Chapter 3 - Developments of auxiliary chemical geothermometers applied to the Los Humeros and Acoculco high-temperature geothermal fields (México)

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DEVELOPMENTS OF AUXILIARY CHEMICAL GEOTHERMOMETERS APPLIED TO THE LOS HUMEROS AND ACOCULCO HIGH-TEMPERATURE GEOTHERMAL FIELDS (MÉXICO)

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3.1 Introduction

The knowledge of the temperature of the deep geothermal fluids, rock permeability and water reservoir capacity are three key parameters for developing deep geothermal energy. Since 1965, one of the major applications of fluid geochemistry in the exploration of the potential geothermal reservoirs involves estimation of their temperature using classical chemical, isotope and gas geothermometers on fluids collected from geothermal wells and thermal springs, such as:

- Na-K (Fournier 1979; Michard, 1979; Giggenbach, 1988), Na-K-Ca (Fournier and Truesdell, 1973), K-Mg (Giggenbach, 1988), SiO_2 (Fournier and Rowe, 1966; Fournier, 1977; Michard, 1979);
- $\delta^{18}O_{H2O-SO4}$ (Lloyd, 1968; Mizutani and Rafter, 1969; Kusakabe and Robinson, 1977; Sakaï, 1977; Seal *et al.*, 2000; Zeebe, 2010; Boschetti, 2013);
- CO_2-CH_4-H_2S-H_2, CO_2-CH_4-H_2, CO_2-CH_4, H_2-Ar, CO_2-Ar (D'Amore and Panichi, 1980; Marini, 1987; Giggenbach and Goguel, 1989; Giggenbach, 1987, 1991).

Most of the solute geothermometers are based on empirical or semi-empirical laws derived from known or unknown chemical equilibrium reactions between water and minerals occurring in the geothermal reservoirs. Unfortunately, these classical tools do not always yield concordant estimations of reservoir temperatures, even at very high temperatures, in acidic environments, for example. Discrepancies in temperature estimates may also be due to different processes occurring during the geothermal fluid ascent up to the surface and its cooling: mixing with surface cold waters or seawater, degassing, precipitation/dissolution processes, etc.

Since the early 1980s, numerical multicomponent geochemical models are also being developed for direct application to chemical geothermometry for geothermal exploration (Reed, 1982; Michard and Roeckens, 1983; Reed and Spycher, 1984; Spycher *et al.*, 2014; Peiffer *et al.*, 2014a). These models allow numerical calculations of equilibration temperature of the geothermal water with respect to a suite of reservoir minerals, and thus the estimation of the reservoir temperature. Multicomponent geothermometry is not intended to replace classical geothermometers, but rather to supplement these geothermometers, and by doing so to increase confidence in temperature estimations. However, such approach cannot be applied carelessly and without a sound conceptual understanding of the area being studied (Al and pH poorly determined, for example). For this approach, a state of full chemical equilibrium is necessary and the conditions of this equilibrium state are not always reached.

Since the early 1980s, in parallel, several auxiliary geothermometers combining a major with a trace element, like Na-Li (Fouillac and Michard, 1981; Kharaka *et al.*, 1982; Michard, 1990; Sanjuan *et al.*, 2014), Mg-Li (Kharaka and Mariner, 1989), Na-Rb, Na-Cs, K-Sr, K-Mn, K-Fe, K-F and K-W (Michard, 1990; Sanjuan *et al.*, 2016a, b; 2017), have been also developed and are available for specific types of geothermal fluids and geological environments.

BRGM aims to develop and validate this type of auxiliary chemical geothermometers and the $\delta^{18}O_{H2O-SO4}$ isotope geothermometers in order:

- to improve the geochemical methods for geothermal exploration in volcanic fields such as Los Humeros and Acoculco, with high-temperature (HT) and relatively low permeability;
- to acquire a better knowledge about the circulation of HT deep fluids and their possible interaction with more superficial waters in this type of geothermal fields, from chemical and isotopic water analyses from surface thermal springs.

In the Los Humeros field, where numerous deep wells were drilled and are presently producing, the temperature values measured at the bottom-hole and estimated using classical water and gas geothermometers, will be used to test and calibrate these auxiliary geothermometers on the fluids collected from the deep geothermal wells. Some neighbouring thermal springs will be also sampled.

In the Acoculco field, where only two deep wells were drilled (EAC-1 in 1994, at a depth of 2000 m, and EAC-2 in 2008, at a depth of 1900 m, 500 m east of EAC-1; Peiffer *et al.*, 2014b), but were not productive, these auxiliary geothermometers will be applied on fluids collected from surface thermal springs.

The temperatures estimated for the waters collected from the thermal springs during this study will be compared with those given by the classical gas and water geothermometers, with reference to the deep temperatures close to 290-330°C measured at a depth of about 2000 m in both los Humeros (Arellano *et al.*, 2003; Pinti *et al.*, 2017) and Acoculco fields (Peiffer *et al.*, 2014b). These temperatures correspond to a gradient of 14°C/100 m, three times higher than the baseline gradient measured within the Trans-Mexican Volcanic Belt (Ziagos *et al.*, 1985).

In order to be able to obtain relevant results, the BRGM activities have been planned as follows:

- a preliminary literature review relative to the geological, geophysical and geochemical data about the Los Humeros and Acoculco geothermal fields, with the collaboration of the other partners, especially the Mexican partners (CFE, for example), in order to collect the main geological information and most of the geochemical data of the fluids sampled from Los Humeros deep wells and from thermal Acoculco springs);
- the participation to a campaign of fluid sampling and on site measurements in the Los Humeros and Acoculco geothermal areas (from deep wells at Los Humeros and from thermal springs at Acoculco), with the collaboration of CNR (Matteo Lelli's team) and Mexican teams (Ruth Alfaro, CFE…);
- chemical (major and some trace species) and isotope ($\delta^{18}O_{H2O}$, $\delta^{18}O_{SO4}$, $\delta^{11}B$, $\delta^{7}Li$, $^{87}Sr/^{86}Sr$…) analyses of the waters collected during the campaign of fluid sampling, in the BRGM laboratories ;
- data interpretation, including the use of thermodynamic considerations, and main conclusions.

3.2 Literature review

Several interesting papers have been found during the literature review carried out by BRGM, among which the main ones are:

- Arzate *et al.* (2018), Peiffer *et al.* (2018), Carrasco-Núñez *et al.* (2018, 2017a and b), Pinti *et al.* (2017), García-Soto *et al.* (2016), Norini *et al.* (2015), Arellano Gomez *et al.* (2003, 2008, 2015), Bernard *et al.* (2011); García-Gutiérrez (2009), Barragán-Reyes *et al.* (2008, 2010), Gutiérrez-Negrín and Izquierdo-Montalvo (2010), Izquierdo *et al.* (2008, 2009), Lopez Romero (2006), Martínez-Serrano (2002), Portugal *et al*. (2002), Prol-Ledesma (1998), and Cortés *et al.* (1997) for the Los Humeros geothermal field;
- Sosa-Ceballos *et al.* (2018), Avellán *et al.* (2017), García-Palomo *et al.* (2017), Canet *et al.* (2010, 2015a, 2015b), Peiffer *et al.* (2014b, 2015), Lermo *et al.* (2009), Lopez-Hernández *et al.* (2009), Verma (2001), Lopez-Hernández and Castillo-Hernández (1997), Tello Hijonosa *et al.* (1995), Tello Hijonosa (1986, 1987, 1991), Ledezma-Guerrero (1987) for the Acoculco geothermal field.

3.2.1 Los Humeros geothermal field

The main existing data of fluids from geothermal wells and neighbouring thermal springs used for this study are presented below.

Documents and Excel sheets provided by CFE in 2017 have allowed to collect geological, temperature and pressure logs from 16 wells located in the Los Humeros geothermal field (wells H-5, H-12, H-22, H-23, H-24, H-25, H-26, H-27, H-28, H-29D, H-41, H-43, H-49, H-56, H-58, H-59). Fluid and gas geochemical data collected between 1987 and 2017 are available for only 13 of these wells (absence of data for the wells H-5, H-25 and H-26). Measurements of water stable isotopes (δD and $\delta^{18}O$) have been performed by CFE, between 2013 and 2016, on fluids from 29 wells (wells H-3, H-6, H-7, H-9, H-11, H-12, H-13R, H-15, H-17, H-19, H-20, H-29, H-30, H-31, H-32, H-33, H-34, H-35, H-37, H-38R, H-39, H-40, H-41, H-42, H-43, H-44, H-45, H-48, H-49).

Chemical data for two neighbouring thermal springs (El Tesoro and Noria Nuevo Pizarro) were also found in the tables of fluid monitoring given by CFE.

Detailed fluid geochemical data from the geothermal wells of Los Humeros field and neighbouring springs are also given by:

- Prol-Ledesma (1998) during pre- and post- exploitation of the Los Humeros geothermal field (gas and water chemical and isotopic data from deep wells, including the stable isotopes of water and $\delta^{18}O$ values of dissolved sulphates);
- Arellano-Gomez *et al.* (2003) for five deep wells (H-1, H-6, H-7, H-8 and H-12), including gas and water chemical and isotopic data (water stable isotopes);
- Barragan-Reyes *et al.* (2010) for several deep wells (stable isotopes of water and gas chemical composition), and neighbouring springs (stable isotopes of water);
- Bernard *et al.* (2011) for several deep wells (water chemical and isotopic data, with boron isotopic data for 4 water samples);
- Pinti *et al.* (2017) for several deep wells (He, Ne and Ar noble gas isotopic abundances, with stable isotopes of water).

The geological and geothermal setting are presented in Chapter 1. The figure 3.2.1.1a, extracted from Pinti *et al.* (2017), and the figure 3.2.1.1b, extracted from Carrasco *et al.* (2017a), show a general view of the location of most of the Los Humeros geothermal wells.

a) **b)**

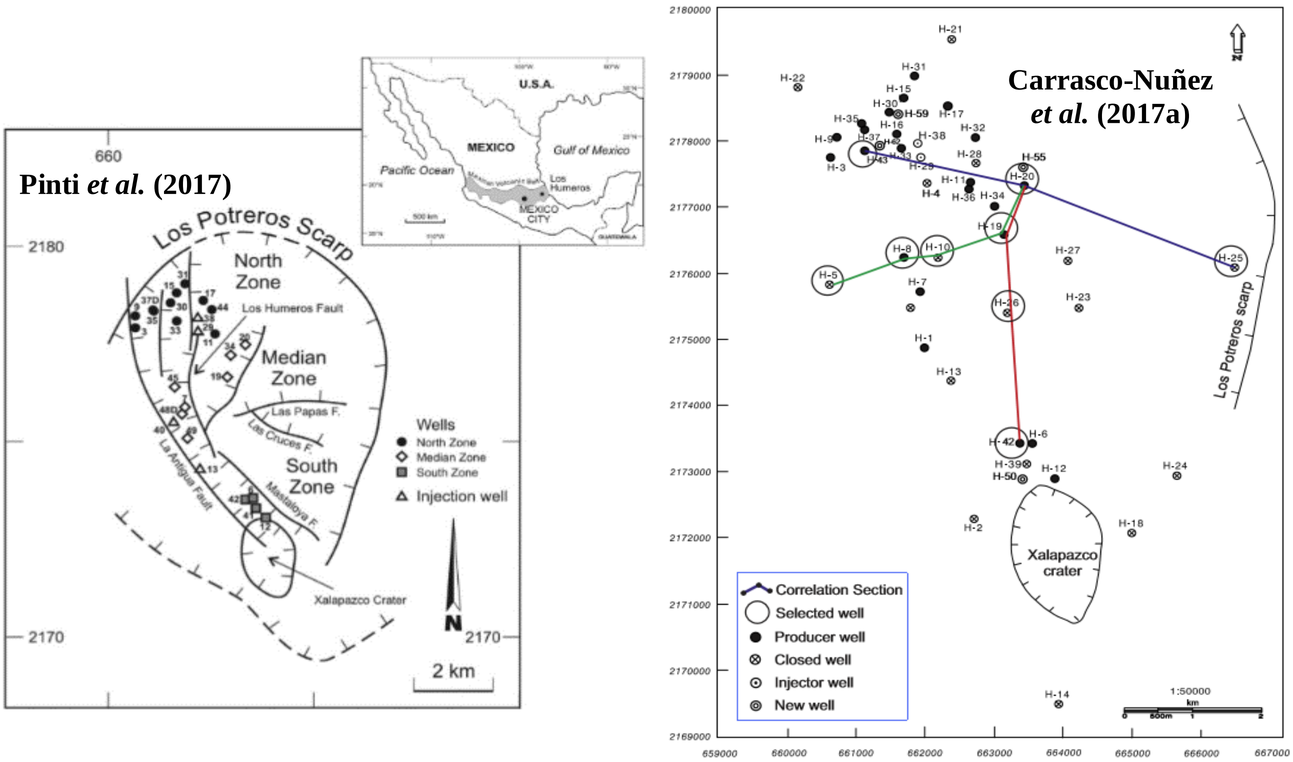

Figure 3.2.1.1 - a) Simplified tectonic map of the central part of the Los Humeros caldera with the major faults and the position of the production and re-injection wells (from Pinti et al., 2017). b) Location of the main geothermal wells within Los Humeros geothermal field (from Carrasco et al., 2017a).

From the geothermal reservoir consisted of medium-to low-permeability pre-caldera andesites, the wells produce biphasic fluid, with variable but high fractions of steam and limited liquid water contents, with enthalpy values over 2400 kJ/kg (Gutiérrez-Negrín and Izquierdo-Montalvo, 2010), except for some wells as H-1, which has always produced water with a low enthalpy of 1500-1700 kJ/kg. Some geothermal fluids reach 400°C in the northern production area.

3.2.2 Acoculco geothermal area

Geochemical data for waters sampled from 39 thermal springs located in the Acoculco geothermal area, with temperature values ranging from 13 to 49°C, have been collected in the CFE report 34-86 (Tello Hinojosa, 1986). Chemical data for 10 gas samples from the Acoculco caldera are also presented in this report. All these data have been interpreted by Tello Hijonosa (1986), and some main conclusions and recommendations were given. Some of these data were also presented and interpreted by Lopez-Hernández *et al.* (2009). Partial chemical data (pH, Na, K, SO_4, B) are presented for samples of drilling fluid collected from the EAC-1 exploration well in the Acoculco area, in a CFE document (Tello Hijonosa *et al.*, 1995).

Peiffer *et al.* (2014b) have reported geochemical data for waters from four Acoculco thermal springs and associated non-condensable gases (fig. 3.2.2.1). They integrated some of the previous data obtained by Tello Hijonosa (1986), interpreted all the results and drew up some main conclusions, among which the estimation of deep temperatures ranging from 243 to 353°C, using gas geothermometry (CO_2-Ar, CH_4-CO_2, CO_2 and H_2S). These values are in agreement with the measured well bottom hole temperatures (267 and 300°C). They might explain the intense hydrothermal alteration observed in the upper 800 m of volcanic rocks, with most abundant alteration minerals being quartz, amorphous silica, calcite, pyrite, clays (illite, smectite, kaolinite), and hematite.

The presence of a deep-water reservoir was not revealed during the EAC-1 drilling (depth of 2000 m), in 1994, in the locality of Los Azufres. However, a few permeable layers, at depths of 70 m and 300-450 m, and inflow of warm water together with significant amount of gas were observed (López-Hernández and Castillo-Hernández, 1997; López-Hernández *et al.*, 2009). The second well of 1900 m deep (EAC-2), drilled in 2008, 500 m east of EAC-1, showed a promising deep temperature of 267°C accompanied by low permeability similar to that of the EAC-1 well.

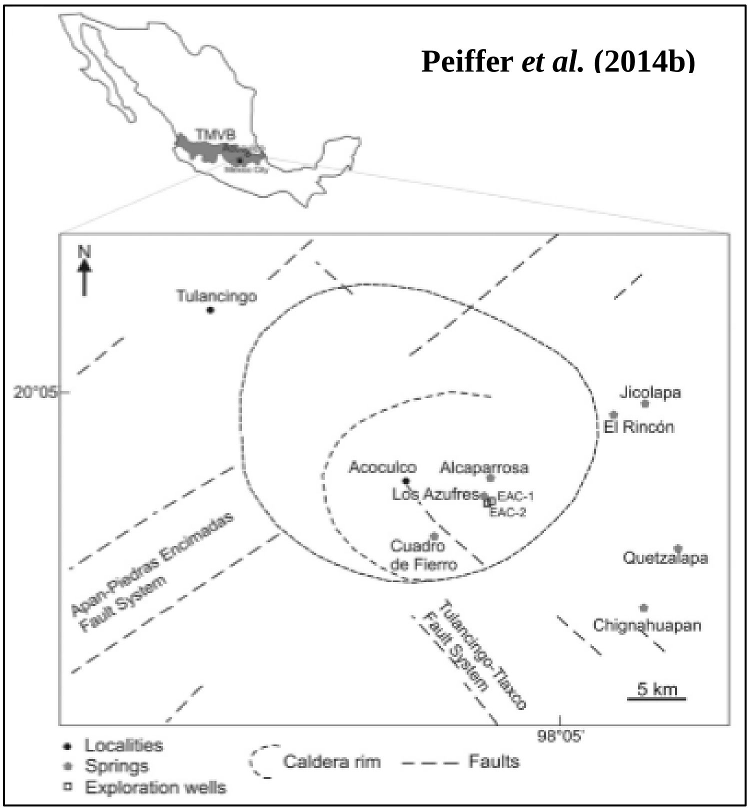

Figure 3.2.2.1 - a) Location of the Acoculco caldera within the Trans-Mexican Volcanic Belt (TMVB) and schematic map of the Tulancingo-Acoculco caldera complex with the position of the main fault systems, thermal springs and the two exploration wells (modified in Peiffer et al., 2014b, after López-Hernández et al., 2009).

According to Peiffer *et al.* (2014b), the high grade of alteration of the volcanic deposits induces low rock permeability and acts as a caprock probably impeding the recharge of the system by meteoric waters (López-Hernández *et al.*, 2009), and causing the absence of thermal manifestations within the caldera complex. Instead, springs with close to ambient temperatures are reported as well as hydrothermally altered grounds, cold diffuse soil degassing and bubbling pools (Polak *et al.*, 1982; Tello-Hijonosa, 1986; Bernard-Romero, 2008).

Cold degassing is probably due to conductive cooling of the deep gases on their way to the surface. Los Azufres, where EAC-1 well was drilled, and Alcaparrosa are the only two regions with noticeable active degassing (H_2S smell), bubbling pools and springs with temperatures of 16-25°C (fig. 3.2.2.1). The only springs with temperature significantly above the ambient temperature are located outside the caldera towards the east and south-east at Chignahuapan (49°C, inside a thermal bath resort), Quetzalapa (30°C), Jicolapa (32°C) and El Rincón (32°C; fig. 3.2.2.1). Apart from Chignahuapan spring, all these springs are characterized by bubbling.

The geological and geothermal setting are presented in Chapter 1.

