



Research papers

Origin of light hydrocarbons in gases from mud volcanoes and CH₄-rich emissionsF. Tassi^{a,b,*}, M. Bonini^b, G. Montegrossi^b, F. Capecchiacci^{a,b}, B. Capaccioni^c, O. Vaselli^{a,b}^a Dept. of Earth Sciences, University of Florence, via G. La Pira 4, 50121 Florence, Italy^b CNR-IGG Institute of Geosciences and Earth Resources, via G. La Pira 4, 50121 Florence, Italy^c Dept. of Earth and Geological-Environmental Sciences, University of Bologna, Piazza di Porta S. Donato, 40127 Bologna, Italy

ARTICLE INFO

Article history:

Received 20 July 2011

Received in revised form 7 December 2011

Accepted 9 December 2011

Available online 14 December 2011

Editor: B. Sherwood Lollar

Keywords:

Mud volcanoes

Light hydrocarbons

Fluid source

Fluid geochemistry

Northern Apennines

Tectonic setting

ABSTRACT

This paper presents new chemical data of hydrocarbon-rich gases discharged from mud volcanoes and CH₄-rich emissions located in different areas of Italy (Northern Apennines and Sicily). The determination of C₅–C₁₀ alkanes, cyclics and aromatics was carried out by GC–MS, while the main gas species and C₁–C₄ hydrocarbons were analyzed by GC–TDC and GC–FID, respectively. Methane is by far the most abundant component of all the investigated gas emissions, with the exception of part of those discharging close to Mt. Etna volcano, which are CO₂-rich. The gas samples collected from the Emilia Apennine and Sicily show δD–CH₄ and δ¹³C–CH₄ values typical of thermogenic gases. Most gases from the Romagna Apennine discharge methane with a biogenic isotopic signature. Non-methane hydrocarbons of biogenic gases are almost exclusively C₂–C₄ alkanes, with minor amounts (fraction of μmol/mol) of C₄₊ compounds, including few aromatics and cyclics, likely deriving from minor thermogenic contribution not evidenced by the δ¹³C–CH₄ and δD–CH₄ values. The Etnean gases, whose R/Ra and δ¹³C–CO₂ values indicate a strong contribution from a hydrothermal fluid source related to the nearby volcanic system, show a significant enrichment of aromatics compounds (up to 36% of the non-methane organic gas fraction), which is likely produced by catalytic reforming processes, such as dehydrocyclization of alkanes.

The thermogenic gases from the Apennines and southwestern Sicily are characterized by the presence of more than 20 different cyclic compounds with concentrations up to several μmol/mol. Cyclic compounds are likely formed by i) thermal cracking and ii) uncompleted aromatization of alkanes occurring at depth > 3 km and temperatures not exceeding 120–150 °C.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Mud volcano is a non-genetic, descriptive term that is referred to a superficial geological phenomenon in which a complex mixture of gas (mainly CH₄), liquid and solid material is continuously or explosively excreted at the surface mostly in a sedimentary environment due to pressurized fluids at depth. Mud volcanoes of variable shape and size (from a few m² to more than 100–200 km²) occur in both sub-aerial and sub-marine environments. They are formed as a result of the extrusion of mud, clasts and fluids caused by the release of high-pressure mud trapped at depth driven by very different mechanisms, such as rapid pressurization in a sedimentary basin and/or buoyancy (Milkov, 2000; Dimitrov, 2002; Kopf, 2002). Occasionally, they are the loci of explosive and paroxysmal events possibly triggered by seismic events, fault failure and drilling (Manga et al., 2009, and references therein). Mud volcanoes are often associated with rapid, subduction-related burying of organic-rich sediments, mainly located along convergent plate margins, where sediments,

accumulated in deep-sea trenches at high rates, are affected by increasing stresses and temperatures related to the subduction process (Higgins and Saunders, 1974; Brown, 1990; Fryer, 1996; Kopf et al., 2001; Kopf, 2002; Deville et al., 2003; Yassir, 2003).

More than 900 continental mud volcanoes are recognized worldwide, whereas thousands of mud volcanoes supposedly occur in deep water areas (Milkov, 2000, 2005; Milkov et al., 2003; Etiope and Milkov, 2004). The origin of water discharged from mud volcanoes may be related to migration of formation waters, brines, freshened waters from mineral dehydration reactions or gas hydrate dissociation, and meteoric water (Martin et al., 1996; Robertson and Ocean Drilling Program Leg 160 Scientific Party, 1996; Slack et al., 1998). The gas phase typically consists of CH₄, with relevant concentrations of CO₂ and higher hydrocarbons (e.g. Stamatakis et al., 1987; Lavrushin et al., 1996; Blinova et al., 2003; Schmidt et al., 2005). On the contrary, mud volcanoes located near volcanic areas emit CO₂-rich gases (e.g., Chiodini et al., 1996; Giammanco et al., 2007). Investigations on the origin of light hydrocarbon gases discharged from emissions in different natural environments generally rely on the chemical and stable isotopic compositions of light alkanes (Bernard et al., 1978; Schoell, 1980, 1983, 1988; Chung et al., 1988; Whiticar, 1999). Noble gas isotopes and ¹⁴C–CH₄ age dating can be used to

* Corresponding author at: Dept. of Earth Sciences, University of Florence, via G. La Pira 4, 50121 Florence, Italy. Tel: +39 0552757477; fax: +39 055284571.

E-mail address: franco.tassi@unifi.it (F. Tassi).

distinguish abiogenic vs. biogenic sources and fossil vs. recent diagenetic origins, respectively (Kessler et al., 2005; Sherwood Lollar et al., 2006). Misleading information from these geochemical parameters can be caused by secondary post-diagenetic processes, such as oxidation and molecular separation during migration of CH₄-rich fluids (James and Burns, 1984; Etiope et al., 2009a). According to the classification proposed by Etiope et al. (2009a), more than 76% of the terrestrial mud volcanoes from 12 different countries discharge thermogenic CH₄, i.e. produced by degradation of organic matter occurring within relatively deep reservoirs at temperatures > 100 °C.

Plinius, in his *Historia Mundi Naturalis* (77 AD), has provided the very first description of the Italian mud volcanoes. They mostly occur along the external compressive margin of the Apennine chain (Pellegrini et al., 1982; Martinelli and Judd, 2004). They are relatively small (up to 3–4 m in height) and characterized by rare explosive events that are occasionally related to local seismic activity (Martinelli et al., 1989; Bonini, 2009). Studies on the origin of gases from the Italian mud volcanoes based both on the main chemical composition and on stable isotopes of methane suggest that they are mostly related to thermogenic processes (Capozzi and Picotti, 2002; Grassa et al., 2004; Etiope et al., 2007, 2009a,b).

In the present work we report original data of hydrocarbons emitted from mud volcanoes, located in northern (Emilia-Romagna) and southern (Sicily) Italy. The dataset includes two CH₄-rich gas vents and one well located at Portico di Romagna and Bagno di Romagna, respectively, as well as a CH₄-rich bubbling gas emission located at Fondachello, along the southeastern Sicilian coast. Most of the mud volcanoes and gas emissions of the present paper were already investigated by previous authors on the basis of the composition of the major compounds and the isotopic signatures of CH₄ and CO₂ (e.g.,

Chiodini et al., 1996; D'Alessandro et al., 1997; Minissale et al., 2000; Capozzi and Picotti, 2002, 2010; Grassa et al., 2004; Pecoraino and Giammanco, 2005; Rizzo et al., 2006; Etiope et al., 2007, 2009a,b). We focused this study on the composition of C₂–C₁₀ alkane, cyclic and aromatic compounds. At our best knowledge, in the literature a complete dataset of hydrocarbons of gases from mud volcanoes as that presented in this work is not available. The aims of this work are to: i) provide new insights on the origin of these organic gases, and ii) investigate the chemical–physical conditions acting at the fluid source and their relation with the regional/local geological and tectonic setting.

2. Regional setting of mud volcanoes of Italy

The Apennine fold-and-thrust belt developed in the framework of the European–African convergence, as a result of convergence and subduction of oceanic and continental crust at the collisional boundaries of the Corsica–Sardinia and Calabrian microplates, and Adriatic–Africa margins (e.g., Boccaletti et al., 1971; Malinverno and Ryan, 1986; Royden et al., 1987; Dewey et al., 1989). Mud volcanoes of Italy basically occur along the external front of this belt at three main geographical locations, namely: 1) Northern Apennines (Pede-Apennine margin of Emilia-Romagna), 2) Central Apennines (eastern Marche–Abruzzo), and 3) Sicily (Martinelli and Judd, 2004; see Fig. 1a).

2.1. Northern Apennine mud volcanoes

The Northern Apennines is a thrust belt-foredeep-foreland system, in which Late Oligocene–Miocene siliciclastic turbidite sequences have

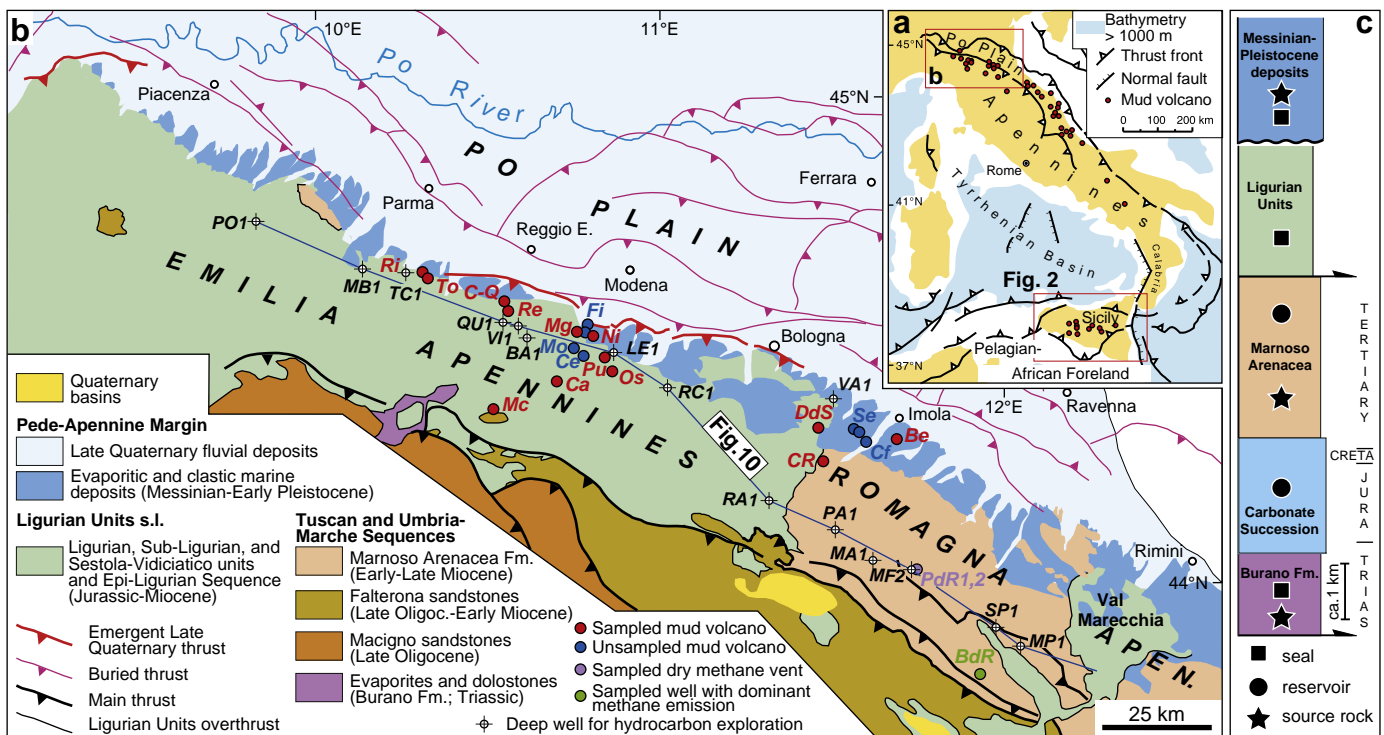


Fig. 1. (a) Geographic and tectonic location of mud volcanoes of Italy (modified from Bonini, 2009). (b) Geological and structural sketch map of the Emilia-Romagna Apennines, showing the position of the main mud volcanoes and methane vent fields (modified from Bonini, 2007). Location of deep wells is from Videpi Project (available at www.videpi.com). Acronyms of mud volcanoes (sampled: red circle; not sampled: blue circle) are: Ri, Rivalta; To, Torre; C–Q, Casola–Querzola; Re, Regnano; Mc, Macognano; Ca, Canalina; Mg, Montegibbio; Mo, Montardone; Ce, Centora; Fi, Fiorano; Ni, Nirano; Pu, Puianello; Os, Ospitaletto; DdS, Dragone di Sassuno; Se, Val Sellustra; Cf, Casalfumanese; Be, Bergullo; Acronym of the sampled dry methane seep (violet circle): PdR, Portico di Romagna; Acronym of the sampled well (green circle): BdR, Bagno di Romagna. Acronyms of the considered deep wells: PO1, Pozzolo 1; MB1, Monte Bosso 1; TC1, Torre Chiara 1; QU1, Querciola 1; VI1, Viano 1; BA1, Baiso 1; LE1, Levizzano 1; RC1, Rio Ciano 1; RA1, Radicosa 1; VA1, Varignana 1; PA1, Palazzuolo 1; MA1, Marradi 1; MF2, Montefreddo 2; SP1, Spinello 1; MP1, Montepietra 1. (c) Schematic lithostratigraphic column showing the position of the main hydrocarbon reservoirs, seal and source rocks in the Northern Apennines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

