doi: 10.22564/brjg.v5i2.2255

Revista Brasileira de Geofísica, 1987, Vol. 5, 275-282

ISOTOPIC AND GEOCHEMICAL STUDY OF THE VAPOR DOMINATED GEOTHERMAL SYSTEM OF COPAHUE, NEUQUEN, ARGENTINE REPUBLIC

HÉCTOR OSVALDO PANARELLO, MANUEL LEVÍN,
MIGUEL CLEMENTE ALBERO

Instituto de Geocronología y Geologia Isotópica (INGEIS)
Pabellón INGEIS — Cuidad Universitaria, 1428 Buenos Aires, Argentina

JOSÉ LUIS SIERRA, MARIO OMAR GINGINS.

Ente Provincial de Energia del Neuquén
Rioja 385, 8300 Neuquén, Argentina.

The first isotopic and geochemical data on samples of fresh waters, hot waters and vapor condensates from the geothermal system Copahue-Caviahue are presented.
^{3}H, ^{2}H and ^{18}O analyses, suggest that the recharge of meteoric water in the deep seated reservoir occur at around 2000 m a.s.l. In addition a shallower hot water reservoir show a recent recharge at the same altitude.
$\delta^{13}C$ of the CO_2 coming with vapor in one of the fumaroles ("Las Maquinitas") —6,8‰ vs PDB and the high gas-vapor ratio account for its magmatic origin and for the existence of a magmatic fed hydrotermally altered pipe.
$\delta^{18}O$ and $\delta^{2}H$ data on vapor of the "Copahue-1", first drilled geothermal well, sampled recently and two years ago, show an evolution in the isotopic content as well as in the gas vapor ratio. This fact along with the geochemical and geophysical evidences allow the establishment of a preliminary model for the geothermal reservoir.

Os primeiros dados geoquímicos e isotópicos obtidos em amostras de águas termais e não-termais, e em vapores condensados provenientes do sistema Copahue-Caviahue são apresentados.
Análises ^{3}H, ^{2}H e ^{18}O mostram que a recarga de águas meteóricas do reservatório profundo ocorreram a aproximadamente 2000 m acima do nível do mar. Além disso, um reservatório mais superficial de águas termais mostra uma recarga recente à mesma altitude.
δ^{3} do CO_2 carregado pelo vapor de uma das fumarolas ("Las Maquinitas") -6,8‰ x PDB e a alta razão gás-vapor indicam a sua origem magmática e a existência de um conduto de alimentação magmática hidrotermicamente alterado.
Dados de δ^{18} e $\delta^{2}H$ no vapor do primeiro poço geotérmico perfurado, "Copahue-1", amostrado recentemente e há dois anos atrás, mostram uma evolução na composição isotópica assim como na razão gás-vapor. Este fato, e evidências geofísicas e geoquímicas, permitem o estabelecimento de um modelo preliminar para o reservatório geotérmico.

(Traduzido pela Revista)

INTRODUCTION

The Copahue geothermal system is one of the few vapor dominated fields still remaining unexploited. It has been widely studied from the geological, geophysical and chemical points of view. From the earliest work of Groeber & Corti (1920), geologic, geophysical, and geochemical studies have been carried out (Groeber & Perazzo, 1941; Corti & Manuele, 1942; Dalo, 1960; Jurío, 1977; and as well as other internal reports). As a result of these studies, a good general knowledge of the geothermal system has been acquired. Nevertheless, several questions still remain unanswered.

Since about 30 years ago the isotopic techniques have shown their usefulness in solving a great number of problems in geothermal exploration and exploitation (Craig, 1952; White et al., 1963; Araña & Panichi, 1974; Panichi et. al., 1974; Panichi & Gonfiantini, 1977; Panichi et al., 1977; Sakai, 1977; and others), however they have been hardly used in the study of Argentine geothermal resources.

The aims of this work are, by using isotope techniques as well as by new geochemical determinations, the clarification of some of the following questions concerning the Copahue geothermal field:

1. The origin of the geothermal water and vapor. The possible relationship with the present meteoric cycle and eventually the location of the recharge area.
2. The temperature of the deep geothermal reservoir.
3. The origin of geothermal gases and the causes of warm water mineralization.

To carry out this study two field trips were made. Fluids from principal natural manifestations and the only well drilled up to now were sampled and chemical and isotopic analyses carried out.

The data obtained show reasonable agreement with the preliminary model of the geothermal system based on results of earlier studies as well as geological and geophysical evidences.

