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Study of the Water-Rock-Interaction Processes in the Hidden Geothermal System of Acoculco Puebla (México) by using a Geochemometric Modeling

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ABSTRACT

The study of water-rock interaction (WRI) processes through an integral modelling of fluid and rock geochemistry is being used as a new geochemometric tool for the prospection of the hidden Geothermal System of Acoculco (GSA) located in the state of Puebla, Mexico. The results of a comprehensive WRI study carried out at GSA are reported for elucidating the main transport mechanisms of major and trace elements that occur in this geothermal system, including the determination of deep reservoir temperatures with less uncertainty. Sampling and analysis of rock and fluid samples were conducted, and a new geochemical model is proposed for explaining the main geochemical signatures, and the behaviour of major and trace elements in this complex geothermal system. Because the rare earth elements (REE) are elements present at very low concentrations in most minerals and fluids, their relative abundances may reflect the interaction of unique chemical properties of the system. A comprehensive geochemical interpretation has been carried out by using the major signatures of REE in selective samples of rocks and fluids. Deep reservoir temperatures were calculated by applying new gas geothermometry equations, together with their associated uncertainties. The computed temperatures were compared with bottom hole temperatures (BHT) logged in two exploratory wells (EAC-1 and EAC-2). From the integration of all these geochemometric studies, a more realistic geochemical model of GSA is proposed in this work.

1. INTRODUCTION

The GSA is a hidden geothermal system, characterized by active hydrothermal alteration (argillic alteration), scarce cold springs with acidic fluids, and cold-gas emissions (also referred as Kaipohans), characterised by near ambient surface temperatures. Based on an early exploration programme carried out by the Federal Commission of Electricity (in Spanish: "Comisión Federal de Electricidad", CFE) of Mexico through the drilling of two exploratory wells (EAC-1 and EAC-2), anomalous geothermal gradients of approximately 150°C/km were measured (Lorenzo Pulido *et al.,* 2011). From this anomalous geothermal gradient, GSA has been preliminary considered as a promissory hot-dry rock geothermal system of high-temperature (López-Hernández *et al.,* 2009). The GSA is a complex geothermal system typified by impermeable layers and sealed faults by either calcite or silica precipitation (Pandarinath *et al.*, 2019). These petrophysical properties of the rock-formation have limited the upflow transport of fluids and gases from deep-seated sources towards the surface. New non-conventional geochemical exploration tools have been used to obtain a better knowledge of this hidden geothermal system, as well as to describe the main geochemical processes that govern at the deep conditions (Santoyo *et al*., 2019). With these purposes, a comprehensive geochemical programme was carried out for almost four years to achieve such geochemical challenges. The present work also describes the results of the geochemical analysis carried out in selective samples of rocks, fluids and gas emissions collected within the GSA. The analysis of the composition of rare earth elements in rock and fluid samples was used as signatures to trace the major hydrogeochemical features of the GSA. Details of this original geochemical study is outlined in the present study.

2. GEOLOGICAL SETTING

The GSA is located within the Trans-Mexican volcanic belt (TMVB), which is considered geologically a magmatic arc that extends from the states of Nayarit to Veracruz. The origin of the TMVB is the result of the subduction of the Cocos and Ribera plates below the North American plate. Being precise the GSA is georeferenced between the coordinates 19° 50' and 20° 0' North latitude and 98° 4' and 98° 15' West longitude, at 130 km NE of México city (Figure 1).

