ISSN 0016-7029, Geochemistry International, 2017, Vol. 55, No. 12, pp. 1079–1089. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © V.Yu. Rusakov, T.G. Kuzmina, M.A. Levitan, E.S. Toropchenova, A.V. Zhilkina, 2017, published in Geokhimiya, 2017, No. 12, pp. 1088–1099.

Heavy Metal Distribution in the Surface Layer of Bottom Sediments of the Kara Sea

V. Yu. Rusakov*, T. G. Kuzmina, M. A. Levitan, E. S. Toropchenova, and A. V. Zhilkina

Vernadsky Institute of Geochemistry and Analytical Chemistry (GEOKhI), Russian Academy of Sciences, pr. Kosygina 19, Moscow, 119991 Russia

**e-mail: rusakov@geokhi.ru*

Received December 2, 2016; in final form, February 21, 2017

Abstract—This paper addresses the distribution of heavy metals (Co, Ni, Cu, Zn, Cd, Sn, Sb, Pb, and Bi) as well as Si, Al, Fe, and Mn in the surface (0–2 cm) layer of bottom sediments of the Kara Sea. The contents of these elements are determined in each of the previously distinguished facies-genetic types of terrigenous sediments: fluvial, glacial, estuarine, shallow water–marine, “background” marine, and relict sediments. It is shown that these types reflect the modern conditions of accumulation of river discharge material, which forms fans of two greatest Siberian rivers, Ob and Yenisei. The main stages are distinguished in heavy metal accumulation. The first stage is related to the avalanche sedimentation of terrigenous sediments in the estuary and characterized by the elevated contents of Co, Ni, Cu, Zn, Cd, Sb, and Bi. The second stage reflects the mechanical differentiation of sedimentary material by waves and bottom currents in a shallow-water sea part adjacent to the estuarine zone, with accumulation of Pb- and Sn-bearing “heavy” ore minerals. The deep-water background terrigenous–marine sediments accumulate mainly Ni, Zn, and Cd, as well as Mn. The relict sediments differ in the high contents of Si, Mn, and Sn.

Keywords: heavy metals, surface bottom sediments, facies-genetic types, Kara Sea

DOI: 10.1134/S0016702917090075

INTRODUCTION

Maximum concentrations of heavy metals (HM) in seas are observed on the geochemically active barriers (Emelianov, 1998). One of these barriers is the water–bottom sediment interface, which is inhabited by a community of benthic organisms serving as the main food for large marine animals, fish and mammals of shelf seas. The HM contents in the surface layer of bottom sediments play important role in biological cycles (Demina et al., 2006, 2010, 2015; Demina, 2011).

When economic activity is low, the main source of pollutants, including HM, in the Kara Sea, is the fresh-water run-off of the two greatest Siberian Rivers, Ob and Yenisei. Based on estimates by Il’in (2009), the Ob’ River annually supplies in the Kara Sea 2180 Cu, 13000 t Zn, 2200 t Ni, and 112850 t Mn, while Yenisei River, 4720 t Cu, 1350 t Zn, and 2700 t Ni. Most part of suspended and dissolved metal species transferred by these rivers are accumulated in sediments on the river–sea sediment barrier zone (Lisitsyn, 1994, Gordeev, 2012). According to Il’in (2009), the average HM contents (in μg/1g of dry sediment) in the surface layer of the bottom sediments of the Kara Sea are 36.2 Cu (APC < 35), 28.3 Zn (APC < 150), 34.7 Ni (APC < 30), 14.2 Pb (APC < 30), 0.18 Cd (APC < 0.25), 5.37 Co, and 33.5 Sn. Thus, the average concentrations of such metals as Cu and Ni exceed approximate permissible concentrations (APC) for unpolluted sediment.

Other studies (Demina et al., 1978, 2006, 2010; Demina, 2011) showed that HM in the mouth zones of the rivers are accumulated as insoluble particulate matters and detrital minerals (>90%), i.e. inaccessible (or weakly accessible) for their bioassimilation by living organisms. At the same time, metal species available for biota (labile) usually account for no more than a few percents of their total content. Exceptions are Cu and Mn, the labile species of which may reach 10% and more. Metals that are accessible for biota also include species adsorbed on clay mineral particle (Luoma and Bryan, 1981; Luoma, 1989). However, Zavarzin (2003) indicates that the metal-organic complexes of multivalent metals such as Fe, in terrigenous clays form bridge between negatively-charged surface of a clay mineral and carboxyl group in humic acid, thus protecting organic compounds on the clay surface from chemical and biological oxidation. This conclusion is supported by direct observations. In particular, the general suppression of biogenic processes was noted by (Lisitsyn, 1994) for the second stage of marginal filter, which reflects the avalanche sedimentation zone of clay minerals. Taking into account this fact, the fraction of labile metal species in sedimentary material of river discharge may be considered to be very insignificant.

The river–sea barrier zone is a complex multistage system of barriers, at the boundary of which chemical elements are precipitated with different intensity owing to different processes (Lisitsyn, 1994; Galimov et al., 2006; Gordeev, 2012; *Siberian...,* 2003). In this relation, at least two most important problems must be solved to decipher the tendencies of HM accumulation in the surface sediments within this zone. The first problem is to reveal zones of excess accumulation of HM. The second problem is to determine the mechanism of their accumulation. The solution of the second problem is tightly related to unraveling relations between HM and rock-forming elements (in our case, this is Si, Al, and Fe), which are precipitated with variable intensity on different barriers of the indicated zone. In the framework of this paper, we attempted to compare the HM contents (without separation of their forms) in different facies-genetic types of sedimentary deposits, which reflect the different stages of precipitation of the river discharge material: riverine, terrigenous–estuarine, terrigenous–shallow water–marine, terrigenous–marine (background), and relict ones.

Material presented in the paper (Fig. 1) was collected by M.A. Levitan during the Cruise of R/V "Boris Petrov" in 2000, 2001, and 2003 (stations BP00..., BP01..., BP03...) (Berichte..., 2001, 2002, 2003) and by V.Yu. Rusakov during Cruise of R/V "Akademik Mstistlav Keldysh" in 2015 (stations 51... and 52...). The work is a continuation of previous studies and devoted to the HM distribution in the surface (0–2 cm) layer of bottom sediments of the Kara Sea, as well as their concentrations in the previously distinguished chemotypes of sediments (Rusakov et al., 2015, 2017).

METHODS

Bottom sediments in the study area were collected using *Okean* grab and *BOKS-4* box corer. Wet sediment was dispersed by ultrasound and then subjected to water-mechanical separation using sieve and decantation at the Laboratory of Geochemistry of Sedimentary Rocks of the Vernadsky Institute of Geochemistry and Analytical Chemistry, analyst L.A. Zadorina. The results of grain-size analysis are shown in Table 1. Prior to and after separation, the samples were studied under the binoculars by V.Yu. Rusakov in order to estimate the contents of separate components, as well as for visual control of the quality of water-mechanical analysis.

