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Mantle origin of methane in the Black Sea

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Складено нову карту виходів газу і грязьових вулканів у Чорному морі. Основу карти складають опубліковані координати близько 5000 газових виходів і 80 грязьових вулканів. Проаналізовано стабільний ізотопний склад метану для аутигенних карбонатів і осадів. Ізотоп δ^{13}C карбонатів і осадів утворює дві різні щільні групи залежно від умов геологічного середовища. Для оцінювання раніших класифікацій метану застосовано діаграми змін значень δ^{13}C залежно від значень δD і δ^{13}C та від відношень C1/(C2+C3). Виявилося, що походження метану більшості зразків є неоднозначним. За даними сейсмічного методу відбитих хвиль, живильні канали газових викидів і грязьових вулканів проникають у передмезозойський фундамент під підняттям Полшкова, хребтами Андрусова і Тетяєва і прогином Сорокіна на глибину до 12 км. У центрі Чорного моря живильний канал грязьового вулкана досягає поверхні мантії, де глибина становить 19 км. Найбільшу концентрацію газових виходів зафіксовано на потрійному зчленуванні мантійних розломів у північно-західній частині Чорного моря. Оцінено здатність різних механізмів зумовити безпрецедентну концентрацію метану у водній товщі Чорного моря. В осадових відкладах у районах виходів газів і грязьових вулканів поширений термогенний метан — результат постгенетичного перетворення біогенного метану палеоген-неогенових відкладів. Біологічний метан, утворений внаслідок переробки органічної речовини, відіграє незначну роль у накопиченні найбільшого у світі резервуара анаеробного метану в Чорному морі. Неорганічний метан формує величезне вмістище розчиненого газу у водному стовпі Чорного моря глибше 150—200 м. Уявну убогість абіогенного метану пояснюємо його рециркуляцією мікробами, неправильною класифікацією походження і вироблення хімічним синтезом з ізотопом δ^{13}C біогенного метану.

Ключові слова: Чорне море, просочування газу, грязьові вулкани, живильні канали, абіогенний метан.

Introduction. The Black Sea is the most isolated and the largest anoxic water reservoir in the World Ocean. Below 150—200 m water depth a total amount of dissolved methane is estimated to be 96 Tg [Reeburg et al., 1991]. Isotope and geochemical results indicate that basin mean flux of methane from the seafloor to the water column is 4.7 Tg yr^{-1} [Schmale et al., 2011]. However, this emission is balanced by the removal of 4.6 Tg yr^{-1} of methane due to its oxidation in the anaerobic water column and upward diffusion to the atmosphere [Reeburg et al., 1991]. Although these figures are only rough estimates, they give an idea of enormous methane reserves in the Black Sea and its low annual net input.

In the Black Sea the origin of near-bottom methane from seepage and mud volcanoes (MVs) areas is reported to be mostly related to high microbial activity [Hunt, Whelan, 1978; Faber et al., 1978; Amouroux et al., 2002; Michaelis et al., 2002; Rusanov et al., 2002; Blinova et al., 2003; Mazzini et al., 2004, 2008; Lein, Ivanov, 2005; Ivanov, Lein 2006; Bahr et al., 2007; Knab et al., 2009; Sahling et al., 2009; Pape et al., 2010; Egorov et al., 2011; Römer et al., 2012].

Meanwhile combining stable isotope carbon signature and molecular composition determinations of hydrocarbons made it possible to identify thermogenic origin for methane from rock clasts and mud breccia from the Kozakov MV in the Sorokin Trough of the NE Black Sea [Stadnitskaia et al., 2007]. There is the minor thermogenic admixture in methane from the nearby Odessa, NIOZ, Tbilisi and Unnamed MVs. Methane seems to be a product of the thermal oil-cracking process of an initial source occurred below the Maycopian Series shale [Bohrmann et al., 2003; Stadnitskaia et at., 2007].

Kruglyakova et al. [2009] performed the comprehensive geochemical analysis of hydrocarbons from different geological features in the Black Sea. The sediments from the MSU, Strakhov, Kornev, Malyshev and Uzhmorgeologiya MVs and outside of them contain distinct concentration of oil compounds that indisputably evidences for hydrocarbons of epigenetic origin. There are well-defined unsaturated elements of oil in petroleum seepage on the Arkhangelsky Ridge that resulted from oil biodegradation.

A thorough multimethod examination of migration processes in the deep subsurface of the Batumi seep area revealed enrichments in the thermogenic homologues in vent gas. This corroborated the assumption of secondary genesis of these compounds most likely associated with oil transformation from the Maycopian series rather than from decomposing shallow hydrates [Pape et al., 2010). Light carbons and high molecular weight impurities indicate the prevailing thermogenic origin for oil and gas from the Pechori and Iberia Mounds and Colkheti Seep within the Batumi seep area, eastern Black Sea [Reitz et al., 2011].

A definite spatial relationship was found between faults and gas seeps in the NW Black Sea that allowed us to first suggest the possibility of a deep abiogenic source of methane in this area [Kutas et al., 2004; Starostenko et al., 2010].

The arithmetic majority of publications on the biological methane may create impression that it dominates in the Black Sea. However, this notion is enough problematic for a number of reasons. The assertion of methane origin was based on studies of samples from the seafloor or the Holocene sediments shallower than 5 m depth. The feeder channels of gas seeps and MVs were seismically registered only up to 0.5 km bsf. The relationship was rarely analyzed between shallow faults and gas venting features. No attempts were undertaken to determine the thermal regime of the sedimentary cover although temperature is one of major regulating factors for methane origin. Assessments were not made how much organic matter is required to produce an enormous quantity of methane in the Black Sea water column. The hydrocarbon potential of the Maycopian series was not estimated as a possible source for producing abundant thermogenic methane in sediments.

Based on an analysis of recent information on gas releases and MVs distribution, the fault tectonics in the crystalline crust and mantle, seismically derived depth penetration of vertical gas pathways and the paleotemperature regime in the sedimentary cover, the aim of this study is to assess the potential for abiogenic methane in the Black Sea.

Materials and methods. This study is based on generalization, interpretation and use of appropriate information available from the Black Sea. To date, there are published coordinates for ca. 5000 gas seeps and 80 MVs in the Black Sea (Fig. 1). The exact number of gas releases from these features is not known mainly due to poor coverage of echo sounding and high resolution seismic surveys. The detailed characterization of the different aspects of gas seepage from venting structures is given elsewhere [Starostenko et al., 2010; Egorov et al., 2011; Shnuykov et al., 2013].

