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Geochemical and Isotopic Characteristics of the Laguna Colorada Geothermal Area – SW Bolivia

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ABSTRACT

Laguna Colorada geothermal area, located in the Southwest part of Bolivia has several hydrothermal manifestations including hot springs, mud pools, and fumaroles. Two drainage basins comprise the survey area, Laguna Colorada in the north flank and Challviri in the south flank whereas Sol de Mañana, which is the most important geothermal field with a potential of more than 100 MWe, is located at the intersection of both. Twenty-five water samples coming from cold springs, rivers, hot springs, mud pools, shallow groundwater, and geothermal wells were sampled and analysed showing the chemical and isotopic characteristics of the area. From the ternary diagrams, three types of water were found: rivers show a bicarbonate composition whereas mud pools and the shallow groundwater indicate a sulphate type; the third type of water corresponds to the cold springs, which show a chloride composition partially equilibrated with the ignimbrite rock and trending to the mature water of the geothermal reservoir. Conservative components such as chloride, boron and arsenic indicate that all the samples follow the bedrock composition ratio from the rivers, shallow waters, cold springs, hot springs to the geothermal reservoir in correlative order. This can be useful for tracing the fluid and mark the up-flow and in-flow zones. Stable isotopes such as δ18O and δD mainly indicate a meteoric water source and show water-rock interaction and high temperature processes in the geothermal reservoir and boiling in the mud pools. 14C was used to date the samples around ten thousand years ago, it also was confirmed with tritium values. In general, isotope value shows that the geothermal reservoir gets recharge from meteoric water of the intermediate and regional flow system of both drainage basins, this water might stem from the last raining season in the area around eight thousand years ago. Today, the area is a cold desert with a negative hydric balance.

1. INTRODUCTION

Bolivia is a landlocked country in South America located on the border of “The ring of fire”, characterized by subduction between the South America and Nazca tectonic plates; as a result, Bolivia has substantial geothermal potential. In the 1970s, the Geological Bolivian Service (GEOBOL) performed an inventory survey of all the geothermal manifestations in the country finding more than 70 hydrothermal sites distributed in the three geographic Andes regions of the country: Western Andes mountain range, Altiplano highlands, and East Andes mountain range (Carrasco and Delgadillo, 1976).

In 1976, Empresa Nacional de Electricidad (ENDE) explored several geothermal fields supported by the United Nations Development Programme (UNDP); consequently, three sites were considered as the most important: Laguna Colorada, Sajama and Empexa. Figure 1 shows the location of all the geothermal sites in Bolivia (Delgadillo, 2000).

Since then, all the effort for the geothermal development has been concentrated on Laguna Colorada; between 1988 and 1994, six deep wells were drilled in Sol de Mañana geothermal field, finding a high enthalpy reservoir with temperature around 260°C. However, due to a change of political situation, the project was suspended until 2008 (Bona and Coviello, 2016).

Following a political change that emphasized the use of renewable energy sources, WestJEC and Japan International Cooperation Agency (JICA) carried out a feasibility study for a 100 MWe geothermal plant (JETRO, 2008) confirming the potential of 100 MWe for 30 years in the Sol de Mañana field (JICA, 2013). Therefore, ENDE is carrying out several steps for devolving the geothermal field, including funding and bidding processes.

Geochemical and isotopic characteristics of the geothermal area are essential to understand the source and the behaviour of the resource; besides, the information help in the reservoir engineering to find the optimal production for a sustainable exploitation (Axelsson, 2016).

This study will focus on understanding the geochemical and isotopic characteristics of the greater Laguna Colorada geothermal area. The study area comprises the thermal springs scattered across the entire Laguna Colorada area. Additionally, a potential area (Sol de Mañana) marked for the establishment of a geothermal power plant inside the Laguna Colorada also comprises part of the study.

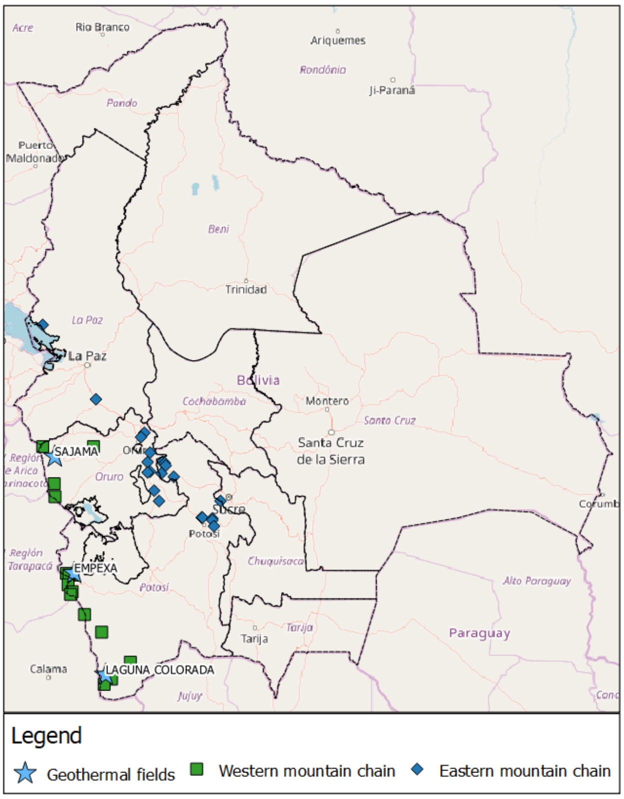

Figure 1: Geothermal sites in Bolivia (Modified from Carrasco and Delgadillo, 1976).

2. BACKGROUND INFORMATION

2.1 Survey and Study Location

The survey area is located in the southwest of Bolivia, inside the Eduardo Avaroa national park between the meridians 67°55'-67°89' western longitude and 22°15'-22°45' southern latitude, at an altitude extending from 4270 to 5500 m a.s.l. at the Laguna Colorada Lake and the top of Pabellon hill respectively. The area has a cold desert climate (BWk) according to the Koppen-Geiger climate classification, with an average temperature of 0.8°C, annual precipitation of 77 mm and strong winds of 15 m/s with predominantly southwest to northeast direction during the afternoon (Peel et al, 2007).

Sol de Mañana geothermal field is located in the middle of the survey area at an altitude of 4980 m a.s.l. It is the most prominent site of surface activity in the survey area, with several hydrothermal manifestations including fumaroles and mud pools.

2.2 Regional Geology

The Altiplano highlands surrounding the geothermal field were formed during the subduction of the Nazca plate below the South American plate around twenty-five millions years ago, when faults allowed magma to ascend to the surface. The volcanism in the survey area can be divided into eight periods, but the rocks exposed at the surface were principally formed during the Tertiary and Quaternary periods (Choque, 1996), as shown in Figure 2.

The oldest eruption site, Cerro Amarillo volcano, is located in the south of the project and is of medium Miocene age. Later, upper Miocene lavas (Lmios) were deposited in a long and active period with four main centres of distribution: Cerro Borotera, Cerro Lagunitas, Chillahuita I and Cerro Negro. The third volcanic period was during the lower Pliocene lavas (Lplii) with the Cerro Muerto volcano along with small lava flows in the south, most of which are covered by a younger volcanic period (ENDE, 2010).

Upper Pliocene lavas (Lgplis), characterized for tuff and cracked rocks forming land flats probably result from a large heterogeneous flow in the N-S direction where today we see the younger Putana, Cerro Michina and Tocopuri volcanos, at the border with Chile. In addition, a second pyroclastic flow occurred in the lower Pleistocene period (Lgplei), forming flat lands similar to those before. The latest volcanic events left prints of lava flows in the Pleistocene period (Lple), eruptive from that period have a large distribution in the survey area. Also the Pleistocene volcanos such Tocopuri, Apacheta and Putana show the presence of fumaroles and indicate current activity (Huaranca et al, 2016).

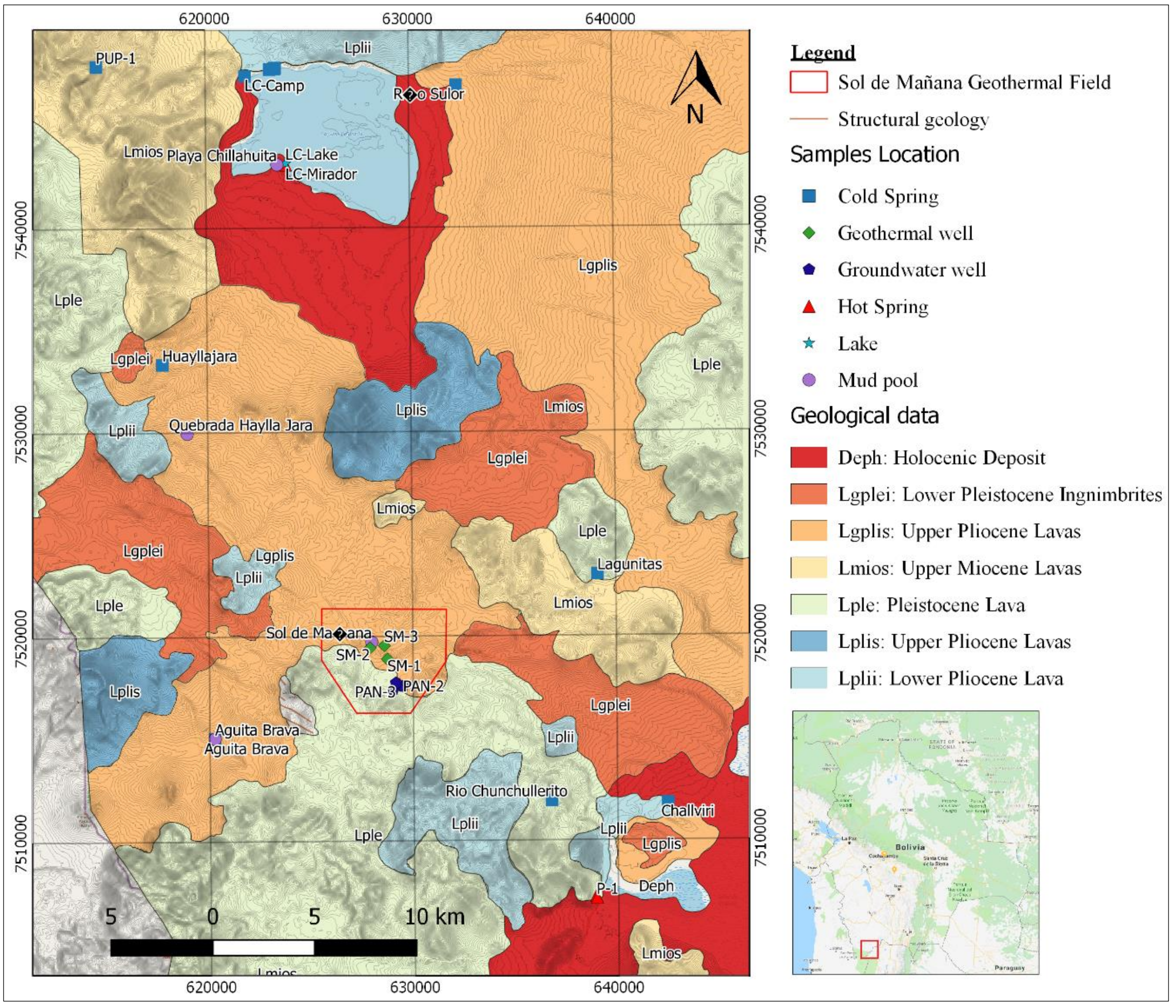

Figure 2: Geological map of the project site (Modified from Choque, 1996).

