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GEOCHEMISTRY

Chemical and Isotopic Uniformity of the Bottom Convective Water Layer in the Black Sea

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The deep anaerobic water column of the Black Sea is composed of two water masses. The upper mass is stratified in terms of temperature, salinity, and potential density. The lower quasi-uniform mass is located below 1680–1800 m [1–4]. The volume of the bottom water (400–500 m thick) is comparable with that of the aerated surface layer. The uniformity of bottom waters is confirmed by measurements of salinity and potential temperature, while in situ temperature measurements show its downward increase. The virtually uniform bottom water mass (bottom convective layer, BCL) is characterized by a neutral or slightly negative thermohaline stability and following hydrological parameters: S = 22.333 psu, θ = 8.885–8.886°C, σ_θ = 17.235 kg/m^3. The position of the upper BCL boundary is laterally variable, although its general topography remained practically stable during repeated measurements over several years. The BCL is overlain by a transitional layer (20–50 m thick) with elevated gradients of temperature, salinity, potential density, and thermohaline stability. Heat and salt fluxes are directed upward. At present, mixing of deep waters under such stratification is attributed to processes of double diffusion [1, 4, 5] induced by the geothermal heat flux from the basin bottom. These new concepts of the hydrophysical structure of basinal deep waters were developed during the past 15 years. However, they are not reflected adequately in hydrochemical studies.

In this communication, we present results of the hydrochemical structure of deep waters based on detailed studies of the BCL and the stratified water/BCL transitional layer. The studies were carried out in the northeastern part of the basin during four expeditions of the R/V *Akvanavt* in the summer and autumn seasons of 1999–2002 (Fig. 1). Samples for hydrochemical studies were collected using a cassette of 5 l Niskin bathometers combined with the SeaBird CTD sonde. At each station, 3–6 horizons were sampled within the BCL. Hydrochemical parameters were determined on board using recommended and accepted methods [6].

Deep waters of the Black Sea within the BCL are characterized by hydrophysical uniformity and relatively stable chemical composition. Table 1 presents data on the hydrochemistry of bottom waters obtained from depths exceeding 1750 m at seven stations during Cruise 33 of the R/V *Akvanavt* in 2001. Their analysis reveals that the standard deviations from average values of all hydrochemical parameters fall into error limits of the applied analytical techniques. The errors do not

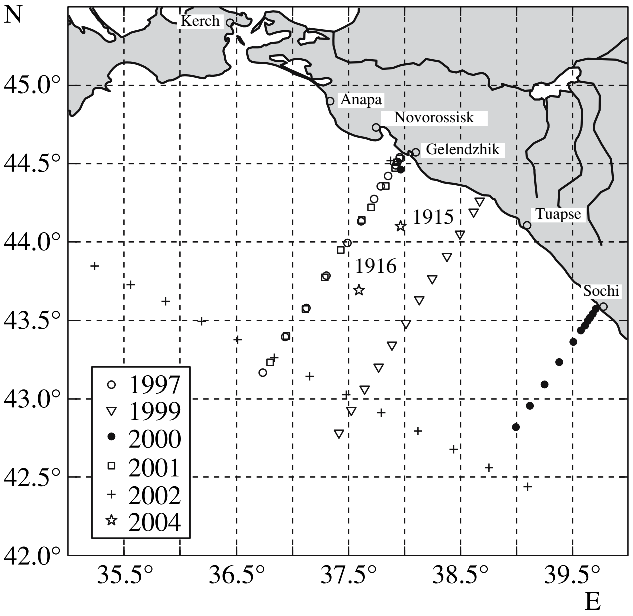

Fig. 1. Location of stations in cruises of the R/V *Akvanavt* in the years 1999–2002.

