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Hydrocarbon gases in deposits from mud volcanoes in the Sorokin Trough, north-eastern Black Sea

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Abstract Hydrocarbon gases were determined in sediments from three mud volcanoes in the Sorokin Trough. In comparison to a reference station outside the mud volcano area, the deposits are characterized by an enrichment of high-molecular hydrocarbons (C_2–C_4), an absence of unsaturated homologues, a predominance of iso-butane in comparison with n-butane, and the presence of gas hydrate. The molecular composition of the hydrocarbon gases suggests their deep sources and thermogenic origin. In the pelagic sediments at the reference station, the methane concentration is relatively low (up to 49 ml/l); maximum concentrations are reached in deposits of the Dvurechenskii mud volcano (up to 400 ml/l). It was the first time that gas hydrate was sampled at the Dvurechenskii mud volcano. The gas extracted by dissociation of hydrate samples was dominated by methane (99.5%) with low amounts of ethane and propane (less than 0.5%). The isotopic composition of the methane varies between −62 and −66‰ PDB in $\delta^{13}C$, and between −185 and −209‰ SMOW in δD, indicating a mainly biogenic origin with an admixture of thermogenic gas.

Introduction

The presence of active fluid vents and mud volcanoes in the Black Sea has been suggested by several authors since the late 1980s (Ivanov et al. 1989; Kremlev and Ginsburg 1989; Konyukhov et al. 1990). Yet, it could not be documented before the TTR-6 expedition in 1996 (Woodside et al. 1997; Ivanov et al. 1998; Bouriak and Akhmetjanov 1998). Multidisciplinary investigations of the Sorokin Trough were continued in 2001 during the TTR-11 cruise (Kenyon et al. 2002). As a result of the two cruises, about 10 mud volcanoes were discovered, gas hydrates and authigenic carbonates with bacterial mats were sampled, and a high content of hydrocarbon gases in the sediments was documented.

The data presented in this paper were collected in 2002 during the MARGASCH cruise with RV *Meteor* (M52/1). This cruise was dedicated to multidisciplinary studies of cold seep structures in the deep Black Sea (Bohrmann and Schenck 2002; Bohrmann et al. 2003-this issue; Krastel et al. 2003-this issue). One of the main targets was detailed investigation of some active mud volcanoes in the Sorokin Trough and associated deposits of shallow gas hydrate.

In general, four mud volcanoes and one reference station were investigated for molecular and isotopic composition of hydrocarbon gases. The reference core (M52/1 #39 TGC-6) was taken in the southern part of the study area, about 5.5 km from the Dvurechenskii mud volcano (Fig. 1). It is represented by homogeneous hemipelagic mud, soupy on the top, with some shell debris layers.

Geological setting

The Sorokin Trough extends along the south-eastern margin of the Crimean Peninsula at water depths of 800–2,000 m (Fig. 1). It is about 150 km long and 45–50 km wide. The trough is filled with Oligocene–Quaternary sediments subdivided into three main units. The lower unit consists of Oligocene–Early Miocene clay deposits (Maikopian Formation) with a thickness of over 5 km. The thickness of the overlying Middle

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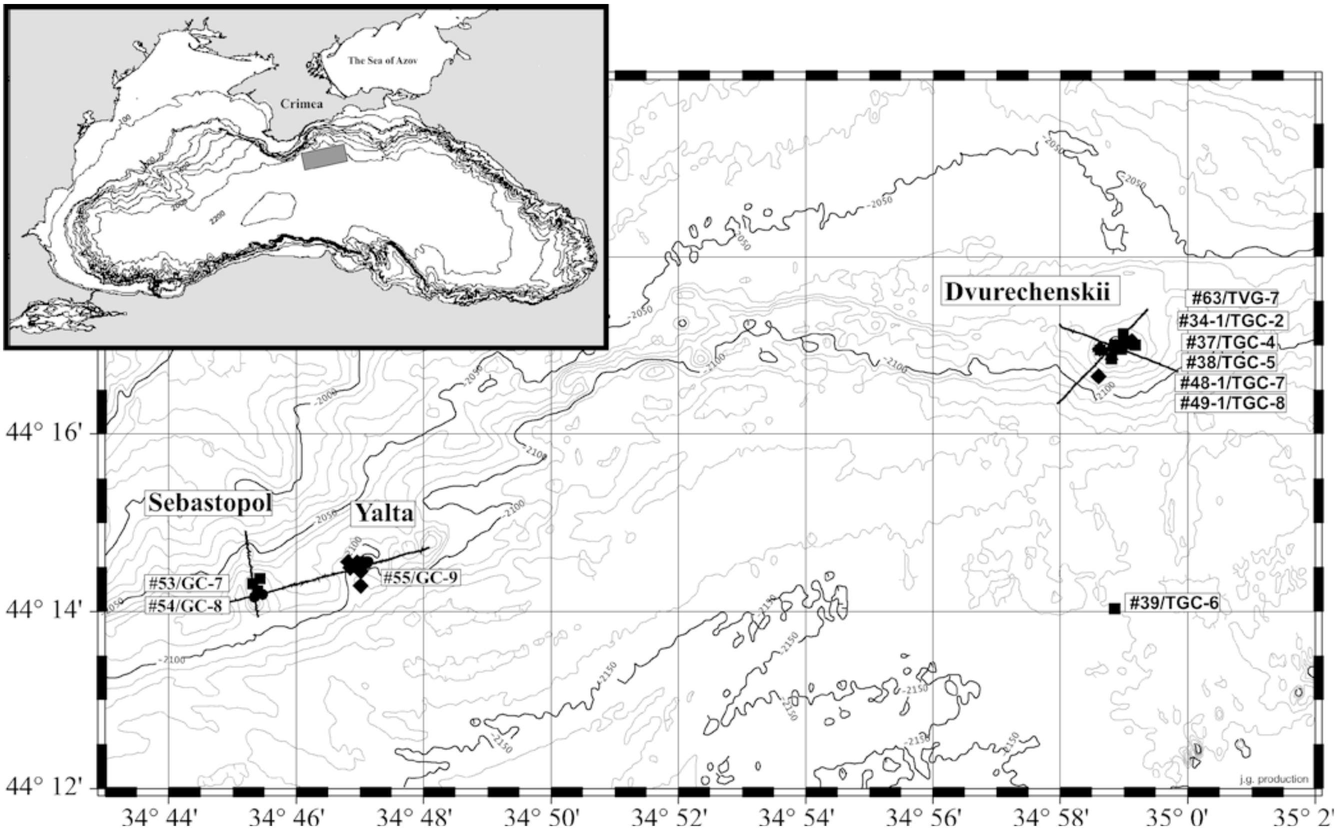


