

Reservoir equilibrium temperatures at the Ahuachapan and Berlin geothermal fields (El Salvador) constrained by the organic gas species composition

Tassi, F.¹, Vaselli, O.^{1,2}, Capaccioni, B.³, Montegrossi, G.², Barahona, F.⁴, Caprai, A.⁵

⁽¹⁾ Dept. of Earth Sciences, University of Florence, Via La Pira 4, Florence, 50121, Italy

⁽²⁾ CNR – Institute of Geosciences and Earth Resources, Via G. la Pira, 4, Florence, 50121, Italy

⁽³⁾ Dept. of Earth and Geological-Environmental Sciences, P.zza di Porta S. Donato, 40127 Bologna, Italy

⁽⁴⁾ Universidad de El Salvador, Boulevard de los Héroes, San Salvador.

⁽⁵⁾ CNR – Institute of Geosciences and Earth Resources, Via Moruzzi 1, 56124 Pisa, Italy

Introduction

The chemical composition of natural gas discharges in volcanic and hydrothermal systems is controlled by complex physical-chemical processes. In this respect, interactions between circulating thermal fluids and shallow environment, as well as inputs from external sources (e.g. radiogenic elements, air and bacterial activity) and boiling and steam condensation processes often play a fundamental role. **Gas scrubbing** can be regarded as any secondary physical-chemical process, comprehending dissolution into the aqueous phase and formation of precipitates (e.g., sulphur, sulfides, fluorides, sulfates) from either gas-water or gas-water-rock reactions, able to modify, at least partially the composition of the gas species in thermal fluids. When the chemical and isotopic features of fluid discharges are used to investigate thermochemical conditions governing the deep reservoirs, the influence of scrubbing has to be severely evaluated.

Main Aims

In a geothermal area the compositional differences between fluids from wells and natural gas vents are likely to be mainly related to the physical-chemical processes that may occur in the shallower part of the fumarolic conduits. As a consequence, the comparison between well and fumarolic gas chemistry has to be considered particularly useful to understand the effects that the shallow processes may have as deep fluids rise from the source area to the surface. Accordingly, the main goal of this study, based on the chemical data of the gas samples collected from both geothermal wells and fumaroles from Ahuachapan-Chipilapa and Berlin geothermal fields (El Salvador), is to evaluate the usefulness of light hydrocarbons as possible geo-indicators for volcanic and geothermal systems, since this group of gas species has similar chemical-physical features and, consequently, they are supposed to show similar behaviour in response to secondary processes.

Effects of scrubbing processes on gas composition

Among the possible secondary interactions able to modify the composition of the geothermal fluids, selective dissolution in water of the gas species rising along the fumarolic ducts, can be considered the most suitable physical-chemical process. To verify this hypothesis the analytical data of fumaroles from Berlin-Chinameca and Ahuachapan-Chipilapa geothermal fields were compared with the expected compositions produced by dissolution-driven fractionation in water of the geothermal fluids of the two areas. We calculated the composition of a residual gas produced by dissolution of a gas phase in water on the basis of the water-vapour distribution coefficients of each gas species with respect to that of CO₂ by the following equation:

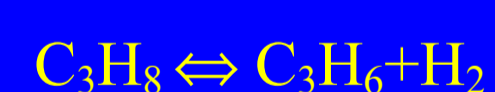
$$X_i/X_{CO_2} = X_{i,0}/X_{CO_2,0} / \{y[(1/S_{CO_2})-1]+1\}$$

where the variables are defined as follows: X_i, i-compound content after dissolution in water of the initial gas phase; X_{CO₂}, CO₂ content after dissolution in water of the initial gas phase; X_{i,0}, i-compound content of the initial gas phase; X_{CO₂,0}, CO₂ content of the initial gas phase; S_i, water-vapour distribution coefficient of the i-compound; S_{CO₂}, water-vapour distribution coefficient of CO₂; y, gas fraction dissolved in water.

The values of X_{i,0} and X_{CO₂,0} are taken from the mean composition of the production wells of Ahuachapan-Chinameca and Berlin-Chinameca geothermal fields, which in our model represents the initial gas phases that could be affected by dissolution during their uprise through the shallow aquifers. Starting from the selected initial gas compositions, two different series of theoretical compositions (lines A-C and B-C for the Ahuachapan-Chipilapa and Berlin-Chinameca geothermal fields, respectively), are produced by substituting in the reported equation increasing y values (ranging from 0 to 0.8) to simulate increasing gas-water interaction (Figure 2a-d). The S_i/S_{CO₂} ratio remains almost constant at temperature ≥ 100 °C, thus the solubility data used to solve equation of dissolution are those at 100 °C.