3.2.3 Main remarks

If all the dissolved major species (Na, K, Ca, Mg, HCO_3, Cl, SO_4, SiO_2) and stable water isotopes (δD and $\delta^{18}O$) were determined among most of the existing geochemical data, few trace elements (only B, Li, F, NH_4, Fe, Al and As) were studied. Very few data were also found for $\delta^{18}O_{SO4}$ and $\delta^{11}B$ values, and $^{87}Sr/^{86}Sr$ ratios. No value was found for $\delta^{7}Li$ values. The campaign of fluid sampling planned by BRGM was therefore very important and necessary to test and develop our auxiliary chemical geothermometers, integrating trace elements such as Rb, Cs, Sr, Mn, F and W, and the $\delta^{18}O_{H2O-SO4}$ geothermometer. It has also contributed to acquire new isotopic data of $\delta^{11}B$ and $\delta^{7}Li$ values.

The table 3.2.3.1 summarizes the existing chemical and isotopic data obtained on the scarce thermal waters of the Los Humeros and Acoculco areas.

Thermal spring	Date	T	Cond.	pH	Na	K	Ca	Mg	HCO_3	Cl	SO_4	SiO_2	F	B	NH_4	Li	Rb	Cs	Fe	Al	TDS	δD	$\delta^{18}O$	Reference
		°C	µS/cm		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	g/l	‰	‰	
El Tesoro	06/03/2015	15	791	8.1	87.4	11.1	10.9	26.0	396	58.6	10.2	58.1				0.089					0.7			*CFE monitoring (database table)*
El Tesoro	13/10/2015	14	774	7.2	83.7	11.3	47.3	23.5	390	58.6	5.8	31.9									0.7			*CFE monitoring (database table)*
El Tesoro	15/04/2016	16	762	6.6	82.9	10.2	42.8	34.1	380	49.6	1.8	55.0				0.067					0.7			*CFE monitoring (database table)*
El Tesoro	17/11/2016	23	783	7.8	79.3	9.8	39.7	30.4	405	60.1	3.4	63.8				0.072					0.7			*CFE monitoring (database table)*
El Tesoro	27/02/2017	15	791	8.1	87.4	11.1	10.9	26.0	396	58.6	10.2	58.1				0.089					0.7			*CFE monitoring (database table)*
Nuevo Pizarro (Noria)	16/10/2015		1686	7.3	303	26.1	31.4	18.9	498	208	99.0	21.3		2.47		0.378					1.2			*CFE monitoring (database table)*
Nuevo Pizarro (well)	25/02/2015	17	1758	7.3	360	1.21	19.4	1.52	552	211	124	29.5		2.50							1.3			*CFE monitoring (database table)*
Nuevo Pizarro (well)	09/11/2016	17	1737	7.1	312	28.9	37.1	25.1	708	195	98.0	44.7		3.20		0.375					1.5			*CFE monitoring (database table)*
Nuevo Pizarro (well)	09/02/2017	17	1758	7.3	360	1.21	19.4	1.52	552	211	124	29.5		2.50							1.3			*CFE monitoring (database table)*
Nuevo Pizarro (spring)	13/04/2016	17	1763	6.7	295	29.4	35.2	30.4	522	169	11.8	17.7		2.30		0.411					1.1			*CFE monitoring (database table)*
Baños Chignahuapan	21-25/04/2006	47.5		7.0	87.0	14.0	196	26.0	735	106	28.0	19.0	0.7	1.80	0.5	0.360					1.2	-70	-10.4	*Peiffer et al. (2014)*
Baños Chignahuapan	02/07/1986	49	1440	6.5	95.4	14.4	173	30.6	831	118	39.0	24.3		3.20	2.0	0.372	< 0.1	< 0.1	< 0.5		1.3	-69	-9.6	*Tello Hijonosa (1986)*
Baños Quetzalapa	18/06/1986	32	1942	5.8	157	18.6	193	47.9	1479	23.5	0	53.6		0.74	2.0	0.149	< 0.1	< 0.1	< 0.5		2.0	-60	-8.7	*Tello Hijonosa (1986)*
Agua Salada	03/07/1986	21	2070	6.5	435	70.5	79.1	34.6	1459	192	0	85.0		34.5	0.24	0.216	< 0.1	< 0.1	0.7		2.4			*Tello Hijonosa (1986)*
Capulines	01/07/1986	20	1030	6.0	77.9	18.4	77.0	76.0	716	5.9	16.3	52.9		0.80	< 0,1	0.131	< 0.1	< 0.1	< 0.5		1.0			*Tello Hijonosa (1986)*
El Rincón	19/06/1986	32	878	5.6	12.9	12.9	144	10.3	500	9.8	36.9	64.7		0.09	1.6	< 0.1	< 0.1	< 0.1	< 0.5		0.8	-65	-9.3	*Tello Hijonosa (1986)*
Baños Jicolapa	21-25/04/2006	25.4		6.2	29.0	15.0	265	12.0	894	7.7	0	63.0	0.6	1.00	0.1						1.3	-66	-10.2	*Peiffer et al. (2014)*
Baños Jicolapa	03/07/1986	32	1381	6.5	31.4	15.6	230	17.2	927	17.6	0	66.9		1.25	0.4	< 0.1	< 0.1	< 0.1	< 0.5		1.3	-67	-9.5	*Tello Hijonosa (1986)*
Los Azufres	21-25/04/2006	21.4		5.5	55.0	15.0	56.0	11.0	137	7.8	218	33.2	0.2	2.00	7.8						0.5	-72	-10.5	*Peiffer et al. (2014)*
Los Azufres	25/06/1986	25	1214	6.0	124	28.4	99.8	29.8	0	37.2	2298	31.3		167	94	< 0.1	< 0.1	< 0.1	< 0.5		2.9			*Tello Hijonosa (1986)*
Los Azufres	25/06/1986	25	829	6.6	17.7	30.1	64.4	15.8	47.5	19.6	211	36.8		36.6	86	< 0,1	< 0.1	< 0.1	2.66	4.49	0.6	-68	-8.1	*Tello Hijonosa (1986)*
Los Azufres	25/06/1986	25	1931	7.0	332	36.5	198	79.4	1231	94.1	340	23.4		266	81	0.159	< 0.1	< 0.1	< 0.5	0	2.7			*Tello Hijonosa (1986)*
Cuadro de Fierro	20/06/1986	23	1876	3.4	42.3	13.6	145	87.2	0	13.7	1245	32.5		1.48	7.6	< 0.1	< 0.1	< 0.1	7.5	64	1.6	-79	-10.8	*Tello Hijonosa (1986)*
Alcaparrosa	29/05/2013	17		2.4	15.8	8.5	9.7	1.3	0	2.2	538	52.0									0.6			*Peiffer et al. (2014)*
Alcaparrosa	21-25/04/2006	12.2		2.4	11.0	6.7	10.0	1.6	0	8.6	515	53.0									0.6	-69	-10.7	*Peiffer et al. (2014)*
Alcaparrosa	24/06/1986	15	1945	2.2	13.7	9.48	36.4	9.2	0	13.7	1272	63.8		12.6	9.8	< 0.1	< 0.1	< 0.1	< 0.5		1.4	-68	-9.4	*Tello Hijonosa (1986)*

Table 3.2.3.1 - Existing chemical and isotopic data of the main thermal springs discharging from the Los Humeros and Acoculco geothermal areas, with literature references.

3.3 Water sampling and analytical results

3.3.1 Water sampling

The campaign of water sampling was carried out by BRGM, in collaboration with CFE, University of Michoacana and CNR Lelli's team, from March 20 to 28, in the Los Humeros and Acoculco geothermal fields (fig. 3.3.1.1). Fluid samples were collected from seven geothermal wells and four thermal springs located in the Los Humeros area, from eight thermal springs located in the Acoculco area, and from three neighbouring crater lakes (lagunas), as points of surface reference. Their locations are reported in figure 3.3.1.1 and in table 3.3.1.1.

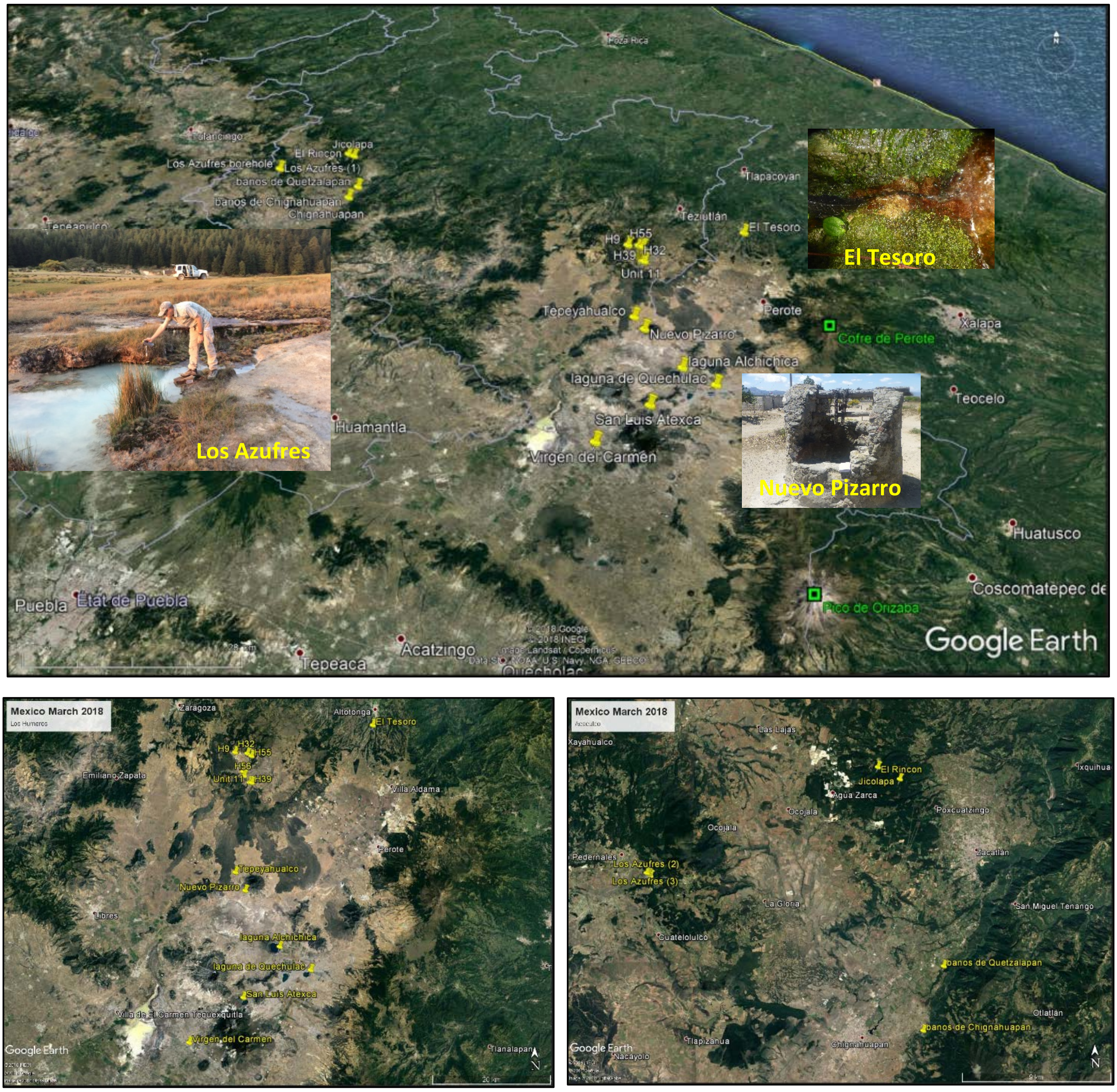

Figure 3.3.1.1 - Location of the geothermal wells and thermal springs which were sampled during the campaign of water sampling carried out by BRGM between March 22 and 28, 2018, in the Los Humeros and Acoculco areas.

Among the two-phase geothermal waters from Los Humeros field, very rich in steam, those which indicated the most high fractions of liquid water were selected with the valuable help of CFE (table 3.3.1.1).

Collection of the fluid samples in the field was accompanied by appropriate on-site measurements such as water temperature, conductivity, pH redox potential and alkalinity. The temperature, conductivity, pH and redox potential measurements were performed on the raw water samples, whereas alkalinity was analysed on fluid samples filtered at 0.45 µm. Absolute uncertainty concerning the pH measurements was 0.05 pH units and relative uncertainty concerning the other parameters varied from 5% to 10%, depending on the parameter and the range of measured values. All these measurements are given in table 3.3.1.1.

Area	Sampling point	Specific enthalpy	Location		Location (ED50 UTM North zone 14)			Depth	Date	T	Cond. 25°C	pH	Eh	Alk.	Alk.
		J/g	Longitude (°E WGS84)	Latitude (°N WGS84)	X	Y	Z (m)	m		°C	µS/cm		mV	meq/l	mg/l HCO_3
Los Humeros area	**Los Humeros H-39**		-97.44192672	19.64813614	663433	2173524	2901	2890	22/03/2018 12:00	61.9	591	7.14	-260	4.45	272
	Los Humeros Unit-11 (fluid mixing)		-97.44426546	19.64789310	663188	2173495	2896		22/03/2018 12:50	52.7	1294	7.00	-240	4.56	278
	Los Humeros H-56	2006	-97.45238985	19.65824117	662325	2174632	2840	2380	22/03/2018 13:25	74.1	1196	7.58	-346	5.68	347
	Los Humeros H-49	1640	-97.45575398	19.66414467	661967	2175282	2824	2030	22/03/2018 13:55	68.0	1051	7.70	-270	4.64	283
	Los Humeros H-9		-97.46771954	19.69284192	660683	2178448	2756	2752	22/03/2018 15:05	66.8	752	7.17	-295	4.63	283
	Los Humeros H-32		-97.44843294	19.69107099	662707	2178270	2815	2818	22/03/2018 15:35	67.8	595	6.67	-235	1.55	95
	Los Humeros H-55	≈ 2600	-97.44178982	19.68610194	663409	2177726	2830		22/03/2018 16:08	68.9	254	7.55	-335	0.73	45
	El Tesoro		-97.25200094	19.73436294	683253	2183272	2080		23/03/2018 09:30	22.5	787	7.49	220	6.05	369
	El Tesoro (in front of the first spring)				683259	2183302	2080		23/03/2018 10:00	21.0	610	7.50	240		
	Noria Nuevo Pizarro		-97.45232003	19.49040046	662501	2156054	2342	20.18	23/03/2018 11:45	16.0	2090	8.82	130	11.21	684
	Pozo Hacienda San Miguel Barrientos		-97.57049400	19.50323691	650084	2157367	2352		23/03/2018 12:45	18.5	441	7.81	210		
	Pozo de Pochintoc							95	23/03/2018 13:45	20.2	660	7.80	190		
	Virgen del Carmen		-97.53992885	19.26677171	653514	2131220	2364		23/03/2018 15:46	19.1	2080	7.10	205	12.36	754
	Pozo de Tepeyahualco		-97.46732500	19.51728056	660899	2159015	2426	130	24/03/2018 10:10	23.8	4970	6.75	-50	33.70	2056
	Laguna de Atexcac		-97.45423537	19.33296456	662456	2138625	2363		24/03/2018 14:15	22.0	12640	8.63	50	2.05	125
	Laguna de Alchichica		-97.39758881	19.40821429	668331	2147009	2324		23/03/2018 16:45	18.5	13250	9.07	106	41.75	2547
	Laguna de Quechulac		-97.34922053	19.37386715	673448	2143255	2342		24/03/2018 16:30	20.4	894	8.73	160	6.75	412
Acoculco area	**Los Azufres 1**		-98.14404722	19.92236110	589656	2203350.946	2840		26/03/2018 15:05	25.4	1489	6.41	-355		
	Los Azufres 2		-98.14442500	19.92255830	589616	2203372.57	2840		26/03/2018 16:00	19.2	693	3.22	-51		
	Los Azufres 3		-98.14504444	19.92286940	589551	2203406.67	2840		28/03/2018 09:45	26.6	1735	7.94	-140		
	Jicolapa		-97.99911898	19.98534263	604784	2210405.375	2230		27/03/2018 09:45	30.7	1372	6.31	-241		
	El Rincon		-98.00717601	19.98889439	603939	2210793.463	2304		27/03/2018 11:00	26.6	550	5.67	110		
	Baños de Quetzalapa		-97.99399722	19.83767500	605418	2194065.117	2171		27/03/2018 16:00	30.0	1964	6.37	135		
	Baños de Chignahuapan		-97.98183170	19.87221460	606669	2197895.496	2190		28/03/2018 07:30	49.0	1448	6.51	-271		

Table 3.3.1.1 - Field data corresponding to the campaign of fluid sampling carried out by BRGM between March 22 and 28, 2018, in the Los Humeros and Acoculco geothermal areas.

Collection and conditioning of all the water samples followed the classical procedures recommended for each of the chemical and isotopic analyses to be performed. Thus:

- for the chemical analysis of major anions and some trace elements, such as Cl, SO_4, Br, F, NH_4 and PO_4, the water samples were filtered at 0.45 µm and collected in 100 ml polyethylene bottles;
- for the chemical analysis of major cations, the water samples were filtered at 0.45 µm, then acidified using Suprapur HNO_3 and collected in 100 ml polyethylene bottles;
- in order to avoid silica precipitation, the samples of hot water for silica analysis (high contents) were collected in 50 ml polyethylene bottles and immediately diluted by a factor of 10 using Milli-Q water;
- for the chemical analysis of the other trace elements, such as B, Sr, Li, Ba, Mn, Fe, Al, Cs, Rb, Ge, As, Nd, Ag, Cd, Co, Cr, Cu, Ni, Pb and Zn, as well as for the isotopic Li and Sr analyses, the water samples were filtered at 0.2 µm, then acidified using Suprapur HNO_3 and collected in 50 ml polyethylene bottles;
- for the isotopic analysis of B, the water samples were filtered at 0.45 µm, then acidified using Suprapur HNO_3 and collected in 1 l polyethylene bottles;
- untreated fluid samples for the isotopic analysis of D and ^{18}O in the water and of ^{13}C in the carbon dioxide were collected in 100 ml and 1 l polyethylene bottles, respectively;
- for the isotopic analysis of ^{18}O in the dissolved sulphate, cadmium acetate was added to the water samples collected in 1 l polyethylene bottles.

3.3.2 Analytical results

All the chemical analyses for both major and trace elements in the collected water samples were done in the BRGM laboratories using standard water analysis techniques such as Ion Chromatography, Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Flame Emission Spectrophotometry, TIC analysis and Colorimetry. The chemical analysis results, for which the analytical precision is better than ± 5% for the major elements and ± 10% for the trace elements, are given in tables 3.3.2.1 and 3.3.2.2. Except for Los Azufres 2 water sample (pH = 3.22), the ion balance (I. B.) values (tabl. 3) traduce a good quality of the major specie analyses.

The isotopic analyses of the water samples (δD and $\delta^{18}O$ of the water, $\delta^{18}O$ of the dissolved sulphate, plus the $\delta^{7}Li$, $\delta^{11}B$, $^{87}Sr/^{86}Sr$) were also performed in the BRGM laboratories using Thermo Ionization Mass Spectrometry and Neptune Multi Collector ICP-MS. More details relative to the BRGM analytical procedures are given in Millot *et al.* (2011). The isotopic analysis results are given in table 3.3.2.3.

The absolute uncertainty for the analyses of δD and $\delta^{18}O$ in the water samples was ± 0.8‰ and ± 0.1‰, respectively. The absolute uncertainty for the $\delta^{18}O$ analyses of the dissolved sulphate was ± 0.1‰. The external reproducibility of the $\delta^{7}Li$ and $\delta^{11}B$ analyses was estimated at around ± 0.5‰ and ± 0.3‰, respectively, and the in-run precision of the $^{87}Sr/^{86}Sr$ ratio was generally better than $\pm 10 \times 10^{-6}$ ($2\sigma_m$).

