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REVIEW

Effect of Phytoplankton and Microorganisms on the Isotopic Composition of Organic Carbon in the Russian Arctic Seas

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Abstract—Carbon isotope composition of suspended organic matter (CIC_{SOM}) and of organic carbon of the bottom sediments (CIC_{BS}) was studied in a series of expeditions (starting in 1993) to the White, Kara, Chukchi, and Barents seas in the Russian Arctic. For each sea, CIC_{SOM} and CIC_{BS} was found to depend primarily on the ratio of OM produced in the water and OM of terrigenous origin. While in the White Sea, where the primary production (PP) is 5.3 times higher than the yearly inflow of terrigenous OM, $\delta^{13}C$ of SOM carbon is –29.1‰, in the Chukchi Sea, where PP is more than 300 times higher than the inflow of terrigenous OM, $\delta^{13}C$ of SOM carbon is –21.8‰. In the Barents and Chukchi seas, a considerable effect of suspended material arriving with the currents from the neighboring seas on formation of the CIC_{SOM} was demonstrated. The difference between CIC OM of the bottom sediments form CIC_{SOM}, the main component of organic matter in the sediments of all shelf seas, was demonstrated for the first time for all the seas studied. This results from production of additional microbial OM due to CO_2 assimilation at the water–sediment redox boundary or in near-bottom water.

Key words: carbon isotopic composition, suspended organic matter, Arctic seas, microbial CO_2 fixation, secondary production of microbial biomass

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The isotopic and molecular composition of carbon of suspended organic matter (SOM) and of organic matter (OM) of marine bottom sediments (BS) is determined by OM arriving with river flow and aerosols (allochthonous OM) and by OM synthesized by marine organisms (autochthonous OM). The isotopic composition ($\delta^{13}C$) of allochthonous OM varies within a broad range, from –12 to –30‰ and depends on the biochemical characteristics of photosynthesis of terrestrial plants (C_3- or C_4-type photosynthesis), the ratio of soil and peat OM, etc. [1, 2].

Autochthonous OM, mostly the biomass of plankton carrying out C_3 photosynthesis, has significantly different $\delta^{13}C$ values, from –16 to –23‰. In the open sea, where autochthonous OM predominates, carbon isotopic composition (CIC OM) is therefore usually heavier than $\delta^{13}C$ = –25‰, while OM of the coastal waters and sediments is usually lighter than –25‰ [2].

The composition of the bottom sediment OM depends on the SOM precipitating from the water column. The isotopic composition of OM in the sediments is usually believed to inherit the isotopic composition of SOM [2]; $\delta^{13}C$ of the bottom sediments is therefore much more often determined than the CIC of SOM. The data on the Arctic shelf seas are a good illustration. Carbon isotopic composition of the BS in this region was originally investigated by American and Canadian researchers in the early 1980s [3]. In the 1990s, when foreign researchers acquired the possibility to work in the Russian Arctic, hundreds of analyses were carried out for OM of the bottom sediments of the Chukchi, Kara, East Siberian, and Laptev seas [4–8].

However, CIC_{SOM} has never been analyzed. Only our biogeochemical team collected the samples of sediments and suspensions during the expedition of the 49th cruise of the *Dmitrii Mendeleev* r/v to the Kara Sea (September to October 1993) and demonstrated that the $\delta^{13}C$ values for the carbon of SOM and of the bottom sediment OM were not identical [9]. These data suggested changes in CIC OM during transport of the suspension in the water column or at the water–sediment interface, probably due to microbial processes.

This conclusion was confirmed by the study of CIC_{SOM} in the Black Sea and in the meromictic Lake Mogil'noe (Kil'din Island, Barents Sea). Significant changes in CIC_{SOM} caused by newly formed OM of microbial origin were revealed in the redox barrier in the chemocline of these environments inhabited by autotrophic microorganisms [10, 11].

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Table 1. Isotopic composition ($\delta^{13}C$, ‰) and content of organic carbon (C_{org}, %) in suspensions from different horizons of the water column and fluff layer of the White Sea

Station, depth, m	No. 6042, 61 m		No. 6049, 80 m		No. 6056, 133 m		No. 6058, 300 m		No. 6066, 264 m		Average values	
	C_{org}	$\delta^{13}C$	C_{org}	$\delta^{13}C$	C_{org}	$\delta^{13}C$	C_{org}	$\delta^{13}C$	C_{org}	$\delta^{13}C$	C_{org}	$\delta^{13}C$
1. *Surface water	–	–29.3	0.49	–29.2	0.65	–28.6	–	–28.6	–	–	0.57	–28.9
2. Near-bottom water (1–2 m above the sediments)	0.37	–29.0	0.44	–28.0	0.19	–29.0	–	–30.5	–	–	0.33	–29.1
3. Over-bottom water (8–10 cm above the sediments)	1.27	–27.7	1.90	–27.7	–	–27.4	1.08	–28.4	2.84	–27.3	1.77	–27.7
4. Fluff layer	1.65	–26.6	1.78	–25.8	1.60	–25.4	1.73	–25.8	1.69	–25.8	1.65	–25.9

Note: * Samples 1 and 2 were collected with a bathometer, samples 3 and 4, with a Niemistö corer.

The goal of this review is analysis of the empirical material related to the effect of phytoplankton and microorganisms on the carbon isotopic composition of SOM and OM of the sediments in the shelf seas of the Russian Arctic.

Bottom sediments and suspensions were sampled in late summer to early autumn 1993–2007 in expeditions of the Shirshov Institute of Oceanology, Russian Academy of Sciences, to the White, Barents, and Kara seas, as well as in the RUSALCA Russian–American expedition to the Chukchi Sea. These seas, except for the White and Barents seas, are located on the continental terrace of the Arctic Ocean, to the north of the Polar Circle, and have depths not exceeding 100 m. Ice cover is sustained for long periods, and the temperatures of air and water are low even in summer. Supply of biogenic elements with the river flow varies by more than an order of magnitude, with the river flow from 3.1 (White Sea) to 0.18% of the seawater volume (Chukchi Sea) [12].

The water was sampled with Rosette bathometers. Sediment samples were collected with gravity corers, dredges, and Niemistö-type hermetic corer. Physicochemical characteristics (pH, Eh, salinity, alkalinity, and the contents of dissolved oxygen and methane) were determined in the water samples, as well as the total number of microbial cells determined by direct count on membrane filters. In the bottom sediment samples, the chemical composition of silt water was analyzed, as well as the content of methane and organic carbon. The rates of microbial methanogenesis, methane oxidation, dark CO_2 fixation, and sulfate reduction were determined with radioactively labeled carbon and sulfur compounds. The methods and results of the microbiological and biogeochemical research are described in our publications [9, 13–23].

These works describe also the procedure for treatment of the samples of organic matter from bottom sediments and suspended organic matter in order to determine their carbon isotopic composition. MI-1305 (Ukraine) and Delta Plus (Germany) mass spectrometers were used to measure the $\delta^{13}C$ values.

ISOTOPIC COMPOSITION OF ORGANIC CARBON IN THE ARCTIC SEAS

White Sea

Location of the sampling stations and $\delta^{13}C$ values presented on Fig. 1 demonstrate that all the samples of SOM from subsurface and near-bottom water had similar CIC, from –28.1 to –30.5‰, with the average value of –29.1‰. Thus, terrigenous OM arriving with the Northern Dvina flow is the main component of suspended organic carbon. The absence of noticeable variations in CIC_{SOM} along the vertical profile of the water column, with depths varying from 36 m in the Dvina Bay (station 6046) to 300 m in the central basin (st. 6058), does not suggest a considerable effect of aquatic microflora on CIC_{SOM}.

