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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 surface 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 MW_e, 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 collected 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, mud pools and the shallow groundwater indicate a sulphate type while a third type of water was found in cold springs and shows 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 and 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 $\delta^{18}\text{O}$ and δD mainly indicate a meteoric water source and show water-rock interaction as well as high temperature processes in the geothermal reservoir and boiling in the mud pools. ^{14}C was used to date the samples to around ten thousand years ago what was also confirmed by 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 in South America located on the border of “The ring of fire”, characterized by the subduction between the South America and Nazca tectonic plates. As a result, Bolivia has substantial geothermal potential. In the 1970s, the Bolivian Geological 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 the most important: Laguna Colorada, Empexa and Sajama. Figure 1 shows the location of all geothermal sites in Bolivia (Delgadillo, 2000).

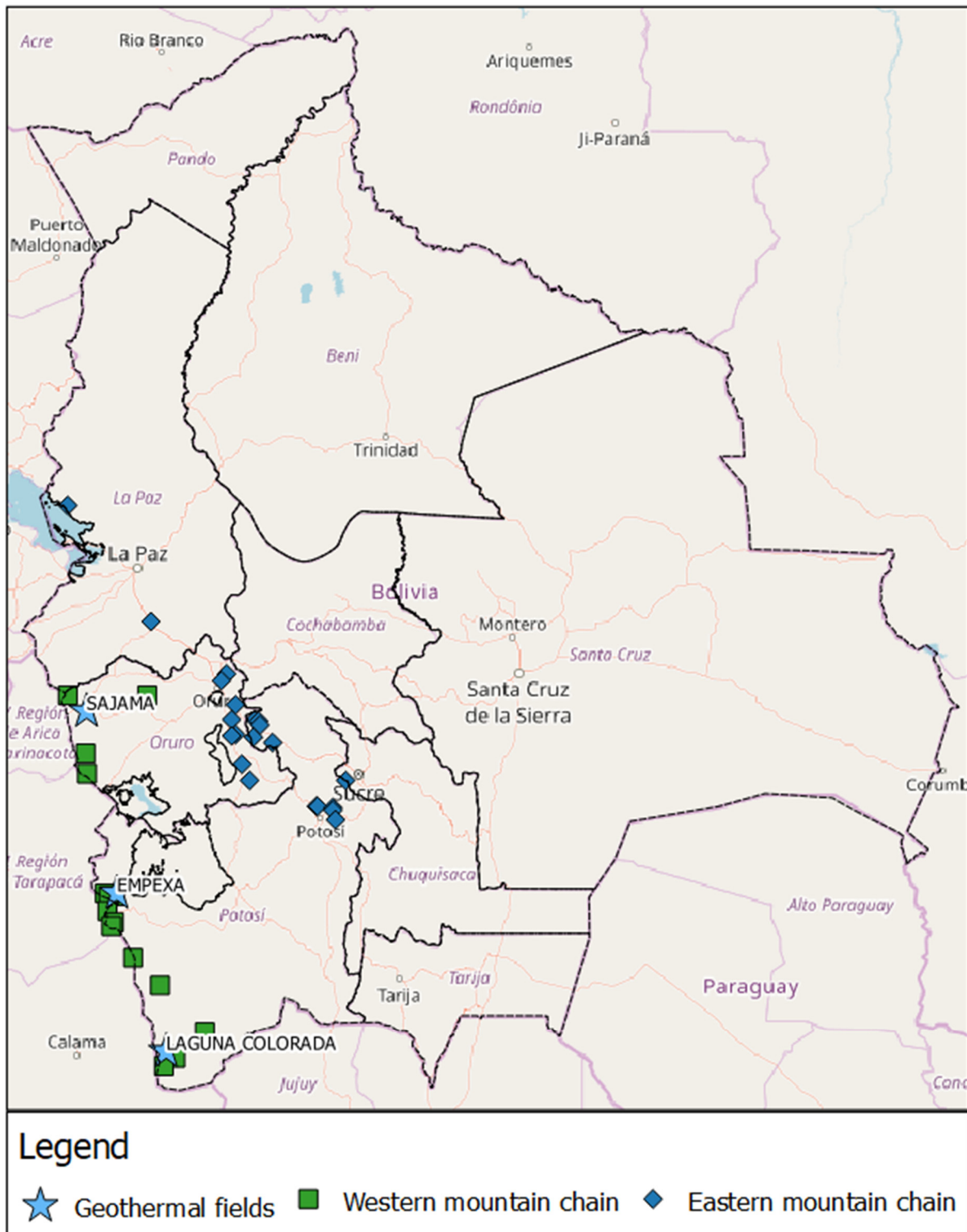


FIGURE 1: Geothermal sites in Bolivia (modified from Carrasco and Delgadillo, 1976)

Since then, all efforts for the geothermal development have 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 a temperature of around 260°C. However, due to political reasons, the project was suspended until 2008 (Bona and Coviello, 2016).

Following a political change in 2008 renewable energy sources became a priority again and WestJEC and Japan International Cooperation Agency (JICA) carried out a feasibility study for a 100 MW_e geothermal plant (JETRO, 2008) confirming the potential of 100 MW_e for 30 years in the Sol de Mañana field (JICA, 2013). Therefore, ENDE is currently working on steps to develop the geothermal field further, 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. This information is crucial to find the optimal production strategy and area 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.

2. BACKGROUND

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 ranging 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 million 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 mostly 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 prospect and is of medium Miocene age. Later, upper Miocene lavas (Lmios) were deposited in a long 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 (Lplii) when the Cerro Muerto volcano was active along with small lava flows in the south, most of which were covered by a younger volcanic period (ENDE, 2010).

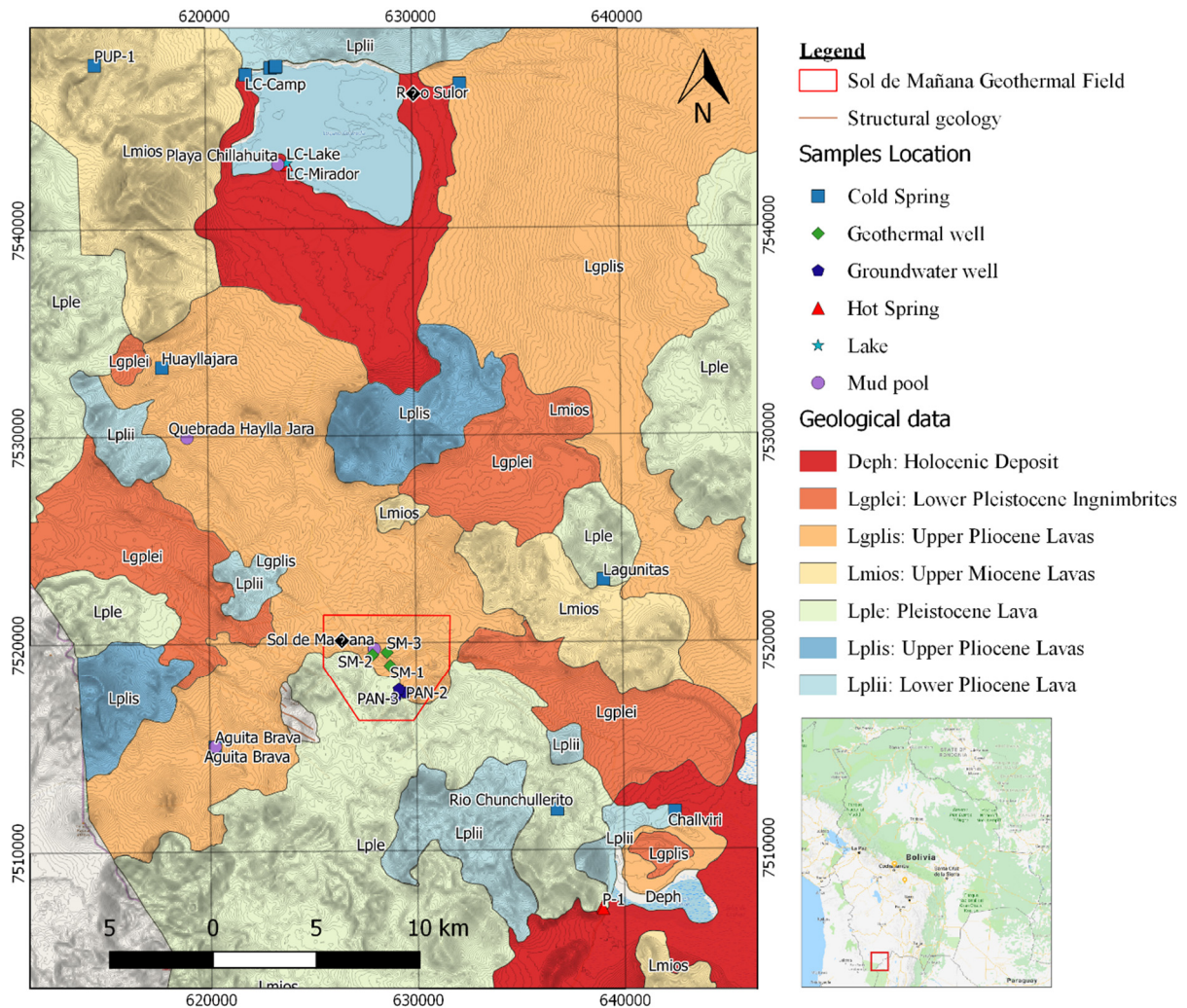


FIGURE 2: Geological map of the southernmost geothermal fields in Bolivia, including Laguna Colorada and Sol de Mañana sites (modified from Choque, 1996)

Upper Pliocene lavas (Lgplis), characterized by tuff and cracked rocks forming land flats, probably originate from a large heterogeneous flow in the N-S direction and are today covered by 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 in the upper Pleistocene. The latest volcanic events left prints of lava flows in the Pleistocene period (Lple), eruption from that period cover large parts of the survey area. Also, the Pleistocene volcanos Tocopuri, Apacheta and Putana have visible surface manifestations such as fumaroles which indicate current activity (Huaranca et al., 2016).

2.3 Hydrogeology

The survey area is located inside the closed drainage basin Altiplano. Two main drainage basins lead to the lake and salt desert, namely Laguna Colorada and Challvirí. 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 while the remaining springs emerge from Neogene period lavas. A hydrogeological map of Laguna Colorada area (including also the Sol de Mañana geothermal field) is shown in Figure 3 (ENDE, 2010).