Fig. 1 Location map of seafloor sampling locations of the Sorokin Trough study area. *TGC* Thermistor gravity corer, *GC* gravity corer, *TVG* TV grab sampler

Miocene–Pliocene terrigenous sediments is about 1 km, and the Quaternary sediments vary in thickness from several tens of meters to about 2 km (Tugolesov et al. 1985).

Plastic clay from the Maikopian Formation protrudes through the upper sedimentary cover and builds several diapiric ridges oriented subparallel to the coastline (Andreev 1976; Morgunov et al. 1976). The tops and slopes of diapiric structures are complicated by mud volcanoes.

Materials and methods

Most of the sediment samples of the MARGASCH cruise were taken with the gravity corer (GC), which provides long cores of up to 600 cm. The gravity corer was partly equipped with a temperature sensor (TGC). The extraction of the core from the plastic liner on the ship's working deck was followed by a subsampling procedure for geochemical analyses, taking into consideration the lithological peculiarities of each core in order to obtain as much geochemical information as possible.

For the gas analysis, a headspace technique was applied, adapted for shipboard conditions (Bolshakov and Egorov 1987; Bohrmann and Schenck 2002). The results are calculated according to the volume of wet sediment.

Gas from gas hydrate aggregates was obtained immediately on deck by spontaneous degassing in salt-saturated water. A gas chromatograph with a flame ionisation detector was used for quantification of methane and its homologues as well as unsaturated compounds. The total relative error of the definitions for this method (by parallel definitions) was 6.7%. In addition, isotopic analyses of hydrate gas and gas from the sediments were carried out. The total organic carbon (TOC) content was determined from the same intervals as the gas samples.

Several carbonate crusts and concretions were collected from the sediments and analysed for carbon isotopic composition. All isotopic measurements were performed in the VSEGINGEO in Moscow. Isotopic values are given in ‰ versus PDB for carbon (C) and SMOW for deuterium (D).

Results and discussion

Table 1 and Figs. 2, 3, 4 and 5 summarize the TOC content and molecular composition of hydrocarbon gases collected in the Sorokin Trough. Figure 2 shows that the methane concentration of the reference core increases from 0.1 ml/l at the top to 49.2 ml/l at the bottom of the core. The presence of unsaturated hydrocarbons (ethylene and propylene) and the absence of heavy homologues indicate a mainly biogenic origin of this gas. The TOC content varies from 0.27 to 2.46%.

Although mud breccia was not taken from the Sebastopol and Yalta mud volcanoes (Figs. 3, 4), the methane concentrations in the hemipelagic sediments are still much higher than the background value (up to 200 ml/l). In addition to methane, the contents of saturated hydrocarbons (including C_4) are high, while unsaturated hydrocarbons cannot be found. The TOC content is rather constant around 1.4% in sediments from the Yalta mud volcano deposits, and increases

Table 1 TOC and hydrocarbon gas contents in sediment samples (*n.d.* not determined)