GEOLOGICAL AND CLIMATIC APPROACH

Working area

The Copahue geothermal field is located in the NW of the Neuquén province, near the chilean border at about 37° 50'S and 71° 05'W, 300 km from Neuquén city. Altitude of the system ranges from 1600 to 2300 m a.s.l. The present topographic conditions show a juvenile evolution of the area with moderately craggy shapes.

Copahue Volcano, 2930 m a.s.l. is located west of the studied area. North and east a sharp scarp of about 400 m limits the area from the sorrounding plateau.

The scarp is cut by permanent water streams, Agrio River, Trolope creek and others, which drain the Copahue Caviahue depression (Figure 1).

Geology

The volcano-tectonic depression of Copahue consists of a thick sequence of Tertiary magmatic rocks.

The existance of a strong thermal anomaly in this area is believed to be due to the presence of a magma chamber formed as a result of recent volcanic activity.

With exclusion of the rather small andesitic lava flows, the remaining area of geothermal interest is covered by the volcanic Palao Co Formation of Pliocene age. The exposed thickness of the sequence is greater than 2000 m overlying Tertiary sedimentary rocks (lower Miocene), outcropping 20 km north of Copahue (Pilún Challá valley). Those sedimentary layers were found between 1800 and 2000 m depth by geolectrical prospecting.

The Palao Co Formation is represented by a volcanic platform of basalt-andesite-rhyolite composition, consisting of lavas as major constituents, and pyroclastic deposits.

