

## Fluid Inclusion, Hydro-Geochemistry and Isotopic Fluid Composition of the “Los Azufres” Geothermal Field, Central Mexico

Eduardo González-Partida<sup>1</sup>, Gilles Levresse<sup>1</sup>, Jordi Tritlla<sup>1</sup>, Saul Venegas-Salgado<sup>2</sup>, Germán Ramírez-Silva<sup>2</sup>, Antoni Camprubí<sup>1</sup>, and Alejandro Carrillo-Chavez<sup>1</sup>

1 Prog. Geofluidos, Centro de Geociencias, Campus Juriquilla, UNAM. 76230 Querétaro, México.

2 Comisión Federal de Electricidad, A.P. 31-7; C.P. 58090 Morelia Mich. México.

Email: [egp@geociencias.unam.mx](mailto:egp@geociencias.unam.mx)

**Keywords:** geothermal, hydro-geochemistry, isotopic fluid composition, Central Mexico

### ABSTRACT

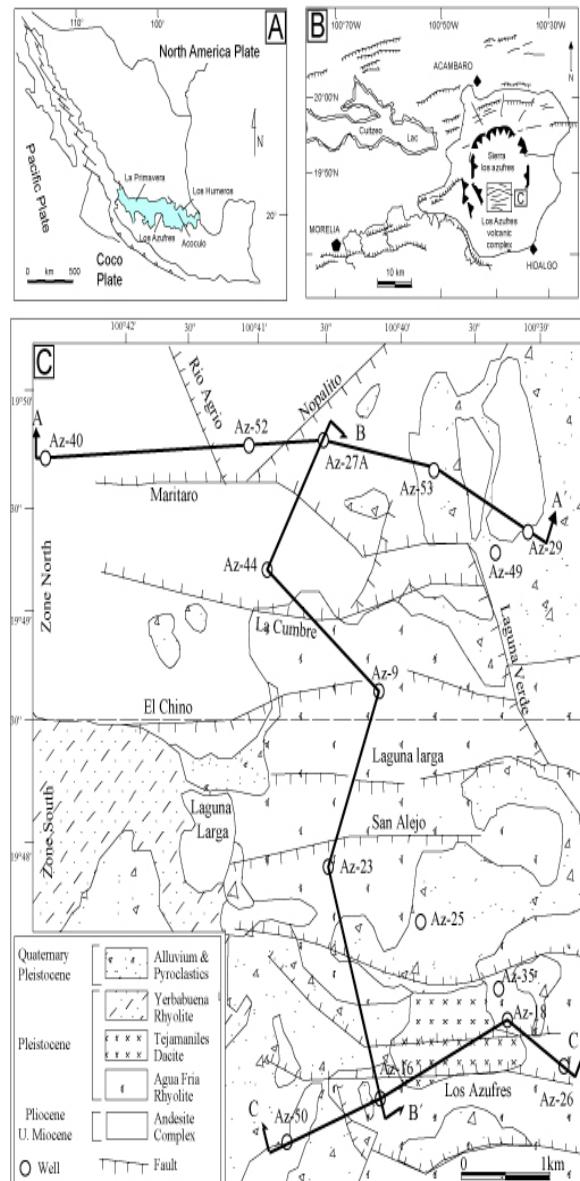
Hydrothermal alteration at Los Azufres geothermal field is mostly propylitic with a progressive dehydration. The temperature increases with depth. Argillic and advanced argillic alteration zones overprint the propylitic zone due to the activity of gases in the system. The deepest fluid inclusions (proto-fluid) are liquid-rich, low salinity fluids dominated by NaCl with calculated salinities around 0.8 wt % NaCl equivalent. The homogenous temperatures (Th) are located around  $325 \pm 5^\circ\text{C}$ . The boiling zone presents a Th around  $300^\circ\text{C}$  and salinities between 1 and 4.9 wt % NaCl equivalent, implying a vaporization process and a very important participation of non-condensable gases (NCG), mostly  $\text{CO}_2$ . The upper part of the geothermal reservoir (from 0 to 700 m depth) presents positive clathrate melting temperatures with  $\text{Th} \approx 150^\circ\text{C}$ , which is the evidence of a high gas concentration. The current water produced at the geothermal wells is NaCl rich (geothermal brine) and it is fully equilibrated with the host rock at temperatures between  $300^\circ\text{C}$  and  $340^\circ\text{C}$ . The hot springs are acid-sulfate, indicating that they are fed by meteoric water heated by geothermal steam. The NCG related to the steam dominant zone are composed mostly by  $\text{CO}_2$  (80 to 98% of all the gases). The gases represent between 2 to 9 wt % of the total fluid mass of the reservoir.