2.3 Hydrogeology

The survey area is located inside the Altiplano closed drainage basin, two main drainage basins lead to the lake and salt desert, namely Laguna Colorada and Challviri. Hot and cold springs, groundwater wells and geothermal wells around the survey area give us information about the hydrogeology. The Polques and Laguna Colorada-Mirador hot springs emerge from Holocene deposits; the remaining springs emerge from Neogene period lavas. The hydrogeological map is shown in Figure 3 (ENDE, 2010).

The area of the basins draining towards Laguna Colorada Lake is around 1,436 km²; the main rivers are Sulor, Quebrada Callejón, Aguaditas and Quebrada Pabellon. In some cases, it is possible to observe a large erosion produced for the flow of water and snow, in other cases the topography consists of flat sand lands without any presence of water on surface (ENDE, 2010).

The local groundwater can be classified in three hydrogeological units depending on the lithology, permeability, recharge and aquifer discharge (MMyA, 2017):

a) *Groundwater in porous non-consolidated aquifers,* located in quaternary sediments around the south border of Laguna Colorada Lake, its use could be limited by a possible salinization of the aquifers, it is considered to be recharged by meteoric water.
b) *Groundwater in fractured aquifers,* with a medium to high productivity, represent the second group. The groundwater flowing in the stratovolcanoes Laguna Colorada and Pupusitas belongs to this group and is found in the springs, which feed the Laguna Colorada lake. In addition, waters in Neogene and Quaternary tuff rocks, which extend to the east and northeast of the drainage basin, are included in the group; the main feature is the Sulor river.
c) *Groundwater in local and limited aquifers (porous or fractured rocks).* Local aquifers with low or no production belong to this group, and are mainly found in two geological formations from the Neogene and Quaternary; i.e. the Aguita Brava and Negra Muerta stratovolcanoes.

Laguna Colorada Lake, which is the lowest point of the study area and gets continuous inflow from Huayllajara and Sulor rivers, also receives concentric groundwater flow from the surrounding highlands.

From the north flank of the lake, the groundwater percolates down through fractured volcanic rocks, and reappears on surface at the edge of the lake as cold or hot springs with flowrates from 3 to 60 L/s. However, on the southern banks of the lake the groundwater passes through the sand and gravel- sediments. This gives rise to few hot springs on the southern side of the lake. Below that, groundwater flows on the ignimbrite basement rocks. Figure 4 shows the hydrogeological profile for Laguna Colorada lake.

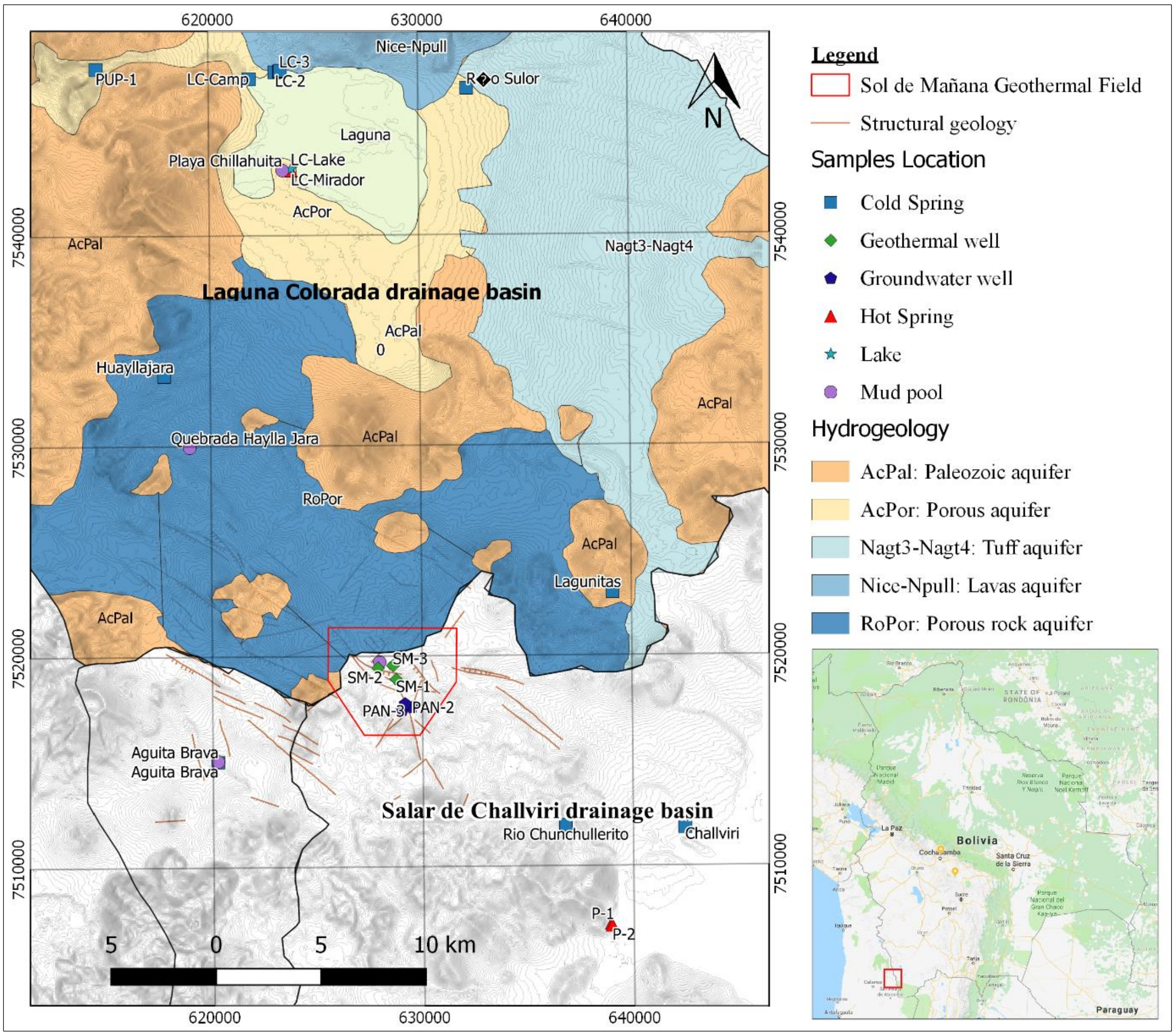

Figure 3: Hydrogeological map (based in ENDE, 2012 and MMyA, 2017).

Regarding the hydric balance of the lake, precipitation in the survey area is low - around 77 mm per year with more rain in December to April as shown in Figure 5. On the other hand, the estimated potential evapo-transpiration is expected to reach 1,900 mm per year (MMyA, 2017). Therefore, the water balance is negative with a moisture effective index of -54.7 and the survey area is classified as arid zone (E) according to the Thornthwaite climate classification (Campero, 2014).

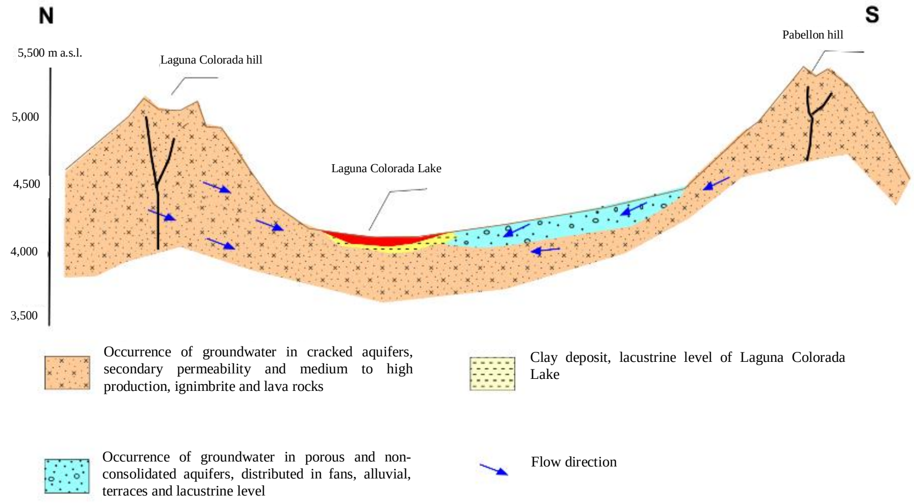

Figure 4: Hydrogeological profile for Laguna Colorada drainage basin (MMyA, 2017).

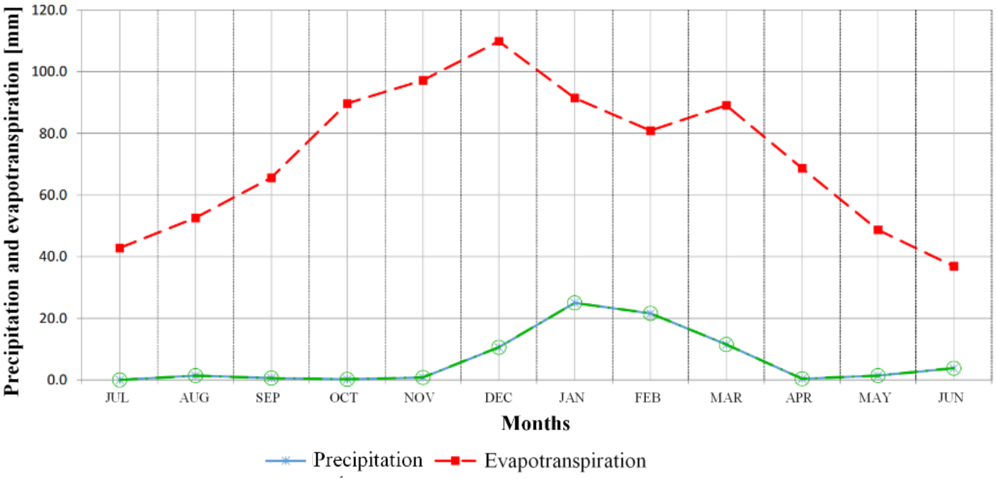

Figure 5: Precipitation and evapotranspiration (Campero, 2014).

