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Methane seeps in the Black Sea: discovery, quantification and environmental assessment

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Abstract

This review describes methodology and software developments for acoustic data acquisition and determining parameters of gas bubble streams; shows geographical distribution of more than 3000 seeps in the Black Sea; presents data on methane fluxes from the deep-sea mud volcanoes; gives a model for evaluation of gas exchange in the water environment and methane emission from gas seeps to water column and atmosphere; explains modern views on the impact of cold seeps on the hydrochemical characteristics of the marine environment, the vertical water exchange, methanotrophic chemosynthesis and trophic structure of water; reveals a new form of life in the anoxic water column of the Black Sea, which is represented by a symbiotic community of anaerobic archaea and methane oxidizing and sulfate-reducing bacteria; contains estimates of potential environmental hazards due to methane discharge from the bottom of the Black Sea, and outlooks the possible use of cold seeps as a resource factors because they can be indications for shallow or deep hydrocarbon accumulations.

Keywords: Black Sea, gas seeps, methane emission

Introduction

Detailed historical overview of the last decades investigation of the Black Sea gas seeps are given in the most recent monograph

“Methane seeps in the Black Sea: environment-forming and ecological role” (Egorov *et al*. 2011). The visual observation of gas bubble escapes from the seafloor in the Black Sea was firstly reported from the Bulgarian bay of Balchik and was treated as ordinary regional shallow gas indication (Dimitrov *et al*. 1979). However, in April 1989 methane seeps were discovered in the anoxic zone of the Black Sea during acoustic survey over the north-western shelf edge and the upper slope (Polikarpov and Egorov 1989). Afterwards, numerous seeps have been found by acoustic detection of plumes of emanating gas bubbles down to a water depth of 2070 m (Egorov *et al*. 2003, 2011). Most of these seeps are located along the shelf edge and on the upper slope (Figure 1), particularly at the paleo-deltas and canyons of the largest Black Sea rivers: Danube, Dnepr, Dniester and Don (Egorov *et al*. 2003). The deepest seeps have been discovered recently in association with faults and mud volcanoes in the central Black Sea basin (Egorov *et al*. 2003, Krastel *et al*. 2003).

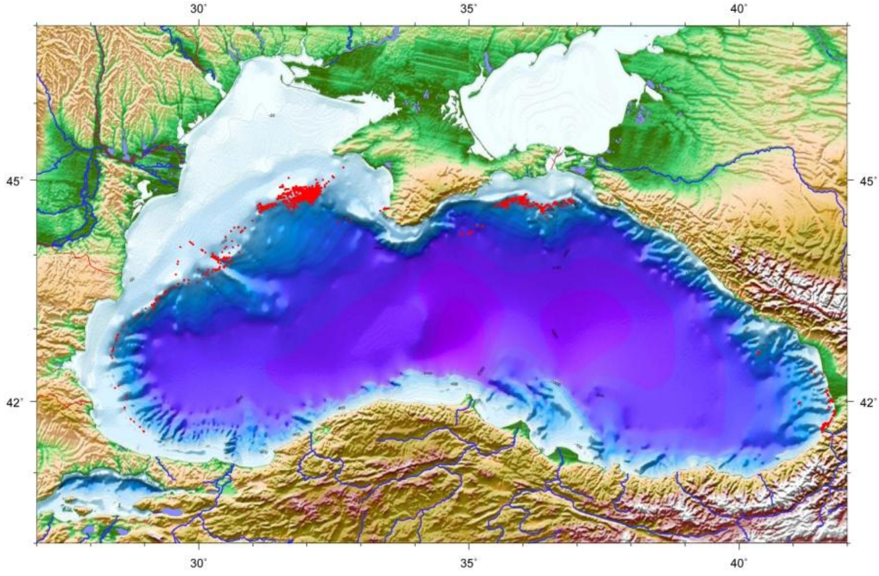


Figure 1. Distribution of methane seeps (dark spots) in the Black Sea (Egorov *et al*. 2003, 2011).