According to López-Hernández et al (2009), the geothermal system of Acoculco is located within a larger caldera complex, known as Tulancingo-Acoculco (TAC). The TAC is the oldest structure and has a diameter of ≈32 km and rocks from the Pliocene (3.0-2.7 Ma), while the GSA has a diameter of ≈18 km and rocks from the Pleistocene (1.7-0.24 Ma). However, Sosa-Ceballos et al. (2018) y Avellán *et al.* (2019) in recent studies rule out the existence of the TAC, and conclude that the active period of the GSA corresponds to the Pliocene. A division of the GSA by means of the following major geological units is proposed by: (i) lithological units formed prior to the formation of the caldera (Pre-caldera); (ii) lithological units formed during the formation of the caldera (Syn-caldera); (iii) lithological units formed early after the formation of the caldera (Early post-caldera); (iv) lithological units formed late after the formation of the caldera (Late post-caldera) and (v) the lithological units formed independently of the formation of the caldera (Extra-caldera). A recent geological map of Acoculco has been therefore updated by Avellán *et al*. (2019). The eruption that caused the formation of the GSA (Syn-caldera) took place at about 2.731 ± 0.184 Ma ago. Anomalous geothermal manifestations related to the GSA can be geographically divided into two major zones: (Zone 1) inside-caldera (Los Azufres: AZ; Alcaparroza: AP, and Chignahuapan: CHIG); and (Zone 2) outside-caldera (Jicolopa: JI; Quetzalapa: QTZ; and Chignahuapan: CHIG). Both geothermal zones are characterized by cold soil-gas fluxes or emissions of CO_2, H_2S and CH_4, among others (López-Hernández et al., 2009; Peiffer e*t al.,* 2014).

