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EXPERIMENTAL ARTICLES

Carbon Isotopic Composition in Suspended Organic Matter and Bottom Sediments of the East Arctic Seas

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Abstract—The samples of water and bottom sediments of the East Siberian and Chukchi Seas collected during the second Russian–American RUSALCA expedition were used to analyze patterns of the isotopic composition of carbon in the organic matter (OM) of suspended material (SOM) and bottom sediments (BOM). Similar to other marine environments, the SOM isotopic composition depended on the ratio between the terrigenous and planktonic OM, both in the water body as a whole and in its parts. Thus, in the East Siberian Sea the carbon of SOM was poorer in ^{13}C ($\delta^{13}C = -24.51‰$) than the open part of the more productive Chukchi Sea ($\delta^{13}C = -22.16‰$). In the less productive coastal waters of the Chukchi Sea, the ratio of terrigenous OM increased, resulting in a $\delta^{13}C$ shift to lower values (−23.40‰). Due to the influx of reduced products of anaerobic diagenesis of the sediments, elevated total number of microorganisms and dark CO_2 fixation were found in the near-bottom water at the water–sediment biogeochemical barrier. The newly formed biomass of autotrophic microorganisms shifted the carbon isotopic composition of the near-bottom suspended material to more positive $\delta^{13}C$ values, with the average values of −23.39 and −20.37‰ for the East Siberian and Chukchi Sea, respectively. Changes in the carbon isotopic composition of OM resulting from microbial activity continued in the upper sediment layers. When the rate of biomass synthesis increased that of biomass consumption, the ^{13}C content increased further. At higher rates of OM mineralization, ^{12}C accumulated in its remaining part.

Keywords: carbon isotopic composition, carbon cycle, suspended organic matter, microbial processes, Arctic seas

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The isotopic signature (IS) of organic matter (OM) is an important geochemical parameter of marine environments, since it characterizes the ratio between two major sources of organic matter: isotopically light ($\delta^{13}C < -25‰$) OM of terrestrial plants arriving with the terrigenous flow, and heavier ($\delta^{13}C > -22‰$) OM synthesized by phytoplankton in the basin [1]. During the last twenty years, large-scale measurements of the $\delta^{13}C$ values of organic matter of the bottom sediments (BOM) were carried out by American and Canadian researchers in all the Eastern Arctic shelf seas: Chukchi [2–4], East Siberian [5], and Laptev Sea [6]. Generalization of these data [4] resulted in the expected conclusion that the carbon IS becomes heavier as water moves from the coastal sediments and estuaries of the big Siberian rivers (major sources of isotopically light terrigenous OM) to the open sea, where organic matter is produced by phytoplankton. Authors of a collective monograph on OM of the Arctic Seas (2004) made the same conclusion [1]. Although the isotopic composition of suspended organic matter (SOM) was very poorly studied, in both works the transfer of suspended organic matter by currents was postulated as a factor responsible for occasional violation of the pattern of lateral variations in the $\delta^{13}C$ of BOM.

Investigation of the carbon isotopic composition of OM of the Arctic seas by Russian researchers commenced in 1993 by the Kara Sea expedition of R/V *Akademik Mstislav Keldysh* [7]. The results of this work and the subsequent expeditions to the White, Barents, and Kara seas were summarized by Lein and Ivanov [8]. The 2004 expedition by the Russian–American RUSALCA program was the first study of the carbon IS of organic matter in the Chukchi Sea [9, 10].

In these cases, not only the IS of the bottom sediments, but also the IS of SOM was studied, both for the upper water horizons, where it was determined by three major components (OM of aerosols, of river inflow, and of phytoplankton) and for the near-bottom horizons, contacting with the upper sediment horizon.

The first of such works revealed that the carbon IS of OM of the bottom sediments of the Kara Sea differed significantly from that of the surface layers of the water column [7]. This effect was subsequently con-

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firmed by abundant material collected at the large area of the shallow Kara Sea [11–14]. Comparison of the isotopic date with the results of other biogeochemical studies showed that heavier carbon isotopic composition in BOM and SOM of the near-bottom horizons resulted from the activity of microbial communities at the near-bottom water–bottom sediment interface [13]. Variations in the IS of organic matter in near-bottom water and upper sediment horizons caused by microbial activity were thoroughly studied in the White Sea [14].

The main goal of the present work was to obtain new data on the carbon IS of the surface and near-bottom suspended material and of the bottom sediment upper horizons in the East Siberian and Chukchi seas and to elucidate the major mechanisms responsible for development of the carbon IS in these neighboring, albeit significantly different, East Arctic seas.

The data presented in Table 1 show that these seas do not differ significantly in most of their morphological characteristics (water area, average depth, and water volume). The river inflow and the flow of terrigenous OM to the East Siberian Sea are, however, three and five times, respectively, higher than these parameters for the Chukchi Sea. Moreover, primary production in the Chukchi Sea was six times higher than in the East Siberian Sea, while the ratio between autochthonous OM (primary production) and allochthonous OM (river inflow) was 30 times higher (Table 1).

MATERIALS AND METHODS

The samples of suspended matter and bottom sediments were collected during the second expedition (August–September 2009) of the RUSALCA project (Fig. 1).

