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Compositional Link Between Thermal Fluids in Mexican Deep Reservoirs

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ABSTRACT

Fluids from four geothermal reservoirs in Mexico (Cerro Prieto and Las Tres Vírgenes in NW-Mexico; Los Humeros and Los Azufres in Central Mexico) are compared with formation water from oil field reservoirs in SE-Mexico, located offshore (Pol-Chuc) and onshore (Activo Luna, Samaria-Sitio Grande). Geothermal fluids are extracted from more shallow depths (350 – 3,500 m) with maximum temperature conditions of 400°C, while oil field waters are encountered at depths between 3,000 and 6,200 m. The fast accumulation of thick sedimentary piles in the Gulf basin explains low temperature conditions from 140°C (Activo Samaria-Sitio Grande) to 170°C (Activo Luna) under extremely high pressure conditions (up to 800 bar).

An increasing mineralization of groundwater with depth is observed in deep Mexican reservoirs, whereby gravity-driven separation represents the principal physical process for the descent of heavy Cl-brines. A linear ^{18}O-isotopic gradient of 0.43 ‰ per 100 m is proposed as a temperature and pressure dependent regional trend for the isotopic evolution of deep formation water in Mexican geothermal and oil reservoirs.

Additionally, local effects cause an individual chemical and isotopic evolution of each reservoir fluid: Oil field waters from the Gulf of Mexico are characterized by a heterogeneous, saline to hypersaline, NaCl and NaCaCl composition, formed by varying mixing proportions between three components - meteoric water, seawater and/or evaporated seawater. Low Cl/Br ratios exclude the influence of halite dissolution from salt domes as a potential Cl-source. In the case of geothermal fluids, chemical and isotopic fingerprints are mainly defined by high-temperature hydrothermal reactions during convective circulation of boiling fluids. Low saline (brackish to marine), NaCl-type water reflect the average composition in Mexican geothermal reservoirs, although Los Humeros fluids can range from NaCl to $NaHCO_3$ and $NaHCO_3ClSO_4$-types. The simultaneous enrichment in Ca^{++} and depletion of Mg^{++} in oil field groundwater is caused by the partial dolomitization of carbonate host rock. Potassium concentrations of geothermal fluids above the evaporation trajectory reflect the addition of K^+ through water/rock interaction, perhaps as albitization of K-feldspar.

Measured ^{14}C-activities between 0.8 pmC and 28.2 pmC for oil field water reflect enhanced infiltration processes during late Pleistocene and/or early Holocene as a period of increased humidity in the Gulf region. Probably, the origin of meteoric and marine components in geothermal fluids from Mexican reservoirs can – although low ^{14}C-concentrations indicate the possible dilution by dead carbon from magmatic CO_2 sources - be attributed in parts to this interglacial recharge event. Elevated δD-ratios with average values of -10.0‰ support the hypothesis of warmer climatic conditions during this period.

1. INTRODUCTION

Geothermal and petroleum wells represent a unique and exclusive medium to study deep groundwater and crustal processes in reservoir depths below 1,000 m. In Mexico, four geothermal fields - Cerro Prieto and Las Tres Vírgenes in NW-Mexico (State of Baja California), as well as Los Humeros and Los Azufres in Central Mexico (States of Michoacán and Puebla, respectively) - are now used for geothermal electricity production (Fig. 1). The reservoirs are between 350 and 3,500 m with maximum temperature conditions of 400°C, as in Los Humeros. On the other hand, petroleum reservoirs in SE-Mexico - Activo Luna and Samaria-Sitio Grande, both in the State of Tabasco, and Activo Pol-Chuc, located offshore the Gulf coast (Fig. 1) - are encountered at a depth between 3,000 and 6,200 m. The accumulation of more than 10,000 m of Jurassic to Tertiary sediments within the Gulf of Mexico explains low temperature conditions from 140°C (Activo Samaria-Sitio Grande) to 170°C (Activo Luna) under extremely high pressure conditions (up to 800 bar). Origin and circulation of these individual flow systems have been published in a series of articles and reports, such as for Cerro Prieto (Lippmann et al., 1991; Halfman et al., 1986; Grant et al., 1984; Truesdell et al., 1981), Las Tres Vírgenes (Portugal et al., 2000a), Los Azufres (Birkle et al., 2001), Los Humeros (Arellano et al., 2003; Cedillo 1999), Activo Luna (Birkle et al., 2002), Activo Samaria Sitio-Grande (Birkle & Maruri, 2003), and Activo Pol-Chuc (Birkle, 2003).

