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Geochemical Study of Thermal Waters Around Cordillera Sillapaca, Lampa, Puno, Peru

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ABSTRACT

In this study, a geological regional reconnaissance aimed to closer understand the hot spring systems related to geological units; also, it allowed the collection of representative samples such as rocks, precipitates and hot spring waters. Solid samples were chemically analyzed using X-ray diffraction. The thermal manifestations are surrounded by sedimentary and igneous rock units with an age range between the Cretaceous and Miocene; where the oldest rocks are sandstone and limestones of Cretaceous age (Hualhuani and Arcurquina Formations). The volcanic activities were developed during Oligocene to Miocene and volcanic deposits are distributed throughout the study area (Tacaza, Palca, Maure and Sillapaca Groups). The hot water manifestations occurred in areas with high and low sulphidation processes related to epithermal deposits of Au-Ag and Pb-Zn-Cu; minerals are associated to intrusive and/or subvolcanic bodies of dacite-andesitic composition. The structural geology shows that rocks are affected by the regional faults named as Lagunillas (NW-SE system), faults are active since Mesozoic times, and are visible as a parallel line to the axis of the Sillapaca Cordillera; rock permeability is the main factor for meteoric water filtration, circulation and geothermal systems recharge.

The thermal manifestations around Cordillera Sillapaca are basically hot springs with temperatures on the range of 18 to 83 °C, pH with values between 3.39 to 7.75 and electrical conductivity from 0.053 a 35.7 mS/cm. According to the geochemical interpretations the water samples are classified in Cl (mature waters), SO_4 (volcanic waters) and bicarbonate waters. The Piper diagram for two groups, Na.K-Cl and Ca.Mg-Cl.SO_4. The waters with high Cl concentration could be associated with reservoirs at depth, and during the ascent interacts with Paleocene-Eocene detritus rocks, or with evaporite environments associated with marine sedimentary rocks (probably from the Upper Cretaceous) with high B concentration. Geothermometers were used to estimate the temperatures of geothermal reservoirs based on the fluid-mineral equilibrium. All cases show that chemical components are not in equilibrium with minerals in the reservoir. The temperature estimation is <200 °C for Pinaya, while Jaraña, Atecata and Coline zones have low enthalpy systems with temperatures below 150 °C. It is an interpretation that reservoir rock contains sandstones (Hualhuani Formation) and conglomerates with calcareous matrix (Puno Group). The δ^2H and δ^{18}O isotopic diagram also show the meteoric water origin of hot springs.

The geological and geochemical result allowed proposing a conceptual model for the Cordillera Sillapaca. The heat source would be associated to a dacitic - andesitic subvolcanic body, similar to a dome with a radiometric age less than 1 Ma.

1. INTRODUCTION

The Sillapaca Cordillera is located on the southern of Peru, at the north side of Lagunillas Lagoon near to Arequipa-Juliaca highway; on the west and east side emerge geothermal fluids with temperatures on the range of 19.6 °C to 83 °C. The study area is located between the parallels 15°41'30" - 15°27' 03" and 71° - 70°45'20", the altitudes vary from 4,300 to 4,700 meters without evidence of recent volcanism. This area belongs to Santa Lucia and Paratia districts, Lampa province, Puno region. The geothermal manifestations are distributed in four areas: Jaraña, Pinaya, Atecata and Coline (Fig. 1).

The study shows the geochemical characterization for geothermal fluids and their relation with geology. The aim of the study was to understand the physical-chemical process affecting the fluids at depth (water-rock interaction, mixture) and the relation between geological and tectonic process, thus, rocks and faults. The fluid circulation through the shallow crust is particularly active because of three main reasons: (1) abrupt morphology; (2) perturbed vertical thermic profiles induced by subduction plates and the elevation of the mantle which is convenient for fluid convection (e.g. Oliver 1986, 1992; Sverjensky & Garven 1992); (3) active faults which provides open feeders for fluid circulation (Barnes et al., 1978).

2. GEOLOGY

The Sillapaca Cordillera is located between the boundaries of Occidental Cordillera and Occidental Altiplano (Carlotto et al., 2010). Hot springs are surrounded by sedimentary and igneous rock units, the range of age are between Cretaceous to Miocene. The oldest rock units are sandstones and limestones from Cretaceous located at the north - east area and recognized as Hualhuani and Arcurquina Formation. The oldest rock sequences are covered by conglomerate rock layers from Paleogene age, conglomerate outcrops are located at the west of Pinaya and recognized as Puno Group. The sedimentary rock sequences (Hualhuani Formation, Arcurquina Formation and Puno Group) were intruded by granodiorite and tonalite bodies from Oligocene. After this period, volcanism time lasted from Oligocene to Miocene; the volcanic sequences are distributed around the study area and were recognized as Tacaza, Palca, Maure and Sillapaca Group.

The petrography analysis shows that Hualhuani and Arcurquina formation at Atecata, contain sandstone with quartz and micrite limestone interbedded with thin thick layers of mudstone. The Puno Group (Eocene - Oligocene) has shale and mudstone layerings; the clastic rocks are covered by volcanic sequences from Tacaza, Palca, Maure and Sillapaca groups. The Tacaza Group has a thin sequence of lithic tuffs with a predominant sequence of andesitic lava on the base of the sequence. The average thickness of the sequence Tacaza Group in Pinaya is 200 m and in Jarpaña is 400 m. The Palca Group has welded lithic tuffs and crystal tuff with quartz, the thickness of the sequences varies from 280 to 350 m, and the ages are between 22 to 18 Ma (Cereceda et al., 2010). The Maure Group appears in few areas and contains interbedded sequences of limonite, limestone and sandstone of fluvial origin, the tick unit is 100 m. The Sillapaca Group has three main volcanic sources located in the following summits: Callatia, Turputa and Sillapaca (Fig. 1). The volcanic deposits contain andesitic lavas and breccias with gray to dark gray color, porphyritic texture and with plagioclase, amphibole and pyroxene minerals. Specifically, the lavas from Sillapaca Group in Callatia have few quartz with propilitic hydrothermal alteration and silicified rocks; lavas at Turputa have argillic hydrothermal alteration and advanced silicification. Finally, rocks are affected by regional faults, part of the Lagunillas fault system with NW-SE trends; faults are active since Mesozoic times and lineaments are visible parallel to the Sillapaca Cordillera (Fig 1).

The lithostratigraphy inside the study area allows confirming that before the volcanic events existed sedimentary sequences with quartz grains which in turn contains Si element (Hualhuani Formation). The carbonate rocks have Ca elements (Arcurquina Formation) and the clastic rocks contain Ca and Fe elements (Puno Group). The volcanic units have effusive events (Tacaza and Sillapaca Group), explosive (Palca Group) and erosion (Maure Group). Therefore, the volcanic sequences contain Fe inside the effusive events, Si inside the explosive events and Si-Ca inside erosion events. The percentage of elements was analyzed in chemical diagrams (Fig. 2).

