Geothermal System Associated with the Sierra Nevada Volcano, Araucanía Region, Chile

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ABSTRACT

The geothermal system associated with the Pleistocene-Holocene Sierra Nevada volcano in the Araucanía Region of Chile has surface manifestations extending from the north-western flank of the volcano to Manzanar and Malalcahuello. Baños del Toro, located on the northwestern flank of the volcano, has numerous fumaroles and acid pools (acid sulfate waters, T=~90°C, pH=2.1, TDS=3080 mg/L); while Aguas de la Vaca, near the base of the volcano, has a bubbling spring (chloride-sulfate waters, T=~60°C, pH=7.0, TDS=950 mg/L). Five shallow (<120m) wells (2 at Manzanar and 3 at Malalcahuello) in the Cautín River Valley discharge alkaline (pH= 9-10) waters with relatively low TDS (130-210mg/L). The main heat source of the geothermal system is apparently the magmatic system of the Sierra Nevada volcano. Liquiñe-Ofqui Fault Zone (LOFZ) that transects the area provides conduits for the flow of the geothermal waters. The geothermal reservoirs are mainly hosted in the volcanic rocks interbedded with glacial deposits that cover the North Patagonian Batholith. This batholith forms an impermeable barrier, and thus constitutes the lower boundary of the geothermal system and also controls the lateral flow of fluids. An equilibrium temperature of 210°C is derived from the gas geothermometry (CO_2/Ar-H_2/Ar) of the Baños del Toro fumaroles. Geothermal fluids from the upflow area on the northwestern flank of the volcano migrate northwards to the Cautín River Valley. This northward migration of the geothermal water is stopped by the Melipeuco Pluton, causing its accumulation to form reservoirs near Manzanar and Malalcahuello. This geothermal system thus has, (1) high enthalpy aquifers (>200°C) on the northwestern flank of the Sierra Nevada volcano and 2) low-enthalpy resources (<100°C) in the Cautín River Valley that have been tapped to form spas at Manzanar and Malalcahuello.

1. Introduction

Chilean geothermal systems are among the least studied and understood ones, despite their immense potential (Lahsen, 1988; Lahsen *et al.*, 2010) as economical and local source of energy in a country looking left and right for clean source(s) to meet the demand. However, time is running out to initiate some of the ambitious mining projects that have been kept on hold due to the lack of energy needed to develop and run those projects, as

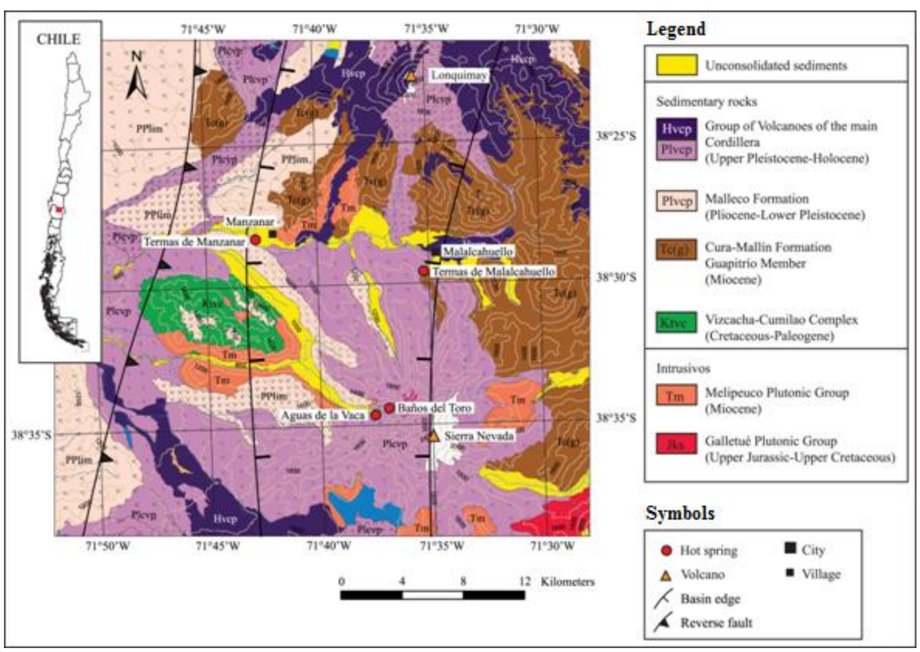

Figure 1. Geological map of the studied area (after Suárez and Emparan, 1997, updated from Emparan *et al.*, 1992), with structural features from Bertín (2010).

well as for meeting the growing energy demand for domestic and industrial purposes. As a consequence, the Chilean Government is compelled to approve conventional mega power projects despite huge environmental concern, e.g., repeated glacial-lake outburst floods (Dussaillant *et al.*, 2009). The present paper describes the Sierra Nevada geothermal system of the south-central volcanic zone of Chile, based on geochemical and isotopic techniques. Te goal of this work is to expand the knowledge of the geothermal systems of the southern Andes.