The picture is different at the water–sediment interface. The data presented in Table 1 demonstrate significant weighting of OM carbon isotopic composition (from –29.1‰ in the water column to –27.7‰ in near-bottom water and –25.7‰ in the upper sediment layers) occurs at the boundary between near-bottom water and the uppermost sediment layer (warp), which is collected only with the Niemistö corer. Interestingly, the average $\delta^{13}C$ value for 15 samples of organic carbon from upper Holocene sediments (–25.85‰) [21] was almost identical for the value for modern sediments. Thus, sediment formation was stable and the modes of CIC formation for marine sediments did not change throughout the upper Holocene. Only in earlier lake sediments were significant changes in CIC OM of the bottom sediments observed, with $\delta^{13}C$ = –30.33‰ [21].

We suggest that the changes in CIC OM at the water–sediment geochemical barrier results from development of chemoautotrophic microorganisms,

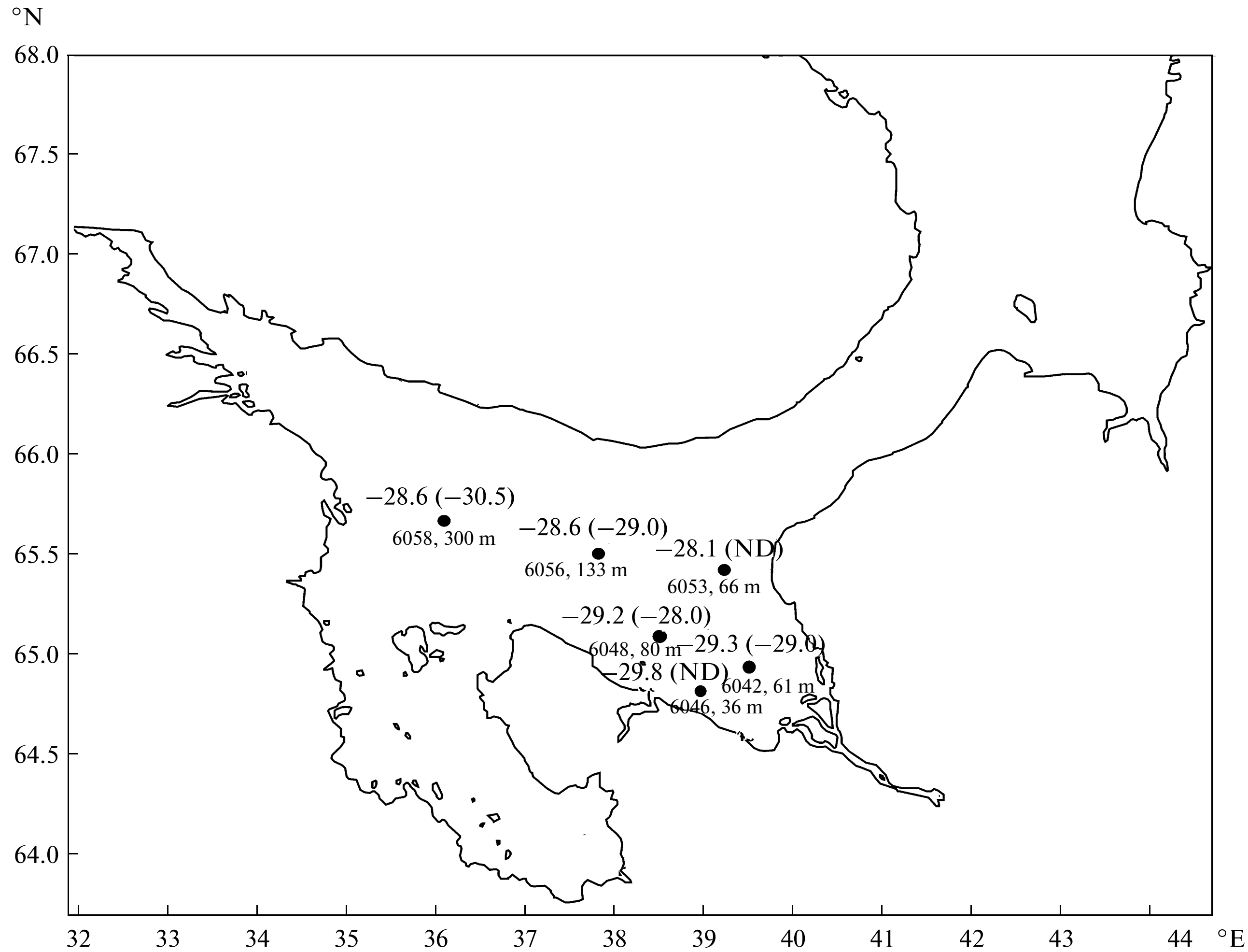

Fig. 1. Isotopic composition ($\delta^{13}C$) of organic carbon in the White Sea suspension. Numbers without parentheses designate the suspension from the surface water horizons; numbers in parentheses designate the suspension from near-bottom water collected with bathometers; ND stands for no data.

which accumulate biomass via CO_2 fixation due to the energy of oxidative metabolism, utilizing the reduced compounds formed during anaerobic decomposition of OM in the sediments. The data presented in Table 2 demonstrate that reducing compounds (e.g., methane) migrate from deep sediments to the water–sediment boundary. This table demonstrates also an increase in methane oxidation rate in the upper sediment layers, compared to its rate in the water column, as well as an increase in the rates of microbial dark CO_2 fixation by one to two orders of magnitude (Table 2).

Most chemoautotrophic microorganisms are known to utilize the C_3 pathway, resulting in OM of the biomass with $\delta^{13}C$ values from −16 to −23‰. Addition of the newly formed organic matter of the chemoautotrophs' biomass to OM precipitating from the water column results in much heavier $\delta^{13}C$ values for SOM of the near-bottom water, OM of the warp, and BS (Table 1). Increased C_{org} content in the near-bottom water and upper sediment horizons compared to C_{org} content in the water column is direct evidence of formation of additional OM (Table 1).

Kara Sea

The samples of suspensions and upper sediment layers were collected during expeditions of the Institute of Oceanology, Russian Academy of Sciences, in August to September 1993 (49th cruise of the *Dmitrii Mendeleev* r/v) and September 2007 (54th cruise of the *Akademik Keldysh* r/v). The material was collected mainly at the meridional transsection from the Ob estuary to 77°N (Fig. 2). During the 1993 expedition, samples of suspension and bottom sediments were also collected at the meridian section from the Yenisei estuary to 76°N (st. 4404 and 4405 for suspensions and st. 4398, 4399, 4400, 4412, and 4410 for sediments; see Fig. 2). During the 2007 expedition, suspensions were sampled at three stations in the southwestern Kara Sea

Table 2. Profiles of methane (μl dm^{-3}) and the daily rates of microbial methane oxidation (MO, nl dm^{-3}) and dark CO_2 assimilation (DCA, μg C dm^{-3}) in the water column and upper sediment horizons of the White Sea

Station no.		St. 6042, 61 m			St. 6056, 133 m			St. 6048, 80 m
Parameters		CH_4	MO	DCA	CH_4	MO	DCA	CH_4
Water column		0.16–0.26	0.05–0.25	0.18–0.48	0.05–0.06	0.01–0.04	0.12–0.35	
Near-bottom water (1–2 m above the sediments)		0.15	0.05	0.18	0.06	0.02	0.12	
Over-bottom water (8–10 cm above the sediments)		–	0.02	–	0.14	0.02	–	0.19
Fluff layer		3.63	6.30	104	0.20	–	–	1.08
Sediments	0–2 cm	6.14	–	170	–	6.39	22.5	4.86
	2–5 cm	7.00	5.02	89	–	–	–	6.44
	5–10 cm	7.41	4.85	27	4.66	–	30.4	9.46

Table 3. Isotopic composition ($\delta^{13}C$, ‰) of organic carbon in the surface horizon (0–3 cm) of the Kara Sea bottom sediments according to the results of the 1993 expedition

