

Non-methane Volatile Organic Compounds (VOCs) at El Chichón volcano (Chiapas, México): Geochemical features, origin and behavior

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Resumen

Se presenta un estudio de las características geoquímicas de la fracción orgánica en las fumarolas del volcán Chichón (Estado de Chiapas, México) para obtener información sobre el origen de los compuestos orgánicos volátiles exceptuando el metano (VOCs) y los procesos que rigen su comportamiento. Los VOCs en fumarolas y pozas burbujeantes consisten principalmente de alcanos (C₂-C₅) cuya abundancia total tiene un orden de magnitud menor que el metano, y concentraciones altas de aromáticos (benceno y tolueno) y C₂-C₃ alquenos (principalmente propano e iso-butano). Se encontraron también concentraciones significativas de compuestos de azufre substituidos que en su mayoría pertenecen al grupo de los heterocíclicos. Esta composición, similar a la de las emisiones gaseosas relacionadas a sistemas geotérmicos, sugiere que la producción de gases orgánicos en el volcán El Chichón es principalmente debida a procesos termogénicos. La abundancia total de VOCs es relativamente baja en comparación con la composición típica de fluidos hidrotermales, lo que podría estar relacionado a una contribución importante de fluidos de origen magmático al reservorio que alimenta las emisiones termales del cráter. Sin embargo, la ausencia de compuestos de O-substituidos parece indicar que la composición de los fluidos hidrotermales no es afectada por el aporte de especies orgánicas producidas en profundidades someras por la descomposición de material vegetal reciente, como aquél sepultado por los productos de la erupción de 1982.

Palabras clave: VOC, El Chichón, fluidos termales, química orgánica.

Abstract

Geochemical features of the organic gas fraction in fumarolic fluids at El Chichón volcano (Chiapas State, Mexico) are studied to investigate the origin of non-methane volatile organic compounds (VOCs) and the processes governing their behavior. VOCs from fumaroles and bubbling pools mainly consist of C₂-C₅ alkanes, with total abundance one order of magnitude less than that of methane, and relatively high concentrations of aromatics (benzene and toluene) and C₂-C₃ alkenes (mainly propene and iso-butene). Significant concentrations of S-bearing compounds, mostly of the heterocyclic group, are also detected. This composition is similar to that of gas emissions of geothermal systems. The production of organic gases at El Chichón may be due to thermogenic processes. Total VOC abundance is relatively low when compared with typical hydrothermal gas discharges, and may be attributed to magmatic-related fluids in the main reservoir feeding the thermal manifestations of the crater. As absence of O-bearing compounds seems to indicate that the hydrothermal fluids are not significantly affected by organic species produced at shallow depth by decomposing vegetation, such as that buried by the volcanic products of the 1982 eruption.

Key words: VOC, El Chichón volcano, thermal fluid, organic chemistry.

Introduction

Non-methane volatile organic compounds (VOCs) are frequently released in gas emissions of geothermal and volcanic systems (e.g. Capaccioni *et al.*, 1993; Darling, 1998; Tassi, 2004). Hydrocarbon gas compounds are

generally produced in these environments by degradation of organic material, mainly buried in sedimentary formations, by bacteria-driven (biogenic) reactions at low temperature (<150 °C) or by thermogenic processes at 150-350 °C, such as catalytic reforming and/or thermal cracking (e.g. Des Marais *et al.*, 1981; Mango, 2000; Taran

and Giggenbach, 2003). Under hydrothermal conditions the relative concentration of light (C_2 - C_3) alkene-alkane pairs is regulated by chemical reactions able to approach a metastable equilibrium (e.g. Seewald, 1994; Capaccioni and Mangani, 2001; Tassi *et al.*, 2005a). Thus such compounds may be used as geoindicators for geothermal prospection and volcano monitoring (Capaccioni *et al.*, 2005; Tassi *et al.*, 2005b; 2007). Despite these encouraging results, the composition of the organic gas fraction in thermal fluid discharges is rarely determined and, consequently, the systematics and the behavior of organic compounds from volcanic and geothermal environments may not be appropriately constrained.

In this paper the composition of C_2 - C_{15} organic compounds of gases from low temperature (<100 °C) discharges is discussed in order to provide new insights into the geochemical processes and the thermodynamic conditions at El Chichón volcano, Chiapas, Mexico (Fig. 1a).

