



Scrubbing process and chemical equilibria controlling the composition of light hydrocarbons in natural gas discharges: An example from the geothermal fields of El Salvador

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[1] The compositional features of fluids from both fumarolic discharges and productive geothermal wells of Ahuachapan-Chipilapa, Berlin-Chinameca, and San Vicente geothermal systems (El Salvador) are described and discussed in order to investigate the complex geochemical interactions involving geothermal fluids within the shallowest part of the hydrothermal circulation pathways. Our results highlight that secondary processes are able to strongly affect and modify the chemical characteristics of geothermal gases once they discharge to the surface as natural manifestations, mainly in relation to the chemical-physical properties of each gas species. The effects of both gas dissolution in shallow aquifers and gas-water-rock chemical interactions on gas discharge composition make it difficult to get a correct evaluation of the thermodynamic conditions that characterize the geothermal reservoirs by applying the common geoindicators based on the chemical equilibria of the $\text{H}_2\text{O}-\text{CO}_2-\text{H}_2-\text{CH}_4-\text{CO}$ system. Differently, the composition of the $\text{C}_1-\text{C}_2-\text{C}_3$ alkanes and the C_3 and C_4 alkane-alkene pair, established within the geothermal reservoirs under the control of chemical reactions, remains stable in samples collected from discharging gas vents. These results suggest that the relative abundances of hydrocarbons characterized by similar structure and molecular size seem to be mainly regulated by the diffusion velocity of gases through the liquid-dominated system. Therefore the chemical features of the light organic gas fraction of naturally discharging fluids can be successfully utilized for the evaluation of geothermal reservoir temperatures and redox conditions, providing useful indications in terms of geothermal exploration and exploitation. On this basis, the distribution, speciation, and relative abundances of light hydrocarbons can also be considered highly promising in geochemical monitoring of active volcanic systems.

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1. Introduction

[2] The chemical composition of natural gas discharges in volcanic and hydrothermal systems is controlled by complex physical-chemical processes [e.g., *Giggenbach*, 1997]. 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 [e.g., *Giggenbach*, 1980; *Giggenbach et al.*, 1986; *Chiodini and Marini*, 1998], often play a fundamental role. Several geochemists [e.g., *Ellis and Mahon*, 1977; *Armannson et al.*, 1982; *Hedenquist and Lowenstern*, 1994] agree that hydrothermal systems are able to completely dissolve magmatic-related gas compounds producing acidic fluids and promoting strong hydrothermal alteration, which is at the base of the mineral/ore forming processes. Generally speaking, gas scrubbing can be regarded as any secondary physical-chemical process, comprehending dissolution into the aqueous phase and formation of precipitates (e.g., sulfur, 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 [e.g., *Symonds et al.*, 1994, 2001]. The effects of this phenomenon were first recognized by *Doukas and Gerlach* [1995] to explain low SO₂ emissions before and between the 1992 eruption of Crater Peak at Mount Spurr. Reaction path modeling has been used to describe magmatic gas scrubbing taking place during interactions of magmatic gas with air-saturated water and rock [*Symonds et al.*, 2001; *Marini and Gambardella*, 2005].

[3] Whatever the conceptual model adopted, these studies have stressed the importance that the influence of secondary interactions can assume for the chemical features of natural discharging fluids, especially those related to hydrothermal systems.

This suggests that, when the chemical and isotopic features of fluid discharges are used to investigate thermochemical conditions governing the deep reservoirs, the influence of secondary processes has to be severely evaluated. Geothermometers based on equilibrium reactions involving gas species, e.g., CO₂-CH₄-H₂-H₂S [*D'Amore and Panichi*, 1980; *Arnosson and Gunnlaugsson*, 1985], CO₂-CH₄ [*Giggenbach*, 1996; *Taran*, 1986], CO₂-CO [*Chiodini et al.*, 2001] and H₂-Ar [*Giggenbach*, 1991], commonly adopted to calculate reservoir temperatures in geothermal areas, are able to provide reliable results especially when gases from deep wells, like those used for the exploitation of geothermal energy that allow a rapid up-flow of fluids toward the surface without significant interactions with the surrounding environment, are considered. Nevertheless, in active volcanoes and hydrothermal systems these artificial gas conduits are rarely present. This can represent a serious limitation for both geochemical investigations of geothermal resources [e.g., *D'Amore and Nuti*, 1977; *Bertrami et al.*, 1985; *Arnosson*, 1990; *D'Amore*, 1991] and geochemical monitoring of active volcanoes [e.g., *Menyailov*, 1975; *Giggenbach*, 1987; *Marini et al.*, 1991; *Chiodini et al.*, 1993].

[4] In a geothermal area the compositional differences between fluids from wells and natural gas vents, which have the same source but characterized by different fluid pathways, 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. According to these considerations, the main goal of this study, based on the chemical data of the gas

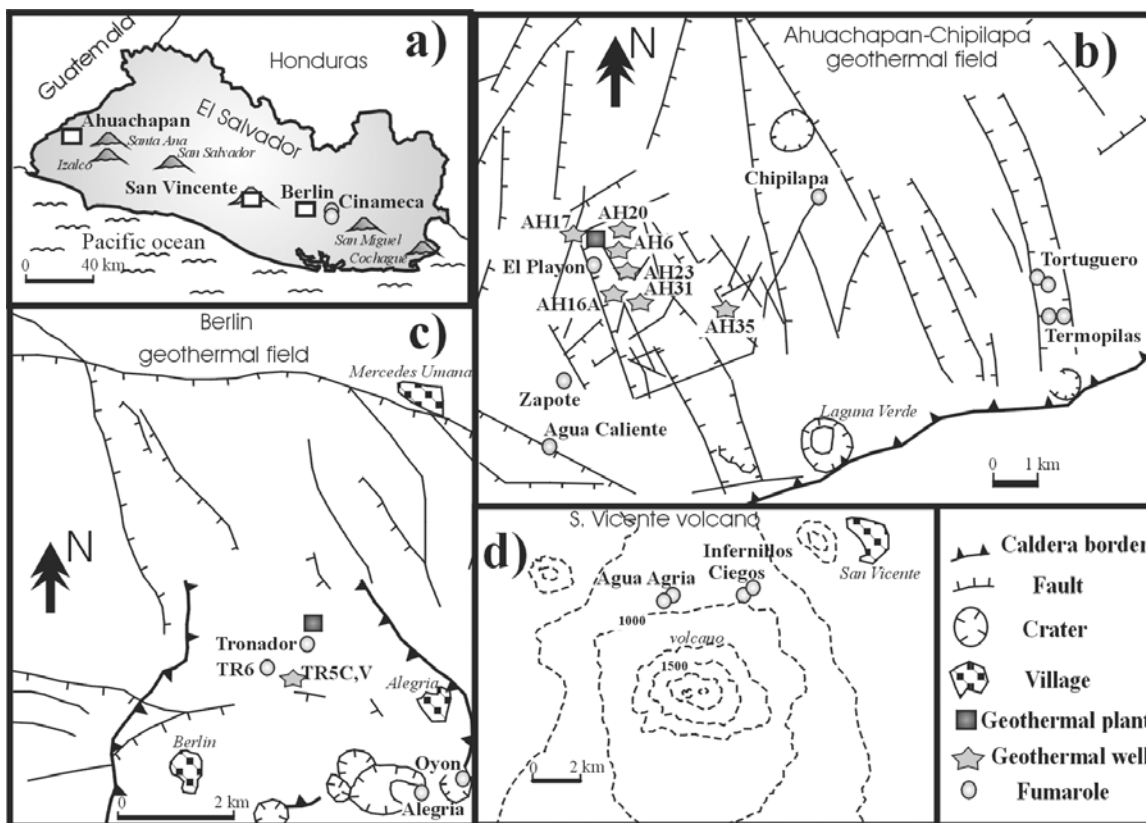


Figure 1. Schematic maps of (a) El Salvador, (b) Ahuachapan-Chipilapa geothermal field, (c) Berlin geothermal field, and (d) San Vicente volcano. The location of the gas sampling sites is also reported.

samples collected from both geothermal wells and fumaroles from Ahuachapan-Chipilapa, Berlin, Chinameca and San Vicente geothermal fields (El Salvador) (Figure 1), is to evaluate the effects of secondary processes on the chemical composition of naturally discharging gases in hydrothermal environment. A particular attention is devoted to verify the usefulness of light hydrocarbons as possible geo-indicators for volcanic and geothermal systems [e.g., Tassi *et al.*, 2005a, 2005b], since this group of gas species has similar chemical-physical features and, consequently, they are supposed to show similar behavior in response to secondary processes.

2. General Features of the Geothermal Systems of El Salvador

2.1. Geothermal Energy Exploitation Activity

[5] The exploration of geothermal resources in El Salvador commenced in 1954 and is still on, although it was suspended because of the 1980–1992 civil war [Huttrer, 2001]. Within the framework of this activity, ten geothermal areas,

characterized by medium-to-high temperature (180–300°C) fluids, have been identified [Monterrosa, 1998]. Geothermal energy production in the Ahuachapan-Chipilapa geothermal field, located approximately 80 km west of San Salvador, started in 1975. Forty wells have been drilled (590 to 1524 m deep) in an area of approximately 5 km², but presently only 8 wells, able to produce up to 63 MW, are in continuous operation [Jacobo, 2003]. Geothermal exploration at the Berlin field started in 1976 [Cuellar, 1981] and developed in 1978–1981, when five wells were drilled. Since 1992, when two 5 MW backpressure power units were installed, the Berlin geothermal field has continuously been exploited. From 1997 to 1999, 18 wells (8 producers and 10 injectors), at depth between 1500 and 2400 m, were drilled and a power plant was constructed, for a total geothermal capacity of 56 MW. After 2000, four wells were drilled in the southern part of the geothermal field in order to assess the possibility of installing a third power unit of 28 MW [Renderos, 2002]. Presently, the geothermal plants installed in El Salvador are able to produce about 161 MW (95 MW from Ahuachapan-Chipilapa and 66 MW from Berlin), accounting for the 24% of the coun-

try electricity output [Rodríguez and Herrera, 2003]. San Vicente geothermal system, close to the homonymous volcano (Figure 1a), has been discovered only in the late 1970s, with the drilling of an exploration well and few shallow boreholes. Further geophysical (gravimetric and geoelectric) investigations have allowed to estimate an energy production of about 50 MW [Huttrer, 2001].

2.2. Geology Overview and Chemistry of the Geothermal Fluids

[6] El Salvador is a seismologically active region of the southern-east coast of Central America, where the Cocos plate is subducting under the Caribbean plate at rates of 92 mm/yr along the Middle America Trench that is located 100 km offshore [Schmidt-Thomé, 1975; Weber, 1978; Bourgois et al., 1984]. Parallel to this trench runs the Central American graben, a 20-km-wide E-W oriented tectonic depression that in the southern part borders a Quaternary volcanic chain (Figure 1a), whose magmas likely represent the heat source of the widespread geothermal activity in the region. The location of the four distinct geothermal areas (Ahuachapan-Chipilapa, Berlin, Chinameca and San Vicente) the present study is referred to, is reported in Figures 1a–1d.

[7] The Ahuachapan-Chipilapa geothermal field (Figure 1b) is located in western El Salvador between the Santa Ana volcanic complex and the Guatemala border (Figure 1a). 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 [Gonzales Partida et al., 1997]. The volcanic sequence of the Concepcion de Ataco caldera, whose volume approaches about 63 km³ [Gonzales Partida et al., 1997], is composed by basaltic andesites to dacitic-ryolitic [Aumento et al., 1982] alternated layers of tuff, lava and pyroclastic sequences [Montalvo, 1994]. 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 [Gonzales Partida et al., 1997], 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 [Jacobo, 2003]. Geophysical measurements suggest that Ahuachapan and Chipilapa can be regarded as two distinct hydrothermal systems [Romo et al., 1997], separated by a hydrological barrier resulting by an uplift structure [Gonzales Partida et al., 1997]. Nevertheless, the chemical and isotopic features of the geothermal fluids of the two areas seem to indicate the existence of a common deep reservoir. When the exploitation activity commenced, fluids were characterized by a temperature of about 230–260°C with chloride contents up to 9000 mg/L [D'Amore and Mejia, 1999]. As the geothermal exploitation proceeded the chemical features of the main reservoir significantly changed, as testified by the compositional evolution of the geothermal wells that suffered (1) a decrease of the Cl contents down to about 6000 mg/L, (2) an increase of SO₄ contents, and (3) an increase of CO₂, H₂S and H₂ partial pressures [Truesdell et al., 1989; Nieva et al., 1997; Jacobo, 2003].

[8] The Berlin geothermal field (Figure 1c), 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 [Jacobo, 2003], 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; Figure 1c) are located [D'Amore and Mejia, 1999]. At Berlin, the chemical-physical conditions of the reservoir are quite different with respect to those of the Ahuachapan-Chipilapa field. The maximum temperature measured in the geothermal wells, that reach a depth of 2300 m, was up to 305°C [Montalvo and Axelsson, 2000]; Cl contents, when the exploitation activity started, were up to 11,000 mg/L [D'Amore and Mejia, 1999]. Furthermore, reinjection has been adopted since the beginning of the geothermal energy production, while at Ahuachapan-Chipilapa no fluid reinjection

has presently been performed. Reinjecting fluids strongly affected both the chemical and the isotopic parameters of the Berlin geothermal reservoir. Chloride contents progressively lowered down to about 3000–7000 mg/L [Montalvo and Axelsson, 2000; Jacobo, 2003], while the $\delta^{18}\text{O}$ and δD isotopic ratios were intermediate between those of the local recharge meteoric water and the reinjected water [Renderos, 2002].