Station no.	Coordinates	Depth, m	C_{org} content, %	$\delta^{13}C$, ‰	
				Our data	Data of Fernanders, Sicra, 2000
Ob–open sea section					
4414	73°40′ N–73°30′ E	26	1.52	–27.8	–26.8
4395	74°13′ N–73°00′ E	31	0.57	–25.0	–25.4
4396	75°00′ N–73°00′ E	30	1.09	–25.5	–25.2
4397	75°59′ N–73°00′ E	150	1.25	–25.7	–24.4
Yenisei–open sea section					
4410	71°36′ N–83°19′ E	32	1.85	–26.1	–26.8
4412	71°49′ N–83°53′ E	14	1.15	–26.0	–26.5
4400	74°59′ N–80°00′ E	35	1.06	–25.4	–25.4
4399	74°14′ N–79°58′ E	40	–	–24.7	–24.6
4398	76°00′ N–80°00′ E	55	9.62	–23.5	–24.4

Table 4. Isotopic composition ($\delta^{13}C$, ‰) of suspended organic matter in the upper water column along the Ob–St. Anne trough meridional transsection (Kara Sea), 1993 expedition

No.	Sampling procedure	Coordinates	$\delta^{13}C$, ‰
1	Station 4418, precipitate from the suspension collected in a bathometer	68°50′ N 73°40′ E	–28.6
2	Sample 28, suspension separation along the movement	from 70°39.76′ N 73°35.85′ E to 69°40.00′ N 73°40.76′ E	–28.7
3	Sample 27, suspension separation along the movement	from 70°56.89′ N 73°33.85′ E to 70°39.86′ N 73°35.85′ E	–29.0
4	Station 4419, precipitate from the suspension collected in a bathometer	71°00′ N 73°20′ E	–28.1 –28.6
5	Station 4420, precipitate from the suspension collected in a bathometer	72°10′ N 72°50′ E	–28.6
6	Sample 29, suspension separation along the movement, Ob estuary	72°26.41′ N 73°30′ E	–29.4
7	Sample 30, suspension separation along the movement, near Belyi Island	73°10.00′ N 73°40′ E	–28.3
8	Sample 31, suspension separation along the movement	73°20.00′ N 73°35′ E	–26.0

Note: Samples 1–6 were collected from the Ob River; samples 7 and 8 were collected in the open sea (see Fig. 2).

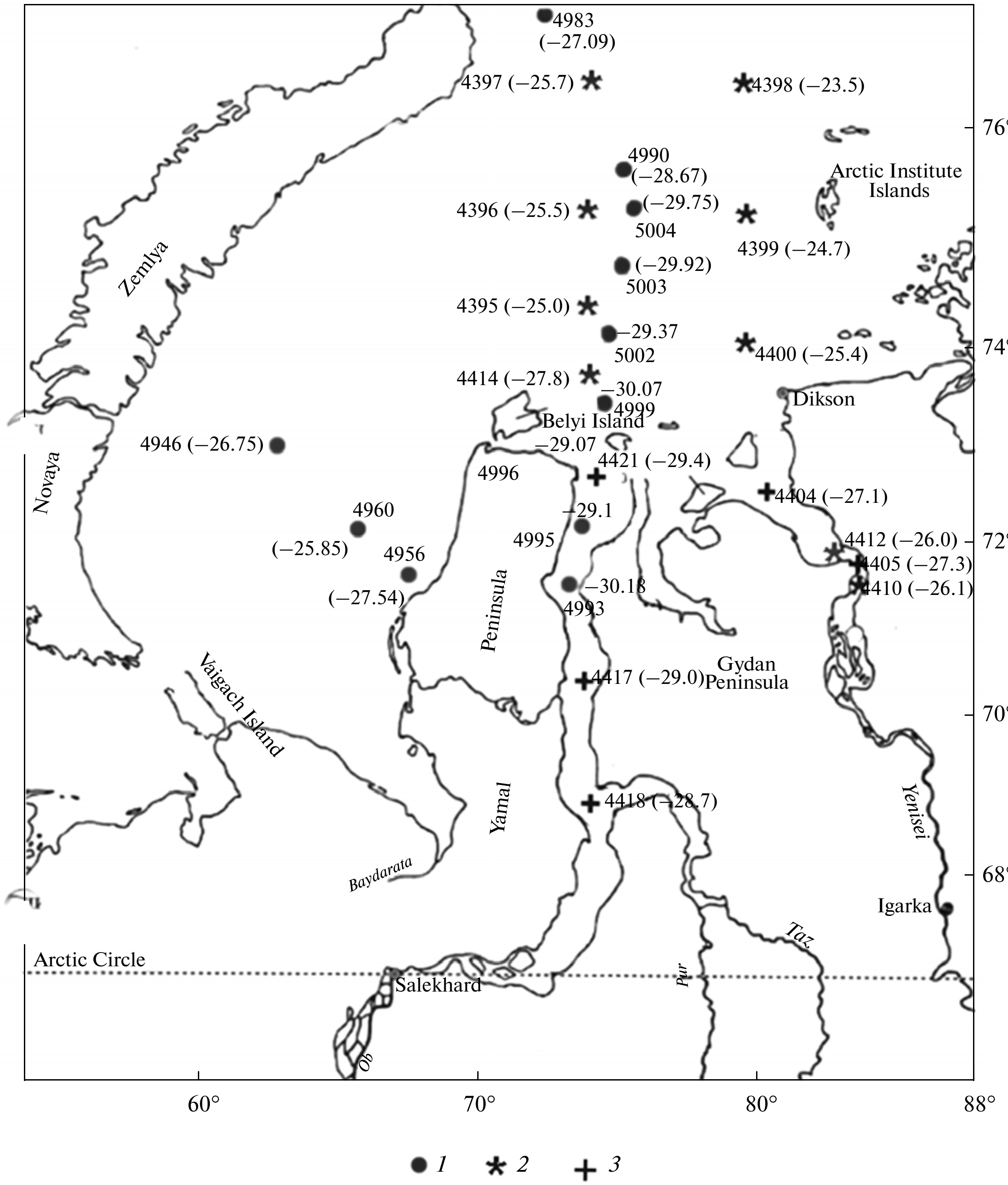

Fig. 2. Location of the stations for sampling suspensions and bottom sediments during the 1993 and 2006 Kara Sea expeditions and the isotopic composition of organic carbon ($\delta^{13}C$, ‰) of suspensions and bottom sediments. Suspension, 2006 (*1*), sediments, 1993 (*2*), and suspension, 1993 (*3*).

(see Fig. 2, st. 4946, 4960, and 4956). At the time of sampling, microbiological investigation of the Kara Sea water and sediments was carried out; these results have been published [9, 13, 14, 23].

The $\delta^{13}C$ values of OM of the sediments obtained in our laboratory (Table 3) are similar to those reported subsequently for these stations by other authors [5]. Table 4 and 5 present the $\delta^{13}C$ values for SOM obtained at the Ob section stations in 1993 and 2007, respectively.

The results of the 1993 expedition demonstrate significant changes of CIC_{SOM} in the south–north direction. The lowest ^{13}C content in OM was revealed in the samples from the Gulf of Ob ^{13}C from −28.1 to −29.4‰ (Table 4) and in the Yenisei estuary sediments (st. 4410, 4412, Table 3). In the open sea (sam-

Table 5. Isotopic composition ($\delta^{13}C$, ‰) of suspended organic matter in the surface and near-bottom water horizons of the Kara Sea, 2007 expedition

Station no.		Ob–St. Anne trough meridional transsection									Southeastern Kara Sea		
		4993 22 m	4995 11 m	4996 20 m	4499 27 m	5002 29 m	5003 60 m	5004 120 m	4990 125 m	4983 550 m	4956 33 m	4960 120 m	4946 140 m
Coordinates	N	71° 14.20′	72° 10.01′	72° 34.19′	72° 57.15′	75° 10.10′	75° 26.40′	75° 33.20′	76° 08.99′	76° 55.51′	71° 15.02′	71° 24.47′	71° 58.20′
	E	72° 29.66′	73° 14.38′	73° 49.78′	73° 17.10′	72° 56.50′	72° 31.40′	72° 31.30′	72° 29.68′	70° 17.87′	65° 50.21′	64° 50.82′	60° 59.4′
Salinity, g/l	Surface	0.05	3.5	–	10.0	19.0	19.0	19.0	27.0	34.3	32.2	31.0	28.1
	Near-bottom	0.05	8.0	–	27.0	25.0	29.0	33.0	34.0	34.7	32.6	33.8	33.8
T°C	Surface	7.2	4.9	3.2	3.0	3.0	3.0	2.5	1.5	2.0	6.0	6.5	6.0
	Near-bottom	+7.2	4.3	2.3	–0.1	–1.1	–1.1	–0.9	–0.9	0.4	4.1	–1.1	–1.2
$\delta^{13}C$, ‰	Surface	–30.18	–29.11	–29.07	–30.07	–29.37	–29.92	–29.75	–28.27	–27.62	–27.54	–25.85	–26.75
	Near-bottom	–30.18	–26.61	–	–28.48	–28.16	–28.71	–	–28.67	–24.77	–26.51	–25.72	–25.54