Volcanological setting and geochemical features

El Chichón volcano ($17^{\circ}22'N$, $93^{\circ}14'W$; 1,100 m a.s.l.) is the youngest volcano in the Chiapanecan Volcanic Arc (CVA; Fig. 1) between the eastern end of the Trans-Mexican Volcanic Belt (TMVB) and the northwestern end of the Central American Volcanic Arc (CVCA; Fig. 1) (Damos and Montesinos, 1978; Duffield *et al.*, 1984; Luhr *et al.*, 1984; García-Palomo *et al.*, 2004; Mora *et al.*, 2007; Layer *et al.*, this issue) (Fig. 1a). El Chichón Volcano produced potassic alkaline magmas (e.g. Luhr *et al.*, 1984), whose genesis was likely related to extensional tectonism associated with the triple junction between the North American, Caribbean and Cocos plates (Nixon, 1982). The most recent eruption occurred in 1982 (e.g. Sigurdsson *et al.*, 1984; Carey and Sigurdsson, 1986) after a quiescence time of at most 550 years (Tilling *et al.*, 1984; Espíndola *et al.*, 2000). The eruption left a sub-circular crater partly covered by an acidic crater lake with a maximum diameter of 1.1 km, featuring intense

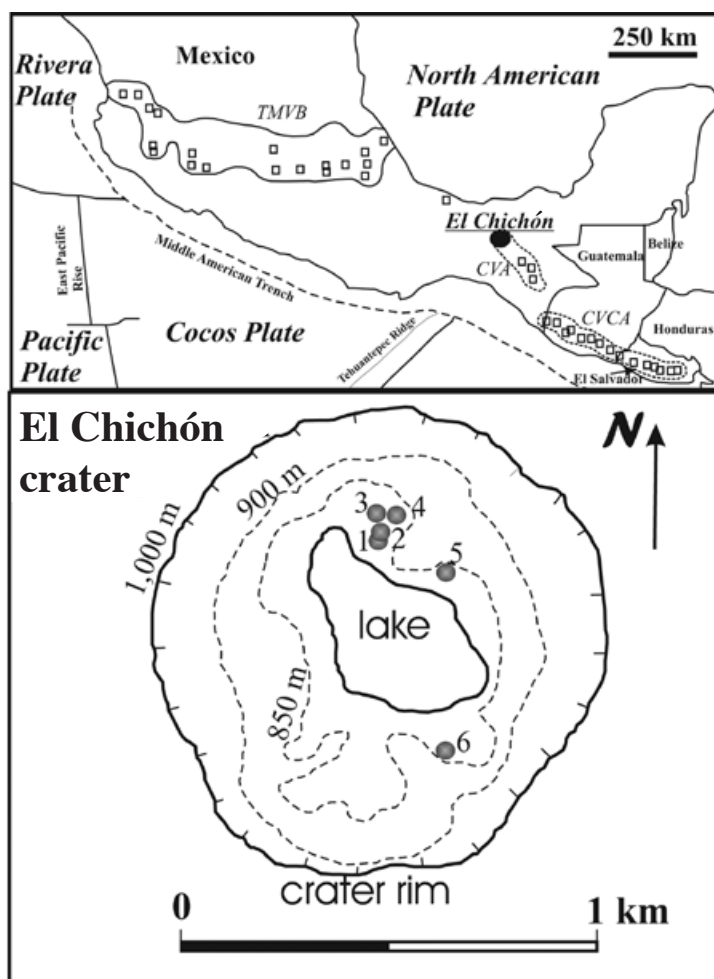


Fig. 1. (a) Tectonic setting of Mexico. The Trans-Mexican Volcanic Belt (TMVB), the Chiapas Volcanic Arc (CVCh), and the so-called “Cordillera Volcanica Centro Americana” (CVCA) are reported. (b) El Chichón crater with the location of i) the collected gas discharges and ii) the site of soil gas sampling.

current hydrothermal activity (Taran *et al.*, 1998; Rouwet *et al.*, 2004; 2008). Fluid discharges have relatively low temperatures (< 100 °C) and include hot mud, boiling and bubbling pools, thermal springs, fumaroles and areas of diffuse degassing (Fig. 1b).