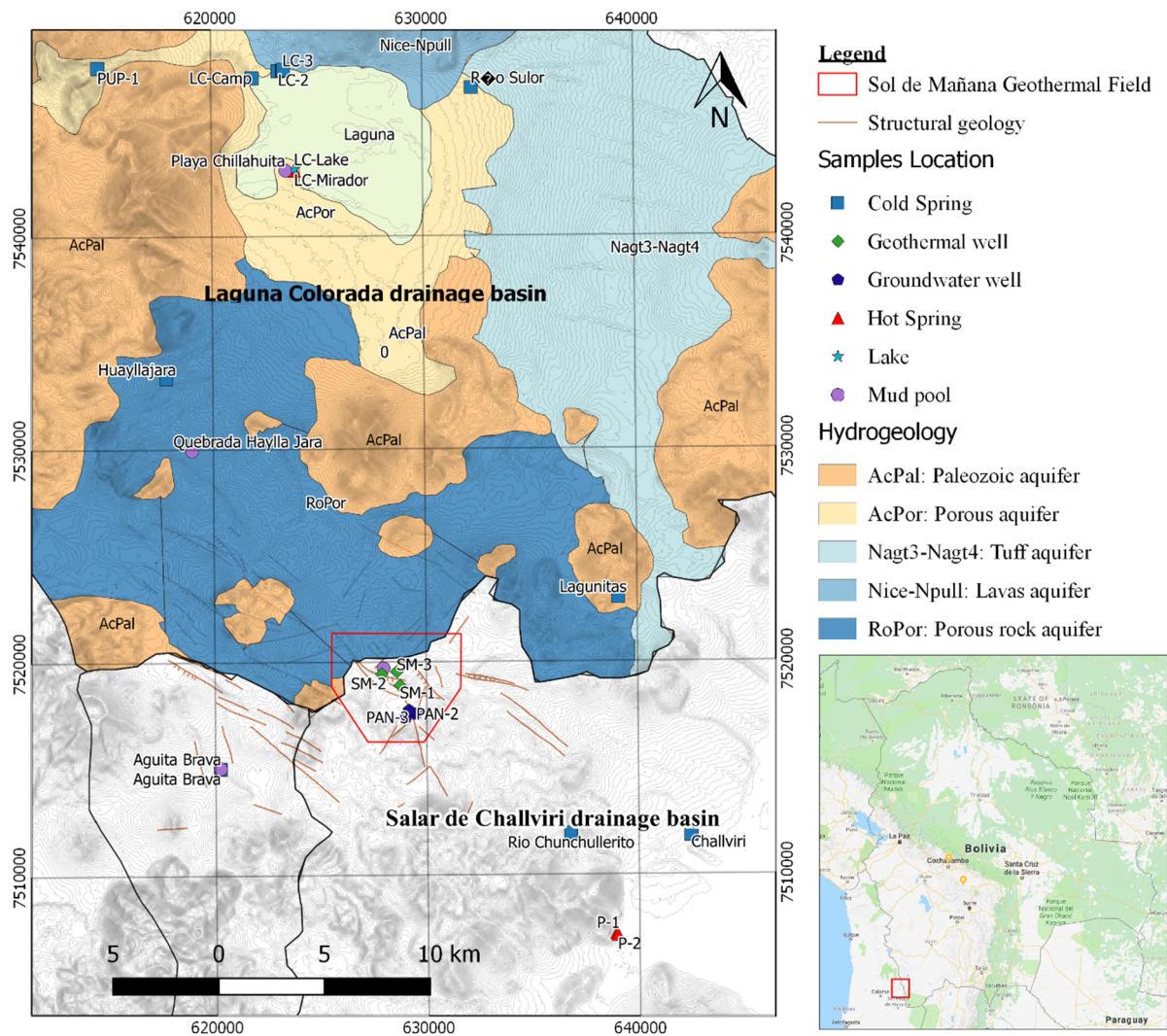


FIGURE 3: Hydrogeological map of the Laguna Colorada drainage basin (based on ENDE, 2012; MMyA, 2017)

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 Pabellón. In some cases, it is possible to observe erosion caused by the flow of water and snow, in other cases the topography consists of flat sand lands without any presence of water at the surface (ENDE, 2010).

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

- Groundwater aquifer in porous non-consolidated rocks* – found in quaternary sediments around the southern border of Laguna Colorada Lake, its use could be limited due to a possible salinization of the aquifers, it is assumed to be recharged by meteoric water.
- Groundwater aquifer in fractured rocks* – has medium to high productivity, representing 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. This groundwater type can be found, e.g. in the Sulor river.

- c) *Local limited groundwater aquifers (in 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 the Huayllajara and Sulor rivers, also receives concentric groundwater flow from the surrounding highlands.

From the north flank of the Laguna Colorada lake (Figure 4), the groundwater percolates down through fractured volcanic rocks before reappearing 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 sand and gravel sediments. This gives rise to a few hot springs on the southern side of the lake. Underneath, groundwater flows in the ignimbrite basement rocks.

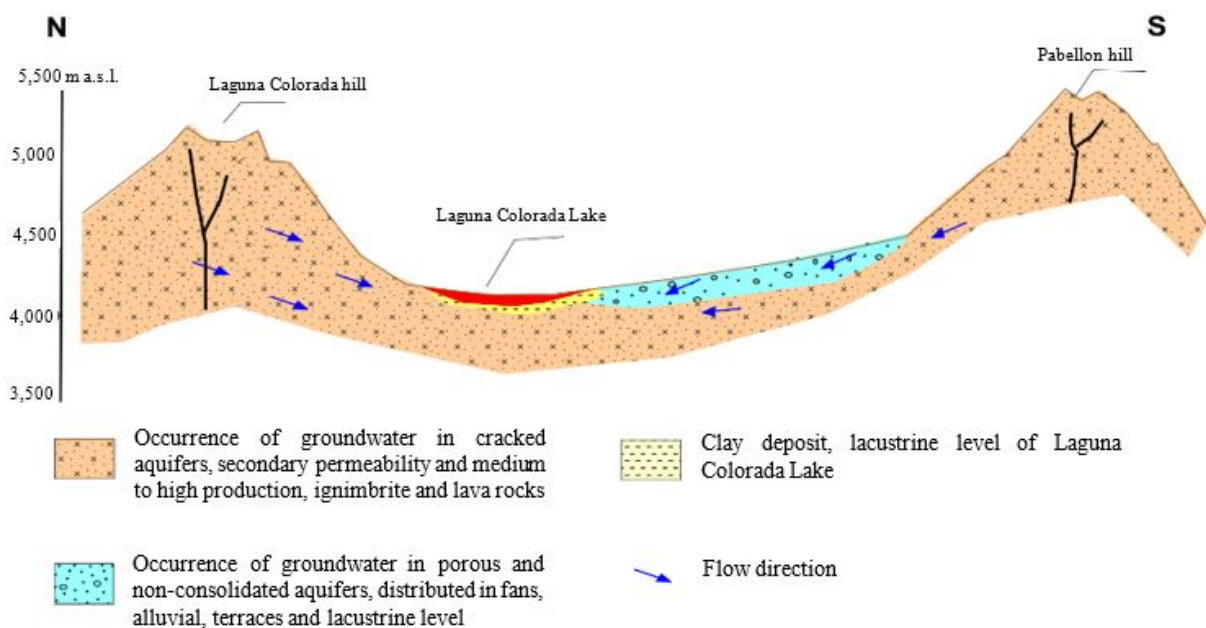


FIGURE 4: Hydrogeological cross-section for Laguna Colorada drainage basin (MMyA, 2017)

Regarding the hydrologic balance of the lake, precipitation in the survey area is around 77 mm per year with more rain in December to April as shown in Figure 5. On the other hand, the estimated potential evaporation 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 an arid zone (E) according to the Thornthwaite climate classification (Campero, 2014).

2.4 Surface exploration

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

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

- The geothermal fluid is meteoric water heated to 270°C due to a magma chambers.

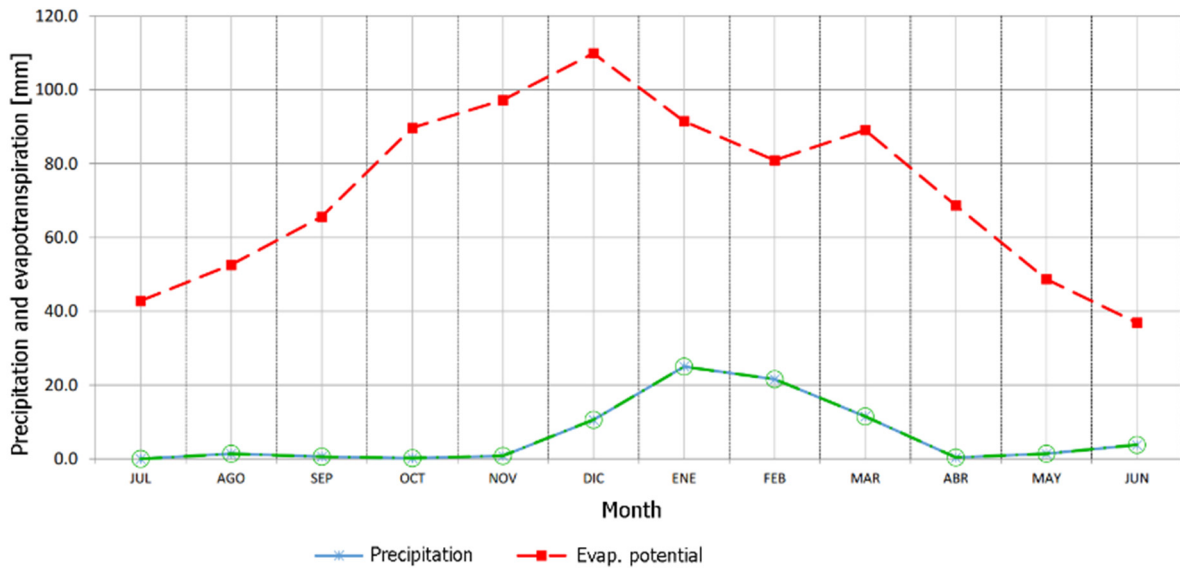


FIGURE 5: Precipitation and evaporation for Laguna Colorada drainage basin (Campero, 2014)

- 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 while the circulation fluid pattern that alters the rocks is related to the fracture system.