[9] Chinameca, a relatively small geothermal area located few tens of km east of the Berlin caldera (Figure 1a), is marked by the presence of fumaroles, locally named “Infernillos de Chinameca,” suggesting the presence of hot fluids at depth, but no geothermal exploration have been carried out and little is known about its geological and structural settings. In the present study we will be referring to the Berlin-Chinameca geothermal field as a unique system, although the two areas are likely characterized by distinct hydrothermal reservoirs.

[10] San Vicente is a Quaternary stratovolcano (2183 m a.s.l.) (Figure 1d), located in the central region of El Salvador (Figure 1a), which rises inside the Pliocene Central American graben. Its activity started in the Tertiary with mild and episodic emissions of tholeiitic lavas. In the Pleistocene several paroxysmic events took place, leading to the collapse of the old edifice, known as La Carbonera, and giving rise to the formation of the caldera structure [Barberi *et al.*, 1995]. The modern San Vicente volcano grew during the Holocene within the caldera. Its edifice consists of two prominent cones that are largely composed of andesite lava flows. On the basis of their morphology, the easternmost cone appears to be the youngest, suggesting that the focus of volcanism has migrated east-northeastward with time. No historical eruptions have been recorded from this apparatus, although volcano-related events, like lahars, have occurred several times (e.g., in 1774, 1934, 1996 and 2001) [Major *et al.*, 2001]. A preliminary investigation carried out by the Salvadorian State Agency for Electric Power indicated a relatively high geothermal gradient ($0.2^\circ\text{C}/\text{m}$), suggesting the presence of a hydrothermal reservoir at a depth ranging between 1100 and 1300 m, characterized by a temperature of about 250°C , consistent with that estimated on the basis of the chemistry of the fumarolic fluids [Aiuppa *et al.*, 1997]. Presently, a moderate fumarolic activity, whose physical-chemical features are almost identical to those of the fumaroles seeping out at Ahuachapan-Chipilapa and Berlin-Chinameca geothermal fields, is present in two areas (Agua

Agria and Infernillos Ciegos, respectively) along the northern and western flanks of the volcano (Figure 1d) [Aiuppa *et al.*, 1997].

3. Sampling and Analytical Methods

[11] Gas samples were collected during two sampling campaigns carried out in February and April 2004 at (1) Ahuachapan-Chipilapa (8 fumaroles and 7 geothermal wells), (2) Berlin-Chinameca (6 fumaroles and 2 geothermal wells), and (3) San Vicente (4 fumaroles) geothermal areas (Figures 1a–1d). Gas samples from the geothermal wells were collected as separated steam from an industrial separator where gas pressure was about 7 bars. Gases were stored into pre-weighted and pre-evacuated 50-mL Thorion-tapped pyrex tubes, containing 20 mL of a 0.15M $\text{Cd}(\text{OH})_2$ and 4M NaOH suspension. Acidic gases (CO_2 , HF and HCl) and water vapor were dissolved into the alkaline solution, H_2S reacted with Cd^{2+} and precipitated as CdS, while residual gases were collected in the headspace. Separate aliquots of condensate were devoted to the analysis of Cl and F. Inorganic gas compounds were analyzed by acidimetric titration (CO_2), ion chromatography (Cl, F, SO_2 , H_2S) and gas chromatography (N_2 , O_2 , CO, H_2 , He, Ar and Ne), following the procedure described by Montegrossi *et al.* [2001]. To obtain a satisfactory separation of H_2 , He and Ne peaks a 10 m long molecular sieve column, at the temperature of 0°C and using Ar as gas carrier, was utilized. The organic gas fraction (CH_4 , C_2 - C_9 hydrocarbons, $\text{C}_4\text{H}_4\text{O}$, $\text{C}_4\text{H}_4\text{S}$, $\text{C}_5\text{H}_6\text{O}$, $\text{C}_5\text{H}_6\text{S}$ and $(\text{CH}_3)_2\text{S}$) was analyzed by gas chromatography. The complete separation of the peaks of the 30 different organic gas compounds was performed by using 2 different chromatographic columns: (1) a 10 m long stainless steel column ($N = 2$ mm) packed with Chromosorb PAW 80/100 mesh coated with 23% SP 1700, for the determination of C_1 - C_5 hydrocarbons, and (2) a 2.5 m long stainless steel column ($N = 2$ mm) packed with Chromosorb PAW 100/120 mesh coated with 10% TCEP, for the determination of C_6 - C_9 hydrocarbons [Tassi *et al.*, 2004].

[12] Analytical precision is $<5\%$ for major gas components and $<10\%$ for minor and trace compounds.

4. Results

4.1. Gas Temperature and Composition of the Inorganic Gas Fraction

[13] The outlet temperatures, the H_2O contents and the composition of the inorganic gases (dry gas

Table 1. Chemical Composition of the Dry Gas Fraction (Inorganic Gases) and Outlet Temperatures of the Fumaroles and the Geothermal Wells From the Ahuachapan-Chipilapa, Berlin-Chinameca, and San Vicente Geothermal Fields^a

	Name	Location	T, °C	CO ₂	H ₂ S	N ₂	Ar	O ₂	Ne	H ₂	He	CO	H ₂ O
1	El Playon	Ahuachapan	99.4	828,965	1,266	157,977	852.8	992.1	0.561	9,988	4.196	1.189	992,930
2	Chipilapa	Ahuachapan	99.7	948,492	2,954	46,294	92.18	1,463	0.056	698.6	8.170	1.216	996,116
3	Agua caliente M2	Ahuachapan	99.2	952,606	31,180	15,587	160.8	7.184	0.096	486.4	5.044	<0.001	988,168
4	Zapote	Ahuachapan	101.7	893,874	4,608	91,500	620.4	6,563	0.406	2,799	18.36	1.117	995,991
5	Termopilas hervideros	Ahuachapan	94.7	932,148	2,551	59,118	670.3	1,199	0.432	4,324	10.52	1.831	993,760
6	Termopilas fumarola	Ahuachapan	100.5	943,767	4,610	47,607	367.2	59.31	0.237	3,454	9.324	1.960	995,987
7	El Tortuguero hervideros	Ahuachapan	93.0	951,050	10,320	35,114	118.4	1,444	0.066	1,912	4.725	1.745	988,377
8	Tortuguero Fumarola	Ahuachapan	98.9	964,609	5,868	25,935	92.29	1,154	0.050	2,352	2.792	1.568	995,617
9	Tronador	Berlin	99.4	952,288	10,394	34,780	215.1	206.5	0.135	2,169	5.658	1.536	997,917
10	TR6	Berlin	98.0	950,342	7,810	35,210	427.8	3,940	0.281	2,345	1.148	0.838	997,600
11	Laguna Alegria	Berlin	98.5	947,452	36,090	12,821	32.76	285.7	0.024	3,310	8.227	1.570	975,351
12	Oyon Crater	Berlin	97.7	955,221	31,323	8,290	28.11	52.45	0.022	5,070	2.266	2.676	976,027
13	Infernillos Cinameca hervideros	Cinameca	98.0	935,358	13,938	48,797	335.2	207.3	0.229	1,491	1.294	1.324	998,353
14	Infernillos Cinameca Fumarola	Cinameca	99.4	759,627	2,400	229,598	1621	818.9	1.071	5,980	6.094	1.428	997,786
15	Infernillos Ciegos Hervideros	San Vicente	92.0	970,656	11,973	13,606	213.7	1,068	0.132	2,464	1.519	0.792	993,572
16	Infernillos Ciegos Fumarole	San Vicente	101.7	936,944	9,587	43,708	535.0	2,472	0.336	6,802	4.629	1.897	997,345
17	Agua Agria hervideros	San Vicente	92.0	950,054	9,063	35,302	290.8	3,039	0.188	2,246	6.261	1.390	986,917
18	Agua Agria Fumarole	San Vicente	100.0	960,139	5,335	30,162	153.7	65.64	0.100	4,173	5.583	1.520	996,885
19	AH 6	Ahuachapan	150	949,868	18,866	27,934	176.4	<0.001	n.d.	3,199	2.051	3.691	997,817
20	AH 16A	Ahuachapan	150	960,005	16,519	22,695	216.2	27.03	n.d.	573.0	<0.001	1.535	996,297
21	AH 17	Ahuachapan	150	983,283	7,709	8,693	75.86	<0.001	n.d.	332.1	2.936	2.235	995,057
22	AH 20	Ahuachapan	150	979,935	13,027	6,482	34.70	<0.001	n.d.	492.2	<0.001	1.574	995,922
23	AH 23	Ahuachapan	150	971,160	3,912	24,320	68.79	<0.001	n.d.	501.7	7.823	1.446	995,885
24	AH 31	Ahuachapan	150	982,287	8,722	8,426	93.20	<0.001	n.d.	441.6	2.031	2.491	995,664
25	AH 35	Ahuachapan	150	966,018	15,030	18,330	132.9	8.638	n.d.	352.5	5.842	0.947	996,527
26	Berlin 5V	Berlin	180	971,785	11,926	14,810	112.4	<0.001	n.d.	1,481	<0.001	0.864	997,017
27	Berlin 5C	Berlin	180	982,343	9,429	7,430	58.73	<0.001	n.d.	811.9	2.514	0.774	996,778

^aOutlet temperatures are in °C. Gas contents are in $\mu\text{mol/mol}$.

fraction) of the fumarolic discharges and the geothermal wells from the three El Salvador geothermal fields are reported in Table 1.

[14] The fumarolic outlet temperatures range in a narrow interval (between 92 and 101.7°C) close to the temperature of boiling water at atmospheric pressure, while the temperatures of the Ahuachapan-Chipilapa and Berlin-Chinameca geothermal wells, measured at the outlet of the water-steam separator, were about 150 and 180°C, respectively, which are significantly lower than those measured at well bottoms [D'Amore and Mejia, 1999] likely due to steam-liquid separation process.

[15] H₂O is largely the dominant component (up to 998,377 $\mu\text{mol/mol}$) in both the fumaroles and the geothermal wells, whereas the dry gas fraction is

mainly represented by CO₂ (between 759,627 and 983,283 $\mu\text{mol/mol}$) and H₂S (up to 36,090 $\mu\text{mol/mol}$), as typically occurs for geothermal fluids [e.g., Giggenbach, 1980, 1991]. Among the residual gases, N₂ (up to 229,598 $\mu\text{mol/mol}$) and H₂ (up to 9,988 $\mu\text{mol/mol}$) are the most abundant compounds, O₂ and Ar contents show large variations (between <0.001 and 6,563 and 28.11 and 1,621 $\mu\text{mol/mol}$, respectively), while only minor contents of He (up to 18.36 $\mu\text{mol/mol}$) and CO (up to 3.691 $\mu\text{mol/mol}$) were measured. The relatively low Ne contents (1.071 $\mu\text{mol/mol}$) seem to exclude any significant air-contamination during the gas sampling. The composition of our geothermal gases from both Ahuachapan-Chipilapa and Berlin-Chinameca geothermal fields is consistent

with those reported by *Renderos* [2002] and *Jacobo* [2003].

4.2. Origin of Steam and Inorganic Gases

[16] The geothermal reservoirs are mainly recharged by meteoric water, although, the $\delta^{18}\text{O}$ and δD values of steam from the geothermal wells [e.g., *Nieva et al.*, 1997; *Montalvo and Axelsson*, 2000; *Renderos*, 2002] suggest that a significant contribution of andesitic water [*Taran et al.*, 1989; *Giggenbach*, 1992] cannot be ruled out [*D'Amore and Mejia*, 1999]. The presence of a deep component is also supported by the carbon ($\delta^{13}\text{C}$ in CO_2) and helium isotopic composition, whose values are between -1.5 and -2.8 ‰ PDB-V [*Snyder et al.*, 2001, 2003] and 5 and 7 (as $\text{R}/\text{R}_{\text{air}}$) [*Snyder et al.*, 2001], respectively. The N_2/Ar ratios are generally higher (up to 502) than that of the air (83.6), consistent with those reported by *D'Amore and Mejia* [1999] and *Jacobo* [2003], and suggest a considerable contribution of non-atmospheric N_2 , as commonly observed in fluids discharging in areas located along convergent plate boundaries [*Giggenbach*, 1996]. Differently, the Ar/Ne ratios, approaching those of ASW (Air Saturated Water: 1,700 to 940 for pure water at temperature ranging from 20 to 80°C), indicate that the atmospheric-related compounds are added to the hydrothermal systems as dissolved phases in the meteoric-originated water recharging the geothermal reservoirs. The O_2/Ar ratios (between 0 and 15.87) are significantly lower than that of ASW (≈ 20), and this is likely related to O_2 -consumption by redox reactions among gas species and during water-rock interaction.

4.3. Composition of the Organic Gas Fraction

[17] The organic fraction composition (dry gas fraction) of fumarolic and geothermal well discharges is reported in Table 2.

[18] Up to 25 different hydrocarbons were detected and quantified. Among the alkanes, methane is the most abundant compound (between 7.64 and $839.5 \mu\text{mol}/\text{mol}$), while ethane (up to $68.47 \mu\text{mol}/\text{mol}$), propane (up to $86.94 \mu\text{mol}/\text{mol}$) and the C_4 - C_9 normal- and iso-alkanes progressively decrease as the molecular size increases. A similar behavior is also shown by the relative abundances of benzene (up to $9.135 \mu\text{mol}/\text{mol}$), toluene (up to $2.06 \mu\text{mol}/\text{mol}$), xylene (the sum of its meta- and para-isomers; up to $0.452 \mu\text{mol}/\text{mol}$) and ethylbenzene (up to $0.329 \mu\text{mol}/\text{mol}$), all pertaining to

the aromatics group. Iso-butene and propene are by far the most abundant alkenes (up to 23.13 and $9.257 \mu\text{mol}/\text{mol}$, respectively), while traces of trans-2-butene and cis-2-butene were detected only in few cases (Table 2). Besides the C-H species, five further organic gas compounds, dimethylsulfide, thiophene, methyl-thiophene, furane and methyl-furane, were detected in some gas samples, although in very low amounts ($\leq 0.068 \mu\text{mol}/\text{mol}$; Table 2).