The dry gas phase of fumaroles and boiling pools in El Chichón crater contains mainly CO₂ (up to 99 % by vol.) plus relatively high concentrations of H₂, N₂ and H₂S, (up to 5.9, 5 and 3.1 % by vol., respectively), and minor concentrations (<0.5 % by vol.) of CO, He and atmospheric-related compounds. Highly acidic gas species (HF, HCl and SO₂) are present as traces (Taran *et al.*, 1998; Tassi *et al.*, 2003). This composition was interpreted as the result of strong inputs of magma-related fluids, as shown by the values of helium and carbon (in CO₂) isotope ratios, in a hydrothermal reservoir that scrubs the typical highly soluble gas compounds (Taran *et al.*, 1998; Tassi, *et al.*, 2003). An important role may also be played by interaction processes of deep fluids with volcanic and sedimentary rocks (limestone and evaporite) basement (Tassi *et al.*, 2003; Taran *et al.*, 2008; Rouwet *et al.*, this issue). S in sulfur species of water and gas discharges and C in CO₂ isotopic composition suggest that the deep system is dominated by highly reducing conditions and by the presence of organic material (Taran *et al.*, 1998).

Sampling and analytical methods

Gas samples were collected from a fumarole (# 1 and 2; Table 1), corresponding to the discharging site of the Soap Pool (Taran *et al.*, 1998), and three boiling pools (# 3, 4 and 5) in the north-eastern sector of the crater (Fig. 1b). We follow the procedure described in Montegrossi *et al.* (2001). One soil gas sample (# 6) was collected in the southern inner part of the crater (Fig. 1b) with a Stütz probe at a depth of 70 cm in the soil. Inorganic compounds and methane were analyzed by gas chromatography and ion chromatography (Montegrossi *et al.*, 2001). Gas samples for the determination of VOC composition were stored into pre-evacuated 12 mL glass vials equipped with pierceable rubber septum (Labco Exetainer®). During the first phase of the analytical procedure, the organic volatiles were pre-concentrated and transferred from the sampling vials into a Thermo Trace GC Ultra gas chromatograph by using a manual SPME (solid-phase micro-extraction) device introduced through the silicon membrane of the glass vial to expose the gas mixtures to a divinylbenzene (DVB)-Carboxen-polydimethylsiloxane (PDMS), 50/30 µm, 2 cm long fibre assembly (Supelco; Bellefonte, PA, USA) for 15 min (Arthur and Pawliszyn, 1990). The GC system was coupled with a Thermo DSQ Quadrupole Mass Spectrometer for analytical separation and detection

of VOCs in the mass range 40-400 *m/z*. The transfer-line temperature was 230 °C. The mass detector was equipped with an EI (Electron Impact) ionization system with an ionization energy of 70 eV. The source temperature was 250 °C. The analyses were desorbed from the SPME fibre through direct exposure for 2 min in the GC injection port, heated at 230 °C. The chromatographic column was a 30 m x 0.25 mm i.d. 0.25 µm film thickness TR-5MS fused silica capillary column (Thermo). The carrier gas was helium at 1.3 mL/min flow-rate in constant flow mode. The column oven temperature was programmed, as follows: 35 °C (hold 10 min), rate 5.5 °C/min to 180 °C (hold 3 min), rate 20 °C/min to 230 °C (hold 6 min). Compounds were identified by comparison of the mass spectra with those of the NIST-05 library.

Concentrations of C₂-C₅ alkanes and C₃-C₄ alkenes (Table 1) were determined by a Shimadzu 14a gas-chromatograph equipped with a Flame Ionization Detector (FID) using a 10 m long stainless steel column (ϕ = 2 mm) packed with Chromosorb PAW 80/100 mesh coated with 23% SP 1700 with helium as carrier gas (Tassi *et al.*, 2004). Analytical precision was <5 %. VOC quantification was performed using an external standard calibration procedure based on a 13 components gas standard mixture. Alkanes were determined with reference to hexane, heptane and decane; alcohols to phenol; cyclics to cyclohexane; Cl-bearing compounds to dichloromethane; aromatics to benzene and p-xylene; ketones to acetone; aromatic aldehydes to benzaldehyde; aliphatic aldehydes and esters to butanal; S-bearing compounds to dimethylsulphoxide; heterocycles to furan. The analytical error was <10%. The detection limit was determined by linear extrapolation from the lowest standard in the calibration curve using the area of a peak having a signal/noise ratio equal to 5.