2.4 Surface Exploration

As mentioned in the introduction chapter, surface exploration started in the 1980s when UNDP and ENDE were charged to carry out the geological, geophysical and geochemical surface exploration. The geological information suggested the existence of magma chambers below the volcanic axis and an important heat source in the west part of the manifestation area (ENDE, 1986).

WestJEC in 2008, carried out a review and complementation of the surface studies including the geochemical and geophysical data obtained in the 1980s. Their conclusions were as follows (JETRO, 2008):

- The geothermal fluid is meteoric water heated to 270°C due to the magma chambers.
- There are upflow zones where the fluid rises and boils; this is the source of hydrothermal manifestations such as fumaroles and mud pools.
- Based on gravimetric and resistivity data, there is a relationship between the anomalies and the hydrothermal alteration. The low resistivity layer corresponds to high argillic alteration, and the circulation fluid pattern that alters the rocks is related to the fracture system.

In 2014, a magnetotelluric survey was carried out in order to obtain more information and extend the exploration area to Apacheta (located 9 km to the southwest). Figure 6a shows the gravimetric and resistivity anomalies and Figure 6b shows a resistivity profile section; the reservoir could be inside these two anomalies and the cap rock would be in the rock around 30 ohm-m (Ramos, 2014).

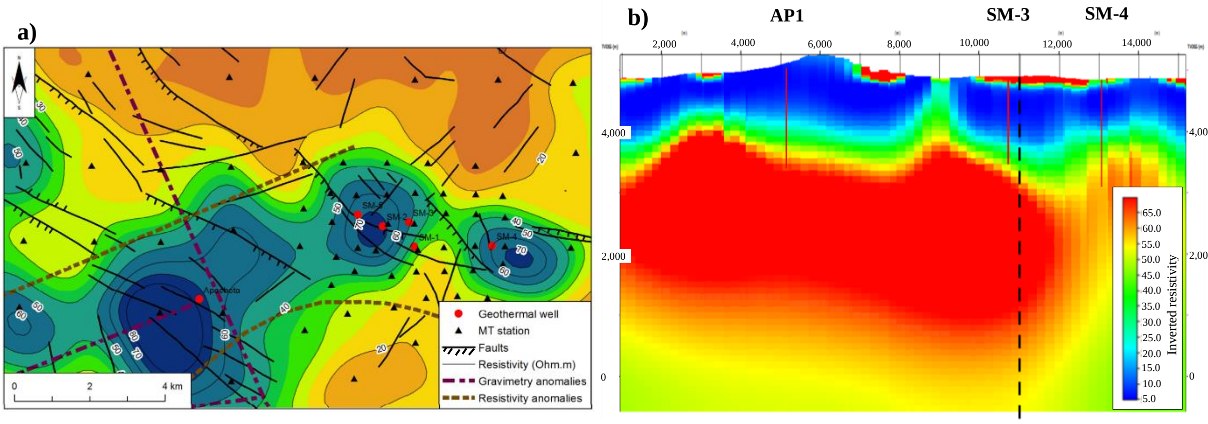

Figure 6: a) Gravimetric and resistivity anomalies and resistivity map at 3500 m a.s.l. (modified from JETRO, 2008); b) MT resistivity profile (Espitalier et al, 2015).

2.5. Exploration Geothermal Wells

The favourable results of the surface exploration gave reason to continue with the drilling of a production well. The deep drilling started in 1987 in Apacheta, unfortunately, the results obtained were discouraging (ENEL, 1991). However, the drilling continued in Sol de Mañana between 1989 and 1994 with better results. To date four production wells and one reinjection well have been drilled there.

The production well SM-01 was drilled to a depth of 1180 m. The main rock type is ignimbrite of Dacite composition; the lithology indicates three alteration zones: heulandite from 0 to 400 m depth, quartz and chlorite from 400 to 780 m depth and epidote from 780 to 1180 m depth. (Ramos, 2015)

The lithology of production well SM-02 is characterized by four alteration zones: Clay minerals from 0 to 400 m depth, wairakite from 525 to 800 m depth, wairakite and epidote from 800 to 950 m depth and adularia from 950 to 1486 m depth. Figure 7 shows the temperature logs and lithology information for these two wells.

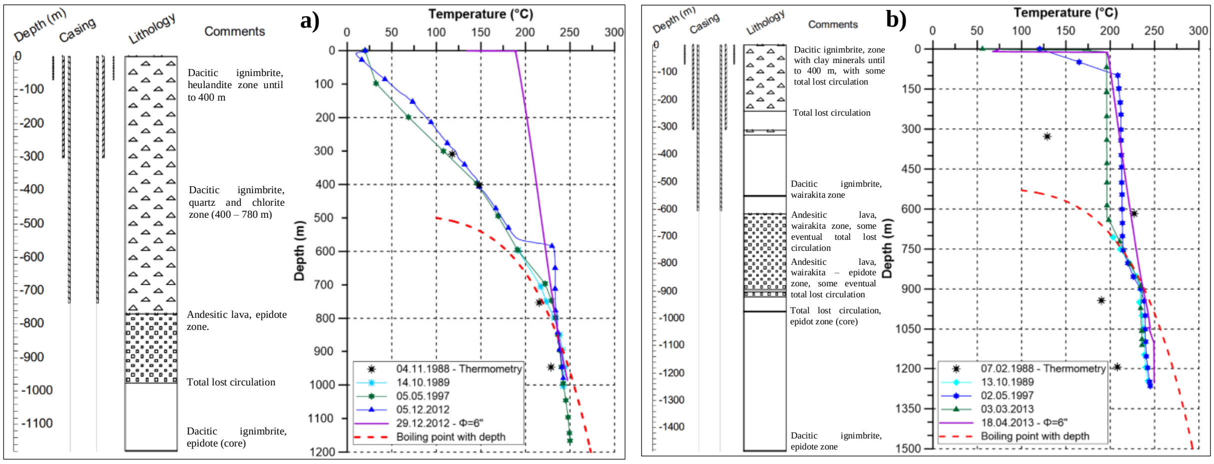

Figure 7: a) Lithology and temperature log for production well SM-01; b) Lithology and temperature log for production well SM-02 (modified from Ramos, 2015).

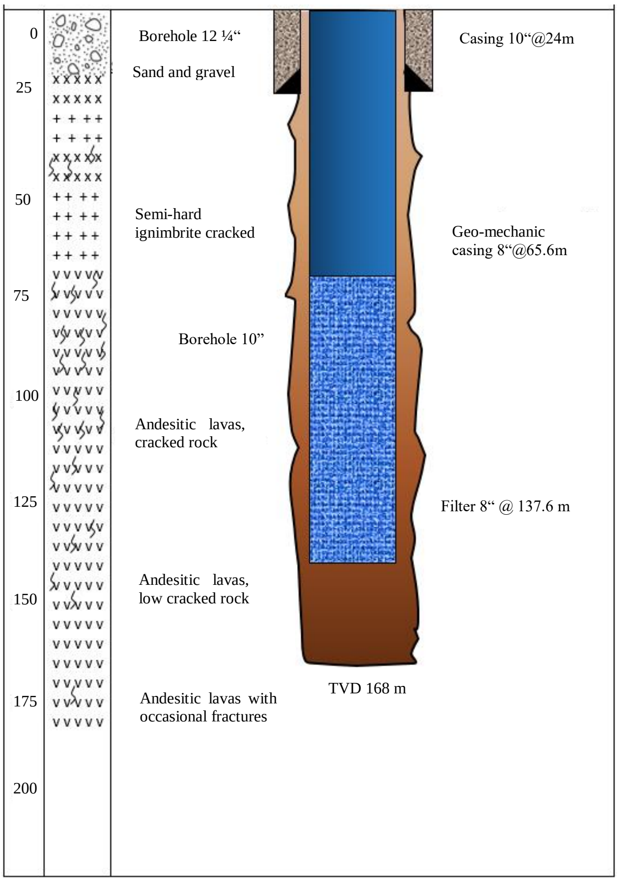

Figure 8: Lithology of the ground water wells (modified from ENDE, 2018).

2.6 Groundwater Wells

Three groundwater wells were drilled in the beginning of 2018 in order to supply water for further geothermal drilling, which is due to start in the next few years. The wells are located in Sol de Manana geothermal field, about 4 km southeast of the geothermal wells. They were designed with a depth up to 200 m and the following steps: (ENDE, 2018)

- Step 1: Borehole of 12 ¼", @ 24 m depth, casing of 10 ½".
- Step 2: Borehole of 9 7/8", @ 170 m depth, casing and filters of 8".

Figure 8 shows the lithology of the wells characterized by:

- From 0 to 50 m of depth, sand and gravel;
- From 50 to 100 m of depth, semi-hard ignimbrite fractured;
- From 100 to 125 m of depth, andesitic lavas, fractured rock;
- From 125 to 150 m of depth, andesitic lavas with few fractures;
- From 150 to 175 m of depth, andesitic lavas with occasional fractures

The aquifer geometry was calculated according to the tested dimensions. Assuming a resistivity of 15 - 100 ohm-m, the aquifer area was estimated to reach from an elevation of 4,750 m a.s.l., down to 4,650 m a.s.l. (ENDE, 2018).

3. METHODOLOGY

3.1 Field Sampling and Analysis of Water Samples

Water sampling has an important role in geochemistry; it is useful in conceptual model design and monitoring of environmental processes. Sampling requires well trained professionals to reduce the possible errors associated with the survey (Arnórsson, 2000). For hydrogeology purposes, the assumption that the chemical component concentration in the subsurface is the result of the inflow of water to the aquifer and the rock water exchange reaction toward its corresponding flow (Appelo and Postma, 2004).