The water was sampled with 5-L bathometers of the Rosette probing complex. Bottom sediments were collected with a direct-flow geological corer and a bottom dredge. The total number of microorganisms (TNM) was determined by direct microscopy of the membrane filters. For chemical analysis of the pore water, it was obtained by centrifugation of the bottom sediments. Eh and the contents of methane and organic and mineral carbon were determined. Suspended matter was collected by filtration through GF/F filters.

The rates of microbial processes (sulfate reduction, dark CO_2 fixation, and autotrophic methanogenesis) were determined using radioisotopes: $Na_2^{35}SO_4$, $NaH^{14}CO_3$ (with analysis of the label transfer to the biomass and soluble exometabolites), and $NaH^{14}CO_3$ (with analysis of ^{14}C transfer to methane), respectively. The analytical procedures developed in our laboratory have been previously published [7, 9, 12]. Carbon IS of suspended matter and bottom sediments were determined using the standard techniques of $\delta^{13}C$ determination on a Delta Plus mass spectrometer (Germany).

Table 1. Hydrological and geochemical characteristics of the East Siberian and Chukchi seas

Parameter	East Siberian Sea	Chukchi Sea
Area, $\times 10^3$ km^2	913	595
Average depth, m	54	71
Water volume, $\times 10^3$ km^3	48.7	42.1
Yearly river flow, km^3	250	78
Terrigenous OM, $\times 10^6$ t C per year	3.0	0.6
Primary production, $\times 10^6$ t C per year	7.0	42
Ratio between autochthonous and allochthonous OM	2.3	70

RESULTS

The data on the East Siberian Sea (Table 2) show that the isotopically lightest SOM was found in the upper water horizons. The $\delta^{13}C$ values varied from –23.97 (st. WN-1) to –25.31‰ (st. LS-3), with the average of –24.51‰ Most SOM samples from the near-bottom water (except st. SS-4) and BOM samples (except st. WN-3) had heavier isotopic composition than the surface SOM (–22.81 to –24.35‰ for near-bottom water and –21.32 to –24.76‰ for bottom sediments, Table 2). Thus, in the near-bottom water and the upper horizons of the bottom sediments the precipitating suspension was supplemented with OM which was poorer in ^{12}C than the surface samples. Enhanced $\delta^{13}C$ values probably resulted from an increased number of microorganisms, which was always higher in the near-bottom water than in the upper water layers (on average, twice as high, see Table 2).

Research in limnological and marine biogeochemistry revealed that the flows of dissolved organic compounds and reduced inorganic compounds (CH_4, NH_4, H_2S, etc.) arriving from the bottom sediments into the near-bottom water result from diagenesis of the sediments, which are actively used by autotrophic and heterotrophic microorganisms from the near-bottom water. These processes result in significant increases in TNM and amount of SOM.

At some stations in the East Siberian Sea dark CO_2 fixation (DF) in the near-bottom water was higher than in the surface samples, so autotrophic CO_2 assimilation by the near-bottom microflora may be assumed. This process may result in formation of OM with $\delta^{13}C$ from –18.0 to –20.0‰, shifting the total isotopic composition of SOM to lower ^{12}C content.

Carbon isotopic composition of SOM and bottom sediments of the Chukchi Sea was studied at 21 stations (Fig. 1 and Tables 3–5). The southern and cen-