All the geochemical data obtained during this study have been uploaded and stored in the GEMEX Open Access Database (OADB), as well as the required information.

Area	Sampling point	Date	T °C	Cond. 25°C µS/cm	pH	Eh mV	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Alk. mg/l HCO_3	Cl mg/l	SO_4 mg/l	NO_3 mg/l	SiO_2 mg/l	TDS g/l	I.B. %
Los Humeros area	Los Humeros H-39	22/03/2018 12:00	61.9	591	7.14	-260	119	23.8	< 0.5	< 0.5	268	46.5	2.3	< 0.5	745	1.20	0.31
	Los Humeros Unit-11 (fluid mixing)	22/03/2018 12:50	52.7	1294	7.00	-240	270	36.9	2.2	< 0.5	307	98.8	227	< 0.5	733	1.68	2.37
	Los Humeros H-56	22/03/2018 13:25	74.1	1196	7.58	-346	244	38.4	1.0	< 0.5	383	147	63.6	< 0.5	931	1.81	1.31
	Los Humeros H-49	22/03/2018 13:55	68.0	1051	7.70	-270	212	35.8	1.1	< 0.5	305	129	86.1	< 0.5	834	1.60	-0.71
	Los Humeros H-9	22/03/2018 15:05	66.8	752	7.17	-295	146	30.9	< 0.5	< 0.5	283	69.5	39.0	0.8	538	1.11	0.41
	Los Humeros H-32	22/03/2018 15:35	67.8	595	6.67	-235	82.6	12.4	2.6	< 0.5	95	86.1	6.3	< 0.5	567	0.85	-1.68
	Los Humeros H-55	22/03/2018 16:08	68.9	254	7.55	-335	34.4	5.6	< 0.5	< 0.5	51	38.4	13.8	< 0.5	155	0.30	1.51
	El Tesoro	23/03/2018 09:30	22.5	787	7.49	220	84.6	11.0	34.5	30.2	369	63.9	12.0	7.9	78.3	0.69	-0.71
	Noria Nuevo Pizarro	23/03/2018 11:45	16.0	2090	8.82	130	410	46.3	17.4	18.0	684	240	115	43.0	47.9	1.62	1.47
	Virgen del Carmen	23/03/2018 15:46	19.1	2080	7.10	205	85.3	8.2	273	107	755	99.1	557	2.3	91.0	1.98	-1.45
	Pozo de Tepeyahualco	24/03/2018 10:10	23.8	4970	6.75	-50	659	30.9	315	133	2056	775	0.6	< 0.5	91.8	4.06	0.99
	Laguna de Atexcac	24/03/2018 14:15	22.0	12640	8.63	50	2022	92.7	16.6	604	1474	3854	264	5.7	68.7	8.40	1.78
	Laguna de Alchichica	23/03/2018 16:45	18.5	13250	9.07	106	2506	218	6.8	431	2547	3259	1088	< 0.5	4.0	10.06	-3.78
	Laguna de Quechulac	24/03/2018 16:30	20.4	894	8.73	160	82.1	7.7	16.7	62.3	412	90.7	19.5	1.0	14.6	0.71	0.04
Acoculco area	Los Azufres 1	26/03/2018 15:05	25.4	1489	6.41	-355	147	29.3	104	28.7	463	36.0	353	< 0.5	77.4	1.24	-2.87
	Los Azufres 2	26/03/2018 16:00	19.2	693	3.22	-51	12.8	8.2	23.0	6.0	< 10	0.7	225	< 0.5	75.3	0.35	-43.53
	Los Azufres 3	28/03/2018 09:45	26.6	1735	7.94	-140	210	33.7	153	46.5	463	52.0	644	< 0.5	56.1	1.66	-2.37
	Jicolapa	27/03/2018 09:45	30.7	1372	6.31	-241	31.7	15.1	278	13.4	958	7.6	4.3	< 0.5	152	1.46	4.76
	El Rincon	27/03/2018 11:00	26.6	550	5.67	110	12.3	12.0	90.7	5.2	291	2.3	48.4	< 0.5	140	0.60	-0.22
	Baños de Quetzalapa	27/03/2018 16:00	30.0	1964	6.37	135	150	16.8	291	37.4	1436	16.1	0.8	< 0.5	114	2.06	2.47
	Baños de Chignahuapan	28/03/2018 07:30	49.0	1448	6.51	-271	93.0	14.2	191	25.9	756	115	26.5	< 0.5	44.1	1.27	-0.34

Table 3.3.2.1 - Chemical composition (major species) of the geothermal and thermal waters collected during the campaign carried out by BRGM between March 22 and 28, 2018, in the Los Humeros and Acoculco geothermal areas.

Area	Sampling point	Date	T	NH_4	PO_4	F	B	Br	Sr	Ba	Mn	Li	Rb	Cs	Ge	Al	As	Fe	W	Ag	Cu	Zn	Ni	Pb	Co	Cd	U
			°C	mg/l	mg/l	mg/l	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Los Humeros area	**Los Humeros H-39**	22/03/2018 12:00	61.9	0.11	0.67	13.4	951	32.0	1.52	0.71	7.05	397	240	305	60.1	4193	42323	38	86.5	< 0.01	< 0.1	1.96	0.35	< 0.05	< 0.05	0.06	< 0.01
	Los Humeros Unit-11 (fluid mixing)	22/03/2018 12:50	52.7	0.15	0.70	20.6	1819	73.7	41.2	5.92	25.9	619	315	330	56.0	3310	21721	90	85.4	0.02	< 0.1	0.32	0.65	< 0.05	< 0.05	< 0.01	< 0.01
	Los Humeros H-56	22/03/2018 13:25	74.1	5.51	0.84	4.2	256	90.9	11.0	1.06	18.7	871	392	705	47.6	2042	8077	110	84.5	< 0.01	0.53	0.42	0.65	0.07	< 0.05	0.01	< 0.01
	Los Humeros H-49	22/03/2018 13:55	68.0	3.59	0.33	4.0	593	94.9	16.2	1.08	8.66	676	259	370	46.3	2362	3838	38	103	< 0.01	0.16	0.46	0.48	< 0.05	< 0.05	< 0.01	< 0.01
	Los Humeros H-9	22/03/2018 15:05	66.8	5.33	1.15	7.0	1459	56.8	2.09	0.64	19.9	1182	178	122	8.0	2430	5E+05	105	22.9	< 0.01	0.77	0.69	0.65	< 0.05	< 0.05	< 0.01	< 0.01
	Los Humeros H-32	22/03/2018 15:35	67.8	0.14	0.15	9.3	1447	< 10	38.6	12.1	22.9	394	99.6	94.8	21.0	1925	54597	58	23.4	< 0.01	0.20	0.39	0.70	< 0.05	< 0.05	0.06	< 0.01
	Los Humeros H-55	22/03/2018 16:08	68.9	10.8	0.16	1.3	43.20	22.8	6.03	1.58	23.1	131	38.3	52.2	7.89	245	3379	22	9.93	0.10	< 0.1	0.47	0.33	< 0.05	< 0.05	0.10	< 0.01
	El Tesoro	23/03/2018 09:30	22.5	< 0.05	0.17	0.4	1.267	153	237	41.6	< 0.1	121	22.1	< 0.5	< 0.5	2.49	2.37	< 20	0.20	< 0.01	< 0.1	0.17	< 0.1	< 0.05	< 0.05	0.01	0.97
	Noria Nuevo Pizarro	23/03/2018 11:45	16.0	< 0.05	14.58	1.5	2.711	568	230	61.1	1.7	421	22.6	< 0.5	< 0.5	2.60	32.8	< 20	1.25	< 0.01	2.58	2.31	2.98	0.08	0.73	0.33	2.62
	Virgen del Carmen	23/03/2018 15:46	19.1	0.51	< 0.05	0.8	1.493	244	2488	91.3	132	108	13.3	< 0.5	< 0.5	1.61	3.05	< 20	< 0.05	< 0.01	0.40	1.45	0.26	< 0.05	< 0.05	0.65	0.03
	Pozo deTepeyahualco	24/03/2018 10:10	23.8	0.27	< 0.05	1.1	19.79	1139	3112	6110	311	1787	49.3	7.39	< 0.5	4.41	137	8118	0.14	0.01	< 0.1	2.24	1.93	< 0.05	0.78	0.28	0.25
	Laguna de San Luis Atexca	24/03/2018 14:15	22.0	0.27	< 0.05	0.5	65.56	5429	105	16.4	13.8	2667	104	21.9	< 0.5	6.50	93.8	< 20	0.32	0.01	0.31	0.22	0.76	0.05	0.07	0.12	0.17
	Laguna de Alchichica	23/03/2018 16:45	18.5	0.49	< 0.05	< 1	39.89	4822	31.9	14.2	5.03	2460	305	1.3	< 0.5	7.49	114	< 20	1.59	0.01	0.18	0.57	0.23	< 0.05	< 0.05	0.98	1.92
	Laguna de Quechulac	24/03/2018 16:30	20.4	0.11	< 0.05	0.5	0.561	158	89.6	21.6	8.22	2.87	7.61	< 0.5	< 0.5	5.06	3.48	< 20	< 0.05	< 0.01	1.33	0.23	< 0.1	< 0.05	< 0.05	0.42	0.92
Acoculco area	**Los Azufres 1**	26/03/2018 15:05	25.4	14.04	1.13	0.2	253	52.7	1732	39.2	1219	38.6	66.8	2.39	3.99	40.1	135	42	0.45	< 0.01	< 0.1	1.12	0.17	< 0.05	< 0.05	0.02	< 0.01
	Los Azufres 2	26/03/2018 16:00	19.2	< 0.05	< 0.05	0.5	1.444	< 10	133	24.3	1160	6.47	19.3	< 0.5	< 0.5	12762	24.3	8284	< 0.05	< 0.01	0.18	105	5.81	0.18	5.31	0.04	0.01
	Los Azufres 3	28/03/2018 09:45	26.6	7.66	2.39	0.3	354	74.6	2500	114	2258	81.3	71.3	2.14	5.53	69.5	8421	70	1.09	< 0.01	1.01	1.37	2.43	0.09	0.9	0.07	0.08
	Jicolapa	27/03/2018 09:45	30.7	0.81	0.08	0.7	1.915	20.7	1242	311	179	95.3	58.3	5.99	1.07	6.08	1.37	70	< 0.05	< 0.01	0.24	0.78	0.18	< 0.05	< 0.05	1.19	< 0.01
	El Rincon	27/03/2018 11:00	26.6	0.49	< 0.05	0.5	0.124	33.3	424	159	120	13.2	33.8	1.81	< 0.5	6.54	13.3	2854	< 0.05	< 0.01	0.23	3.49	0.23	< 0.05	0.11	0.08	< 0.01
	Baños de Quetzalapa	27/03/2018 16:00	30.0	1.01	< 0.05	0.4	2.240	44.3	1070	726	132	138	31.3	11.9	2.6	1.20	1.25	< 20	< 0.05	< 0.01	0.14	0.23	< 0.1	< 0.05	< 0.05	0.15	< 0.01
	Baños de Chignahuapan	28/03/2018 07:30	49.0	0.57	< 0.05	0.8	3.076	182	691	147	27.2	374	63.9	63.1	0.98	25.8	24.1	311	0.14	< 0.01	0.17	0.89	0.18	< 0.05	< 0.05	0.03	0.05

Table 3.3.2.2 - Chemical composition (minor and trace species) of the geothermal and thermal waters collected during the campaign carried out by BRGM between March 22 and 28, 2018, in the Los Humeros and Acoculco geothermal areas.

Area	Sampling point	Date	T	δD	$\delta^{18}O$	$\delta^{18}O_{SO4}$	$\delta^{7}Li$	$\delta^{11}B$	$^{87}Sr/^{86}Sr$
			°C	‰	‰	‰	‰	‰	
Los Humeros area	**Los Humeros H-39**	22/03/2018 12:00	61.9	-63.8	-1.2	9.3			
	Los Humeros Unit-11 (fluid mixing)	22/03/2018 12:50	52.7	-45.9	1.5	4.0		-2.50	
	Los Humeros H-56	22/03/2018 13:25	74.1	-61.6	-1.1	1.2	7.2	-2.23	0.704310
	Los Humeros H-49	22/03/2018 13:55	68.0	-58.3	-0.3	0.9		-0.74	
	Los Humeros H-9	22/03/2018 15:05	66.8	-53.1	1.2	3.4			
	Los Humeros H-32	22/03/2018 15:35	67.8	-61.5	-0.9	4.8	2.3	-2.52	0.704283
	Los Humeros H-55	22/03/2018 16:08	68.9	-51.3	0.5	5.2			
	El Tesoro	23/03/2018 09:30	22.5	-79.3	-11.1	3.7			
	Noria Nuevo Pizarro	23/03/2018 11:45	16.0	-38.4	-5.1	4.3			
	Virgen del Carmen	23/03/2018 15:46	19.1	-87.2	-11.9	3.4	12.4		0.707095
	Pozo de Tepeyahualco	24/03/2018 10:10	23.8	-73.7	-9.4		8.9	8.55	0.706862
	Laguna de Atexcac	24/03/2018 14:15	22.0	-23.4	0.0	11.8	10.1	6.49	0.706864
	Laguna de Alchichica	23/03/2018 16:45	18.5	-12.2	1.0	17.7			
	Laguna de Quechulac	24/03/2018 16:30	20.4	-30.0	-1.4				
Acoculco area	**Los Azufres 1**	26/03/2018 15:05	25.4	-69.5	-8.1	4.7	44.8	-4.42	0.705065
	Los Azufres 2	26/03/2018 16:00	19.2	-62.1	-8.4				0.704778
	Los Azufres 3	28/03/2018 09:45	26.6	-29.8	0.1	5.6		-5.61	0.705045
	Jicolapa	27/03/2018 09:45	30.7	-67.5	-10.0	5.3	4.9	-6.79	0.707262
	El Rincon	27/03/2018 11:00	26.6	-68.3	-10.1		5.1		0.707114
	Baños de Quetzalapa	27/03/2018 16:00	30.0	-64.2	-9.1	6.5	5.5	-1.20	0.706804
	Baños de Chignahuapan	28/03/2018 07:30	49.0	-70.8	-10.1	6.0	4.7	-0.17	0.706272

Table 3.3.2.3 - Isotopic composition of the geothermal and thermal waters collected during the campaign carried out by BRGM between March 22 and 28, 2018, in the Los Humeros and Acoculco geothermal areas.

3.4 Data interpretation and discussion

3.4.1 Los Humeros high-temperature geothermal waters

a) Chemical characteristics of the fluids

The geothermal Na-HCO_3-Cl waters discharged from Los Humeros wells (fig. 3.4.1.1), completely deleted in calcium and magnesium, enriched in silica (fig. 3.4.1.2) and boron (among the highest ones in the world), with TDS and pH values ranging from 0.3 to 1.8 g/l and 6.67 to 7.58, respectively, traduce a high interaction process with the reservoir rocks, at high temperature.

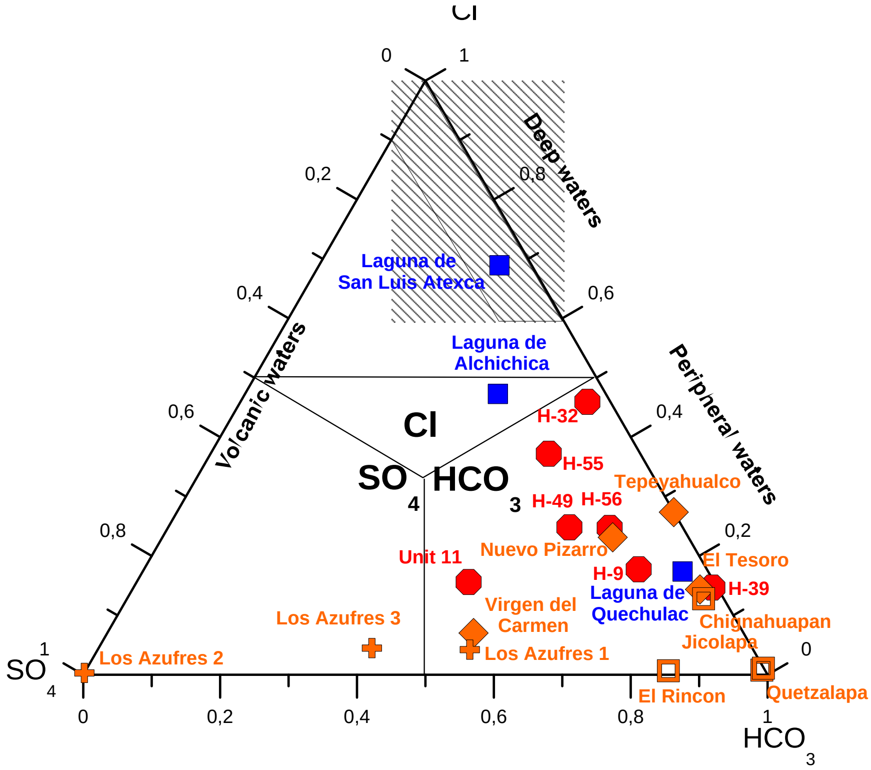

Figure 3.4.1.1 - Position of the geothermal and thermal waters collected in the Los Humeros and Acoculco areas in the Cl-HCO_3-SO_4 ternary diagram of Giggenbach (1988).

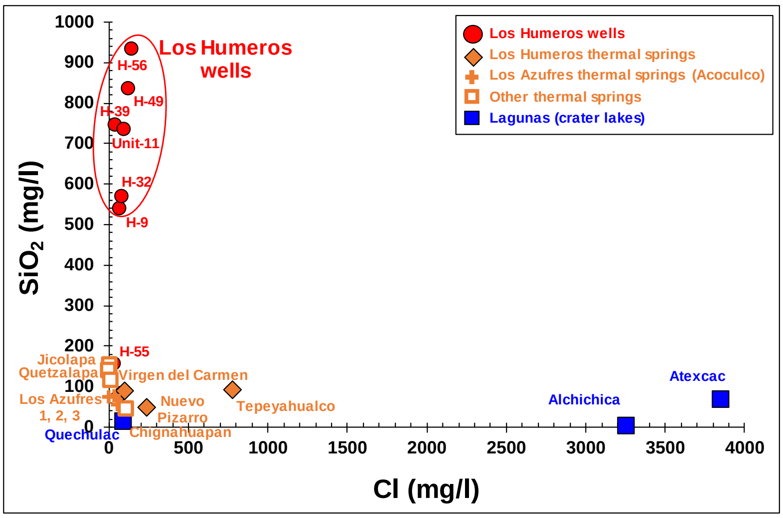

Figure 3.4.1.2 - Diagram SiO_2 - Cl for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas.

b) *Water origin*

The isotopic δD and $\delta^{18}O$ values for the Los Humeros wells show a wide dispersion probably related to boiling, mixing, phase separation and condensation phenomema (fig. 3.4.1.3). The high values of $\delta^{18}O_{H2O}$ of the geothermal waters towards the right of the Global Meteoric Water Line (GMWL) are not only in concordance with high-temperature values, but also suggest a low water-rock ratio of the geothermal reservoir, when compared with the lower values observed in the Krafla geothermal field, in North-Iceland (tabl. 3.4.1.1), where the fluids are also biphasic, but the water-rock ratio is much higher. This is in agreement with a reservoir consisting of medium- to low-permeability pre-caldera andesites.

