

## Manganese and Iron in the White Sea: Sedimentation and Diagenesis

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**Abstract**—Iron and manganese in bottom sediments studied along the sublatitudinal transect from Kandalaksha to Arkhangelsk are characterized by various contents and forms depending on sedimentation environments, grain size of sediments, and diagenetic processes. The latter include redistribution of reactive forms leading to enrichment in Fe and Mn of the surface sediments, formation of films, incrustations, and ferromanganese nodules. Variations in the total Fe content (2–8%) are accompanied by changes in the concentration of its reactive forms (acid extraction) and the concentration of dissolved Fe in the interstitial water (1–14  $\mu\text{M}$ ). Variations in the Mn content in sediments (0.03–3.7%) and the interstitial water (up to 500  $\mu\text{M}$ ) correspond to a high diagenetic mobility of this element. Changes in the valence of chemical elements results in the redox stratification of sediment strata with maximum concentrations of Fe, Mn, and sulfides. Organic matter of sediments with a considerable terrestrial constituent is oxidized by bottom water oxygen mainly at the sediment surface or in anaerobic conditions within the sediment strata. The role of inorganic components in organic matter oxidation changes from surface sediments, where manganese oxyhydroxide dominates among oxidants, to deeper layers, where sulfate of interstitial water serves as the main oxidant. Differences in river runoff and hydrodynamics are responsible for geochemical asymmetry of the transect. The deep Kandalaksha Bay serves as a sediment trap for manganese (Mn content in sediments varies within 0.5–0.7%), whereas the sedimentary environment in the Dvina Bay promotes its removal from sediments (Mn 0.05%).

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### INTRODUCTION

The program of the White Sea investigation developed by the Shirshov Institute of Oceanology involves many problems of its nature, including physical, geological, and biological aspects. In this work, we present the data on geochemical properties of sediments from the longest transect across the White Sea between the Kandalaksha and Dvina bays obtained during Cruise 55 of the R/V *Professor Shtokman* in 2003 (Fig. 1). Our study is focused on Mn and Fe distribution in sediments, as well as the relation of these elements to material sources and their behavior in diagenetic processes. Mn and Fe not only constitute a considerable proportion in the metallic matrix of sediments and participate in biogeochemical sedimentary cycles, but also determine the behavior and fate of many other chemical elements.

The composition of waters and sediments of the White Sea, which replaced the Early Holocene periglacial lake, is formed by the mixing of fresh river water runoff with saline sea water inflow from the Barents Sea. Coastal abrasion coupled with the frost weathering of crystalline rocks, nearshore snow melting, groundwater runoff, and atmospheric transport play an important role in the sedimentary material delivery. Aerosols

may contribute as much as 20% to the sedimentary material budget (A.P. Lisitsyn, personal communication). However, terrigenous material delivered by river discharge represents the main sediment source. It is distributed according to laws of mechanical (grain size and density), biological, and physicochemical (flocculation and coagulation) differentiation. The delivery of both allochthonous (river discharge) and autochthonous (marine production) organic matter considerably contributes to the sediment formation. These general regularities of all mediterranean seas connected with the ocean by narrow and shallow straits have many specific features in the White Sea, such as irregularity of coastline, cold climate, abundant river runoff, and tides.

The generally shallow (mean depth 49 m, maximum depth up to 340 m) study region is connected with the Barents Sea via the Gorlo Strait, 40 km wide and 37 m deep (Fig. 1). Three large bays (Dvina, Onega, and Kandalaksha) begin from river estuaries. The largest Severnaya Dvina and Onega rivers discharge 80% of the total river runoff (110 and 20  $\text{km}^3/\text{yr}$ , respectively). One-half of the annual runoff is discharged during May and June (Elisov, 1997). Fresh water and ice distributed by the main cyclonic surface current evacuate to the Barents Sea. Subsequently, they are replaced by colder

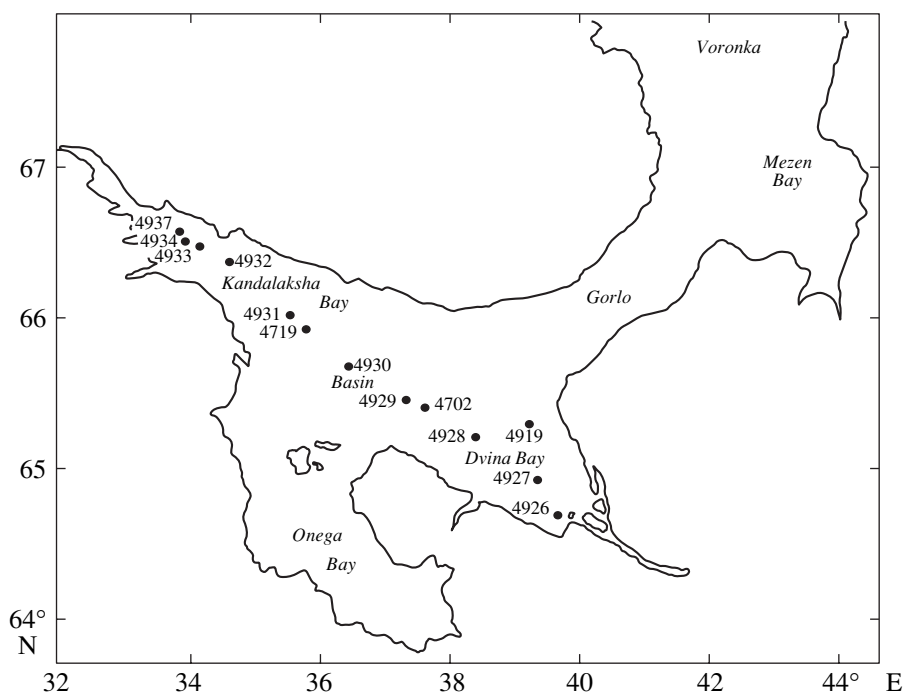


Fig. 1. Location of geological sampling stations of the R/V *Professor Shtokman* in the White Sea (cruise 55, August 2003).

and more saline Barents Sea water flowing in the opposite direction through the Gorlo Strait (Timonov, 1947). The inflow from the Barents Sea along the Kola Peninsula coast increases considerably due to tidal currents, which act as a compressing pump (Lukashin et al., 2003). The balance of outflow and inflow is estimated at 2000 km<sup>3</sup>/yr. Since the volume of the White Sea (without Gorlo and Voronka straits) is 4000 km<sup>3</sup>, its total water exchange lasts 2 yr (Stunzhas and Borodkin, 2004). However, the time of exchange is apparently different for various water masses of the stratified water column.

Tidal effects, which amplify the turbulent mixing, are especially noticeable in shallow-water and near-shore areas. Height of the tidal wave decreases from 7 m in the north (near the Gorlo Strait) to 2 m in the south (Onega Bay). The major water body is stratified; i.e., it shows stepped density structure. The mixed and freshened surface layer (0–15 m) with salinity as low as 2‰ in bays is replaced by denser marine water with salinity 27–29‰ at a depth of 20–60 m (Stunzhas and Borodkin, 2004). This intermediate watermass is fed by the Barents Sea water from the Gorlo Strait during summer season, whereas the deep water with a salinity more than 29‰ and temperature less than –1°C inflows from the Barents Sea during winter. The deep water is rather uniform. However, investigations carried out during last decades (Lukashin et al., 2003; *Kompleksnye issledovaniya...*, 1994) show that stepped structures and seasonal variations occur not only in the intermediate water, but also in the deep water. The very high oxygen content, no less than 7 ml/l (80% of saturation),

in the deep water is also an evidence of its constant and rapid renewal.

It is noted that areas adjacent to river mouths discharging into the White Sea are characterized by low concentrations of suspended matter ranging from 0.5–1 mg/l in the Kandalaksha Bay (Lukashin et al., 2003) to 5 mg/l in the Dvina Bay (Artem'ev, 1993). The latter value is much lower (up to 100 times) than those typical for southern Russian rivers. This is explained by regulation of river runoff in reservoir and lake systems (Nevesskii et al., 1977). The content of dissolved mineral components in the river runoff varies from 20 mg/l in the Kandalaksha Bay to 210 mg/l in the Dvina Bay (Leonov and Chicherina, 2004). In order to estimate the contents of dissolved Mn and Fe in the river runoff, we can refer to generalized data in (Gordeev, 1983): 10 and 40 µg/l, respectively. Corresponding values for sea water are 0.1 and 5 µg/l, respectively. Average Mn and Fe concentrations in the river suspended matter (0.5 and 24 mg/l, respectively) show considerable variations, especially in high-latitude drainage areas (Strakhov et al., 1968).

Rivers of the Russian North are enriched in humic organic matter. According to early estimates by Skopintsev and Krylova (1955), the dissolved C<sub>org</sub> content in the Severnaya Dvina river is 12.7 mg/l, which accounts for 90% of total (sum of dissolved and particulate) organic matter (Romankevich and Vetrov, 2001). According to these authors, average contents of dissolved and particulate C<sub>org</sub> in the White Sea water are 8 and 0.25 mg/l, respectively. The content of organic mat-

ter in the White Sea surface water was 50% higher in the 1990s owing to the industrial contamination of river runoff (Maksimova, 1996). Both the particulate river runoff and mineralization of river waters considerably change during spring inundations and autumn rain floods. The amount of suspended matter and, in part, dissolved components decreases at the river-sea boundary within the salinity range of 2–10‰ owing to flocculation of organic matter and coagulation of colloidal clay minerals (Lisitsyn, 1994). In the Kandalaksha Bay, this salinity barrier occurs in the upper part of the pycnocline at a short distance (1–2 km) from the river mouths (Lukashin et al., 2003).

