



## Chloride and Boron behavior in fluids of Los Humeros geothermal field (Mexico): A model based on the existence of deep acid brine

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### ABSTRACT

Geothermal field Los Humeros, Mexico, is characterized by a high steam fraction in the well fluids, by extremely high B concentrations in separated water (grams per liter, with a magmatic B signature,  $\delta^{11}\text{B} \pm 2\sigma = -0.8 \pm 1.6\text{‰}$ ), by the absence of correlation between B and Cl concentrations and by positive correlation between B content in separated water and fluid enthalpy. Such behavior is consistent with the existence of moderately acid brine (pH 3–5) at depth with a high B concentration (500–600 mg/kg). In this case a 3-level model can be suggested for Los Humeros: (1) immature, moderately acid brine at depth which is boiling at a temperature  $\sim 350^\circ\text{C}$  producing the HCl-bearing vapor with a high B content; (2) partial condensation of this vapor at the upper level accompanying water–rock interaction and neutralization; (3) formation of a shallow water-dominated aquifer above a lithologic low-permeability boundary as has been proposed by other authors. A thermochemical computer code has been used to model boiling of an aqueous fluid at  $350^\circ\text{C}$  with 0.1 M of NaCl, 0.05 M of  $\text{H}_3\text{BO}_3$  and variable amount of HCl (0.001–0.1 M), then a partial condensation of the produced vapor at  $250^\circ\text{C}$  and then separation of the steam–water mixture at  $150^\circ\text{C}$ . Results of simulation are in a qualitative agreement with the observed data.

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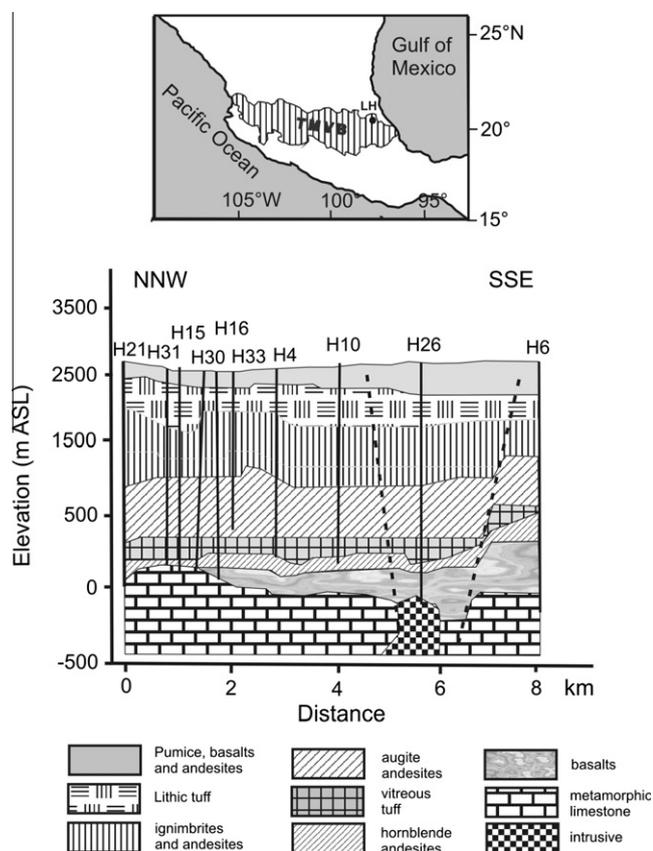
### 1. Introduction

Los Humeros is a caldera-type hydrothermal system located in the eastern part of the Trans-Mexican Volcanic Belt (TMVB, Fig. 1). More than 40 deep wells have been drilled here (1000–2800 m from the surface). The most productive wells drain from a two-phase reservoir and produce steam for a 40 MW geothermal power plant. The system is composed mainly of a complex mixture of evolved volcanic rocks with different lithology and a subordinate amount of basalts (Verma, 2000). The presence of a large partially solidified magma chamber is suggested at a depth of 7–8 km (Castillo-Roman et al., 1991; Verma, 2000). The regional basement is composed of intrusive and metamorphic rocks of Paleozoic age (Arellano et al., 2003). A remarkable feature of the system is the presence of metamorphic limestone and scarn-type rocks underlying the volcanic sequences (e.g., Martínez-Serrano, 2002). The caldera is located in a semi-arid zone with a low recharge potential. A two-layer hydrological structure has been proposed for Los Humeros: the upper reservoir filled with water-dominated fluid and hydrostatic pressure profile and the lower steam-dominated aquifer with a low liquid water fraction and a quasi-static pressure

profile (Arellano et al., 2000, 2003; Portugal et al., 2002; Tello, 2005; Gutierrez-Negrin and Izquierdo-Montalvo, 2010, among others). Because of a high vapor fraction in the fluid (high enthalpy) at the well heads, the separated water generally is highly variable in salinity; variations in Cl content for a well may be orders of magnitude with a mean Cl concentration  $\sim 50$  mg/kg and a maximum of less than 1000 mg/kg (Tello, 1992, 2005; Arellano et al., 2003). The condensed total fluid (vapor + water) at the surface represents an aqueous solution with neutral or slightly alkaline pH, low Cl, variable but low (generally, less than 100 mg/kg)  $\text{SO}_4$ , and unusually high B and As contents. One feature which makes this hydrothermal system unique among other high-temperature hydrothermal systems is extremely high B concentrations in separated waters (Arellano et al., 2003; Tello, 2005, among others). According to Arellano et al. (2003) and Tello (2005) who, as many other authors, have used the same data set based on the analyses provided by the Mexican Comision Federal de Electricidad (CFE), B concentration in separated water is variable even for a single well and may reach a concentration up to 5000 mg/kg. The other unusual (but not unique) feature is the lack of correlation between Cl and B in Los Humeros hydrothermal fluid. Water-dominated hydrothermal systems always demonstrate a strong positive correlation between B and Cl with a Cl/B ratio in a wide range, from  $\sim 1$  for Ngawha, New Zealand (weight ratio, i.e., Ellis and Mahon, 1977)

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**Fig. 1.** Location of Los Humeros geothermal field relative to Trans-Mexican Volcanic Belt (TMVB, upper panel) and a simplified SSE-NNW cross-section of Los Humeros (from Arellano et al., 2003) with position and numbers of wells.

to ~1000 for Cerro-Prieto, Mexico (i.e., Truesdell et al., 1981). Other hydrothermal systems with no Cl–B correlation (to the authors' knowledge) are The Geysers (USA), Larderello (Italy) and Krafla (Iceland). The Geysers and Larderello produce superheated steam with a high B content (up to 50–100 mg/kg, D'Amore and Truesdell, 1979, 1984; Truesdell et al., 1989). The Krafla system hydrologically is similar to Los Humeros with the steam-enriched hot lower reservoir and a water-dominated and cooler shallow aquifer (e.g., Arnórsson, 1996). The only difference is that Krafla fluids contain much lower B concentrations (<10 mg/kg). Fluids from some wells at these fields have low (< 100 mg/kg) and variable Cl content. The presence of Cl in superheated steam of The Geysers, Larderello and Krafla was attributed by Truesdell et al. (1989) to the boiling of a hypothetical acid Cl-bearing brine beneath the steam-dominated reservoir. Dissolved molecular HCl is stable at low pH and partitions into the vapor phase (e.g., Simonson and Palmer, 1993).

