Light hydrocarbons in gas-emissions from volcanic areas and geothermal fields

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(Received June 29, 1992; Accepted December 10, 1992)

Geochemical investigation of gas emissions at low temperatures in areas of Quaternary volcanism shows a systematic enrichment of aromatic hydrocarbons and alkenes in fumaroles from active volcanic areas (Vulcano and Phlegrean Fields, Italy; S. Miguel, Terceira and Graciosa, Azores; Chichón, Mexico; Uzon and Geyser Valley, Kamchatka) and geothermal systems (Larderello area, Italy) with respect to those pertaining to areas of recent but exhausted volcanism (Vulsini and Sabatini volcanic districts, Torre Alfina volcano, Italy). The general behaviour of hydrocarbons in the investigated gas-emissions, together with thermodynamic and experimental data (taken from the industrial treatment of petroleum) suggest possible abiogenic processes acting on degradation of alkane hydrocarbons when source temperatures exceed 150° and acid species together with high active-surface area clay minerals are available. Benzene shows very similar enrichments in emissions from Vulcano beach and Phlegrean Fields, Kamchatka and Azores, pointing out the possible occurrence of catalytic reactions at the source. Alkenes display significant relative increases in crater fumaroles from Chichón volcano. Moreover, lower carbon-number alkenes (propene and ethene) progressively appear with increasing alkenes/alkanes ratio, suggesting an increasing importance of thermal-cracking reactions. The general similarities in distribution patterns from different active volcanic environments allow us to reappraise the influence of the nature of sources and to emphasize the effects of abiogenic reactions.

With reference to areas of active volcanism, the distribution of hydrocarbons can represent a useful parameter to evaluate the prevailing physico-chemical conditions and their time-space variabilities. Accordingly they can give a significant contribution to the geochemical monitoring of active volcanic areas.

INTRODUCTION

Natural gaseous emissions have been currently investigated for geothermal purposes or geochemical surveillance of active volcanoes, and significant information is available on the chemical composition of fumarolic gases in a wide range of temperature (Martini *et al.*, 1980; 1984; 1991; Carapezza *et al.*, 1981; Le Guern *et al.*, 1982; Gerlach, 1982; Giggenbach *et al.*, 1986; Matsuo, 1988). With reference to light hydrocarbons, however, only few data have been provided. Ellis (1957) and Matsuo (1961), who firstly discussed the chemical composition of fumarolic gases in terms of equilibrium ther-

modynamics, suggested that methane detected at Showanshinzan (Japan) and Wairakei (New Zealand) might have an extra-magmatic origin. Giggenbach *et al.* (1986) also agreed with this conclusion and hypothesized the occurrence of two main end members mixing into a cooler two-phase hydrothermal zone surrounding the magmatic system: a magmatic component characterized by the presence of H₂S and SO₂, low contents of methane and an hydrothermal component low in SO₂ but high in methane. The kinetics of reactions involving methane are very slow, and equilibrium is approached only within the slow moving two-phase hydrothermal zone, where redox conditions are controlled by rock

composition. Equilibrium is on the contrary quenched within a magmatic gas phase rapidly ascending towards the earth's surface. Tedesco and Sabroux (1987) suggested a re-examination of the influence of catalysis on the Fischer-Tropsch synthesis of methane by hydrogenation of carbon dioxide during the fluid uprising. According to Martini *et al.* (1986), the flow of magmatic gases through an aquifer leads to a selective absorption of highly soluble acid gases, such as SO₂, HCl and HF, and to a consequent enrichment of slightly soluble species, such as H₂, N₂, O₂ and methane in the residual gas phase. The same authors interpreted methane as

the result of decaying organic matter.

However, sufficient information on the presence of light hydrocarbons in natural gas emissions is not available. In this paper new data are presented and discussed on the concentration and distribution of these chemical components in fumarolic gases from active and recent volcanic systems as well as geothermal areas not directly related to volcanic activity (Table 1).