Core no.	Depth	TOC	Hydrocarbon gas/wet sediment (ml/l)								
	(cm b.s.f.)	(%)	C_1	C_2	C'_2	C_3	C'_3	i-C_4	n-C_4	C'_4	C_1/C_{2+}
M52/1 #34 TGC-2	0	1.06	38.6	0.0381	n.d.	0.0036	n.d.	0.0006	0.0001	n.d.	908
	50	n.d.	152.8	0.1537	n.d.	0.0026	n.d.	0.0006	n.d.	n.d.	974
	100	1.01	326.4	0.2820	n.d.	0.0022	n.d.	0.0001	n.d.	n.d.	974
	150	1.01	44.5	0.0267	n.d.	0.0037	n.d.	0.0005	n.d.	n.d.	1,439
	200	n.d.	25.2	0.0229	n.d.	0.0030	n.d.	0.0006	n.d.	n.d.	951
	250	1.01	78.6	0.0737	n.d.	0.0021	n.d.	n.d.	n.d.	n.d.	1,038
	300	n.d.	38.6	0.0305	n.d.	0.0015	n.d.	0.0004	n.d.	n.d.	1,190
	320	0.99	32.6	0.0508	n.d.	0.0011	n.d.	n.d.	n.d.	n.d.	629
M52/1 #39 TGC-6	0	2.29	0.3	0.0005	0.0002	0.0004	n.d.	n.d.	n.d.	n.d.	269
	20	0.55	0.3	0.0003	0.0000	0.0002	n.d.	n.d.	n.d.	n.d.	450
	40	2.06	0.2	0.0005	0.0002	0.0002	0.0001	n.d.	n.d.	n.d.	207
	70	2.46	0.2	0.0010	0.0002	0.0003	n.d.	n.d.	n.d.	n.d.	167
	90	1.88	0.06	0.0006	0.0001	0.0001	n.d.	n.d.	n.d.	n.d.	71
	120	0.73	0.07	0.0008	0.0001	0.0001	n.d.	n.d.	n.d.	n.d.	72
	135	0.53	0.08	0.0010	0.0000	0.0001	n.d.	n.d.	n.d.	n.d.	74
	150	n.d.	4.5	0.0012	0.0001	0.0003	n.d.	n.d.	n.d.	n.d.	2,781
	200	0.27	7.4	0.0017	0.0001	0.0002	n.d.	n.d.	n.d.	n.d.	3,738
	250	0.69	26.7	0.0018	0.0002	0.0001	n.d.	n.d.	n.d.	n.d.	12,284
	300	0.64	30.4	0.0026	n.d.	0.0001	n.d.	n.d.	n.d.	n.d.	11,040
	320	n.d.	21.5	0.0018	n.d.	0.0001	n.d.	n.d.	n.d.	n.d.	10,914
M52/1 #49 TGC-8	0	1.17	35.6	0.0470	n.d.	0.0072	n.d.	0.0015	n.d.	n.d.	639
	50	1.26	117.2	0.1397	n.d.	0.0069	n.d.	0.0008	0.0004	n.d.	793
	100	n.d.	118.7	0.1588	n.d.	0.0061	n.d.	0.0010	0.0006	n.d.	713
	200	1.16	99.4	0.1219	n.d.	0.0080	n.d.	0.0012	0.0006	n.d.	754
	300	1.29	118.7	0.2515	n.d.	0.0075	n.d.	0.0021	0.0003	n.d.	454
	400	n.d.	103.9	0.1778	n.d.	0.0035	n.d.	0.0002	n.d.	n.d.	572
	490	1.11	89.0	0.1041	n.d.	0.0036	n.d.	0.0004	n.d.	n.d.	823
M52/1 #53GC-7	0	n.d.	0.2	0.0002	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	966
	100	n.d.	13.9	0.0078	n.d.	0.0003	n.d.	n.d.	n.d.	n.d.	1,722
	200	n.d.	47.5	0.0302	n.d.	0.0008	n.d.	n.d.	n.d.	n.d.	1,532
	310	n.d.	40.1	0.0260	n.d.	0.0008	n.d.	n.d.	n.d.	n.d.	1,491
M52/1 #54 GC-8	0	1.29	32.6	0.0178	n.d.	0.0061	n.d.	0.0017	n.d.	n.d.	1,278
	50	1.2	51.9	0.0229	n.d.	0.0100	n.d.	0.0025	0.0008	n.d.	1,435
	100	n.d.	41.5	0.0165	n.d.	0.0072	n.d.	0.0019	0.0006	n.d.	1,589
	150	3.32	40.1	0.0178	n.d.	0.0122	n.d.	0.0042	0.0008	n.d.	1,145
	200	n.d.	34.9	0.0178	n.d.	0.0136	n.d.	0.0050	0.0006	n.d.	945
	250	9.5	44.5	0.0216	n.d.	0.0183	n.d.	0.0075	0.0011	0.0012	895
	300	6.13	35.6	0.0184	n.d.	0.0180	n.d.	0.0085	0.0011	0.0010	756
	360	9.65	46.0	0.0229	n.d.	0.0216	n.d.	0.0100	0.0011	0.0018	802
	402	1.64	19.3	0.0095	n.d.	0.0083	n.d.	0.0037	n.d.	n.d.	894
M52/1 #55 GC-9	0	1.33	1.0	0.0025	0.0002	0.0003	n.d.	n.d.	n.d.	n.d.	316
	20	n.d.	34.1	0.0292	n.d.	0.0028	n.d.	n.d.	n.d.	n.d.	1,067
	50	1.37	100.2	0.0826	n.d.	0.0076	n.d.	0.0004	0.0006	n.d.	1,099
	100	1.48	135.0	0.1041	n.d.	0.0097	n.d.	0.0010	0.0008	n.d.	1,167
	130	n.d.	117.2	0.0902	n.d.	0.0091	n.d.	0.0008	0.0014	n.d.	1,154
	160	n.d.	62.3	0.0610	n.d.	0.0080	n.d.	0.0008	0.0011	n.d.	878