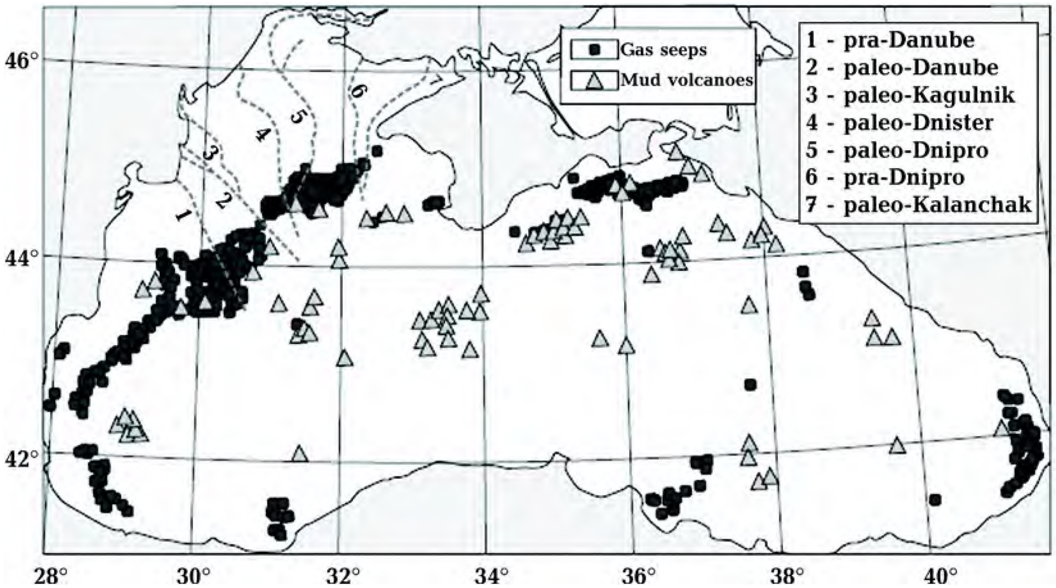


Fig. 1. Location of gas seeps and mud volcanoes in the Black Sea. Distribution is based on the compilations from [Pape et al., 2010; Starostenko et al., 2010; Egorov et al., 2011; Schmale et al., 2011; Römer et al,. 2012; Shnuykov et al., 2013].

Fig. 2 presents location of the sites from which the methane composition of samples is discussed in this study.

Recently, 16 regional multichannel 2D seismic lines of common depth point method across MVs have been published for the central Black Sea and Sorokin Trough [Shnuykov et al., 2015]. Depth penetration of reflections from 15 profiles is 9—12 km. One of them characterizes the seismic section of the entire crust down to the Moho discontinuity. As the examples, Figs. 3, 4 demonstrate the portions of the regional seismic reflection lines across the Mantle MV in the central Black Sea and the Kazakov MV in the Sorokin Trough, respectively. The feeder

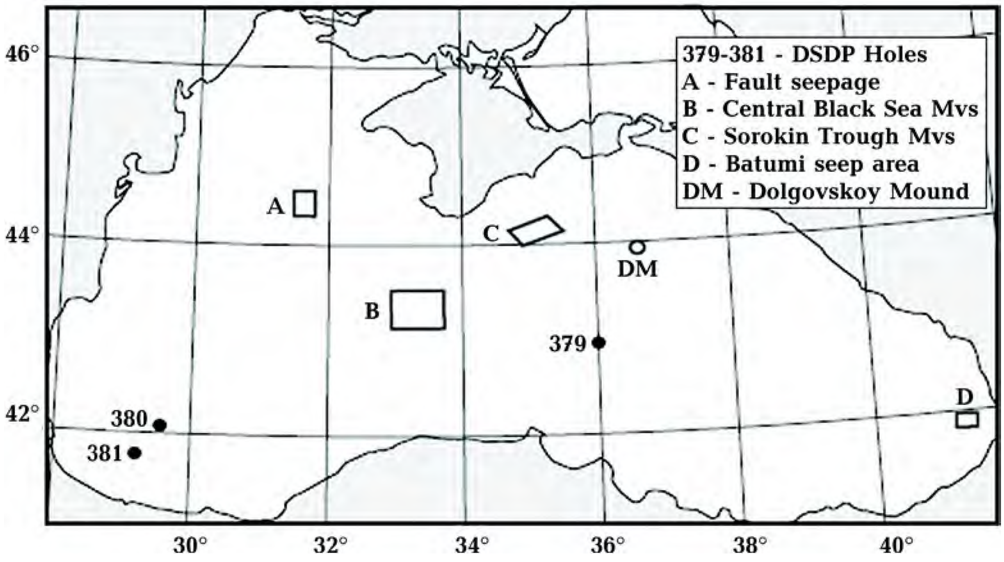


Fig. 2. Location of the samples presented in Table.

channel of the first MV penetrates the 17 km thick sedimentary cover and crystalline basement reaching the uppermost sub-Moho depths. Its coordinates are 43° 39.9′ N and 33° 09.29′ E. The second MV has feeder channel which terminates at a 10 km depth in the Pre-Mesozoic rocks. The coordinates of the Kazakov MV are 44° 17.54′ N and 35° 10.50′ E.

Fig. 5 presents the most detailed map of the faults in the crystalline crust and mantle developed from the potential fields [Starostenko et al., 2010b]. The pattern of these faults was validated by the international "Geology without Limits" project [Nikishin et al., 2014]. The locations of 135 out ca. 150 seismic-derived faults on the surface of the crystalline crust completely coincide with those from magnetic and gravity fields [Rusakov, Pashkevich, 2017].

The numerical reconstruction of the thermal regime and subsidence analysis were especially performed for the sedimentary cover in the B and C areas (Fig. 6, *a*, *b*). This reconstruction is based on the deep geological structure derived from seismic information, geological history and physical properties of different layers. Input data, necessary corrections and calculation procedure are described elsewhere [Kutas et al., 1998; Shnyukov et al., 2013; Starostenko et al., 2014]. Among them are heat flow map, seismic reflection and refraction profiles, heat flow density on the crystalline basement and mantle surface, radiogenic sedimentary layers, thermal conductivity, allowances for influence of a sedimentation rate, sediments compaction, crustal thinning, and climate variations in temperature on the seafloor etc. A principal advantage of this approach is solving the non-stationary equation of thermal conductivity of heat transfer [Carslaw, Jaeger, 1959] that significantly increases the quality of restoring temperature evolution. The subsidence models were obtained using a well-developed approach [Allen, Allen, 2013].