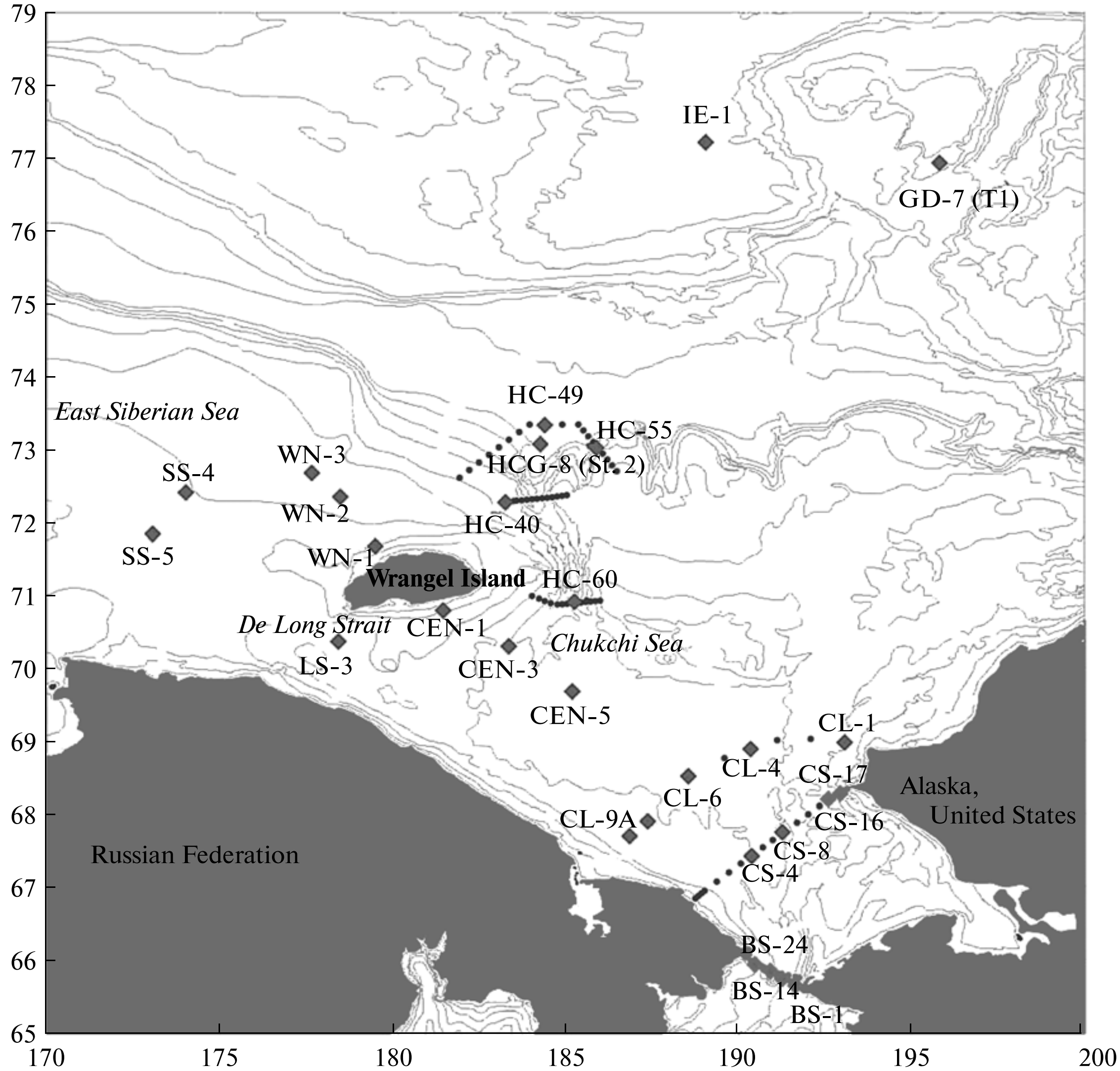

Fig. 1. Localization of the sampling stations (diamonds) along the station profiles (dots) in the Chukchi and East Siberian seas during the 2009 expedition. Abbreviations for the sampling profiles: BS, Bering Strait; CL, Cape Lisburne; CEN, Central; CS, Chukchi South; HC, Herald Canyon; IE, Ice Edge; LS, De Long Strait; SS, Siberian Shelf; WN, Wrangel North; GC, Geologic Dredge.

tral parts of the sea were studied in more detail: 8 open-sea stations with relatively high primary production and 4 coastal stations affected by terrigenous flow and coastal currents. These are stations CS-16 and CS-17 near Alaskan coast, which are affected by the eastern branch of the current from the Bering Sea, and stations CL-9A and CEN-1, which are affected by the main branch of the East Siberian current via the De Long Strait and by the northern branch of this current to the eastern shores of the Wrangel Island, respectively (Fig. 1).

Comparison of the ranges and average values of $\delta^{13}C$ showed that autochthonous OM prevailed in the SOM of open-sea water, with the average $\delta^{13}C$ value for 8 samples –22.16‰ (range from –20.77 to –23.83‰), while the average value for the coastal water was –23.40‰ (range from –24.08‰22.73 to –24.08‰) (Table 3). Among the open-sea stations, enrichment with OM of phytoplankton origin was especially pronounced in the case of three stations, CEN-5, CEN-3, and HC-60 (Table 3), which were the ones most remote from the continents and the Wrangel Island, i.e., from potential sources of allochthonous isotopically light OM (Fig. 1).

SOM in the near-bottom water of all 12 stations of the southern and central Chukchi Sea was enriched with the heavy isotope ^{13}C compared to SOM of the surface waters (Table 3). The average $\delta^{13}C$ value for SOM from near-bottom water was –20.37‰ for the open sea and –21.37‰ for the coastal water. Thus, the SOM isotopic composition becomes considerably

Table 2. Carbon isotopic composition ($\delta^{13}C$, ‰) of suspended organic matter, total number of microorganisms (TNM, 10^3/mL) in the surface and near-bottom horizons of the water column, and $\delta^{13}C$ values for the surface horizon (0–2 cm) of the East Siberian Sea sediment

Station no. and depth, m	Coordinates	Surface water		Suspension from near-bottom water		$\delta^{13}C$, ‰ of the sediment
		$\delta^{13}C$, ‰	TNM	$\delta^{13}C$, ‰	TNM	
SS-4, 45	71°53′N 173°04′E	–24.11	78	–24.70	120	–22.21
SS-5, 39	70°23′N 178°14′E	–24.51	76	–22.58	140	–23.72
WN-1, 28	71°39′N 179°33′E	–25.09	110	–24.35	170	–24.76
WN-2, 42	72°20′N 178°36′E	–23.97	110	–23.07	130	–21.46
WN-3, 70	72°40′N 177°40′E	–24.05	100	–22.81	270	–27.64
LS-3, 47	70°23′N 178°14′E	–25.31	160	–22.85	150	–21.32
Average δ^{13} C values, ‰		–24.51	106	–23.39	190	–23.52

Table 3. Carbon isotopic composition ($\delta^{13}C$, ‰) of suspended organic matter in the surface and near-bottom horizons of the water column and in the upper horizon of the bottom sediments of the Chukchi Sea

Station no.	Depth, m	Surface water suspension	Near-bottom water suspension	Sediment
A. Open-sea stations				
CS-4	46	–21.47	–20.23	–23.07
CS-5	37	–22.93	–20.79	–22.65
CL-1	42	–22.31	–18.99	–
CL-4	50	–23.83	–19.71	–
CL-6	42	–22.42	–20.36	–22.04
CEN-5	54	–21.73	–20.62	–20.91
CEN-3	50	–21.89	–22.01	–21.03
HC-60	37	–20.77	–20.30	–20.71
Average values		–22.16	–20.37	–21.72
B. Coastal stations				
CS-16	45	–22.73	–20.61	–23.67
CS-17	38	–23.70	–20.69	–24.93
CEN-1	27	–23.10	–22.34	–22.69
CL-9aL		–24.08	–21.84	–
Average values		–23.40	–21.37	–23.76

enriched with isotopically high carbon in the course of SOM precipitation in the water column.