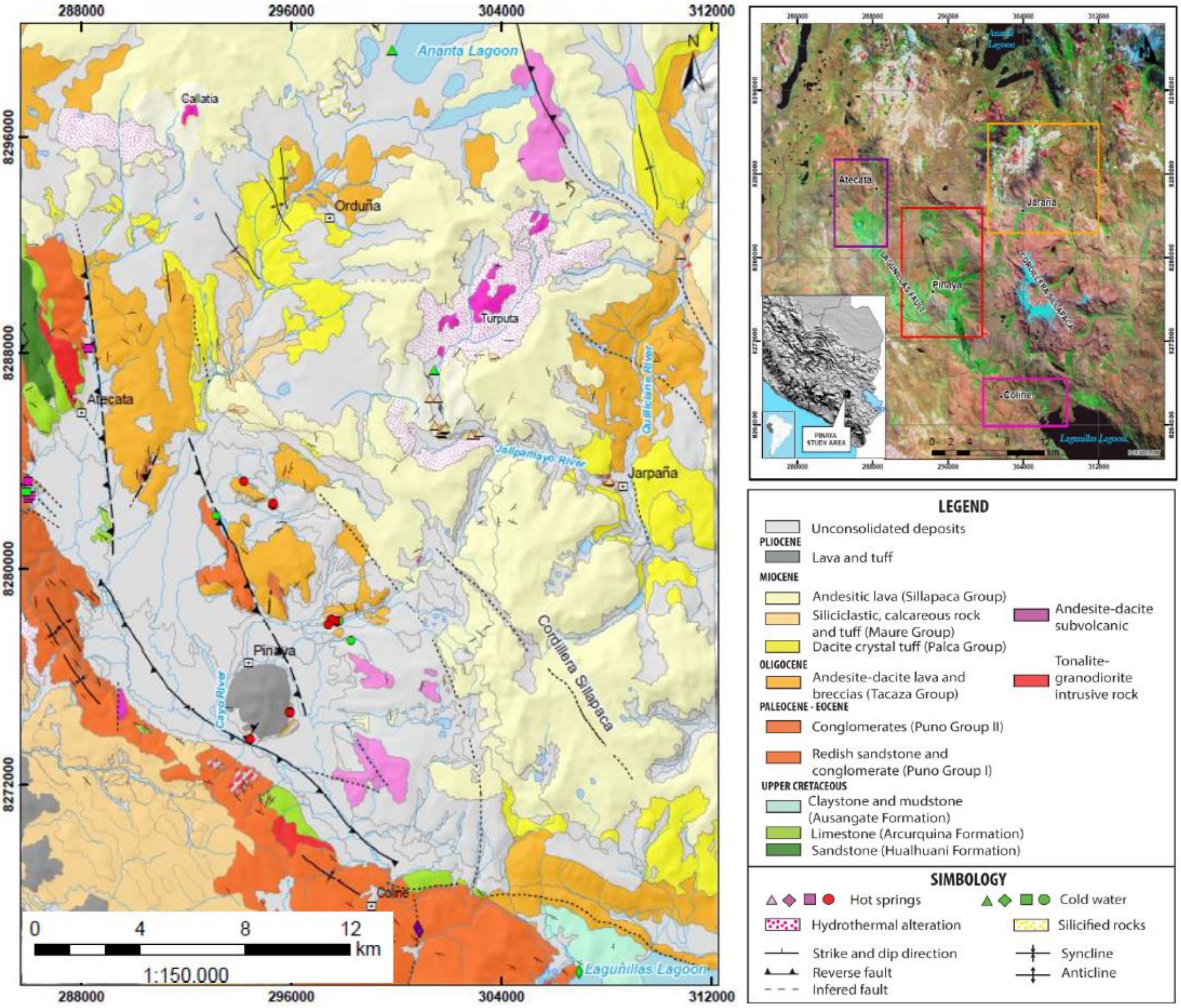

Fig. 1. Geologic map and hot spring location around Cordillera Sillapaca.

3. METHODOLOGY, SAMPLING AND ANALYSIS

The fieldwork around the Sillapaca Cordillera has an area around 700 km^2, the work was about the petrographic identification and description of lithologic rock units on surface. The chemical analysis on rocks was focused on lavas and tuffs. The lineaments were analyzed using satellite imagery and the geological structures were identified on outcrops around hot springs. Also, water, hot spring deposits, and rocks around thermal waters were sampled for future analysis.

Samples of water were collected from four geothermal areas around Sillapaca Cordillera and samples from lagoons were used as a reference for comparison. A total of 30 samples of water were collected using plastic bottles with high density. Three samples were collected for the analysis of dissolved cations (Li, Na, K, Ca, Mg, B, As, Si and trace elements). The first sample, after the filtration through a MILLIPORE filter of 0.45 μm, were acidified using ultra-pure HNO_3; a second one was taken without addition of acid, to determine anions (Cl, F, Br, SO_4 and CO_3, HCO_3) (non-preserved sample). And third sample, to determine the isotopic composition. The samples were important to explain the chemistry of the thermal water (Giggenbach y Goguel, 1989; Marini, 2000). During the fieldwork sampling, the outlet temperature (± 0,1 °C), pH (± 0,1 units) and electric conductivity parameters were measured using a multiparameter equipment (WTW 340I). The analyses were as follows: 1) dissolved metals (Li, Na, K, Ca, Mg, B, As, Si) by inductively coupled plasma mass spectrometry. 2) F, Cl, SO_4, by ion chromatography; using a Dionex ICS-2000 Ion Chromatograph, 3) SiO_2 by Molybdosilicate Method and 4) HCO_3 was analyzed volumetrically by titration with 0.1 N HCl. The accuracy and precision of the results were calculated analyzing certified materials and making repetitive analysis and sample dilution. The analytic error was less than 5 % (Murray and Wade, 1996). The isotopic analysis (δ^2H and δ^{18}O) was made in LaGeo laboratories at El Salvador using mass spectrometry (Delta S).

The precipitates at hot springs deposited around the hot springs hole (fresh and old) were collected randomly on the field. The quantity of the samples were not more than 200 gr and were analyzed with SHIMADZU XRD-6000 X-ray equipment, totally automated (Cu radiation), with a monochromator equipment CM-3121 for a Cu tube, scintillation detector of NaI (sodium iodide), energy of 40 Kv, 30 mA and presents a range sweeping from 2º to 163º. The diffractograms were programmed through the software PMGR-RXD-6000-V4.1 proper from the equipment. On the other hand, the radiometric ages K-Ar and Ar- Ar for rocks were analyzed on SERNAGEOMIN laboratories from Chile, using the spectrometer Argus VI (multicollector, CDD in ^{36}Ar); Thermo Scientific Laser of CO_2 (10.6µ); Photon Machines.

4. RESULTS AND DISCUSSION

4.1 Lithogeochemistry

The geochemical result of 32 samples in volcanic rocks collected from the Tacaza, Palca and Sillapaca groups were represented in TAS diagram (Total Alkali Silica) (Fig. 2A, Le Maitre et al., 1989), where shows the silica variation between 60 to 75 wt% and the total alkali is higher than 6 wt%. The Tacaza Group lavas are grouped inside the traquiandesite rock field; while the Sillapaca Group lavas are inside the calco-alkaline rock series which are typical from subduction setting. The volcanic event Callatia formed a group with the volcanic event Sillapaca, and the volcanic event Sillapaca formed a group with samples from the volcanic event Turputa (Fig. 2 A).

According to the K_2O vs SiO_2 diagram (Rickwood, 1989, Fig. 2B), the Tacaza and Sillapaca lavas have a high K (>3 wt%). Samples from the Tacaza Group have an intermediate composition; while samples from Sillapaca Group have a felsic composition. Lava samples from Tacaza Group plot inside basaltic-andesitic rock field; while lava samples from Sillapaca Group plot in the andesitic, dacitic and rhyolite rock field. The FeO total vs SiO_2 diagram (Fig. 2 C), shows the Tacaza Group and Callatia event plotted inside the medium and high content composition of iron (>4 wt%). Similarly, other groups of samples from Tacaza and Sillapaca groups have medium to low amount of Fe less than 2 wt%. Therefore, the Tacaza Group volcanic rocks have K_2O and FeO_{total} high comparing with Sillapaca Group lavas. The Sillapaca event plot in two groups between medium and low amount of FeO_{total}; also, Sillapaca Group lavas come from evolved magmas, regarding the amount of SiO_2.