Table 6. Profiles of methane (μl dm^{-3}), isotopic composition of organic matter ($\delta^{13}C$, ‰), and the daily rates dark CO_2 assimilation (DCA, μg C dm^{-3}) in the water column and upper sediment horizons of the Kara Sea

	Sampling horizons	St. 4999, 27 m			St. 4990, 125 m			St. 4983, 550 m		
		CH_4	DCA	$\delta^{13}C$	CH_4	DCA	$\delta^{13}C$	CH_4	DCA	$\delta^{13}C$
Water column	Surface water	0.45	0.44	–30.01	0.25	0.14	–28.27	0.36	0.07	–25.85
	Near-bottom water	0.42	0.55	–28.48	0.25	0.03	–28.67	0.04	0.02	–25.72
	Over-bottom water	19.9	0.85	–	1.44	0.12	–	0.20	0.12	–
Sediment, cm	0–1 cm	237.0	2.24	–25.70	104.0	98.0	–24.80	30	4.6	–23.70
	1–7 cm	110.0	45.3	–	153.0	113.0	–	33	12.6	–

ple 31, 72°30′N, Table 4), CIC_{SOM} was significantly heavier than in the Gulf of Ob (up to –26.0‰). The carbon isotopic composition of organic matter in the sediments of the Ob ($\delta^{13}C$ values from –25.0 to –25.7‰, st. 4395–4397) and Yenisei profiles ($\delta^{13}C$ values from –23.5 to –25.4‰, st. 4398–4400) was still heavier.

Weighting of CIC_{SOM} from the Gulf of Ob to the open sea was confirmed by the 2007 expedition. While in subsurface water of three Gulf of Ob stations the $\delta^{13}C$ values varied from –29.7 to –30.18‰ (Table 5, st. 4993, 4495, 4996), this value was –27.62‰ at the northernmost st. 4983 (Table 5). Progressive dilution of the River Ob fresh water (carrying isotopically light terrigenous OM) with salt seawater carrying isotopically heavier phytoplankton is the main factor responsible for the CIC changes in surface water.

In the southwestern part of the Kara Sea, which is protected from the Ob inflow by the Yamal peninsula, CIC_{SOM} differs from that of the other stations, since saline water from the Barents Sea, containing SOM with different carbon composition, arrives to this region through the Kara Strait (see Fig. 3, Table 5).

Analysis of the isotopic composition of the suspension along the water column profile (Table 5) revealed that the $\delta^{13}C$ values for the surface and near-bottom horizons were almost identical. At all marine stations, except for st. 4990, suspensions from the near-bottom samples were enriched with ^{13}C compared to suspensions from the surface horizons (up to 2.85‰ at st. 4983, Table 5). Together with the results of the 1993 expedition, these data demonstrate that the carbon isotopic composition of the bottom sediments is enriched with ^{13}C by at least 2‰, compared to suspended carbon of the surface horizons [9]. We therefore compared all available data, both our results and the published ones, on the $\delta^{13}C$ values of organic carbon in suspensions and the upper sediment layer of the Kara Sea in the zone affected by the Ob waters between 70 and 75°E. These data are combined on Fig. 3, with 72°30′N as the northern border of active distribution of the Ob fresh water (see salinity data, st. 4996, Table 5).

The data presented on Fig. 3 confirm the earlier conclusion that the CIC of both SOM and OM of the BS changes regularly from the Ob estuary to the St. Anne trough. Comparison of the $\delta^{13}C$ values of the

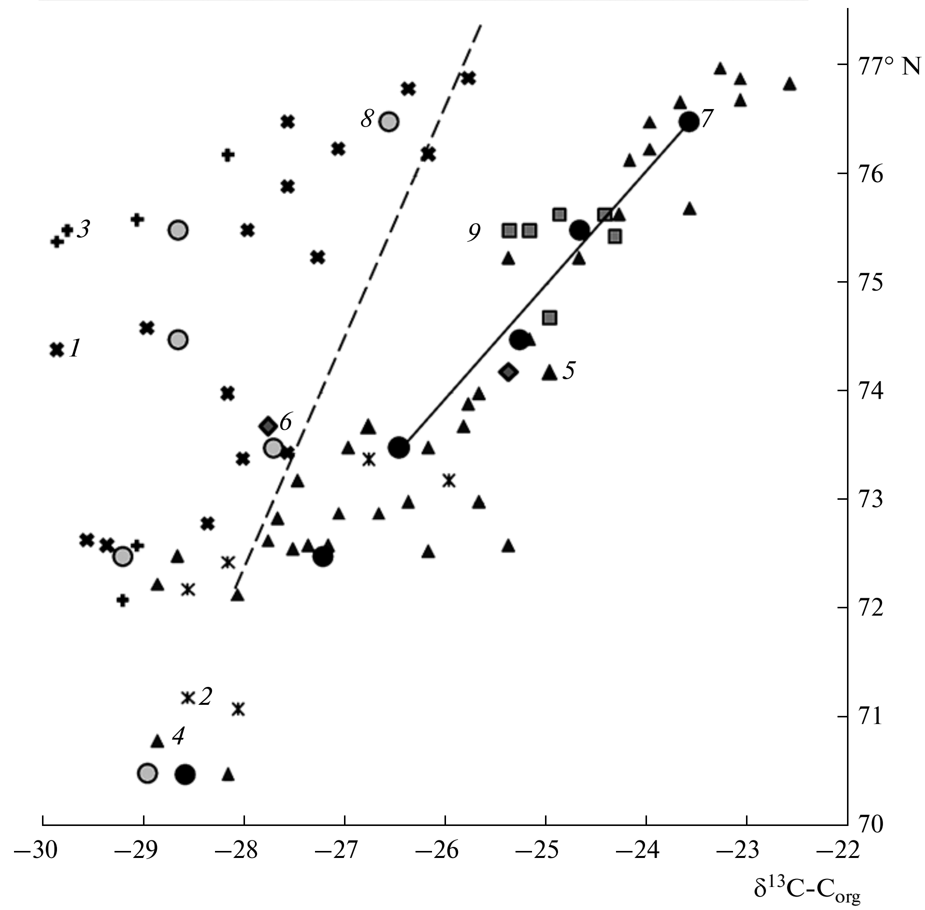

Fig. 3. Isotopic composition of organic carbon (δ^{13}C, ‰) for suspensions and upper sediment horizons sampled in the Kara Sea between 70 and 75°E and in the direction from the Ob estuary (from 70°00′ to 702°30′ N) to the open sea (from 72°30′ to 77°00′ N). Suspensions: [24] (*1*), [9] (*2*), [23] (*3*); sediments: [23] (*4*), [9] (*5*), [5] (*6*), [6] (*7*); average data for the sediments sampled within 1°N (*8*); average data for suspensions sampled within 1°N (*9*).

suspension and sediments at the geographically close stations always demonstrated enrichment of the sediments with ^{13}C. Variation of the δ^{13}C values for the sediment samples collected within 1° northern latitude do not exceed 2.5‰, while the average values of CIC OM for the sediments increase in the south–north direction (Fig. 3).

The δ^{13}C values of the samples of suspended carbon from the surface water horizons collected at different times [9, 23, 24] exhibit more differences than do the values for sediments, which may be explained by the annual changes in the volume of the Ob river flow and the primary production values.