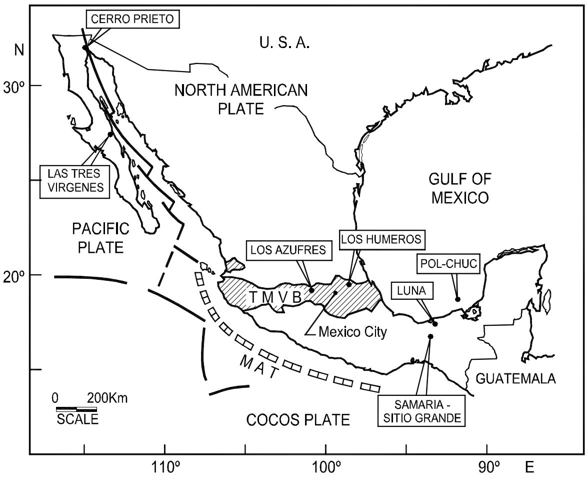

Figure 1: Location of the described geothermal and petroleum fields.

This paper compares the chemical and isotopic composition of deep fluids from different geothermal and petroleum reservoirs and tectonic regimes in Mexico to define common chemical-physical processes in deep groundwater systems, such as gravity dependent increase of salinity, and mineralization by water-rock interaction. The significance and validation of interpretations of chemical and isotopic characteristics of local sites is shown in a regional, large-scale context.

2. LOCATION AND HYDROGEOLOGICAL DESCRIPTION OF THE RESERVOIRS

The Cerro Prieto geothermal field in northern Baja California is hosted in deltaic sands and shales of the southern Salton through. Fluids are extracted from depths between 800 and 3,000 m with an average reservoir thickness of 1,900 m and temperatures above 260°C. At Las Tres Vírgenes geothermal reservoir in Southern Baja California, four production wells and three injection wells were drilled to a maximum depth of 1,100 m (since 1988). The volcano-sedimentary Grupo Comondú with a maximum thickness of 750 m covers the granodioritic basement intrusion (López, 1998).

Los Azufres is one of several Pleistocene silicic volcanic centers with active geothermal systems in the E-W trending Transmexican Volcanic Belt. A 2700 m thick interstratification of lava flows and pyroclastic rocks of andesitic to basaltic composition (Dobson & Mahood, 1985) provide the main aquifer with fluid flow through fractures and faults that sometimes reaches the surface (Birkle et al., 2001). The production wells extract vapor and liquid from a depth between 350 and 2,500 m. A silicic sequence of rhyodacites, rhyolites and dacites with thickness up to 1,000 m (Dobson & Mahood 1985) form a caprock seal to the aquifer, allowing the geothermal system to pressurize. The NaCl rich fluids reach temperature values as high as 320°C, but temperatures of 240-280°C are normal in the field.

The Los Humeros geothermal field is located in the eastern part of the Transmexican Volcanic Belt with a total of 42 wells of which 22 are currently used for electricity generation. Metamorphized carbonate forms the basement below a low-liquid-saturation reservoir, which is located at a depth between 1,950 and 2,700 m (850 - 100 m a.s.l.). Basalt and hornblende andesite of intermediate permeability form the host rock of the lower reservoir, whereas augite andesite represents the upper geothermal reservoir (800 – 1,700 m) (Cedillo, 1997; Arellano et al., 2001). Both aquifers are separated by impermeable vitreous tuff, and overlain by low permeable lithic tuffs, ignimbrites. At the top, pumice, olivine basalts and andesites from shallow aquifers systems.