VOLCANIC ACTIVITIES

Active volcanic areas

The last eruptive activity occurred at

Table 1. Description of the samples investigated

Sample	Location	Typology	Date of sampling
Active volcanic areas			
RJ1	Vulcano beach (Italy)	Bubbling gases	February 1991
FM1	Vulcano beach (Italy)	Submarine emission	February 1991
BG4	Phlegrean Fields (Italy) (Solfatara crater)	Fumarolas	January 1992
PS4	Phlegrean Fields (Italy) (Pisciarelli site)	Bubbling gases	January 1992
KUZ	Uzon caldera (Kamchatka)	Bubbling gases	October 1990
KGV	Geysir Valley (Kamchatka)	Fumarolas	October 1990
FU	S. Miguel island (Azores) (Furnas site)	Bubbling gases	October 1991
ES	S. Miguel island (Azores) (Esguicho site)	Bubbling gases	October 1991
RG	S. Miguel island (Azores) (Ribeira Grande site)	Bubbling gases	October 1991
CV	S. Miguel island (Azores) (Caldera Velha site)	Bubbling gases	October 1991
GR	Graciosa island (Azores) (Graciosa caldera site)	Fumarolas	October 1991
TE	Terceira island (Azores) (Terceira caldera)	Fumarolas	October 1991
CH1	Chichón volcano (Mexico)	Bubbling gases	November 1991
CH3	Chichón volcano (Mexico)	Fumarolas	November 1991
Recent volcanic areas and geothermal fields			
LT1	Latera caldera (Italy)	Potizza	May 1990
LT2	Latera caldera (Italy)	Potizza	May 1990
TA	Torre Alfina volcano (Italy)	Potizza	May 1990
GG1	Sabatini volc. complex (Italy)	Potizza	July 1990
GG2	Sabatini volc. complex (Italy)	Potizza	July 1990
MZ	Manziana crater (Italy)	Potizza	July 1990
SPp	S. Pisano geoth. well (Italy)	Geoth. fluid	September 1990
SPs	S. Pisano geoth. field (Italy)	Bubbling gases	September 1990
MR	Monterotondo geoth. field (Italy)	Fumarolas	September 1990

Fig. 1. Investigated areas.

Vulcano (Fig. 1) in 1888–1890 was characterized by hydromagmatic explosions, producing thin ash deposits at a distance not exceeding few hundred meters from the vent (Frazzetta *et al.*, 1984; Dellino *et al.*, 1990). After this last eruptive period, the volcanic system remained in a fumarolic stage with the main clusters of emissions located on the northern crater rim and near Baia di Levante beach. The crater fumaroles have shown interesting time- and space-related variations (Martini *et al.*, 1980; Carapezza *et al.*, 1981; Cioni and D'Amore, 1984). However, due to their almost complete lack of hydrocarbons our attention has been devoted to the beach manifestations.

Phlegrean Fields are located inside a huge caldera (Fig. 1), possibly related to a giant ignimbrite eruption 35,000 years ago (Rosi *et al.*, 1983). The last eruptive event occurred in 1538 with the

build up of Monte Nuovo, a 140 m high tuff cone. At present, gas emissions are located inside and just outside the Solfatara crater (Bocca Grande, 159°C, and Pisciarelli, 98°C, respectively). Their physico-chemical characters suggested an origin from boiling aquifers (Martini *et al.*, 1984).

The axis of the Mid-Atlantic ridge crosses the Azores submarine plateau in a north-south direction (Fig. 1). The historical documentation on volcanic activity started after the Portuguese settlement in 15th century, and only ten volcanoes are considered still active. Besides the surtseyan eruption of Capelinhos at Faial in 1957–58 (Machado and Forjaz, 1968), strombolian activity with lava flows occurred in 1761 at Terceira, four explosive eruptions were recorded for San Miguel in 1563, 1638, 1640 and 1811, and solfataric activity was reported for Graciosa

(Booth *et al.*, 1983; Forjaz pers. comm.).

Chichón volcano (Fig. 1) consists almost entirely of pyroclastic deposits and lava domes, directly overlying the sedimentary substratum. It erupted explosively on March 29, 1982, after a period of quiescence of about 350 years, and produced a pumiceous fallout followed by surges and pyroclastic flows. At present an intense fumarolic activity occurs inside the crater (Carey and Sigurdsson, 1986).

The manifestations at Uzon caldera and Geyser Valley, Kamchatka (Fig. 1) with bubbling gases, steaming pools and geysers can be considered as related to active volcanism, although no information about their volcanic histories is available (Piip, 1937; Vakin *et al.*, 1982).

Areas of recently exhausted volcanism

Gaseous emissions in these areas are represented by surface manifestations of residual thermal anomalies and characterized by almost pure CO₂ (mofettas) or by CO₂ plus H₂S (potizzas).