Thus, analysis of available data demonstrates that, similarly to the White Sea (Table 1, Fig. 3), in the Kara Sea the CIC OM changes significantly at the water–bottom sediment boundary. In the near-bottom water and in the sediments, organic carbon contains suffi-

Table 7. The values of δ^{13}C, ‰ for SOM and OM of the upper sediment horizon in different regions of the Kara Sea

Region	Borders	Suspension		Sediments		Autochthonous OM, %[1]
		Number of samples	δ^{13}C, average	Number of samples	δ^{13}C	
Gulf of Ob	68–71° N	10	–29.2	10	–29.2	0
Zone of mixing of seawater and fresh water	72–72°30′ N	15	–28.7	15	–27.2	7%
Sea	73–77° N	20	–27.5	36	–24.3	31%

Note: [1] Allochthonous ON δ^{13}C = –29.2‰; autochthonous OM δ^{13}C = –22.0‰.

ciently more ^{13}C than in the suspension in the water column.

The data on methane content at the water–sediment boundary (Table 6) suggest intense processes of microbial oxidation of the reduced compounds formed in anaerobic sediments and enhanced CO_2 assimilation at this boundary, resulting in formation of microbial biomass with isotopic composition different from that of suspended organic matter. This results in changes in the $\delta^{13}C$ values of the total organic carbon of the sediments.

The average $\delta^{13}C$ values for suspended organic matter and for the upper sediment horizon at different sites between 70 and 75°E (see Fig. 3) are presented in Table 7.

Chukchi Sea

The Chukchi Sea, washing the shores of the Chukotka and Alaska peninsulas, is the easternmost shallow shelf sea of the Arctic Ocean. Since the flow of freshwater is limited to three small rivers (the Amguyema, Kobuk, and Noatak), while the flow of salt water from the Bering Sea via the Bering Strait and from the East Siberian Sea via the Del Long Strait is considerable, the water balance of this sea is different from that of other Arctic seas (Fig. 4). The samples of suspension and sediments from the Chukchi Sea were collected during the RUSALCA Russian–American expedition on the *Professor Khromov* r/v in August 2004. American biologists collected SOM samples for isotopic analysis at the same time and often at the same stations [25]. The main results of our biogeochemical team have already been published [15, 20].

All the sampling stations and $\delta^{13}C$ values for SOM carbon from the upper water layers and for the upper (0–3 cm) sediment layer are presented on Fig. 4. In the absence of pronounced river flow, the lightest OM with $\delta^{13}C$ value below –24.0‰ was detected in the sites of marine water inflow from the Bering and East Siberian seas. For example, stations 6 and 17 were situated in the zone affected by the Bering Sea current, which, after entering the Chukchi Sea, turns in the northeastern direction along the Alaskan coast. The $\delta^{13}C$ values for SOM at these stations were –24.3 and –24.1‰, respectively.

In the western part of the sea, isotopically light SOM was revealed at stations 27, affected by the coastal branch of the current from the East Siberian Sea via the De Long Strait ($\delta^{13}C$ = –24.5‰), and 85, at the Herald Canyon, where the northern branch of this current turns (δ^{13}CSOM = –24.0‰) (see Fig. 4).

At most of the stations of the central Chukchi Sea (stations 11, 14, 25, 23, and 106) and at station 7 in the western Bering Strait (through which the Chukchi Sea water enters the Bering Sea), $\delta^{13}C$ values vary from –19.5 (st. 14) to –22.6‰ (st. 25). Only at station 20, at the northeastern point of the northern section of the Chukchi Sea (st. 20–25), the isotopic composition of SOM was somewhat lighter (to –24.4, –24.6‰) due to admixtures of isotopically light SOM brought by the Bering Sea current (Fig. 4, stations 17 and 18).

The same pattern was observed for bottom sediments: at the stations of the central part of the sea (11, 13, 15—southern section; 22 and 20—northern section) and at station 106, the $\delta^{13}C$ values for organic carbon of the sediments were heavier than –23.0‰ (see Fig. 4). Only in the sediments of stations 25 and 85 the $\delta^{13}C$ values for organic carbon of the sediments were –23.2 and –23.0‰, respectively, due to the water flow from the East Siberian Sea via the De Long Strait. At stations 1 and 18, affected by the Bering Sea water, still lighter CIC OM of the bottom sediments was detected ($\delta^{13}C$ = –24.6 and –24.3‰, respectively) (see Fig. 4).

The average $\delta^{13}C$ value for all 14 SOM samples of the upper water column (Fig. 4) was –23.1‰, while for 8 samples from the stations not affected by the currents from the Bering and East Siberian seas (stations 7, 11, 14, 23, 25, and 106, Fig. 5), the average $\delta^{13}C$ SOM = –21.5‰.

The results of analysis of the CIC_{SOM} along the sections of the water column at the stations of the central part of the sea are presented on Fig. 4. Although the $\delta^{13}C$ values in individual samples vary from –19.1 to –23.7‰, the average $\delta^{13}C$ value for 24 samples (–21.8‰) is close to the one for the surface horizons (–21.5‰, see above).

The average $\delta^{13}C$ value for ten samples of organic carbon from the upper layer of bottom sediments is –23‰; it is –22.4‰ for six stations at the central part of the sea and –23.8‰ for the stations affected by the currents from the East Siberian Sea (st. 25 and 85) and the Bering Sea (st. 17 and 18).

Barents Sea

The hydrological regime of the Barents Sea differs significantly from that of the White and Kara seas, where river flow plays a noticeable role in the water budget, bringing fresh water and terrigenous organic matter. In the Barents Sea, the yearly river flow is 1663 km^3 of fresh water, i.e., about 2.2% of the 74000 km^3 of the ocean water arriving to the southern and central parts of the sea from the Norwegian Sea with the Nordkapp current. The southern arms of the Siberian branch of the Transpolar drift, which brings yearly 15000 km^3 of water and drift ice from the Arctic ocean to the northern part of the sea via the northern border between Franz Joseph Land and Spitsbergen (Fig. 5).

The samples for determination of the carbon isotopic composition of suspensions were collected during the Arktika-98 complex expedition on the *Akademik Fedorov* r/v (October to November 1998). The results of microbiological investigations by this expedition have been published earlier [16, 22]. The literature