The Activo Luna and the Samaria-Sitio Grande oil reservoirs are located onshore within the southeastern coastal plain of the Gulf of Mexico. Both oil fields form part of the NW-SE trending Villahermosa uplift horst structure, which is separated from the Comalcalco basin to the NW, and from the Macuspana basin to the SE by the Comalcalco and Frontera faults. The Villahermosa uplift comprises between 5,000 m and 10,000 m of Tertiary and Mesozoic sediments in the western and eastern part, respectively (Salvador, 1991). Formation water is produced as an undesired co-product of the petroleum exploitation, mainly from Jurassic to Cretaceous limestone and dolomite formations. The initial piezometric level of the water-hydrocarbon contact was encountered at a depth between 5,900 m and 6,100 m (Luna), and between 3,800 m and 4,500 m (Samaria-Sitio Grande), respectively. The Pol-Chuc reservoir, together with the adjacent Abkatún, Batab, Caan, and Taratunich oil fields, is located within the Gulf of Mexico, about 60 km offshore from the town Ciudad de Carmen. Dolomitized carbonates in Paleocene breccia and Upper Cretaceous calcareous sandstone as part of NW-SE trending anticlines form the principal Pol reservoir at a production depth between 2,900 and 4,800 m. The original water-oil contact was detected at a depth of 3,960 m.

3. METHODS

Basic chemical and isotopic data was collected from a variety of previous published articles and reports: Portugal et al. (2000b) and Mazor & Mañon (1979) describe chemical data, and $\delta^{18}O$ and δD values for the Cerro Prieto fluids. Chemical data from 24 fluids samples from the Los Humeros geothermal field were taken from González et al. (2001) and Arellano et. al (2001), isotopic data from Portugal et al. (2001) and Arellano et al. (2003), as well as extraction depths from the mentioned articles. Data from geothermal wells in Las Tres Vírgenes were derived from Portugal et al. (1998, 2000a). Chemical analysis from 17 geothermal wells in Los Azufres were taken from González et al. (2000), stable isotope data from Birkle et al. (2001) and Nieva et al. (1983, 1987). Chemical and isotopic composition and interpretations about the origin of formation water from the Activo Luna oil field were taken from Birkle et al. (2002); hydrochemical data from 28 production wells of the Samaria-Sitio Grande reservoir are given in Birkle & Maruri (2003), Birkle & Lima (2004) and Birkle & Angulo (2004). The chemical-isotopic composition of Pol-Chuc fluids from 29 production wells as well as interpretations of the hydrogeological-isotopic reservoir model were extracted from Birkle (2003).

4. RESULTS

4.1 Chemical Characterization

The Schoeller diagram (Fig. 2a,d) shows the major elemental distribution in reservoir fluids of several Mexican geothermal and petroleum fields. The oil field brines are characterized by a Na-Cl and Na-Ca-Cl composition, partially reaching supersaturated conditions with maximum Cl concentrations of 228 g/l. The carbonate basement of the Mexican Gulf explains their enrichment in Ca and HCO_3 (up to 54,420 mg/l and 1769 mg/l, respectively). In detail, Activo Luna fluids are characterized by a range of fluid types, varying from drinking water to hypersaline water composition (Fig. 2a). The Samaria-Sitio Grande and Pol-Chuc fluids are characterized by a very similar, narrow-range, saline to extreme hypersaline Na-Cl composition (Figs. 2a,b). The elevated Ca content of Na-Ca-Cl waters (17 out of 28 samples) indicate dolomitization as main mechanism for the cationic composition of the Samaria-Sitio Grande fluids, where Mg-rich water converts calcite to dolomite.

Geothermal fluids are far less concentrated: Most of them are characterized by brackish water composition, with Cerro Prieto fluids near the mineralization of marine water. Cerro Prieto and Las Tres Vírgenes fluids are very homogeneous NaCl brines (Fig. 2c), whereas relatively elevated concentrations of Li (up to 33.1 mg/l) characterize most of the Los Azufres fluids as Na-Li-Cl type (15 out of 17 samples). In general, Cerro Prieto, Las Tres Vírgenes and Los Azufres formation waters show affinity by similar chemical compositions (Figs. 2c-d).

The Los Humeros reservoir is composed of low mineralized groundwater with maximum Cl-concentration of 1,479 mg/l (Fig. 2d). The abundance of HCO_3 and SO_4 in some aquifer sections, as well as variations in their Cl-content, cause a widespread chemical diversity: NaCl-type water is dominant at the Los Humeros reservoir (11 of 24 wells), but individual samples of Na (well H-31), $NaHCO_3$ (H-16), $NaClHCO_3$ (H-6, H-18, H-30), $NaHCO_3Cl$, (H-1, H-8, H-12), $NaSO_4$ (H-15, H-16R), $NaClSO_4$ (H-16, H-17), and $NaHCO_3ClSO_4$ type (H-7) reflect the heterogeneous character of the reservoir fluids (well sample in parenthesis). Barragán et al. (1999) explain the variable character of the fluids by elevated bicarbonate and sulfate fractions in the condensed fraction.

