

Molecular and isotopic composition of free hydrocarbon gases from Sicily, Italy

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[1] Chemical and isotopic data have been used as geochemical tracers for a genetic characterization of hydrocarbon gases from a total of eleven manifestations located in Eastern and Central-Southern Sicily (Italy). The molecular analysis shows that almost all the samples are enriched in methane (up to 93.2% Vol.), with the exception of four gas samples collected around Mt. Etna showing high mantle-derived CO₂ content. Methane isotope signatures suggest that these are thermogenic gases or a mixture between thermogenic gases and microbial gases. Although samples from some mud volcanoes in Southern Sicily (Macalube di Aragona) show isotope signatures consistent with a mixing model between thermogenic and microbial, by combining the molecular compositions (C₁/(C₂ + C₃)) and the methane isotope ratios (δ¹³C₁), such a process seems to be excluded. Therefore, the occurrence of secondary post-genetic processes should be invoked. Two main hypotheses have been considered: the first hypothesis includes that the gas is produced by microbial activity and altered post-genetically by microbial oxidation of methane, while according to the second hypothesis thermogenic gas have modified their molecular ratios due to vertical migration. **INDEX TERMS:** 1040 Geochemistry:

Isotopic composition/chemistry; 1055 Geochemistry: Organic geochemistry; 1099 Geochemistry: General or miscellaneous. **Citation:** Grassa, F., G. Capasso, R. Favara, S. Inguaggiato, E. Faber, and M. Valenza (2004), Molecular and isotopic composition of free hydrocarbon gases from Sicily, Italy, *Geophys. Res. Lett.*, 31, L06607, doi:10.1029/2003GL019362.

1. Introduction

[2] Hydrocarbon gases may be generated by two principal processes, microbial or thermogenic alteration of kerogen, each of them leads to different molecular and isotope compositions. For this reason, the stable hydrogen (δD) and carbon (δ¹³C) isotope compositions as well as the molecular composition have been used as suitable parameters to assess the source and the origin of natural gases. In this study, such an approach has been utilised for a geochemical characterization of eleven gas manifestations from Sicily (Italy) occurring in different geological environments. Gases were

sampled from natural gas seeps from the peripheral areas of Mount Etna or from mud volcanoes, (Figure 1), emitting also brackish-highly saline waters [Parello *et al.*, 1995; Favara *et al.*, 2001]. Some samples were also collected from some artificial wells drilled for hydrocarbons or carbon dioxide exploitation, also located close to the Mount Etna.

2. Gas Geochemistry

[3] In Figure 1 the location of sampling sites is reported. Collected gases have considerably varying CO₂ (0.2–96.4%Vol.) and CH₄ contents (0.5–93.2%Vol.), nitrogen is generally below 5% except for some samples where 17% Vol. is reached (Table 1). These samples are also characterized by relatively high He contents (from hundreds to thousands of ppmv). As can be seen from the triangular diagram plot (Figure 2) which considers the relative concentrations of CO₂, CH₄ and N₂, the samples can be classified into two main types: methane-dominated showing a methane content >50% vol. and carbon dioxide-dominated with CO₂ contents >50% vol. NA, ST and P39 samples are located in proximity of the CO₂ vertex with carbon dioxide contents ranging from 86 to 96% Vol. All the other samples (P2, P3, FO, FC, SN3 and BR) lie very close to the CH₄ vertex with the exception of VS sample showing an intermediate composition between CH₄ and CO₂.

[4] The CO₂-enrichment in NA, P39, ST and VS samples is consistent with a magmatic origin of the CO₂ as the carbon isotope composition of CO₂ in these emissions (−2.8 to +1.3‰ vs. V-PDB) reflects the interaction between magmatic gases derived from the Etnean degassing system and shallow cold groundwaters or hydrothermal systems [Chiodini *et al.*, 1996; D'Alessandro *et al.*, 1997; Giammanco *et al.*, 1998]. All these sites, are also characterized by ³He/⁴He ratios (R/Ra = 6.5 ± 1 [Caracausi *et al.*, 2003] confirming the presence of a relevant mantle-derived helium component. CH₄-rich gas manifestations located around Mount Etna volcano reveal different He isotope signatures. Although FO, SN3 and BR sites show comparable methane contents (85.7–91.7% Vol.), thus suggesting a common origin of gases, the He isotope ratios highlight: (a) values close to 0.03 R/Ra for SN3 and BR sites thus indicating the presence of a crustal gas contribution in these samples; (b) values distinctly higher than those of BR and SN3 sites, in the range typical for the Etnean magmatic end-

