Research Article

Groundwater Chemistry and Overpressure Evidences in Cerro Prieto Geothermal Field

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In order to understand the geological and hydrogeological processes influencing the hydrogeochemical behavior of the Cerro Prieto Geothermal Field (CP) aquifer, Mexico, a characterization of the water samples collected from geothermal wells was carried out. Different hydrochemical diagrams were used to evaluate brine evolution of the aquifer. To determine pressure conditions at depth, a calculation was performed using hydrostatic and lithostatic properties from CP, considering geological characteristics of the study area, and theoretical information about some basin environments. Groundwater shows hydrogeochemical and geological evidences of the diagenetic evolution that indicate overpressure conditions. Some physical, chemical, textural, and mineralogical properties reported in the lithological column from CP are explained understanding the evolutionary process of the sedimentary material that composes the aquifer.

Dedicated in memory of Dr. Ramiro Rodríguez C.

1. Introduction

Different authors have observed that the origin of some brines around the world can be caused by diagenesis evolution and porewater trapped during burial [1–3]. Commonly, porewater shows characteristics according to the depositional environment [4]. The different stages of diagenesis are composed of burial and compaction of material in sedimentary basins; the sandstones and shales undergo changes in their physical, chemical, textural, and mineralogical properties which are reflected in the sediment density, the compaction of the granular package, and loss of porosity [5]; additionally, a chemical alteration occurs in sandstones generating cementation and lithification as a product of chemical precipitation affecting detrital grains, dissolution, recrystallization, or mineralogical alteration [6]. Silica is the most abundant cementing agent in sandstones, compared to calcium carbonate, either calcite or aragonite, since the latter dissolves more easily in contact with groundwater, mainly the second [7]. In the diagenetic stages, interstitial fluids are constantly lost in most shales [8]; this phenomenon can occur at low depth and can last

for thousands or hundreds of thousands of years or have a longer duration and greater depth; but when it suddenly occurs and the permeability of the medium is so low that it does not allow the interstitial fluid to leak, an increasing degree of stress can be generated [9]; this geological event is known as overpressure [10]. Overpressure is an abnormally high pressure in the subsoil that exceeds the hydrostatic pressure at a certain depth; this pressure is carried out in the pores where the pressure of the interstitial fluids increases as the overcoat increases [11, 12]. Overpressure indicates that the high pressures developed during compaction do not dissipate efficiently [10] and can generate hydraulic fracturing in the system (stress applied to compressible rock and fluid expansion). These processes generate overpressured fluids related to porosity reduction, changes on porewater flow, and diagenetic reactions due to compaction and disequilibrium in a sedimentary basin [12–14]. Also overpressure can be related to chemical compaction due to changes in mineralogy (e.g., ion exchange, dissolution/precipitation) or to diagenetic processes and fluid expansion by thermal water in pore space.

FIGURE 1: Localization of Cerro Prieto Geothermal Field and sampled wells.

Cerro Prieto Geothermal Field (CP), located in north-western Mexico ($32^{\circ}24'43''\text{N}$, $115^{\circ}14'41''\text{W}$), is a brine with high-temperature geothermal system characteristics. Several studies about the origin and behavior of CP groundwater have been reported [15–18]. According to geological evidences, a large accumulation of sedimentary material from a continental and marine origin, overlying the depositional basin, is related to the origin of brine [17]. The sedimentary material shows diagenetic evolution evidences and porewater trapped between sediment grains during burial processes. The porewater is saline with high Cl^- , Na^+ , Ca^{2+} , and K^+ concentration; in geothermal brines this characteristic is common [1, 2, 10]; the composition depends mainly on the primary origin, mineralogical composition of the sediments and their modification due to diagenetic processes (e.g., facies distribution), and hydrothermal characteristics [15, 19]. Among the most evident diagenetic processes in CP are cementation, mineral replacement, recrystallization, authigenesis, and growth of concretions and nodules [16]. On the other hand, in deep sedimentary basins as CP, mechanical processes of deformation related to burial mechanisms are common; likewise, hydrostatic and lithostatic conditions increase with depth due to an increase of the superposed fluids hydraulically connected, through the pore and the pressure exerted by sediments overload [10]. If pore pressure in deep aquifers like CP is higher than expected from hydrostatic conditions, anomalous pressure (overpressure) can be generated; overpressure is common mainly within 2–4.5 km depth [10–12].