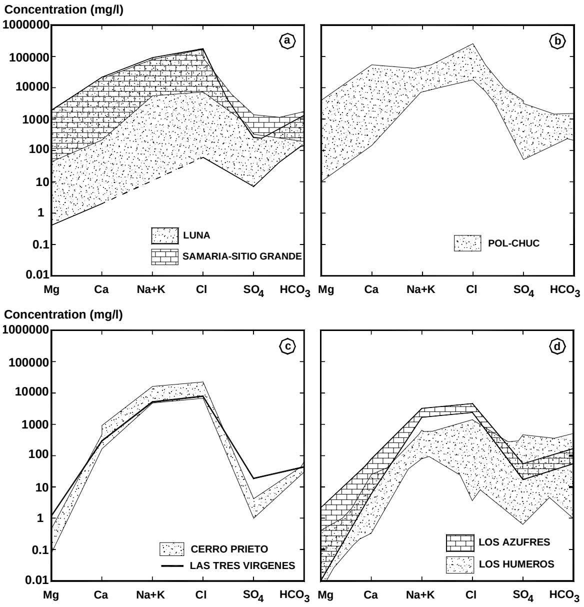

Figure 2: Schoeller-Diagram: Major elemental characterization of Mexican oil field waters (Figure 2a,b) and geothermal waters (Fig. 2c,d).

As a major characteristic of geothermal fluids from Las Tres Vírgenes, Los Azufres and Los Humeros reservoirs, high-temperature water-rock interaction processes with volcanic host rock cause fluid enrichment in SiO_2 (62 – 1,359 mg/l). As SiO_2 represents one of the major chemical compounds of geothermal fluids, the silica content should be considered for the chemical classification of geothermal water. The trace elements Li, Cs and Rb represent an appropriate method to distinguish deep reservoir fluids (Fig. 3). While oil field waters are characterized by a linear trend from the central part of the diagram towards the Li-corner, geothermal fluids from Cerro Prieto and Los Azufres show trends towards the Cs corner. Los Humeros and Las Tres Vírgenes fluid composition is not shown due to the lack of available analytical data from Cs and Rb.

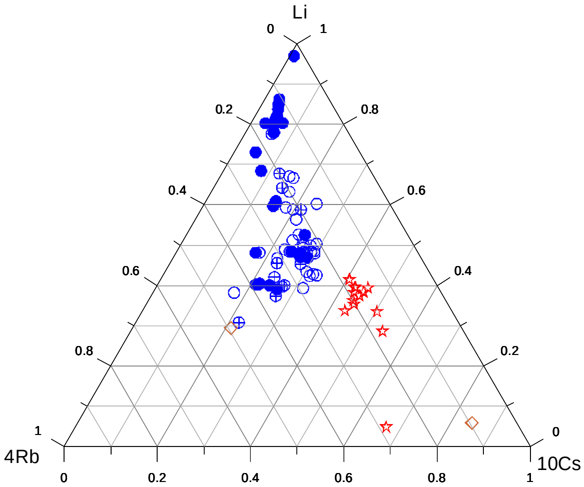

Figure 3: **Ternary Li-Rb-Cs classification of geothermal (Cerro Prieto, Los Azufres) and oil field water (Activo Luna, Samaria-Sitio-Grande, Pol-Chuc) (Legend in Fig. 4).**

4.2 Vertical Tendencies and Mixing Processes

Worldwide, a general increase of groundwater salinity and mineralization with circulation depth can be explained by, a) gravity driven separation processes due to differences in fluid density and, b) temperature and pressure intensified water-rock interaction processes, such as halite dissolution, carbonate precipitation, dolomitization, sulfate reduction and methane formation. Ion exchange processes between Ca and Na - with Na as the more mobile phase - cause stockwork zoning with a typical sequence $CaHCO_3$-$CaSO_4$-$NaSO_4$-NaCl with increasing depth, as observed in Southern Germany (Käss, 1967). Typically, regions with stagnant flow conditions and retarded water exchange processes are characterized by $CaCl_2$-type fluids (Tschuchrow, 1965). On the other hand, hydrothermal reactions may accelerate exchange processes, causing a homogeneous distribution of NaCl-type fluids throughout the stockwork. The abundance of NaCl-type deep water can be correlated with following processes:

