Preliminary conceptual model of the Cerro Blanco caldera-hosted geothermal system (Southern Puna, Argentina): Inferences from geochemical investigations


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ABSTRACT

The Cerro Blanco Caldera (CBC) is the youngest collapse caldera system in the Southern Central Andes (Southern Puna, Argentina). The CBC is subsiding with an average velocity of 0.87 cm/year and hosts an active geothermal system. A geochemical characterization of emitted fluids was carried out based on the chemical and isotopic compositions of fumaroles, and thermal and cold springs discharged in this volcanic area with the aim of constructing the first hydrogeochemical conceptual model and preliminary estimate the geothermal potential.

The main hydrothermal reservoir, likely hosted within the pre-caldera basement rocks, has a Na⁺-Cl⁻ (HCO₃⁻) composition with estimated temperatures ≥135 °C. The unconsolidated, fine-grained Cerro Blanco ignimbrite likely acts as the cap-rock of the hydrothermal system. The presence of phreatic eruption breccias in the surrounding area of the geothermal fumaroles supports the effectiveness of the pyroclastic deposit as sealing rocks.

The isotopic data of water (δ¹⁸O and δD) indicate a meteoric recharge of the hydrothermal reservoir, suggesting as recharge areas the sectors surrounding the CBC, mainly towards the W and NW where large outcrops of the pre-caldera basement exist. A fault-controlled hydraulic connection between the hot springs and the hydrothermal reservoir is proposed for the Los Hornitos area. The fumaroles show the typical compositional features of hydrothermal fluids, being dominated by water vapor with significant concentrations of H₂S, CH₄ and H₂.

Considering the high geothermal gradient of this area (∼10⁴ °C/km) and the relatively high fraction of mantle He (∼39%) calculated on the basis of the measured R/Ra values, the hydrothermal aquifer likely receives inputs of magmatic fluids from the degassing magma chamber. The preliminary geothermal potential at CBC was evaluated with the Volume Method, calculating up to E = 11.4*10¹⁸ J. Both the scarce presence of superficial thermal manifestations and the occurrence of an efficient cap-rock likely contribute to minimize the loss of thermal energy from the reservoir. The results here presented constitute the necessary base of knowledge for further accurate assessment of the geothermal potential and ultimately the implementation of the geothermal resource as a viable energy alternative for small localities or mining facilities isolated from the National Interconnected System due to their remote localization.

1. Introduction

Andean South American countries constitute promising sites for geothermal exploration due to their position upon the Pacific Ring of Fire, where magmatic and tectonic features favor the development of geothermal systems. Despite the proven existence of this resource in South America, only one geothermal plant is currently producing electrical energy. This is the recently inaugurated (September 2017)
Cerro Pabellón 48 MW installed power geothermal plant, in Chile. Prior to this, a 0.67 MW binary prototype unit was in operation for a short period of time until 1996 (Bertani, 2010) in the Copahue geothermal field (Neuquén Province, Argentina). During the last years, there has been a renewed interest for developing the geothermal resource in Argentina due to the increasing demand for new sources of energy. The aforementioned fostered by a recently regulatory framework aimed to promote the use of non-conventional renewable energies. The most interesting high-temperature geothermal systems in Argentina are located in the western sector (Central and Southern Volcanic Zones of the Andes), likely associated with the Neogene-Quaternary volcanic arc (Fig. 1a). Geothermal systems related to magmatic intrusions are generally the hottest (T ≥ 220 °C) and most prolific producers of geothermal electricity worldwide (Stimac et al., 2015). Particularly, young silicic calderas, as Cerro Blanco (Northwestern Argentina), are ideal geological settings for the development of large long-lived geothermal systems (e.g. Campi Flegrei, Long Valley Caldera; Goñi and Janik, 2000). The formation of a caldera requires the accumulation of magma at shallow depth, which implies a high heat flux in the upper crust. Moreover, faulted and fractured intra-caldera rocks can act as great reservoirs for fluids, due to their secondary permeability capable to trap meteoric waters, which are heated by subjacent magmas (Stimac et al., 2015). In addition, the Cerro Blanco Caldera (CBC; Fig. 1a and b) represents an important geothermal target because it is the youngest collapse caldera system in the Southern Central Andes (Middle Pleistocene-Holocene; Viramonte et al., 2008; Montero-López et al., 2009, 2010; Fernández-Turiel et al., 2019, Báez et al., 2015). CBC is part of the volcanic activity related to the Cerro Blanco Volcanic Complex (CBVC), located in the southern limit of the Andean Plateau (Catamarca Province, Argentina). Despite the existence of recent publications focused on the volcanic aspects of the CBVC (Fernández-Turiel et al., 2019; Báez et al., 2015, 2017), the hydrothermal activity in this area is still scarcely investigated (Viramonte et al., 2005a; Chiodi, 2015). Fluid geochemistry constitutes a valuable tool for geothermal prospections and the development pre-feasibility investigations (e.g. D’Amore and Panichi, 1980; Giggenbach, 1991, 1997a). In this work, we present the results of a geochemical survey carried out on the hydrothermal manifestations related to CBC to provide insights into (i) the physicochemical conditions acting on the fluid reservoir, (ii) the primary fluid source(s) and (iii) secondary processes controlling the fluid chemistry. Eventually, the very first hydrogeochemical conceptual model and a preliminary estimation of the geothermal potential are proposed.