Analytical data must have certain levels of accuracy and reliability to be considered in the geochemical interpretation. Quality control is also a concern for the analytical laboratory; the precision of methods can be checked by repeated analysis of the same sample. Ionic balance (Equation 1) is a good approach to obtain an idea of the accuracy of the analysis checking whether the sum of anions determined is close to the sum of cations determined (Ármannsson and Ólafsson, 2006).

$$CBE(\%) = \frac{\sum Z_{cat}M_{cat} - \sum Z_{an}M_{an}}{\sum Z_{cat}M_{cat} - \sum Z_{an}M_{an}} \cdot 100 \qquad (1)$$

where Z_i = Charge of an ion; M_i = Molar concentration of the ion [mol/kg]

Several water samples surveys have been carried out in Laguna Colorada by different institutions since 1989. The current one was performed in 2018; moreover, Hidrogema and Nippon Koei collected data in 2016 as well as JICA in 2013 and PNUD 1989 (Neumann and Huaranca, 2018). Results from all surveys were considered in the present report.

Spectrolab and ENDE carried out the sampling survey between 6 and 8 March 2018 and on 13 April 2018. Sample bottles, procurement and treatment process followed the standard Bolivian guidelines from NB 416, Potable water – Sampling (IBNORCA, 2005) and chemistry analysis followed AWWA, APHA and WEF standard guidelines published in Standard methods for the examination of water and wastewater (Greenberg et al, 1980).

Samples from the geothermal wells were collected using a Weber separator during the well production test, obtaining two-phase samples. Although an international advisor collected the samples in 2013, the treatment for silica was not properly carried out. As a consequence analyses were carried out by two processes, the first one using nitric acid for acidifying were called “as received” and the other one using sodium hydroxide and heating to 100°C for about 40 minutes were called “digested”. Due to this incident, silica digested concentration reported in this project is not completely reliable (Villarroel, 2014).

3.2 Classification of Geothermal Fluids

Ellis and Mahon classified geothermal waters in four kinds, based in the distribution of the concentration of major anions (Ellis and Mahon, 1977):

a) *Alkali-chloride water,* with pH from 4 to 11, mostly sodium-potassium chloride waters.
b) *Acid-sulphate water,* results of the oxidation of H_2S forming SO_4, most constituents likely dissolved from surface rock. This kind of water is not useful for subsurface properties estimation.
c) *Acid-sulphate-chloride water,* is a mixture of alkali-chloride water with sulphate water, can be formed from the oxidation of H_2S to SO_4 in alkali-chloride or sulphur rock dissolution followed by oxidation.
d) *Bicarbonate water,* might derive from CO_2 gas during the steam condensing or be the result of water mixing. It is rather common in old geothermal systems and the surrounding outflow areas, most commonly at equilibrium and useful for estimation of subsurface properties.

Geothermal fluids are found at the deepest levels of a geothermal system, Arnórsson et al. (2007) refer to the mature geothermal fluid in equilibrium as *primary geothermal fluids.* These fluids are a mixture of up to three fluid components: meteoric water, seawater and magmatic volatiles. Primary fluids rise to the surface, and could begin to form *secondary geothermal fluids* after various processes:

- *Depressurisation boiling,* goes to the formation of vapour phase and boiled liquid;
- *Vapour condensation,* produce steam heated water with high concentration of sulphate or bicarbonate, commonly in shallow groundwater or surface water;
- *Mixing of CO_2 gas,* from magmatic or a depth source with ground water; and
- *Mixing of geothermal water,* shallow and/or cool water might mix with geothermal water.

Methods to classify waters often involve diagrams where samples are characterized by their component concentrations. A convenient way to differentiate between geothermal water and other water types is using the Cl-SO_4-HCO_3 and Na-K-Mg ternary diagrams.

Spreadsheets for geothermal water geochemistry developed by Powell and Cumming (2010) were used for the calculations and ternary diagrams. Cross-plots and ternary diagrams are used through measured concentrations data and formulas based in equilibrium reactions and empirical relationships to find trends and characteristics of waters (Powell and Cumming, 2010).

3.2.1 Cl-SO_4-HCO_3 triangular diagram

One of the diagrams used for classification of water according to the scheme outlined by Ellis and Mahon is the Cl-SO_4-HCO_3 ternary diagram. Most geochemical techniques may be confidently applied only to specific types of fluid, for example, solute geothermometers are only expected to work if the water is classified as mature. Therefore, it is recommended to classify water based on major anions. The diagram shows anion composition for four typical groups of thermal waters: *Volcanic and steam-heated, mature and peripheral waters* to evaluate compositional trends (Giggenbach, 1991).

The data is expressed as a percentile point with a relation between the three constituents and is obtained by summing the concentration of each component in ppm as it is shown in Equation 2:

$$S = C_{Cl} + C_{SO_4} + C_{HCO_3} \tag{2}$$

where: S = Sum of all the concentrations; C_i= Concentration of the anion in ppm

Therefore, the percentage of each anion can be calculated as:

$$Cl\,(\%) = 100(\tfrac{C_{Cl}}{S})\,; \qquad SO_4(\%) = 100(\tfrac{C_{SO_4}}{S}); \qquad HCO_3(\%) = 100(\tfrac{C_{HCO_3}}{S}) \tag{3}$$

3.2.2 Na-K-Mg triangular diagram

In addition to the previous diagram, the Na-K-Mg ternary diagram classifies water according to their cation equilibrium and allows for the estimation of temperature assuming a complete equilibrium between K^+, Na^+ and Mg^{2+} in feldspars and other minerals. Waters is be classified into fully equilibrated, partially equilibrated and immature waters according to the equilibrium of magnesium, potassium and sodium minerals and their temperature deduced (Giggenbach, 1991). The mathematical relation shows two reactions, which depend of the temperature:

$$K - feldspar + Na^+ = Na - feldspar + K^+ \tag{4}$$

$$0.8\,Kmica + 0.2\,chlorite + 5.4\,silica + 2K^+ = 2.8Kfeldspar + 1.6H_2O + Mg^+ \tag{5}$$

In a similar way of the preview diagram, the data is expressed as a point according to their three components concentration, but the concentrations are scaled to correct for the difference in their typical relative concentrations in different waters:

$$S = \frac{C_{Na}}{1000} + \frac{C_K}{100} + \left(C_{Mg}\right)^{0.5} \tag{6}$$

$$\%Na = \frac{C_{Na}}{10S} \qquad \%K = \frac{C_K}{S} \qquad \%Mg = 100\left(\frac{C_{Mg}}{S}\right)^{0.5} \tag{7}$$

where: S= Sum of all the scaled concentrations; C_i= Concentration of the canion in ppm

3.3 Tracing Fluid Origin

In a geothermal system, thermal waters might ascend from the reservoir to the surface through fractures or up-flow zones; forming different types of waters, as mentioned in section 3.2. During such ascent, several processes may affect the water composition, for example mixing with a shallow cold water can change the components concentration due the lower concentrations in the latter water. However, chemical equilibria between water and the rock might be traced applying mixing models or linear relationships between conservative components (Arnórsson, 2000).

Non-reactive or conservative constituents play an important role in tracing the origin of geothermal fluids. In particular, stable isotopes and components such boron, chloride and bromide are commonly used for this purpose (Óskarsson and Ármannsson, 2015). For example, stable carbon isotopes permit to estimate the flow patterns and mixing processes of fluids from different sources (Tabaco et al, 1991).

3.3.1 Hydrogen and oxygen stable isotopes

Stable isotopes in water are commonly used as tracers for the origin of the geothermal solutions or dissolved components; the isotope pairs used are δD as a ratio ($^2H/^1H$) and $\delta^{18}O$ as a ratio ($^{18}O/^{16}O$), expressed as per mil (‰) deviations from Standard Mean Ocean Water (SMOW). By definition, ocean water has δ-values close to 0‰, but due to processes such as evaporation and precipitation, fractionation is observed. The isotope ratio in precipitation is known to depend on the altitude, season changes, latitudes and temperature effects, however after precipitation little changes are observed – particularly in the hydrogen isotope ratio (Craig, 1961).

The relationship between $\delta^{18}O$ and δD values of meteoric water has been fitted by a linear equation, generally referred to as the "Global Meteoric Water Line" (GMWL), and is based on precipitation data from locations around the globe (Craig, 1961).

$$\delta D = 8\delta^{18}O + 10 \tag{8}$$

where: δD= Deuterium expressed in per mil (‰); $\delta^{18}O$= Oxygen 18 expressed in per mil (‰)

As a result of the first isotopic surveys and analyses in Laguna Colorada, Scandiffio and Alvarez (1992) defined a local water meteoric line (LMWL) with available data in the geothermal field and including isotopic composition from El Tatio geothermal field, located in the Chilean Andes, about 30 km NW of Laguna Colorada (Giggenbach, 1978). They proposed a relationship between $\delta^{18}O$ and δD with a slope of eight and an intersection around five (Sandiffio and Alvarez, 1992).

$$\delta D = 8\delta^{18}O + 5 \tag{9}$$

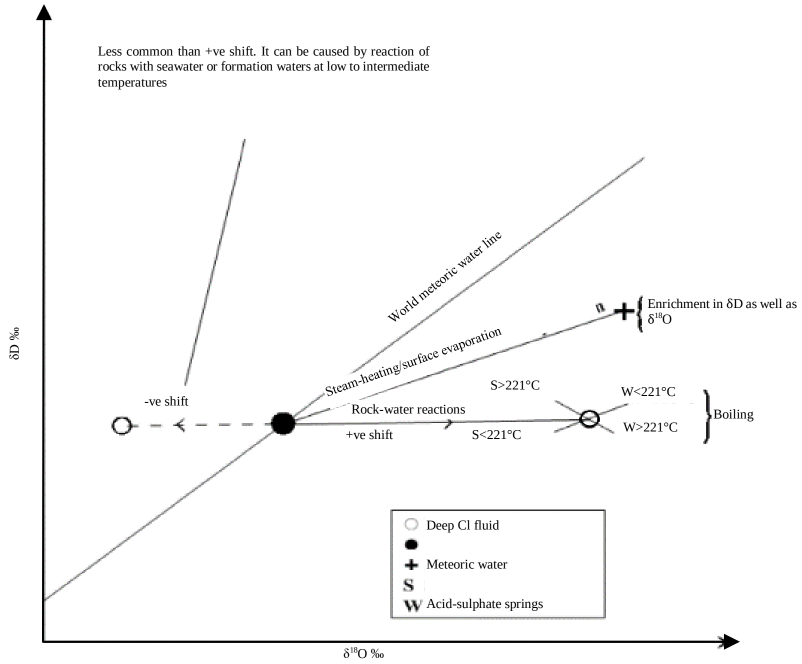

Figure 9: Schematic trend in isotope changes (Nicholson, 1993).