a) Gravitational descent of heavy Cl-waters

b) Abundance of fossil marine water

c) Formation of hydrothermal, magma-derived fluids in correlation with HCl and H_2S from volcanic gases

d) Dissolution processes from saline interlayers

In the studied geothermal and oil reservoir fluids in Mexico, a general increase of ^{18}O (Fig. 4) and salinity concentrations can be observed with depth. On a regional scale, an isotopic gradient of 0.43‰ / 100m for $\delta^{18}O$ can be derived, which could reflect a general temperature and pressure related increase of the stable isotope composition ("Regional trend" in Fig. 4). Besides, vertical separation of the fluids by differences in density could represent an additional formation factor, as indicated by a similar linear increase of Cl with depth.

Any deviation from this linear trend must be due to additional local effects, which form the observed isotopic variety of each reservoir. Oil field waters are characterized by a wide range of isotopic values, which is mainly due to mixing processes between two components - meteoric water ("M" in Fig. 4) and evaporated seawater ("S" en Fig.

4). Figure 4 illustrates the end-member components for the Activo Luna (Birkle et al., 2002), Samaria-Sitio Grande and Pol-Chuc reservoir fluids. As end-member components are normally not preserved, the ^{18}O concentration of the meteoric and seawater component represent the observed maximum and minimum values, respectively. The dominance of mixing processes in Mexican oil reservoirs is also supported by a linear, positive correlation between the ^{18}O and Cl contents of oil field waters (Fig. 5).

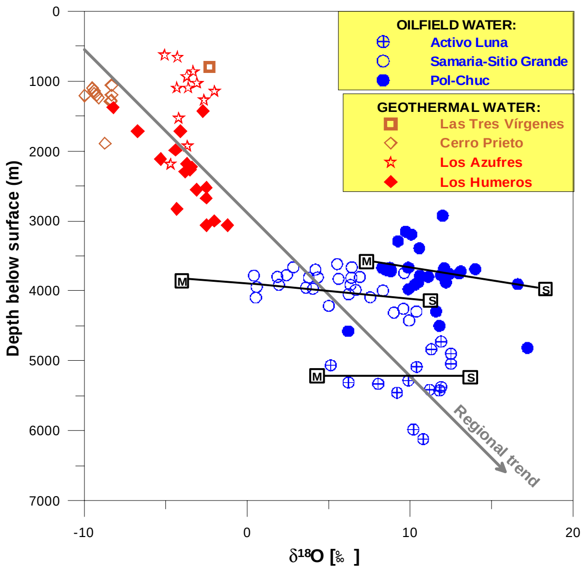

Figure 4: Depth related increase of δ^{18}O-values as a regional effect of deep formation water. Also shown are local processes, such as mixing between meteoric ("M") and evaporated seawater ("S") in petroleum reservoirs.

Dissolution processes from saline layers or salt domes can probably be excluded in the formation of hypersaline brines due to low Cl/Br-ratios, such as between 88 and 290 at the Pol-Chuc reservoir (Birkle, 2003), or ratios of 74 to 260 in Samaria-Sitio Grande. On the other hand, positive trends between Br and I concentrations of the mentioned oil field waters could indicate the partial breakdown of Br-rich organic matter and the posterior enrichment of the water phase with organic Br. Na/Cl ratios close to seawater composition (0.86) support the hypothesis of a non-dissolution origin of brine mineralization, as halite has a molar ratio of 1.0.