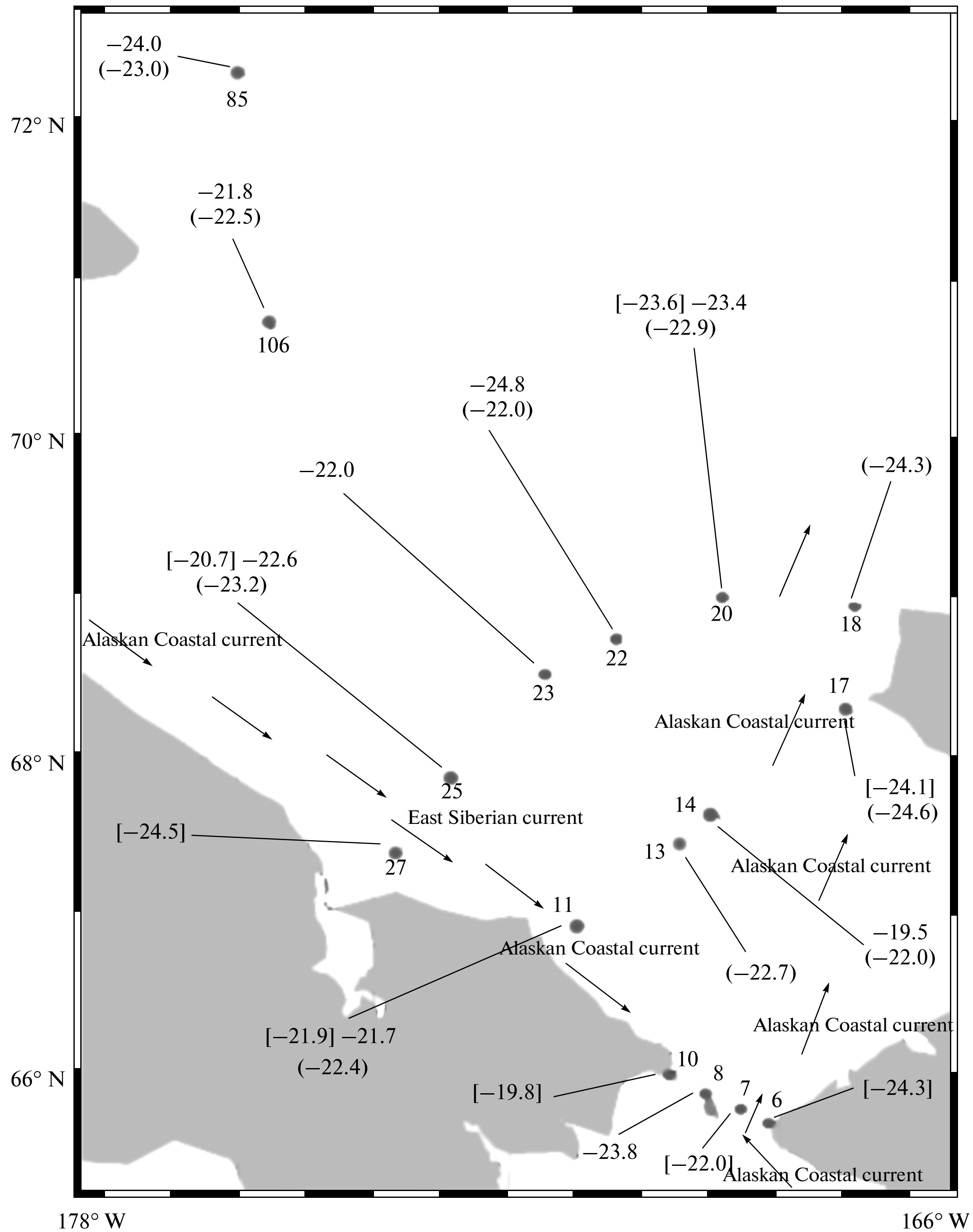

Fig. 4. Location of sampling stations for suspension and sediment samples in the Chukchi Sea and the isotopic composition of organic carbon ($\delta^{13}C$) of suspensions and bottom sediments. Numbers in parentheses designate our data for sediments, numbers without parentheses designate our data for suspensions, and numbers in square brackets designate American data for suspensions [25].

data on the $\delta^{13}C$ values of suspensions [26] and the results of foreign investigators on CIC OM of the upper bottom sediments of the Barents Sea [27, 28] were also used. The sampling sites for SOM and bottom sediments are shown in Fig. 5.

The data presented in Table 8 demonstrate that CIC_{SOM} at the most high-latitude sites (stations 1–5), located in the zone containing drift ice, varied from −21.0 to −24.9‰ (nine samples) with an average value of −23.6‰. The carbon isotopic composition of

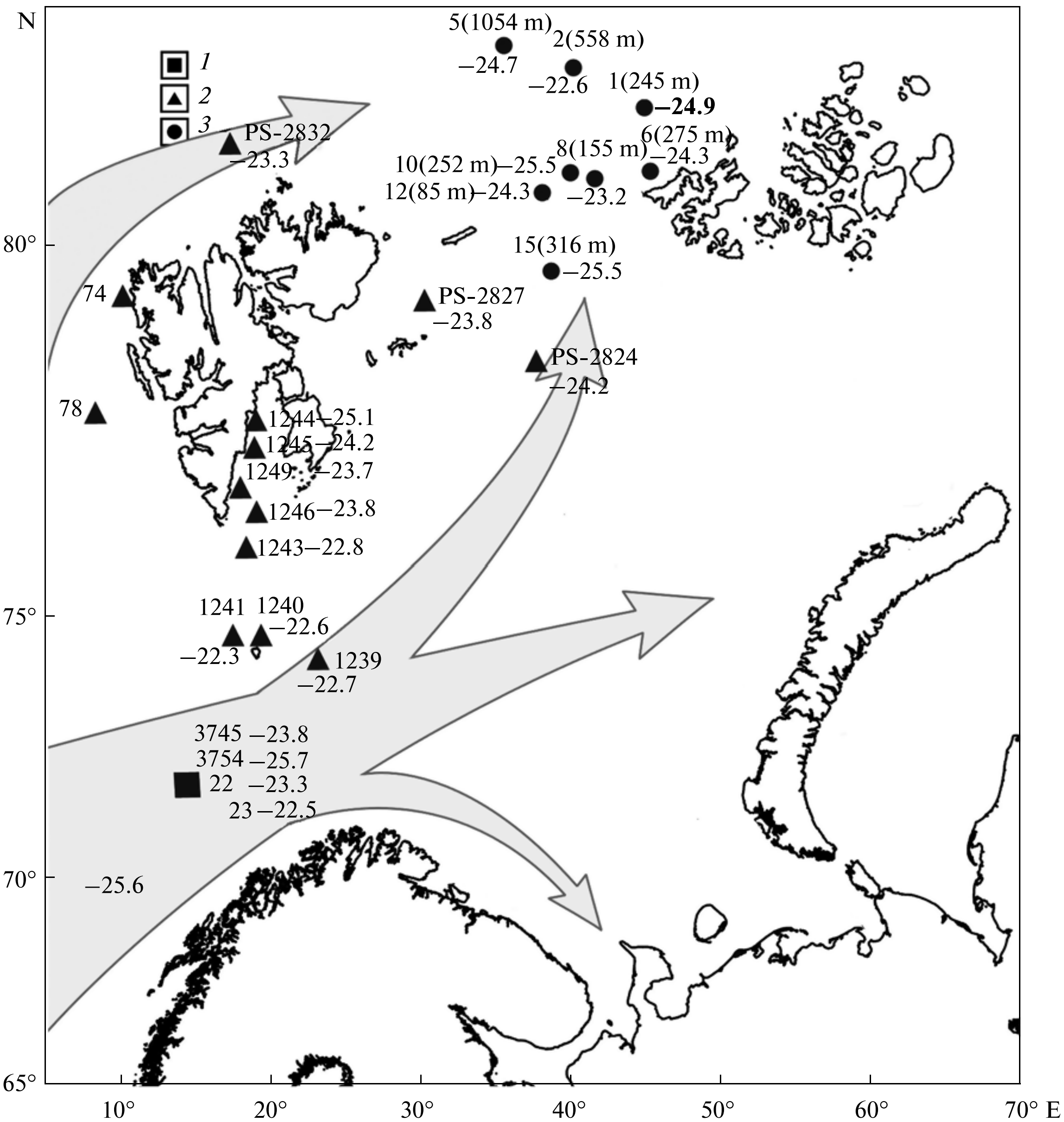

Fig. 5. Location of sampling stations for suspension and sediment samples in the Barents and Norwegian seas and the isotopic composition of organic carbon ($\delta^{13}C$) of suspensions and bottom sediments. Five samples for the bottom sediments from the region of the Haakon Mosby volcano [17] (*1*), bottom sediments [27, 28] (*2*), and suspension (our data) (*3*).

SOM in the samples collected at more southern sites (stations 6–15) varied from –23.8 to –26.4‰. The average $\delta^{13}C$ value for 16 samples from this region was –25.0‰. Since in both investigated regions SOM contained less ^{13}C than is typical of the biomass of Arctic phytoplankton ($\delta^{13}C$ values from –20.0 to –22.0‰), this suggests inflow of isotopically lighter terrigenous OM with aerosols. Their isotopic composition, according to our measurements of OM in the snow cover, has practically the same $\delta^{13}C$ values as the suspension: –25.4, –23.8, and –25.8‰, with the average of –25‰ (Table 8).

Variations in CIC_{SOM} along the water column do not suggest any regularities in the $\delta^{13}C$ values in different horizons of the Barents Sea water (Table 8).