filled the foredeep basins that developed in front of the northeastward-migrating chain (Ricci Lucchi, 1986; Boccaletti et al., 1990). Sedimentation in the foredeep basins was interrupted by the progressive overthrusting of the Ligurian Units (LU; i.e., highly-tectonized ophiolites and their Jurassic to Eocene sedimentary cover), which achieved their current tectonic position as uppermost units in the Apennine nappe pile (e.g., Principi and Treves, 1984). The exposed Northern Apennine belt can be distinguished into two sectors: i) the Emilia Apennines to the northwest and ii) the Romagna Apennines to the southeast (Fig. 1b). The LU are mainly outcropping in the Emilia Apennines, with the underlying siliciclastic deposits being exposed only at tectonic windows and along the axial ridge. In contrast, the Romagna Apennines are characterized by the dominant outcropping of the Marnoso Arenacea foredeep siliciclastic sequence, with the LU cropping out as tectonic 'klippes' (Fig. 1b).

Mud volcanoes of relatively small size occur dominantly in the Emilia Apennines, where they are closely associated with the presence of LU in outcrop, and also when the LU are overlain by Messinian-to-Early Pleistocene deposits (Fig. 1b). In the Romagna Apennines, where the LU are thin or totally missing, the presence of mud volcanoes is restricted to an area southwest of Imola (Fig. 1b). The Emilia and Romagna mud volcanoes are roughly distributed sub-parallel to the Apennine foothills and adjacent to the Pede-Apennine margin. The latter represents the main physiographic element separating an uplifted and exposed accretionary wedge from the topographically flat Po river Plain, where the most external thrusts are buried beneath Pliocene–Quaternary sediments (Pieri and Groppi, 1981; Fig. 1b).

Mud volcanoes and seeps are closely related to petroleum systems, which in this region are considered to include three oil reservoirs, named (e.g., Lindquist, 1999): (1) Porto Garibaldi (Plio-Pleistocene and minor Miocene biogenic gas); (2) Marnoso Arenacea (Tertiary thermal gas, oil and condensate), and (3) Meride/Riva di Solto (Triassic thermal oil and gas). The position of the main hydrocarbon reservoirs, source and sealing rocks in the sedimentary sequence is shown in Fig. 1c. The mud volcanoes settled in the LU are driven by thermogenic methane (Etiope et al., 2007) that is likely sourced from both the Marnoso Arenacea, which attains thickness exceeding 3 km, and deeper, mostly Triassic, rocks (Riva, et al., 1986; Pieri, 2001; Capozzi and Picotti, 2002, 2010). In this view, the escaping methane would represent a mixing derived from the Marnoso Arenacea and Meride/Riva di Solto total petroleum systems. The Marnoso Arenacea sequence also provides most of the formation water expelled from the mud volcanoes (Lindquist, 1999; Capozzi and Picotti, 2002). Although heterogeneous, the LU act as an efficient impermeable barrier to the vertical migration of the ascending fluids. This suggests that fluid overpressure produced by the fluids accumulating underneath the impermeable LU represents a primary cause controlling mud volcanism (Bonini, 2007). A similar role is likely played by the Pliocene–Pleistocene claystones for the small-sized Romagna mud volcanoes, which are driven by biogenic methane (Etiope et al., 2007) of the Porto Garibaldi petroleum system (Fig. 1b).

2.2. Sicily mud volcanoes

The southward-verging Apennine–Maghrebian fold-and-thrust belt of Sicily is a Neogene–Quaternary thin-skinned accretionary wedge that progressively migrated southward over the Pelagian–African foreland. During this movement, stratigraphic successions pertaining to different Late Paleozoic to Cenozoic paleogeographic domains were involved (Ghisetti and Vezzani, 1984; Lentini et al., 1991, 1994; Butler et al., 1992; Catalano et al., 1996, 2000a, b; Finetti et al., 2005). At a regional scale, the Apennine–Maghrebian collision belt is interpreted as being tectonically sandwiched between two imbricated continental blocks: i) the Panormide block

on the hanging-wall, whose leading edge is manifested by a major E–W-trending crustal oblique thrust (i.e., the Mount Kumeta–Alcantara Fault; Ghisetti and Vezzani, 1984), and ii) the Pelagian block made of African crust on the thrust belt footwall (Roure et al., 1990; Finetti et al., 2005; Catalano et al., 2011; Fig. 2). South of the Mount Kumeta–Alcantara fault the Apennine–Maghrebian fold-and-thrust belt consists of a thick clastic sequence of Miocene–Pliocene sediments deposited in a system of amalgamated thrust-top basins (e.g., Butler et al., 1992; Catalano et al., 2000a, b). The Siculo-Calabrian Rift Zone delimits the Apennine–Maghrebian collision belt to the east, deforming the Ionian offshore area and the easternmost sector of Sicily, including the eastern flank of the Mount Etna volcano (Monaco and Tortorici, 2000; Catalano et al., 2008; Fig. 2).

The petroleum systems of Sicily are associated with both the (1) Neogene Apennine–Maghrebian fold-and-thrust belt and its (2) Pelagian foreland, where oil and thermogenic gases are related to Late Triassic–Early Jurassic source rocks and similarly aged traps (Granath and Casero, 2004; Bertello et al., 2008). Mud volcanoes occur in eastern and south-western Sicily (Fig. 2) essentially over the thick clastic sequences filling the system of Miocene to Pleistocene foredeep and piggy-back basins (Caltanissetta Basin). Mud volcanoes and other seeps of Sicily release either thermogenic methane or gases with isotope signatures that were interpreted as produced by mixing of thermogenic and microbial gases (Grassa et al., 2004). The origin of gases driving most of the mud volcanoes and seeps of central Sicily is presumably related to the presence of commercial hydrocarbons in the Apennine–Maghrebian fold-and-thrust belt, consisting of thermo- and biogenic gas-charged Tertiary reservoirs (Granath and Casero, 2004; Bertello et al., 2008). However, it is also possible that part of the thermogenic gas could be released from the deeper petroleum system through deeply rooted faults, such as for the normal faults around the Mount Etna volcano (Fig. 2).

3. Methods

3.1. Gas sampling

Gases of mud volcanoes and from CH₄-rich emissions were sampled using a plastic funnel up-side-down positioned above the bubbling mud pools and connected through silicone/tygon tubes to pre-evacuated 250 mL glass flasks equipped with Thorion® valves (Vaselli et al., 2006). The same apparatus was used to collect gases emitted from the CH₄-rich vents of Portico di Romagna. Dissolved gases from the Bagno di Romagna well, where no free gas was available, were collected using the “equilibrated headspace” method described by Chiodini (1996). The CO₂-rich gases were also collected with pre-evacuated 50 mL glass flasks partly filled with a 4 M NaOH solution for the determination of the major gases. Carbon dioxide solubilizes into the alkaline solution, whereas CH₄, N₂, O₂ and noble gases accumulate in gas vial headspace (Vaselli et al., 2006).

3.2. Analysis of the main gas species

The analysis of the main gas compounds (CH₄, CO₂, N₂, Ar, O₂ and He) was carried out using a Shimadzu 15A Gas Chromatographic (GC) system equipped with a 9 m long molecular sieve column and Thermal Conductivity Detector (TCD). Carbon dioxide in the CO₂-rich gases was analyzed in the alkaline solution as CO₃²⁻ by acidimetric titration with 0.1 N HCl. The C₂–C₄ alkanes were analyzed with a Shimadzu 14A gas-chromatograph equipped with a Flame Ionization Detector (FID) using a 10 m long stainless steel column packed with Chromosorb PAW 80/100 mesh coated with 23% SP 1700. The analytical error for both the GC and titration analysis is <5%.

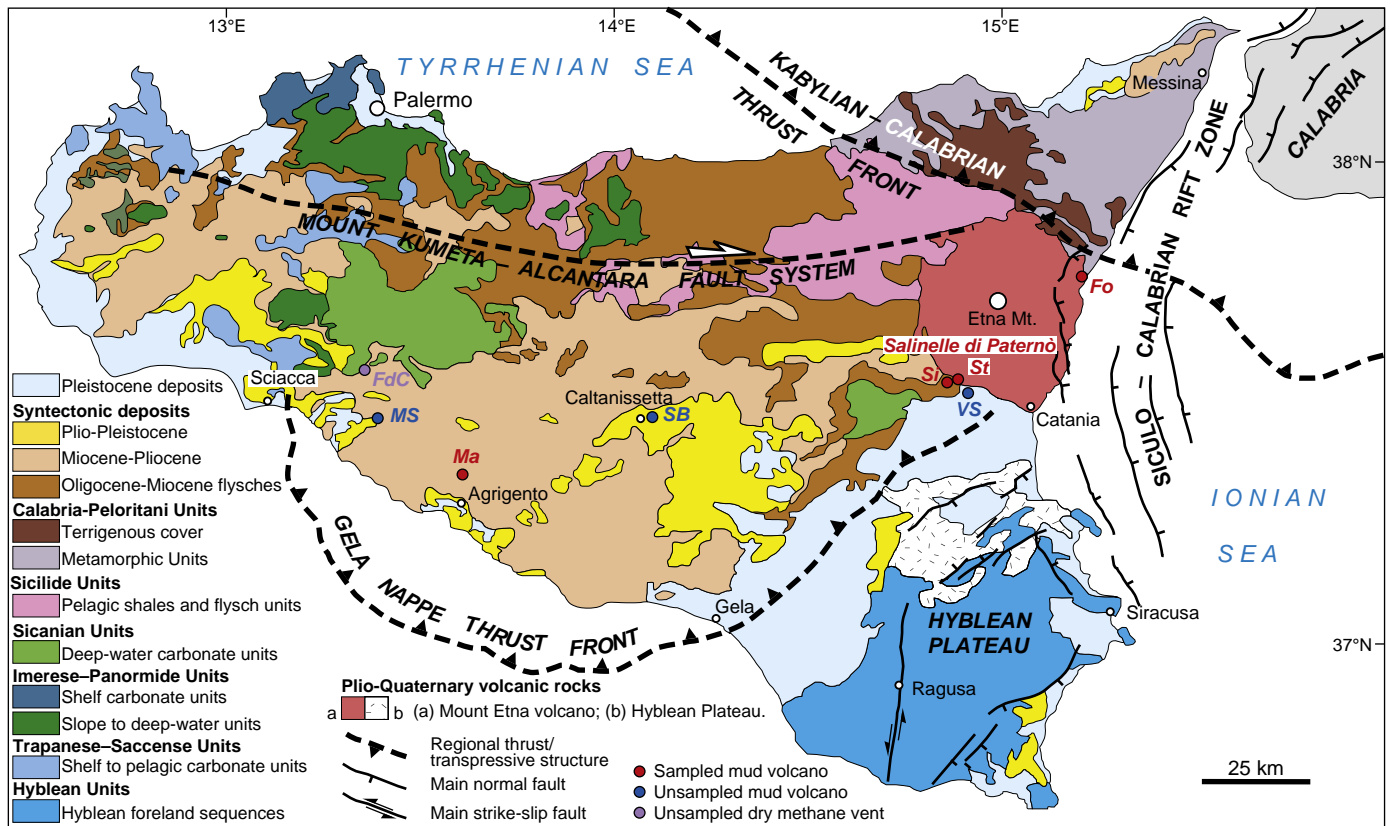


Fig. 2. Geological structural sketch map of Sicily (compiled and modified from Catalano et al., 2000a, b, 2008; Accaino et al., 2011). The position of the main mud volcanoes (sampled: red circle; not sampled: blue circle) and the Fuoco di Censo dry methane seep (violet circle) is also indicated (after Etiope et al., 2002; Grassa et al., 2004). Acronyms of mud volcanoes (sampled: red circle; not sampled: blue circle) are: Ma, Maccalube di Aragona; Si, Simeto; St, Stadio; Fo, Fondachello; MS, Monte Sara; SB, Santa Barbara; VS, Vallone Salato. Acronym of the sampled dry methane seep (violet circle): FdC, Fuoco di Censo. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.3. Analysis of the C_4+ hydrocarbons