4.4. Origin of the Organic Gases

[19] The presence of many different organic gas compounds, which is consistent with the compositional characteristics observed in other hydrothermal systems [e.g., *Capaccioni et al.*, 1993, 2004; *Tassi*, 2004; *Tassi et al.*, 2005a, 2005b], can be regarded as a peculiar feature for geothermal fluids. Organic matter ("kerogen") is likely the main hydrocarbon source [e.g., *Gunter*, 1978; *Des Marais et al.*, 1981; *Mango*, 2000], since abiotic synthesis from inorganic constituents contributing to hydrocarbon production at hydrothermal conditions, though possible [e.g., *Berndt et al.*, 1996; *Horita and Berndt*, 1999], can be regarded as negligible [e.g., *Welhan*, 1988; *Darling*, 1998; *Mango*, 2000; *Taran and Giggenbach*, 2003]. The ratio between CH_4 and light hydrocarbons can provide some useful information on the temperature conditions characterizing the genetic process of these compounds. The $\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$ ratio ranges between 2 and 108 and indicates that the hydrocarbons are thermogenically produced ($T > 150^\circ\text{C}$) [e.g., *Oremland et al.*, 1987; *Whiticar and Suess*, 1990]. This implies that (1) the organic matter evolved at depth, possibly within the geothermal reservoirs, and (2) no significant contribution by bacterial activity, which typically occurs in shallow environments at $T < 50^\circ\text{C}$ generating almost pure CH_4 [*Hunt*, 1984], was added to the geothermal fluids.

[20] The previously mentioned presence of sulfur-substituted hydrocarbons in some of our gas samples can be considered a common feature for natural gases [e.g., *Mangani et al.*, 2004], these compounds being easily produced in presence of H_2S even at low-to-medium temperatures. Differently, the two relatively unstable oxygen-substituted heterocyclic, furane and methyl-furane, that were detected only in two fumaroles of the Berlin-Chinameca geothermal field (Laguna Alegria and Oyon Crater gas samples; Table 2), are rarely found in geothermal gases being typical of fuma-

Table 2. Chemical Composition of the Dry Gas Fraction (Organic Gases) in the Fumaroles and the Geothermal Wells From the Ahuachapan-Chipilapa, Berlin-Chinameca, and San Vicente Geothermal Fields^a

Name	Location	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₃ H ₆	i-C ₄ H ₁₀	n-C ₄ H ₁₀	i-C ₄ H ₈	t-2-C ₄ H ₈	c-2-C ₄ H ₈	i-C ₃ H ₁₂	n-C ₃ H ₁₂	2,3-dimethyl-C ₄ H ₁₀
1	El Playon	147.1	12.04	6.070	0.369	0.432	1.478	1.104	<0.0001	<0.0001	0.1189	0.4271	0.1911
2	Chipilapa	40.67	1.696	0.470	0.019	0.140	0.153	0.219	<0.0001	<0.0001	0.0023	0.0314	0.0023
3	Agua caliente M2	86.39	2.284	0.387	0.019	0.115	0.060	0.058	<0.0001	<0.0001	0.0035	0.0098	0.0014
4	Zapote	51.07	1.823	0.438	0.023	0.406	0.191	0.394	<0.0001	<0.0001	0.0196	0.0208	0.0113
5	Termopilas hervideros	89.66	1.624	0.206	0.015	0.035	0.034	0.111	<0.0001	<0.0001	0.0243	0.0545	0.0101
6	Termopilas fumarola	82.10	1.490	0.186	0.013	0.027	0.047	0.077	<0.0001	<0.0001	0.0191	0.0236	0.0061
7	El Tortuguero hervideros	56.14	0.981	0.116	0.008	0.057	0.019	0.033	<0.0001	<0.0001	0.0019	0.0062	0.0047
8	Tortuguero Fumarola	38.66	0.645	0.074	0.005	0.010	0.013	0.036	<0.0001	<0.0001	0.0075	0.0167	0.0062
9	Tronador	99.03	0.979	0.063	0.005	0.019	0.068	0.064	<0.0001	<0.0001	0.0190	0.0283	0.0357
10	TR6	78.30	2.384	0.435	0.032	1.502	0.303	0.771	0.0587	0.0209	0.0203	0.0132	0.0061
11	Laguna Alegria	144.0	1.256	0.066	0.025	0.005	0.006	0.015	<0.0001	<0.0001	0.0061	0.0229	0.0100
12	Oyon Crater	7.639	0.174	0.025	0.011	0.002	0.002	0.007	0.0013	<0.0001	0.0009	0.0015	0.0009
13	Infernillos Cinameca hervideros	109.5	5.977	2.286	0.100	0.199	0.563	0.487	0.0116	<0.0001	0.0858	0.1571	0.0160
14	Infernillos Cinameca Fumarola	304.7	18.87	8.047	0.379	0.743	0.167	0.282	<0.0001	<0.0001	0.0340	0.0433	0.0202
15	Infernillos Ciegos Hervideros	293.8	4.581	0.499	0.025	0.037	0.054	0.070	0.0264	<0.0001	0.0064	0.0124	0.0172
16	Infernillos Ciegos Fumarole	839.5	13.165	1.440	0.077	0.102	0.169	0.199	<0.0001	<0.0001	0.0138	0.0355	0.0313
17	Agua Agria hervideros	45.19	0.859	0.111	0.005	0.039	0.018	0.015	<0.0001	<0.0001	0.0035	0.0058	0.0018
18	Agua Agria Fumarole	123.4	2.434	0.324	0.015	0.022	0.045	0.047	<0.0001	<0.0001	0.0009	0.0056	<0.0001
19	AH 6	217.4	43.83	56.60	5.083	7.208	11.743	9.973	0.0216	0.0070	1.5721	2.5428	0.1039
20	AH 16A	379.7	68.47	86.94	9.257	7.031	18.047	23.13	<0.0001	<0.0001	2.5973	4.4334	0.0446
21	AH 17	56.18	5.213	3.272	0.317	0.395	0.767	0.731	<0.0001	<0.0001	0.0351	0.0525	0.0093
22	AH 20	57.08	5.379	3.419	0.350	1.808	1.467	1.921	<0.0001	<0.0001	0.2404	0.3339	0.0159
23	AH 23	187.9	28.06	25.935	2.126	1.661	6.973	2.417	<0.0001	<0.0001	1.5306	1.6752	0.0850
24	AH 31	14.84	1.244	0.621	0.059	0.180	3.762	0.689	<0.0001	<0.0001	0.0320	0.0498	0.0061
25	AH 35	88.63	7.526	4.155	0.360	1.722	4.532	0.949	<0.0001	<0.0001	0.0590	0.1521	0.0109
26	Berlin 5V	151.5	9.789	3.951	0.319	1.373	0.999	2.828	<0.0001	<0.0001	0.1099	0.2541	0.0094
27	Berlin 5C	113.7	4.094	0.950	0.111	0.527	1.769	1.691	0.0035	<0.0001	0.0434	0.0925	0.0034

^a Gas contents are in μmol/mol.

Table 3. Mean Contents, Standard Deviations, and Molecular Volumes of the Fumaroles and the Geothermal Wells From the Ahuachapan-Chipilapa, Berlin-Chinameca, and San Vicente Geothermal Fields for Selected Gas Species^a

	Molecular Volume	(<i>mean well</i>)	Std. Dev. Wells	(<i>mean fum</i>)	Std. Dev. Fumaroles	(<i>mean fum</i>)/(<i>mean well</i>)
H ₂ S	43.4	11,624	4,723	11,129	10,630	0.96
CO ₂	42.9	966,572	11,396	924,319	53,074	0.96
N ₂	38.7	15,389	8,190	53,736	55,852	3.49
Ar	32.0	107.1	58.24	377.9	389.0	3.53
H ₂	26.5	906	927.3	3432	2349	3.79
He	23.8	2,565	2,700	5,847	4,140	2.28
CO	39.5	1,720	0,940	1,414	0,560	0.82
CH ₄	42.1	140.4	111.4	145.7	190.2	1.04
C ₂ H ₆	65.1	19.26	23.00	4,058	5,220	0.21
C ₃ H ₈	90.5	20.63	30.92	1,178	2,230	0.06
n-C ₄ H ₁₀	116.4	5,545	5,870	0,188	0,350	0.03
n-C ₅ H ₁₂	144.9	1,144	1,520	0,051	0,100	0.04
n-C ₆ H ₁₄	174.4	0,622	0,540	0,044	0,050	0.07
n-C ₇ H ₁₆	204.9	0,125	0,152	0,009	0,014	0.07
n-C ₈ H ₁₈	237.4	0,069	0,068	0,006	0,009	0.08
n-C ₉ H ₂₀	271.2	0,026	0,027	0,002	0,004	0.09
i-C ₄ H ₁₀	114.9	2,429	2,720	0,216	0,376	0.09
i-C ₅ H ₁₂	141.3	0,727	0,948	0,021	0,031	0.03
i-C ₆ H ₁₄	170.2	0,257	0,178	0,011	0,020	0.03
i-C ₇ H ₁₆	200.7	0,178	0,135	0,002	0,004	0.01
i-C ₈ H ₁₈	232.3	0,169	0,145	0,002	0,003	0.01
i-C ₉ H ₂₀	240.8	0,066	0,048	0,001	0,002	0.01
C ₆ H ₆	119.3	3,171	2,760	1,609	1,490	0.51
C ₇ H ₈	149.7	0,534	0,623	0,063	0,050	0.12
m-p-C ₈ H ₁₀	178.5	0,130	0,133	0,011	0,010	0.09
C ₃ H ₆	82.4	1,996	3,170	0,063	0,116	0.03
i-C ₄ H ₈	101.9	4,917	7,400	0,221	0,299	0.04

^aMean contents are in $\mu\text{mol/mol}$, standard deviations are in $\mu\text{mol/mol}$, and molecular volumes are in cm^3/mol . Definitions: (*mean fum*), fumaroles; (*mean well*), geothermal wells. Mean contents were calculated on the basis of the composition of the dry gases. The (*mean fum*)/(*mean well*) ratios were also reported.

rolic emissions in active volcanic systems [Tassi, 2004; Capaccioni *et al.*, 2005].

5. Effects of Scrubbing Processes on Gas Composition

5.1. Inorganic Gas Compounds

[21] A first evaluation of the possible influence of scrubbing processes on the contents in the fumaroles of the main inorganic gas compounds (CO₂, H₂S, N₂, Ar, H₂, He and CO), as the fumarolic fluid migrates up to the surface, can be carried out by comparing the mean contents of each gas species in the fumaroles (*mean fum*) with those in the geothermal wells (*mean well*). It is worthy to point out that the composition of the whole analyzed gas species, which are constrained to a “closure” to 1,000,000 $\mu\text{mol/mol}$, are dramatically affected by the constant sum problem [e.g., Chayes, 1960; Meisch, 1969]. Consequently, the behavior of H₂O, which practically only depends

on vapor-liquid distribution during retrograde boiling of rising fluids at decreasing pressure conditions, is able to strongly control the contents of the other gas constituents being by far the most abundant compound. Therefore the (*mean fum*)/(*mean well*) ratios of inorganic gas compounds (Table 3) are more conveniently referred to the dry gas fraction. O₂, whose presence is likely related to near-surface air contamination, was not considered in the present discussion. As shown in Figure 2, the values of the (*mean fum*)/(*mean well*) ratio indicate that CO₂ and H₂S contents in the fumaroles are slightly lower than those of the geothermal wells, while CO seems, although at limited extent, depleted along the fumarolic pathways. On the contrary, N₂, Ar, H₂ and He contents are strongly enriched in the fumaroles. Moreover, all the inorganic gas species, with the only exception of CO, are characterized by standard deviation values of the fumaroles significantly higher than those of geothermal wells (Table 3). This compositional scattering observed for the fumarolic discharges

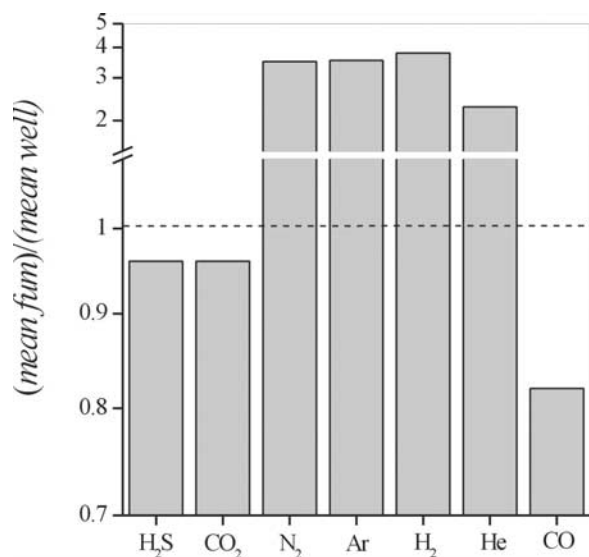


Figure 2. Histograms of the $(\text{mean fum})/(\text{mean well})$ ratios of CO₂, H₂S, N₂, Ar, H₂, He, and CO. Gas compositions are referred to the dry gas fraction.

is likely to be ascribed to the influence of secondary processes affecting the uprising fluids. 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. Actually, the presence of aquifers overlying the geothermal reservoirs at both Berlin [Montalvo and Axelsson, 2000] and Ahuachapan-Chipilapa [Rodriguez et al., 1997] geothermal systems was evidenced. These relatively cold aquifers likely interact with the fumarolic fluids at very shallow depth, as also supported by the outlet temperature of the fumaroles (<101.7 °C), which are close to the boiling point of water at 1 atm. 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. Similarly to what described by Chiodini et al. [1996], who calculated the composition of a CO₂-rich gas phase separated in a single step from a liquid phase, we calculated the composition of a residual gas produced by dissolution of a gas phase in water on the basis of the water-vapor distribution coefficients of each gas species with respect to that of CO₂ by the following equation:

$$X_i/X_{CO_2} = X_{o,i}X_oX_{o,CO_2}/\{y \cdot [(1/S_i/S_{CO_2}) - 1] + 1\} \quad (1)$$

where the variables are defined as follows: X_i , i -compound content after dissolution in water of the initial gas phase; X_{CO_2} , CO₂ content after dissolution in water of the initial gas phase; $X_{o,i}$, i -compound content of the initial gas phase; X_{o,CO_2} , CO₂ content of the initial gas phase; S_i , water-vapor distribution coefficient of the i -compound; S_{CO_2} , water-vapor distribution coefficient of CO₂; y , gas fraction dissolved in water.