Discussion and conclusions. Much effort has been undertaken to study isotope composition of methane in sediments of the Black Sea, with purpose of elucidating its origin and postgenetic alternations. These results are presented in Table. They obviously display that the $\delta^{13}C$ values of authigenic carbonates form 2 distinct tight groups. The first cluster consists of samples from the Fault seeps, Odessa MV, Diapiric structure and Dolgovskoy Mound. The values of $\delta^{13}C$ range from −41.9 to −35.9 ‰. The second group includes the Vassoevich and Kozakov MVs whose values of isotopic determinations are significantly heavier (from −19.7 to −18.6 ‰).

The stable isotopic values of methane from the bottom sediments can also be divided into 2 assemblages. The most numerous group from the DSDP Holes, Fault seep area, TREDMAR, Odessa and NIOZ MVs, Batumi seep area (2) is characterized by $\delta^{13}C$ values more negative than −50 ‰. The second cluster includes Batumi seep area (1) and Kovalevsky MV area with intermediate $\delta^{13}C$ values from −43.0 ‰ to −31.4 ‰. The average $\delta^{13}C$ value for methane of the sediments from 4 gas seepage sites and 5 MVs is 50.9 ‰ and 55.6 ‰, respectively.

The recent overview of the methane origin in marine sediments was presented by Bohrmann and Torres [2016]. As for the modern Black Sea, the methane genesis is in line with the notions of this overview. Methane is supposed to originate mostly from the decomposition of organic matter while a minor contribution is made by biological degradation of oil and biogenic reduction of carbon dioxide through anaerobic microbial activity, thermogenic transformation and temperature cracking of crude oil from the Maikopian sediments [Reeburg et al., 1991; Ivanov, Lein, 2006; Stadnitskaia et al., 2007; Kruglyakova et al., 2009; Pape et al., 2010].

A new "clumped isotope" technique yields that the formation temperature of biological gas is less than 50 °C while that of thermogenic gas varies from 157 to 221 °C [Stolper et al., 2014]. The Archaeal consortium is the main anaerobic methanogen in the Black Sea [e. g. Egorov et al., 2011]. As the upper temperature for their life is experimentally shown to be 121 °C [Kashefi, Lov-

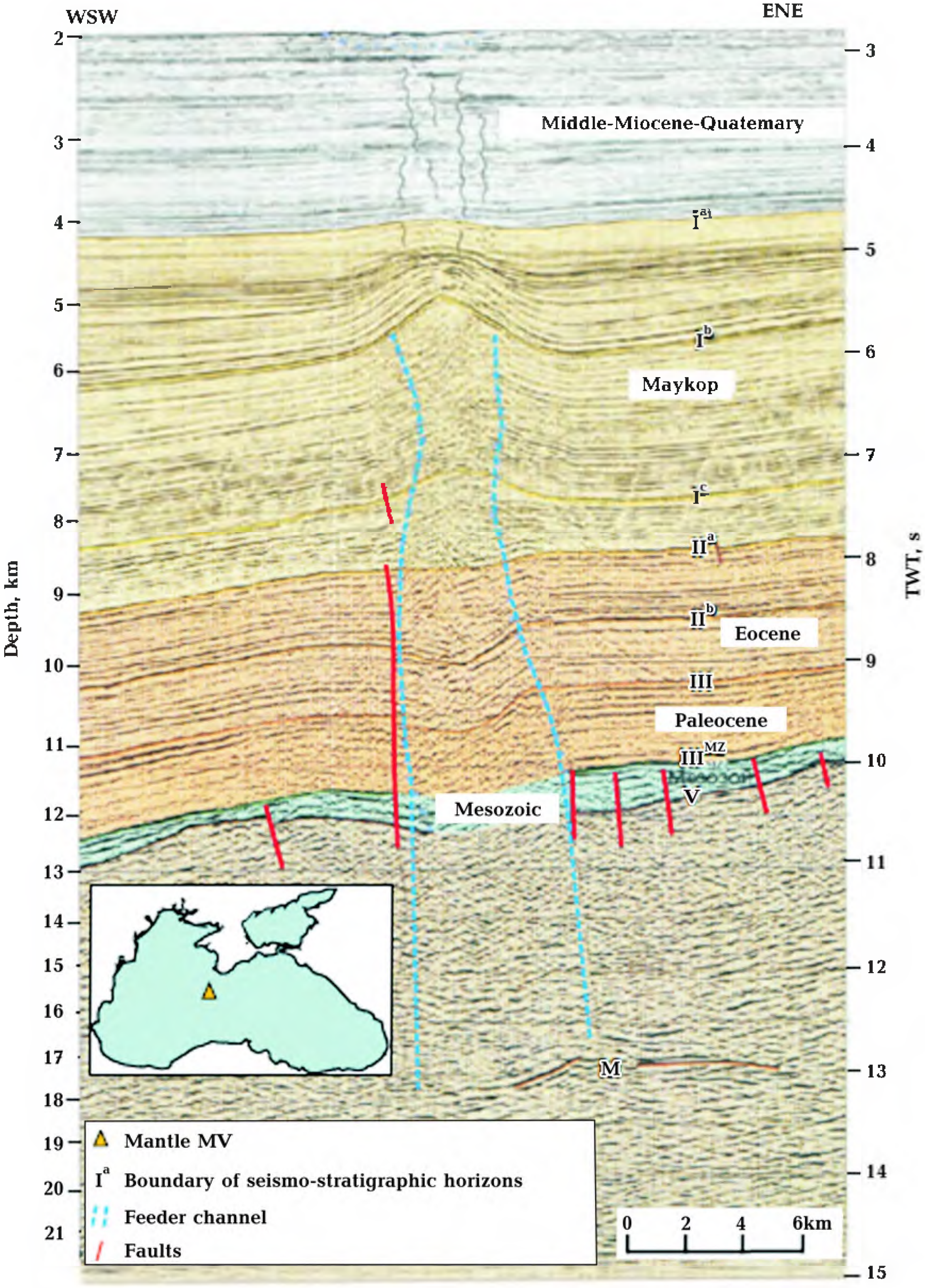


Fig. 3. Fragment of a regional seismic line across the Mantle MV (modified from [Shnuykov et al., 2013]).