A part of sediment collected from the sample surface to a depth of 2 cm was taken for chemical analysis. It was preliminarily dried in an oven and manually ground in an agate mortar to a powder. Chemical composition was determined at the Laboratory of Mineral Analysis of the Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences by XRF (Si, Al, Fe, Mn, Co, Ni, Cu, Zn, Pb, analyst T.G. Kuzmina) as well as by induction coupled plasma mass spectrometry (Cd, Sn, Sb, and Bi, analyst E.S. Toropchenova). Analysis results are given in Table 1.

MATERIALS AND DISCUSSION

Grain-size composition. In spite of the wide diversity of the grain-size composition of sediments, two types are predominant in them: silt and pelite–silt sediments dominated by fraction 0.063–0.01 m and silt sand dominated by fraction 0.25–0.125 mm. The former reflect mainly the composition of sedimentary material of estuarine zone and background terrigenous–marine sediments. The latter are riverine, shallow-terrigenous sediments and partially relict sediments, which were subjected to the wave and current influence. Correlation matrix of the chemical composition and grain-size fractions (not shown in paper) revealed strong positive correlations (>0.5) between sand fractions and Sb, Cd, Bi, as well as between silt and Fe (Table 2). This indicates that such HM as Sb, Cd, and Bi in bottom sediments are mainly restricted to the detrital minerals of sand fraction. The strong correlation of Fe with Ni and Cu reflects their coprecipitation with Fe oxyhydroxides. Mn (one of the essential polyvalent metals in the studied sediments) shows no significant positive correlation with the grain-size fractions and the studied HM. This element shows only a weak positive correlation with Ni and Fe, as well as with silt and pelite fractions. The absence of the high HM positive correlation with Mn can be explained by its partial diagenetic reduction from sediments.

Factor analysis. Calculation of factor loads on the chemical composition of the studied samples showed that such metals as V, Co, Ni, Cu, and Zn have high positive correlation with Al, Fe, and Mg within one most significant 1-st factor (Fig. 2). This factor explains 36.2% of chemical variations in bottom sediments and characterizes the composition of Mg–Fe aluminosilicates, i.e., clay minerals negatively correlating with Si. The high positive correlations for the indicated chemical elements within this factor demonstrate a weak differentiation of the mineral composition of sediments, with a high percentage of instable femic and salic minerals, as well as hydromica predominance. This conclusion is confirmed by the wide range of Si (22–32 wt %) and Al (3.2–4.7 wt %) (Table 1), as well as by low alumina–silica module (Al_2O_2/SiO_2 = 0.10–0.19), approaching average values typical of magmatogenic rocks (Ronov and Migdisov, 1965) (Fig. 3). Remained three factors show no any significant correlations of HM with other chemical elements, which suggests the predominance of lithogenic and/or detrital forms of HM in the studied sediments (Fig. 2), which we indicated above.

Facies-genetic types of sediments. Previous chemical studies of the surface layer of bottom sediments (Rusakov et al., 2015, 2017) allowed us to distinguish

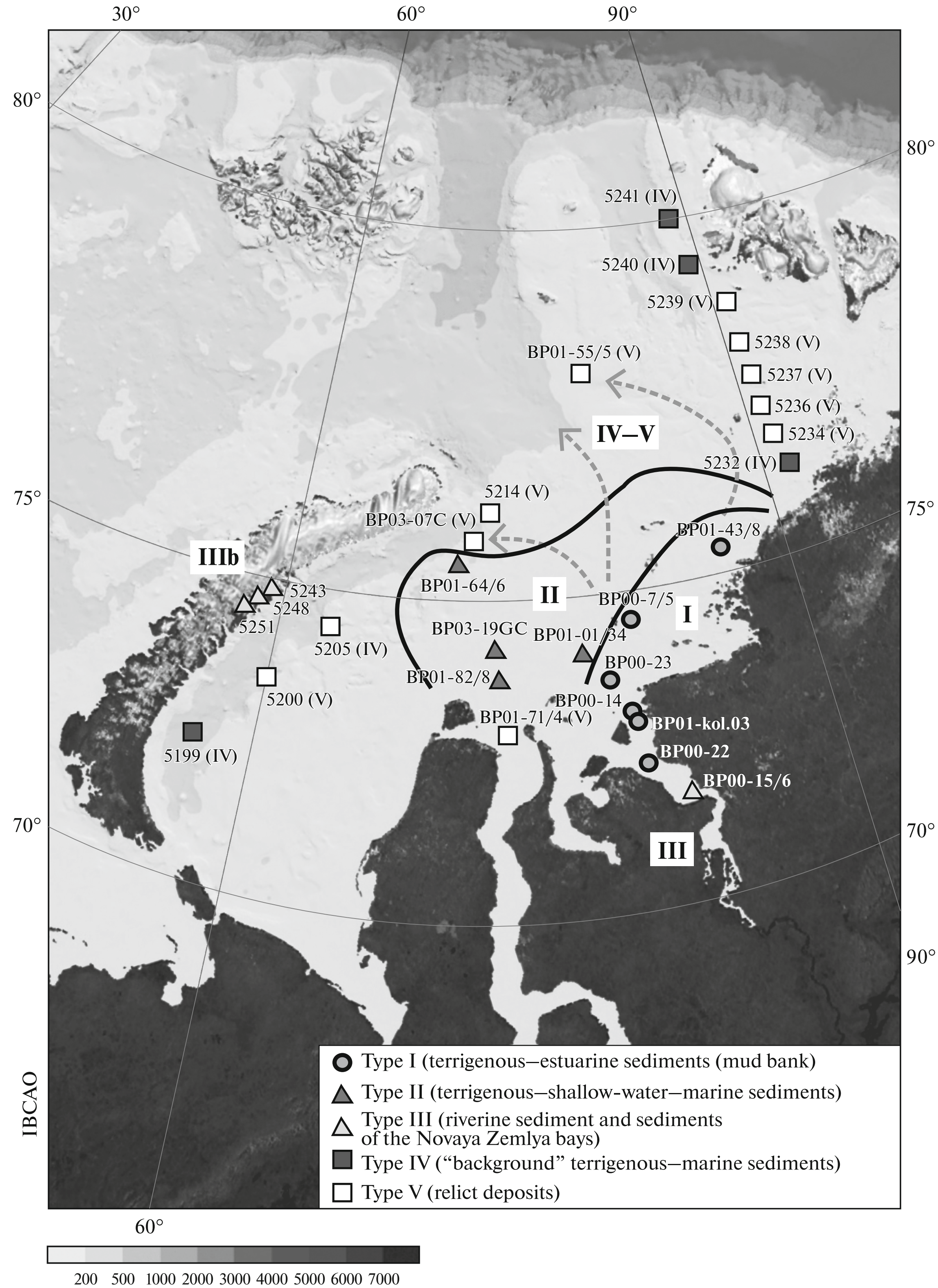

Fig. 1. Map of the studied area and position of bottom sediment sampling stations classified according to the facies-genetic type. IIIb—sediments of the Novaya Zemlya bays.