2. Geological and volcanic features

CBVC (Fig. 1a and b) was recognized as a nested caldera system with associated domes and pyroclastic deposits (Seggjario et al., 2000; Arnost et al., 2005; Viramonte et al., 2005a, 2005b). All erupted products are rhyolitic/rhyodacitic in composition and middle Pleistocene-Holocene in age (Báez et al., 2015 and references therein). CBVC was built on a complex basement that includes (i) Neoproterozoic-Lower Paleozoic metamorphic rocks of low to medium grade, Ordovician volcano-sedimentary sequences, (ii) Upper Paleozoic continental deposits and (iii) Cenozoic deposits that infill Paleogene foreland basins (Seggjario et al., 2000). Furthermore, CBVC overlies a Miocene-
Pleistocene volcanic sequence consisting of several andesitic-dacitic stratovolcanoes aligned in a SW-NE direction (La Hoyada Volcanic Complex, LHVC), which constitutes the San Buenaventura range (Seggiaro et al., 2000; Montero López et al., 2010; Bustos et al., 2019). CBVC stratigraphy consists of two main ignimbrite units separated by major unconformities that represent periods of quiescent volcanic activity (Báez et al., 2015). The oldest is Campo de la Piedra Pómez Ignimbrite (Pleistocene) related to the largest caldera collapse in the evolution of the CBVC. The youngest ignimbrite unit is Cerro Blanco Ignimbrite (Holocene) that represents further reactivations of the CBVC resulting in the nesting of at least two collapse calderas. The youngest activity in the CBVC also includes the emplacement and destruction of several lava domes (Báez et al., 2017). It is important to highlight that CBVC had at least two large-scale eruptions (Volcanic Explosivity Index ≥ 6) over the past 100,000 years including one of the greatest Holocene volcanic events in the Central Andes (Fernández-Turiel et al., 2019; Báez et al., 2015). In addition, the CBC is subsiding at an average velocity of 0.87 cm/year (Brunori et al., 2013; Henderson and Pritchard, 2013; López, 2016) and hosts an active geothermal system (Viramonte et al., 2005a; Chiodi, 2015; Chiodi et al., 2017). The main tectonic structures in the study area consist of reverse faults with NNE-SSW to NE-SW orientation in response to the NW-SE shortening associated with vertical extension, developed in the Southern Puna from Miocene to Pliocene (Viramonte et al., 2005a). From Pliocene to present, the tensional field changed to a NE-SW extensional regime associated with strike-slip and late normal reactivation of reverse faults (Marrett and Emerman, 1992; Montero López et al., 2010). The recent extension in the Southern Puna was associated either with the gravitational collapse of the plateau or episodic lithospheric thinning and delamination under Puna’s thick crust (Oucea et al., 2013; Schoenbohm and Strecker, 2009).

3. Geothermal manifestations at CVCB

According to the classification proposed by Moeck (2014), the studied geothermal system can be interpreted as a volcanic field type due to, as follows: i) its location in a magmatic arc above a subduction zone in a convergent plate margin in association with recent magmatism (recent magmatism sensu McCoy-West et al., 2011), ii) the occurrence of a magma chamber providing the heat source, iii) the structural control on fluid circulation. The surface manifestations of the Cerro Blanco Geothermal System (CBGS) are situated in the northern sector of CBC (26.7588° S-67.7394° W, 4132 m a.s.l.) associated with a NE-SW extensional regime controlled with strike-slip and late normal reactivation of reverse faults (Marrett and Emerman, 1992; Montero López et al., 2010). The recent extension in the Southern Puna was associated either with the gravitational collapse of the plateau or episodic lithospheric thinning and delamination under Puna’s thick crust (Oucea et al., 2013; Schoenbohm and Strecker, 2009).

4. Sampling and analytical methods

4.1. Water and gas sampling

Nine water samples from 3 bubbling pools (LH1-LH3), 4 cold springs (EM1, EM3, CBVF1-CBVF2), 2 creeks (EM2 and RLH) and 1 snow sample (CBN) were collected. Water temperature, pH and electrical conductivity were measured in the field using portable instruments (Hanna HI 98195; accuracy: ± 0.15 °C, ± 0.02 and ± 1%, respectively). Alkalinity (expressed as HCO₃⁻) and silica were analyzed in situ by (i) acidimetric titration using HCl 0.03 N, phenolphthalein and bromophenol blue as indicators, and (ii) molecular spectrophotometry (Hanna HI 96770C; ± 1 mg/l), respectively (Table 1). At each sample point, 4 aliquots (2 filtered samples at 0.45 μm and acidified with ultrapure HCl and HNO₃ for the analysis of major cations and trace elements, respectively, 1 filtered sample for the analysis of anions and 1 unfiltered sample for the analysis of water isotopes) were collected.

Gas samples from bubbling pools (LH1, LH2, LH3) were sampled using a plastic funnel up-side-down positioned above the bubbles and connected through tygon tubes to the sampling flasks. The latter consisted of (i) a pre-evacuated 60 mL glass thorium tamped bottle filled with 20 mL of a 4 N NaOH solution for the analysis of the gas chemical composition (Gilgenbach and Goguel, 1989) and (ii) a pre-evacuated 60 mL glass flask for the analysis of the carbon isotopic ratio in CO₂ (Vaselli et al., 2006). One fumarole (CBa) was sampled with the same devices used for the bubbling gases. At this sampling site, a steam condensate (for the analysis of the δD and δ¹⁸O values of water) was collected using a water-cooler glass condensing system.

One water sample (EM1) for the analysis of the dissolved gases was collected in a 50 mL glass flask equipped with a rubber septum. In the laboratory, a 10 cc headspace was created in the flasks by injecting H₂ through the septum. Following a modified method based on Chioldini (1996), the chemical composition was computed by considering the measured concentrations of gases stored in the headspace on the basis of: i) headspace gas pressure and volume, ii) volume of water in the flask and iii) solubility coefficients of each gas compound (Whitfield, 1978). The location (coordinates) of the sampling sites is reported in Tables 1 and 2 and plotted in Fig. 1b.

