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The Redox Profile of the Bottom Sediments in the Ob River's Mouth Area

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Abstract—By the data of cruise 54 of the R/V *Akademik Mstislav Keldysh* (September 2007), the results of geochemical studies of the redox processes in the bottom sediments of the Ob River's near-mouth area as applied to the redox indicator elements such as manganese, iron, and sulfur are presented. The characteristics of the bottom sediments and the distribution of these elements in them testify not only to the significant role of the mixing processes in the formation of the geochemical profile of the bottom sediments in the estuary but also to the role of the postsedimentation (diagenetic) processes.

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INTRODUCTION

The redox profile of marine sediments is formed by the chemical elements interacting with the organic matter (OM) and with each other in the course of the postsedimentation processes, the transforming from higher to lower oxidation degrees, and the changing of their forms and solubility. In the bottom sediments, the main oxidants of OM, either produced in the sea or supplied from the land, are oxygen, nitrates, oxyhydroxides of manganese (III, IV) and iron (III), sulfates, and carbon dioxide. The oxidants listed are reduced in the energetic and microbiological series of corresponding reactions to give water, ammonia, bivalent forms of manganese and iron, hydrogen sulfide, and methane. The study of each of the redox pairs is still very much questionable. This report presents the results of the studies of the geochemical effects of the redox reactions in the bottom sediments of the Ob River estuary involving manganese, iron, and sulfur. The study was carried out in September 2007 during cruise 54 of the R/V *Akademik Mstislav Keldysh* in the course of the expedition to the Kara Sea. The authors were aware of the recent results of the national and international research performed during the expeditions of the R/Vs *Dmitrii Mendeleev* (1993) [18], *Akademik Boris Petrov* (1997–2003) [34], and other R/Vs [36].

MATERIALS AND METHODS

The bottom sediments were examined in a submeridional profile 275 miles length from the southernmost freshwater station in the Ob River delta (71°N) to the estuary and open sea (75°N), where the northernmost station of the profiles 500 considered was located beyond the inner shelf (Table 1, Fig. 1) [11, 20].

The bottom sediments were sampled by means of dredgers and geological tubes, including Neimisto tubes, allowing one to simultaneously sample a small amount of the near-bottom water over the sediment. The sampling was often complicated in the area of the coarse–silty and sandy sediments.

The moisture of the sediments (air drying to constant mass at 105°C) was the maximum in the southern organogenic oozes (over 60%) and the minimum in the coarse-silty sediments (below 30%, station 5001). The moisture was also somewhat decreased in the compacted oozes within the sediment mass (Table 1).

The redox potential measured using a platinum electrode (E_{Pt}) may be as close as one likes to the thermodynamic Eh value allowing one to calculate the free energies of the reactions (ΔG^0) and the concentrations of the components involved for any temperature. However, the difference in the measurements caused by the nonideality of the platinum surface may result in incorrect conclusions not only concerning the concentrations of the interacting substances but also the processes proper. Nevertheless, we use the E_{Pt} measurements as qualitative features allowing one to characterize, to a degree of conventionality, the level of the oxidation of the marine environment and the occurring reactive phases. We used needle-shaped platinum electrodes introduced into the sediment or collected sample, a silver chloride reference electrode, and a solution of potassium ferri- and ferrocyanides to control the electrode system [4, 21, 41]. All the values obtained are given related to the standard hydrogen electrode (+200 mV addition, Table 1).

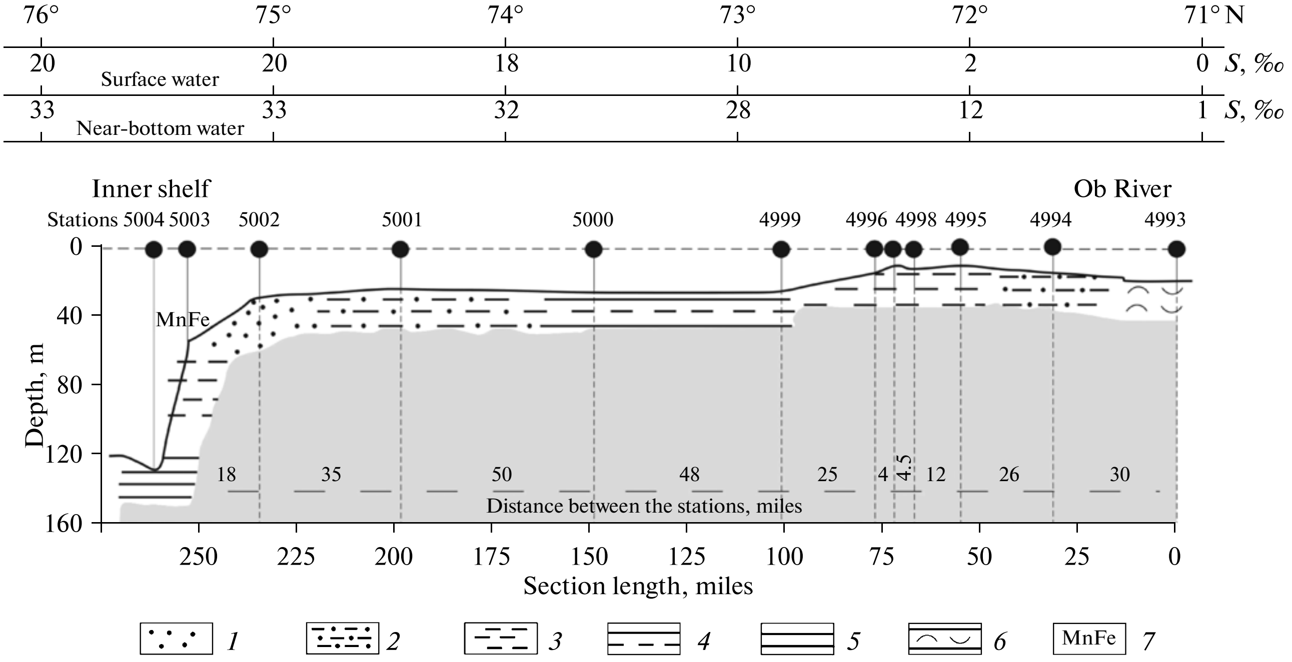

Fig. 1. Lithological and grain-size submeridional profile of the surface bottom sediments (0–7 cm) across the Ob River's estuary (the upper numerals are the latitudes; the lower ones are the salinities (‰) of the surface and near-bottom waters). *1*—medium-grain sands; *2*—coarse siltstones; *3*—fine-silty oozes; *4*—fine-silty oozes with an increased content of calyey matter; *5*—silty–clayey oozes; *6*—black sapropel-like oozes; *7*—iron–manganese concretions.