The aim of this paper is to consider a model which would explain high and variable B concentrations in separated water of Los Humeros well fluids, low and variable Cl concentrations, and lack of Cl–B correlation (Cl–B “decoupling”). The model is based on the hypothetical presence of acid brine in a lower, third reservoir, which is the source of vapor for the upper two-phase aquifer of Los Humeros. In this case, the main reason for the observed variability of Cl, B and Cl/B should be the dependence of the partitioning of B into the vapor phase only on temperature, whereas the HCl partitioning depends on both temperature and pH. A computer code is used for quantifying the model.

There have been a number of works for and against the presence of an acid brine at the base of the Los Humeros system, (Tello, 1992, 1997; Verma et al., 1998; Arellano et al., 2003; Izquierdo et al., 2000, 2005, 2009). However, no studies have explained or even discussed

the Cl–B behavior in Los Humeros fluids. Here an attempt is made to show that the observed B–Cl behavior in Los Humeros fluids can be evidence of the presence of an acid solution at the base of the system. There is no detailed discussion of the origin of such a brine and the origin of its acidity (magmatic volatiles, high-temperature NaCl hydrolysis or something else), this will be done elsewhere.

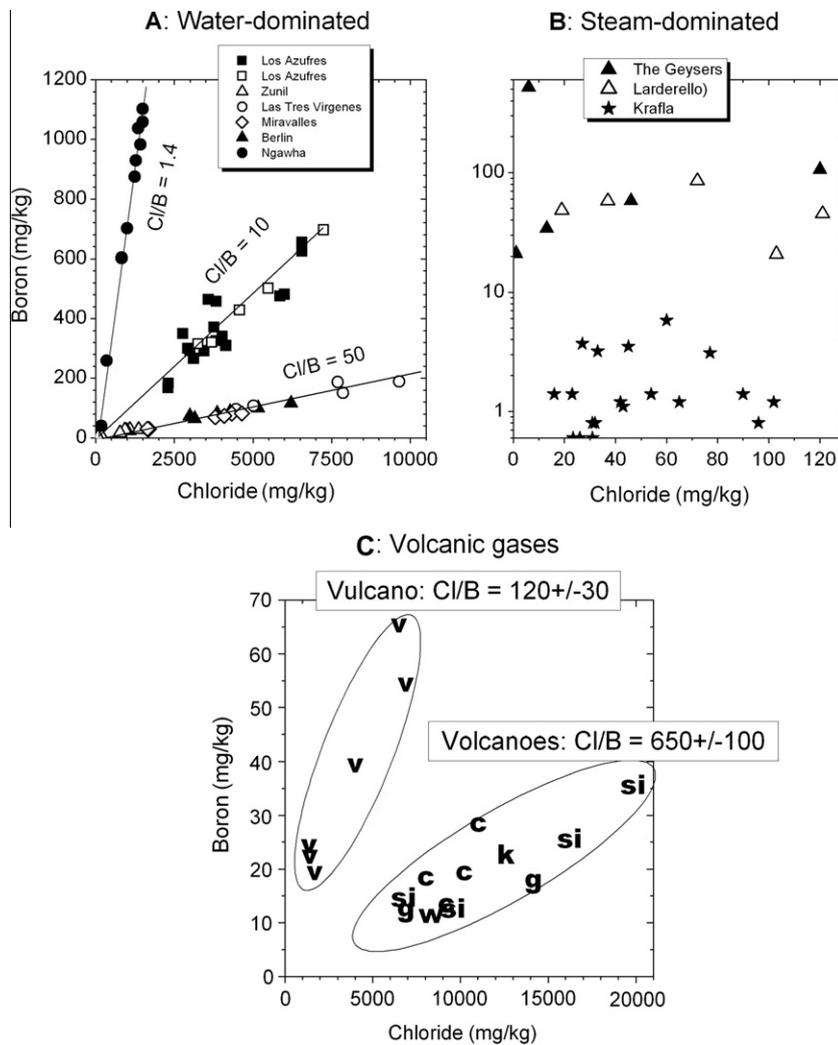
## 2. Boron and chloride in volcanic and hydrothermal fluids

Deep hot hydrothermal fluids from geothermal wells are characterized by a wide range of Cl/B ratios, but they are usually, between 10 and 100 (e.g., Ellis and Mahon, 1977). Generally, B and Cl are well correlated, and all Na–Cl waters discharging within a geothermal field including hot springs and geothermal wells show as a rule a single linear trend indicating a common source of B and Cl (e.g., Arnórsson and Andresdottir, 1995). It can be suggested that in most cases the source of Cl and B in discharging thermal waters has a secondary origin: a hydrothermal solution which homogenizes Cl and B content and whose chemical composition was determined by water–rock interaction and a contribution from additional sources like magmatic volatiles, seawater, etc. Sometimes it could be a combination of two mixing trends, like at Roturua, New Zealand, geothermal field (Giggenbach and Glover, 1992) or at El Chichon volcano (Taran et al., 2008) indicating mixing of two or more waters originating from different aquifers. The highest B content in geothermal fluid, ~800 mg/kg, and the lowest Cl/B ~1.4 (weight ratio) was reported for the Ngawha geothermal system in New Zealand (Ellis and Mahon, 1977; Sheppard, 1987; Aggarwal et al., 2003). Evaporation processes concentrate B and Cl and other conservative elements in the residual water with little change in their relative amounts. Several plots of Cl–B correlation for fluids of different geothermal systems are shown in Fig. 2a. Fluids from Central America geothermal systems (Zunil, Miravalles, Berlin) have a very similar Cl/B ratio, near 50, whereas fluids from Los Azufres, Mexico, are more enriched in B with Cl/B ~10. A high Cl/B ratio of ~1000 was reported in Cerro-Prieto, Mexico, hot hydrothermal system (e.g., Truesdell et al., 1981; not shown on the plot). All the data are plotted for water-dominated hydrothermal systems, where wells drain from a one-phase reservoir of hot water or from a two-phase reservoir with a low steam fraction. The published data on Cl and B concentrations in well fluids of vapor-dominated systems are quite limited and available only for The Geysers and Larderello fields. The caldera-type Krafla system in Iceland is similar to Los Humeros in respect to the hydrological structure but it differs from the latter by very low B content. The B–Cl plot for these fields based on data by Truesdell et al. (1989) and Arnórsson and Andresdottir (1995) is shown in Fig. 2b. In contrast to water-dominated systems, Cl and B concentrations in fluids of The Geysers, Larderello and Krafla are not correlated.

High-temperature volcanic gases can be considered as a proxy for the magmatic source contributing to hydrothermal fluids. Some data from andesitic and more evolved arc volcanoes are shown in Fig. 2c. Volcanic gas condensates usually have Cl/B weight ratio >500. Gases from volcanoes with magmas contaminated by crustal material, like Italian volcanoes, are characterized by a higher B content and lower Cl/B ratios (Vulcano, Fig. 2c). It follows from data reported by Goff and McMurtry (2000) and Taran et al. (1995) that Cl/B in volcanic gases correlates well with Cl/B in associated rocks but usually Cl/B in the gas phase is higher than Cl/B in the associated rock. The same is true for thermal waters of Iceland (Arnórsson and Andresdottir, 1995).