According to geochemical evidences, the origin of geothermal brine at CP could be governed by mixing processes related to a hydrothermal environment and the sedimentary material located at depth which shows burial diagenesis evolution with hydrogeochemical evidences of an overpressurized environment. The aim of the present study was to evaluate hydrogeochemical behavior of geothermal groundwater

and its relation with diagenetic processes, including overpressure.

2. Localization

Cerro Prieto Geothermal Field (CP), located in Mexicali Valley, SE of Mexicali City, in Baja California State, Mexico (Figure 1), is a Basin of Salton Sea [17]. Climate is arid with temperatures up to 40°C in July and to 4°C in winter. The average annual precipitation is 55 mm/year and the average annual evaporation is 2200 mm/year [23]. Groundwater at CP is extracted from geothermal wells that are in constant exploitation to generate electricity. The Comisión Federal de Electricidad of Mexico (CFE) operates and manages the Geothermal Field. CP power production is up to 720 MW and is composed of five individual units: CP1, CP2, CP3, CP4, and CP5; each unit has a total capacity of production with a specific number of production wells. Sampled wells are indicated in Figure 1. Their localization in the five individual CP units is included in Table 1. All the wells are located in zone “beta,” 1500 to 3100 m depth [17].

2.1. CP Geology. The lithology around CP is composed of gneiss (quartz-feldspars), shale (quartz-mica), marble, amphibolite, and quartzite from Permian to Jurassic [24] and metamorphic, granitic, and granodiorite rocks which are intruded by batholithic rocks [16], together with dacite and andesite from Miocene and rhyodacite from Quaternary [25]. The tectonic basin was filled by sedimentary material that, due to burial, compaction, and diagenesis processes, evolved to gray shales from Late Miocene (shales and silt shales that vary from light gray to black); this unit overlies the granitic basement and the mafic intrusive and is interlayered by permeable sandstones (composed of quartz and feldspars; arkoses type). The thickness is near 3000 m [21, 26]. Immediately above a layer of brown shale (shale and silt shale),

TABLE 1: Major elements concentration values at CP groundwater samples measured in summer 2010.