The C_4+ hydrocarbons were analyzed by GC–MS (Gas Chromatography coupled with Mass Spectrometry) using the Solid Phase Micro-Extraction (SPME) technique (Arthur and Pawliszyn, 1990) to extract volatile organic compounds (VOCs) from the gas mixture and inject them in the GC–MS (Davoli et al., 2003; Mangani et al., 2003; Florez Menendez et al., 2004). From an operative point of view, gases are transferred from the sampling glass flasks into a pre-evacuated 10 mL glass vial sealed with a silicone rubber membrane. A manual SPME device is introduced through the silicon membrane into the vial to expose the gaseous mixtures to a divinylbenzene (DVB)-Carboxen-polydimethylsiloxane (PDMS), 50/30 μm , 2 cm long fiber assembly (Supelco; Bellefonte, PA, USA) for 15 min. A Thermo Trace GC Ultra gas chromatograph coupled with a Thermo DSQ Quadrupole Mass Spectrometer is used for analytical separation and detection (Tassi et al., 2011). The mass spectrometer operates in full scan mode, in the mass range 40–400 m/z . The transfer-line temperature is set at 230 °C. The mass detector is equipped with EI with an ionization energy of 70 eV, whereas the source temperature is 250 °C. The gas chromatograph is equipped with a split/splitless injection port operating in the splitless mode with a dedicated SPME liner (0.75 mm i.d.). Analytes are desorbed from the SPME fiber through direct exposure at 230 °C for 2 min in the GC injection port. The chromatographic column is a 30 $m \times 0.25$ mm i.d. 1.4 μm film thickness TR-V1 fused silica capillary column (Thermo). The carrier gas is helium set to a flow-rate of 1.3 mL/min in constant pressure mode. The column oven temperature program is, as follows: 35 °C (hold: 10 min), ramp at 5.5 °C/min to 180 °C (hold: 3 min), ramp at 20 °C/min up to 230 °C (hold:

6 min). The organic compounds detected by the quadrupole detector are identified according both to their retention time of the chromatographic peak and to their mass spectra. The mass spectra database of the NIST05 library (NIST, 1995) is used for comparison. Quantitative analyses were performed using an external standard calibration procedure on the basis of calibration curves constructed measuring the instrumental signal of Accustandard® standard mixtures of compounds pertaining to the following functional groups: alkanes (12 C_4 – C_{10} alkanes, at concentrations ranging from 100 to 200 ppbv), cyclic compounds (5 C_5 – C_6 species, at 20 ppbv), aromatic compounds (15 species at concentrations ranging from 100 to 5000 ppbv) (Tassi et al., 2011). The values of the Relative Standard Deviation (RSD), calculated from five replicate analyses of the gas mixture in which the compounds of interest are present at a concentration of 50 ppbv, were <5%. The limit of quantification (LOQ) was determined by linear extrapolation from the lowest standard in the calibration curve using the area of a peak having a signal/noise ratio of 5 (Mangani et al., 2003).

3.4. Analysis of the $\delta^{13}\text{C}$ – CO_2 , $\delta^{13}\text{C}$ – CH_4 and δD – CH_4 ratios

The $^{13}\text{C}/^{12}\text{C}$ ratios of CO_2 (expressed as $\delta^{13}\text{C}$ – CO_2 ‰ V-PDB) were measured with a Finnigan Delta S mass spectrometer after purification of the gas mixture by standard procedures (Evans et al., 1998). Internal (Carrara and San Vincenzo marbles) and international (NBS18 and NBS19) standards were used in order to estimate external precision. Analytical error and the reproducibility were ± 0.1 ‰.

The analyses of the $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$ ratios of CH_4 (expressed as $\delta^{13}\text{C}$ – CH_4 ‰ V-PDB and δD – CH_4 ‰ V-SMOW, respectively) were

performed by mass spectrometry (Varian MAT 250) according to the procedure described by Schoell (1980). Analytical error was $\pm 0.15\%$.

4. Results

4.1. Chemical composition of the main gases

The chemical composition of the main gas compounds (in mmol/mol) of the 21 gas discharges (13 mud volcanoes (Fig. 3a), 2 dry gas vents (Fig. 3b), 1 well from Emilia-Romagna (Fig. 1b), and 4 mud volcanoes and 1 bubbling gas from Sicily, southern Italy (Fig. 2)), analyzed in the present study, is reported in Table 1. These gases are dominated by CH₄ that ranges from 931 to 988 mmol/mol, with the only exception of the Vallone Salato (VS), Simeto (Si) and Stadio (St) gases (Fig. 2), which have relatively high CO₂ concentrations (from 582 to 935 mmol/mol). Significant contents of N₂, CO₂, O₂ and Ar (up to 41.5, 17.9, 2.85 and 1.05 mmol/mol, respectively) characterize the CH₄-dominated gases, whereas He does not exceed 0.026 mmol/mol. VS, Si and St gases have significant CH₄ (up to 390 mmol/mol) contents, whereas those of N₂, O₂ and Ar are in the same range as those in the CH₄-dominated gases.

4.2. $\delta^{13}\text{C-CO}_2$, $\delta^{13}\text{C-CH}_4$ and $\delta\text{D-CH}_4$ ratios

The $\delta^{13}\text{C-CO}_2$ values in the CH₄-dominated gas discharges (Table 2) vary within a wide range, comprised between -13.3 and 35.6% V-PDB, whereas those in the CO₂-rich gases are quite similar (ranging from -2.11 to 0.14% V-PDB). Most gases pertaining to the former group have $\delta^{13}\text{C-CH}_4$ and $\delta\text{D-CH}_4$ values clustering between -47.5 to -39.6% V-PDB and -182 to -170% V-SMOW, respectively. Similar carbon and hydrogen isotopic values were measured in CH₄ of the three CO₂-rich gas samples. On the contrary, Dragone di Sassuno (DdS), Bergullo (Be), Cà Robano (CR) and Bagno di Romagna (BdR) gases show more negative $\delta^{13}\text{C-CH}_4$ and $\delta\text{D-CH}_4$ values ($<-60\%$ V-PDB and $>-192\%$ V-SMOW, respectively).

4.3. Chemical composition of C₂–C₁₀ hydrocarbons

Up to 54 different hydrocarbons, pertaining to the alkane (27 compounds), aromatic (4 compounds) and cyclic (23 compounds)

groups, were recognized (Table 2). The total hydrocarbon abundances range from 235 to 3410 $\mu\text{mol/mol}$. Ethane concentrations are up to one order of magnitude higher than the sum of all other alkanes. Benzene is the most abundant aromatic compound, although its concentrations in the CH₄-dominated gases slightly exceed those of C₇H₈. On the contrary, the C₆H₆/C₇H₈ ratios of the CO₂-rich gases reach values as high as 73. Methylated C₅, C₆ and C₈ cyclics show higher concentrations than those having ethyl, propyl and butyl branches. The alkane/100-cyclic-aromatic ternary diagram (Fig. 4) allows to distinguish three different groups of gases: 1) "MVA", including the CH₄-dominated gases from the Emilia Apennines, i.e. Rivalta (Ri), Torre (To), Casola-Querzola (C-Q), Macognano (Ma), Regnano (Re), Canalina (Ca), Puianello (Pu), Nirano (Ni), Montegibbio (Mg), Ospitaletto (Os), Portico di Romagna (PdR1 and PdR2) (Fig. 1b), and the Maccalube di Aragona (Ma) gas from Sicily (Fig. 2), display proportionally high concentrations of cyclic compounds; 2) "MVB", consisting of the three CO₂-rich gases (VS, Si and St; Fig. 2) and the CH₄-rich gas from Fondachello (Fo) (Fig. 2), is dominated by aromatics; 3) "MVC", which has relatively low concentrations of both cyclic and aromatic compounds and includes the DdS, Be and CR mud volcanoes and the BdR well (Fig. 1b).

5. Discussion

5.1. Origin of gas compounds

The investigated gas emissions show N₂/Ar ratios ranging from 40 to 53, i.e. intermediate between those of air saturated water (ASW: N₂/Ar = 38.3 at 20 °C in pure water) and air (83.6). This suggests that N₂ and Ar have an atmospheric origin and are mainly added to the uprising gases as air dissolved in the meteoric water that recharges the system. The relatively low O₂ concentrations (≤ 2.85 mmol/mol) indicate that air contamination of the gas samples have occurred during the gas sampling only at limited extent. Helium in the CH₄-dominated gases from Emilia-Romagna is mostly produced by the decay of radiogenic elements within the crust, as indicated by the relatively low ³He/⁴He ratios (<1 R/R_a, where R is the ³He/⁴He measured ratio and R_a is the ³He/⁴He ratio in air: 1.39×10^{-6} ; Mamyrin and Tolstikhin, 1984) reported in literature (Minissale et al., 2000). The isotopic composition of He (R/R_a ~6.5) of the MVB gases (Allard et al., 1997;



Fig. 3. (a) View of a typical mud volcano of the Emilia Apennines (Puianello); the tallest cone in the background is ca. 3 m high. (b) Everlasting fire fed by a CH₄ emission at Portico di Romagna (July 2010).

Table 1
Chemical and isotopic ($\delta^{13}\text{C}\text{-CO}_2$, $\delta^{13}\text{C}\text{-CH}_4$ and $\delta\text{D}\text{-CH}_4$) composition of gases from mud volcanoes of Emilia and Romagna Apennines and of Sicily (Italy). Gas concentrations are in mmol/mol; $\delta^{13}\text{C}$ (in CO_2 and CH_4) and $\delta\text{D}\text{-CH}_4$ ratios are expressed as ‰ V-PDB and ‰ V-SMOW, respectively; n.a.: not analyzed.

	Ri	To	C-Q	Mc	Re	Ca	Pu	Ni	Mg	Os	PdR1	PdR2	DdS	CR	Be	BdR	Ma	VS	Fo	St	Si
CH_4	956	973	974	976	965	975	982	981	980	982	952	945	988	984	988	931	975	390	971	57.9	85.5
CO_2	17.9	16.5	14.2	13.9	14.8	11.7	9.46	9.75	4.97	11.8	13.4	11.8	2.12	2.54	3.03	48.6	13.8	582	5.64	935	908
N_2	25.1	8.75	10.8	7.49	18.5	12.8	6.80	7.50	14	5.60	32.7	41.5	8.50	12.5	7.80	18.8	9.75	26.3	21.6	5.90	6.40
Ar	0.50	0.22	0.25	0.17	0.35	0.28	0.14	0.15	0.29	0.14	0.78	1.05	0.2	0.31	0.19	0.43	0.24	0.61	0.53	na	na
O_2	0.98	1.17	0.58	2.85	1.25	0.68	1.85	1.77	0.89	0.69	1.29	1.11	0.85	1.08	0.77	1.14	1.11	1.29	1.09	1.40	0.51
He	0.016	0.026	0.011	0.008	0.012	0.008	0.011	0.006	0.008	0.005	0.005	0.005	0.002	0.003	0.002	0.004	0.011	0.095	0.007	0.013	0.018
$\delta^{13}\text{C}\text{-CH}_4$	-43.1	-41.6	-39.6	-43.2	-44.5	-42.5	-43.3	-47.5	-46.2	-45.8	-41.6	-40.9	-60.8	-66.7	-68.9	-60.1	-45.1	-43.7	-40.9	-47.3	-46.8
$\delta\text{D}\text{-CH}_4$	-182	-180	-170	-176	-171	-182	-179	-182	-181	-180	-175	-171	-211	-202	-192	-193	-178	-171	-173	-177	-175
$\delta^{13}\text{C}\text{-CO}_2$	28.3	27.5	22.6	27.8	na	9	35.6	13.5	na	15.1	10.3	na	na	-8.48	-13.3	-3.82	-2.44	-2.11	na	-0.32	0.14
	Emilia Apennines											Romagna Apennines									
												Sicily									

Caracausi et al., 2003; Pecoraino and Giammanco, 2005; Rizzo et al., 2006) indicates significant contribution from a mantle source related to the proximity of Mount Etna volcano, whereas at the Maccalube di Aragona mud volcanoes He ($R/R_a=0.7$) is predominantly crustal (Favara et al., 2001; Caracausi et al., 2003; Grassa et al., 2004). The marked mantle-derived He isotopic signature of the CH_4 -rich Etnean gas (Fo) is apparently in contrast with its composition, typical of crustal gases. According to Caracausi et al. (2003) and Grassa et al. (2004), the composition of this gas emission is determined by selective dissolution of CO_2 , whose solubility in water is significantly higher than that of CH_4 and the atmospheric gases. This suggests that the gases from the Etnean area (Fo, VS, Si and St), although compositionally different (Table 1), are affected by significant fluid contribution from a common deep (mantle) source.