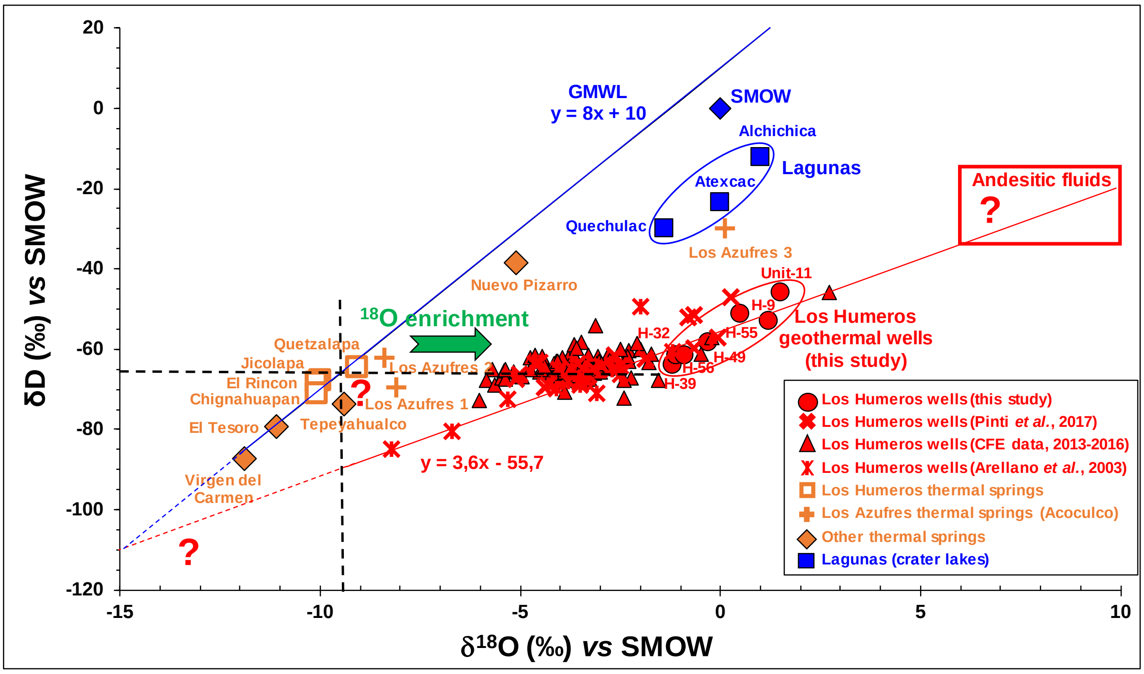

Figure 3.4.1.3 - Diagram δD - $\delta^{18}O$ for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas.

According to Arrellano *et al.* (2003) and Barragán *et al.* (2010), the isotopic composition of the water molecule would be dominated by two main processes.

The first process would be a mixing of recharge meteoric water with a deep fluid-type andesitic water (δD ≈ -20‰ and $\delta^{18}O$ ≈ 6‰), as defined by Giggenbach (1992), leading to a positive correlation between δD and $\delta^{18}O$, with a slope close to 3.0. In this case, from the literature existing data, the intersection of the mixture line with the GMWL would result to vary from -14.5‰ to -11‰ for $\delta^{18}O$, and from -105‰ to -78.5‰ for δD (Portugal *et al.*, 2002; López-Romero, 2006; Barragán Reyes *et al.*, 2010; Bernard *et al.*, 2011). These values are lower than those measured for the meteoric waters in Los Humeros area (Oriental Basin), which are generally close to -10.7‰ for $\delta^{18}O$ and -77.3‰ for δD (Quijano *et al.*, 1981). From these values, the proportion of andesitic water was estimated to be between 25% and 50% (Portugal *et al.*, 2002; Barragán Reyes *et al.*, 2010; Bernard *et al.*, 2011).

The second process would be boiling and phase separation. At fluid temperatures higher than 220°C, ^{18}O is preferentially partitioned into the fluid phase, while deuterium is slightly partitioned into the vapor phase. The resulting fractionation scatters the points a few per mil perpendicular to the main mixing trend in the corresponding δD - $\delta^{18}O$ diagram.

According to data from Verma *et al.* (1998), Arellano *et al.* (2003), Tello (2005) and Bernard (2008), the total geothermal fluid (steam + water) from Los Humeros is characterized by average values of δD ≈ -62‰ and $\delta^{18}O$ ≈ -3‰.

Another assumption for the origin of the geothermal waters could be the contribution of meteoric water with a δD value similar to that of the geothermal fluid, affected by a strong water-rock interaction process at high-temperature and low water-rock ratio, which enriches its ^{18}O content (up to 7-8‰). The wide dispersion observed for the isotopic values in the δD - $\delta^{18}O$ diagram could be explained by different water-rock interaction factors and processes such as kinetic fractionation at temperatures close to boiling temperatures (Giggenbach and Stewart, 1982), with characteristic slopes of 3.0-3.5, and phase separation. In this case, the isotopic values for the meteoric water would be slightly heavier than those reported by Quijano *et al.* (1981) for the Los Humeros area, but they coincide with hydrologic studies that identify the main recharge to Los Humeros area from the Sierra Madre Oriental, with groundwater flow in a NE-SW direction (Prol-Ledesma, 1998). According to Cedillo Rodríguez (2000), recharge might also occur locally, from rainfall infiltrating the reservoir through its fault and fracture systems.

In this study, the data obtained for the water isotopic values are in the range of the previous data and it is difficult to give a preference about the different assumptions. According to the first assumption, the δD and $\delta^{18}O$ values for the meteoric water were estimated to be close to -110‰ and -15‰, respectively (fig. 3.4.1.3). For the second assumption, these values would be rather close to -65‰ and -9.5‰, respectively (fig. 3.4.1.3). Other arguments and more information about the water recharge and origin of the Los Humeros geothermal waters would have to be probably proposed in the works carried out by other teams like CNR, within the framework of the task 4.3 of this project.

The Los Humeros geothermal waters are also characterized by high Cl/Br ratios with respect to the thermal waters (fig. 3.4.1.4), much higher than that of seawater, which could be partially explained by supply of Cl from the degassing magma chamber.

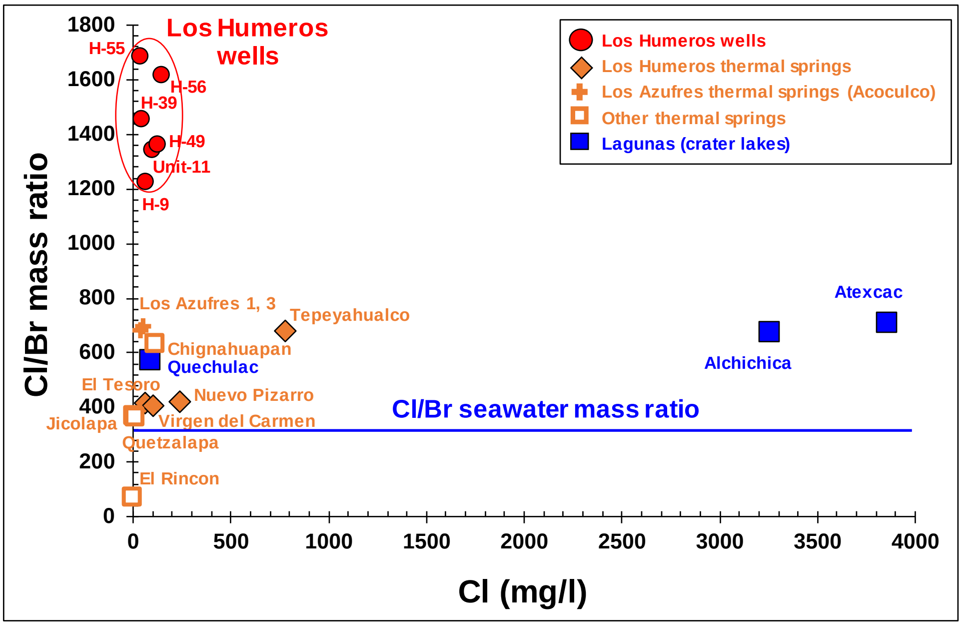

Figure 3.4.1.4 - Diagram Cl/Br - Cl for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas.

c) *Processes of water-rock-gas interaction*

The high boron concentrations of these geothermal waters (from 43 to 1819 mg/l; fig. 3.4.1.5) and their $\delta^{11}B$ values (-2.52 to -0.74‰; fig. 3.4.1.6) are close to those previously determined by Bernard *et al.* (2011), which range from 214 to 932 mg/l and from -1.7 to 0.3‰, respectively, and by Tello (2005) and Arellano *et al.* (2005), which vary from 118 to 3168 mg/l.

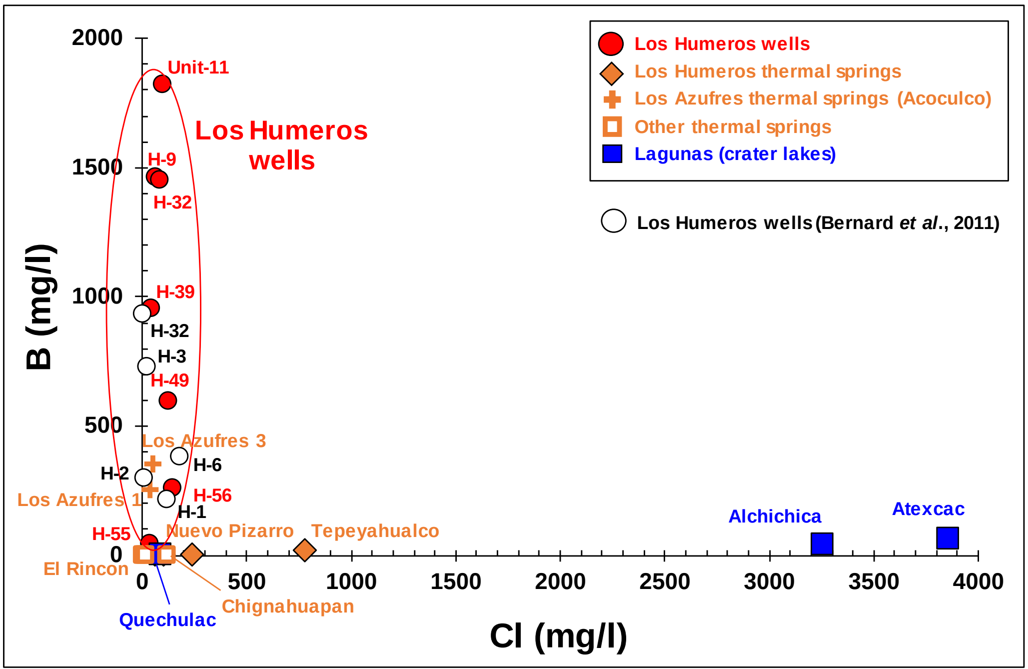

Figure 3.4.1.5 - Diagram B - Cl for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas.

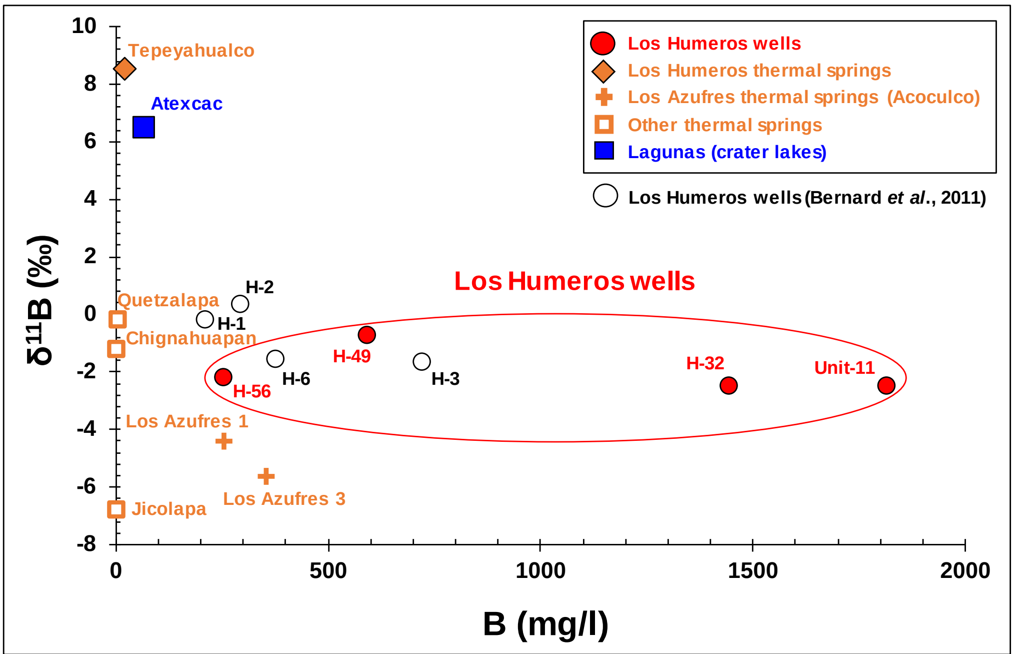

Figure 3.4.1.6 - Diagram $\delta^{11}B$ - B for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas.

High B concentrations as those observed for these geothermal waters are rare in the world (fig. 3.4.1.7). Natural hydrothermal solutions have generally B concentrations from 1 to 10 mg/l in high-temperature two-phase fluids from basaltic aquifers of Iceland such as Krafla, Nesjavellir, etc. (Arnórsson and Andrésdóttir, 1995; Aggarwal *et al.*, 2000; HITI-FP6 project, 2014).

B concentrations higher than 100 mg/l were only observed in fluids from aquifers composed of sedimentary and metamorphic rocks (Larderello, Italy; The Geysers, California; Ngahwa, New Zealand), of dacite-rhyolite volcanic rocks (Los Azufres, Mexico), and of marine carbonate and magmatic rocks, in the Yunnan-Tibet geothermal belt, in China.

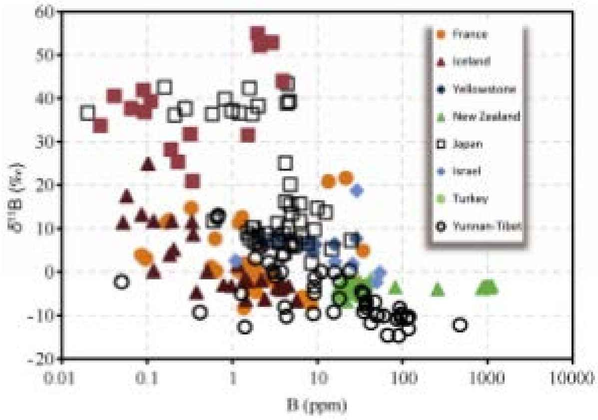

Figure 3.4.1.7 - Diagram δ^{11}B - B for worldwide geothermal waters (after Lü et al., 2014).

In contrast, similar δ^{11}B isotopic values (from -3.7 to -1.5‰) were observed in the high-temperature basaltic waters from Icelandic geothermal fields (Krafla, Nesjavellir, etc.; Aggarwal *et al.*, 2000; FP6-HITI project, 2010; tabl. 3.4.1.1) as well as in the Ngahwa (Aggarwal *et al.*, 2003) and Lardarello (Pennisi *et al.*, 2001) geothermal fields. These values are lower for the Yunnan-Tibet thermal waters (-6.0 to -6.8‰; Lü *et al.*, 2014). Tonarini *et al.* (1998) suggest that δ^{11}B of exsolved fluids during tourmaline crystallization from pegmatites of the Elba Island could vary between -6 and -2‰ at temperatures ranging from 300 to 600°C. As a matter of fact, the δ^{11}B data related to the Tuscan magmatic Province show negligible variations. The restricted range in δ^{11}B values compared to the total concentration variations suggest that the B isotope ratios reflect differences in the δ^{11}B values of the rock rather than the results of secondary processes, such as phase separation or deposition of secondary minerals (Aggarwal *et al.*, 2000).

According to Arnórsson and Andrésdóttir (1995), the variable B and Cl concentrations and Cl/B ratios in high-temperature geothermal waters, as well as high B concentrations can be attributed to a combination of several processes. They include: i) supply of these elements from the degassing magma chamber, ii) supply from the rock with which the water interacts, and iii) phase separation in producing aquifers of wells.

Aggarwal *et al.* (2003) suggested a main source of B in Ngawha to be the greywacke wall rocks and the reason for such high B concentrations (up to 1000 mg/l) to be a lower 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/l in condensates of 300°C volcanic vapors from Vulcano, in Italy. They interpreted these values as the result of mixing of a magmatic endmember with about 70 mg/l 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 and variable Cl concentrations in the Los Humeros geothermal waters could be the result of mixing of magmatic fluid from a deep magmatic chamber, the heat and fluid source for the system, leaching of wall rocks of the deep aquifer at a low fluid/rock ratio and phase separation process. Bernard *et al*. (2011) proposed a model based on the existence of deep acid brine to explain the B and Cl behavior in the geothermal fluids of the Los Humeros geothermal field.