The data presented in Table 3 also show that the IS of upper sediments did not inherit the IS of SOM from the surface water horizons. At stations CS-16 and CS-17, C_{org} of the sediments was enriched with the light ^{12}C, while at other stations C_{org} was enriched with the heavy ^{13}C compared to SOM of the surface water (Table 3).

Four stations at the northern part of the Chukchi Sea provided additional data on the carbon isotopic composition of SOM of the surface and near-bottom horizons, as well as of organic carbon of the upper sediment horizons (Table 4, Fig. 1). While the $\delta^{13}C$ values

Table 4. Carbon isotopic composition (δ^1 C, ‰) of suspended organic matter in the surface and near-bottom horizons of the water column and in the bottom sediments of the northern part of the Chukchi Sea

Station no.	Depth, m	Surface water suspension	Near-bottom water suspension	Sediment
HC-55	94	–22.21	–21.24	–20.19
HC-49	142	–24.05	–22.65	–21.83
GD-7	665	–21.63	–18.19	–
IE-1	660	–24.26	–26.80	–
Average values		–23.03	–22.21	–21.01

SOM of the surface and near-bottom horizons, as well as of C_{org} of the upper sediment horizons, determined at these stations varied significantly, the pattern reported above was still confirmed: the lightest carbon was found in SOM of the upper horizons of the water column (average $\delta^{13}C$ for four stations was –23.03‰, Table 4), and the carbon of the near-bottom suspension and upper sediments was enriched with ^{13}C to –22.21 and –21.01‰, respectively (Table 4). The possible mechanisms responsible for the changes in the carbon IS of near-bottom SOM and upper sediment horizons will be discussed below, after description of the experimental data, including those on $\delta^{13}C$ of the Bering Strait surface suspension (Table 5) and new data on $\delta^{13}C$ of organic carbon in the samples collected along the vertical profile of the Chukchi Sea bottom sediments (Table 6).

The information on the carbon IS of suspended material brought via the Bering Strait from the Bering Sea is required for understanding the formation of the IS of SOM in the upper water horizons of the southern and central parts of the Chukchi Sea. The $\delta^{13}C$ values for SOM from the upper horizons of the Bering Strait water column are presented in Table 5. At three stations of the eastern and central parts of the 24-station section (BS-1, BS-7, and BS-14), the $\delta^{13}C$ values varied within a narrow range, from –18.83 to –19.59‰, with the average of –19.19‰. These values probably indicate the phytoplanktonic origin of all suspended

Table 5. Carbon isotopic composition ($\delta^{13}C$, ‰) of suspended organic matter, total number of microorganisms (TNM, cells/mL), and dark CO_2 assimilation (nM C dm^{-3} day^{-1}) at the stations of the Bering Strait profile (samples from the surface water horizons)

Station no.	$\delta^{13}C$, ‰	TNM	Dark CO_2 fixation
BS-1	–19.59	1500	165
BS-7	–18.83	800	96
BS-14	–19.15	720	69
BS-24	–23.20	550	54
Average values	–19.19	1007	110

OM at the surface horizons of these stations. At station BS-24, located close to the coast of the Chukchi Peninsula (see Fig. 1), $\delta^{13}C$ = –23.20‰, indicating a considerable admixture of terrigenous OM.

American and Canadian researchers associated the differences in the carbon isotopic composition of the central and eastern parts of the Chukchi Sea with the heterogeneity of the water masses arriving to this sea via the Bering Strait [1–4]. Most of the Bering Sea water arriving to the Chukchi Sea via the central and western parts of the Bering Strait are formed in the Gulf of Anadyr in the northwestern part of the Bering Sea. These so-called Anadyr waters (AW, see [2, 4]) have extremely high levels of biogenic elements (NO_3^- concentration exceeds 20 μM) and have primary production of up to 720–840 g/m^2 per year with the average annual production of 470 g/m^2. The $\delta^{13}C$ values of the bottom sediments of the Gulf of Anadyr and the western part of the Bering Strait vary therefore from –20.0 to –21.0‰. The flow of Anadyr waters into the western part of the Chukchi Sea is responsible for high primary production in this region (250–300 g/m^2 per year) [4].

Via the eastern part of the Bering Strait, the Bering Sea waters formed at the North American coasts under the influence of the Yukon River flow into the Chukchi Sea. These waters, termed Alaskan shelf waters (ASW-4) have higher temperature, lower levels of biogenic elements, and significantly lower primary production than the Anadyr waters (Table 6). As a result, OM of the sediments in the zone of penetration of these waters becomes enriched with terrigenous OM to $\delta^{13}C$ from –23.0 to –24.0‰ (Fig. 2).