## 3. Boron and chloride in Los Humeros fluids

Several typical analyses of separated water from geothermal wells of Los Humeros are shown in Table 1. These are samples col-



**Fig. 2.** Cl–B relationships for geothermal fluids (upper panel) and volcanic gases (lower panel). Data for fluids from water-dominated fields (A) are from Arellano et al. (2005) – Los Azufres; this work – Los Azufres; Verma et al. (2006) – Las Tres Virgenes; Marini et al. (2003) – Miravalles; Adams et al. (1990) – Zunil; Tenorio-Mejia et al. (1997) – Berlin; Sheppard (1987) and Aggarwal et al. (2003) – Ngawha. Data for steam-dominated systems and Krafla (B) are from Truesdell et al. (1989) and Arnórsson and Andresdóttir (1995), respectively. C: Volcanoes: v – Vulcano; si – Satsuma Iwojima; k – Kudryavy; c – Colima; w – White Island; g – Galeras. Data for volcanic gases are from Goff and McMurtry (2000), Taran et al. (1995, 2002).

lected in 2006–2007 and analyzed by standard techniques (i.e., Giggenbach and Goguel, 1989). In these samples Cl ranges from 3.2 to 180 mg/kg and B from 214 to 932 mg/kg. The isotopic composition of B varies from +0.3‰ to –1.7‰ with a mean value of  $-0.8 \pm 1.6$  ( $2\sigma$ ). Details of the B isotope analyses can be found in Pennisi et al. (2000). Note that B isotopic composition does not depend on B concentration. The values of  $\delta^{11}\text{B}$  may indicate the magmatic origin of B in Los Humeros fluids (e.g., Palmer and Swihart, 2002; Leeman and Sisson, 2002) but the source of B, a direct contribution from magmatic fluid or leaching from magmatic rocks, is impossible to distinguish.

Data for enthalpies of fluids from individual wells are taken from reports of CFE within the same time period. The enthalpy is a measure of the steam fraction in the reservoir tapped by a well (e.g., Ellis and Mahon, 1977; Nicholson, 1993). For a single-phase reservoir filled with liquid water, the enthalpy of the fluid should be close to the enthalpy of liquid water at reservoir temperature. Fluids from wells draining from a steam-dominated reservoir should have enthalpy close to the enthalpy of saturated steam. For example, water at 300 °C has an enthalpy  $\sim 1350$  kJ/kg and saturated vapor  $\sim 2750$  kJ/kg (Keenan et al., 1969). Intermediate values of enthalpy indicate that a given well drains from a two-phase reservoir with a

steam fraction that can be estimated if the reservoir temperature is known. The enthalpy can be directly measured using a separator and measuring water and steam flow rates separately, or using a special device like a “James nozzle” (James, 1970; Nicholson, 1993). Enthalpy of geothermal fluids usually is measured with a 5–15% of relative error (e.g., Hirts et al., 1993).

A set of Cl and B concentrations with enthalpies of well fluids when samples were taken is presented in Table 2. Most of the data have already been published. The largest data sets can be found in Tello (1992, 2005), i.e., from the CFE data base. Arellano et al. (2003) used the same data set. The authors’ data are obtained in 2006–2007. A much larger data set can be found in unpublished reports of the CFE. The concentrations of Cl and B in the total fluid (separated steam + separated water) are calculated using data on enthalpies and separation conditions using standard rules (e.g., Nicholson, 1993). Considering relatively high errors in determining the enthalpies and thus, steam fractions, the calculated solute concentrations in total fluid (steam + water), especially at high enthalpies may have relative errors higher than 100%.

Fig. 3a–c demonstrates the Cl–B relationship and relationships between enthalpy of fluids and Cl and B concentrations in separated water. In contrast to correlations observed for fluids of other

**Table 1**

Selected chemical composition (mg/kg) of separated water from some wells of Los Humeros. Also are shown are enthalpies of fluids and isotopic composition of B in separated water. Samples are collected in 2006–2007.

Well #	H-1	H-2	H-3	H-6	H-32
H (kJ/kg)	1280	2726	2242	2081	2436
pH	8.1	7.5	6.6	7.5	6.9
Na	269	150	168	196	10
K	44	32	28	40	2.0
Ca	1.2	2.0	0.9	0.5	0.0
Mg	0.012	0.08	0.02	0.02	0.007
Li	0.71	0.81	0.49	0.63	0.22
Rb	0.26	0.28	0.21	0.24	0.08
Cs	0.35	0.31	0.29	0.29	0.08
Cl	120	11.1	27	180	3.2
F	6.4	2.0	–	6.9	11
SO <sub>4</sub>	114	89	90	37	16
HCO <sub>3</sub>	361	222	325	203	143 <sup>a</sup>
B	214	295	725	380	932
As	4.7	–	–	–	29
SiO <sub>2</sub>	799	839	900	1000	479
$\delta^{11}\text{B}^b$	$-0.2 \pm 0.4$	$0.3 \pm 0.5$	$-1.7 \pm 0.4$	$-1.6 \pm 0.4$	–

<sup>a</sup> The charge balance is partially provided by 46 mg/kg of NH<sub>4</sub>.

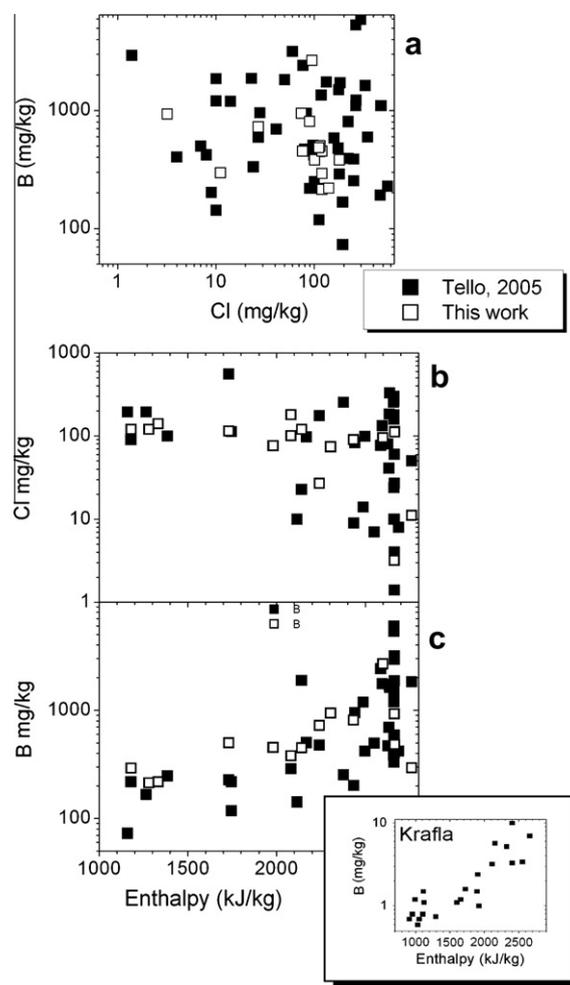
<sup>b</sup> average values (and associated SD) of two independent measurements. The in-run standard deviation of each measurement is lower than 0.5 permil (same analytical design as in Pennisi et al., 2000).

**Table 2**

Selected data on B and Cl concentrations (mg/kg) and Cl/B weight ratios in separated water and total fluid in well fluids of Los Humeros. Separation pressure ~5–8 bar. Data on the fluid enthalpies are from Tello (2005), Arellano et al. (2003) and reports of Comision Federal de Electricidad (CFE, 2009). U2 and U3 are separators unifying several wells.