VOC composition

The concentration of methane and VOCs expressed as ppb by vol. in the dry gas phase of the hydrothermal fluid discharges and in the soil gas of El Chichón crater is reported in Table 1. For comparison, we also show the VOC composition of *i*) “hydrothermal” fluids, based on the mean composition of gas discharges collected at three hydrothermal systems (Yellowstone, USA; Tendaho, Ethiopia; Tatun, Taiwan), and *ii*) “low-temperature” fluids, based on the mean composition of gas discharges related to low-enthalpy systems in Tuscany, Italy (e.g. Fournier, 1989; D’Amore *et al.*, 1997; Minissale *et al.*, 1997; Lee *et al.*, 2005) (Table 1). A total of 33 and 57 different species were identified in the El Chichón fluid discharges and the soil gas, respectively (Table 1). VOC concentrations vary over a wide range (from 0.1 to 7,375 ppbv) but the fluid discharges (# 1-5) are characterized by the presence

Table 1

	1	2	3	4	5	6	hydrothermal low-temperature	
methane	345,111	39,398	18,681	48,729	2,065	262,820	2,411,359	1,670,670
ethane	7,375	979	312	1,062	50	218	49,169	487
propane	1,362	199	78	217	12	108	9,473	22
propene	216	989	79	111	13		46	
i-butane	167	25	4	29	3	4	2,021	1
n-butane	242	36	16	42	3	2	1,311	1
1-butene	47	3	9	4	2			
i-butene	57	77	86	107	52	8	3,495	4
t-2-butene	55	41	11	49	5		1	
c-2-butene	66	25	9	32	2		1	
i-pentane	63	15	2	22	1	6	951	0.3
n-pentane	40	13	4	16	1	1	1,067	0.2
Acetone							648	
DiMethylSulphide	12	9	10	10	3			
i-Exane	3	3	3	2	1	5	3,349	0.6
3-MethylPentane							1,934	
n-Exane	33	29	8	25	8	3	14,367	11
Exene							2,397	
2-MethylFurane	0.5	0.6	0.1	0.4	0.2			
MethylCycloPentane	10	13	5	13	3		2,291	
2-Butanone						6	27	
EthylAcetate							32	
CycloExane							1,636	3
Benzene	586	255	105	288	26	13	93,886	16
Tiophene	185	131	146	156	14	1	12	
n-Eptane							187	6
3-Methyl 2-Butanedione							0.2	24
MethylCycloExane							51	
TriChloroEtene	27	15	16	10	3	26	22	38
1.2-DiChloroPropane							906	
Pentanal							6	
3.4 DiMethyl 2-Exene							0.2	
4-Ethyl 1-Exene							0.6	26
3-DiMethyl 2-Exane							269	
2.2.5-TriMethylExane							134	2
2.3.4-TriMethyl 2-Pentene							0.5	254
Toluene	150	65	15	78	12	3	682	29
3-Methyl 2-Pentanone							8	
3-Methyl 1-Butanol							120	15
n-Octane							38	
3-MethylTiophene	177	180	169	215	12	0.5	18	
4-Ethyl 3-Exanol							7	
Exanal							1	135
4.5-DiMethylExene							3	185
Octene							1	
2-MethylPropilEster Acid Acetic							1	160
3.3-DiMethyl 1-Butanol							1	122
3.4-DiMethylExene							0.7	666
ChloroExane							0.1	133
EthylBenzene	42	6	4	15	1	0.1	217	7
m-p-Xylene	81	28	19	122	4	2		15

Table 1
(continued)