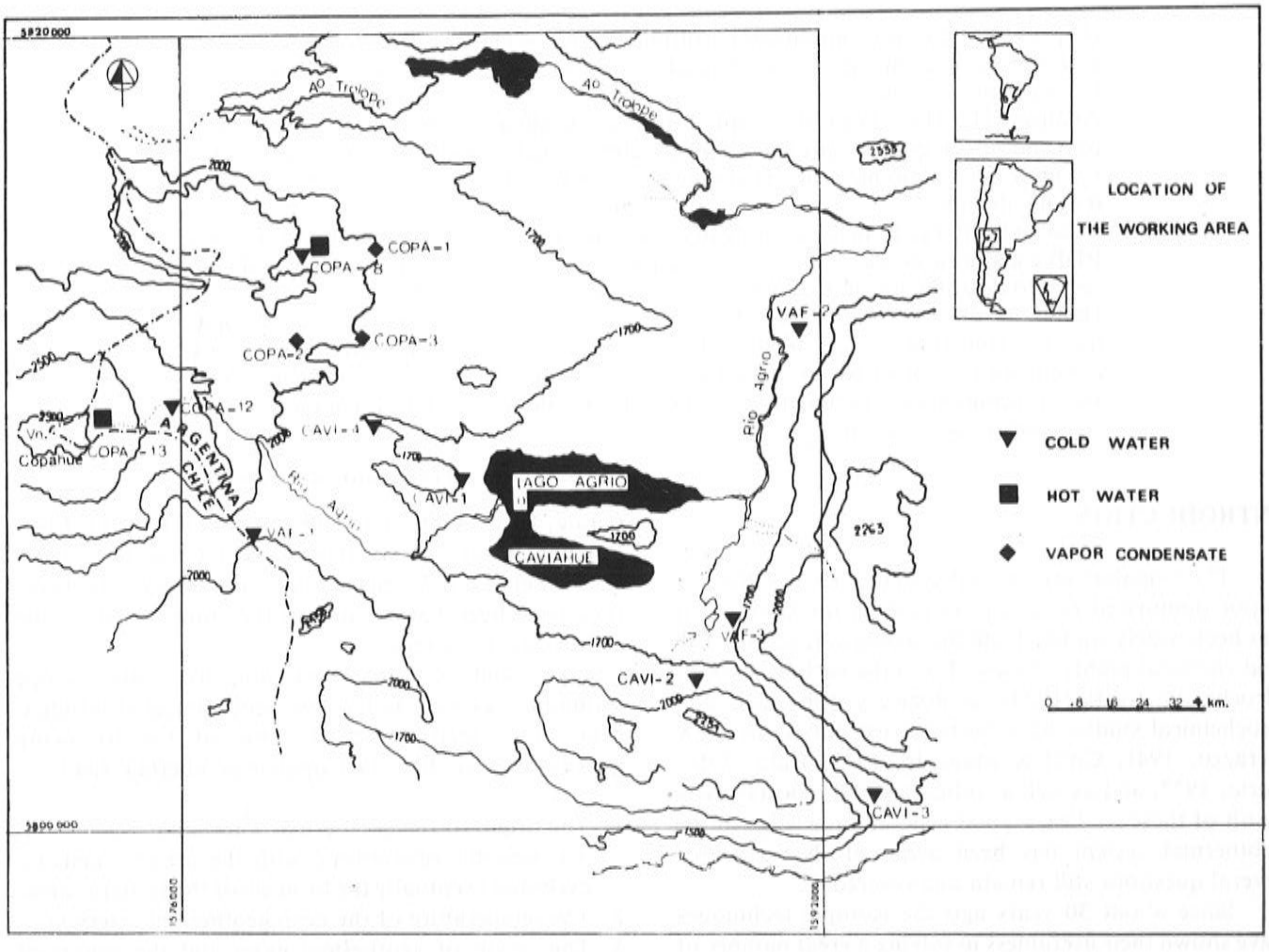

Figure 1 — Working area and sampling points

Copahue-1 well cuts through a trough of 900m of alternating layers of lavas and pyroclastics under the andesitic upper layer.

From a structural point of view, the area is part of a huge volcano-tectonic depression, forming a horst-graben system. Such depression progressively dips to the east. The depression is formed by several structural blocks, the highest one being the Termas de Copahue. This structural system is considered to be of prime importance in trapping geothermal fluids.

The Termas of Copahue horst is strongly fractured and faulted and favors circulation of the geothermal fluids.

The lateral extension of this block is nearly 15 km². The faults, running WSW-ENE, and reactivated during the post glacial periods, are considered to be probable paths for the upward movement of trapped fluids.

Hydrogeology

The surface runoff is directly related to structural characteristic.

There are two important water stream systems, one governed by regional fractures in the WNW-ESE direction and other by recent fractures.

Groundwater circulation is irregular, due mainly to the vertical and lateral variations in the permeability of the formations. For instance in the Palao Co formation, lava, toba, breccia and kynerites are found, being the lava products generally more permeable than pyroclastic due to their intense fracturing. Thus, it is almost impossible to delineate continuous layers acting as aquifer and aquicludes. Therefore deep circulation believed to be mainly due to secondary permeability mantained through active tectonics.

The more recent tectonic lineaments have SWS-ENE direction and the higher density of faults is inside the horst Termas de Copahue.

Climate

The lack of precise climatic data makes it difficult to establish an hydrogeological balance in the area. However precipitation of more than 2000 mm as snow and rain, with low evapotranspiration due to low temperature and poor vegetal development, would ensure infiltration and adequate recharge for the geothermal system.

THECNIQUES AND EXPRESSION OF THE RESULTS

To carry out this study, the following isotope and chemical analysis were performed:

- ^{3}H, ^{2}H and ^{18}O of vapor condensates, hot water and cold water.
- ^{13}C and ^{18}O on CO_2 of geothermal gases
- Gas chromatography of geothermal gases
- Major and trace elements dissolved in hot and cold waters.

Hydrogen for deuterium isotope analysis, was extracted according to Coleman et al. (1982) by reducing water with hot zinc at (485 ± 2)°C. Oxygen-18 concentration in waters was determined by the method of Epstein & Mayeda (1953) and Roether (1970) which consist of water equilibration with CO_2 at (25.0 ± 0.1)°C. Extracted gases and CO_2 coming from geothermal exhalations were measured against a proper reference in a Micromass 602-D mass spectrometer after criogenic purifications, as described in Panarello et al. (1980). Results are expressed as δ ‰. The ^{18}O standard for waters and CO_2 is V-SMOW (Gonfiantini, 1978) and for ^{13}C is PDB (Craig, 1957).

Tritium samples were measured by liquid scintillation counting on previously enriched waters with an enrichment factor of about 10. Results are expressed in tritium units (T.U.)

Non condensible gases were collected in one liter bottle partially filled with 3N NaOH under vacuum. CO_2, SO_2 and H_2S were determined by tritation of the solution while CH_4, Ar, N_2, and O_2, by gas-chromatography. Chemical concentrations are expressed in the usual from: $mg.L^{-1}$.

When possible, *in situ* pH, temperature and conductivity were measured.

RESULTS AND DISCUSSION

Waters

1. Cold water samples (CAVI-1, 2, 3, 4; VAF 1, 2, 3 and COPA 8, 12) (Table 1).

As presented in Fig. 1, δ^2H vs $\delta^{18}O$ plot, the values fit the meteoric water line $\delta^2H = 8\,\delta^{18}O + 10$ ‰ defined by Craig (1963). There is no correlation between the isotopic composition and the altitude, mainly due to:

a — Air masses producing precipitation at Copahue are of Pacific origin and discharge most of their moisture as rain or snow in the Chilean territory and over the cordillera. The remaining vapor mixes with the vapor of top mountain isotopic composition and become more depleted as the altitude decreases. This process is believed to be responsible for a positive slope in the $\delta^{18}O$ vs altitude plot for the precipitation on the Argentine side.

b — Frequently the collection altitude does not represent the actual catchment area altitude.