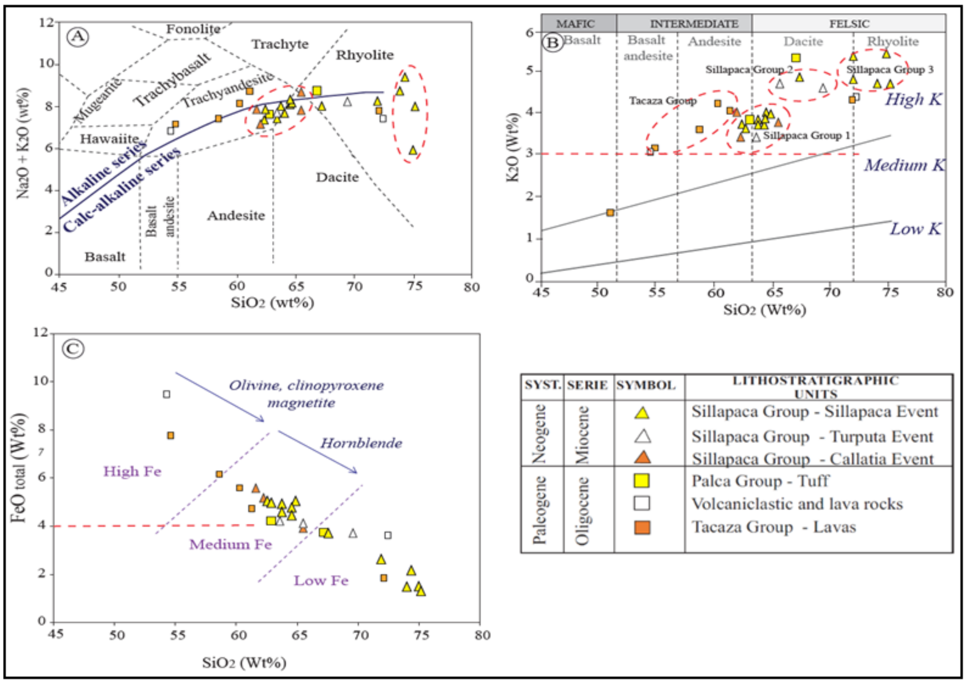

Fig 2. (A) TAS diagram (Total Alkali vs. Silica) (Le Maitre et al., 1989), (B) K_2O vs. Silica relation (Rickwood, 1989) and (C) FeO total vs. SiO_2 relation in volcanic rocks from Cenozoic.

The major elements such as MgO, CaO and Na_2O vs SiO_2 (Fig. 3 A, B y C) are represented in the Harker diagram (Harker, 1909), the diagrams shows that Tacaza Group lavas have high amount of MgO between 2 to 4.53 wt%. The volcanic rocks of Tacaza Group and Callatia event have CaO high, it varies between 4 and 8 wt% (Fig. 3 A y B). The diagrams MgO vs SiO_2 and CaO vs SiO_2 show a negative correlation, while the magmatic segregation increases. In the case of the diagram Na_2O vs SiO_2, most of the volcanic rocks have higher amount (more than 3 wt%) and the correlation is positive (Fig. 3 C).

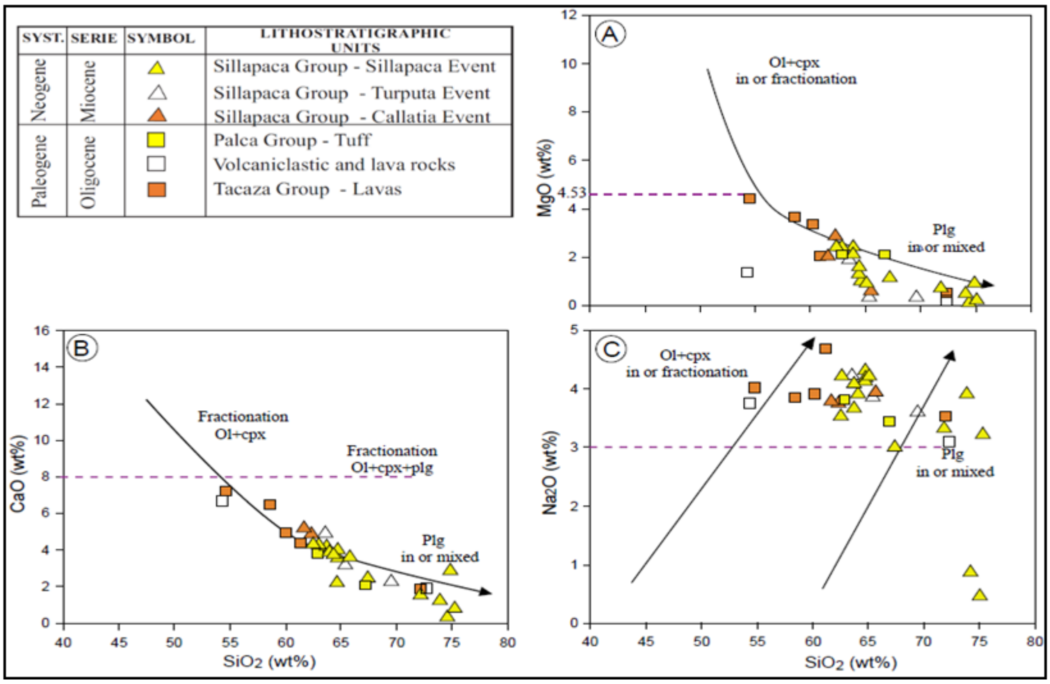

Fig. 3. A), B) and C) Harker diagrams for Cenozoic volcanic rocks.

4.2 Geochronology for lava rocks

The radiometric dating results obtained for the Turputa andesite (Sillapaca Group) is between 19.74 to 20.1 Ma (Table 01) and have a correlation with the age of Tacaza Group rocks at Orcopampa Mine (Swanson, 2002). From the results, three volcanic events could be identified: the first volcanic event is the subvolcanic intrusion which generates lava deposits; then, a second intrusion of subvolcanic bodies in Turputa were affected by hydrothermal and silicification process. Finally, a third lava event covers the andesitic lavas with hydrothermal alteration. The andesitic lava deposits located around the Cordillera Sillapaca, apparently have as a feeder the lineament NW-SE on the Cordillera Sillapaca where volcanic deposits could be seen on both sides of the slopes. The radiometric results in this study (13.19 to 14.87 Ma) are similar with the results obtained by Klinck et al. (1986) and Wasteneys (1990) (14±0.6, and 16.24±0.4 Ma, respectively). However, the radiometric dating results for the lava dome at Pinaya had an interesting result; andesitic rock have a plateau age between 863 ± 22 ka and 953 ± 95 ka, which represents an age less than 1 Ma and is relevant result for the identification of a heat source. The age results in Pinaya dome is important because it has a relation with recent magmatism and is suitable for a heat source for a geothermic reservoir at depth.