In 2014, a magneto-telluric survey was carried out in order to obtain more information and extend the exploration area to Apacheta (located ~9 km southwest of Sol de Mañana). Figure 6a shows a map with gravimetric and resistivity anomalies including Apacheta and Sol de Mañana, and Figure 6b shows a resistivity cross-section from west to east in the same

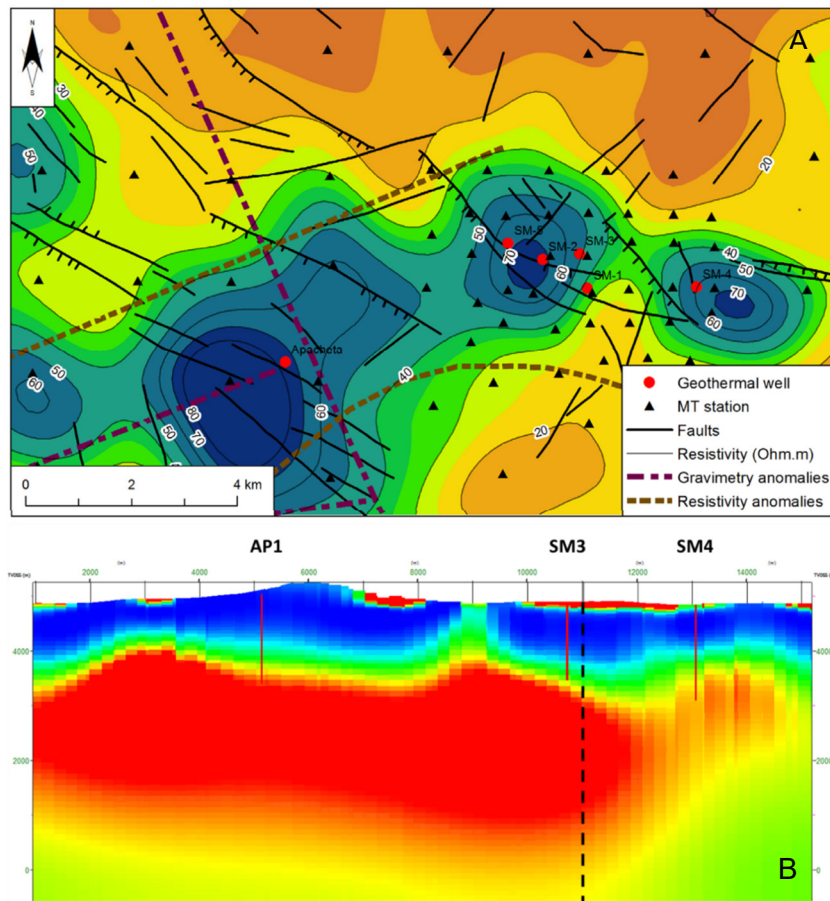


FIGURE 6: a) A resistivity map at 3500 m a.s.l. with gravimetric and resistivity anomalies of the Sol de Mañana area, including Apacheta (modified from JETRO, 2008); b) MT resistivity cross-section stretching from Apacheta through Sol de Mañana (Espitalier et al., 2015)

area. The reservoir could be located inside the two main anomalies seen on the map and the cap rock would be the rock with a resistivity of around 30 Ωm (Ramos, 2014).

2.5 Geothermal exploration wells

The 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.

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.

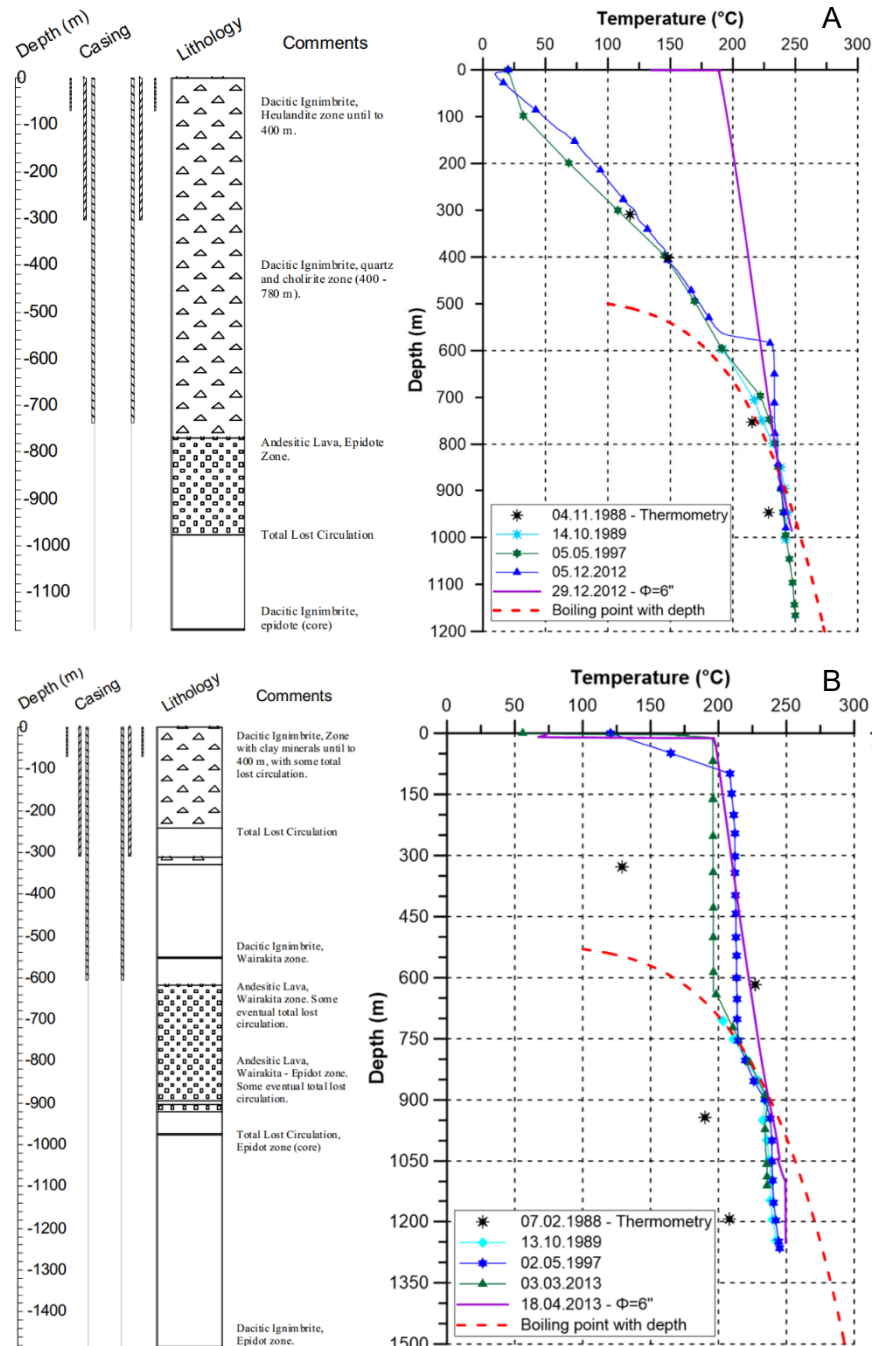


FIGURE 7: Lithology and temperature log for production well: a) SM-01; and b) SM-02 (modified from Ramos, 2015)

2.6 Groundwater wells

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

- Step 1: Borehole of 12 ¼”, @ 24 m depth, casing of 10 ½”.
- Step 2: Borehole of 9 ⅞”, @ 170 m depth, casing and filters of 8”.

Figure 8 shows the lithology of the wells:

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

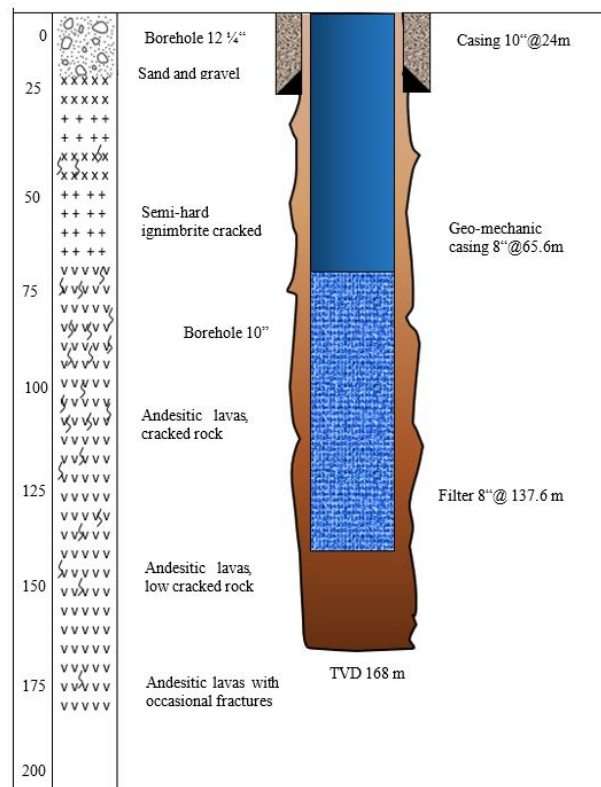


FIGURE 8: Lithology of the ground water wells in the Sol de Mañana field (modif. from ENDE, 2018)

3. METHODOLOGY

3.1 Field sampling and analysis of water samples

Analytical data must have certain levels of accuracy and reliability to be considered in the geochemical interpretation. Therefore, quality control is a concern in the laboratory. The precision of a method can be checked by repeated analysis of the same sample. Ionic balance (Equation 1) calculation is a way to check whether the sum of anions determined is the same as the sum of cations and is a valuable method to estimate the accuracy of the analysis (Ármansson and Ólafsson, 2006).

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

where Z_i = Charge of an ion; and
 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 with the most recent one being performed in 2018: Hidrogema (Huaranca et al., 2016) and Nippon Koei (2017) collected data in 2016 as well as JICA (2013) in 2013 and PNUD in 1989 (Neumann and Huaranca, 2018). Results from all surveys were considered in the present report.

Spectrolab and ENDE carried out a sampling survey in March and 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 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. Analyses were carried out using 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 concentration reported in this project is not completely reliable (Villarrol, 2014).

3.2 Classification of geothermal fluids

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

- a) *Alkali-chloride water*, with pH from 4 to 11, mostly sodium-potassium chloride waters.
- b) *Acid-sulphate water*, resulting from the oxidation of H₂S forming SO₄, 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, it can be formed from the oxidation of H₂S to SO₄ in alkali-chloride or sulphur rock dissolution followed by oxidation.
- d) *Bicarbonate water* might derive from CO₂ 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) refers 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 can form *secondary geothermal fluids* through various processes:

- *Depressurisation boiling*, forming a vapour phase and a boiled liquid phase;
- *Vapour condensation* produces steam heated water with high concentrations of sulphate or bicarbonate, commonly in shallow groundwater or surface water;
- *Mixing of CO₂ gas*, from a magmatic or another deep source with groundwater, and
- *Mixing of geothermal water* with shallow and/or cool 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-SO₄-HCO₃ 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 together with formulas describing equilibrium reactions and empirical relationships to find trends and characteristics of waters (Powell and Cumming, 2010).

