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First Geochemical Data from Cerro Pabellón Geothermal Project (Apacheta Region, Chile)

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ABSTRACT

Cerro Pabellón (Chile) is the newly developed geothermal field by Geotermica del Norte (GDN) and it is the first under production in South America. It is located in ‘Pampa Apacheta at 4500 m a.s.l.’. No surface manifestations indicate the presence of a deep liquid geothermal resource at high enthalpy (250°-260°C). A shallow borehole (187 m depth) drilled by Codelco (Corporación Nacional del Cobre, Chile) for water research found steam g (at 88°C due to the high elevation) instead of a cold water aquifer. In 2002, the exploration mining lease (330 km^2) was assigned to Geotérmica del Norte (GDN). From 2009 to 2017, thirteen wells were drilled to explore the field. All the productive wells found permeability in the geothermal reservoir, hosted in volcanic products. To the present knowledge, the geothermal system is hosted in a graben structure (Apacheta graben) bounded by two NW-SE oriented faults.

The geothermal reservoir is liquid dominated and the fluid shows very low gas content. Fluid samples depict a mature system with a chemistry typical of a volcanic-hosted field. Geothermometers indicate apparent temperature equilibrium in the range of 280°-290°C, as compared to 255°C measured in wells, indicating higher temperatures may possibly be found deeper in the system.

1. INTRODUCTION

Cerro Pabellón (Chile) is the first geothermal system industrially exploited in South America. Located in the “Pampa Apacheta” area at about 4500 m a.s.l. in the Antofagasta region, about 8 km from the Chile-Bolivia border, the area is covered by volcanic and volcanoclastic rocks of Neogene to Quaternary age, erupted by the numerous volcanic summits that commonly exceed 5000 m a.s.l. The geothermal production pole is developed inside the depressed structure of the Apacheta Graben, while the reinjection pole is located out of this structure. Figure 1 shows a map of the geothermal field with the wells drilled between 2009 and 2017. A full summary of the different phases of Cerro Pabellón project development is in Cappetti et al. (2020).

At present, six production wells feed a 48 MW gross high enthalpy binary power plant. The depth of the wells ranges between 452 and 2900 m. All the natural fluid is reinjected, maintaining a temperature higher than 90 °C in order to avoid silica scaling problems. The aim of this paper is to present a first geochemical assessment of the Cerro Pabellón geothermal system (hereafter referred as CP) by analyzing chemical and isotopic characteristics of the fluid produced by the six production wells.

Differently from others geothermal known resources of the region (El Tatio is only 60 km to the south), Cerro Pabellón is considered a ‘blind’ system. Only two dry, superheated fumaroles (109°-118°C) located on the top of Cerro Apacheta (Urzua et al., 2002; Tassi et al., 2010) indicate the existence of a volcanic heat source at depth in the area.

Based on gas and steam condensate analysis, Urzua et al. (2002) infer that the fumaroles are an expression of the geothermal system. Considering a redox buffer FeO/FeO1.5 value of -4 (oxidizing conditions) a 250°C deep equilibrium temperature is found, while standard RH value of -2.8 (Giggenbach, 1987) gives 325°C reservoir temperature. The observed oxygen shift for the fumarolic condensate could derive from intensive water-rock interaction at high temperature or mixing with a magmatic component. Tassi et al. (2010) found highly acidic gas species, namely HCl and SO_2, in the same fumaroles sampled by Urzua et al. (2002). Although the authors confirm a more oxidizing redox state for the fumaroles (-3.4), giving temperatures of >320°C, HCl and SO_2 are related to degassing magma bodies and could not be found in geothermal conditions involving a liquid dominated reservoir. This would rule out the fumaroles as surface expression of the Cerro Pabellón geothermal system.

CP wells CP-1, CP-1A, CP-2, CP-5, CP-5A and CP-6 were sampled during flow tests for chemical analysis in 2010, 2016 and 2017. The first available data refer to wells CP-1 and CP-2 (June and December 2010 respectively), CP-5 and CP-5A were sampled in June 2016, CP-1A at the beginning of July 2017, while CP-6 was opened only a few days and was collected at the end of 2017.

Sampling was carried out by GDN personnel in order to collect the water, steam and non-condensable gasses (here in after, NCG) discharged during flow tests. Chemical analyses were performed both by ENEL and CEGA (Centro de Excelencia en Geotermia de Los Andes) laboratories. The gas samples presented were analyzed by ENEL Laboratories in Larderello, Italy. The isotopic composition of the liquid phase was determined by CNR of Pisa (Italy).