Well	Operation areas (individual units)	Depth (Km)	T (°C)	pH	CE mS/cm	TSD Calculated	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	HCO ₃ (mg/L)	Cl ⁻ (mg/L)	SO ₄ (mg/L)	% IB	B (mg/L)	SiO ₂ (mg/L)
M 104	CP3	1.73	88.4	7.73	20.45	20613.2	261.6	50.9	6250	1187.5	41.5	11962.5	13.5	-2.8	13.26	851.7
M 117A	CP3	2.89	91.2	7.7	35	17315.5	140.2	34.7	5575	1185	18.4	9375	0.09	3.3	14.65	980.1
M 119A	CP2	3.1	87.9	6.79	35	34506.9	379.1	38.3	9850	2682.5	10.7	20150	0.09	-4.5	17.42	1401.7
M 127	CP2	2.5	76.8	7.61	24.8	21457.8	288.3	31.1	6087.5	1352.5	28.4	12812.5	5.9	-6.7	18.4	847.4
M 133A	CP3	2.49	80.8	7.49	35.45	36545.4	819.4	53.9	10750	1840	19	22200	14.2	-5.6	19.86	853.9
M 148A	CP2	2.99	85.8	7.43	26.8	27327.2	379.1	28.7	8300	1652.5	21.3	15875	7.1	-2.7	18.45	1074.3
M 155	CP3	2.9	80.5	7.44	36.65	38863.8	735.5	44.9	11325	2050	27.2	23800	0.09	-6.8	27.92	890.2
M 198	CP4	2.8	91.8	7.52	21.85	25601.2	187.6	56.9	7587.5	1577.5	16.6	15250	0.09	-5.6	28.8	915.9
M 200	CP3	2.84	82.8	7.42	25.85	22151.3	183.6	25.1	6312.5	1690	28.4	12950	0.09	-5.2	22.35	973.7
112	CP1	2.65	86	7.25	33.05	31216.4	533.1	47.9	9125	1992.5	14.8	18250	0.09	-3.6	15.8	1260.5
233	CP2	2.64	88.9	7.53	4.34	23971.6	189.5	29.9	7275	1490	23.7	13700	3.6	-2.6	16.6	1262.6
311	CP3	2.94	85.1	7.56	43	23548.8	288.3	23.9	7137.5	1432.5	11.8	13550	5.4	-2.5	21.9	1091.4
323	CP3	2.9	94.6	7.67	26.75	27018.9	286.3	53.9	7437.5	1482.5	37.9	16750	0.09	-10.8	22	973.7
343	CP3	2	95.8	7.48	28.5	34309.7	789.8	59.9	9712.5	1447.5	14.3	21587	29	-9.4	17.56	667.7
403	CP4	2.89	82.8	7.32	16.1	15503	167.8	59.9	4540	1030	42.6	8950	4.4	-3.2	28.85	727.6
407	CP4	2.99	88.4	7.91	18.95	20042.6	108.6	35.9	5815	1185	19	11887.5	8.5	-7	16.7	969.4
611	CP3	2.52	88.4	7.87	52.85	33262.9	730.5	53.9	9875	1585	19	20100	22.4	-5.2	21.61	877.4
222 D	CP2	3.14	92.2	7.74	29.75	28719.9	296.2	27.5	8062.5	1907	9.5	17300	0.09	-7.9	11.25	1114.9
E-23	CP2	2.95	71.1	58.5	39344.1	39344.1	580.5	21.6	11175	2717.5	28.4	23750	0.09	-6.6	24.2	1080.7
E-29	CP2	2.69	83.3	7.12	79.4	44491.3	785.8	14.4	13200	2962.5	21.3	26600	0.09	-4.1	26.55	918
E-47A	CP3	2.89	91.7	7.47	61	35074.6	647.6	16.8	10650	2247.5	16.6	20500	0.09	-2.1	21.97	995.1
T 350A	CP2	2.9	82	6.88	82.2	49251.2	1032.6	22.8	14312.5	2782.5	15.4	29700	0.09	-5.7	28.55	1393.1
T 395	CP2	2.65	80.1	7.92	4.88	23924.2	337.6	27.5	7037.5	1420	4.7	14062.5	6.3	-4.6	10.25	1016.5
T 400	CP1	2.1	89.6	7.9	19.73	12945.5	122.4	33.5	3910	560.5	20.7	7570	33.6	-5.2	9.11	680.5
611*A	CP3	2.52	87.6	7.85	52.4	33217.5	704.9	37.1	10087.5	1595	20.1	19875	22.5	-4	22	877.4

the gray shale covers interlayered permeable sandstones and sands cemented by carbonates, about 500 m thickness [21]. In these zones, a rapid distribution of geothermal fluids enhances the recharge. Erratic mudstone layer and unconsolidated clastic sediments (clays, silts, sand, and little gravel) overlie all the previous units. The thickness of these units is between 400 and 2500 m [26]. Sedimentary material shows evidence of the diagenetic evolution and recrystallization processes due to an incipient low grade metamorphism.

The geological evolution of CP is a complex blend of rifting, rapid deltaic sedimentation, and large scale strike-slip faulting located within the Salton Basin [16, 19, 21, 27]. The Geothermal Field is placed in a shear zone where NW-SE and NE-SW fault systems intersect. The more important faults are Cucapá, Imperial, Cerro Prieto, and Michoacán [21]. This fault system is part of a major regional lineament that penetrates deep into the crustal and basement rocks and serves as conduit for geothermal flow. The system originates in a tectonic basin of 5200 m depth, filled by alluvial and deltaic sediments from Tertiary to Quaternary [21].

Vonder Haar and Howard [27] observed that, in sandstone and shale units, a mineral dissolution/precipitation took place along microfractures, originating secondary porosity and newly precipitated hydrothermal minerals, causing a reduction of permeability. Likewise, Elders et al. [20] observed cementation, mineral replacement, recrystallization, authigenesis, and growth of concretions and nodules; these processes are related to diagenesis.