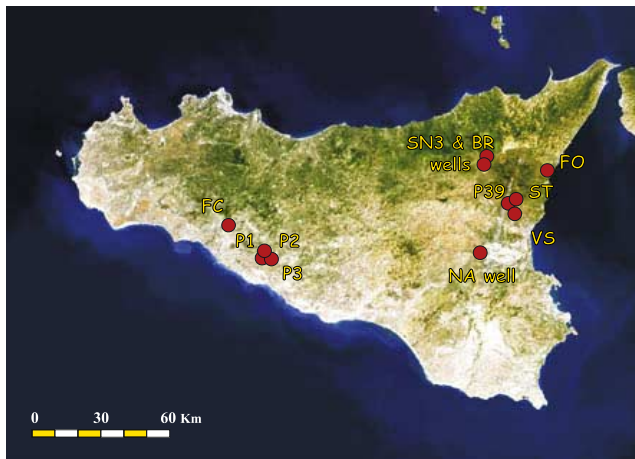


Figure 1. Sampling sites are located in two main areas: Eastern and Central-Southern Sicily. Seven samples were collected around the Mount Etna edifice some of them strictly connected to the volcanic degassing system [Caracausi et al., 2003]. P39 sampling point, a gas vent located on the southwestern flank of the volcano, is characterized by high soil CO₂ emission [Giammanco et al., 1998]. ST and VS samples were collected within the same area, from mud volcanoes emitting large amount of gases [Chiodini et al., 1996], mainly CO₂ (ST sample) or CO₂ and CH₄ in almost equal proportions (VS sample). FO sample has been collected as bubbling gas from a CH₄-dominant emission. NA is a CO₂-dominant exploiting well, located along a NE-SW fault system, about 40 Km southwest of Mt. Etna; BR and SN3 samples were collected from two borehole wells for HC exploitation located in the Northwestern flank of Mt. Etna. Other sampling sites are located in Southern Sicily. FC is a natural gas seep (Fuoco di Censo), without water. It is a typical example of “everlasting fires” [Etioppe et al., 2002]. P1, P2 and P3 samples were collected both as free gases from mud volcanoes and as bubbling gases from mud pools in the area of “Macalube di Aragona”.

member ($6 \div 7$ R/Ra [Marty et al., 1994]) at FO sample. The high variability of CH₄ contents in the gas samples collected around the Etnean edifice was explained taking into account two different processes. On the bases of the temporal trend of CH₄ and He contents and CO₂ flux

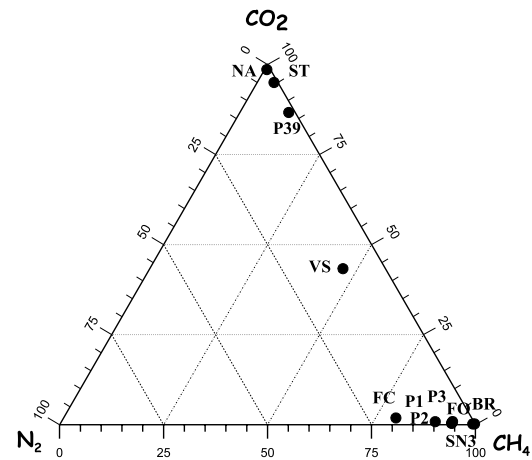


Figure 2. CO₂-CH₄-N₂ triangular plot. The chemical composition of sampled gaseous manifestations fall in two main groups. CO₂-dominated samples represented from Etnean gas (NA, ST and P39 sites) and CH₄-dominated samples that include all remaining samples. The chemical composition of Vallone Salato samples show a intermediate composition with almost equal amounts of CO₂ and CH₄.

observed during one year of gas monitoring, Giammanco et al. [1998] indicated that at P39 site the source of methane is compatible with an origin from a shallower hydrocarbon reservoir. Rising towards the surface along the same tectonic discontinuities volcanic gases and hydrocarbons are mixed, after the last interaction between volcanic fluids and hydrothermal waters.