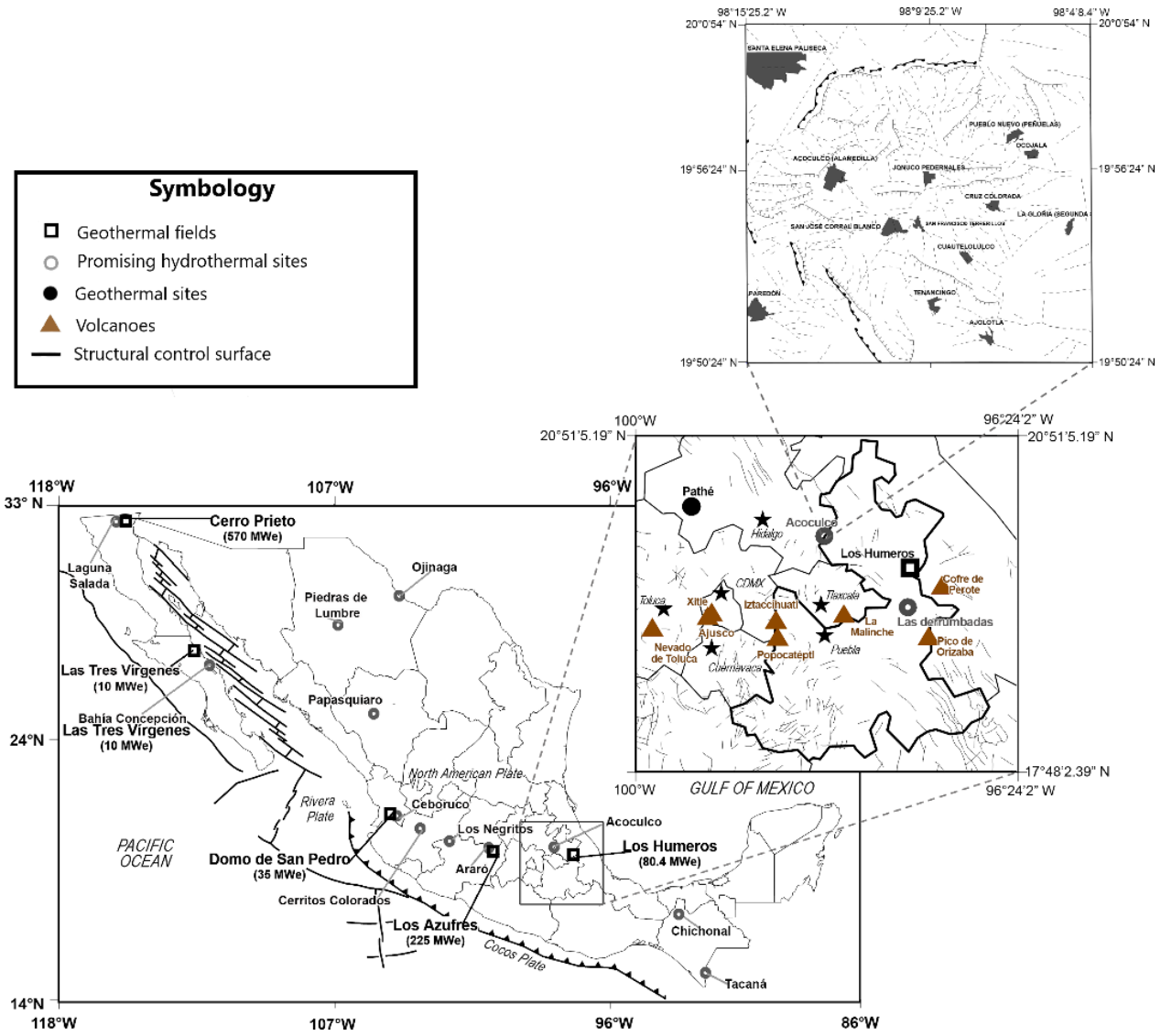

Figure 1: General map of Mexican geothermal fields under exploitation (black squares), potential promissory sites (gray circles), and simplified projection from the study area of the Geothermal System of Acoculco (GSA).

3. WORK METHODOLOGY

To carry out the proposed geochemical study in the GCA, an integrated work methodology was developed. A schematic flow diagram showing the methodology to study the water rock interaction processes is presented in Fig. 2. The work methodology basically involved three major phases for studying the fluid and rock fractionation. The first phase was related to conventional field work for the collection of representative fluid and rock samples in the GSA, as well as the chemical analysis of such collected samples. The second phase, related with fluid fractionation, considered the classical hydrogeochemical tasks for fluid classification, solute and gas geothermometry, and the REE interpretation in fluid samples; whereas the third phase was related to the study of the REE fractionation in parental rock samples.

4. FLUID GEOCHEMISTRY

During the fluid sampling programme, 78 water samples were collected in the promising areas of GSA. Ternary plots of major anions for water classification (Giggenbach, 1988) show the main abundances of these anions (Fig. 3). A clear dilution process is observed in the water samples collected in the Zone 1 of the GSA (Fig. 3a), where most of the samples are classified as steam heated waters (AP), whereas a few samples are identified as peripherical waters (CHIG). This variation may be explained by a decrease in the fluid pH (acidification) mainly due to the oxidation of H_2S in the steam heated waters, resulting in a very high concentration of sulphate waters together with a low content of bicarbonate (HCO_3). For the Zone 2 (Fig. 3b), all the collected samples fall in the peripheral water section, which indicates a mixing process either with surface water or a CO_2 dissolution.

Based on the Piper classification that considers the composition of the anions and cations, the GSA samples may be classified into 2 geochemical groups: (i) calcium sulfate waters (AP and AZ) and (ii) calcium bicarbonate waters (CHI, JI and QTZ): Fig. 4.

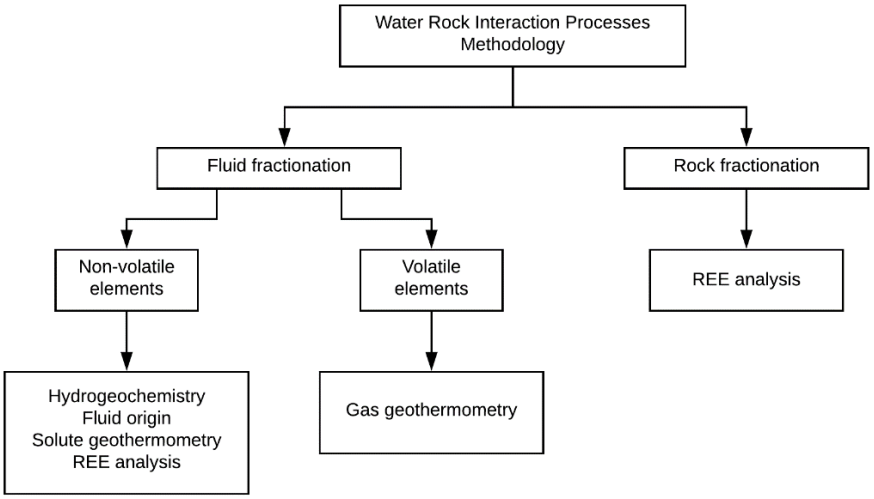

Figure 2: Integrated work methodology developed for the study of water-rock interaction processes in the GSA