The beginning of this century was marked by a sharp increase in international multidisciplinary researches on Black Sea gas seeps, which were focused on: analysis of localization, spatial distribution and environmental role of seeps (Gevorkyan *et al*. 1991; Egorov *et al*. 2003; Shnukov *et al*. 1999; Egorov *et al*. 1998); study of geological conditions of gas hydrate generation (Shnukov *et al*. 1995; Naudts *et al.* 2006); studying the mechanism of bacterial oxidation of methane and formation of microbial build-ups in anoxic waters (Ivanov *et al*. 1991; Polikarpov *et al*. 1993; Michaelis *et al*. 2002); determination the age and genesis of methane in the Black Sea (Lein *et al*. 2002; Gulin *et al*. 2003), and quantification of emission of gaseous methane to the Black Sea water column and overlying atmosphere (Artemov *et al*. 2007; Egorov *et al*. 2003, 2011).

In 2000-2011, there were carried out a number of international marine expeditions on research vessels “Professor Vodyanitskiy” (Ukraine), “Professor Logachev” (Russia), “Meteor” (Germany), “Poseidon” (Germany) and “Maria S. Merian” (Germany) equipped with advanced single- and multi-beam echo-sounders, manned underwater submersibles, landed automatic probe stations, TV-guided vehicles and other instruments allowing remote detection and mapping of the gas seeps, their direct visual observation and sampling of the emanating gas, surrounding seawater, bottom sediments and the associated methanogenic microbial structures.

The purpose of this paper is to introduce main results of our studies of the gas seeps in the Black Sea performed since the first discovery of this phenomenon in 1989 and to assess state of these explorations at the present time.

Methodology development and main outcomes: brief overview

Acoustic detection and quantification of gas seeps

It is well known that echo-sounding observation of the water column is an efficient method for the detection of bubble releases from the seafloor. Echo responses from numerous gas bubbles, rising towards the sea surface, combine on echograms into vertically elongated figures, which shape resembles flares (Figure 2a). This analogy is especially vivid if applied to color echograms where high levels of the echo-signal are coded with red hues. At the same time, "echographic gas flares " are merely “acoustic images” of real gas bubble streams, the physical size of which is difficult to estimate from echograms as illustrated in Figure 2.

Specialized software for acquisition and processing of acoustic data, accessible through the ETHERNET interface of the scientific echosounder SIMRAD EK-500, was developed (Artemov 2006) and regularly employed during a number of scientific cruises to obtain such data as: the area of a venting site; total number of bubbles, released per a time period; size spectrum and rise velocity of bubbles at different depths through the water column.

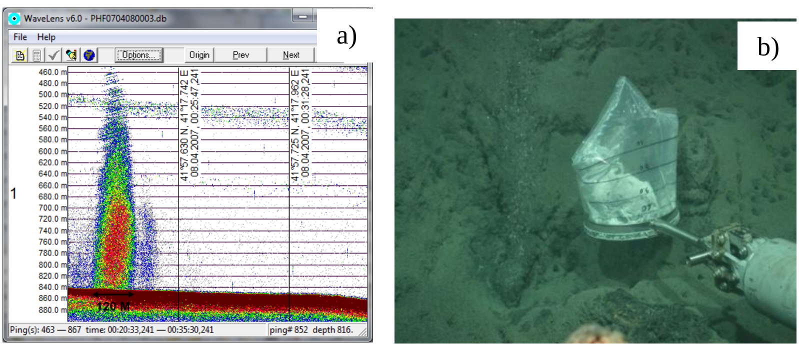


Figure 2. a) Echogram of the gas flare from seep site recorded at a ship speed of 1.9 kn with the narrow beam 18 kHz Parasound parametric echosounder. b) Photo of the same seep site obtained during the measurement of bubbling gas flux using the ROV QUEST-4000. To the right from the gas outlet the manipulator with the plastic bag can be recognized. The bag, 19 cm in diameter and 5.5 liters in volume, filled up with gas for 1 min 35 sec, so *in situ* gas flux was, approximately, 3.5 liter/minute. The photo is the property of MARUM University of Bremen.