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Table 1. Hydrophysical and hydrochemical characteristics of the bottom convective layer in the Black Sea, according to data obtained during Cruise 33 of the R/V *Akvanavt* in 2001 (depths ≥1750 m, seven stations)

Parameter	Value
S, psu	22.332–22.333
T, °C	9.055–9.103
θ, °C	8.884–8.886
σ_θ	17.234–17.236
H_2S, μM	$\frac{369–381\ (34)}{376 \pm 3\ (0.9\%)}$
Alk, μM	$\frac{4375–4551\ (32)}{4450 \pm 45\ (1.0\%)}$
pH	$\frac{7.51–7.56\ (32)}{7.53 \pm 0.02\ (0.3\%)}$
NH_4, μM	$\frac{85.8–100.6\ (24)}{94.4 \pm 4\ (4.3\%)}$
PO_4, μM	$\frac{7.42–7.67\ (34)}{7.52 \pm 0.06\ (0.8\%)}$
Si, μM	$\frac{321–335\ (35)}{330 \pm 3\ (1.0\%)}$
Mn, μM	$\frac{4.0–4.3\ (27)}{4.1 \pm 0.1\ (2\%)}$
CH_4, μM	$\frac{11.8–13.4\ (29)}{12.5 \pm 0.4\ (3.4\%)}$

Note: Here and in Table 2, the numerator shows the range of values and the number of measurements (in parentheses); the denominator shows the average ± standard deviation and the relative standard deviation (in parentheses).

Table 2. Hydrogen sulfide concentration and alkalinity of waters in the bottom convective layer, according to observations of the years 1999–2002

Time and sites of sampling	H_2S, μM	Alk, μM
1999, depth ≥1750 m, 7 stations	$\frac{367–379\ (26)}{376 \pm 3\ (0.9\%)}$	$\frac{4419–4530\ (19)}{4478 \pm 33\ (0.7\%)}$
2000, depth ≥1750 m, 5 stations	$\frac{375–385\ (18)}{380 \pm 3\ (0.7\%)}$	$\frac{4400–4529\ (18)}{4485 \pm 44\ (1.0\%)}$
2001, depth ≥1750 m, 7 stations	$\frac{369–381\ (34)}{376 \pm 3\ (0.9\%)}$	$\frac{4375–4551\ (32)}{4450 \pm 45\ (1.0\%)}$
2002, depth ≥1750 m, 7 stations	$\frac{368–400\ (36)}{376 \pm 6\ (1.7\%)}$	–

exceed 1% for the volumetric methods (H_2S, Alk) and 5% for the photometric methods (NH_4, PO_4, Si, and Mn). The errors are similar for the potentiometric (pH) and chromatographic (NH_4) methods.

The data on hydrogen sulfide and alkalinity demonstrate that average concentrations of chemical components in bottom waters of the northeastern Black Sea remained stable at least during four years of observation regardless of sampling sites (Table 2).

The available data indicate only the relative uniformity of the chemical composition in the bottom water layer. We can observe lateral and vertical heterogeneities against the general average background. For example, bottom waters are characterized by an elevated H_2S content at the remote offshore stations along the profile of 2000 and the southeastern end of the profile of 2002, where the upper BCL boundary rises to 1640–1680 m. This is evident from average values of H_2S (2000) and its maximal values (up to 400 μM) recorded in the profile of 2002 (Table 2). Some stations show that the H_2S concentrations within the BCL in the southeastern segment of the profile 2002 (Station 1320) are 10–15 μM higher as compared with their values at Station 1330, which is located at the northwestern end of the profile (Fig. 2). The figure also demonstrates that the depth of the upper BCL boundary in the profile of 2002 increases from 1640 m in the southeast to 1810 m in the northwest. As in the profile extending from Sochi (2000), the highest position of the upper BCL boundary in the southeastern part of the study area is attributed to high heat flow from the seafloor [7].

The less distinct vertical heterogeneity in the distribution of hydrochemical characteristics within the BCL is reflected in development of water layers and lenses with elevated concentrations of components (in particular, H_2S) near the bottom and, locally, in the upper part of the uniform layer. The nature of these low anomalies in the distribution of hydrochemical characteristics is probably similar to that of the reticular thermohaline stability in the BCL, i.e., the appearance of lenses with negative stability within the BCL against the background of neutral parameters [7]. As a whole, the bottom layer is uniform. This is also indicated by the vertical gradient of hydrochemical parameters. For example, the average vertical H_2S gradient below the upper BCL boundary is ±0.03 μM/m. Gradients of other hydrochemical parameters are similarly low. Therefore, both absolute and relative deviations from the average values of all hydrochemical parameters in the BCL waters are low (Tables 1, 2). In fact, these values are determined by the detection limits of analytical methods.