However, δ^2H and $\delta^{18}O$ values show good correlation with the measured temperature of the sampled waters:

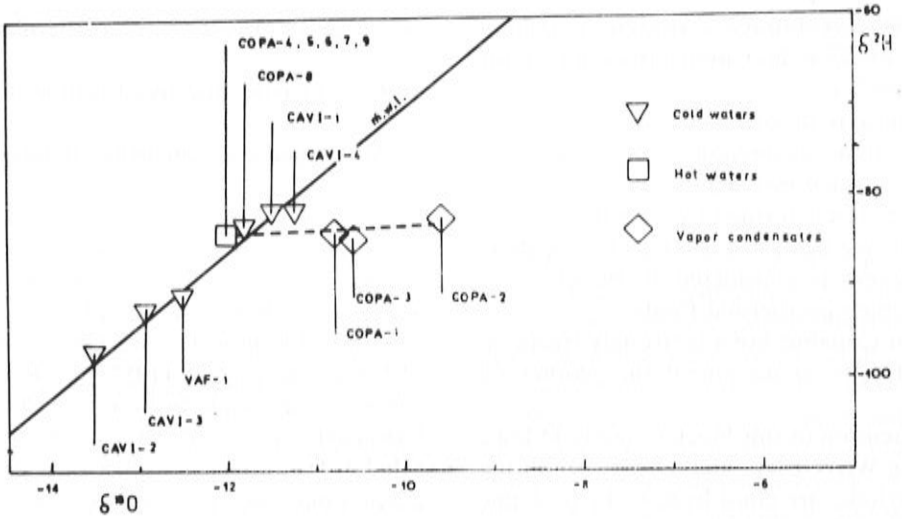

Figure 2 — Isotopic composition of sampled waters

$\delta^{18}O = 0.32\,T - 15.7$ ‰ $r = 0.85$
$\delta^2H = 2.42\,T - 112.0$ ‰ $r = 0.86$

where T is expressed in: degrees Celsius and 'r' is the correlation coefficient.

Tritium levels range from 1.8 T.U. to 4.5 T.U. suggest some residence time of which water as snow before melting.

Precipitation waters collected at Caviahue, covering the 1983-1984 years show rather erratic δ^2H and $\delta^{18}O$ values. ^3H concentration varies between 3.8 and 6.8 T.U.

From the chemical point of view these waters are sodium bicarbonated, with low mineralization, showing sulfate and chloride concentrations under 1 mg L^{-1} with exception of CAVI-4 that presents higher sulfate content. Sulfate is probably due to loss of H_2S trough fractures and further oxidation. Indeed, "los Baños" creek, where this sample was collected flows across the "Mellizas" fault.

2 — Warm waters (COPA 4, 5, 6, 7, and 9).

Warm water samples are isotopically homogeneus, with $\delta^{18}O = (-12.0 \pm 0.2)$ ‰ and $\delta^2H = (-84.0 \pm 0.5)$ ‰, fitting the meteoric water line, without significant evaporation. Their tritium contents ranges from 1.7 to 3.6 T.U. which are similar to those of cold waters.

Chemically, they are also an homogeneous group, with low chloride contents. This fact together with tritium values evidence a short residence time.

These waters are calcium-magnesium sulfate, slightly acid (pH = 5.7 — 5.9), with high CO_2 fugacities (20 to 100 kPa). It is possible then that thermalism is not only due to the contact with hot rock, but also to heat transport from the hot gases making impossible the application of geothermometers because mineral fuid equilibrium is not reached. However, "Agua de Vichy", with the Lowest magnesium content is perhaps the sample of highest temperature.

Despite other complex mechanisms, the main hemireactions involved in mineralization are:

$CO_2\ (g) + H_2O \rightleftharpoons HCO_3^- + H^+$

$H_3BO_3\ (v) \rightleftharpoons H_2BO_3^- + H^+$

$S^{2-} + 4H_2O \rightleftharpoons SO_4^{2-} + 8H^+ + 8e^-$

3. Vapor condensates (COPA — 1, 2 and 3)

All the vapor condensate samples are enriched in oxygen-18. In the δ^2H-$\delta^{18}O$ diagram (Fig. 2) these samples define a straigh line intercepting the meteoric water line over values $\delta^{18}O = -12$ ‰ and $\delta^2H = -84$‰, similar in isotopic composition to COPA-8 and to the group 2 composed of the warm water samples. All the three values look like waters of meteoric origin, slightly enriched. There is no evidence of juvenile waters with $\delta^{18}O = +7$ to 9.5 ‰ (Taylor, 1967, Craig, 1963). Thus the possibility of its occurrence is limited to less than 11%.