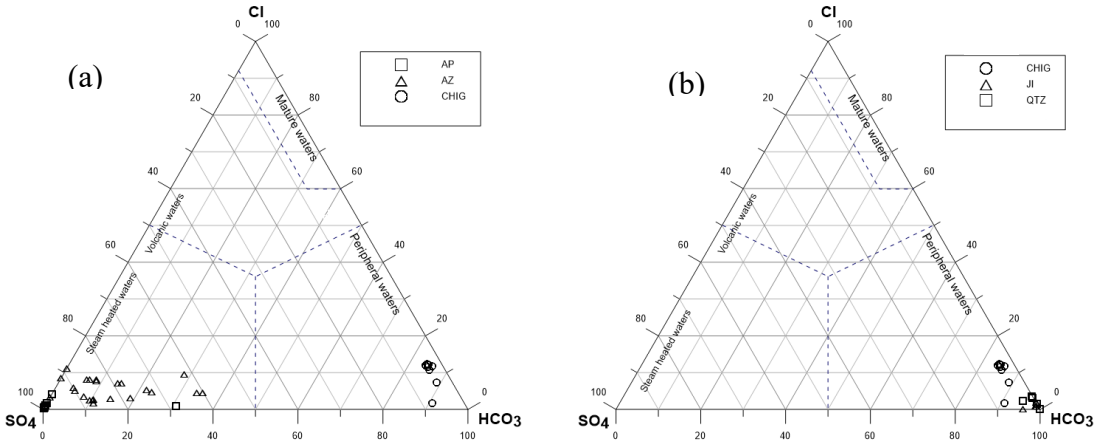

Figure 3: Ternary diagrams showing the compositional variation of major anions of the water samples collected in the Zones 1 (a) and 2 (b).

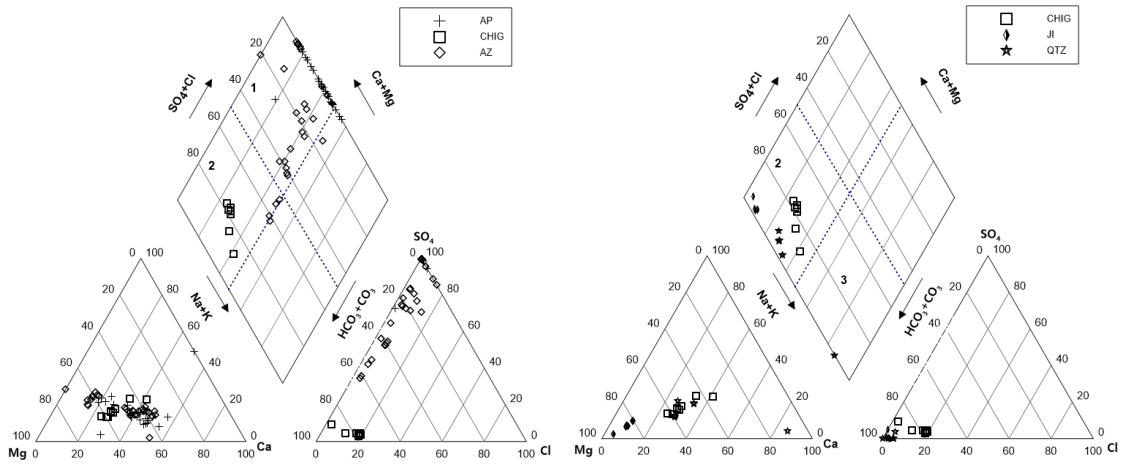

Figure 4: Piper diagram showing the geochemical classification of the two groups of fluids of the GSA.

4.1 Rare Earth Elements

The analysis of the composition of the REE in hydrothermal fluids for the understanding of the main water-rock processes has not been studied until two decades ago. Gimeno Serrano *et al.* (2000) ponted out that the absence of studies of REE in geothermal fluids is mainly due to the low sensitivity of geoanalytical techniques, the lack of reliable field data, and geochemical models. With the new

advances of geoanalytical techniques, such as ICP-MS, the analysis of REE have passed to be from a tedious and difficult task to a more reliable routine due to the lower limits of detection achieved with these new techniques (Verma *et al.,* 2002).