Some subsurface processes can change the isotopic composition of waters. One of them, water-rock interaction with high-temperature contact surface can lead to increase in the $\delta^{18}O$ isotope ratio although the δD ratio stays constant. This is called the "oxygen isotope shift". Generally, rocks are rather more enriched in oxygen-18 than meteoric water and therefore, after the water-rock interaction, the water becomes more enriched in $\delta^{18}O$ whereas rock becomes more depleted. This process leads to a positive displacement of oxygen-18 on the $\delta^{18}O$ – δD diagram (Ellis and Mahon, 1977).

Figure 9 shows a schematic trend in isotope signatures of meteoric water with the processes involved with the changes in the composition (Nicholson, 1993).

3.3.2 Carbon isotopes

The CO_2 source in geothermal systems has been studied for a long time, two models have tried to explain it: a) magma source as main source of CO_2 in the depth and b) fluid rock exchange during the flow in the geological system (Ellis and Mahon, 1977).

Both model can be complement each other, in fact, CO_2 and derived components could come from the following sources:

- Magmatic source;
- Carbonated rocks and rock fluid reaction exchange;
- Oxidation of organic-sedimentary material;
- Recharge of meteoric water, i.e. atmosphere.

Additionally, the age distribution of different aquifers through dating the age of springs can be deduced using ^{14}C contents which has a half time of 5,730 ± 40 yrs (Godwin, 1972). The source of this isotope is the high radiation at the upper boundary of the atmosphere. From there ^{14}C is dissolved in precipitation and infiltrated to the aquifer (Vogel, 1970).

When an unconfined aquifer flows toward the lowest point on the surface and forms a spring, the age of the spring water might be equal to the average age in the aquifer, the relationship between the apparent age of the discharge (t) and the ^{14}C contain is expressed as (Vogel, 1970):

$$A = A_o e^{-\lambda t} \tag{10}$$

where: A= activity at time t; Ao= initial activity; λ= the decay constant; t= time

3.3.3 Tritium (^3H)

Tritium is formed in the upper atmosphere by neutron bombardment of nitrogen nuclei and passes via precipitation into groundwater. The natural content varies from 2 to 20 tritium units (TU) depending on local conditions. After atomic bomb tests in the 1950s, the tritium content temporarily increased by a factor of thousand, especially in the northern hemisphere; however, nowadays it has returned to pre-1950s levels (Vogel, 1970).

3.3.4 Boron-chloride relationship

Chloride and boron are conservative constituents in geothermal systems, they provide information on the source of the fluid as tracer and evaluate mixing of hot and cold water in ascending flow. Boron and chloride concentrations in rock vary both within volcanic and sedimentary rocks.

Rainwater, surface water and non-thermal groundwater generally have lower B concentrations than thermal water, and rainwater typically reflects the Cl/B concentration ratio of its source, i.e. ocean water (Arnórsson and Andrésdóttir, 1995).

3.3.5 Deuterium-chloride relationship

Deuterium isotopic information together with chemical analyses of the water may give information about the groundwater flows and the chemical reactions that have taken place. In some cases, the ground water, which is initially meteoric in origin, passes through chloride rich formations whereby it acquires considerable amounts of chloride without changing the deuterium content (Árnason and Tómasson, 1970).

Chloride is a conservative component in geothermal systems; it is preferentially partitioned to the liquid phase and is neither leached nor deposited along hot-water conduits in the upper parts of geothermal systems. Deuterium, which is also conservative, is useful to observe the mechanism of boiling, mixture with cold water and steam loss, because water and steam constitute the only major reservoirs of deuterium and hydrogen in geothermal systems (Truesdell et al, 1977).

3.3.6 Arsenic-chloride relationship

Arsenic is a pervasive trace component in geothermal systems. The range of As concentration found in natural water is large, from less than 0.5 ppb to more than 5 ppm in natural water (Smedley and Kinniburgh, 2001) and up to 50 ppm in geothermal fields (Webster and Nordstrom, 2003), the aforementioned value was observed in the El Tatio geothermal field (Ellis and Mahon, 1977).

The presence of arsenic in geothermal fluids can be due to water-rock interaction; most reservoir fluids are under-saturated with respect to arsenopyrite and other arsenic minerals. In addition, there often exists a linear relationship between As and Cl. The source of the Cl ion could be associated with magma intrusion, host rock leaching or seawater, whereas As is derived mainly by host rock leaching (Webster and Nordstrom, 2003).

3.3.7 Silica-chloride relationship

Water formed by mixing of geothermal water and cold ground or surface water possesses many chemical characteristics, which serve to distinguish it from unmixed geothermal water. Geothermal water is characterized by equilibrium conditions between solutes and alteration minerals, whereas the composition of cold water appears mostly determined by the kinetics of the leaching process, the mixed waters tend to acquire characteristics intermediate between those (Arnórsson, 1985).

4. RESULTS

In total 26 water samples have been analysed, 3 from geothermal wells, 4 from groundwater wells, 9 from cold springs, 4 from hot springs, 4 from rivers and surface waters and 2 from mud pools.

As mentioned above, hot springs, cold springs and groundwater were sampled and analysed following the standard guidelines for potable water in Bolivia and the standard methods of analyses (APHA/AWWA).

Quality control is expressed in terms of ionic mass balance giving a reliable result as shown in Figure 10; most of the samples have less than 5% of error between cations and anions, but seven samples ion balance error between 5 and 10%. However, they are also considered reliable.

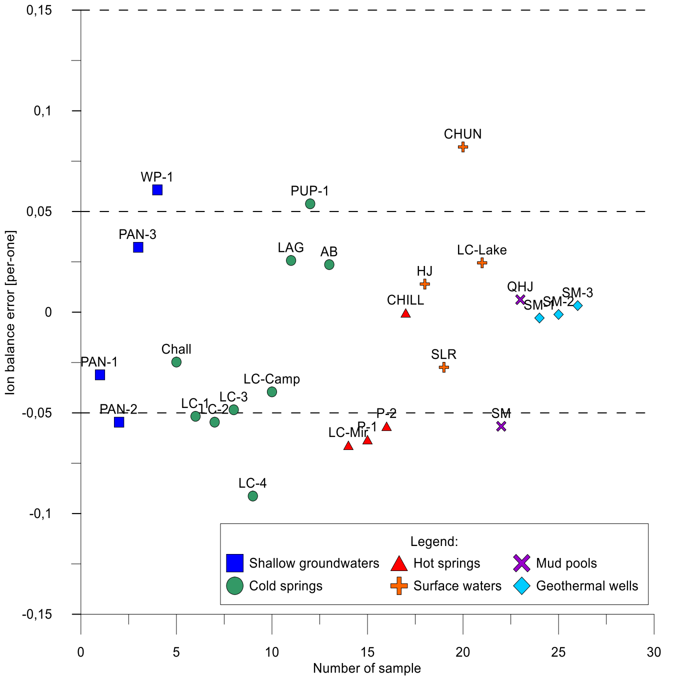

Figure 10: Ion balance error for all the samples.

4.1 Chemical Characteristics

Based in the diagram showed in Figure 11, Laguna Colorada geothermal area presents the three types of waters; groundwater and mud pool samples are classified as volcanic and steam heated waters, the rivers and some cold-spring samples as peripheral water and most common cold and hot spring samples as well as geothermal wells samples as mature water.

All samples from Sol de Mañana geothermal field are classified as immature water, excepting a mud-pool located in Huayllajara and the geothermal wells, which are already in equilibrium at a temperature of 260°C. Several water and gas geothermometers were employed by Villarroel in 2016 showing average temperatures of 260°C and 270°C respective (Villarroel, 2016).

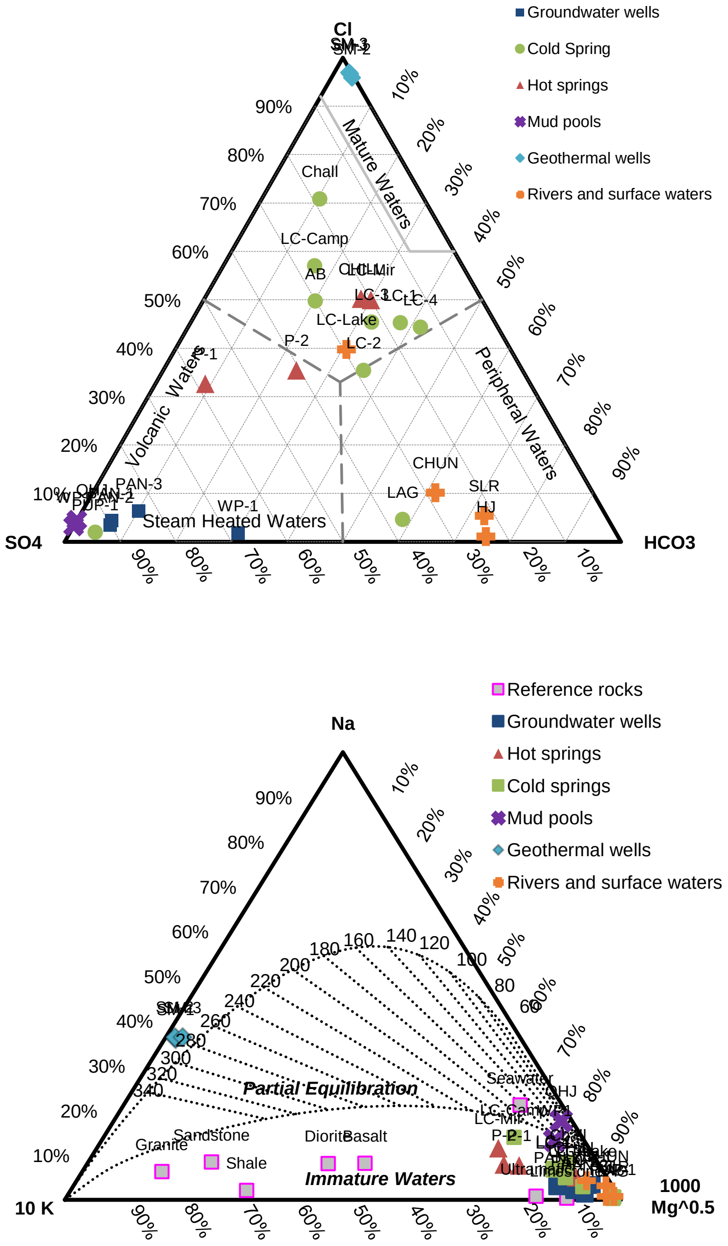

Figure 11: a) Cl-SO4-HCO3 ternary diagram, b) Na-K-Mg ternary diagram for Laguna Colorada geothermal area.