The distribution of suspended matter in sea water is controlled by both biological productivity and hydrodynamics, including tidal processes. The spring-summer phytoplankton bloom mainly represented by diatoms and flagellates creates maximum concentration of suspended matter (more than 1 mg/l) in surface waters. However, increased concentrations of suspended matter may also appear within the water column due to the sinking of plankton remains after the bloom. High contents of suspended matter are also noted in the bottom water (especially, at shallow depths), e.g., in the Gorlo area, where the Barents Sea water flowing over the sill and accelerated by tides is enriched in suspended matter owing to the resuspension of sediments. These processes may be reflected in the Si/Al ratio variation in suspended matter. The ratio decreases with depth, reaches the lowest values in the layer of increased suspension concentration, and then increases near the bottom due to resuspension of sediments. Similar patterns are noted for the particulate  $C_{org}$  distribution, one-third of which is related to diatoms: the  $C_{org}$  content decreases with depth to less than 0.1 mg/l (Lukashin et al., 2003). The carbonate content in both suspended matter and sediments is negligible (less than 1.5%). The content of amorphous  $SiO_2$  (represented by opal of diatoms) in sediments is less than 2.5% (Nevesskii et al., 1977), although diatoms dominate in both plankton and sediment flux onto the bottom (Lukashin et al., 2003). The composition of suspended matter apparently undergoes seasonal changes, so that the proportion of lithogenic component increases during winter, whereas the content of organic matter is higher in warm seasons.

The coastline of the western White Sea is of tectonic origin. Metamorphic rocks, mainly granite gneisses, are exposed here on coasts of shallow-water bays. The low eastern coast represents a subsided part of the Russian Platform. In the Gorlo area of rapid currents, on shoals, and at river mouths, the bottom is covered with pebbles, gravel, and sand. On slopes, the coarse sediments are replaced by sand and mud, whereas sediments of the central White Sea (the "Basin") are represented by clayey mud. Ferromanganese nodules occur in the Gorlo Strait and some other regions. According to (Klenova, 1974), the thickness of recent sediments varies from zero in erosion areas to 22 cm in the central

part of the Basin, 100–150 cm near the coast, and up to 3 m off river mouths. Sedimentation rates are low (~2 cm/ka) in the central part of the White Sea, and exceed 30 cm/ka near the coast. According to isotope data (R. Aliev, personal communication), sedimentation rates may be much higher (up to 1–3 mm/yr). Recent sediments are underlain by late glacial dark gray homogeneous microfossil-free clays. The local occurrence of varved clays suggests the existence of an ancient glacier lake in the present White Sea area (analogy with the Baltic Sea). The White Sea was formed in the glacier lake area at the end of deglaciation, i.e., not earlier than 12 ka BP.

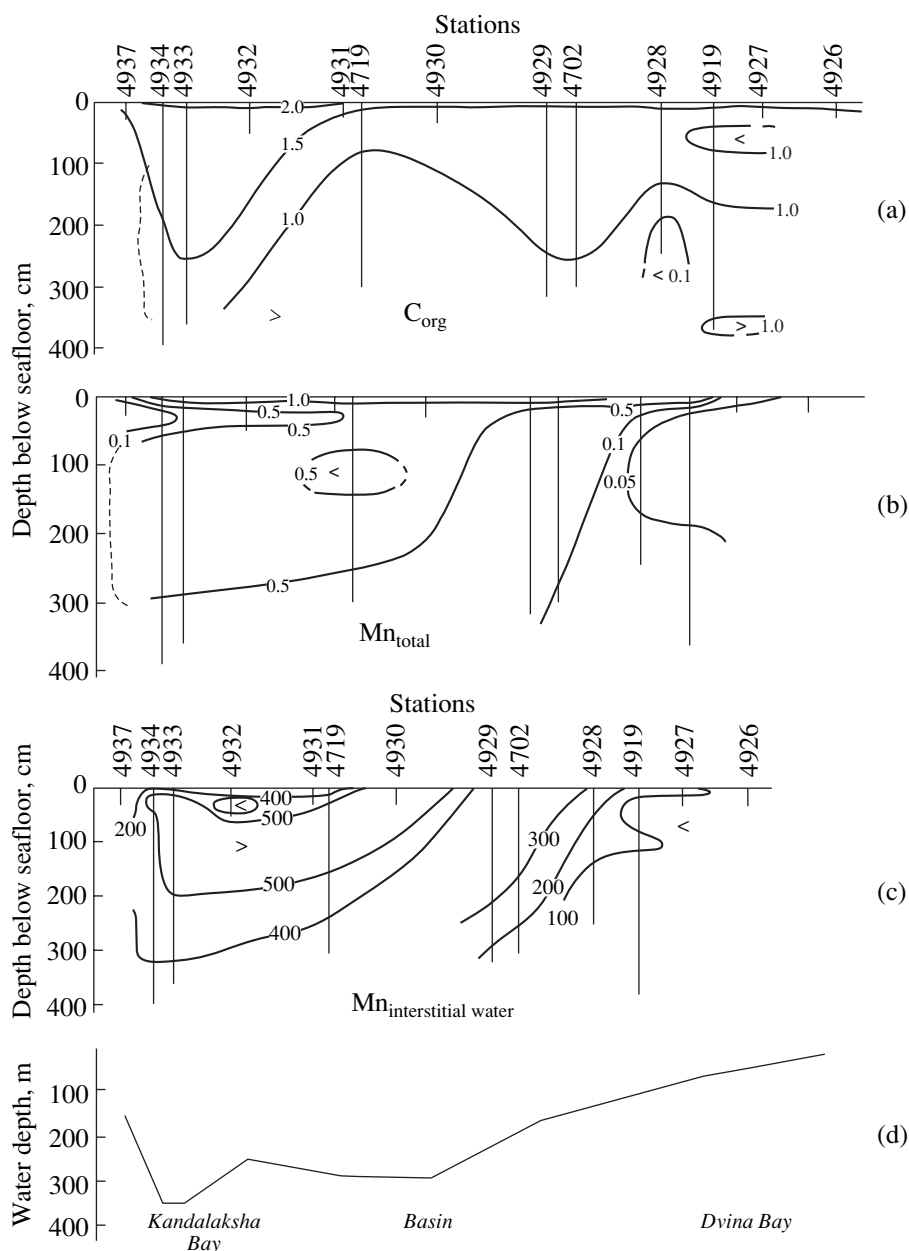
The aim of this work is to study the composition and main properties of the metallic constituent in sediments based on two sediment-forming elements (Mn and Fe). Similarities and dissimilarities of these chemical elements allow us to assess specific features of sedimentation and diagenesis in the White Sea.

## MATERIALS AND METHODS

Samples of White Sea sediments were collected from the Kandalaksha–Arkhangelsk transect (Fig. 1) using the grab sampler *Ocean* (40 × 60 cm<sup>2</sup>), the Niemisto corer (diameter 5 cm), and gravity corer (diameter 18 cm). The grab sampled up to 25-cm-thick surface sediments, the Niemisto corer recovered 60-cm-long cores, and the gravity corer retrieved sediment cores up to 4 m long. A part of sediment samples was processed aboard the ship immediately after their recovery (analyses for reactive forms of Mn and Fe in sediments, Mn and Fe dissolved in the interstitial water, as well as water content). Another part was dried and subsequently studied in the shore-based laboratory (analysis of the bulk content of chemical elements).

Reactive forms of Fe were determined after the treatment of a fresh sediment sample with 3.5N  $H_2SO_4$  without heating and the subsequent analysis of the extract for contents of Fe(II) and Fe(III). We used 0.02N  $K_2Cr_2O_7$  for the detection of Fe(II) and KJ and 0.02N  $Na_2S_2O_3$  for the determination of Fe(III). The method used for the analysis of marine and oceanic sediments allows us to estimate mainly the content of hydroxide forms of both bivalent and trivalent Fe, carbonate Fe, and partially Fe of layered silicates (Sokolov, 1980).

Interstitial water was extracted from fresh sediment samples (~30 cm<sup>3</sup>) by centrifuge (3000 rpm during 30 min). Solutions obtained were filtered through Millipore filters (0.45 μm) using a vacuum pump. The volume of extracted solution specimens commonly did not exceed 5–10 ml. In order to determine dissolved Mn and Fe, the interstitial water specimens were diluted ten times with the filtered surface sea water that did not contain these elements in dissolved forms (concentrations below their detection limits). Photometric technique with formaldoxim was applied to determine the



**Fig. 2.** Distribution of (a)  $C_{org}$  and (b)  $Mn_{total}$  (b) in dried sediment samples (%) and of (c) dissolved Mn in interstitial water ( $\mu M$ ). Water depth at stations is shown below (d).