Well no.	Cl	B	Cl tot	B tot	Cl/B	H (kJ/kg)
<i>From Tello (2005) and Arellano et al. (2005)</i>						
H1	90	218	57	162	0.41	1179
H3	175	477	42	114	0.37	2242
H7	83	946	12	137	0.088	2441
H8	76	453	28	164	0.17	1981
H9	50	1822	–	–	0.027	2762
H12	41	695	2.2	37	0.059	2634
H13	140	219	94	147	0.64	1332
H15	7	199	0.6	18	0.035	2551
H16	4	402	0.2	16	0.010	2663
H17	24	332	1.0	13	0.072	2661
H18	112	118	53	56	0.95	1747
H19	23	1873	6.6	536	0.012	2141
H20	114	446	4.5	18	0.26	2665
H23	194	167	63	63	0.31	2064
H30	10	1202	0.4	48	0.008	2661
H31	8	420	0.2	11	0.02	2689
H32	27	591	1.1	23	0.046	2663
H34	9	202	1.3	30	0.045	2436
H35	1.4	2929	0.1	115	0.0005	2663
H36	60	3168	2.4	125	0.019	2663
H37	10	1863	0.4	73	0.0054	2663
<i>This study</i>						
H1	120	214	83	148	0.56	1280
H1	120	292	89	216	0.41	1180
H6	101	380	6.6	185	0.27	2081
H7	95	2670	34	129	0.036	2600
H8	120	452	15	197	0.27	2142
H8	76	453	94	147	0.17	1981
H12	74	942	28	164	0.079	2305
H13	140	219	4.3	64	0.64	1332
H32	3.2	932	13	119	0.003	2663
H18	115	500	0.13	37	0.23	1730
U2	111	482	89	216	0.23	2665
U3	90	809	55	240	0.11	2434

(water-dominated) geothermal systems (Fig. 2a), no correlation is seen for Los Humeros fluids, similar to data for The Geysers and Larderello steam-dominated fields and the Krafla field in Iceland (Fig. 2b). Chloride–enthalpy and B–enthalpy plots (Fig. 3b and c) for Los Humeros are different. There is no correlation between Cl



**Fig. 3.** (a) Cl–B relationship in separated waters from geothermal wells of Los Humeros. (b and c) Cl and B in separated waters as a function of enthalpy of fluids. Inserted is B–enthalpy plot for Krafla geothermal field (modified from Arnórsson and Andresdóttir, 1995).

and enthalpy, and a positive trend can be seen on the B–enthalpy plot. A similar positive trend occurs but with much lower concentrations of B, as reported by Arnórsson and Andresdóttir (1995), for the Krafla geothermal system (Fig. 3c, insert). These findings may be interpreted by invoking at least two reasons: (1) different sources of Cl and B in Los Humeros fluids and (2) different behavior of H<sub>3</sub>BO<sub>3</sub> and Cl at phase separation (boiling). Metamorphic basement and scarn-type rocks of the interface between limestone and magmatic intrusions (Verma, 2000; Arellano et al., 2003; Rocha et al., 2010) at depth would be a possible additional source for B. However, there are two strong arguments against this possibility: (1) The isotopic composition of B is not consistent with a significant contribution from limestone and rather indicates a B originating from leaching a magmatic source (Palmer and Sturchio, 1990; Tonarini et al., 2007). The magmatic-dominated setting is also supported by the  $\delta^{13}\text{C}$  of CO<sub>2</sub> of about  $-3.5\text{‰}$  V-PDB and very high, almost mantle <sup>3</sup>He/<sup>4</sup>He ratios, higher than 7Ra (Bernard, 2008; Ra =  $1.4 \times 10^{-6}$ , the atmospheric ratio). Some variations observed in the B isotopic composition could be related to isotopic fractionation at boiling; the heavier <sup>11</sup>B isotope prefers the vapor phase (Spivack et al., 1990), and this may be a reason for the positive  $\delta^{11}\text{B}$  in the fluid of H-2 well (Table 1) with the highest enthalpy (steam fraction) though all values are within analytical error. (2) According to the exploitation characteristics of Los Humeros wells, the main inflow zones are located above the metamorphized

limestone strata, which has a low permeability and is almost unaltered (e.g., Rocha et al., 2010). On the other hand, Cl and B can be transported with vapor to the main vapor-dominated aquifer through fractures or through the main upflow zone where the underlying intrusive body cuts the overlying limestone (Arellano et al., 2003; Gutierrez-Negrin and Izquierdo-Montalvo, 2010) from a lower aquifer as HCl and H<sub>3</sub>BO<sub>3</sub>. Molecular HCl has a distribution coefficient between vapor and liquid water >1 (Truesdell et al., 1989; Simonson and Palmer, 1993; Palmer et al., 2004), and at high temperature and low pH the equilibrium: H<sup>+</sup> + Cl<sup>-</sup> = HCl<sup>0</sup>(aq) is shifted to the right (e.g., Simonson and Palmer, 1993; Tagirov et al., 1997). Therefore, the concentration of HCl<sup>0</sup> is higher in Cl-bearing solutions at low pH and consequently, is higher in the vapor produced by boiling of such a solution. The concentration of H<sub>3</sub>BO<sub>3</sub> in the vapor phase depends only on temperature and B concentration of the water phase (see below).

#### 4. Distribution of B and Cl between water and steam

Variations in Cl/B in the total fluid and separated water of Los Humeros (Table 2) are most probably related to the existence of the acid brine at depth and a process of phase separation (boiling) with different partitioning of HCl and H<sub>3</sub>BO<sub>3</sub> into the vapor phase. Indirect evidence of such a process could be the relationship between enthalpy and chemistry of the separated water shown in Fig. 3. Boron concentrations in the separated water of Los Humeros reach values up to 5000 mg/kg (Table 2, Tello, 2005). However, mean concentration of B in the total fluid (steam + water) is near 150 mg/kg, a value close to B concentrations in the superheated vapor of The Geysers steam-dominated field (D'Amore and Truesdell, 1979, 1984; Truesdell et al., 1989). This value (150 mg/kg) may also indicate a high initial vapor fraction at boiling of hypothetical brine.

Concentrations of B and Cl in the vapor phase are governed by the distribution coefficients of H<sub>3</sub>BO<sub>3</sub> and HCl between water and vapor. Boric acid is the main species of B in solutions with pH <8. Therefore, concentration of B in the vapor phase at pH <8 depends only on the total B concentration in the liquid phase and distribution coefficient:  $K_d^{(B)} = m_{B,v}/m_{B,l}$ , where  $m_{B,v}$  and  $m_{B,l}$  are concentrations of B in vapor and liquid, respectively. As an approximation, temperature dependence of  $K_d^{(B)}$  can be expressed as

$$\log K_d^{(B)} = 0.0083t \text{ } ^\circ\text{C} - 3.56 \quad (1)$$

This expression is a best fit for a combination of curves proposed by different authors (Fig. 4a). As it can be seen from Fig. 4a, H<sub>3</sub>BO<sub>3</sub> always prefers the liquid phase, but at high temperature, close to critical point, a significant part of the B partitions into the vapor phase (>20% at 350 °C). Concentration of B in the vapor phase as the result of a single-step steam separation can be written as:

$$M_{B,v} = m_{B,o} K_d^{(B)} / (K_d^{(B)} Y - Y + 1) \quad (2)$$

where  $B_o$  is B concentration in the total fluid (steam + liquid) and  $Y$  is the weight fraction of steam in the steam–water mixture. This expression is derived from the mass balance for a closed system boiling (e.g., Giggenbach, 1980).