The reactive forms of iron were extracted from the moist samples of the sediments stored with no aeration by their treatment with 3.5 N H_2SO_4 under cooling with the following Fe(II) titration with a 0.02 N $K_2Cr_2O_7$ solution and the Fe(III) determination with KI and a 0.02 N $Na_2S_2O_3$ solution [28]. When using this procedure, the iron transforms into a solution of hydroxides; carbonates; hydrotroilite; and, partly, the most labile layered silicates of loams (glauconites and leptochlorites). These samples were also tested for the forms of sulfur [5] (Table 2). The carbon dioxide and C_{org} were determined in dry sediment samples (105°C) using high-temperature catalytic decomposition with an AN 7529 device with following CO_2 conversion into the $CaCO_3$ content (Table 1).

The interstitial waters were separated from the sediment with a centrifuge at 3000 rpm during 30 min on board the vessel within 6 hours or earlier after the drill core's raising. The sediments were very dense, and 30–40 ml of the sediment gave 5–10 ml or below of interstitial water. After the filtration through the membrane filters (Millipore, 0.45 μm), the dissolved manganese and iron in the interstitial waters were determined with formaldoxime and ferrozine, respectively [12, 39]. The manganese, iron, and aluminum in the solid phase of the sediment were determined from dry samples (105°C) after the acidic decomposition (HF + $HClO_4$) by means of atomic absorption flame spectroscopy (Table 1).

CHARACTERISTICS OF THE BOTTOM SEDIMENTS

According to the scale of the values of the redox potential (E_{Pt}) applied by the authors and tested with marine and oceanic sediments (from –350 to +650 mV relative to the normal hydrogen electrode at 20°C) [4, 21, 22], the E_{Pt} values over +400 mV corresponded to the presence of oxidized manganese and iron forms in the sediment matter, usually as Mn(IV) and Fe(III) oxyhydroxides. At E_{Pt} values below +200 mV, the sulfide forms are stable (hydrotroilite, pyrite, and organic sulfides). At zero and negative E_{Pt} values, the sediments contain free hydrogen sulfide, being commonly detected by its odor [22]. In the sediments of the profile considered, the high E_{Pt} values (+400 mV and over) are characteristic only for a thin mobile warp on the sediment surface formed owing to the reductive processes in the subsurface layers. The dissolved Mn(II) and Fe(II) forms appeared in these layers under the diffusion and oxidation on the surface by the oxygen dissolved in the near-bottom water and the water-insoluble Mn(III, IV) and Fe(III) oxyhydroxides, just the presence of which determines the high E_{Pt} values. The bulk of the sediments is represented by grey reduced oozes of various density and watering. The presence of black patches and bands points to sulfide formation (E_{Pt} from 0 to +200 mV) and even to the appearance of free hydrogen sulfide (at the layer of 180 cm and below, E_{Pt} up to –180 mV, station 5004, Table 1). Only on the sediment's surface, as a rule, was

Table 1. Geochemical characteristics of the bottom sediments in the Ob River's mouth area

Layer, cm	Description of the sediment	E_{Pt}, (Eh), mV	H_2O, %	C_{org}	$CaCO_3$	Al	Fe	Mn	Fe	Mn
				% in the dry sediment					µM in the interstitial water	
Station 4993, 71°14.90 N, 72°51.51 E, 23 m depth										
D										
0–2	Brown warp (1mm) on black semiliquid ooze compacted downwards to a degree	+20	64.9	1.52	0.34	6.37	6.45	0.174	41.2	44.0
2–5		+50	62.6	1.25	0.59	6.72	5.92	0.163	11.1	27.3
5–15		+20	61.1	1.15	0.34	6.56	5.38	0.164	2.26	88.6
Station 4996. 72°34.19′ N 73°49.28′ E, 18 m depth										
D										
0–4	Brown semiliquid	+476	60.4	1.10	1.82	6.94	7.09	0.332	0.35	183
4–7	Grey, many animals	+50	59.5	1.35	0.59	7.30	7.29	0.270	6.23	260
7–15	Darker and denser, denser	+5	51.5	1.12	1.07	7.20	6.89	0.261	7.32	245
Station 4999, 72°57.17 N, 73°16.97 E, 20 m depth										
D										
0–3	Brown semiliquid	+440	40.8	0.65	0.50	4.87	4.16	0.200	1.09	2.50
3–6	Grey, many animal	+50	46.1	0.63	1.00	6.26	5.00	0.073	2.10	102
6–12	Grey, uniform, denser	+20	43.0	0.70	1.16	6.72	5.52	0.070	3.89	87.2
Station 5000, 73°45.90 N, 72°56.61 E, 29 m depth										
D										
0–2	Brown semiliquid	+375	40.3	0.52	0.25	5.40	3.27	0.104	0.62	13.4
2–8	Dark grey, soft	+40	39.3	0.61	0.32	5.73	3.80	0.102	5.84	95.9
8–12	The same, denser and cloddy	+130	34.9	0.37	0.25	5.97	3.74	0.041	1.56	74.2
NT										
5–10	Dark grey, dense	+20	33.8	0.35	1.07	5.96	3.42	0.050	2.18	85.2
10–20	Denser	+35	37.3	0.62	0.16	6.7	4.52	0.053	3.58	129

Table. (Contd.)