Table 01. Radiometric dating results around Sillapaca Cordillera

Samples Number	Location	Litology	Method	Material	Age	Error_ Ma (+/-)	Samples Number	Location	Litology	Method	Material	Age	Error_ Ma (+/-)
GE-38-2-2015-015	Turputa	Subvolcanic	K-Ar	Whole rock	19.2	0.8	GE-38-2-2015-030	Turputa	Andesite lava	Ar/Ar	Fundamental mass	19.99	0.02
GE-38-2-2015-020	Atecata	Dacite subvolcanic	K-Ar	Biotite	25.7	0.1	GE-38-2-2015-031	Turputa	Andesite lava	Ar/Ar	Fundamental mass	19.97	0.02
GE-38-2-2015-022	Pinaya	Andesite-dacite subvolcánic	Ar/Ar	Biotite	0.842	0.22	GE-38-2-2015-033	Cordillera Sillapaca	Andesite lava	Ar/Ar	Fundamental mass	14.87	0.02
GE-38-2-2015-022	Pinaya	Andesite-dacite subvolcanic	Ar/Ar	Amphibole	0.953	95	GE-38-2-2015-035	Cordillera Sillapaca	Andesite lava	Ar/Ar	Fundamental mass	14.161	0.014
GE-38-2-2015-023-A	Turputa	Andesite-dacite subvolcánic	Ar/Ar	Fundamental mass	20.01	0.04	GE-38-2-2015-038	Turputa	Andesite lava	Ar/Ar	Fundamental mass	19.91	0.02
GE-38-2-2015-027	Turputa	Andesite lava	Ar/Ar	Fundamental mass	20.1	0.05	GE-38-2-2015-042	Cordillera Sillapaca	Andesite lava	Ar/Ar	Fundamental mass	13.19	0.02
GE-38-2-2015-028	Turputa	Andesite lava	Ar/Ar	Fundamental mass	19.74	0.02							

4.3 Geochemistry of geothermal fluids

Hot springs around Cordillera Sillapaca have a temperature between 18 to 83 °C, the pH values are on the range of 3.39 to 7.75, the electric conductivity is between 0.053 to 25.7 mS/cm and discharge values oscillate in 0.2 to 12 L/s. Most of the hot springs have high values of Cl and SO_4, the values are on the range of 105.2 to 12983 mg/L and 29.1 to 1874 mg/L. The chemistry ratio SO_4/Cl is high for waters with low pH values, which indicate that associated with hydrothermal alteration zones and mixing processes occur between three water types: acid-sulphate waters, chloride water and meteoric water. Besides, thermal waters contain high concentration values in elements as it follows: Na from 260 mg/L to 6459.7 mg/L, K from 5.4 mg/L to 544 mg/L and for Ca and Mg from 26 mg/L to 1479.9 mg/L and 12.3 mg/L to 169.9 mg/L. Also, trace elements (Si, B, As, Rb, Cs, Sr, Co, Cu, Ti, Zn, Mo, Mn, Sb, Fe, and Ni) are present in thermal waters (see more results in: http://geocatmin.ingemmet.gob.pe/geocatmin/ go to: Geotermia/evaluación geotérmica.

4.3.1 Water chemistry

The water analysis results are represented on the ternary diagram Cl-SO$_4$-HCO$_3$ (Giggenbach, 1988; Fig. 4a). The diagram shows that waters from Cordillera Sillapaca zone plot in the Cl (mature waters) and SO$_4$ (volcanic water) fields. However, two samples (32U-P-14A and 32U-P-16) are mixed with peripheral waters. The Piper diagram (Fig. 4b) shows that waters are grouped between Na.K-Cl and Ca.Mg-Cl.SO$_4$ fields. Waters with high Cl concentration could be associated with deep reservoirs interacting with Paleocene-Eocene detritic rocks through their way to the surface, or with evaporitic environments related with sedimentary rocks from upper Cretaceous. Moreover, waters have a reactive interaction with volcanic rocks which contain sulfur minerals. The interaction produces lixiviation and dissolve trace elements from rocks and sulfur, the interaction recharge waters with the anion SO$_4$. On the other hand, the Jarpaña area would be acting as a zone of salt precipitation (brine) that comes from Jaraña and Chupahuito hot springs and then by out flow mixing with Jarpaña hot springs. These waters by evaporation process concentrate and precipitate the salts increasing the content of dissolved ions, such as Cl with amounts up to 12982 mg/L and Li with 20 mg/L, and in the precipitates (brines) appears the mineral LiPO$_4$.

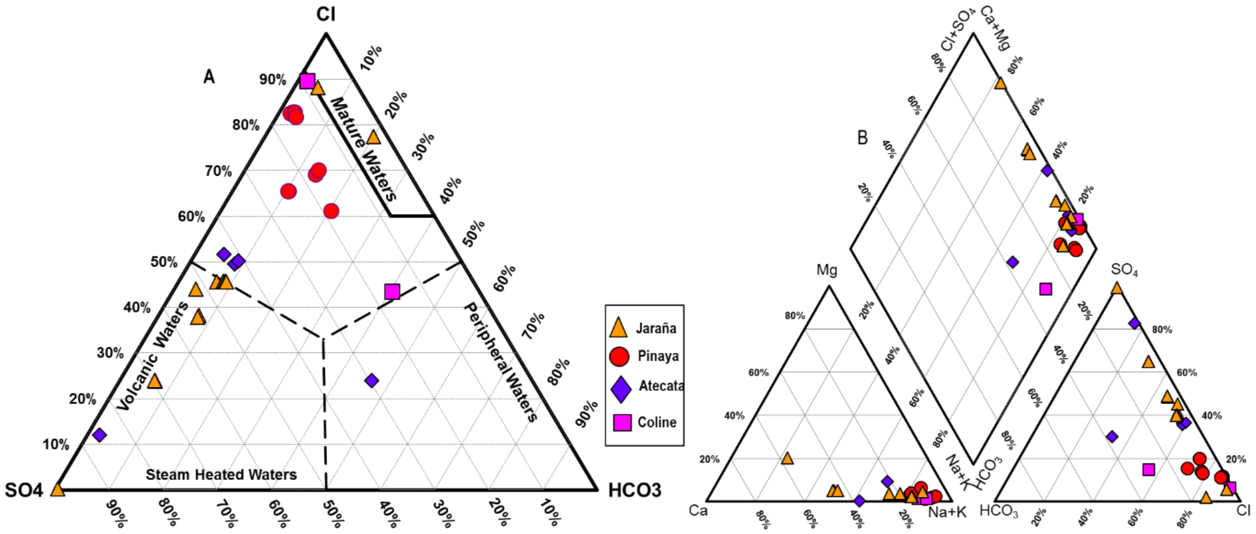

Fig. 4. Plot of data for thermal waters located around the Cordillera Sillapaca, using: a) Ternary and b) Piper diagrams.

The Cl, B, Li, Rb and Cs are trace elements chemically inert; thus, they are not altered with the addition to the liquid phase and allow understanding the origin of waters. Chemical proportions in Cl to B, Li, Rb and Cs elements on thermal waters around Cordillera Sillapaca are very similar, which implies the absence of shallow temperature variation and implies type of rock inside the hydrothermal system. However, the variable concentration of elements such as Cl, B, Li, Rb and Cs in waters, probably is affected by a secondary process of water – rock interaction. The results of relative concentration of the species Cl, Li and B were plotted in the ternary diagram of Giggenbach (1991a, Fig. 5). The ternary diagrams shows that waters have a common origin, plots are located at the Cl corner because of the predominant amount comparing with B and Li; with low steam absorption B/Cl. Therefore, the results indicate that waters are associated to old hydrothermal systems and probably the fluid migrated from old rocks.

The relative concentration of Li, Rb and Cs and particular process which could affect concentration in waters are represented in the ternary diagram Li-Rb-Cs (Fig. 6, Giggenbach, 1991). It is interesting to notice that samples have a common origin related with reservoirs with similar characteristics. The data plots are far from earth crust composition standards, probably, waters have lost part of the Rb from minerals with secondary process such as illite and potasic feldspar that incorporates Rb into their structure up to 300ºC. The precipitation result of quartz during the rise of thermal waters produce the reduction of Li concentration, which in turn incorporates inside their structure with temperatures lower than 200ºC. The chemistry proportions of Li/Cs on thermal waters (cold waters are excluded) are on the range of 1.46 to 23.8 that reflects the water-rock interaction. Low relations of Li/Cs are evidence of waters that discharge in an area with outflow that corresponds with waters from Jaraña and Pinaya. While, the high proportion of Li/Cs points the lateral flow areas (Giggenbach, 1991) such as waters from Atecata and Coline.