Geothermometry based on alkanes/alkenes

De-hydrogenation reaction of the C₃ alkene-alkane pair is given by:



As shown in the log(C₃H₆/C₃H₈) vs. temperature diagram (Figure 5) (where temperature values are those calculated with the C₁-C₂-C₃ alkane geothermometer, since alkanes and alkenes pertain to the same compositional sub-system and are supposed to be produced by a common source), geothermal gases are clustered in a narrow area at higher oxidizing conditions even than those of the HM redox buffer, suggesting that: i) the alkenes-alkanes reaction is able to control the C₃H₆/C₃H₈ ratios; ii) the C₃H₆-C₃H₈ couple equilibrates at redox conditions that are to be considered unusual for geothermal systems. Magmatic-related fluid inputs may be invoked to justify the redox conditions of the Ahuachapan-Chipilapa and Berlin-Chinameca geothermal systems. Accordingly, the high C₃H₆-C₃H₈ ratios of Laguna Alegria (LA) and Oyon Crater (OC), which represent the most recent craters of the Tecapa-Berlin volcanic system, are possibly due to particularly conspicuous addition of highly-oxidizing hot fluids, whose occurrence is also supported by both the presence of oxygen-substituted hydrocarbons (C₃H₄O and C₃H₆O), typically produced at high temperature, and the relatively high H₂ and CO contents.

The C₃H₆/C₃H₈ log-ratios in the fumaroles and the geothermal wells are in the same range. Therefore, the C₃H₆-C₃H₈ geothermometer, as well as that of the C₁-C₂-C₃ alkanes, seems to be not significantly affected by secondary processes occurring along the fumarolic pathways, likely due to the minimum difference between the molecular volumes of these two compounds (C₃H₆/C₃H₈ molecular volume ratio = 0.91).

The Ahuachapan-Chipilapa geothermal field is located in western El Salvador between the Santa Ana volcanic complex and the Guatemala border (Figure 1). It lies within the 6-km-wide Pleistocene caldera of Concepcion de Ataco that is part of the Apaneca volcanic complex (also known as the Cuyanausol Range) consisting of roughly E-W oriented Pleistocene and Holocene stratovolcanoes. The post-caldera cones of Cerro El Aguila (2036 m a.s.l., the highest peak of the complex) and Cerro Los Naranjos volcanoes, at the eastern end of the Apaneca Range, and the young craters of Laguna Verde stratovolcano may have been active during the Holocene. The tectonic structure is controlled by E-W, associated to the Central American graben, and NE-SW trending fault systems. The geothermal field, which is characterized by numerous hot springs, bubbling pools and fumaroles, is the largest one under exploitation in El Salvador. Its heat source seems to be related to the presence of an andesite-basalt magmatic chamber (0.1 Ma) located at the depth of 9 km. Geophysical measurements suggest that Ahuachapan and Chipilapa can be regarded as two distinct hydrothermal systems, separated by a hydrological barrier resulting by an uplift structure. Nevertheless, the chemical and isotopic features of the geothermal fluids of the two areas seem to indicate the existence of a common deep reservoir.

Effects of scrubbing processes on organic gases

The fumarolic and the geothermal well discharges are characterized by the presence of many different hydrocarbons. Besides of methane, C₂-C₉ normal-alkanes and their isomers, C₂-C₄ alkenes, C₆-C₈ aromatics and several heterocyclics and S-substituted hydrocarbons are present. Among this variegated group of organic gas species, hydrocarbons pertaining to the same structural series show regular compositional variations in response to secondary processes. As shown in Figure 2a-d, where the theoretical compositional trends for the dissolution model are also reported (lines A-C and B-C), the C₂-C₈ normal-alkanes contents of the fumarolic gases are less abundant than those of the geothermal wells. It must be underlined that this is exactly the contrary of what expected following the dissolution-driven mechanism. Similar results can also be obtained by considering the iso-alkanes and aromatics series (here not reported). This clearly indicates that the fractionation of normal-alkanes along the fumarolic ducts likely depends on a chemical-physical process not related to gas dissolution in water. Tentatively, the molecular dimension of each gas compound, which constitutes the main distinctive parameter for structurally homologous hydrocarbons, can be taken into account. Actually, the values of the (mean fum)/(mean well) ratios for the C_n-C_{n+1} pairs of the normal-alkanes are inversely correlated (R² = 0.88) with the C_n/C_{n+1} molecular volume ratios (Figure 3). Moreover, this secondary process practically has the same effects [(mean fum)/(mean well) ≈ 1] on hydrocarbons characterized by almost equal molecular volumes (C_n/C_{n+1} molecular volume ratio > 0.82). Such results can be explained when considering that, as shown by the Stokes-Einstein equation, diffusion coefficients of non-dissociating solutes in dilute solutions are mainly regulated by their molecular volumes.

