone (LOFZ).

Figure 2 (below). Simplified geological map of the Cordón Caulle geothermal area.
Fumarolic gas samples were collected from Las Sopas, Los Venados, and El Azufral zones (Fig. 7). On a dry basis, the main constituents are alkali gases CO$_2$ and H$_2$S. Relative amounts of CO$_2$ and H$_2$S remain similar in Las Sopas-Los Venados, in the range of 4.7 to 6.9 mole % H$_2$S and 90 to 94 mole % CO$_2$. El Azufral shows lower CO$_2$ (~82-83 mole %) and higher H$_2$S (~13 mole %) relative to Las Sopas-Los Venados, a first hint on two separate sources for these gases. Graphically, the relative abundances of CO$_2$ and H$_2$S appear in the CH$_4$-CO$_2$-H$_2$S ternary diagram (Fig. 3). A second indication that Las Sopas-Los Venados and El Azufral have different origins is given by the N$_2$-CO$_2$-Ar ternary diagram (Fig. 4), used to determine to which degree gas samples are a mixture of magmatic and atmospheric components. Air, air-saturated groundwater (ASW) and magmatic gases have N$_2$/Ar ratios of about 80, 40, and 800 or greater, respectively (Giggenbach and Goguel, 1989). Las Sopas and Los Venados show N$_2$/Ar ratios close to the ASW composition, indicating that these samples arise from ASW which has been deeply convected into the system, whereas El Azufral shows N$_2$/Ar ratios in the range of ~340-550 indicating a greater contribution of magmatic gases (Fig. 4).
The oxidation-reduction (redox) conditions prevailing at the Cordón Caulle geothermal system are described by the so-called \( R_H \) factor = \( \log(f_{H2}/f_{H2O}) \sim \log(x_{H2}/x_{H2O}) \), where \( x_i \) is the analytical mole fraction of the gas \( i \) (Giggenbach, 1987; 1991; 1997; Giggenbach and Goguel, 1989). \( R_H \) is preferable to \( f_{O2} \) since \( O_2 \) contents drop by far below detection limits in lower temperature (<350°C) hydrothermal systems (Giggenbach, 1987). \( R_H \) assumes equilibrium of the vapor phase at depth according to \( 2H_2O (g) = 2H_2(g) + O_2(g) \). Due to shallow steam-condensing or evaporation processes, assessment of \( R_H \) is made by plotting \( CH_4/CO_2 \) and \( CO/CO_2 \) ratios (Giggenbach and Goguel, 1989), rather than by directly using \( x_{H2}/x_{H2O} \) ratios reported during analysis. In the \( CH_4/CO_2-CO/CO_2 \) grid (Fig. 5), which is also a gas geothermometer, equilibrated liquid and vapor lines represent the state of equilibrium of a sample for a number of redox states. In a mature rock-buffered system, the usual and expected redox state is represented by \( R_H = -2.8 \). This value corresponds to the attainment of equilibrium of the aqueous phase at depth with the \( Fe^{2+}/Fe^{3+} \) content of the rock phase, with fayalite and hematite as thermodynamic proxies (Giggenbach, 1987). For \( R_H = -2.8 \), Las Sopas-Los Venados gases plot in the liquid region leading to some disagreement with the premise of a vapor-dominated system. For \( R_H = -3.2 \), Las Sopas-Los Venados samples plot in the two-phase
region representing gases equilibrated under a mixture of liquid and vapor equilibrated gases (Fig. 5), which best approaches the condition of a vapor-dominated system. The recent incursion of high-temperature, highly oxidizing volcanic fluids, which are largely governed by the SO$_2$-H$_2$S redox buffer (Giggenbach, 1987; Gignebach and Goguel, 1989; Giggenbach, 1997), would result in the shift of $R_H$ from -2.8 to -3.2. The presence of young volcanic fluids is in agreement with the vast record of historic eruptions at Cordón Caulle. For $R_H = -3.2$, reservoir temperatures are estimated to be over 250°C, and any value of $R_H$ higher than -3.2 (e.g. $R_H = -2.8$) will produce even greater temperatures (Fig. 5).