In the present work special emphasis has been given to the interpretation of the REE behaviour exhibited by these trace elements in some rock and fluid samples selectively collected in the GSA. The REE concentration patterns normalized to chondrite (Sun & McDonough, 1989) are shown in the Fig. 5. Samples from geothermal Zone 1 of the GSA shows a well-defined concentration pattern of REE in the acidic fluid samples (pH< 3), where the change of this physicochemical parameter seems to control the pattern shape, and the level of REE fractionation exhibited in fluids (pH> 3.5) as a result of the water/rock interaction processes.

Gimeno Serrano *et al.* (2000) proposed that at least four hypotheses that may be considered for the geochemical interpretation of REE patterns in acidic waters: (i) the formation of aqueous complexes, (ii) original patterns (only primary minerals), (iii) patterns after weathering (secondary minerals), and (iv) combination of the above processes. Gimeno Serrano *et al.* (2000) and Shakeri *et al.* (2015) pointed out that the fluid pH plays an important role on the REE fractionation, which is given by an inverse correlation between the REE concentration and the fluid pH. This correlation is nearly observed in most of the samples collected in the zone 1, where the REE concentration levels clearly exhibit a decrease pattern as the pH increases. These water samples are also characterised by negative anomalies of europium (Eu). For the geothermal zone 2, it is observed that the water samples exhibit very low concentrations of REE, which seem to be nearly correlated with pH measurements ranging from neutral to basic, besides there is not a clear defined pattern. Each geothermal site actually displays a different pattern, and only the QTZ sample shows a positive Eu anomaly. CC water sample shows a low pH, which is likely due to the proximity to the zone 1 (AZ).