Partitioning of Cl into vapor in significant amount is possible only as HCl. Hydrochloride acid partitioning was experimentally studied by Simonson and Palmer (1993) after finding HCl in superheated steam from geothermal fields The Geysers and Larderello (Truesdell et al., 1989) and discussed in many later studies (see Palmer et al. (2004) for review). Because the concentration of the dissolved HCl in water (HCl<sup>0</sup>) depends on the total Cl concentration and pH, the resulting concentration of HCl in the vapor phase is a

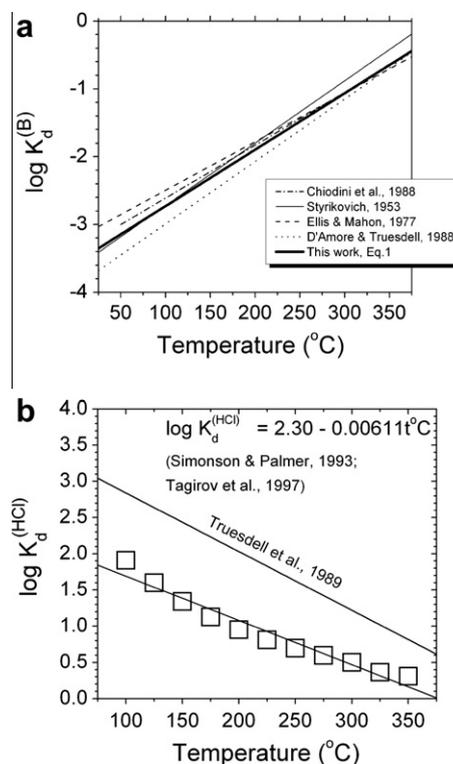


Fig. 4. Temperature dependence of distribution coefficients between vapor and liquid water for boric acid (a) and hydrogen chloride (b). See text for details.

complex function of temperature, pH and Cl of the boiling water and steam fraction (enthalpy) of the formed steam–water mixture.

Concentration of Cl in the vapor phase depends on the activity of the total Cl,  $a_{Cl}$ , and pH:

$$Cl_v = a_{Cl} \cdot K_d^{(HCl)} 10^{\log Ka - pH} / (K_d^{(HCl)} Y - Y + 1) \quad (3)$$

Table 3

Input file for the program HSC-7. 0.1 mmol of HCl, 350 °C, 0.1 M NaCl and 0.05 M of H<sub>3</sub>BO<sub>3</sub>. 40 mmol of CO<sub>2</sub> is added to extend the zone of boiling.

Species	Moles
<i>Vapor phase</i>	
CO <sub>2</sub> (g)	
HCl (g)	
H <sub>3</sub> BO <sub>3</sub> (g)	
HBO <sub>2</sub> (g)	
NaCl(g)	
H <sub>2</sub> O(g)	
<i>Aqueous phase</i>	
H <sub>2</sub> O	55.51
CO <sub>2</sub> (aq)	0.04
BO <sub>2</sub> (aq)	
B(OH) <sub>4</sub> (aq)	
H <sub>3</sub> BO <sub>3</sub> (aq)	0.1
H <sub>2</sub> BO <sub>3</sub> (aq)	
HBO <sub>2</sub> (aq)	
H <sup>+</sup> (aq)	1.0E-07
OH <sup>-</sup> (aq)	1.0E-07
HCl(aq)	0.0001-0.1
NaCl(aq)	
Na <sup>+</sup> (aq)	0.1
Cl <sup>-</sup> (aq)	0.1
HCO <sub>3</sub> <sup>-</sup> (aq)	

Here  $K_d^{(\text{HCl})}$  is the distribution coefficient of HCl between vapor and liquid:

$$K_d^{(\text{HCl})} = m_{\text{HCl,v}}/m_{\text{HCl,l}} \quad (4)$$

and  $K_a$  is the constant of association  $\text{H}^+ + \text{Cl}^- = \text{HCl}$ :

$$K_a = m_{\text{HCl}}/a_{\text{H}^+}a_{\text{Cl}^-} \quad (5)$$

Temperature dependence of  $K_d^{(\text{HCl})}$  is shown in Fig. 4b using  $K_a$  as was reported by Tagirov et al. (1997) at saturation pressure and data by Palmer et al. (2004).

## 5. Computer simulation

A direct application of Eq. (3) is difficult because pH and activity of  $\text{Cl}^-$  depend on the vapor fraction: the higher the vapor fraction, the more concentrated the remaining liquid solution. Therefore, the thermodynamic modeling was carried out using a thermochemical computer code HSC-7 (Roine, 2006). A simple composition was taken: a solution of  $\text{NaCl} + \text{H}_3\text{BO}_3 + \text{CO}_2(\text{aq})$  (0.1 M, 0.05 M and 0.04 M, respectively) with a variable amount of HCl (0.0001–0.1 M). The reason of such a choice for NaCl and  $\text{H}_3\text{BO}_3$  concentrations is explained in the next section. The dissolved  $\text{CO}_2$  is included because the presence of  $\text{CO}_2$  provided a range of

steam fractions at given boiling temperature in a narrow range of pressures slightly lower than the saturation pressure for pure water. Table 3 shows the composition of the initial solution and chemical species taken into account by the program. The HSC code computes the multi-component, two-phase (steam–water) equilibrium using the SOLGASMIX program (Eriksson, 1975) that minimizes the total Gibbs free energy of the system and uses an approximation of Pitzer (1995) for calculation of the activity coefficients. The thermodynamic data base of HSC for dissolved species and gases is compiled mainly from the SUPCRT data set (Johnson et al., 1992) as updated by Sverjensky et al. (1997). Data for  $\text{HCl}^\circ$  in the HSC data base were modified according to Tagirov et al. (1997).

Results at 350 °C are shown in Table 4. Concentrations of B in the vapor phase do not depend on the HCl added to the solution, i.e., on pH of the parent brine. In contrast, the pH of the liquid phase is proportional to the amount of HCl added to the brine and to the fraction of water in the steam–water mixture. Variations in the initial concentration of NaCl from 0.1 M to 1.0 M (not shown) have negligible effect on the HCl concentrations in the vapor phase. The main factor controlling these concentrations at given temperature is the amount of the added HCl or pH of the NaCl–brine. Thus, the concentration of B in the vapor phase at given B concentration in the brine depends only on the temperature

**Table 4**

Results of modeling. Single-step steam separation from a solution (0.1 M NaCl, 0.05 M  $\text{H}_3\text{BO}_3$ , 0.04 M  $\text{CO}_2$ ) at 350 °C with different amount of HCl added and different steam fractions. All concentrations in mg/kg.