Table 1. Stations, sea depths, grain-size fractions, and content of chemical elements classified by genetic types (Type) in the surface layer of the Kara Sea bottom sediments. Si, Al, Fe, and Mn (wt %); Co, Ni, Cu, Zn, Pb, Cd, Sn, Sb, and Bi (ppm)

Station no.	Depth, m	Gravel	Sand	Silt	Pelite	Type	Si	Al	Fe	Mn	Co	Ni	Cu	Zn	Pb	Cd	Sn	Sb	Bi
BP00-7/5	38	0	0.95	83.77	15.28	I	22.96	3.89	3.42	0.273	27	70	31	85	21	0.2	2.04	1.89	0.29
BP00-14/4	19	0	1.31	73.34	25.35	I	24.34	3.90	3.276	0.072	34	71	42	93	17	0.26	6.52	1.94	0.31
BP00-43/8	48	0.27	1.77	69.57	28.39	I	23.19	4.08	3.29	0.529	20	73	35	90	21	0.13	2.34	2	0.31
BP00-22	15	0.07	10.64	63.01	26.28	I	25.29	3.93	2.902	0.093	30	70	40	94	19	0.18	2.19	1.95	0.3
BP00-23	33	0	49.17	37.57	13.26	I	25.30	3.93	2.93	0.072	27	67	36	85	20	0.25	2.38	2.17	0.36
BP00-23/7	33	0.07	11.57	61.66	26.7	I	26.03	3.83	2.898	0.066	22	65	35	84	13	0.15	2.95	1.71	0.32
BP01-kol.03	17	0	0.9	72.22	26.88	I	24.26	3.89	3.147	0.083	31	67	45	91	19	0.08	2.28	1.79	0.24
Mean	–	–	–	–	–	**I**	**24.48**	**3.92**	**3.123**	**0.17**	**27**	**69**	**38**	**89**	**19**	**0.18**	**2.96**	**1.92**	**0.3**
BP01-01/34	91	0	4.84	68.34	26.83	II	26.53	4.38	2.321	0.058	26	51	30	84	26	0.15	19.5	2.18	0.3
BP01-64/6	99	0	4.74	65.97	29.29	II	26.61	3.93	2.545	0.059	17	52	23	84	23	0.18	4.77	2.01	0.32
BP01-82/8	29	0	4.72	68.36	26.92	II	26.32	3.61	2.916	0.083	20	52	21	143	19	0.12	2.97	1.87	0.31
BP03-19GC	34	2.06	5.95	65.41	26.58	II	26.23	3.65	2.783	0.076	20	48	23	80	20	0.13	3.07	2.14	0.31
Mean	–	–	–	–	–	**II**	**26.42**	**3.89**	**2.641**	**0.069**	**21**	**51**	**24**	**98**	**22**	**0.15**	**7.58**	**2.05**	**0.31**
BP00-15/6	6	0	31.74	42.09	26.17	III	27.44	3.66	2.699	0.089	27	60	27	79	16	0.17	2.67	2	0.31
5248	200	0.74	36.75	52.6	9.91	III	25.53	4.71	2.657	0.131	27	85	37	117	5	0.22	2.78	1.29	0.27
5251	130	0	0.34	86.45	13.21	III	25.74	4.51	2.573	0.38	28	86	34	126	10	0.29	2.95	1.73	0.24
5243	120	0.4	1.53	84.71	13.36	III	24.52	4.69	2.811	1.047	25	75	36	110	8	n.d.	n.d.	n.d.	n.d.
Mean	–	–	–	–	–	**III**	**25.81**	**4.39**	**2.685**	**0.412**	**27**	**77**	**34**	**108**	**10**	**0.23**	**2.8**	**1.67**	**0.27**
5199	330	0.13	5.04	72.81	22.02	IV	23.76	3.41	2.286	2.58	23	69	23	101	14	0.27	2.1	2.55	0.21
5205	190	0	14.21	67.89	17.9	IV	22.18	3.99	3.584	1.309	26	79	25	99	9	0.3	1.78	2.87	0.26
5232	51	0	15.94	59.73	24.33	IV	25.41	4.01	2.8	0.827	27	62	25	80	4	0.12	1.6	1.39	0.16
5240	290	0	6.22	74.31	19.47	IV	21.96	4.36	3.437	1.078	31	90	27	95	7	0.15	2.22	2.54	0.26
5241	330	0	3.51	75.07	21.42	IV	24.47	4.29	2.926	0.687	29	77	16	94	9	0.15	2.4	1.21	0.27
Mean	–	–	–	–	–	**IV**	**23.56**	**4.01**	**3.007**	**1.296**	**27**	**75**	**23**	**94**	**9**	**0.2**	**2.02**	**2.11**	**0.23**
5200	205	0	57.74	31.08	11.18	V	28.29	3.40	2.048	1.217	26	54	7	64	8	0.15	1.31	1.45	0.14
BP03-07C	108	0	27.46	52.05	20.49	V	29.82	3.55	1.946	0.059	19	41	13	66	16	0.16	3.25	2.12	0.3
BP01-55/5	83	0.38	23.65	50.48	25.49	V	29.15	3.47	1.932	0.06	21	41	7	60	26	0.13	2.8	2.28	0.31
BP01-71/4	23	0	42.95	42.34	14.71	V	31.58	3.13	1.81	0.061	20	38	9	74	16	<DL	65.5	2.24	0.32
5214	159	0.41	48.07	39.78	11.74	V	22.18	3.82	2.118	0.132	20	39	8	70	9	0.06	1.87	0.7	0.16
5234	47	46.75	29.06	17.69	6.5	V	28.97	3.37	2.09	0.536	22	45	14	56	10	0.1	1.19	1.02	0.13
5236	90	0	55.5	33.1	11.4	V	30.15	3.26	2.037	0.218	19	37	11	56	7	0.06	1.18	0.88	0.12
5237	128	2.86	35.72	43.93	17.49	V	28.02	3.59	2.51	0.326	23	50	14	68	14	0.07	1.6	1.17	0.16
5238	108	0	67.8	23.97	8.23	V	31.68	3.17	1.701	0.331	20	38	10	53	15	0.07	1.06	0.97	0.12
5239	242	0	70.41	23.73	5.86	V	30.75	3.27	1.929	0.446	12	61	11	57	17	0.08	1.13	1.12	0.13
Mean	–	–	–	–	–	**V**	**29.06**	**3.40**	**2.012**	**0.339**	**20**	**44**	**10**	**62**	**14**	**0.1**	**8.09**	**1.4**	**0.19**
UCC upper continental crust (Rudnick, Gao. 2003)						–	31.27	4.08	4.1	0.07	15.55	53.14	23.17	62	17.29	0.09	2.96	0.33	0.14

Content of grain-size fractions is given in wt %, n.d. data are absent; <DL below detection limit.