Static temperature and pressure logs in the wells show a conductive thermal gradient in the upper zone, followed at depth by a convective zone with a thermal gradient near zero (Baccarin et al., 2020). Maximum measured temperatures in wells are 250°-260°C. In the surroundings, a regional cold aquifer exists, and its level is continuously monitored by two shallow wells drilled by GDN (Perdiz-1 and Cachimba-1), one in the northeastern and one in the southern part of the field, respectively (Figure 1). Their static level in 2019 (4200 m a.s.l.) is different from the hydrostatic pressure gradient measured in the geothermal system, indicating that the two systems are not hydraulically connected (Baccarin et al., 2020). No samples are yet available from these two shallow wells.

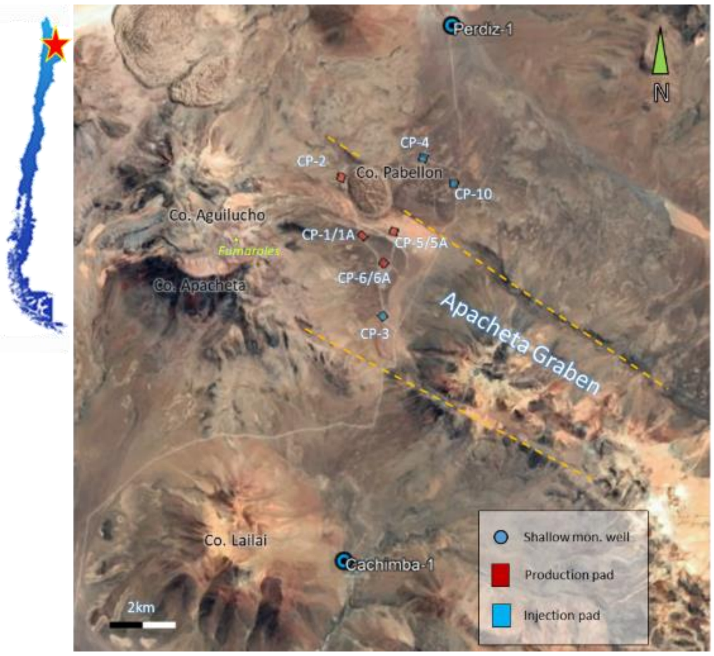

Figure 1: Satellite view showing the location of geothermal project and wells at Cerro Pabellón. Yellow dashed lines indicate schematic simplified major fault system.

2. MATERIALS AND METHODS

CP water samples were collected from a weir box located downstream of an atmospheric cyclonic separator ($P_{atm} \sim 0.6$ bar). Temperature, pH and total alkalinity were determined on-site. Total alkalinity was measured by titration with 0.1 M ultrapure HCl. For determinations of anions, cations, trace metals and ammonia, one filtered (0.45 µm) and two filtered-acidified (with HNO_3 and with HCl, respectively) water samples were collected in 500 mL polyethylene bottles. For H_2S determination, a 250 mL polyethylene bottle was collected and stabilized with zinc acetate solution. For determination of silica content, 5 mL of sample were diluted in a 100 mL polyethylene bottle filled with Milli-Q water. An aliquot was stabilized with a solution of HNO_3/H_2O_2 for analysis of As and Sb. The isotopic composition of waters was analyzed on samples collected in 100 mL amber glass bottles.

CP steam and NCG samples were taken with a portable cyclonic separator connected to the flow line before the atmospheric expansion stage, keeping the flashing pressure at about 4-5 bar. Once condensed, the aliquots were divided as described above for chemical determinations of species carried in the vapor phase.

NCG samples were collected in two-way 250 mL glass flasks tapped with Teflon valves attached at the end of the sampling line. After rinsing, the bottom valve of the flask was shut and gas was manually pumped with a syringe through a three way valve into the flask. Residual gas was collected in pre-evacuated 300 mL glass flasks, equipped with a Teflon stopcock, filled with 100 mL of a 4M NaOH. Unfortunately, the only reliable NCG data collected with NaOH was collected at CP-1 in 2010; the other samples were found to be affected by heavy air contamination and were therefore discarded. Even for some of the “natural” gas sampled, i.e. without soda, the air contamination is significant and thus the analysis not reliable. The gas/steam ratio was measured through a volume displacement technique, as described in Enel internal procedures, using a so-called “gasometer” in situ.