The lack of ^{18}O vs. Cl correlation tendencies for geothermal fluids reflects the minor effect of mixing processes in geothermal reservoirs (Fig. 6). In Los Humeros, the lower reservoir (depth > 2000 m) is characterized by a linear increase of δ^{18}O values with depth, which is also congruent to measured temperatures and geothermometers (Tovar & López, 1999). For the Los Humeros and Los Azufres reservoir, boiling processes of ascending fluids cause the formation of vapor- and liquid dominated reservoir zones, explaining a larger range in δ^{18}O-isotopic composition as observed in Cerro Prieto fluids (Fig. 6). The existence of convective flow systems explains, a) minor isotopic and chemical variations of geothermal liquids as observed for oil field waters, and b) the homogeneous distribution of NaCl-type water throughout the geothermal reservoir. Similarities between the Los Azufres and Las Tres Vírgenes geothermal fluids are reflected by the proposed mixture of about 70% of "fossil" meteoric water with 30% of a magmatic component (Birkle et al., 2001; Portugal et al., 2000a), whereas the primary mixing of seawater and Colorado river water (Truesdell et al., 1981) could explain the wider chemical range for Cerro Prieto fluids (Cl = 5,500 mg/l – 22,700 mg/l).

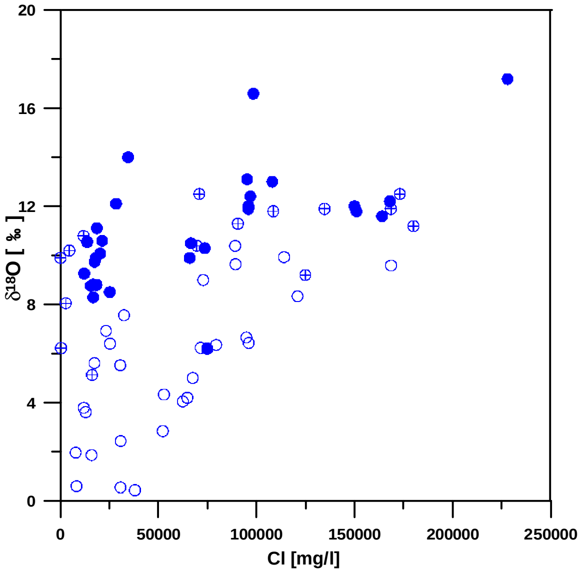

Figure 5: Linear tendencies between ^{18}O and Cl-concentrations for groundwater of the Activo Luna, Samaria-Sitio Grande and Pol-Chuc petroleum reservoirs. (Legend in Fig. 4).

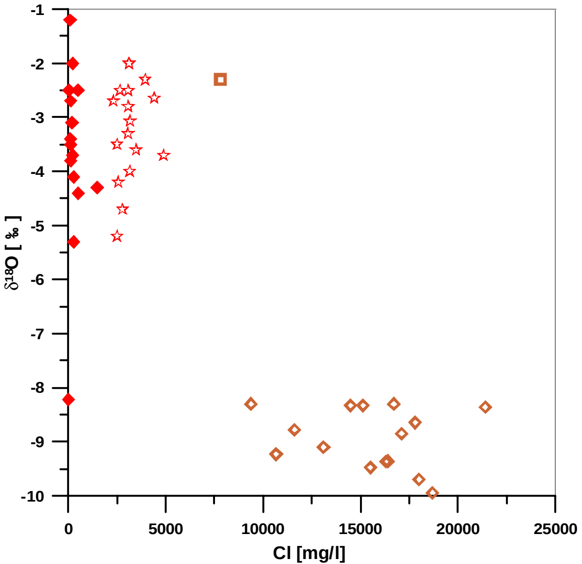

Figure 6: Correlation diagram between Cl and ^{18}O values for geothermal fluids from Las Tres Vírgenes, Cerro Prieto, Los Azufres and Los Humeros (Legend in Fig. 4).

4.3 Water-rock interaction

In the hypothetical case of water-rock interaction as the main formation process of reservoir fluids, a positive ^{18}O shift and constant deuterium values should be observed. However, all Mexican reservoirs are characterized by a positive trend of both stable isotopes (Fig. 7). In general, groundwater from Mexican geothermal reservoirs is more depleted in δ^{18}O and δD as in petroleum reservoirs, indicating cooler climatic conditions during recharge and/or less fractionation of primary seawater during evaporation at the surface. The isotopic evolution of oil field brines can be reconstructed, assuming an extreme reduction of up to 60 times of the initial seawater volume during evaporation, as shown by Pierre et al. (1984). A regressive trend during a process called "super-evaporation" explains – besides mixing processes with meteoric water - the broad range in