A new approach based on the use of calibrated echo-sounder, digital data recording and processing techniques, mathematical modeling and GIS technology has been proposed and applied for better understanding the methane seepage phenomenon.

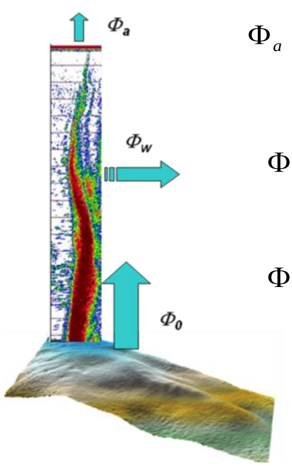
Methane flux originated from gas bubble streams has been regarded as composed of three constituents:

– initial upward flux Φ_0, governing methane intake from the bottom to the water column;

– dispersed flux Φ_w, evolved from gas exchange between rising bubbles and surrounding water;

– flux to the atmosphere Φ_a, produced by bubbles reached the sea surface.

To achieve evaluation of gas fluxes, the assumption was taken that each flux constituent is linearly dependent on the seep productivity N (1/m) which characterizes the frequency at which gas bubbles come to the water column and is numerically equal to the amount of gas bubbles contained in the water layer of 1 m thickness above the bottom (Figure 3).



$$\Phi_a = \Phi_0 - \Phi_w = N(\overline{s_0} \cdot \overline{m_0} - \int_0^{H_0} \overline{s(h)} \cdot \frac{\partial \overline{m(h)}}{\partial h} \cdot dh)$$

$$\Phi_w = N \cdot \int_0^{H_0} \overline{s(h)} \cdot \frac{\partial \overline{m(h)}}{\partial h} \cdot dh$$

$$\Phi_0 = N \cdot \overline{s_0} \cdot \overline{m_0}$$

Figure 3. Constituents of methane flux originated from gas bubble streams. Notation: $\overline{s_0}$ is the mean initial bubble rising speed, $\overline{m_0}$ is the mean initial methane content in bubbles, $\overline{s(h)}$ is the mean bubble rising speed depending on depth, $\partial\overline{m(h)}$ is the mean change of methane content in bubbles depending on depth, and H_0 is the release depth of bubbles.

The seep productivity N was determined from acoustic measurements in a thin bottom layer of the water column. Rather point than volume model of sound scattering was used as this made it feasible to estimate individual intensity of gas bubble streams and methane flux to the water column and atmosphere as well.

Methane content and rising speed of bubbles at any point of their trajectory were estimated using the mathematical model of gaseous exchange with surrounding water. It was found that models based on the 1st Fick's law and equation of state of ideal gases (IGEOS) or real gases equation of state by Peng - Robinson (PREOS) can be applied for quantitative analysis of gas bubble behavior in the water column. The major difference of our models from others documented by various researchers concerns the algorithmic representation of bubble evolution from "clean" to "dirty" modes depending on the area of stagnant cap at the rear of rising bubble, where adsorbed surfactants accumulate due to the surface convection and cause the Marangoni effect (Clift *et al*. 1978).

For shallow sea models for ideal and real gases give almost identical results (Figure 4a). However, for deep sea the real gas model predicts a much longer life-time and rising height of methane bubble due to growing influence of van der Waals forces (Figure 4b).