	1	2	3	4	5	6	hydrothermal low-temperature	
2.5-DiMethylTiophene	38	11	15	22	8		11	
5.5-DiMethyl 2-Exanol						1	38	
1-Methyl 2-EthylCisCycloExane							24	
o-Xylene	8	4	3	9	0.4	0.3	41	5
Styrene						0.1		
1.1.2-TriChloro 2-MethylPropane							12	
Eptanal						4		15
Pirene						2	14	
1-Methyl 3-EthylBenzene	2	1	1	2	1			
3-DiMethylEptane						0.5	24	5
Butoxy-2-Etanol						3		3
2-DiMethylCycloExanol							24	
DiMethylSulphoxide	7	6	3	3	2	8		2
1-Ethyl 4-MethylBenzene	4	2	1	8	2			
2-DiMethylEptane						4	83	4
2-BromoOctane							14	
Decane						0.6	21	15
1.2.3-TriChloro 2-MethylPropane						3	57	
3.3-DiMethylOctane							21	4
1.3.5-TriMethylBenzene	1	0.9	0.6	1.5	0.3		9	
Benzaldehyde	7	7	5	11	4	0.6	17	0.5
6-Methyl 2-Eptanone						0.5		9
3-MethylEthylCycloExane							11	9
2Ethyl 1-Exanol							2	10
Octanal						9		3
Limonene								0.2
1-Methyl 4MethylEthylBenzene	0.8	0.4	0.7	0.5	0.4			3
DiChloroBenzene						0.4		1
1-Metoxy 1-MethylEtoxy 2-Propanol								
2-EtoxyEtanol						9		3
2-Propanol								11
2Ethyl 1-Exanol						0.5	4	9
Undecane						1.1	26	6
Phenol						0.3	8	4
1-Ethyl 2.4DiMethylBenzene	1.7	1	1.2	1.1	1.9			
3Methyl 1.2CycloPentanediol								
AcetoPhenone						0.8		8
Nonanal						0.6	7	19
Dodecane						0.5	11	5
1.2.3.4 Naftalene TetraHydrato						0.5		0.8
Acid Benzoic EthylEster						0.2		0.7
Decanal						0.6		21
Naftalene	4	3	5	6	2	0.2	5	0.2
TriDecane						0.3	3	1.4
Benzotiazole						0.7		22
FenoxoPropanol						0.3		4
Tetradecane						0.2	2	1.6
Pentadecane							2	1
Exadecane							2	0.9
VOCs total	11,070	3,173	1,146	2,689	251	504	191,964	850

of the same organic species. Their composition can be considered relatively homogeneous. Generally speaking, C_2-C_5 alkanes largely represent the most abundant group of VOCs in El Chichón gas samples (Table 1). However, as shown in Fig. 2a-b, the mean composition of the 5 gas discharges is significantly different from that of the soil gas. El Chichón hydrothermal fluids are contained by relatively high concentrations of alkenes (11.7 % of the total VOC composition), aromatics (10.7 %) and S-bearing compounds (8.4 %), while the O- and Cl-bearing organic species found in the soil gas (15.7 and 5.9 %, respectively; Fig. 2b), are present in very small amounts (<0.4 %). The VOC composition of El Chichón fluid discharges shows striking differences when compared with typical fluids of hydrothermal systems (Fig. 2c), as the latter are significantly rich in aromatics (49.5 %) (e.g. Capaccioni *et al.*, 1993; 1995; 2005). Notice that the pie charts of relative proportions of the main group of VOCs clearly show compositional features of soil gas resembling those

of gases produced at relatively low temperature (Fig. 2b,d). The distribution of alkanes in the organics of El Chichón gas discharges, is poor in C_{6+} species that are present in significant amounts in soil gas, as in hydrothermal and low-temperature fluids (Fig. 3). On the other hand, the distribution of aromatics shows no significant differences among the four types of fluids considered, especially those produced by analogous reaction series (Tassi, 2004), i.e. benzene, toluene and xylenes (Fig. 4). Thus the VOC composition of El Chichón fluid discharges, though partly resembling that found in other hydrothermal fluids also presents distinctive features as follows:

- 1) total VOC concentration is two orders of magnitude lower than in typical hydrothermal fluids;
- 2) several light VOCs (< C_5) were detected;
- 3) heavy VOCs (C_{6+}) are present only as aromatics and aromatic-derived species (i.e. benzaldehyde and 2,5-dimethylthiophene).