We interpret the evolution of this system as a deep fluid, mainly water, that boils and circulates through fractures connected to the surface. Boiling is accompanied by a drop of pressure, which in turn favors an increasing steam evolution with the brine ascending towards the surface. During this ascent, the fluid changes from steam-dominated to steam in the shallowest zone, where mixing with perched aquifers and meteoric water occurs. Stable isotope data ( $\delta^{18}\text{O}\text{‰} - \delta\text{D}\text{‰}$ ) of the geothermal brine indicates the occurrence of mixing between meteoric water and a minor magmatic component. The enrichment in  $\delta^{18}\text{O}\text{‰}$  is due to the rock-water interaction at relatively high temperatures.

### 1. INTRODUCTION

The geothermal reservoir of Los Azufres is located in the eastern central portion of the Michoacan state, in central Mexico, and was first discovered in 1972. Currently, the geothermal field has an installed capacity of 88 MW, within an area of  $35 \text{ km}^2$  with plans to expand the capacity of the geothermal field up to 128 MW with the installation of two more units of 20 MW each. This field is a typical high-enthalpy hydrothermal system related to a volcanic caldera and intense fracturing (Ferrari et al., 1991). Based on its

geochemical and petrological characteristics, it can be classified as a “low sulfidation” system (González, 1999).



**Figure 1.** (A) Regional tectonic framework of Mexico and distribution map of the main geothermal zones. (B) General structural map of the Los Azufres caldera and geothermal field. (C) Detailed geologic map of Los Azufres, location of the geothermal wells and location of the cross sections.

## 2. GEOLOGICAL SETTING

Los Azufres geothermal field is located in the Trans-Mexican Volcanic belt (Figure 1). The local basement is made up of a group of andesitic rocks with some paleo-soil layers, basaltic rocks and volcanic agglomerates interstratified with the andesites. A sequence of acid volcanic rocks (Agua Fría rhyolite), lake sediments, the San Andrés dacite, and ignimbrite deposits (Yerbabuena rhyolite) are unconformably overlaying the basement. Basic volcanic rocks, representing the last volcanic stage at Los Azufres, outcrop as basalts and cinder cones at east and west of the geothermal field. The whole rock geochemistry from the different units shows a calc-alkaline trend (Cathelineau et al., 1987). Structural geologic studies by Garduño, (1988) and Ferrari et al., (1991) indicate the existence of three, almost vertical, main fault systems. The major fault system has an E-W trend and cuts the other two with NE-SW and N-S trends. These faults are the major cause of the secondary porosity in the geothermal reservoir. The E-W fault system, which is closely related with the Acambay fault, has a lateral displacement, mainly affecting the south part of the Los Azufres Caldera.