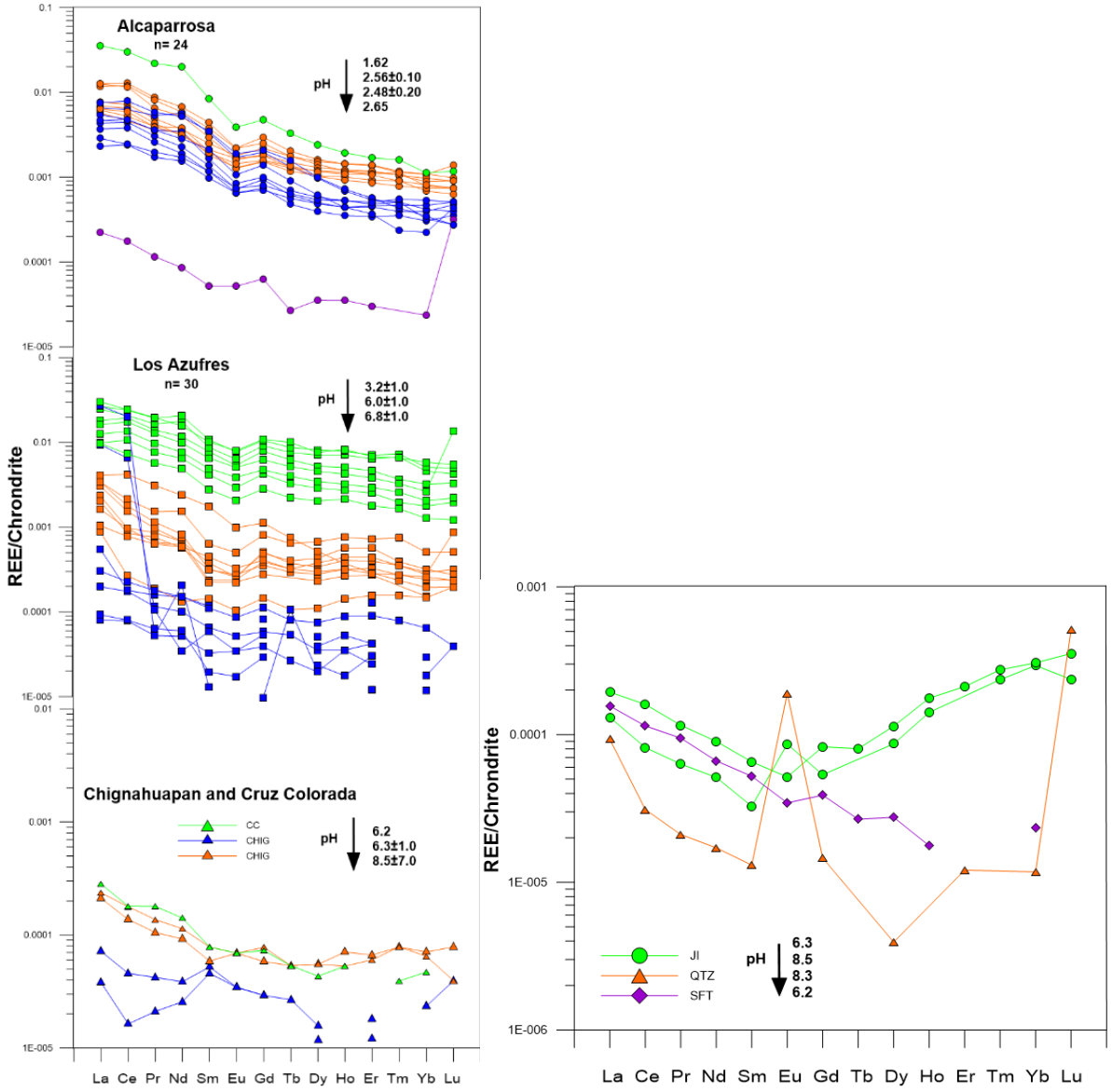

Figure 5: Concentration of rare earths elements normalized to chondrite in fluid samples collected from zone 1 (left) and zone 2 (right). The pH values of each sample are indicated by the arrow in each plot.

5. ROCK GEOCHEMISTRY

A total of 65 samples of surface rocks were collected in the GSA for the analysis of trace elements. The composition of 45 samples were additionally compiled from the literature (Sosa-Ceballos *et al.,* 2018; Verma, 2001) to make a more representative data set. All samples were classified according to the type of lava (acid, intermediate and basic) for further analysis, this classification was made based on the information of the geological map reported by Sosa-Ceballos *et al.* (2018). For the interpretation of the REE geochemistry, their concentrations were normalized to chondrites by using the methodology proposed by McDonough and Sun (1995). Figure 6 shows the variety of REE patterns found in different types of rocks. Most REE patterns display an enrichment in light rare earth elements (LREE) with relatively flat patterns to a strongly depleted pattern for heavy rare earth elements (HREE). Within the main differences in the REE patterns, the negative europium anomaly is the one that stands out the most, being very noticeable in acidic rocks, decreasing in intermediate rocks and disappearing in basic rocks. Fulignati *et al.* (1998) remarked that the hydrothermal alteration is an important signature in europium anomalies, causing negative anomalies in altered rocks. Fresh rocks, such as rhyolite (acid composition) show a strong europium anomaly, whereas rocks such as latites (intermediate composition) display a very weak europium anomaly. The negative anomaly of europium is evident either at temperatures above 250 °C or in an extremely reducing chemical environment. These conditions actually support the stability of Eu^{2+} to reside in the parent rocks, whereas the Eu^{3+} as it exhibits a greater solubility, it is more susceptible to be leached from the parent rock (Fulignati et al., 1998).

As a reference, the global average of the REE composition in acidic (purple) and basic (red) rocks reported by (Parker, 1967) is plotted. In the case of acidic rocks, a greater enrichment (with respect to the standard) of the heavy rare earth elements (HREE) is observed. The basic rocks present the opposite case, with a greater enrichment of the LREE.