The “Schoell” $\delta^{13}\text{C}\text{-CH}_4$ vs. $\delta\text{D}\text{-CH}_4$ diagram (Schoell, 1980) (Fig. 5) suggests that CH_4 in both the MVA and MVB gases has a thermogenic origin, i.e. produced by decomposition of organic matter buried in sediments at $T > 100^\circ\text{C}$ (e.g., Whiticar and Suess, 1990). These data are in agreement with those reported by other authors (Minissale et al., 2000; Capozzi and Picotti, 2002; Grassa et al., 2004; Etiope et al., 2007) for most of the investigated gases (Re, To, Ri, Ni, Os, PdR1, Ma, Fo, VS, and St). Differently, microbial carbonate reduction (e.g., Whiticar, 1999) seems to be the main cause for the production of CH_4 in the MVC gases. It is worth noting that the $\delta^{13}\text{C}\text{-CH}_4$ and $\delta\text{D}\text{-CH}_4$ values of the Be and PdR gases, reported by Etiope et al. (2007) and Minissale et al. (2000), respectively, are consistent with our data. On the contrary, the carbon isotopic signature of CH_4 in the DdS gas (-43.8% V-PDB) reported by Minissale et al. (2000), for which a thermogenic origin was suggested, is significantly different from both the $\delta^{13}\text{C}\text{-CH}_4$ (-58.4% V-PDB) reported by Etiope et al. (2007) and $\delta^2\text{H}\text{-CH}_4$ (-60.1% V-PDB; present study; Table 1) values. The evolution of the CH_4 isotopic signature of the DdS gas from thermogenic to biogenic values could be related to the documented decrease of the discharge activity from this mud volcano, a hypothesis that was already claimed by Etiope et al. (2007).

In the “Bernard” $\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$ vs. $\delta^{13}\text{C}\text{-CH}_4$ diagram (Bernard et al., 1978) (Fig. 6) the MVC gases plot within the field of microbial hydrocarbon production, whereas the remaining samples seem to be related to mixing between microbial and thermogenic fluids. Post-genetic processes, such as molecular fractionation and secondary methanogenesis related to subsurface anaerobic biodegradation, may have changed the original chemical and isotopic composition of the MVA and MVB gases. Molecular fractionation and anaerobic biodegradation can cause an increase of the $\text{CH}_4/\text{C}_2 +$ ratios from reservoir to surface (Deville et al., 2003; Etiope et al., 2007, 2009a; Milkov and Dzou, 2007; Waseda and Iwano, 2008). Therefore, these secondary processes may explain the relatively high $\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$ ratios of the MVA and MVB gases, higher than those typical of thermogenic gases (Fig. 6). The extremely variable $\delta^{13}\text{C}\text{-CO}_2$ signature of the MVA and MVC gases (from -13.3 to 35.6% V-PDB) suggests that CO_2 is related to anaerobic oxidation of heavy hydrocarbons (Pallasser, 2000) followed in most cases by secondary methanogenesis, particularly for those gas samples characterized by high $\delta^{13}\text{C}\text{-CO}_2$ values ($>10\%$ V-PDB; Table 1). This process, which depends on the type of microbial communities and physical-chemical reservoir conditions (Wang et al., 2005), is able to strongly enrich the residual CO_2 in ^{13}C (Etiope et al., 2009b). The CO_2 origin of the MVB gases, whose $\delta^{13}\text{C}\text{-CO}_2$ values range from -2.11 to 0.14% V-PDB (Table 1), is likely related to a common magmatic source, also indicated by the helium isotopic signature, with some CO_2 contribution from carbonate rocks (Chiodini et al., 1996; D’Alessandro et al., 1997).

Light alkanes ($\text{C}_2\text{-C}_9$) of thermogenic gases are mainly produced by thermal cracking processes affecting organic matter even at relatively low temperatures ($<100^\circ\text{C}$; Hunt, 1984; Mango, 1997, 2000), whereas bacteriogenesis typically produces $\text{C}_1\text{-C}_3$ alkanes. The distribution of $\text{C}_2\text{-C}_{10}$ alkane concentrations (Fig. 7) suggests that the MVC

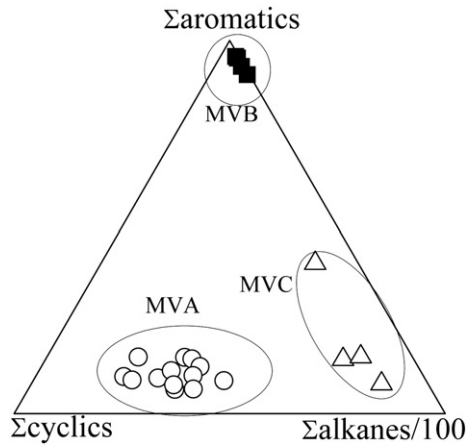


Fig. 4. Σ alkanes/100– Σ aromatics– Σ cyclics ternary diagram of gases from mud volcanoes and gas emissions of Emilia-Romagna and Sicily (Italy). MVA gases (open circles): Rivalta (Ri), Torre (To), Casola–Querzola (C–Q), Macognano (Ma), Regnano (Re), Canalina (Ca), Puianello (Pu), Nirano (Ni), Montegibbio (Mo), Ospitaletto (Os), Portico di Romagna (PdR 1 and PdR2) and Maccalube (Ma); MVB gases (closed squares): Fondachello (Fo), Vallone Salato (VS), Simeto (Si) and Stadio (St); MVC gases (open triangles): Dragone di Sassuno (DdS), Bergullo (Be), Cà Robano (CR), and Bagno di Romagna (BdR).

gases have significant amounts of C_{4+} compounds, although their concentrations are lower than those of MBA and MVB gases. This may imply that the MVC gases suffer a lesser contribution from a thermogenic source, which is not detectable on the basis of the CH_4 isotopic signature. The relatively low concentrations of the C_3 – C_8 alkane in the MVB gases with respect to those of the MVA ones (Fig. 7) are likely to be related to i) the type of source rock feeding these emissions, and/or ii) post-genetic molecular fractionation due to fluid migration (Thompson, 2004, and references therein). The occurrence of heat and hydrothermal fluid contribution from the Mount Etna volcano (Caracausi et al., 2003; Grassa et al., 2004) may also cause the C_{3+} alkanes depletion in the MVB gases, since these compounds are characterized by low stability at increasing temperature.

Branched hydrocarbons are indicative of catalytic cracking via carbonium-ion mechanism, whereas free radical cracking, taking place in a relatively deep environment, preferentially produces normal

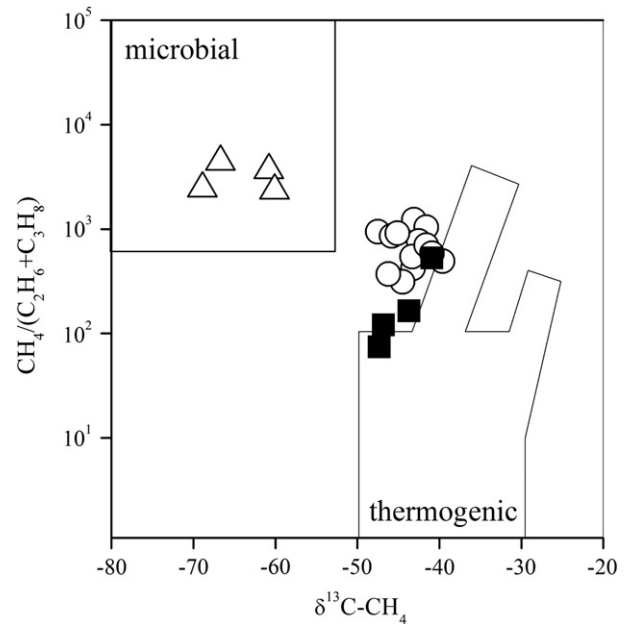


Fig. 6. $CH_4/(C_2H_6+C_3H_8)$ vs. $\delta D-CH_4$ plot of gases from mud volcanoes of Emilia-Romagna and Sicily (Italy). Symbols as in Fig. 4.

alkanes (Hunt et al., 1980; Hunt, 1984; Tannebaum and Kaplan, 1985). The production of high iso/normal alkane ratios is related to biodegradation processes (Tissot and Welte, 1978), whereas normal alkanes are favored as temperature increases (Astafev et al., 1973). The iso/normal alkane ratios are also used for investigations aimed at identifying the type of organic source, since enrichment in normal alkanes is considered to be related to the decomposition of sapropelic organic matter, whereas light hydrocarbons from humic organic matter bear isoalkanes (Dai, 1992; Hu et al., 2008).

As shown in Fig. 8, the iso/normal ratios of the C_4 – C_{10} alkane compounds in the MVA and MVC gases are quite similar, thus this parameter seems not to be useful to distinguish thermogenic and biogenic hydrocarbons in gases originated by a low temperature source. On the contrary, the iso/normal ratios of the MVB gases are significantly

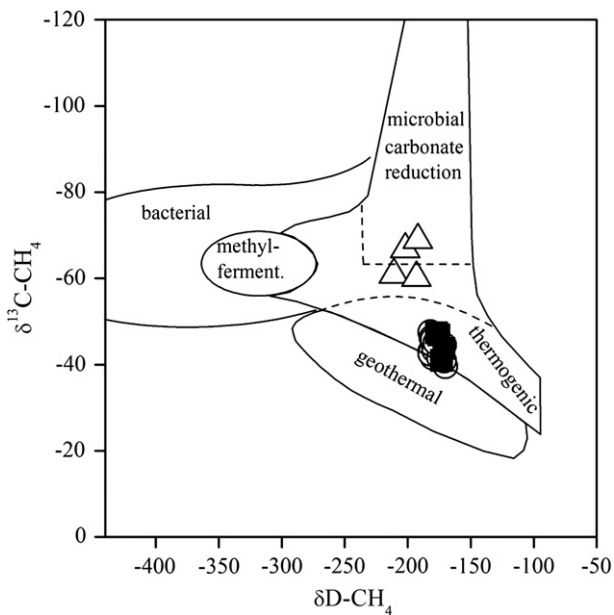


Fig. 5. $\delta^{13}C-CH_4$ vs. $\delta D-CH_4$ plot of gases from mud volcanoes of Emilia-Romagna and Sicily (Italy). Symbols as in Fig. 4.

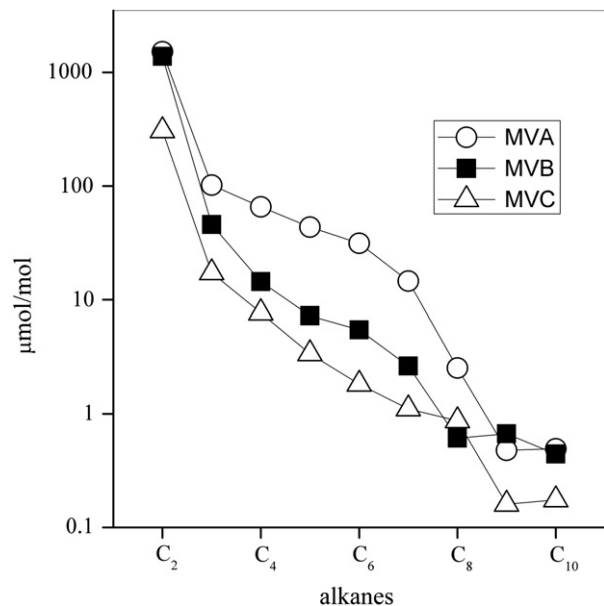


Fig. 7. Mean values of C_2 – C_{10} hydrocarbon concentrations (in $\mu mol/mol$) in the gases from the mud volcanoes pertaining to the MVA, MVB and MVC groups (mean values). Symbols as in Fig. 4.