The Latera caldera (Fig. 1) consists of a huge polygenetic structure produced by a series of ignimbrite-forming eruptions (Sparks, 1975; Metzeltin and Vezzoli, 1983; Nappi *et al.*, 1991) occurring during a period of about 0.17 m.y. Its youngest activity has been dated at 110,000 years ago (Santi, 1990).

Other samples pertain to the small quaternary center of Torre Alfina (Fig. 1), whose products are only represented by minor lava flows.

Explosive paroxysmal eruptions with subordinate effusive episodes characterized the Sabatini Volcanic District (Fig. 1) during a period of 0.6 m.y., and the development of the volcano-tectonic depression of Bracciano lake followed the exhaustion of the eruptive activity about 40,000 years ago (De Rita and Funicello, 1985).

Geothermal areas not related to recent volcanism

Geothermal wells at Monterotondo and Sasso Pisano, pertaining to the well known area of Larderello (Fig. 1), are mainly vapour-

dominated systems. The productive, high permeability aquifer is located in Triassic evaporites covered by impervious shales of allochthonous series (Ligurids). The bottomhole temperatures often exceed 260°C (Squarci, 1981).

SAMPLING AND ANALYTICAL PROCEDURES

The sampling apparatus included a vacuum vial partially filled with 4 N NaOH solution (Giggenbach, 1975), which might concentrate up to several hundred times the uncondensable gases, such as H₂, N₂, O₂ and light hydrocarbons. The total quantity of sample collected (included water vapour if present) varies from 1 to 10 grams, depending on the relative amounts of uncondensable gases.

The analysis of organic fractions was carried out with a Dani 86.10 gas chromatograph (Mangani *et al.*, 1991) equipped with a Flame Ionization Detector (FID). A glass column (2 m long, 2 mm I.D.) was packed with Carbowax B 80/100 mesh coated with 1% of SP 1000. The temperature of the column was set at 30°C for 2 minutes and then increased up to 220°C with a rate of 30°C/min. The injector and detector temperatures were 150°C and 220°C respectively. Nitrogen was used as carrier gas and the flow rate was set at 30 ml/min. Qualitative analysis was carried out using the retention time and the mass spectrum obtained by the gas chromatograph (GC) coupled with a double focussing mass spectrometer (MS) of a model VG 70-70 H (VG analytical Ltd., Manchester, U.K.). The MS was equipped with a Tecknivent Vector/one data system (Tecknivent, St. Louis, USA). Calibration was performed by using standard mixtures obtained with permeation tubes (Mangani and Ninfali, 1988). The very slow kinetics of possible reactions involving hydrocarbons at sample storage temperatures prevent any kind of modification after collection.

RESULTS

Table 2 shows the analytical data for the inorganic components. Carbon dioxide concentra-

Table 2. Main chemical composition of gases (in volume percent)

Active volcanic areas									
Sample	RJ1	FM1	BG4	PS4	FU	ES	RG		
temp. °C	94	97	155	89	96	98	95		
CO ₂	92.88	94.67	98.82	99.13	99.05	99.11	99.39		
H ₂ S	1.15	1.32	0.59	0.44	0.43	0.53	0.22		
H ₂	0.54	1.94	0.14	0.14	0.16	0.25	0.30		
N ₂	4.75	1.84	0.28	0.27	0.35	0.09	0.08		
O ₂ *	380	75	0.3	0.8	8.3	2.2	2.1		
CO*	—	0.24	0.19	—	—	—	0.015		
Sample	CV	GR	TE	CH1	CH3	KUZ	KGV		
temp. °C	97	91	91	94	97	89	97		
CO ₂	99.54	99.19	97.59	78.00	91.28	93.23	94.44		
H ₂ S	0.09	0.13	0.98	4.71	6.15	3.96	3.61		
H ₂	0.13	0.08	0.83	12.17	1.46	0.15	0.12		
N ₂	0.21	0.48	0.22	4.90	0.82	1.85	1.58		
O ₂ *	6.3	112	5.7	47	1.1	11	28		
CO*	—	0.017	0.048	0.67	0.09	—	—		
Recent volcanic areas and geothermal fields									
Sample	LT1	LT2	TA	GG1	GG2	MZ	SPp	SPS	MR
temp. °C	cold	cold	cold	cold	cold	cold	93	95	98
CO ₂	94.57	92.55	93.25	98.29	98.41	97.13	88.94	90.76	89.33
H ₂ S	0.311	0.301	0.037	0.086	0.055	1.097	2.678	—	1.996
H ₂	—	—	—	—	—	—	3.988	2.710	3.323
N ₂	4.390	5.980	5.290	0.840	0.788	1.745	1.026	4.580	1.713
O ₂	0.4505	0.8105	0.6928	0.0019	0.0004	0.0013	0.0029	0.1300	0.0310

(*) values expressed in ppm.