Table 2. Correlation of HM with grain-size composition, as well as with Fe and Mn

Fractions and chemical elements	Correlation			
	positive		negative	
	strong	weak	weak	strong
Gravel	–	–	Co	–
Sand	Sb, Cd, Bi	Pb, Sn	Ni, Cu, Mn	–
Silt	Fe	Ni, Cu, Zn, Mn	–	–
Pelite	–	Mn	–	–
Fe	Ni, Cu	Co, Zn, Mn	–	Sb
Mn	–	Ni, Fe	–	–

Dash denotes correlation is not revealed.

five chemotypes (Fig. 4). According to classification proposed by Frolov (1992), the studied sediments can be ascribed to two large genetic groups: relict detrital and newly formed supergene groups. The latter consist of a mixture of clay and detrital minerals (terrisupergene minerals). More detailed facies analysis of the modern sediments of the West Arctic shelf performed by Gurevich (2002) revealed eight types of bottom sediments, some of which spatially coincide with distinguished chemotypes. In particular, the deltaic and estuary sediments coincide with chemotypes III and I, the sediments of shallow-water plains, with chemotype II, while basins and trench sediments correspond to chemotype IV. Sediments of shallow- and deep-water plains include chemotypes IV and V. The latter can be explained by the lithological and geochemical heterogeneity of sediments of marine plains, which contains both discharge material and "ancient" relict sediments.

Thus, the distinguished chemotypes practically completely coincide with facies–genetic types of the modern deposits of the Kara Sea, but previously distinguished types are additionally supplemented by relict sediments, which sharply differ in chemical composition from Holocene sediments of the river discharge. On this basis, five previously distinguished chemotypes will be termed as facies-genetic types (further, types). They form subsequent lithological-facies set, which reflects the accumulation of river-borne sedimentary material on different boundaries of the barrier river–sea zone: (1) Poorly differentiated continental–riverine sediments (type III); (2) Terrigenous–estuarine sediments that are accumulated in the avalanche sedimentation zone of the riverine suspended matter (type I); (3) Terrigenous–shallow-water–marine sediments of the transition zone (type II); (4) Terrigenous–marine background sediments (type IV).

The marine–glacial sediments of the Novaya Zemlya bays are distinguished as a separate subtype (IIIb). They reflect the composition of the finest mainly clay minerals, which are supplied by thawed waters of the Novaya Zemlya glaciers in the archipelago bays (stations 5243, 5248, and 5251).

The type V sediments have principally different source of sedimentary material: relict pre-Holocene (possibly, Pleistocene) sediments. In terms of gain-size composition, they are subdivided into two groups. The first group represented by the coarser-grained gravel-sand and sand sediments is exposed on the seafloor and was subjected to erosion by bottom currents and waves. The second group represented by fine silt and pelite–silt sediments was produced by the erosion and subsequent transfer of the fine fractions of relict sediments in the hydrodynamically calm sea areas (Fig. 4). The former (coarser grained) serve as "parental" rocks with respect to the latter group (finer grained). Since the main mechanism of decomposition of "parental" rocks is hydrodynamic (mechanical) influence of waves and currents, the finer fractions transferred from floor erosion area did not lose their geochemical link with "parental" rocks and preserved their affiliation to type V.

Most distinctive features of the mentioned types can be illustrated in the **Si–Al/Si** diagram (Fig. 3). Linear distribution of values in the diagram for most stations indicates prevailing mechanical (grain-size) differentiation of sedimentary material at different stages of its sorting (Ronov and Migdisov, 1965). In particular, the coarser grained gravel–sand and sand sediments of type V fall in the left lower part of the linear trend. They are characterized by the high Si content > 27 wt %, mainly in form of quartz, and low alumina–silica module <0.13. The exception is station 5214 located on the northern slope of the Eastern Novaya Zemlya Basin, the sediments of which have higher Al content. This trend is continued into type I sediments, which reflect the zone of avalanche sedimentation of riverine suspended matter. As compared to type V, they have the lower Si contents <26 wt % and higher aluminum–silica module >0.14, i.e., are more clayey. Marine–glacial deposits of bays as well as sediments of transition and marine zones maximally deviate from liner trend. Such deviation from the linear trend indi-

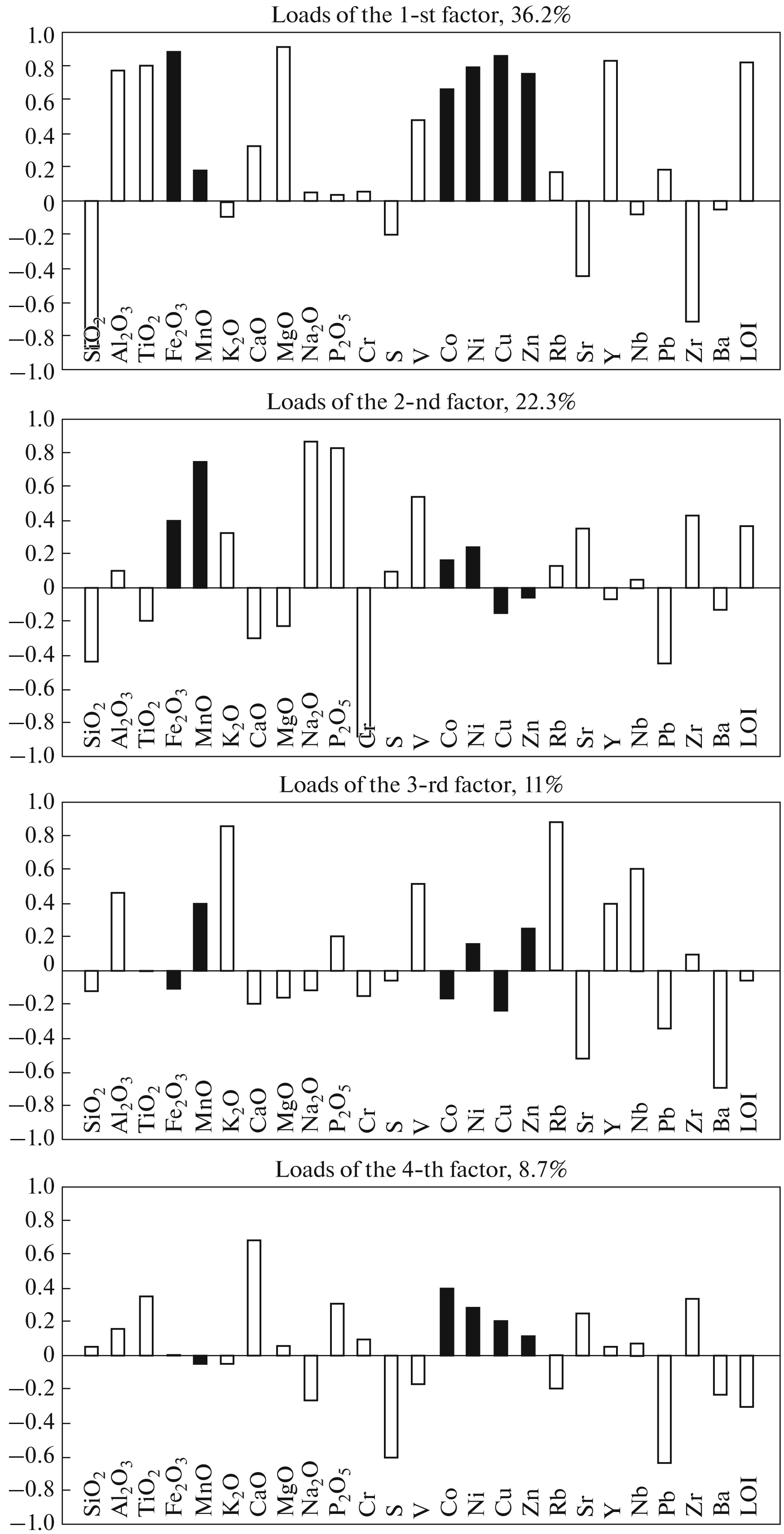

Fig. 2. Loads of chemical elements on the factors controlling chemical variations of the surface layer of bottom sediments of the Kara Sea. HM, as well as Fe and Mn are shown by black.

