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The pattern of $\delta^{13}C_{org}$ versus HI/OI relation in recent sediments as an indicator of geochemical regime in marine basins: comparison of the Black Sea, Kara Sea, and Cariaco Trench

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Abstract

An approach is suggested to evaluate the geochemical regime of marine basins. By comparative study of the carbon isotopic composition of organic matter and its hydrogen index to oxygen index ratio in recent sediments a significant role of chemosynthetic bioproduction in the Black Sea, and extensive oxidative diagenesis of the organic matter in the Kara Sea have been demonstrated. The relative role of chemosynthetic production in the Cariaco Trench seems to be different compared to that in the Black Sea.

Keywords: Black sea; Kara sea; Cariaco trench; Carbon isotopes; Pyrolysis study; Chemosynthesis

1. Introduction

The carbon isotopic composition ($\delta^{13}C$, ‰) of organic matter in sediments is often used to identify its source and the type of diagenetic transformation (e.g. Galimov, 1995). Rock-Eval pyrolysis data, including the hydrogen index (HI) to oxygen index (OI) ratio, is routinely used for evaluation of hydrocarbon potential and structural characteristics of organic matter (e.g. Espitalié et al., 1977). A combination of these two techniques for organic material from recent marine sediments promises further insight in its diagenesis. This paper aims to demonstrate the benefits of this approach for evaluation of redox conditions in marine basins. Geochemical peculiarities of three marine basins, the Black Sea, the Kara Sea of the Arctic Ocean, and the Cariaco basin are considered. The reason for comparing them is that they are similar in one main feature, while they are different in others. The Black Sea is distinguished by its hydrogen sulfide regime in the water column and a significant input of terrestrial material due to Danube River discharge. The Kara Sea, like the Black Sea, has a strong continental influence due to the discharge of the great Siberian rivers, Ob' and Enisey. However, in contrast to the Black Sea this is a well oxygenated shallow sea. The Cariaco basin is similar to the Black Sea in that it is an anoxic basin, but it has no major river discharging into it. These basins have been studied at different

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times by a geochemical group from the V.I. Vernadsky Institute (Moscow, Russia) during cruises of the research vessel (R/V) "Akademic Boris Petrov" (Report on the 14th Cruise of the R/v "Akademic Boris Petrov", 1991; Galimov et al., 1996; Galimov et al., 1998; Kodina et al., 1996; Kodina et al., 1999).

2. Methods

The primary data and full details of the analytical procedures are presented in the literature sources mentioned above. The following is a short description of the methods used. The pyrolysis of organic matter was performed by use of a Rock-Eval II instrument at the temperature range from 300 to 600 °C with the rate of temperature rise of 25 °C/min. HI is determined as the yield of reduced products of pyrolysis (S_2) relative to the total organic carbon (mg HC/g TOC) and OI is the yield of the oxygen bound organic carbon (S_3) relative to TOC (mg CO_2/g TOC). The hydrogen index HI is a function of the relation H/C in organic matter. The oxygen index OI reflects the relative content of oxygen containing functional groups. In our experience, the range from 300 °C ordinarily used for pyrolytic study of fossilized organic matter, provides more reliable interpretation than lower temperature regimes, sometimes used for young sediments. The reproducibility of S_2 and S_3 are within 15–20%. The Rock-Eval analyses were performed at least in duplicate, and repeated if the difference between the first two runs exceeded 20%. The standard deviation from the averaged values was well within ± 15%. The use of HI/OI relation excludes uncertainty related to the determination of TOC contents. T_{max} (temperature of the maximal yield of S_2) is a measure of maturation of organic matter. In the studied recent sediments, T_{max} varied mainly from 350 to 420 °C. To avoid the effects of admixture of fossilized organic matter, the samples with $T_{max} \geq 425$°C were excluded from consideration. Such samples represented less than 5% of the data collection.

The organic carbon content (C_{org}) was measured using a "Carlo Erba" CHNS analyzer with a reproducibility better than 15% in the range of C_{org} from 0.2% to 8%. Carbon isotope compositions were determined by use of a VARIAN-MAT-230 mass-spectrometer. All the carbon isotopic results presented here are given relative to the V-PDB standard ($^{13}C/^{12}C = 0.0112372$). The decarbonated and dried sediment samples were oxidized at 900 °C in oxygen flow, and the purified CO_2 was used for the isotope analysis. Precision was ± 0.2‰.

3. Results and discussion

3.1. The Black Sea

Fig. 1 shows the $\delta^{13}C$-distribution for organic carbon in the surface layer (0–1 cm) of the sediments in the north-western part of the Black Sea. The samples were collected in 1995 and 1997 within the EROS program (Galimov et al., 1998).

The Danube River delivers to its mouth terrestrial material with isotopically light organic carbon, which is characterized by $\delta^{13}C$ values of about − 26‰ to − 28‰. This results in isotopically depleted organic matter in sediments of the littoral region of the sea. The shelf area more remote from the coast is characterized by relatively higher $\delta^{13}C$ values, typical for marine conditions ($\delta^{13}C$ − 22‰ to − 23‰). However, in the deep sea deposits the organic carbon again becomes isotopically light (less than − 25‰).

The ^{13}C-depletion of the organic carbon in the deep sea sediments is characteristic not only of the recent deposits, but also for the sediments through the whole studied sedimentary profiles. The $\delta^{13}C$ values for organic carbon vary mainly between − 24‰ and − 26‰ (Fig. 2).

One might suggest that isotopically light carbon is characteristic of plankton in the Black Sea in general (Freeman et al., 1994). In that case, the higher $\delta^{13}C$ values for the shelf area are exceptional and might be due to a high biodegradation rate and the effect of exhaustion of the inorganic carbon source with the light carbon isotope (e.g. Deuser, 1970). However, it is seen from Fig. 2 that marine bioproducers in the surface waters of the Black Sea show $\delta^{13}C$ values from about − 20.5‰ to − 22.5‰ (Kodina et al., 1996).

The traditional interpretation for isotopically depleted carbon in marine sediments is that it is due to a contribution of terrestrial material (e.g. Calvert and Fontugne, 1987). However the Rock Eval data disagrees with such an interpretation. Fig. 3 presents a

