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Genesis of Organomineral Deposits in Lakes of the Central Part of the Baraba Lowland (South of West Siberia)[1]

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Abstract—A quantitative assessment of the fractionation of elements during sedimentation is made based on long-term comprehensive studies with the participation of geochemists, hydrobiologists, soil scientists, and chemists. Analytical studies of the chemical composition of water, soil, bottom sediments, and biota were carried out at the Center for Collective Use of Scientific Equipment for Multielement and Isotope Studies and at the Institute of Catalysis, Novosibirsk. Based on a mineralogical and geochemical approach, we chose lakes with different types of biogenetic formation and different classes of organomineral sediments and performed detailed studies of the relationship between the organic and mineral parts of the sediments. It has been established that the organomineral sediments of different classes and biogenetic types of formation differ not only in the contents of major elements (Si, Ca, C, and O) but also in the group composition of organic matter. The direct effect of the transformation of organic matter on the mineral composition of bottom sediments has been revealed. The contents of other elements vary in a narrow range of values. At the same time, the difference in the contents of elements between organomineral sediments of different types and classes is comparable with their difference within a class. The leading role in the formation of the geochemical and mineral compositions of the organomineral sediments of small lakes belongs to intricate biological, biochemical, and physicochemical processes depending mainly on azonal factors and occurring under prolonged freezing-up (anaerobic conditions).

Keywords: small lakes, Baraba Lowland, organomineral sediments

INTRODUCTION

The quantitative characterization of the chemical and mineral composition of organomineral bottom sediment matter remains one of the fundamental problems of sedimentology geochemistry. Our approach for solving this problem is factual material accumulation, new data and development of special methods.

Currently, active sapropel formation occurs in small lakes against the background of terrigenous ablation and aeolian processes. The main processes of sapropel formation include synthesis of organic and mineral material and its transformation. For many years, organic matter of sedimentary rocks and modern bottom sediments has been divided into two main facial-genetic types: sapropelic and humus, meaning, respectively, the organic matter of inferior and higher plants according to the classification of organic matter facial-genetic types, suggested by G. Potonie, N.B. Vassoevich, V.A. Uspensky, and O.A. Radchenko. It became obvious that sometimes organic matter of inferior plants corresponds by many components to the organic matter composition of higher plants and vice versa due to research methods improvement. In modern geochemistry of organic matter, it has been established that sapropelic organic matter has a complex composition, and it is the material-petrographic composition of organic matter (i.e. the ratio of three biocenotic groups of initial material: phytoplankton, phytobenthos, and zoological component) that is the most infor-

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mative in the genetic sense. Eventually another interpretation of sapropel definition appeared by studying sapropel deposits as a nonmetallic mineral resource. According to it, sapropels are formed under anaerobic conditions as a result of physicochemical and biological transformations of plant and animal residues with active participation of mineral and organic components, which interact actively with each other (Kemp et al., 1999; Helmond et al., 2015). This definition implies that the composition of bottom sediments organic matter includes both the decay products of higher aquatic vegetation (macrophytes) and, directly, buried macrophyte residues. Therefore, in this work, small lakes bottom sediments of the Baraba Lowland will be classified as organic-mineral silts, since they have mainly a mixed composition of organic matter. However, there are the sapropel deposits in all studied lakes according to the modern definition of sapropel as a nonmetallic mineral resource.