Layer, cm	Description of the sediment	E_{Pt}, (Eh), mV	H_2O, %	C_{org}	$CaCO_3$	Al	Fe	Mn	Fe	Mn
				% in the dry sediment					μM in the interstitial water	
Station 5001, 74°35.04 N, 72°45.54 E, 24 m depth										
D										
0–2	Brown semiliquid	+460	17.3	0.10	0.25	4.00	1.59	0.041	0.86	16.0
2–7	Dark grey, dense	+70	28.1	0.27	0.25	4.72	2.72	0.032	1.63	57.9
LDT										
5–35	Dark grey, coarse siltstone, white flakes, hydrotroilite patches	+50	27.5	0.29	0.25	4.40	2.82	0.038	1.65	79.9
35–47	Distinctly bordered, very dark and dense, coarse siltstone	+100	21.8	0.22	0.16	4.60	2.24	0.026	2.18	42.4
47–53	Much watered, fine-silty with brown-ochric cavities	+60	26.0	0.20	0.16	4.53	2.27	0.040	1.17	101
53–66	Similar to 5–35 but with ochric patches	+110	30.2	0.38	0.16	4.82	2.89	0.029	2.10	40.9
66–82	Analogue of 35–47	+60	27.8	0.27	0.16	5.01	2.66	0.029	1.24	48.6
Station 5004 D. 75°34.34 N, 72°24.71 E, 160 m depth										
D										
0–2	Brown semiliquid	+545	48.9	0.67	0.75	6.50	5.16	0.066	0.85	4.82
2–7	Grey, denser	+100	44.0	0.58	0.16	7.96	5.00	0.067	0.62	83.4
7–12	More denser, dark patches of hydrotroilite at 5–14 cm	+40	42.6	0.57	0.25	6.80	4.46	0.077	1.71	104
LDT. 75°33.32 N, 72°34.96 E, 120 m depth										
14–20	Grey, soft, dark patches (5–14) are substituted with watered grey ooze and ocher	+15	58.4	0.75	1.00	7.90	8.27	0.108	3.11	136
50–60	From 20 to 107 cm, the hydrotroilite content increases (black strips on the grey background), and the sediment is compacting	+10	50.0	0.70	0.41	7.70	6.15	0.066	1.82	106
100–107		+20	56.5	0.71	0.50	7.68	7.53	0.107	1.24	126
125–140	Dark grey with hydrotroilite patches; their number, as well as the sediment density, increases to the core's end. A seeming H_2S odor	+50	54.3	0.87	0.34	7.70	7.45	0.086	1.87	135
180–200		–20	48.2	0.72	0.25	8.20	6.32	0.074	2.65	123
300–320		–140	46.5	0.75	0.25	8.06	6.07	0.077	–	99.2

Note: D is a dredger, NT is a Neimisto tube, and LDT is a large diameter tube.

Table 2. Forms of reactive iron and sulfur compounds (% in the dry sediment) in the bottom sediments of the Ob River's mouth area

Station	Layer, cm	H_2O, %	Reactive iron				Forms of sulfur						ΣS_{H_2S}
			total	including			sulfate S	S^{2-}	S^0	S_{pyrite}	S_{org}		
				Fe^{2+}	Fe^{3+}	sulfide Fe					total	in bitumens	
4993	2–5	64.1	3.08	2.40	0.42	0.26	0.060	0.146	0.040	0.014	0.106	0.016	0.306
4996	7–15	58.0	3.03	2.36	0.62	0.05	0.102	0.021	0.029	0.014	0.170	0.055	0.234
4999	3–6	48.0	1.89	1.26	0.61	0.02	0.096	0.007	0.002	0.012	0.082	0.029	0.103
5000	2–8	47.9	1.58	1.12	0.40	0.06	0.096	0.027	0.028	0.015	0.062	0.014	0.133
″	10–20	35.8	1.35	1.00	0.24	0.11	0.071	0.056	0.044	0.011	0.054	0.013	0.166

Note: $Fe_{sulfide} = Fe_{monosulfide} + Fe_{pyrite}$; S^{2-} is monosulfide sulfur.

the brown semiliquid warp (thinner than 1mm) revealed, being carried easily with the near-bottom currents and often washed-off during the sampling. Along with the diagenetic origin, one may suppose the precipitation of solid oxyhydroxides from the near-bottom water in the case of the formation of increased concentrations of dissolved manganese. However, no cases as such were found in the near-bottom water of the Ob River estuary, at least in view of the detection limit of the method used (0.1 μM of Mn^{2+}). In the sediments of the seaward part of the estuary (stations 5001 and 5004), oxidation evidence was registered within the sediment mass (47–53 and 14–20 cm, Table 1) where grey oozes with ochric patches were found. Here, the oxidation might be caused by the permeation of oxygen-containing near-bottom water through the water-bearing layers formed by irregular sedimentation or by benthos.