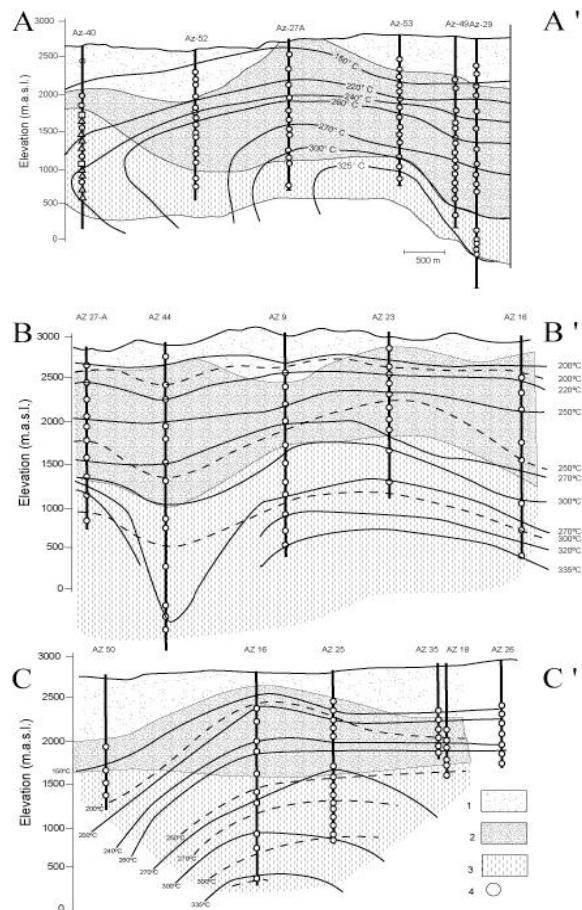
The main surface hydrothermal activity in the caldera is associated with the E-W fault system. These faults allow fluids to ascend and cause an alteration zone, with the development of siliceous and clay sinters, "hot" soils, hot springs, mud volcanoes and smokers. The deepest wells at Los Azufres reservoir reach 3600 m (Well Az-44). The host rocks are mostly andesites and minor rhyolites. Hydrothermal alteration is evidenced by the presence of calc-silicates, whose paragenesis define the different alteration zones: (1) a deep alteration zone, characterized by the assemblage epidote + clinozoisite + actinolite + tremolite  $\pm$  garnet, and chlorite + smectite + illite in the clay fraction, the chlorite being more abundant; (2) an intermediate zone defined by the occurrence of epidote + laumontite + wairakite, and illite + smectite + chlorite within the clay fraction; and (3) a shallow zone characterized by the predominance of laumontite. The assemblage of chlorite + quartz + calcite are present in all three zones in variable quantities, with significantly more calcite in well Az-40. The surface sinters are composed by elemental sulfur + alunite + kaolinite + quartz + pyrite. A general zoning of the calc-silicate zone can be observed in the alteration zones, with zeolite-group minerals in the upper part and epidote-clinozoisite assemblages at the deepest levels. An argillic alteration zone overlies the calc-silicate zone and is the main surface manifestation of the hydrothermal alteration. In some parts, there is a mineral assemblage composed of kaolinite + alunite + sulfur + quartz (advanced argillic alteration zone) formed due to a process of steam-heated shallow groundwaters. Pyrite, pyrrhotite, marcasite, chalcopyrite, bornite, covellite, digenite and idaite are the main sulfides present at Los Azufres. Hematite is the only metal oxide present in the mineral assemblages (González, 2000a, 2001).

## 3. FLUID INCLUSION DATA

Fluid inclusions are commonly found in the hydrothermal minerals (calcite, prehnite, wairakite, anhydrite, quartz and epidote), and are sampled from drill cuttings and core slices. These fluid inclusions represent aliquots from the early fluids in the system. A complete sample dataset for 15 geothermal wells is presented in González-Partida et al., (2000b). A cross section of the geothermal field is based on 15 geothermal wells, with location of the studied samples represented in figure 2. The iso-concentrations of the paleo-

brine (proto-fluid) and the average Th are indicated in the same figure.