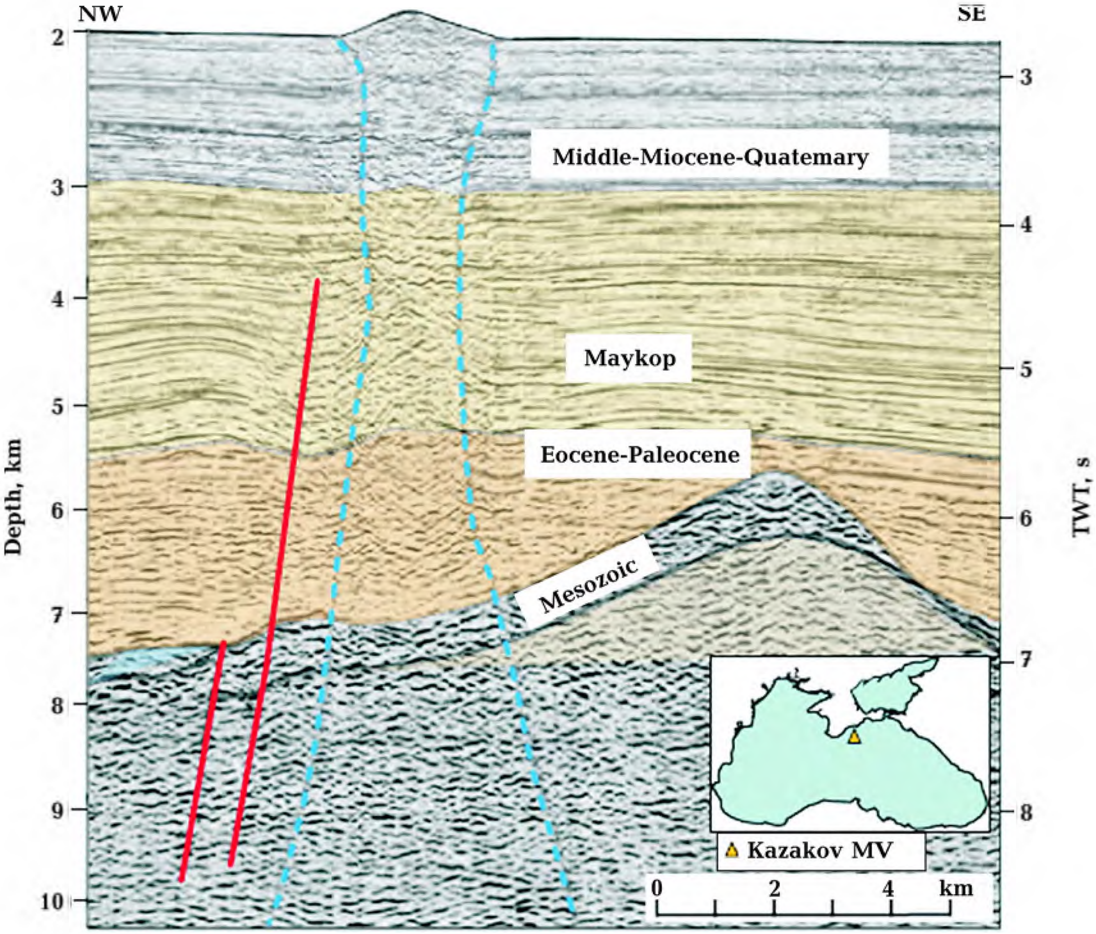


Fig. 4. Fragment of a regional seismic line across the Kazakov MV (modified from [Shnuykov et al., 2013]). See Fig. 3 for symbols.

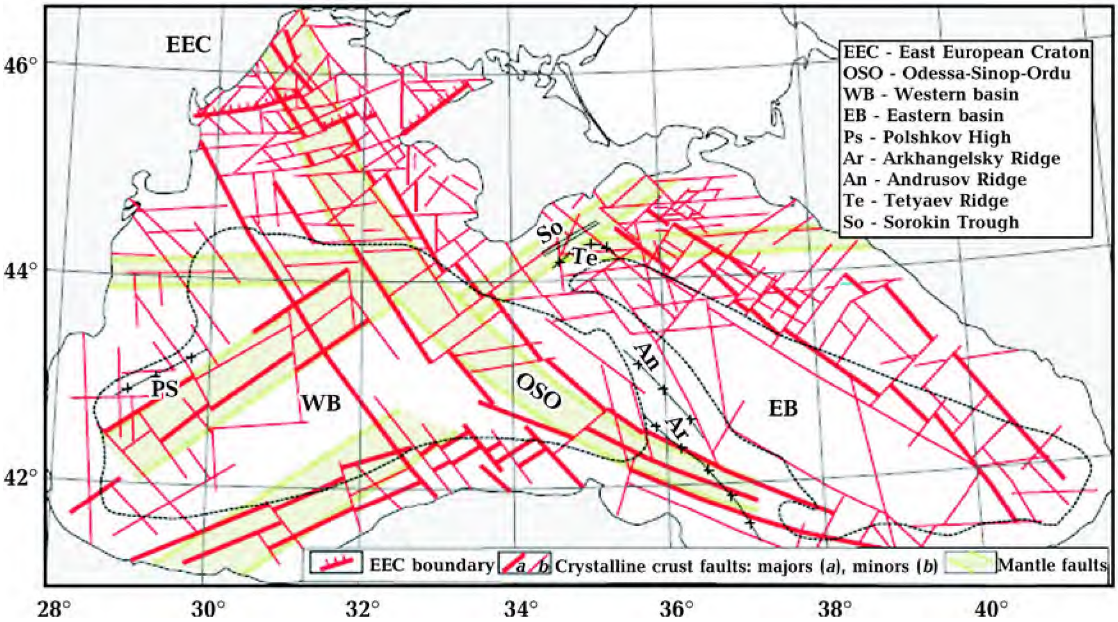
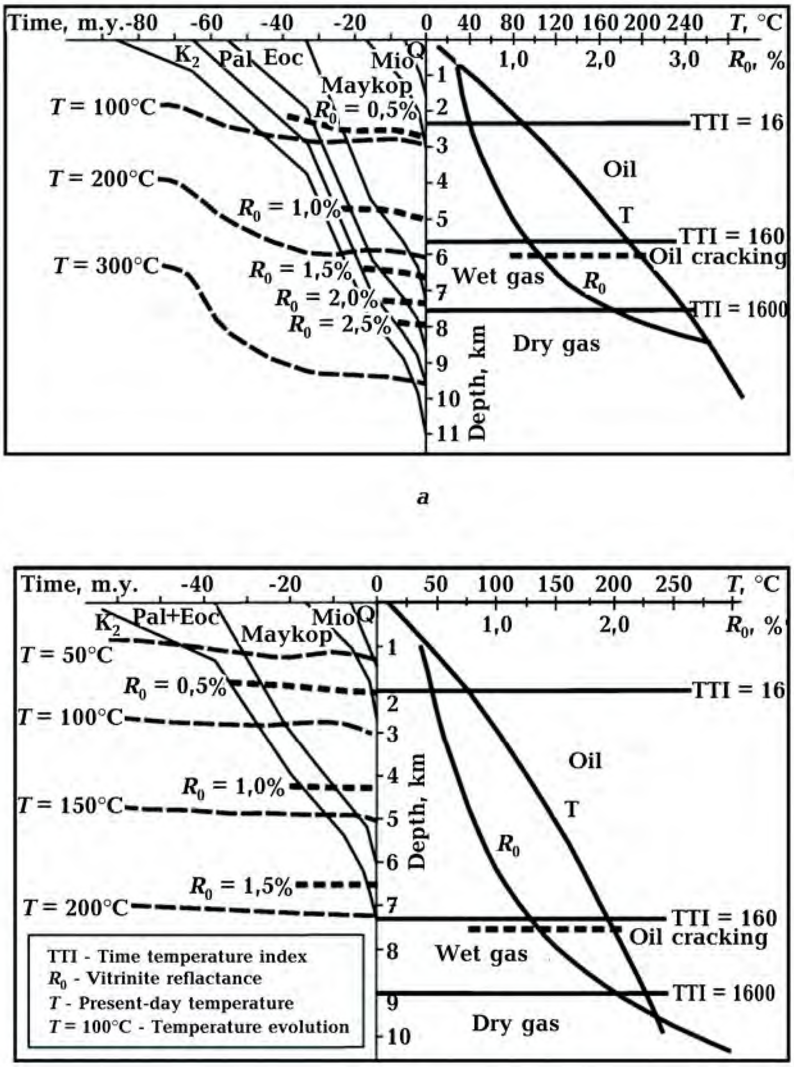