"—" means below the detection limit.

tions in all the samples exceed 90%, with minor amounts of hydrogen sulphide, nitrogen and oxygen. Not negligible contents of hydrogen and carbon monoxide are found only in active volcanic areas. This last shows maximum concentrations of 0.70 ppm in the crater fumaroles from Chichòn volcano.

Among hydrocarbons, fifteen components pertaining to five homologous series have been identified. These components often amount to less than 1% of the total gas mixture (Tables 3 and 4). The concentrations of methane are invariably above 90% of the total organic fraction.

Normal alkanes, the second most abundant species, display decreasing contents with increasing carbon number in the homologous series. Isoalkanes are represented by isobutane and isopentane with concentrations up to thousands of

ppb. Cyclo-alkanes occurring as cyclopentane and cyclohexane were detected only at the Azores and at Chichòn volcano.

Among alkenes, butene characterizes the samples from active volcanic and geothermal areas. Propene was detected at Phlegrean Fields, at San Miguel and Graciosa and at Chichòn volcano, while ethene was found only in the sample from Chichòn volcano.

Significant amounts of aromatics showed a common character of all the areas examined. Benzene was found to be an ubiquitous component, while toluene was detected in some samples only.

DISCUSSION

Figure 2 represents the distribution of alkanes, aromatics and hydrogen, where an in-

Table 3. Concentration of hydrocarbons (in ppm for methane and in ppb for the others)

Active volcanic areas							
Sample	RJ1	FM1	BG4	PS4	FU	ES	RG
methane	3720	2400	120	86	20	48	37
ethene	—	—	—	—	—	—	—
ethane	570	178	1798	1115	235	960	—
propene	—	—	13	—	10	—	—
propane	498	100	154	98	19	570	109
i-butane	60	48	9	5	—	274	—
i-butene	66	32	9	4	13	32	22
1-butene	—	—	—	—	—	—	—
tr-2-butene	—	—	—	—	—	—	—
cs-2-butene	—	—	—	—	2	—	9
n-butane	78	8	16	10	—	172	—
cyclopentane	—	—	—	—	—	14	2
i-pentane	12	2	—	—	2	81	2
n-pentane	18	6	1	—	2	74	3
cyclohexane	—	—	—	—	51	21	12
benzene	2889	763	2020	1032	303	373	164
toluene	—	—	—	—	115	176	148
Sample	CV	GR	TE	CH1	CH3	KUZ	KGV
methane	19	27	3700	38	11	7900	3300
ethene	—	—	—	1244	—	—	—
ethane	204	—	5913	1486	465	18750	9900
propene	—	22	—	1054	62	—	—
propane	32	52	50	484	64	274	1320
i-butane	2	2	9	155	21	17	—
i-butene	7	6	71	553	52	21	—
1-butene	—	—	—	190	25	—	—
tr-2-butene	—	—	—	104	11	—	—
cs-2-butene	55	—	94	294	34	—	—
n-butane	3	5	6	294	57	21	660
cyclopentane	—	—	—	155	3	—	—
i-pentane	1	5	13	397	9	8	—
n-pentane	2	18	10	397	8	4	330
cyclohexane	18	21	51	2488	78	—	—
benzene	248	156	998	2332	319	11390	4290
toluene	17	114	—	—	—	—	—

“—” means below the detection limit.

crease of both aromatics and hydrogen can be observed from areas of recent volcanism, to geothermal areas and to active volcanic areas. After an increase of both hydrogen and aromatics, a sharp shift towards the hydrogen corner occurs for samples collected at volcanic systems where historical activities are reported. These two trends can be tentatively interpreted by considering an initial common and then independent sources for aromatics and hydrogen.