As to the morphology, the bottom sediments in the freshwater part of the section (station 4993, 23 m depth, Fig. 1) looking like sapropel-like oozes are separated from the seaward part with a small elevation (bar) of gravitation genesis (stations 4994–4996 of depths of 18 m or shallower, Fig. 1). Here, with the seaward moving, the coarse-silty sediments are substituted by fine silty oozes extending seawards for over 150 miles (station 5000, 29 m depth, Fig. 1). Farther into the sea, the sediments anew coarsened, from coarse siltstones at station 5001 (24 m depth) to sands at the margin of the inner shelf (station 5002, 35 m depth). The sediments of the outer shelf adjacent to the Ob Bay estuary are represented by fine silty (station 5003, 47 m depth) and silty–clayey oozes (station 5004, 120 m depth, Fig. 1). The grain sizes determined to a great extent the material composition of the sediments in which alumosilicates and quartz are prevailing in ratios varying regularly from the mouth to the estuary and farther to the open sea. Note that the Ob River is a powerful quartz source for the sediments of the Kara Sea [14]. The inverse correlation between these components [9] allows one to evaluate more completely the sediment composition on the basis of the direct determination of the Al (Table 1, Fig. 2). In view of this, in the freshwater and saltish mouth area (station 4993), where much organic matter is present and the sediments are fine-grained, alumosilicates are prevailing (7% Al, a quartz content of 30%). Farther to the sea, with the fractionation of the sediment matter by size and density, the quartz content in the sediments increases up to the outer part of the estuary to reach 50% in the coarse-silty and sandy sediments; the Al content decreases to 4% (stations 5001 and 5002). The finest fraction is carried to the open sea because of the permanent rewashing. The sediments of the outer shelf adjacent to the estuary, in which the Al content (7–8%, station 5004) approaches the average values for marine sediments, contain 25% or below of quartz.

Along with the mechanical sizing of the fractional sediment matter, the zone of the riverine and marine water mixing is characterized by physicochemical mechanisms of coagulation and flocculation of the loamy solutions, dissolved, and particulate organic matter. The general characteristics of these processes are known, including those for the Ob River mouth area [17, 38]. The results of cruise 49 of the R/V *Akademik Mstislav Keldysh* introduced certain corrections and completed the previous data. At the salinity of 0.6‰ or below (station 4994), by the measurements with a Coulter counter [2], the gravitational sedimentation of 50% of the silty–clayey (6–15 μm) riverine particulate matter takes place, and, at the salinity of 6‰ (station 4996), the particulate matter becomes mainly clayey (96%) (4.7 μm). The highly developed surface of the particulate matter and the sediments formed from it promotes the sorption processes involving the loamy minerals; oxyhydroxides of metals; and organic residues, including, along with amorphous organic matter, silicon, carbonate, and chitin fragments as well. At 15–20‰, after the pronounced clarification of the water, the intensified development of diatom algae was noted, which resulted in considerable fluctuations of the particulate matter concentration and grain size (the increase of the median diameter to 24 μm) [2, 30].

RESULTS AND DISCUSSION

The content of C_{org} in the bottom sediments (Table 1, Fig. 2) of the Ob River estuary is determined by the supply of terrigenous OM with the riverine runoff, the physicochemical processes in the zone of the riverine and marine water mixing, and by the OM production by plankton and benthos, on the one hand, and by the oxidation and decomposition processes, on the other hand. The concentration of the OM dissolved in the riverine water, by the data from the cruise considered, was as high as 12 mg of C/l (station 4993) [1], which is close to the results of the expeditions of the R/V *Akademik Boris Petrov* (7.2–10.1 mg of C/l [37] with an annual average value of 7.7 mg of C/l [36]). The optical characteristics and high C/N ratio of the OM dissolved in the estuary water and the 60–75% humic matter testify to its terrigenous origin (the fraction of the plankton OM is quite small) [27, 37]. Within the total content in the estuary water, the dissolved OM is considerably prevailing over its particulate forms, which are much variable spatially and temporally in view of the contrasting seasonal effects. The direct C_{org} determination in the particulate matter results in 2.7–6.9% [1]. The two-week observations of September 1999 in the seaward part of the estuary (near station 5001) using sedimentation traps point to the changes in the particulate matter composition from diatoms and copepods to flagellates and protozoa, and the spectrum of the amino acids in the particulate matter changes from phyto- to zooplankton. Within the flux of the particulate matter to the bottom (2202 mg/m^2 day), about half (1101 mg/m^2 day) is constituted by the OM, whereas the lithogenic part is secondary (890 mg/m^2 per day) [35].

As already mentioned, the OM with prevailing humic substances is quite resistant to decomposition and involving into the biochemical but not into the physicochemical transformations. As noted above, the growth of the salinity from 0.5 to 6‰ in the mixing zone causes the coagulation and flocculation of both the loamy forms of particulate matter the dissolved and particulate organic forms. This determines the high OM content in the freshwaters and the saltish sediments of the “deposition center” of the river located between 71 and 73°N (C_{org} over 1%, stations 4993–4996, Table 1, Fig. 2), where the total content of particulate matter in the near-bottom water decreases from over 5 to 0.1–0.5 mg/l [2, 10]. Farther, when moving seawards, the content of organic matter in the estuary sediments decreases (C_{org} of 0.5–1% at stations 4999–5001 and below 0.5% at station 5001), and the fine-silty oozes are substituted by coarse-silty sediments and sands, and freshwaters are more and more replaced with seawaters. At the output of the mixing zone, in the area of great depth and finer sediments, the content of C_{org} in them increases (over 0.5%, station 5004).

The organic carbon buried in the bottom sediments is the final link in the chain of the transformations to which the dissolved and particulate OM is subjected under the sedimentation, bioactivity, and diagenetic processes. Note that the C_{org} content in the particulate matter from the Ob Bay (2–7% [9]), as a rule, is higher by an order of magnitude than that in the upper layers of the bottom sediments (0.1–1.5%, Table 1). This fact represents the processes of the OM utilization and recycling on the bottom sediment surface proceeding under the impact of microorganisms and benthos. As a result, a considerably smaller amount of OM is buried in the sediments compared to that supplied with the riverine particulate matter (roughly, a 1 : 10 ratio), and the OM amount passed into sediments shows zonal variability. The most effective is the zone of coagulation and flocculation of the OM in the riverine water coinciding with the zone of the highest concentrations of C_{org} in the sediments and of the dissolved C_{org} in the interstitial waters (Fig. 2, stations 4993–4996). The higher C_{org} content in the sediments at the transition from the inner to the outer shelf (station 5004) is caused by the high bioproductivity of this zone [29, 30].