Major anions (Cl, SO_4, F and Br) and ammonia were analyzed by ion-chromatography (IC Thermo Scientific Dionex ICS-3000). Major Cations (Na, K, Ca and Mg), silica, boron and trace elements (As, Li, Rb, Cs, Sr, Sb and Hg) were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-OES Agilent 5100 System). H_2S was measured by iodimetric titration. Gas analyses were performed with a Varian CP-3800 gas-chromatograph.

The $^{18}O/^{16}O$ and $^{2}H/H$ isotopic ratios (expressed $\delta^{18}O$ and δD ‰ V-SMOW) in water samples were determined using a Finnigan Delta Plus XL mass spectrometer according to standard protocols. Oxygen isotopes were analyzed using the CO_2 - H_2O equilibration method. Hydrogen isotopic ratios were measured on H_2 after the reaction of 10 mL of water with metallic zinc at 500°C. The experimental error was +0.1 ‰ and +1 ‰ for $\delta^{18}O$ and δD values, respectively.

3. RESULTS AND DISCUSSION

3.1 Liquid phase chemistry

For liquid samples collected at the weir box, the ionic balance shows a deviation in the range of ±10%, which is considered acceptable. The chemical composition of the main elements (mg/L), pH, steam fraction and gas-steam ratio (weight %) are reported in Table 1.

Table 1. Separated brine composition, sampled at weir box, and gas phase analysis. Bdl = below detection limit; nd = not determined. G/S is in weight %; brine analysis is in ppm, gas analysis is in X mmol/mol.

WELL	SAMPLING DATE	STEAM FRACTION	G/S	pH	Na	K	Ca	Mg	Cl	SO4	F	Br	SiO_2	B	HCO_3	Li	Rb	Cs	Sr	Sb	As	TDS
CP_1	11/06/2010	0.21	0.54	6.89	5182	871	543	0.17	10066	22	10.9	10.4	531	273	34	59	9.5	32	13.4	9.5	71	16769
CP_1A	05/07/2017	0.36	0.60	6.95	4452	729	538	0.36	8214	28	0.5	7.5	429	293	51	50	6.4	26	12.8	1.8	79	14146
CP_2	10/12/2010	0.32	0.61	7.12	3498	666	597	0.81	6808	33	11.5	6.5	362	258	67	31	3.0	22	10.9	1.6	65	11778
CP_5	11/06/2016	0.48	0.87	6.74	4343	638	528	0.04	7447	29	0.7	6.5	276	265	48	34	4.3	20	8.3	1.7	34	13095
CP_5A	26/06/2016	0.33	0.38	6.84	4724	793	645	0.13	9045	32	0.8	7.7	363	312	46	50	6.3	21	12.1	2.1	44	15385
CP_6	04/12/2017	0.21	0.60	6.82	5668	1125	541	0.21	8986	27	1.5	11.7	574	343	48	62	9.5	32	13.4	2.9	84	16569

WELL	CP_1		CP1A	CP2	CP5	CP5	CP5
SAMPING DATE	10/06/2010	11/06/2010	05/07/2017	10/12/2010	09/06/2016	09/06/2016	11/06/2016
g/s (wt %)	0.54		0.6	0.61	0.87		
CO2	2.18E+00	2.18E+00	2.37E+00	2.45E+00	3.51E+00	3.52E+00	3.52E+00
H2S	6.01E-03	8.71E-03	6.09E-03	5.57E-03	8.14E-03	7.38E-03	6.43E-03
CH4	bdl	bdl	1.22E-03	bdl	3.70E-03	3.69E-03	bdl
H2	bdl	bdl	2.19E-03	2.53E-03	6.66E-03	5.90E-03	5.00E-03
N2	2.71E-02	3.69E-02	1.14E-01	6.00E-02	4.96E-02	3.58E-02	3.28E-02
CO	4.45E-06	4.92E-06	1.05E-05	5.06E-06	1.85E-05	1.73E-05	1.79E-05
He	2.89E-05	2.90E-05	9.99E-05	4.30E-05	3.70E-05	3.32E-05	5.71E-05
Ar	1.35E-03	nd	nd	nd	nd	nd	nd
Water	9.96E+02	9.96E+02	9.95E+02	9.95E+02	9.93E+02	9.93E+02	9.93E+02

The recalculated pH at reservoir conditions, using the software Watch 2.4 (Bjarnason, 2010), displays slight acidity, between 5 and 6.2, at reservoir conditions. The difference observed between computed-downhole pH values and those measured at surface (close to neutrality from 6.7 to 7.1) is due to the loss of CO_2 during flash. The water type is sodium-chloride, with a relatively high concentration of K (from 638 to 1125 ppm), Ca (from 528 to 645 ppm), B (from 258 to 343 ppm), Li (from 31 to 62 ppm) and As (from 34 to 84 ppm). Very low Mg content (from 0.04 to 0.81 ppm) is observed. Well CP-5 shows a much higher steam fraction than the others as a consequence of a steam cap developed in the higher zone of the reservoir in this location. In fact, the well is only 500 m deep and produces from a very shallow fracture in the reservoir, compared to other wells.