from 1.2 to 9.65% (in the sapropel layer) at the Sebastopol mud volcano.

Analyses of the gas composition in these cores show a clear predominance of iso-butane in comparison with n-butane (Fig. 4). This ratio clearly indicates a strong process of biodegradation (Tissot and Welte 1978). Such a predominance is also observed in thermogenic gases associated with places of active fluid venting (Kvenvolden et al. 1979; Kvenvolden and Field 1981; Kvenvolden and Pettinga 1989; Sassen et al. 1994; Kruyglyakov et al. 1996; Egorov and Ivanov 1998). In general, such mud volcano gases are characterized by a dry composition, with a C_1/C_{2+} ratio in the range of 316 to 1,722 (Table 1).

At both volcanoes, the $\delta^{13}C$ value of methane is about −58‰. According to Schoell (1980), this value corresponds to thermogenic gas, yet it is close to the boundary (−60‰). Such an intermediate isotope ratio suggests that it is a mixture of thermogenic and biogenic methane (Chung et al. 1988). Based on the lithological composition of the cores (hemipelagic sediments without any evidence of mud breccia), we can infer that samples from the Sebastopol and Yalta mud volcanoes were not taken from their active parts. However, the molecular composition of hydrocarbon gases and their isotopic signature suggest that active vents are located nearby.