The geothermal system associated with the Sierra Nevada volcano has surface manifestation extending from the northwestern flank of this volcano to the Cautín River Valley, near Curacautín, in the Araucanía Region (IX Region) of Chile (Figure 1). These manifestations have been studied along with those in other parts of Chile by Hauser (1997, 2000), Risacher and Hauser (2008) and Risacher *et al.* (2011). Transient electromagnetic (TEM) studies near Manzanar and Malalcahuello show the existence of low resistivity anomaly only at Manzanar around 80 to 250 m below surface, with a thickness of at least 100 m (Reitmayr, 2007). Reitmayr (2007) attributed the low resistivity zone at Manzanar to the presence of mineralized hot waters.

2. Geological Setting

The geothermal system associated with the Sierra Nevada volcano has been identified as Sierra Nevada Volcanic Geothermal System (hereafter referred as only "geothermal system") in this work. The term "volcanic geothermal system" used for the geothermal system associated with this volcano is synonymous with the geothermal systems in young igneous environments (Goff and Janik, 2000). The studied geothermal system is located in the south central Andes (Fig.1), west of the Main Cordillera of the southern Andes, which is an active volcanic arc, built on the eroded surface of the upper Jurassic-Miocene volcanic arc. In the studied area, there are numerous outcrops of the Melipeuco Plutonic Group belonging to the North Patagonian Batholith (Mpodozis and Ramos, 1990; Pankhurst *et al*., 1992; Suárez and Emparan, 1997). In the central part of the studied area, there is an outcrop of the Viscacha-Cumilao Complex, composed mainly of andesitic and subordinate massive basalt (Suárez and Emparan, 1997). In the northeastern part of the studied area, there are outcrops the Guapitrío Member (with alternating pyroclastic deposits and lava flows) of the Cura-Mallín Formation, which overlies the Melipeuco Plutonic Group. The outcrops of the Malleco Formation, consisting of a continental volcanic sequence of Pliocene-Pleistocene age (Suárez and Eparan, 1997), occur in the western part of study area. The rocks belonging to the Group of Volcanoes of the Main Cordillera overlain the aforementioned sequences and consists of Upper Pleistocene-Holocene products (Suárez and Eparan, 1997), with basalts and basaltic andesites (Hickey-Vargas *et al*., 1984, 1986, 1989; López Escobar *et al*., 1993, 1995).

The most remarkable structural feature of the southern Andes is the Liquiñe-Ofqui Fault Zone (LOFZ), an intra-arc fault zone that extends about 1200 km between 38° and 47°S (Cembrano *et al*., 1996; Folguera *et al*., 2002; Adriasola *et al*., 2006; Rosenau *et al*., 2006). Subvertical structures of LOFZ facilitate the infiltration of meteoric water that recharges the geothermal systems located along the fault zone (Cembrano and Lara, 2009).

3. Sierra Nevada Volcano

It is a dormant Pleistocene-Holocene volcano (Gonzalez-Ferran, 1995) with a broad base (~30 km diameter) that lies unconformably over the rocks of the Cura-Mallín Formation and North Patagonian Basalt (Figure 1). The extent and disposition of the lava flows and pyroclastic deposits of this volcano indicate the occurrence of glaciations earlier than volcanism (Suárez and Emparan, 1997). Although the age of the last eruption is unknown, it predates the last glacial event (Llanquihue 20000 years ago, Mercer, 1976, Heusser, 1990). Major element geochemistry of its products indicates they are basaltic to basaltic andesitic in composition, with silica concentration between 53 to 61%. According to TAS (total alkalis vs. silica, Le Bas *et al.*, 1986) diagram, they are mainly basaltic andesitic and to a lesser extent andesitic (Muñoz, 2011).