4.2 Fluid Origin

A summarized results of the isotopic analysis is shown in Table 1, Isotopic samples took place in 2016 (Neumann and Huaranca, 2018) determining stable isotopes from 3 types of sampled water (geothermal wells, mudpool and springs). The isotope composition of the geothermal wells (represented by the blue square points in the Figure 12 below) was calculated using values for the steam condensate and brine samples, and the steam fraction during sampling (calculated based on the reservoir temperature and sampling pressure). These samples show an oxygen shift of about 4‰ towards more enriched values for ^{18}O; assuming that deuterium values are preserved from the initial water. This is commonly observed in geothermal fluids and is caused by reactions between the fluid and host rock, which is typically quite enriched in ^{18}O.

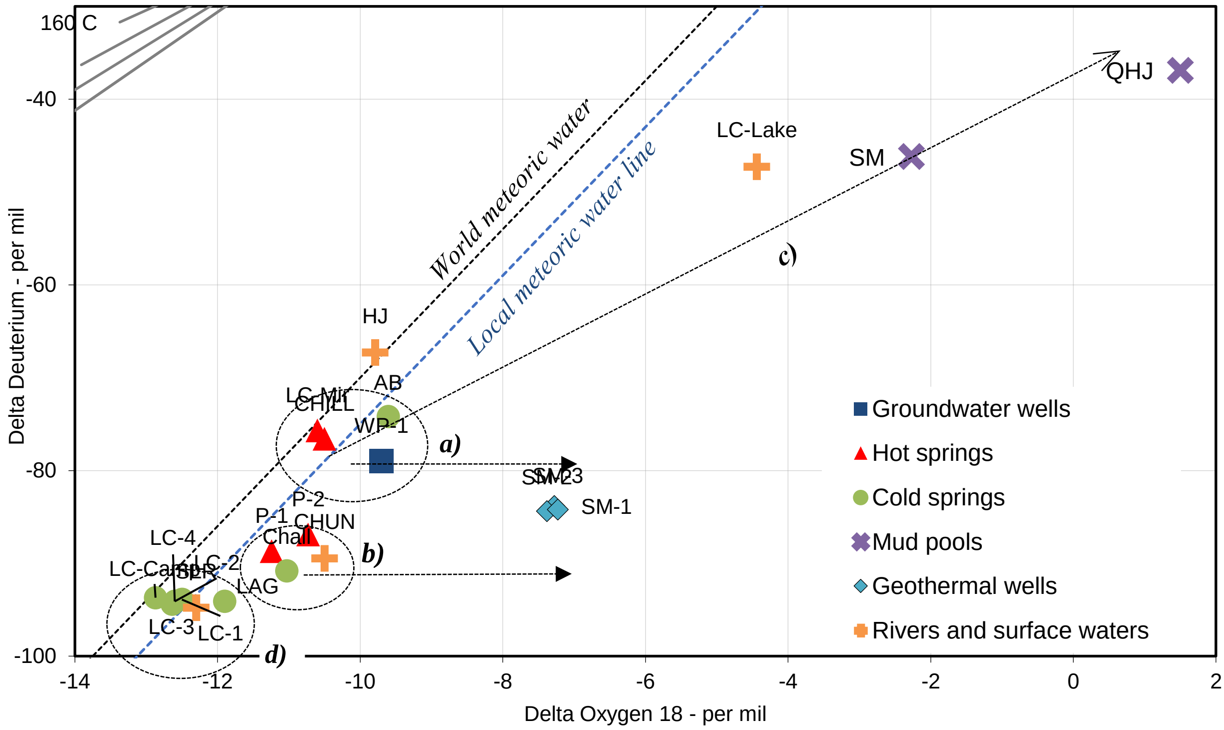

Figure 12: Delta oxygen 18 and delta deuterium diagram. a) Oxygen shift in Laguna Colorada meteoric water due to water-rock interaction; b) Oxygen shift in Challviri basin meteoric water due to water-rock interaction; c) Oxygen and deuterium enrichment due to evaporation from the mud pools. d) The most depleted water samples are found on the north flank of the Laguna Colorada Lake.

Springs samples, even thermal hot springs such Polques or LC-Mirador, are located much closer to the local meteoric line, indicating that the groundwater are recharged by only precipitation and have not reacted substantially with rock. A sample from Laguna Colorada Lake was also analysed and shows a fractionation in deuterium and oxygen-18, where the isotope composition of the lake is more enriched (heavier) than the springs. This is because of the evaporation of the water.

Huayllajara mud pool shows oxygen-18 and deuterium values much heavier than the springs, due to the evaporation and possibly water-rock interaction i.e. dissolution of the surrounding rock and soil in the acidic fluid of the mudpool. However, fumaroles isotopes composition analysed by Sandiffio and Alvarez in 1992 found a similar line with samples from El Tatio, concluding that fumaroles are formed by boiling of the same meteoric water that feeds the geothermal reservoir (Sandiffio and Alvarez, 1992).

In order to use the half-life of ^{14}C (5,730 years) for age determination, it is important to estimate the initial activity of the radiocarbon. Therefore, the knowledge about the percent of radiocarbon that is still active in the geology region is required. The climate in south and east Bolivia was extremely pluvial from 12,500 to 8,500 years ago, in the so-called Tauca phase (Pasig, 2003) followed by a dry period which was repeatedly interrupted by short steps of heavy precipitation. However, at present the precipitation is around 77 mm/a (Neumann and Huaranca, 2018).

The isotopic composition and the estimated age of the water are explained by Neumann and Huaranca (2018) based on the sampling survey in 2016. Six spring waters were analysed and dated from 2,900 to 15,600 years before present and two samples date from around 10,500 years ago. This age is in good agreement with age determinations of groundwater in Silala, which is located 30 km to the north of the geothermal field (Sergeomin, 2005). This suggests that the main recharge of the groundwater must have taken place relatively quickly during the short period of heavy precipitation although more recent water may have seeped into the ignimbrite aquifer at higher levels. Evaporation of the water from this infiltration could have displaced the local meteoric line. However, it seems that fossil waters feed the hot springs, providing a constant flow in spite of the arid climate in the project area and the unfavourable hydric balance (Neumann and Huaranca, 2018).

Regarding the stable carbon isotope ^{13}C, the data is between -8.3‰ and -13.8‰, compared to PDB, indicating that the main source of carbon dioxide is the atmosphere, with a limited presence of organic material, possibly due to a thin layer of vegetation at the recharge location. Additionally, there is a relationship between ^{14}C and δ^{13}C. The younger the waters are, the more enriched they are in δ^{13}C; this is also observed in the project site, giving reliability to the dating estimation (Huaranca et al, 2016).

In the study area, waters samples have very low tritium values from 0.00 to 0.12 TU, demonstrating that the spring waters must have been in place before the year 1960. However, two samples: Lagunitas and Sulor may have an influence of up to 5% water formed after 1960. The low tritium values are consistent with the results of age dating of the ^{14}C method (Neumann and Huaranca, 2018).

The chloride and boron relationship is shown in the Figure 13, where is also shown the seawater and bedrock molar ratios (basaltic ratio of 30 according to Turekian and Wedepohl, 1961). Considerable variations in B and Cl concentration were observed; rivers and shallow waters with the lowest concentration, increasing concentrations in the cold springs and hot springs and the highest concentration in the geothermal reservoir. The graphic also shows a linear relationship between the concentration for almost all the samples excluding mud pool and river samples. Concentrations in cold springs and hot springs are in concordance with a formation by mixing of groundwater and geothermal fluid. The observed chloride-boron ratio is similar to the bedrock ratio and indicates that water-rock interaction controls the B and Cl content of the water. In contrast, mud pools are concentrated in boron than chloride with reference to the bedrock ratio; this could be due to condensation of boron-rich and chloride-poor steam in the mud pool or dissolution of rock, which is also richer in boron than chloride.

Table 1: Isotope parameters of samples in the study area

No.	Sample Name	$\delta^{18}O$ [‰SMOW]	δ D [‰SMOW]	$\delta^{13}C$* [‰PDB]	^{14}C* [pmc]	^{14}C Age* [ya]	^{3}H* [TU]
1	Challviri	-11.03	-90.8				
2	LC-1	-12.5	-93.9				
3	LC-2	-12.6	-94.1				
4	LC-3	-12.64	-94.4				
5	LC-4	-12.6	-94.1				
6	LC-Mirador	-10.6	-75.7	-8.3	25.1 ± 0.14	10,358 ± 45	0.03
7	LC-Camp	-12.87	-93.7				
8	LC-Lake	-4.44	-47.3				
9	P-1	-11.24	-88.7	-9.8	8.3 ± 0.8	15,638 ± 88	0.01
10	P-2	-10.73	-86.9				
11	PUP-1						
12	Huayllajara	-9.79	-67.3				
13	Aguita Brava	-9.61*	-74.2*	-10.3	24.1 ± 0.14	10,870 ± 39	0.06
14	Lagunitas	-11.9*	-94.1*	-13.8	58.3 ± 0.23	3,594 ± 23	0.10
15	Río Sulor	-12.3	-94.8	-10.6	63.1 ± 0.23	2,933 ± 32	0.09
16	Rio Chunchullerito	-10.5*	-89.5*	-9.0	44.0 ± 0.17	5,909 ± 32	0.04
17	Playa Chillahuita	-10.5*	-76.6*				
18	Sol de Mañana	-9.7*	-79.0*		36.4 ± 0.18		
19	Quebrada Hayllajara	1.5*	-36.9*				
20	SM-1	-7.3**	-83.8**				
21	SM-2	-7.4**	-84.4**				
22	SM-3	-9.0**	-89.5**				

(*) Values obtained from (Naumann and Huaranca, 2018)
(**) Values obtained from (Villarroel, 2016)

A contour map of chloride concentrations is also shown in Figure 14 and demonstrates the variation of chloride between the cold springs and the hot springs. It may be observed that the southern border of the Laguna Colorada lake has higher concentration than the other springs located in the north site, In addition, Polques and Aguita Brava have higher chloride concentration.