Overall, Cerro Pabellón geothermal fluid is quite similar to El Tatio (60 km south of CP), reported by Giggenbach (1978): they show high levels of calcium and low alkalies, evidencing these features as a common fingerprint for geothermal systems in this area.

Intense leaching from the host rock in a long living system without surface discharge (liquid phase) leads to an increase of solutes in the fluid and development of secondary mineral precipitation (propylitic facies development). The high chloride content (up to 9738 ppm) may primarily derive from magmatic HCl degassing (Giggenbach, 1992) and interacting with deep penetrating waters giving rise to the geothermal system. The presence of superheated steam fumaroles (up to 118 °C) discharging possible traces of volcanic gas species (HCl and SO_2) on the top of the Apacheta Volcano (Tassi et al., 2010) would confirm the existence of an active magmatic system that is scrubbed by the hydrothermal aquifer(s) below Pampa Apacheta. The very high Ca (up to 691 ppm) has to be linked to the low carbon content (P_{CO2} of the system is very low, see paragraph 3.2 for details) that prevents calcite deposition and hence allows calcium to keep its ionic aqueous form. In order to identify the processes that affected the composition of thermal waters at depth, the combination of two conservative elements, such Cl and B, represents a common technique in geochemical applications. In Figure 2, a binary diagram that shows Cl/B ratios of CP wells is reported.

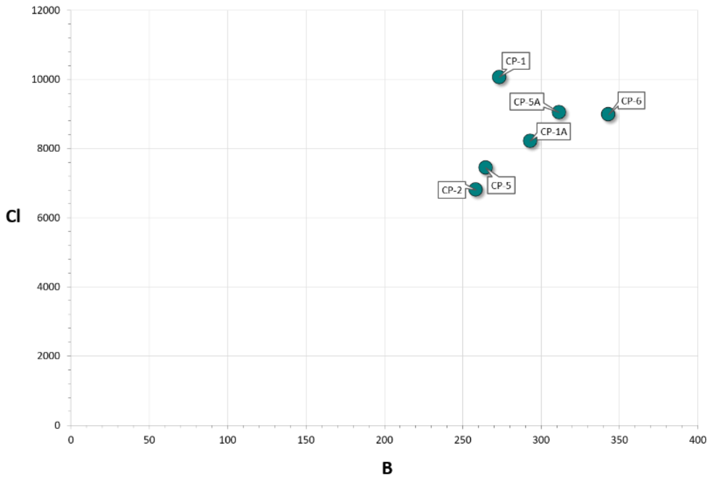

Figure 2: Cl vs. B binary diagram for CP brines; values are in ppm (mg/L).

The behavior of these two species is quite similar, although Cl, compared to B, shows a major affinity to the liquid phase (D'Amore and Giannelli, 1984). Except for the anomalous CP-1, most probably related to an analytical error, all others CP samples are aligned on a linear trend ($R^2 = 0.9509$), which indicates that: 1) Cl and B share a common origin; and, 2) CP-2 and CP-6 area are possibly affected by some dilution process. CP-2 was sampled just a few days after drilling. The drilling fluid used was water from the shallow aquifer, for which some analysis are in Risacher et al. (1999). Figure 3 shows Mg vs. Cl contents of wells and shallow waters, with the CP-2 point shifted towards the Perdiz point, indicating mixing between deep geothermal fluid and groundwater used for drilling.

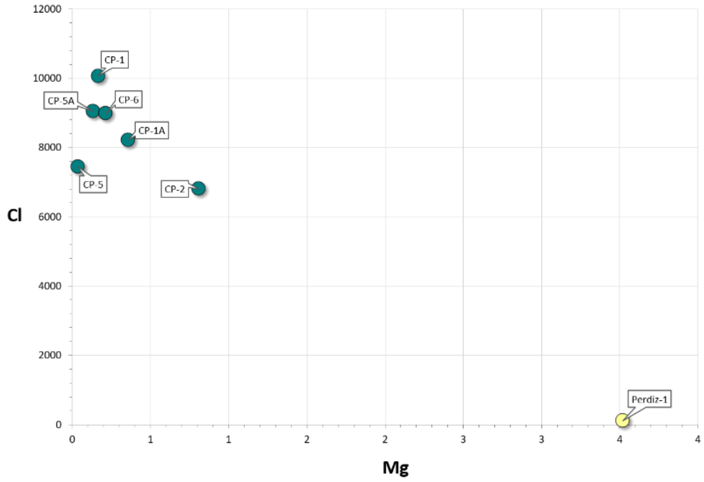

Figure 3: Cl vs. Mg binary diagram for CP brines (green dots) and shallow water well Perdiz-1 (yellow dot); values are in ppm (mg/L).