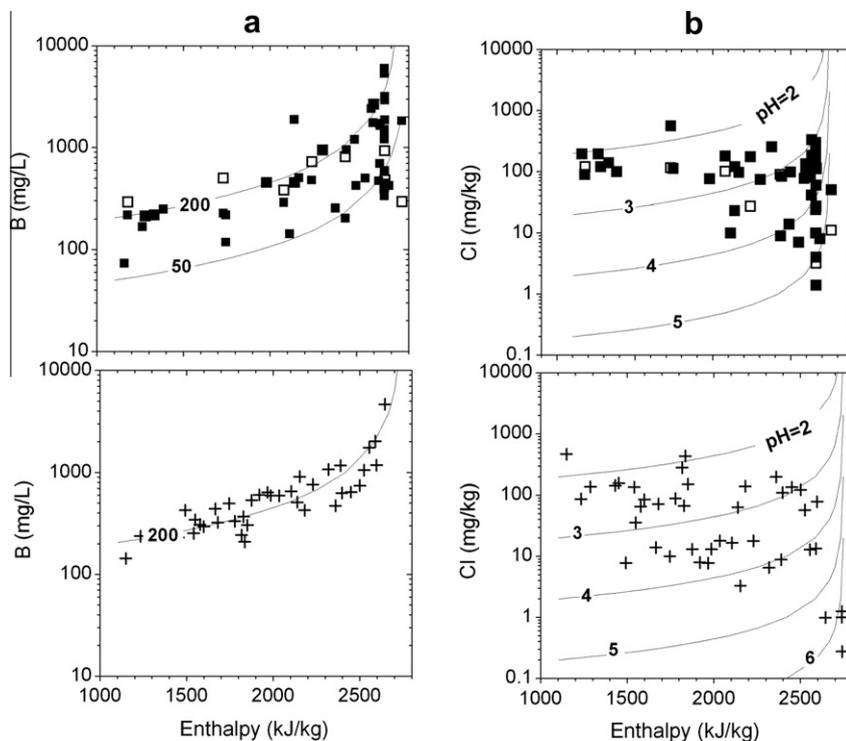
Steam fraction Y	HCl <sup>l</sup> (aq)	B(aq)	HCl(v)	B(v)	pH	(Cl/B) <sub>v</sub> weight	H (kJ/kg)
<i>0.1 mmol HCl</i>							
0.90	1.4	2192	3.9	356	5.83	0.001	2478
0.88	1.4	1998	3.9	346	5.56	0.001	2455
0.83	1.4	1739	3.9	292	5.47	0.001	2409
0.74	1.4	1426	4.3	238	5.35	0.002	2335
0.60	1.8	1134	4.6	184	5.20	0.002	2209
0.45	1.8	864	5.3	151	5.06	0.003	2071
0.33	2.1	745	6.0	130	4.97	0.004	1968
0.26	2.1	691	6.4	119	4.91	0.005	1898
0.20	2.5	648	6.7	108	4.87	0.006	1850
<i>1 mmol HCl</i>							
0.90	13.1	2192	38	356	4.83	0.01	2478
0.88	13.5	1998	38	335	4.58	0.01	2455
0.83	13.8	1750	40	292	4.47	0.01	2414
0.74	14.5	1426	42	238	4.35	0.02	2335
0.60	16.3	1134	47	184	4.20	0.02	2209
0.45	18.4	864	52	151	4.07	0.03	2075
0.34	20.2	745	58	130	3.98	0.04	1972
0.26	21.6	691	63	119	3.92	0.05	1898
0.20	23.0	648	66	108	3.88	0.06	1850
<i>10 mmol HCl</i>							
0.91	131	2192	72	356	3.83	0.09	2481
0.88	134	1998	76	335	3.56	0.11	2454
0.83	138	1750	83	292	3.48	0.12	2412
0.75	146	1426	95	238	3.35	0.16	2338
0.61	162	1134	121	184	3.21	0.24	2212
0.45	183	864	157	151	3.07	0.34	2078
0.34	202	745	193	130	2.98	0.43	1971
0.26	217	691	221	119	2.92	0.49	1905
0.20	230	648	376	108	2.88	0.61	1852
<i>100 mmol HCl</i>							
0.91	1308	2192	3829	356	2.84	0.9	2483
0.88	1329	1998	3829	335	2.58	1.0	2460
0.84	1368	1750	3935	292	2.50	1.2	2427
0.77	1432	1426	4112	238	2.40	1.5	2359
0.65	1597	1134	4538	184	2.28	2.1	2248
0.49	1772	864	5105	151	2.14	3.0	2111
0.37	1978	745	5707	130	2.05	4.0	1998
0.28	2152	691	6168	119	1.99	4.9	1921
0.20	2287	648	6558	108	1.95	5.5	1871

of boiling and variations in the B concentration of the brine, whereas the concentration of HCl in the vapor phase at given temperature depends on the pH of the Na–Cl brine.

## 6. Application to Los Humeros

Arellano et al. (2003) developed a “two-level” model of the Los Humeros geothermal system. They assumed that a hot (>300 °C) vapor-dominated reservoir underlies a water-dominated aquifer with a lithologic boundary (low permeable altered tuffs) separating the reservoirs. It can be assumed also that this vapor is derived from deeper brine with unknown salinity; this brine should underlie the limestone horizon, and vapor rises to the vapor-dominated reservoir above the limestone layer through fractures or more permeable contacts between limestone and intrusive bodies (Fig. 1). Boron concentrations in the brine can be estimated to be about 4–5 times greater than the mean B concentration in the total fluid sampled from wells of Los Humeros. With a value of ~100–150 mg/kg B in the total fluid, the concentration of B in the brine should be ~500–600 mg/kg. The reason for such a suggestion is that the distribution coefficient of B between vapor and liquid at 350 °C is ~0.2 (Eq. (1); Fig. 4a), and the thermal fluid tapped by geothermal wells was initially a pure vapor formed after liquid phase separation (Arellano et al., 2003). It is assumed also that the brine is acid with a pH that promotes the partitioning of HCl into the vapor. This vapor partially condenses and neutralizes during interaction with the wall rocks. It follows from Table 4 that depending on the steam fraction during primary boiling at 350 °C, the calculated concentrations of B in the vapor varies between about 100–300 mg/kg which is close to the range of B concentrations determined in the total fluid (Table 2).

Such a model for the Los Humeros geothermal system can be supported by comparison of the chemistry of separated water from geothermal wells (Fig. 3) and the simulated B and Cl concentrations in a process that can be called “stochastic”. In the model, the concentrations of B in the vapor phase vary from about 100 to 300 mg/kg and depend on the steam fraction during the initial boiling (single-step steam separation) at 350 °C. A random series of B concentrations can be generated in the vapor phase after first boiling within this interval (100–300 mg/kg) using uniform or any other distribution. Another uncontrolled and independent process is condensation of this vapor in the upper productive aquifer. Again a random series of steam fractions (enthalpies) can be generated for the final fluid that is assumed to be tapped by wells. Then, a value of the enthalpy will correspond to a value of the B concentration. After “separation” of this fluid with the given enthalpy and B concentration at 150 °C a series of B concentrations in the separated water can be calculated. This virtual process corresponds to the real fluid separation using cyclone separators at the Los Humeros field for producing dry steam. If the concentration of HCl<sup>o</sup> in the parent solution were constant, the Cl and B behavior in the vapor phase would be similar. However, the acidity of the parent solution decreases as HCl partitions into vapor, and additionally, the acidity of the parent solution can vary due to different internal reasons, such as the local degree of neutralization of wall rocks and a local injection of magmatic fluid. Chloride in the derived fluid, according to the model, is controlled by both variations in pH of the brine and variations in the fraction of the produced vapor phase. The “stochastic” simulation of the Cl behavior in the steam–water mixture of the upper steam-dominated reservoir is generally the same as for B but by considering an additional random variable, pH of the boiling deep brine. The range of pH variations is chosen between 2 and 5 which approximately corresponds



**Fig. 5.** (a) Upper panel is the observed data (same as Fig. 3c). The lower panel shows result of “stochastic” simulation of water separation at 150 °C from a fluid of different enthalpies and a random concentration of B in the total fluid (100 mg/kg < B < 300 mg/kg). Theoretical lines (Eq. (6)) correspond to constant B concentration in total fluid (50 and 200 mg/kg on the upper panel and 200 mg/kg on the lower panel). (b) Upper panel is the observed data for Cl–enthalpy relationship in separated water (same as Fig. 3b). The lower panel shows results of simulation with random pH of the parent brine (2 < pH < 6) and condensation with the random steam fraction (enthalpy). Theoretical lines correspond to HCl concentrations in initial vapor at different pH (numbers on line). See text for more details.

to the concentration range of Cl in the total fluid (~1–100 mg/kg, see Table 4). The corresponding Cl concentration in the vapor separated from brine at 350 °C was calculated as  $\log C_{Cl}$  (mmol/kg) = 4-pH (best fit of the results of modeling, Table 4).