[5] Gas samples, collected in selected Etnean sites (VS and FO), are enriched in methane and high in helium content. They have markedly mantle-derived helium signatures. Recently their compositions were related to a selective dissolution of highly soluble species (such as CO₂) in shallow aquifers, thus causing a progressive enrichment of less-soluble gases such as He and CH₄ [Caracausi et al., 2003].

[6] The chemistry of the gases released from FC site and the Macalube area was not yet studied in detail. Favara et al. [2001], in a preliminary geochemical characterization of gas emitted from the Macalube area, suggested that the gas emission seems to be related also to a chemical fractionation of CO₂ dissolved in water

Table 1. Molecular and Isotopic Composition of Collected Samples^a

Site	N ₂ (%Vol.)	O ₂ (%Vol.)	CO ₂ (%Vol.)	C ₁ (%Vol.)	C ₂ (ppm)	C ₃ (ppm)	$\frac{C_1}{(C_2+C_3)}$	$\delta^{13}C_{CH_4}$	δD_{CH_4}
BR	0.1	0.0	0.2	91.8	36454	17970	17	-58.7	-173
FC	17.4	3.8	1.8	76.4	5911	826	113	-35.1	-146
FO	5.4	0.3	0.4	91.4	25017	93	36	-40.5	-170
NA	0.9	0.2	96.4	0.5	198	16	25	-52.9	n.d.
P1	5.3	1.2	0.5	92.1	230	7	2172	-47.9	-190
P2	9.1	1.7	0.8	88.3	557	18	1537	-48.0	-191
P3	5.0	0.9	0.9	93.2	578	26	1545	-48.3	-188
P39	1.6	0.1	86.3	11.7	3181	n.d.	37	-35.9	-155
SN3	0.5	1.6	0.2	85.7	42805	41817	10	-59.2	-186
ST	0.9	0.1	94.9	4.1	403	10	98	-36.0	-133
VS	9.9	2.4	42.0	45.1	4490	805	85	-47.9	-185

^a $\delta^{13}C$ and δD are reported in delta units per mil vs. VPDB and SMOW, respectively. n.d. = not determined.

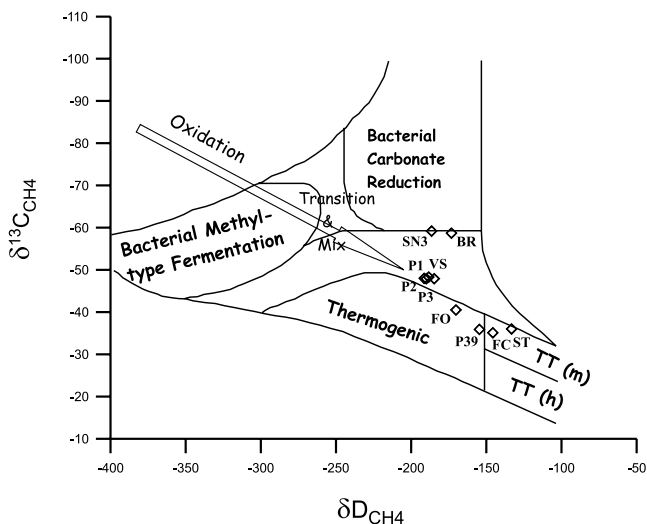


Figure 3. $\delta^{13}\text{C}_{\text{CH}_4}$ - $\delta\text{D}_{\text{CH}_4}$ classification diagram. Methane in four sites (ST, FO, P39 and FC) is generated by thermal decomposition of organic matter. All the other samples show intermediate values between thermogenic and microbial isotope signatures. TT(m) = dry gas from marine source rocks; TT(h) = gases from humic organic matter [Schoell, 1980, 1983].

rather than to a pristine CH_4 -rich gas source. The brackish waters associated with hydrocarbons emission at Macalube site show an high DIC (Dissolved Inorganic Carbon) content in the range between 60 and 120 mmol l^{-1} . A CH_4 output of about 400 tons year^{-1} was estimated for this site [Etioppe *et al.*, 2002]. At the Macalube sites Helium concentration is also high, ranging from 150 to 200 ppmv with $^3\text{He}/^4\text{He}$ ratios close to $R/R_a = 0.7$. The origin of this gas in these samples can be interpreted as mixing between two end-members: a prevailing crustal component and a deep ^3He -rich end-member. At FC site the output of methane (86 % vol.) was previously estimated in about 6.0 tons year^{-1} [Etioppe *et al.*, 2002].