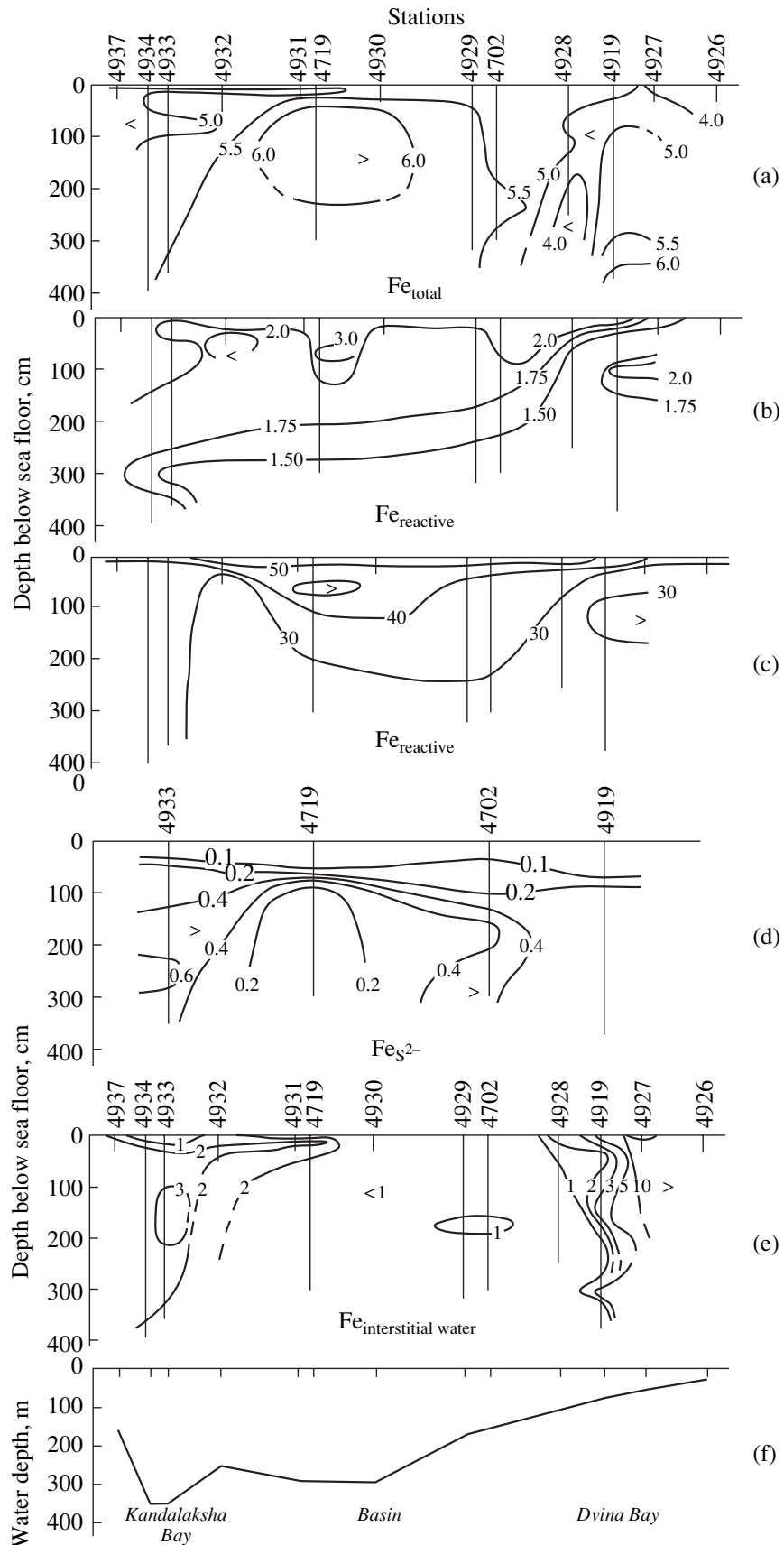
Mn content (detection limit  $0.2 \mu M$ ). Fe was determined using ferrozene with the detection limit of  $0.02 \mu M$  (Rozanov, 2003). This method allowed us to determine Fe(II) and the sum of Fe(II) and Fe(III).

The water content was determined in the shipboard laboratory using a drying box (temperature  $105^{\circ}C$ ). The total metal content, as well as  $C_{org}$  and  $CO_2$ , were determined in the shore-based laboratory using dried sediment samples. Specimens were digested by the successive treatment with HF and  $HClO_4$  with heating. Flame version of the atomic absorption method was applied for the final detection.  $CO_2$  and  $C_{org}$  were determined with an AN-7529 express analyzer. The content

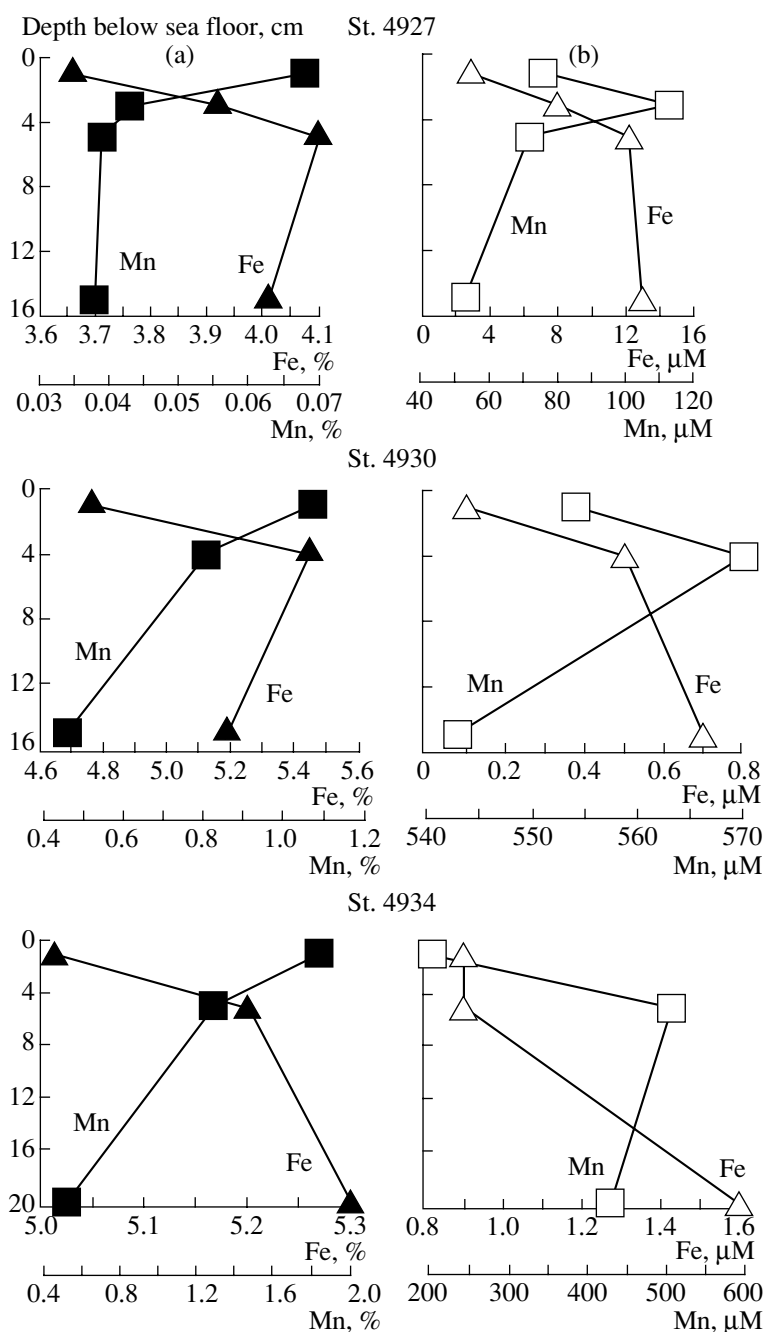
of sulfide Fe was calculated from results of direct determinations of sulfide sulfur (hydrotroilite) and pyritic sulfur (Kokryatskaya et al., 2003).

## RESULTS

The analytical results are presented in the table and profiles showing the distribution of individual sediment components (Figs. 2–4). In order to compile the profiles, we also used data obtained during Cruise 49 of the R/V *Professor Shtokman* in 2001 (stations 4702 and 4719).



**Fig. 3.** Distribution of (a)  $Fe_{total}$ , (b)  $Fe_{reactive} = Fe(II) + Fe(III)$ , (c) proportion of  $Fe_{reactive}$  in  $Fe_{total}$ , (d)  $Fe_{S^{2-}}$  (%) in dried sediment samples, and (e) dissolved Fe in interstitial water ( $\mu M$ ). Water depth at stations is shown below (f).



**Fig. 4.** Distribution of Fe and Mn in the (a) surface layer of sediments and (b) interstitial water of the White Sea. Dvina Bay (St. 4922); Basin (St. 4930); and Kandalaksha Bay (St. 4934).

*Organic matter* delivered to sediments from terrigenous sources and as marine plankton remains undergoes significant alteration and mineralization in the course of settling and at the sediment surface. A minor portion (about 5%) of the total organic matter settled onto the bottom is subjected to diagenetic alterations within the sediment strata (Romankevich and Vetrov, 2001). Analytical data on the  $C_{org}$  content (table) reflect just this portion. Nevertheless, the residual organic matter is responsible for many biogeochemical alter-

tations commonly realized by the chemoorganotrophic microbial activity (Kuznetsov et al., 1962).

Despite a high biological productivity of the Dvina Bay, where the summer primary production is up to  $2.7 \text{ g C/m}^2/\text{day}$  (Leonov et al., 2004), the  $C_{org}$  content in sediments here ( $\sim 1\%$ ) is slightly lower, as compared to 1.5% in the Kandalaksha Bay sediments (Fig. 2). This may be related to not only higher hydrodynamics of the Dvina Bay, but also coarser grain size of the sediments

Manganese and iron in sediments (%) and interstitial water ( $\mu\text{M}$ ) of the White Sea, cruise 55 of the R/V *Professor Shokman* (August 21–30, 2003)