[22] The values of $X_{o,i}$ and X_{o,CO_2} are taken from the mean composition of the production wells of Ahuachapan-Chinameca (samples 19–25; Table 1) and, separately, Berlin-Chinameca (samples 26–27 Table 1) geothermal fields, which in our model represents the initial gas phases that could be affected by dissolution during their uprising 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) (Figures 3a–3f), are produced by substituting in equation (1) increasing y values (ranging from 0 to 0.8) to simulate increasing gas-water interaction. When the mean compositions of the Ahuachapan-Chipilapa and the Berlin-Chinameca production wells do not significantly differ, lines A–C and B–C, are coincident (Figures 3a and 3b). The S_i/S_{CO_2} ratio remains almost constant at temperature $\geq 100^\circ\text{C}$ [Chiodini et al., 1996], thus the solubility data used to solve equation (1) are those at 100°C [Lide, 2001].

[23] As shown in Figures 3a–3c, where CO₂ versus N₂ (a), Ar (b) and He (c) contents are reported, at least part of the fumarolic gases tends to fit the theoretical compositions resulting from the selective dissolution process, suggesting that gas inputs from different sources, such as air dissolved into the shallow aquifers, are likely to be significant. Differently, CO contents measured in all the fumaroles are strongly lower than the expected abundances (Figure 3d), possibly because CO behavior, at slightly acidic condition, is controlled by the CO-HCOOH reaction [Shock, 1993], and this can explain the low standard deviation value in the fumaroles ($0.56 \mu\text{mol/mol}$; Table 3) with respect to that of the geothermal wells ($0.94 \mu\text{mol/mol}$; Table 3). On the contrary, H₂S (Figure 3e) and H₂ (Figure 3f) seem to be in excess with respect to the dissolution trends, possibly in relation with the production of these reduced gas species during gas-water-rock interactions at relatively high temperatures, as typically occurs in volcanic-hydrothermal environment [e.g., Giggenbach, 1980, 1987, 1996].

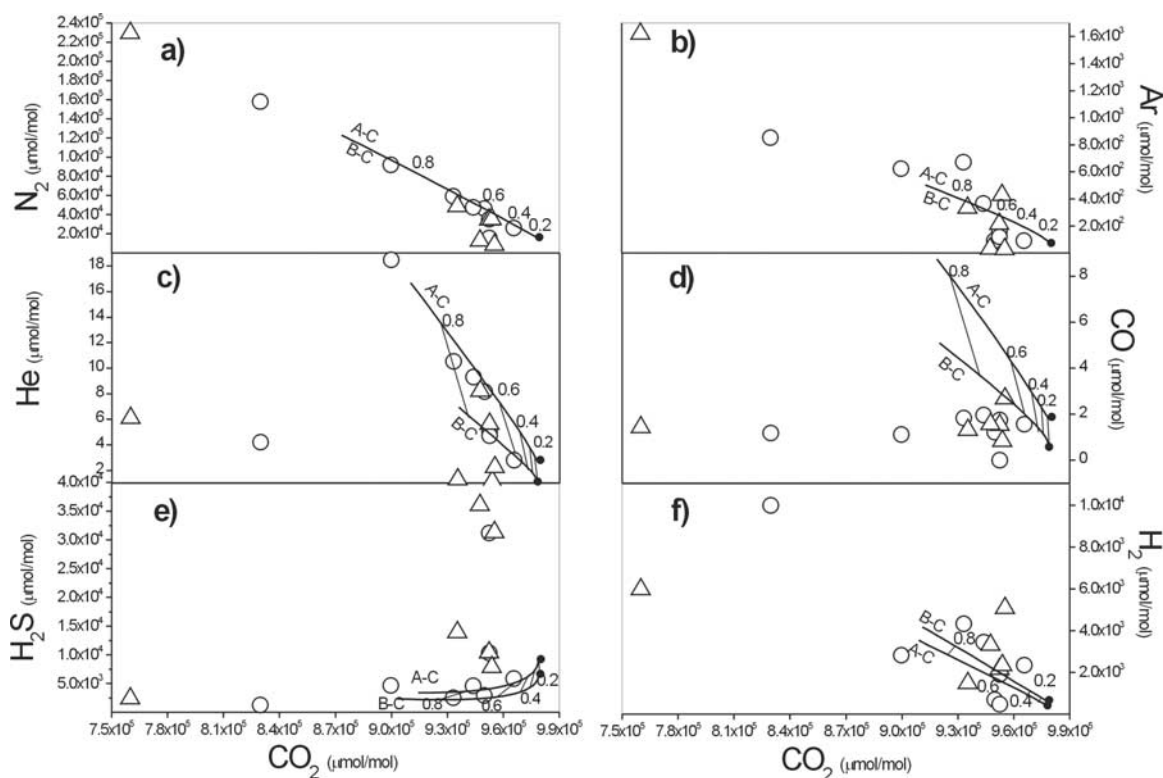


Figure 3. Binary diagrams of CO₂ versus (a) N₂, (b) Ar, (c) He, (d) CO, (e) H₂S, and (f) H₂ contents (dry gas fraction) in fumaroles from the Ahuachapan-Chipilapa and Berlin-Chinameca geothermal fields. Expected compositions (A-C and B-C lines for Ahuachapan-Chipilapa and Berlin-Chinameca, respectively) produced by dissolution-driven fractionation process acting on geothermal fluids of the two areas are also reported.

[24] Summarizing, the simple model of selective gas dissolution in water seems to be able to describe, at least at first approximation, the effects of scrubbing processes on fumarolic fluids only for CO₂, whose chemical reactivity, in CO₂-rich geothermal fluids rising through CO₂-saturated environment at slight acidic conditions dominating the shallower hydrothermal pathways of these geothermal fields [D'Amore and Mejia, 1999; Jacobo, 2003], is relatively low, and those gas compounds that are chemically inert. Differently, the behavior of the most reactive gas species cannot easily be predicted, depending on complex chemical interaction involving gas, water and rock phases.

5.2. Organic Gas Compounds

[25] As already mentioned, 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, C₃-C₄ alkenes, C₆-C₈ aromatics and several heterocyclics and S-substituted hydrocarbons are present (Table 2). Among this variegated group of organic gas species, hydrocarbons pertaining to the

same structural series show regular compositional variations in response to secondary processes. In fact, the (*mean fum*)/(*mean well*) ratios (calculated on the basis of the dry gas fraction) of the C₂-C₉ normal-alkanes (Figure 4), the C₄-C₉ iso-alkanes and the aromatics (Figure 5) series progressively decrease as their molecular size increases. As shown in Figures 6a–6d, where the theoretical compositional trends calculated from (1) (solubility data from Lide [2001] and Cabani *et al.* [1981]) 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.

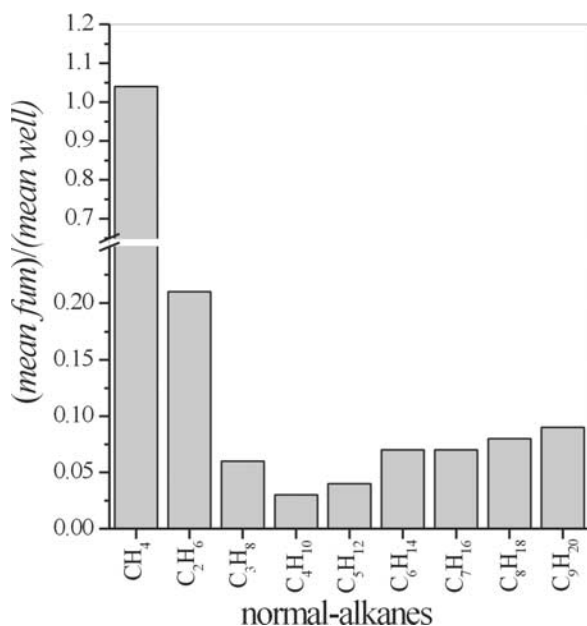


Figure 4. Histogram of the $(mean\ fum)/(mean\ well)$ ratios of the C_1 - C_9 normal-alkanes series.

Actually, the values of the $(mean\ fum)/(mean\ well)$ ratios for the C_n - C_{n+1} pairs of the normal-alkanes (Table 4) are inversely correlated ($R^2 = 0.88$) with the C_n/C_{n+1} molecular volume ratios (Figure 7). Moreover, this secondary process practically has the same effects [$(mean\ fum)/(mean\ well) \approx 1$] on hydrocarbons characterized by almost equal molecular volumes (C_n/C_{n+1} molecular volume ratio >0.82 ; Table 4). 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 [Wilke and Chang, 1955; Bird et al., 1960; Reid et al., 1987].

[26] Therefore the diffusion process seems to represent the main parameter controlling the fractionation of iso-structural hydrocarbons in fumarolic fluids during their uprising from the geothermal reservoirs to the surface. Accordingly, several studies [e.g., Leythaeuser et al., 1979; Hunt, 1984; Igari and Sakata, 1992] have emphasized the role of diffusion as a mechanism able to control the compositional changes of light hydrocarbon (C_2 - C_7 alkanes) in natural gases migrating from source to reservoir-type rocks.

6. Geothermometry

[27] Physical-chemical conditions (temperature, pressure and redox potential) of geothermal reser-

voirs are commonly investigated on the basis of the compositional features of gas and water phases discharged by exploration and production wells [e.g., Fouillac and Michard, 1981; Arnorsson et al., 1983; Bertrami et al., 1985; D'Amore and Truesdell, 1985; Giggenbach, 1988, 1991; Chiodini and Cioni, 1989]. These studies are extremely important to assess the energy potential of geothermal fields, as well as to control the evolution of deep thermal fluids during geothermal exploitation [e.g., Fournier, 1981; Arnorsson and Gunnlaugsson, 1985; D'Amore and Mejia, 1999]. The application of geothermometric techniques to naturally discharged fluids could provide these useful data even in areas where no wells have already been drilled, allowing, at least, a better evaluation of the geothermal potential of unexplored thermal systems at relatively low costs. In spite of these considerations, as also shown by the results of the present work, the chemical features of fumaroles and thermal springs seem to be deeply affected by secondary processes during the relatively slow circulation of geothermal fluids along their natural pathways.

6.1. Thermodynamic Equilibrium in the H_2O - H_2 - CO_2 - CO - CH_4 System

[28] The composition of hydrothermal gas discharges can usefully be represented by the H_2O - H_2 - CO_2 - CO - CH_4 system, whose equilibrium

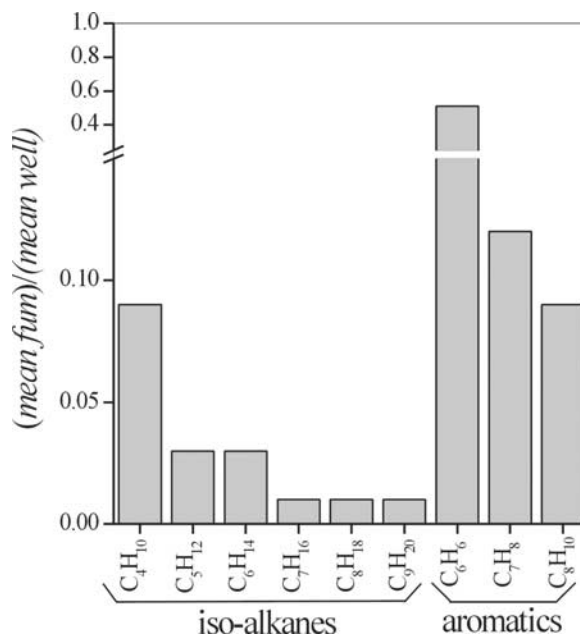


Figure 5. Histogram of the $(mean\ fum)/(mean\ well)$ ratios of both the C_4 - C_9 iso-alkanes and C_6 - C_8 aromatics series.