The BCL is separated from the overlying stratified water mass by a transitional layer (20–50 m thick), which is called the deep density jump layer (DDJ layer) [3]. It is characterized by elevated gradients of *T*, θ, *S*, σ_θ, and thermohaline stability. The heat and salt fluxes are directed upward from the BCL toward the stratified water column. The transitional layer is also characterized by a sharp increase in the gradients of concentrations of H_2S and biogenic elements [7]. Figure 2 shows the vertical distribution of the potential temperature and hydrogen sulfide at stations 1320, 1322, and 1330 in

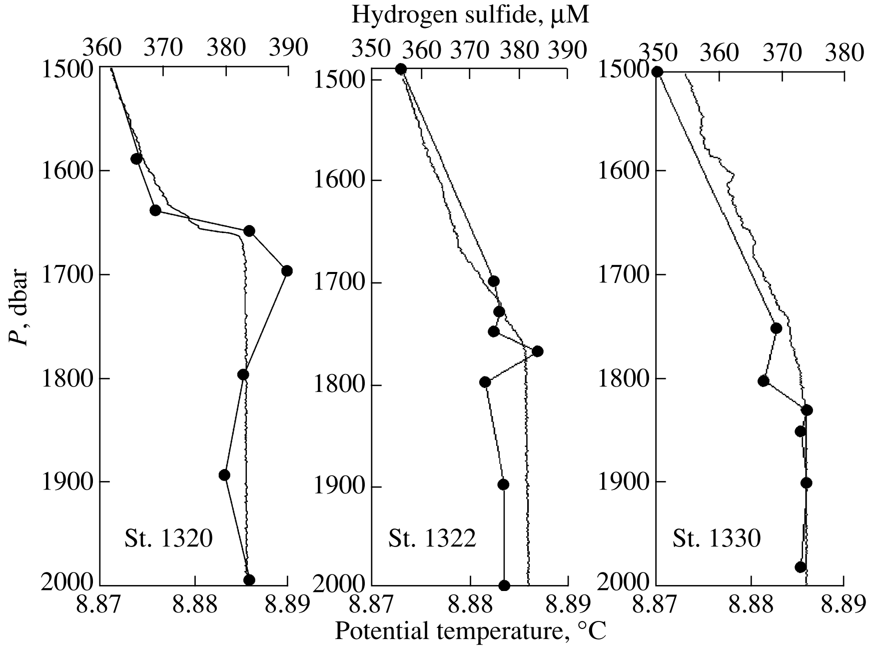

Fig. 2. Potential temperature and hydrogen sulfide concentration in deep waters of the Black Sea at stations 1320, 1322, and 1330 during the expedition of 2002.

2002. It is seen that the temperature jump in the transitional layer can be manifested differently. It can be sharp (e.g., Station 1320), less developed (Station 1322), and obscure (Station 1330). Depending on the hydrophysical parameters, the H_2S gradient is also differently developed.

The H_2S gradient does not exceed 0.1 μM/m in the depth interval from 1000 m to the lower BCL boundary. According to our observations, the gradient sharply increases to 0.23–0.75 μM/m in the DDJ layer. As was mentioned, the H_2S gradient is close to zero (±0.03 μM/m) at deeper levels of the BCL. Like heat and salt fluxes, fluxes of H_2S and biogenic elements are directed toward the overlying stratified water mass.

The H_2S gradient determined for the DDJ layer (0.23–0.74 μM/m) is comparable with that at the upper boundary of the H_2S-contaminated zone (0.5–0.6 μM/m). The assessment of the upward H_2S flux from the BCL and its role in the general distribution and budget of hydrogen sulfide in the basin is a task for further studies.

Many researchers have studied the sulfur isotopic composition in sulfates and hydrogen sulfide of the Black Sea. The results of these studies are summarized in [8, 9]. The available data demonstrate that the average isotopic composition of sulfates ($\delta^{34}S$) in the oxygen-rich and H_2S-contaminated zones of the sea is 18.5 and 19.5 ‰, respectively. The Black Sea receives annually $2.82 \cdot 10^6$ t of sulfates (average $\delta^{34}S$ 4.6‰) brought by rivers and $\sim 540 \cdot 10^6$ t of sulfates (average $\delta^{34}S$ 19.8‰) provided by the deep current through the Bosporus Strait.