The magmatic system of the Sierra Nevada volcano is presumed to be the heat source of the geothermal system, based on the spatial distribution of the manifestations with respect to the volcano (Figure 1) and the water and gas geochemistry described here. The composition of water and gas of the manifestations close to the volcano indicates proximity to the volcanic heat source (discussed later). The large size and relative age of this volcano, with respect to younger adjacent volcanoes (*e.g.*, Lonquimay, which is still in construction phase), implies a stable heat source at depth ideal for exploitation.

4. Surface Manifestations

Baños del Toro (5727164 N, 272122 E; 1341 m.a.s.l.), located on the northwestern flank of the Sierra Nevada volcano, is characterized by fumaroles and acid pools (discharge temperature=90˚C, pH=2.1; TDS=3000 mg/l. Aguas de la Vaca (5726641 N, 271116 E; 1070 m.a.s.l.), located on the western flank of this volcano near its base, has a bubbling spring (discharge temperature=57˚C; pH=7; TDS=950 mg/l). At Manzanar (5739046 N, 263729 E; 745 m.a.s.l.) there are two shallow wells (dug one of 4 m depth and another drilled one of 120 m depth); while at Malalcahuello (5736642 N, 274555 E; 970 m.a.s.l.), there are three wells drilled to depths of 25, 80 and 120 m. Thermal waters (discharge temperature=~50˚C; pH=9-10; TDS=130-210 mg/l) from these shallow wells at Manzanar and Malalcahuello, in the Cautín River Valley, are being used in spas. The aforementioned Universal Transverse Mercator (UTM) coordinates of the geothermal manifestations are on the Ellipsoid 19 and Datum 19S.

5. Methodology

Thermal and non-thermal waters for geochemical and isotopic analysis were sampled in High Density Polyethylene (HDPE) bottles of 200 ml, following the procedures (viz., filtration using 045µm cellulose filter, Whatman 7141-104; acidifying the filtered sample for cation analysis, etc.) recommended by Giggenbach and Goguel (1989). Chemical analysis for cations and anions were carried out in the Geochemical Laboratory of the Department of Geology at the Universidad de Chile, Santiago. Cations were analyzes using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Perkin Elmer, Model OPTIMA 7400V

CYCLONIC, 2009). Anions (except HCO_3^- and CO_3^{2-}) were analyzed using Ion Chromatography technique (Metrohm IC 861 Advanced Compact, 2009). HCO_3^- and CO_3^{2-} were analyzed by volumetric titration (Giggenbach and Goguel, 1989). Stable isotope analysis (D and O^{18}) were carried out in the Environmental Isotope laboratory of the Chilean Commission of Nuclear Energy (CCHEN), using Laser Spectrometry.

Thermal gases for geochemical analysis were sampled in the evacuated Giggenbach bottles (Giggenbach and Goguel, 1989), containing 100 ml of NaOH (6N) to absorb the acid gases (CO_2, H_2S, SO_2, HCl and HF, and 15 ml of $ClCd_2$ (1N) added to prevent the H_2S oxidation to SO_2. Non-condensable gases (He, H_2, O_2, N_2, CO, CH_4, Ar) are collected in the headspace of the bottle. Chemical analysis of gas samples were carried out in the Wairakei Analytical Laboratory of GNS Science, Taupo, New Zealand. Non-condensable gas (He, H_2, O_2, N_2 and Ar) were determined using Thermal Conductivity Detector (TCD), while CH_4 content was determined using Flame Ionization Detector (FID). CO_2 and H_2S were determined using Iodometric Method (APHA, 1998).

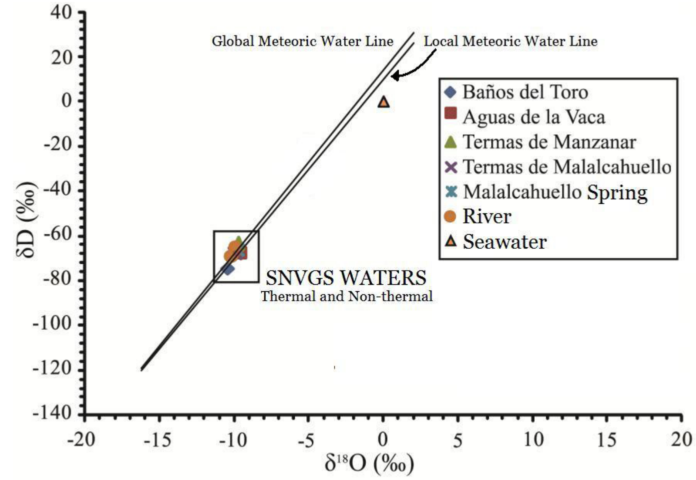

Figure 2. The isotopic compositions of thermal and non-thermal waters. SNVGS: Sierra Nevada Volcanic Geothermal System.