Therefore, the diffusion process seems to represent the main parameter controlling the fractionation of iso-structural hydrocarbons in fumarolic fluids during their uprise from the geothermal reservoirs to the surface. Accordingly, several studies have emphasized the role of diffusion as a mechanism able to control the compositional changes of light hydrocarbon (C₂-C₇ alkanes) in natural gases migrating from source to reservoir-type rocks.

The Berlin geothermal field (Figure 1), located 100 km east of San Salvador at an elevation between 600 and 900 m a.s.l., is associated to the Pleistocene Tecapa-Berlin volcanic complex that consists of a series of peripheral volcanic cones emerging around the Berlin caldera. The latter formed after the final activity (0.1 Ma) of the old Berlin volcano, which is characterized by basaltic to andesitic lava flows and scoria and andesitic to dacitic ignimbrites, and is marked by a NE-SW oriented fault system and a NNW-SSE transverse fault, along which several hot fluid discharges are aligned. Geophysical investigations suggest that the heat source of the Berlin geothermal field is a recent andesite magma chamber that lies at a depth of about 6 km, south of the present geothermal field where the most recent volcanic edifices (El Hoyon and Cerro de Alegria) are located. At Berlin the maximum temperature measured in the geothermal wells, that reach a depth of 2300 m, was up to 305 °C.

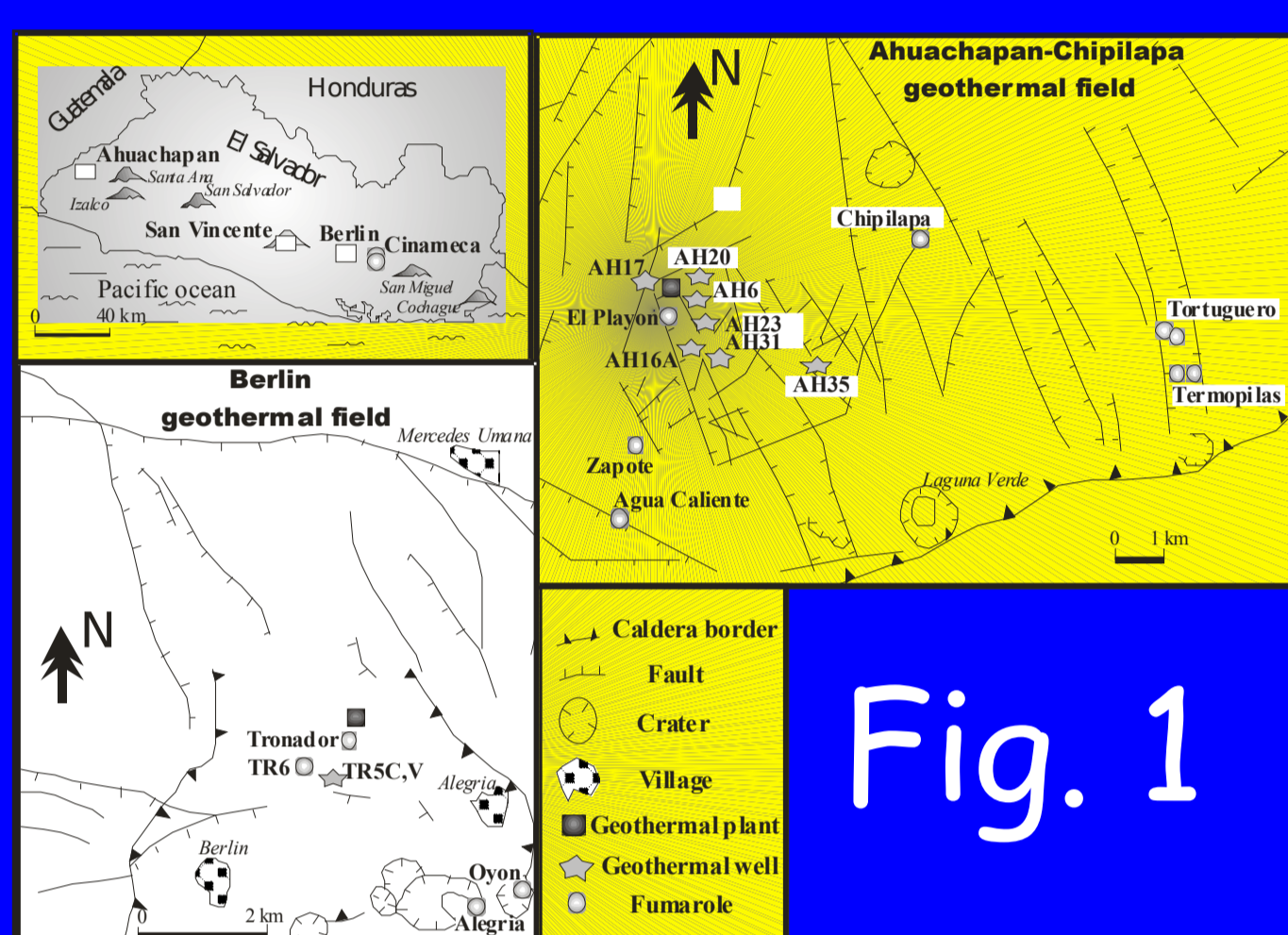


Fig. 1

Geothermometry based on alkanes

The C₁-C₂-C₃ alkanes are thermodynamically controlled, by the following pressure-independent equilibrium reaction:



As shown by the log(CH₄/C₂H₆) vs. log(C₂H₆/C₃H₈) diagram (Figure 4), geothermal gases plot within the isotherms 220-260 °C of the CH₄-C₂H₆-C₃H₈ equilibrium, in agreement with the temperatures measured at depth ranging from 1500 to 2400 m in the Berlin geothermal field, and slightly higher than those found in the Ahuachapan-Chipilapa geothermal field at shallower depth (600-1500 m). Gases from both fumaroles and geothermal wells are in the same range of equilibrium temperatures, although hydrocarbon contents in fumaroles are strongly affected by secondary interactions. Actually, the effects of gas diffusion which seems to represent the main process able to control the (mean fum)/(mean well) ratios of the iso-structural hydrocarbons of geothermal fluids rising through shallow aquifers, are to be considered negligible for the (CH₄/C₂H₆)/(C₂H₆/C₃H₈) log-ratios since the CH₄/C₂H₆ and the C₂H₆/C₃H₈ molecular volume ratios are very similar (0.65 and 0.72, respectively). Differently, the CH₄/C₂H₆ and C₂H₆/C₃H₈ log-ratios, considered separately, are significantly higher in the fumaroles (triangles; Figure 4) than in the geothermal wells (circles; Figure 4), depending on the largely different molecular volumes of CH₄, C₂H₆ and C₃H₈ (42.1, 65.1 and 90.5, respectively).