The data on OM isotopic composition of the Chukchi Sea surface sediment horizons were presented above (Tables 2 and 4). Additionally, at two stations of the 2004 expedition [7] and two stations of the 2007 expedition we collected the material characterizing the carbon IS of OM in the Chukchi Sea Quaternary sediments (175–213 cm). In brief, the geochemical features of these sediments described in detail in our previous work [7] are as follows. Pelitic and aleuro–pelitic diatomic olive green or greenish-gray silts with numerous black hydrotroilite inclusions prevailed in the open sea. The content of organic carbon was 1.6–2%, while carbonate carbon content did not exceed 0.4% (wt/wt) of dry sediment. Apart from the surface horizon (0–3 cm), the sediment had negative Eh values, which together with high levels of organic carbon favored the development of anaerobic sulfate-reducing and methanogenic organisms. The highest rates of sulfate reduction (up to 81 μM at the southern stations and up to 1.5 μM dm^{-3} day^{-1} at the northern ones) were found in the upper parts of the cores (3–70 cm), while the highest rates of methanogenesis (up to 270 nL dm^{-3} day^{-1} at the southern stations and up to 14 nL dm^{-3} day^{-1} at the northern ones) were restricted to deeper sediment horizons [10].

Microbial processes had a significant effect on the salt composition of pore water. For example, the sediments of the southern part of the open sea exhibited decreased sulfate concentrations already in the surface layer (0–3 cm), while the total alkalinity of the sediments increased to 10–12 mg-eq/L at the depth of 70–80 cm. A unique feature of these sediments was inverse occurrence of extremely high concentrations of biogenic elements: ammonium nitrogen (up to 15 mM), phosphorus (up to 0.4 mM), and silicon (up to 0. 8 mM). These extreme levels of biogenic elements were found in the pore water of the uppermost sediment horizon, while in deeper layers the concentrations decreased. The usual distribution of phosphorus and ammonium nitrogen with the concentrations gradually increasing with depth was observed only in the northern part of the open sea [10].

Unlike the deep-water marine sediments, the coastal sediments (from the depths not exceeding 45 m) had more coarse granulometric composition, lower content of organic carbon (<1%), and significantly less active microbial processes [10].

Some additional geochemical characteristics of the sediments of the East Siberian and Chukchi seas obtained as results of the 2009 expeditions are summarized in Table 7. In general, they confirm the earlier conclusions concerning the anaerobic nature of the sediments, increase in the total alkalinity with sediment depth, and localization of the highest sulfate reduction rates in the upper part of the sediment core. Similar to the previous studies, the highest rates of methanogenesis occurred in deeper sediment layers, below the peak of sulfate reduction rates. Finally, further proof is provided for all the indices of the geochemical activity being lower than in the central part of the Chukchi Sea (Table 7, st. HC-8 and GD-3).

The first data on methane distribution in the sediments of the two seas under study (Table 7) was a significant addition to available information. At all four stations, methane content increased with depth, with the highest methane concentrations (17.7–16.6 μM) found at 135–170 cm of the HC-8 station of the central part of the sea. The highest CH_4 concentrations were observed in the sediment horizons with the highest rates of methanogenesis (Table 7). In the deepest sediment horizons, the rate of methanogenesis was lower by an order of magnitude, so that the highest methane concentration in the lower layers of the core of st. GD-7 (0/31–0.46 μM) was significantly lower than at st. HC-8.

Table 6. Comparative characteristics of Anadyr waters (AW) and Alaskan shelf waters (ASW) arriving from the Bering Sea to the Chukchi Sea via the Bering Strait [4]

Parameter	AW	ASW
Temperature, °C	<1.5	>2.0
Salinity, ‰	32.5	<31.8
NO_3^-, μM	>20	<1.0
Primary production, g/m^2 per year	250–300	50–80
Carbon isotopic composition of the sediments affected by the waters, $\delta^{13}C$, ‰	–21...–20	–24...–23

DISCUSSION

American and Canadian expeditions of the 1980s–1990s were aimed at the geochemical investigation of the upper sediment horizons of the American and Russian parts of the Chukchi Sea and eastern East Siberian Sea. Much attention was paid to investigation of the carbon isotopic composition of OM in the sediments. Naidu et al. generalized the results of isotopic analysis of over 100 samples as a map with the $\delta^{13}C$, contour lines (Fig. 2). In the most productive central zone of the Chukchi Sea, most data occurred between the eastern and western contour lines with $\delta^{13}C$ = –21‰. A broad band of sediments with $\delta^{13}C$ from –21 to –22‰ bordered this zone from the southwest. In the zone of the Chukchi Peninsula coast affected by the East Siberian current, sediments with $\delta^{13}C$ < –23‰ were found. Similar $\delta^{13}C$ values were observed in the eastern part of the sea along the Alaskan coast (Fig. 2).

In the shallow sediments of the East Siberian Sea collected in its eastern part around the Chauna Bay, the $\delta^{13}C$ values varied from –23 to –24.5‰ (Fig. 2). Our values obtained for the sediments of this sea along two sections, from the Chauna Bay to the open sea (SS on Fig. 1) and from the northwestern shore of the Wrangel Island to the open sea (WN on Fig. 1), fell within the range from –21.46 to –27.64‰ with the average value of –23.52‰ for the seven samples from the East Siberian Sea and the De Long Strait (Table 2).