3. Origin of Hydrocarbon Gases

[7] Hydrocarbon gases originate from microbial decay or thermogenic alteration of organic matter. Microbial gases are characterized by $\delta^{13}\text{C}_{\text{CH}_4}$ values lower than -50‰ , and a δD lower than -150‰ , while thermogenic gases usually have $\delta^{13}\text{C}_{\text{CH}_4}$ composition between -50 and -20‰ . Microbial gases are essentially enriched in methane (C_1) with respect to the higher molecular weight hydrocarbon gases (C_{2+}) resulting in values for “Bernard parameter” expressed as $\text{C}_1/(\text{C}_2+\text{C}_3)$ in the range 10^3 – 10^5 . On the contrary, $\text{C}_1/(\text{C}_2+\text{C}_3)$ ratios less than 50 are also typical values for thermogenic hydrocarbon gases.

[8] All the $\delta^{13}\text{C}$ values of methane from this study are lighter than -35‰ vs. VPDB, while the $\delta\text{D}_{\text{CH}_4}$ values range from -145 to -191‰ vs. SMOW. Almost all the sampled gases show a C_{2+} hydrocarbon contents less than 2.5%. Only, BR and SN3, differ from the other samples, displaying C_{2+} hydrocarbon contents higher than 5%Vol.

[9] The origin of the gases was investigated by using of two classification schemes considering isotope data and the combination of both molecular and isotope values. The

$\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta\text{D}_{\text{CH}_4}$ values show that methane in four sites (ST, FO, P39 and FC) is generated by thermal decomposition of organic matter (Figure 3) [Schoell, 1980]. Among these, FC and ST samples fall within the TT(m) field thus resulting as thermogenic dry gases. All the other samples show intermediate values between thermogenic and microbial isotope signatures thus suggesting that hydrocarbon gases are the result of the admixture of microbial methane and thermally generated gases. Similar evidences can be also carried out by the Bernard classification diagram (Figure 4) [Bernard *et al.*, 1978], which correlates the isotope composition of methane ($\delta^{13}\text{C}_{\text{CH}_4}$) and the “Bernard parameter” ($\text{C}_1/\text{C}_2+\text{C}_3$). However the hypothesis of a mixing between thermogenic and microbial gases seems to be compatible only for samples from Etnean sites. Such a mixing process has been modelled considering two different compositions and isotope values for each end-member (theoretical mixing curve 1: thermogenic ($\text{C}_1/\text{C}_2+\text{C}_3$) = 10 and $\delta^{13}\text{C}_{\text{CH}_4} = -40\text{‰}$, microbial ($\text{C}_1/\text{C}_2+\text{C}_3$) = 10^4 and $\delta^{13}\text{C}_{\text{CH}_4} = -100\text{‰}$; theoretical mixing curve 2: thermogenic ($\text{C}_1/\text{C}_2+\text{C}_3$) = 40 and $\delta^{13}\text{C}_{\text{CH}_4} = -35\text{‰}$, microbial ($\text{C}_1/\text{C}_2+\text{C}_3$) = 5000 and $\delta^{13}\text{C}_{\text{CH}_4} = -55\text{‰}$, Figure 4). From mixing curve 1, the contribution of thermogenic methane has been estimated about 70% for SN and BR and about 80% at Na site. VS site displays a fraction of about 35% of thermogenic gas computed from mixing curve 2.

[10] As seen, the samples from “Macalube di Aragona” mud volcanoes, fall far from any possible theoretical curve representing the mixing process above discussed. For these samples, the occurrence of post-genetic processes