Thermal waters contain high arsenic concentrations (0.2 to 4.5 mg/L) related with lixiviation process of rocks with metallic sulfurs, with abundant amount of oligoelements in solution such as Ag, Fe, Cu, Pb and Zn; comparable with the mineralogy obtained from precipitates using XRD. The high concentration of Sr (0.4 to 48.6 mg/L) in thermal waters shows the interaction between ascending thermal waters and volcanic rocks (Delalande et al., 2011). The strontium in thermal waters show a positive correlation with Ca (R^2=0.9073, Fig. 7), which indicates the blending with carbonate waters (Han et al., 2010).

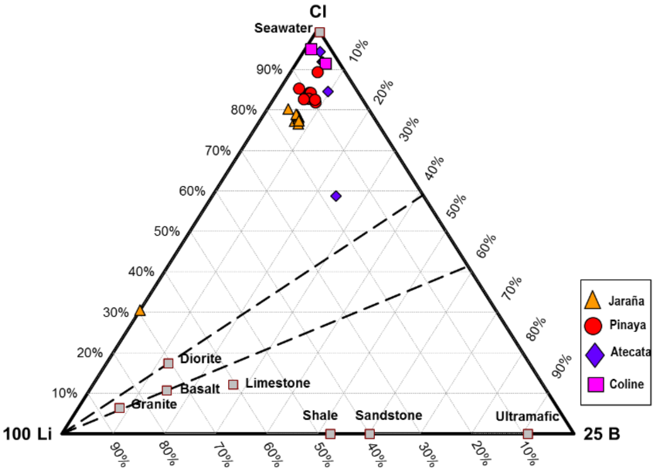

Fig. 5. Cl-Li-B ternary diagram (Giggenbach, 1998).

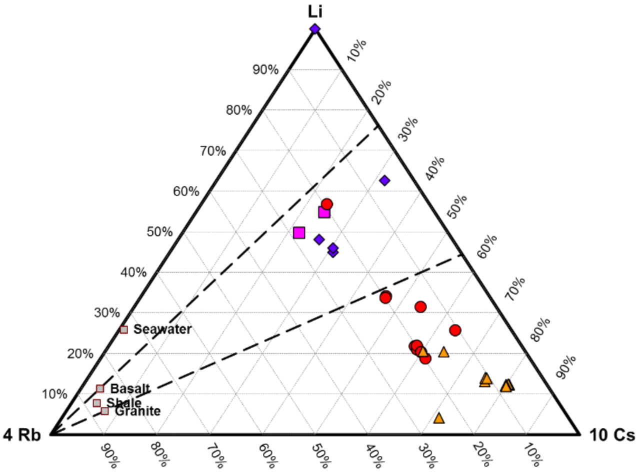

Fig. 6. Li–Rb–Cs diagram.

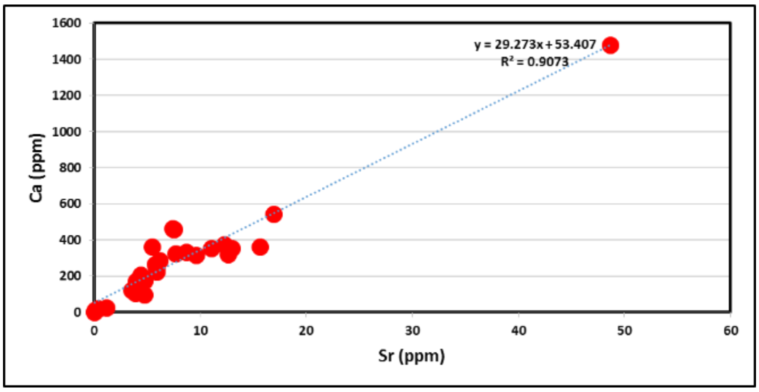

Fig. 7. Plot of Ca vs. Sr concentrations in all thermal water samples.

4.3.2 Mineralogy of precipitates around hot springs

The weather conditions, pH and water temperature have influence in the behavior and transfer of ionic elements, fluids have influence in the ionic element extraction from rocks and produce hydrothermal alteration. The ionic saturation in water originates precipitate deposition on the surface around thermal waters vents (Custodio & Llamas, 1976). The precipitate deposits inside the study area have in common calcite minerals. The calcite mineral has 100% of concentration and silica is < 5% inside the four areas. The gypsum minerals have >30% concentration in Jaraña and Atecata. Aragonite mineral is > 30% only presented in Jaraña (Fig. 8). The minerals with Ca, Mg, Na and Fe elements have higher concentrations in Jaraña and Atecata. The Fe and Ti minerals have a major presence in Jaraña. Minerals with Al element have low concentrations in Jaraña and Atecata. The precipitate deposits with mineral amount of metallic elements such as Pb, Ag, Cu, Mo and Zn, are located inside Jaraña and with lower amount in Atecata. Other uncommon minerals such as cometite (18.75%) and lithium phosphate (0.86%) minerals have been identified (Fig. 8); which is an interesting result because cometite contains Cu element and the lithium phosphate includes the Li element.

4.3.3 Geothermometry

The average of temperature using silica geothermometers gave two results, the lowest one was using chalcedony mineral (18 ºC) and the highest result was using conductive quartz until 169ºC. However, the hot springs 32u-P-027 and 23u-P-028 samples have low flow on surface and are affected by evaporation process, as consequence, results are not reliable; similar to cold and acid water results. The temperature results for silica were calculated using the Fournier and Potter (1982) equation. Figure 9 shows the hot spring plots that indicates the equilibrium between SiO_2 species (quartz, chalcedony and alpha cristobalite). The variety of SiO_2 species occurs inside the geothermal system reservoir around Cordillera Sillapaca. The blending phase was calculated using log (C^2_K/C_{Mg}) in front of log (C_{SiO2}) for water samples with temperatures results between 60 to 140ºC.

The geothermometers of Na-K from Fournier (1979), Truesdell (1976), Giggenbach (1988), Tonani (1980), Nieva & Nieva (1987) and Arnorsson (1983) gave the following range temperature results: 83 - 226 °C, 33 - 198 °C, 104 – 240 °C, 52 – 235 °C, 73 – 212 °C and 46 – 205 °C. However, the geothermometers of Na-K applied to geothermal systems for the Cordillera Sillapaca gave anomalous high temperature results suggesting a deep level location. Moreover, the K-Mg geothermometers from Giggenbach (1986) estimated temperatures between 41 – 139 °C. Samples 32u-P-027 and 32u-P-028 have low flow on surface and are affected by evaporation process; therefore, temperatures would not be reliable. The Na-K-Ca geothermometer from Fournier (1981) was used for deleting the effects produced for Ca concentrations on the geothermometer Na-K. The temperatures calculated using the Na-K-Ca geothermometer is on the range of 47-216 ºC, which are lower than Na-K geothermometer. Also, the Na-K-Ca-Mg-corr geothermometer from Fournier and Potter (1979) was applied for waters in the study area to obtain realistic results. The temperatures are estimated on the range of 47-137 ºC, which have a correlation with quartz and K-Mg geothermometers respectively.

The ternary diagram from Giggenbach (1988), (Fig. 10) shows thermal waters plots from Jaraña zone which do not reach the water-rock equilibrium. The plots are inside the immature waters field, with the exception of sample 32u-P-028; this sample has low flow and it is exposed to evaporation process allowing the ionic concentration and precipitation in waters. Besides, thermal waters has a high magnesium (Mg) concentration, this element tends to be soluble in low temperatures (<100ºC) thermal waters. All thermal waters have a blending between geothermal fluids and meteoric water in high amount, the blending gets into the area from the outcrops around. The probable equilibrium temperature Na-K inside reservoirs is lower than 200ºC, but it is the highest result for Pinaya followed from Jaraña, Atecata and Coline zones.