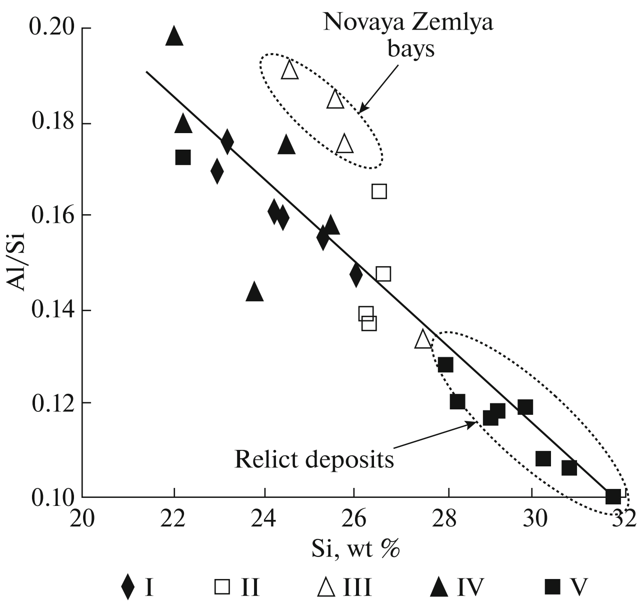

Fig. 3. Ranges of the differentiation of the surface layer of bottom sediments of the Kara Sea by separate types: (I) terrigenous–estuarine sediments (mud bank); (II) terrigenous–shallow water marine sediments, (III) riverine sediments and sediments of the Novaya Zemlya bays; (IV) "background" terrigenous–marine sediments, (V) relict sediments.

cates that their chemical composition was controlled by not only grain-size differentiation, but also by other factors. The latter include additional influx of amorphous silica from the photic layer and alumina with thawed waters from the Novaya Zemlya continental glaciers.

HM. In order to unravel the main tendencies of HM distribution in bottom sediments of estuary and open sea, it is necessary to analyze their distribution at different stages of precipitation of the river discharge material according to the distinguished types of sediments. In particular, the total HM distribution along the above mentioned facies-genetic series shows insignificant and gradual decrease of their contents from type III poorly differentiated continental deposits to the transition zone of type II sediments (Fig. 5, upper plot). The seaward part shows the insignificant increase of their total contents. The lowest total HM contents reflect the composition of the older relict clastic sediments of type V. Thus, the total HM distribution indicates that they are in general weakly sensitive to the precipitation of material on the different barriers of the river–sea zone, evenly accumulating in sediments of former four types.

Exception is **Cu**, the most significant contents of which occur in type I sediments (Fig. 5). Thus, the main part of copper is mainly precipitated in the estuary in the zone of avalanche sedimentation of riverine suspended matter. This is also confirmed by a tight correlation of Cu with Fe (Table 2), which indicates a coprecipitation of copper and iron in the estuarine zone and adjacent sea part (type I). The main precipitation mechanism is supposedly the flocculation of Fe hydroxides in electrolyte (sea water), which is

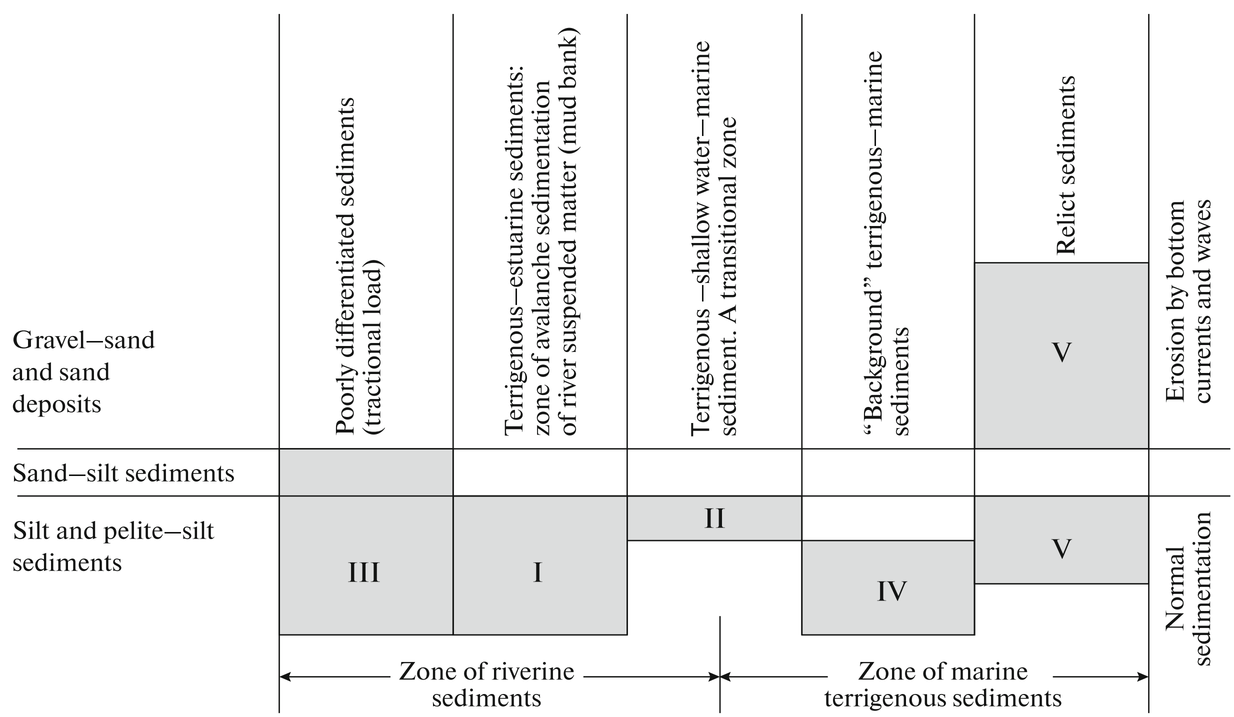

Fig. 4. Relations between the grain-size composition and types (I–V) of the surface layer of bottom sediments of the Kara Sea. See text for explanation.