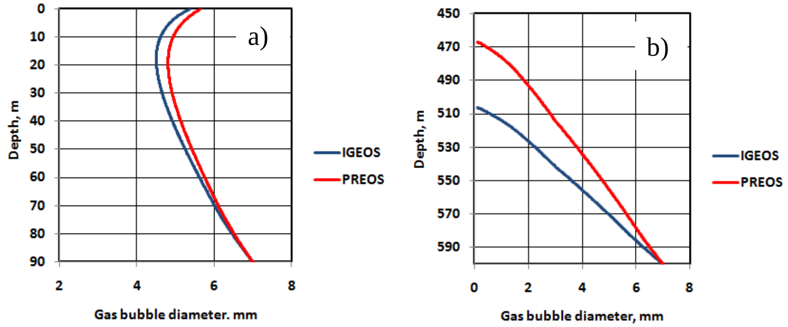


Figure 4. Evolution of 7 mm diameter bubble with 99% initial content of methane simulated with IGEOS and PREOS models: a) for water depths 90m; b) for water depths 600 m.

Appraisal of methane flux - results summary

It was found that at the vast area of the Black Sea stretching from the Danube Canyon to the Kerch-Taman region only 1.6% of methane from gas bubble streams reaches the atmosphere in gas phase, while 98.4% dissolves in the water column (Table 1).

Table 1. Integral estimates for the studied regions of the Black Sea

Region	Number of detected seeps	Methane flux (m^3 y^{-1})	
		water column	atmosphere
West (including Danube Canyon, Paleo-Dnieper)	2693	18.8 10^6	3.8 10^5
Kerch-Taman	594	5.9 10^6	1.4 10^4
Sorokin Through	10	2.6 10^5	0
Total	3297	25.0 10^6	4.0 10^5

Thus, the most part of methane carbon from gas bubble streams at this area transfers to the water column and enters into the biogeochemical cycles and bio-production process of the Black Sea.

Underwater observation and biogeochemistry of the seep-related microbial structures

Our first underwater observations, which were carried out in 1990 with the scientific submarine “Benthos-300”, have revealed broad fields of chimney-like structures located in the NW Black Sea within the methane seeps area in permanently anoxic waters at depths of 200-230 m (Ivanov *et al*. 1991; Polikarpov *et al*. 1992). Comprehensive underwater inspection of this area was conducted in 2001 with the submersible “Jago” (Germany), finding the carbonate chimneys up to 4 m high at a depth around 230 m (Michaelis *et al*. 2002). These structures represent carbonate build-ups, the upper part of which is covered by massive microbial mats consisting of methanotrophic archaea (Figure 5).

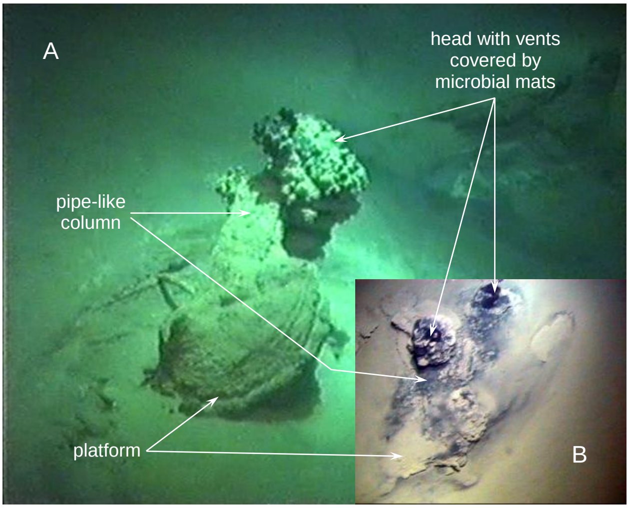


Figure. 5 Underwater photos of the methane-seep-related microbial buildups growing at the upper slope of the NW Black Sea. The pictures were made from research submarine Benthos-300 in December 1990, water depth 230 m (A); and with the Ocean Floor Observation System (OFOS) at site of the dredging performed during the present study, water depth ~650 m, vertical view (B) (Gulin *et al*. 2005)