3.2.1 Cl-SO₄-HCO₃ triangular diagram

One of the diagrams used for classification of water according to the scheme outlined by Ellis and Mahon (1977) is the Cl-SO₄-HCO₃ 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, i.e. its chemical composition suggests that it is in equilibrium with the relevant minerals. Therefore, it is recommended to classify water based on major anion concentrations. A diagram published by Giggenbach (1991) shows anion composition for four typical groups of thermal waters to evaluate compositional trends.

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:

$$S = C_{Cl} + C_{SO_4} + C_{HCO_3} \quad (2)$$

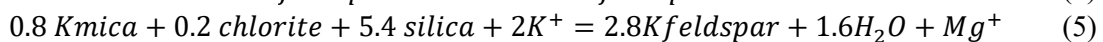
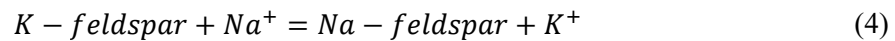
where S = Sum of all the concentrations; and
 C_i = Concentration of the anion in ppm.

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

$$Cl (\%) = 100\left(\frac{C_{Cl}}{S}\right); SO_4 (\%) = 100\left(\frac{C_{SO_4}}{S}\right); HCO_3 (\%) = 100\left(\frac{C_{HCO_3}}{S}\right) \quad (3)$$

3.2.2 Na-K-Mg triangular diagram

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



Similar to the previous diagram, each data sample is expressed as a point according to concentration of the three components, but the concentrations are scaled to correct for the difference in their typical relative concentrations in different waters:

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

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

where S = Sum of all the scaled concentrations and
 C_i = Concentration of the cation 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 this ascent, several processes may affect the water composition, for example mixing with shallow cold water can change the components concentration. 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 as boron, chloride and bromide are commonly used for this purpose (Ellis and Sewell, 1963; Arnórsson and Andrésdóttir, 1995). 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 ($^2H/^1H$) and $\delta^{18}O$ ($^{18}O/^{16}O$), 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 (equation 8), 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 (‰); and
 $\delta^{18}O$ = 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 from the geothermal field including isotopic composition from the El Tatio geothermal field, located in the Chilean Andes about 30 km NW of Laguna Colorada. They proposed a local linear relationship between $\delta^{18}O$ and δD with a slope of eight and an intersection around five (Sandiffio and Alvarez, 1992).

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

Some subsurface processes can change the isotopic composition of waters. One of them, water-rock interaction with high-temperature contact surface, can lead to an increase in the $\delta^{18}O$ isotope ratio while the δD ratio is 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 rocks become more depleted. This process leads to a positive shift of ^{18}O on the $\delta^{18}O - \delta D$ diagram (Ellis and Mahon, 1977).

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

3.3.2 Carbon isotopes

The CO_2 source in geothermal systems has been studied for a long time and two models have been developed in the attempt to explain it: a)

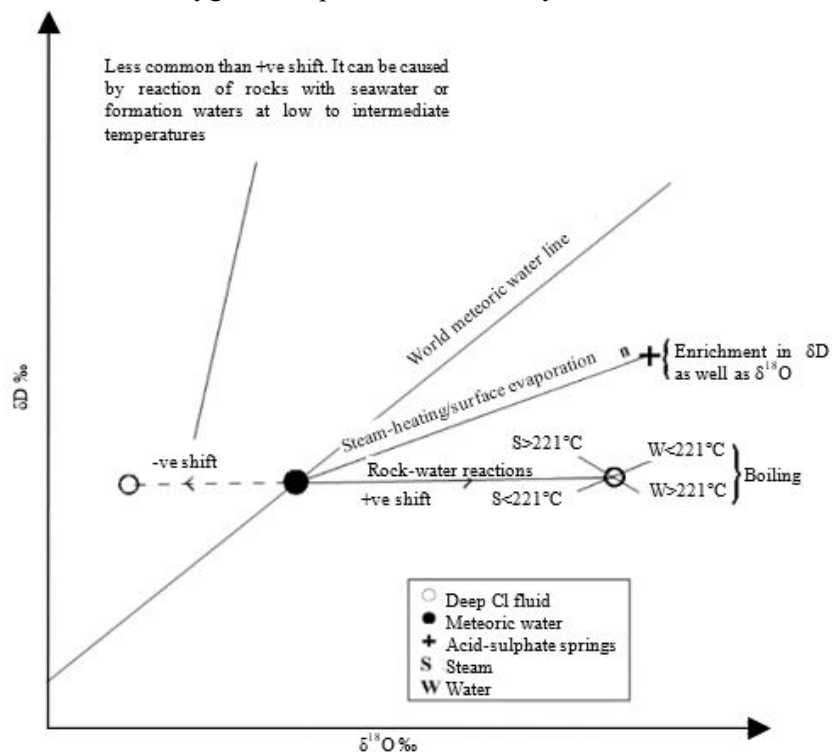


FIGURE 9: Schematic trend in isotope changes (Nicholson, 1993)

magma as main source of CO₂ at depth and b) fluid rock interaction in the geological system (Ellis and Mahon, 1977).

The two models complement each other, in fact, CO₂ and derived components could come from one or several of the following sources:

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

Additionally, the age distribution of different aquifers can be deduced by dating the age of springs using ¹⁴C contents which has a half time of $5,730 \pm 40$ yrs (Godwin, 1972). The source of this isotope is strong radiation at the upper boundary of the atmosphere. From there ¹⁴C 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 ¹⁴C contained is expressed as (Vogel, 1970):

$$A = A_0 e^{-\lambda t} \quad (10)$$

where A = Activity at time t ;
 A_0 = Initial activity;
 λ = The decay constant; and
 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 the 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 in the form of tracer and can be used to evaluate mixing of hot and cold water in ascending flow. Boron and chloride concentrations in rock vary both within volcanic and sedimentary rocks (Arnórsson and Andrésdóttir, 1995).

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 (Ellis and Sewell, 1963).

3.3.5 Deuterium-chloride relationship

Deuterium isotopic information together with chemical analyses of the water can give information about the groundwater flow and the chemical reactions that have taken place. In some cases, the groundwater, initially meteoric in origin, passes through chloride rich formations whereby it acquires considerable amounts of chloride while the deuterium content remains unchanged (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 in 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, since 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). Very high values (about 50 ppm) have been observed in the El Tatio geothermal field in Chile, which is situated about 30 km away from Laguna Colorada (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 intrusions, 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 can be said 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 to be mostly determined by the kinetics of the leaching process. Mixed waters tend to acquire characteristics intermediate between those (Arnórsson, 1985).

4. RESULTS

In total 26 water samples have been analysed; three from geothermal wells, four from groundwater wells, nine from cold springs, four from hot springs, four from rivers and surface waters and two from mud pools. Table 1 summarizes the chemistry parameters and composition of all samples.

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.

The ionic mass balance is used for quality control (Figure 10). Most of the samples have discrepancies less than 5% between cations and anions, but the ion balance error of seven samples lies between 5 and 10%. They are still considered reliable.