		Los Humeros field, Mexico (this study)				*Nesjavellir and Krafla fields, Iceland (FP6-HITI project; Sanjuan et al., 2014)*								
Well		**Unit-11 (fluid mixing)**	**H-39**	**H-49**	**H-56**	**NJ-16**	**NJ-10**	**NJ-14**	**NJ-16**	**NJ-19**	**KS-01**	**K-05**	**K-27**	**K-37**
Parameters	**Unit**	**22/03/2018**	**22/03/2018**	**22/03/2018**	**22/03/2018**	**11/06/2008**	**11/06/2008**	**11/06/2008**	**11/06/2008**	**11/06/2008**	**13/06/2008**	**13/06/2008**	**13/06/2008**	**12/06/2008**
Cond. 25°C	µS/cm	**1294**	**591**	**1051**	**1196**	**860**	**872**	**965**	**860**	**783**	**930**	**820**	**1087**	
pH		7.00	7.14	7.70	7.58	8.42	9.03	8.79	8.42	8.11	9.36	9.21	8.72	
Eh	mV	-240	-260	-270	-346	-103	-31	-341	-103	-44	-305	-239	-284	
Na	mg/l	270	119	212	244	145	157	161	145	126	175	180	206	268
K	mg/l	36.9	23.8	35.8	38.4	29.0	33.4	32.8	29.0	31.4	36.4	17.8	32.1	48.8
Ca	mg/l	2.2	< 0.5	1.1	1.0	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	0.34	8.83	3.13	1.46
Mg	mg/l	< 0.5	< 0.5	< 0.5	< 0.5	11.7	< 0.5	< 0.5	11.7	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Alk.	mg/l HCO_3	307	268	305	383	296	257	159	296	128	400	162	237	
Cl	mg/l	98.8	46.5	129	147	69.7	129	193	69.7	162	76.1	45.0	39.2	64.7
SO_4	mg/l	227	2.3	86.1	63.6	90.5	81.6	44.0	90.5	35.9	40.6	248	296	130
SiO_2	mg/l	733	745	834	931	697	752	718	697	797	1001	361	538	1333
TDS	g/l	**1.68**	**1.20**	**1.60**	**1.81**	**1.34**	**1.41**	**1.31**	**1.34**	**1.28**	**1.73**	**1.02**	**1.35**	**1.85**
F	mg/l	20.6	13.4	4.0	4.2	1.25	1.57	1.11	1.25	1.13	1.68	0.89	0.98	2.72
B	mg/l	1819	951	593	256	1.82	1.52	1.76	1.82	3.77	2.68	0.54	0.56	2.38
Br	µg/l	73.7	32.0	94.9	90.9	200	500	700	200	600	200	< 500	< 500	< 500
Sr	µg/l	41.2	1.52	16.2	11.0	3.0	2.5	2.3	3.0	2.0	2.1	29.3	15.5	14.1
Ba	µg/l	5.92	0.71	1.08	1.06	2.5	1.0	0.8	2.5	1.0	0.1	1.5	5.2	3.0
Mn	µg/l	25.9	7.05	8.66	18.7	0.6	1.0	0.6	0.6	0.5		0.9	1.0	23.8
Li	µg/l	619	397	676	871	157	290	287	157	263	254	119	186	745
Rb	µg/l	315	240	259	392	96	140	198	96	108	209	138	167	273
Cs	µg/l	330	305	370	705	2.4	6.5	7.5	2.4	4.2	6.7	3.7	5.9	12.1
Ge	µg/l	56.0	60.1	46.3	47.6	59.8	60.6	39.6	59.8	42.7	39	34.6	34.2	49.0
As	µg/l	21721	42323	3838	8077	8.5	5.6	9.7	8.5	22	384	2.1	2.8	202
Zn	µg/l	0.32	1.96	0.46	0.42	1.1	0.6	0.8	1.1	1.1	0.6			4.2
Ni	µg/l	0.65	0.35	0.48	0.65	0.30	0.30	0.20	0.30	0.40	0.10	0.30	0.20	0.70
B/Cl	molal ratio	60	67	15	6	0.09	0.04	0.03	0.09	0.08	0.12	0.04	0.05	0.12
Na/K	molal ratio	12.5	8.5	10.1	10.8	8.5	8.0	8.4	8.5	6.8	8.2	17.2	10.9	9.3
Na/Li	molal ratio	132	90	95	84	279	163	170	279	145	208	458	334	108
Na/Rb	molal ratio	3190	1836	3047	2310	5620	4156	3029	5620	4343	3120	4860	4580	3647
Na/Cs	molal ratio	4735	2246	3317	1998	349560	139190	124346	349560	173665	151343	281880	201592	127947
K/Sr	molal ratio	2007	35086	4952	7822	21635	29940	31969	21635	35129	38842	1363	4642	7752
δD	‰	-45.9	-63.8	-58.3	-61.6	-71.1	-73.1	-69.9	-71.1	-68.3	-102.2		-79.9	-58.9
$\delta^{18}O$	‰	1.5	-1.2	-0.3	-1.1	-5.4	-5.7	-5.8	-5.4	-3.9	-6.3		-10.5	-7.3
$\delta^{18}O_{SO4}$	‰	4.0	9.3	0.9	1.2	-0.1	3.6		-0.1				-6.2	-5.9
$\delta^{7}Li$	‰				7.2	8.1	7.8	8.0	8.1	6.8	6.8	8.1	6.5	7.1
$\delta^{11}B$	‰	-2.50		-0.74	-2.23	-2.68	-2.19	-3.37	-2.68	-2.84	-5.45		-3.98	
$^{87}Sr/^{86}Sr$					0.704310	0.7036201	0.7034461	0.7035571	0.7036201	0.7035351	0.7034731	0.7032241	0.7032021	

Table 3.4.1.1 - Comparison of water chemical and isotopic data obtained in three high-temperature (≥ 290°C) geothermal fields: Los Humeros in Mexico, and Krafla and Nesjavellir in North-Iceland.

The low Sr concentrations and the $^{87}Sr/^{86}Sr$ ratios of these geothermal waters, ranging from 1.52 to 41.2 µg/l (fig. 3.4.1.8) and 0.704283 to 0.704310 (fig. 3.4.1.9), respectively, suggest these waters are in contact with andesite rocks in the reservoir, which is in good agreement with the well observations (Arellano *et al.*, 2003). Lower Sr isotopic values between 0.7032 and 0.7036 (FP6-HITI project, 2010) are observed for the high-temperature geothermal fluids from North-Iceland (Krafla, Nesjavellir, etc.) in contact with basalts in the reservoir (tabl. 3.4.1.1).

The high Li concentrations and the δ^7Li values of the Los Humeros geothermal waters, varying between 131 and 1182 mg/l, and between 2.3 ant 7‰ (tabl. 3.3.2.2 et 3.3.2.3), respectively, confirm that these waters interacts with volcanic rocks at high-temperatures. If the average Li concentrations are slightly higher than those observed in the high-temperature geothermal waters from the North-Iceland basaltic reservoirs (from 119 to 745 µg/l), the isotopic values are close (from 6.5 to 8.1‰; FP6-HITI project, 2014; tabl. 3.4.1.1). Note that the Cs concentrations analysed in the Los Humeros geothermal waters (from 52 to 705 µg/l) are much higher than those observed in the North-Icelandic geothermal dilute waters (from 2 to 12 µg/l) whereas the Rb concentrations are closer (FP6-HITI project, 2010; tabl. 3.4.1.1).

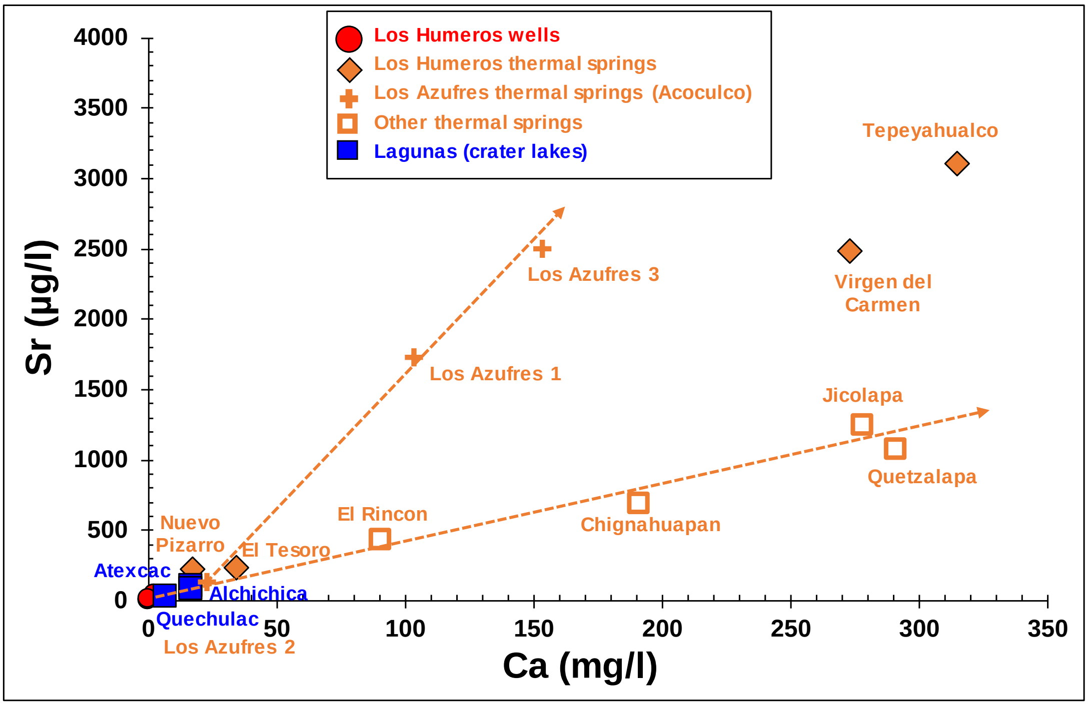

Figure 3.4.1.8 - Diagram Sr - Ca for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas.

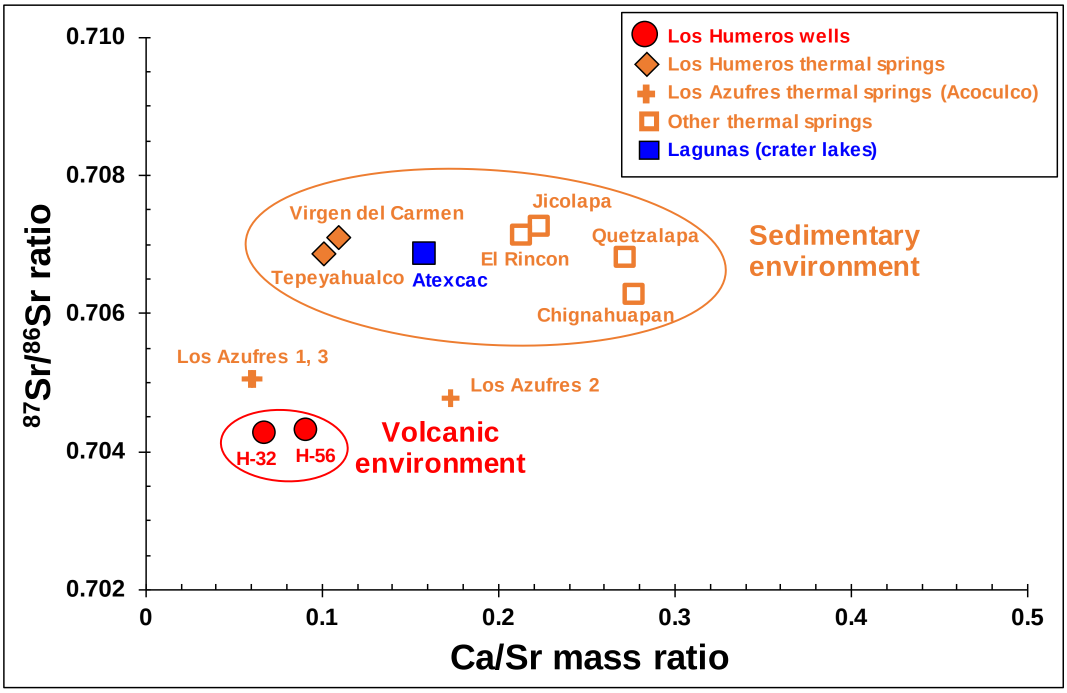

Figure 3.4.1.9 - Diagram $^{87}Sr/^{86}Sr$ - Ca/Sr for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas.

d) Geothermometry

The Na-K-Mg ternary diagram from Giggenbach (1988) and the main classical geothermometers such as Silica-quartz, Na-K, Na-K-Ca and K-Ca, as well as the isotopic $\delta^{18}O_{H2O-SO4}$ geothermometric relationships established by Kusakabe and Robinson (1977) and Zeebe (2010), indicate that the full chemical equilibrium is reached for most of these waters at about 290 ± 30°C (fig. 3.4.1.10; tabl. 3.4.1.2 and 3.4.1.3). For the H-55 well, which has a very low fraction of liquid water, the temperature estimated using Silica-quartz is underestimated (163°C) because the concentration of dissolved silica is decreased by probable dilution of steam condensate. For the H-32, H-39 and H-55 water samples, the isotopic $\delta^{18}O_{H2O-SO4}$ geothermometer also gives underestimated temperature values (112 to 228°C), indicating that the isotope equilibrium conditions are not attained for these samples.

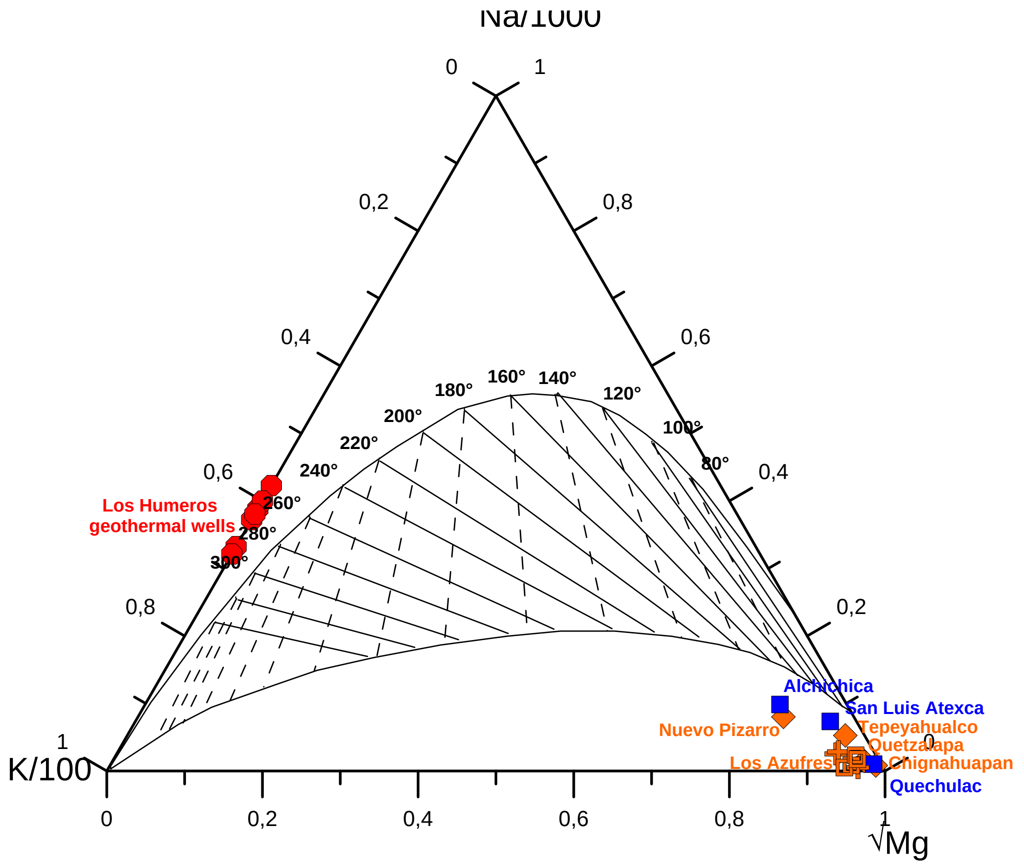

Figure 3.4.1.10 - Position of the geothermal and thermal waters collected in the Los Humeros and Acoculco areas in the Na-K-Mg ternary diagram of Giggenbach (1988).

This temperature range is concordant with the presence of an upper liquid-dominated reservoir area, located in augite andesites, between 1025 and 1600 m a.s.l., with neutral pH at 290-330°C, suggested in numerous studies (Arellano *et al.*, 2003; Gutiérrez-Negrín and Izquierdo-Montalvo, 2010). The other deeper, two-phase, low-liquid saturation reservoir area, with high fractions of steam, is located in basalts and hornblende andesites, between 800 and 100 m a.s.l., with low pH fluids at temperatures of between 300 and 400°C.

Area	Sampling point	Date	$T_{measured}$ °C	T_{Qz} °C	$T_{Chalced.}$ °C	$T_{Na\text{-}K\ (1)}$ °C	$T_{Na\text{-}K\ (2)}$ °C	$T_{Na\text{-}K\ (3)}$ °C	$T_{Na\text{-}K\text{-}Ca\ (\beta=1/3)}$ °C	$T_{Na\text{-}K\text{-}Ca\ (\beta=4/3)}$ °C	$T_{Na\text{-}K\text{-}Ca\text{-}Mg}$ °C	$T_{K\text{-}Mg\ (1)}$ °C	$T_{K\text{-}Mg\ (2)}$ °C	$T_{Ca\text{-}K\ (1)}$ °C	$T_{Ca\text{-}K\ (2)}$ °C
Los Humeros area	**Los Humeros H-39**	22/03/2018 12:00	61.9	292	297	284	284	294							
	Los Humeros Unit-11 (fluid mixing)	22/03/2018 12:50	52.7	304	312	233	245	258	231	264				334	256
	Los Humeros H-56	22/03/2018 13:25	74.1	317	329	251	258	271	247	307				386	293
	Los Humeros H-49	22/03/2018 13:55	68.0	320	334	260	266	278	248	292				371	282
	Los Humeros H-9	22/03/2018 15:05	66.8	263	259	293	290	300							
	Los Humeros H-32	22/03/2018 15:35	67.8	265	261	244	254	267	210	165				228	176
	Los Humeros H-55	22/03/2018 16:08	68.9	163	139	255	262	274							
	El Tesoro (existing data)	*17/11/2016*	*23.0*	*114*	*83*	*221*	*235*	*250*	*172*	*80*	*13*	*54*	*23*	*131*	*99*
	El Tesoro	23/03/2018 09:30	22.5	124	95	227	240	254	177	88	11	56	26	141	107
	Nuevo Pizarro well (existing data)	*09/11/2016*	*17.0*	*97*	*65*	*189*	*210*	*226*	*182*	*142*	*24*	*80*	*56*	*194*	*150*
	Noria Nuevo Pizarro	23/03/2018 11:45	16.0	100	68	210	227	242	206	196	30	97	77	257	198
	Virgen del Carmen	23/03/2018 15:46	19.1	132	104	193	213	229	145	39	34	37	4	83	59
	Pozo deTepeyahualco	24/03/2018 10:10	23.8	133	104	129	159	178	142	97	33	62	34	137	104
Acoculco area	***Los Azufres (existing data)***	*21-25/04/2006*	*21.4*	*84*	*51*	*334*	*320*	*327*	*207*	*83*	*85*	*74*	*48*	*144*	*110*
	Los Azufres (existing data)	*25/06/1986*	*25.0*	*81*	*48*	*305*	*299*	*308*	*207*	*101*	*58*	*78*	*53*	*163*	*125*
	Los Azufres (existing data)	*25/06/1986*	*25.0*	*70*	*36*	*207*	*224*	*240*	*177*	*106*	*36*	*72*	*56*	*158*	*121*
	Los Azufres 1	26/03/2018 15:05	25.4	124	94	284	283	294	201	103	62	79	54	164	125
	Los Azufres 3	28/03/2018 09:45	26.6	107	76	253	260	273	192	104	53	77	51	161	123
	Jicolapa (existing data)	*03/07/1986*	*32.0*	*116*	*86*	*462*	*407*	*403*	*218*	*50*	*149*	*70*	*43*	*112*	*83*
	Jicolapa	27/03/2018 09:45	30.7	162	137	452	400	397	213	46	172	72	46	107	79
	El rincon (existing data)	*19/06/1986*	*32.0*	*114*	*84*	*702*	*545*	*521*	*250*	*45*	*170*	*72*	*45*	*114*	*85*
	El Rincon	27/03/2018 11:00	26.6	157	132	691	540	516	253	51	189	78	53	121	91
	Baños de Quetzalapa (existing data)	*18/06/1986*	*32.0*	*105*	*74*	*216*	*231*	*246*	*168*	*74*	*59*	*62*	*33*	*124*	*93*
	Baños de Quetzalapa	27/03/2018 16:00	30.0	145	118	209	226	241	161	62	97	63	34	110	82
	Baños de Chignahuapan (existing data)	*02/07/1986*	*49.0*	*71*	*37*	*245*	*254*	*267*	*173*	*64*	*80*	*62*	*33*	*115*	*86*
	Baños de Chignahuapan	28/03/2018 07:30	49.0	96	64	247	255	268	172	61	96	63	35	112	83
	Agua salada (existing data)	*03/07/1986*	*21.0*	*128*	*99*	*254*	*261*	*274*	*213*	*165*	*51*	*99*	*81*	*230*	*178*
	Capulines (existing data)	*01/07/1986*	*20.0*	*105*	*73*	*310*	*303*	*312*	*202*	*86*	*9*	*57*	*38*	*146*	*111*

T_{Qz}: Fournier (1977); $T_{Chalced.}$: Michard (1979)

Recommended value (shaded cells)

$T_{Na\text{-}K\ (1)}$: Michard (1979); $T_{Na\text{-}K\ (2)}$: Fournier (1979); $T_{Na\text{-}K\ (3)}$: Giggenbach (1988).