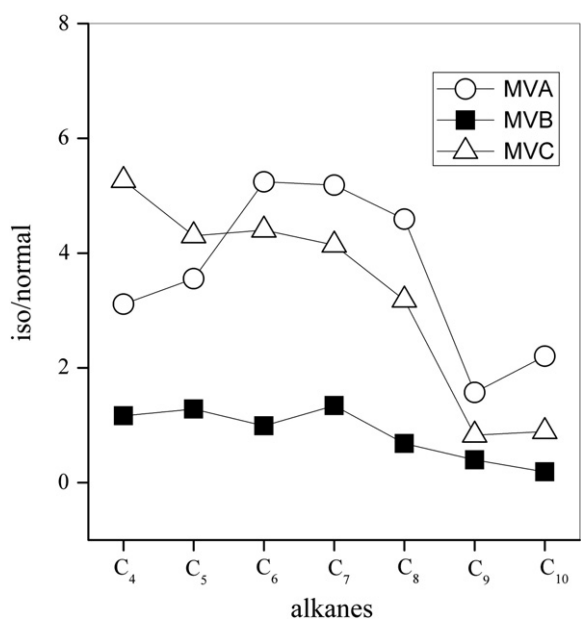


Fig. 8. Mean values of iso/normal ratios of the C₄–C₁₀ alkane compounds in the gases from the mud volcanoes pertaining to the MVA, MVB and MVC groups (mean values). Symbols as in Fig. 4.

lower, a feature that may be related to i) relatively high temperatures at the source of fluids, since the normal alkanes are more stable at increasing temperature, and/or ii) a different type of kerogen.

5.2. Origin of aromatic compounds

Monocyclic aromatic compounds are a significant fraction of the total organic carbon in oil reservoirs, as well as in fluids from hydrothermal and volcanic systems (Somerville et al., 1987; Simoneit et al., 1988; Fisher and Boles, 1990; Giggenbach and Corales, 1992; Darling, 1998; Capaccioni et al., 2000, 2004). Occurrence of these compounds in natural fluids depends on several factors, including the type of source matter, secondary fractionation and decomposition processes (Bennet and Larter, 1997; Dale et al., 1997). For example, thermal maturation of lignin and cellulose is known to produce relatively high concentration of aromatics (Leythaeuser et al., 1979). Furthermore, enrichments both in C₆H₆ and in C₇H₈ can be caused by phase- and migration-related compositional fractionation (Thompson, 1987). The ubiquitous presence of aromatic compounds in fluid discharges from different environments is also related to the high stability of the aromatic ring itself (C₆H₆) at high temperature, even under highly oxidizing conditions (Katritzky et al., 1990). Formation of aromatic compounds may proceed through catalytic “reforming” processes, such as dehydrogenation of cycloalkanes and dehydrocyclization of alkanes, whose efficiency is favored by temperatures ranging from 100 to 350 °C and presence of catalytic agents, such as free acids, aluminosilicates and sulfur gas species (Capaccioni et al., 1993, 1995; Mango, 1994; Mèriaudeau and Naccache, 1997). These conditions are typical of hydrothermal systems, where monoaromatics may also be produced by thermal decomposition of alkylated aromatic compounds with long side chains (Savage and Klein, 1987; Smith and Savage, 1991; Kissin, 1998). This supports the idea that the MVB mud volcanoes (Fig. 4), which show relatively high concentrations of aromatic compounds, are significantly affected by a high convective heat flow related to the activity of Mount Etna volcano, as also suggested by their mantle He isotopic signature (Table 1). The high C₆H₆/(C₇H₈ + C₈H₁₀) ratios of these gases (up to 22), a common feature for hydrothermal/volcanic fluids (Capaccioni et al., 1995; Darling, 1998; Taran and Giggenbach,

2003; Tassi, 2004), are likely caused by the occurrence of oxidative decarboxylation and/or demethylation reactions affecting methylated mono- and poly-cyclic aromatic compounds (Taylor et al., 1997; McCollom et al., 2001).

5.3. Origin of cyclic compounds

A certain quantity of cyclic hydrocarbons is always present in sediments. The compositional features of these compounds are strongly related to: sedimentary environment, biological sources and diagenetic processes (Duan, 2000; Duan and Ma, 2001; Duan et al., 2004). Enrichments of methylhexane are found to occur in oils from terrigenous source rocks, whereas dimethylcyclopentane with different structures, deriving mainly from lipids of aquatic organisms, is a typical feature of light hydrocarbons of marine-derived oils (Leythaeuser et al., 1979; Dai, 1993; Wang and Zhang, 2008). Notwithstanding the abundance of cycloalkanes within the main sources of organic gases, these compounds were recognized in relatively low concentrations in gas discharges related to hydrothermal activity in sedimentary environments, and they are almost absent in hydrothermal and volcanic fluids (Tassi, 2004; Tassi et al., 2009a, 2010), as well as in soil gases (Tassi et al., 2009b), likely because these organic compounds have low stability at oxidizing conditions and temperature typical of hydrothermal/magmatic systems. The presence of several different cycloalkanes at concentrations even higher than those of the aromatic compounds (Table 2), although the latter are stable in a relatively wide range of redox and temperature conditions, represents the most peculiar features of the MVA gases. The origin of these organic compounds could be related to the type of source rock. However, the MVA gases display the same cyclic compositions (in Fig. 9a the cyclic concentrations are expressed in % with respect to the total cyclic abundances), including those produced by different petroleum systems, such as those from Emilia Apennine (Re), Romagna Apennine (PdR1) and Sicily (Ma), (Fig. 9b). This supports the idea that the origin of the cyclic compounds found in the Apennine and Sicilian thermogenic gases depends on specific chemical–physical conditions characterizing these zones, i.e. high pressures and temperature not exceeding 120–150 °C. At these conditions, cycloalkanes could be produced by thermal cracking of preexisting organic material. However, it is worth of note that numerous reaction pathways for the production of aromatic compounds proceed through dehydrogenation of cycloalkane intermediates formed from cyclization of alkanes (Davis, 1999, and references therein). Therefore, it is reasonable to suppose that the presence of cycloalkanes in the MVA gases can also be related to the occurrence of reforming processes at temperature too low to complete alkane aromatization that typically occur at hydrothermal conditions.

The paucity of cycloalkanes in the MVB gases is likely related to the relatively high temperatures caused by addition of hot hydrothermal fluids from the Mount Etna volcanic system. The MVC gases mostly derive from bacteria activity, which are not able to produce C₄₊ compounds including cycloalkanes, whose presence at low concentrations is likely related to trivial thermogenic contribution.

5.4. Hydrocarbon composition vs. fluid source regions

The structural setting of the Emilia and Romagna Apennines may offer a key to decipher the development and/or the origin of the two dissimilar MVA and MVC gas typologies. A regional cross-section longitudinal to the chain (constrained by logs from deep wells for hydrocarbon exploration available at www.videpi.com) shows the position of mud volcanoes and dry CH₄ seeps in relation to the structural setting and nappes pile geometry (Fig. 10). More specifically, most of the MVA gases occur in the Emilia sector, where the LU provide an overburden layer that may approach or even exceed 4 km in thickness, as documented by some deep wells (e.g., Querciola 1, Viano 1, Rio Ciano 1 wells; Figs. 1b and 10). Conversely, the MVC

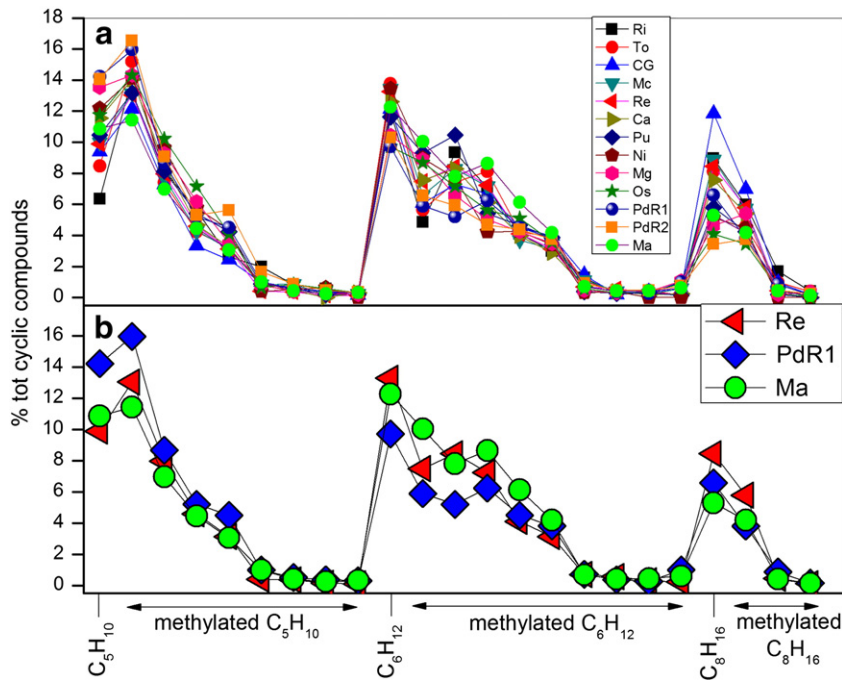


Fig. 9. (a) Concentrations of cyclic compounds with respect to the total cyclic abundance in (a) the investigated gas samples and (b) the Re, PdR1 and Ma gases.

gases are from the Romagna Apennines, where the LU are mostly absent, or exhibit a thickness lower than ~1.5 km at the transition zone to the Emilia Apennines (Radicosa 1 and Varignana 1 wells; Figs. 1b and 10). As a result, there is little or no upper impermeable barrier to the escape of gases in the Romagna Apennines.

MVA gases of both Emilia mud volcanoes and some Romagna seeps (PdR1 and PdR2) likely represent a mix sourced from both the Marnoso Arenacea and the Upper Triassic dolostones (Burano Fm.; Lindquist, 1999; Pieri, 2001). Owing to its fracture permeability, the Marnoso Arenacea may also host the main fluid reservoirs sealed by the overlying LU (Pieri, 2001, and references therein). This implies that fluid reservoirs are expected to be located beneath the Marnoso Arenacea–LU interface. On the basis of the setting of some Emilia mud volcanoes, it can be roughly estimated that the development of the MVA gases, characterized by abundance of cyclic compounds, requires the overburden to exceed a thickness of ~3 km (Fig. 10).

Estimation of a paleogeothermal gradient is crucial for assessing the temperature of the source region of gases. Although difficult to be assessed, a reasonable paleo-geothermal gradient of 25 °C/km (acting since the Miocene) has been considered for the thermal evolution of the Marnoso Arenacea basin according to temperature measurements in deep well bores, vitrinite data, and heat flow distribution (Zattin et al., 2000). A similar geothermal gradient has also been assumed by Capozzi and Picotti (2002) for estimating the source depth of thermogenic methane released from the Regnano mud volcano. Therefore, a mean geothermal gradient of 25 °C/km, the ~3 km-thick minimum overburden apparently required to form the MVA gases, would correspond to temperatures >75 °C, i.e. approaching thermodynamic conditions favorable for the occurrence of reforming processes able to produce cyclic-rich thermogenic gas. Gases from Macalube di Aragona (Ma), pertaining to the MVA group, are likely produced by this genetic mechanism, and, consequently, are related to a deep fluid source whose temperature is regulated by a normal geothermal gradient.

The genesis of the MVC gases would instead require lower temperature (≤ 50 °C) and pressure that could broadly be estimated to correspond to depths not exceeding 1.5–2 km, as suggested by the

MVC-type DdS mud volcano, where the thickness of the underlying LU may vary between ca. 1200 and 1500 m (Figs. 1b and 10). These findings are in accordance with the MVC gas type determined for the CR mud volcano, which lies directly over the outcropping Marnoso Arenacea, thereby without any LU overburden (Figs. 1 and 10). The observation that other mud volcanoes in the region (for example Be) release MVC gas sourced from the Pliocene–Pleistocene deposits suggests that this gas type can originate from different source rocks, and that its formation is mostly depending upon burial depth and temperature.

The above scenario is in apparent contrast with the Emilia mud volcanoes that discharge the deep originated MVA gases. They are indeed located in the area where the Marnoso Arenacea is lifted by a fold anticline, referred to here as Sassuolo Anticline, and the LU cover is only ~1 km thick (Figs. 1b and 10). In our interpretation, the Sassuolo Anticline may act as collector of fluids generated in the deeper along-strike sectors, where the LU package is as thick as 3–4 km, or more (Fig. 10). Such gases would flow through the permeable layers in the periclinal terminations of the Sassuolo Anticline, in response to the lateral pressure gradient in the Marnoso Arenacea layer driven by the thickness variation of the overlying (and impermeable) LU overburden. In such a way, the rising gases may collect at the fold crest, and this might explain the concentration of mud volcanoes discharging MVA gases in this sector of the Pede–Apennine margin, where the LU package is thin and the brittle elements associated with the folding may provide efficient depth-to-surface structural conduits for the rising fluids (e.g., Bonini, 2007).