4.2. Chemical and isotopic analyses of water samples

Major cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, Li⁺ and NH₄⁺) and anions (F⁻, Cl⁻, SO₄²⁻, Br⁻ and NO₃⁻) were analyzed by ion-chromatography (IC: Metrohm 861 and 761, respectively). The analytical error was ±5%. Boron was analyzed by molecular spectrophotometry (MS; Beckman DU 520) using the Azomethine-H method (Bencini, 1985). The analytical error was ±5%.

Trace elements were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) using an Optima 8000 PerkinElmer spectrometer. The analytical error was ±10%.

The ¹⁸O/¹⁶O and δ¹⁸O/δ²H ratios in water (expressed as δ¹⁸O-H₂O and δ²H-H₂O % vs. V-SMOW, respectively) were analyzed using an Ultra High-Pressure Isotopic Water Analyzer Picarro L2130-i laser spectrometer. The analytical errors for δ¹⁸O-H₂O and δ²H-H₂O values were ± 0.25‰ and ± 1.20‰, respectively.
4.3. Chemical and isotopic analysis of dissolved and bubbling gases

Inorganic gases (N₂, O₂, H₂, CO, Ar, Ne and He) in the headspace of the soda flasks, as well as those collected in the headspace of the dissolved gas vial (N₂, O₂, CO, Ar, He, Ne, CO₂ and H₂S), were analyzed by gas chromatography (GC) using a Shimadzu 15A instrument equipped with a Thermal Conductivity Detector (TCD). Carbon dioxide and H₂S in the alkaline solution were analyzed as CO₃²⁻, by acidimetric titration with a HCl 0.1 N solution, and SO₄²⁻, by IC after oxidation with H₂O₂, respectively. Light hydrocarbons, including CH₄, were determined by using a Shimadzu 14A gas chromatograph (GC), equipped with a 10-m-long stainless-steel column packed with Chromosorb PAW 80/100 mesh coated with 23% SP 1700 and a Flame Ionization Detector (FID). The analytical errors for GC analyses were ≤5%.

The δ¹³C/¹²C ratio of dissolved CO₂ (expressed as δ¹³C-CO₂‰ vs. V-PDB) in EM1 was computed from the δ¹³C values measured in CO₂ of the flask headspace (δ¹³C-CO₂STRIP), using the ε₁ factor for gas–water isotope equilibrium proposed by Zhang et al. (1995), as follows:

ε₁ = δ¹³C-CO₂estrip - δ¹³C-CO₂STRIP × 0.0049 × (T(°C) - 1.3) (1)

The δ¹³C-CO₂STRIP analysis was carried out with a Finningan Delta Plus mass spectrometer after extracting and purifying CO₂ by using liquid N₂ and N₂-trichloroethylene cryogenic traps (Evans et al., 1998; Vaselli et al., 2006). The δ¹³C/¹²C ratios of CO₂ (expressed as δ¹³C-CO₂‰ vs. V-PDB) of the bubbling gas flasks were measured by using 2 mL of the soda solution after the addition of ~5 mL of anhydrous phosphoric acid for the extraction of CO₂. Isotopic equilibration was achieved in a thermal bath at the temperature of 25 ± 0.1 °C for at
Table 1

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<th>ID</th>
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<td>1390</td>
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<td>1680</td>
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<td>1550</td>
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Table 2

Chemical composition (in μg/L) of minor elements of thermal waters from Los Hornitos area, Southern Puna, Argentina.

<table>
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<th>ID</th>
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least 8 h. The extracted CO₂ was treated as previously described for the CO₂STRIP. The 13C/12C ratios were analyzed with a Finningan Delta Plus mass spectrometer. Carrara and San Vincenzo marbles (Internal), as well as NBS18 and NBS19 (International) standards were used to estimate the external precision. The analytical errors were ± 0.05‰ and ± 0.1‰, respectively. The Helium isotopic ratios (expressed as R/Ra, where R is the 3He/4He measured ratio and Ra is the 3He/4He ratio in the air: 1.39 × 10⁻⁶; Mamyrin and Tolstikhin, 1984) and those of 4He/²⁰Ne were determined by using a double collector mass spectrometer (VG 5400-TFT) according to the method described by Ingugiazzo and Rizzo (2004). The analytical error was ± 1%. The R/Ra values were corrected for atmospheric contamination using the 4He/²⁰Ne ratios (Poreda and Craig, 1989a,b), as follows:

\[
Rc/Ra = \left( \frac{R}{Ra_{measured}} \right) - \left( \frac{1}{r} \right)
\]

where \( r \) is (4He/²⁰Ne)air/(4He/²⁰Ne)measured and that of (4He/²⁰Ne)air is 0.421 at the estimated altitude of recharge of approximately 4000 m (Hoke et al., 1994).

5. Results

5.1. Chemical and stable isotopic (δ¹⁸O and δD) composition of waters

The chemical-physical parameters as well as the chemical and isotopic composition of the CBC waters are listed in Table 1. Based on the chemical composition, 3 groups of waters can be distinguished (Fig. 3):

1) Group 1 (Na⁺-Cl⁻(HCO₃⁻) waters) includes thermal waters (LH1, LH2 and LH3 samples) emerging from the Los Hornitos zone, which shows nearly neutral to slightly acidic pH values (from 6.87 to 6.41), relatively high outlet temperatures (up to 67.4 °C) and TDS values (up to 5200 mg/L). These waters are also characterized by relatively high outlet temperatures (up to 67.4 °C) and TDS values (up to 5200 mg/L). These waters are also characterized by relatively high outlet temperatures (up to 67.4 °C) and TDS values (up to 5200 mg/L). These waters are also characterized by relatively high outlet temperatures (up to 67.4 °C) and TDS values (up to 5200 mg/L).