Table 1. Chemical and isotopic composition of thermal and non-thermal waters.

	pH	T (°C)	Na	K	Ca	Mg	Li	Cl	SO_4	HCO_3	CO_3	SiO_2	B	Fe	Al	δD	$\delta^{18}O$
			mg/l													‰	
Thermal Waters																	
BT	2.1	89	48	5.0	211	82	0.2	15	3796	0	0	323	0.3	131	322	-75	-10
AV	7.0	57	167	29	95	6.4	2.1	332	174	58	0	125	18	0	0	-68	-9.5
MR1	9.7	52	69	2.0	1.4	0	0.3	19	50	38	11	59	0.6	0	0	-63	-9.7
MR2	9.7	48	70	1.9	1.2	0	0.4	19	101	44	9.6	60	0.8	0	0	-64	-9.7
ML1	9.4	44	40	1.6	4.2	0	0.3	15	47	33	0.6	47	1.0	0	0	-68	-9.9
ML2	9.5	43	53	1.9	3.5	0	0.3	16	48	33	2.4	47	0.6	0	0.1	-68	-10
Non-thermal Waters																	
RB	7.8	17	10	1.0	28	3.6	0.2	2.1	41	37	0	9.8	0	0.2	0.2	-65	-10
RC	7.8	7	17	2.1	8.1	3.3	0.3	2.6	42	44	0	28	0	0	0	-69	-10
MLV	6.7	9	17	2.6	8.3	1.7	0.2	5.4	11	49	0	39	0	0.1	0.1	-66	-9.8

BT: Baños del Toro, AV: Agua de la Vaca, MR: Manzanar, ML: Malalcahuello, RB: Río Blanco, RC: Río Cautín V: Cold Spring

6. Water Chemistry

The chemical and isotopic compositions of water of the thermal and non-thermal waters are summarized in Table 1. Thermal waters from the acid pools (pH 2.1) of the Baños del Toro are Ca-Mg-SO_4 in composition; while those from Aguas de la Vaca spring are Na-Cl-SO_4 in composition with neutral pH. Relatively higher Cl content in Aguas de la Vaca waters is an indication of proximity to the mature water reservoir above the upflow zone. Relatively higher Ca and Mg contents compared to that of Na indicates non-equilibrium conditions of water-rock interaction (Giggenbach *et al.*, 1983, Giggenbach, 1988, Giggenbach, 1991a) for Baños del Toro waters, probably due to leaching of Ca and Mg ions from the wall-rock through a neutralization process during the ascent of the geothermal fluid to the surface (D'Amore and Arnórsson, 2000). Thermal waters from the shallow wells at Manzanar and Malalcahuello are Na-SO_4(-HCO_3) type and alkaline (pH=9-10) in nature.

According to stable isotopes (D and ^{18}O) composition, the water recharging the geothermal system is meteoric (Figure 2). Acid pools at Baños del Toro do not show an enrichment of heavy isotopes normally expected for such pools by evaporation (Giggenbach, 1991b). It is probably due to steep slope of the fumaroles field, preventing accumulation of the discharged fluid in such pools that would have favored evaporation.

6.1 *Relative Cl-SO_4-HCO_3 Composition*

Relative contents of Cl, SO_4 and HCO_3 (Figure 3) in the thermal waters show the acid sulfate waters of the Baños del Toro, plot quite expectedly in the steam heated water field; which coincides with its spatial location in the highest part of the liquid dominated geothermal system (Henley and Ellis, 1983; Nicholson, 1993), i.e. the slopes of the Sierra Nevada volcano. The acidic nature of