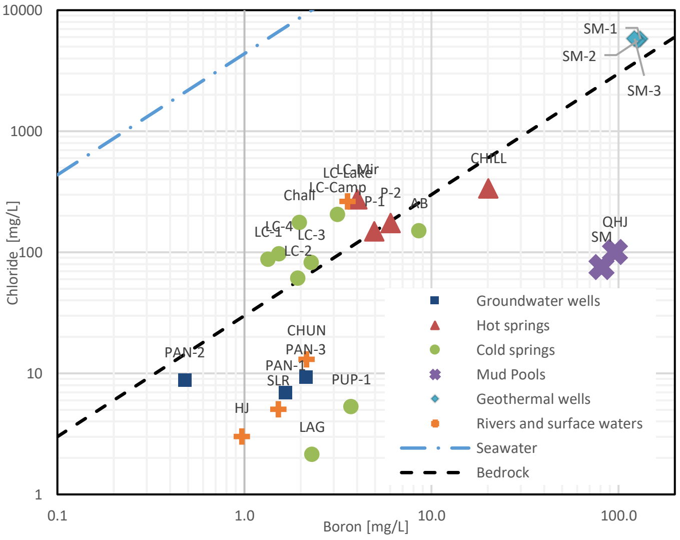

Figure 13: Variation of Cl with B.

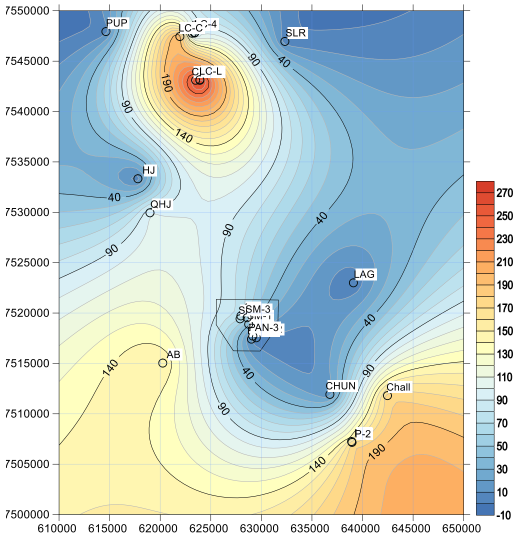

Figure 14: Contour map of Cl.

Figure 15 shows the deuterium chloride relationship in the Laguna Colorada samples. No clear signs of mixing are observed. However, in 1978 Giggenbach made a similar analysis of El Tatio geothermal field, expected for steam separation from a water with an initial temperature of 260°C, a chloride content of 5500 ppm and isotopic composition of -78 ‰ for deuterium. The analysis assumes that the well and high chloride spring discharges to be related by straight forward single step steam separation processes. It suggests some considerable rock-water oxygen-shift or evaporation at above ambient temperatures caused by steam heating, with two processes affecting the thermal water during their migration are steam separation and dilution by local meteoric waters (Giggenbach, 1978).

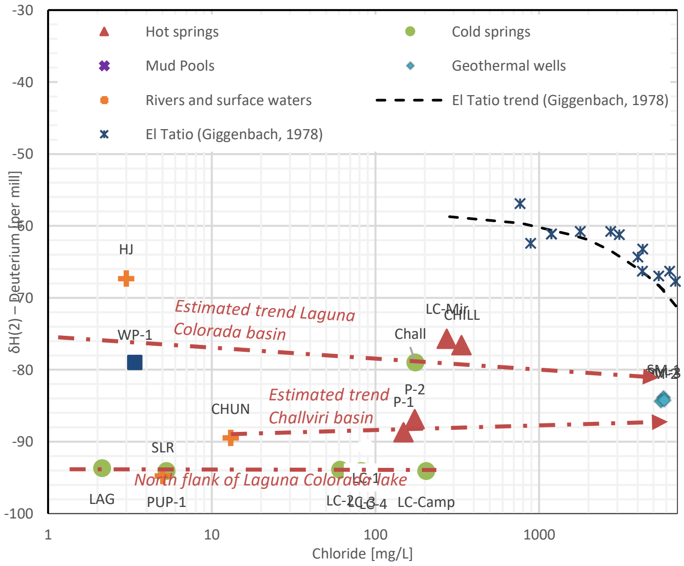

Figure 15: Variation of δD with Cl.

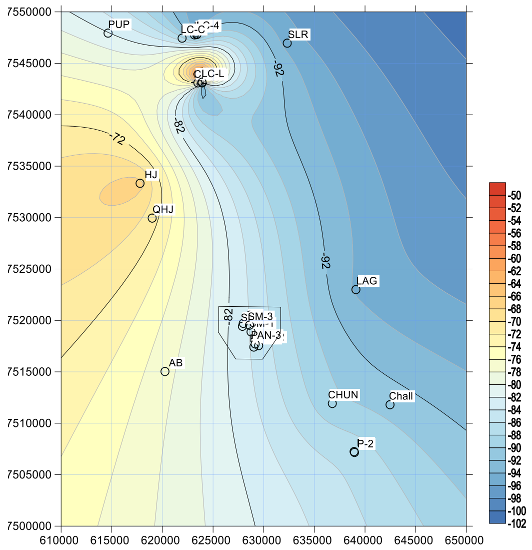

Figure 16: Contour map for δD excluding the mud pools.

Under the same assumption, there could be a relationship for Laguna Colorada, for the samples Aguita Brava, Polques and Mirador, going through Sol de Mañana mud pool to finally reach the reservoir, Figure 16 shows the contour map for deuterium distribution in the area.

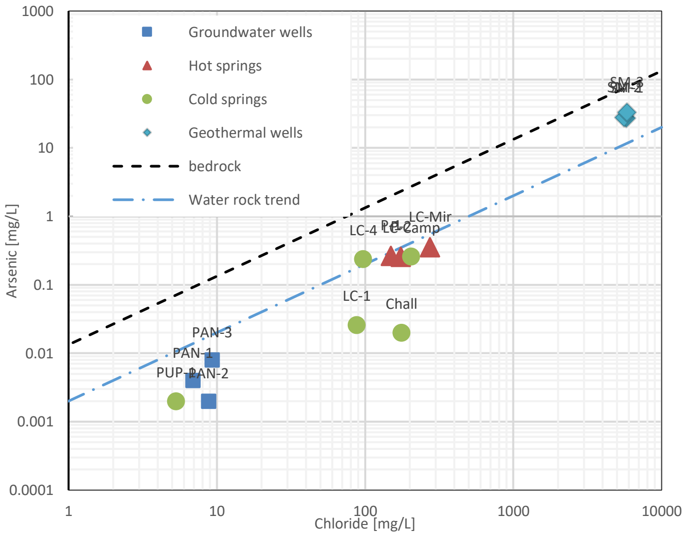

Figure 17: Variation of As with Cl.

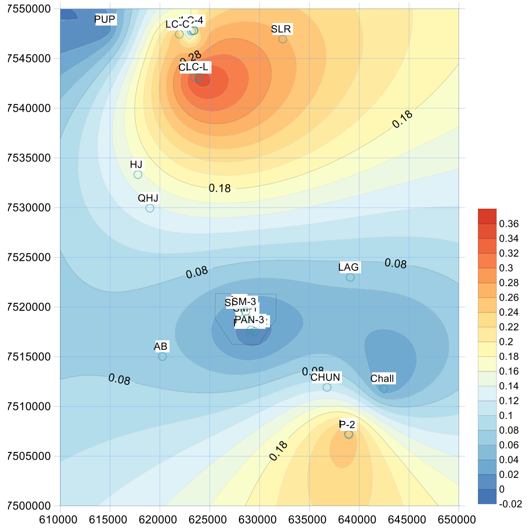

Figure 18: Contour map of As in the geothermal area excluding the geothermal well samples.

The samples from Laguna Colorada geothermal area have an As concentration between 1 ppb and 35 ppm which seems increase with the sample temperature and chloride concentration as shown in Figure 17. In comparison with other geothermal fields, As shown in Figure 18, Laguna Colorada Lake and Challviri Lake have very high arsenic concentration. Other examples of geothermal fields with high As are Wairakei in New Zealand which reaches up to 5.2 ppm (Ritchie, 1961) and Los Azufres in Mexico around 24 ppm (Birkle and Merkel, 2000). However, the El Tatio geothermal field in Chile located 30 km from Laguna Colorada has arsenic concentration up to 50 ppm.

5. DISCUSSION

The study area involves two drainage basins, Laguna Colorada basin reaching to the northeast with a drainage point in the Laguna Colorada Lake at 4,370 m a.s.l. and Challviri basin to the southeast with a drainage point at 4,530 m a.s.l. The Sol de Mañana geothermal field is located at the border of both, at 4,900 m a.s.l. elevation.

In a similar was as the samples were classified according their chemistry characteristics, it is also possible to differentiate the different sources of the water and figure out a hydrogeological groundwater flow model. As shown in the background information, the hot and cold springs sampled discharge constantly throughout the whole year, with flow rates ranging from 3 to 60 L/s depending on the spring. Carbon isotopes suggest that the age of the waters is from 2,900 to 15,600 years before the present. Aguita Brava and Polques located in Challviri basin discharge water from 10,500 to 15,000 years old. Due to the constant flow rates and the high age of the waters Neumann and Huaranca (2018) suggest that the groundwater is "fossil water" recharged during the last rain season in the survey area, around mid-Holocene. This statement also fits the results of the present study; although the waters are relatively cold the concentration of conservative components suggests partial water rock interaction, during the long residence time. However, there is little or no oxygen shift observed for the hot and cold springs on the delta plot, where the samples follow the meteoric line.

According to the isotopic characteristics and the source of the water shown in the Figures 12 and 15, the following water sources may be inferred:

a) *North flank Laguna Colorada lake,* cold springs samples such LC-1, LC-2, LC-3, LC-4, LC-Camp located in the north site of the Laguna Colorada lake are lighter in Oxygen and deuterium and get the source from meteoric water located norther site from the survey area.
b) *Challviri drainage basin,* samples such Polques and Challviri belong to this group located in the southern flank of the survey area, the samples are heavier than the North flank of Laguna Colorada Lake but lighter than Laguna Colorada drainage basin, they are dating up to 15,000 years ago.
c) *Laguna Colorada drainage basin,* samples such LC-Mir, Aguita Brava, and WP-01, are heaviest meteoric water found in the survey area, dating up to 10,000 years ago.
d) *Geothermal reservoir,* Sol de mañana geothermal reservoir is located in the watershed of those two drainage basin at 2,000 meters depth; it has a huge water-rock interaction from Challviri and Laguna Colorada water basin, perhaps located in the regional flow system.

