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GEOCHEMISTRY

Study of Gas Biogeochemical Parameters of Gaseous Fluids from the Bottom of the Black Sea

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Gaseous fluid flows from sediments into bottom water of seas and oceans attract attention of oceanographers, particularly specialists in gas geochemistry [1]. Fluid flows from the Black Sea bottom were the main study object in Cruise 61 of the R/V *Professor Vodyanitskii*, carried out in the Ukrainian segment of the Black Sea in June–July, 2004. The expedition was organized and conducted by the Division of Marine Geology and Sedimentary Ore Formation, National Academy of Sciences of Ukraine. Gas biogeochemical parameters were investigated at the Institute of Oceanology (Moscow). These works were aimed at studying spatial variations in gas biochemical parameters in seawater and bottom sediments in the zone of local fluid flows.

Bottom water was sampled in fluid discharge areas detected by multibeam sonar as a gaseous plume. Samples were taken closest to the fluid discharge site in the depth interval of 200–2000 m. Specially designed equipment and methods were used for the study of gas biogeochemical parameters [2]. Water samples were taken with a hermetic bottom bathometer from the bottom layer of 1.5–2.0 m above the seafloor, with the bathometer cartridge at several meters above the bottom, and by integration of the bathometer from the water column located 100–150 m above the bottom. Bottom sediments were sampled by a gravity corer with a plastic container that fills with sediments in situ. In the case of spontaneous degassing of gas-saturated sediment after dismantling of the corer on deck, the released gas mixture inflated the container and the gas sample was taken by syringe for chromatographic analysis. Then, sediment samples were taken at different levels of the core. The content of gas components (hydrocarbons, helium, hydrogen, carbon dioxide, and permanent gases) and biochemical parameters, such as the ATP content and alkaline phosphomonoesterase activity (APHA), were simultaneously determined in water and sediment samples.

The article presents new factual data on underwater fluid discharge areas. Methane and carbon dioxide appeared to be most informative among gas components. Hydrogen, helium, and homologues of methane were not detected, because their concentration in the analyzed gas mixture was below the sensitivity of the chromatograph. The gas mixture was either sampled immediately from the plastic container of the gravity corer (or hermetic core catcher) or was extracted by phase-equilibrium degassing of seawater and sediment samples. In both cases, air was the main gas carrier. Therefore, oxygen and nitrogen were also measured methodologically. In total, approximately 100 samples were analyzed. The gas mixture contained methane (0.0–89.8 vol %) and carbon dioxide (0.0–15.5 vol %). The total content of oxygen and nitrogen varied from 8.65 to 100 vol %. Table 1 presents data on various gas mixtures obtained from the gravity corer container and hermetic core catcher or extracted from water and sediment samples.

Biochemical parameters were measured in the same water and sediment samples. In addition, certain intervals of the core and bottom and surface water samples were analyzed to estimate biological activity of seawater medium in study areas. Table 2 presents gasometric and biochemical data.

The data from Tables 1 and 2 make it possible to disclose some peculiarities in the distribution of gas biogeochemical parameters. In the study areas, bottom water is saturated with methane and carbon dioxide. The biological activity of water is sufficiently high and

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Table 1. Variations in concentrations of gas components measured in gas mixtures, vol %

Study object	Methane	Carbon dioxide	Oxygen + + nitrogen
Container of gravity corer, core catcher	0.01–89.8	0.0–2.81	8.65–100
Water	0.0–0.41	0.0–6.47	93.5–100
Sediments	0.01–12.4	0.64–5.35	84.1–99.3

Table 2. Variations in values of gas biogeochemical parameters in bottom water and sediments

Sea medium	Methane, ml/l(kg)	CO_2, ml/l(kg)	ATP, ng/l (g)	APHA, E/l(g)
Water	0.0–0.82	0.0–52.9	337–2520	55–2810
Sediment	0.0–80.8	17.5–120	55–640	144–575

sometimes exceeds the activity in surface waters. Spontaneous degassing of the gravity corer on the deck is primarily accompanied by the release of volatile components. This is indicated by the high content of methane and signs of carbon dioxide inside the plastic container. Nevertheless, sediments preserve a high residual content of both gas components and high biological activity. Moreover, carbon dioxide is always present in sediments in variable concentrations, whereas methane is not a constant component.