2) Group 2 (Na⁺(K⁺)-HCO₃⁻ waters), including the EM1 and EM3 cold springs and the EM2 creek from El Médano area, shows relatively low outlet temperatures (≤ 17.1 °C), pH values ranging between 6.65 and 8.15, and low TDS values (up to 610 mg/L).

3) Group 3 (Ca²⁺-HCO₃⁻ waters) refers to two cold springs (CBVF1 and CBVF2) located within the western sector of the CBC, where strongly altered rocks of the LHVC crop out, and the RLH creek from Los Hornitos zone. These samples have slightly alkaline pH (between 7.17 and 7.85) and show low outlet temperatures ≤ 14.3 °C and TDS values (up to 280 mg/L).

Trace element concentrations of the thermal water samples are listed in Table 2. The highest values were measured for Sr, Cs, As and Rb (up to 5,060, 2,160, 1680 and 1550 μg/L, respectively), followed by Fe, Mn, Ba and Se (up to 440, 370, 71 and 19 μg/L, respectively).

The oxygen and hydrogen isotopic data (expressed as δ¹⁸O-H₂O and δD-H₂O‰ vs. V-SMOW, respectively) for the thermal waters vary in a narrow range, from −5.43 to −5.20 and from −31.66 to −30.78‰ vs. V-SMOW, respectively, whereas those of the cold springs and creeks...
vary from $-5.31$ to $-3.38$ and from $-35.14$ to $-20.47$ ‰ vs. V-SMOW, respectively. The $\delta^{18}O$–H$_2$O and $\delta^D$–H$_2$O values of the snow sample (CBN) are significantly more negative than those determined in the water samples, being $-7.37$ and $-40.1$ ‰ vs. V-SMOW, respectively. Finally, the $\delta^{18}O$–H$_2$O and $\delta^D$–H$_2$O values of the steam condensate (CB) from the fumarole are $-5.1$ and $-49$ ‰ vs. V-SMOW, respectively (Table 1).

5.2. Chemical and stable isotopic ($\delta^{13}C$–CO$_2$ and R/Ra) composition of gases

The outlet temperature of the CBa fumarole is 93.7 °C (Table 3). The chemical composition of this gas sample (Table 3) is dominated by water vapor (89% by vol.), whereas CO$_2$ is largely the most abundant dry gas compound (950 mmol/mol), followed by N$_2$ (36 mmol/mol), H$_2$S (14 mmol/mol) and H$_2$ (0.037 mmol/mol). Helium is present at relatively low concentrations (0.0014 mmol/mol) whereas CO was below the analytical detection limit (0.001 mmol/mol). The concentrations of the atmospheric gases (O$_2$, Ar and Ne) are 0.71, 0.34 and 0.00018 mmol/mol, respectively. Methane is the most abundant organic gas (0.022 mmol/mol), whereas heavier hydrocarbons have significantly lower concentrations ranging from 0.00011 mmol/mol (i-C$_5$H$_{12}$) to 0.0054 mmol/mol (C$_2$H$_6$). The chemical composition of the bubbling pools (Table 3), expressed as dry gas fraction since water vapor mostly condensed in the liquid phase at the surface, is dominated by CO$_2$ (between 730 and 880 mmol/mol) and N$_2$ (up to 260 mmol/mol), with minor concentrations of CH$_4$ (up to 0.011 mmol/mol), Ar (up to 5.9 mmol/mol), O$_2$ (up to 2.5 mmol/mol), He (up to 0.0019 mmol/mol) and Ne (up to 0.0031 mmol/mol). Hydrogen was detected only in LH2 sample (0.011 mmol/mol), with concentrations comparable with that measured in the fumarole, whilst H$_2$S, CO and hydrocarbons were not detected. The chemical composition of the EM1 dissolved gases (Table 3) is characterized by dominant CO$_2$ and N$_2$ (up to 560 and 420 mmol/mol, respectively), and relatively high concentrations of atmospheric gases (Ar, O$_2$ and Ne: 9.6, 7.9 and 0.0062 mmol/mol, respectively), whereas those of He and CH$_4$ were 0.054 and 0.011 mmol/mol, respectively. Hydrogen, H$_2$S, CO and hydrocarbons were not detected.

The isotopic composition of the gas samples is listed in Table 3. The $\delta^{13}C$–CO$_2$ values span in a narrow range, from $-9.56$‰ to $-5.23$‰ vs.
V-PDB. The Rc/Ra (where Rc is the corrected isotopic ratio calculated according to the ^4He/^20Ne ratio) values measured in two selected samples (CBa and LH2) were 2.16 and 1.11, respectively.