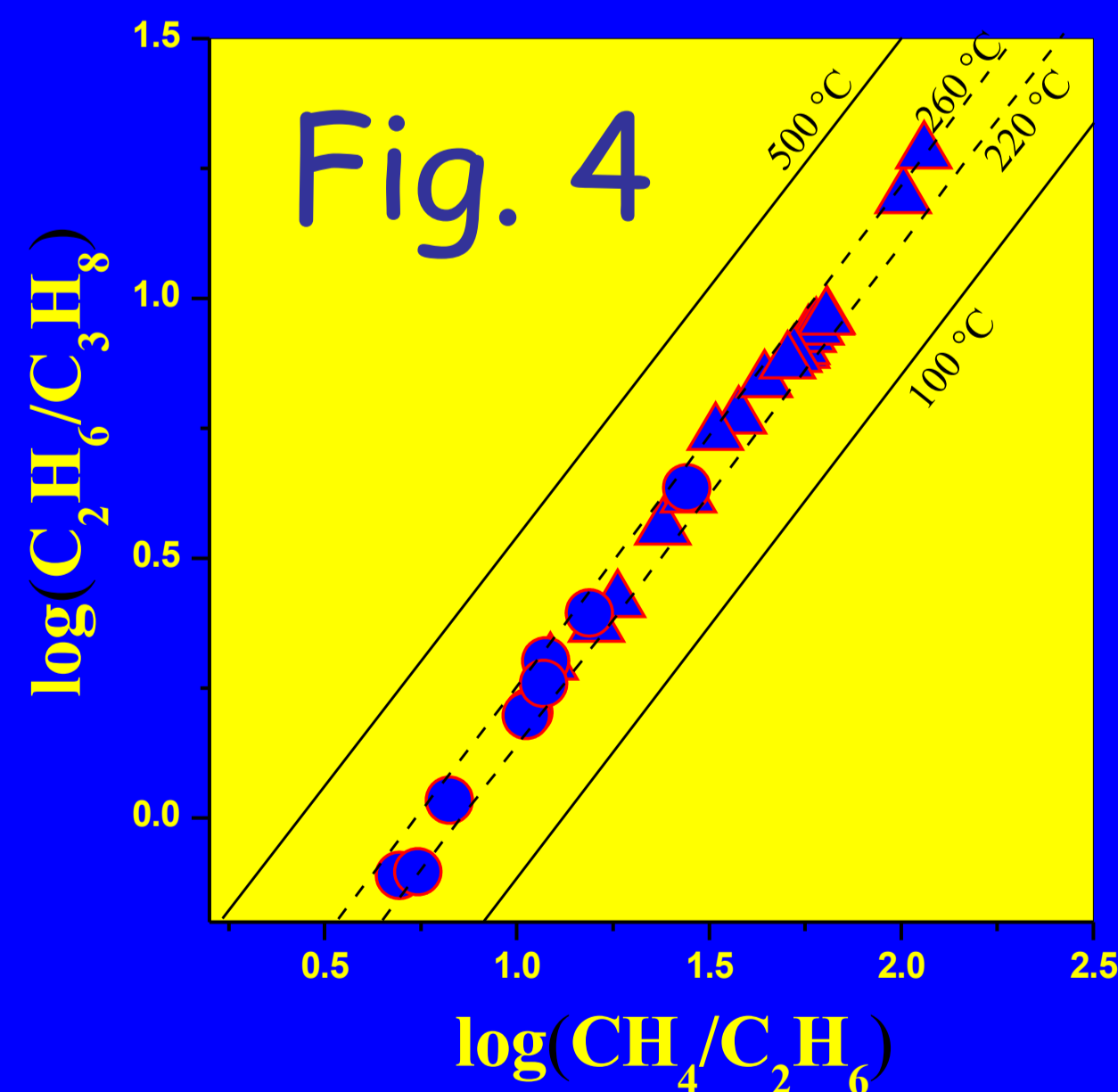


Fig. 4

Among the possible chemical reactions involving the C₄ unsaturated-saturated pairs, de-hydrogenation of the iso-C₄ alkane to form the iso-C₄ alkene can be considered:



As shown in Figure 6, the i-C₄H₈/i-C₄H₁₀ ratio, as that of the C₃-C₃ alkane-alkene pair, seems to be established at relatively high oxidizing conditions, although gas samples are significantly scattered along the y axis, possibly due to the fact that this alkene-alkane reaction has not attained thermodynamic equilibrium in the considered temperature range. The molecular volumes of the two iso-C₄ hydrocarbons are indeed almost identical, thus we can hypothesize that the diffusion process is not able to significantly affect the i-C₄H₈/i-C₄H₁₀ ratio. Nevertheless, it seems not reasonable that two almost identical chemical processes, i.e., the de-hydrogenation reactions of the C₃ and the C₄ alkane-alkene pairs, can show a distinct thermodynamic response. Consequently, the interaction between the two C₄-isomers, i-C₄H₈ and n-C₄H₁₀, remains the most likely mechanism able to explain the gas distribution shown in Figure 6.