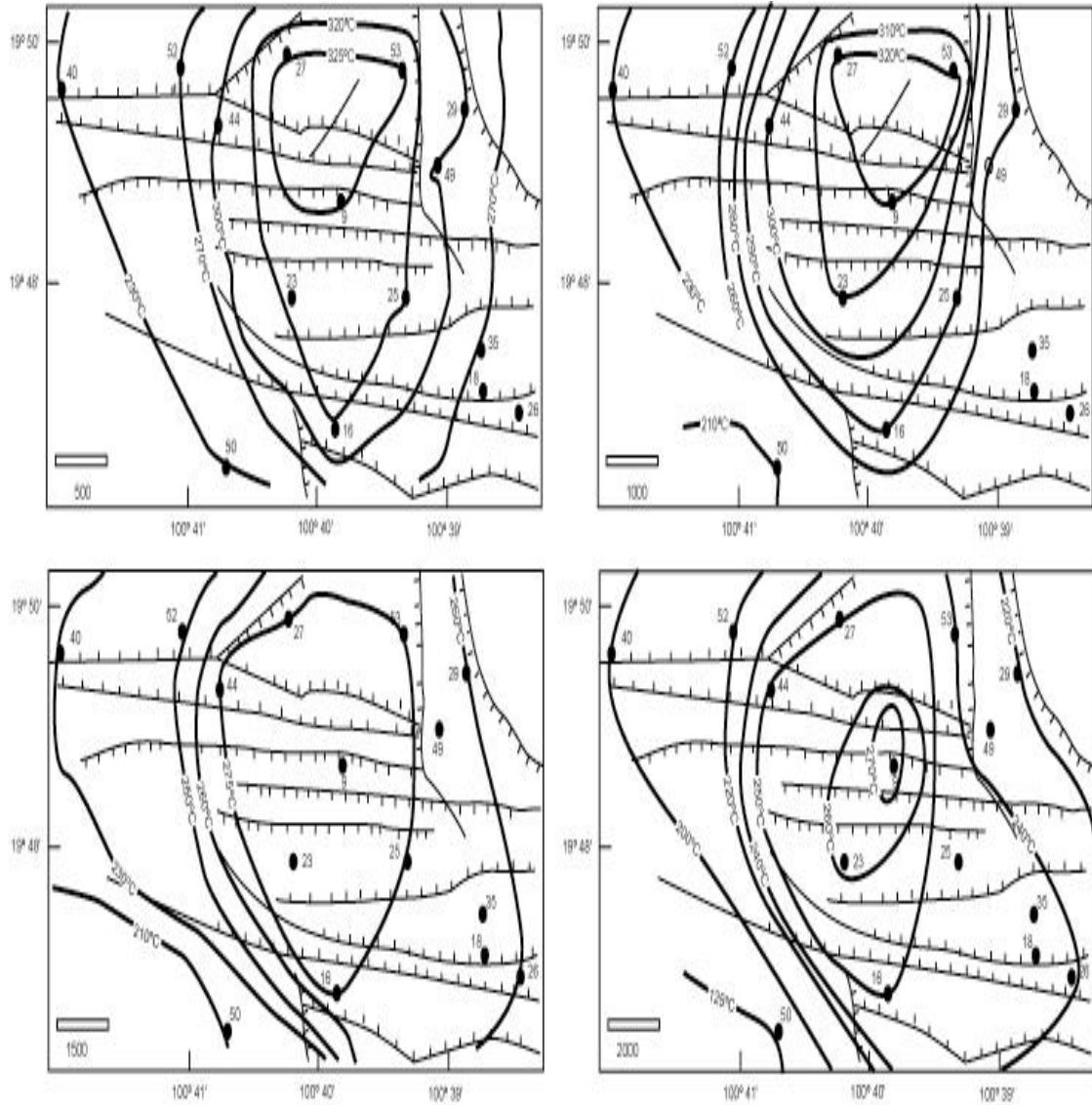
The freezing runs show that the fluid inclusions present a first melting temperature (eutectic temperature,  $T_e$ ) around  $-21.5 \pm 0.5$  °C, which indicates a NaCl-dominated brine. The final ice melting temperatures ( $T_{mi}$ ) show a zone distribution: (a) a deepest zone, close to the base line 0 (0 meter above sea level; zone 3 in figure 2) has a  $T_{mi}$  between -0.1 and -0.7 °C, with salinities comprised between 0.88 to 1.23 wt % equivalent NaCl; (b) an intermediate zone is located between levels 1000 and 2500 m.a.s.l. (zone 2 in Figure 2) and consists of the mixture of L+V and V-dominated fluid inclusions. It shows a  $T_{mi}$  between -0.7 and -2.4 °C, which corresponds to calculated salinities of 1.2 to 4.9 wt % NaCl; and (c) a shallow zone, located between the surface and the steam-rich zone (steam cap, zone 1 in Figure 2), with positive ice-melting temperatures (presence of clathrate), indicating a strong chemical change in the paleo-brine. The last melting temperatures in this zone are located between



**Figure 2.** Cross-sections indicating iso-concentration zones of the paleo-brine (fluid inclusions) and isotherms obtained from microthermometric analyses of fluid inclusions. Solid lines correspond to average homogenization temperatures zones, where: 1 = clathrate positive fusion temperatures; 2 = fusion temperatures from -0.7 to -2.4 °C; 3 = fusion temperatures from -0.5 to -0.7 °C; 4 = microthermometric analysis on quartz (black circle); 5 = microthermometric analysis on epidote (black triangle); 6 = microthermometric analysis on calcite (black squares); 7 = microthermometric analysis on prehnite (black asterisks).

+0.1 and +7°C, indicating the presence of CO<sub>2</sub> with some other gases. This high concentration of CO<sub>2</sub> in this sector of Los Azufres was already found by Suárez in 1997.