2.2. CP Hydrogeology. Some authors consider that CP brine may have been formed from marine evaporite dissolved and partly by evaporated Colorado River water [16, 19, 21, 28–31]. However, according to geological evidences, a large accumulation of sedimentary material, overlying the depositional basin, from a continental and marine origin and mixing with meteoric water [30–33], was related to the origin of brine [17]. The sedimentary material shows diagenetic evolution evidences and porewater trapped between grains during burial processes. Isotopic evaluations (^{18}O , ^2H) and chemical analysis (Cl^- and Br) elaborated by Coplen [34] and Birkle et al. [35] suggest that Salton Sea was the probable predecessor of high chlorinated groundwater of CP.

3. Methodology

A hydrogeological and hydrogeochemical study was carried out in geothermal groundwater samples from CP following standard methods of APHA-AWWA [38]. Water samples were collected from geothermal wells that are in constant exploitation. Temperature, pH, and conductivity were measured in the field during the summer of 2010 and calibrated to the water temperature at each site. The chemical analyses for the major elements, B and SiO_2 , were performed at the Analytical Chemistry Laboratory of the Geophysics Institute, UNAM, Mexico (the laboratory participates in international calibration exercises of chemical analyzes of geothermal waters). Boron was determined by colorimetry through reactions with carminic acid (Method 4500-B C) APHA-AWWA [38]. SiO_2 was determined by atomic absorption

spectrophotometry with flame and UV-visible spectroscopy (molybdosilicic acid method). Major ions were analyzed following standard methods [38]. HCO_3^- and CO_3^{2-} were determined by volumetry (titrating with HCl), Ca^{2+} and Mg^{2+} were determined by volumetry (titrating with EDTA), Cl^- was determined by potentiometry with selective electrodes (4500- Cl^-) [38], Na^+ and K^+ were determined by atomic emission spectrophotometry (3500- Na^+ and K^+), and SO_4^{2-} was determined by turbidimetry (4500- SO_4^{2-}). Analytical quality was assessed through ionic balance (less than 10%) and the use of certified (NIST) reference solutions.

In order to evaluate brine evolution of CP, different techniques were used: (a) Carpenter [39] evaluated the behavior of major elements using a plot with concentrations as a function of dissolved chloride concentration, considering the composition of seawater during evaporation and diagenesis; using chemical results of CP groundwater a similar evaluation was elaborated; (b) Davisson and Criss [40] devised a diagram to determine the geochemical evolution of mineralogy in brines applying an evaluation of $\text{Na}_{(\text{deficit})}$ and $\text{Ca}_{(\text{excess})}$ in water samples; hydrogeochemical results of samples from CP were evaluated with this diagram; (c) Boschetti [3] considers B-Cl concentrations to explain the evolutionary process in the groundwater; B-Cl diagram was used to determine the dominant geological environment in CP. A geochemical simulation with the measured water concentrations was carried out using the Phreeqc© program to determine saturation indexes.

In order to determine pressure conditions, a calculation was performed using hydrostatic and lithostatic properties from CP, considering geological characteristics of the study area and theoretical information about some basin environments. To estimate pressure conditions ($P_l(h)$) exerted by a geological column at a depth (h) offshore in a geologic formation, (1) was used [12]:

$$P_l(h) = g \int_0^{h_w} \rho_{\text{sea}} dh + g \int_{h_w}^h \rho_b dh. \quad (1)$$

It is necessary to take into account pure water column weight at sea level $h = 0$, depth of seawater column h_w , seawater density $\rho_{\text{sea}} = 1100 \text{ kg/m}^3$, gravity constant $g = 9.78 \text{ (m/s}^2\text{)}$, and material density (rock or sediments) ρ_b . The integral about overburden weight of sediments can be replaced by a sum of the individual weights of layers [12]:

$$P_l(h) = g \int_0^{h_w} \rho_{\text{sea}} dh + g \sum_{i=1}^n d_i [\rho_w \varphi_i + \rho_{ri} (1 - \varphi_i)], \quad (2)$$

where it is important to consider the number of layers (ni) with thickness d_i (i is the layer number measured in m), rocks density ρ_{ri} (kg/m^3), porosity φ_i , and water density ρ_w (which can change with salinity variation, while temperature and pressure dependence is relatively small or negligible).