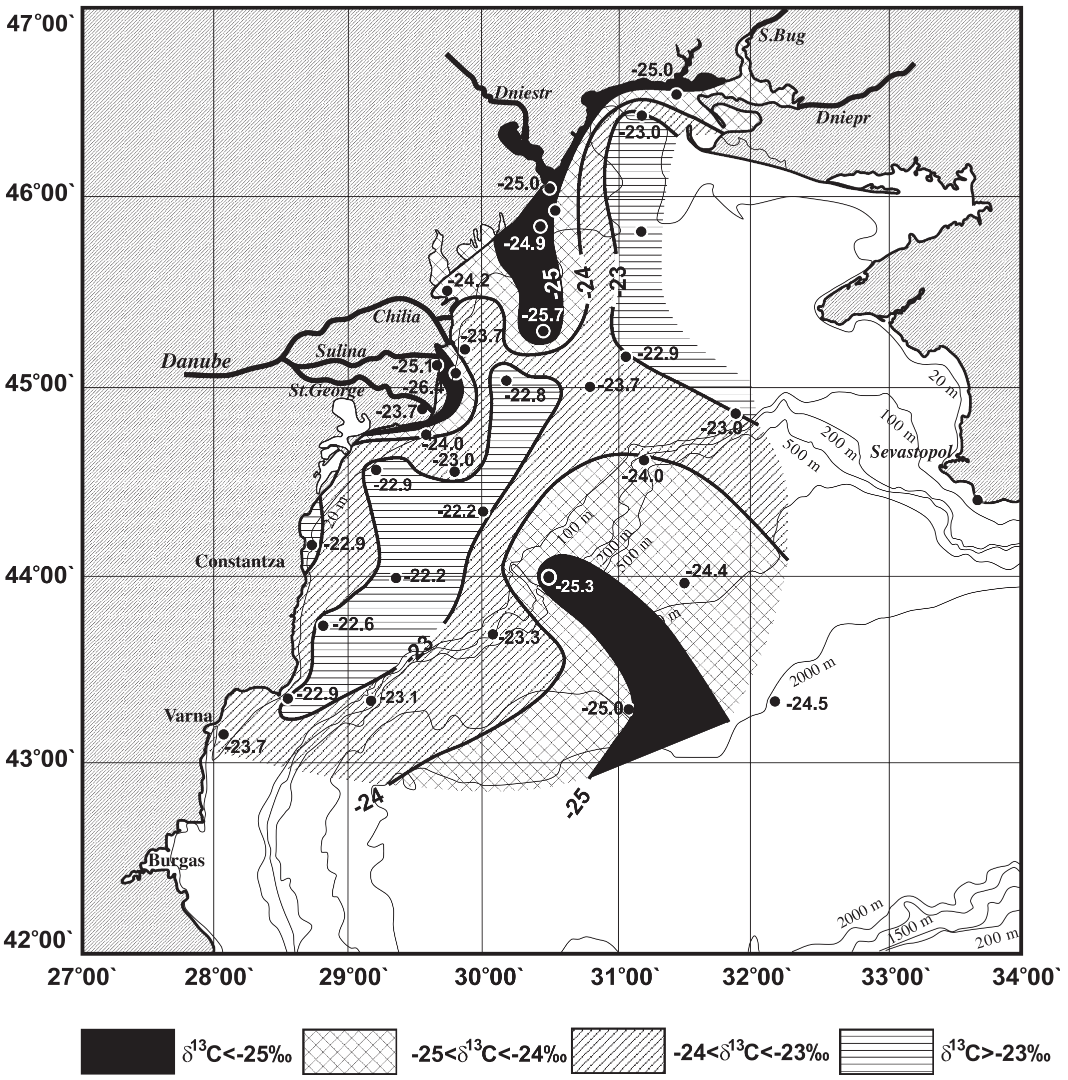

Fig. 1. Distribution of the δ^{13}C values of organic carbon in the surface layer (0–1 cm) of sediments in the north-western part of the Black Sea.

plot of the δ^{13}C versus the HI/OI values for organic carbon from Black Sea sediments. The samples with a significant input of terrestrial material have relatively low δ^{13}C values. As terrestrial organic matter is enriched in the oxygen bearing compounds such as carbohydrates and lignin, it is characterized by a higher oxygen content and hence a lower HI/OI ratio. In contrast, plankton-derived material containing more lipids is characterized by a higher HI/OI ratio. At the same time, organic carbon that originates from marine plankton is depleted in the light isotope compared to terrestrial carbon. This causes the correlation between δ^{13}C and HI/OI ratio, which is visible in Fig. 3. This correlation reflects mixing of organic matter from the two end members in different proportions. Variability of the end members can worsen the correlation. However, in the present case the data points for the deep sea organic carbon fall away from the mixing line. Organic matter in the deep sea sediments shows a relatively high hydrogen to oxygen ratio index, which is similar to that of plankton or bacterial material. This is evidence that a different

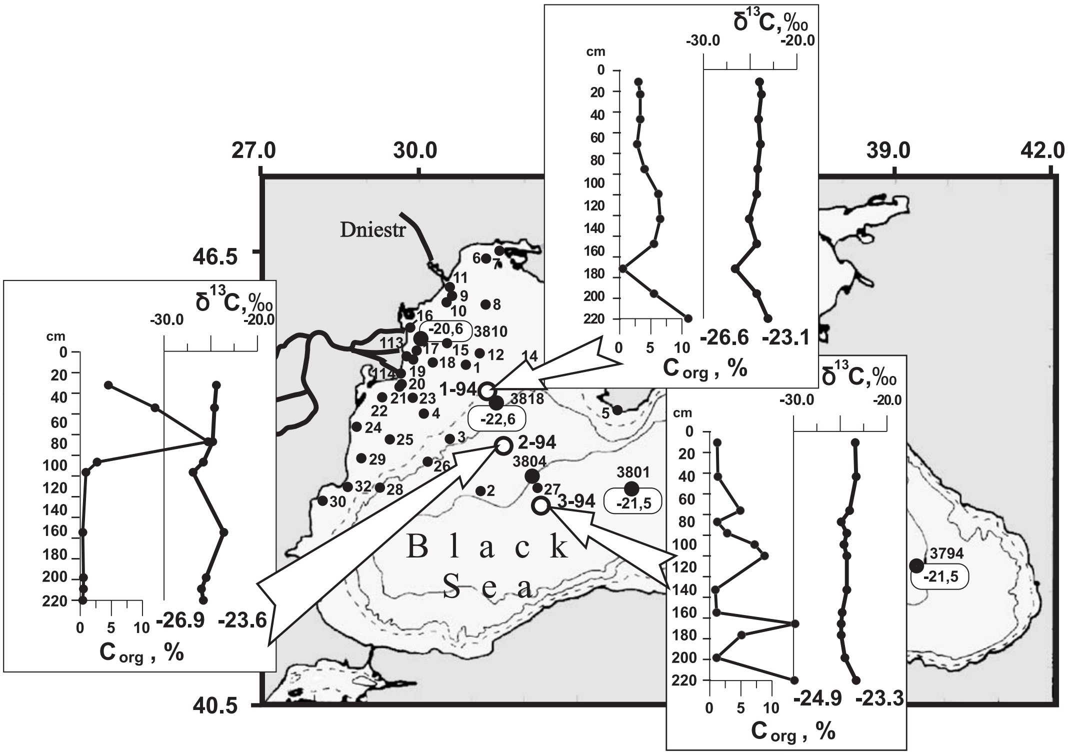

Fig. 2. Variations of δ^{13}C values (‰) and concentration of organic carbon (C_{org}, %) in sedimentary profiles (cm-scale) in Black Sea bottom deposits. The site numbers are indicated. The dashed line is the boundary of the hydrogen sulfide zone. In the ovals, δ^{13}C values obtained for marine plankton at the corresponding sites are indicated.

mechanism from that of simple mixing of organic matter from marine and terrestrial sources is needed to obtain the isotopic composition of the deep sea organic carbon in the Black Sea.