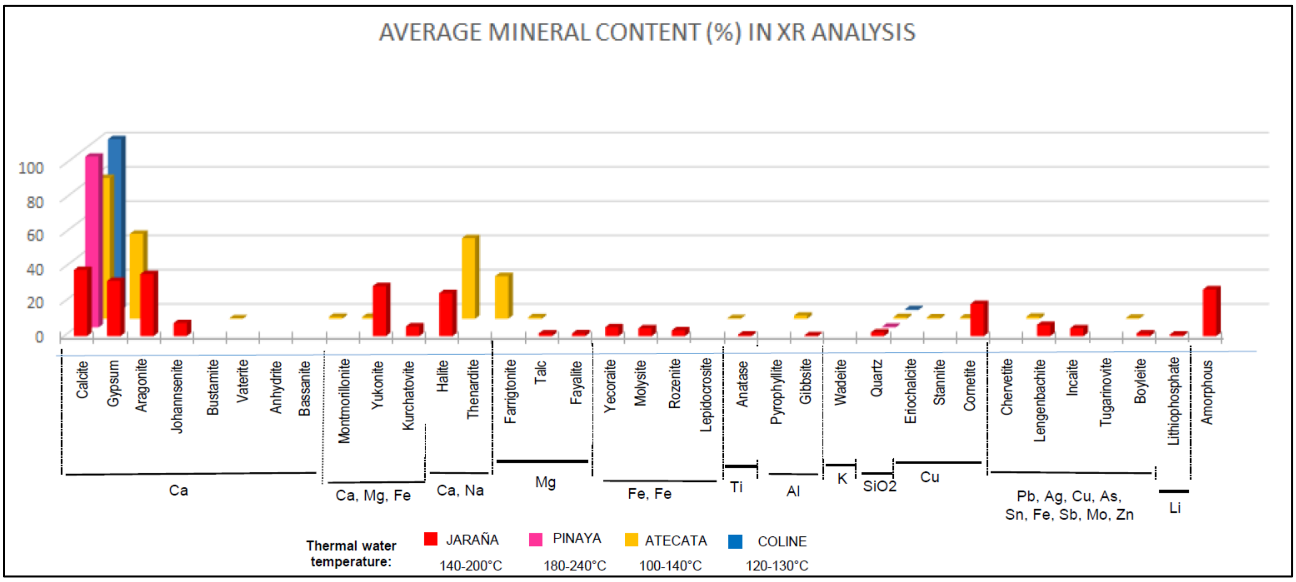

Fig. 8. Schematic chart of mineral concentration in precipitate deposits, located around hot springs in Jaraña, Pinaya, Atecata and Coline in percentage (%).

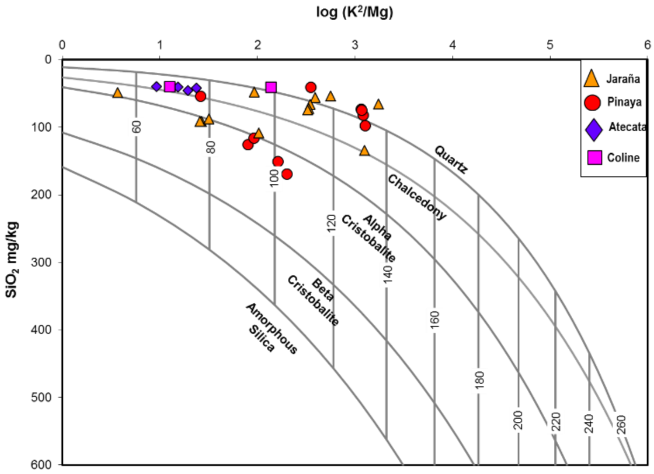

Fig. 9. Plot of the thermal water from around Cordillera Sillapaca in the silica content versus K2/Mg diagram gives low temperatures (60–140 °C).

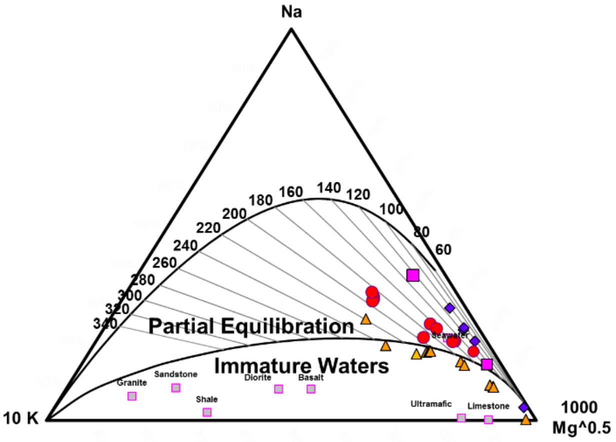

Fig. 10. Plot of Na–K–Mg Giggenbach diagram.

4.3.4 Isotopic data evaluation

The analysis result for stable isotopes (δ^2H y δ^{18}O) have δ^2H values on the range of -70.1‰ to –132.4‰ and δ^{18}O values on the range of –4.94‰ to –17.75‰, the results were plotted using the diagram δ^2H vs δ^{18}O (Fig. 11); the global meteoric water line was used as reference according to Craig (1961). The diagram shows a wide variation range between hot spring waters and waters from lagoons, which is logical, because of the wide area extension, recharge conditions and evaporation process. The shallow water evaporation (e.g. rivers, lagoons, etc.) is responsible for important changes on the isotopic composition for waters. The evaporation process occurs under no equilibrium conditions (unsaturated atmosphere) and the relative kinetic effect is higher on δ^{18}O rather than δ^2H. Also, the δ^{18}O and δ^2H diagrams show that thermal waters have a common meteoric origin, thermal waters are heated for conductivity at depth, probably related to a heat source associated to intrusive bodies controlled by Sillapaca and Cusco-Lagunillas-Mañazo faults (Carlotto et al., 2005).

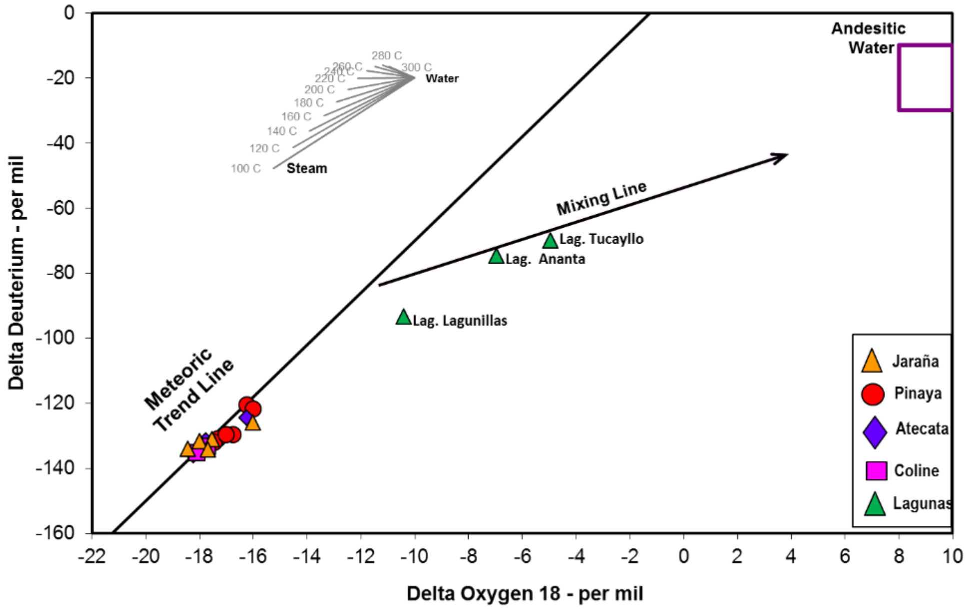

Fig. 11. Plot of δ^{18}O y δ^{2}H diagram. GMWL Global Meteoric Water Line ($\delta^{2}H = 8\ \delta\ ^{18}O$ + 10‰ SMOW; Craig, 1961) and the range of andesitic water as proposed by Giggenbach (1992a).