Within the studied upper layer of the sediments, the C_{org} content varies slightly, both in the upper part of Ob Bay, where it is somewhat decreased from 1.5‰ on the surface to 1.15% at 20 cm (station 4993, Table 1), and in the estuarine area, where the C_{org} is even increased a little in the sediment mass from 0.1% on the surface to 0.3% at 80 cm (station 5001). In the marine part of the section adjacent to the estuary, the C_{org} content also increases a little with the sediment depth (station 5004, Table 1), which is caused now by the features of the sedimentation in the Kara Sea. Considering the accumulation of carbon in the bottom sediments, note the quite small carbonate content, which is barely as high as 1% (converted into calcium carbonate) (Table 1), which is characteristic for the Arctic aquatic areas.

Quantitatively, the redox system of the bottom sediments may be characterized by the distribution and transformations of manganese, iron, and sulfur compounds, being the primary agents of the diagenetic transformations and OM utilization. The diagenesis makes the corrections in the initial concentrations of these components subjected alternately to dissolution, migration, and sedimentation in different layers.

The manganese content in the marine sediments (the clarke) amounts to 0.06–0.09% [7]. An increased Mn content is found in the bottom sediments of the southern part of the mixing zone of the Ob River and the Kara Sea waters. This content is lower in the freshwater and saltish sediments (0.17%, station 4993, Table 1) and higher (0.33%, station 4996) where the salinity of the riverine water increases to 2–6‰ (Table 1, Fig. 2). Within this zone of the marginal filter, as already mentioned, several areas of riverine matter sedimentation with the distance from the mouth are conventionally distinguished, namely, the gravitational, physicochemical, and biological area [16]. Of course, no distinct border may take place between these areas because of the real parallelism and superposition of the dominant processes. The mechanical fractionation of the sediment matter by grain size and density does not exclude the interaction of the riverine and marine waters to change the salinity and cause the coagulation of colloids. As applied to the manganese, iron, and many other elements, of greatest importance is the physicochemical stage related to the coagulation of the colloids in the riverine water under the impact of the electrolyte (seawater) [40]. At the salinity from 2 to 7‰, manganese is the most intensively isolated from the riverine water and passes into the sediments. When we compare the content of manganese in the riverine particulate matter (0.22–0.39% [9, 10]) to that in the bottom sediments of the estuary, it becomes obvious that only the sediments of the coagulation zone (station 4996, Fig. 1), where the salinity of the near-bottom water is about 6‰ and the manganese concentration amounts to 0.3% (Table 1), are close to the composition of the particulate matter. In the other bottom sediments, both upstream (station 4993) and downstream (station 4999 and farther to the north), the content of manganese is considerably lower (Table 1, Fig. 2). By this, we mean that the manganese supplied to the sediments with the solid particulate matter, mainly as oxyhydroxide or as a sorbate, passes into the interstitial solution and, then, because of the difference in the concentrations, to the near-bottom water. The authors really noted a high manganese content in the interstitial water (up to 260 μM at the most), which caused a flux of dissolved manganese from the sediments to the near-bottom water with an incomparably lower dissolved manganese content. Manganese, especially its labile fraction represented by Mn(III, IV) oxyhydroxides, under the increased OM content, is easily reduced to Mn(II). The compounds of the latter are well soluble but also easy for oxidation as promoted by their accumulation and sorption on the solid particles.

With the distance seawards from the mouth, the manganese content in the sediments decreases form 0.07% in the fine-silty to 0.03% in the sandy sediments of the inner shelf margin (stations 4999 and 5001, respectively). This decrease, as already mentioned, is determined by the lowering of the loamy alumosilicate fraction in the sediment and the increase of the quartz amount. The situation is restored only in the marine sediments of the outer shelf, where the content of manganese is equal to the clarke and even exceeds it in some of the interlayers (station 5004, Table 1).

The vertical distribution of the manganese in the bottom sediments is affected by both the irregularities in the sedimentation [14] and the diagenetic redistribution caused by the organic matter [32]. The supply of this latter also was not regular, both in the coarse-silty sediments of the estuary and in the silty–clayey marine sediments adjacent to the estuary from the north. In the former case (station 5001), this redistribution takes place in the background of the decreased manganese content (below 0.04%) because of the low content of the loamy fraction, being a primary carrier of this element. This is supplemented by the outwashing of manganese from the sediments owing to the organic matter. At that, the thin surface layer (2 mm) is simultaneously enriched in both the dissolved manganese from the interstitial water and the solid-phase manganese. The other layer of the diagenetic distribution at this station is the intermediate one with brown ochric cavities and patches (47–66 cm, Table 1), in which, along with a higher C_{org} content, an increased content of manganese is also found in both the solid phase and the interstitial water. At that, the relative positions of the corresponding C_{org}, iron, and manganese layers (iron below manganese) points to the superposition of the diagenetic processes onto the irregular supply of the sediment matter.

A similar view takes place in the marine silty–sandy sediments of the seaward part of the estuary but, in this case, in the background of considerably higher concentrations of manganese (0.07–0.11%, station 5004, Table 1). Here, the enrichment of the surface layer in both the dissolved manganese (and iron as well) and the solid-phase forms of these elements is registered. Within the sediments' mass, the irregularity in the distribution of the OM, manganese, and iron caused either by the appearance of ochric layers (14–20 cm) or by the formation of loamy "pillows" (100–140 cm) takes place as well [14, 15].

As already mentioned, the most common manifestation of the diagenesis in the bottom sediments of the mouth area is the appearance of quite high concentrations of dissolved manganese in the interstitial water, amounting to over 260 μM in the sediments characterized by the maximum coagulation and manganese content (station 4996, Table 1, Fig. 2). Nearer to the sea (stations 4999–5001), the amount of dissolved manganese in the interstitial waters of the estuarine sediments decreases, especially in the sandy sediments (station 5001), but it still remains high (50–100 μM). In the marine sediments of the outer shelf adjacent to the estuary (station 5004), the concentrations of manganese in the interstitial waters are also increased

Fig. 2. Chemical components (C_{org}, Mn, Fe, and Al) in the surface sediments and interstitial waters of the Ob River's mouth area (the numerals at the isolines are the concentrations).