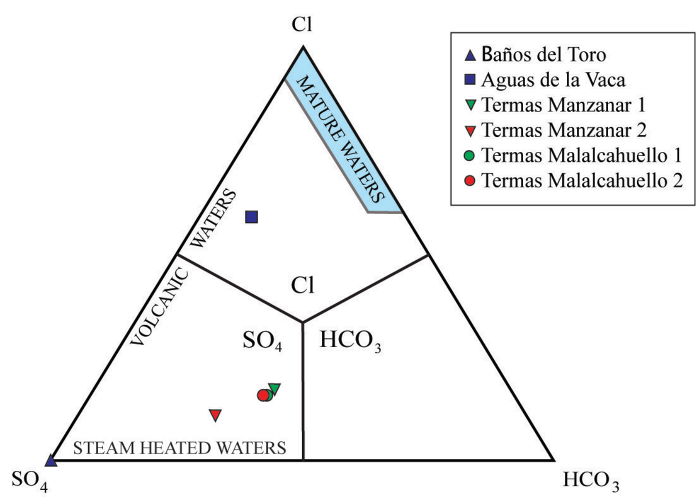

Figure 3. Relative Cl, SO_4, HCO_3 concentrations (mg/l) of the thermal waters.

such waters causes intense leaching of the rocks in contact near/on the surface, so the composition of such thermal waters does not provide information on reservoir conditions.

Aguas de la Vaca thermal waters are Na-Cl-SO_4 type with neutral pH, unlike the acid sulfate-chloride waters (Ellis and Mahon, 1977). They could be formed at depth by oxidation of sulfide (in H_2S) present in the alkali chloride waters to form bisulfate (HSO_4^-) due to neutralizing and buffer action of the confining rocks (Ellis and Mahon, 1977). Neutral pH of the Agua de la Vaca thermal waters suggests a high temperature regime underneath; as such waters become acidic with the lowering of temperature causing increase in the dissociation constant value for bisulfate (HSO_4^-) ion (Ellis and Mahon, 1977; Arnórsson *et al*., 2007). This type of Cl-SO_4 thermal water is common in geothermal systems associated with andesite volcanoes (*e. g.*, Guanacaste, Costa Rica, Giggenbach and Corrales, 1992; Miravalles, Costa Rica, Gherardi *et al*., 2002). The high content of HCO_3^- and SO_4^- with respect to Cl in thermal water at Manzanar and Malalcahuello hot springs indicate an evolution of thermal waters caused by the action of 2 buffers of pH, viz., (1) HSO_4^-/SO_4^{2-} and (2) CO_2/HCO_3^- (Arnórsson *et al*., 2007).

6.2 Relative Content of Cl, Li and B

Based on the relative contents of Cl, Li and B in thermal waters (Figure 4), thermal waters of Aguas de la Vaca have undergone absorption of magmatic vapors (with a high B/Cl ratio) and water-rock interaction (with basaltic rocks); while thermal waters of Manzanar and Malalcahuello are produced by water rock interaction (with basaltic rocks).

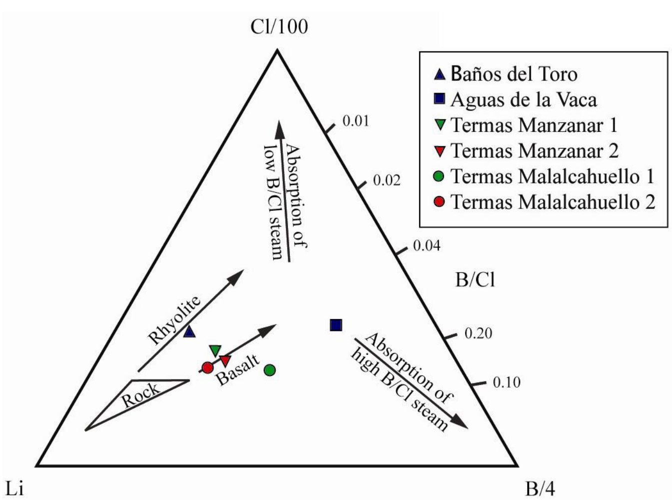

Figure 4. Relative Cl, Li, B concentrations (mg/l) of the thermal waters.

Since the equilibrium temperatures for Manzanar and Malalcahuello thermal waters is less than 150°C (as discussed in next section), the B/Cl value decreases; as compared to the B/Cl values of the thermal waters in the higher enthalpy zones (Aguas de la Vaca). This is because B behaves incompatibly at temperature above 150°C (Ellis and Mahon 1964, 1967; Ellis, 1970); while Cl behaves incompatibly at all temperatures (Ellis, 1970; Michard, 1991). Moreover, the relative content of Li with respect to B and Cl in Manzanar and Malalcahuello thermal waters increases with respect to Aguas de la Vaca, as Li serves as a tracer of water-rock interaction (Giggenbach 1991a). On the other hand, thermal waters Baños del Toro are affected by intense leaching of rocks by these waters and show an unlikely tendency of water-rock interaction with rhyolite, perhaps because Cl is released before B in the volcanic rocks, for Cl being more incompatible than B (Ellis and Mahon, 1964).