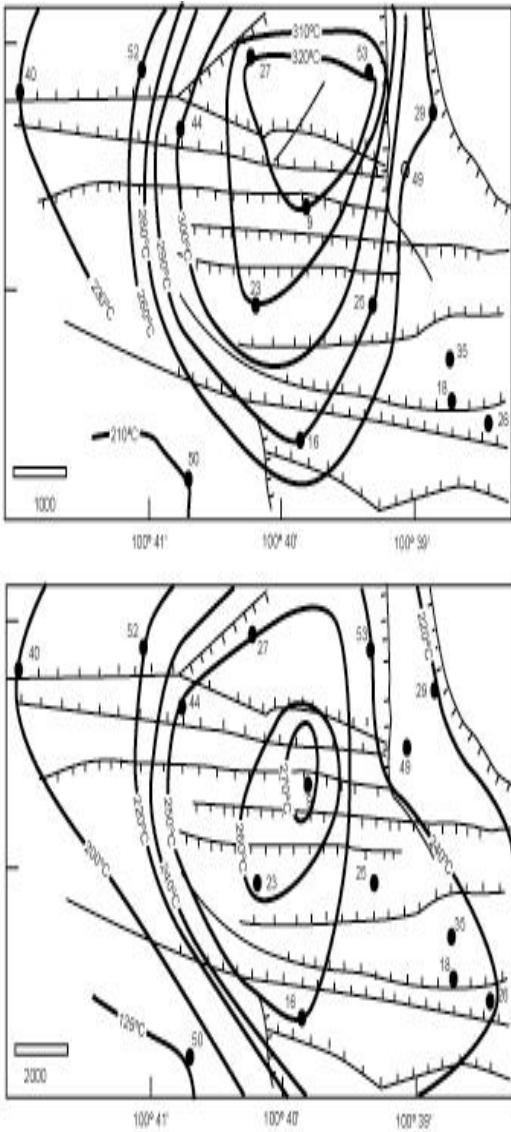
The measured homogenization temperatures were used to plot isotherms on the cross-section of figure 2. The boiling process starts at the isotherm  $\approx$ 300°C, which coincides with the increase of both the fluid inclusions calculated salinity and gases (Suárez et al., 1997). The shape of the isotherms



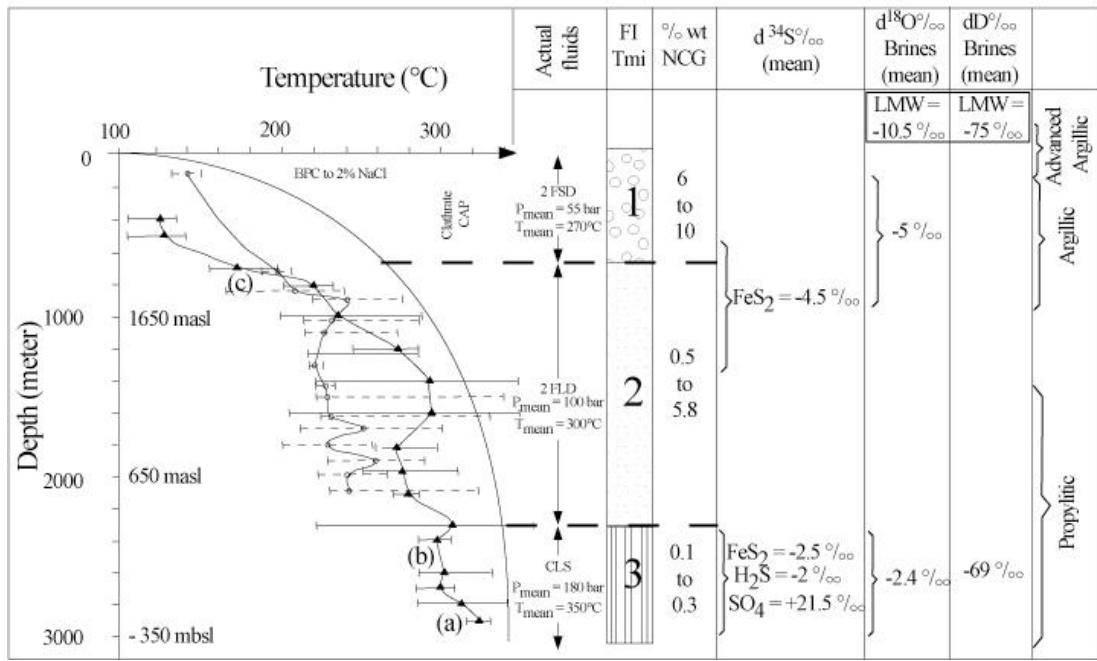
**Figure 3.- Isotherms of the homogenization temperatures (of fluid inclusions) of the geothermal reservoir at, 500, 1000, 1500 and 2000m.a.s.l.(above).**