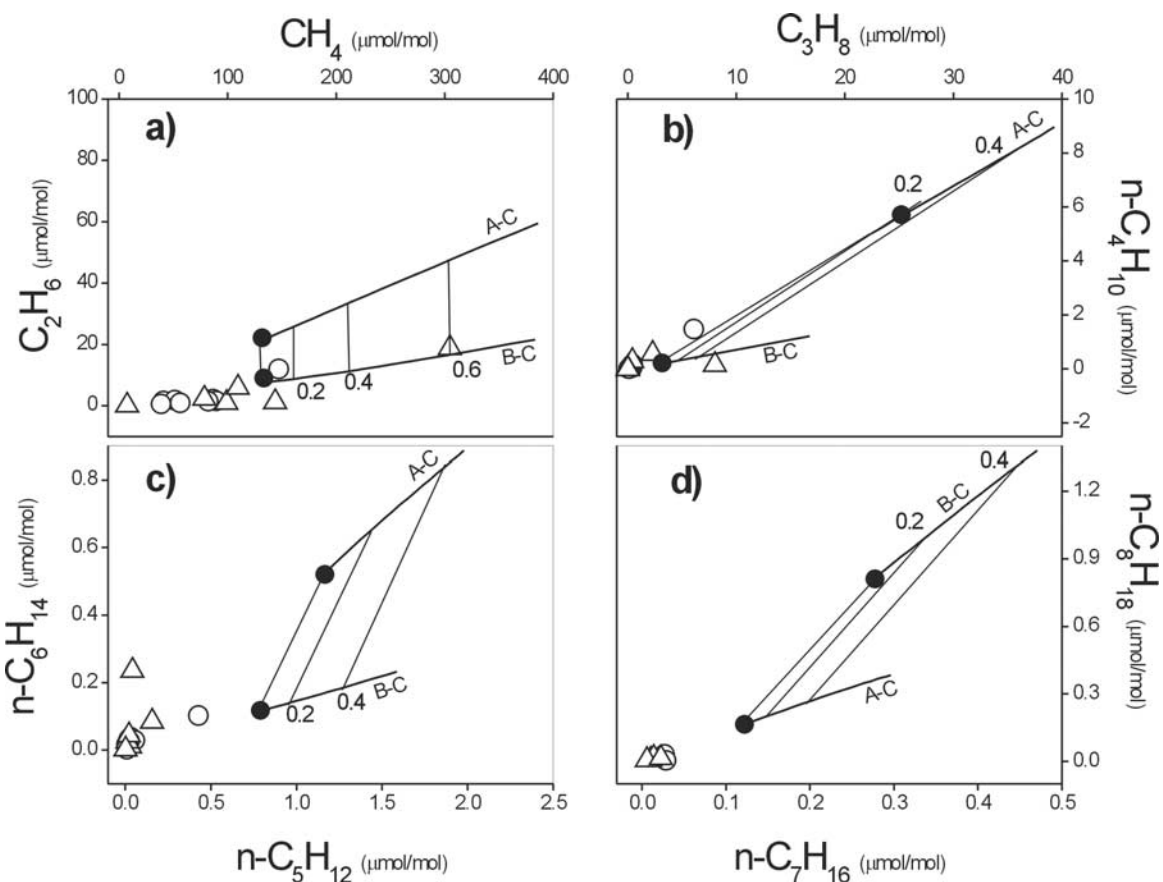
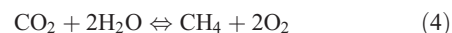
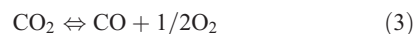
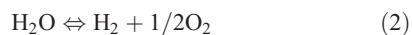


Figure 6. Binary diagrams of (a) CH_4 versus C_2H_6 , (b) C_3H_8 versus $n\text{-C}_4\text{H}_{10}$, (c) $n\text{-C}_5\text{H}_{12}$ versus $n\text{-C}_6\text{H}_{14}$, and (d) $n\text{-C}_7\text{H}_{16}$ versus $n\text{-C}_8\text{H}_{18}$ (dry gas fraction) in fumaroles from the Ahuachapan-Chipilapa and Berlin-Chinameca geothermal fields. Expected compositions (A-C and B-C lines for Ahuachapan-Chipilapa and Berlin-Chinameca, respectively) produced by dissolution-driven fractionation process acting on geothermal fluids of the two areas are also reported.

constrains may be provided by the following three reactions:



[29] *Chiodini and Marini* [1998] extensively investigated this restricted compositional system to evaluate the effects of secondary boiling and steam condensation processes on thermodynamic equilibrium in fluids from thermal discharges and wells

Table 4. Ratios Between the Mean Contents for Selected Gas Species of the Fumaroles and the Geothermal Wells From the Ahuachapan-Chipilapa, Berlin-Chinameca, and San Vicente Geothermal Fields^a

	(mean well) Ratio	(mean fum) Ratio	(mean fum)/(mean well) Ratio	Molecular Volume Ratio
$\text{CH}_4/\text{C}_2\text{H}_6$	7.28	35.91	4.93	0.65
$\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$	0.933	3.440	3.69	0.72
$\text{C}_3\text{H}_8/n\text{-C}_4\text{H}_{10}$	3.720	6.270	1.69	0.78
$n\text{-C}_4\text{H}_{10}/n\text{-C}_5\text{H}_{12}$	4.850	3.690	0.76	0.80
$n\text{-C}_5\text{H}_{12}/n\text{-C}_6\text{H}_{14}$	1.840	1.160	0.63	0.83
$n\text{-C}_6\text{H}_{14}/n\text{-C}_7\text{H}_{16}$	4.980	4.890	0.98	0.85
$n\text{-C}_7\text{H}_{16}/n\text{-C}_8\text{H}_{18}$	1.810	1.500	0.83	0.86
$n\text{-C}_8\text{H}_{18}/n\text{-C}_9\text{H}_{20}$	2.650	2.980	1.12	0.88

^aThe (mean fum)/(mean well) and the molecular volume ratios were also reported.

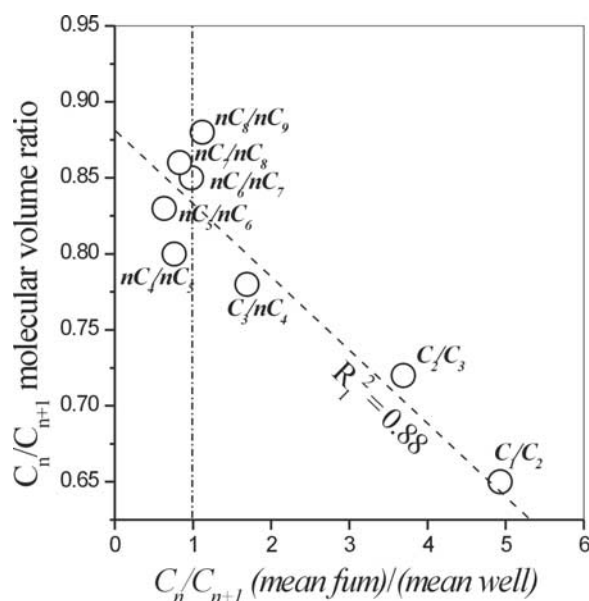


Figure 7. Binary diagram of molecular volume ratios versus $(\text{mean fum})/(\text{mean well})$ ratios for the C_n - C_{n+1} pairs of the normal-alkanes series.

seeping out in a wide range of volcanic and non-volcanic environments. These authors have evidenced that the H_2/H_2O , CO/CO_2 and CH_4/CO_2 log-ratios, which constitute the most suitable geothermometers for hydrothermal fluids [Giggenbach, 1987, 1991], strongly depend on (1) different kinetic responses of each compound to changes of thermodynamic parameters as thermal fluids rise up to the surface, (2) vapor-liquid distribution coefficients of the different gas species, and (3) fraction of separated vapor or condensed steam.

[30] Following a similar approach, the analytical data of fumaroles and geothermal wells from El Salvador geothermal fields are graphically compared with the computed theoretical compositions of gases that have attained chemical equilibrium at different temperatures (150, 200, 250, 300 and 350°C) in (1) pure saturated vapor (*vapor*), (2) liquid (*liquid*), and (3) coexisting vapor plus liquid phases, assuming that redox conditions are governed by the $FeO/FeO_{1.5}$ buffer proposed by Giggenbach [1987]. In the $\log(CH_4/CO_2)$ versus $\log(CO/CO_2)$ diagram (Figure 8) all gas samples plot out of the theoretical grid between the *vapor* and the *liquid* lines for hydrothermal fluids. This result may be due to the different kinetics characterizing the chemical behavior of CO and CH_4 . The former is, as well as H_2 , a fast-reacting species, while the latter is one of the slowest species

to equilibrate [Nehring and D'Amore, 1984; Giggenbach, 1987; Chiodini et al., 1993]. Moreover, it has to be considered that redox conditions of the geothermal reservoirs may not be controlled by a single buffer system. Low CH_4/CO_2 ratios (and consequently unrealistic high CH_4 - CO_2 equilibrium temperature), whose dependence on fO_2 is four times larger than that of the CO/CO_2 ratio (equations (3) and (4)), could be due to more oxidizing conditions with respect to those constrained by the $FeO/FeO_{1.5}$ buffer, possibly in relation to magmatic-related fluid inputs into the roots of the geothermal systems, as suggested for other volcanic systems (i.e., Phlegrean Fields, Ischia, Teide) by Chiodini and Marini [1998]. Ahuachapan-Chipilapa, Berlin-Chinameca and San Vicente geothermal fields are indeed located in active volcanic areas, as also supported by the mantle signature of the helium isotopic ratios (up to 7.1 R/R_{air}) [Snyder et al., 2003]. Therefore the presence of deep-circulating SO_2 -rich fluids, able to interact with the geothermal reservoirs, cannot be excluded, although SO_2 was detected in neither the discharging fluids nor the geothermal wells (Table 1), possibly because, as previously suggested, this highly soluble compound is totally dissolved into the geothermal liquid-dominated system.

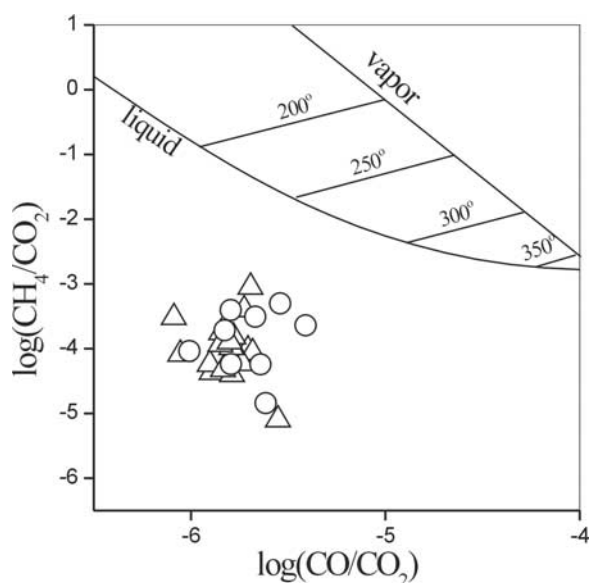


Figure 8. $\log(CH_4/CO_2)$ versus $\log(CO/CO_2)$ binary diagram. The computed theoretical compositions (FeO - $FeO_{1.5}$ buffer system) of (1) pure saturated vapor, (2) vapor separated from liquid in a single step, and (3) liquid phases [Chiodini and Marini, 1998] are also reported. Open triangle, fumarole; open circle, geothermal well.

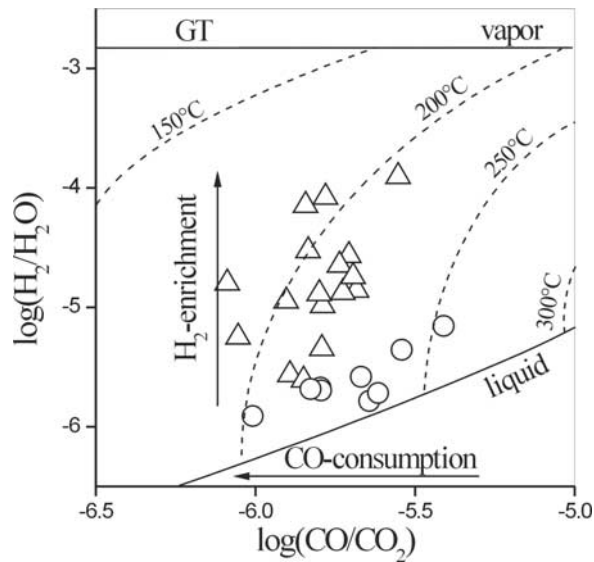


Figure 9. Log(H_2/H_2O) versus log(CO/CO_2) binary diagram. The computed theoretical compositions (FeO-FeO_{1.5} buffer system) of (1) pure saturated vapor, (2) vapor separated from liquid in a single step, and (3) liquid phases [Chiodini and Marini, 1998] are also reported. Symbols as in Figure 8.

[31] In the log(H_2/H_2O) versus log(CO/CO_2) diagram (Figure 9) gas samples plot within the expected compositional field for vapors produced through boiling of a liquid phase at initial temperature ranging between 180 and 250°C. Such temperatures are significantly lower than those estimated for Ahuachapan-Chipilapa geothermal fluids ($\approx 260^\circ C$) [Truesdell et al., 1989] and measured in the deep wells from the Berlin geothermal field (up to 310°C) [D'Amore and Mejia, 1999], likely due to partial reequilibration of both the H_2 - H_2O and CO - CO_2 pairs, indicating that both the fumaroles and the geothermal wells show clues of compositional readjustment at decreasing temperature and pressure conditions during fluid rise. Furthermore, the large variation shown by the H_2/H_2O ratio (more than 2 log-units) (Figure 9) seems to be mainly depending on the strong influence of secondary interactions (i.e., gas-water-rock reactions) on H_2 contents in fumaroles (Figure 2 and Table 3). Similarly, the CO/CO_2 log-ratios are likely dependent on CO -consumption at shallow depth due to formate production from CO [Shock, 1993], a process that may have continued in the time-interval (about two weeks) between the collection and the analysis of gas samples, leading to a general lowering of the CO - CO_2 equilibrium temperatures (Figure 9).