A final remark concerns the possibility that the thrust faults producing the Sassuolo Anticline may also provide deeply-rooted pathways able to transfer upwards the thermogenic gas originated in the Triassic source rocks. A similar setting can also explain the occurrence of the MVA gases released at the PdR1 and PdR2 dry seeps of Romagna, where the LU are missing and the Marnoso Arenacea is only ~1 km-thick (see Montefreddo 1 and 2 well logs available at www.videpi.com). Such a lithostratigraphic setting markedly differs from that of the Emilia mud volcanoes releasing the same type (MVA) gases. However, the discharge of the MVA gases at the PdR1 and PdR2

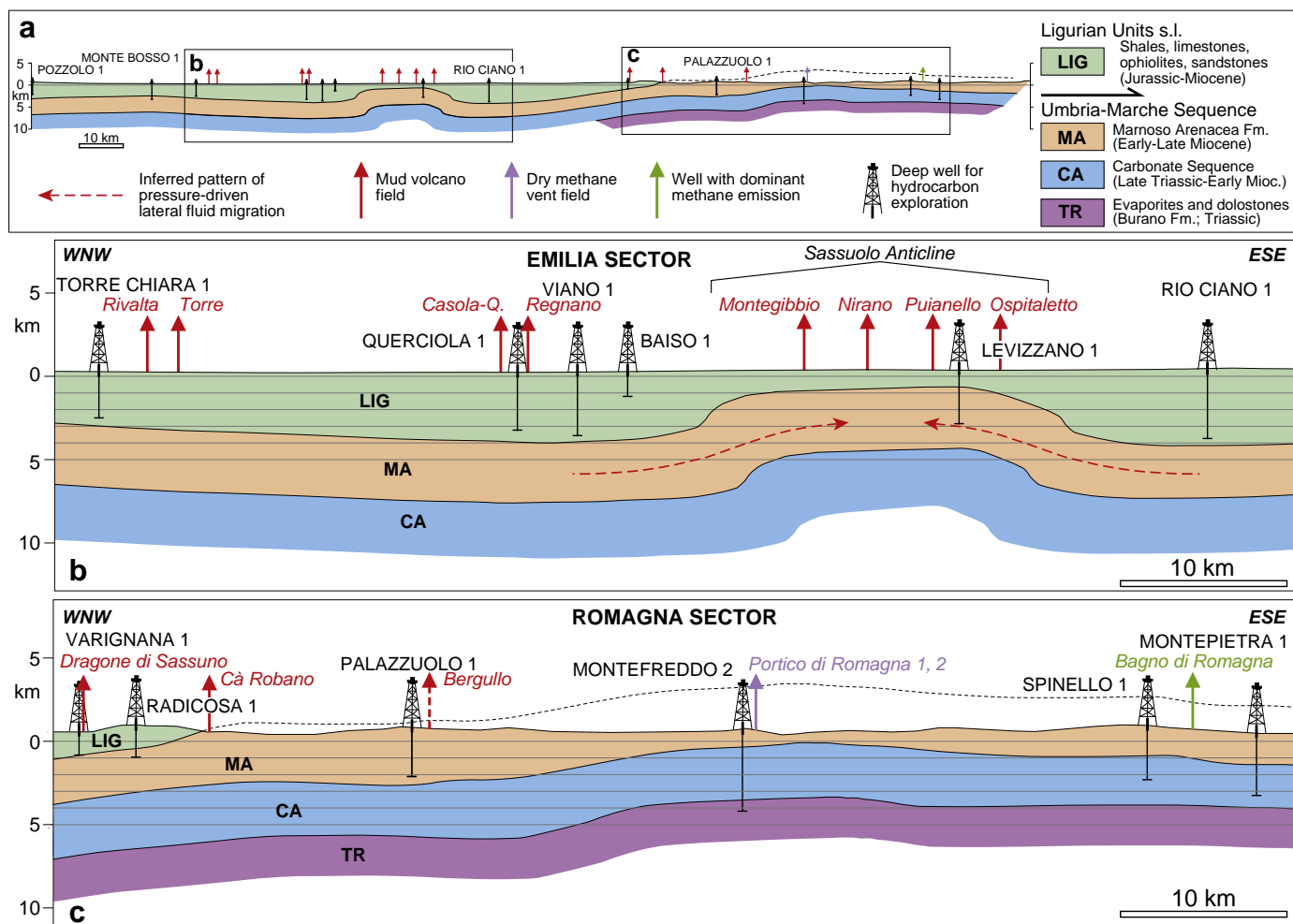


Fig. 10. Schematic regional cross-section along-strike the Romagna and the Emilia Apennines (blue trace in b). The sampled mud volcanoes as well as the dry methane vent and the CH_4 -rich well are projected on the profile to allow comparison with vertical stratigraphy. The Romagna sector is adapted from Anelli et al. (1994). Note the lateral pressure gradient in the Marnoso Arenacea layer and the inferred gas/fluid migration toward the Sassuolo Anticline core, which is supposedly driven by the lateral thickness variation of the impermeable (overlying) Ligurian Units overburden. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

seeps can be explained by considering that these gas emissions are situated above the core of a large thrust-related anticlinorium (Bonini, 2007), where (likewise the Sassuolo Anticline) the brittle elements associated with this fold may function as conduits releasing MVA gases mostly supplied from the Triassic source rocks.

6. Concluding remarks

The composition of light hydrocarbons (alkane, cyclic and aromatic compounds) of the gas discharges investigated in the present study evidences two distinct groups of thermogenic gases, which cannot be distinguished using the classic Schoell and Bernard geochemical parameters: 1) Aromatic-rich gases (MVB) from mud volcanoes (VS, Si, St) and a CH_4 -rich emission (Fo) located in the south-eastern sector of Sicily which are fed by significant fluid contribution of a hydrothermal system related to the activity of Mount Etna volcano, which favors the aromatization of alkanes and cycloalkanes; 2) cyclic-rich gases (MVA) from mud volcanoes in the Emilia Apennines and in the south-western sector of Sicily, as well as CH_4 -rich emissions (PdR1 and PdR2) in the Romagna Apennines. All these emissions are fed by organic sources located at depths ≥ 3000 m, a genetic environment characterized by high pressure and temperatures in the 100–120 °C temperature range. At these conditions the production of cyclic compounds may proceed through both i) thermal cracking of heavier organic molecules

and ii) catalytic reforming process likely consisting of incomplete aromatization of light alkanes.

Biogenic gases discharged from emissions located in the Romagna Apennines show relatively low concentrations of C_4+ hydrocarbons. The presence of these compounds indicates the occurrence of small fluid contribution from a thermogenic component that is not shown by the CH_4 isotopic features, being masked by the dominant biogenic signature.

Summarizing, our results have highlighted that the gas composition of the investigated mud volcanoes and seeps reflects the complex, though intimate, interplay between the geological assessment and the chemical–physical conditions of the fluid reservoirs. Accordingly, light hydrocarbon speciation is to be regarded as a geochemical tool able to retrieve information on the fluid source and on gas genetic mechanisms in complex geological environments.

Acknowledgments

Two anonymous reviewers are warmly thanked for their helpful and useful suggestions on an early draft of the manuscript. We also thank W. D'Alessandro a G. Pecoraino (INGV Palermo) for their help during the sampling campaign in Sicily.

This research was financed by the Laboratory of Fluid Geochemistry of the Department of Earth Sciences of Florence and by a project of Ciudad de la Energía (Spain): Chemical composition of free- and

diffuse-gases in CO₂-rich natural analogs (Resp. for the CNR-IGG: O. Vaselli).