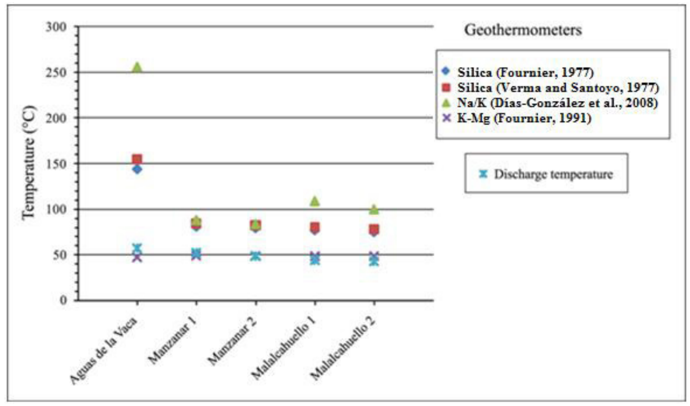

Figure 5. Reservoir temperatures estimated using conventional geothermometers.

6.3 Sub-Surface Temperature and Equilibrium Conditions

Aqueous geothermometers cannot be used in the case of Baños del Toro, because the chemistry of the acid water pools does not provided information of the conditions at depth. Due to low temperature expected for Manzanar and Malalcahuello empirically calibrated geothermometers in the expected range of temperature could be used; viz., (a) Silica geothermometer (Fournier, 1977; Verma and Santoyo, 1997), with pH correction proposed by D'Amore and Arnórsson (2000) because of more alkaline pH of Manzanar and Malalcahuello thermal waters, (b) Na/K geothermometer (Díaz-González *et al*., 2008) and (c) K/Mg geothermometer (Fournier, 1991). The temperatures derived from aforementioned geothermometers (Figure 5) were verified by multimineral equilibria technique (Reed and Spycher, 1984). It was done using WATCH v. 2.4 (April 2010 release) software, which was first described by Arnórsson *et al*. (1982). The diverse range of temperatures estimated from different geothermometers, including those from multimineral equilibria, indicates that the thermal waters of Aguas de la Vaca do not come from a reservoir in equilibrium. Conventional silica and cation geothermometers indicate that thermal waters in Manzanar and Malalcahuello comes from reservoir(s) in partial equilibrium within a temperature range of 70-80˚C, indicated by multimineral equilibria.

7. Gas Geochemistry

The chemical composition of gas samples of Aguas de la Vaca and Baños del Toro are summarized in Table 2. According to the relative content of H_2, He and Ar the gas sample from Baños del Toro has an intermediate composition between magmatic and a meteoric end members. The gas sample from Aguas de la Vaca has air contamination (Giggenbach, 1991a), hence it has not been used for geothermometry or other interpretations. According to H_2/Ar-CO_2/Ar gas geothermometer (Figure 6, Giggenbach and Goguel, 1989), the Baños del Toro gas sample indicates the presence of a liquid dominated reservoir with a temperature of 216˚C.

Table 2. Chemical composition of the gas samples.

Sampling Location	CO_2	H_2S	He	H_2	Ar	N_2	CH_4
	(mmol/mol) dry gas						
Baños del Toro	727	55	0.01	6.7	1.7	180.1	<0.005
Aguas de la Vaca	136	14	0.03	0.4	9.3	780.8	<0.005

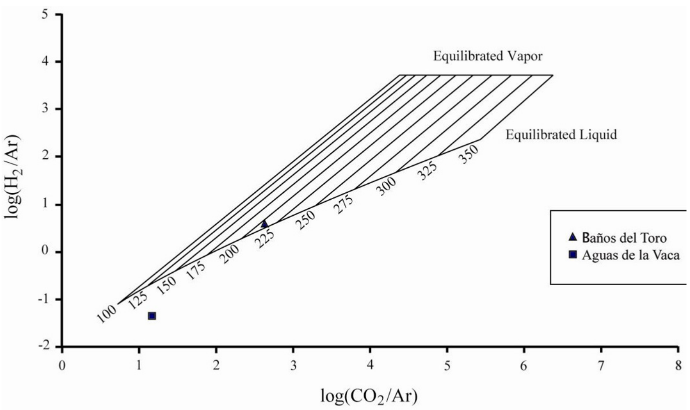

Figure 6. H_2/Ar - CO_2/Ar geothermometer applied to Baños del Toro gas sample.