Figure 4 shows a depth vs. temperature plot. On this figure, boiling curve for a fluid with 2 wt. % NaCl equivalents is shown, which takes into account water table at the surface because the Agria River discharges water to the local aquifer. The same plot (figure 4) shows the data from the end member wells (Az 29, the hottest, and Az 40, the coolest), the sulfur isotopic composition from the geothermal fluids, data on the distribution of wt% of non-condensable gases (NCG) and the alteration types for the different defined zones. At the depth of 2300 m, where

indicates a decrement in the homogenization temperatures at the deepest part of wells Az-50 and Az-40. In order to corroborate this local low temperature gradient, four different sections at altitudes of 500, 1000, 1500 and 2000m were obtained (figure 3). These sections show a group of isotherms distributed almost concentrically, with the highest temperatures around wells Az-27, Az-9 and Az-52 and low temperatures to the SW and W, where Az-50 and Az-40 wells are located.



boiling occur, the gathered data show a wider dispersion and go beyond the L + V zone defined by the boiling curve. At a depth of 700 m, where mixing between geothermal and meteoric fluids takes place, the data plots underneath the boiling curve, showing positive melting temperatures that suggests the presence of non-condensable gases (NCG). As a result of the temperature profiles obtained after plotting the average fluid inclusion data temperatures for the two end-members, it is clear that the fluids at well Az-40 are cooler than at well Az-29, at any depth.



**Figure 4.** Temperature vs. depth diagram showing the boiling curve for water with 2wt% NaCl equivalent salinity (BPC). The water table level is considered to coincide with the surface. Temperature data for well Az-29 are presented by solid lines. Temperature data for well Az-40 are in dashed lines; where F.I. = Fluid inclusions; 1 = positive fusion temperature; 2 = fusion temperatures from  $-0.7$  to  $-2.4$  °C; 3 = fusion temperatures from  $-0.5$  to  $-0.7$  °C; (a), (b) and (c) are points (samples) where the thermodynamic data were calculated. NCG = distribution in wt % of the non-condensable gases. Isotopic behavior of  $\delta^{34}\text{S}^{\circ/\text{oo}}$ ,  $\delta^{18}\text{O}^{\circ/\text{oo}}$  and  $\delta\text{D}^{\circ/\text{oo}}$ : types of hydrothermal alteration with respect to depth

Currently, Los Azufres geothermal field is divided into two well-defined sectors with different thermodynamic characteristics (Suárez et al., 1997). The northern sector is a liquid single-phase reservoir, characterized by a hydrostatic vertical profile with an average pressure of 90 bars and mean temperature of around 300°C. The southern sector presents three different horizons (figure 4): (1) a shallow 2-phase steam dominated (2FSD) layer with around 55 bar and 270°C as initial conditions; (2) an intermediate 2-phase liquid dominated layer (2FLD), at approximately 100 bars and 300 °C; (3) and a deep compressed liquid layer (CLS), at 180 bars and 350 °C.

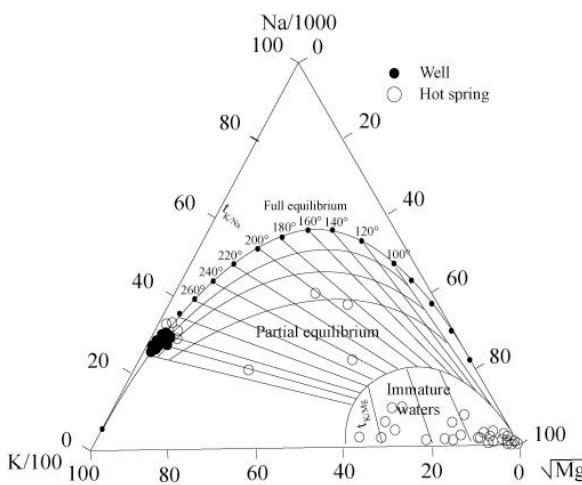
The non-condensable gases produced during steam extraction are mainly composed of CO<sub>2</sub> ( $\geq 90$  wt. % of total NCG; figure 4). The wt % of NCG display a vertical distribution. At deepest levels (CLS zone in figure 4), the wt % of NCG varies from 0.1 to 0.3. At the intermediate zone (2FLD) the wt % varies from 2.8 to  $\approx 3$ , while at the uppermost zone (2FSD) the wt % varies between 6 and 8. Since boiling is an important process at Los Azufres system (González et al., 2000a), we conclude that some physico-chemical parameters (mainly pressure) have changed between the time of mineral formation and the start of field production.