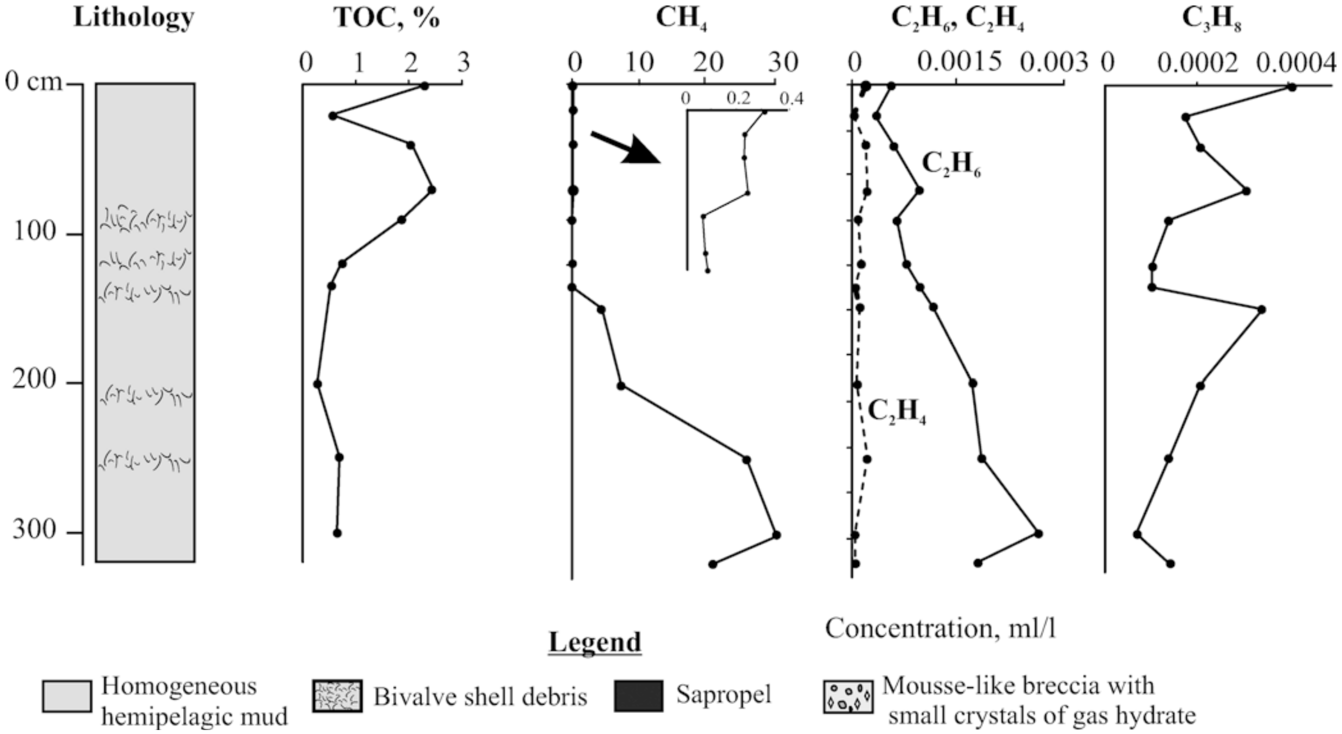


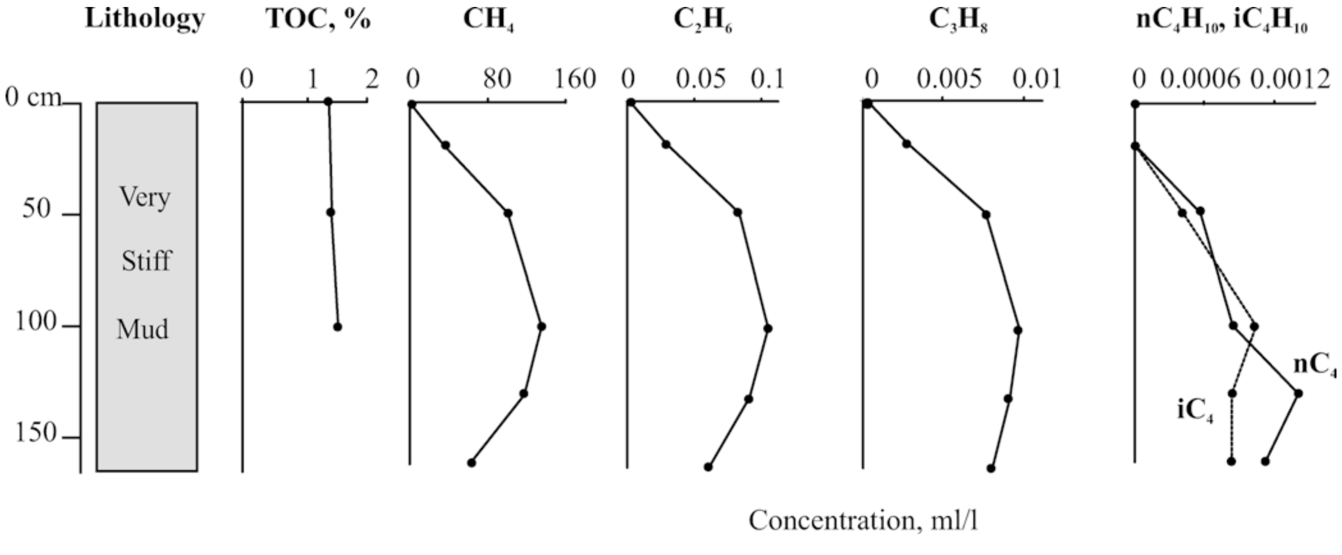
Fig. 2 Lithology, TOC content and hydrocarbon composition of core M52/1 #39 TGC-6 (reference core)

Gas composition and concentrations from the mud breccia generally differ from those in the reference core. Figure 5 demonstrates the vertical distribution of TOC and hydrocarbons along with the lithology of the cores from the crater of the Dvurechenskii mud volcano (#34 TGC-2 and #49 TGC-8). They consist of mousse-like breccia with small crystals of gas hydrate throughout the whole core depth.

The composition and vertical distribution of hydrocarbon gases in these two cores unambiguously indicate the presence of migrated gases. A very high concentration of saturated hydrocarbons in the mud breccia and the absence of any unsaturated hydrocarbons prove a thermogenic origin of the gas. A predominance of iso-butane in comparison to n-butane suggests a high rate of migration.

Gas hydrate has been observed in all the cores at the Dvurechenskii mud volcano (Bohrmann and Schenck 2002). In most cases, it appears in the form of small isometric inclusions with sizes of up to 1–5 mm, and in a few cases up to 1 cm. It is associated with homogeneous, dark grey, gas-saturated mud breccia. Hydrate gas

Fig. 3 Lithology, TOC content and hydrocarbon composition of core M52/1 #55 GC-9 (Yalta mud volcano)