Sampling instrument	Interval, cm	Lithological description	Iron				Manganese		$\text{CaCO}_3$ , %	$\text{H}_2\text{O}$ , %		
			$\text{Fe}_{\text{tot}}$	Fe(II) reactive	Fe(III) reactive	Fe(II) interstitial water	Fe(II + III) interstitial water	$\text{Mn}_{\text{tot}}$			Mn interstitial water	
1	2	3	4	5	6	7	8	9	10	11	12	13
St. 4919 (65°17.00' N, 39°15.00' E), depth 69 m												
Gr	0–1	Clayey warp with sand admixture, reddish brown, semiliquid	6.01	0.23	3.02	2.49	8.18	1.06	163	1.88	9.22	71.5
NC	1–3	0.5–16 cm: clayey aleurite (aleuropelite), brownish gray with rare hydrotroilite inclusions, plastic	–	–	–	2.73	2.46	–	132	–	–	–
	0–2	The same	6.13	0.51	1.94	–	–	0.216	–	1.66	7.63	72.3
	2–5	"	6.13	0.94	0.68	–	–	0.067	–	1.26	4.72	58.6
	5–8	"	6.31	1.40	0.59	–	–	0.052	–	1.03	3.90	68.8
	8–12	"	4.47	0.87	0.24	2.90	3.60	0.043	59.8	1.03	3.06	65.4
	15–20	Clayey mud, dark gray	–	0.77	0.16	2.00	4.10	–	49.1	1.02	2.07	61.5
GC	20–25	The same	4.29	0.70	0.10	–	–	0.040	–	0.83	2.66	64.7
	25–30	"	4.35	0.63	0.14	–	–	0.038	–	0.85	2.25	62.7
	30–35	"	4.23	0.84	0.13	0.40	1.90	0.040	40.8	1.12	2.72	61.5
	35–40	"	4.29	0.71	0.07	–	–	0.041	–	0.97	3.16	62.4
	40–45	"	4.41	0.62	0.09	–	–	0.042	–	1.03	2.32	60.6
	45–50	"	4.53	0.69	0.24	–	–	0.043	–	0.98	2.41	63.5
	50–55	"	4.29	0.70	0.13	–	–	0.042	–	0.85	3.16	56.7
	55–60	"	4.41	0.41	0.08	–	–	0.055	–	0.95	3.31	55.4
	60–63	"	4.60	0.51	0.11	–	–	0.036	–	0.80	4.15	43.5
	90–105	First signs of hydrotroilite at 50 cm; frequency of hydrotroilite inclusions increases with depth	5.58	2.26	0.49	2.10	2.50	0.038	107	1.13	4.31	63.7
138–150	50–180 cm: homogeneous greenish gray aleuropelite with hydrotroilite, fossil-free (a shell at 138 cm)	5.09	1.65	0.17	–	5.50	0.056	86.2	1.14	3.81	60.9	
195–210	180–285 cm: color change to reddish brown, density increases, hydrotroilite content decreases	5.09	1.04	0.34	<0.1	<0.1	0.056	82.5	0.93	4.72	55.1	
260–275	285–370 cm: sharp increase in hydrotroilite content (spots, secretions, and lenses), denser at 310 cm, with soft black inclusions	5.25	0.95	0.16	<0.1	<0.1	0.050	68.2	0.79	3.84	52.7	
310–325		5.64	1.28	0.23	–	–	0.053	32.6	0.48	1.48	49.5	
355–371		6.07	1.17	0.11	–	<0.1	0.065	49.5	1.57	1.25	44.5	

Table (Contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13
		St. 4926 (64°37.28' N, 39°33.92' E), depth 16 m										
Gr	0-1	0-0.5 cm: aleuritic-clayey sand, brown	2.81	0.44	0.60	9.00	14.20	0.045	86.2	1.97	11.5	51.1
	1-6	0.5-16 cm: greenish gray aleurite, with organic matter (?) inclusions, becomes denser downward	1.69	0.22	0.29	-	-	0.030	32.8	0.72	4.90	26.8
		St. 4927 (64°55.0' N, 39°20.0' E), depth 56 m										
Gr	0-1	0-0.5 cm: sandy aleuritic warp, brown, liquid	3.66	0.33	1.33	1.60	2.90	0.068	76.0	1.42	4.72	65.2
	2-3	1-16 cm: aleuropelite, dark gray, cloddy, with hydrotroilite inclusions	3.92	0.77	0.25	4.40	8.00	0.043	113	1.49	3.72	60.4
	3-5		4.10	0.93	0.17	8.00	12.2	0.039	72.0	1.26	3.81	56.6
	10-15		4.01	1.00	0.26	7.70	13.0	0.038	53.0	1.22	3.40	54.6
		St. 4928 (65°10.50' N, 38°25.18' E), depth 95 m										
Gr	0-2	0-4 cm: clayey warp with sand, pebbles and shells, brown	8.10	0.06	5.13	1.90	2.80	0.780	298	1.85	5.11	70.4
	2-5	4-16 cm: aleuritic pelite, light gray, with dark inclusions	5.29	1.00	0.80	2.50	3.00	0.136	223	1.60	4.24	65.7
	5-10		5.29	0.69	0.21	0.41	2.00	0.077	271	1.31	3.54	43.1
NC	5-10	4-35 cm: aleuritic-pelitic mud, greenish gray, with sand and hydrotroilite inclusions	5.34	0.73	0.21	0.25	0.57	0.124	246	1.36	3.40	38.7
	11-16			1.53	0.65	0.90	2.00		202	1.31	3.31	67.3
	21-26		5.19	1.44	0.42	0.57	1.60	0.055	203	1.29	3.16	70.5
	26-30		5.29	1.76	0.38	0.82	1.70	0.060	211	1.25	3.04	67.7
GC	70-80	40-176 cm: homogeneous brownish gray clay, abundant hydrotroilite mottles form layering; below 140 cm: rare hydrotroilite mottles; brownish shade becomes more distinct	4.61	1.24	0.18	1.40	1.40	0.017	111	1.02	2.43	64.0
	90-100	176-190 cm: brown aleuropelite with sand and gravel	5.19	1.07	0.24	0.07	1.23	0.034	104	1.03	2.61	65.1
	150-160		4.61	0.76	0.10	0.66	0.82	0.043	90.8	0.89	2.50	57.3
	205-215		3.40	0.48	0.03	-	-	0.081	43.8	0.15	0.68	23.4
	240-250		3.01	0.34	0.03	-	-	0.008	20.5	0.07	0.56	17.4
		St. 4929 (65°27.03' N, 37°23.02' E), depth 152 m										
Gr	0-3	Aleuropelite, olive gray, liquid	5.02	n.d.	7.66	<0.1	<0.1	5.060	34.2	1.71	2.91	71.2
GC	30-50	25-40 cm: aleuropelite, gray, cloddy, with alternating gray and olive bands, enriched in hydrotroilite; below 64 cm: homogeneous, grayish green, with hydrotroilite ("marble" structure), becomes denser downward	5.50	1.16	0.26	<0.1	<0.1	0.330	306	1.25	1.25	66.7
	90-100		5.70	1.32	0.11	0.70	0.70	0.302	339	1.08	2.41	62.1
	170-180		5.48	1.51	0.28	1.07	1.20	0.263	340	1.07	2.00	61.0
	300-310		5.65	0.89	0.09	0.53	0.67	0.150	200	0.92	1.82	58.3





Table (Contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13
NC	12–17	Pelite, greenish gray, with hydrotrillite; at 310 cm: transition to aleuropelite with rare hydrotrillite spots	5.15	1.49	0.34	1.10	2.10	0.67	530	1.53	3.82	72.1
	22–27		5.03	1.07	0.20	0.80	2.40	0.41	523	1.56	2.66	59.7
	32–37		5.52	1.78	0.23	1.20	2.50		532	1.56	3.07	72.7
	42–47		4.90	1.78	0.26	1.80	2.60	0.43	536	1.51	2.57	72.6
	47–52		5.21	1.96	0.27	1.40	1.90	0.61	524	1.38	3.32	73.1
	70–95		4.66	1.82	0.41	1.40	2.00	0.62	530	1.61	3.23	72.3
GC	120–135		5.09	1.66	0.14	2.60	3.00	1.04	526	1.84	3.00	72.1
	170–185		5.76	2.02	0.17	2.50	3.60	0.91	515	1.83	2.25	71.4
	240–255		5.33	1.74	0.15	2.20	2.80	0.87	458	1.71	2.75	58.8
	300–315		5.46	1.29	0.08	1.60	2.20	0.32	407	1.49	2.75	58.8
	340–355		5.64	1.68	0.11	–	1.70	0.21	292	1.54	2.41	63.6
St. 4934 (66°29.91' N, 33°58.75' E), depth 339 m												
Gr	0–2	Aleuropelitic warp, dark brown	5.01	n.d.	2.37	<0.1	0.90	1.83	203	2.18	4.56	78.3
	2–5	Aleuropelitic, light brown	5.20	0.07	2.25	–	0.90	1.29	506	2.05	3.81	76.9
GC	10–20	Aleuropelitic, greenish gray, homogeneous, without inclusions	5.30	1.57	0.49	0.70	1.60	0.52	428	1.72	3.81	76.9
	40–50		5.15	1.69	0.42	1.80	2.30	0.41	510	1.60	3.56	
	100–110		5.09	2.11	0.12	1.20	2.50	0.63	476	1.70	3.75	73.5
	200–210		5.32	1.80	0.10	1.20	2.20	0.70	472	1.45	2.32	67.7
	300–310		5.42	1.68	n.d.	1.00	3.00	0.25	458	1.34	3.16	64.7
	380–390		5.50	1.70	0.20	–	1.50	0.15	273	1.27	3.90	62.7
St. 4937 (66°39.41' N, 33°50.83' E), depth 156 m												
Gr	0–1	Aleuropelitic, aleuropelitic warp, reddish brown, grayish green, with black hydrotrillite inclusions	5.24	0.32	1.99	–	0.47	0.158	108	1.27	3.11	73.9
	1–3		4.76	1.03	0.24	–	4.31	0.055	120	1.75	4.15	65.3
	3–5		4.22	1.07	0.24	–	2.70	0.051	113	1.42	2.57	66.7
	5–10		4.41	1.09	0.23	–	2.61	0.043	98.5			66.7
	10–20		4.37	1.08	0.14	–	2.08	0.068	117	1.42	1.91	66.1

Note: Lithological description of cores by N.K. Fedorova (SEVMORGE0); (Gr) grab sampler; (NC) Niemisto corer; (GC) gravity corer; (–) no data. Here and in Fig. 4: (St.) station. (n.d.) Not detected.

promoting the mineralization of organic matter and removal of its decay products. On the contrary, organic matter accumulates more intensely in sediments of the Kandalaksha Bay characterized by a calmer hydrodynamic regime. As will be shown below, accumulation rates of mobile forms of Fe and Mn are also higher here. However, along with an eastward decreasing trend along the profile, the  $C_{\text{org}}$  distribution in sediments demonstrates common patterns: a very high concentration (up to 2%) in the surface layer (0–10 cm) and gradual (but not equal) decrease in subsurface sediment layers. In sediments from the Kandalaksha Bay, the  $C_{\text{org}}$  concentration is 1.5% at a depth of 200–250 cm below seafloor and >1% in deeper sediments (Fig. 2). In sediments from the central part of the sea and the Dvina Bay, the isoline of 1.5%  $C_{\text{org}}$  is close to the surface, whereas the 1% level occurs at a depth of 100–250 cm and the  $C_{\text{org}}$  content is even lower in the deeper sediments. Meanwhile, both lower and higher  $C_{\text{org}}$  values appear in sediments from the Severnaya Dvina region. We suggest that these patterns are related to an uneven supply and distribution of the sedimentary material. Detailed lithological study of the White Sea sediments is needed for a more substantiated consideration of sedimentation processes in the studied regions.