References

- Accaino, F., Catalano, R., Di Marzo, L., Giustiniani, M., Tinivella, U., Nicolich, R., Sulli, A., Valenti, V., Manetti, P., 2011. A crustal seismic profile across Sicily. *Tectonophysics* 508, 52–61.
- Allard, P., Jean-Baptiste, P., D'Alessandro, W., Parello, F., Parisi, B., Flehoc, C., 1997. Mantle-derived helium and carbon in groundwaters and gases of Mount Etna, Italy. *Earth and Planetary Science Letters* 148, 501–516.
- Anelli, L., Gorza, M., Pieri, M., Riva, M., 1994. Subsurface well data in the northern Apennines. *Memorie della Società Geologica Italiana* 48, 461–471.
- Arthur, C.L., Pawliszyn, J., 1990. Solid phase microextraction with thermal desorption using fused silica optical fibers. *Analytical Chemistry* 62, 2145–2148.
- AstaFev, V.P., Makhmudov, A.K., Zhelonkin, A.I., 1973. Significance of isobutane/butane ratios in hydrocarbon gases in searching for petroleum (according to Baltic and Bielorussian data). *Tr. Vses. Neft. Nauchno-Issled. Geologorazved. Inst.* 338, 35–38.
- Bennet, B., Larter, S.R., 1997. Partition behaviour of alkylphenols in crude oil/brine systems under subsurface conditions. *Geochimica et Cosmochimica Acta* 61, 4393–4402.
- Bernard, B.B., Brooks, J.M., Sackett, W.M., 1978. Light hydrocarbons in recent Texas continental shelf and slope sediments. *Journal of Geophysical Research* 83, 4053–4061.
- Bertello, F., Fantoni, R., Franciosi, F., 2008. Exploration Country Focus: Italy. Search and Discovery Article #10165, Posted 16 October 2008. <http://www.searchanddiscovery.net/documents/2008/08158bertello/index.htm> 2008available at.
- Blinova, V.N., Ivanov, M.K., Böhrmann, G., 2003. Hydrocarbon gases in deposits from mud volcanoes in the Sorokin Trough, North-Eastern Black Sea. *Geo-Marine Letters* 23 (3–4), 250–257.
- Boccaletti, M., Elter, P., Guazzone, G., 1971. Plate tectonic models for the development of the Western Alps and Northern Apennines. *Nature Physical Sciences* 234, 108–111.
- Boccaletti, M., Ciaranfi, N., Cosentino, D., Deiana, G., Gelati, R., Lentini, F., Massari, F., Moratti, G., Pescatore, T., Ricci Lucchi, F., Tortorici, L., 1990. Palinspastic restoration and paleogeographic reconstruction of the peri-Tyrrhenian area during the Neogene. *Palaeogeography, Palaeoclimatology, Palaeoecology* 77, 41–50.
- Bonini, M., 2007. Interrelations of mud volcanism, fluid venting, and thrust-anticline folding: examples from the external northern Apennines (Emilia-Romagna, Italy). *Journal of Geophysical Research* 112, B08413. doi:10.1029/2006JB004859.
- Bonini, M., 2009. Mud volcano eruptions and earthquakes in the Northern Apennines and Sicily, Italy. *Tectonophysics* 474, 723–735.
- Brown, K.M., 1990. The nature and hydrogeologic significance of mud diapirs and diatremes for accretionary systems. *Journal of Geophysical Research* 95, 8969–8982.
- Butler, R.W.H., Grasso, M., La Manna, F., 1992. Origin and deformation of the Neogene–recent Maghrebien foredeep at the Gela Nappe, SE Sicily. *Journal of the Geological Society of London* 149, 547–556.
- Capaccioni, B., Martini, M., Mangani, F., Giannini, L., Nappi, G., Prati, F., 1993. Light hydrocarbons in gas-emissions from volcanic areas and geothermal fields. *Geochemical Journal* 27, 7–17.
- Capaccioni, B., Martini, M., Mangani, F., 1995. Light hydrocarbons in hydrothermal and magmatic fumaroles: hints of catalytic and thermal reactions. *Bulletin of Volcanology* 56, 593–600.
- Capaccioni, B., Tassi, F., Vaselli, O., 2000. Organic and inorganic geochemistry of low temperature gas discharges at the Baia di Levante beach, Vulcano Island, Italy. *Journal of Volcanology and Geothermal Research* 108, 173–185.
- Capaccioni, B., Taran, Y., Tassi, F., Vaselli, O., Mangani, G., Macias, J.L., 2004. Source conditions and degradation processes of light hydrocarbons in volcanic gases: an example from El Chichon volcano (Chiapas State, Mexico). *Chemical Geology* 206, 81–96.
- Capozzi, R., Picotti, V., 2002. Fluid migration and origin of a mud volcano in the northern Apennines (Italy): the role of deeply rooted normal faults. *Terra Nova* 14, 363–370.
- Capozzi, R., Picotti, V., 2010. Spontaneous fluid emissions in the Northern Apennines: geochemistry, structures and implications for the petroleum system. In: Goffey, G.P., Craig, J., Needham, T., Scott, R. (Eds.), *Hydrocarbons in Contractual Belts: Geological Society, London, Special Publications*, 348, pp. 115–135. doi:10.1144/SP348.7.
- Caracausi, A., Favara, R., Giammanco, S., Italiano, F., Paonita, A., Pecoraino, G., Rizzo, A., Nuccio, P.M., 2003. Mount Etna: geochemical signals of magma ascent and unusually extensive plumbing system. *Geophysical Research Letters* 30 (2), 1057. doi:10.1029/2002GL015463.
- Catalano, R., Di Stefano, P., Sulli, A., Vitale, F.P., 1996. Paleogeography and structure of the central Mediterranean: Sicily and its offshore area. *Tectonophysics* 260, 291–323.
- Catalano, R., Franchino, A., Merlini, S., Sulli, A., 2000a. A crustal section from North Algerian to the Ionian ocean (Central Mediterranean). *Memorie della Società Geologica Italiana* 55, 71–85.
- Catalano, R., Franchino, A., Merlini, S., Sulli, A., 2000b. Central Western Sicily structural setting interpreted from seismic reflection profiles. *Memorie della Società Geologica Italiana* 55, 5–16.
- Catalano, S., De Guidi, G., Monaco, C., Tortorici, G., Tortorici, L., 2008. Active faulting and seismicity along the Siculo–Calabrian Rift Zone (Southern Italy). *Tectonophysics* 453, 177–192.
- Catalano, S., Torriss, S., Tortorici, G., Romagnoli, G., 2011. Active folding along a rift-flank: the Catania region case history (SE Sicily). *Journal of Geodynamics* 51, 53–63.
- Chiodini, 1996. Gases dissolved in groundwaters: analytical methods and examples of application in central Italy. In: Pacini (Ed.), *Environ. Geochem. Congress, Castelnuovo di Porto, Rome*, pp. 135–148, 22–26 May.
- Chiodini, G., D'Alessandro, W., Parello, F., 1996. Geochemistry of gases and waters discharged by the mud volcanoes at Paterno, Mt. Etna (Italy). *Bulletin of Volcanology* 58, 51–58.
- Chung, H.M., Gormly, J.R., Squires, R.M., 1988. Origin of gaseous hydrocarbons in subsurface environments: theoretical considerations of carbon isotope distribution. *Chemical Geology* 71, 97–103.
- D'Alessandro, W., De Gregorio, S., Dongarrà, G., Gurrieri, S., Parello, F., Parisi, B., 1997. Chemical and isotopic characterization of the gases of Mount Etna (Italy). *Journal of Volcanology and Geothermal Research* 78, 65–76.
- Dai, J.X., 1992. Identification of different alkane gas. *Science in China, Series B* 22 (2), 185–193.
- Dai, J.X., 1993. Identification of coal formed gas and oil type gas by light hydrocarbons. *Petroleum Exploration and Development* 20 (5), 26–32.
- Dale, J.D., Shock, E.L., MacLeod, G., Aplin, A.C., Larter, S.R., 1997. Standard partial molal properties of aqueous alkylphenols at high pressures and temperatures. *Geochimica et Cosmochimica Acta* 61, 4017–4024.
- Darling, W.G., 1998. Hydrothermal hydrocarbon gases: 1. Genesis and geothermometry. *Applied Geochemistry* 13, 815–824.
- Davis, B.H., 1999. Alkane dehydrocyclization mechanism. *Catalysis Today* 53, 443–516.
- Davoli, E., Gangai, M.L., Morselli, L., Tonelli, D., 2003. Characterization of odorants emissions from landfills by SPME and GC/MS. *Chemosphere* 51, 357–368.
- Deville, E., Battani, A., Griboulard, R., Guerlais, S., Herbin, J.P., Houzay, J.P., Muller, C., Prinzhofer, A., 2003. The origin and processes of mud volcanism: new insights from Trinidad. In: Van Rensbergen, P., Hillis, R.R., Maltman, A.J., Morley, C.K. (Eds.), *Subsurface Sediment Mobilization: Geol. Soc. London, Spec. Publ.*, 216, pp. 475–490.
- Dewey, J.F., Helman, M.L., Turco, E., Hutton, D.H.W., Knott, S.D., 1989. Kinematics of the western Mediterranean. In: Coward, M.P., Dietrich, D., Park, R.G. (Eds.), *Alpine Tectonics: Geol. Soc. London, Spec. Publ.*, 45, pp. 265–283.
- Dimitrov, L., 2002. Mud volcanoes – the most important pathways for degassing deeply buried sediments. *Earth-Science Reviews* 59, 49–76.
- Duan, Y., 2000. Organic geochemistry of recent marine sediments from the Nansha Sea, China. *Organic Geochemistry* 31, 159–167.
- Duan, T., Ma, L.H., 2001. Lipid geochemistry in a sediment core from Ruergai Marsh deposit (Eastern Qinghai – Tibet plateau, China). *Organic Geochemistry* 32, 1429–1442.
- Duan, Y., Wu, B., Zheng, G., Zhang, H., Zheng, C., 2004. The specific carbon isotopic compositions of branched and cyclic hydrocarbons from Fushun oil shale. *Chinese Science Bulletin* 49, 369–373.
- Etiopie, G., Milkov, A.V., 2004. A new estimate of global methane flux from onshore and shallow submarine mud volcanoes to the atmosphere. *Environmental Geology* 46, 997–1002.
- Etiopie, G., Martinelli, G., Caracausi, A., Italiano, F., 2007. Methane seeps and mud volcanoes in Italy: gas origin, fractionation and emission to the atmosphere. *Geophysical Research Letters* 34. doi:10.1029/2007GL030341.
- Etiopie, G., Feyzullayev, A., Milkov, A.V., Waseda, M., Mizobe, K., Sun, C.H., 2009a. Evidence of subsurface anaerobic biodegradation of hydrocarbons and potential secondary methanogenesis in terrestrial mud volcanoes. *Marine and Petroleum Geology* 26, 1692–1703.
- Etiopie, G., Feyzullayev, A., Baciu, C.L., 2009b. Terrestrial methane seeps and mud volcanoes: a global perspective of gas origin. *Marine and Petroleum Geology* 26, 333–344.
- Evans, W.C., White, L.D., Rapp, 1998. Geochemistry of some gases in hydrothermal fluids from the southern Juan de Fuca ridge. *Journal of Geophysical Research* 15, 305–313.
- Favara, R., Gioia, C., Grassa, F., Inguaggiato, S., Proietto, F., Valenza, M., 2001. Studio geochimico delle manifestazioni fluide presenti nell'area della riserva naturale integrale "Maccalube di Aragona". *Natural Siciliano* 25, 137–154.
- Finetti, I.R., Lentini, F., Carbone, S., Del Ben, A., Di Stefano, A., Forlin, E., Guarnieri, P., Pipan, M., Prizzon, A., 2005. Geological outline of Sicily and lithospheric tectonodynamics of its Tyrrhenian margin from new CROP seismic data. In: Finetti, I.R. (Ed.), *CROP PROJECT: Deep Seismic Exploration of the Central Mediterranean and Italy*, pp. 319–375. Cpt. 15.
- Fisher, J.B., Boles, J.R., 1990. Water–rock interaction in Tertiary sandstones, San Joaquin basin, California, U.S.A.: Diagenetic controls on water composition. *Chemical Geology* 82, 83–101.
- Florez Menendez, J.C., Fernandez Sanchez, M.L., Fernandez Martinez, E., Sanchez Uria, J.E., Sanz-Mendez, A., 2004. Static headspace versus head space solid-phase microextraction (HS-SPME) for the determination of volatile organochlorine compounds in landfill leachates by gas chromatography. *Talanta* 63, 809–814.
- Fryer, P., 1996. Evolution of the Mariana convergent plate margin system. *Reviews of Geophysics* 34, 89–125.
- Ghisetti, F., Vezzani, L., 1984. Thin-skinned deformations of the western Sicily thrust belt and relationships with crustal shortening: mesostructural data on the Mt. Kumeta–Alcantara fault zone and related structures. *Bollettino della Società Geologica Italiana* 103, 129–157.
- Giammanco, S., Parello, F., Gambardella, B., Schifano, R., Pizzullo, S., Galante, G., 2007. Focused and diffuse effluents of CO₂ from mud volcanoes and mofettes south of Mt. Etna (Italy). *Journal of Volcanology and Geothermal Research* 165, 46–63.