C_{org} in the sediments: 0.5, 0.75, 1.0, 1.25, 1.25.

Mn (%) in the sediments: 0.05, 0.10, 0.20, 0.25, 0.30.

Mn (μM) in the interstitial water: 50, 100, 150, 200.

Fe (%) in the sediments: 3, 4, 5, 6, 7.

Fe (μM) in the interstitial water: 2, 5, 7, 10.

Al (%) in the sediments: 5, 6, 7.

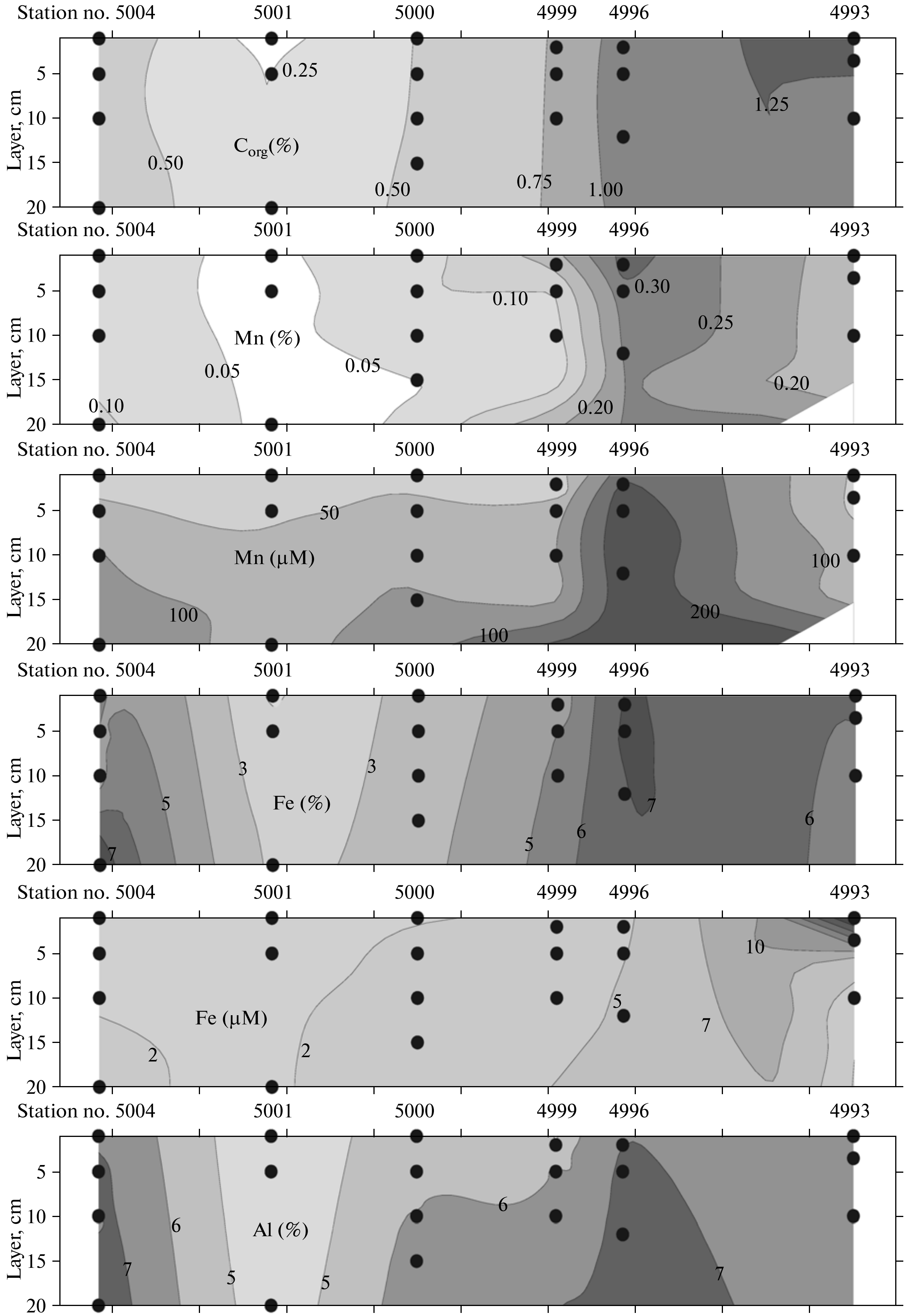
Station no. 5004
5001
5000
4999
4996
4993
Layer, cm
5
10
15
20
C$_{org}$(%)
0.25
0.50
0.50
0.75
1.00
1.25
Mn (%)
0.05
0.05
0.10
0.10
0.20
0.20
0.25
0.30
Mn (μM)
50
100
100
100
200
Fe (%)
3
3
5
5
6
6
7
7
Fe (μM)
2
2
5
7
10
Al (%)
5
5
6
6
7
7

Table 3. Relationships of the forms of the reactive iron and sulfur compounds in the bottom sediments of the Ob River's mouth area

Station	Layer, cm	% of Fe_{react}			% of ΣS_{H_2S}			
		Fe^{2+}	Fe^{3+}	Fe_{sufide}	S^{2-}	S^0	S_{pyrite}	S_{org}
4993	2–5	77.81	13.59	8.60	47.76	13.09	4.43	34.72
4996	7–15	77.87	20.51	1.62	9.05	12.48	6.07	72.40
4999	3–6	66.61	32.22	1.17	6.62	2.30	11.40	79.68
5000	2–8	70.66	25.48	3.86	20.69	20.98	11.64	46.69
″	10–20	74.48	17.58	7.94	33.88	20.82	6.85	32.45

(100 μM and over). These concentrations remained in the sediment mass as well, including the variations caused by the irregularities in the sedimentation. The high concentrations of dissolved manganese in the interstitial water as such result, as already noted, in the flux of this element from the sediments to the near-bottom water [26]. A part of this flux is realized in the formation of the warp of the manganese oxyhydroxides on the sediment surface or of iron–manganese concretions, which were found in the seaward part of the estuary (station 5003). The remaining part of the dissolved manganese is spread by the near-bottom water.