The *distribution of Fe in sediments* in the Kandalaksha–Arkhangelsk transect reflects the supply of sedimentary material, its grain size, and conditions of sedimentation and diagenesis. Sediments from river mouth areas and the open sea differ considerably. Areas with the relatively low total Fe content occur locally along the transect (Fig. 3), including the Kandalaksha Bay (stations 4933, 4934, and 4937), where the Fe content is less than 5% owing to an admixture of coarse material. However, the most distinct Fe minimum occurs in the Severnaya Dvina mouth area (stations 4919 and 4926–4928), where the total Fe content in sand decreases to less than 2%. The chemical composition of sediments (table, Fig. 3) reflects an uneven distribution of the material delivered by the river.

On the contrary, sediments from the central White Sea (the Basin area: stations 4702, 4719, and 4929–4931) represented by aleuritic-pelitic mud are rather uniform in the grain size distribution due to the delivery of sorted fine fractions of the sedimentary material to these regions. The Fe content is up to 6% or even more in these sediments (Fig. 3). Increased Fe content (more than 5.5%) is also detected in lower layers (below 300 cm) at marginal stations (4933 in the Kandalaksha Bay and 4919 in the Dvina Bay). This is apparently related to changes in the sedimentation environment during previous time intervals. In the central part of the sea, where the isochronous layer is thinner, the relatively high Fe content occurs at 50 cm (stations 4702 and 4929), whereas the Fe content decreases again in the deeper sediments. The profile of total Fe content in White Sea sediments looks rather symmetrical (higher at the center and lower at margins), although it demon-

strates an obvious increasing trend in sediments of the Kandalaksha Bay (Fig. 3a).

The general iron distribution pattern becomes more prominent if we compare *reactive forms of Fe* in sediments and dissolved forms of Fe in the interstitial water. Reactive forms transferred into solution by acid leaching mainly include iron hydroxides (partially, layered silicates of the leptochlorite type) and minor amounts of carbonates, phosphates, and sulfides. The reactive Fe constitutes more than 50% of the total Fe content in the thin surface layer, and its proportion decreases in subsurface layers to less than 30% (Fig. 3). This situation, typical of many types of marine sediments, is commonly interpreted as diagenetic ageing of hydroxides and silicates that are transformed into more stable and, hence, less reactive forms. However, the situation is not so simple: increase in the content of reactive Fe may also be related to a higher amount of its supply during sedimentation. This is observed in the Kandalaksha Bay, in the Basin, and even in the Severnaya Dvina mouth (table, Fig. 3), where the reactive Fe content in some layers is noticeably higher than the background values of <1.5% (e.g., station 4919, interval 75–150 cm). Along with Fe(II), Fe(III) is also present among the reactive forms of Fe (table). The presence of oxidized Fe in White Sea sediments together with sulfides is an evidence of thermodynamic nonequilibrium in the upper sediment layers. The content of trivalent Fe considerably decreases with depth in sediment cores and practically disappears in lower layers, suggesting that sediments approach the thermodynamic and diagenetic equilibrium. A minor increase in the Fe(III) content may be related to analytical errors of its determination, in particular, owing to the interaction of Fe(II) with Mn(IV), which always exists in sediments, especially in their upper layers.

The diagenetic Fe redistribution, which involves a much less proportion of the total Fe (relative to Mn) contained in sediments, is manifested in some enrichment of the surface sediments in Fe (table, Fig. 3). The rusty brown film on the sediment surface is enriched in both Fe and Mn. This is well expressed in the Severnaya Dvina mouth area (6–8% Fe, stations 4919 and 4928). The formation of ferromanganese nodules and other authigenic forms reported from various regions of the White Sea is also related to the diagenetic migration of Fe (Neveskii et al., 1977; Strekopytov et al., 2005).

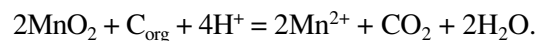
The *distribution of Fe in the interstitial solution* illustrates the migration process (table, Fig. 3). High concentrations of dissolved Fe in the interstitial water are also found at the transect margins. The dissolved Fe content in interstitial water from the Kandalaksha Bay sediments is up to 3  $\mu\text{M}$  or more. Even higher concentrations (table, up to 14  $\mu\text{M}$ ) are detected in surface sediments from the Dvina Bay. Deeper within the sediments, the Fe concentration considerably decreases to <1  $\mu\text{M}$  or even 0.1  $\mu\text{M}$  in the Dvina Bay.

It is impossible to explain the high dissolved Fe concentrations in interstitial water from the White Sea sediments in terms of the solubility of known solid phases, iron oxides and hydroxides, or sulfides. The presence of these solid phases thermodynamically assumes Fe ion concentrations of significantly less than 0.1  $\mu\text{M}$  (Krainov et al., 2004; Stumm and Morgan, 1996). The observed pattern is apparently controlled not by ionic Fe, but by organic (possibly humic) complexes that are quite stable against destruction in natural conditions. The delivery of iron humates by the Severnaya Dvina discharge apparently surpasses their supply from other rivers (Leonov and Chicherin, 2004). The discharge of northern Russian rivers formed in forest and swamp landscapes predetermines the high dissolved Fe content in the interstitial water of Dvina Bay sediments. The presence of colloidal forms of Fe in the interstitial water is also possible, as they pass through the used filter with 0.45- $\mu\text{m}$  pores. It is noticeable that Fe(III) is present among both dissolved forms of Fe in the interstitial water and reactive forms in the solid phase of sediments. Moreover, the Fe(III) often prevails over Fe(II) (table). We attempted to explain this phenomenon relative to the reactive Fe in the solid phase of sediments. This explanation is perhaps also valid for interstitial water, because Fe(III) of humic complexes has a higher stability.

The appearance of *sulfides* as a result of bacterial sulfate reduction, which commonly takes place in sediments with high organic matter content ( $\text{H}_2\text{SO}_4 + 2\text{C} = \text{H}_2\text{S} + 2\text{CO}_2$ ), may serve as a graphic evidence of the reducing diagenesis of marine sediments. Hydrogen sulfide generated in this process interacts with the sediment to form various organic and inorganic derivatives, the total content of which is commonly characterized by the “sum of hydrogen sulfide derivatives  $\Sigma S_{\text{H}_2\text{S}}$ ”. Iron sulfides dominate in this sum, although organic sulfides constitute a noticeable portion among the hydrogen sulfide derivatives in the White Sea, especially in surface sediments (0–10 cm) from the Severnaya Dvina estuary. Organic sulfides prevail among other species in this area characterized by a very low  $\Sigma S_{\text{H}_2\text{S}}$  level of <0.05% (Kokryatskaya et al., 2003). In deeper layers of the White Sea sediments with higher  $\Sigma S_{\text{H}_2\text{S}}$ , which commonly does not exceed 0.5%, iron sulfides prevail among the hydrogen sulfide derivatives. Such  $\Sigma S_{\text{H}_2\text{S}}$  values seem to be lower than one might expect for sediments with high contents of  $\text{C}_{\text{org}}$  (1–2%) and reactive Fe (1.5–2%) (Strakhov, 1976; Volkov, 1984) observed in the White Sea sediments. The major part of the total organic matter in sediments—terrigenous organic matter delivered with the river discharge from forest and swampy drainage areas—is more stable and less suitable for the vital activity of sulfate-reducing bacteria, relative to the planktonic organic matter produced in the sea.

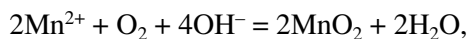
The content of *sulfide Fe* ( $\text{Fe}_{\text{S}_2}$ ) represented by hydrotroilite (iron monosulfide, FeS) and pyrite ( $\text{FeS}_2$ ) commonly does not exceed 0.5% in White Sea sediments (average 0.2–0.4%). Sulfate reduction already starts at the sediment surface, including the oxidized film. Hydrogen sulfide first interacts with iron hydroxides to form hydrotroilite and pyrite. Colloidal or cryptocrystalline hydrotroilite stains the sediment with dark gray or black color. The content of sulfide Fe increases downward the section and reaches stable values of ~0.2–0.4% already at a depth of 50–100 cm (table, Fig. 3). A higher value (0.6%) is recorded in sediments of the Kandalaksha Bay, where iron sulfides are mainly represented by hydrotroilite (station 4933). On the contrary, hydrotroilite (typical for the surface layer) is replaced by pyrite (the most stable iron sulfide) in deeper sediments of the central White Sea (Fig. 3, stations 4719 and 4702). In sediments from the area close to the Severnaya Dvina estuary, where sedimentation conditions are variable, an intercalation of layers with domination of hydrotroilite or pyrite takes place. This is accompanied by other changes in the sediment composition. For example, an increase in hydrotroilite at the base of core 4919, where pyrite predominates (table, interval 310–325 cm), is accompanied by an increase in contents of reactive Fe and  $\text{C}_{\text{org}}$  in sediments and dissolved Fe in the interstitial water. This process is likely related to an increase in the reducing potential of sediments from this interval that hinders the transformation of hydrotroilite to pyrite, which is a more oxidized species than monosulfide.