To estimate pressure in a reservoir unit from CP it was considered that the study area is located onshore, few meters above seawater level; therefore the integral including the weight of seawater column is zero; the distinctive strata units, their thickness, and depth of each sampled well were

FIGURE 2: Variations in dissolved (a) Na^+ , (b) Ca^{2+} , (c) K^+ , (d) Mg^{2+} , (e) HCO_3^- , and (f) SO_4^{2-} concentrations as a function of dissolved chloride concentration. The solid line on each plot is the seawater evaporation-dilution curve for each cation; circle is the ionic composition of seawater.

considered; the porosity values reported by Olson [41] and Hiriart Le Bert [42] in the geologic material from CP were used (between 0.15 and 0.25), for lithological units without reported porosity; theoretical values proposed by distinct authors studied unlike geological material and depth were used (e.g., mudstone and shales, slate, quartz, feldspars, uncemented sandstones, or sandstones as reservoirs) [43–46].

4. Results and Discussion

4.1. Major Elements in CP Groundwater. Table 1 shows the major solutes concentration in CP groundwater.

In Table 1 chemical results from the studied wells are shown. Total dissolved solids were calculated from

conductivity measures showing values between 12945.5 and 49251.2 mg/L. These values are comprised between saline water (>1,000 mg/L) and brine (>35,000). All the sampled wells are located at beta reservoir [17, 47]. To explain geochemical variations in CP brine it is necessary to evaluate the composition and removal of solutes by salt precipitation according to diagrams proposed by Carpenter [39] where the circle represents the solute-chloride composition of normal seawater; the line represents the limit between evaporation-dilution curves of seawater and freshwater (Figure 2).

Figure 2 shows that groundwater in CP is dominated by high concentrations of Na^+ , K^+ , Ca^{2+} , and Cl^- . When Cl^- concentration increases Na^+ , K^+ , and Ca^{2+} concentrations also increase in ratios 1:1, 1:1, and 2:1, respectively

FIGURE 3: Mineralogy and paragenesis reported in lithology from CP, depth of sampled geothermal wells (modified by [20]), and estimated porosity considering geological characteristics.

(Figures 2(a), 2(b), and 2(c)). Bicarbonate ion, Mg^{2+} , and SO_4^{2-} have a low concentration (Figures 2(d), 2(e), and 2(f)), Na^+ values are parallel and near coincident with their respective evaporation-dilution curve (Figure 2(a)), Ca^{2+} values cross the evaporation-dilution curve (Figure 2(b)), and K^+ also increases with Cl^- but the values are enlarged relative to the seawater evaporation-dilution curve (Figure 2(c)). In CP brine, Mg^{2+} concentrations lie well below the seawater evaporation trajectory indicating significant depletion of the element. According to Hanor [48] and Kharaka and Hanor [1] Mg^{2+} concentrations in brines decrease when temperature increases in the subsurface, and when alkalinity decreases [49]. Evaporation of continental waters has a more variable concentration range in water samples from CP due to evaporating mixtures of continental and marine water with meteoric water [50].

In CP brine depleted and enriched concentrations of some major elements are a consequence of reactions linked with the hydrothermal processes and water-rock interactions. Major elements concentrations are controlled by the alteration and formation of minerals like feldspar-K, plagioclases, quartz, biotite, amphibole, chlorite, pyrite, wairakite, prehnite, muscovite, epidote, and talc, as reported in CP by Elders et al. [20] and Izquierdo et al. [16] and shown by calculated saturation index values (Figures 3 and 4).

The K^+ origin is restrained by alteration of feldspar-K, illite, and biotite and by muscovite formation. Very low SO_4^{2-} and HCO_3^- concentrations in CP could be inhibited by the water interactions with anhydrite, dolomite, talc, pyrite, or calcite (Table 1; Figures 2 and 3); Elders et al. [20] report pyrite formation at depth. Low concentration of Mg^{2+} and high concentration of Ca^{2+} could be related to dolomitization of limestone as major source of Ca^{2+} ; and low Mg^{2+} contents are associated with the evolution of chlorites and micas when temperature and depth increase according to mineralogy reported in CP (Figure 3); similar behavior has been reported previously in hydrothermal brines with diagenetic evolution

evidences [51] (Figure 3). Albite reactions at depth at high temperature can be linked with the slight Na^+ decrease [16, 30, 31].

4.2. Saturation Index. Results of saturation index calculations are shown in Figure 4. From these results amorphous silica (SiO_2 am), albite, k-feldspar, and in some cases k-mica show a behavior close to equilibrium with the fluid. Besides, quartz, chalcedony, talc, and crysocolle are oversaturated. Dolomite, calcite, and aragonite are undersaturated at some sites and oversaturated at others, in agreement with Figures 2 and 3.