Thus, the formation of the manganese concentration in the bottom sediments, especially in their surface layer, resulted from the recycling, including the sedimentation of particulate matter containing Mn(III, IV) oxyhydroxides, the sorbed and organic manganese, and the subsequent reductive diagenesis and desorption, including the transition of Mn(II) ions to the interstitial solution. The increased concentrations in the interstitial waters cause a flux of dissolved manganese from the sediments and, at a sufficient concentration for the oxidation by oxygen dissolved in the near-bottom water, solid Mn(III, IV) oxyhydroxides are formed anew, which constitute the warp on the surface of the bottom sediments, and are spread over the estuary by the near-bottom currents. Unlike the Ob River estuary, the Yenisei River mouth area is characterized by suboxidative conditions appearing in places in the near-bottom water and allowing for the coexistence of particulate Mn(III, IV) and dissolved Mn^{2+}; at that, the concentrations of this latter may increase to 10 μM [9, 33, 36]. In this case, the oxygen content amounted to 4 ml/l; i.e., it was too high for the steady existence of dissolved manganese in amounts as such. The known data on anoxic basins testify to the considerably lower oxygen concentrations causing Mn^{2+} oxidation and precluding the appearance of dissolved manganese [23, 25]. In the near-bottom water of the Ob River estuary, where, really, the concentration of dissolved oxygen was not below 6 ml/l [19], no increased concentrations of dissolved manganese were registered by the authors. The Yenisei phenomenon considered is probably caused by the high dynamics of the near-bottom processes, the absence of chemical equilibrium, and by the uncertainty of the composition and properties of the involved colloidal and organic forms of manganese.

The content of iron in bottom sediments of the profile across the Ob River estuary also shows great variability caused by the processes in the river–sea boundary zone. The range of variations is quite wide: from 1.6% in the sandy and coarse-silty sediments at the inner shelf edge (station 5001, Table 1) to over 7% in the sediments of the zone of coagulation and flocculation (station 4996). Note that the clarke concentration of the iron for loams and shales is close to 5% [7]. The zone of high iron concentrations, beginning from sapropel-like calyey oozes in the freshwater part of the profile (6.5%, station 4993), reaches its maximum in the silty–clayey oozes of the coagulation zone (7.3%) and lenses out gradually to the minimum values in the sands of the seaward margin of the estuary (Fig. 2). In the marine sediments of the northern part of the estuary, where the silty–clayey fraction is prevailing (station 5004), the content of iron tends to the clarke values (5–6%, Table 1).

As in the case of manganese, the content of iron succeeds to the irregularity of the sedimentation in this area, to which the diagenetic irregularity may be superposed. This may be seen by the vertical distribution of iron not only in surface sediments but also in the more ancient Holocene layers. In the coarse-silty sediments of quite low iron content (station 5001), its growth is registered in the subsurface layers. This growth is, evidently, of diagenetic character related to the transition of the reactive iron forms to the interstitial solution and their following oxidation near the surface either by the oxygen of the near-bottom water or by the Mn(IV) always occurring on the sediment surface. Another jump in the iron content may be noted in the layer of 53–66 cm just below that of 47–53 cm enriched in manganese. The relative position of the enriched layers (iron below manganese), along with the increased OM content in them, as well as the ochric and brown patches in the sediment core, point to the redox stratification. In this case, evidently, the OM acts as a reductant (increased C_{org} content) but with an oxidant character within the sediment mass. One may assume the existence of water-bearing layers in the coarse-silty sediments being conjoint to the surface oxic waters or an impact by polychaetes characterized by tubular structure and the capability to pump the near-bottom water through their tubes. The latter assumption is hardly feasible because of the small sizes of the polychaetes. One may also assume the initial burial of a layer enriched in Mn(IV), e.g., owing to iron–manganese concretions (IMC), which, under the interaction with OM, may act both as a source of metals and as an oxidant for iron (ochric patches). The latter assumption is confirmed by the finding of the IMC in the surface layer of station 5003 in immediate proximity to the sediments considered (Fig. 1).

In the marine sediments adjacent to the estuary from the direction of the outer shelf, the mentioned irregularities in the iron content (station 5004, Table 1) may also be diagenetic, because they are associated with the layers enriched in OM and manganese. In this case, a key factor of this irregularity may be the irregular supply of OM, being the motive force of the mobilization and dissolution of metals.

In the interstitial water, the content of dissolved iron or, rather, of its fraction constituted mainly by inorganic forms, which may be detected with ferrozene, is at the level of 1–3 μM. These concentrations are considerably higher in the interstitial water of the sediments of the coagulation zone (over 7 μM, station 4996) and incomparably higher (over 40 μM, station 4993) in the interstitial water of the freshwater sediments of the lower course of the river (Table 1). The high concentrations of dissolved iron as such in the interstitial waters of the Ob River‘s lower course provide the transition of a considerable part of the dissolved iron from the bottom sediments into the near-bottom water, the transfer to the estuary, and further to the open sea despite the losses in the coagulation zone. As is known, the transition of the dissolved iron from the sediments to the oxic water of the near-bottom layer is quite hindered compared to the manganese or even excluded [39], but one must not deny it completely because of the existence of organic forms characterized by other parameters of solubility.