According to our data collected during the 2004 Chukchi Sea expedition, the average $\delta^{13}C$ value of the open sea sediments of the central and southern parts of the Chukchi Sea was –22.54‰. In two samples from

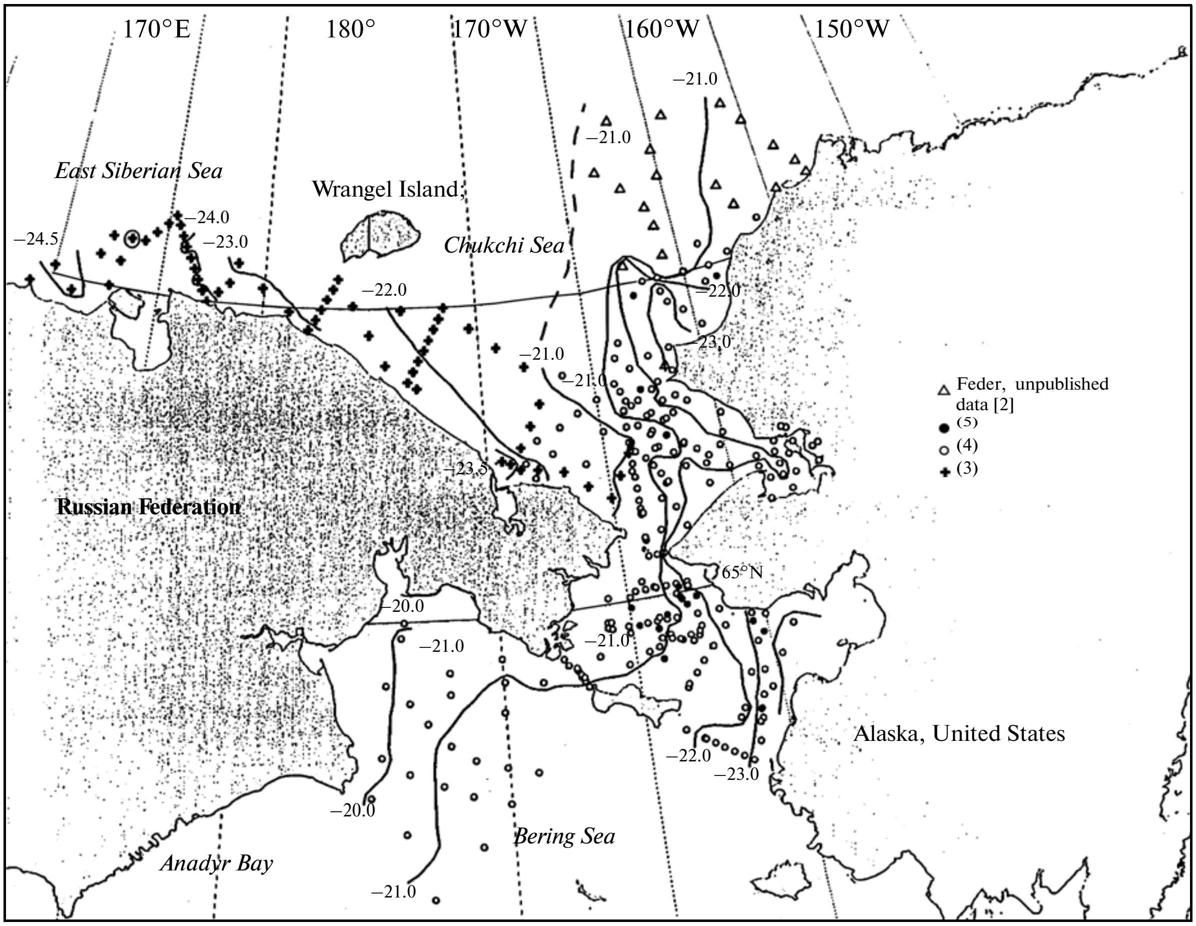

Fig. 2. Carbon isotopic composition ($\delta^{13}C$, ‰) of organic matter in the upper sediment horizons of the Chukchi and East Siberian seas according to the data of four American and Canadian expeditions of 1980s–1990s (from Naidu et al., 2000 [2]).

the Alaskan coastal zone were significantly poorer in ^{13}C (to the values of –24.6‰) [7]. According to the data of the 2009 expedition, the average $\delta^{13}C$ values were –23.52‰ for 6 samples of the open sea sediments (Table 2) and –23.76‰ for 4 samples of the coastal sediments (Table 3).

Carbon of OM of the sediments of the open Chukchi Sea were more than 0.02‰ richer in ^{13}C than the East Siberian Sea sediments ($\delta^{13}C$ = –23.52‰. The share of carbon of phytoplanktonic and terrigenous origin may be calculated from the equation of material–isotopic balance:

$$A_{sed} \times 100\% = B_{fito} \times \% + (100 - x)\% - C_{ter},$$

where A_{sed} is $\delta^{13}C$ of the sediment OM, ‰; B_{fito} is $\delta^{13}C$ of the phytoplanktonic carbon, ‰; C_{ter} $\delta^{13}C$ of terrigenous carbon, ‰; $x\%$ is the share of carbon of phytoplanktonic origin; and $(100 - x)\%$ is the share of terrigenous carbon.