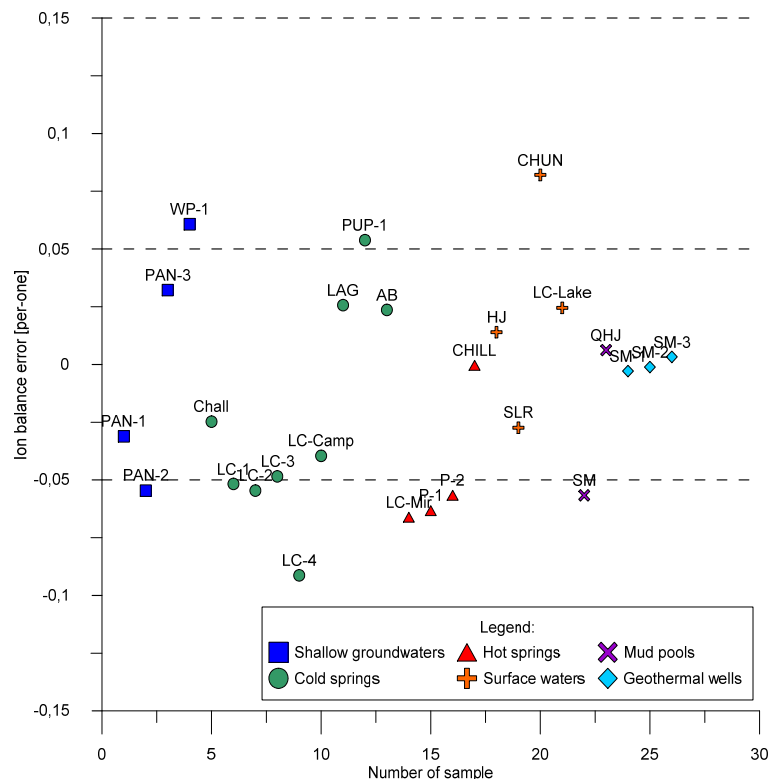


FIGURE 10: Ion balance error for all samples included in this work

TABLE 1: Chemical components concentration

N	Sample Label*	Date of collection	Source **	UTM east	UTM north	Elevation	Temp (°C)	pH	Cond (µS/cm)	Na (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)	SiO ₂ (ppm)	B (ppm)	Cl (ppm)	F (ppm)	SO ₄ (ppm)	HCO ₃ (ppm)
1	PAN-1 ^a	06.03.18	SW	629020	7517410	4,832	33.1	7.5	590.0	48.79	16.7	4.52	4.21	79.22	1.66	6.90	0.36	142.3	10.00
2	PAN-2 ^a	13.04.18	SW	629499	7517550	4,832	26.0	7.2	505.0	39.81	17.0	37.7	7.29	113.1	0.48	8.80	0.16	224.9	16.00
3	PAN-3 ^a	07.03.18	SW	629156	7517716	4,837	32.7	7.3	609.0	56.27	18.7	2.75	2.66	85.76	2.13	9.30	0.53	122.8	15.00
4	WP-1 ^c	22.01.89	SW			4,860	20.0	6.7	374.0	59.80	6.60	22.2	2.90	83.50		3.40	0.25	126.0	56.10
5	Chall ^a	06.03.18	CS	642469	7511805	4,398	18.7	7.4	829.0	125.6	8.03	1.84	1.69	64.52	1.97	175.9	0.32	46.40	26.00
6	LC-1 ^a	07.03.18	CS	623161	7547764	4,297	21.1	7.7	495.0	79.88	10.8	1.34	1.04	65.46	1.34	87.60	0.48	33.00	73.00
7	LC-2 ^b	16.04.14	CS	623377	7547795	4,300	21.4	7.8	474.0	55.04	10.1	9.62	2.93		1.93	61.00		49.16	62.10
8	LC-3 ^b	16.04.14	CS	623399	7547809	4,300	21.7	7.7	549.0	62.19	9.50	14.0	1.22		2.28	82.50		40.16	59.00
9	LC-4 ^a	07.03.18	CS	623426	7547839	4,299	22.0	8.2	493.0	83.37	10.3	1.13	1.00	60.36	1.53	97.00	0.51	30.40	91.50
10	LC-Camp ^a	07.03.18	CS	621943	7547443	4,291	20.2	7.9	993.0	172.3	15.1	0.85	0.83	68.94	3.15	204.6	0.41	95.40	59.00
11	LAG ^b	24.06.16	CS	639100	7523000	4,723	8.0	7.4	80.4	5.69	2.48	6.41	3.40	23.59	2.30	2.14		17.20	27.24
12	PUP-1 ^a	08.03.18	CS	614632	7547935	4,846	12.6	7.7	765.0	22.43	4.16	80.8	12.6	53.23	3.72	5.30	0.37	248.5	12.00
13	AB ^b	23.06.16	CS	620251	7515034		82.0	7.6	813.5	31.04	5.99	66.1	32.8	37.78	8.58	150.8		91.10	61.29
14	LC-Mir ^a	07.03.18	HS	623921	7543095	4,297	30.3	8.5	1,506	225.7	32.0	4.31	2.01	79.26	4.02	273.9	0.45	109.3	165.0
15	P-1 ^a	06.03.18	HS	638919	7507249	4,396	39.8	8.2	1,236	178.1	34.0	4.52	3.31	101.2	4.96	149.0	0.95	266.7	41.00
16	P-2 ^a	06.03.18	HS	638961	7507161	4,398	39.7	8.4	1,274	189.0	41.5	3.46	3.28	104.7	6.05	174.3	0.78	200.0	118.0
17	CHILL ^c	23.02.89	HS	623500	7543100	4,310	31.0	7.0	1,480	259.0	28.8	37.1	21.4	96.90	20.2	337.0		145.0	189.2
18	HJ ^b	14.07.16	R	617794	7533331	4,590	0.8	8.3	441.5	34.12	9.99	35.3	18.5	64.14	0.97	3.00		66.00	209.3
19	SLR ^b	25.06.16	R	632323	7546956	4,353	2.0	7.3	149.3	17.10	2.17	7.21	5.30	8.330	1.52	5.03		20.50	68.10
20	CHUN ^b	24.06.16	R	636771	7511924	4,459	5.0	7.6	262.4	44.64	1.72	14.4	1.94	43.71	2.15	13.07		36.50	79.45
21	LC-Lake ^b	19.06.16	R	623915	7543159	4,300	3.8	7.4	1,572	241.5	23.0	44.1	26.8	84.53	3.56	261.9		194.3	202.9
22	SM ^b	25.06.16	MP	627979	7519716	4,900	36.0	2.4	4,200	823.0	32.7	18.0	25.5	32.19	81.3	75.40		2,253	
	QHJ ^b	25.06.16	MP	618990	7529950	4,480	30.0	2.0	9,375	838.0	9.30	4.00	14.6	29.08	96.0	100.5		2,141	
23	SM-1 ^d	01.01.13	GW	628746	7518887		260	7.0		3,281	569	166	0.03	633.5	131	5,786	3.07	22.14	177.5
24	SM-2 ^d	25.04.13	GW	627895	7519430		258	7.1		3,208	548	151	0.02	1,046	127	5,583	3.20	22.72	217.1
25	SM-3 ^d	23.02.13	GW	628597	7519539		255	4.3	590.0	3,346	559	170	0.08	480.5	122	5,822	3.13	23.68	158.8

(*) According to the sample date, the laboratory of analysis are: (a) Spectrolab, located in the city of Oruro – Bolivia; (b) U.M.S.S.-C.A.S.A., located in the city of Cochabamba – Bolivia; (c) ENEL, located in Italy (Scandifio and Alvarez, 1992); (d) Thermochem, located in California – USA (Villaruel, 2014).

(**) The sample sources are: SW: Shallow ground water; CS: Cold springs; HS: Hot springs; L: Lake; R: River; MP: Mud pool; GW: Geothermal wells.

4.1 Chemical characteristics

Based on the diagrams shown in Figure 11, samples from the Laguna Colorada geothermal area represent all 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.

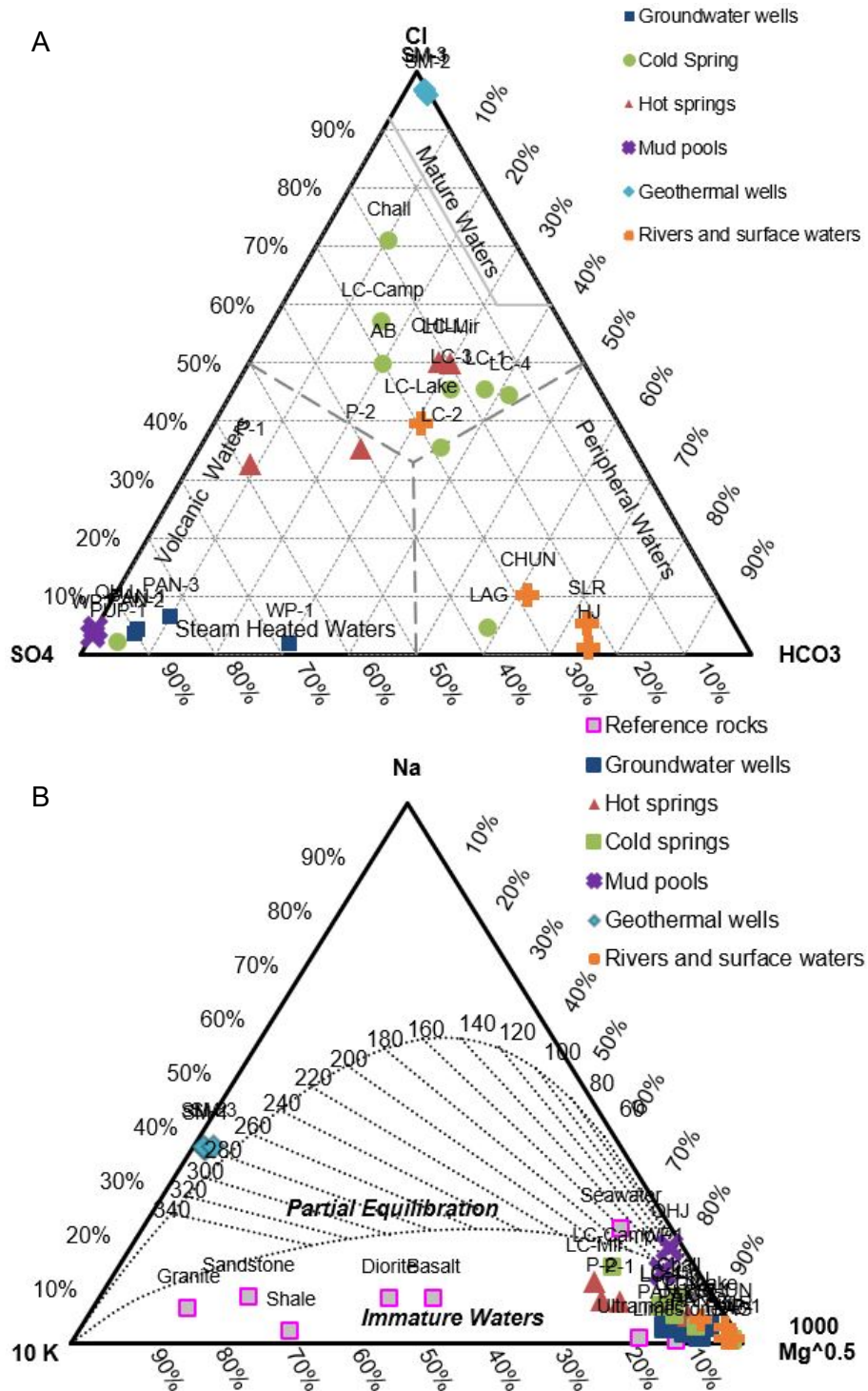


FIGURE 11: Ternary diagrams for Laguna Colorada geothermal area; a) Cl-SO₄-HCO₃ diagram; b) Na-K-Mg diagram

All samples from Sol de Mañana geothermal field are classified as immature water except for a mud-pool located in Huayllajara and the geothermal wells which are in equilibrium at a temperature of 260°C. Several water and gas geothermometers were employed by Villarroel (2014) showing average temperatures of 260 and 270°C, respectively.

4.2 Fluid origin

Summarized results of the isotopic analysis are shown in Table 2. Isotopic sampling 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 Figure 12) was calculated using results for the steam condensate, brine samples, and the steam fraction during sampling (retroactive 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 composition. This is commonly observed in geothermal fluids and is caused by reactions between the fluid and host rock which is typically enriched in ^{18}O .