Fig. 5. Map of the crystalline crust and mantle faults derived from the anomaly of magnetic and residual gravity fields (simplified from [Starostenko et al., 2015]).



a

b

Fig. 6. Models of sedimentation, thermal and maturity history in the areas of B (*a*) and C (*b*) in the Black Sea. See Fig. 2 for areas location.

ley, 2003], they cannot produce thermogenic methane.

Two approaches are widely used to diagnose the origin of methane. The combination of the $\delta^{13}C$ and δD values is a useful empirical indicator of its genesis [Whiticar, 1999] in the absence of postgenetic transformation during vertical migration through a sedimentary cover [Etiope, Sherwood Lollar, 2013]. Microbial methane is characterized by values of $\delta^{13}C$ from −110 to −55 ‰ and δD from −400 to −150 ‰. Thermogenic gas has the $\delta^{13}C$ values of −(55—20) ‰ and δD −(300—100) ‰. The diagram of $\delta^{13}C$ vs. C1/(C2 + C3) was proposed to distinguish between biogenic and thermogenic gas [Bernard et al., 1978]. Bacterial methane is documented by C1/C2 + C3 values from 10^3 to 10^5 and $\delta^{13}C$ values in a range of −(90—60) ‰. Thermogenic gas has C1/(C2 + C3) less than 10^2 and $\delta^{13}C$ heavier than −52 ‰.

An attempt was undertaken to apply once more these diagrams to the data from the Black Sea (see Table) to analyze earlier classifications of methane. Methane is of microbial origin in the sediments from the DSDP Holes, Fault seepage, Odessa, NIOZ MVs, Batumi seep area (2) because the $\delta^{13}C$ values are more negative than 50 ‰. Within the δ^{13}C values range of −(50—20) ‰ the identification gives uncertain results without information on δD values or data on molecular fractionation of gas because biological and thermogenic methane cannot be distinguished from each other. Therefore, the stable carbon isotope values −(43.0—31.4.6) ‰

Stable carbon isotope values for methane from sedimentary rocks in the Black Sea. See Fig. 2 for the location of samples

Area	Structure	Number of samples	δ^{13}C ‰, VPDB	Type of sediments	References
A	DSDP Holes 379—381 (depth: 33—1066 m bsf)	22	−(80.4—54.2) −66.2	Terrigeneous and Coccolith mud	[Faber et al., 1978]
	Fault seepage	3	−(74.2—65.7) −69.6	Clay, sapropel	[Mazzini et al., 2004]
	Fault seepage	7	−(46.9—25.6) −41.9	Authigenic carbonate	
B	Kovalevsky MV	4	−(50.7—31.6) −43.0	Mud breccia	[Mazzini et al., 2004]
	TREDMAR MV	1	−50.7	Mud breccia	
	Vassoevich MV	14	−(24.5—8.5) −18.6	Authigenic carbonate	
C	Odessa MV	7	−(70.4—66.5) −68.0	Clay	[Mazzini et al., 2004]
	Odessa MV	9	−(44.9—35.5) −40.1	Authigenic carbonate	
	Kazakov MV	7	−(56.0—55.3) −55.7	Mud breccia clay	
	Kazakov MV	26	−(23.1—5.6) −19.7	Authigenic carbonate	
	NIOZ MV	7	−(67.4—49.1) −61.4	Mud breccia	
	Diapiric structure	4	−(39.1—38.4) −38.5	Authigenic carbonate	
DM	Dolgovskoy Mound	35	−(40.6—31.0) −35.9	Authigenic carbonate	[Bahr et al., 2007]
D	Batumi seep area (1)	109	−(33.9—28.1) −31.4	Lithified coccolith ooze	[Bahr et al., 2007]
	Batumi seep area (2)	4	−(53.0—2.0) −52.5	Cocolith ooze, sapropel	[Pape et al., 2010]

for methane from sediments of the Kovalevsky MV and Batumi seep area (1) strongly suggest its mixture composition of biogenic and thermogenic gas. As for authigenic carbonates, the $\delta^{13}C$ values of $-(46.9—8.5)$ ‰ indicate origin due to microbial oxidation of methane whose primary sources are not discussed [Peckmann et al., 2001; Mazzini et al., 2004]. In these cases methane type may be elucidated by the analysis of isotope signature and molecular fractionation of hydrocarbon gas in host sediments for authigenic carbonates.