[32] In conclusion, the different chemical-physical behavior of the various compounds involved seems to imply severe limitations to the use of the H_2O - H_2 - CO_2 - CO - CH_4 system for geothermometric purposes, especially when analytical data are referred to the composition of naturally discharged fluids.

6.2. Thermodynamic Equilibria Among Hydrocarbons

[33] Thermodynamic properties and chemical behavior of aqueous organic species at hydrothermal conditions were extensively investigated only in recent times [Shock and Helgeson, 1990; Shock, 1990a]. Shock [1990b] first claimed that these compounds may attain metastable equilibrium over geologically significant periods of time. Accordingly, laboratory experiments, conducted at 300 to 350°C and 350 bar to examine chemical interactions of light hydrocarbons with water under the redox control of Fe-bearing mineral buffers, have demonstrated that alkene-alkane, alkene-ketone and alkene-alcohol pairs are able to achieve metastable equilibrium states within the timescale from hundreds to thousands of hours [Seewald, 1994, 2001]. In relation to the results of these investigations, the possible application of organic gas composition to geothermometry has been extensively debated [e.g., Sugisaki and Nagamine, 1995; Taran and Giggenbach, 2003; Capaccioni et al., 2004]. Several authors [e.g., Giggenbach, 1997; Taran and Giggenbach, 2003] have stressed the fact that hydrolysis reactions regulating the C_1 - C_2 - C_3 - C_4 alkane system in natural environment are not reversible processes, since the reversibility of the stepwise breakage of C-C bonds is largely limited by a kinetic barrier [Stocchi, 1991]. Barker and Takach [1992] suggested that the production of alkanes is not thermodynamically controlled, although, at high temperatures, this process possibly converges to equilibrium. On the other hand, Darling [1998], assuming a thermal breakdown mechanism for the production of CH_4 from C_{2+} alkanes, formulated an empirical relationship between the CH_4/C_2H_6 ratio and the temperature of deep thermal fluids that moderately well fits a range of hydrothermal systems worldwide. Furthermore, Capaccioni and Mangani [2001], on the basis of the composition of La Solfatara volcano fumaroles (Phlegrean Fields, Italy), stressed that the C_1 - C_2 - C_3 alkanes, characterized by similar solubility [Lide, 2001], for hydrothermal fluids with relatively long residence time at depth and in presence of abundant catalysts (such as free acids, allumosilicates and sulfur species), may be

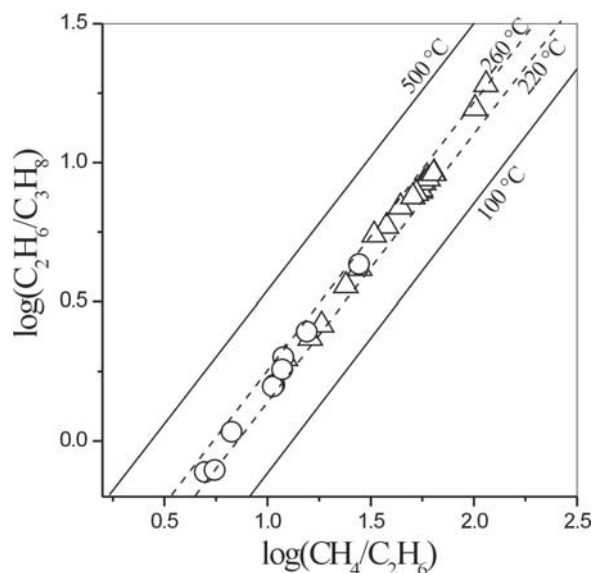


Figure 10. Log(CH₄/C₂H₆) versus C₂H₆/C₃H₈ binary diagram. Isotherms (in °C) refer to the equilibrium: 2C₃H₈ = C₂H₆ + CH₄. Symbols as in Figure 8.

thermodynamically controlled, in gases released from a single liquid phase, by the following pressure-independent equilibrium reaction:



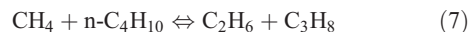
[34] According to thermodynamic data [Reid et al., 1987; Barin, 1989], the temperature dependence of the equilibrium constant of reaction (5) is

$$\log(\text{CH}_4/\text{C}_2\text{H}_6) - \log(\text{C}_2\text{H}_6/\text{C}_3\text{H}_8) = -0.0828 + 457.42/T \quad (6)$$

[35] As shown by the log(CH₄/C₂H₆) versus log(C₂H₆/C₃H₈) diagram (Figure 10), geothermal gases plot within the isotherms 220–260°C (dashed lines) 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) [D'Amore and Mejia, 1999] and with those calculated with the Na-K-Ca geothermometer [Fournier and Truesdell, 1973] by Snyder and Fehn [2002]. This represents an important result because it seems to constitute one of the rare examples of thermodynamic equilibrium attained among the C₁-C₂-C₃ alkanes [Sugizaki and Nagamine, 1995; Capaccioni and Mangani, 2001]. A second fundamental indication is that gases from both fumaroles and geothermal wells are in the same range of equilibrium temperatures (Figure 10), although, as previously ob-

served (Figures 4 and 5), 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; Table 4). Differently, the CH₄/C₂H₆ and C₂H₆/C₃H₈ log-ratios, considered separately, are significantly higher in the fumaroles than in the geothermal wells (Figure 10), depending on the largely different molecular volumes of CH₄, C₂H₆ and C₃H₈ (42.1, 65.1 and 90.5, respectively; Table 3).

[36] A similar approach can be adopted to investigate the C₁-C₂-C₃-C₄ alkane system, whose internal equilibrium is regulated by the following reaction [Capaccioni and Mangani, 2001]:



[37] The temperature dependence of the equilibrium constant of reaction (7) (at T > 200°C) is given by

$$\log(\text{CH}_4/\text{C}_2\text{H}_6) - \log(\text{C}_3\text{H}_8/n\text{-C}_4\text{H}_{10}) = -0.0567 + 477/T \quad (8)$$

[38] As shown in Figure 11, both geothermal wells and fumaroles are scattered in a wide area, indi-

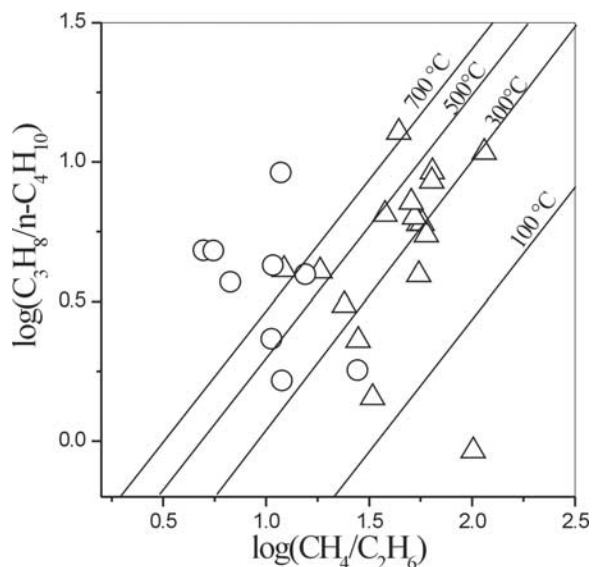
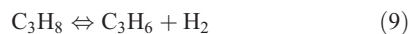


Figure 11. Log(CH₄/C₂H₆) versus C₃H₈/n-C₄H₁₀ binary diagram. Isotherms (in °C) refer to the equilibrium: CH₄ + n-C₄H₁₀ ⇌ C₂H₆ + C₃H₈. Symbols as in Figure 8.

cating equilibrium temperatures ranging from 50 to >700°C. This result may be ascribed to two possible reasons: (1) reaction (7) has not attained a complete equilibrium, possibly in relation to further chemical reactions involving n-C₄H₁₀, and (2) secondary processes. Concerning the first hypothesis, we believe that the apparent disequilibrium of reaction (7) is mainly due to the interaction between n-C₄H₁₀ and its isomer, i-C₄H₁₀. It is worthy of note that the CH₄/C₂H₆ molecular volume ratio is significantly different with respect to that of C₃H₈-n/C₄H₁₀ (0.65 and 0.78, respectively; Table 4); thus the composition of the C₁-C₄ alkanes may also depend on the influence of the diffusion process.

[39] Further reactions among light hydrocarbons that can usefully be utilized for evaluating deep temperatures in geothermal and volcanic systems are those of de-hydrogenation processes [e.g., *Capaccioni and Mangani, 2001; Tassi et al., 2005b*], which result in saturated-unsaturated conversion of the alkane-alkene pairs without strong structural changes.

[40] De-hydrogenation reaction of the C₃ alkene-alkane pair is given by



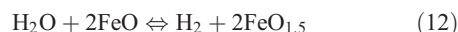
whose temperature dependence is given by

$$\log(\text{C}_3\text{H}_6/\text{C}_3\text{H}_8) + \log f_{\text{H}_2} = 7.15 - 6,600/T \quad (10)$$

[41] As shown by (10), the relative abundances of C₃H₆ and C₃H₈ are regulated, besides of the temperature, by the hydrogen fugacity, which in turn is instantaneously governed by redox conditions. As suggested by *Giggenbach [1987]*, the most suitable parameter to describe redox potentials of natural fluids is:

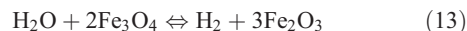
$$R_{\text{H}} = \log(f_{\text{H}_2}/f_{\text{H}_2\text{O}}) \quad (11)$$

[42] The R_H values referring to the FeO-FeO_{1.5} couple, which is considered the most suitable redox buffer system for hydrothermal fluids [*Giggenbach, 1987*], are fixed by the generalized reaction [*Giggenbach et al., 1986*]:



[43] However, as suggested by the distribution of gas samples in Figure 8, the redox conditions dominating the geothermal reservoir of both Ahuachapan-Chipilapa and Berlin-Chinameca geothermal fields are likely more oxidative than

those expected when the FeO-FeO_{1.5} buffer is predominating. Therefore the redox buffer system involving hematite and magnetite (HM), which is possibly in equilibrium with geothermal gases at relatively high oxidation potential [*Giggenbach, 1987*], was also adopted. The R_H values referring to the hematite-magnetite couple are fixed by the reaction



[44] Hence, assuming that changes of log f_{H₂O} with temperature are closely approximated by the following equation [*Giggenbach, 1980*]:

$$\log f_{\text{H}_2\text{O}} = 5.51 - 2048/T \quad (14)$$

and using the temperature dependences of the equilibrium constants of reactions (12) and (13) proposed by *Giggenbach [1987]*, hydrogen fugacity can be linked to temperature through the following equations:

$$\log f_{\text{H}_2} = 2.71 - 2048/T \quad (15)$$

$$\log f_{\text{H}_2} = 0.91 - 2318/T \quad (16)$$

[45] Finally, by combining (10) with (15) and (16), the theoretical relationship between the C₃H₆/C₃H₈ ratios and temperature for gases equilibrated at the typical redox conditions for hydrothermal and volcanic environments, respectively, can be obtained.

[46] As shown in the log(C₃H₆/C₃H₈) versus temperature diagram (Figure 12) (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 (1) as already observed in volcanic gases [*Taran and Giggenbach, 2003*], reaction (9) is really able to control the C₃H₆/C₃H₈ ratios and (2) the C₃H₆-C₃H₈ couple equilibrates at redox conditions that are to be considered unusual for geothermal systems [e.g., *Giggenbach, 1980, 1987*]. Magmatic-related fluid inputs able to affect the redox conditions of the Ahuachapan-Chipilapa, Berlin-Chinameca and San Vicente geothermal systems were already invoked to justify gas distribution in the binary diagram (Figure 8) describing the thermodynamic equilibria of the CH₄/CO/CO₂ redox system. Accordingly,

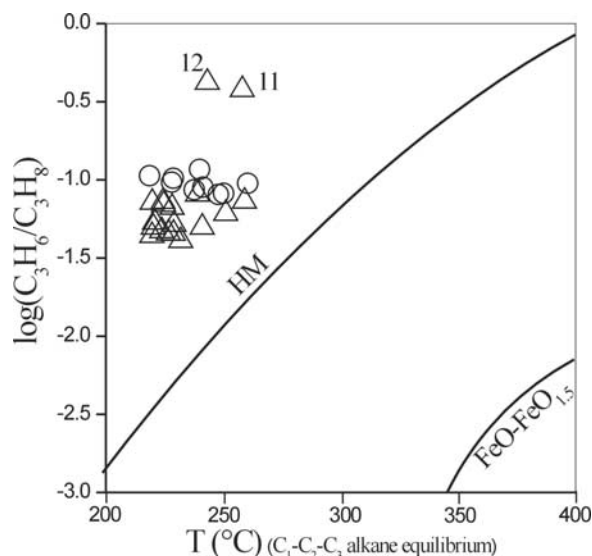
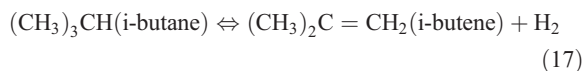


Figure 12. $\log(C_3H_6/C_3H_8)$ versus $(C_1-C_2-C_3)$ -calculated temperature diagram. Solid lines represent the positions of the GT and HM redox buffer systems. Symbols as in Figure 8.

the high $C_3H_6-C_3H_8$ ratios of Laguna Alegria and Oyon Crater (samples 11 and 12; Figure 12), which represent the most recent craters of the Tecapa-Berlin volcanic system [D'Amore and Mejia, 1999], 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 (C_4H_4O and C_5H_6O ; Table 2), typically produced at high temperature [Montegrossi et al., 2003], and the relatively high H_2 and CO contents.