TABLE 2: Isotope parameters of samples used in this work

No.	Sample name	$\delta^{18}\text{O}$ [‰SMOW]	δD [‰SMOW]	$\delta^{13}\text{C}^*$ [‰PDB]	$^{14}\text{C}^*$ [pmc]	^{14}C age* [a]	$^3\text{H}^*$ [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	Río 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, 2014)

Spring samples, even thermal hot springs such Polques or LC-Mirador, are located much closer to the local meteoric water line, indicating that the groundwater is recharged only by precipitation and has not reacted substantially with rock. A sample from Laguna Colorada Lake was also analysed and shows a

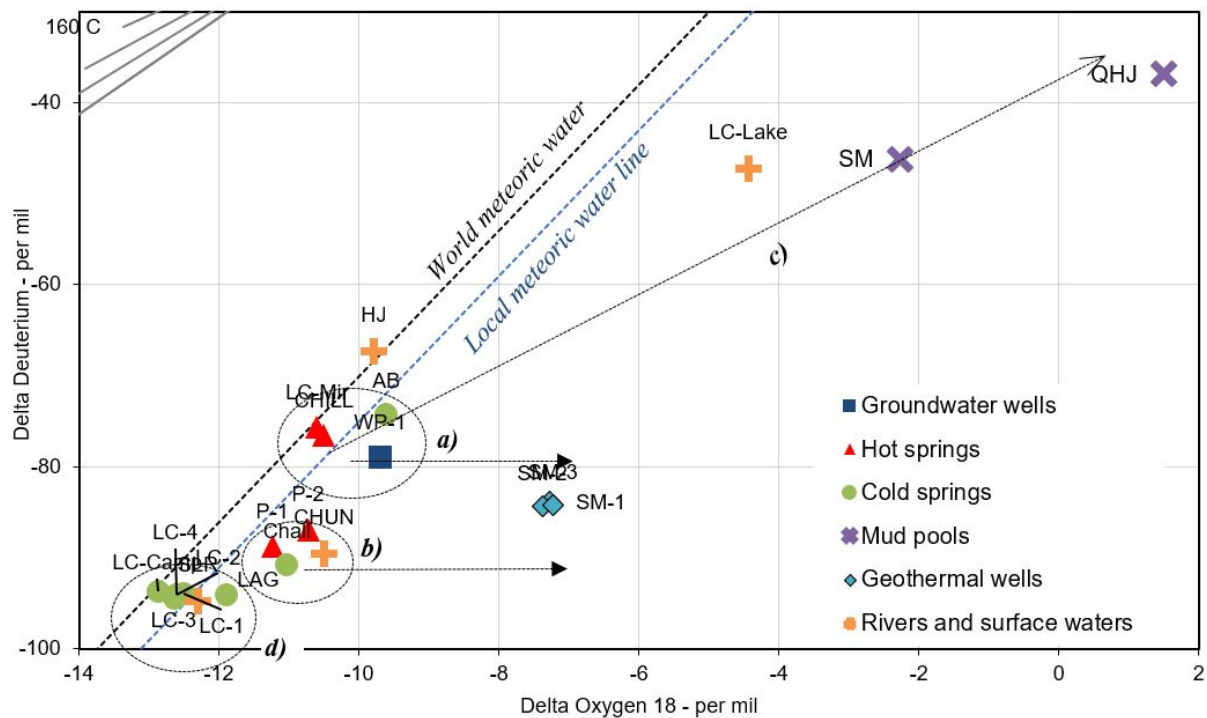


FIGURE 12: $\delta^{18}\text{O}$ and δD diagram a) ^{18}O shift in Laguna Colorada meteoric water due to water-rock interaction; b) ^{18}O shift in Challviri basin meteoric water due to water-rock interaction; c) ^{18}O and D enrichment due to evaporation from the mud pools; d) The most depleted water samples are found at the north flanks of the Laguna Colorada Lake

fractionation in deuterium and oxygen-18 where the isotope composition of the lake is more enriched (heavier) than in the springs. This is due to the evaporation of water.

Huayllajara mud pool shows higher oxygen-18 and deuterium values than the springs due to the evaporation and possibly water-rock interaction, i.e. dissolution of the surrounding rock and soil into the acidic fluid of the mud pool. However, fumarole isotopes composition analysed by Sandiffio and Alvarez in 1992 were found to follow a similar linear relationship as samples from El Tatio, Chile. Fumaroles were found to be sourced by 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 region is required. The climate in south and east Bolivia was extremely pluvial from 12,500 to 8,500 years ago during the so-called Tauca phase (Pasig, 2003) followed by a dry period which was repeatedly interrupted by short intervals of heavy precipitation. Currently, the precipitation is around 77 mm/a (Neumann and Huaranca, 2018).

The isotopic composition and the estimated age of the water were analysed by Neumann and Huaranca (2018) following their sampling survey in 2016. Six spring waters were analysed and dated from 2,900 to 15,600 years before present and two samples dated 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). That suggests that the main recharge of groundwater must have taken place relatively quickly during the short periods of heavy precipitation, although more recent water may have seeped into the ignimbrite aquifer at shallower levels. Evaporation of the water from the infiltration could have displaced the local meteoric line. However, it seems that fossil waters feed the hot springs, providing a constant flow despite 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 point lies 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 the thin layer of vegetation at the recharge location. A known relationship between ^{14}C and $\delta^{13}\text{C}$ can also be used for quality control. The younger the waters are, the more enriched they are in $\delta^{13}\text{C}$. This relation also observed at the project site, confirming the reliability to the dating estimation (Huaranca et al., 2016).

In the study area, waters samples have very low tritium content 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% of water precipitated after 1960. The low tritium values are consistent with the results of the age dating with the ^{14}C method (Neumann and Huaranca, 2018).

The chloride and boron relationship are shown in the Figure 13 together with 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 show the lowest concentrations, intermediate concentrations can be found in cold and hot springs while the geothermal reservoir has the highest concentrations. The graphic also shows a linear relationship between the concentrations in almost all the samples excluding mud pool and river samples. Concentrations in cold and hot springs are in concordance with values expected when mixing 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 have higher concentrations of boron than chloride with reference to the bedrock ratio. This could be due to dissolution of rock, which is richer in boron than chloride, or possibly condensation of boron-rich and chloride-poor steam in the mud pool.

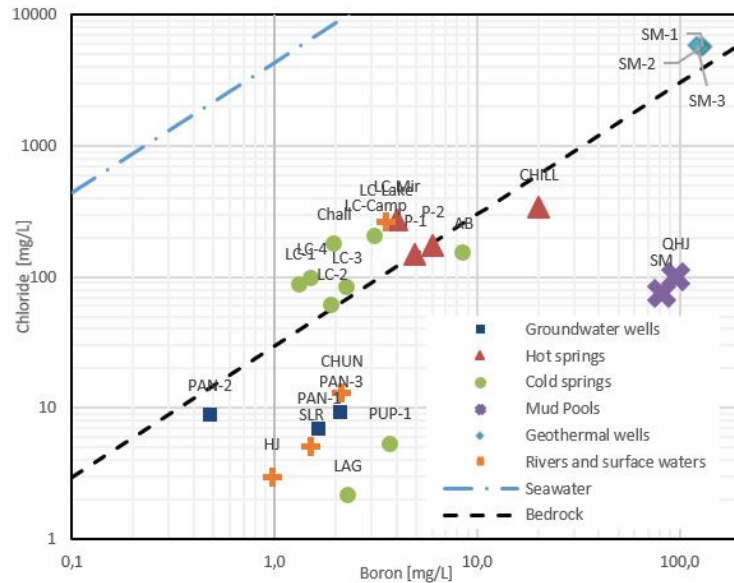


FIGURE 13: Relation between Cl and B

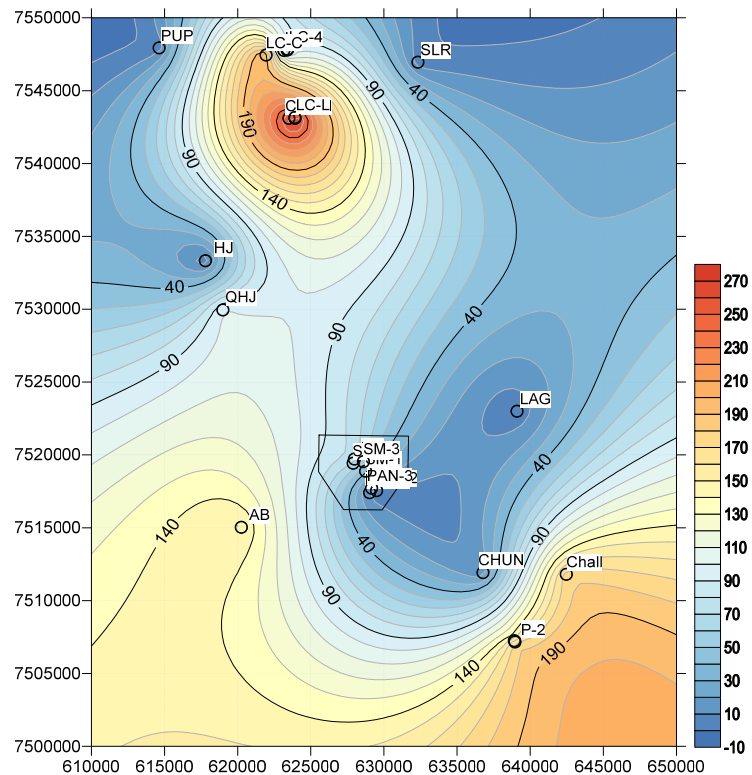


FIGURE 14: Contour map of Cl (ppm) concentration for the Laguna Colorada and Sol des Mañana sites

A contour map of chloride concentrations is shown in Figure 14 and illustrates the variation of chloride

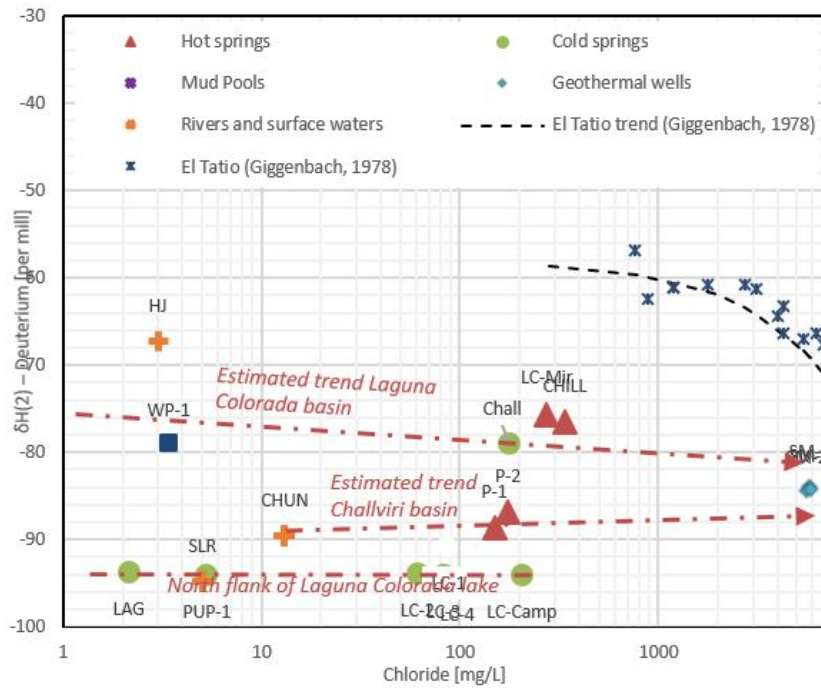


FIGURE 15: Deuterium (δD (‰)) chloride relationship for Laguna Colorada

concentration between the cold and hot springs. It can be observed that the southern border of the Laguna Colorada lake has higher concentrations than the springs located in the northern site. In addition, Polques and Aguita Brava have higher chloride concentrations.

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 the El Tatio geothermal field where he analysed chloride content of 5500 ppm and isotopic composition of -78 ‰ for deuterium. It was assumed that the well fluid and high chloride spring discharges are related by straight forward single step steam separation processes. The author also suggested that the considerable oxygen isotope shift observed was due to water-interaction or evaporation at above ambient temperatures caused by steam heating with the two processes affecting the thermal water during its migration, being steam separation and dilution by local meteoric waters (Giggenbach, 1978).