I believe that the most plausible explanation is that the observed phenomenon is related to the hydrogen sulfide regime of the Black Sea. It has been suggested that there is a layer of high microbial activity in the redox zone where molecular oxygen and hydrogen sulfide coexist (Sorokin, 1982; Karl and Knauer, 1991). Chemosynthetic bioproduction may have been comparable to photosynthetic bioproduction in this zone. Biochemical oxidation of H_2S is a source of energy during chemosynthetic bioproduction (Jorgensen et al., 1991). The bacterial bioproduction in the redox zone is estimated to be about 50–100 mg/m^3 and 40–60 mg/m^3 day from this amount is chemosynthetic bioproduction (Sorokin and Avdeyev, 1991). Indeed, as shown in Fig. 4, there is a spike of particulate organic carbon (POC) concentration at the boundary of the anoxic zone.

Laboratory experiments show that chemosynthetic thiosulfate oxidizing bacteria fractionate carbon isotopes more strongly than photosynthetic organisms (Ruby et al., 1987). Therefore, the biomass of bacteria must have been depleted in the ^{13}C isotope 4–6‰ more compared to that of marine plankton. Again, it follows from Fig. 4 that at the interval of overlapping of toxic and anoxic regimes, where chemosynthesis is expected to be most intense, there is a significant shift towards more negative δ^{13}C values (Kodina et al., 1996). It should be noted that Fry et al. (1991) did not find any significant carbon isotopic change at the top of the sulfide zone in the Black Sea.

Below the redox zone, bacterial production sharply decreases. However, chemosynthesis is a characteristic of not only the redox zone but occurs throughout the whole profile of the anaerobic water column of the

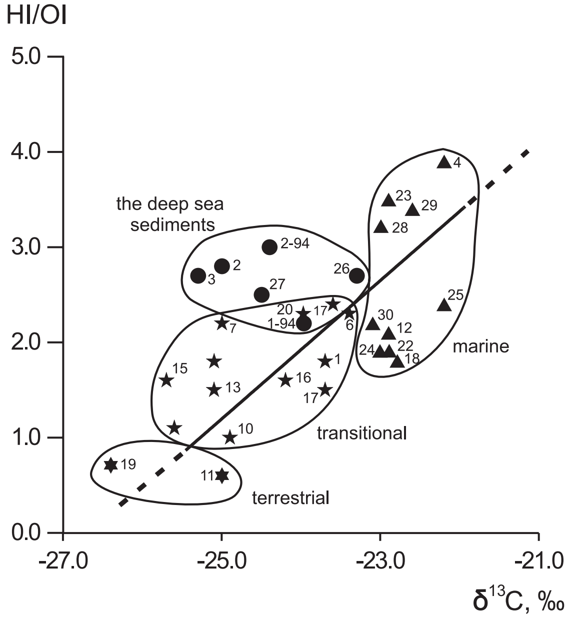

Fig. 3. δ^{13}C values vs. HI/OI relationship for the organic matter from the sub bottom sediments of the Black Sea. The data are parceled out in accordance with the prevailing source of the organic matter.

Black Sea, but much less intense (Sapozhnikov, 1992).

It has been reported that there is a regular trend of decreasing δ^{13}C values of CO_2 with depth in the Black Sea, from about 0‰ to −2‰ at the surface to −6‰ to −7‰ at the bottom (Deuser, 1970; Fry et al., 1991). This must have led to a gradual change of δ^{13}C of organic carbon with depth to more negative values, which is actually observed (Calvert and Fontugne, 1987; Freeman et al., 1994).

On the basis of the considerations stated above the following geochemical model for the Black Sea can be proposed (Fig. 5). River discharge delivers organic carbon with δ^{13}C values from −28‰ to −26‰. Mixing of the land-derived material with the autochtonous marine bioproduction gives δ^{13}C values of about −25‰ to −23‰ for the littoral organic carbon. On the shelf area, planktonic material dominates as a source of organic carbon in sediments. In the hydrogen sulfide zone, chemosynthetic bacteria produce additional organic matter with hydrogen index to oxygen index ratios similar to that of planktonic origin, but with a different isotopic composition that results in relatively isotopically light organic carbon in the deep sea sediments.

3.2. The Kara Sea

The Kara Sea is a shallow water sea with a mean depth of about 110 m. The deepest part is the Novaya Zemlya Trough where depths exceed 400 m. The Kara Sea is distinguished by the strong influence of continental river discharge. The Ob' and Enisey rivers deliver about 1200 km^3/year of river water into the Kara Sea (compared to 180 km^3/year of the Danube). Ob' and Enisey drainage basins occupy nearly 5.5 million km^2 (compared to 0.82 million km^2 of the Danube). The general geochemical characteristics of the Kara Sea can be found elsewhere (Danyushevskaya et al., 1980; Lisitzin, 1994; Gordeev, 2000).

The data discussed here was obtained by analysis of samples collected during the 22nd cruise of the R/V "Academik Boris Petrov" (Galimov et al., 1996). Fig. 6 shows the location of the sampling

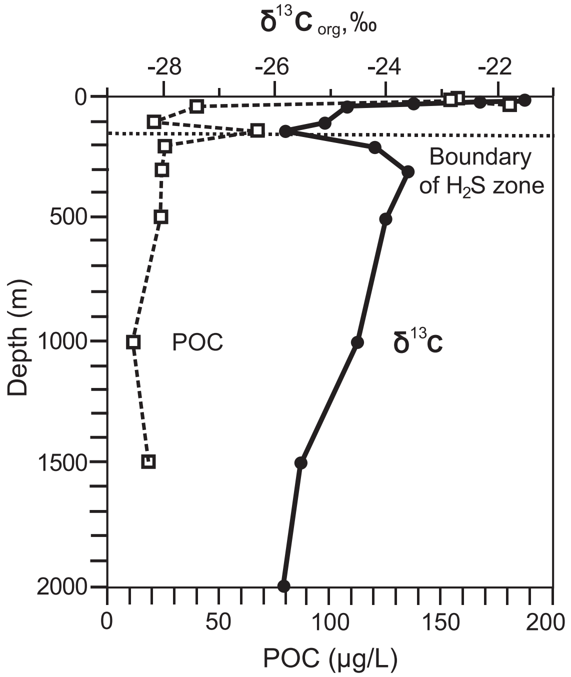

Fig. 4. Variation of δ^{13}C values and concentration of particulate organic carbon (POC) in the water column of the Black Sea (data from Kodina et al., 1996).