According to traditional concepts of unchanging IS of SOM carbon throughout the water column, the ratio of carbon of phytopkanktonic origin in the sediments of the East Siberian and Chukchi seas is 40.7 and 72.2%, respectively, assuming B_{fito} of –19.19‰ (the value for suspended OM of the Bering Strait surface water, see Table 5) and C_{ter} = –26.5‰ (averaged data for 13 samples of the Lena and Anadyr rivers delivering terrigenous OM from the northeastern part of the Asian continent) [1]. The difference between two seas may result from significant differences in the balance of OM of terrigenous and phytoplanktonic origin: while in the Chukchi Sea primary production is 70 times higher than terrigenous OM, this ratio for the East Siberian Sea is 2.3 (Table 1).

Our previous work on carbon isotopic composition of the Arctic seas showed that the ratio of the allochthonous and autochthonous OM was the main factor, though not the only one responsible for the carbon IS of the bottom sediments. It was shown for the White and Cara seas that microbial processes of the water column, especially of the near-bottom water, may affect the carbon IS of OM precipitating into the upper sediment horizons [9, 13].

Comparison of the $\delta^{13}C$ values of suspended OM from the surface and near-bottom water horizons, as well as of the bottom sediment OM, revealed that the

Table 7. Characteristics of the bottom sediments of the East Siberian Sea (stations SS-4 and WN-1) and the Chukchi Sea (stations HC-8 and GD-7). MG and SR are designations for the rates of methanogenesis and sulfate reduction, respectively

Station no. and depth, m	Horizon, cm	Eh, mV	CH_4, μM dm^{-3}	Alk, mg-eq	Dark CO_2 fixation, μM C dm^{-3} day^{-1}	MG, nM dm^{-3} day^{-1}	SR, μM dm^{-3} day^{-1}
SS-4, 45 m	0–2	+120	0.28	3.0	1.17	0.17	1.3
	8–12	–170	0.79	4.4	0.45	1.92	1.89
	32–37	–290	1.39	5.5	0.28	2.17	1.06
	58–63	–210	1.13	5.0	0.11	3.75	0.47
	90–95	–240	1.45	5.2	0.07	4.08	0.21
	115–120	–180	1.69	5.0	0.15	3.42	0.32
WN-1, 28 m	0–2	+180	0.38	3.2	0.97	5.5	3.97
	10–15	–230	1.62	4.5	1.05	5.25	3.60
	22–26	–130	0.65	5.0	0.72	9.25	3.80
HC-8, 98 m	5–10	0	0.41	3.4	1.4	2.54	5.9
	50–55	–80	0.81	4.0	0.12	11.90	11.0
	90–95	–190	14.4	4.0	0.10	6.67	3.13
	135–140	–100	17.5	4.5	0.11	17.90	4.20
	165–170	–100	16.6	4.5	0.13	33.9	4.05
GD-7, 565 m	0–2	+60	0.58	3.0	1.60	0.48	0.51
	5–10	–40	0.57	4.0	0.12	1.25	1.07
	30–35	–60	0.39	4.5	0.07	1.50	2.12
	50–55	–80	0.35	4.5	0.06	2.30	1.28
	100–105	–110	0.31	4.5	0.09	2.00	0.50
	170–172	–110	0.46	4.5	0.06	3.50	0.88

processes occurring in the sediments and near-bottom water affected the IS of OM formed in the surface water (Tables 2–4, 8). At 19 out of 22 stations, the near-bottom suspension was enriched with ^{13}C compared to SOM of the surface horizons. The data presented in Table 9 show that at all the stations studied, both total numbers of microorganisms (TNM) and the rates of dark CO_2 fixation were higher in the near-bottom water than in the surface horizons. This pattern is rather common and results from inflow of additional energy substrates originating from anaerobic processes of OM decomposition in the bottom sediments. Enhanced dark CO_2 fixation in near-bottom water suggests enhanced activity of chemoautotrophic microorganisms producing OM similar to that of phytoplanktonic origin it its isotopic composition ($\delta^{13}C \sim -20‰$). Ammonium ions produced during aerobic mineralization of autochthonous OM may be an additional substrate for chemoautotrophs, especially in the central part of the Chukchi Sea (stations CS-8 and CL-6a, see Fig. 1). Both TNM and dark CO_2 fixation were significantly lower in the near-bottom waters of all three East Siberian Sea stations (LS-3, WN-1, and WN-3, Table 9).

Comparison of the $\delta^{13}C$ values in near-bottom water and upper sediment horizons (Tables 2–4) revealed that the processes affecting the IS of OM occurred in the sediments as well. At all 17 stations, the $\delta^{13}C$ values of the sediments were different from those of the near-bottom water. At 7 stations, enrichment of OM with the heavy ^{13}C isotope due to chemosynthetic processes continued in the sediments. At other 10 stations, however, the carbon of OM in the sediments became depleted of ^{13}C. According to the data of Table 9, the rates of dark CO_2 assimilation in these sediments were higher than in the near-bottom water, so that isotopically heavy carbon was formed in the sediments. However, apart from OM production, active anaerobic OM consumption occurred in the sediments; its scale may be assessed from the rates of sulfate reduction. Comparison of OM production via dark CO_2 fixation and OM consumption via sulfate reduction in the Chukchi Sea sediments (st. CS-8 and CS-6a, Table 9) shows that OM consumption was significantly higher than its production. It is logical to assume that sulfate reducers preferentially consume the fresher, isotopically heavy OM produced in the course of photo- and chemosynthesis. This results in a higher ratio of isotopically light terrigenous OM in residual OM, so the IS of OM of the bottom sediments