4.3. $\text{Na}_{(\text{deficit})}$ - $\text{Ca}_{(\text{excess})}$ Plot. Figure 5 was used to explain the initial composition of brines and the nature of fluid-rock interactions. In the diagram, Basinal Fluid Line (BFL) is a straight line with a unit slope that indicates a $2\text{Na}-1\text{Ca}$ exchange relationship [40]; BFL represents the effect of plagioclase albitization on water composition. Seawater evaporation trajectory is a representation of the natural trends for seawater evaporation which is formed by large positive $\text{Na}_{(\text{deficits})}$ and small negative $\text{Ca}_{(\text{excess})}$; reactions involving seawater evaporation follow a vertical descent and afterwards produce large deficits along a horizontal trend. Halite dissolution in seawater or freshwater can produce negative values along a slope of 1:4.

To determine the origin and geochemical evolution of CP brine, an evaluation of $\text{Na}_{(\text{deficit})}$ and $\text{Ca}_{(\text{excess})}$ was applied to explain the initial composition and nature of fluid-rock interaction (Figure 5). All the analyzed water samples from CP were located right and over the seawater evaporation trajectory (SET) in the $\text{Na}_{(\text{deficit})}$ - $\text{Ca}_{(\text{excess})}$ diagram (Figure 5) indicating that the fluids are a product of brine that passed the point of halite precipitation evaporated (along of $\text{Na}_{(\text{deficit})}$ axis). The horizontal line of CP has a large positive $\text{Na}_{(\text{deficit})}$ and a small negative $\text{Ca}_{(\text{excess})}$, but the fluid is more enriched in $\text{Ca}_{(\text{excess})}$ than expected from seawater evaporation.

Dolomitization produces elevated Ca contents, increasing $\text{Ca}_{(\text{excess})}$ without changing the $\text{Na}_{(\text{deficit})}$, and can explain

FIGURE 4: Saturation index diagrams.

FIGURE 5: Diagram $\text{Na}_{(\text{deficit})}$ and $\text{Ca}_{(\text{excess})}$. Diamonds correspond to the CP sampled wells.

the phenomenon observed in CP. Other dissolved minerals could interact in the evolutionary processes to brine aside from the above-mentioned ones, such as calcite, anhydrite, quartz, halite, and illitization to smectite transformation. Often, these geochemical processes are treated separately but in some situations the origin is linked to a mixing of processes and is not mutually exclusive [1]. Illite formation involves reactions relevant for diagenesis: (a) release of water during transformation of feldspar to kaolinite and smectite; (b) potassium and silica budget [2, 52]. Some of these processes can occur in CP.

Geology of CP shows equilibrium with clays (Figure 4); groundwater shows high concentrations of K^+ . Also reactions between calcite, illite, and K^+ to form K-feldspar could be involved in brine evolution. According to the results (Figures 2 and 5) the origin of CP groundwater is a consequence of an evolution of dissolved evaporative products (e.g., halite), residual water remaining during the dissolution precipitation of seawater evaporites, and different water-rock interactions (e.g., clays, siltstones, and shales) but could have a slight contribution to exchange reactions 1Ca for 2Na in the aquifer by albitization of plagioclases, which could change the ionic composition of fluids (Figure 5), according to the following

FIGURE 6: CP overpressure: chloride versus boron concentration (mg/L; fields and paths from [3]). Dashed lines represent binary mixings where specific geological environments dominate. Diamonds correspond to the CP sampled wells.

reaction proposed by Carpenter [39], Hanor [48], and Demir and Seyler [53]:

4.4. Overpressure

4.4.1. B-Cl Plot. Some hydrogeochemical evidences (Figures 2 and 5) shown in a B-Cl plot (Figure 6) indicate that overpressurized fluids participate in the evolutionary process of the CP geothermal brine. Boron behavior helps to define these geologic environments because B is adsorbed by clay minerals and is released into the fluid in a deep environment, mainly when tectonic stresses by vertical and/or lateral compaction are high and temperature increases with depth, and stronger geologic deformations are generated [10, 12, 54].