The original fluid phase started boiling during its ascent through the fractured host rock. The deepest sampled fluid inclusions present a relatively low salinity (approximately 0.7 eq. wt % NaCl). The salinity recorded at the paleo-boiling zone is two to five times higher than the original salinity (from 1.0 to 4.9 eq. wt % NaCl), indicating the importance of the boiling process. It is also known that the high content of some gases (mostly CO<sub>2</sub>) can extensively contribute in lowering the fusion temperature of ice crystals within fluid inclusions. Boiling produces a massive CO<sub>2</sub> and volatile separation, which were initially dissolved

within the liquid phase, causing the resulting fluid to be more oxidizing than in the deepest reservoir.

#### 4. GEOCHEMISTRY OF FLUIDS

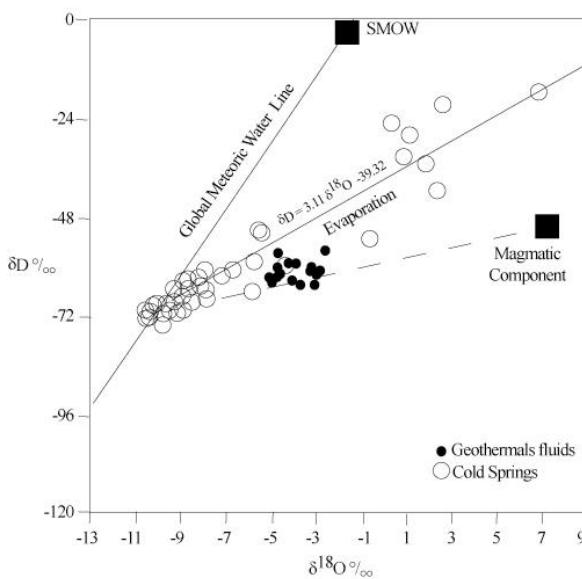
Tello, (1991; 1996), studied the hydrogeochemistry of Los Azufres geothermal field. He found that Cl and Na dominate the electrolyte composition of the geothermal brine. The Cl concentration ranges between 1485 mg/l and 7297 mg/l, and Na concentration varies between 914 mg/l and 4442 mg/l. The brine has also high concentrations of SiO<sub>2</sub>, K and B, whereas Ca and Mg present relatively low concentrations (González et al., 2000a). The equilibrium state and the temperatures of the geothermal system can be deduced from the ternary Na-K-Mg diagram of figure 5. The entire geothermal well samples fit very closely to Na-K lines, indicating that they reached water-rock equilibrium at temperatures between 300°C to 340°C. Some of the water samples taken from surface springs match the geothermal waters, suggesting that they are modified to some extent by the hydrothermal system or belong to it. The bicarbonate-Na springs are displaced towards the Mg corner and present temperatures lower than 100°C, calculated after the K/Mg geothermometer. This indicates that the bicarbonate-Na springs are composed by shallow waters equilibrated with the host rock at relatively low temperatures. Moreover, the sulfate-acid springs also fall in the region of shallow waters, but show a K/Mg temperatures over 100°C, indicating that these are waters of relatively recent infiltration heated up by geothermal steam.



**Figure 5.** Ternary diagram Na-K-Mg showing the evolution of the Los Azufres thermal waters from wells and springs. The diagram shows the fields for the different equilibrium states (immature-partial equilibrium-full equilibrium) and isotherms (Giggenbach, 1989).

## 5. STABLE ISOTOPES

Figure 6 shows the  $\delta^{18}\text{O}\text{‰}$ - $\delta\text{D}\text{‰}$  corrected data for the discharge water from the Los Azufres geothermal wells and hot springs. The samples from geothermal wells present a shift towards high  $\delta^{18}\text{O}\text{‰}$  values, characteristic of the geothermal fluids, due to water-rock interaction processes at relatively high temperatures and to boiling of the fluids at depth. Most of the spring samples fit the global meteoric water line, showing some mixing with heavier waters and/or effect of evaporation. However, some spring samples, especially those with a sulfate-rich chemistry, present a modified isotopic composition and plot along an evaporation line. Surface water samples (lakes) present an isotopic composition characteristic of highly evaporated waters at ambient temperature.



**Figure 6.** Stable isotopes ( $\delta\text{D}\text{‰}$  vs.  $\delta^{18}\text{O}\text{‰}$ ) plot for samples of the geothermal brine and surface manifestations (hot springs) of Los Azufres. (SMOW = Standard Meteoric Oceanic Water).

## 6. CONCLUSIONS

The proto-fluid (fluid inclusions) at the Los Azufres geothermal system is a near-neutral, sodium chlorine brine that originated a deep propylitic alteration of the host rock in the productive zone. At depth, the geothermal field is dominated by a pressurized liquid, yielding to steam at more shallow depths. The gradual change from liquid to the steam phase occurs through boiling and is accompanied by changes in the hydrothermal alteration mineralogy. The type of alteration goes from propylitic to argillic by the means of an oxidation-acidification process, which includes the release of NCG (mainly  $\text{CO}_2$ ).