$\delta^{18}O$-values. Average δD ratios of -10‰ (range: -33.0‰ to +43.0‰) of oil field waters in comparison to recent, local meteoric water (δD = -21.0‰ to -45.3‰), indicate warmer climatic conditions in SE-Mexico during reservoir recharge. A general use of the terms "magmatic water" and "andesitic water", proposed by Giggenbach (1992) and Taran et al. (1989), should be avoided for deep crustal fluids: many samples from Mexican oil field brines are congruent in their $\delta^{18}O$ and δD composition to the "andesitic water type", but a thick sedimentary sequence of more than 10 km in the Mexican Gulf basin exclude the possibility of ascending andesitic water from a deep situated magma chamber. On the other hand, significant isotopic discrepancies between the standard "andesitic water type" and geothermal fluids reflect the limited contribution of magmatic fluids to explain formation and origin of Mexican reservoir fluids.

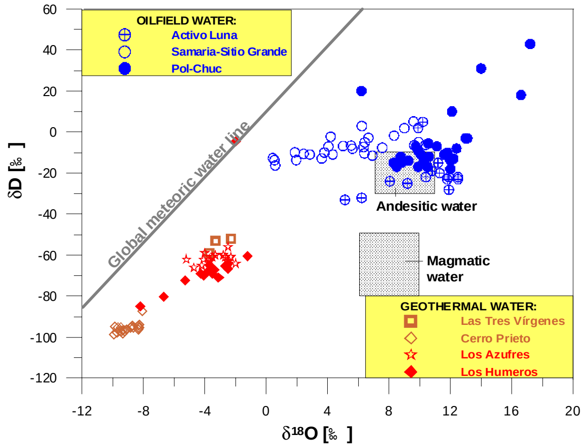

Figure 7: Correlation between $\delta^{18}O$ and δD ratios for geothermal and petroleum reservoir fluids in Mexico.

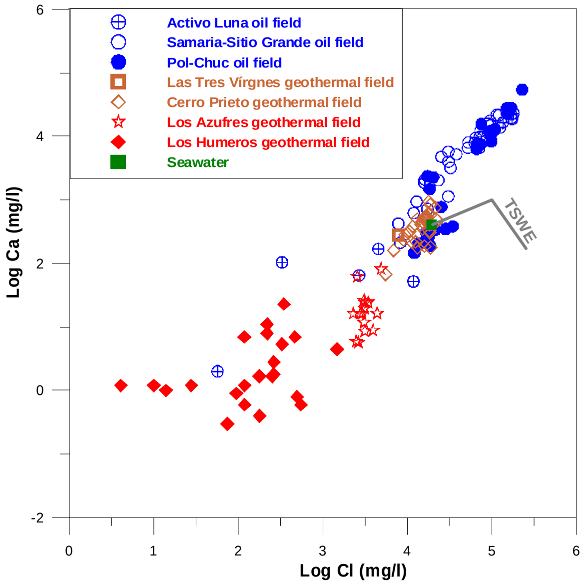

Figure 8: Seawater evaporation trajectory (TWSE) in terms of Cl^- and Ca^{++} .

The partial impact of dolomitization processes in Mexican oil field basins – although the NaCl water type remains dominating - is indicated by the simultaneous enrichment in Ca^{++} (Fig. 8) and depletion in Mg^{++} in comparison to the trajectory line of evaporating seawater (TSWE).

Some diluted Activo Luna petroleum field waters are close to the cationic composition of Los Humeros fluids. On the other hand, potassium concentrations of geothermal fluids above the evaporation trajectory reflect the addition of K^+ through water/rock interaction, perhaps as albitization of K-feldspar. Formation water from petroleum fields is – except minor enrichment of some Samaria Sitio-Grande samples – little affected by potassium exchange (Fig. 9).

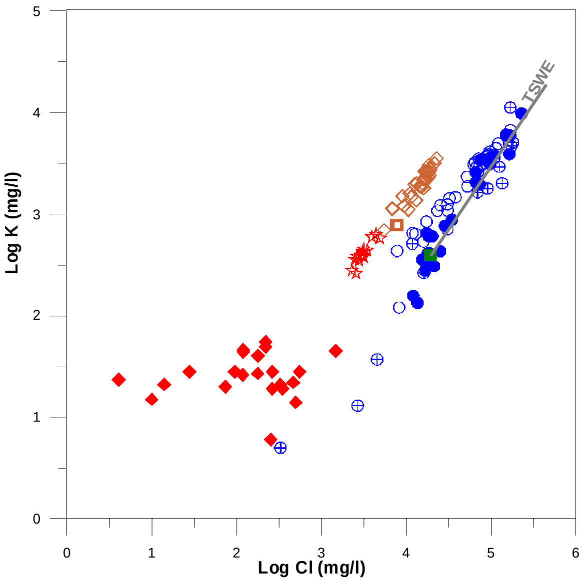

Figure 9: Seawater evaporation trajectory (TWSE) in terms of Cl^- and K^+ .