Isotopic data did not confirm the suggestion of the effect of the suspension released from thawing ice on the CIC_{SOM} in the zone of drift ice [26]. The $\delta^{13}C$ value of the first-year ice varied from –24.6 to –27.5‰ (the average value for seven samples was –26.1‰), while suspensions from younger ice had the average $\delta^{13}C$ value of –24.5‰ (range from –23.8 to –25.0‰) [26]. Both average values for $\delta^{13}C$ values of OM suspended in the drift ice are significantly lighter than the average

Table 8. Isotopic composition ($\delta^{13}C$, ‰) of suspended organic matter in the Barents Sea

Station no.	Depth, m	Coordinates	Sampling horizon, m	$\delta^{13}C$, ‰	Coordinates	Sampling horizon, m	$\delta^{13}C$, ‰
Our data					**Data of Kodina et al. [26]**		
1	245	81°34′ N	130	–24.9	81°51′ N	under ice	–24.2
		44°18′ E			39°19′ E		
2	558	81°47′ N	under ice	–22.6	81°58′ N	under ice	–26.3
		40°46′ E	100	–23.2	38°18′ E	near-bottom	–27.0
5	1054	82°00′ N	100	–24.7			
		37°33′ E	near-bottom	–21.9			
6	275	80°38′ N	25	–24.3			
		44°26′ E	50	–24.3			
			near-bottom	–24.9			
8	155	80°28′ N	15	–23.2	79°17′ N	0	–25.9
		42°08′ E	100	–23.8	40°15′ E		
			near-bottom	–23.4			
10	252	80°33′ N	90	–25.5			
		40°30′ E	near-bottom	–25.3			
12	85	80°17′ N	0	–24.3			
		39°21′ E	near-bottom	–24.9			
15	316	79°39′ N	0	–25.5			
		38°38′ E	100	–25.6			
			near-bottom	–24.1			
7						0	–24.5
9					79°17′ N	0	–26.4
					40°15′ E		

$\delta^{13}C$ for the water column in the zone of drift ice (–23.6‰) (Table 8).

Thus, the $\delta^{13}C$ value of suspensions in the central Barents Sea (average for 16 samples collected at stations 6–16) is –25.0‰ (see Table 8).

The results on the CIC of OM of the Barents Sea bottom sediments published by Schubert and Calvert [27] and Winkelmann and Knies [28] are presented in Table 9. The average $\delta^{13}C$ value for seven sediment samples collected to the north of 77°N is –24.3‰, while in the sediments to the south of 77°N, the sediments are significantly richer in ^{13}C ($\delta^{13}C$ = –23.0‰, Table 9). Thus, the pattern for the Barents Sea is the same as for the White and Kara seas: the carbon isotopic composition of the bottom sediments differs from the CIC_{SOM}, being richer in the heavy isotope ^{13}C. The difference between the $\delta^{13}C$ values for SOM and OM of the bottom sediments in the central part of the sea if 2.0‰ (Table 9).

EFFECT OF PHYTOPLANKTON AND MICROORGANISMS ON FORMATION OF THE CIC OM

The isotopic composition of suspended organic matter is formed in the upper water column of marine environments, where terrigenous organic matter arrives, both as suspensions in the river flow and as aerosols. Isotopically heavy OM is formed in the same surface layer as a result of photosynthesis.

The ration between terrigenous and planktonogenic OM is the main factor determining the $\delta^{13}C$ values of SOM and OM of the bottom sediments. This suggestion is confirmed by abundant material of investigations in the Arctic seas. Weighting of the CIC OM of the bottom sediments from the coastal sediments to marine ones has been demonstrated for the Beaufort Sea [3], East Siberian Sea [3, 4], and Laptev Sea [5]. Changes in the CIC OM of the Kara Sea sediments along the Ob and Yenisei meridional profiles has been originally demonstrated by the authors on the materials of the 1993 expedition (see Tables 4 and 8). The

Table 9. Carbon isotopic composition ($\delta^{13}C$, ‰) of the upper sediment horizons in the Barents and Norwegian seas

No.	Station no.	Depth, m	Coordinates		$\delta^{13}C$, ‰
			N	E	
			Barents Sea		
1	PS-2832	–	81°10′	16°15′	–23.3
2	PS-2827	–	79°25′	30°20′	–23.8
3	PS-2824	–	78°40′	40°00′	–24.2
4	1265	87	78°22′	16°22′	–25.2
5	1266	250	78°21′	15°15′	–23.7
6	1244	96	77°50′	19°09′	–25.1
7	1245	180	77°30′	19°07′	–24.2
Average value for the sediments north of 77° N					–24.3
8	1249	156	76°56′	15°15′	–23.7
9	1246	153	76°46′	19°25′	–23.8
10	1243	333	76°00′	16°34′	–22.8
11	1241	297	74°49′	17°34′	–22.3
12	1240	94	74°49′	19°10′	–22.6
13	1239	178	74°26′	20°50′	–22.7
Average value for the sediments south of 77° N					–23.0
			Norwegian Sea		
14	3745-M-1		72°00′	14°44′	–23.8
15	3754		72°00′	14°44′	–25.7
16	22	1255	72°00′	14°43′	–23.3
17	23	1265	72°00′	14°43′	–22.5
18	74	200	79°29′	12°02′	–25.0
19	78	123	78°10′	09°52′	–25.3
Average value for Norwegian Sea sediments					–24.3

Note: Samples 1–3 from Schubert and Calvert [27]; samples 4–13 from Winkelmann and Knies [28]; samples 14–19 from Lein and Ivanov [17].

same expedition revealed also regular variations in the CIC for suspended OM and differences between the CIC values for SOM and OM of the bottom sediments collected at the same sites. SOM contained less ^{13}C than OM of the bottom sediments (Tables 4, 5, and 7, Fig. 3).

A significant difference between the $\delta^{13}C$ values for suspended OM and OM of the bottom sediments was revealed in other Russian Arctic seas: the White (Fig. 1, Table 1), Barents (Tables 8 and 9), and Chukchi (Fig. 4) seas. Rachold and Hubberton observed the same pattern in the Laptev Sea: the CIC_{SOM} value for the matter brought by the Lena River was –26.6‰ and $\delta^{13}C$ for the Yana River SOM was –26.2‰. The isotopic composition of the Laptev Sea BS varied from –26.6 to –22.8‰ [30].

Since the Russian Arctic shelf seas are the terminal reservoirs for the flow of the full-flowing rivers draining the northern part of Eurasia, terrigenous OM of the river flow is among the major components of SOM and of OM of the sediments formed out of this suspension. Our results and the literature data on the CIC_{SOM} of some rivers flowing into the Arctic seas, which are presented in Table 10, demonstrate that the CIC_{SOM} for most of the northern rivers is close to $\delta^{13}C$ = –26.0‰, which is characteristic of carbon produced by polar terrestrial plants via C_3 photosynthesis.

The lighter CIC_{SOM} of the Northern Dvina and Ob (–29.2‰, Table 10) results from intense growth of freshwater phytoplankton in their estuaries. It utilizes isotopically lighter CO_2 and bicarbonate for photosynthesis than do marine phytoplankton [31].

In the Arctic seas with insignificant river inflow (the Barents and Chukchi seas), seawater from the neighboring reservoirs has a pronounced effect on the CIC_{SOM}. This may be exemplified by the Chukchi Sea (Fig. 4). While the coast of the Chukotka Peninsula is washed with the waters arriving from the East Siberian Sea via the De Long Strait, the Bering Sea current with the suspension differing in its isotopic composition from SOM of the central Chukchi Sea flows into the western part of the sea (Fig. 4).

Table 10. Average carbon isotopic composition for suspensions of Siberian rivers and suspension and sediments of the Arctic seas

Sea	Main rivers	$\delta^{13}C$, ‰					
		River		Shelf		Sea	
		SOM	Sediments	SOM	Sediments	SOM	Sediments
White	Northern Dvina	–29.2*	–	–	–	–29.1	–25.7
Kara	Ob	–29.2	–29.2	–28.7	–27.2	–27.5	–24.3
	Yenisei	–27.2	–26.1	–	–	–	–24.5
Laptev	Lena	–27.1**	N.d.	N.d.	–26.4**	–	–23.7**

Notes: * Due to the absence of data on CIC SOM for river water, the result from station 6042, the closest to the Northern Dvina estuary, was used (Fig. 1).