The *distribution of Mn in sediments* is much more affected by the reducing diagenesis than Fe distribution. Concentration of Mn in surface sediments of the White Sea is apparently related to diagenesis. Concentrations exceeding the Mn clarke abundance of 0.08% (Ronov and Yaroshevsky, 1967) by more than an order of magnitude are consistent with the concept of Mn transport in the suspension as Mn(III, IV) oxyhydrates that are easily transformed into dissolved Mn(II) under conditions of oxygen depletion (especially, sulfate reduction in sediments). This process leads to consumption of organic matter and reduced inorganic sediment components (Fe(II) and  $\text{S}^{2-}$ ). Microbes possibly participate in the process. It is schematically expressed by the equation:



A two times or more decrease of the Mn content in subsurface sediments (relative to the clarke value) indicates that the reactive Mn dominates over the less mobile (lithogenic) form in sediments of the White Sea. The lithogenic form remains in sediments, whereas the reactive form is reduced and dissolved in the interstitial or bottom water, resulting in the migration of Mn in both the sediments and the near-bottom water layer. At the contact with seawater oxygen, Mn(II) is oxidized

and transformed into insoluble  $\text{MnO}_2$  or the more general form  $\text{Mn(III,IV)O}_x$ :



thus causing enrichment of surface sediments in Mn. The quite mobile warp of  $\text{MnO}_2$  and Mn-rich suspended matter is transported by bottom currents and accumulated in depressions and the distal (relative to both sedimentary material sources and primary sedimentation sites) central part of the sea.

The processes described above are reflected by Mn distribution patterns in sediment sections. High contents of organic matter ( $C_{\text{org}} > 1\%$ ) in sediments of the Dvina Bay, which represents the most productive region of the White Sea due to abundant supply of nutrients, promote intense reducing reactions. The sand-aleurite grain size of the Dvina Bay sediments provides favorable conditions for the washout of dissolved Mn, its transfer into bottom water, and migration in both particulate and dissolved forms within the near-bottom water and sediment layers. The Mn content (table, Fig. 2) in the surface layer of near-shore sediments (0.05–0.07%, stations 4926 and 4927) slightly exceeds its concentration in subsurface sediments (0.04%), although a reddish brown film enriched in iron and manganese hydroxides commonly occurs at the sediment surface, which is difficult to sample because of its small thickness (no more than 1 mm). At more remote stations (4919 and 4928), a thicker Mn-rich layer (2–10 cm) occurs in sediments with the Mn content of 0.1–0.2%. The Mn content may be up to 1% in the surface warp. The Mn content in subsurface layers is low (less than 0.05%); i.e., the reactive Mn is removed from the sediments due to its reduction. A slight increase in the Mn content (up to 0.05–0.06%), which is accompanied by changes in other components ( $C_{\text{org}}$ , Fe, Al, and others in the table) and is possibly related to oscillations in sedimentation, is only observed below 200 cm in core 4919. The presence of sand interbeds characteristic for the area near the Severnaya Dvina mouth results in even lower concentrations of Fe, Mn, and other components. For example, sediments from the level of 250 cm in core 4928 contain 3% Fe and only 0.01% Mn.

Sediments from the Basin and the deep part of the Kandalaksha Bay contain considerably more Mn. Its content in sediments ranges within 0.1–0.5% and reaches 2–5% in a warp at the sediment surface (table, Fig. 2). The highest Mn content for subsurface sediments (almost 1%) is fixed in the Kandalaksha Bay.

Thus, Mn distribution is asymmetric in the transect, with maximum values (0.5–0.7%) in the Kandalaksha Bay, intermediate values (0.1–0.5%) in the Basin, and minimum concentrations (less than 0.05%) in the Dvina Bay. Manganese concentration isolines of 0.1 and 0.05% separate the Dvina Bay from the central White Sea (Fig. 2). The Mn content decreases with depth in sediment layers. The 0.5% Mn isoline occurs

at 300 cm in the Kandalaksha Bay, rises to the sediment surface in the Basin sediments, and occurs only in the mm-scale surface film of Dvina Bay sediments. Hence, conditions of diagenetic Mn mobilization are substantially different in the Dvina and Kandalaksha bays.

The high total Mn content in sediments from the Kandalaksha Bay is repeated in the interstitial water. The dissolved Mn concentration is the highest (more than 500  $\mu\text{M}$ ) in this region (Fig. 2). On the contrary, the dissolved Mn content in the interstitial water of Dvina Bay sediments commonly does not exceed 100  $\mu\text{M}$ , and intermediate values characterize the Basin sediments. Therefore, asymmetry in the distribution of dissolved Fe and Mn along the Kandalaksha Bay–Dvina Bay transect is expressed by substantially higher Mn concentrations in the western part (Fig. 2) and higher Fe concentrations in the east (Fig. 3).

Vertical distribution patterns of Mn dissolved in interstitial water within sediment sections reflect both diagenetic and sedimentological characteristics, which control the composition of sediments and the migration of elements. The highest dissolved Mn concentrations occur in surface or subsurface sediment layers. Abundance of fresh organic matter in the surface sediments leads to the intense reduction of  $\text{MnO}_2$ , transfer of Mn into solution, and its removal from sediments. The process of Mn removal often governs the confinement of the dissolved Mn maximum several millimeters or centimeters below rather than the sediment surface, where it is washed out by bottom water. The maximum concentration layer (table, Fig. 2c) formed here creates the flux of dissolved Mn from sediments to the bottom water. A surface sediment or near-bottom suspension layer enriched in solid manganese phases occurs above the maximum. This layer is characterized by distinct enrichment in Mn, as well as formation of a Mn-rich warp at the sediment surface, films on shells, and ferromanganese nodules in some cases. As was noted above, this layer is very thin in the Dvina Bay and thickest in the Kandalaksha Bay.

When comparing distribution patterns of dissolved Fe and Mn concentrations in the interstitial water from the studied sediments, we see that location of maximum values depends on both differences in the solubility of solid phases, which contain these elements, and differences in their redox properties. The Mn-rich surface layer is commonly underlain by Fe-rich sediments (Fig. 4), which corresponds to their different redox potential values. Similar patterns characterize the distribution of dissolved forms of Mn in subsurface sediment layers that control the Mn flux, and in less extent, the Fe flux toward the sediment surface. This is observed at the qualitative level in all cores of the transect including those from the Dvina Bay (Fig. 4, station 4927), Basin (station 4930), and Kandalaksha Bay (station 4934), but the best evidence is observed in Mn-rich sediments from the western part of the sea.

## DISCUSSION

We explain such a considerable diversity of Mn and Fe distribution patterns in White Sea sediments by different sources of these elements and variations in sedimentation environments. The composition of terrigenous material discharged by rivers is rather uniform, and the difference discussed above is caused by mixing of the Mn-rich Barents Sea water flowing into the White Sea with the Mezen Bay water enriched in suspended matter (Neveeskii et al., 1977). As shown by Timonov (1947), the major portion of suspended matter (including the hydromicaceous material) is transported from the White Sea to the Barents Sea, but a part of the suspended matter is transported with the bottom current, which is accelerated by tidal currents, through the Gorlo Strait into the White Sea and further distributed by the main cyclonic current. However, asymmetry of the distribution of Mn (and partially Fe) in the White Sea is mainly related to the diagenetic efflux of these elements from sediments, which is especially prominent in the east (Dvina Bay). This is evident from the comparison of the sediment mass accumulated in the Dvina Bay and the Mn content in sediments (commonly, below 0.05%), which is considerably lower than that in the material of river runoff feeding the sedimentation. Dissolved and particulate forms of Fe and Mn are distributed throughout the White Sea by currents. The western part of the White Sea and the deep Kandalaksha Bay serve as peculiar sediment traps on the path of this flux, and the Mn-rich suspended matter may be accumulated here. Sediments contain enough organic matter to create favorable conditions for Mn concentration in the interstitial water.

Thus, the combination of enhanced Mn delivery, appropriate depths, and sufficiently high content of organic matter promote the accumulation of Mn in the Kandalaksha Bay and adjacent White Sea region in both the solid phase of sediments and interstitial waters. Concentrations of dissolved Mn (more than 500  $\mu\text{M}$  or about 30 mg/l) recorded in the interstitial water are extremely high, although Thamdrup et al. (1994) have reported even higher concentrations in marine sediments. Such high concentrations of dissolved Mn may lead to the removal of this element from the solution, for example, by the precipitation of manganese carbonates or sulfides, as shown by experiments and thermodynamic calculations (Savenko, 2005) and present-day processes in the Baltic Sea (Kuleshov and Rozanov, 1998; Suess, 1979). However, such authigenic minerals have not been found in the White Sea sediments so far, possibly, owing to the absence of any well developed carbonate- or sulfide-forming processes in the sea. Hydrodynamics of the White Sea, which is separated from the ocean (Barents Sea) by the narrow and shallow Gorlo and Voronka straits with the two-layer opposite currents, is also characterized by the two-layer density stratification of water column that might lead to stagnation of the lower dense water mass. However,

shallow depths and intense hydrodynamics amplified by tides provide an almost complete aeration of the water column and rules out the development of anoxic conditions in the deep water. This is observed, for example, in the Black Sea and some other basins.

The transfer of Mn and the subordinate Fe to pelagic areas is typical for marine basins and the World Ocean as a whole. The Mn concentration in the clayey mud from the central White Sea Basin is several times higher than the Clarke value. The above statement is also supported by the *pelagic shift*, a term introduced by Strakhov (1976, 2000) to consider the concentration ratio of chemical elements in near-shore sediments and muds from the most remote deep-water pelagic zone. Geochemical and lithological implications of this parameter are as follows: the higher the value of this indicator, the stronger the migration ability of an element in marine sedimentation. According to V. Kalinenko, the pelagic shift in the White Sea is as follows: Cr 3, Fe 4, Ni 8, Co 10, and Mn 12 (Neveeskii et al., 1977). Significant difference between the migration ability of these elements is related to changes in their dispersion degree (up to colloidal and dissolved forms) during migration that provides their transfer to the pelagic zone and delivery to the pelitic mud.