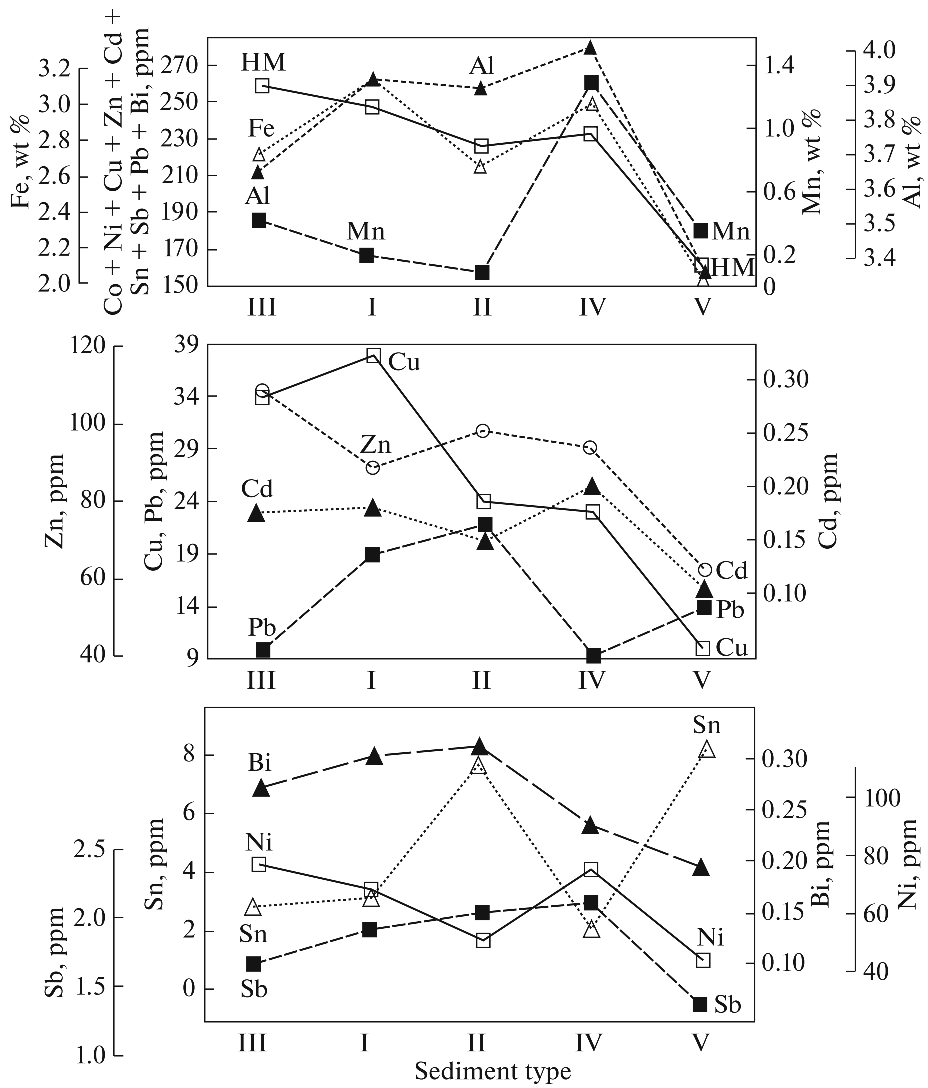

Fig. 5. Contents of HM and major elements in different types of the surface layer of the Kara Sea bottom sediments.

accompanied by sorption of dissolved Cu. As a result, most part of labile Cu precipitates in the estuarine zone at the fresh–salt water mixing boundary. It should be noted that Fe hydroxides are the most powerful natural sorbent in marine environment. The lowest Cu contents were found in the transition zone and background marine sediments of the open sea. In particular, the average Cu content in type-I sediments is 38 ppm, which is almost two times higher than those of the background marine sediments of the Kara Sea and over three times higher than those of the type V relict deposits (Table 1). The higher Cu contents were also found in sediments of the Novaya Zemlya bays (subtype IIIb). Its source in the latter is likely the decomposition products of the archipelago sedimentary rocks.

Beyond the zone of avalanche sedimentation of the river suspended matter (type I terrigenous–estuarine sediments), the Fe, Al, and Mn contents simultaneously decrease simultaneously with total HM, thus reflecting the composition of type-II terrigenous–shallow-water–marine sediments (Fig. 5). Such simultaneous decrease of the afore-mentioned elements in the transition zone reflects a hydrodynamic effect of bottom currents and waves, which remove finer and light fractions from terrigenous sediments (Fig. 4), thus leading to their enrichment in heavy subfraction. This is the area of accumulation of **Pb and Sn**, which are incorporated in ore minerals of sand fraction. The high Pb contents are also typical of zones of avalanche sedimentation of riverine suspended matter, while its lowest contents were found in the background marine sediments (Table 1). Thus, the main part of Pb is precipitated in the estuarine zone (type I) and in the adjacent shallow-water sea zone (type II). The maximum Pb contents were reached in the transitional, most hydrodynamically active zone with hydraulic differentiation of sedimentary material, which facili-

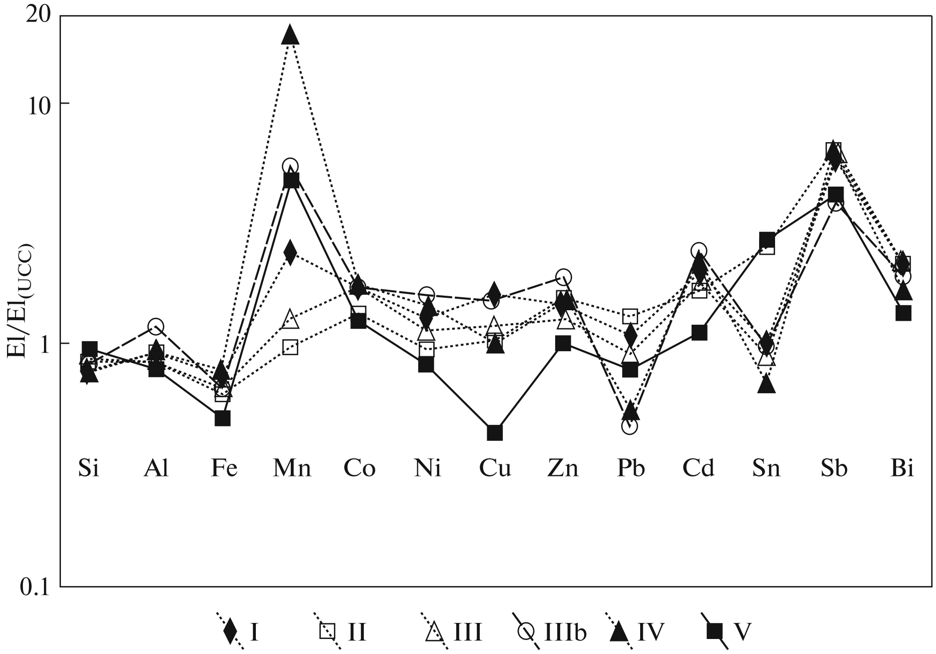

Fig. 6. Upper crust-normalized element abundance in the surface layer for the separate types of the Kara Sea bottom sediments. IIIb are sediments of the Novaya Zemlya bays Other symbols are shown in Fig. 3.

tates the accumulation of heavy ore minerals. Sn is also accumulated in heavy fraction, which is confirmed by its high content in coarse-grained sediments of types II (7.58 ppm) and V (8.09 ppm). This metal was likely incorporated in cassiterite, the placers of which frequently occur on the shallow-water shelves and inshore zones, where its concentrations can reach economic values.