5 CONCEPTUAL MODEL

The conceptual model (Fig. 12) for the geothermal system around Cordillera Sillapaca was created using geological and chemical results on the current study. The geothermal systems around Cordillera Sillapaca are liquid dominated. The isotopic composition of δ^{2}H y δ^{18}O indicates that fluids come from meteoric waters from highest summits of Cordillera Sillapaca and Turputa Hill. Meteoric waters infiltrate through rocks and are heated by conduction at depth; then, fluids ascend by difference of density (upflow and outflow) using the NE-SW oblique faults derived from Lagunillas regional faults, which brings permeability. The temperature assigned for the geothermal reservoirs using the quartz geothermometer is less than 150 ºC and for cationic geothermometers is less than 200ºC.

The heat source is associated to the dacitic-andesitic subvolcanic located at Pinaya with radiometric age less than 1 Ma; the subvolcanic rock has a morphology similar to a dome. The emplacement of the circular dome is associated to regional faults, which cut lithological sequences and the magmatism is associated to a back arc magmatism. Faults have a great depth and transmit the heat though other areas such as Jaraña. The reservoir rock could be associated to the conglomerate sequences with calcareous matrix from Puno Group, which is a fluid result characteristic. On Jaraña zone, rocks have hydrothermal alteration such as argillic and silicification, hydrothermal alteration generates a rock layer with clays that could represent a seal layer horizon overlaying a probable geothermal reservoir located at depth.

The chemical thermal fluid properties are Na-Cl and Ca.Mg-SO_4-Cl. The high Cl and Na concentration have a relation with the fluid circulation at depth. The B is trapped by absorption inside clays reducing their concentration; this is caused by the lateral path of thermal fluids in a prolonged time through rocks (White, 1957; Nicholson, 1993). Moreover, the Ca.Mg-SO4-Cl waters come from the blending between three types of water: 1) chloride water or mature, 2) saline water and 3) meteoric water.

The complete resource estimation of geothermal reservoir resource around Cordillera Sillapaca requires geophysical information and drill holes; which will be considered in future studies.

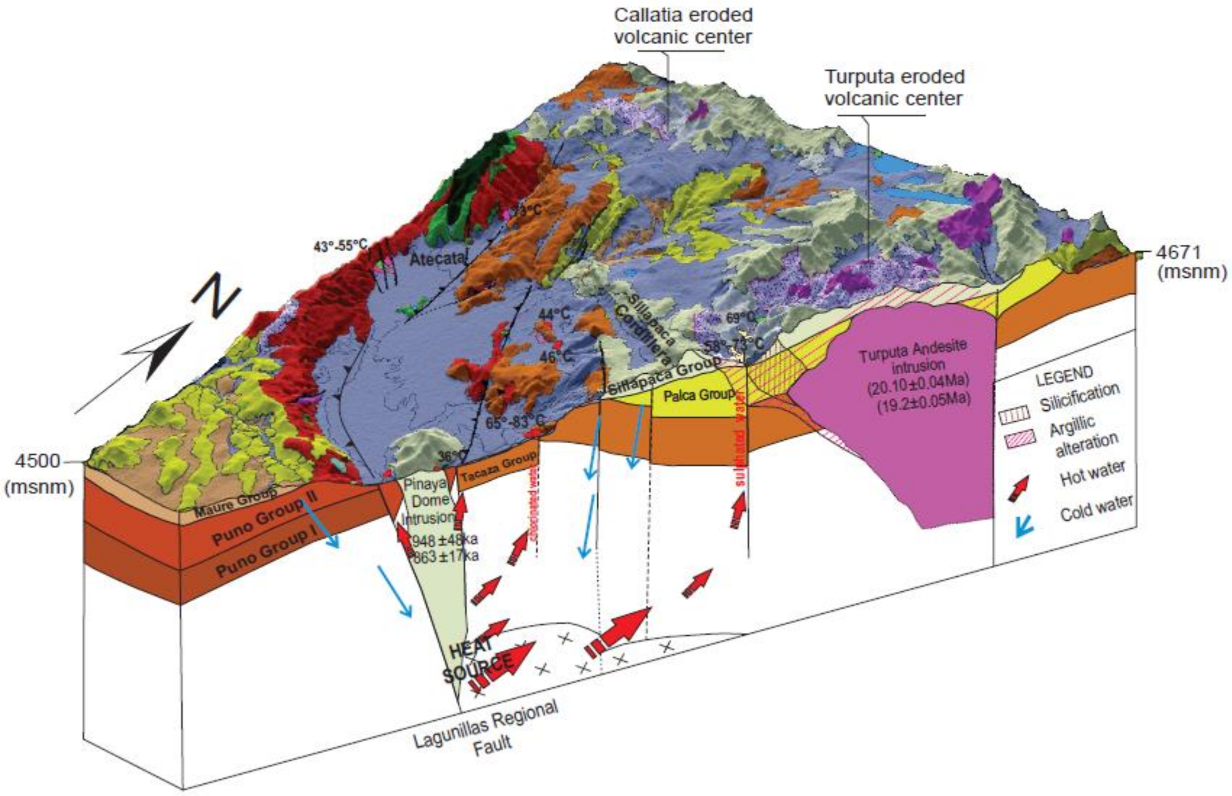

Fig. 12. Conceptual model of geothermal system and surface manifestations around Cordillera Sillapaca.

CONCLUSIONS

Thermal manifestations circulate through Miocene rocks with associated to epithermal ore deposits of Au-Ag, also, Pb-Zn-Cu economic elements; mineralization is associated with intrusive rocks and/or dacitic-andesitic subvolcanic rocks around Jaraña (Pinaya Rockmaster Resource Corp).

The hot springs chemical characteristics at Pinaya, Jaraña, Atecata and Coline geothermal zones, gave three water types: 1) chloride-sulphate alkaline Na-SO_4.Cl, 2) sulphate-chloride alkaline earth, and 3) bicarbonate alkaline earth. Hot springs are the result of the water-rock interaction and blending process (chloride, sulphate and bicarbonate waters). Chloride waters come from zones at depth where the hard dissolution in rocks generates Na ions and it is blended with sulphate calcic waters with high amount of HCO_3. Similarly, the fluid circulation through rocks generates lixiviation process for evaporate sequences rich in sulphate minerals (e.g. gypsum, anhydrite) and lixiviation of calcareous sequences (e.g. calcite), lixiviation process incorporates SO_4 and Ca into water chemistry, which are associated to lithological sequences of Puno Group. Boron presence in waters is associated to the interaction between water and rocks units such as sedimentary rocks, andesitic volcanic rocks, dioritic, and granodioritic intrusive rocks. The relation between stable isotopes $\delta^{18}O$ and $\delta^{2}H$ indicates the origin of geothermal fluids at Pinaya, Jaraña, Atecata and Coline geothermal zones, waters comes from meteoric waters up to 4300 meters and infiltrates through Lagunillas regional system faults.

The geothermal system has as a main heat source the Pinaya dome location on surface with a chronological age of 948 ± 48 ka and 863 ± 17 ka, the heat is transmitted by conductivity through deep faults. The heat source and energy for geothermal reservoirs at Pinaya and Jaraña would be associated with a conductive heat of magmatic bodies located at depth. On the other hand, geothermal systems at Atecata and Coline have a heat source associated to geothermal gradient, which in turn have a relation with conductive heat using permeable rocks. Hot springs with meteoric origin infiltrate through rocks using fractures and faults part of the Lagunillas regional system faults.

The temperature estimation for geothermal reservoir based on geothermometry and chemistry in liquid phase gave a result less than 200°C. Pinaya could be considerate as a system with medium enthalpy; however, the Jaraña, Atecata and Coline zones present a trend to low enthalpy systems below 150°C. The results bring an idea about the reservoir rock composition, which would be represented by sandstones from Hualhuani Formation and conglomerates with calcareous matrix from Puno Group.