The fluid zoning ( $\text{Tmi}$ ) observed within the fluid inclusions is in agreement with the distribution of the NCG: the increase in apparent salinity in the boiling zone and the formation of clathrate in the advanced argillic alteration zone (clathrate cap). The isotopic behavior of the species analyzed follows the same general trend.

The deepest fluids in the northern sector of Los Azufres geothermal field (Maritano zone) are liquid-phase, low salinity and NaCl-bearing brines with temperatures ranging from 150 to 325 °C. The corresponding analyzed fluid inclusions are composed of a diluted brine of around 0.8 wt % NaCl equivalent salinity. The salinity recorded at the boiling zone at a temperature of 300°C is 2 to 5 times higher (1 to 4.9 wt % NaCl equivalent), implying an important loss of steam. The fluid inclusions from the top of the reservoir (from 0 to 700 m depth) have positive melting temperatures, indicating a high concentration of gases (mainly  $\text{CO}_2$ ) and fluid temperatures of ca. 150°C. The vertical cooling of the reservoir is product of boiling of the brine during its ascent (sudden drop of pressure and temperature), which also produces a sudden increase of the salinity, density and enthalpy of the fluid upwards.

## ACKNOWLEDGMENTS

This research is funded by project UNAM-PAPIIT # IN107203. The authors wish to thanks the CFE geothermy office, Morelia, Michoacan, Mexico.

## REFERENCES

- Cathelineau, M., Oliver, H. R., Nieva, G. D., 1987. Geochemistry of volcanic series of the Los Azufres geothermal field (México): Geof. International. 26, 273-290.
- Ferrari, L., Garduño, M. V., Pasquare, G., Tibaldi, A., 1991. Geology of Los Azufres caldera, Mexico, and its relationships with regional tectonics. Journal of Volcanology and Geothermal Research. 47, 129-148.
- Garduño, M. V., 1988. La Caldera de Los Azufres y su relación con el sistema regional E-W: Geotermia Revista Mexicana de Geoenergía. 4, 49-61.
- Giggenbach, W. F., 1989. Technique for the interpretation of water and analyses in geothermal exploration. Chemistry Division. Department of scientific and Industrial Research. Petone N. Z. 65 p.
- González, P. E., 1999. Comportamiento de Fluidos en un sistema hidrotermal actual-caso de Los Azufres Mich. México. Revista Mexicana de Ciencias Geológicas. 16, 2, 208-216.
- González, P. E., 2000a. Evidencias de evolución de un fluida básica a ácido a partir del análisis de la alteración hidrotermal del campo geotérmico de Los

Azufres Mich. Revista Mexicana de Ciencias Geológicas. 17, 1, 76-82.

González, P. E., Birkle, P., Torres, A. I., 2000b. Evolution of the hydrothermal system at the geothermal field of Los Azufres Mexico, based on fluid inclusion, isotopic and petrologic data. *Journal of Volcanology and Geothermal Research*. 104, 277-296.

González, P. E., 2001. Especies sulfurosas del sistema hidrotermal actual del campo geotérmico de Las Azufres Mich.: Distribución y comportamiento isotópico. *Revista Mexicana de Ciencias Geológicas*. V, 18, 1, 103-110.

Suárez, M., Samaniego, F., Tello, R. M., 1997. An updated survey of non-condensable gases evolution at Los Azufres Mexico, geothermal reservoir. *Proceedings, 22 Workshop on Geothermal Reservoir Engineering*. Stanford University, Stanford. 27-33.

Tello, H., 1991. Características geoquímicas de los fluidos de Los Azufres Mich. CFE-GPG. Depto. De Exploración. 60p.

Tello, H., 1996. Características químicas e isotópicas del pozo AZ-22 Los Azufres Mich. CFE-GPG. Depto. De Yacimientos. Informe, OIY-AZ-7 96.

Torres, A. I., 1996. Wasser/Gesteins-wechselwirkung im geothermischen Feld von Los Azufres, Mexiko. Mineralogische, thermochemische und isotopengeochemische Untersuchungen. *Tuebinger Geowissenschaftliche Arbeiten*, Reihe E, 2.

Valley, J., Taylor, H., O'Neil, J., 1986. Stable isotopes. *Reviews in Mineralogy* 16, Mineralogical Society of America. 570p