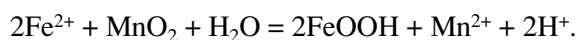
Despite the high content of total organic carbon (1–2%) in White Sea sediments, the composition of organic matter is not optimal for deep reduction processes. The organic matter is largely represented by stable allochthonous humic components, while more reactive forms of planktonic origin are subordinate (Kokryatskaya et al., 2003; Romankevich and Vetrov, 2001). It should be added that the Fe-rich swamp waters affect the composition of organic matter in the river discharge (Kholodov and Butuzova, 2004; Strakhov et al., 1968). This explains an increased Fe concentration in the White Sea sediments, especially in the Dvina Bay. The amount and composition of the organic matter turn out to be sufficient to reduce Mn and partially Fe, but they are obviously insufficient for an overall sulfate reduction. The composition of organic matter in high latitudes is possibly more suitable for methane formation.

We can approximately estimate the thickness of sediments that provide the surface layer with Mn due to its upward diffusion and its oxidation by the bottom water oxygen. The average Mn content in the surface layer (0–10 cm) of Dvina Bay sediments at station 4919 is 0.17% (1.06% in the surface warp 0–1 cm and 0.043% in the layer 8–12 cm). The lower sediments contain 0.04% Mn (table). Hence, 0.13% of Mn ( $0.17 - 0.04 = 0.13$ ) was extracted from ~30 cm-thick subsurface sediment layer due to its reduction ( $\text{MnO}_2 \rightarrow \text{Mn}^{2+}$ ) and transferred by diffusion to the surface layer (10 cm). Taking the Clarke concentration of Mn 0.08% for the mineral component of suspended matter in the White Sea, we conclude that one-half of Mn is removed from the sediment during diagenesis to enrich the surface layer. The estimate for core 4928 located at the outer

boundary of the Dvina Bay shows that the diagenetic reworking of 50-cm-thick subsurface sediments provides the Mn enrichment of the 10-cm-thick surface layer (0.24% Mn as compared to the residual concentration of 0.04% in subsurface sediments). If the Mn content in sediments is higher, as in the Kandalaksha Bay, the subsurface sediment layer that provides the Mn enrichment of the surface layer may be much thinner. At station 4933, mobilization of Mn from the underlying 6.2-cm-thick layer with an average Mn concentration of 0.5% is necessary to maintain the observed Mn enrichment of the upper 10 cm of sediments (average Mn concentration 1.33%). This is qualitatively reflected as an increase in the dissolved Mn content in the interstitial water, which is more than two times higher in the Kandalaksha Bay sediments (500  $\mu\text{M}$ ), as compared to the Dvina Bay (160  $\mu\text{M}$  at station 4919 and 300  $\mu\text{M}$  at station 4928). The dissolved Mn content in the interstitial water is considerably lower (less than 100  $\mu\text{M}$ ) in underlying sediments and as low as 20  $\mu\text{M}$  in sand from the lower part of the core 4928 (interval 240–250 cm). The latter is related to decrease in the total Mn content (0.008%) and the reducing ability of sediments ( $C_{\text{org}}$  0.07%).

A part of Mn obviously migrates from subsurface sediment layers to the bottom water bypassing the surface oxidized layer. In this case, the process of reducing diagenesis, which removes the dissolved Mn from sediments, involves considerably thicker sediment strata. The scheme considered above simplifies (quantitatively, but not essentially) the geochemical cycle of Mn, because its content in the sediment-forming suspended matter may be higher or lower than the Clarke value. The Mn content may be higher if the suspended matter is enriched in manganese oxyhydroxides formed from the dissolved Mn flux from sediments. The content may be lower if the suspended matter interacts with organic matter in the bottom water or at the sediment–water interface. Both dissolved  $\text{Mn}^{2+}$  and fine  $\text{MnO}_2$  particulates formed in these processes may be distributed by bottom currents. As noted above, the residual Mn concentration in sediments may exceed 0.4%, but it necessarily becomes lower than the Mn content in the sediment-forming particulate material during reduction.

In order to complete the consideration of manganese and iron cycle in sediments, we have to note that the manganese dioxide ( $\text{MnO}_2$ ) accumulated in the surface layer serves as an additional oxidant of organic matter delivered to sediments.  $\text{MnO}_2$  also oxidizes the bivalent Fe that is formed in lower sediment layers and diffused toward the sediment surface, where it is oxidized again and precipitated within the surface layer:



The newly formed iron oxyhydroxide, in turn, also participates in the oxidation of organic matter delivered to the sediment. Thus, a successive chain of oxidants is formed:  $\text{O}_2$ —(possibly,  $\text{NO}_3^-$ )— $\text{MnO}_2$ — $\text{FeOOH}$ . Sul-

fates of the interstitial water serve as an additional oxidant of organic matter. Their role is negligible in surface sediments and noticeable in deeper sediment layers. Sulfate reduction resulting in the generation of hydrogen sulfide represents an anaerobic microbiological process. In surface sediments, this process is restricted and realized only in microniches enriched in organic matter. Data on the excess Mn and Fe, as well as the content of hydrogen sulfide derivatives, allow us to estimate the amount of organic matter ( $C_{\text{org}}$ ) consumed for their formation. We can also evaluate the potential capability of hydroxides accumulated in the surface layer to oxidize organic matter during diagenesis.

Based on data presented in the table and Figs. 2 and 3, we assume the average excess Mn content (% dry weight, relative to the Clarke concentration of 0.08%) accumulated in the surface layer of sediments (0–5 cm) due to diagenetic migration is as follows: 0.4% for the Dvina Bay, 1.7% for the Basin, and 2.2% for the Kandalaksha Bay. Corresponding values for Fe hardly exceed 0.5% throughout the entire White Sea, although one can see considerable variations that reflect variable sedimentation regimes, which are especially characteristic for the Dvina Bay (Fig. 2). The content of iron sulfides in the surface layer is negligible:  $\Sigma S_{\text{H}_2\text{S}}$  does not exceed 0.05%, which may also be applied to the White Sea as a whole. Then, we can calculate the  $C_{\text{org}}$  consumption for the surface layer (0–5 cm) using the known stoichiometric relationship (Roazanov et al., 1980; Strakhov, 1976):

$C_{\text{org}}(\%) = 0.109\text{Mn}(\%) - 0.04\%$  for the Dvina Bay, 0.19% for the Basin and 0.24% for the Kandalaksha Bay);

$C_{\text{org}}(\%) = 0.054\text{Fe}(\%) - 0.03\%$  (arbitrarily, for all White Sea sediments);

$C_{\text{org}}(\%) = 0.75 S_{\text{H}_2\text{S}}(\%) - 0.04\%$  (arbitrarily for all White Sea sediments).

Thus, the total  $C_{\text{org}}$  consumption providing Mn and Fe accumulation, as well as generation of hydrogen sulfide derivatives in the surface layer (5 cm) of sediments is as follows:  $0.04 + 0.03 + 0.04 = 0.11\%$  in the Dvina Bay;  $0.19 + 0.03 + 0.04 = 0.26\%$  in the Basin; and  $0.24 + 0.03 + 0.04 = 0.31\%$  in the Kandalaksha Bay.

Let us note that we consider here the anoxic (anaerobic) diagenesis stage when the main portion of organic matter delivered to the bottom has already undergone decay at the sediment surface under the action of bottom water oxygen. We only can evaluate the relationship between aerobic and anaerobic diagenesis based on the most general considerations, according to which approximately 10% of the primary organic matter remains in sediments, whereas 90% is oxidized at the bottom surface (Romankevich and Vetrov, 2001). If we assume the average  $C_{\text{org}}$  content in White Sea sediments as 1–1.5%, the initial sedimentary material settled onto the bottom must contain 20–30% of  $C_{\text{org}}$ . Of course,

this is a rough estimate that varies in different regions of the sea, but suggests the scopes and mechanisms of organic matter alteration at different stages of diagenesis.

As shown for similar sediments (Glud et al., 1994; Rozanov, 1988, 1995), oxidation of organic matter by the bottom water oxygen at the sediment surface with the participation of benthic organisms and aerobic bacteria is restricted to the warp and upper thin (millimeter-scale) layer of sediments, where the  $C_{org}$  content is more than an order of magnitude lower.  $Mn^{2+}$  migrated from subsurface sediments is oxidized by oxygen within the same surface layer. Anaerobic diagenesis involves a much thicker subsurface sediment layer and considerably lower  $C_{org}$  concentrations. As shown above, the  $C_{org}$  content in the surface (0–5 cm) sediment layer varies within 1.5–2% and is almost two times less in the upper few meters of the sediment. Some uncertainty is introduced by the confrontation of oxidizing (participation of oxygen) and reducing (sulfate reduction) stages (Romankevich and Vetrov, 2001), although the case in point is oxidation of organic matter in both cases. Therefore, it seems more reasonable to distinguish aerobic and anaerobic stages of diagenesis bearing in mind the participation of oxygen, which oxidizes the major portion of organic matter in the surface layer, and of other oxidants (nitrates, manganese and iron oxyhydroxides, sulfates, and carbon dioxide), which oxidize the buried organic matter in deeper sediment layers after the consumption of oxygen.