Under the same assumption, there could be a similar relationship for Laguna Colorada. Figure 16 shows the contour map for deuterium distribution in the area.

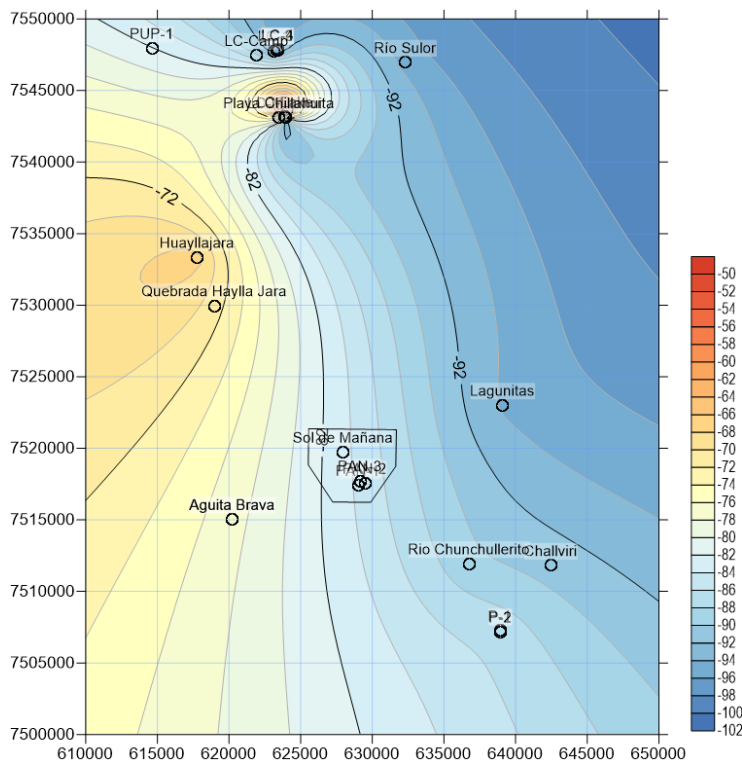


FIGURE 16: Contour map of δD (‰) without mud pools for the Laguna Colorada and Sol des Mañana sites

Laguna Colorada Lake and Challviri Lake have very high As concentrations (Figure 18). Other examples of geothermal fields with high As concentrations are Wairakei in New Zealand which reaches up to 5.2 ppm (Ritchie, 1961) and Los Azufres in Mexico which has concentrations 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.

The samples were classified according to their chemical characteristics. It was possible to differentiate the different sources of water and figure out a hydrogeological groundwater flow model. 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 ranges from 2,900 to 15,600 years. Aguita Brava and Polques located in Challviri basin discharge water which is 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 the mid-Holocene. This statement is reinforced by the results of the present study. Although the waters are relatively cold the concentration of conservative components suggest partial water rock interaction during the long residence time. However, there is little or no oxygen shift observed in the hot and cold springs on the delta plot, where these samples simply 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 grouped:

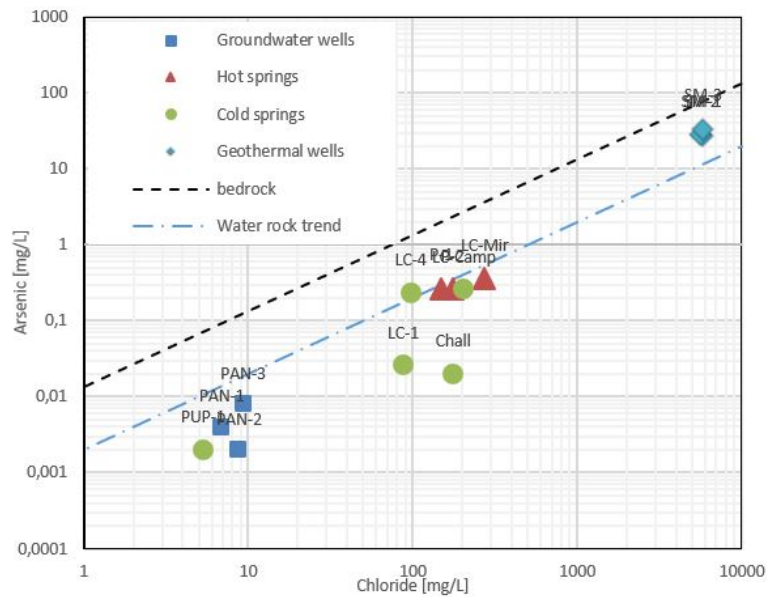


FIGURE 17: Variation of As with Cl (bedrock line based on Turekian and Wedepohl, 1961; water rock trend based on ENDE data)

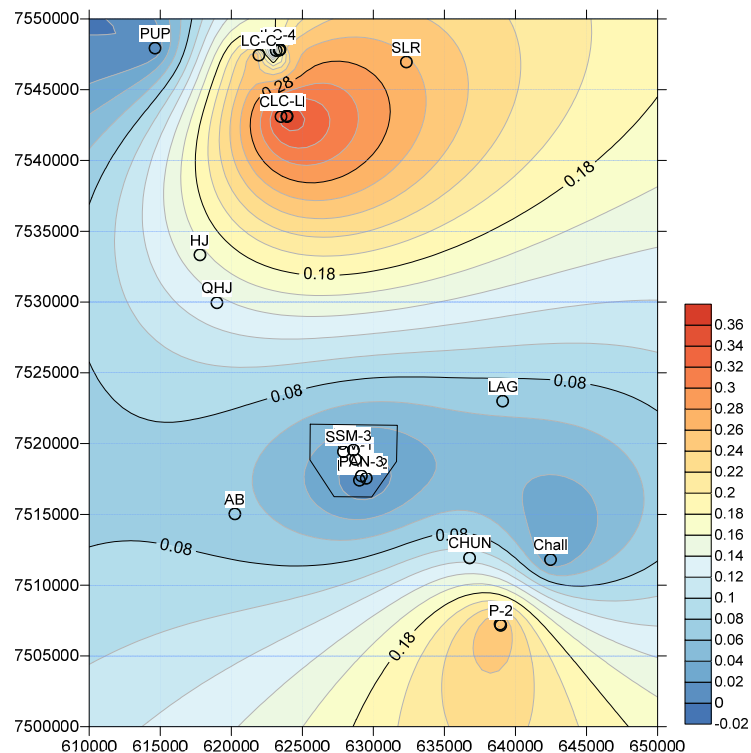


FIGURE 18: Contour map of As for the Laguna Colorada and Sol des Mañana sites, excluding the geothermal well samples

the PAN wells (Figure 3) which are sulphate waters 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 thousand 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 could be recent meteoric water in an inflow zone through the local flow system. PAN and WP01 both 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.

5.3 Challviri drainage basin

The waters sampled from the Challviri drainage basin are from the Challviri cold spring which is chloride immature water, the Chunchellerito River that is bicarbonate water and the hot spring of Polques which is sulphate water. They follow the local meteoric water line with more enriched isotopic composition than the Northern flank of Laguna Colorada Lake and have been dated to five to fifteen thousand years ago. As for the samples from the northern flanks of the Laguna Colorada Lake, some water-rock interaction is 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 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 been subjected to different flow regimes, experiences, and time-scales during the 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 $\mu S/cm$ measured in the liquid phase. The chemical composition of the reservoir liquid as well as the geothermometry were calculated using the WATCH program and water/gas geothermometers, respectively (Villaruel 2014). The samples were classified as completely mature and chloride neutral with 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.

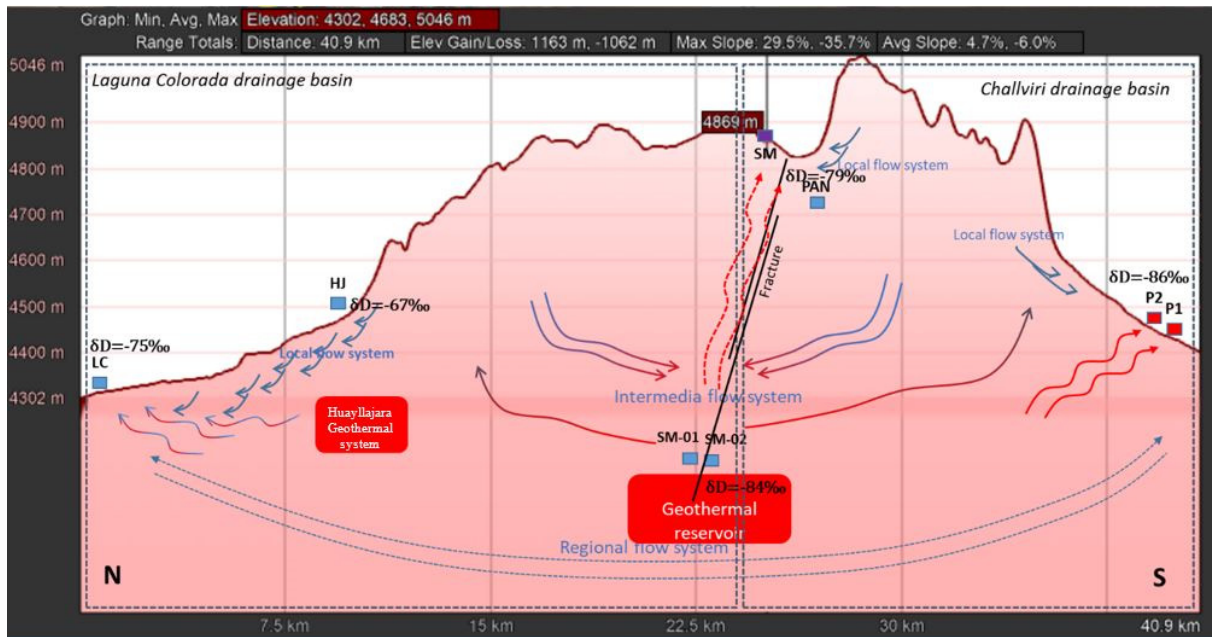


FIGURE 20: Conceptual model of the groundwater flow for Laguna Colorada and Challviri drainage basins

6. CONCLUSIONS

Based on the chemical and isotopic composition of the 26 samples collected, four different water groups have been identified: Cold springs north of the Laguna Colorada lake; water from springs in the Challviri drainage basin; spring and well samples from the Laguna Colorada drainage basin; and the geothermal fluid at Sol de Mañana.