The extrapoled value on the meteoric water line and the highly fractured characteristics of the horst Termas de Copahue determine this zone, and particulary the Anfiteatro place at around 2000 m a.s.l., as the more likely recharge area for both, the shallower type 2 waters and the deeper, vapor system. Water Longer residence time of water in the deep reservoir, is evidenced by its null or low tritium content.

Non condensible gas samples.

Besides water and vapor, non condensible geothermal gases were also sampled.

These gas samples were analysed in order to determine the volumetric percent of SO_2, H_2S, CO_2,

Table 1 – Isotopic and Chemical analyses of water samples

Sample N°	Location	Coll. T °C	Tipe	Alt. m a.s.l.	$\delta^{18}O$ ‰	δ^2H ‰	^3H T.U.	pH	HCO_3^- mg/L	Cl^- mg/L	SO_4^{2-} mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	Fe mg/L	SiO_2 mg/L	Na^+ mg/L	K^+ mg/L	Li^+ mg/L
COPA-1 A	Las Maquinitas	130	vapor		–10,8	–84,2	0,8 ± 0,7											
COPA-2 A	Well Copahue-1	140	vapor	2000	– 9,6	–82,7	0,6 ± 0,7											
COPA-4	Ferruginosa	51	liquid	2020	–11,9	–84,7	1,7 ± 0,7	5,9	489	3	19	59	29	0,1				
COPA-5	Sulfurosa	61	liquid	2020	–11,9	–84,2	2,5 ± 0,7	6,6	474	2	13	51	30	0,10	90	53	23	0,06
COPA-6	del Mate	51,5	liquid	2020	–11,9	–84,3	–	5,9	282	< 1	23	39	13	0,18	100	38	19	<0,05
COPA-7	de Vichy	34	liquid	2010	–12,0	–84,3	3,3 ± 0,7	5,9	287	2	12	61	9,5	0,1	80	19	6,2	<0,05
COPA-8	Los Baños creek	–	liquid	2040	–11,8	–83,3	2,4 ± 0,7	6,9	286	2	12	52	20	0,28	71	24	7,8	<0,05
COPA-9	Pesqueira	26	liquid	–	–12,2	–83,3	–	6,3	276	3	–	53	20	0,28	80			
COPA-12	Spring on the volcano	–		2010	–11,9	–84,6	3,6 ± 0,7											
COPA-13	Volcano lake	30	liquid		– 3,7	–	0,9 ± 0,7											
COPA-20	Copahue pool		vapor		–12,8	–90,2	–											
CAVI-1	Caviahue tap water	13	liquid		–11,5	–81,7	3,9 ± 0,4											
CAVI-2	Spring	7	liquid		–13,5	–97,2	1,8 ± 0,4	6,2										
CAVI-3	Spring	10	liquid	1424	–12,9	–92,5	4,5 ± 0,4	6,6										
CAVI-4	Water fall	12	liquid	1620	–11,3	–81,9	3,6 ± 0,5	6,8	21	< 1	13	2,9	2,4	–	12	2,9	0,8	<0,05
VAP-1	Spring	8	liquid		–12,5	–90,1	4,8 ± 0,7											
VAP-2	Spring	10	liquid	1670	–12,9	–93,5	3,2 ± 0,7	7,4	42	< 1	5	3,3	1,2	0,25	20	5,3	1,7	<0,05
VAP-3	Spring	11	liquid	1674	–13,6	–94,5	1,8 ± 0,7	7,1	30	< 1	5	1,8	0,9	0,1	20	3,6	1,7	<0,05

N_2, Ar, H_2 and CH_4 by gas chromatography. Final results, corrected for the presence of air fixed during sampling, are listed in Table 3.

On each sample the temperature has been determined by application of the empiric gas geothermometer of D'Amore & Panichi (1980). These temperatures are also listed in the last column of Table 3.