[47] It must be underscored that the C_3H_6/C_3H_8 log-ratios in the fumaroles and the geothermal wells are in the same range (Figure 12). Therefore the $C_3H_6-C_3H_8$ geothermometer, as well as that of the $C_1-C_2-C_3$ alkanes, seems to be not significantly affected secondary processes occurring along the fumarolic pathways, likely due to the minimum difference between the molecular volumes of these two compounds (C_3H_6/C_3H_8 molecular volume ratio = 0.91). This consideration confirms once again that a strong relation exists between the diffusion process and the (*mean fum*)/(*mean well*) ratios.

[48] Among the possible chemical reactions involving the C_4 unsaturated-saturated pairs, de-hydrogenation of the iso- C_4 alkane to form the iso- C_4 alkene can be considered:



[49] The temperature dependence of the equilibrium constant of reaction (17) is given by

$$8.18 - 5,780/T - 270,398/T^2 \\ = \log[(CH_3)_2C = CH_2]/[(CH_3)_3CH] + \log f_{H_2} \quad (18)$$

[50] The theoretical compositions for gases equilibrated at redox conditions governed by the FeO/FeO_{1.5} and the HM buffer systems, respectively, were obtained by combining (18) with (15) and (16), respectively. As shown in Figure 13, the i- $C_4H_8/i-C_4H_{10}$ ratio, as that of the C_3-C_3 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 reaction (17) has not attained thermodynamic equilibrium in the considered temperature range. The molecular volumes of the two iso- C_4 hydrocarbons are indeed almost identical (Table 3), thus we can hypothesize that the diffusion process is not able to significantly affect the i- $C_4H_8/i-C_4H_{10}$ ratio. Nevertheless, it seems not reasonable that two almost identical chemical processes, i.e., the de-hydrogenation reactions of the C_3 and the C_4 alkane-alkene pairs, can show a distinct thermodynamic response. Consequently, as also supported by the lack of equilibrium of the $C_1-C_2-C_3-C_4$ alkane system (Figure 11), the interaction between the two C_4 -isomers, i- C_4H_{10} and n- C_4H_{10} , remains the most

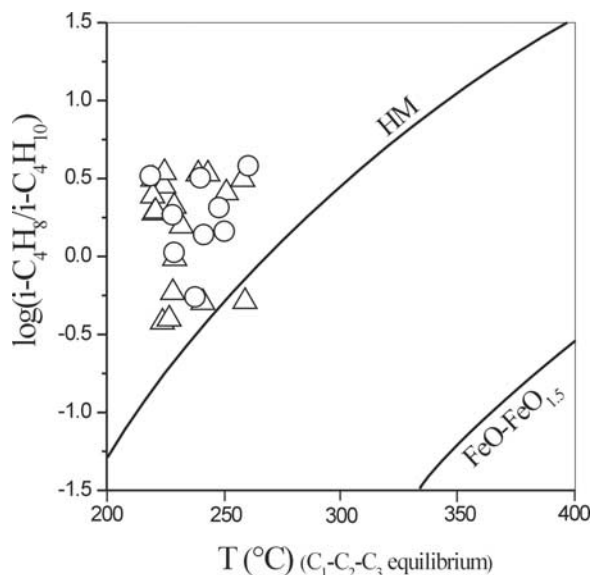


Figure 13. $\log(\text{iso-}C_4H_8/\text{iso-}C_4H_{10})$ versus $(C_1-C_2-C_3)$ -calculated temperature diagram. Solid lines represent the positions of the GT and HM redox buffer systems. Symbols as in Figure 8.

likely mechanism able to explain the gas distribution shown in Figure 13.

7. Conclusions

[51] Temperature-dependent interactions between gas species stored within geothermal reservoirs, where fluids have long residence times and the physical-chemical conditions (temperature, pressure) are particularly favorable to the proceeding of chemical reactions, are likely to be able to achieve a complete equilibrium. This is confirmed by the reliable temperature estimations commonly obtained by applying the geothermometric techniques based on the composition of the deep production wells [e.g., *Arnorsson et al.*, 1983; *Bertrami et al.*, 1985, *Giggenbach*, 1991], which are likely very similar to that thermodynamically established at depth since exploited fluids rapidly move toward surface and are almost isolated by the shallow environment. On the contrary, it is reasonable to suppose that the compositional features of geothermal reservoirs are rarely maintained by fumarolic discharges, mainly due to the influence of secondary processes that may take place during the slow gas ascension along the natural pathways. The composition of naturally discharging fluids from fumaroles of Auhachapan-Chipilapa and Berlin-Chinameca geothermal fields, when compared to that of the geothermal wells of the same areas, have indeed shown that (1) dissolution-driven fractionation due to the interaction of geothermal fluids with shallow aquifers is able to control, at least partially, N₂, Ar, He and CO₂ contents in fumarolic gases; (2) fumarolic gases, with respect to gases from geothermal wells, are strongly enriched in H₂ and slightly depleted in CO and H₂S, likely due to complex secondary gas-water-rock chemical reactions; (3) organic gases of geothermal fluids are significantly depleted at relatively shallow depth by scrubbing processes (i.e., dissolution in shallow aquifers); (4) 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; and (5) 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 [*Capaccioni and Mangani*, 2001] of the chemical reaction among

the C₁-C₂-C₃ alkanes, whose behavior is commonly that of a non-reversible process [*Taran and Giggenbach*, 2003], 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.

Acknowledgments

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References

- Aiuppa, A., M. L. Carapezza, and F. Parello (1997), Fluid geochemistry of the San Vicente geothermal field, *Geothermics*, 26, 83–97.
- Armansson, H., G. Gislason, and T. Hauksson (1982), Magmatic gases in well fluids aid the mapping of the flow pattern in a geothermal system, *Geochim. Cosmochim. Acta*, 46, 167–177.
- Arnorsson, S. (1990), Gas chemistry of geothermal systems, in *Geochemistry of Gaseous Elements and Compounds*, edited by S. Augustithis, pp. 187–222, Theophrastus, Athens.
- Arnorsson, S., and E. Gunnlaugsson (1985), New gas geothermometers for geothermal exploration: Calibration and application, *Geochim. Cosmochim. Acta*, 49, 1307–1325.
- Arnorsson, S., E. Gunnlaugsson, and H. Svavarsson (1983), The chemistry of geothermal waters in Iceland. III. Chemical geothermometry in geothermal investigations, *Geochim. Cosmochim. Acta*, 47, 567–577.
- Aumento, F., P. Viale, M. Choussy, and A. Santan (1982), Alteration mineralogy of the Auhachapan geothermal field, *Trans. Geotherm. Resour. Council.*, 6, 7–10.
- Barberi, F., S. G. Rotolo, and A. Aiuppa (1995), Petrology of Chichontepeque volcano (El Salvador), *Period. Mineral.*, 64, 89–91.
- Barin, I. (1989), *Thermochemical Data on Pure Substances*, Part I, John Wiley, Hoboken, N. J.
- Barker, C., and N. E. Takach (1992), Prediction of natural gas composition in ultradeep sandstone reservoirs, *Am. Assoc. Pet. Geol. Bull.*, 76, 1859–1873.
- Berndt, M. E., D. E. Allen, and W. E. Seyfried (1996), Reduction of CO₂ during serpentinization of olivine at 300°C and 500 bar, *Geology*, 24, 351–354.
- Bertrami, R., R. Cioni, E. Corazza, F. D'Amore, and L. Marini (1985), Carbon monoxide in geothermal gases: Reservoir temperature calculations at Larderello (Italy), *Trans. Geotherm. Resour. Council.*, 9, 299–303.
- Bird, R. B., W. E. Stewart, and E. N. Lightfoot (1960), *Transport Phenomena*, 780 pp., John Wiley, Hoboken, N. J.
- Bourgeois, J., J. Azema, P. Baumgartner, J. Tournon, A. Dasmét, and J. Aubouin (1984), The geologic history of the Caribbean-Cocos plate boundary with special references to the Nicoya ophiolitic complex (Costa Rica) and D. S. D. P.

- (Legs 67 and 84 off Guatemala): A synthesis, *Tectonophysics*, 108, 1–32.
- Cabani, S., P. Gianni, V. Mollica, and L. Lepori (1981), Group contribution to the thermodynamic properties on non-ionic organic solutes in dilute aqueous solution, *J. Solution Chem.*, 10, 563–595.
- Capaccioni, B., and F. Mangani (2001), Monitoring of active but quiescent volcanoes using light hydrocarbon distribution in volcanic gases: The results of 4 years of discontinuous monitoring in the Campi Flegrei (Italy), *Earth Planet. Sci. Lett.*, 188, 543–555.
- Capaccioni, B., M. Martini, F. Mangani, L. Giannini, G. Nappi, and F. Prati (1993), Light hydrocarbons in gas-emissions from volcanic areas and geothermal fields, *Geochem. J.*, 27, 7–17.
- Capaccioni, B., Y. Taran, F. Tassi, O. Vaselli, F. Mangani, and J. L. Macias (2004), Source conditions and degradation processes of light hydrocarbons in volcanic gases: An example from the Chichon Volcano (Chiapas State, Mexico), *Chem. Geol.*, 206, 81–96.
- Capaccioni, B., F. Tassi, M. Maione, F. Mangani, and O. Vaselli (2005), Organics in volcanic gases: A review on their distribution and applications to volcanic surveillance, *Eos Trans. AGU*, 86(52), Fall Meet. Suppl., Abstract B23D-03.
- Chayes, F. (1960), On correlation between variables of constant sum, *J. Geophys. Res.*, 65, 4185–4193.
- Chiodini, G., and R. Cioni (1989), Gas geobarometry for hydrothermal systems and its application to some Italian geothermal areas, *Appl. Geochem.*, 4, 465–472.
- Chiodini, G., and L. Marini (1998), Hydrothermal gas equilibria: The H₂O-H₂-CO₂-CO-CH₄ system, *Geochim. Cosmochim. Acta*, 62, 2673–2687.
- Chiodini, G., R. Cioni, and L. Marini (1993), Reactions governing the chemistry of crater fumaroles from Vulcano Island, Italy, and implications for volcanic surveillance, *Appl. Geochem.*, 8, 357–371.
- Chiodini, G., W. D'Alessandro, and F. Parello (1996), Geochemistry of gases and waters discharged by the mud volcanoes at Paternò, Mt. Etna (Italy), *Bull. Volcanol.*, 58, 51–58.
- Chiodini, G., L. Marini, and M. Russo (2001), Geochemical evidence for the existence of high-temperature hydrothermal brines at Vesuvio Volcano, Italy, *Geochim. Cosmochim. Acta*, 65, 2129–2147.
- Cuellar, G. (1981), Geothermal development in El Salvador, in *Resources of the Pacific Region*, *Stud. Geol.*, vol. 12, pp. 21–25, Am. Assoc. of Pet. Geol., Tulsa, Okla.
- D'Amore, F. (1991), Gas geochemistry as a link between geothermal exploration and exploitation, in *Application of Geochemistry in Geothermal Reservoir Development*, edited by F. D'Amore, pp. 93–117, UNITAR, New York.
- D'Amore, F., and T. J. Mejia (1999), Chemical and physical reservoir parameters at initial conditions in Berlin geothermal field, El Salvador: A first assessment, *Geothermics*, 28, 45–73.
- D'Amore, F., and S. Nuti (1977), Notes on the chemistry of geothermal gases, *Geothermics*, 6, 39–45.
- D'Amore, F., and C. Panichi (1980), Evaluation of deep temperatures of hydrothermal systems by a new gas geothermometer, *Geochim. Cosmochim. Acta*, 44, 549–556.
- D'Amore, F., and A. H. Truesdell (1985), Calculation of geothermal temperatures and steam fractions from gas composition, *Trans. Geotherm. Resour. Council*, 9, 305–310.
- Darling, W. G. (1998), Hydrothermal hydrocarbons gases: 1. Genesis and geothermometry, *Appl. Geochem.*, 13, 815–824.
- Des Marais, D. J., J. H. Donchin, A. H. Truesdell, and N. L. Nehring (1981), Molecular carbon isotopic evidence for the origin of geothermal hydrocarbons, *Nature*, 292, 826–828.
- Doukas, M. P., and T. M. Gerlach (1995), Sulfur dioxide scrubbing during the 1992 eruptions of Crater Peak, Mount Spurr Volcano, Alaska, in *The 1992 Eruptions of Crater Peak Vent, Mount Spurr Volcano, Alaska*, edited by T. E. C. Keith, *U.S. Geol. Surv. Bull.*, 2139, 47–57.
- Ellis, A. J., and W. A. J. Mahon (1977), *Chemistry and Geothermal Systems*, 392 pp., Elsevier, New York.
- Fouillac, C., and G. Michard (1981), Sodium-lithium ratio in water applied to the geothermometry of geothermal waters, *Geothermics*, 10, 55–70.
- Fournier, R. O. (1981), Application of water chemistry to geothermal exploration and reservoir engineering, in *Geothermal Systems: Principles and Case Histories*, edited by L. Rybach and L. J. P. Muffler, pp. 109–143, John Wiley, Hoboken, N. J.
- Fournier, R. O., and A. H. Truesdell (1973), An empirical Na-K-Ca geothermometer for natural waters, *Geochim. Cosmochim. Acta*, 37, 1255–1275.
- Giggenbach, W. F. (1980), Geothermal gas equilibria, *Geochim. Cosmochim. Acta*, 44, 2021–2032.
- Giggenbach, W. F. (1987), Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand, *Appl. Geochem.*, 2, 143–161.
- Giggenbach, W. F. (1988), Geothermal solute equilibria, derivation of Na-K-Mg-Ca geothermometers, *Geochim. Cosmochim. Acta*, 52, 2749–2765.
- Giggenbach, W. F. (1991), Chemical techniques in geothermal exploration, in *Application of Geochemistry in Geothermal Reservoir Development*, edited by F. D'Amore, pp. 253–273, UNITAR, New York.
- Giggenbach, W. F. (1992), Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin, *Earth Planet. Sci. Lett.*, 113, 495–510.
- Giggenbach, W. F. (1996), Chemical composition of volcanic gases, in *Monitoring and Mitigation of Volcano Hazards*, edited by M. Scarpa and R. I. Tilling, pp. 222–256, Springer, New York.
- Giggenbach, W. F. (1997), Relative importance of thermodynamic and kinetic processes in governing the chemical and isotopic composition of carbon gases in high-heat flow sedimentary basins, *Geochim. Cosmochim. Acta*, 61, 3763–3785.
- Giggenbach, W. F., M. Martini, and E. Corazza (1986), The effects of hydrothermal processes on the chemistry of some recent volcanic gas discharges, *Period. Mineral.*, 55, 15–28.
- Gonzales Partida, E., V. Torres Rodriguez, and P. Birkle (1997), Plio-Pleistocene volcanic history of the Ahuachapan geothermal system, El Salvador: The Concepcion de Ataco caldera, *Geothermics*, 26, 555–575.
- Gunter, B. D. (1978), C₁-C₄ hydrocarbons in hydrothermal gases, *Geochim. Cosmochim. Acta*, 42, 137–139.
- Hedenquist, J. W., and J. B. Lowenstern (1994), The role of magmas in the formation of hydrothermal ore deposits, *Nature*, 370, 519–527.
- Horita, J., and M. E. Berndt (1999), Abiogenic methane formation and isotopic fractionation under hydrothermal conditions, *Science*, 285, 1055–1057.
- Hunt, J. M. (1984), Generation and migration of light hydrocarbons, *Science*, 226, 1265–1270.
- Huttrer, G. W. (2001), The status of world geothermal power generation 1995–2000, *Geothermics*, 30, 1–27.