Sb, Cd, and Bi are also tightly related to sand fraction (Table 2). However, they show no significant increase in the transition zone of type II sediments, because they are involved in the minerals of lighter fraction, and as a result, more hydrodynamically mobile fraction. The Cd behavior mimics the Fe and Al behavior. Its highest contents were found in the background marine sediments (Cd = 0.2 ppm) and in the Novaya Zemlya bays (Cd = 0.22–0.29 ppm), while the minimum values occur in the type V relict deposits (Cd = 0.1 ppm) (Table 1). Such Cd behavior can be explained by its dual nature, i.e., its simultaneous occurrence both in sand material consisting of Fe-rich aluminosilicate minerals and in the finer clay fractions and Fe hydroxides.

HM incorporated in the finer silt fractions such as **Ni and Zn**, as well as Mn oxyhydroxides, are mainly accumulated beyond the transition zone, in the open sea, in the type IV background terrigenous–marine sediments (75 ppm, 94 ppm, and 1.3 wt %, respectively). In this sediment, the sum of HM, Fe, Al, and Mn shows simultaneous growth, which is less significant for HM and most significant for Mn. As mentioned above, the background marine sediments differ in the highest Mn contents, which precipitates in suspended matter owing to the influence of biogenic processes (Lukashin et al., 2000), flocculation in Fe-organic colloids (Gordeev, 2012), as well as reduction in bottoms sediments (Rozanov, 2015). The highest Ni and Zn contents also occur in sediments of the Novaya Zemlya bays, where they reach maximum of known values (Ni = 75–85 ppm, Zn = 110–126 ppm).

Type V relict sediments have the lowest total HM. Exception is Sn, which is concentrated in the coarser and heavy fractions in the bottom erosion areas of ancient sedimentary rocks of the Kara Sea, reaching the maximum content of 8.1 ppm.

Figure 6 displays abundances of chemical elements normalized to the average upper continental crust (UCC) (**El./El.$_{\mathbf{(ucc)}}$**). The average UCC composition was calculated as the average value from several references listed in (Rudnick and Gao, 2003), and shown in Table 1. The values above and below 1 denote how much the content of definite element is higher or lower than its average content in the upper continental crust.

Sediments of the avalanche sedimentation zone located mainly in the estuary and near the exit from it (type I) are enriched relative to UCC in Mn, Co, Ni, Cu, Zn, Cd, Sb, and Bi, which indicates their excess accumulation in the terrigenous–estuary deposits. The Pb and Sn contents, which are involved in "heavy" ore minerals, practically coincide with their average content in the UCC. The content of rock-forming elements (Si and Al) indicates that sediments of the "mud bank" in terms of its chemical composition reflect the first stage of geochemical differentiation of continental metamorphic and volcanic rocks, which is expressed in the separation of silica and aluminum. The alumina–silica module in type I sediments is higher than those typical of continental sedimentary rocks. The Al_2O_3/SiO_2 ratio is 0.15–0.17 in type I sediments, while these values in the continental sedimentary rocks are as low as 0.08 (glacial and arid) and 0.09 (humid) (Ronov and Migdisov, 1965). This stage was marked by the accumulation of HM restricted to the clastic and clay minerals. This conclusion is also confirmed by other researchers. In particular, Demina et al. (2006) notes that HM in the bottom sediments of the Ob and Yenisei estuary mainly occur in the geochemically inert (lithogenic or clastic) form.

Type II sediments, which reflect the transitional (from river to marine) facies sedimentation conditions, are characterized by the highest Pb and Sn contents, which are incorporated in sand-fraction ore minerals. As mentioned above, these sediments were formed through mechanical differentiation, which leads to their enrichment in "heavy" subfractions and removal of the "lighter" and fine mineral particles. The aluminum–silica module in this zone decreases, reaching values close to those of continental deposits (~0.14).

Type IV background terrigenous–marine sediments reflect deep-water facies sedimentation conditions of the high-latitude shelf seas. Unlike the previous terrigenous–estuarine and terrigenous shallow-water–marine sediments, the main role in the terrigenous–marine deposits belong to the finer sedimentary material, which passed through the main barrier zone of the avalanche sedimentation of river suspended matter and was transferred in the deepest and hydrodynamically calm shelf areas. A distinctive feature of the latters, in addition to the finer grained size composition (pelite–silt deposits), is the extremely high Mn contents (18.5! times exceeding its contents in the UCC (Fig. 6)), which is accumulated owing to the precipitation of mainly biogenic–marine particulate matters (Lukashin et al., 2000, Gordeev, 2016). These sediments also contain the main part of HM, which are incorporated in the finer and "light" fractions: Ni, Zn, and Cd, as well as Fe. Such sediments demonstrate the highest degree of silica and alumina separation among terrigenous deposits of the high-latitude shelf seas, which is expressed in the maximum value of the alumina–silica module (~0.18, Fig. 3).

The marine–glacial deposits of the Novaya Zemlya bays (subtype IIIb) are sharply different from other sediments of this lithological–facies series. As mentioned above, they reflect the composition of the archipelago sedimentary rocks. The brightest features of glacial deposits of this type are the extremely high contents of Al, as well as some HM, such as Ni, Cu, Zn, and Cd, which is not typical of terrigenous deposits. High values of alumina–silica module (~0.18, Fig. 3) indicate a significant role of fine clay material, which accumulates Ni, Zn, and Cd. The Cu contents are comparable with those of sediments of the estuary zone (34–37 ppm, Table 1). As mentioned above, such Cu contents reflect the high accumulation rates of sedimentary material at the first stage of geochemical differentiation of continental material.

In terms of composition, type V relict deposits exposed on the Kara Sea floor are sharply different. Their distinctive feature is the wide grain-size composition from silt-pelite to gravel-sandy sediments (Fig. 4), which is caused by their mechanical erosion and relatively high contents of Mn (comparable with bay sediments), Sn (comparable with shallow–marine terrigenous sediments of transition zone), as well as extremely low contents of Fe and Cu (Fig. 6). The elevated Mn contents may reflect the composition of ancient sedimentary rocks of the archipelago, which were accumulated under marine conditions in the Devonian and/or Early Carboniferous (Khain, 2001).