A combined $\delta^{13}C_{CH_4}$ and hydrocarbon compositional analysis $(C1/(C2+C3))$ of authigenic carbonates was performed for the sediments of MVs in the Sorokin Trough [Mazzini et al., 2004]. The methane from NIOZ MV is of biological origin with slight thermogenic contamination whilst the samples of mud breccia and clay from the Odessa, Kazakov and Kovalevsky MVs contain mixture gas of both methane origins because of inputs from different sources. The values of the $\delta^{13}C$ for methane from the Odessa and Kozakov MVs are lighter than −55 ‰. Therefore, determinations of methane nature by only $\delta^{13}C$ values have no isotope basis and should be considered with caution. Accordingly, in a grey area there are the classifications of microbial methane based only on the $\delta^{13}C$ values more negative than −55‰ [Hunt, Whelan, 1978; Faber et al., 1978; Amouroux et al., 2002; Michaelis et al., 2002; Rusanov et al., 2002; Knab et al., 2009].

The carbon isotopic values of methane from the sediments hosting carbonate crusts are 25—30 ‰ lighter than authigenic carbonates at all studied sites [Mazzini et al., 2004]. If so, the $\delta^{13}C$ methane values of the sediments from the Vassoevich, Kovalevsky, TREDMAR MVs in the Central Black Sea is ca. 47 ‰. Based on widespread practice mentioned above, it is reasonable to suggest that the methane origin in this case is rather thermogenic than abiogenic.

Stadnitskaia et al. [2007] obtained additional results also by an analysis of molecular and carbon isotopic composition and suggested that hydrocarbon gases from the Kazakov, Odessa, NIOZ, Tbilisi and Unnamed MVs in the Sorokin Trough are products of non-microbial oil cracking process. The methane of dissociation of hydrate samples from the Dvurecheskii MV (the Sorokin Trough) is mainly of biogenic origin with an admixture of thermogenic gas [Blinova et al., 2003].

Well-defined unsaturated elements of oil in petroleum seepage on the Arkhangelsky Ridge and enrichments in the thermogenic homologues in vent gas on Pechori and Iberia Mounds and Colkheti Seep offshore Georgia indisputably revealed oil transformation [Kruglyakova et al., 2009; Reitz et al., 2011]. In all these cases an initial source seems to occur in the Maykopian Formation or even deeper. The further information is needed to support these speculations.

In the abiotic concept, the multistage process of the hydrocarbon formation is governed by the transformation and maturation of organic matter under specific temperature and pressure conditions [e. g. Hantschel, Kauerauf, 2009]. The widely used thermal maturity parameters of organic matter are vitrinite reflectance (R_0) and modified Lopatin's time-temperature index (TTI) [Waples, 1979, 1980]. They both depend on the thermal regime of sedimentary cover delineating hydrocarbon generation process and the subsequent cracking of oil to methane. TTI can be determined from subsidence history and temperature change with time in source rocks.

In the Central Black Sea (see Fig. 6, *a*, Area B) the formation of oil (oil window) occurs at 2.3—5.5 km depth within the Maikopian Formation whose depth varies from 2.2 to 7.2 km. The fraction of ultimate generation of liquid hydrocarbon is 2—92 % in the interval of oil window because R_0 ranges from 0.6—1.2 % [Waples, 1979]. At a depth of 6 km TTI is equal to16 and natural oil cracking takes place [Waples, 1980]. The most favourable conditions for generation of wet gas are identified at 6.0—7.5 km depth in the Lower Maikopian and Upper Eocene sediments where $ITI = 160 \div 1600$ and $R_0 = 1.3 \div 2.2$ %. Dry gas is formed below 7.5 km.

In the Sorokin Trough (see Fig. 6, *b*, Area C) oil window occurs in the Middle Miocene—Maikopian sediments (2.0—7.5 km) where R_0 is 0.5—1.6 %. The fraction of ultimate generation of oil ranges from 1 to 100 %. Gas generation occurs in the Eocene—Paleocene sediments (below 7.2 km). Thus, these assessments corroborate the ability of oil producing from biodegradation and temperature cracking of organic matter in the sediments of the Black Sea. Therefore, thermogenic gas is a secondary product of postgenetic transformation of biologically derived hydrocarbons in the sedimentary cover.

No commercial oil or gas fields were discovered in the Maikopian sediments which were penetrated by the Sürmene-1, Yassihöyük-1 and Sinop-1 wells in water depth between 1680 and 2150 m in the Turkish sector [Şen, 2013]. It is not surprised. Intensive sulphate reduction and massive hydrogen sulfide contamination of the Maycopian waters resulted in a catastrophic decrease in organic matter (to <1 %) at an early stage of diagenesis of sediments [Bazhenova et al., 2003]. This caused relatively small-scale producing of liquid hydrocarbons which could not form industrial accumulations.

In line with these inferences Reeburgh et al. [1991] revealed that annual methane production from organic matter in the best-case is only 0.25 Tg. It implies that about 400 years are needed to produce 96 Tg methane in the Black Sea water column meanwhile a residence time for methane is maximum of 20 years [Reeburgh, 1991]. Ivanov and Lein [2006] suggested that the total annual methane (12.44 Tg) mostly from carbon dioxide-reducing methanogens is consumed in the process of anaerobic oxidation. Therefore, results from these independent assessments available in the Black Sea unequivocally point out that biological methane from organic matter plays negligibly small role in accumulating the world's largest anaerobic reservoir (96 Tg).

Meanwhile, there exists a very real possibility of inputting crystalline crust and mantle methane into the Black Sea. The characteristics of the gas chimneys structure have been derived from high-quality seismic data in the Bulgaria deep sector of the Black Sea [Tari et al., 2009, 2011]. The vertical feeder channels of gas seeps from the Polshkov High distinctly indicate gas migration to the Maycopian Series from deeper sources. During dominantly upwelling along syn-rift faults and their reactivated continuations in the post-rift sedimentary cover gas discharges to the intra-Tertiary packages. The seismic sections undoubtedly demonstrate that gas sources don't occur at depth shallower than the uppermost basement of the Polshkov High because the syn-rift faults (gas pathways) cut it. The vertical conduits of methane seeps of the Andrusov and Tetyaev Ridges pierce to 2 km into crystalline basement [Hydrocarbon ..., 2007].