Looking at other conservative species, a relatively large amount of lithium (up to 62 ppm), cesium (up to 32 ppm) and rubidium (up to 9.5 ppm) is also found in CP water samples (Table 1). Prolonged water-rock interaction, related to long-term circulation pathways, leads to enrichment of these rare alkali elements. Li-Rb-Cs and Li-Cl-B ternary diagrams are plotted in Figure 4.

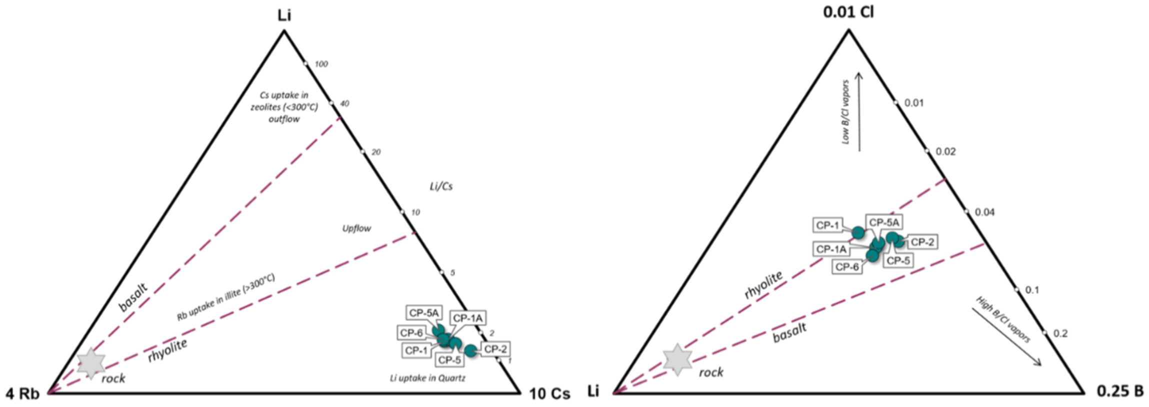

Figure 4: Li-Rb-Cs (left) and Li-Cl-B (right) ternary diagrams for CP wells.

In Figure 4 (left), all the data points are far removed from the main rock composition area (grey star in diagram), as expected for geothermal mature fluids, and are clustered in a roughly linear trend close to Cs corner. This positioning reflects an actual Cs-enrichment derived from leaching of volcanic products with very low Li/Cs ratios. Progressive absorption of magmatic vapors rich in HCl and H_3BO_3 into the liquid brine can explain the positioning of data points in Figure 4 (right) (Giggenbach, 1991a). The high arsenic (As) content found in all CP water samples (34-84 ppm) is also related to leaching of the extremely acid volcanic product associated to extrusion of dacitic domes (Domo Pabellóncito, Domo ChacInca), which represent the latest volcanic events of the area and display the highest As content from XRF analysis (Ahumada and Mercado, 2010).

Regarding gases, CO_2 is the dominant species with very low concentrations of others, with H_2 and CH_4 being strongly depleted. Well CP-5 shows a higher G/S ratio and CO_2 content because of the presence of the steam cap. An N_2/Ar ratio of 20 (for CP-1) is close to the air-saturated groundwater value of 38, while the He-Ar value of 0.02 is very low, describing a system with a small contribution of deep gasses.

3.2 Geothermometry

The calculated values for quartz geothermometer on silica concentration range from 226°-256°C (Fournier & Potter, 1982) that are in perfect agreement with downhole temperatures measured on static logs (230°-260°C).

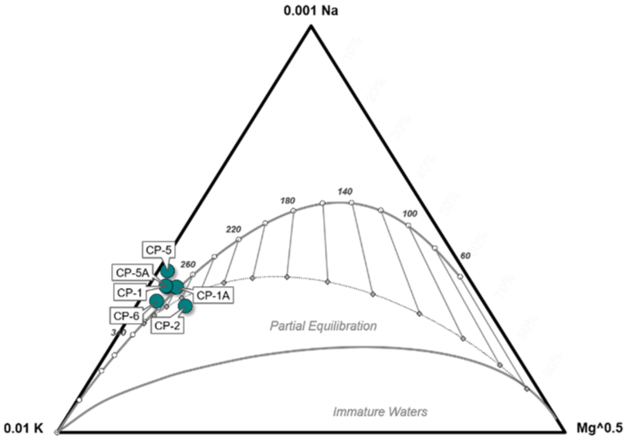

Figure 5: Na-K-Mg ternary diagram.