6. Discussion

6.1. Processes controlling the chemical and isotopic composition of waters

According to the $\delta^{18}$O–D$_2$O and $\delta^2$H–D$_2$O diagram (Fig. 4), where the Local Meteoric Water Line (LMWL: ($\delta^D = (8.01 \pm 0.08) \delta^{18}O + (15.2 \pm 0.7)$‰; Gonfiandini et al., 2001) was reported, the CBC waters have a meteoric origin. EM2, CBVF1 and CBVF2 plots slightly off of the LMWL (Fig. 4), possibly due to evaporation in a high-altitude hyper-arid environment, which causes kinetic fractionation that often increases the $\delta^{18}$O values of residual surface waters (Gat, 1996; Stewart, 1975; Fiorella et al., 2015; Bershaw et al., 2016), a process also invoked to explain the isotopic data of stream water across the Andean Plateau (Bershaw et al., 2016). The main compositional features of Group 1, i.e. i) relatively high TDS values (up to 5169 mg/L), ii) slightly acidic pH, iii) high Li$^+$ concentrations and iv) high B and Ba concentrations, are typical of hydrothermal fluids related to geothermal and volcanic systems (Giggenbach, 1988, 1991). Relatively high concentrations of As, Cs, Rb and Mn (Table 2), in the range of contents characterizing waters discharges in hydrothermal environment (e.g. Aiuppa et al., 2006; Kaasalainen and Stefánsson, 2012; Wilson et al., 2012; Göb et al., 2013), were also measured. Such high concentrations of Li, Rb and Cs (up to 7.6 and 2.1 mg/L) are likely related to the high concentrations of these elements in rocks of rhyolitic and andesitic composition (Nicholson, 1993), which were recognized in the study area. Iron concentrations are low (<0.44 mg/L), in the range of those characterizing chloride-rich fluids (Nicholson, 1993). Nevertheless, the Na$^-$/Cl$^-$ mol-ratios (Fig. 5a) are higher than the stoichiometric ratio expected for typical geothermal brines (e.g. Giggenbach, 1997a).

Such a Na$^-$ excess may be caused by intense leaching of Na-silicates (e.g. feldspars and their alteration products), which are abundant in the study area. The relatively high HCO$_3^-$ values of these waters (Table 1) were likely due to CO$_2$ dissolution, a process that seems to be
particularly efficient for the LH3 sample having a \((\text{HCO}_3^- + \text{CO}_3^{2-})/\text{Ca}^{2+}\) mol-ratio of 2.4 (Fig. 5b). Travertine precipitation (Mors et al., 2016) is likely the cause of the \((\text{SO}_4^{2-})/(\text{Ca}^{2+} + \text{Mg}^{2+})\) mol-ratio > 1.

The \(\text{B}/\text{Cl}^-\) ratios (between 0.01 and 0.02), lower than those typically found in fluids from geothermal systems (e.g. Giggenbach, 1991), are in the range of those characterized by heated aqueous solutions in contact with rhyolite (Ellis and Mahon, 1964, 1967; Giggenbach, 1995). Furthermore, the relatively high Cl and B contents suggest the addition of these two elements possibly through absorption of low \(\text{B}/\text{Cl}\) magmatic vapors (Giggenbach, 1991, Fig. 6).

The cold waters pertaining to groups 2 and 3 are related to a shallow, short-live circulation source, as indicated by their low TDS contents and outlet temperatures (Table 1). However, different processes are proposed to explain their chemical composition accordingly both the geological framework and the location of the samples (Fig. 1). The Na\(^+\) (K\(^+\))-HCO\(_3^-\) composition of the cold waters from El Médano area (Group 2) was probably caused by low-temperature alteration of glass contained in the alkali-rich volcanic rocks, the latter being extensively present in the area (Arnosio et al., 2008; Báez et al., 2015). This process involves considerable hydrogen exchange for Na\(^+\) and K\(^+\) ions, with little variation in other major- or trace-element contents (Cerling et al., 1985). The relatively high \(\text{SO}_4^{2-}\) content shown by the EM1 sample (Fig. 3c) is likely due to the dissolution of \(\text{H}_2\text{S}\)-bearing gases phase into the shallow aquifer, as also suggested by both its location near the caldera border (Fig. 1) and the relatively high \(\text{CO}_2\) content in the dissolved gases (Table 3). On the other hand, an incipient oxidation of sulfur-bearing minerals (e.g. pyrite) affecting the hydrothermal altered rocks of LHVC (Ricci et al., 1999) could also explain its \(\text{SO}_4^{2-}\) content. However, it is likely that this process is acting more effectively in the CBVF1 and CBVF2 (Group 3) cold springs from the western sector of the caldera (Fig. 3c), where strongly altered rocks of the LHVC occur.

6.2. Origin of gases

The CBa fumarole shows the typical features of hydrothermal fluids, as follows: i) dominant water vapor, ii) occurrence of \(\text{H}_2\text{S}, \text{CH}_4\) and \(\text{H}_2\) at significant concentrations and iii) lack of magmatic gases (\(\text{SO}_2, \text{HCl}\) and HF). The relatively high \(\text{N}_2/\text{Ar}\) ratio, i.e. higher than that of air (Fig. 7a; Giggenbach, 1992) indicates the presence of extra-atmospheric \(\text{N}_2\) likely from sediments overlying the subducted slab which can produce \(\text{N}_2/\text{Ar}\) ratios up to 2000 (Matsuo et al., 1978; Giggenbach, 1997b; Sano et al., 2001). The \(\text{N}_2\) excess/\(^{3}\text{He}\) ratios, between \(1.43 \times 10^7\) and \(5.5 \times 10^9\) (Table 4), are consistent with this deep origin for \(\text{N}_2\) being in the range commonly found in gases discharging from arc volcanoes (Snyder et al., 2003).