Fig. 3 demonstrates a portion of regional seismic reflection line across a buried mud volcano in the Central Western Black Sea Basin [Shnyukov et al., 2013]. The distinguishable vertical zone of distortions in time lines is registered in the Middle and Upper Neogene sediments. The top of the Maycopian sediments forms the closure whose amplitude reaches up to 800 m. The syncline-like curvature of reflectors is observed at the base of the Maycopian horizon that reflects sharp velocity sag due to significant increase in the gas concentration in the sedimentary deposits. The velocity anomaly increases with the age up to the Cretaceous indicating the presence of gas. The feeder channel penetrates the 17 km thick sedimentary cover and crystalline basement reaching the uppermost sub-Moho depths. The depth penetration of methane pathway of the Kazakov MV in the Sorokin Trough is 10 km in the Pre-Mesozoic basement (see Fig. 4). Its feeder channel is identified by subvertical zone of the lost correlation of seismic reflections. The characterization of dynamics and decrease in the velocity of seismic waves indicate the presence of gaseous hydrocarbons. The depth penetration of the MVs feeder channels in the Sorokin Trough is more than 9 km (see Fig. 6).

Crystalline crust and mantle derived helium was revealed in the vicinity of the Vodyanitskiy MV in the Sorokin Trough and in the Dnepr paleo-delta [Holzner et al., 2007]. This implies the existence of faults that cross the mantle—crust boundary, the crystalline crust and the sedimentary cover for vertical gas migration to the seafloor. Near-subsurface faults were mapped in and around the mud volcanoes by the high resolution 3D seismic data in the Sorokin Trough while the regional single channel profile (190 km in length) collected by SSC "Yuzhmorgeologia" of Gelendzhik in the vicinity of the Sevastopol MV penetrated the Lower Cretaceous sediments [Wagner-Friedrichs, 2007]. Based on these data, the shallow faults were suggested to be related to the deeper faults reaching deep layers and serving as fluid migration conduits to the seafloor. The pattern of the crystalline crust fault (see Fig. 5) distinctly supports this assertion.

Overlapping the zones of the near-subsurface diapiric ridges and terminating the feeder channels in the crystalline crust (Fig. 7) implies a common source of gas and fluids which migrate within the vertical zone along individual conduits of each volcano in the Sorokin Trough.

In respect with the depth penetration of the MVs feeder channels in the Central Black Sea form 2 groups. The first of them embodies the Goncharov, Kovalevskii, Vassoevich and Malyshev MVs whose feeder channels terminate in the Lower Eocene at a depth of 10 km (Fig. 8). The second cluster consists of the Kornev, MSU, Strakhov MVs which feeder channels reach 12 km depth (the Lower Eocene) or even more (the Mantle MV). It is worth mentioning that the MVs are situated in the area of intersecting the mantle faults (see Fig. 7, 8). The highest concentration of gas seeps distribution is observed at the triple junction of the mantle faults in the NW Black Sea (see Fig. 1, 4). In contrast to the all above mentioned cases, there are practically no discovered MVs in the central parts of the Black Sea beyond the area B where the mantle faults are unknown (see Fig. 1, 5).

As can be seen in Fig. 1, on the both sides of the shelf break in the NW Black Sea gas seeps are related to the canyons of the Kalanchak, Dnipro, Dnister, Kagulnik, and Danube palaeo-rivers [Starostenko et al., 2010]. The canyons are V-shaped nar-

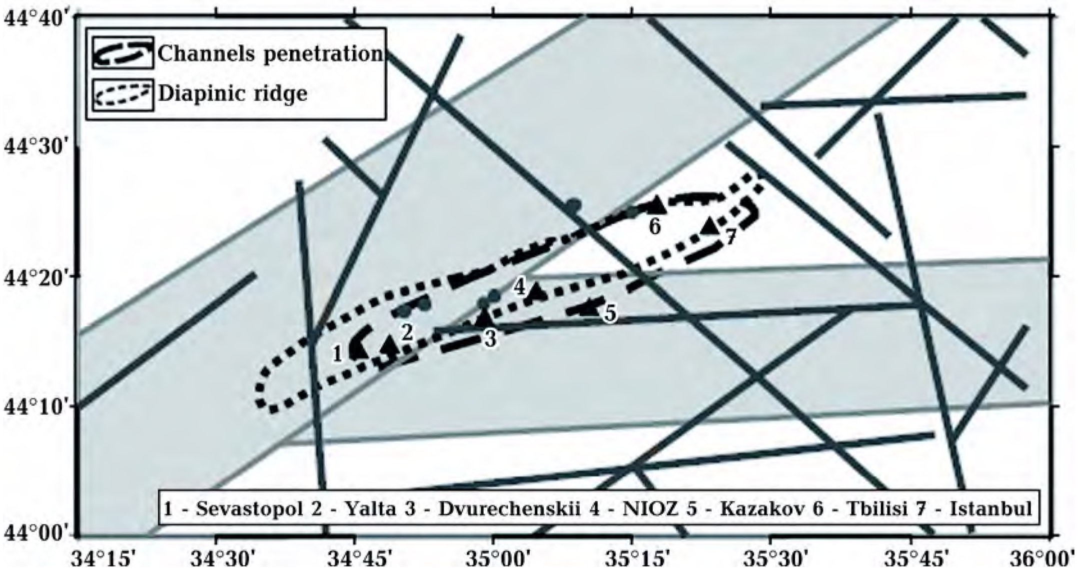


Fig. 7. Pre-Mesozoic MVs feeder channels at 9 km depth and diapiric ridge in the Sorokin Trough. The contour of the diapiric ridge is from [Wagner-Friedrichs, 2007]. Data on depth penetration are from [Shnyukov et al., 2013]. See Fig. 2 for areas location and Fig. 5 for symbols.