The data on the isotopic composition of H_2S are approximately two times more as compared to the data on sulfates. The $\delta^{34}S$ (H_2S) value varies in the entire anaerobic zone from –32.6‰ at the upper boundary to –42‰ at 2200 m (average –39.6‰). According to published data, the vertical section of H_2S-contaminated waters comprises the upper (up to a depth of 300 m), intermediate (300–1500 m), and deep (>1500 m) zones. The maximal isotopic variability is characteristic of the upper zone, where the $\delta^{34}S$ (H_2S) value ranges from –32.6 to –40.8‰ (average –38.1‰). The intermediate zone is characterized by the practically uniform isotopic composition of sulfur in H_2S (average –40.0‰). The sulfur isotopic composition in deep waters of the sea is least known. According to available data, like the upper layer, the deep layer is characterized by heavier isotopic composition ($\delta^{34}S$ from –37.4 to –40.3‰, average –38.4‰) [8].

Extremely low values of the sulfur isotopic composition in H_2S (approximately –40‰) and the high sulfur fractionation factor (difference between isotopic compositions of sulfur and hydrogen sulfide) of about 60‰ imply very low rates of bacterial sulfate reduction. The slightly heavier isotopic composition of sulfur in H_2S recorded in the upper and bottom zones is explained by the intensification of sulfate reduction [12] and the influx of isotopically heavier H_2S from the bottom sediments in the deep zone [8, 9].

In order to confirm the isotopic uniformity of the BCL, samples were taken at two stations from depths exceeding 1500 m near Gelendzhik in the northeastern