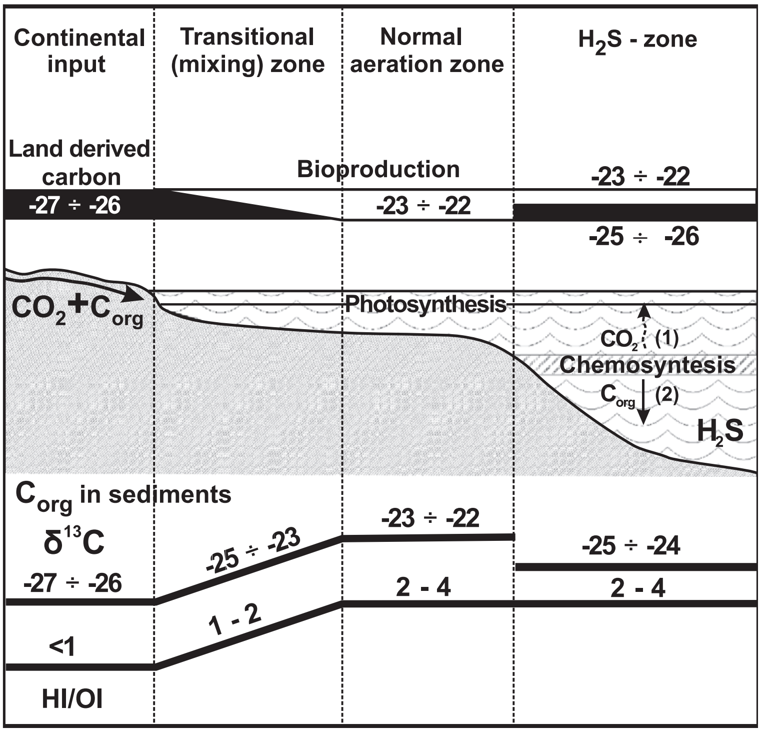

Fig. 5. A model describing geochemical zonation in the Black Sea characterized by the presence of chemosynthetic production of organic matter in the redox layer.

stations in the Kara Sea. About 160 locations have been sampled. Also, zonation of the redox state of subsurface sediments is shown. During the cruise, redox potential (Eh) was measured throughout the sediment cores. As an indicator of the redox state of the subsurface sedimentary profile we used a conventional parameter: the thickness of the sediments above the boundary of Eh-transition from positive to negative values. Sediments with a well-developed oxidized layer characterized by positive Eh-values persisting to a considerable depth (defined in Fig. 6) are shown by dense hatching. This is typical for the Novaya Zemlya trough (depression along the south–east coast of the Novaya Zemlya island) and the adjacent area. The less dense hatching corresponds to normal redox conditions.

Fig. 7 presents δ^{13}C values of organic carbon in the surface layer of the sediments. δ^{13}C values of about -22‰ are characteristic of planktonic organic carbon in the North Atlantic. These values are typical for sediments just offshore of the north and south tips of the Novaja Zemlya, where Atlantic waters enter the Kara Sea. The south-eastern part of the Kara Sea has sediments dominated by isotopically light organic carbon derived from terrestrial plants. The most isotopically depleted organic carbon with δ^{13}C values of -26‰ to -28‰ occurs at the Ob' and Enisey river mouths.

Fig. 8 presents the δ^{13}C versus HI/OI plot for organic matter from the surface layer of sediments at different sites in the Kara Sea. The mixing line appears to be similar to that observed for the case of the Black Sea. However, a large number of samples have hydrogen to oxygen index ratios lower than samples with the most isotopically depleted organic matter. From their pyrolysis characteristic these samples might be considered as representatives of land-derived organic matter. However, their carbon isotopic composition ranging from -23‰ to -24‰ corresponds to altered planktonic or mixed type of organic matter rather than typical terrestrial material.

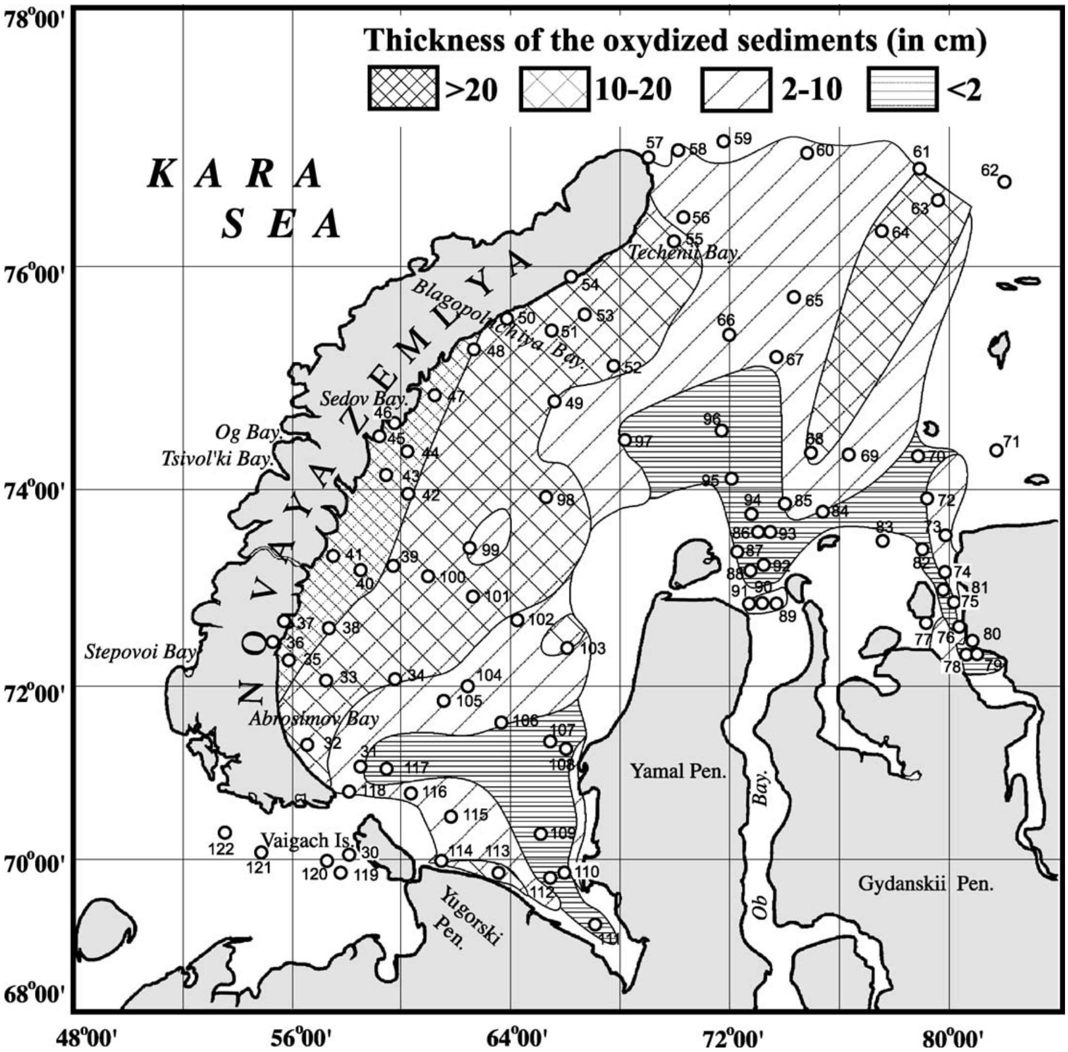

Fig. 6. Zonation of the redox conditions in the Kara Sea. The dense hatching corresponds to higher oxidated states. The latter is evaluated based on the thickness (in cm) of the sub-bottom sediments retaining positive Eh-values. Also the sampling site numbers are indicated.