- Igari, S., and S. Sakata (1992), Fractionation of light hydrocarbons through GC columns packed with rocks and minerals: Implication for natural gas migration, *Geochem. J.*, *26*, 37–43.
- Jacobo, P. E. (2003), Gas chemistry of the Ahuachapan and Berlin geothermal fields, El Salvador: Report n° 12, in *Geothermal Training in Iceland*, pp. 275–304, United Nations Univ.-Geotherm. Training Programme, Reykjavik.
- Leythaeuser, D., R. G. Schaefer, C. Cornford, and B. Weiner (1979), Generation and migration of light hydrocarbons (C₂–C₇) in sedimentary basins, *Org. Geochem.*, *1*, 191–204.
- Lide, D. R. (Ed.) (2001), *Handbook of Chemistry and Physics*, 82nd ed., CRC Press, Boca Raton, Fla.
- Major, J. J., S. P. Schilling, C. R. Pullinger, C. D. Escobar, and M. M. Howell (2001), Volcano-hazard zonation for San Vicente volcano, El Salvador, *U.S. Geol. Surv. Open File Rep.*, *01-367*, 22 pp.
- Mangani, G., A. Berlani, B. Capaccioni, F. Tassi, and M. Maione (2004), Gas chromatographic-mass spectrometric analysis of hydrocarbons and other neutral organic compounds in volcanic gases using SPME for sample preparation, *Chromatographia*, *58*, 1–5.
- Mango, F. D. (2000), The origin of light hydrocarbons, *Geochim. Cosmochim. Acta*, *64*, 1265–1277.
- Marini, L., and B. Gambardella (2005), Geochemical modeling of magmatic gas scrubbing, *Ann. Geophys.*, *48*(4/5), 739–753.
- Marini, L., A. Agostini, R. Cioni, M. Guidi, and O. Leon (1991), Gagua Pichincha volcano, Ecuador: Fluid geochemistry in volcanic surveillance, *J. Volcanol. Geotherm. Res.*, *46*, 21–35.
- Meisch, A. T. (1969), The constant sum problem in geochemistry, in *Computer Application in Earth Sciences*, edited by D. F. Merriam, pp. 161–176, Springer, New York.
- Menyailov, I. A. (1975), Prediction of eruptions using changes in composition of volcanic gases, *Bull. Volcanol.*, *39*, 112–125.
- Montalvo, F. E. (1994), Geochemical evolution of the Ahuachapan geothermal field, El Salvador: Report n° 9, in *Geothermal Training in Iceland*, pp. 211–236, United Nations Univ.-Geotherm. Training Programme, Reykjavik.
- Montalvo, F., and G. Axelsson (2000), Assessment of chemical and physical reservoir parameters during six years of production-reinjection at Berlin geothermal field (El Salvador), paper presented at World Geothermal Congress, Int. Geotherm. Assoc., Kyushu-Tohoku, Japan, 28 May to 10 June.
- Montegrossi, G., F. Tassi, O. Vaselli, A. Buccianti, and K. Garofano (2001), Sulfur species in volcanic gases, *Anal. Chem.*, *73*, 3709–3715.
- Montegrossi, G., F. Tassi, O. Vaselli, and A. Minissale (2003), Heterocyclic compounds in volcanic and geothermal systems: Case studied from Vulcano Island (Sicily, Italy) and Larderello (Central-Northern Italy), paper presented at 4th FIST Congress, GEOITALIA, Bellaria, Italy, 16–18 Sept.
- Monterrosa, V. (1998), Present status of geothermal development in El Salvador and contribution of UNU Fellows in the geothermal scenario and management, in *Geothermal Training in Iceland: 20th Anniversary Workshop*, edited by L. S. Georgsson, pp. 21–28, United Nations Univ.-Geotherm. Training Programme, Reykjavik.
- Nehring, N. L., and F. D'Amore (1984), Gas chemistry and thermometry of the Cerro Prieto, Mexico, geothermal field, *Geothermics*, *13*, 75–89.
- Nieva, D., M. Verma, E. Santoyo, E. Portugal, and A. Campos (1997), Geochemical exploration of the Chipilapa geothermal field, El Salvador, *Geothermics*, *26*, 589–612.
- Oremland, R. S., L. G. Miller, and M. J. Whiticar (1987), Sources and flux of natural gases from Mono Lake, California, *Geochim. Cosmochim. Acta*, *51*, 2915–2929.
- Reid, R. C., J. M. Prausnitz, and B. E. Poling (1987), *The Properties of Gases and Liquids*, McGraw-Hill, New York.
- Renderos, R. E. (2002), Chemical characterization of the thermal fluid discharge from well production tests in the Berlin geothermal field, El Salvador: Report n° 12, in *Geothermal Training in Iceland*, pp. 205–232, United Nations Univ.-Geotherm. Training Programme, Reykjavik.
- Rodriguez, J. A., and A. Herrera (2003), International geothermal development: Geothermal El Salvador, *GRC Bull.*, *32*(4), 159–162.
- Rodriguez, V. T., P. Birkle, E. G. Partida, D. Nieva, M. P. Verma, E. P. Marin, and F. Castellanos (1997), Isotopic zoning and origin of the aquifers in the discharge area of the geothermal fields of Ahuachapan and Chipilapa, El Salvador, *Geothermics*, *26*, 613–626.
- Romo, J. M., C. Flores, R. Vega, R. Vasquez, M. A. Perez Flores, E. Gomez Treviño, F. J. Esparza, J. E. Quijano, and V. H. Garcia (1997), A closely-spaced magnetotelluric study of the Ahuachapan-Chipilapa geothermal field, El Salvador, *Geothermics*, *26*, 627–656.
- Seewald, J. S. (1994), Evidence for metastable equilibrium between hydrocarbons under hydrothermal conditions, *Nature*, *370*, 285–287.
- Seewald, J. S. (2001), Aqueous geochemistry of low molecular weight hydrocarbons at elevated temperatures and pressures: Constraints from mineral buffered laboratory experiments, *Geochim. Cosmochim. Acta*, *65*, 1641–1664.
- Shock, E. L. (1990a), Geochemical constraints of the origin of organic compounds in hydrothermal systems, *Origin Life Evol. Biosphere*, *20*, 331–367.
- Shock, E. L. (1990b), Do amino acids equilibrate in hydrothermal fluids?, *Geochim. Cosmochim. Acta*, *54*, 1185–1189.
- Shock, E. L. (1993), Hydrothermal dehydration of aqueous organic compounds, *Geochim. Cosmochim. Acta*, *57*, 3341–3349.
- Shock, E. L., and H. C. Helgeson (1990), Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures, *Geochim. Cosmochim. Acta*, *54*, 915–945.
- Schmidt-Thomé, M. (1975), The geology in the San Salvador area (El Salvador, Central America), a basis for city development and planning, *Geol. Jahrb.*, *13*, 207–228.
- Snyder, G., and U. Fehn (2002), Origin of iodine in volcanic fluids: ¹²⁹I results from the Central American Volcanic Arc, *Geochim. Cosmochim. Acta*, *66*, 3827–3838.
- Snyder, G., R. Poreda, A. Hunt, and U. Fehn (2001), Regional variations in volatile composition: Isotopic evidence for carbonate recycling in the Central American volcanic arc, *Geochem. Geophys. Geosyst.*, *2*(10), doi:10.1029/2001GC000163.
- Snyder, G., R. Poreda, U. Fehn, and A. Hunt (2003), Sources of nitrogen and methane in Central American geothermal settings: Noble gas and ¹²⁹I evidence for crustal and magmatic volatile components, *Geochem. Geophys. Geosyst.*, *4*(1), 9001, doi:10.1029/2002GC000363.
- Stocchi, E. (1991), *Chimica Industriale: Organica* (in Italian), EDISCO, Torino, Italy.
- Sugisaki, R., and K. Nagamine (1995), Evolution of light hydrocarbon gases in subsurface processes: Constraints from chemical equilibrium, *Earth Planet. Sci. Lett.*, *133*, 151–161.
- Symonds, R. B., W. I. Rose, W. I. Bluth, and T. M. Gerlach (1994), Volcanic-gas studies: Methods, results, and applica-

- tions, in *Volatiles in Magmas, Rev. Mineral.*, vol. 30, edited by M. R. Carroll and J. R. Holloway, pp. 1–66, Mineral. Soc. of Am., Washington, D. C.
- Symonds, R. B., T. M. Gerlach, and M. H. Reed (2001), Magmatic gas scrubbing: Implications for volcano monitoring, *J. Volcanol. Geotherm. Res.*, *108*, 303–341.
- Taran, Y. A. (1986), Gas geothermometers for hydrothermal systems *Geochem. Int.*, *3*, 111–126.
- Taran, Y. A., and W. F. Giggenbach (2003), Geochemistry of light hydrocarbons in subduction-related volcanic and hydrothermal fluids, in *Volcanic, Geothermal, and Ore-Forming Fluids: Rulers and Witnesses of Processes Within the Earth, Spec. Publ.*, *10*, edited by S. F. Simmons and I. J. Graham, pp. 61–74, Soc. of Econ. Geol., Littleton, Colo.
- Taran, Y. A., B. G. Pokrovsky, and A. D. Esikov (1989), Deuterium and oxygen-18 in fumarolic steam and amphiboles from some Kamchatka volcanoes: “Andesitic waters,” *Dokl. Akad. Nauk SSSR*, *304*, 440–443.
- Tassi, F. (2004), Fluidi in ambiente vulcanico: Evoluzione temporale dei parametri composizionali e distribuzione degli idrocarburi leggeri in fase gassosa (in Italian), Ph.D. thesis, 292 pp., Univ. of Florence, Florence, Italy.
- Tassi, F., G. Montegrossi, and O. Vaselli (2004), Metodologie di campionamento ed analisi di fasi gassose (in Italian), *Internal Rep. CNR-IGG 1/2004*, 24 pp., Cons. Naz. delle Ric.-Ist. di Geosci. e Georisorse, Florence, Italy.
- Tassi, F., C. Martinez, O. Vaselli, B. Capaccioni, and J. Viramonte (2005a), The light hydrocarbons as new geoindicators of equilibrium temperatures and redox conditions of geothermal fields: Evidence from El Tatio (northern Chile), *Appl. Geochem.*, *20*, 2049–2062.
- Tassi, F., O. Vaselli, B. Capaccioni, C. Giolito, E. Duarte, E. Fernandez, A. Minissale, and G. Magro (2005b), The hydrothermal-volcanic system of Rincon de la Vieja volcano (Costa Rica): A combined (inorganic and organic) geochemical approach to understanding the origin of the fluid discharges and its possible application to volcanic surveillance, *J. Volcanol. Geotherm. Res.*, *148*, 315–333.
- Truesdell, A. H., Z. Aunzo, G. Bodvarsson, J. Alonso, and A. Campos (1989), The use of Ahuachapan fluid chemistry to indicate natural state conditions and reservoir processes during exploitation, paper presented at XIV Workshop on Geothermal Reservoir Engineering, Stanford Univ., Stanford, Calif.
- Weber, H. S. (1978), Mapa geologico de la Republica de El Salvador: Hoja San Salvador, scale 1:100000, Bundesanst. für Geowiss. und Rohstoffe, Hannover, Germany.
- Wehlan, J. A. (1988), Origin of methane in hydrothermal systems *Chem. Geol.*, *71*, 183–198.
- Wilke, C. R., and P. Chang (1955), Correlation of diffusion coefficient in dilute solution, *AIChE J.*, *1*, 264–270.
- Whiticar, M. J., and E. Suess (1990), Hydrothermal hydrocarbon gases in the sediments of the King George Basin, Bransfield Strait, Antarctica, *Appl. Geochem.*, *5*, 135–147.