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Reference

Arnórsson, S. (1983) - Chemical Equilibria in Icelandic Geothermal Systems: Implications for Chemical Geothermometry Investigations, Geothermics, 12, 119-128.

Barnes, I., Evans, W. C. & White, l. D. (1978) - Global distribution of CO2 and major zone of seismicity. US Geological Survey Open-File Report, 78 –39.

Carlotto, V.; Jaillard, E.; Carlier, G.; Cárdenas, J.; Cerpa, Luis.; Flores, T.; Latorre, O. & Ibarra, I. (2005) - Las cuencas terciarias sinorogénicas en el Altiplano y en la Cordillera Occidental del sur del Perú. Sociedad Geológica del Perú. Volumen Especial, n. 6.

Carlotto, V.; Quispe, J.; Acosta, H.; Rodríguez, R.; Romero, D.; Cerpa, L.; Mamani, M.; Díaz, E.; Navarro, P.; Jaimes, F.; Velarde, K.; Lu, S.; Cueva, E. (2010) - El control de los dominios tectónicos en la metalogénesis del Perú. Congreso Peruano de Geología, 15, Cusco, 2010, *Resúmenes extendidos*. Lima: Sociedad Geológica del Perú, p. 515-518.

Craig, H. (1961) - Isotopic variations in meteoric waters. Science 133, 1702–1703.

Cereceda, I.; Cerpa, L.; Mamani, M.; Torres, D.; Muñoz, L.; Aguilar, R. (2010) - Características geoquímicas del volcanismo Cenozoico del sur del Perú en el sector Condoroma-Ocuviri: implicancias en la estratigrafía volcánica y mineralización. Congreso Peruano de Geología, 15, Cusco, 2010, Resúmenes extendidos. Publicación Especial Lima: Sociedad Geológica del Perú 2010, p. 911-915.

Custodio, E. & Llamas, M. (1976) - Hidrología Subterránea. Editorial Omega. Tomo 1.

Delalande, M., Bergonzini, L., Gherardi, F., Guidi, M., Andre, L., Abdallah, I., Williamson, D. (2011) - Fluid geochemistry of natural manifestations from the Southern Poroto-Rungwe hydrothermal system (Tanzania): preliminary conceptual model. J. Volcanol. Geotherm. Res. 199, 127–141.

Fournier, R.O. (1979) - Geochemical and hydrologic considerations and the use of enthalpy-chloride diagrams in the prediction of underground conditions in hot spring system. *Journal of Volcanology and Geothermal Research* 5, 1-16.

Fournier, R.O., and Potter R. W.II. (1979) - Magnesium correction to Na-K-Ca geothermometer. Geochim. Cosmochim. Acta, 43, 1543-1550.

Fournier R.O. and Potter R.W. II (1982) - "A revised and expanded silica (quartz) geothermometer," Geothermal Resources Council Bulletin, 11, 3-12.

Fournier, R. O. (1981) - *Application of water geochemistry to geothermal exploration and reservoir engineering, in Rybach*, L., and Muffler, L. J. P., eds, Geothermal Systems: Principles and Case Histories: John Wiley & Sons, New York , p. 109 – 143.

Giggenbach, W.F. (1988) - Geothermal solute equilibria; derivation of Na-K-Mg-Ca geoindicators. *Geochimica et Cosmochimica Acta*, 52(12): 2749-2765.

Giggenbach, W.F. (1991) - Chemical techniques in geothermal exploration. In Applications of geochemistry in geothermal reservoir development, (Ed) D'Amore, United Nations Institute for Training and Research, USA, Pub., 1991, 119-144.

Giggenbach, W.F. (1991a) - Chemical techniques in geothermal exploration. En: D'Amore, F. (Ed.), Applications of Geochemistry in Geothermal Reservoir Development. UNITAR/UNDP Centre on Small Energy Resources, Rome, Italy, pp 119–144.

Giggenbach WF (1992a) - Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin. *Earth Planet. Sci.* Lett. 113, 495-510

Giggenbach, W. F., Goguel, R. L. (1989) - Collection and analysis of geothermal and volcanic water and gas discharges, unpublished report. Chemistry Division, Department of Scientific and Industrial Research Petone, New Zealand, 81p.

Giggenbach, W.F. (1986) - Graphical techniques for the evaluation of water/ rock equilibration conditions by use of Na, K, Mg, and Ca-contents of discharge waters, *Proceedings* NZ Geothermal Workshop 8th, New Zealand.

Harker, A. (1909) - The Natural History of Igneous Rocks. Hafner, New York (1965 facsimile of original edition).

Han, D.M, Liang, X., Jin, M.G., Currell, M.J., Song, X.F. & Liu, C.M. (2010) – Evaluation of groundwater hydrochemical characteristics and mixing behavior in the Daying and Qicun geothermal systems, Xinzhou Basin. *Journal of Volcanology and Geothermal Research*.189, pp. 92-104.

Klinck, B.A.; Ellison, R.A.; Hawkins, M.P. (1986) - The geology of the Cordillera Occidental and Altiplano West of Lake Titicaca Southern Peru. British Geological Survey, INGEMMET.

Le Maitre, R.W.; Bateman, P.; Dudek, A.; Keller, J. (1989) – A Classification of Igneous rocks and Glossary of terms: Recommendations of the International Union of Geological Sciences. Subcommission on the Systematics of Igneous Rocks. Blackwell Scientific Publications, Oxford.

Marini, L., (2000) - Geochemical techniques for the exploration and exploitation of geothermal energy. Taller Proyecto FONDEF 1051, Noviembre 2000, Departamento de Geología, Universidad de Chile, 82p.

Murray, K. & Wade, P. (1996) - Checking anion-cation charge balance of water quality analyses: limitations of the traditional method for non potable waters. *Water SA*, 22(1): 27-32.

Nicholson, K. (1993) - Geothermal fluids: Chemistry and exploration techniques. Berlin: Springer-Verlag, 278 p.

Nieva, D., Nieva, R. (1987) - Developments in geothermal energy in Mexico, part 12—A cationic composition geothermometer for prospection of geothermal resources. Heat recovery systems and CHP 7, 243–258.

Oliver, J. (1986) - Fluids expelled tectonically from orogenic belts: their role in hydrocarbon migration and other geological phenomena. Geology, 14, 99– 102.

Oliver, J. (1992) - The spots and stains of plate tectonics. Earth-Science Reviews, 32, 77 –106.

Rickwood P.C. (1989) - Boundary lines within petrologic diagrams which use oxides of mayor and minor elements. Lithos. 22, 247 – 263.

Sververjensky, G. H. & Garven, G. (1992) - Tracing great fluid migrations. Nature, 365, 481 –482.

Swanson, K. (2002) *Geology of the Orcopampa 30 Minute Quadrangle southern Peru, with Special Focus on the Evolution of the Chinchón and Huayta Calderas*. Dissertation for doctor of Philosophy in Geology. University of Nevada, Reno.

Tonani F. (1980) – Some remarks on the application of geochemical techniques in geothermal exploration. In: Proc. Adv. Eur. Geoth. Res., Second symposium Strasboug, 428-443.

Truesdell, A.H. (1976) - Summary of Section III - Geochemical Techniques in Exploration, Proceedings, the Second United Nations Symposium on the Development and Use of Geothermal Resources, San Francisco, CA, 1, 1iii-1xiii.

White, D.E. (1957) - Thermal waters of volcanic origin. *Geological Society of America Bulletin*, 68(12): 1637-1658.

Wasteneys, H. 1990. Epithermal silver mineralization associated with a mid-Tertiary diatreme; Santa Barbara, Santa Lucia.