$T_{Na\text{-}K\text{-}Ca}$: Fournier and Truesdell (1973).

$T_{Na\text{-}K\text{-}Ca\text{-}Mg}$: Fournier and Potter (1979).

$T_{K\text{-}Mg\ (1)}$: Giggenbach (1988); $T_{K\text{-}Mg\ (2)}$: Michard (1990).

$T_{Ca\text{-}K\ (1)}$: Fournier and Truesdell (1973); $T_{Ca\text{-}K\ (2)}$: Michard (1990).

Table 3.4.1.2 - Classical chemical geothermometers applied on waters from the Los Humeros and Los Azufres geothermal areas.

Area	Sampling point	Date	$T^{18}O_{H2O\text{-}SO4\ (1)}$ °C	$T^{18}O_{H2O\text{-}SO4\ (2)}$ °C	$T^{18}O_{H2O\text{-}SO4\ (3)}$ °C	$T^{18}O_{H2O\text{-}SO4\ (4)}$ °C	$T^{18}O_{H2O\text{-}BaSO4}$ °C	$T^{18}O_{H2O\text{-}CaSO4\ (1)}$ °C	$T^{18}O_{H2O\text{-}CaSO4\ (2)}$ °C
Los Humeros area	**Los Humeros H-39**	22/03/2018 12:00	176	171	112	113	138	186	194
	Los Humeros Unité 11 (fluid mixing)	22/03/2018 12:50	360	387	267	246	281	394	405
	Los Humeros H-56	22/03/2018 13:25	368	398	273	251	287	403	415
	Los Humeros H-49	22/03/2018 13:55	418	464	315	283	322	463	476
	Los Humeros H-9	22/03/2018 15:05	372	403	277	254	290	408	420
	Los Humeros H-32	22/03/2018 15:35	263	269	185	178	208	282	291
	Los Humeros H-55	22/03/2018 16:08	289	299	207	197	228	311	321
	El Tesoro	23/03/2018 09:30	126	117	69	74	96	132	139
	Noria Nuevo Pizarro	23/03/2018 11:45	192	189	125	126	151	204	212
	Virgen del Carmen	23/03/2018 15:46	121	112	65	70	92	127	134
	Pozo deTepeyahualco	24/03/2018 10:10							
Acoculco area	**Los Azufres 1**	26/03/2018 15:05	147	140	87	91	114	155	162
	Los Azufres 3	28/03/2018 09:45	268	275	189	182	212	287	297
	Jicolapa	27/03/2018 09:45	121	112	65	70	92	127	134
	El Rincon	27/03/2018 11:00							
	Baños de Quetzalapa	27/03/2018 16:00	118	109	63	68	89	124	131
	Baños de Chignahuapan	28/03/2018 07:30	114	104	59	64	86	120	126

$T^{18}O_{H2O\text{-}SO4\ (1)}$: Lloyd (1968); $T^{18}O_{H2O\text{-}SO4\ (2)}$: Mizutani and Rafter (1969); $T^{18}O_{H2O\text{-}SO4\ (3)}$: Zeebe (2010); $T^{18}O_{H2O\text{-}SO4\ (4)}$: Zheng (1999).

Recommended value (shaded cells)

$T^{18}O_{H2O\text{-}BaSO4}$: Kusakabe and Robinson (1977).

$T^{18}O_{H2O\text{-}CaSO4\ (1)}$: Chiba *et al.* (1980); $T^{18}O_{H2O\text{-}CaSO4\ (2)}$: Boschetti *et al.* (2011).

Table 3.4.1.3 - Classical isotope geothermometers applied on waters from the Los Humeros and Los Azufres geothermal areas.

Among the different Na-Li geothermometric relationships existing in the literature (Michard and Fouillac, 1981; Kharaka *et al.*, 1982; Michard, 1990; Sanjuan *et al.*, 2014; 2016b; 2017), only the Na-Li auxiliary geothermometer defined for North-Icelandic high-temperature geothermal dilute waters (Sanjuan *et al.*, 2014; tabl. 3.4.1.4), give concordant temperature estimations (320 ± 30°C) with those estimated using the classical Silica-quartz, Na-K and Ca-K geothermometers, and the isotopic $\delta^{18}O_{H2O-SO4}$ geothermometer, for most of the Los Humeros geothermal waters (apart H-9 and H-32 waters). The Na-Cs auxiliary geothermometer defined by Sanjuan *et al.* (2016a, b) also yields concordant temperature values (300 ± 30°C) for all the waters, and to a lesser extent, with lower estimated temperature values, and only for some waters, the Na-Rb, K-Sr and K-W auxiliary geothermometers defined by Sanjuan *et al.* (2016b). These estimations range from 227 to 255°C, 241 to 319°C, and 244 to 248°C, respectively.

Area	Sampling point	Date	$T_{Na-Li\ (1)}$ °C	$T_{Na-Li\ (2)}$ °C	$T_{Na-Li\ (3)}$ °C	$T_{Na-Rb\ (1)}$ °C	$T_{Na-Rb\ (2)}$ °C	$T_{Na-Cs\ (1)}$ °C	$T_{Na-Cs\ (2)}$	T_{K-Sr} °C	$T_{K-Fe\ (1)}$ °C	$T_{K-Fe\ (2)}$ °C	T_{KF} °C	T_{KW} °C
Los Humeros area	**Los Humeros H-39**	22/03/2018 12:00	155	337	78	264	255	174	331	309	164	112	201	215
	Los Humeros Unité 11 (fluid mixing)	22/03/2018 12:50	127	309	67	219	230	151	289	210	164	113	244	244
	Los Humeros H-56	22/03/2018 13:25	160	343	80	245	244	178	339	262	160	109	172	246
	Los Humeros H-49	22/03/2018 13:55	151	334	77	223	232	162	309	241	193	143	167	248
	Los Humeros H-9	22/03/2018 15:05	239	419	108	223	231	140	270	319	148	96	184	191
	Los Humeros H-32	22/03/2018 15:35	185	368	90	222	231	149	286	147	112	60	159	146
	Los Humeros H-55	22/03/2018 16:08	166	348	82	216	227	157	301	154	96	45	76	96
	El Tesoro (existing data)	*17/11/2016*	*72*	*248*	*42*									
	El Tesoro	23/03/2018 09:30	97	276	54	128	172			101	135	83	64	56
	Nuevo Pizarro well (existing data)	*09/11/2016*	*87*	*265*	*49*									
	Noria Nuevo Pizarro	23/03/2018 11:45	78	255	45	63	124			170	243	195	141	139
	Virgen del Carmen	23/03/2018 15:46	90	268	51	103	155			49	118	67	73	
	Pozo deTepeyahualco	24/03/2018 10:10	139	321	72	74	133	45	116	91	44		118	82
Acoculco area	***Los Azufres (existing data)***	*25/06/1986*	*41*	*213*	*27*									
	Los Azufres 1	26/03/2018 15:05	18	184	14	157	192	52	126	100	175	123	71	100
	Los Azufres 3	28/03/2018 09:45	32	202	23	141	181	44	114	98	167	115	84	123
	Jicolapa	27/03/2018 09:45	147	329	75	256	250	102	205	81	118	66	85	
	El Rincon	27/03/2018 11:00	80	258	47	293	270	96	195	92	30		71	
	Baños de Quetzalapa (existing data)	*18/06/1986*	*74*	*250*	*43*						*80*	*29*		
	Baños de Quetzalapa	27/03/2018 16:00	72	248	43	117	164	82	174	88	162	110	74	
	Baños de Chignahuapan (existing data)	*02/07/1986*	*168*	*350*	*83*									
	Baños de Chignahuapan	28/03/2018 07:30	170	353	84	182	207	134	259	90	78	27	87	58
	Agua salada (existing data)	*03/07/1986*	*43*	*214*	*28*						*140*			
	Capulines (existing data)	*01/07/1986*	*106*	*287*	*58*									

$T_{Na-Li\ (1)}$: Fouillac and Michard (1981); $T_{Na-Li\ (2)}$: Sanjuan *et al.* (2014); $T_{Na-Li\ (3)}$: Sanjuan *et al.* (2017). [shaded cell] Recommended value

$T_{Na-Rb\ (1)}$, $T_{Na-Cs\ (1)}$, $T_{K-Fe\ (1)}$, T_{KF}, T_{KW}: Michard (1990).

$T_{Na-Rb\ (2)}$, $T_{Na-Cs\ (2)}$, T_{K-Sr}, $T_{K-Fe\ (2)}$: Sanjuan *et al.* (2016a, b).

Table 3.4.1.4 - Auxiliary chemical geothermometers applied on waters from the Los Humeros and Los Azufres geothermal areas.

Thermodynamic binary diagrams representating log (H_4SiO_4) as a function of log (Na/K), log (Ca/K^2), log (Mg/K^2), log (Na/Li), log (Na/Cs), log (Na/Rb) and log (K^2/Sr) were constructed in order to illustrate these results (figs. 3.4.1.11 and 3.1.4.12).

In the log (H_4SiO_4) - log (Na/K) diagram (fig. 3.4.1.11), the equilibrium reaction (equation 1) at different temperatures was determined using the thermometric relationships given by Fournier (1977) for Silica-quartz and by Giggenbach (1988) for Na-K; the other equilibrium reaction (equation 2) at different temperatures was defined using the thermometric relationships given by Fournier (1977) for Silica-quartz and by Michard (1979) for Na-K.

In the log (H_4SiO_4) - log (Ca/K^2) diagram (fig. 3.4.1.11), the equilibrium reaction (equation 1) at different temperatures was determined using the thermometric relationships given by Fournier (1977) for Silica-quartz and by Michard (1990) for Ca-K; the equilibrium reaction (equation 2) at different temperatures was defined using the thermometric relationships given by Michard (1979) for Silica-chalcedony and by Michard (1990) for Ca-K.

In the log (H_4SiO_4) - log (Mg/K^2) diagram (fig. 3.4.1.11), the equilibrium reaction (equation 1) at different temperatures was determined using the thermometric relationships given by Michard (1979) for Silica-chalcedony and by Giggenbach (1988) for K-Mg; the equilibrium reaction (equation 2) at different temperatures was defined using the thermometric relationships given by Michard (1979) for Silica-chalcedony and by Michard (1990) for K-Mg.

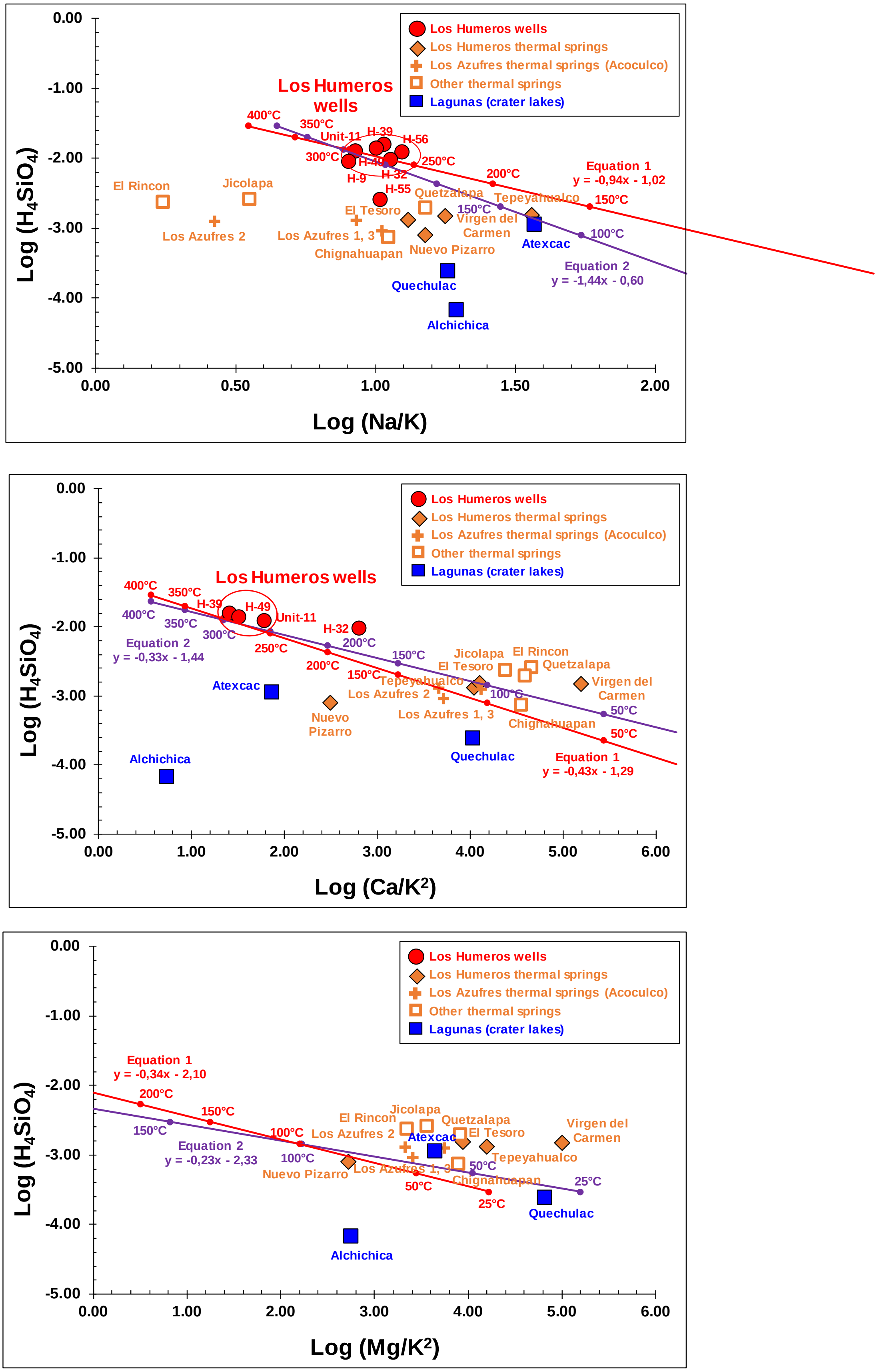

Figure 3.4.1.11 - Diagrams log (H_4SiO_4) as a function of log (Na/K), log (Ca/K^2) and log (Mg/K^2) for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas (all the concentrations are given in mol/l).

In the log (H_4SiO_4) - log (Na/Li) diagram (fig. 3.4.1.12), the equilibrium reaction (equation 1) at different temperatures was determined using the thermometric relationships given by Fournier (1977) for Silica-quartz and by Sanjuan *et al.* (2014) for Na-Li; the equilibrium reaction (equation 2) at different temperatures was defined using the thermometric relationships given by Michard (1979) for Silica-chacedony and by Fouillac and Michard (1981) for Na-Li.

In the log (H_4SiO_4) - log (Na/Cs) diagram (fig. 3.4.1.12), the equilibrium reaction (equation 1) at different temperatures was determined using the thermometric relationships given by Fournier (1977) for Silica-quartz and by Sanjuan *et al.* (2016a, b) for Na-Cs; the equilibrium reaction (equation 2) at different temperatures was defined using the thermometric relationships given by Michard (1979) for Silica-chalcedony and by Michard (1990) for Na-Cs.

In the log (H_4SiO_4) - log (Na/Rb) diagram (fig. 3.1.4.12), the equilibrium reaction (equation 1) at different temperatures was determined using the thermometric relationships given by Fournier (1977) for Silica-quartz and by Sanjuan *et al.* (2016a, b) for Na-Cs; the equilibrium reaction (equation 2) at different temperatures was defined using the thermometric relationships given by Fournier (1977) for Silica-chacedony and by Michard (1990) for Na-Cs.

In the log (H_4SiO_4) - log (K^2/Sr) diagram (fig. 3.1.4.12), the equilibrium reaction (equation 1) at different temperatures was determined using the thermometric relationships given by Fournier (1977) for Silica-quartz and by Sanjuan *et al.* (2016a, b) for K-Sr; the other equilibrium reaction (equation 2) at different temperatures was defined using the thermometric relationships given by Fournier (1977) for Silica-chalcedony and by Michard (1990) for K-Sr.

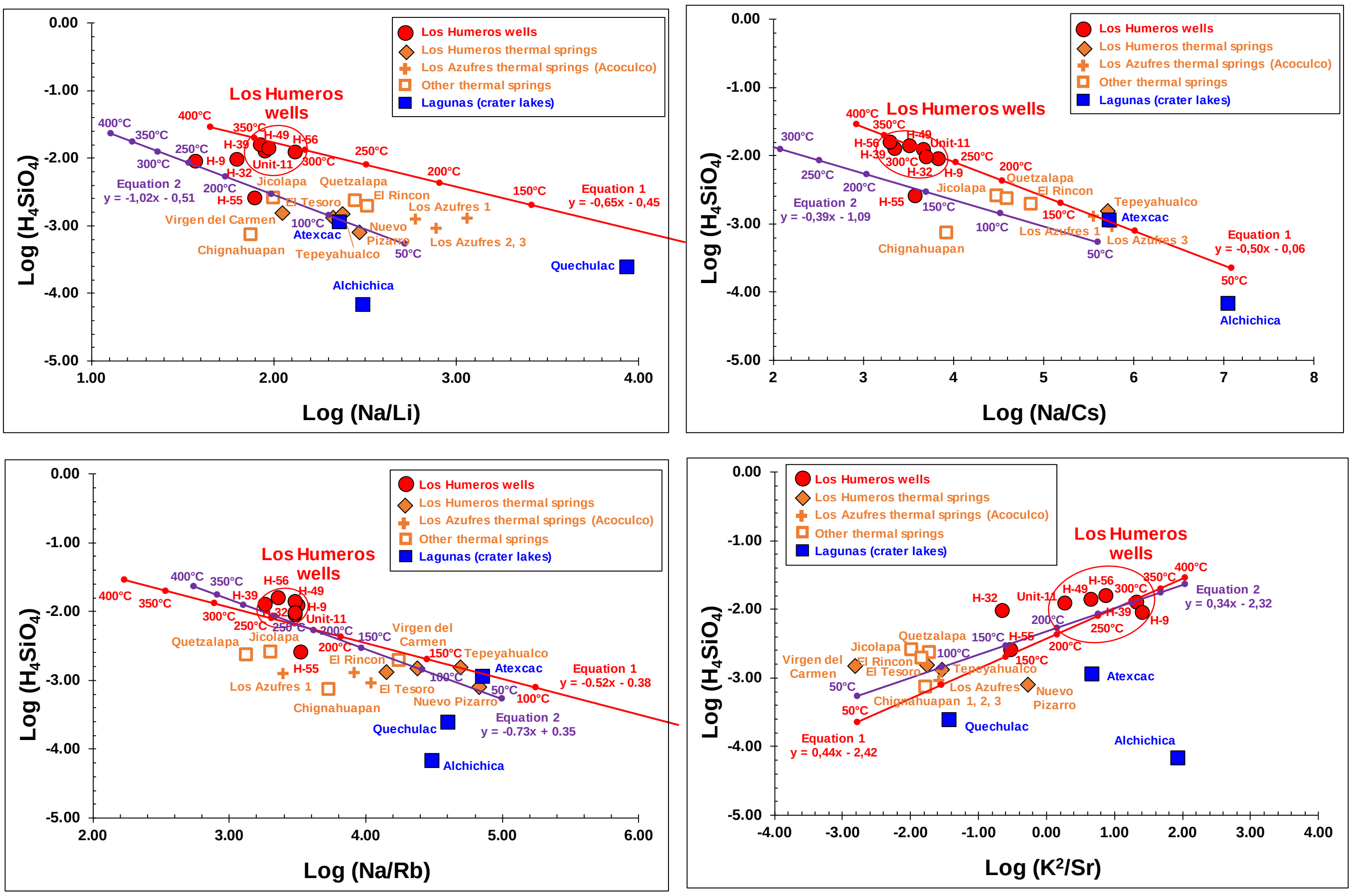

Figure 3.1.4.12 - Diagrams log (H_4SiO_4) as a function of log (Na/Li), log (Na/Cs), log(Na/Rb) and log (K^2/Sr) for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas (all the concentrations are given in mol/l).