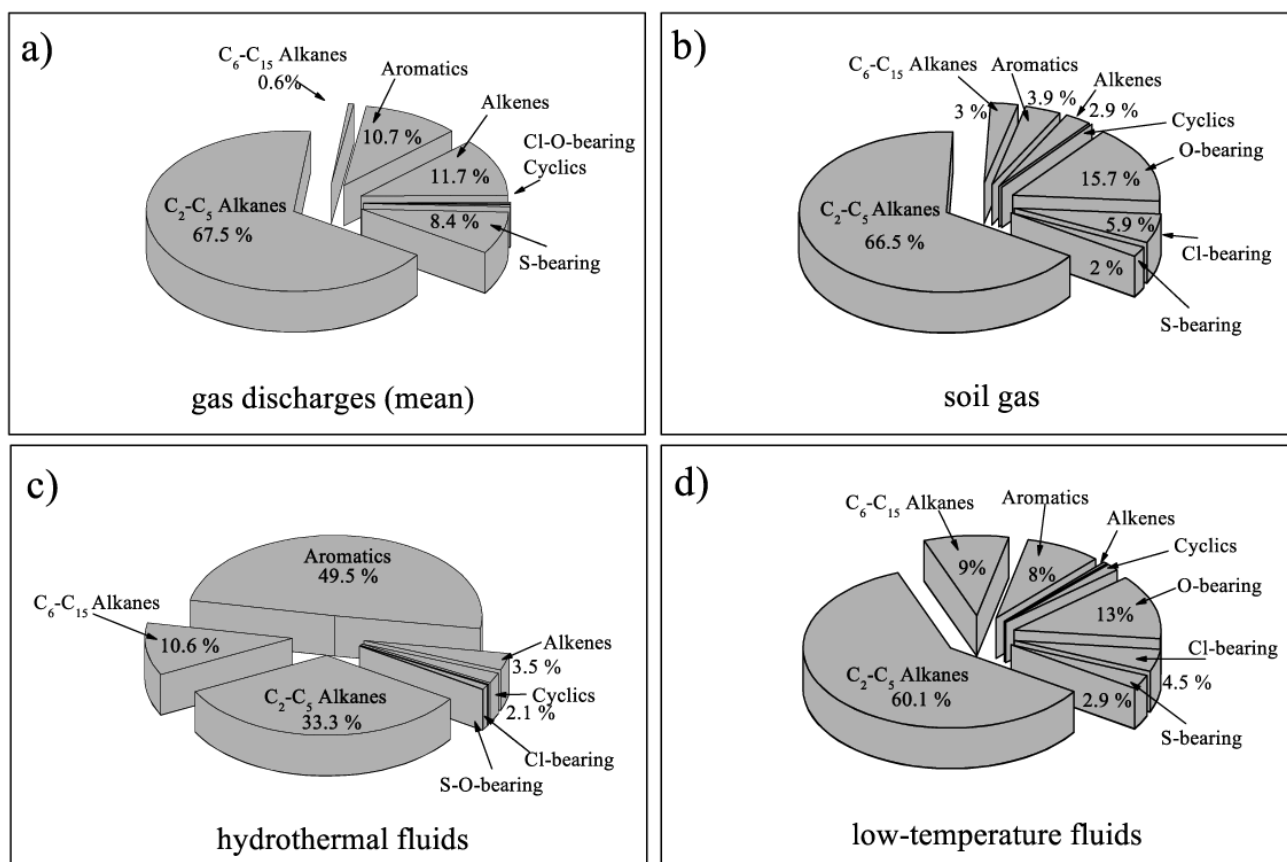


Fig. 2a,d. Pie diagrams showing the relative abundances, expressed in % with respect to the total VOC concentrations, of the various groups of VOCs in a) El Chichón gas discharges, b) soil gas of El Chichón crater, c) fluid discharges of hydrothermal systems and d) fluid discharges of low-temperature systems.