The increase of aromatics with respect to alkanes passing from recent to active volcanic areas, already pointed out in Fig. 2, is shifted sharply towards the alkenes corner in Fig. 3. The samples from Chichón volcano show the maximum shift. However the evidence of historical records of volcanic activities does not provide a sufficient explanation; in fact the samples from Vulcano show a lower increase in alkenes than those from the Azores where eruptive episodes

Table 4. Concentration of hydrocarbons (in ppm for methane and in ppb for the others)

Sample	Recent volcanic areas and geothermal fields								
	LT1	LT2	TA	GG1	GG2	MZ	SPp	SPs	MR
methane	0.280	0.360	0.730	0.786	0.749	0.027	3.367	2.010	3.606
ethane	31343	39388	8254	7484	4526	1481	100572	89930	40809
propane	5278	6775	3050	203	212	41	22178	6566	5393
i-buthane	439	674	529	116	109	5	7127	1897	789
i-butene	—	—	—	—	—	7	87	874	737
n-buthane	1057	1302	606	116	117	7	4292	1255	1448
i-pentane	247	286	290	177	176	1	1396	418	286
n-pentane	276	342	161	98	95	1	1014	298	191
cyclohexane	21	25	64	93	88	—	251	158	147
benzene	42	46	193	151	146	10	2081	2762	5115
n-hexane	100	68	—	132	152	—	503	242	—
toluene	—	—	171	146	137	—	1193	1730	1609

“—” means below the detection limit.

Fig. 2. Relative distribution of normal alkanes, aromatic hydrocarbons and hydrogen for all the investigated samples. Closed stars: recently exhausted volcanic areas; closed squares: Uzon and Geyser Valley; closed triangles: Phlegrean Fields; open circles: Vulcano island; open triangles: Azores islands; closed circles: El Chichón volcano.

are dated back to much earlier time.

Information from industrial processes of oil refineries can provide some details about the parameters controlling possible reactions between different hydrocarbons (Girelli, 1969). Two main types of processes can be considered:

catalytic reforming and thermal cracking. Temperature, hydrogen partial pressure, and several catalytic agents represent the controlling parameters. Catalytic reforming includes different processes in which catalytic agents, rather than temperature and pressure, play the

Fig. 3. Relative distribution of normal alkanes, aromatics and alkenes. Closed stars: recently exhausted volcanic areas; closed squares: Uzon and Geyser Valley; closed triangles: Phlegrean Fields; open circles: Vulcano island; open triangles: Azores islands; closed circles: El Chichòn volcano.

most important role. The main reactions involved are the following (Girelli, 1969):

These consist respectively of dehydrogenation of C_6 cycloalkanes (1) and of dehydrocyclization of normal alkanes (2), to produce benzene and hydrogen. The best industrial results are obtained in the temperature range of 450–500°C, hydrogen partial pressure from 15 to 40 atm and catalytic agents composed by platinum supported by aluminum beds impregnated with halogen acids. Intermediate products of reactions (1) and (2) are represented by iso- and cyclo-alkanes.

Processes of thermal cracking consist on the breakage of carbon-carbon bond ("cracking" s.s.) and the breakage of carbon-hydrogen bond:

The first is prevailing during thermal cracking of high carbon number molecules, while the second is preferred when low carbon number molecules represent the starting material. The industrial reactions are carried out at temperatures of the order of 1000°C. As shown by reactions (3) and (4) the most important products of thermal cracking are represented by alkenes, hydrogen and methane.

Several authors (Weiss and Roloff, 1963; Sarkisyan, 1972; Blank *et al.*, 1973; Zimmerle, 1985) stressed the importance of clay minerals as catalysts during the transformation of organic matter. In particular Hunt (1979) concluded that smectite-type clay minerals can play an important role in the production of hydrocarbons from organic matter, due to their large active surface area.

From a thermodynamic point of view, the relative stabilities of alkanes, aromatics and alkenes, can be well expressed in the diagram of Fig. 4, where the variation of free energies of formations for carbon atom is reported against tem-

Fig. 4. Relationships between free energies of formation (expressed as Kcal/g for each carbon atom) and temperature for different compounds (modified from Girelli, 1969).

perature (Girelli, 1969). According to its relatively high concentrations observed in any of the gas emissions investigated, methane appears as the component with the highest stability at any temperature. Ethane appears also more stable with respect to benzene and alkenes up to 600°C, while at temperatures above 350°C the stability of benzene is greater with respect to high carbon number normal alkanes. Among alkenes, always less stable than normal alkanes, butene is prevailing below 350°C; propene in the temperature interval 350–700°C and ethene above 700°C display relatively higher stabilities.