In the Na-K-Mg ternary plot (Giggenbach, 1988) in Figure 5, all the points representing the wells fall close to the full-equilibrium indicating higher equilibrium temperature (≈ 280 °C) with respect to those measured in the wells. Very low Mg content explains the position of the points slightly above the full equilibrium curve, and could be due to fast removal of Mg from the liquid by secondary mineral precipitation. The CP-2 position is shifted slightly below the equilibrium curve due to its higher Mg content, as a dilution effect. Assuming the slow equilibrating Na-K geothermometer values to be correct, and considering the thermal gradient found in the wells (Baccarin et al., 2020), a temperature of about 280 °C could be found in the deep root of the system at 1500m a.s.l., some 800-1200 m below the actual depth of the wells, closer to the heat source of the system.

The K-Mg-Ca geoindicator (Figure 6) represents a tool for determination of CO_2 partial pressure and temperature of "last equilibrium" of waters with the same rock assemblage of Na-K-Mg system. As suggested by Giggenbach and Goguel (1989), P_{CO2} in geothermal fluids is likely controlled by the conversion of Ca-Al silicates to calcite, involving the formation of K-mica.

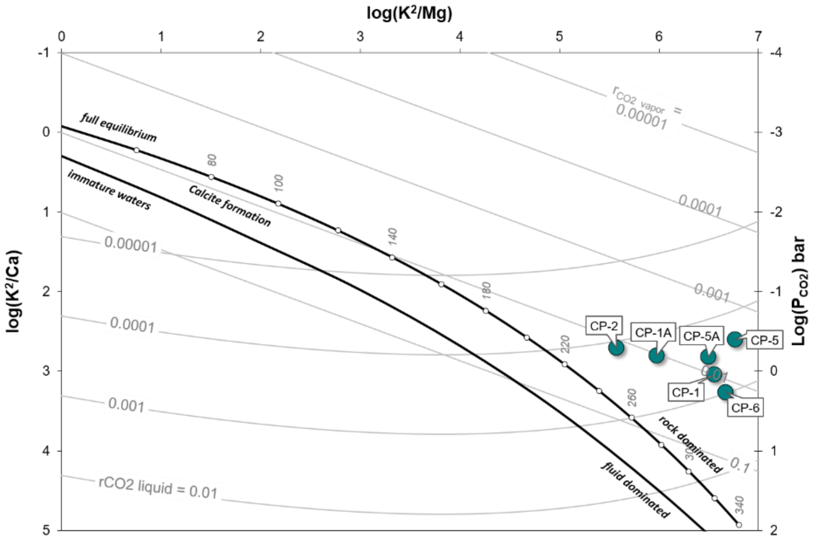

Figure 6: K-Ca-vs. K-Mg-temperature binary diagram

Data points for CP wells plot above the full equilibrium line and above the calcite formation field. The shift in data points due to Mg removal does not significantly affect the point positions, considering that CP-2 well still remains in the rock dominated field, despite its higher Mg content. The CO_2 content of the deep, rising waters is thus too low to induce rock alteration, as described above. The low CO_2, mirrored by the high Ca content, is an indication of decoupling between the geothermal system and the source of CO_2 that originates from a deeper zone corresponding to a degassing magmatic system located below the geothermal reservoir.

For the gas phase only for CP-1, sampled in 2010, a complete gas analysis is available, as stated above, and only for this sample the evaluation of combined CO_2/Ar vs. H_2/Ar geothermometers is possible. In the graph (not shown), the point is slightly below the equilibrium liquid line at a CO_2/Ar temperature of 245°C. For the other wells, CO_2 geothermometer (Arnorsson et al., 1998) calculations show higher temperatures in the range of 266°-286°C, similar to those obtained with Na-K estimates.

3.3 Origins of waters

Deep water isotopic composition (total discharge) was calculated considering the steam fractions in Table 1 with a temperature of 250°C, as measured by static logs in wells. Isotopic fractionation factors from Truesdell et al. (1977) at the surface boiling point (85.8°C) were applied.