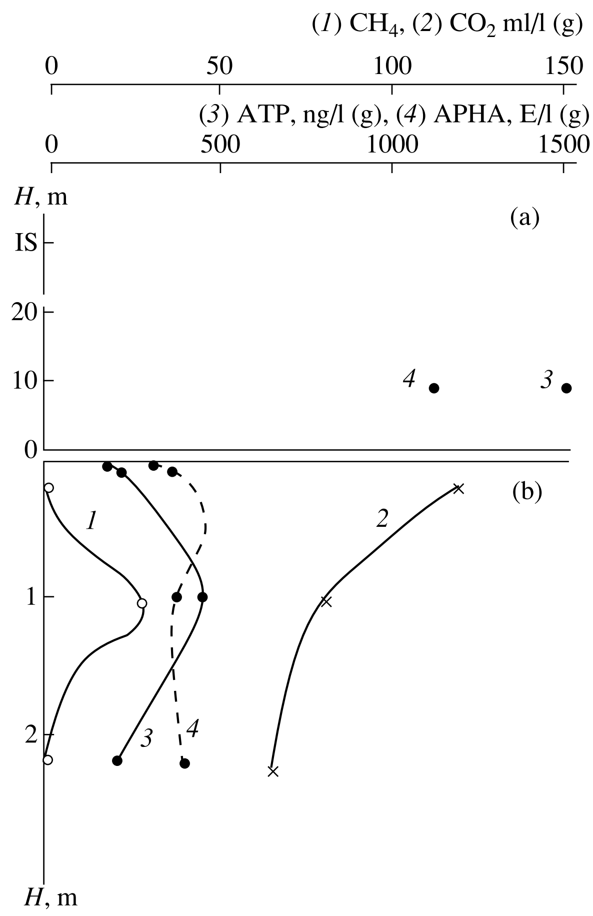

Fig. 1. Vertical distribution of gas biogeochemical parameters in (a) water and (b) sediments in the Dvurechenskii Volcano area. (*1*) Methane; (*2*) carbon dioxide; (*3*) ATP; (*4*) APHA. (IS) integral sample.

The vertical distribution of gas biogeochemical parameters in the bottom water layer is variable in different sampling sites. Figures 1–3 demonstrate data on the integral water sample taken at 100–150 m above the seafloor, the near-bottom layer located 1.5–2.0 m above the seafloor, and the sediment core. Values of all the measured gas biogeochemical parameters are several times higher than the background values at Station 5779 (2020–2060 m bsl). The content of methane in the sediment core at 100 cm is two to three orders higher than its background values. In addition, the plastic container included several liters of gas mixture released by spontaneous sediment degassing. In the course of processing of a core >12 cm in diameter, small gas hydrate (GH) crystals detected at the same level were taken for gasometric analysis. The crystals (up to a few centimeters across) rapidly diminished in size. We placed some of the crystals, which included a small quantity of host sediments, into a hermetic vessel to study the released gas mixture. During the first rapid sampling of the GH-hosted gas mixture, the methane content was an order of magnitude higher (4.69 vol %) than that of carbon dioxide (0.45 vol %). At the terminal stage of spontaneous degassing of the GH-including sediment sample in the hermetic vessel, the contents of methane and carbon dioxide increased to 7.59 and 8.07 vol %, respectively. The spontaneous degassing of GH crystals in a hermetic vessel in laboratory conditions is well consistent with the process of natural degassing of the core inside the plastic container on the deck. In the latter case, the methane and carbon dioxide contents during the first sampling of gas mixture from the container were 64.4 and 0.45 vol %, respectively. During the sampling 5–7 min later, their concentrations increased to 89.8 and 1.54 vol %, respectively.