Recent microbiological, isotopic, molecular and petrographic analyses showed that such microbial build-ups were formed as a result of anaerobic oxidation of methane seeping from the bottom sediments, which was operated by a consortium of archaea and sulphate-reducing bacteria (Polikarpov *et al*. 1993; Boetius *et al*. 2000; Thiel *et al*. 2001; Michaelis *et al*. 2002). During observations conducted in greater water depths in 1993 with the submersible "Sever-2" (Ukraine), similar carbonate buildups were found at a depth of 1738 m, in an area of deep faults and rock outcrops south-west of the Crimean Peninsula (Shnukov *et al*. 1995). During dredging in this area a carbonate chimney was recovered from 1555 m water depth (Gulin *et al*. 2003; Shnukov *et al*. 2004). The most recent finding of the buildups was achieved in 2007 using the deep-sea ROV QUEST-4000, allowing discovery of the Black Sea methane seeps located deeper than the upper boundary of the gas-hydrate stability zone (> 725 m), and a broad field of unusual microbial structures growing at methane seeps in the deeper part of the Dnepr paleo-delta area at water depth more than 730 m (Gulin and Artemov 2007).

Stable carbon isotope analysis of the taken samples showed that carbonates of the buildups were isotopically light, indicating a high presence of the ^{13}C-depleted methane carbon in the carbonates (Ivanov *et al*. 1991; Polikarpov *et al*. 1993; Michaelis *et al*. 2002). As no carbonate structures in the form of chimneys were found in the oxic waters, it was assumed that the Black Sea microbial buildups are formed as a result of anaerobic bacterial oxidation of methane seeping from the bottom sediments (Ivanov *et al*. 1991; Polikarpov *et al*. 1992). This has been argued recently by radiotracer, molecular and petrographic analyses of the Black Sea carbonate buildups, showing that anaerobic oxidation of methane is mediated by methanotrophic archaea in syntrophy with sulfate reducing bacteria (Thiel *et al*. 2001; Michaelis *et al*. 2002).

The earlier ^{14}C-dating has showed that age of carbonates in the base part of the Black Sea microbial buildups is in the range of 5100 years at water depth of 230 m (Ivanov *et al*. 1991) to 17500 years at depth of 1738 m (Shnukov *et al*. 1995, 2003). This dating, however, combines the age of both methane-derived carbon and carbon of bicarbonates dissolved in seawater (Gulin *et al*. 2003). Thus, the given ages may be considerably differernt from the actual time of origin of the Black Sea microbial buildups.

Therefore, we have developed an approach allowing calculation the absolute age of the microbial buildups at different depths of the Black Sea by applying the evaluation of growth rate of the buildups based on the combining data on ^{14}C-dating and stable carbon isotope analyses of the methane-derived carbonates and their initial components: methane and seawater bicarbonates (Gulin *et al*. 2003). The overall results of ^{14}C-dating of the carbonate structures from different depths of the north-western Black Sea slope show a gradual increase of the carbonate age with water depth (Table 2). The age-depth relationships for the base and middle parts of the chimneys are almost parallel, suggesting a similar growth rate of the deeper and shallower buildups. The best fit lines of these trends are: ^{14}C-age (year) = 4094.5 e $^{0.000796\ m}$ (r^2 = 0.985) and 2795.2 e $^{0.000916\ m}$ (r^2 = 0.961), respectively. Assuming a linear growth of carbonate chimney, its absolute age may be roughly assessed by doubling the difference between the radiocarbon dating of the base and middle parts of the buildups. Using the above mentioned exponential curve fitting of the age-depth trends, an extrapolation to maximal depth, where the buildups were found (~ 2100 m, Aloisi *et al*. 2002), gives an approximate time of origin of the deepest chimneys as 5316 years, while for the shallowest buildups (~ 200 m, Polikarpov *et al*. 1992) this estimation is 2888 years.