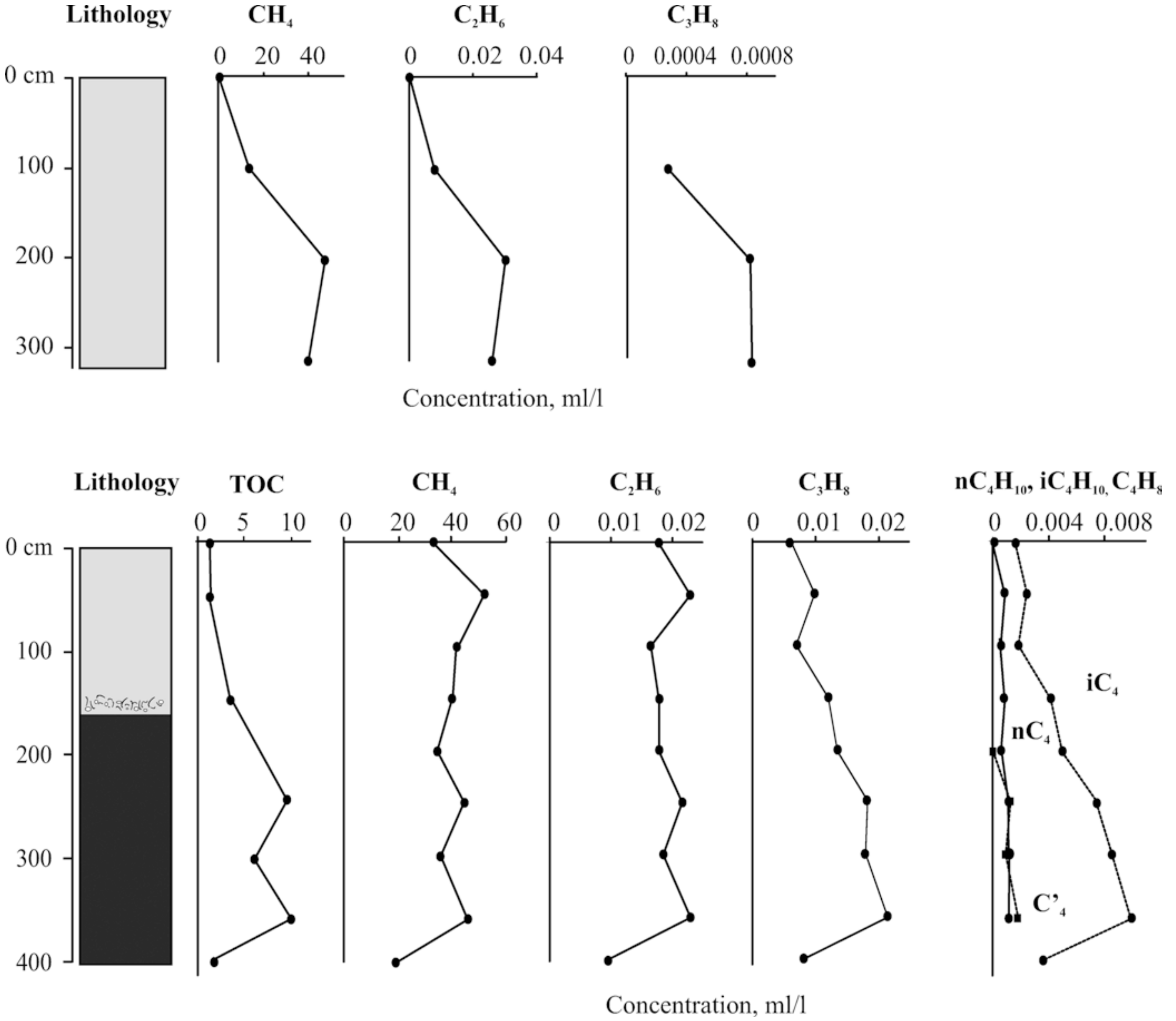


Fig. 4 Lithology, TOC content and hydrocarbon composition of cores M52/1 #53 GC-7 (*top*) and M52/1 #54 GC-8 (*bottom*; Sebastopol mud volcano)

mainly consists of methane (99.5%) with a low C_2–C_3 content (less than 0.54%; Table 2).

The carbon isotopic analysis of the methane component from the gas hydrate shows a strongly negative ratio (from −62 to −66‰), which is mostly characteristic for bacterial, with probably an admixture of thermogenic methane (Table 2). The value of $\delta^{13}C$ in ethane is −26.3‰, that of CO_2 is −25.5‰. The combined use of both carbon and hydrogen isotope parameters is of high diagnostic value in identifying the origin of natural gases (Schoell 1980; Whiticar 1999). The δD value varies from −185 to −209‰. Figure 6 shows that the methane mainly originates from bacterial CO_2 reduction (Whiticar 1999), but various secondary effects can obscure the signature of source(s) under certain conditions. The gas signature could be the result of mixing of different sources of CH_4: vertically migrated (thermogenic gas) and an admixture of bacterially generated methane.

We suggest that part of the methane present in the gas mixture was generated as a result of biodegradation of hydrocarbons accumulated below the mud volcano. Such a scenario has been described in the literature (Rise and Threlkeld 1983; Brekke et al. 1997) as the generation of "secondary" biogenic methane, which has the same chemical and isotopic characteristics as shallow "primary" biogenic methane.

Gas migration from the deep sources, its deposition, and re-deposition along mud volcano channels and deep faults was inferred from an analysis of acoustic anomalies in a sedimentary section of the Black Sea (Gainanov et al. 1998; Ivanov et al. 1998), which can be considered as giving indirect evidence of such a process.