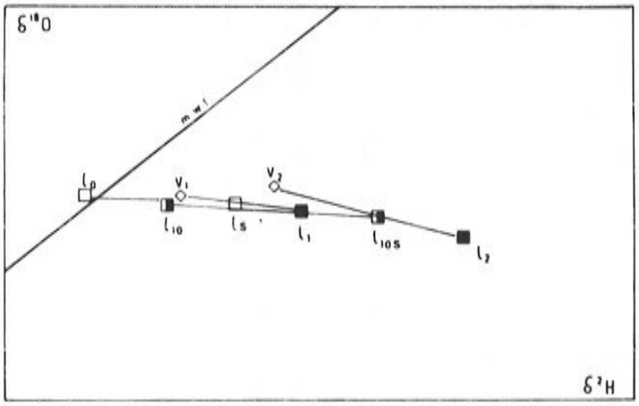

Figure 3 — Hypothetic isotopic evolution in the Copahue-1 well

Qualitative reservoir model

The geothermal well, COPA-2 has been sampled twice, in 1982 (Jurío, personnal communication) and 1985. The values obtained for δ^2H and $\delta^{18}O$ are:

Sampling date	$\delta^{18}O$ (‰)	δ^2H (‰)	gas-vapor ratio (10^2)
1982-02	- 10.5	- 84.0	3.38
1985-02	- 9.6	- 82.7	2.25

During this interval the well remained open to the atmosphere and its well head pressure dropped exponentially.

The 1982 value is similar to those of the present natural manifestations, while the 1985 results show a shift towards enriched $\delta^{18}O$ values. This fact together with the lowering of the pressure and the gas vapor ratio enable the formulation of a possible qualitative reservoir model for the sequential evolution of the water and vapor system, as follows: (Fig. 3)

a- Fresh water input in the recharge area ℓ_0
b- Heating by contact with hot rock and oxygen shift to ℓs
c- Partial vaporization of ℓs to yield a vapor composition v_1 and the hypothetic remaining liquid ℓ_1 at 240°C.
d- Mixing of the remaining water ℓ_1 with fresh water from the recharge producing a mixture of isotopic composition ℓ_{10}
e- Further heating and shift from ℓ_{10} to ℓ_{10s}
f- Partial vaporization of ℓ_{10s} to yield the more enriched vapor v_2 and the hypothetic liquid ℓ_2, g- etc.

Table 2 – $\delta^{13}C$ and $\delta^{18}O$ values for CO_2 of non condensable fraction.

Sample	Location	Gas	$\delta^{13}C$	$\delta^{18}O$
COPA-1D	Las Maquinitas	CO_2	– 6,8	25,2
COPA-2D	Pozo Copahue 1	CO_2	–10,9	26,6
COPA-3D	Las Máquinas	CO_2	–10,7	28,8

This model would render more enriched ^{18}O values for the vapor with the lowering of an assumed water table due to the decrease of recharge by hydrothermal deposits and free outlet of steam (White et al., 1971).

A special case within the sampled manifestations is "Las Maquinitas", since non condensible gases seem to be magmatics. Its CO_2 exhibit a $\delta^{13}C$ = — 6,8‰ (TABLE 2), close to the average value for primary carbonatites (Craig, 1963; Allard et al., 1977). In addition this group of fumaroles present a high gas-vapor ratio (about 3). These facts as well as geophysical evidences enable the assumption of the existence of a magmatic fed hydrothermal altered pipe.

From the above evidences as well as those from deep geoelectric prospection, we propose the preliminary scheme, shown in Fig. 4, as indicative of the fluid circulation pattern at depth within the study area.

Table 3 – Air corrected chemical composition in volume porcent of dry gas and Reservoir temperature in °C.

Sample	Location	SO_2	H_2S	CO_2	N_2	Ar	H_2	CH_4	T
COPA-11	Copahue	0,10	0,43	72,83	18,14	0,18	4,46	3,85	249
COPA-22	Las Máquinas	0,34	0,38	76,00	19,78	1,02	1,29	1,18	222
COPA-21	Las Maquinitas	0,18	0,54	62,90	18,65	0,06	9,55	8,11	273
COPA-23	Pozo Copahue-1	0,13	0,18	68,76	18,91	0,19	5,98	5,88	243