Analysis of the pattern shows that all these samples are from the sediments with the highest oxidation state. As seen from Fig. 7, the data for the highly oxygenated part of the sea deviate significantly from the mixing line. A similar deviation, but in the opposite direction and reflecting a different phenomenon, is characteristic of the Black Sea.

Fig. 9 illustrates the proposed model for the Kara Sea. It is similar to that for the Black Sea (Fig. 5) for three zones out of four. But the peculiarity of the Black Sea is its hydrogen sulfide zone. The organic matter deposited there has the same HI/OI ratio as planktonic material, but is relatively enriched in the light carbon isotope. The peculiarity of the Kara Sea is the zone of highly oxygenated water along Novaya Zemlya. The organic carbon in sediments shows the same isotopic composition as planktonic material but much lower HI/OI ratios, reflecting a higher oxygen index. In the given case this is not a property of the initial biological material, but has been acquired during oxidative diagenesis. Part of the organic carbon was oxidized to CO_2. This organic carbon was lost.

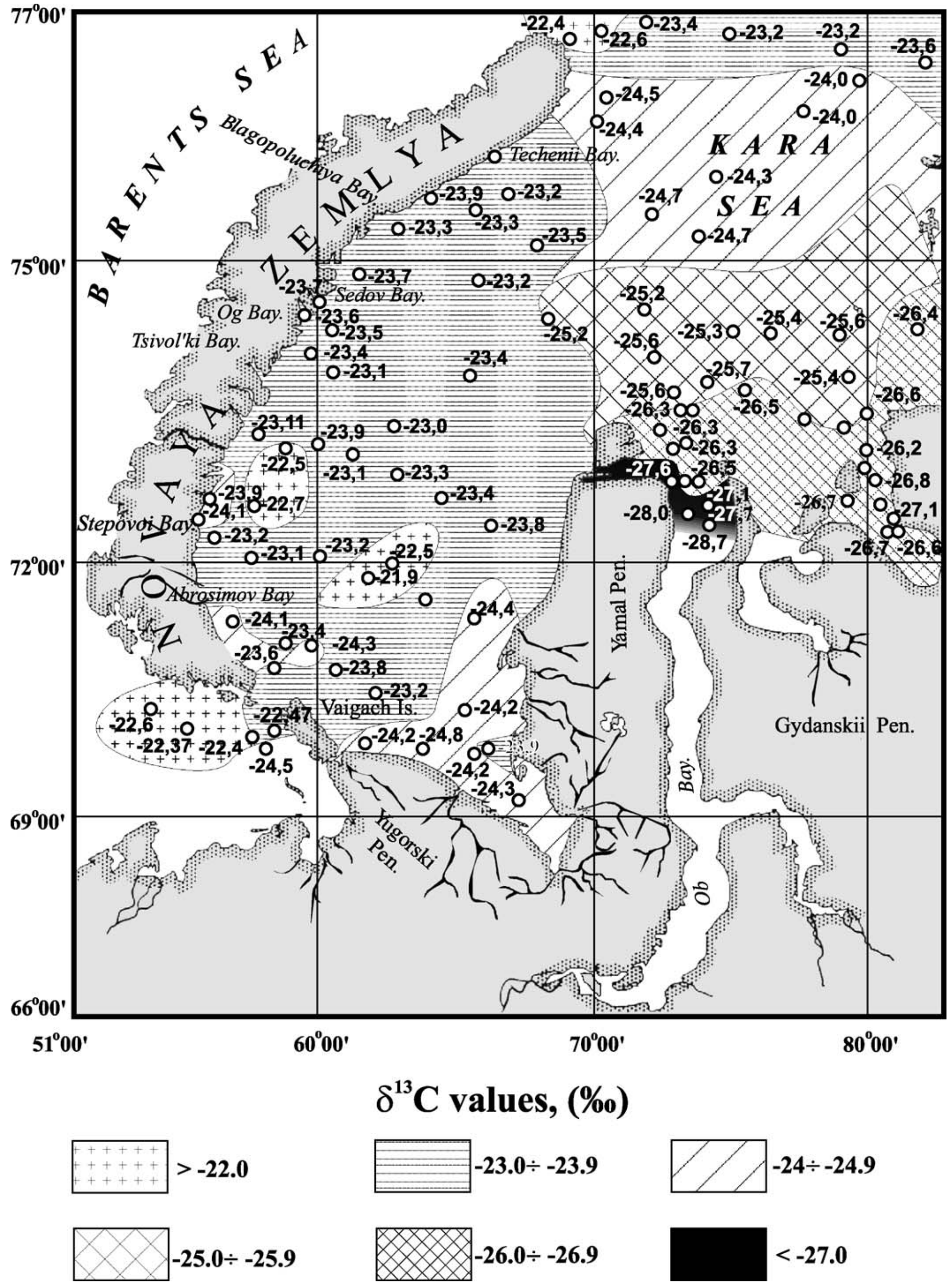

Fig. 7. Distribution of the δ^{13}C values of organic carbon in the surface layer (0–1 cm) of the sub-bottom sediments in the Kara Sea.

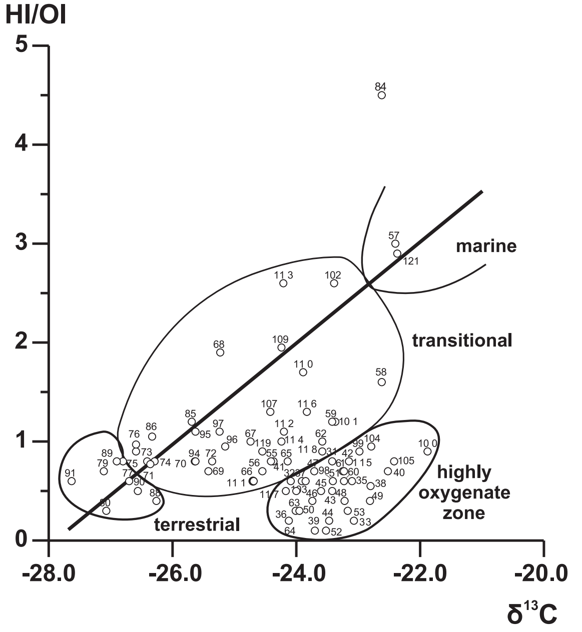

Fig. 8. δ^{13}C values vs. HI/OI relationship for organic matter from sub-bottom sediments in the Kara Sea. The number beside the data point is the site number.

But some oxygen atoms were incorporated into structures of the organic compounds (as ether bridges, oxygen of hydroxyl and carboxyl groups, etc.) thus increasing the oxygen index of the organic matter.