Table 2. Radiocarbon age (years before present) of microbial carbonate buildups found at different depths of the north-western Black Sea slope (Gulin *et al*. 2003, Egorov *et al*. 2011)

Water depth, m	Middle part of buildup	Base part of buildup
230	3400 ± 105	5100 ± 150
700	–	6655 ± 165
1120	8500 ± 120	9200 ± 200
1555	9800 ± 700	13800 ± 300
1738	15150 ± 380	17500 ± 540

These ages correspond, respectively, to the first appearance of hydrogen sulfide in the deepest Black Sea waters and to the stabilization of the upper boundary of anoxic zone around the present day level. It is known that the Black Sea was a freshwater lake before the incursion of Mediterranean water through the Bosphorus Strait at about 6000 - 7500 years ago as a result of the rise in global sea level (Hay 1991, Ryan *et al*. 1997). This has led to a density stratification of the water column and the beginning of the anoxic conditions development in the deep-sea waters nearly 5000-7000 years before present (Degens *et al*. 1980; Calvert *et al*. 1987, 1991; Hay *et al*. 1990, 1991; Wakeham *et al*. 1995). A gradual salinization of the Black Sea followed until some 3000 years ago the existing salinity and upper level of anoxic waters became established (Deuser 1974).

Thus, the age of the Black Sea carbonate structures at different depths of the continental slope may reflect dynamics of the long-term rising of the oxic/anoxic interface in the water column. This resulted in a change from aerobic to anaerobic oxidation of the seeping methane when oxygen has depleted at the respective depth. This suggestion allows for the consideration that the methane-derived microbial buildups are unique objects for further detailed tracing of the evolution of anoxic conditions in the Black Sea.

Conclusions

Studies in the Black Sea conducted from 1989 to present days revealed a previously unknown chemoecological and resource factor in the Black Sea – numerous methane-emitting gas bubble streams. At gas bubble outlets various biogeochemical and hydrodynamic effects are originated including gas exchange between gas bubbles and the water environment, the creation of zones of upwelling and vertical mixing of water, transferring from the bottom to the water column bacteria, sediment particles, as well as oil. Depending on water depth, initial size, rising speed, as well as some other parameters, gas bubbles can completely dissolve in the water column or reach the sea surface releasing to the atmosphere methane, one of the most important greenhouse gas.

The fields of methane seeps, located in the anoxic Black Sea waters, are characterized with presence of chimney-like carbonate buildups, which are formed due to anaerobic methane oxidation by arhaea in syntrophy with sulfate reducing bacteria. ^{14}C-dating of these microbial structures has shown a gradual increase of the age of carbonates of these buildups with depth. Comparing the radiocarbon age of the base and middle parts of the microbial structures gives an approximate time of origin of the deepest and shallowest microbial buildups as about 5300 and 2900 years before present, respectively. These dates correspond to the first appearance of hydrogen sulfide in the deepest Black Sea waters and to the stabilization of the upper boundary of the anoxic zone around the present day level.

References

Aloisi, G., Abegg, F., Blinova, V., Drews, M., Greinert, J., Ivanov, M., Bohrmann, G. (2002) Seafloor sampling results. In: Marine gas hydrates of the Black Sea (MARGASCH): R/V Meteor cruise report M52/1 (eds., G. Bohrmann & S. Schenck). GEOMAR, Kiel, Germany: 102-116.

Artemov, Yu. G. (2006) Software support for investigation of natural methane seeps by hydroacoustic method. *Mar. Ecol. J*. 5(1): 57-71.

Artemov, Yu. G., Egorov, V.N., Polikarpov, G.G., Gulin, S.B. (2007) Methane emission to the hydro – and atmosphere by gas bubble streams in the Dnieper paleo-delta, the Black Sea. *Mar. Ecol. J*. 6(3): 5-26.