Among the above mentioned conditions, the occurrence of acid species, metals, hydrogen, as well as fine-grained smectites (Capaccioni *et al.*, 1991) at relatively high temperatures, can be normally observed in the environments of active volcanoes and, at a lower extent, in geothermal

areas. The distribution of hydrocarbons in gaseous emissions here considered could then mainly result from abiogenic reactions occurring at the prevailing conditions of the different systems. The source of hydrocarbons can be organic matter rapidly buried by volcanoclastic sediments (Zimmerle, 1985) in volcanic areas, or contained in the sedimentary rocks of geothermal fields.

The relative depletion in alkanes, the increase of aromatics and of alkenes passing from recent to active volcanic areas, could be related to the fulfilment of thermal and catalytic conditions able to trigger reactions of the type (1) to (4). In particular, the maximum enrichment of benzene at Vulcano beach (Fig. 2) could result from the occurrence of catalysts in the source aquifer (reactions 1 and 2), such as soluble acid species (SO_2 , HCl and HF) and clay minerals (mainly smectites). On the contrary, alkenes enrichment seems to be mainly related to thermal effects (reactions 3 and 4), as suggested by the displacing of crater fumaroles of Chichón volcano towards the alkenes corner (Fig. 3). This conclusion well agrees with the relatively high contents of components equilibrated at high temperatures, such as carbon monoxide and hydrogen (Tedesco and Sabroux, 1987), and with the progressive appearance of lighter alkenes (propene and ethene), whose relative stabilities are reversed with increasing temperature (Fig. 4). Moreover, the occurrence of cyclohexane could testify an incomplete reaction of type (2). The relative thermodynamic stabilities seem to suggest the increase of aromatics/alkanes ratio in gases from active volcanic areas (Fig. 2) as resulting from processes occurring at minimum temperatures of 350°C, even if the temperatures of the reactions (1) and (2) can be lowered by catalysts. Moreover, the present aromatics/alkanes ratios may result from an independent depletion of alkanes due to reactions of type (3) and (4). Finally, hydrogen and methane always appear as final products of all the reactions considered.

CONCLUSIONS

The results obtained through the investigation of gaseous emissions from different volcanic environments suggest the following inferences: 1) no evidences disagree with an origin of hydrocarbons from decaying of organic matter; 2) the composition of hydrocarbons in volcanic gases appears to be mainly controlled by the physico-chemical conditions occurring during their generation and uprising towards the surface, while their total contents seem to be related with the amounts of organic matter available at the source; 3) fumaroles interpreted as supplied by extensive boiling aquifers show the highest relative increase of aromatics, probably due to catalytic and thermal reactions of the type (1) and (2); 4) suitable catalysts seems to occur in active volcanoes, where acid species (SO_2 , HCl and HF) in the uprising fluids and smectites and other clay minerals in the hosting rocks are available; 5) high temperature fluids reaching the surface after minor interactions with aquifers (crater fumaroles) point out a significant increase of alkenes together with a gradual appearance of propene and ethene; in this case thermal reactions of the type (3) and (4) are expected to prevail.

The systematic increase of benzene, the appearance of butene and propene, and the relative decrease in normal and iso-alkanes concentrations passing from areas of recent volcanism to presently active volcanic areas, seem to indicate general processes affecting the organic fraction of gaseous emissions, favoured by temperatures in the range of 250–500°C, with acid species and probably clay minerals (mainly smectites) acting as catalysts.

According to the available data on the free energies of formation, further increases in concentrations of alkenes with respect to aromatics should correspond to processes occurring at higher reaction temperatures.

Mofettas and potizzas from areas of recently exhausted volcanism do not show evidences of significant catalytic and thermal reactions among normal alkanes. Gases from Larderello

geothermal field point out a minor increase of species, such as aromatics and alkenes, produced by catalytic and thermal reactions, while the highest total amount of hydrocarbons can be related to a high content of organic matter available in the sedimentary source rocks. Catalytic and thermal reactions affect gases from Vulcano beach, Phlegrean Fields, Uzon caldera, Geyser Valley, Terceira and Graciosa, probably due to significant accumulation of acid species in the boiling aquifers, leading to a severe argillification of hosting rocks. Finally, at Chichòn volcano and at a minor extent at S. Miguel island, reactions dominated by thermal cracking of normal alkanes seem to represent the prevailing processes.

Acknowledgments—This work was financially supported by Gruppo Nazionale Vulcanologia, and C.N.R. Centro di Studio per la Mineralogenesi e la Geochimica Applicata.

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