Several carbonate concretions and crusts were recovered from all studied mud volcanoes. Massive

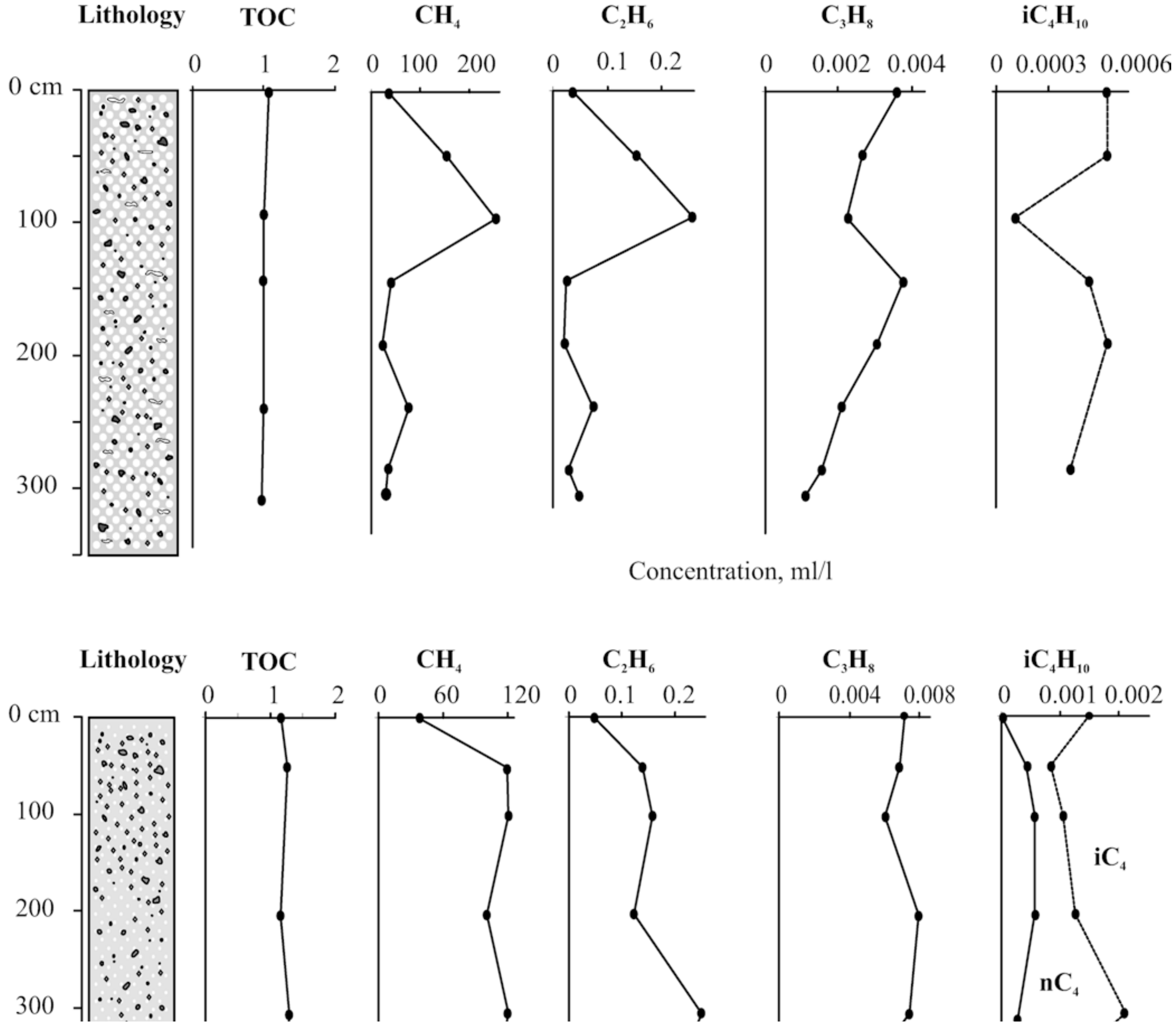


Fig. 5 Lithology, TOC content and hydrocarbon composition of cores M52/1 #34 TGC-2 (*top*) and M52/1 #49 TGC-8 (*bottom*; Dvurechenskii mud volcano)

crusts with bacterial mats were obtained from the Yalta mud volcano. For the first time, carbonate concretion was found in the mud breccia of the Dvurechenskii mud volcano. This carbonate shows a very negative δ^{13}C value (−39.9‰), which suggests authigenic carbonate precipitation due to bacterial methane oxidation.

Conclusions

High concentrations of hydrocarbon gases uncorrelated with TOC content indicate their allochtonous nature. The molecular composition of the hydrocarbon gases from all venting sites suggests that they come from deep sources.

Isotopically very heavy δ^{13}C of ethane (−26.3‰), high concentrations of saturated hydrocarbons, and a clear predominance of iso-butane over n-butane at the Dvurechenskii mud volcano strongly suggest that the venting fluids are generated at a deep source and have a high migration rate. On the other hand, we see isotopically light methane in gas hydrate from the same location; the average δ^{13}C value of −64‰ is a clear sign of microbial processes. We believe that a significant part of the methane has been produced by the process of biodegradation of hydrocarbons in the deep sediments.