4.4.2. Pressure Conditions Estimated due to Overburden. Some authors [55, 56] estimated pressure at depth at CP considering the host rock density at a specific depth. The obtained values were in the range between 0.5 and 42 MPa. Those calculations considered only geothermal water conditions from the extraction zone and no lithologic information was used from the stratigraphic columns of each site. To confirm hydrogeochemical evidence of overpressure, a calculation to determine pressure conditions was performed using hydrostatic and lithostatic properties from CP and theoretical information about some basin environments (Figure 7). It is necessary to consider that normal pressure increases with depth according to the hydrostatic pressure gradient (10 MPa/Km), higher or lower values of this gradient, and

their associated depths are considered abnormal pressures (e.g., overpressure). Lithostatic pressure is equivalent to the total charge of the overlaying sediments in a geological formation and increases according to the lithostatic pressure gradient (23 MPa/Km) [10–12, 57].

In general, overpressured systems can take place when porewater is not expelled from rock at a proper rate, remaining under hydrostatic pressure. Overpressured volume rock must be trapped by low permeability layers where fluids move slowly, even when there is high pressure in the environment. The overpressure affects the effective stress that acts between the grains within the rock and generates a change in the compaction. In many areas of active sedimentation rate around the world, porewater pressure in deep groundwater (>1 km) is higher than would be expected from hydrostatic circumstances [10, 57–59]. It is necessary to consider thermal expansion in the pore space (increasing volume) and increment of the system temperature by thermal conditions and by fluid movement and mineral phases transition [11]. According to Swarbrick et al. [11] and Kauerauf and Hantschel [12] secondary overpressure by chemical cementation may occur at large depths when porosity is reduced by dissolution-diffusive transport-precipitation of silica cement (temperature affects diffusion-precipitation rate) or by fluid expansion processes when gas or thermal solutions are originated in highly permeable facies interconnected locally at certain depth levels generating compaction, rearrangement of grains, and reduction in the pore space. Some of these conditions could occur in CP aquifer [22].

The results obtained confirm that in CP overpressure is present (Figures 7 and 8). Positive anomalies with an increase of depth are shown between 0.6 and 3.1 km; this phenomenon can be caused by a hydraulic seal. Overpressure coincides with lithology variation in CP [22], when sedimentary material composed of sand and clay changes to shale and sandstone due to clay and sand diagenesis and shale compaction (Figure 7). In CP, sandstone is hosted by a low permeability layer of shale and siltstones creating adequate conditions for this process. Overpressure in CP brine could occur as a consequence of a rapid sedimentation, deposition, and accumulation rates of fine-grained material along time and due to the stress increase in sediments, compressibility, or expansion of fluids by hydrothermalism.

Geological evidence in CP indicates that mineralogical changes occur at depth, mainly by diagenetic processes (Figure 5). According to the geochemical behavior observed in CP, it is possible that mineral dissolution precipitation processes generated this phenomenon; osmosis, buoyancy, and tectonic or magmatic process can generate changes in mineralogy (e.g., feldspar to illite or smectite to illite conversion), diagenesis, and carbonate or silicate cementation. In CP, sandstones and shales units reveal clogging, mineral dissolution, and mineral precipitation along microfractures as indicated by Vonder Haar and Howard [27]. In the study area the calcite dissolution and/or cementation more likely develops where cold water interacts with hotter rocks or precipitation of quartz and k-feldspar occurs when hot waters interact with colder rocks [16, 20]. Exchange of Na^+ by K^+ with a higher ion radius is carried out in mineral transformations and increases

FIGURE 7: CP geology cross section. Stratigraphic column was modified from Lira [21] and Peña et al. [22].

the volume of the solid matrix [12]; this process is controlled by temperature and K^+ availability in minerals.

The permeability of sandstones in CP facilitates reactions between rocks and hydrothermal fluids (e.g., dissolution of some minerals); these reactions can reduce or increase the porosity and also generate secondary fracturing or microfracturing and modify physical properties [16, 21], which could cause overpressure (Figures 7 and 8). Sandy shale and siltstone facies in CP are most amenable to increased microfracturing. In sandstones (where high temperature dominates) and shales from CP, mineral dissolution precipitation takes place along microfractures, which originates secondary porosity and newly precipitated hydrothermal minerals, causing a reduction of permeability.