5.1 North Flanks of Laguna Colorada Lake

Cold spring samples, located in the outflow zones of the Laguna Colorada have an average temperature of 20°C and conductivity from 474 to 829 µS/cm. They are classified as neutral chloride waters according to the anion ternary diagram. All the samples are immature but trending to the same cation equilibrium as the geothermal well samples.

The isotopic characteristics follow the local meteoric water line, are more depleted in δD and $\delta^{18}O$ than the Challviri basin, but clearly meteoric in origin. The water source could be in the northern site of the study area, in a lighter isotopic region and flowing constantly from north to south, getting the outflow zone in the north border of the Lake as shown in the Figure 19.

Conservative components such As and B suggest a partial exchange with the rock for cold springs. The extent of these reactions between the water and the rock despite the low temperature may indicate that the ground flow corresponds to the intermediate flow system with a longer residence time than rivers and the shallow ground water. However, no ^{3}H or ^{14}C analyses have been carried out for these samples.

5.2 Laguna Colorada Drainage Basin.

Samples such as LC-Mirador, which is a chloride immature water and the shallow groundwater samples from the PAN wells, which are sulphated water belong to this group. The isotopic composition follows the meteoric water line with the most enriched deuterium and oxygen-18 values, LC-Mirador has been dated to 10 thousands years ago and the water shows partial water rock interaction.

PAN samples represent the groundwater located in a recharge zone around 4 km southeast of the geothermal wells. Unfortunately, during the survey it was not possible to analyse their isotopic composition, however, Sandiffio and Alvarez (1992) collected a sample WP01 with similar characteristics as the PAN samples, this sample was taken from a shallow well of 127 m depth. WP01 has a δD value of -79 ‰ and seems recent meteoric water in an inflow zone through the local flow system. PAN and WP01 have a temperature of almost 30°C, which can be explained by conductive heating from the ignimbrites observed in the lithology of the groundwater wells.

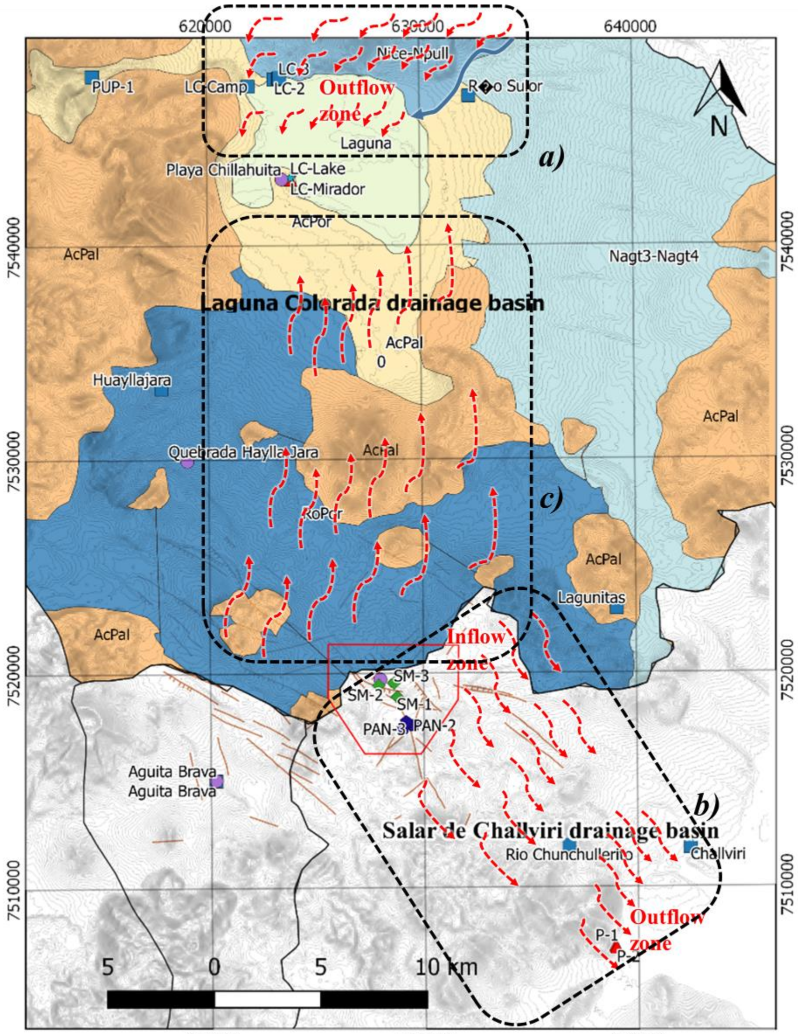

Figure 19: Ground water flows direction. a) North flank Laguna Colorada Lake; b) Challviri drainage basin; c) Laguna Colorada drainage basin.

5.3 Challviri Drainage Basin

The waters sampled from the Challviri drainage basin are from the Challviri cold spring, which is chloride immature water, Chunchellerito River that is bicarbonate water and the hot spring of Polques, which is sulphate water. They follow the local meteoric water line with heavier isotopic composition than the North flank of Laguna Colorada Lake and have been dated from five to fifteen thousand years ago. As for the samples from the northern flanks of the Laguna Colorada Lake, some water-rock interaction suggested by the concentration of conservative components. The extent of water-rock interaction increases with residence time and temperature.

The hot springs (Polques-1 and Polques-2) flow from ignimbrite rocks which indicates a hot source. Due to the far distance from the reservoir, the elevated temperature cannot be explained by a boiling process. Rather, it may be explained by conductive heat flow from the hot rock. Although their origin is considered to be meteoric, they show a positive oxygen shift (less than 2 ‰) suggesting oxygen isotope exchange with the host rock. Sandiffio and Alvarez (1992) suggest that the water comes from an ignimbrite hosted Pliocene aquifer, located north of the springs and which feeds the Polques and Challviri springs. As shown in the Figure 19, the flow direction might be from north to south.

The different isotope signatures can be explained by the distance from the coast; the Challviri basin is located 200 meters higher and further to the southwest (i.e. closer to the ocean) than Laguna Colorada and the prevailing wind blows from southwest to northeast. However, samples have different flow regime, experience, and time-scale while process of recharging and infiltrating underground.

5.4 Geothermal Reservoir

The samples from the Sol de Mañana geothermal system (SM-wells) have a temperature around 260°C and a conductivity of 22,000 μS/cm measured in the liquid phase. The chemical composition of the reservoir liquid as well as the geothermometry were calculated using WATCH program and water/gas geothermometers respectively by Villarroel (2016), and yielded a classification of completely mature and chloride neutral water at a temperature of 260°C.

Isotopic data shows δD of -83.8 to -89.5 ‰, and although the source of this water is meteoric in origin the oxygen isotope shift and the solute concentrations show that it has undergone significant water rock interaction - about 100 times more than the cold springs and 1000 times more than the shallow groundwater and the rivers. The isotopic delta diagram indicates a recharge from the two drainage basins. No age determinations have been carried out on the geothermal brines.

Figure 20 summarizes the regional, intermedia and local flow systems in the survey area based on the isotopic and chemical composition of the samples.

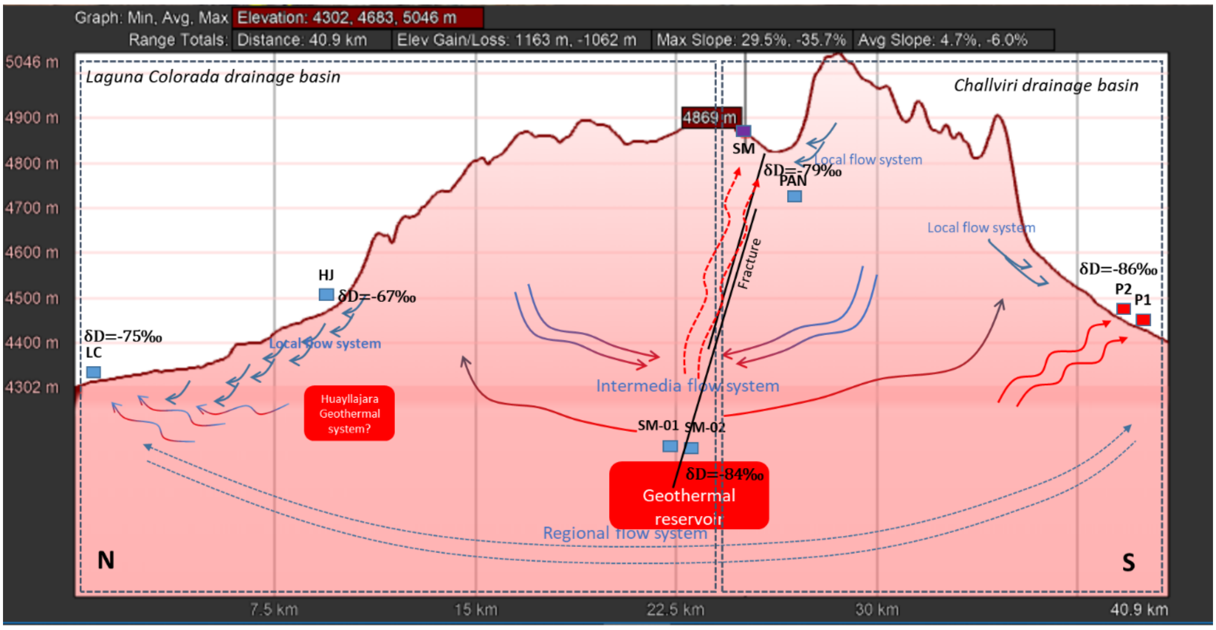

Figure 20: Conceptual model of the ground flow water.

6. CONCLUSIONS

Based on the chemical and isotopic composition of the 26 samples collected, four different types of water have been identified.

Hot and cold springs have constant flow rates (3 to 60 L/s) and discharge old waters dated from about 3,000 to 15,000 years ago. As in its current state, the survey area has negative water balance and arid characteristics, is cannot provide enough water for the springs. Therefore, it is likely that the aquifers supplying the springs have been recharged during the last humidity season (8,000 y.a.).

The concentrations of conservative components such as boron and arsenic and their relation to chloride concentation suggests some water-rock interaction in many of the samples. The extent of the water-rock interaction depends on the temperature and the residence time of the water, in increasing order from the surface waters and shallow ground water toward the reservoir and largely following the component concentration ratios of the ignimbrite.

Two water drainage basins and their corresponding flow systems have been identified; Laguna Colorada located in the north side of Sol de Mañana, and Challviri on the south side. The Sol de Mañana geothermal reservoir is located near the watershed and is recharged by a mixture of the regional ground water flow system of both basins.

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