Boetius, A., Revenschlag, K., Schubert, C.J., Rickert, D., Widdel, F., Gieseke, A., Armann, R., Jorgensen, B. B., Witte, U., Pfannkuche, O. (2000) A marine microbial consortium apparently mediating anaerobic oxidation of methane. *Nature* 407: 623-626.

Calvert, S.E., Vogel, J.S., Southon, J.R. (1987) Carbon accumulation rates and the origin of the Holocene sapropel in the Black Sea. *Geology* 15: 918-921.

Clift, R., Grace J.R., Weber M.E.. (1978) Bubbles, Drops, and Particles. Elsevier, New York: 380 p.

Degens, E.T., Stoffers, P., Olubic, S., Dickman, M.D. (1980) Varve chronology: Estimated rates of sedimentation in the Black Sea deep basin. In: Initial Reports of the Deep Sea Drilling Project, vol. 42B (ed., D.A. Ross). U.S. Government Printing Office, Washington, DC, USA: 499-508.

Deuser, W.G. (1974) Evolution of anoxic conditions in Black Sea during Holocene. In: The Black Sea - Geology, Chemistry and

Biology (eds.) E.T. Degens, D.A. Ross. The American Association of Petroleum Geologists, Tusla, Oklahoma, USA: 133-136.

Dimitrov, P., Dachev, V., Nikolov, H., Parlichev, D. (1979) Natural gas seepages in the offshore area of Balchik Bay. *Oceanology* 4: 43–49 (in Bulgarian).

Egorov, V.N., Luth, U., Luth, C., Gulin, M.B. (1998). Gas seeps in the submarine Dnieper Canyon, Black Sea: acoustic, video and trawl data. In: U. Luth, C. Luth and H. Thiel (Editors), Methane gas seep explorations in the Black Sea (MEGASEEBS), Project Report. Ber. Zentrum Meeres- u. Klimaforsch. Universität Hamburg, Hamburg: 11-21.

Egorov, V.N., Polikarpov, G.G., Gulin, S.B., Artemov, Y.G., Stokozov, N.A., Kostova, S.K. (2003) Present-day views on the environment-forming and ecological role of the Black Sea methane gas seeps. *Mar. Ecol. J.* 2 (3): 5-26 (in Russian).

Egorov, V.N., Artemov, Yu.G., Gulin, S.B. (2011) Methane seeps in the Black Sea: environment-forming and ecological role (ed., G.G. Polikarpov). ECOSEA-Hydrophysics, Sevastopol: 405 p.

Gevorkyan, V.H., Burakov, V.I., Isagulova, U.K., Semeonov, D.V., Malahov, V.P., Oleinik, F.I., Gryazanov, A.S., Shevchenko, A.F. (1991) Gas venting sea bottom build ups in the north-western Black Sea part. (Doklady*) USSR Acad. Sci*. 297 (4): 80–85 (in Russian).

Gulin, S.B., Artemov, Yu.G. (2007) Study of the Black Sea methane seeps during international expedition of RV "Meteor" (Germany) in February 2007. *Mar. Ecol. J.* 6(2): 98-100.

Gulin, S.B., Polikarpov, G.G., Egorov, V.N. (2003) The age of microbial carbonate structures grown at methane seeps in the Black Sea with an implication of dating of the seeping methane. *Marine Chemistry* 84(1-2): 67-72.

Hay, B.J., Arthur, M.A., Dean, W.E., Neff, E.D., Honjo, S. (1991) Sediment deposition in the Late Holocene abyssal Black Sea with climatic and chronological implications. *Deep-Sea Research* 38 (suppl. 2): 1211-1236.

Ivanov, M.V., Polikarpov, G.G., Lein, A.Yu., Galtchenko, V. N., Egorov, S. B., Gulin M. B., Gulin, I. I., Miller, Yu. M., Kuptsov, V. I. (1991) Biogeochemistry of carbon cycle at the methane seeps of the Black Sea. Proc. *USSR Acad. Sci*. 320(5): 1235-1240 (in Russian).