It should be noted that the oxidative loss of organic carbon is not significant. It is seen from Fig. 10 that concentrations of organic carbon in the highly oxygenated region of the Kara Sea show a similar range of values compared to other parts of the Kara Sea. However, it is important to note that the quality of the oxidized organic matter is quite different. Aerobic diagenesis leads to the destruction of chemical structures, which are precursors of the substrates for bacteria. Therefore microorganisms utilize highly oxidized organic matter less readily. This may be exemplified by comparison of the geochemical profiles of sub-bottom sediments at sites with different redox zones within the Kara Sea (Fig. 11). For example, Site 88 is situated close the Ob' river mouth. It represents a classical geochemical zonation. Decrease of the concentration of SO_4^{2-} ion with depth reflects the sulfate reduction process. Simultaneously the alkalinity increases at the expense of biochemical

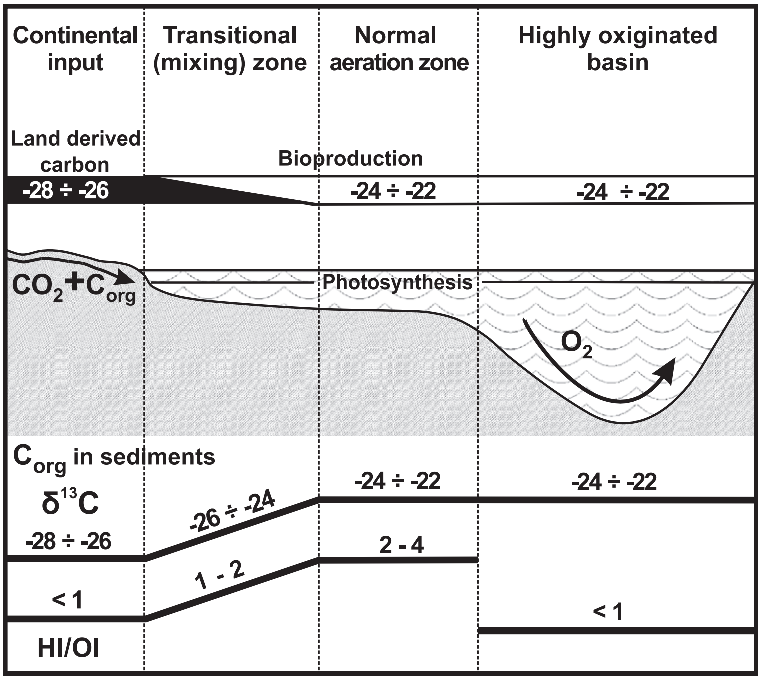

Fig. 9. A model describing geochemical zonation in the Kara Sea characterized by the presence of diagenetic oxidation of organic carbon.

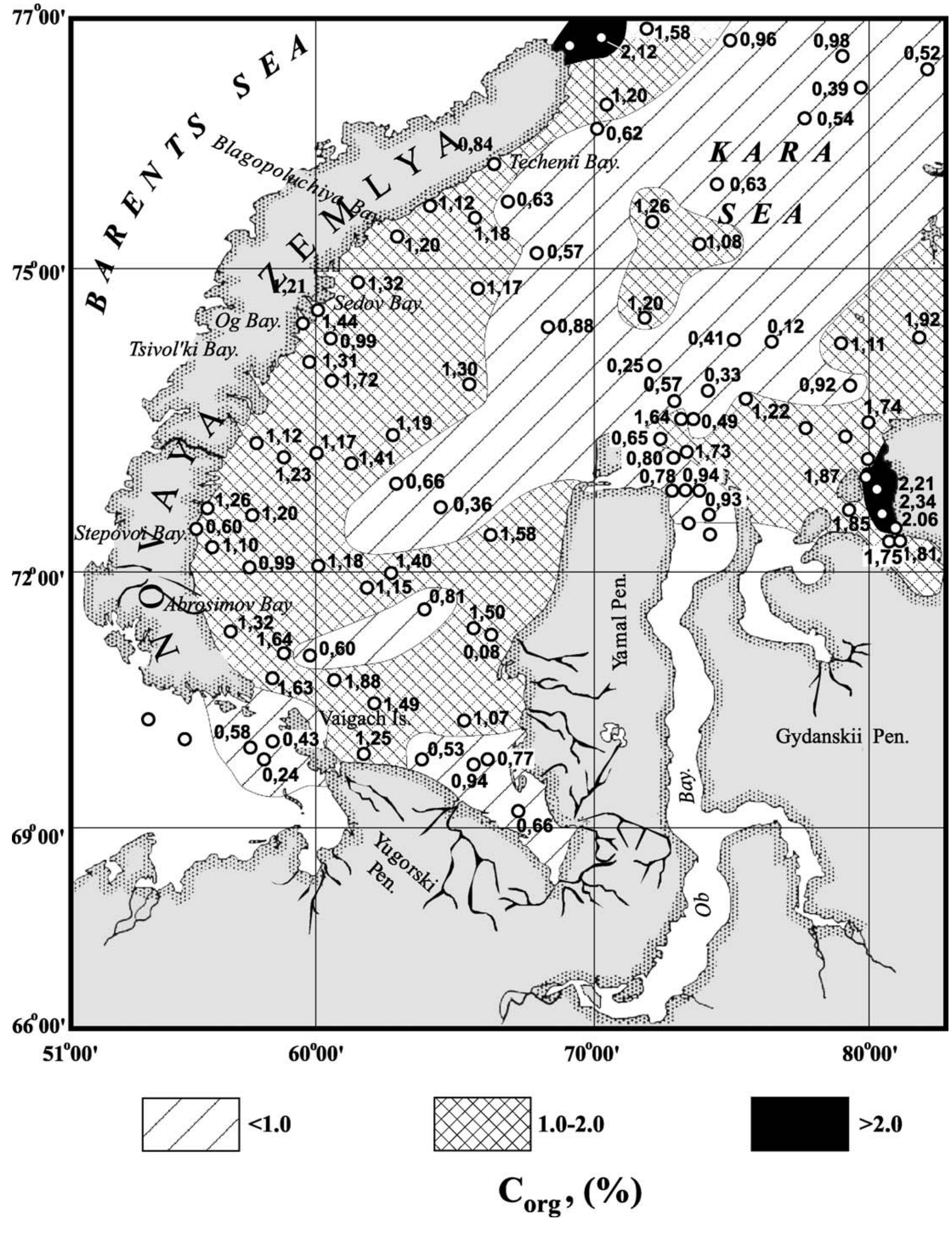

Fig. 10. Concentration of organic carbon (in %) in the surface layer (0 – 1 cm) of sub-bottom sediments in the Kara Sea. Different density of hatching marks the zones different in the C_{org} (%).