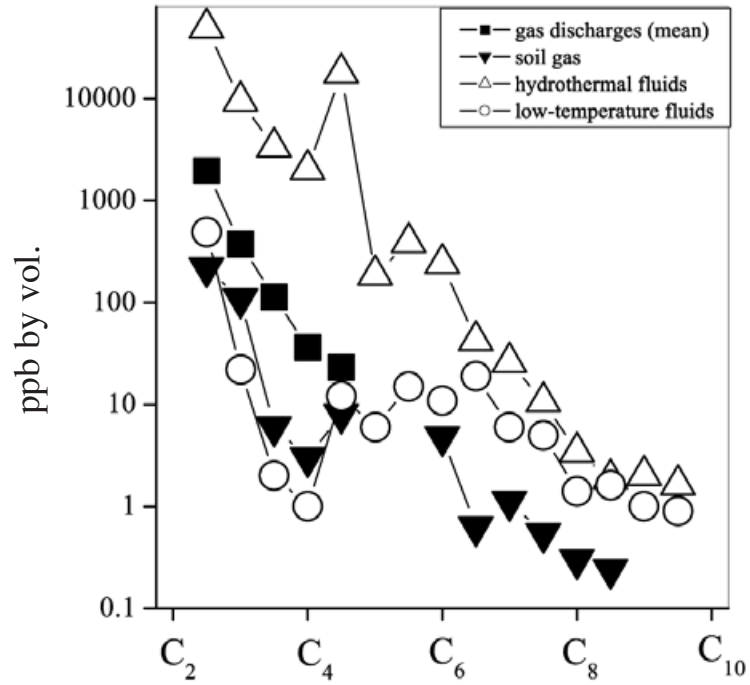


Fig. 3. Distribution pattern of the concentrations of C₂-C₁₆ alkanes in i) El Chichón gas discharges, ii) soil gas of El Chichón crater, iii) fluids of hydrothermal systems and iv) fluids of low-temperature systems. Concentrations are in ppb by vol.

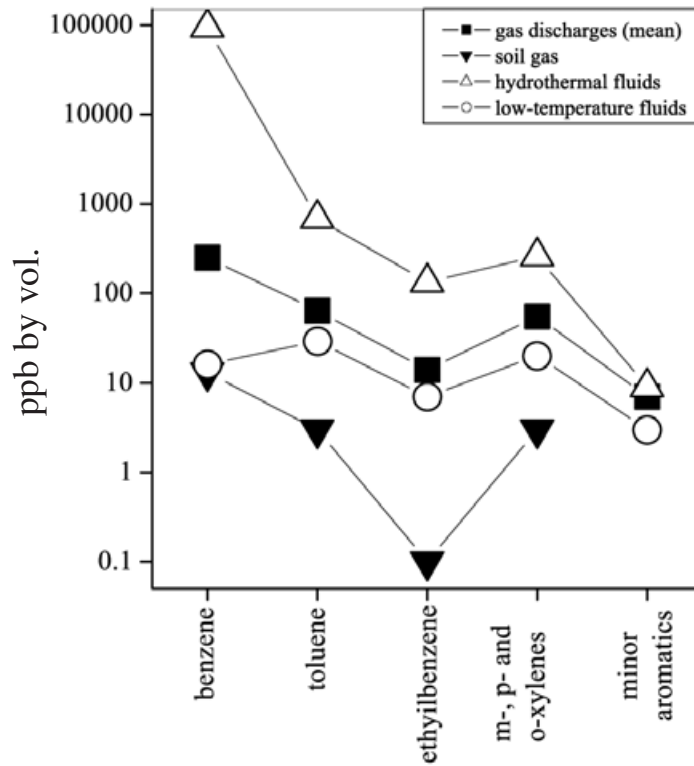


Fig. 4. Distribution pattern of the concentrations of aromatics in i) El Chichón gas discharges, ii) soil gas of El Chichón crater, iii) fluids of hydrothermal systems and iv) fluids of low-temperature systems. Concentrations are in ppb by vol.

VOC origin

VOCs in the natural environment are almost exclusively produced by degradation of organic matter (“kerogen”) (e.g., Gunter, 1978; Des Marais *et al.*, 1981; Mango, 2000). Abiotic synthesis of organic species can originate from inorganic constituents (e.g., Berndt *et al.*, 1996; Horita and Berndt, 1999), but may be regarded as negligible (e.g., Welhan, 1988; Darling, 1998; Mango, 2000; Taran and Giggenbach, 2003).