Results of simulation and the observed data are shown in Fig. 5. The observed Cl and B behavior as a function of the fluid enthalpy are the same as in Fig. 3b and c. Similarity between observed and simulated data for B (upper and lower panels of Fig. 5a, respectively) is consistent with the proposed physical model in which B is produced by the “initial” boiling at depth including the assumption of the initial B concentration and temperature of boiling. The scattering of modeled data points (Fig. 5a, lower panel) is provided by the presumed random distribution of B concentrations in the initial vapor. A line shown in the same plot corresponds to a constant B concentration of 200 mg/kg in the initial 350 °C vapor,  $m_{B,o}$ . This line is derived from the mass balance at a single-step separation of a steam–water mixture at 150 °C:

$$m_{B,w} = m_{B,o} / (K_d^{(B)} y - y + 1) \quad (6)$$

where  $m_{B,w}$  is B concentration in separated water and other notation as for Eq. (1).

Two theoretical lines with initial B concentrations of 50 and 200 mg/kg are shown on the upper panel of Fig. 5a. Therefore, it could be suggested that the observed scattering in B concentrations could be caused by non-controlled variations in the initial B concentration in the “parent” vapor. In turn, these initial variations should be the result of variations in both vapor fraction and temperature of boiling at depth.

The simulated Cl–enthalpy behavior is even more scattered than that observed in separated water of Los Humeros (Fig. 5b). It should be repeated that Cl concentration in the vapor separated from the brine almost does not depend on the total Cl in the range 0.1–1 M NaCl. Therefore, it is impossible to predict the salinity of this hypothetical brine from the model, only its B content. Again, theoretical lines corresponding to different pHs of boiling brine are shown on both panels of Fig. 5b.

Temperature of boiling can be one more variable controlling B and HCl concentrations in the vapor phase. At lower temperatures the concentrations decrease and vice versa. A gentle range of random variations in the temperature ( $\pm 5^\circ$ ) gives the same pattern for B–enthalpy behavior and virtually does not affect the Cl–enthalpy relationship (not shown on plots). The behavior of the system at temperatures close to critical point (374 °C for pure water and ~400 °C for a brine with salinity of 0.5 M of NaCl, Bischoff and Rosenbauer, 1988) is more complicated and beyond of the scope of this study.

## 7. Discussion

### 7.1. Limitations of the model and other potential processes responsible for B–Cl decoupling

The model for the Cl–B behavior in Los Humeros fluids is consistent with the presence of an acid Na–Cl solution (brine) beneath the productive aquifer. This is the simplest model based on the single-step (closed system) boiling of a NaCl + H<sub>3</sub>BO<sub>3</sub> solution of variable pH. The addition of other components to the solution will not modify the main results of the modeling because (i) Cl and H<sub>3</sub>BO<sub>3</sub> are not redox-dependent and (ii) their partition to vapor depends by definition only on concentrations in the solution and pH for Cl. An application of a more complicated mechanism of phase separation such as multi-step boiling-condensation or a Rayleigh mechanism requires more sophisticated calculations which it seems will not change the main result on the final Cl–B decoupling for boiling acid solutions. Much more interesting is a question

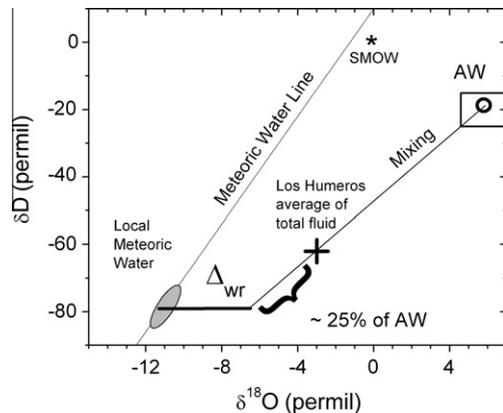
about whether or not other natural processes may exist producing aqueous fluids within a single hydrological system with the resulting independent behavior of Cl and B. Any binary mixing will result in a mixing line. Ternary mixing with meteoric water as one of the endmembers (zero-concentrations of both Cl and B) will result in compositions limited by two binary mixing lines, confined in a mixing triangle like data for Rotorua, New Zealand (Giggenbach and Glover, 1992). An apparent Cl–B decoupling can show mixing of more than two fluids from different sources but with at least one of the endmembers having an exotic composition – very high B and very low Cl. It could be, for example, mixing of seawater, meteoric water and a solution of H<sub>3</sub>BO<sub>3</sub>. Therefore, this mixing mechanism seems to be improbable for Los Humeros fluids.

However, there is still no direct evidence for the existence of an acidic brine at Los Humeros. Core and cutting samples from some deep wells do not show acidic alteration (Izquierdo et al., 2005, 2009), though Flores et al. (2010) reported pyrophyllite in cores of the deep H-43 well that discharges a high-enthalpy fluid, and its separated water (<5 wt.%) has a pH 4–5. There are no wells at Los Humeros producing acid Cl–SO<sub>4</sub> waters like some wells at Miravalles, Costa Rica (Marini et al., 2003) or Tatun, Taiwan (Ellis and Mahon, 1977). Izquierdo et al. (2005) have suggested that low pH in some wells of Los Humeros is a result of exploitation and reinjection due to H<sub>2</sub>S oxidation or, as an alternative, direct injections of magmatic volatiles into the system. The reinjection and oxidation of H<sub>2</sub>S (by dissolved O<sub>2</sub>) hypothesis contradicts to the very low SO<sub>4</sub> concentrations in separated waters of Los Humeros. The injection of magmatic fluids cannot be excluded; however this hypothesis requires an explanation for the high B content in the resulting hydrothermal fluid. On the other hand, the injection could occur into a lower water-dominated aquifer containing high-salinity and high-B brine resulting in lowering the pH of this brine.

One more mechanism for the irregular B enrichment of fluids cannot be excluded. In zones of dry superheated vapor B can precipitate as boric acid, H<sub>3</sub>BO<sub>3</sub> (sassolite), at temperatures <170 °C, as metaborate, HBO<sub>2</sub>, at >170 °C (e.g., Arnovitz and Grew, 2002) or complex borates. Precipitation–sublimation of these B compounds may control B concentration in hydrothermal vapor. This mechanism requires a primary source of B and has too many uncertainties to be applied to Los Humeros.