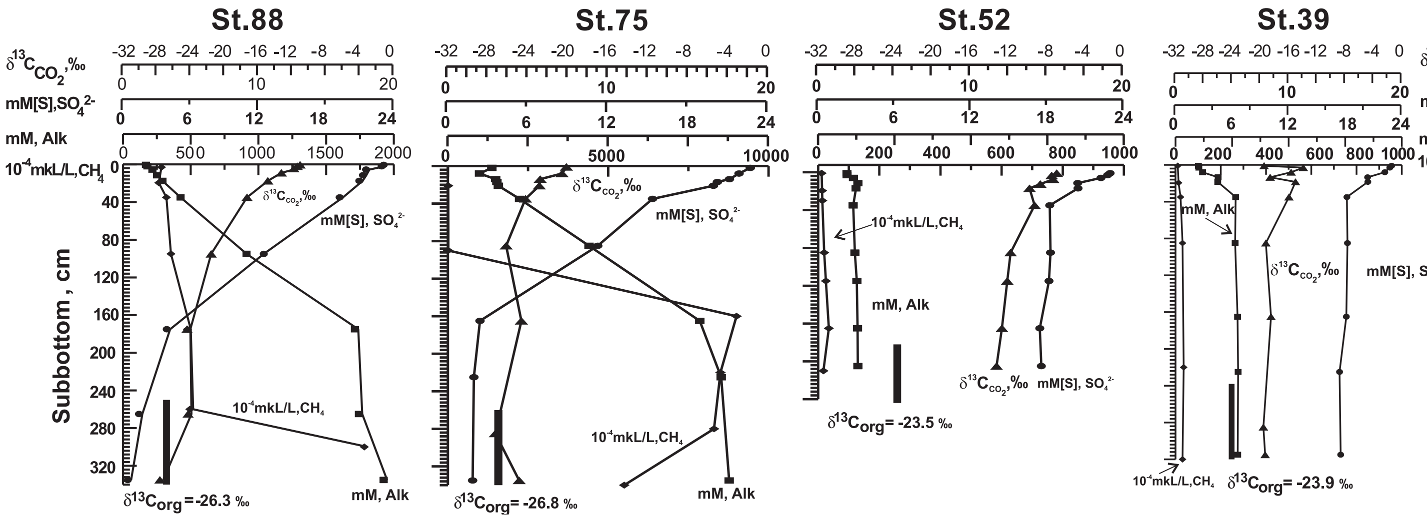

Fig. 11. Variation of geochemical parameters with depth in sub-bottom sediments at sites with different redox zones in the Kara Sea. The data are from Galimov et al. (1996).

oxidation of organic matter. Input of CO_2 released during oxidation of organic matter is indicated by the gradual change of its isotopic composition. The $\delta^{13}C$ value of CO_2 in the interstitial water changes from a value which is characteristic of local sea water to that which corresponds to organic carbon. When the sulfate reduction process is almost completed, methane generation starts. The same features are observed for Site 75, which is located in an area with similar geochemical characteristics. The picture is different for Site 52 located in the northern part of the Novaya Zemlya trough, within the highly oxidized area. Sulfate reduction as indicated by sulfate concentration and alkalinity, is restricted to shallow depth. The isotope composition of interstitial CO_2 changes slowly and in the studied part of the core is still far from the $\delta^{13}C$ value characteristic of organic carbon. Methane generation is weak. The same is characteristic for Site 39.

3.3. The Cariaco basin

The third region examined in this paper is the Cariaco basin. The Cariaco Trench is a unique anoxic basin in the Atlantic Ocean situated on the continental slope offshore Venezuela (Fig. 12). It is about 200 km long and 50 km wide with a maximum depth of about 1400 m. The Cariaco basin is separated from the open ocean by a sill at about 150 m below the water surface. Because of the limited oxygen supply, the deep Cariaco waters have become anoxic. Below 300 m hydrogen sulfide appears in the water and its concentration increases with depth.

The Cariaco basin was studied by an expedition on the R/V "Akademic Boris Petrov" in 1991 (Report on the 14th Cruise of the R/v "Akademic Boris Petrov", 1991). We were not authorized to collect samples from numerous locations with research limited to the study of three sites offshore of Venezuela. Therefore, it is not possible to present the $\delta^{13}C$–HI/OI relationship for the subsurface layer sediments. However, the data obtained from the sedimentary cores and the water column provide a basis for comparison with the situation in the Black Sea. Here the data for Site 8 are presented (Fig. 13).

The oxygen and sulfide containing zones overlap between 330 and 390 m. The shift in the carbon

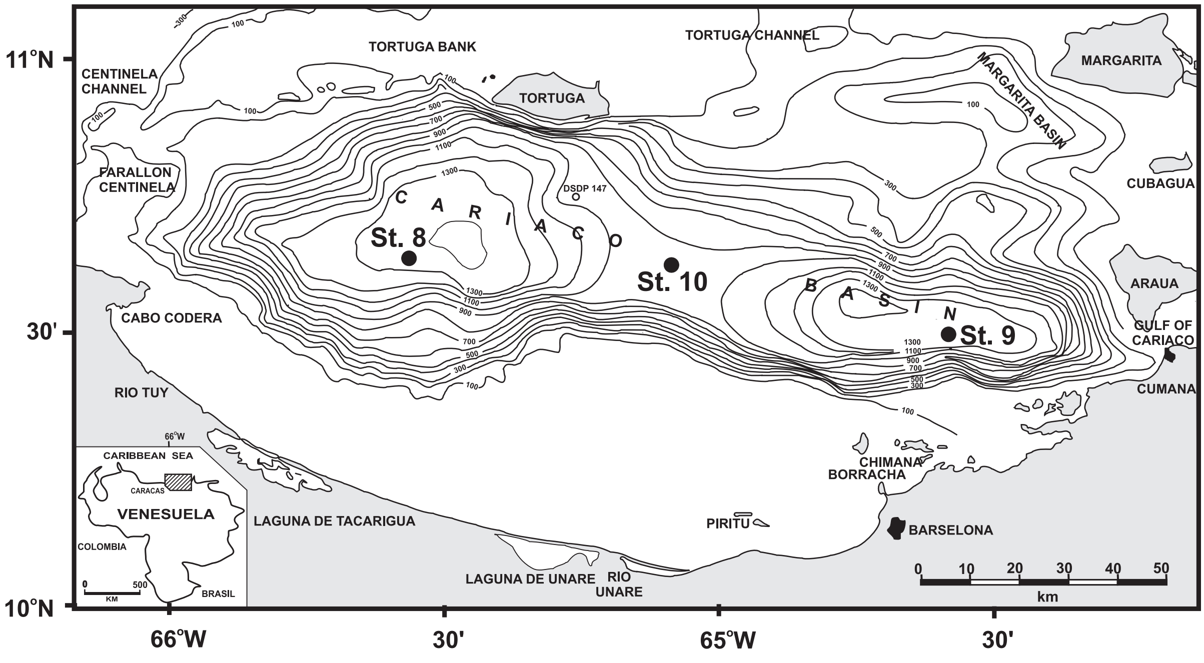

Fig. 12. Location of the sites studied in the Cariaco basin during the 14th cruise of R/v "Akademic Boris Petrov".