Isotopic values in separated brine and deep downhole values are reported in Table 12 for CP-1A, CP-5 and CP-5A. The other wells (CP-1, CP-2 and CP-6) were not sampled for isotopic determination. In Figure 7, the δD-H_2O vs. $\delta^{18}O$-H_2O diagram is shown.

Table 1: Water isotopic values (‰ SMOW) from CP-1A, CP-5 and CP-5A wells

WELL	BRINE SAMPLES		TOTAL DISCHARGE	
	$\delta^{18}O$	δ D	$\delta^{18}O$	δ D
CP_1A	-2.3	-68.9	-4.4	-81.2
CP_5	-1.6	-61.2	-4.4	-77.5
CP_5A	-2.4	-68.4	-4.3	-79.6

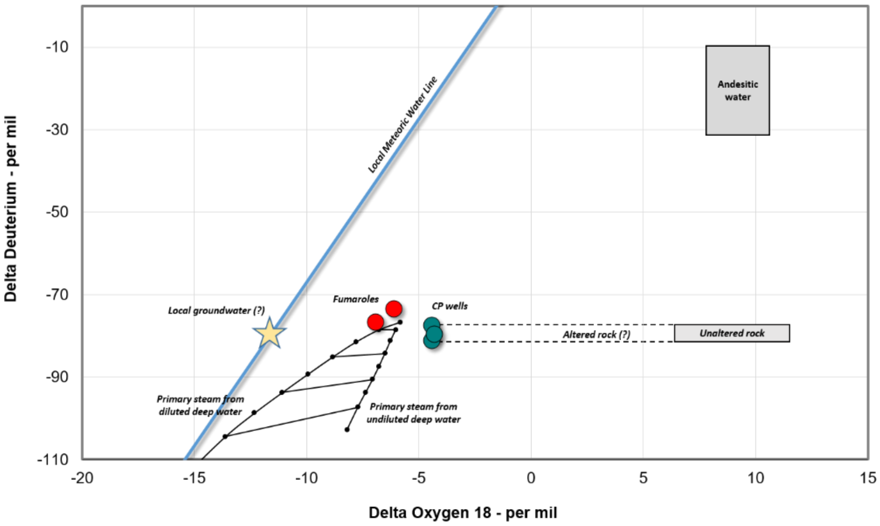

Figure 7: δD-H_2O vs. $\delta^{18}O$-H_2O binary diagram. CP brine samples are reported together with fumaroles (red dots) sampled by Urzua et al. (2002). The Local Meteoric Water Line (LMWL) from Boschetti et al., (2019) is also shown.

The δ^2H and $\delta^{18}O$ data are similar for the three CP wells and fall in the range -5‰ to -3‰ for oxygen and -72‰ to -80‰ for deuterium. CP data points show a very strong oxygen shift related to the LMWL, possible a consequence of ^{18}O-exchange between water and rock at elevated temperatures (Truesdell & Hulston, 1980). Considering a local meteoric recharge with an isotopic composition of -80‰ and -12‰ for deuterium and oxygen, respectively (orange star in the graph), an ^{18}O-shift of about seven delta is obtained. Some authors reported similar isotopic shifts for meteoric components (Munoz-Saez et al., 2018) in nearby areas. The magnitude of the oxygen shift is related both to temperature, the degree of exchange and relative proportions and ^{18}O composition of the exchanging water and rock (Giggenbach, 1991b). In Figure 7, the isotopic ^{18}O values for volcanic fresh rocks sampled close to the CP site are reported (black filled box; Longstaffe et al., 1983; Valley and Taylor, 1986), while ^2H is the one corresponding to the thermal water. A fractionation factor ε between water and rock of 9‰, like the one in Figure 7 between CP fluid and fresh rocks, corresponds to a temperature of about 250°C if equilibrium with quartz is invoked (Giggenbach, 1991b). Of course, this is a maximum value for ε, given the absence of direct determination on reservoir minerals. An input of an external source of water, the so-called "andesitic water", could not be ruled out *a priori*, with a possible contribution of about 40%.

In the diagram of Figure 7, the isotopic composition of steam formed from the brine at 250°C is reported following Giggenbach and Stewart (1982), considering the dilution groundwater isotopic values as above. It is interesting that the position of fumarolic condensate sampled by Urzua et al. (2002) is close to the apex of the field.