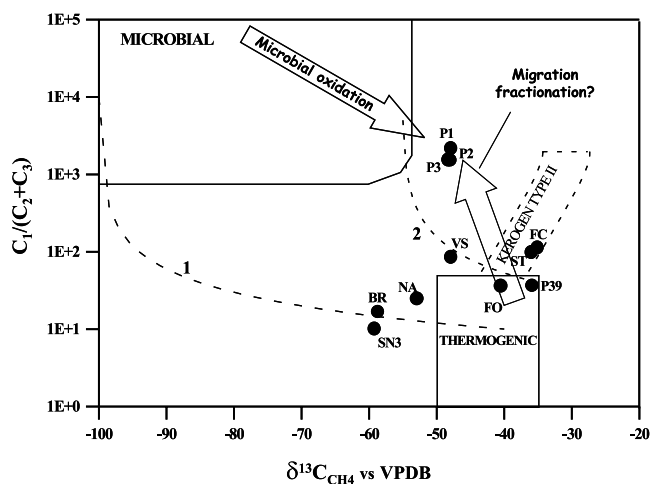


Figure 4. Modified “BERNARD” diagram [after Bernard *et al.*, 1978] considering the molecular composition of hydrocarbon gases ($\text{C}_1/\text{C}_2+\text{C}_3$) and data for the carbon isotope ratio of methane. In the same figure, the curves 1 and 2 represent a theoretical mixing process between thermogenic and microbial end members (theoretical mixing curve 1: thermogenic ($\text{C}_1/\text{C}_2+\text{C}_3$) = 10 and $\delta^{13}\text{C}_{\text{CH}_4} = -40\text{‰}$, microbial ($\text{C}_1/\text{C}_2+\text{C}_3$) = 10^4 and $\delta^{13}\text{C}_{\text{CH}_4} = -100\text{‰}$; theoretical mixing curve 2: thermogenic ($\text{C}_1/\text{C}_2+\text{C}_3$) = 40 and $\delta^{13}\text{C}_{\text{CH}_4} = -35\text{‰}$, microbial ($\text{C}_1/\text{C}_2+\text{C}_3$) = 5000 and $\delta^{13}\text{C}_{\text{CH}_4} = -55\text{‰}$). Trend of migration fractionation [Prinzhofer and Pernaton, 1997; Zhang and Krooss, 2001] is indicated.

modifying the pristine molecular composition and/or isotope values of the gases has to be invoked. There are two ways of interpreting their origin: the first hypothesis includes that the gas is produced by microbial activity and altered post-genetically by microbial oxidation processes [Whiticar and Faber, 1986; Whiticar, 1999]. This methanotrophic reaction, appears to act preferentially on methane rather than higher molecular weight hydrocarbons (ethane and propane). From an isotope point of view, this process should lead to an enrichment in heavy isotopes (both carbon and hydrogen) in the residual methane.

[11] Although less probable, according to the second hypothesis, the gases thermally generated could have modified both molecular ratios and isotope values due to migration or diffusion processes [Prinzhofer and Pernaton, 1997; Zhang and Krooss, 2001]. As a consequence of a greater mobility of methane with respect to higher molecular hydrocarbons, a vertical gas migration or diffusion process should produce a progressive CH₄-enrichment compared with higher hydrocarbons. This could be responsible for a carbon isotope fractionation causing an enrichment in lighter hydrocarbons.

4. Conclusions

[12] In this study we presented a geochemical characterization of natural gas from eleven gas manifestations located in Eastern and Central-Southern Sicily (Italy). The samples can be classified into two main types: methane-dominated having CH₄ content >50% vol. and carbon dioxide-dominated with CO₂ content >50% vol. of The genetic origin of the gases was assessed using molecular data and stable isotope ratios ($\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta\text{D}_{\text{CH}_4}$). The $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta\text{D}_{\text{CH}_4}$ values show that methane at ST, FO, P39 and FC sites is generated by thermal decomposition of organic matter. The samples, FC and ST are probably derived from a mature marine source rock, with maturity beyond the oil window. Such a maturity results in a dry gas with C₁/C₂+C₃ ratio greater than 100. Hydrocarbon gases of mixed origin have been identified at SN3, NA, VS and BR site, resulting from the mixture of microbial methane and thermally generated gases. Molecular composition and isotope values of the gases samples from "Macalube di Aragona" mud volcanoes, do not provide univocal origin, probably because the gas have been affected by secondary post-genetic processes which have modified the original compositional and isotope values. There are two ways of interpreting their origin: the first hypothesis includes that the gas is produced by microbial activity and altered post-genetically by microbial oxidation processes [Whiticar and Faber, 1986; Whiticar, 1999]. The second hypothesis suggests that migration or diffusion process molecular could be responsible for an enrichment in methane compared to higher hydrocarbons

and an enrichment in light carbon isotopes in the methane [Prinzhofer and Pernaton, 1997; Zhang and Krooss, 2001].

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