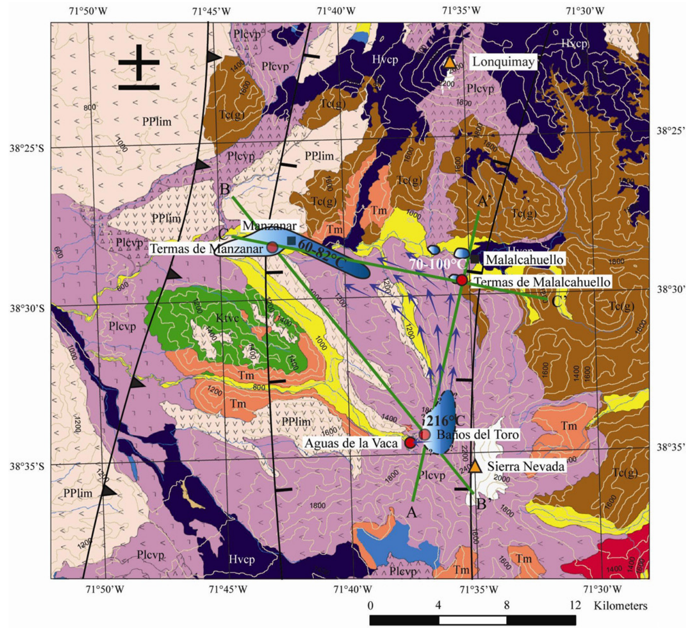

Figure 7. Flow paths of the geothermal fluids indicated by the arrows. Flow of the geothermal fluids from Baños del Toro area towards Malalcahuello (Profile A), but the flow towards Manzanar is stopped by Melipueclo Pluton (Tm, Profile B). Subsequently geothermal fluids flow towards Manzanar and get accumulated to form a vast reservoir, after getting diverted westwards on reaching the poorly permeable Guapitrío Member (Tc) of the Cura-Mallín Formation (Profile C). For the names of other units, please refer to the legend in Figure 1.

8. Integrated Model

All the geothermal manifestations in the area, including shallow wells, reported in the present study are part of one geothermal system. The composition of different thermal waters of the area represents different types of the geothermal fluids in different parts a liquid dominated geothermal system, from its upflow to the outflow zones.

8.1. Geothermal Reservoirs

Considering their disposition (Bertín, 2010), the volcano-sedimentary rocks (Suarés and Emparan, 1997) overlying the North Patagonian Batholith quite likely hosts the geothermal reservoirs. It is substantiated, if not proven, by the presence of a 100 m thick reservoir extending for about at a depth of 80-100 m near Manzanar, inferred from TEM studies (Reitmayr, 2007). The chemical composition of thermal waters suggests that it is located in the outflow part of the geothermal system and has an equilibrium temperature between 60-82°C (Figures 7 and 8). The presence of a 100 m thick (maximum thickness inferred as 600 m from Magnetotelluric studies; Kalberkamp, 2007) geothermal reservoir at 100 m depth extending for about 2 Km has been inferred from TEM studies (Reitmayr, 2007) near Malalcahuello as well (Figures 7 and 8).