- Giggenbach, W.F., Corales, R., 1992. The isotopic and chemical composition of water and steam discharges from volcano-magmatic hydrothermal system of the Guana-caste geothermal province, Costa Rica. *Applied Geochemistry* 7, 309–322.
- Granath, J.W., Casero, P., 2004. Tectonic setting of the petroleum systems of Sicily. In: Swennen, R., Roure, F., Granath, J.W. (Eds.), *Deformation, Fluid Flow and Reservoir Appraisal in Foreland Fold-and-Thrust Belts: AAPG Hedberg Series*, pp. 391–411. n°1.
- Grassa, F., Capasso, G., Favara, R., Inguaggiato, S., Faber, E., Valenza, M., 2004. Molecular and isotopic composition of free hydrocarbon gases from Sicily, Italy. *Geophysical Research Letters* 31, L06607. doi:10.1029/2003GL019362.
- Higgins, G.E., Saunders, J.B., 1974. Mud volcanoes – their nature and origin. *Verhandl Naturf Ges Basel* 84, 101–152.
- Hu, G.Y., Li, J., Li, Z.S., Luo, X., Sun, Q.W., Ma, C.H., 2008. Preliminary study on the origin identification of natural gas by the parameters of light hydrocarbons. *Science in China, Series D: Earth Sciences* 51, 131–139.
- Hunt, J.M., 1984. Generation and migration of light hydrocarbons. *Science* 226, 1265–1270.
- Hunt, J.M., Huc, A.Y., Whelan, J.K., 1980. Generation of light hydrocarbons in sedimentary rocks. *Nature* 288, 688–690.
- James, A.T., Burns, B.J., 1984. Microbial alteration of subsurface natural gas accumulations. *American Association of Petroleum Geologists Bulletin* 68 (8), 957–960.
- Katritzky, A.R., Balasubramanian, M., Siskin, M., 1990. Aqueous high-temperature chemistry of carbo- and heterocycles. 2. Monosubstituted benzenes: Benzyl alcohol, benzaldehyde, and benzoic acid. *Energy & Fuels* 4, 499–505.
- Kessler, J.D., Reeburgh, W.S., Southon, J., Varela, R., 2005. Fossil methane source dominates Cariaco Basin water column methane geochemistry. *Geophysical Research Letters* 32, L12609. doi:10.1029/2005GL022984.
- Kissin, Y.V., 1998. Catagenesis of light aromatic compounds in petroleum. *Organic Geochemistry* 4, 947–962.
- Kopf, A.J., 2002. Significance of mud volcanism. *Reviews of Geophysics* 40, 1005. doi:10.1029/2000RG000093.
- Kopf, A., Klaeschen, D., Masclé, J., 2001. Extreme efficiency of mud volcanism in dewatering accretionary prisms. *Earth and Planetary Science Letters* 189, 295–313.
- Lavrushin, V.U., Polyak, B.G., Prasolov, R.M., Kamenskii, I.L., 1996. Sources of material in mud volcano products based on isotopic, hydrochemical, and geological data. *Lithology and Mineral Resources* 31 (6), 557–578.
- Lentini, F., Carbone, S., Catalano, S., Monaco, C., 1991. Tettonica a thurst della catena appenninico-maghebide: esempi della Lucania e della Sicilia. In: Boccaletti, M., Deiana, G., Papani, G. (Eds.), *Neogene Thrust Tectonics. Studi Geologici Camerti*, pp. 19–26.
- Lentini, F., Carbone, S., Catalano, S., 1994. Main structural domains of the central Mediterranean region and their Neogene tectonic evolution. *Bollettino di Geofisica Teorica e Applicata* 36, 103–125.
- Leythaeuser, D., Schaefer, R.G., Cornford, C., Weiner, B., 1979. Generation and migration of light hydrocarbon (C₂–C₇) in sedimentary basin. *Organic Geochemistry* 4, 191–214.
- Lindquist, S.J., 1999. Petroleum systems of the Po Basin Province of Northern Italy and the Northern Adriatic Sea: Porto Garibaldi (Biogenic), Meride/Riva di Solto (Thermal), and Marnoso Arenacea (Thermal). USGS Open-File Report 99-50-M.
- Malinverno, A., Ryan, W.B.F., 1986. Extension in the Tyrrhenian Sea and shortening in the Apennines as a result of arc migration driven by sinking of the lithosphere. *Tectonics* 5, 227–245.
- Mamyrin, B.A., Tolstikhin, I.N., 1984. Helium Isotopes in Nature. Elsevier, Amsterdam.
- Manga, M., Rudolph, M.L., Brumm, M., 2009. Earthquake triggering of mud volcanoes. *Marine and Petroleum Geology* 26, 1785–1798.
- Mangani, G., Berloni, A., Maione, M., 2003. “Cold” solid-phase microextraction method for the determination of volatile halocarbons present in the atmosphere at ultra-trace levels. *Journal of Chromatography A* 988, 167–175.
- Mango, F.D., 1994. The origin of light hydrocarbons in petroleum: ring preference in the closure of carbocyclic rings. *Geochimica et Cosmochimica Acta* 58, 895–901.
- Mango, F.D., 1997. The light hydrocarbons in petroleum: a critical review. *Organic Geochemistry* 26, 417–440.
- Mango, F.D., 2000. The origin of light hydrocarbons. *Geochimica et Cosmochimica Acta* 64, 1265–1277.
- Martin, J.B., Kastner, M., Henry, P., Le Pichon, X., Lallemand, S., 1996. Chemical and isotopic evidence for sources of fluids in a mud volcano field seaward of the Barbados accretionary wedge. *Journal of Geophysical Research* 101, 20325–20345.
- Martinelli, G., Judd, A., 2004. Mud volcanoes of Italy. *Geological Journal* 39, 49–61.
- Martinelli, G., Bassignani, A., Ferrari, G., Finazzi, P.B., 1989. Predicting earthquakes in Northern Apennines: recent developments in monitoring of Radon 222. *Proceedings of the 4th International Symposium on The Analysis of Seismicity and Seismic Risk, Bechyně Castle, Czechoslovakia*, pp. 192–208. 4–9 September.
- McCormack, T.M., Seewald, J.S., Simoneit, B.R.T., 2001. Reactivity of monocyclic aromatic compounds under hydrothermal conditions. *Geochimica et Cosmochimica Acta* 65, 455–468.
- Mèriaudeau, P., Naccache, C., 1997. Dehydrocyclization of alkanes over zeolite-supported metal catalysts: monofunctional and bifunctional route. *Catalysis Reviews – Science and Engineering* 39, 5–48.
- Milkov, A.V., 2000. Worldwide distribution of submarine mud volcanoes and associated gas hydrates. *Marine Geology* 167, 29–42.
- Milkov, A.V., 2005. Global distribution of mud volcanoes and their significance in petroleum exploration, as a source of methane in the atmosphere and hydrosphere, and as geohazard, in:
- Milkov, A.V., Dzou, L., 2007. Geochemical evidence of secondary microbial methane from very slight biodegradation of undersaturated oils in a deep hot reservoir. *Geology* 35, 455–458.
- Milkov, A.V., Sassen, R., Apanasovich, T.V., Dadashev, F.G., 2003. Global gas flux from mud volcanoes: a significant source of fossil methane in the atmosphere and the ocean. *Geophysical Research Letters* 30, 1037. doi:10.1029/2002GL016358.
- Minissale, A., Magro, G., Martinelli, G., Vaselli, O., Tassi, F., 2000. A fluid geochemical transect in the northern Apennines (central-northern Italy): fluid genesis and migration and tectonic implications. *Tectonophysics* 319, 199–222.
- Monaco, C., Tortorici, L., 2000. Active faulting in the Calabrian arc and eastern Sicily. *Journal of Geodynamics* 29, 407–424.
- NIST/EPA/NIH Mass Spectral Library, 2005. <http://www.nist.gov/srd/nist1a.htm>2005.
- Pallasser, R.J., 2000. Recognising biodegradation in gas/oil accumulations through the $\delta^{13}\text{C}$ compositions of gas components. *Organic Geochemistry* 31, 1363–1373.
- Pecoraino, G., Giammanco, S., 2005. Geochemical characterization and temporal changes in parietal gas emissions at Mt. Etna (Italy) during the period July 2000–July 2003. *TAO* 16, 805–841.
- Pellegrini, M., Brazzorotto, C., Forti, P., Francavilla, F., Rabbi, E., 1982. *Idrogeologia del margine pedeappenninico Emiliano-Romagnolo. Memorie della Società Geologica Italiana* 34, 183–189.
- Pieri, M., 2001. Italian petroleum geology. In: Vai, G.B., Martini, I.P. (Eds.), *Anatomy of an Orogen: The Apennines and Adjacent Mediterranean Basins*. Kluwer Academic Publisher, pp. 533–550.
- Pieri, M., Groppi, G., 1981. Subsurface geological structure of the Po plain, Italy. *Consiglio Nazionale delle Ricerche, Pubbl.* 414, Rome.
- Principi, G., Treves, B., 1984. Il sistema Corso-Appennino come prisma di accrezione. *Riflessi sul problema generale del limite Alpi-Appennino: Memorie della Società Geologica Italiana*, 28, pp. 529–576.
- Ricci Lucchi, F., 1986. The Oligocene to recent foreland basins of the Northern Apennines. In: Allen, P.A., Homewood, P. (Eds.), *Foreland basins: International Association of Sedimentologists Special Publication*, 8, pp. 105–139.
- Riva, A., Salvatori, T., Cavaliere, R., Ricchiuto, T., Novelli, L., 1986. Origin of oils in Po Basin, Northern Italy. *Organic Geochemistry (Advances in Organic Geochemistry 1985)*, 10, pp. 391–400.
- Rizzo, A., Caracausi, A., Favara, R., Martelli, M., Paonita, A., Paternoster, M., 2006. New insights into magma dynamics during last two eruptions of Mount Etna as inferred by geochemical monitoring from 2002 to 2005. *Geochemistry, Geophysics, Geosystems* 7, Q06008. doi:10.1029/2005GC001175.
- Robertson, A.H.F., Ocean Drilling Program Leg 160 Scientific Party, 1996. Mud volcanism on the Mediterranean Ridge: initial results of Ocean Drilling Program Leg 160. *Geology* 24, 239–242.
- Roure, F., Howell, D.G., Muller, C., Moretti, I., 1990. Late Cenozoic subduction complex of Sicily. *Journal of Structural Geology* 12, 259–266.
- Royden, L.H., Patacca, E., Scandone, P., 1987. Segmentation and configuration of subducted lithosphere in Italy: an important control on thrust belt and foredeep-basin evolution. *Geology* 15, 714–717.
- Savage, P.E., Klein, M.T., 1987. Asphaltene reaction pathways. 2. Pyrolysis of n-pentadecylbenzene. *Industrial and Engineering Chemistry Research* 26, 488–494.
- Schmidt, M., Hensen, C., Morz, T., Muller, C., Grevemeyer, I., Wallmann, K., Mau, S., Kaul, N., 2005. Methane hydrate accumulation in “Mound 11” mud volcano, Costa Rica forearc. *Marine Geology* 216 (1–2), 83–100.
- Schoell, M., 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochimica et Cosmochimica Acta* 44, 649–661.
- Schoell, M., 1983. Genetic characterization of natural gases. *American Association of Petroleum Geologists Bulletin* 67, 2225–2238.
- Schoell, M., 1988. Multiple origins of methane in the Earth. *Chemical Geology* 71, 1–10.
- Sherwood Lollar, B., Lacrampe-Couloume, G., Slater, G.F., Ward, J., Moser, D.P., Gihring, T.M., Lin, L.-H., Onstott, T.C., 2006. Unravelling abiogenic and biogenic sources of methane in the Earth’s deep subsurface. *Chemical Geology* 226, 328–339.
- Simoneit, B.R.T., Kawka, O.E., Brault, M., 1988. Origin of gases and condensates in the Guaymas Basin hydrothermal system (Gulf of California). *Chemical Geology* 71, 169–182.
- Slack, J.F.R., Turner, J.W., Ware, P.L.G., 1998. Boron-rich mud volcanoes of the Black Sea region: modern analogues to ancient sea-floor tourmalinites associated with Sullivan-type Pb–Zn deposits? *Geology* 26, 439–442.
- Smith, C.M., Savage, P.E., 1991. Reactions of polycyclic lkylaromatics: structure and reactivity. *AIChE Journal* 37, 1613–1624.
- Somerville, H.J., Bennett, D., Davenport, J.N., Holm, M.S., Lynes, A., Mahieu, A., McCourt, B., Parker, J.G., Stephenson, R.R., Watkinson, R.J., Wilkinson, T.G., 1987. Environmental effect of produced water from North Sea oil operations. *Marine Pollution Bulletin* 18, 549–558.
- Stamatakis, M.G., Baltatzis, E.G., Skounakis, S.B., 1987. Sulfate minerals from a mud volcano in the Katakato area, western Peloponnese, Greece. *American Mineralogist* 72, 839–841.
- Tannebaum, E., Kaplan, I.R., 1985. Role of minerals in the thermal alteration of organic matter-I: generation of gases and condensates under dry condition. *Geochimica et Cosmochimica Acta* 49, 2589–2604.
- Taran, Y.A., Giggenbach, W.F., 2003. Geochemistry of light hydrocarbons in subduction-related volcanic and hydrothermal fluids. *Society of Economic Geologists Special Publication* 10, 61–74.
- Tassi, F., 2004. Fluidi in ambiente vulcanico: Evoluzione temporale dei parametri composizionali e distribuzione degli idrocarburi leggeri in fase gassosa. Ph.D. thesis, Univ. of Florence, Florence, Italy, pp. 292 (in Italian).
- Tassi, F., Capaccioni, B., Capecciacci, F., Vaselli, O., 2009a. Non-methane volatile organic compounds (VOCs) at El Chichon volcano (Chiapas, Mexico): geochemical features, origin and behaviour. *Geofisica International* 48 (1), 85–95.

- Tassi, F., Montegrossi, G., Vaselli, O., Liccioli, C., 2009b. Degradation of C₂–C₁₅ volatile organic compounds in a landfill cover soil. *Science of the Total Environment* 407, 4513–4525.
- Tassi, F., Montegrossi, G., Capecchiacci, F., Vaselli, O., 2010. Origin and distribution of thiophenes and furans in gas discharges from active volcanoes and geothermal systems. *International Journal of Molecular Sciences* 11, 1434–1457.
- Tassi, F., Capecchiacci, F., Bucciati, A., Vaselli, O., 2011. Sampling and analytical procedures for the determination of VOCs released into Air from natural and anthropogenic sources: a comparison between SPME (Solid Phase Micro Extraction) and ST (Solid Trap) methods. *Applied Geochemistry*. doi:10.1016/j.apgeochem.2011.09.023.
- Taylor, P., Larter, S., Jones, M., Dale, J., Horstad, I., 1997. The effect of oil–water–rock partitioning on the occurrence of alkylphenols in petroleum systems. *Geochimica et Cosmochimica Acta* 61, 1899–1910.
- Thompson, K.F.M., 1987. Fractionated aromatic petroleum and the generation of gas-condensates. *Organic Geochemistry* 11, 573–590.
- Thompson, K.F.M., 2004. Interpretation of charging phenomena based on reservoir fluid (PVT) data. Geological Society of London, Special Publication 237, 7–26. doi:10.1144/GSL.SP2004.237.01.02.
- Tissot, B.P., Welte, D.H., 1978. *Petroleum Formation and Occurrence*. Springer, Berlin, Heidelberg, New York.
- Vaselli, O., Tassi, F., Montegrossi, G., Capaccioni, B., Giannini, L., 2006. Sampling and analysis of volcanic gases. *Acta Volcanology* 18, 65–76.
- Wang, X., Zhang, M., 2008. Compositional and geochemical characteristics of light hydrocarbons for typical marine oils and typical coal-generated oils in China. *Chinese Journal of Geochemistry* 27, 407–411.
- Wang, W.C., Zhang, L.Y., Liu, W.H., Kang, Y., Ren, J.H., 2005. Effects of biodegradation on the carbon isotopic composition of natural gas – a case study in the Bamianhe oil field of the Jiyang Depression, Eastern China. *Geochemical Journal* 39, 301–309.
- Waseda, A., Iwano, H., 2008. Characterization of natural gases in Japan based on molecular and carbon isotope compositions. *Geofluids* 8, 286–292.
- Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chemical Geology* 161, 291–314.
- Whiticar, M.J., Suess, E., 1990. Hydrothermal hydrocarbon gases in the sediments of the King-George Basin, Bransfield Strait, Antarctica. *Applied Geochemistry* 5, 135–147.
- Yassir, N., 2003. The role of shear stress in mobilizing deep-seated mud volcanoes: geological and geomechanical evidence from Trinidad and Taiwan. In: Van Rensbergen, P., Hillis, R.R., Maltman, A.J., Morley, C.K. (Eds.), *Subsurface Sediment Mobilization*: Geol. Soc. London, Spec. Publ., 216, pp. 461–474.
- Zattin, M., Landuzzi, A., Picotti, V., Zuffa, G.G., 2000. Discriminating between tectonic and sedimentary burial in a foredeep succession, Northern Apennines. *Journal of the Geological Society of London* 157, 629–633.