CONCLUSIONS

The HM distribution in the surface layer of bottom sediments of the Kara Sea is related to zoning of the precipitation of continental sedimentary matter on the geochemical barriers of the river–sea zone. The first precipitation stage is caused by the sharp decrease of the stream rate in the estuary region, as well as sorption–adsorption processes proceeding in a fresh river–saline sea water mixing zone. This area accumulates terrigenous–estuary deposits, which are characterized by the elevated alumina to silica ratio and high concentrations of HM, which are closely related to the fine clay fractions of sediments: Co, Ni, Cu, Zn, Cd, Sb, and Bi. Transition shallow-marine zone, where bottom sediments are subjected to the elevated hydrodynamic influence of waves and marine currents, accumulate particles of "heavy" ore minerals, including Pb and Sn. In this zone, their concentrations reach values higher than the average contents of analogous metals in the upper continental crust. The background terrigenous–marine sediments accumulate the finest particles of Zn and Cd-bearing clay minerals as well as Ni-bearing Fe oxyhydroxides. This area is also marked by the avalanche sedimentation of Mn supplied by river runoff. In general, the afore-mentioned sediment types characterize the composition of sediments of the Ob and Yenisei fans. As compared to the average UCC composition, these rocks are enriched in HM and Mn.

The marine–glacial sediments of the Novaya Zemlya bays have the extremely high HM contents. They are characterized by the highest contents of all above mentioned metals, except for Pb and Sb, which result from the avalanche accumulation of mainly fine fractions of aluminosilicate minerals, with Al content higher than that of UCC.

Relict pre-Holocene deposits exposed on the Kara Sea floor demonstrate the widest grain-size composition and the highest Si, Mn, and Sn contents, as well as the lowest Fe, Co, Ni, Cu, Zn, Cd, and Bi contents. Note that the Ni, Cu, and Pb contents are lower than in sedimentary rocks of the continental crust.

REFERENCES

Berichte zur Polar- und Meeresforschung (Reports on Polar and Marine Research) (2001–2003).

L. L. Demina, "Estimation of the role of global biological filters in the geochemical migration of trace elements in the ocean: the marginal filter of the ocean," Dokl. Earth Sci. **439** (1), 981–985 (2011).

L. L. Demina, V. V. Gordeev, and L. S. Fomina, "Species of Fe, Mn, Zn, and Cu in river water and suspended particulate matter and their change on the river–sea water mixing zone: evidence from rivers of the Black, Azov, and Caspian sea basins," Geochem. Int., No. 8, 1211–1228 (1978).

L. L. Demina, M. A. Levitan, and N. V. Politova, "Speciation of some heavy metals in bottom sediments of the Ob and Yenisei estuarine zones," Geochem. Int. **44** (2), 182–195 (2006).

L. L. Demina, V. V. Gordeev, S. V. Galkin, M. D. Kravchishina, and S. P. Aleksankina, "The biogeochemistry of some heavy metals and metalloids in the Ob River Estuary–Kara Sea section," Oceanology **50** (5), 729–742 (2010).

L. L. Demina, S. V. Galkin, and D. F. Bud'ko, "Biosorption of heavy metals of the bottom fauna of the Kara Sea," in *Geology of Seas and Oceans. Volume 4. Proceedings of 21th International Conference (School) on Marine Geology, Moscow, Russia, 2015* (GEOS, Moscow, 2015), pp. 23–26.

E. M. Emelianov, *Barrier Zones in Ocean: Sedimentation and Ore Formation, Geoecology* (Yantar. Skaz., Kaliningrad, 1998) [in Russian].

V. T. Frolov, *Lithology. A Textbook* (Mosk. Gos. Univ., Moscow, 1992) [in Russian].

E. M. Galimov, L. A. Kodina, O. V. Stepanets, and G. S. Korobeinik, "Biogeochemistry of the Russian Arctic. Kara Sea: research results under the SIRRO Project, 1995–2003," Geochem. Int. **44** (11), 1053–1104 (2006).

V. V. Gordeev, *Geochemistry of the River–Sea System* (I.P Matushkina, Moscow, 2012) [in Russian].

V. I. Gurevich, *Modern Sedimentogenesis and Geoecology of the Western Arctic Shelf of Eurasia* (Nauch. Mir, Moscow, 2002) [in Russian].

G. V. Il'in, "Distribution of Pollutants in Russian Arctic Shelf Seas," in *Geology and Geoecology of the Eurasian Continental Margins*, (GEOS, Moscow, 2009), Vol. 1, pp. 124–163.

V. E. Khain, *Tectonics of Continents and Oceans* (Nauch. Mir, Moscow, 2001) [in Russian].

A. P. Lisitsyn, "Marginal filer of oceans," Okeanologiya **34** (5), 735–747 (1994).

V. N. Lukashin, VS. V. Lyutsarev, A. D. Krasnyuk, V. P. Shevchenko, and V. Yu. Rusakov, "Suspended matter in estuaries of the Ob' and Yenisei rivers: data from the 28th Cruise of R/V *Akademik Boris Petrov,"* Geochem. Int. **38** (12), 1221–1236 (2000).

S. N. Luoma, "Can we determine the biological availability of sediment-bound trace elements?" Hydrobiologia **176**, 379–396 (1989).

S. N. Luoma and G. W. Bryan, "A statistical assessment of the forms of trace metals in oxidized estuarine sediments employing chemical extractions," Sci. Total Environ. **17**, 165–196 (1981).

A. B. Ronov, and A. A. Migdisov, "Main geochemical features of hydrolyzate elements in weathering and sedimentation," Geochem. Int., No. 2, 131–157 (1965).

A. G. Rozanov, "Redox system of the bottom sediments of the western Kara Sea," Geochem. Int. **53** (11), 987–1001 (2015).

R. L. Rudnick and S. Gao, "Composition of the continental crust," *Treatise on Geochemistry* Ed. by R. L. Rudnick (Elsevier, 2003), **Vol. 3**, pp. 1–64.

"Siberian river run-off in the Kara Sea: characterisation, quantification, variability and environmental significance," *Proceedings in Marine Science 6,* Ed. by R. Stein, K. Fahl, D. K. Fuetterer, E. M. Galimov, and O. V. Stepanets (Elsevier, 2003), **Vol. 6**, p. 204.

V. Yu. Rusakov, M. A. Levitan, T. G. Kuzhmina, E. S. Toropchenova, and A. V. Zhylkina, "Typification of surface layer of bottom sediments of the Kara Sea on the basis of cluster analysis," *Geology of Seas and Oceans: Proceedings of 21rst International Conference (School) on Marine Geology, Moscow, Russia, 2015* (GEOS, Moscow, 2015), pp. 305–309 [in Russian].

V. Yu. Rusakov, T. G. Kuzhmina, M. A. Levitan, E. S. Toropchenova, and A. V. Zhylkina, "Lithological and geochemical typification of surface bottom sediments in the Kara Sea," Oceanology **57** (1), 192–203 (2017).

G. A. Zavarzin, *Lecture on Natural Historical Microbiology,* Ed. by N. N. Kolotilova, (Inst. Microbiol.–Nauka, Moscow, 2003) [in Russian].

Translated by M. Bogina