A supplementary characteristic of the processes of sedimentation and diagenesis may be the data on the determination of the reactive forms of iron, namely, of Fe(II) and Fe(III) in the solid hydroxides, carbonates, sulfides, and several silicates transformed in the course of the analyses into subacid extracts and, by the present concepts, taking an active part in the postsedimentation processes [22, 28]. By the data obtained (Table 2), the reactive iron in the bottom sediments of the Ob River estuary amounts almost to half of the total iron content (Table 1), which is quite a high value compared to the marine and oceanic sediments. The remaining iron is represented by lithogenic forms being practically invariable under the diagenesis. The bulk of the reactive iron (70–80%) is represented by bivalent Fe(II) forms, among which the fraction of sulfide iron is 10% or below (Table 3), which agrees with the general reduced state of the sediments (see the data on E_{Pt} values). However, the reactive iron forms in the bottom sediments always include the oxidized Fe(III) forms, sometimes in considerable amounts (usually 20 and even 30% in the coagulation zone, station 4999, Table 2).

As a rule, the most informative characteristics of the redox conditions in marine reduced sediments are the data on the sulfate reduction. In the anoxic diagenesis prevailing in the studied bottom sediments, sulfates play a primary role as the OM oxidants [5]. The microbial reduction of sulfates results in free hydrogen sulfide, which is bound to the substance of the sediments considered to form iron sulfides (hydrotroilite and pyrite) and other inorganic and organic compounds being commonly considered as the sum of the hydrosulfide derivatives (ΣS_{H_2S}, Tables 2 and 3).

Our attention is engaged by the limited level of the sulfate reduction in the sediments of the high OM content (the riverine part of the estuary). In the marine and oceanic sediments with a C_{org} content of about 1%, as in the case considered, the ΣS_{H_2S} value usually tends to 0.7% and over [5, 6]. The maximum ΣS_{H_2S}, value registered in the area surveyed amounts to 0.306% (station 4993, Table 2). The factors limiting the sulfate reduction may be either the decreased OM or sulfate contents or a deficiency of reactive iron. Really, the decrease of the C_{org} content in the sediments with the distance from the mouth area causes a pronounced ΣS_{H_2S} decrease (almost halved from station 4993 to station 5000, Table 2). No other factors are present in this case; although a small decrease of the sulfate concentration takes place because of the desalination of the interstitial water and is registered at station 4993 (Table 3); it is not so efficient to be a limiting factor. The reactive iron, as noted earlier, is also in sufficient amounts. In the absence of reactive iron capable to bind free hydrogen sulfide, the latter is accumulated, which retards and even stops its further formation, as takes place in the carbonate sediments of tropical lagoons. The main factor limiting the sulfate reduction in the bottom sediments of the Ob River's mouth area is not the total content but the composition of the OM. Unlike the quite labile planktonogenic OM of the marine sediments, the terrigenous OM of the riverine runoff represented mainly by humic substances is characterized by lower reactivity and suitability for the processing by sulfate reducing microorganisms.

Another feature of the sulfate reduction process in the Ob River estuarine zone is the composition of the reduced sulfur forms derived from hydrogen sulfide, among which organic sulfur, including that of bitumens, is of considerable importance and prevailing in the sediments of the zone of colloidal coagulation (stations 4996, 4999, Table 3). The composition as such distinguishes the sediments of the estuary from the marine sediments, in which, as a rule, the sulfur of diagenetic iron sulfides (hydrotroilite and pyrite) is prevailing [5, 6]. The sediments considered are characterized by the prevalence of hydrothroilite (amorphous greasing sulfide of the conventionally ascribed FeS formula) among the iron sulfides, which determines the color of the reduced sediments (from grey to black in patches, lenses, and interlayers). Pyrite FeS_2, as a more stable crystalline form, is not prevailing in the sediments of the estuary as usually takes place in marine sediments. One must note one more feature of the composition of the derivatives of the diagenetic hydrogen sulfide, namely, the relatively high content of elemental sulfur (S^0) comparable to the content of iron sulfide sulfur. This form, appearing under the oxidation of free hydrogen sulfide, may be an intermediate in further transformations, especially in the formation of sulfur-containing organic compounds.

CONCLUSIONS

The redox stratification in the marine bottom sediments is formed by chemical elements changing their oxidation states and solubilities under the chemical and microbial processes involving the OM. The redox profile of the bottom sediments in the mouth area of the Ob River flowing into the Kara Sea is formed on the basis of the known zonality of the sedimentation at the river–sea boundary. The zone of gravitational sedimentation of the riverine matter extending over the entire estuary to the inner shelf edge is supplemented with the zone of physicochemical sedimentation under the mixing of the riverine and marine waters (destruction of riverine colloids at 1–7‰ salinity). The bottom sediments of this zone are characterized by increased contents of OM (C_{org} over 1%), manganese (over 0.3%), iron (over 7%), and of reduced sulfur produced by the microbial reduction of sulfates and the formation of hydrogen sulfide ((ΣS_{H_2S} over 0.3%).

The content of C_{org} in the surface layer of the bottom sediments is lower almost by an order of magnitude than that in the composition of the riverine particulate matter. The bulk of the OM is oxidized by the oxygen of the near-bottom water (6 ml/l) within a thin (millimetric) surface layer. Practically no oxygen permeates below this layer, which makes the sediments considered anoxic. The anoxic diagenesis of these sediments is characterized by the appearance of reduced forms of manganese, iron, and sulfur immediately in the subsurface layers. The appearance of high concentrations of these elements in the interstitial waters (up to 260 μM of manganese and up to 40 μM of iron) causes the formation of the fluxes from the sediment and the transition into near-bottom water, as for manganese, or the appearance of solid phases as the warp of iron and manganese oxyhydroxides or of iron–manganese concretions of the sediment surface. The reduced sulfur exists as iron sulfides, elemental, and organic forms, and these latter may be prevailing in the sediments.

The redox processes within the sediment mass may be represented as the irregularities in the stratification of the layers enriched in manganese, iron, and OM.

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