Krastel, S., Spiess, V., Ivanov, M., Weinrebe, W., Bohrmann, G., Shashkin, P., Heidersdorf F. (2003) Acoustic investigations of mud volcanoes in the Sorokin Trough, Black Sea. *Geo-Marine Letters* 23: 230-238.

Lein, A.Yu., Ivanov, M.V., Pimenov, N.V. (2002) Genesis of Methane from Cold Methane Seeps in the Dnieper Canyon, the Black Sea. *Dokl. Earth Sci*. 387 (8): 979-980.

Michaelis, W., Seifert, R., Nauhaus, K., Treude, T., Thiel, V., Blumenberg, M., Knittel, K., Gieseke, A., Peterknecht, K., Pape, T., Boetius, A., Amann, R., Jørgensen, B.B., Widdel, F., Peckmann, J., Pimenov, N. V., Gulin, M. B. (2002) Microbial reefs in the Black Sea fuelled by anaerobic oxidation of methane. *Science* 297: 1013-1015.

Naudts, L., Greinert, J., Artemov, Y., De Batist, M. (2006) Geological and morphological setting of 2778 methane seeps in the Dnepr paleo-delta, northwestern Black Sea. *Marine Geology* 227(3-4): 177-199.

Polikarpov, G.G., Egorov, V.N. (1989). Active gas-releases from the Black Sea bottom has been discovered. *Visnyk Acad. Sci. of Ukrainian SSR*, 10, Oct. 19: 108. (in Ukrainian).

Polikarpov, G.G., Egorov, V.N., Gulin, S.B., Gulin, M.B., Stokozov, N. A. (1992) Gas seeps from the Black Sea bottom – a new object of molismology. In: Molismology of the Black Sea (ed., G.G. Polikarpov), Naukova Dumka, Kiev: 10-28 (in Russian).

Polikarpov, G.G., Ivanov, M.V., Gulin, S.B., Gulin, M.B. (1993) Deposition of methane carbon in the carbon-ate chimneys grown in anoxic zone at the Black Sea slope. *Proc. Ukrainian Ac. Sci*. 7: 93-94 (in Russian).

Ryan, W.B.F., Pittman, I.I.I., Major, C.O., Shimkus, K., Moskalenko, V., Jones, G.A., Dimitrov, P., Gorür, N., Sakinc, M., Yüce, H. (1997) An abrupt drowning of the Black Sea shelf. *Mar. Geol*. 138: 119-126.

Shnukov, E.F., Sobolevskiy, Yu.V., Kutniy, V.A. (1995) Unusual carbonate build-ups at continental slope of the north-western Black Sea – an apparent consequence of the degassing of sediments. *Lithology and Minerals* 5: 541-461 (in Russian).

Shnukov, E., Pasnikov, A., Kleshtenko, S. (1999) Gas Vents on the Bottom of the Black Sea. NANU Publishing House, Kiev: 133 p. (in Russian)

Shnukov, E.F., Lein, A.Y., Egorov V.N., Kleshenko S.A., Gulin S.B., Artemov, Y.G., Arslanov, H.A, Kutnyi, V.A., Logvina E.A. (2004) Discovery in the Black Sea of deep-water biogenic buildups. *Proc. Ukrainian Ac. Sci*. 1: 118-123 (in Russian).

Thiel, V., Peckmann, J., Richnow, H.H., Luth, U., Reitner, J., Michaelis, W. (2001) Molecular signals for anaerobic methane oxidation in Black Sea seep carbonates and a microbial mat. *Marine Chemistry* 73(2): 97-112.

Wakeham, S.G., Damste, J.S.S., Kohnen, M.E.L., de Leeuw, J.W. (1995) Organic sulfur compounds formed during early diagenesis in Black Sea sediments. *Geochimica et Cosmochimica Acta* 59(3): 521-533.

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