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. In its current state, the survey area has a negative water balance and arid characteristics, and therefore cannot provide enough water to feed the springs. Therefore, it is likely that the aquifers supplying the springs have been recharged during the last humidity season (8,000 a).

The concentrations of conservative components such as boron and arsenic and their relation to chloride concentration 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. Evidence of water-rock interaction increase from the surface waters and shallow ground water toward the reservoir waters, with component concentration ratios largely approaching those of the ignimbrite.

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

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REFERENCES

- Ármannsson, H. and Ólafsson, M., 2006: *Collection of geothermal fluids for chemical analysis*. ÍSOR, Reykjavík, ÍSOR, report ISOR-2006/016, 17 pp.
- Árnason, B., and Tómasson, J., 1970: Deuterium and chloride in geothermal studies in Iceland. *Geothermics*, 2, 1405-1415.
- Arnórsson, S., 1985: The use of mixing models and chemical geothermometers for estimating underground temperature in geothermal systems. *J. Volc. Geotherm. Res.*, 23, 299-335.
- Arnórsson, S., 2000: Mixing processes in upflow zones and mixing models. In: Arnórsson, S. (ed.), *Isotopic and chemical techniques in geothermal exploration, development and use. Sampling methods, data handling, interpretation*. International Atomic Energy Agency, Vienna, 200-211.
- Arnórsson, S., and Andrésdóttir, A., 1995: Processes controlling the distribution of boron and chlorine in natural waters in Iceland. *Geochim. Cosmochim. Acta*, 59, 4125-4146.
- Arnórsson, S., Stefánsson, A., and Bjarnason, J.Ö., 2007: Fluid-fluid interaction in geothermal systems. *Reviews in Mineralogy & Geochemistry*, 65, 229-312.
- Axelsson, G., 2016: Nature and assessment of geothermal resource. *SDG Short Course I on Sustainability and Environmental Management of Geothermal Resource Utilization and the Role of Geothermal in Combating Climate Change organized by UNU-GTP and LaGeo, Santa Tecla, El Salvador*, 23 pp.
- Birkle, P., and Merkel, B., 2000: Environmental impact by spill of geothermal fluids at the geothermal field of Los Azufres, Michoacán, Mexico, *Water Air and Soil Pollution*, 124, 371-410.
- Bona, P., and Coviello, M., 2016: *Assessment and governance of geothermal projects in South America: a methodological proposal*. Economic Commission for Latin America and the Caribbean (CEPAL), (in Spanish), 178 pp.
- Campero, S.A., 2014: *Water balance, humidity conditions and climatic conditions of 124 weather stations*, SENAMHI, La Paz, (report in spanish), 512 pp.

Carrasco, R., and Delgadillo Terceros, Z., 1976: *Primary evaluation of geothermal resources in Bolivia*. United Nations, ENDE, GEOBOL, La Paz. Bolivia, (internal report in Spanish), 78 pp.

Choque, N.M., 1996: *Putana Volcano - Geological letter of Bolivia, scale 1: 100000*. Servicio Nacional de Geología y Minería de Bolivia, publication SGM Serie I-CGB-41 (in Spanish), 1 pp.

Craig, H., 1961: Isotopic variations in meteoric water. *Science*, 133, 1702-1703.

Delgadillo Terceros, Z., 2000: State of Geothermal Resources in Bolivia. Laguna Colorada Projec. *Proceedings of the World Geothermal Congress 2000, Kyushu- Tohoku, Japan*, 153-158.

Ellis, A.J., and Mahon, W.A J., 1977: *Chemistry and geothermanl systems*. New York. Academic. 1977. XI, 392 p.

Ellis, A.J., and Sewell, J.R.: 1963: Boron in rocks and waters of New Zealand hydrothermal areas, *New Zealand J. Sci.*, 6, 589-606.

ENDE, 1986: *Geothermal feasibility study in Laguna Colorada area, geoscientists surface studies*. Empresa Nacional de Electricidad (ENDE), Cochabamba, Bolivia, internal report (in Spanish), 98 pp.

ENDE, 2010: *Preparation studies for the Sol de Mañana geothermal project*. ENDE, internal report, (in Spanish), 250 pp.

ENDE, 2012: *Comprehensive analytical environmental impact assessment study (EEIA-AI) Laguna Colorada geothermal project and electrical transmission line*. ENDE, URS, internal report submitted to ENDE (in Spanish), 16-8 pp.

ENDE, 2018: *Groundwater study "Construction of water wells and alternatives to water supply"*, Empresa Nacional de Electricidad, internal report submitted to ENDE (in Spanish), 41 pp.

ENEL, 1991: *Geothermal feasibility study in Laguna Colorada area, feasibility final report*. ENEL, internal report submitted to ENDE (in Spanish), 395 pp.

Espitalier, J., Siffert, D., Corsini, M., and Yves, M. D., 2015: *Exploratory and conceptual data analysis Report No. 2*. Internal report submitted to ENDE (in Spanish), Kidova, Teranov, 130 pp.

Giggenbach, W.F., 1978: The isotopic composition of waters from the El Tatio geothermal field, Northern Chile, *Geochim. Cosmochim. Acta*, 42-7, 979-988.

Giggenbach, W.F., 1991: Chemical techniques in geothermal exploration. In: D'Amore, F. (coordinator), *Application of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, 119-144.

Giggenbach, W.F., and Goguel, R.L., 1989: *Collection and analysis of geothermal and volcanic water and gas discharges*. DSIR Chemistry report, CD 2401, 82 pp.

Godwin, H.: 1972, Half-life of radiocarbon, *Nature*, 195, 984-984, website: dx.doi.org/10.1038/195984a0

Greenberg, A.E., Connors, J.J., Jenkins, D., and Franson, M.A.H., 1980: *Standard methods for the examination of Water and wastewater* (15th ed). ADHA, AWWA-WPSF, Washington DC, 1134 pp.

Huaranca, W. R., Neumann C., and Vera, M. A., 2016: *Hydrogeological study for the identification of aquifers in the Sol de Mañana field area, Sur Lipez, Potosí*. Hidrogema, ENDE, internal report submitted to ENDE (in Spanish), 179 pp.

IBNORCA, 2005: *Bolvia guidelines NB 496 - Drinking water sampling*, Instituto Boliviano de Normalización y Calidad IBNORCA, first review, (in Spanish), 25 pp.

JETRO, 2008: *Study of feasibility for construction of the Laguna Colorada geothermal plant Potosi, Bolivia*. Japan External Trade Organization (JETRO), internal report submitted to ENDE (in Spanish), 269 pp.

JICA, 2013: *Project preparation for the project construction of Laguna Colorada geothermal plant*. Japan International Cooperation Agency (JICA), internal report submitted to ENDE (in Spanish), 185 pp.

MMyA, 2017: *Water and hydrological integrated balance of the Laguna Colorada unit with climate change analysis*. Environmental and Water Ministry (MMyA), internal report (in Spanish), 158 pp.

Neumann, C., and Huaranca, R., 2018: Hydrogeological exploration of groundwater in the arid and volcanically built western Cordillera of Bolivia. *Grundwasser – Zeitschrift der Fachsektion Hydrogeologie*, 23, (in German), 47-57.

Nicholson, K., 1993: *Geothermal fluids: chemistry and exploration techniques*. Springer-Verlag, Berlin, 268 pp.

Nippon Koei, 2017: *Report on interpretation of the geochemical study analysing if there is a connection between the geothermal system (geothermal reservoir and fumaroles) and surface aquifers*. Nippon Koei, internal report submitted to ENDE (in Spanish), 54 pp.

Pasig, R., 2003: *Origin and dynamics of groundwater in northwestern Chaco in South America*. Dissertation, Würzburg, Deutschland, (in German), 97 pp.

Peel, M.C., Finlayson, B.L., and McMahon, T.A., 2007: Updated world map of the Köppen-Geiger climate classification. *Hydrol. Earth Syst. Sci.*, 11, 1633–1644, website: www.hydrol-earth-syst-sci.net/11/1633/2007/

Powell, T., and Cumming, W., 2010: Spreadsheets for geothermal water and gas geochemistry. *Proceedings of the 35th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA*, 10 pp.

Ramos, P., 2014: *Updating the conceptual model and resource assessment - Laguna Colorada Geothermal Project*. Programa Regional de Entrenamiento Geotermico (PREG), University of El Salvador, San Salvador, El Salvador, final report (in Spanish), 39 pp.

Ramos, P., 2015: Well data analysis and volumetric assessment of the Sol de Mañana geothermal field, Bolivia. Report 30 in: *Geothermal training in Iceland 2014*. UNU-GTP, Iceland, 665-688.

Ritchie, J.A., 1961: Arsenic and antimony in some New Zealand thermal waters [Rotorua-Taupo region], *N.Z. J. Sci.*, 4-2,, 218-229.

Scandiffio, G., and Alvarez, M., 1992: Geochemical report on the geothermal zone of Laguna Colorada, Bolivia. *International Atomic Energy Organisation: Geothermal studies with isotopic and geochemical techniques, Technical Document IAEA/TECDOC, 641* (in Spanish), Vienna, 77-114.

Sergeomin, 2005: *Report about the geoscientific research carried out in Campo de Silala in December 2004*. Servicio Geológico y Minero Bolivia, internal report in Spanish, 54 pp.

Smedley, P.L., and Kinniburgh, D.G., 2001: A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17, 517–568.

Tabaco, F., Verma, M.P., Nieva, D., and Portugal, E., 1991: Geochemical and isotopic characteristics of carbon in the Los Azufres geothermal system, Mich., *Geofísica Internacional*, 30-3, (in Spanish), 173-178.

Truesdell, A.H., Nathenson, M., and Rye, R.O., 1977: The effects of subsurface boiling and dilution on the isotopic compositions of Yellowstone thermal waters, *J. Geophysical Research*, 82-26, 3694-3704.

Turekian, K.K., and Wedepohl, K.H., 1961: Distribution of the elements in some major units of the earth's crust. *Geological Society of America, Bulletin*, 72-2, 175-192.

Villarroel, D., 2014: Geochemical studies of geothermal fluid and evaluation of well test results from wells SM-01, SM-02 and SM-03, Sol de Mañana field, geothermal project, Laguna Colorada, Bolivia. Report 32 in: *Geothermal training in Iceland 2014*. UNU-GTP, Iceland, 697-720.

Vogel, J.C., 1970: Carbon-14 dating of groundwater. *Proceedings of Series Isotope Hydrology*, 1970, Vienna, 225-239.

Webster J.G., and Nordstrom D.K., 2003: Geothermal arsenic. In: Welch A.H., and Stollenwerk K.G. (eds), *Arsenic in ground water*. Springer, Boston, MA, 101-125.