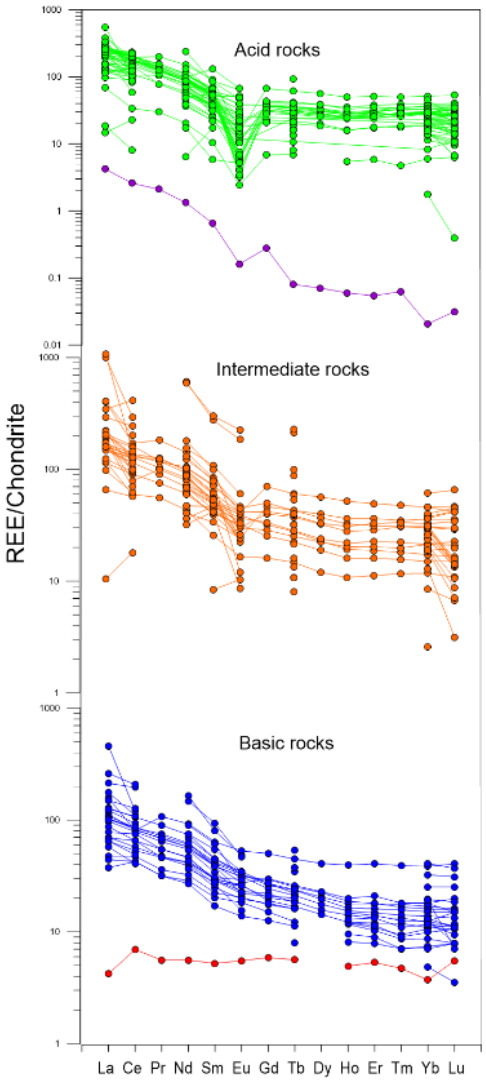

Fig. 6: Concentration of REE normalized to chondrite in some selected rock samples collected in the GSA.

6. GAS GEOTHERMOMETRY

The most used geochemical technique for the estimation of reservoir temperatures is the solute geothermometry, but when plotting the composition of the GSA fluid samples on the Na-K-Mg ternary diagram proposed by Giggenbach (1988), such waters are classified as immature waters. The calculation of deep temperatures obtained from the solute geothermometry are reliable only if the samples are in total or partial equilibrium, constraint that is not fulfil in the collected water samples.

As the geothermal manifestations existing in the GSA are mostly characterized by cold gas emissions (mofettas), gas samples collected in traditional evacuated Giggenbach bottles were selectively collected in the study area. The chemical analyses of these gas samples were carried out by using conventional wet-chemical and gas chromatography methods (Santoyo *et al.,* 1991). In this way, and as a more suitable geothermometric method, gas geothermometry has been applied to estimate reservoir temperatures.

A total of five geothermometers (Table 1) were selected for these purposes: Santoyo *et al.,* (2019); Tarán (1988); Arnórsson and Gunnlaugsson. (1985) and Giggenbach. (1991). New gas geothermometers based on artificial neural networks and recently proposed by Santoyo et al. (2019) were used for the prediction of deep geothermal reservoir temperatures. ANN-1 and ANN-2 were specifically inferred from a multivariate analysis among gas-phase compositional data and bottomhole temperatures (BHT) measurements compiled in a world geochemical database (Pérez-Zarate *et al.,* 2019).

Table 1: List of gas geotermometers applied to estimate reservoir temperatures in the Geothermal System of Acoculco.

ID	Nomenclature	Formula	Units	Reference
1	ANN-1	ANN equation based of CO_2 concentration	mmol/mol	1
2	ANN-2	ANN equation based of H_2S concentration	mmol/mol	1
3	TN88	$t = \frac{4036}{5.94 - \log[XCO2]} - 273.15$	mmol/kg	2
4	AG85	$t = 27.2 + 20.99[\log(H2)]$	mmol/kg	3
5	Gg91	$t = \frac{4625}{10.4 + \log[CH4/CO2]} - 273.15$	mmol/mol	4

(1) Santoyo *et al.,* (2019); (2) Tarán (1988); (3) Arnórsson and Gunnlaugsson. (1985); (4) Giggenbach (1991).

Results of the temperatures calculated by using the gas geothermometers are graphically shown in Fig. 7. Such temperature estimates correspond to 27 gas samples collected from bubbling or soil-gas emissions located in Los Azufres and Alcaparroza zones (Zone 1) of the GSA, and are in total agreement with the bottomhole temperatures measured in the exploration wells EAC-1 (~307ºC) and EAC-2 (~265ºC): Pulido *et al.,* 2011. The temperature estimates are also in full match with homogenization temperatures reported from fluid inclusions (López-Hernández *et al.,* 2009). It is observed that the calculated temperatures with gas geothermometers are very close to the reference temperatures, it is noticeable that ANN-1 y ANN-2 geothermometers from Santoyo *et al* (2019) have the lowest dispersion in comparison with other geothermometric tools, and a better accuracy with respect to the median value computed.