5. Geothermometry

Alkali feldspar geothermometers are the most used tool to determine chemical equilibrium in fluids at depth in a geothermal system [60]. Na/K and Na-K-Ca geothermometers were developed to evaluate the temperature in high enthalpy geothermal systems [61]; these geothermometers are less affected by chemical reequilibration in mixing zones, but the calculated temperature may be affected by mixing

with cold water or by deposition of aluminum-rich minerals or clays [62]. Na/K geothermometers are adapted for temperatures between 180 and 350°C. Na/K geothermometers have been generally used to estimate temperatures at CP [36, 37, 62]. We applied (4) and (5) [61, 62] to evaluate the temperature of CP reservoir:

$$T = \left(\frac{1178}{(1.47 + \log (Na/K))} \right) - 273.15 \quad (4)$$

$$T = \left(\frac{1289}{(1.615 + \log (Na/K))} \right) - 273.15. \quad (5)$$

The temperature range of CP reservoir, calculated with Na/K geothermometer, varies between 236 and 306°C for (4) and between 251 and 318°C for (5) (Table 2).

6. Conclusions

CP shows intermediate brine characteristics (Na-Ca-Cl) with high K^+ , Ca^{2+} , and salinity contents; the relation Na^+/Cl^- is less than 1.

The porewater composition in CP evolved from its primary origin and was modified by the interaction with

FIGURE 8: Plots represent pressure estimated conditions at depth: pressure conditions were calculated with the following values: porewater density $\rho_w = 1040 \text{ kg/m}^3$, shale and mudstone density $\rho_{sh} = 2700 \text{ kg/m}^3$, sandstone density $\rho_{sd} = 2720 \text{ kg/m}^3$, slate density $\rho_{sl} = 2750 \text{ kg/m}^3$, and sedimentary material density $\rho_{sm} = 1650 \text{ kg/m}^3$ [10, 12].

TABLE 2: Results of Na/K geothermometers.

Well	T °C Na/K [36]	T °C Na/K [37]	Well	T °C Na/K [36]	T °C Na/K [37]	Well	T °C Na/K [36]	T °C Na/K [37]
M 104	264	279	112	280	293	222 D	289	302
M 117A	277	290	233	273	286	E-23	292	305
M 119A	306	318	311	270	284	E-29	283	296
M 127	282	295	323	270	284	E-47A	276	290
M 133A	254	268	343	240	255	T 350A	267	281
M 148A	269	283	403	284	297	T 395	271	285
M 155	259	274	407	272	286	T 400	236	251
M 198	274	288	611	247	262	611*A	246	260
M 200	304	316						

minerals of the sedimentary material. Brine characteristics were acquired by deep-burial diagenesis processes and low grade metamorphism at high temperatures. Results show geochemical evidence of overpressured fluids due to compaction.

Groundwater samples from CP show a mixing of marine and continental water; this situation is partially related to a continental and evaporative precursor. The hydrogeochemical evidence indicates that the sedimentary material has porewater between grains, which was trapped during burial processes. The diagenetic processes could have generated high concentrations of Cl^- , Na^+ , K^+ , and Ca^{2+} . Calcium enrichment, Na^+ depletion, and K^+ release could have a relation with a contribution of exchange reactions 1Ca for 2Na in the aquifer by albitization of plagioclases or by illitization processes, respectively, and precipitation of secondary minerals. High K^+ and low Mg^{2+} contents are related to alteration of feldspar-K, illite, biotite, and muscovite formation. Ca-Na exchange with plagioclases could be a geochemical control on the fluids of CP and may directly explain slight $\text{Ca}_{(\text{excess})}$ and $\text{Na}_{(\text{deficit})}$ in the brine.

Overpressure in CP is related to burial mechanisms; secondary overpressure is related to chemical pressure by mineralogical changes and by fluid expansion, which increases with depth. The magnitude of overpressure may be produced by some characteristics of deposit formation (burial), permeability evolution of sedimentary material, and the compressibility of rock and fluid. Secondary overpressure in the system related to chemical pressure and porosity changes due to mineral dissolution can be generated at large depths. Fluid expansion takes place in the reservoir which generates compaction, rearrangement of grains, and reduction of pore space. Boron release at overpressure conditions can be related to high contents of K^+ in water.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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