The ratio of CH₄ to light hydrocarbons may provide insights into the thermodynamic conditions controlling the genetic process of these organic compounds (Mango, 2000, Mango, 2001). The CH₄/(C₂H₆+C₃H₈) ratio in El Chichón gas discharges, as in other hydrothermal systems used for comparison, are <100 (Fig. 5), suggesting that these compounds are thermogenic (T > 150°C) (e.g. Oremland *et al.*, 1987; Whiticar and Suess, 1990). By contrast, El Chichón soil gas shows a relatively high CH₄/(C₂H₆+C₃H₈) ratio (806), which suggests a significant contribution of organics from bacterial activity, as in shallow environments at T <50 °C (Hunt, 1984). Thus the light alkene-alkane pair in the El Chichón crater fluid discharges may be utilized to evaluate equilibrium temperature and redox conditions in the main hydrothermal reservoir (Capaccioni *et al.*, 2004), where the aromatics, which together with the alkanes and alkenes constitute almost the 90 % of VOCs (Fig. 2a), may also be produced. Similarly, the S-bearing compounds, up to 10 % of the total VOC composition (Fig. 2a), can be considered a common feature in fluids equilibrated at medium-to-

high temperature in the presence of H₂S (e.g. Mangani *et al.*, 2004). O-bearing compounds (aldehydes, ketones, organic acids, alcohols and esters), are very rare in fluid discharges (Table 1), they may be due to bacterial metabolism at relatively high oxidizing conditions (Jones, 1968). This explains the relatively high concentrations of these compounds in soil gas and in fluids from low-temperature systems (Fig. 2b,d), where genetic processes for organics can take place under oxidizing condition and in presence of fresh organic matter, typically containing O- and N-bearing compounds. Cl-substitutes may be produced at depth by interaction of organics with Cl-rich fluids in the deep aquifer (Taran *et al.*, 1998). They show similar concentrations in gases from thermal discharges and soil (Table1), possibly because of the high stability of these compounds at various redox conditions (Scheutz *et al.*, 2000).

Concluding remarks

The VOC composition in fluids of the fumaroles and the boiling pools of El Chichón volcano have a composition that is related to thermogenic processes. Accordingly, the lack of O-bearing compounds in the hydrothermal discharges indicates that the production processes of the organic gas fraction essentially proceed at depth, likely within the main hydrothermal reservoir. Consequently, contribution of VOCs from degradation of fresh vegetation buried in the soil, such as that related to the volcanic products of the 1982 eruption, can be considered negligible. It is important to notice that the total VOC abundance measured in El Chichón fluids is

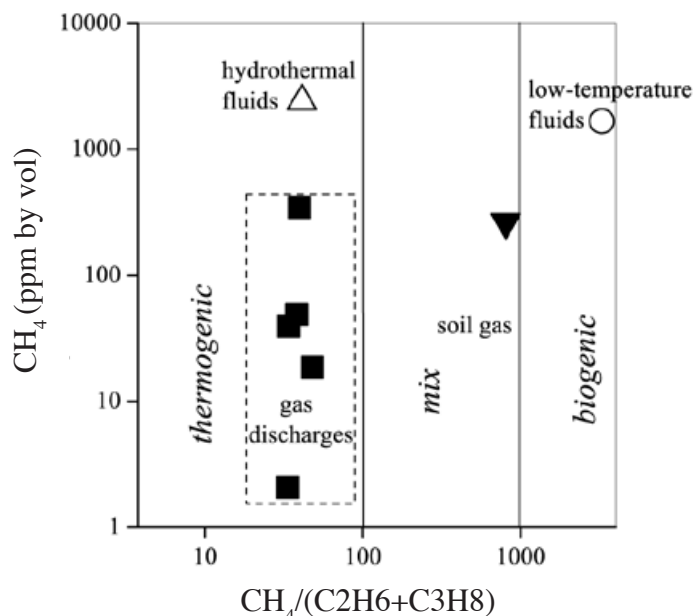


Fig. 5. CH₄ vs. CH₄/(C₂H₆+C₃H₈) binary diagram for gases of i) El Chichón gas discharges, ii) soil gas of El Chichón crater, iii) fluids of hydrothermal systems and iv) fluids of low-temperature systems. Methane concentration is in ppm by vol.

relatively low when compared with those characterizing the typical hydrothermal systems (Table 1), but it is to be considered high with respect to the VOC abundances found in gas emissions of high-temperature fumaroles of active volcanic systems (Tassi, 2004; Schwandner *et al.*, 2004 and references therein). This is in agreement with the chemical and isotopic features of the main gas constituents that were interpreted (Taran *et al.*, 1998; Tassi *et al.*, 2003) as related to a hydrothermal system whose temperature and redox conditions were strongly affected by magmatic inputs.

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