The $H_2$-Ar vs. $CO_2$-Ar geothermometers assume that the $H_2/H_2O$ and $CO_2/H_2O$ mol-ratios in the deep equilibrium liquid phase are related to the Ar/H$_2$O mol-ratio as a function of temperature. The reservoir waters of Cordón Caulle are largely meteoric in origin since the N$_2$/Ar ratios of Las Sopas-Los Venados are dominated by the ASW component (Fig. 4). Because Ar is essentially atmospheric, the Ar/H$_2$O mol-ratio in reservoir waters is taken to be that of air-saturated groundwater (ASW = 0.3x10$^{-6}$; Giggenbach and Goguel, 1989). The $H_2$-Ar method is relatively immune to shallow steam condensing or evaporation due to the very similar and low solubilities of $H_2$ and Ar. Therefore, $H_2$/Ar ratios in the sample tend to be representative of the deep environment, although in practice the quick adjustment of $H_2$ to changes in temperature and redox conditions leads to recording can cooler temperatures closer to surface discharge. The $CO_2$-Ar method, conversely, is more vulnerable to steam condensing or evaporation and “slower” than the $H_2$-Ar system. The $CO_2$-Ar and $H_2$-Ar grid (Fig. 6), which combines the two geothermometers, is presented at $R_H = -3.2$ (in accordance with Fig. 5) suggesting equilibration of the samples under a two-phase environment. Estimates of reservoir temperatures are in the range of 175-230°C. The lowest temperatures correspond to the lowest $CO_2$/Ar and $H_2$-Ar ratios,
found in Los Venados where coincidentally CH$_4$ is higher relative to Las Sopas (Fig. 3). Marginal vapor-gas mixtures are likely to undergo some steam and alkali gas condensing, causing the amount of insoluble gases (e.g. CH$_4$, Ar) to increase relative to more soluble gases (e.g. CO$_2$ and H$_2$S). Therefore we suggest that the source of gases of Los Venados is more marginal and cooler than that of Las Sopas. Temperatures of Las Sopas on the order of 230°C are taken to be the most representative of reservoir conditions, whereas the temperatures of El Azufra1 are neglected because of the less probable attainment of equilibrium under volcanic-hydrothermal conditions.

Figure 6. The H$_4$/Ar vs. CO$_2$-Ar grid showing reservoir temperatures about 230°C (see Las Sopas) for R$_{ii} = -3.2$. 
Figure 7. Schematic profile of the Cordón Caulle geothermal system showing two distinctive hydrothermal environments at depth.

- Outflow (70-100 l/s)
- Los Venados
- Las Sopas
- 1980-1981 dacite eruption
- 1960 dacite eruption
- Cordon Caulle fissure
- El Azufra
- Nevada Cordillera Caldera
- Regional water table

Legend:
- Chloride waters?
- Heat source
- Steam-heated aquifer
- 100°C
- 150°C
- 200°C
- 250°C
- Vapor-dominated reservoir
- Acté-sulfate alteration
- Hot springs
- Fumaroles
DISCUSSION AND CONCLUDING REMARKS

Two hydrothermal environments are proposed to prevail at subsurface in the Cordón Caulle geothermal area: a volcanic environment expressed at surface by recent fissure eruptions and concomitant gas discharges (El Azufral), and a geothermal environment expressed at surface by gas discharges at Las Sopas and Los Venados and hot springs at the Cordillera Nevada Caldera. These end members (i.e. El Azufral vs. Las Sopas-Los Venados) do not differ much at surface displaying intense acid-sulfate alteration consisting of clays, elemental sulfur, pyrite, and quartz. However, subsurface conditions differ in that volcanic fluids are buffered by the \( \text{SO}_2 - \text{H}_2\text{S} \) pair leading to a redox state much lower (or oxidizing) than that of mature rock-buffered geothermal systems (\( R_{\text{H}} = –2.8 \)). This is inferred from the \( R_{\text{H}} = –3.2 \) calculated for Las Sopas-Los Venados, farther from the source of volcanic fluids but still denoting slightly oxidizing conditions. The acid-oxidizing environment of El Azufral would prevail at all the vertical range, resulting in a high-sulphidation epithermal system dominated by pyrophillite, diaspore and quartz. Conversely, in Las Sopas-Los Venados, acid-oxidizing conditions would be limited to the region above the regional water table (Fig. 7). The expected subsurface conditions are those of a low sulphidation epithermal environment with hydrothermal fluids over 230°C, more reducing than in El Azufral (\( R_{\text{H}} = –3.2 \)) and closer to neutrality. Water-rock interaction is probably dominated by adularia, sericite, calcite and quartz at depth (two-phase boiling region) and by silica sinter at surface where the water table is superficial (e.g. Cordillera Nevada area).

ACKNOWLEDGMENTS

This study is funded by the FONDEF Chile Grant No. 1051: “Characterization and Assessment of Geothermal Resources of Central and Southern Chile: Possibilities of Generation of Electric Energy and Direct Applications”. The authors would like to thank CONICYT (National Council of Science and Technology Research, CHILE), Luis Urzúa, David Sussman, Juan Rojas (ENAP), Carlos Palacios, Pablo Letelier and Jaime Martínez (University of Chile), Tom Powell (THERMOCHEM, USA), Javier Labra and Nicolás Pacheco (CONAF National Park Puyehue).

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