Other thermodynamic binary diagrams such as log (Na/Cs), log (Na/Rb), and log (K^2/Sr), as a function of log (Na/Li) may also illustrate these results (fig. 3.4.1.13).

In the log (Na/Cs) - log (Na/Li) diagram (fig. 3.4.1.13), the equilibrium reaction (equation 1) at different temperatures was determined using the thermometric relationships given by Sanjuan *et al.* (2014) for Na-Li and Sanjuan *et al.* (2016a, b) for Na-Cs; the other equilibrium reaction (equation 2) at different temperatures was defined using the thermometric relationships given by Fouillac and Michard (1981) for Na-Li and by Michard (1990) for Na-Cs.

In the log (Na/Rb) - log (Na/Li) diagram (fig. 3.4.1.13), the equilibrium reaction (equation 1) at different temperatures was determined using the thermometric relationships given by Sanjuan *et al.* (2014) for Na-Li and Sanjuan *et al.* (2016a, b) for Na-Rb; the other equilibrium reaction (equation 2) at different temperatures was defined using the thermometric relationships given by Fouillac and Michard (1981) for Na-Li and by Michard (1990) for Na-Rb.

In the log (K^2/Sr) - log Na/Li) diagram (fig. 3.4.1.13), the equilibrium reaction (equation 1) at different temperatures was determined using the thermometric relationships given by Sanjuan *et al.* (2014) for Na-Li and by Sanjuan *et al.* (2016a, b) for K-Sr; the equilibrium reaction (equation 2) at different temperatures was defined using the thermometric relationships given by Fouillac and Michard (1981) for Na-Li and by Sanjuan *et al.* (2016a, b) for K-Sr.

The geothermometric relationships used in this study are as follows (T in K):

Silica-quartz (Fournier, 1977):	$T = 1309 / [0.41 - \log (H_4SiO_4)]$	
Silica-chalcedony (Michard, 1979):	$T = -1015 / [0.125 + \log (H_4SiO_4)]$	
Na/K (Giggenbach, 1988):	$T = 1390 / [\log (Na/K) + 1.52]$	
Na/K (Michard, 1979):	$T = 908 / [\log (Na/K) + 0.70]$	
Ca/K (Michard, 1990):	$T = 3030 / [\log (Ca/K^2) + 3.94]$	
K/Mg (Giggenbach, 1988):	$T = 4410 / [9.60 - \log (K^2/Mg)]$	
K/Mg (Michard, 1990):	$T = 3000 / [5.84 - \log (K^2/Mg)]$	
Na/Li (Sanjuan *et al.*, 2014):	$T = 2002 / [\log (Na/Li) + 1.322]$	
Na/Li (Fouillac & Michard, 1981):	$T = 1000 / [\log (Na/Li) + 0.38]$	(Cl < 0.3 M)
Na/Cs (Sanjuan *et al.*, 2016a, b):	$T = 2585 / [\log (Na/Li) + 0.923]$	
Na/Cs (Michard, 1990):	$T = 2610 / [\log (Na/Cs) + 2.48]$	
Na/Rb (Sanjuan *et al.*, 2016a, b):	$T = 2522 / [\log (Na/Rb) + 1.514]$	
Na/Rb (Michard, 1990):	$T = 1400 / [\log (Na/Rb) - 0.66]$	
K/Sr (Sanjuan *et al.*, 2016a, b):	$T = 2992 / [6.472 - \log (K^2/Sr)]$	
K/Sr (Michard, 1990):	$T = 2450 / [4.44 - \log (K^2/Sr)]$	

where all the specie concentrations must be expressed in mol/l.

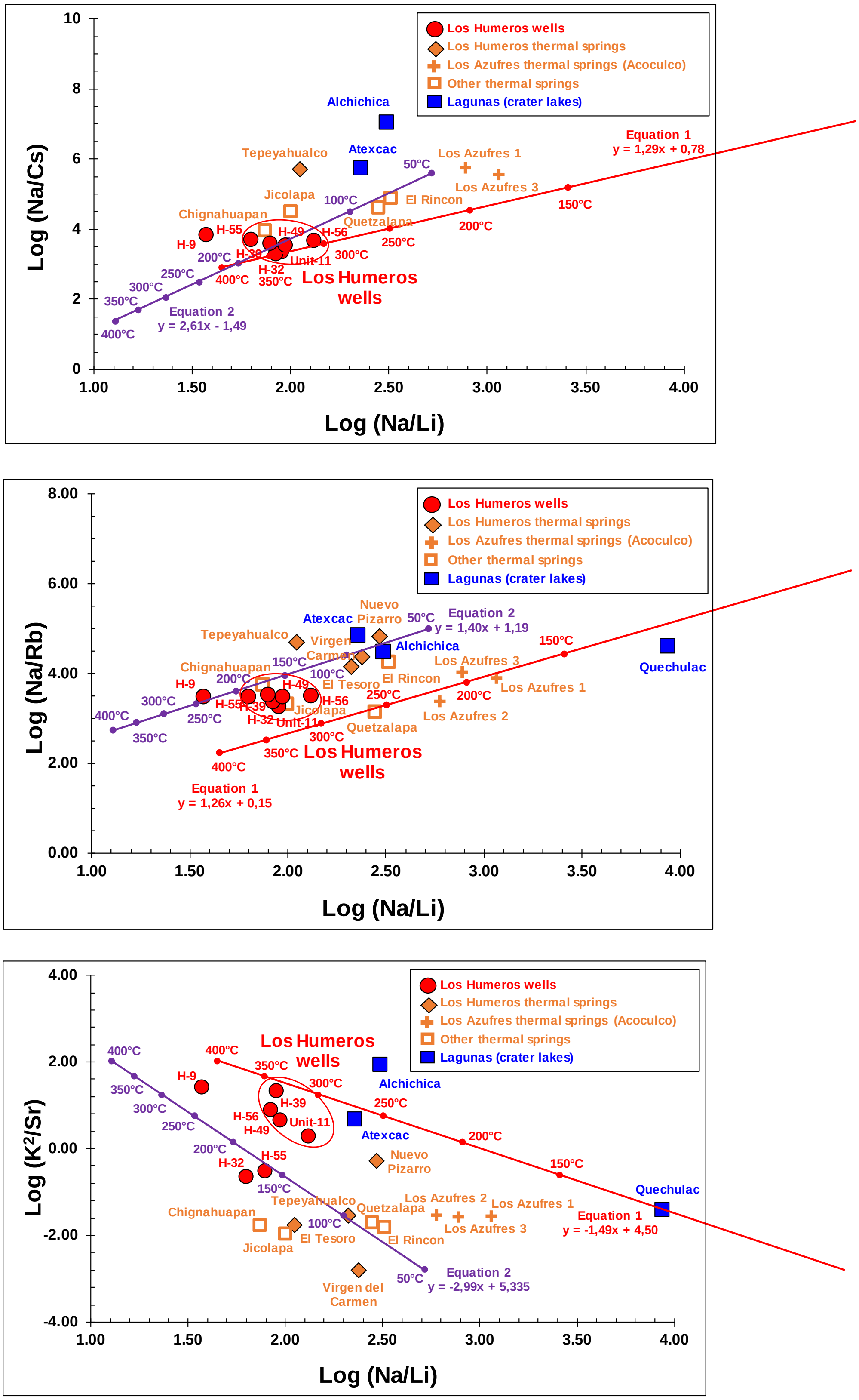

Figure 3.4.1.13 - Diagrams log (Na/Cs), log (Na/Rb), and log (K^2/Sr) as a function of log (Na/Li) for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas (all the concentrations are given in mol/l).

3.4.2 Los Humeros and Acoculco thermal waters

a) *Chemical characteristics of the fluids*

The El Tesoro, Noria Nuevo Pizarro, Virgen del Carmen and Pozo de Tepeyahualco waters from the Los Humeros area, sampled during this study, Na-HCO_3-Cl-(SO_4) type (fig. 3.4.1.1), have temperature, TDS and pH values ranging from 16 to 23.8°C, from 0.69 to 4.1 mg/l and from 6.75 to 8.82, respectively. The water samples collected from the Acoculco area (Los Azufres, Jicolapa, El Rincón, Quetzalapa and Chignahuapan), HCO_3-SO_4-Na-Ca and HCO_3-Na-Ca type (fig. 3.4.1.1), have temperature, TDS and pH values varying from 19 to 49°C, from 0.35 to 2.1 g/l and from 3.22 to 7.94, respectively. The Los Azufres 2 water, SO_4-Na-Ca type (fig. 3.4.1.1), which has the lowest values of pH (3.22) and TDS (0.35 g/l), is probably an acidic steam condensate.

The analytical results obtained in this study for the El Tesoro, Noria Nuevo Pizarro, Jicolapa, El Rincón, Quetzalapa and Chignahuapan thermal waters are close to those found in previous studies, when the analyses have been done (Tello Hinojosa, 1986; López-Hernández *et al.*, 2009; Peiffer *et al.*, 2014b; CFE data). For the Los Azufres thermal springs, waters like Los Azufres 3 with relatively high pH (7.94) had never been previously measured.

b) *Water origin*

Apart the Nuevo Pizarro, Tepeyahualco and Los Azufres waters, all the other waters show composition in δD and $\delta^{18}O$ falling close to GMWL (fig. 3.4.1.3), which indicate a meteoric origin. The position of the Los Azufres 1 and 2 waters, at the right of GMLW suggest an enrichment in ^{18}O due to water-rock interaction at high-temperature and/or low water-rock ratio. That of Los Azufres 3 water could probably result from a boiling process taking into account its $\delta^{11}B$ value and its Cl content. As for the crater lake waters (lagunas), also positioned at the right of GMLW, the Nuevo Pizarro and Tepeyahualco have probably been affected by a process of water evaporation or by a mixing with an evaporated water. Given their similar values in δD, the Chignahuapan, Jicolapa, El Rincón, Los Azufres 1 thermal waters could have the same recharge area. If we consider the second assumption for the origin of the Los Humeros geothermal waters (mainly meteoric water with high water-rock interactions) and the δD values, this area of water recharge could be also close to that of the Los Humeros geothermal waters. The relatively wide dispersion in δD and $\delta^{18}O$ values observed for the Virgen del Carmen, El Tesoro, and Quetzalapa waters suggest that these waters have different recharge areas, probably located in the Sierra Madre Oriental.

The Cl/Br mass ratios of all these waters are much lower (from 70 to 700) than those of the Los Humeros geothermal waters (from 1200 to 1700 ; fig. 3.4.1.4). However, the higher Cl/Br values for the thermal waters are those associated with the Los Azufres 1 and 3, Chignahuapan and Tepeyahualco (600-700). The El Tesoro, Virgen del Carmen, Nuevo Pizarro and Quetchalapa waters indicate similar values of Cl/Br around 400 (fig. 3.4.1.4).

c) *Processes of water-rock-gas interaction*

Los Azufres 1 and 3 thermal waters have B concentrations (253-354 mg/l) much higher than those analysed in the other thermal waters (from 0.12 to 20 mg/l; fig. 3.4.1.5) and specific $\delta^{11}B$ signatures (-5.61 and -4.42‰; fig. 3.4.1.6), which suggest mixing with low proportions of deep geothermal waters enriched in B (probably similar to those from the Los Humeros).

However, the relatively high B concentrations observed in most of the thermal waters and their $\delta^{11}B$ signatures could traduce very small fluxes of deep geothermal waters in these waters, especially for the Chignahuapan thermal water (B ≈ 3 mg/l), which has also a high Cl concentration (115 mg/l). López-Hernández *et al.* (2009) already mentioned that the Chignahuapan thermal water, discharged from a spring located in an area of ancient system faults (Tulancingo-Tlaxco) connecting both zones, might be the farthest SE discharge of the Acoculco hydrothermal system, constituted of a mixture of deep geothermal fluid and shallow waters. Water isotopic data do not differ from meteoric values, because important dilution with shallow meteoric water could mask the deep signature.

The high B and Cl concentrations (≈ 20 mg/l and 775 mg/l, respectively) for the Tepeyahualco water, and its specific $\delta^{11}B$ value (8.55‰), close to that of the Atexcac water (crater lake), suggest that this water is affected by a process of evaporation, like probably the Nuevo Pizarro water.

For most of the thermal waters, the Ca - HCO_3 diagram (fig. 3.4.2.1) shows that these waters interact with calcium carbonates and have high Ca concentrations, compared with the Los Humeros geothermal waters, which are depleted in Ca. Apart the Los Azufres thermal waters, the high Sr concentrations of the other thermal waters, compared with those of the Los Humeros geothermal waters (fig. 3.4.1.8), and their $^{86}Sr/^{87}Sr$ ratios, ranging from 0.706272 to 0.707262 (fig. 3.4.1.9), confirm that these waters are interacting with marine carbonate rocks formed during the Mesozoic period (probably the thick series of Jurassic and Cretaceous limestones, mentionned in Carrasco *et al.*, 2017a).

For Los Azufres thermal waters, the Sr concentrations are high (from 133 to 2500 µg/l), but their $^{86}Sr/^{87}Sr$ signature (from 0.704778 to 0.705065; fig. 3.4.1.9) is closer to volcanic rocks (rhyolites?). These values could also traduce a mixing process between a deep water in contact with volcanic rocks and low proportions of water interacting with sedimentary rocks.

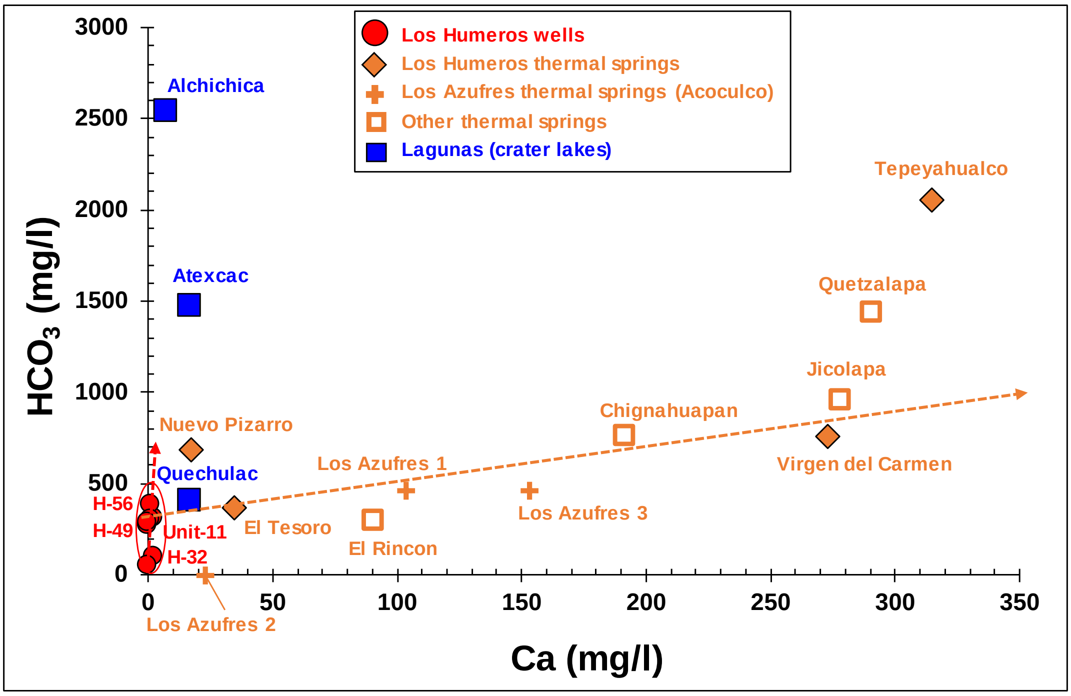

Figure 3.4.2.1 - Diagram HCO_3 - Ca for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas.

d) Geothermometry

The Na-K-Mg ternary plot developed by Giggenbach (1988) indicates that all the thermal waters of the Los Humeros and Acoculco areas are immature, having not reached full chemical equilibrium with the host rocks (fig. 3.4.1.10). In addition, geothermometry cannot be applied to acidic waters. However, the Na-K and Na-Li diagrams (fig. 3.4.2.2) show that the Na/K and Na/Li ratios for numerous thermal waters are close to those of the Los Humeros geothermal waters. Associated with δ^7Li values ranging from 4.7 to 6.5‰ and relatively high B concentrations (especially for the Los Azufres waters), these ratios suggest that very low proportions of deep geothermal waters at about 300°C could be present in these thermal waters.