### 7.2. Sources of boron in Los Humeros fluid

According to the model, the source of B in well fluids of Los Humeros is a hot ( $\geq 350^\circ\text{C}$ ) acidic brine beneath the main productive reservoir with a B content not less than 500 mg/kg and unknown Cl concentration. Natural hydrothermal solutions have B concentrations from 1 to 10 mg/kg in fluids from basaltic aquifers of Iceland (Arnósson and Andresdóttir, 1995), high concentrations, >100 mg/kg, in fluids from aquifers composed of sedimentary and metamorphic rocks (Larderello, Italy; The Geysers, California; Ngahwa, New Zealand) or of dacite–rhyolite volcanic rocks (Los Azufres, Mexico). The highest B content, up to 1000 mg/kg, was reported for the Ngawha geothermal field in New Zealand (Sheppard, 1987; Aggarwal et al., 2003). Aggarwal et al. (2003) suggested a main source of B in Ngawha to be the greywacke wall rocks and the reason for such a high B concentrations (up to 1000 mg/kg) to be a low water/rock ratio deduced from the high O isotope shift (+11‰) of deep water relative to the local meteoric water. Leeman et al. (2005) reported up to 240 mg/kg B in condensates of 300 °C volcanic vapors from Vulcano, Italy. They interpreted these values as the result of mixing of a magmatic endmember with ~70 mg/kg of B and vapor derived from boiling of a modified seawater hot brine that was in contact with B-enriched Vulcano rhyolites and trachytes at low fluid/rock ratio. The observed high B content in



**Fig. 6.** Generalized  $\delta D$ – $\delta^{18}O$  diagram for Los Humeros (LH) thermal fluid. AW – “andesitic water” box (Taran et al., 1989; Giggenbach, 1992);  $\Delta_{wr}$  is the O isotopic shift due to water–rock interaction; SMOW – Standard Mean Ocean Water. Data for local meteoric water and average isotopic composition of LH fluid are from Tello (1992, 2005), Verma et al. (1998), Arellano et al. (2003) and Bernard (2008).

Los Humeros fluids (100–150 mg/kg in the total fluid from geothermal wells or  $\geq 500$  mg/kg in the hypothetical parent brine) may also be the result of mixing of magmatic fluid from the deep magmatic chamber, the heat and fluid source for the system, and leaching of wall rocks of the deep aquifer at a low fluid/rock ratio. According to Arellano et al. (2003), Tello (2005) and Bernard (2008), the O isotopic composition of Los Humeros fluid shows a large positive shift from the meteoric water line (up to +7‰) indicating a low water/rock ratio. A direct magmatic contribution from the magmatic chamber is also evident taking into account high  $^3\text{He}/^4\text{He}$  ratios (7.5Ra, Bernard, 2008), “magmatic”  $\delta^{13}\text{C}$  of  $\text{CO}_2$  ( $\sim -3$ ‰) and a significant deuterium isotopic shift of hydrothermal fluid ( $\sim -60$ ‰ instead of  $\sim -75$ ‰ of the local meteoric water; Arellano et al., 2003; Tello, 2005; Bernard, 2008).

### 7.3. Magmatic contribution and a possible concentration of chloride in deep brine

A generalized plot  $\delta D$  vs.  $\delta^{18}O$  for fluids of Los Humeros is shown in Fig. 6. According to data from Verma et al. (1998), Arellano et al. (2003), Tello (2005) and Bernard (2008), the total fluid (steam + water) is characterized by average  $\delta D \sim -62$ ‰ and  $\delta^{18}O \sim -3$ ‰. These values should be close to the isotopic composition of the parent fluid because at such high temperatures isotopic fractionation between liquid water and vapor is negligible. Isotopic composition of local meteoric water at this elevation ( $\sim 3000$  m above sea level) is  $\delta D \sim -80$ ‰ and  $\delta^{18}O \sim -11$ ‰ (Verma et al., 1998; Tello, 1992; Bernard, 2008). Magmatic fluid could be the main contributor of Cl to the system. If this magmatic fluid is similar to a typical magmatic fluid in subduction zones, its water should have an isotopic composition close to that of “andesitic water” (Taran et al., 1989; Giggenbach, 1992), i.e.  $\delta D \sim -20$ ‰ and  $\delta^{18}O \sim +6$ ‰, and Cl content close to that of seawater ( $\sim 1$  mol% or  $\sim 20,000$  mg/kg). If so, the Los Humeros fluid has approximately 25% of “andesitic water” (Fig. 6) and correspondingly  $\sim 5000$  mg/kg of chloride. Note that the Cl/B ratio in this case is  $\sim 10$ , exactly as in Los Azufres deep thermal fluid (Fig. 2a), 300 km to west.

## 8. Conclusions

Geothermal fluids from Los Humeros geothermal field, Mexico are characterized by a low ( $< 1$ ) and extremely variable Cl/B weight ratio and very high B concentrations in separated water (g/L). Isotopic composition of B ( $-0.8 \pm 1.6$ ‰) suggests its magmatic origin,

though sedimentary origin cannot be ruled out. A similar Cl–B “decoupling” is shown in steam-dominated hydrothermal systems Larderello, Italy, The Geysers, USA and Krafla, Iceland. The latter is characterized by a hydrological structure similar to Los Humeros and, like Los Humeros, produces dry steam and a steam–water mixture. However, high concentrations of B in well fluids have been reported only for Los Humeros.

To explain the unusual behavior of Cl and B in well fluids of Los Humeros a model is proposed which invokes the existence of a deep acid brine boiling at a temperature  $\sim 350$  °C producing  $\text{H}_3\text{BO}_3$  and HCl-bearing vapor that condenses and neutralizes at an upper level where it is tapped by wells. The model is based on the difference in thermodynamic properties of the dissolved  $\text{H}_3\text{BO}_3$  and HCl; partitioning of B to vapor depends only on temperature, whereas partitioning of HCl to vapor depends on the temperature and pH of the boiling brine.

This process was modeled using a thermochemical computer code and an approximation of single-step steam separation at depth. The hypothetical brine, according to calculations, should have B concentration near 500–600 mg/kg; however, the Cl content of the parent brine is not constrained by the model. Concentration of HCl in the vapor phase in the model depends only on the pH of the boiling solution in the range of 0.1–1 M of NaCl.

In order to compare results of modeling and the observed data for Los Humeros a “stochastic” simulation was applied where steam fractions at boiling of the brine in the lower reservoir, liquid fractions at condensation of steam in the upper reservoir and pH of the brine were assessed as random variables with uniform distribution. Results of modeling in terms of B–enthalpy and Cl–enthalpy relationships showed qualitative and even semi-quantitative agreement with the observed Cl/B ratios and relationships between the chemistry and enthalpy of fluids.

Discussion of other processes which potentially could be responsible for the decoupling of Cl and B in natural hydrothermal fluids has showed that mixing of waters of different origin cannot be responsible for such behavior. Therefore, the presence of a lower aquifer filled with hot fluid enriched in B (500–600 mg/kg) with a variable pH of 3–5 is a probable situation explaining not only Cl–B behavior but some other features of this geothermal field.

Assuming only a magmatic source of Cl in the Los Humeros parent thermal solution and taking into account the water isotopic composition of well fluids it can be speculated that the parent brine of Los Humeros has  $\sim 5000$  mg/kg Cl with a Cl/B ratio  $\sim 10$ , similar to thermal fluids of Los Azufres, located within the same Trans-Mexican Volcanic Belt 300 km to west.

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