** According to Rachold and Hubberton [7].

Table 11. Isotopic composition of carbon in suspended organic matter (SOM) and upper horizons of bottom sediments ($\delta^{13}C$, ‰) in the Russian Arctic seas with different ratios of terrigenous and planktonogenous OM

Sea	Area, 10^3 km^2	Riverflow, km^3/year	Terrigenous SOM, 10^3 t C/year			Primary production (PP)		PP/SOM ratio	Isotopic composition, $\delta^{13}C$, ‰	
			River flow	Eolian transfer	Total	g/(m^2 year)	10^6 t/year		SOM	Sediment OM
White	85	250	360	16	376	25	2	5.3	–29.1	–25.7
Kara	920	1480	765	167	932	30–50	37	40	–26.6	–23.6
Chukchi	620	24	14	112	126	20–400	42	330	–21.8	–21.5
Barents	1512	215	90	363	453	20–200	136	300	–25.0	–22.8

Effect of high volumes of water from the neighboring seas, which carry SOM with the $\delta^{13}C$ values typical of those seas, is pronounced in the Barents Sea. In the Barents Sea, primary production of organic matter is more than 300 times higher than SOM inflow from the rivers, which is comparable to the ratio of autochthonous and allochthonous OM in the Chukchi Sea (Table 11). The CIC_{SOM} in the Barents Sea is significantly lighter than in the Chukchi Sea, –25.0 and –21.8‰, respectively (Table 11). This results from the fact that great volumes of water containing isotopically light suspension flow into the Barents Sea with the Nordkapp and Transpolar currents. The Nordkapp current carries 59000 km^3/year of the water with $\delta^{13}C =$ –25.6‰, while the polar waters (15000 km^3/year) contain a suspension with $\delta^{13}C$ = –23.6‰ (see Table 8).

Based on these data, the equation for the matter–isotopic balance can be used to calculate the isotopic composition of the suspension formed in the Barents Sea:

$$\delta^{13}C_BV_B = \delta^{13}C_NV_N + \delta^{13}C_TV_T + \delta^{13}C_XV_B.$$

In this equation, $\delta^{13}C_X$ is the $\delta^{13}C$ value for the suspension formed in the Barents Sea by photosynthesis, $\delta^{13}C_B$ is the $\delta^{13}C$ value measured in the Barents Sea (–25.0‰, Table 11), $\delta^{13}C_N$ and $\delta^{13}C_T$ are the $\delta^{13}C$ value for the suspensions brought by the Nordkapp current from the Norwegian Sea (–25.6‰) and by the Transpolar current (–23.6‰), V_B is the water volume of the Barents Sea (316000 km^3), V_N is the yearly flow from the Norwegian Sea (55000 km^3), and V_T is the yearly flow from the north (19000 km_3).

The calculation demonstrates that the CIC_{SOM} formed in the Barents Sea proper during photosynthesis is characterized by $\delta^{13}C$ = –21.8‰, which is almost identical to the $\delta^{13}C$ value for the CIC_{SOM} in the central part of the Chukchi Sea (Table 11).

Another important factor affecting formation of the CIC of SOM and OM of the sediments is an admixture of isotopically heavier OM of planktonic origin, which dilutes the isotopically light terrigenous OM. Our data summarized in Table 11 suggest that the dilution effect of the isotopically heavy OM of planktonic origin depends directly on the ratio between OM produced via photosynthesis and terrigenous SOM. The ratio of OM of different origin determines the differences in the CIC of SOM of the bottom sediments in different Arctic seas. The lowest surplus of primary production over the input of terrigenous OM (5.3-fold) was observed in the White Sea (Table 11), where the $\delta^{13}C$ value for SOM in almost all the central part of the basin was close to the $\delta^{13}C$ for the Dvina Bay (see Fig. 1). On the contrary, in the Chukchi Sea, where the primary production was 30 times higher than the content of terrigenous organic carbon, SOM is enriched with the isotopically heavy carbon of phytoplanktonic origin (see Table 11). In the Kara Sea suspension, where the primary production was

40 times higher than the inflow of terrigenous OM, CIC_{SOM} had intermediate values.

In the course of its relatively rapid precipitation to the bottom sediments, suspended organic matter, which contains pellets and incompletely mineralized remains of marine invertebrates, as well as peat and soil particles and plant spores originating from the continent, passes through the water column inhabited by heterotrophic microorganisms and some of the suspended OM is decomposed under aerobic conditions.

Data on experimental investigation on the effect of aerobic microorganisms on the component and isotopic composition of SOM are scarce. According to Galimov and Kodina [2], the CIC_{SOM} should become significantly lighter during its transport through the water column. It was demonstrated, however, that, in the Black Sea, in spite of a tenfold decrease in SOM content along the profile of the 100-m aerobic water column [32] and considerable variation in the composition of hydrocarbon biomarkers [33], changes in the $\delta^{13}C$ values of SOM were either not detected [32] or resulted in an increased ^{13}C content in SOM from the zone of photosynthesis to the oxycline [10].

Analysis of the distribution of $\delta^{13}C$ values for SOM in the vertical profiles of the water column of four Arctic seas demonstrates the absence of regular unidirectional changes in these values with depth (Tables 1, [4–6, 8]). However, Tables 1 and 6 demonstrate a significant weighting of organic matter at the near-bottom layer (collected with the Niemistö corer) and in the warp ("fluff layer") and the upper 1–3 cm of the bottom sediments. These data are confirmed by the results of analyses of the CIC_{SOM} in the water column and upper sediment horizons for 11 stations of the Kara Sea [24]. In this case, the average $\delta^{13}C$ value for 30 SOM samples from the water column, for the near-bottom suspension, and for the upper sediment horizon were –27.0, –25.6, and –25.3‰, respectively.

The heavier carbon isotopic composition of OM in the near-bottom water and fluff layer is accompanied by a significant increase in the content of organic carbon: in the White Sea, C_{org} content in the near-bottom suspension and fluff layer is five times higher than in the suspension from the lower water horizons and three times higher than in the suspension from the surface water (Table 1). Since the rate of dark CO_2 fixation in the near-bottom water, especially in the fluff layer, is several orders of magnitude higher than in the water column (Tables 1 and 6), increased C_{org} certainly results from the activity of CO_2-fixing microorganisms, which oxidize reduced carbon and sulfur compounds arriving by diffusion from anaerobic sediments to the water–sediment boundary. The data on methane distribution in the upper sediment horizons of the White and Kara seas (Tables 1 and 6) provide direct confirmation of the vertical flow of reduced compounds from the lower sediment horizons to the surface. Carbon isotopic composition of the biomass of chemoautotrophic microorganisms (using mostly the C_3 pathway of CO_2 fixation) has the same $\delta^{13}C$ value as the phytoplankton, i.e., from –19 to –22‰. An addition of even a small amount of the newly formed microbial OM to precipitating suspended organic matter may therefore result in the weighting of the CIC of the sediment OM.

CONCLUSIONS

1. Wide-scale investigations of the isotopic composition of organic carbon in suspensions and upper horizons of the bottom sediments were carried out for four shelf seas of the Russian Arctic.

2. This research confirmed that the isotopic composition of organic carbon in the sediments did not inherit the isotopic composition of suspended organic matter precipitating from the water column, but is significantly enriched with the heavy ^{13}C isotope.

3. A comprehensive microbiological investigation, which was carried out in parallel with research on the formation of the isotopic composition of organic carbon in bottom sediments, demonstrated that the changes in $\delta^{13}C$ values at the water–sediment boundary resulted from formation of additional organic matter of microbial origin, differing in its isotopic composition from the CIC_{SOM}.

4. The effect of the ratio between the amounts of allochthonous and autochthonous OM on the isotopic composition of suspended organic carbon was demonstrated to take place not only in the shelf–pelagial sections, but also to act as a geochemical characteristics for each sea investigated.

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