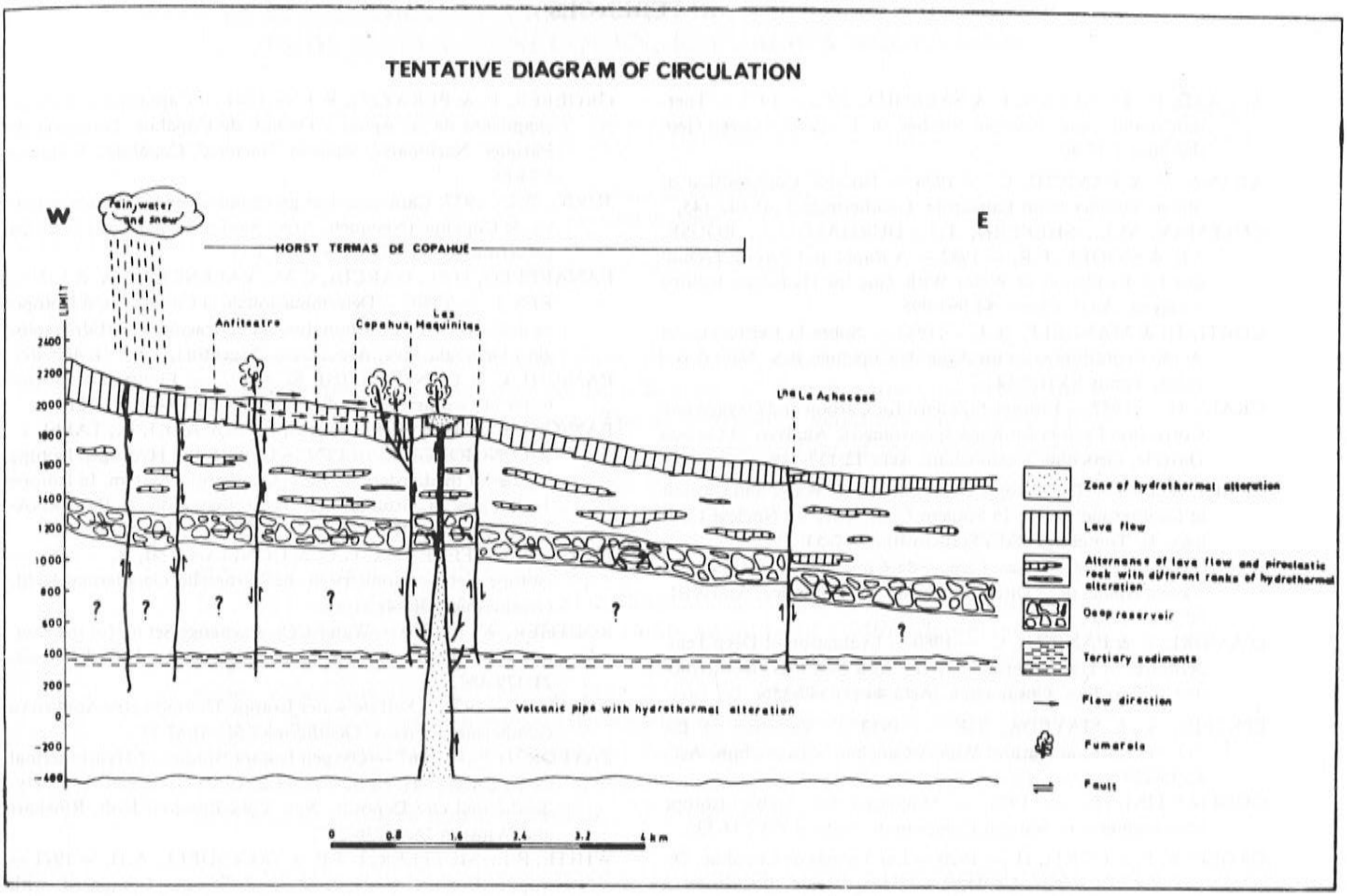

Figure 4 — Tentative circulation scheme

CONCLUSIONS

Based on the results of isotopic and geochemical study, and in conjunction with the available geological and geophysical information, the following preliminary conclusions may be reached:

1- The recharge of both, deep and shallow geothermal reservoirs is meteoric water. The contribution of juvenile water to the deep reservoir, if any, is no more than 11%.
2- The recharge area is located on "Anfiteatro" site and surrondings at about 2000 m a.s.l. in the highgly fractured horst Termas de Copahue.
3- The decrease of the gas fraction and the evolution of the isotopic contents suggest that steam is at least partially produced by boiling from a declining water table.
4- Low mineralization and relatively high tritium content of warm waters account for a short transit time for the circulation in the system. Presence of sulfate in these waters is a consequence of the dissolution and oxidation of hydrogen sulphide rising through the faults.
5- The existence of a tertiary magmatic fed hydrothermal altered pipe is indicated by the high gas-vapor ratio, results of geophysical prospection and the $\delta^{13}C$ of -6.8‰ for the CO_2 evolving from "Las Maquinitas" fumaroles.
6- Physical, chemical and isotopic data contributed to development of a preliminary model for the sequential evolution of water and steam in Copahue well.
7- A tentative circulation scheme is also presented, indicative of the pattern of water circulation in the Termas de Copahue horst.

ACKNOWLEDGEMENTS

We are grateful to F. D'Amore and C. Panichi for their valuable comments on this work. We are indebted to the International Atomic Energy Agency and the Instituto Internazional per le Ricerche Geotermiche, for partial financial support: Research Contract 3988/IG.