The LH1, LH2 and LH3 bubbling pools and the EM1 dissolved gas had \(\text{N}_2/\text{Ar}\) ratios consistent with that of air-saturated water (ASW) (Fig. 7a). According to Fig. 7a, \(\text{He}\) seems to be mostly atmospheric. However, the relatively high He/Ne ratios measured in these samples (i.e. more than an order of magnitude higher than that of air; Table 4), imply a significant extra-atmospheric \(\text{He}\) source. In fact, the \(\text{Rc}/\text{Ra}\) values (Table 4; Fig. 7b), are consistent with those found in gases from the Andean Volcanic Arc (from 0.92 to 5.52; e.g. Hoke et al., 1994; Tassi et al., 2010; Capaccioni et al., 2011), which are lower than the typical values found in other volcanic arcs (between 5 and 8; Poreda and Craig, 1989a,b; Hilton et al., 1993; Giggenbach and Poreda, 1993). Considering that the \(\text{Rc}/\text{Ra}\) ratios of gases from subduction zones are mainly controlled by the crustal thickness, being related to the residence time of fluids in the \(^{4}\text{He}\)-rich crust (e.g. Hilton et al., 1993; Fischer and Chiodini, 2015), the \(\text{Rc}/\text{Ra}\) values of the CBC samples are consistent with the abnormally thick crust of the Southern Puna (Heit et al., 2014), fitting well with those values from hydrothermal systems from the Central Andean Volcanic Zone (e.g. Tassi et al., 2010; Benavente et al., 2016; Peralta Arnold et al., 2017). As far as the \(\delta^{13}\text{C}-\text{CO}_2\) values are concerned, they are consistent with those of mantle \(\text{CO}_2\) (Rollinson, 1993; Sano and Marty, 1995; Hoefs, 1997; Ohmoto and Goldhaber, 1997). However, the \(\text{CO}_2/^{3}\text{He}\) ratios (up to \(2.26 \times 10^{11}\); Table 4; Fig. 7c) are two orders of magnitude higher than

![Fig. 5. (a) Cl\(^-\) vs. Na\(^+\), (b) HCO\(_3^-\) vs. Ca\(^{2+}\) binary diagrams for the cold and thermal waters from the CBC. Symbols as in Fig. 3.](image)

![Fig. 6. Cl\(^-\)/100, Li\(^+\), B/4 ternary diagram (Giggenbach, 1991) for the cold and thermal waters from the CBC. Symbols as in Fig. 3.](image)
the mantle values ($\sim 1.2 \times 10^9$; Marty and Jambon, 1987), suggesting that CO$_2$ derived from a mixture between MORB-related gases and gases from a crustal source such as i) degradation of organic matter and/or ii) subduction of C-bearing material. The first option is unlikely since organic CO$_2$ is characterized by $\delta^{13}C_{CO_2}$ values $\leq -20$‰ vs. V-PDB (Hoefs, 2008), i.e. too negative in comparison with those of the CBC gases. On the other hand, a significant contribution of CO$_2$ from reactions involving C-bearing material, which generally shows $\delta^{13}C_{CO_2}$ values between −2 and +2‰ vs. V-PDB (Rollinson, 1993), seems to be excluded by the more negative CBC carbon signature. Notwithstanding, secondary processes, such as calcite precipitation (Barry et al., 2019) and $^{13}C$-$^{12}C$-fractionation, the latter being related to the dissolution of gaseous CO$_2$ in the hydrothermal aquifer (Gilfílían et al., 2009), may explain a $^{13}C$-enrichment in the CBC gases. In agreement with this hypothesis, extreme $^{13}C$ enrichments (up to $+13$‰ V-PDB) were found in primary calcite and aragonite precipitates from high-altitude lakes in the southern Andean Altiplano (Valero-Garcés et al., 1999). It is important to highlight that, in the geodynamic context of the Southern Puna, the genesis of silicic magmas commonly involves significant contribution of partial melting of the crust (e.g. Caffé et al., 2002; Kay et al., 2011). Therefore, the origin of CO$_2$ in the CBC gases is likely related to degassing crust-contaminated magmas, subsequently affected by secondary processes.

6.3. Temperature estimations of the hydrothermal reservoir

Considering the chemical equilibria in the Na–K–Mg system, commonly adopted for aqueous solutions interacting with the authigenic mineral assemblage (including Na- and K-feldspars, K-micas, chlorite and silica), the LH1-LH3 waters, which show the highest Cl$^-$ concentrations, point to temperatures of 235–237 °C (Fig. 8a). Similar temperatures are indicated by the $(10 K^+/10 K^+ + Na^+)$ vs. $10Mg^{2+}/[10Mg^{2+} + Ca^{2+}]$) geothermometer (Fig. 8b), where the effect of Ca$^{2+}$ in the calculations and the mineral assemblage were considered (Chioldini et al., 1995). Notwithstanding the consistency of the two independent geothermometers, such calculated temperatures should be considered with severe caution due to the incomplete maturity of these CBC waters that is also indicated by the lack of any isotopic shift in the $\delta^{18}O$‰ (Fig. 4).

Water-rock exchange reactions involving Mg proceed relatively fast at low temperatures, thus the K/$\sqrt{Mg}$ and Li/$\sqrt{Mg}$ ratios appear to be good geothermometers for low maturity waters (Fournier, 1991; Inguaggiato et al., 2000). The temperatures estimated on the basis of the for K/$\sqrt{Mg}$ and Li/$\sqrt{Mg}$ ratios, between 121 and 127 °C, and 137 and
144 °C, are actually lower than those calculated in the Na–K–Mg–Ca system (Table 5) and likely reflect equilibria attained during the fluid uprising toward the surface. Saturation index (SI = log AP/Ksp; where AP: ion activity product and Ksp: solubility product) values for various mineralogical species from the emergence temperature 42.7–300 °C were computed using the PHREEQC v. 3.2 (Parkhurst and Appelo, 1999) software package (Inl: Lawrence Livermore National laboratory database) for the LH3 water sample (the sample that most closely approximates to the partial equilibrium line; Fig. 8a). Minerals (except for Analcime, Prhenite, Wairakite and Clinozoisite) seem to attain the mineralogical species from the emergence temperature 42.7 °C, as also invoked to explain the equilibrium temperatures obtained adopting these geothermometric approach are not reliable.