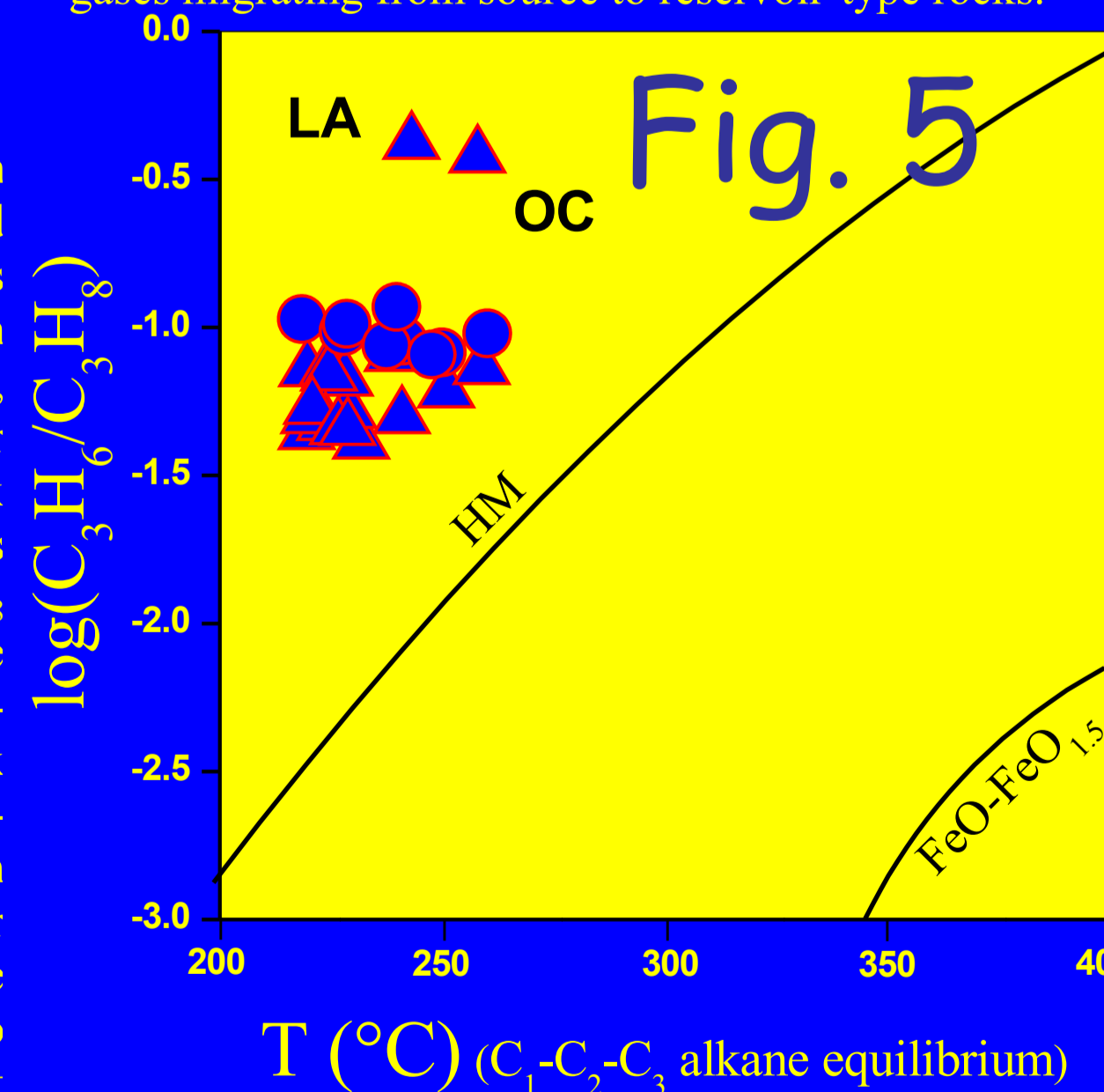


Fig. 5

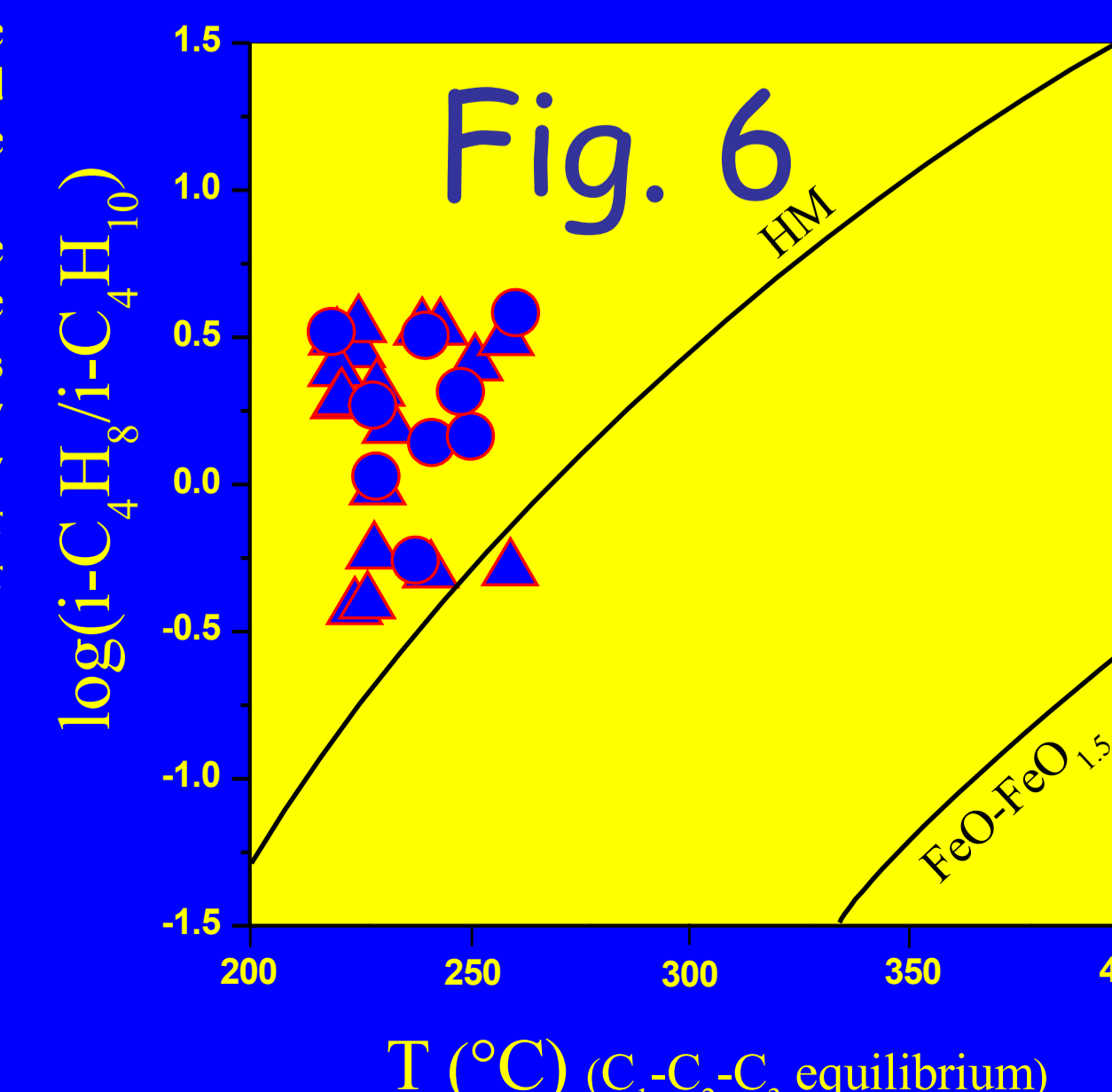


Fig. 6

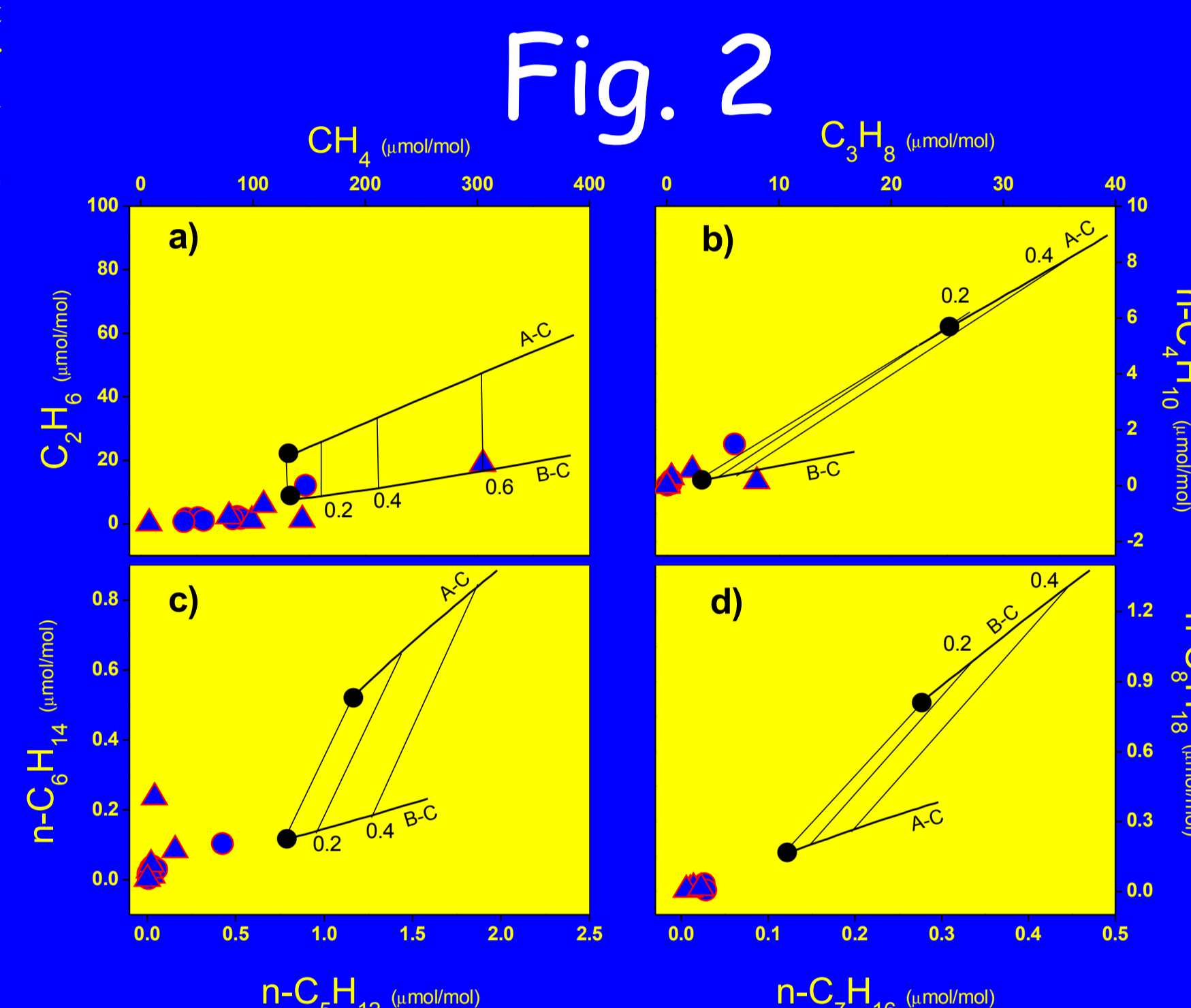


Fig. 2

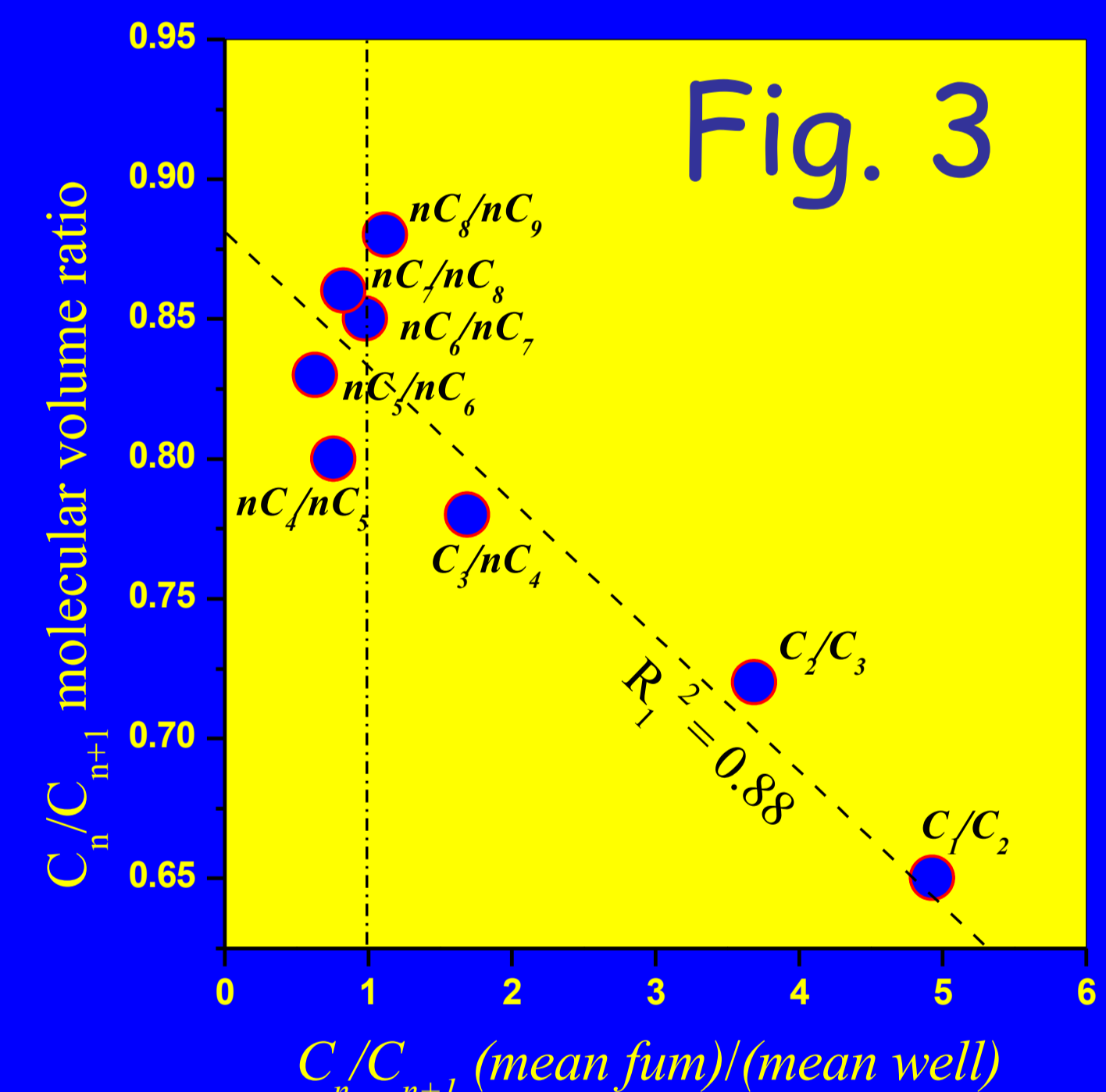


Fig. 3

Conclusions

The composition of naturally discharging fluids from fumaroles of Ahuachapan-Chipilapa and Berlin-Chinameca geothermal fields, when compared to that of the geothermal wells of the same areas, have shown that: 1) organic gases of geothermal fluids are significantly depleted at relatively shallow depth by scrubbing processes (i.e. dissolution in shallow aquifers); 2) the relative abundances of the structurally homogeneous gases pertaining to the C₂-C₉ normal-alkane, iso-alkane and aromatic series in response to secondary interactions appear to be mainly regulated by the diffusion velocity of gases through shallow aquifers, a parameter that is function of the molecular volume of each gas species; 3) the thermochemical equilibrium of reactions among hydrocarbons characterized by similar molecular dimensions and structure, i.e., the C₃-C₃ and the C₄-C₄ alkane-alkene pairs, as well as the very rare metastable equilibrium of the chemical reaction among the C₁-C₂-C₃ alkanes, whose behaviour is commonly that of a non-reversible process, seems to be attained. Therefore, the chemical equilibria among light hydrocarbons can constitute a useful tool to provide reliable estimations of geothermal reservoir temperature and dominating redox conditions, especially during the exploration phase of promising areas for geothermal resources and for the geochemical monitoring of active volcanoes, where only natural gas emissions are available.