More detailed examination of the dynamics of organic matter consumption shows that the scenario of successive decrease of the  $C_{org}$  content depends on the type of sediment sections, marine regions, and depth levels. The contribution of Mn to the anaerobic  $C_{org}$  consumption is highest in the upper sediment layer (0–5 cm), e.g., 40% in the Dvina Bay and 80% in the Kandalaksha Bay. The role of iron and sulfates is commonly subordinate, although they may account for more than one-half of the total  $C_{org}$  oxidation in the Dvina Bay. Similar calculations of the stoichiometric  $C_{org}$  consumption for the reduction of the “excess” Mn, Fe, and sulfates at the level of 100 cm below seafloor yield the following values:  $0.05 + 0.03 + 0.31 = 0.39\%$  for the Kandalaksha Bay,  $0.3 + 0.8 + 0.2 = 1.3\%$  for the Basin, and  $0.01 + 0 + 0.23 = 0.24\%$  for the Dvina Bay. The pattern at the 100-cm level drastically differs from that in the surface layer: the major portion is consumed by sulfate reduction (70% in the Basin sediments and almost 100% in the Kandalaksha Bay), whereas the role of Mn decreases to 10% or less. The contribution of Fe is still significant in the Basin sediments (18%), but its role is negligible in the Dvina Bay. Similar calculations for the deeper layer (300 cm) show that the role of Mn also decreases to zero in the Dvina Bay. However, the role of Mn and Fe is still appreciable in the Basin and Kandalaksha Bay sediments at this level, although they oxidize not more than 10% of  $C_{org}$ . The

role of sulfate increases to 100% in Dvina Bay sediments, but its contribution to the  $C_{org}$  consumption at the 100-cm level is negligible, possibly, except for Basin sediments, where the content of sulfide sulfur slightly increases. In most studied cores, even the process of sulfate reduction and, particularly, reduction of reactive Mn and Fe terminate at the 50–60 cm level (maximum at 100 cm). Minor variations in deeper layers are related to residual processes or changes in sediment composition.

According to the above calculation, estimates of the total  $C_{org}$  amount consumed for anaerobic oxidation within the 300-cm-thick sediment layer vary from 0.23% (Dvina Bay and Basin areas) to 0.38% (Kandalaksha Bay). Summing up these values with the residual  $C_{org}$  content (direct determination), we obtain the following values of the “primary”  $C_{org}$  involved in the diagenesis: 1.7–1.8% for the Dvina Bay and Basin areas and up to 2.4% for the Kandalaksha Bay. Estimation of the  $C_{org}$  consumption in the 300-cm-thick anaerobic sediment layer (relative to the primary  $C_{org}$ ) yields similar values (14–16%) for all studied regions of the White Sea (Fig. 1). Moreover, the major portion of the total consumption is related to the upper 100-cm-thick sediment layer. Estimates for near-shore oceanic sediments yield similar values (Rozanov et al., 1980). According to other estimates, “anaerobic loss” of organic matter is 5–7% in Russian Arctic seas (Romankevich and Vetrov, 2001).

The values of  $C_{org}$  consumption obtained for the White Sea are possibly underestimated, because direct measurements of the residual  $C_{org}$  suggest a more significant (two times higher, instead of 14–16%) consumption. This fact needs explanation or more careful investigations. We have probably underestimated the number of anaerobic oxidants or their recycling. Oxygen can also penetrate the anaerobic zone. Bioturbation and tides possibly promote this process, especially because microaerophile properties of anaerobic sediments is widely accepted at present (Volkov, 1984). Anyway, dynamics of redox diagenesis of sediments in the White Sea is characterized by specific features. In this respect, sediments of the Kandalaksha Bay are distinguished from those of the Basin and, especially, the Dvina Bay.

## CONCLUSIONS

Average Fe and Mn contents in White Sea sediments (upper 4 m in the Kandalaksha Bay–Dvina Bay transect) are close to the Clarke values for sedimentary rocks (5 and 0.08%, respectively), but individual analyses demonstrate considerable variations (Fe 2–8% Fe and Mn 0.03–3.7%), depending on the grain size of sediments, material sources, and influence of diagenetic processes. Organic matter and reduction processes strongly affect concentration and distribution patterns of Mn, whereas the influence is less significant



for Fe and reduced sulfur species. Despite a high  $C_{org}$  content (1–2%), organic matter is characterized by rather low reactivity owing to the prevalence of allochthonous humic components in its composition. This is reflected, in particular, by the restricted development of sulfate reduction (Kokryatskaya et al., 2004).

The Fe content is higher in the central White Sea (more than 6%). It is characterized by mosaic distribution patterns near river mouths, especially off the Severnaya Dvina mouth, with high values (8%) in the thin surface layer and low ones in sand interbeds (less than 2%). The proportion of reactive Fe extracted by acid leaching mainly from iron oxyhydroxides (partially, from layered silicates) decreases downward the core sections from 50% in the thin surface layer to less than 30% in deeper layers. The process of diagenetic stabilization and sedimentary material ageing also involves valence forms: the content of reactive Fe(III), which dominates in the surface layer, decreases downward the section to complete disappearance in its lower part. Diagenetic redistribution of Fe leading to the Fe enrichment of the surface layer and the formation of ferromanganese films or nodules is related to Fe concentration in the interstitial water. The highest concentrations of dissolved Fe occur in surface sediments of the Dvina Bay (up to 14  $\mu\text{M}$ ). This is related to the delivery of iron as metalloorganic complexes with the river runoff. In sediments from the central White Sea (Basin) and Kandalaksha Bay, the Fe content in the interstitial water does not exceed 1–3  $\mu\text{M}$ . Both Fe(II) and Fe(III) are recorded among the dissolved forms of Fe.

The generation of reduced sulfur species, which represent derivatives of bacterial hydrogen sulfide, is restricted in White Sea sediments. At a low concentration level of  $\Sigma S_{H_2S}$  (less than 0.05%), organic sulfides dominate, especially off the Severnaya Dvina river mouth. Higher  $\Sigma S_{H_2S}$  concentrations (commonly not exceeding 0.5%) are related to diagenetic pyrite ( $\text{FeS}_2$ ) or hydrotroilite ( $\text{FeS}$ ), which may incorporate up to 25% of the reactive Fe or up to 10% of the total Fe. The restricted character of sulfate reduction is likely related to a low reactivity of organic matter in White Sea sediments.

The distribution of Mn in White Sea sediments is much more affected by its diagenetic migration, as compared to that of Fe. The Mn concentration in surface sediments may be one order of magnitude higher than the concentration in lower sediment layers (often, <0.05%). The highest Mn concentrations (0.5–0.7%) are observed in Kandalaksha Bay sediments; the intermediate values (0.1–0.5%), in the Basin sediments; and minimum values (0.05%), in the Dvina Bay sediments. Asymmetry of the Mn distribution along the Kandalaksha–Arkhangelsk transect is controlled by the hydrodynamic regime of the White Sea. The Kandalaksha Bay serves as a sediment trap for Mn accumulation. On the contrary, sedimentation environment in the most pro-

ductive Dvina Bay, which delivers a greater amount of organic matter, favors the reduction and transition of Mn to solution and its subsequent efflux from sediments. Washing of sand and warp by bottom currents promotes this process. Mobilization of Mn concentrated in the surface layer due to its leaching from the underlying sediments involves subsurface layers of variable thickness depending on the total primary Mn content. About 30–50 cm of underlying sediments was reworked to provide the Mn concentration of 0.2% in the 10-cm-thick surface layer of the Dvina Bay. Meanwhile, the Mn concentration of >1% in the surface layer of the Kandalaksha Bay was provided by the leaching of Mn from the underlying 10-cm-thick sediments.

In the interstitial water, the content of dissolved Mn, a reducing diagenesis product responsible for the migration of this element in sediments, reaches its maximum in the Kandalaksha Bay. We recorded here the highest concentrations of dissolved Mn ever measured in marine sediments (more than 500  $\mu\text{M}$ ). In sediments from the Basin and Dvina Bay, the concentrations are considerably lower (less than 200–300  $\mu\text{M}$ ), and the maximum dissolved Mn content is noted in subsurface layers.

The mutual disposition of levels with maximum Mn and Fe concentrations in sediments obeys the thermodynamic redox succession, according to which the interval with maximum Mn content is located above that of maximum Fe concentration. Excess of maximum concentrations relative to the background ones is equal to a few percents for Fe (not more than 50%) and one to two orders of magnitude for Mn. Intervals of maximum concentrations of dissolved Mn and Fe in the interstitial water, which provide the maximums in the solid phases, are arranged according to the same succession.

Consumption of organic matter for oxidation at the sediment surface is more than one order of magnitude higher than that for anaerobic processes within the upper sediment layer. After the disappearance of oxygen, the major portion of organic matter in the surface layer (0–5 cm) is oxidized by manganese dioxide and iron oxyhydroxides. In deeper sediment layers (100 cm), sulfates contained in the interstitial water serve as the main anaerobic oxidant of organic matter. Organic matter consumption for anaerobic diagenetic processes (including the reduction of reactive Mn and Fe in the solid phase, as well as sulfates in the interstitial water) in the upper 300-cm-thick sediment layer does not exceed 16% of the primary organic matter buried in sediments after aerobic decay in the surface layer. Meanwhile, the residual  $C_{org}$  content measured by direct determination is almost two times less. The discrepancy may be related to the additional oxidation of organic matter owing to the penetration of oxygen into the upper anaerobic layer of sediments (aerobic-anaerobic diagenesis). Recycling of redox system compo-

nents near the oxygen zone boundary is also among the possible reasons.

In general, the distribution of Mn and Fe in the present-day sediments of the sublatitudinal Kandalaksha–Arkhangelsk transect is characterized by an obvious asymmetry. Relatively high Mn concentrations in sediments and interstitial waters are noted in the central White Sea and, especially, in the Kandalaksha Bay. Increased Fe concentrations occur in sediments from the central White Sea and in the interstitial water of the Dvina Bay sediments. A less distinct asymmetry is noted in the distribution of organic carbon and sulfides. Their concentrations are higher in the Kandalaksha Bay sediments. The geochemical asymmetry is related to not only different material sources, but also variations in hydrodynamic regime, bottom topography, and early diagenetic processes in sediments.

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