We also thank E. Galardi, E. Linares and the technical staff of the Ente Provincial de Energía de Neuquén and Instituto de Geocronología y Geología Isotópica for their collaboration in this work.

REFERENCES

ALLARD, P., LE GUERN, F. & SABROUX, J.C. — 1977 — Thermodynamic and Isotopic Studies in Eruptive Gases. Geothermics 5:37-40.

ARAÑA, V. & PANICHI, C. — 1974 — Isotopic Composition of Steam Samples from Lanzarote. Geothermics 3 (4):142-145.

COLEMAN, M.L., SHEPERD, T.J., DURHAM, J.J., ROUSE, J.E. & MOORE, F.R. — 1982 — A Rapid and Precise Technique for Reduction of Water With Zinc for Hydrogen Isotope Analysis. Anal. Chem. **54**:993-995.

CORTI, H. & MANUELE, R.J. — 1942 — Sobre la Existencia del Acido Pentatiónico en un Agua de Copahue. Rev. Nac. de La Plata, Tomo XVII:7-14.

CRAIG, H. — 1957 — Isotopic Standard for Carbon and Oxygen and Correction Factors for Mass-spectrometric Analysis of Carbon Dioxide. Geochim. Cosmochim. Acta **12**:133-149.

CRAIG, H. 1963 — The isotopic Geochemistry of Water and Carbon in Geothermal Areas. In Spoleto Conference on Nuclear Geology. E. Tomgiorgi (Ed.) Spoleto-Italy: 17-53.

DALO, H.R. — 1960 — Las Termas de Copahue. Análisis de sus Aguas. Anales de la Dirección Nacional de Química, Año XIII, Nº 25:5-23.

D'AMORE, F. & PANICHI, C. — 1980 — Evaluation of Deep Temperatures of Hydrothermal Systems by a New Gas Geothermometer. Geochim. Cosmochim. Acta **44**:(3):549-556.

EPSTEIN, S. & MAYEDA, T.K. — 1953 — Variation of the $^{18}O/^{16}O$ Ratio in Natural Waters Geochim. Cosmochim. Acta 4:213-224.

GONFIANTINI, R. — 1978 — Standards for Stable Isotope Measurements in Natural Compounds. Nature **271**:534-536.

GROEBER, P. & CORTI, H. — 1920 — Las Termas de Copahue. Direc. Nac. de Minas, Geologia e Hidrogeología, Boletín Nº 3 (Serie F), 112 pp.

GROEBER, P. & PERAZZO, R.J. — 1941 — Captación y Aprovechamiento de las Aguas y Fuentes de Copahue. Dirección de Parques Nacionales, Reserva Nacional Copahue, Volumen I:54-88.

JURIO, R.L., 1977. Características geoquímicas de los fluidos termales de Copahue (Neuquén, Argentina) principales implicancias geotérmicas. MINERIA Nº 172:3-11.

PANARELLO, H.O., GARCIA, C.M., VALENCIO, S.A. & LINARES, E. — 1980 —. Determinación de la Composición Isotópica del Carbono en Carbonatos. Su aplicación a la Hidrogeología y Geología. Rev. Asoc. Geol. Argentina, XXXVI: 460-466.

PANICHI, C. & GONFIANTINI, R. — 1977 — Environmental Isotopes in Geothermal Studies. Geothermics **6**(4):143-161.

PANICHI, C., CELATI, R., NOTO, P., SQUARCI, P., TAFFI, L. & TONGIORGI, E. — 1974 — Oxygen and Hydrogen Isotope Studies of the Larderello, Italy, Geothermal System. In Isotope Techniques in Groundwater Hydrology Vol. 2, INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA :3-28.

PANICHI, C., FERRARA, G.C. & GONFIANTINI, R. — 1977 — Isotope Geothermometry in the Larderello Geothermal Field. Geothermics, **5**(1-4):81-88.

ROETHER, W. — 1970 — Water-CO_2. Exchange Set up for the Routine ^{18}O assay of Natural Waters. Int. J. Appl. Radiat. Isot. **21**:379-387.

SAKAI, H. — 1977 — Sulfate-water Isotope Thermometry Applied to Geothermal Systems. Geothermics **5**(1-4):67-74.

TAYLOR, H.P. — 1967 — Oxygen Isotope Studies of Hydrothermal Mineral Deposits. In Barnes, H.L. (Ed.) Geochemistry of Hydrothermal Ore Deposits. New York-London: Holt, Rinehart and Winston Inc.: 236-277.

WHITE, P.E., MUFFLER, L.J.P. & TRUESDELL, A.H. — 1971 — Vapor Dominated Hydrothermal System Compared with Hot-Water Systems. Economic Geology **66**:75-97.