The CO2 geothermometer proposed by Giggenbach and Goguel (1989) assumes that Pco2 is controlled by interactions with crustal rocks, whereas further geothermometric estimations can be carried out based on the dependence of H2 fugacity on temperature (Giggenbach, 1987). To avoid possible problems related to the use of univariant reactions, Giggenbach (1991) proposed the use of CO2/Ar and H2/Ar ratios, assuming that Ar has a meteoric origin. Considering that hydrothermal fluids are O2-free, to prevent the effect of possible air contamination at the surface, Ar* values were computed, as follows:

\[ \text{Ar}^* = \text{Ar} - \frac{O_2}{22} \]  

where the O2/22 ratio is the minimum Ar concentration from air contamination. The dependence of H2 on RH in the two phases can be expressed, as follows:

\[ \log(H_2/Ar^*)_L = R_H + 6.52 - \log(B_{H2}) \]  
\[ \log(H_2/Ar^*)_V = R_H + 6.52 - \log(B_{H2}^*) \]  

where B_{H2} and B_{H2}^* are the vapor/liquid distribution coefficient of H2 and Ar, respectively.

At redox conditions controlled by the D’Amore and Pancioli (1980) redox buffer (DP), the dependence of CO2/Ar* ratios on temperature is given by:

\[ \log(CO_2/Ar^*)_V = \log(P_{CO2}) - 5.51 + 2048/ T + 6.52 - \log(B_{CO2}) \]  
\[ \log(CO_2/Ar^*)_L = \log(P_{CO2}) - 5.51 + 2048/ T + 6.52 - \log(B_{CO2}^*) \]  

where T is in K and B_{CO2} is the vapor/liquid distribution coefficient of CO2 and the dependence of log(P_{CO2}) on temperature is given by:

\[ \log(P_{CO2}) = 0.0168xT - 3.78 \]  

where x is the temperature in Celsius. The combination of the CO2/Ar* and H2/Ar* geothermometers from 150 to 350 °C is graphically displayed in Fig. 10. Both the fumarolic gas sample (CBa) and the LH2 bubbling gas plot below the full equilibrium line with the liquid phase suggesting that they are affected by secondary processes such as: i) CO2 dissolution, as also invoked to explain the measured δ13C–CO2 values, (ii) H2 consumption at shallow deep, where the occurrence of air contamination causes oxidizing conditions and (iii) Ar addition. Thus, deep temperature estimations by using these geothermometric approach are not reliable.

6.4. Geochemical conceptual model

Based on the available geochemical, structural, and hydrogeological data, the following conceptual model is proposed, integrated in the schematic cross section of Fig. 11. A deep Na*–Cl(HCO3) aquifer, which represents the hydrothermal reservoir with temperatures of at least 135 °C (based on silica contents), is possibly hosted into the pre-caldera basement rocks (Bm; mainly in the Miocene volcanic rocks of the La Hoyada volcanic Complex; Fig. 11b), whose permeability is likely caused by the intense fracturing generated during the caldera collapse. The unconsolidated very fine-grained pyroclastic fall deposits of the Cerro Blanco ignimbrite (CBI), characterized by a low permeability, would act as the cap-rock of the hydrothermal system. In
In addition, the hydrothermal alteration of the basal section of the CBI could further decrease the low porosity of this layer. The existence of phreatic eruption breccias in the surrounding area of the geothermal fumaroles (Fig. 2a) requires that the hydrothermal aquifer may suffer over-pressurization, proving the effectiveness of the CBI as sealing rock.

In addition, the presence of pre-caldera basement blocks into the breccias supports the idea that the former could act as the main reservoir for hydrothermal fluids. The occurrence of sinter deposits in the vicinity of the fumaroles implies a water source at temperatures higher than 180 °C in the past and an efficient fluid uprising from the reservoir to the surface, likely favored by the NE-SW fault system. The isotopic data (δ18O and D; Fig. 4) indicate a meteoric recharge of the

Table 5

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<tr>
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<th>K – Mg [G] T (°C) = (4410/14.00 - log K/√Mg) - 273.15</th>
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Fig. 9. Temperature (°C) estimated for the LH3 thermal water by using the saturation indexes for various mineralogical species between the emergence temperature 42.7-300 °C.

Fig. 10. Log(H2/Ar*) vs. log(CO2/Ar*) binary diagram for bubbling and fumarolic gases the Cerro Blanco caldera. Solid lines refer to equilibria in the vapor and liquid phases controlled by the GT redox buffer system at temperatures from 150 to 350 °C (Giggenbach, 1987).
hydrothermal reservoir. According to the $\delta^{18}O$–H$_2$O vertical gradient ($\sim -2.8$‰/km, estimated with calculations based on the chemistry of the cold springs and stream waters that are plotted on the LMWL), the meteoric recharge is likely located at an altitude of 4100–4300 m a.s.l., suggesting that the sectors surrounding the CBC, mainly towards the W and NW where large outcrops of the pre-caldera basement exist, are the sites where meteoric precipitations infiltrate and supply the hydrothermal reservoir.