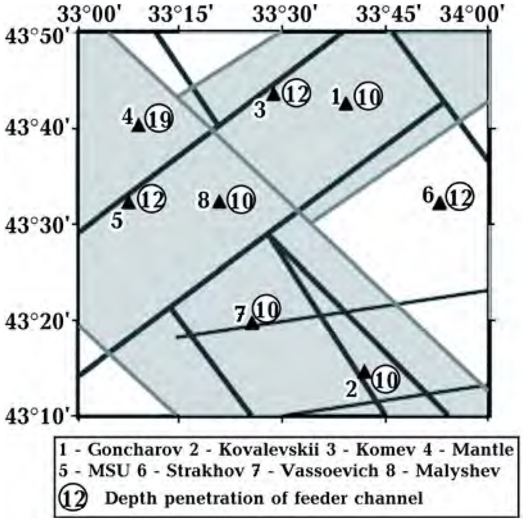


Fig. 8. Depth penetration of MVs feeder channels in the Central Black Sea. Data on depth penetration are from [Shnyukov et al., 2013]. See Fig. 2 for areas location and Fig. 5 for symbols.

row valleys of up to 1200 m depth in the sedimentary cover, which spatially coincide with the deep faults in this area [Starostenko et al., 2015]. The most important of them is the Odessa-Sinop-Ordu fault zone because of its mantle origin. In this transitional zone between the continental and oceanic crust a long-live tectonic activity is maintained from the Cretaceous to date [Nikishin et al., 2014] resulting in numerous faults, slides, fractures, joints and fissures. In turn, they produce pathways for methane migration to the seafloor bottom. The present-day disruption of sedimentary layer geometries, canyons, deep tectonic disturbances provide suitable channels for the vertical migration of methane from the crystalline crust and upper mantle.

The vertical strong gas flows produced anticline-like features in mostly clayey Maycopian Formation (see Fig. 3, 4). This layer is identified as one of the most extensive overpressured zones in the world due to the effect of gas force [Scott et al., 2009].

Foregoing information provides reasonable grounds to conform the possibility for the occurrence of nonorganic methane in the Black Sea. Abiogenic methane is most likely to be able to form a unique huge reservoir of methane in the water column of the Black Sea. There is no another way to explain a serious contradiction between negligible production of biogenic methane and enormous quantity of dissolved gas in the water column. If so, a question arises: why abiogenic methane was not identified in the Black Sea. There are three reasonable explanations of these results. Anaerobic oxidation and sulfate reduction of methane is widespread in sediments of the Black Sea [e. g. Jørgensen et al., 2001; Treudel et al., 2007; Knab et al., 2009]. This multistep and reverse process involves both consumption and production of biological methane [Timmers et al., 2017]. Thus, biological methane may result from recycling of abiogenic methane during microbial activity. As was demonstrated above, in the number of cases the $\delta^{13}C$ values of methane heavier than –50 ‰ were taken to be indicator of the biological origin although they are also characteristic of thermogenic methane. These two types of methane cannot be distinguished without δD values or data on molecular fractionation of gas. Biological methane originates only at temperature below 50 °C [Stolper et al., 2014] which occurs at ca. 1 km bsf in the sedimentary cover (see Fig. 5). In this geological environment the production of biological methane is not enough to form the huge reservoir in the Black Sea water. So, thermogenic methane can be mostly of abiotic origin. Abiotic methane derived by gas-water-rock reaction has $\delta^{13}C$ values more negative than –57 ‰ that can be assumed as an indication of biological activity [Etiope, Sherwood Lollar, 2013]. It is worth mentioning that the virtual predominance of biogenic methane in the Black Sea is a unique phenomenon. For example, composition and methane stable isotopes of 143 terrestrial mud volcanoes indicate that at least 76 % of them release thermogenic gas, with only 4 % biogenic and 20 % with mixed character [Etiope, Baciu, 2009]. In our opinion, the most likely explanation for these differences is the absence of anaerobic microbial processes in the MVs subsurface on land.

A discussion of abiogenic methane formation and its upwelling is far beyond of the scope of this paper. An updated comprehensive review of abiogenic methane on Earth is recently presented by Etiope and Sherwood Lollar [2013].

Finally, the main results of this study are as follows:

- new distribution map of gas seeps and mud volcanoes has been compiled for the Black Sea;
- feeder channels of gas chimneys pierce to several kilometers into crystalline basement at Polshkov High, Andrusov and Tetyaev Ridges and at MVs in the Sorokin Tough. The gas pathway reaches to the mantle subsurface in the Mantle MV of the Central Black Sea;
- the highest concentration of gas seeps distribution is observed at the triple junction of the mantle faults in the NW Black Sea;
- sediments from gas seepage and mud volcanoes areas frequently contain thermogenic methane;
- thermogenic methane results from postgenetic alternation of biogenic methane of the Paleogene—Neogene sedimentary cover;
- biological methane produced from organic matter plays negligibly small role in accumulating the world's largest anaerobic inventory of 96 Tg in the Black Sea;
- nonorganic methane is most likely to form the tremendous reservoir of dissolved gas in the Black Sea water column;
- the absence of identification of abiotic methane is accounted for its recycling by microbial activity, misclassificated origin and producing by chemical syntheses, with its $\delta^{13}C$ values indicating biological origin.

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Mantle origin of methane in the Black Sea

O.M. Rusakov, R.I. Kutas, 2018

A new distribution map of gas seeps and mud volcanoes has been compiled of the Black Sea. It has been derived from the published coordinates for ca. 5000 gas seeps and 80 mud volcanoes. An analysis of the stable isotopic composition of methane has been performed for authigenic carbonates and sediments. The $\delta^{13}C$ values of carbonates and sediments form 2 distinct tight groups depending of the geological environments. The diagrams of values of $\delta^{13}C$ vs. δD and $\delta^{13}C$ vs. $C1/(C2+C3)$ have been applied to assess earlier classifications of methane. The origin of methane from most of samples has turned out to be uncertainly determined. Based on seismic reflection data, the feeder channels of gas releases and mud volcanoes penetrate to the Pre-Mesozoic basement beneath the Polshkov High, Andrusov and Tetyaev Ridges and Sorokin Trough at a depth of up to 12 km. In the Central Black Sea the feeder channel of mud volcano reaches the mantle surface where a depth is 19 km. The highest concentration of gas seeps distribution is observed at the triple junction of the mantle faults in the NW Black Sea. Assessments of different mechanisms have been made for their ability to produce an unprecedented methane concentration in the Black Sea water column. There occurs thermogenic methane in the sediments from gas seepage and mud volcanoes areas. The thermogenic methane results from post genetic alternation of biogenic methane of the Paleogene—Neogene sediments. Biological methane produced from organic matter plays negligibly small role in accumulating the world's largest quantities of anaerobic methane in the Black Sea. Nonorganic methane is most likely to form the tremendous reservoir of dissolved gas in the Black Sea water column below 150—200 m. The seeming scarcity of abi-otic methane is accounted for its recycling by microbial activity, misclassificating origin and producing by chemical syntheses, with its biological metha-ne $\delta^{13}C$ values.

Key words: Black Sea, gas seeps, mud volcanoes, methane isotopic composition, feeder channels, abiotic methane.

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