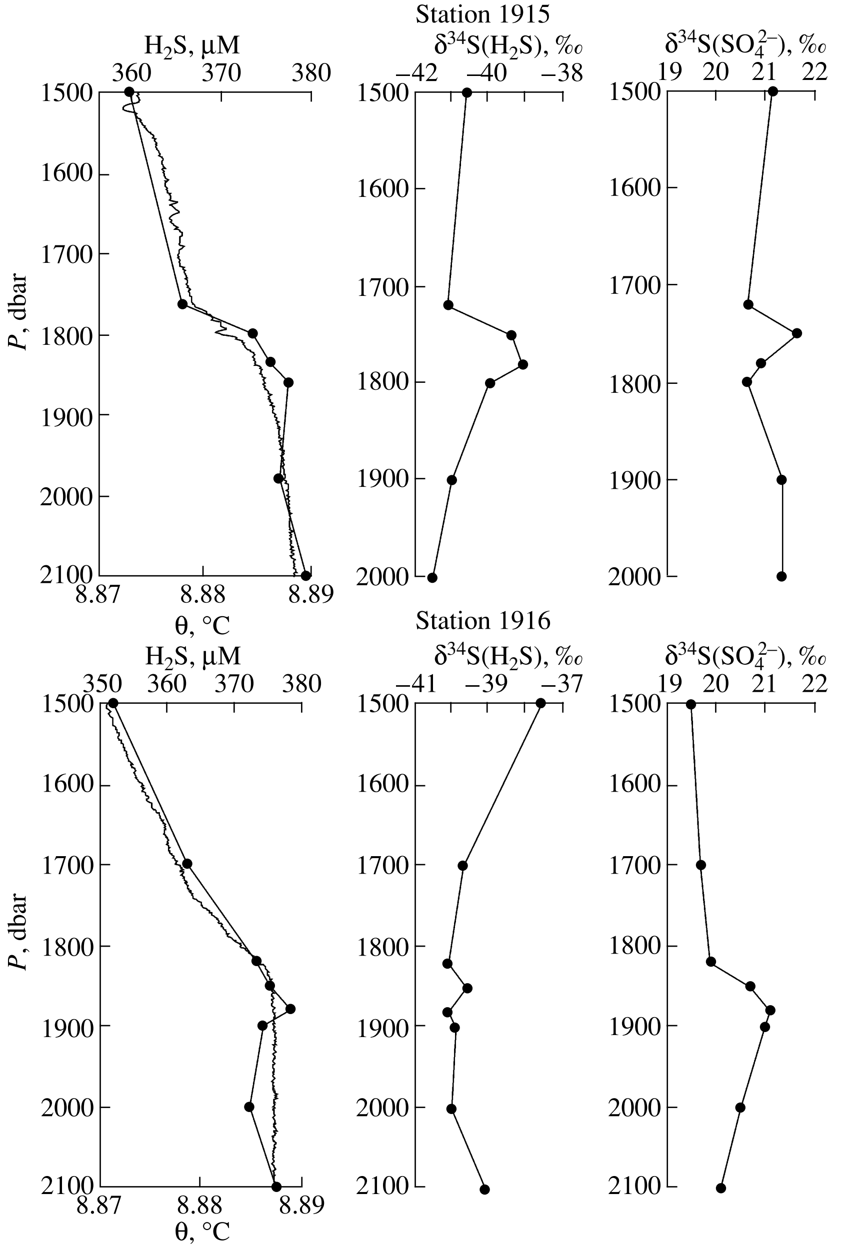

Fig. 3. Potential temperature, hydrogen sulfide concentration, and isotopic sulfur composition of H_2S and SO_4^{2-} in deep waters of the Black Sea.

part of the sea (Fig. 1). Figure 3 demonstrates data on concentrations of H_2S and sulfur isotopic composition in hydrogen sulfide and sulfates. Among 15 water samples examined, 11 samples were taken from the uniform convective layer. In these samples, the $\delta^{34}S$ (H_2S) value ranges from –39.1 to –41.5‰ (average –40.0‰). The sulfur isotopic composition in sulfates, i.e., $\delta^{34}S$ (SO_4), varies from 19.9 to 21.6‰ (average 20.8‰). These data suggest the following regularity: waters of the Black Sea below 300–500 m are uniform with respect to the sulfur isotopic composition in H_2S, the $\delta^{34}S$ (H_2S) values are close to –40‰, and the previously assumed concentration of the heavy sulfur isotope is lacking in the bottom layer. To the contrary, data on the sulfur isotopic composition in sulfates indicate that the $\delta^{34}S$ (SO_4) value in the BCL increases to 20.8‰ as compared to the average value of 19.5‰ in the anaerobic zone of the sea. Such a slight but significant concentration of the heavy sulfur isotope in sulfates is explained by the consumption of sulfates in the course of bacterial sulfate reduction. The absolute diminution of sulfates in waters of the H_2S-contaminated zone (the bottom one included) cannot be recorded, because the concentration of sulfates in waters increases downward due to the salinity growth from 16.0 mM in the surface layer to 17.6 mM at a depth of 2000 m. However, the downward decrease in the SO_4/Cl-value from 0.141 to 0.137 suggests that the sulfate concentration in the bottom layer is approximately 2% lower as compared with the initial one. The slight relative exhaustion of sulfates due to fractionation during sulfate reduction is the process responsible for the growth of the $\delta^{34}S$ value to 20.8‰ in the remaining portion.

Inorganic (carbonate) carbon in deep waters of the Black Sea is enriched in the light ^{12}C isotope. At a depth of 2000m, the $\delta^{13}C$ value in such waters is –6.8‰ [13, 14]. Data on the isotopic composition of inorganic carbon are summarized (with account for later measurements) in [15]. They show that the concentration of the light isotope in the hydrosulfuric zone shows positive correlation with the growth of the total inorganic carbon and the $\Delta C/C_T$ value, i.e., with the relative growth of the inorganic carbon in its total concentration. Special studies of the carbon isotopic composition in waters of the BCL have not been carried out. However, taking into consideration the stability of the alkali reserve and pH value in bottom waters (Tables 1, 2) and, consequently, $\Delta C/C_T$ value of approximately 0.2, we can assume that the isotopic composition of inorganic carbon in waters of the BCL should also be stable.

The available data indicate that waters of the BCL are characterized not only by the hydrophysical uniformity, but also by the hydrochemical and isotopic uniformity. The total mineralization and major salt composition of waters are determined by the influx of transformed Bosporus waters. Like sulfur and carbon isotopic compositions, the concentrations of hydrogen sulfide and biogenic elements are determined by in situ anaerobic processes of the conjugate biogeochemical cycles of carbon and sulfur. Exchange processes at the water–bottom interface also make a contribution to concentrations of the last components.

According to the existing concepts, waters of the BCL have evolved significantly after the initial stage and the growth of its thickness at the present stage is negligible. The uniformity of physical and chemical characteristics of the BCL is related to the mechanism of double diffusion of salts and heat driven by the geothermal heat flow. The neutral thermohaline stability of waters in the BCL and, especially, the presence of lenses of water with negative stability imply relatively rapid convective mixing, which provides the uniformity of hydrological and hydrochemical characteristics of the water mass.

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