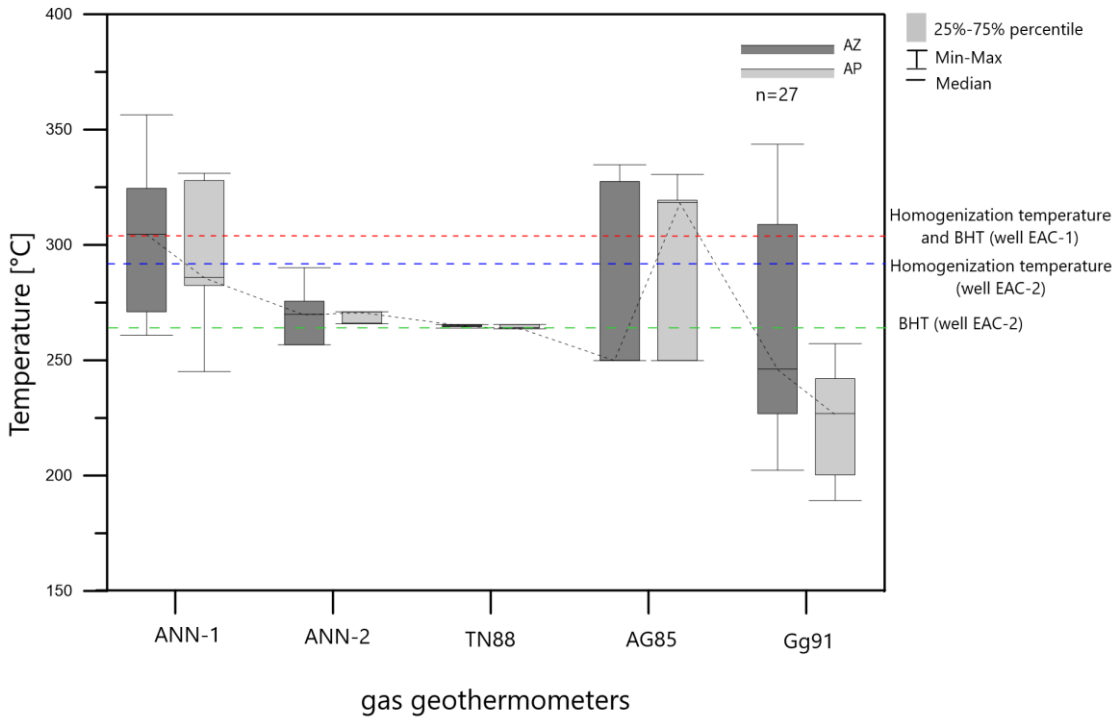

Figure 7: Statistical descriptive plot showing the temperatures calculated by gas geothermometers for some gas samples collected in Los Azufres and Alcaparrosa zones of the Geothermal System of Acoculco.

7. CONCLUSIONS

The geochemical study carried out through the conventional geochemistry of major elements do not provide enough information to elucidate the water-rock interaction processes that occur in the complex GSA. For this reason, it is concluded that hidden geothermal systems such as the GSA require studies related to the geochemistry of trace elements, especially the tracer rare earths elements.

The normalized REE patterns found in the fluids collected in AP and AZ zones have a geochemical signature very similar to the REE patterns present in rocks of intermediate and basic composition. This could indicate that fluids and rocks are in equilibrium with respect to their trace composition.

The high concentrations of REE present in AP and AZ fluids can be attributed to two main factors: (i) acidification of fluids due to H_2S emanations; (ii) to the intense hydrothermal alteration present.

Finally, the temperatures calculated with gas geothermometers are very close to the well measurements and those calculated by fluid inclusions. So, it is concluded that to obtain realistic reservoir temperatures in hidden geothermal systems it is necessary to carry out studies related to the composition of the gas phase.

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