Apparently, the isotopic composition and, thus, the source of methane was very stable over time. This can be concluded from the carbon isotopic composition of the methane-derived carbonates from the Dvurechenskii mud volcano (−39.9‰). In the Black Sea vents, they are usually heavier than the corresponding methane here—the fractionation is about 24‰.

Table 2 Molecular and isotopic composition of hydrocarbons and CO_2 of gas hydrate samples from the Dvurechenskii mud volcano (*n.d.* not determined)

Core no.	Depth	Molecular compositions of hydrated gases (assuming hydrocarbons = 100%)			Hydrogen and carbon isotopic composition of hydrated gases (‰)			
	(cm)	C_1	C_2	C_3	δC_{CH4}	δC_{C2H6}	δD	δC_{CO2}
M52/1 #34 TGC-2		99.6	0.41	0.0012	−66	n.d.	−202	n.d.
M52/1 #37 TGC-4		99.7	0.26	0.0029	−66	−26.34	n.d.	−25.49
M52/1#38 TGC-5		99.6	0.38	0.0006	n.d.	n.d.	n.d.	n.d.
M52/1 #48 TGC-7		99.5	0.54	0.0000	n.d.	n.d.	n.d.	n.d.
M52/1 #49 TGC-8	110	99.5	0.47	0.0012	−62	n.d.	−185	n.d.
M52/1 #49 TGC-8	450	99.6	0.39	0.0006	−63	n.d.	−209	n.d.
M52/1 #63 TVG-7		99.6	0.37	0.0009	n.d.	n.d.	n.d.	n.d.

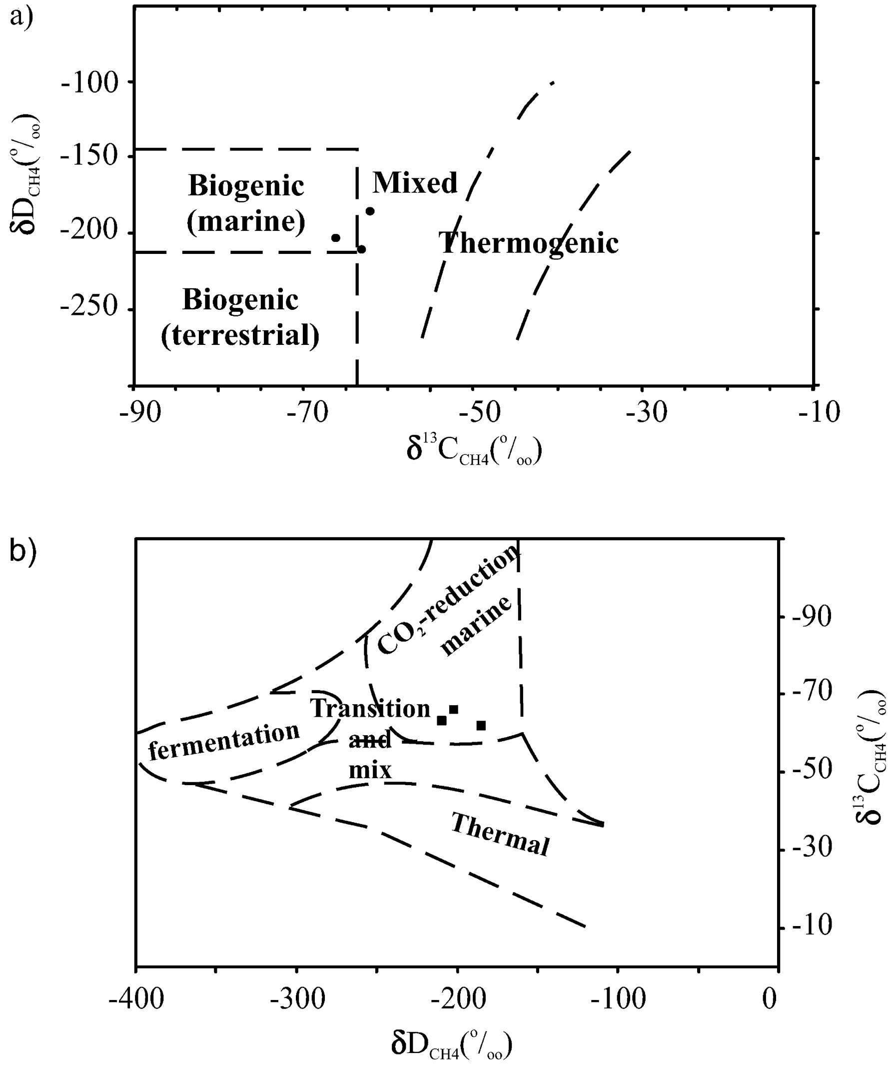


Fig. 6a, b Hydrogen and carbon isotopic composition of methane from gas hydrates of the Dvurechenskii mud volcano. **a** Schoell (1980) and **b** Whiticar (1999)

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