A high similarity between modeling (in the vessel) and natural processes of GH decay indicates that the data on the container are adequate. Hence, the application of plastic container for the study of gas composition and GH origin is efficient. The analysis of obtained data suggests that the composition of the gas mixture inside the container is governed by the rapid influx of methane from GHs and the partial release of methane and carbon dioxide from the remainder of the core. Thus, the gas mixture largely characterizes the GH composition. The content of methane in the GH is more than 90%. Moreover, no admixtures were found, suggesting the correctness of theoretical considerations of GHs. However, at Station 5781 located 300–400 m away from Station 5779, the container included a small amount of gas mixture (0.04 vol % of methane) and sediments are depleted in methane and carbon dioxide (0.52 and 1.75 ml/kg, respectively). Hence, the high gas

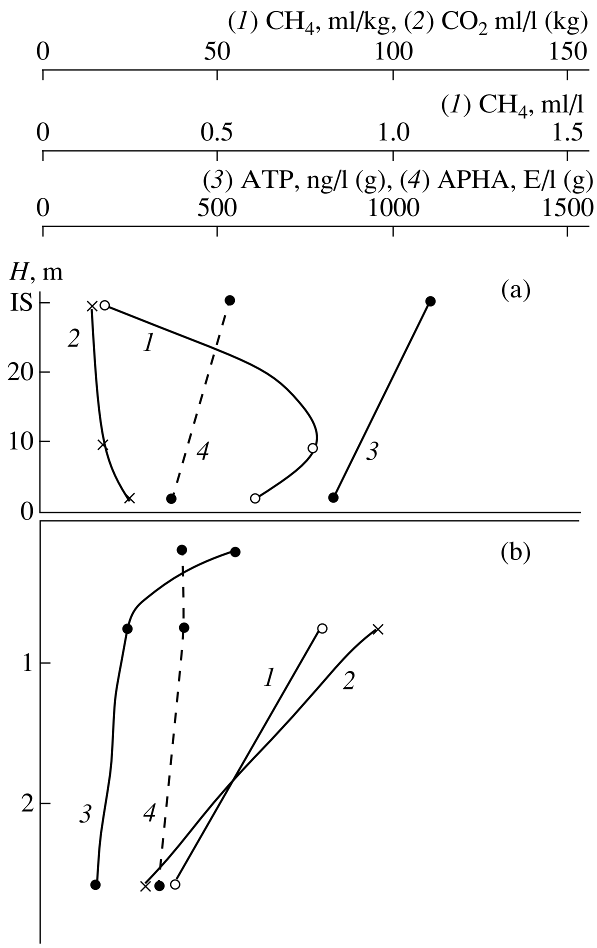

Fig. 2. Vertical distribution of gas biogeochemical parameters in (a) water and (b) sediments in the Vodyanitskii Volcano area. (*1*) Methane; (*2*) carbon dioxide; (*3*) ATP; (*4*) APHA. (IS) integral sample.