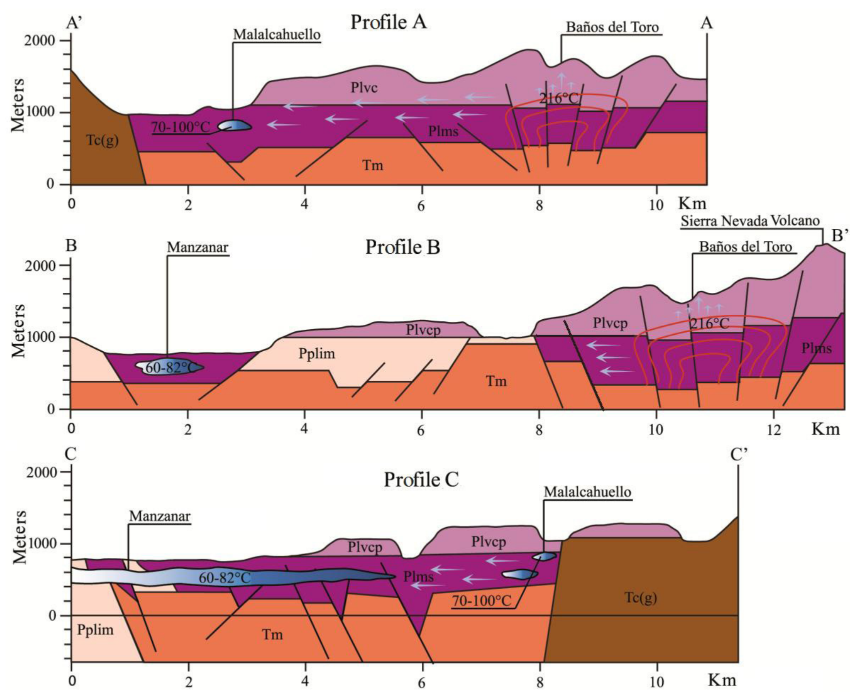

Figure 8. Integrated conceptual model of the geothermal system. Flow of the geothermal fluids from Baños del Toro area towards Malalcahuello (Profile A), but the flow towards Manzanar is stopped by Melipueclo Pluton (Tm, Profile B). Subsequently geothermal fluids flow towards Manzanar and get accumulated to form a vast reservoir, after getting diverted westwards on reaching the poorly permeable Guapitrío Member (Tc) of the Cura-Mallín Formation (Profile C). For the names of other units, please refer to the legend in Figure 1.

A high enthalpy liquid dominated geothermal reservoir is inferred from this study underneath Baños del Toro from gas geochemistry, which suggest an equilibrium temperature of 216°C (Figure 6).

8.2 Geothermal Fluid Flow

The structures associated with the basin formation, located between Lonquimay and Sierra Nevada volcanoes (Bertín, 2010), favor the fluid flow within the geothermal system; whereas, subvertical structures of LOFZ (Cembrano and Lara, 2009) facilitate the infiltration of meteoric water that recharging the geothermal system.

The composition of geothermal waters and gases indicates Baños del Toro's location in the upflow part of the geothermal system and that of Aguas de la Vaca in its outflow part, where re-equilibrium (albeit partial), dilution and boiling has changed the thermal fluid composition considerably. Thermal waters at Manzanar in the outflow part of the geothermal system have undergone a significant dilution and resulting fluid is in equilibrium with the reservoir rocks. However, thermal waters at Malalcahuello have reached only partial equilibrium with the reservoir rocks. It is probably due to insufficient time for the geothermal fluids to re-equilibrate on its way to get accumulated and form extensive reservoir (as suggested by TEM studies; Reitmayr, 2007) near Manzanar. The flow path of the geothermal fluids is shown in Figure 7.

9. Conclusions

The following conclusions can be made from the geochemistry of the thermal waters and gases, geology of the area and limited geophysical (TEM, Reitmayr, 2007) studies. Geothermal fluids emerging from the northern flank of the Sierra Nevada volcano (Baños del Toro) outflows northward to the Cautín River Valley and then to the west to form reservoirs near Malalcahuello and Manzanar (Figures 7 and 8). Thus, all the surface manifestations (including shallow wells) in the studied area belong to one geothermal system identified as the Sierra Nevada Volcanic Geothermal System. The geothermal system is recharged by meteoric water that infiltrated through the subvertical structures of LOFZ. The evolution of major anions is characterized by the action of 2 pH buffers: (1) HSO_4/SO_4 and (2) CO_2/HCO_3, to form SO_4-HCO_3. According to the relative contents of Cl, B and Li the geothermal system can be divided into domains, based on the processes/factors controlling the geochemistry of thermal waters and gases: a volcanic domain near the Sierra Nevada volcano (Baños del Toro and Aguas de la Vaca) and a water-rock interaction domain in the Cautín River Valley (Manzanar and Malalcahuello). The reservoir near Manzanar is in equilibrium at a temperature between 60-82˚C, where that at Malalcahuello is not in equilibrium. High enthalpy liquid dominated reservoir with an equilibrium temperature of 216˚C is located below the Baños del Toro. Further geophysical studies are essential to know the depth and dimensions of this reservoir.

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