5. DISCUSSION

Although the geothermal reservoirs of Cerro Prieto, Las Tres Vírgenes and Los Azufres are formed by different geological host rocks (sedimentary vs. volcanic units) and by mixing of different end-member components - sea water and river water in Cerro Prieto (Truesdell et al., 1981) vs. magmatic and meteoric water in Las Tres Vírgenes (Portugal et al., 2000a) and Los Azufres (Birkle et al., 2001) - the parallelism in the chemical and isotopic tendencies of their reservoir fluids indicate the dominance of gravity, temperature and pressure-driven convection processes. The zoning of the Los Humeros reservoir into two isolated aquifers can explain the wider range in the chemical and isotopic composition of its formation fluids. On the other hand, no pure sample is available of lower reservoir Los Humeros water as it may have vapor only.

Concerning the origin of deep formation water in Mexico, age determinations of geothermal fluids with the ^{14}C-method are affected by dilution processes with magmatic CO_2, lowering the initial ^{14}C activity. Based on ^{14}C and tritium data, Truesdell et al. (1979) reported an average age between 50 and 10,000 years for the Cerro Prieto fluids. Birkle et al. (2001) proposed a Late Pleistocene and/or Early Holocene glacial period for the infiltration of meteoric water into the Los Azufres reservoir and its subsequent mixing with magmatic fluids.

A similar trend was observed for oil field waters from the Gulf of Mexico: The homogeneous distribution of ^{14}C activities (between 0.9 pmC and 28.2 pmC) indicate a common infiltration event at the Mexican Gulf coast during late Pleistocene (40,000 to 10,000 years). Meteoric water and seawater - previously concentrated by evaporation processes at the surface - recharged the Activo Luna (Birkle et al., 2002), Samaria-Sitio Grande (Birkle & Maruri, 2003) and Pol-Chuc (Birkle, 2003) reservoirs. Possibly, the fossil recharge event was related to major periods of increased humidity, such as observed for northern Mexico at the end of late Pleistocene (18-11 ka) and early Holocene (11-8.9

ka) (Ortega-Ramírez et al., 1998). In the Yucatan region, SE-Mexico, lake records indicate drier, glacial conditions from 18,000 to 12,000 yr BP and relatively wet conditions all over Mexico during early-mid Holocene (6000 yr BP) (Metcalfe et al., 2000). The meteoric and marine component of Mexican geothermal reservoirs - characterized generally by depleted ^{14}C-activities - could also be attributed to these interglacial infiltration events. Climatic changes could have caused the transgression of Gulf seawater over the plain coastal area in SE-Mexico, forming isolated lagoons with potential to evaporate stagnant seawater. Similar infiltration processes of meteoric water into reservoir zones during Pleistocene were observed in the Williston basin (Grasby & Betcher, 2000).

6. CONCLUSIONS

In comparison with formation water from oil reservoirs, geothermal fluids are characterized by small variations in their chemical and isotopic composition. These characteristics can be attributed to boiling and convective circulation processes - and of minor importance - by mixing of magmatic water (?) with infiltrating meteoric and/or marine water. On the other hand, the extremely heterogeneous composition of oil field water is related to, a) the infiltration and mixing of two or more components - meteoric water, seawater and/or evaporated seawater - during Late Pleistocene-Early Holocene periods under more humid climatic conditions, b) density driven separation processes with increasing reservoir depth, and, c) the partial dolomitization of carbonate host rock. Probably, major parts of deep groundwater systems in geothermal and petroleum reservoirs were recharged during late Pleistocene and/or early Holocene by meteoric water, and in the case of coastal oil reservoirs - additionally by seawater, previously evaporated at the surface. In none of the deep aquifer systems in Mexican petroleum and geothermal fields, a direct proof for the infiltration of recent surface water can be postulated.

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