Table 8. Isotopic composition of organic matter carbon (δ^{13} C, ‰) in the Quaternary sediments of the Chukchi Sea determined by the 2004 (stations 15 and 106) and 2009 expeditions (stations 7T1 and 2TB)

Station 15		Station 106, depth 72 m		Station 7T1		Station 2TB	
Sediment horizon, cm	δ^{13}C, ‰	Sediment horizon, cm	δ^{13}C, ‰	Sediment horizon, cm	δ^{13}C, ‰	Sediment horizon, cm	δ^{13}C, ‰
0–3	–22.03	0–2	–	0–2	–	0–2	–
3–20	–	2–20	–22.49	7–22	–22.40	5–10	–25.06
20–45	–22.84	20–40	–21.75	22–52	–22.58	–	–
45–70	–21.81	40–65	–22.75	52–70	–	50–55	–21.29
		70–90	–22.75	70–100	–24.12	–	–
		100–120	–22.41	110–120	–	–	–
		120–140	–23.64	120–150	–24.77	–	–
		140–190	–22.54	150–170	–	135–190	–24.31
		190–213	–22.05	180–200	–22.73		
				230–240	–24.07		

Table 9. Total number of microorganisms (TNM, $\times 10^3$/mL), dark CO_2 fixation (μg C dm^{-3} day^{-1}), consumption of organic matter via sulfate reduction (SRC, μg C dm^{-3} day^{-1}), and carbon isotopic composition (δ^{13}C, ‰) of suspended organic matter from the surface and near-bottom water and of the bottom sediments

Station no.	Surface water			Near-bottom water			Surface sediment horizon			
	TNM	Dark CO_2 fixation	δ^{13}C	TNM	Dark CO_2 fixation	δ^{13}C	Eh, mV	SRC	Dark CO_2 fixation	δ^{13}C
					Chukchi Sea					
CS-8	140	0.444	–21.47	800	0.612	–20.23	–145	115	68	–23.07
CL-6a	390	0.420	–22.47	620	0.528	–20.36	+180	252	51	–22.04
					East Siberian Sea					
WN-1	110	0.132	–25.09	170	0.192	–24.35	–80	90	12	–24.76
WN-3	100	0.144	–24.05	270	0.168	–22.81	–90	40	12	–27.64
LS-3	160	0.192	–25.31	260	0.204	–22.85	–50	8	2.6	–21.32

Note: Consumption of organic matter by sulfate reducers (SRC) was calculated from the experimentally measured sulfate reduction rate, with consumption of 24 μg of OM carbon for formation of 32 μg of reduced sulfur.

changes in the direction of lower negative δ^{13}C values than those of the near-bottom water (Table 9).

Carbon isotopic composition of OM in the upper 100–120 cm of the sediment (the average value for 13 samples from 4 cores being –22.59‰, Table 8) was very close to the δ^{13}C = –22.16‰ value of the upper sediment horizons (17 samples, Tables 3 and 4). These data make it possible to state that the biogeochemical conditions of sediment accumulation remained similar to the modern ones during formation of the meter-thick Quaternary sediment layer, while the major processes affecting the carbon IS of organic matter in the sediments were localized in the uppermost sediment layers with the most active microbial processes (Table 7).

Thus, the isotopic composition of suspended organic carbon in the upper water horizons of the East Siberian and Chukchi seas depends on the ratio of isotopically light terrigenous carbon (δ^{13}C = –26.5‰) and the relatively heavy organic carbon of phytoplanktonic origin (δ^{13}C = –19.9‰). Since primary production in the Chukchi Sea is 7 times higher than in the East Siberian sea, SOM of the Chukchi Sea is depleted of ^{13}C (–21.27‰) compared to the suspension of the East Siberian Sea (–23.52‰).

Aerobic and anaerobic microbial processes at the near-bottom water–upper sediment horizons biogeochemical barrier result in changes in the isotopic composition of organic carbon.

In the near-bottom water, under aerobic conditions, OM carbon almost invariably becomes enriched with ^{13}C. The TNM values and the rates of dark CO_2 fixation in the near-bottom water are significantly higher than in the surface water due to the flow of reduced products of anaerobic OM decomposition from the sediments to the near-bottom water. Chemoautotrophic microorganisms use these compounds for synthesis of additional biomass with the carbon IS close to $\delta^{13}C$ values from −20 to −21‰.

In the upper sediment horizon, the carbon IS of OM change depending on the ratio between the rates of microbial synthesis and consumption of organic matter, which may be determined from the rates of dark CO_2 fixation and anaerobic OM degradation via sulfate reduction, the most active anaerobic process in marine sediments.

At the stations with aerobic conditions in the uppermost sediment horizon, active OM production by chemoautotrophic synthesis continues, resulting in further OM enrichment with ^{13}C. The isotopic composition shifts to more positive $\delta^{13}C$ values than those of the near-bottom water.

At most stations, however (13 out of 20), apart from OM production via dark CO_2 fixation, freshly synthesized, isotopically heavy OM is consumed by sulfate reducers and other anaerobic microorganisms. When the rate of OM consumption exceeds the rate of OM production, the carbon IS of the sediments shifts to more negative $\delta^{13}C$ values.

Thus, aerobic and anaerobic microbial processes of OM production and consumption at the biogeochemical barrier between the near-bottom water and the upper sediment horizons result in significant, often multidirectional changes in the carbon IS of SOM formed in the upper water horizons and buried in the bottom sediments.

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