Fluids from the degassing magma chamber contribute significantly ($\sim 39\%$ of primordial helium, considering a R/Ra value of 5.5 for local mantle; Hoke et al., 1994) to the hydrothermal reservoir. Fluids from the fumaroles showed the typical features of hydrothermal fluids: dominant water vapor and significant concentrations of H$_2$S, CH$_4$ and H$_2$. The occurrence of cold springs in the El Médano area (EM1) with Na$^+$.HCO$_3^-$ (SO$_4^{2-}$) composition and low TDS content (Table 1) suggests the interaction between the deep hydrothermal fluids with the water table (Fig. 11b), which in calderas is usually close to the ground surface due to the relatively small topographic gradient (Hurwitz et al., 2003, 2007).

A fault-controlled hydraulic connection between the hot springs and the hydrothermal reservoir is proposed for the Los Hornitos area. Fig. 1a and b highlights that the NNE-SSW tectonic structure that uplifts Los Colorados range towards north, cutting both the pre-caldera basement and the overlying volcanic-sedimentary sequence, could act as a preferential pathway for lateral advection of hydrothermal fluids allowing the emergence of Los Hornitos hot springs towards the south. The low Na/K ratios ($\sim 15$) in these thermal waters indicate that have reached the surface rapidly, and are therefore associated with highly permeable zones (Nicholson, 1993).

Considering: (i) an average depth of the reservoir rock of $\sim 1200$ m estimated by gravimetry studies (Di Filippo et al., 2008, cross section from Báez et al., 2015), (ii) an average surface water temperature of $\sim 10$ °C (Tchilinguirian and Olivera, 2014) and (iii) the calculated reservoir temperatures using the silica content (135 °C), the local
geothermal gradient for the CBC would be around ~104 C/km. Such a high geothermal gradient resembles those proposed for caldera-hosted hydrothermal systems with acidic compositions (Wood, 1995) and would be a consequence of the high heat flow generated by the emplacement (during Holocene) of a magmatic chamber in the upper levels of the crust (~6 km depth; López, 2016).

6.5. Estimated geothermal potential

The estimation of the geothermal potential is usually done by applying the Volume Method (Muffler and Cataldi, 1978; Doveri et al., 2010), which is based on the definition of a reservoir volume, with an associated porosity and an average fluid temperature; given by:

\[
E = Er + Ef = [(1 - \varphi) \times \rho r \times \text{Cr} \times \text{Ax} \times Z (T - T_d)]
+ [\varphi \times pf \times \text{Cl} \times \text{Ax} \times Z (T - T_d)]
\]

(9)

where Er is the heat stored in the solid rocks and Ef in the fluid phase.

The area considered for the calculations (A = 39 km2) coincides with the inner depression of the CBC (Fig. 11a), where the collapse of pre-caldera blocks was mainly focused (Báez et al., 2015) and currently records the higher subsidence rates (Brunori et al., 2013; López, 2016). For the estimations of the geothermal potential, two possible thicknesses were contemplated for the reservoir (Zmin = 500 m and Zmax = 1000 m, both considered as conservative values; e.g. Sorey et al., 1991; Giordano et al., 2014), and the conservative average temperature estimated using the silica content (135°C). Considering a rock density of 2650 kg/m³ (ρr) with an average effective porosity of 0.05 (φ; e.g. Zarrouk and Simiti, 2013), 850 J/kg for the rock specific heat (Cₚ), 4270 J/kg for water specific heat (Cw) and a T₀ of 10°C as air temperature, the following results are obtained:

\[
E_{\text{min}} = 5.22 \times 10^{18} \text{ J} \quad E_{\text{max}} = 1.04 \times 10^{19} \text{ J}
\]

\[
E_{\text{min}} = 4.85 \times 10^{17} \text{ J} \quad E_{\text{max}} = 9.70 \times 10^{17} \text{ J}
\]

It is important to highlight that the estimation of the geothermal potential was made adopting all conservative values. In this sense and taken into account the geological framework, the results are probably underestimated.

7. Conclusions

The geochemical investigation presented in this work provides the baseline of the chemical and isotope composition of the superficial and groundwater systems present in the Cerro Blanco caldera-hosted hydrothermal system. The main hydrothermal reservoir has a Na⁺-Cl(HCO₃)⁻ composition with temperatures of at least 135°C. Considering the high geothermal gradient resulting for this area (~104°C/km) and the relatively high fraction of mantle He (~39%), this aquifer likely receives inputs of magmatic fluids from the degassing magma chamber. Both the scarcely presence of superficial thermal manifestations associated with the CBGS and the occurrence of an efficient cap-rock likely contribute to minimize the loss of thermal energy from the reservoir (Goff and Janik, 2000; Todesco and Giordano, 2010). The preliminary geothermal potential at CBC has been evaluated with the Volume Method, calculating up to E = 11.4×10¹⁸ J. Hence, this system is a promising target to continue geothermal investigations.

Up to date, the only geothermal target considered of interest to continue geothermal investigations in the northwestern Argentina was the Tuzgle-Tocomas geothermal system (Giordano et al., 2013, 2016; Norini et al., 2014; Filipovich et al., 2017). In this sense, the present investigation expands the frontiers of geothermal research in northwestern Argentina, unveiling a promising geothermal system for this region. The results here presented and discussed could constitute the necessary base of knowledge for further accurate assessment of the geothermal potential and ultimately the implementation of the geothermal resource as a viable energy alternative for small localities or mining facilities (e.g. El Peñón and Las Papas localities, La Hoyada mining district, etc.), isolated from the National Interconnected System due to their remote localization. Geophysical studies are required to confirm and improve the proposed conceptual model.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jsames.2019.102213.

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