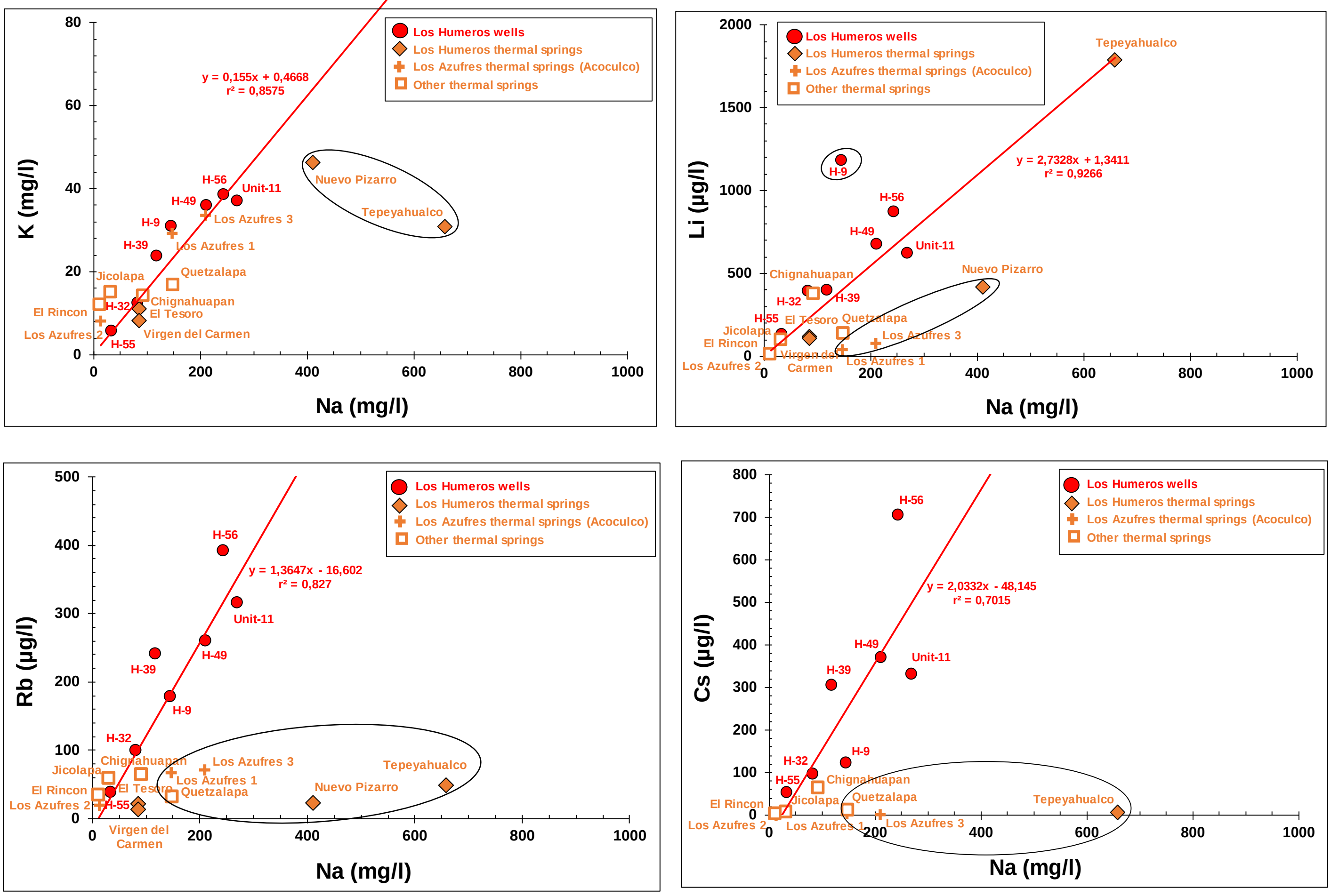

Figure 3.4.2.2 - Diagrams K - Na, Li - Na, Rb - Na, and Cs - Na for the geothermal and thermal waters collected in the Los Humeros and Acoculco areas.

These Na/K and Na/Li ratios, and to a lesser extent, the Na/Rb and Na/Cs ratios (fig. 3.4.2.2), could be the only witness of the presence of very small fluxes of high-temperature geothermal waters in the thermal waters, because the permeability of these areas is low, these geothermal waters are completely depleted in Ca, Mg and Sr whereas the thermal waters have relatively high concentrations in these elements, and the high silica concentrations of the geothermal waters can significantly decrease due to silica precipitation during their cooling and/or their dilution with shallow waters.

In this case, the geothermometers Na/Li and Na/K, and Na/Rb and Na/Cs sometimes, determined by Sanjuan *et al.* (2014; 2016a,b), give temperature estimations ranging from 248 to 353°C (tabl. 3.4.2.4), close to the temperature values measured in the wells and estimated using thermometric relationships.

In the Acoculco area, not only escapes of deep gases from the geothermal reservoir reach the surface (Peiffer *et al.*, 2014b), but also small fluxes of deep waters coud be able to preserve, more or less, their original Na/K and Na/Li ratios, resulting from the temperature of their deep reservoir, even after a significant mixing with cold waters, during their ascent up to the surface.

In such a context (low-permeability environment, presence of low-salinity deep waters with very low concentrations of dissolved calcium, magnesium and strontium, precipitation of dissolved silica or dilution by shallow waters during the ascent and cooling of the deep water, dissolution of marine carbonates which provides relatively high concentrations in calcium, magnesium and strontium to the thermal waters), the application of geothermometers to thermal waters in order to estimate the temperature of deep reservoir is very difficult, but the Na/K and Na/Li ratios, and sometimes the Na/Cs and Na/Rb ratios, the boron concentrations and their isotopes, as well as analyses of associated non condensable gases (Peiffer *et al.*, 2014b) may be useful tools for high-temperature geothermal exploration.

Classical geothermometers such as Silica-chalcedony, Na-K-Ca, K-Mg and Ca-K, based on the fluid equilibration with chalcedony, muscovite, clinochlore, K-felspar and calcite, which can re-equilibrate relatively fast, probably indicate subsurface temperature estimations for these thermal waters, ranging from 60 to 100°C (tabl. 3.4.1.2). The $\delta^{18}O_{H2O-SO4}$ geothermometers defined by Kusakabe and Robinson (1977), Zeng (1999) and Zeebe (2010), as well as the K-Sr and K-F auxiliary geothermometers determined by Sanjuan *et al.* (2016) and by Michard (1990), respectively, also seem to indicate concordant temperature estimations, which vary from 60 to 100°C (tabl. 3.4.1.3 and 3.4.1.4).

The relatively high concentration of dissolved silica analysed in the Atexcac water (fig. 3.4.1.2) could be explained by a thermal water input throughout the bottom of the Atexcac crater lake, according to Macek *et al.* (1994).

3.5. Main conclusions

The main objectives of this study were to develop and validate auxiliary chemical geothermometers such as Na-Li, Na-Cs, Na-Rb, K-Sr, … and the $\delta^{18}O_{H2O-SO4}$ isotope geothermometers in order:

- to improve the geochemical methods for geothermal exploration in volcanic fields such as Los Humeros and Acoculco, with high-temperature and relatively low permeability;
- to acquire a better knowledge about the circulation of high-temperature deep fluids and their possible interaction with more superficial waters in this type of geothermal fields, from chemical and isotopic water analyses from surface thermal springs.

In order to attain these objectives, a preliminary exhaustive literature review about the geological setting and the existing geochemical data on the geothermal and termal waters from Acoculco and the Los Humeros areas was carried by BRGM. After this review, fluid samples were collected by BRGM, between March 22 to 28, 2018, in collaboration with CFE, University of Michoacana and CNR Lelli's team, from seven geothermal wells and four thermal springs located in the Los Humeros area, from eight thermal springs located in the Acoculco area, and from three neighbouring crater lakes (lagunas), as references of surface waters. Among the two-phase geothermal waters from Los Humeros field, very rich in steam, those which indicated the most high fractions of liquid water were selected with the valuable help of CFE. The chemical (major and trace species) and isotopic analyses (δD_{H2O} and $\delta^{18}O_{H2O}$, $\delta^{18}O_{SO4}$, $\delta^{11}B$, $\delta^{7}Li$ and $^{87}Sr/^{86}Sr$ ratios) were performed in the BRGM laboratories, and data interpretation was then carried out.

The geothermal Na-HCO_3-Cl waters discharged from Los Humeros wells, completely deleted in calcium and magnesium, enriched in silica and boron (among the highest ones in the world), with TDS and pH values ranging from 0.3 to 1.8 g/l and 6.67 to 7.58, respectively, traduce a high interaction process with the reservoir rocks, at high-temperature. The high values of $\delta^{18}O_{H2O}$ of these waters towards the right of of the Global Meteoric Water Line (GMWL) are not only in concordance with these high-temperature values, but also suggest a low water-rock ratio of the geothermal reservoir, when compared with the lower values observed in the Krafla geothermal field, in North-Iceland, where the fluids are also biphasic, but the water-rock ratio is much higher. This is in agreement with a reservoir consisting of medium- to low-permeability pre-caldera andesites. The volcanic nature of the reservoir rocks was confirmed by the Sr and Li isotope signatures.

The isotopic δD and $\delta^{18}O$ for the Los Humeros wells show a wide dispersion probably related to boiling, mixing, phase separation and condensation phenomema. Two main assumptions were considered in this study:

- a mixing of recharge meteoric water with a deep fluid-type andesitic water ($\delta D \approx -20‰$ and $\delta^{18}O \approx 6‰$), as defined by Giggenbach (1992), leading to a positive correlation between δD and $\delta^{18}O$, with a slope close to 3.0, and a proportion of andesitic water estimated to be between 25% and 50%, accompanied with processes of boiling and phase separation (Arrellano *et al.*, 2003; Barragán *et al.*, 2010);
- a contribution of meteoric water with a δD value similar to that of the geothermal fluid (average values of $\delta D \approx -62‰$ and $\delta^{18}O \approx -3‰$ for the total geothermal fluid, steam + water, characterized by data from Verma *et al.*, 1998; Arellano *et al.*, 2003; Tello, 2005; and Bernard, 2008), affected by a strong water-rock interaction process at high-

temperature and low water-rock ratio, which enriches its ^{18}O content (up to 7-8‰). The wide dispersion observed for the isotopic values could be explained by different water-rock interaction factors and processes such as kinetic fractionation at temperatures close to boiling temperatures (Giggenbach and Stewart, 1982), with characteristic slopes of 3.0-3.5, and phase separation.

In this study, the data obtained for the water isotopic values are in the range of the previous data and it is difficult to give a preference about the different assumptions. According to the first assumption, the δD and $\delta^{18}O$ values for the meteoric water were estimated to be close to -110‰ and -15‰, respectively. For the second assumption, these values would be rather close to -65‰ and -9.5‰, respectively. In this last case, the isotopic values for the meteoric water would be slightly heavier than those reported by Quijano *et al.* (1981) for the Los Humeros area (Oriental Basin), close to -77.3‰ for δD and -10.7‰ for $\delta^{18}O$, but they would coincide with hydrologic studies that identify the main recharge to Los Humeros area from the Sierra Madre Oriental, with groundwater flow in a NE-SW direction (Prol-Ledesma, 1998).

According to Arnórsson and Andrésdóttir (1995), the variable B and Cl concentrations and Cl/B ratios in high-temperature geothermal waters, as well as high B concentrations can be attributed to a combination of several processes. They include: i) supply of these elements from the degassing magma chamber, ii) supply from the rock with which the water interacts, and iii) phase separation in producing aquifers of wells. The observed high B contents and specific isotopic signatures, as well as the variable Cl concentrations in the Los Humeros geothermal waters, could be the result of mixing of magmatic fluid from a deep magmatic chamber, the heat and fluid source for the system, leaching of wall rocks of the deep aquifer at a low fluid/rock ratio and phase separation process.

The Na-K-Mg ternary diagram from Giggenbach (1988) and the main classical geothermometers such as Silica-quartz, Na-K, Na-K-Ca and K-Ca, as well as the isotopic $\delta^{18}O_{H2O-SO4}$ geothermometric relationships established by Kusakabe and Robinson (1977) and Zeebe (2010), indicate that the full chemical equilibrium is reached for most of these waters at about 290 ± 30°C. This temperature range is concordant with the presence of an upper liquid-dominated reservoir area, located in augite andesites, between 1025 and 1600 m a.s.l., with neutral pH at 290-330°C, suggested in numerous studies (Arellano *et al.*, 2003; Gutiérrez-Negrín and Izquierdo-Montalvo, 2010).

Among the different Na-Li geothermometric relationships existing in the literature (Michard and Fouillac, 1981; Kharaka *et al.*, 1982; Michard, 1990; Sanjuan *et al.*, 2014; 2017), only the Na-Li auxiliary geothermometer defined for North-Icelandic high-temperature geothermal dilute waters (Sanjuan *et al.*, 2014), give concordant temperature values (320 ± 30°C) with those estimated using the classical Silica-quartz, Na-K and Ca-K geothermometers, and the isotopic $\delta^{18}O_{H2O-SO4}$ geothermometer, for most of the Los Humeros geothermal waters (apart H-9 and H-32 waters). The Na-Cs auxiliary geothermometer defined by Sanjuan *et al.* (2016) also yields concordant temperature values (300 ± 30°C) for all the waters and to a lesser extent, with lower temperature estimations and only for some waters, the Na-Rb, K-Sr and K-W auxiliary geothermometers defined by Sanjuan *et al.* (2016). These estimations range from 227 to 255°C, 241 to 309°C, and 244 to 246°C, respectively.

Thermodynamic binary diagrams such as log (H_4SiO_4) as a function of log (Na/K), log (Ca/K^2), log (Mg/K^2), log (Na/Li), log (Na/Cs), log (Na/Rb) and log (K/Sr^2), or representing log (Na/Cs), log (Na/Rb), and log (K^2/Sr) as a function of log (Na/Li), were constructed in order to illustrate these results.

The El Tesoro, Noria Nuevo Pizarro, Virgen del Carmen and Pozo de Tepeyahualco waters from the Los Humeros area, sampled during this study, Na-HCO_3-Cl-(SO_4) type, have temperature, TDS and pH values ranging from 16 to 23.8°C, from 0.69 to 4.1 mg/l and from 6.75 to 8.82, respectively. Those sampled from the Acoculco area (Los Azufres, Jicolapa, El Rincón, Quetzalapa and Chignahuapan), HCO_3-SO_4-Na-Ca and HCO_3-Na-Ca type, have temperature, TDS and pH values varying from 19 to 49°C, from 0.35 to 2.1 g/l and from 3.22 to 7.94, respectively. The Los Azufres 2 water, SO_4-Na-Ca type, which has the lowest values of pH (3.22) and TDS (0.35 g/l), is probably an acidic steam condensate. The Los Azufres 3 water with relatively high pH (7.94) had never been previously sampled and studied.

Apart the Nuevo Pizarro, Tepeyahualco and Los Azufres waters, all the other waters show composition in δD and $\delta^{18}O$ falling close to GMWL, which indicates their meteoric origin. The position of the Los Azufres 1 and 2 waters, at the right of GMLW suggest an enrichment in ^{18}O due to water-rock interaction at high-temperature and/or low water-rock ratio. That of Los Azufres 3 water could result from a boiling process taking into account its $\delta^{11}B$ value and its Cl content. As for the crater lake waters (lagunas), also positioned at the right of GMLW, the Nuevo Pizarro and Tepeyahualco have probably been affected by a process of water evaporation or by a mixing with an evaporated water. Given their similar values in δD and $\delta^{18}O$, the Chignahuapan, Jicolapa, El Rincón, Los Azufres 1 thermal waters (Acoculco area) could have the same recharge area. The relatively wide dispersion in δD and $\delta^{18}O$ values observed for the Virgen del Carmen, El Tesoro, and Quetzalapa waters suggest that these waters have different recharge areas, probably located in the Sierra Madre Oriental. Given the similar δD values measured in the Los Humeros geothermal waters and in the Los Azufres 1 and Chignahuapan thermal waters (Acoculco area), the meteoric water recharge area could be close for these two geothermal fields, following the selected interpretation for the origin of the Los Humeros geothermal waters.

The Cl/Br mass ratios of all these waters are much lower (from 70 to 700) than those of the Los Humeros geothermal waters (from 1200 to 1700). However, the higher Cl/Br values for the thermal waters are those associated with the Los Azufres 1 and 3, Chignahuapan and Tepeyahualco (600-700). The El Tesoro, Virgen del Carmen, Nuevo Pizarro and Quetchalapa waters indicate similar values of Cl/Br around 400.

For most of the thermal waters, the Ca-HCO_3 diagram shows that these waters interact with calcium carbonates and have high Ca concentrations, compared with the Los Humeros geothermal waters, which are depleted in Ca. Apart the Los Azufres thermal waters, the high Sr concentrations of the thermal waters, compared with those of the Los Humeros geothermal waters, and their $^{86}Sr/^{87}Sr$ ratios, ranging from 0.706272 to 0.707262, confirm that these waters are interacting with marine carbonate rocks formed during the Mesozoic period (probably the thick series of Jurassic and Cretaceous limestones, mentionned in Carrasco *et al.*, 2017a). For Los Azufres thermal waters, the Sr concentrations are high, but their $^{86}Sr/^{87}Sr$ signature (from 0.704778 to 0.705065) is closer to volcanic rocks (rhyolites?). These values could also traduce a mixing process between a deep end-member water in contact with volcanic rocks and low proportions of water interacting with sedimentary rocks.

The Na-K-Mg ternary plot developed by Giggenbach (1988) indicates that all the thermal waters of the Los Humeros and Acoculco areas are immature, having not reached full chemical equilibrium with the host rocks. In addition, geothermometry cannot be applied to acidic waters. However, the Na-K and Na-Li diagrams show that the Na/K and Na/Li ratios for numerous thermal waters are close to those of the Los Humeros geothermal waters. Associated with δ^7Li values ranging from 4.7 to 6.5‰ and relatively high B concentrations (especially for Los Azufres waters), these ratios suggest that very low proportions of flux of deep geothermal waters at about 300°C could be present in these thermal waters.

Indeed, these Na/K and Na/Li ratios, and to a lesser extent, the Na/Rb and Na/Cs ratios, could be the only witness of the presence of very small flux of deep high-temperature geothermal waters in the thermal waters, because the permeability of these areas is low, these geothermal waters are completely depleted in Ca, Mg and Sr whereas the thermal waters have relatively high concentrations in these elements, and the high silica concentrations of the geothermal waters can significantly decrease due to silica precipitation during their cooling and/or their dilution with shallow waters. In this case, the geothermometers Na/Li and Na/K, and Na/Rb and Na/Cs sometimes, determined by Sanjuan *et al.* (2014; 2016a,b), give temperature estimations ranging from 248 to 353°C, close to the temperature values measured in the wells and estimated using thermometric relationships.

In the Acoculco area, not only escapes of deep gases from the geothermal reservoir reach the surface (Peiffer *et al.*, 2014b), but also small fluxes of deep waters coud be able to preserve, more or less, their original Na/K and Na/Li ratios, resulting from the temperature of their deep reservoir, even after a significant mixing with cold waters, during their ascent up to the surface.

In such a context (low-permeability environment, presence of low-salinity deep waters with very low concentrations of dissolved calcium, magnesium and strontium, precipitation of dissolved silica or dilution by shallow waters during the ascent and cooling of the deep water, dissolution of marine carbonates which provides relatively high concentrations in calcium, magnesium and strontium to the thermal waters), the application of geothermometers to thermal waters in order to estimate the temperature of deep reservoir is very difficult, but the Na/K and Na/Li ratios, and sometimes the Na/Cs and Na/Rb ratios, the boron concentrations and their isotopes, as well as analyses of associated non condensable gases (Peiffer *et al.*, 2014b) may be useful tools for high-temperature geothermal exploration.

Classical geothermometers such as Silica-chalcedony, Na-K-Ca, K-Mg and Ca-K, based on the fluid equilibration with chalcedony, muscovite, clinochlore, K-felspar and calcite, which can re-equilibrate relatively fast, probably indicate subsurface temperature estimations for these thermal waters, ranging from 60 to 100°C. The $\delta^{18}O_{H2O-SO4}$ geothermometers defined by Kusakabe and Robinson (1977), Zeng (1999) and Zeebe (2010), as well as the K-Sr and K-F auxiliary geothermometers determined by Sanjuan *et al.* (2016) and by Michard (1990), respectively, also seem to indicate concordant temperature estimations, which vary from 60 to 100°C.

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6. Dissemination activities

BRGM participated to three GEMEX meetings, which occurred in Utretch (Netherlands), in March 2017 (F. Gal), in Akureyry (Iceland), in October 2017 (B. Sanjuan), and in Morelia (Mexico), in October 2018.

It has also contributed to a GEMEX e-News document for WP4 - Task 4.3, in 2018.

All the geochemical data obtained during this study have been uploaded and stored in the GEMEX Open Access Database (OADB), as well as the required information, by Eugenio Trumpy from CNR, responsible for maintaining this database.

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Acoculco geothermal system

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