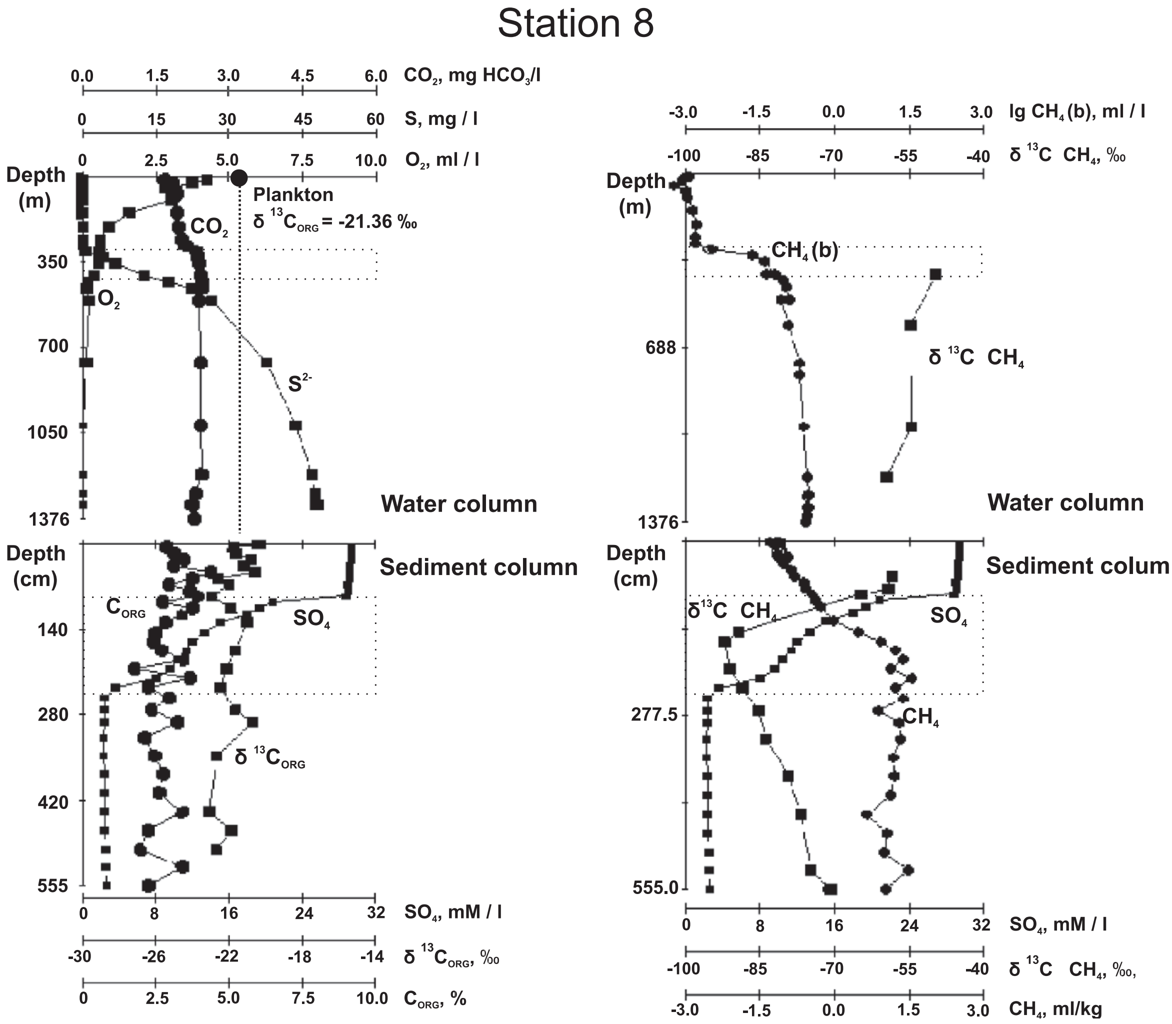

Fig. 13. Variation of geochemical parameters in the water column and the sedimentary profile at St. 8 in the Cariaco basin, as measured during 14th cruise of the R/v "Akademic Boris Petrov" (SO_4^{2-}, CH_4, CO_2, S^{2-}, O_2, C_{org}) and in the V.I. Vernadsky Institute ($\delta^{13}C_{org}$, $\delta^{13}C_{CH4}$). The data are from Report on the 14th Cruise of the R/v "Akademic Boris Petrov" (1991) and Galimov (1995).

dioxide concentration at the upper boundary of the sulfide zone indicates strong microbiological activity in this layer. Methane appears below 350 m, and its $\delta^{13}C$ value is less negative than in the hydrogen sulfide zone of the water column. Depletion of methane in the light carbon isotope is evidence of its microbial oxidation. In these features, the Cariaco Basin is similar to the Black Sea. Therefore, contribution of chemosynthesis to sedimentary organic matter should also be expected in the Cariaco Basin. However, organic carbon in the Cariaco sediments is almost of the same isotopic composition as plankton carbon. The isotopic composition of total organic carbon in the sub-bottom sediments varies between − 21 ‰ and − 23 ‰. Measurements of the isotopic composition of plankton carbon yielded $\delta^{13}C$ values from − 20.5 ‰ to − 22.1 ‰. Our measurements of the carbon isotopic composition of suspended organic matter in the anoxic water of the Cariaco basin gave $\delta^{13}C$ values from − 22.3 ‰ to − 23.1 ‰. These values are very similar to those values reported by Fry et al. (1991) for particulate organic matter at the top of the sulfide zone in the

Cariaco Trench (– 23.1‰ and – 23.2‰). Thus, in contrast to the Black Sea, no significant shift in the δ^{13}C values of the organic carbon is apparent at the oxic/anoxic boundary where chemoautotrophic activity might be at its maximum.

Thus, in spite of the clear evidence for microbial activity in the anoxic water of the Cariaco Trench, chemosynthetic bioproduction has not noticeably contributed to the organic carbon balance. Apparently, photosynthetic bioproduction in the Cariaco basin dominates over chemosynthesis. This may be related to the deeper level of the oxic/anoxic boundary in the Cariaco basin (see also Freeman et al., 1994). This is a characteristic not only for recent sediments. In the Cariaco Trench, the δ^{13}C values of the organic carbon vary around -21.5 ± 1‰ throughout the whole studied sedimentary profile (555 cm), whereas in the Black Sea δ^{13}C values of – 24‰ to – 25‰ are typical for sedimentary organic carbon for at least the last several thousand years.

4. Conclusions

1. The form of the $\delta^{13}C_{org}$ vs HI/OI relation may serve as an indicator of geochemical regime in a marine basin. Deviation of the data-points from the marine-terrestrial mixing line is related to peculiarity of the geochemical regime.
2. In the Black Sea, this approach reveals a significant role for chemosynthetic production of organic matter at the top of the hydrogen sulfide zone and within the anoxic zone.
3. In the Kara Sea the observed deviation of the data points from the $\delta^{13}C_{org}$–HI/OI mixing line is related to extensive oxidative diagenesis of organic matter in the bottom sediments in the region of the Novaya Zemlya Trough.
4. In the sediments of the Cariaco Trench, organic carbon does not show any noticeable shift of δ^{13}C towards more negative values compared to the δ^{13}C of the local plankton in spite of the hydrogen sulfide regime occurring below 350 m. This is likely a consequence of the dominating contribution of photosynthetic bioproducers to the balance of organic carbon in sediments of the Cariaco basin.

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