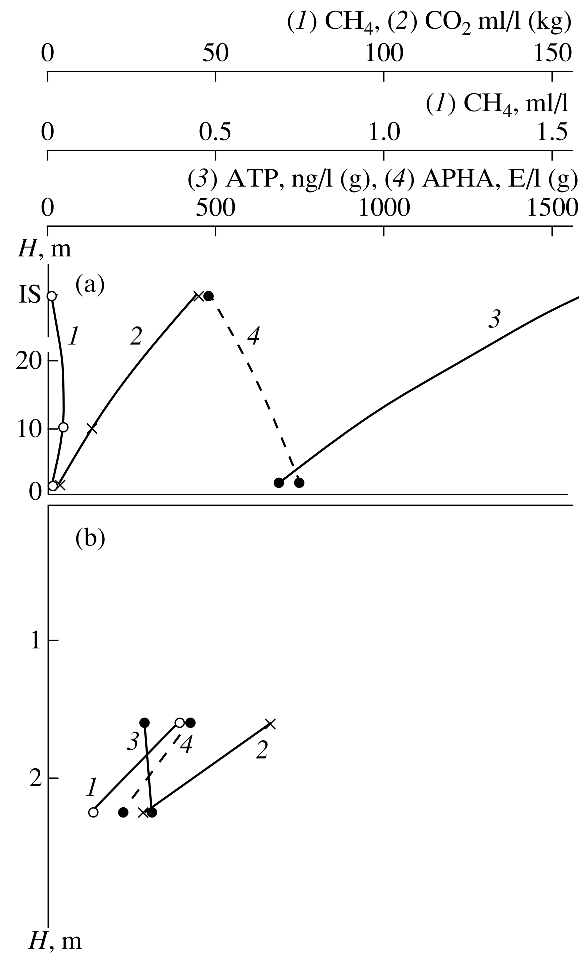

Fig. 3. Vertical distribution of gas biogeochemical parameters in (a) water and (b) sediments in the Dniester paleovalley area. (*1*) Methane; (*2*) carbon dioxide; (*3*) ATP; (*4*) APHA. (IS) integral sample.

content in sediments at Station 5779 (Fig. 1) is a local phenomenon related to the influx of both gases with the fluid flow from deeper levels of the sedimentary section. The discharge of fluids at this site is evident from the high biological activity of bottom water (Fig. 1).

A similar situation was observed at Station 5795, located near the Vodyanitskii mud volcano (Fig. 2) at 810–830 mbsl. During the first sampling, the gas mixture in the container was composed of methane (79.6 vol %) and carbon dioxide (0.26 vol %). The methane content was maximal and biological activity was high, at a level of ~1 m in the sediment core (Fig. 2). At the same level, small GH crystals were detected in the sediments. Chemical analysis revealed that they are almost entirely composed of methane (90–99 vol %). The distribution of gas biogeochemical parameters at this station is similar to that at Station 5779 and is typical of sediments containing GH. The factual material indicates the rapid degassing of a large volume of methane from GHs into the container and the significant mobility of methane and carbon dioxide in fluid flow from sediments into water. This is confirmed by their anomalously high contents in the bottom water layer and high activity of the microbial community in fluid discharge areas (Fig. 2).

At Station 5792, samples for the study of gas biogeochemical parameters were taken from the depth interval of 210–310 m. Sediments appeared to be highly saturated with gas as a result of the fluid influx. This is most evident from the presence of carbon dioxide in bottom water (Fig. 3). The ATP data indicate that the downsection decrease in the carbon dioxide content is accompanied by an increase in methane concentration and high biomass of active living microorganisms. Hence, the interval is characterized by chemolithoautotrophic processes, i.e., reduction of carbon dioxide to methane.

The obtained new data provide new insights into natural processes in the Black Sea. Fluid discharges at the seafloor substantially influence the distribution of gas biogeochemical parameters in the bottom layer. This is an important criterion for the discovery of fluid discharges and study of the mechanisms of their interaction with seawater. The ecosystem approach is based on the postulate of obligatory development of a community of microorganisms in the material and energy flow. Moreover, this community notably influences the component composition of the fluid flow. It has been established that the study areas are characterized by high biological activity of bottom waters and sediments: biochemical parameters in the bottom water layer are an order of magnitude higher as compared to the passive background areas [3]. Their distribution in the geochemical section of the bottom medium also differs from that in typical profiles [4]. Thus, we can make two important inferences. All of the sampling sites are marked by different-intensity fluid flows from the bottom into water; in contrast to fluid discharges on land, biologically active seawater substantially changes the component composition of fluid flows.

In addition, the type of medium influences the results of the phase-equilibrium degassing method, which implies a minimal retention interval of the sample with the air portion (1 day). Correspondingly, data on methane are underestimated, while those on carbon dioxide are overestimated. Nevertheless, the data obtained confirm the presence of methane (8–30 vol %) and carbon dioxide (*n* vol %) in fluid flows, suggesting a significantly higher migration capacity of methane [5]. The fluid flows are related to deep geological processes in the Black Sea region (primarily, geodynamic activity of the earth's interior). Despite the fact that fluid discharges are local processes, they represent an inexhaustible source of hydrocarbons and provide the main contribution to their general balance in the Black Sea.

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