3.4 Geochemical conceptual model

In Figure 8, a tentative geochemical conceptual model is constructed. The cross section cuts the field W-E and SW-NE. Isotherms are reconstructed on the basis of in-well measurements and geothermometric estimations, and becomes deeper close to the supposed intrusive beneath the Cerro Aguilucho-Apacheta volcanic edifices. The known geothermal resource Na-Cl type is mostly hosted in the Apacheta Graben, which structures possibly delimitate the system towards E and W. Eastern well CP-4 found injectivity and shares the same hydrostatic regime of the productive wells (Baccarin et al., 2020), although the temperature profile shows lower values compared to the central part of the graben. Well CP-4 was not tested for production, so a fluid sample is not available. A deep circulating water (natural recharge), not related to the shallow cold aquifer found in Perdiz-1, could be invoked to explain the thermal behavior of this area. Alternatively, the system is simply fading off, with the graben fault acting as a semipermeable barrier for fluid circulation.

Westward, the relationships between the fumaroles and the geothermal reservoir are not clear at the moment, given the uncertainty on fumaroles origin, so that the boundary of the system is still to be clarified. Degassing occurs at depth and gas rises also trough the fumarole conduit up to the surface.

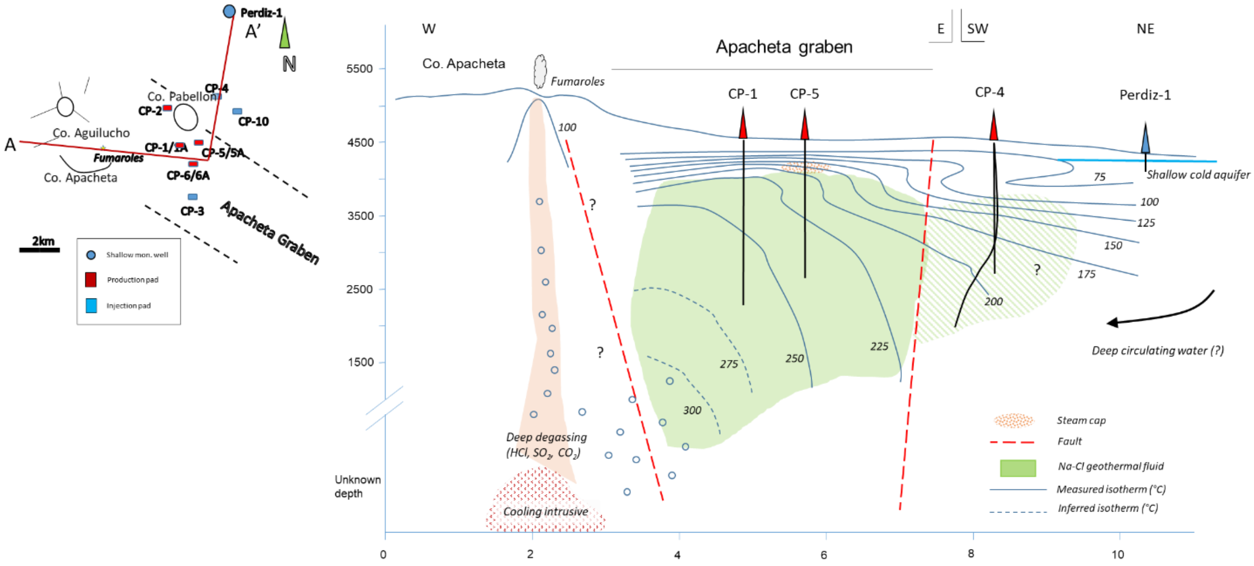

Figure 8: CP geochemical conceptual model. The cross section direction is shown on the right side structural scheme.

CONCLUSIONS

The first preliminary chemical data from the Cerro Pabellón geothermal field are presented in this work. CP is a new geothermal power plant and, therefore, relatively few data are currently available. The fluid is a typical sodium-chloride water, slightly acidic at reservoir condition, with a TDS of 14-17 g/L. Chemically, it shares characteristics typical of other systems in the region: high solutes content enriched in Ca, rare alkalies, and low gas content. The salinity and the noticeable isotopic oxygen shift indicate a system with a very long residence time, and strong interaction with the volcanic andesitic host rock.

The fast responding quartz geothermometer shows temperatures identical to those measured in the wells, while the slow responding Na-K and CO_2 indicates equilibrium temperature of 280°-290°C, so that presumably the system is even hotter at greater depth. As for the present knowledge, the system is hosted in the Apacheta graben structure.

The relationship with the fumaroles present on Cerro Apacheta are not clear, which could have an impact on the extension of the system toward the west, so additional sampling and analysis is needed to clarify this aspect. Finally, to complete the geochemical model of the area, sampling of superficial aquifers and shallow wells is desirable. As more data will become available from well sampling, the model will be refined.

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