There are many classifications and typological characteristics of organic deposits. The following scientific monographs and papers are of a particular interest among numerous recent publications on the formation conditions, location tendencies and chemical properties of organic-mineral deposits: (Lopotko and Evdokimova, 1986; Perminova, 2000; Savchenko, 2004; Shtin, 2005; Kholodov, 2006; Subetto, 2009; Krivonos, 2012; Kurzo et al., 2012; etc.). We should note that they give a comprehensive idea of the current state of studying these sediments. According to these researchers, the main suppliers of organic matter into sediments are bacteria, phytoplankton, zooplankton, and higher plants, both aquatic and near-water ones. The composition and structure of aquatic biocenoses differ from lake to lake significantly, as well as the mineral and geochemical composition of bottom sediments and facial conditions of their burial. These and many other factors predetermine the type and class of small lakes organic-mineral deposits in general, and Baraba Lowland lakes in particular. The organic and mineral matter elemental composition of bottom sediments reflects the genesis conditions. For example, the main components of plants are carbohydrates and lignin. Proteins predominate in zooplankton. Phytoplankton, zooplankton, bacteria and spores are enriched with lipids and lipoids (Tetel'min and Yazev, 2009). These components are parts of living organisms and differ from each other in elemental composition. Only proteins contain nitrogen and sulfur, carbohydrates contain much more oxygen than other components of living matter, and lipids and lipoids are most enriched with carbon and hydrogen (Romankevich et al., 2009).

The aim of this work is to quantify the main characteristics of the studied lakes based on fractionation of elements in the process of sapropel formation depending on hydrochemical conditions, the level of biological productivity and species composition of the dominant species-producers of organic matter, mineralogical and geochemical composition of allochthonous and autochthonous substances of organic and mineral parts of bottom sediments.

OBJECTS AND METHODS OF RESEARCH

Thirty-five small continental lakes located in the central part of the Baraba Lowland were the objects under study. This area belongs to the Ob–Irtysh interfluve. The Baraba Lowland passes into the Vasyugan Plain in the north, turns into the Kulunda Plain in the south, borders with the southwestern part of the Tobol–Ishim Lowland in the west, and is contiguous with the Priob Plain in the east. There are more than 2500 lakes within the Baraba Lowland with a total area of 4900 km^2. There are mostly drainless lakes, and small reservoirs of up to 2.5 km^2 in size occupy the dominant position (97.5%). The peculiar crest topography is a Baraba Lowland feature: alternation of parallel rises (crests) and depressions, elongated from SW to NE, where numerous lakes are located. Due to this surface arrangement, local redistribution of moisture and easily soluble salts occurs—they are transported from the crests into the intercrest space. The soil-forming rocks are lake-alluvial and subaerial loess-like sediments of predominantly aleuropelite granulometric composition with different degrees of salinity. The climate of this region is sharply continental. The average annual air temperature ranges from –1 to 0 °C with monthly maximum in July (+19–20 °C) and minimum in January (–21… –22 °C). The average annual rainfall is 350–375 mm.

All studied lakes are small and shallow in the water area with a depth of less than 2.5 m (Fig. 1). Water was sampled for subsequent analysis using the standard methods during fieldwork (GOST 31861, 2012). Bottom sediments were sampled according to (GOST R 54519, 2011). The sampling site was chosen far from settlements or at maximum distance from them. If they were located in the coastal zone of the reservoir, sampling was performed at the sites that exclude sediment mixing due to anthropogenic activity. A bottom sediments core was taken by a cylindrical sampler with a vacuum shutter designed by NPO "Typhoon", Russia (diameter of 82 mm, length of 120 cm) from a catamaran boat. The bottom sediment core was tested in layers in increments of 3 or 5 cm, depending on the sediment density, to a depth of 50–250 cm from the surface of sediments. The sediment was weighed immediately after sampling and then dried to an air-dry state in the laboratory. Soils were sampled by a metal ring to the depth of the entire soil cross-section. In total, 42 cross-sections of lacustrine bottom sediments and 19 cross-sections of the soil cover were sampled with the total number of samples 564 and 131, respectively, as well as 56 water samples and 27 samples of the soil-forming rocks. Further studies of the chemical composition of water, soil, and bottom sediment samples were carried out in the Analytical Center for multielemental and isotope research of the SB RAS, Novosibirsk, the Laboratory of Geochemistry of Rare, Noble Elements and Ecogeochemistry of the Institute of Geology and Mineralogy SB RAS and the Institute of Catalysis SB RAS. The detailed description of the methods can be found in the previous papers by (Strakhovenko et al. 2014; Yermolaeva et al., 2016; Taran et al., 2018). The mor-

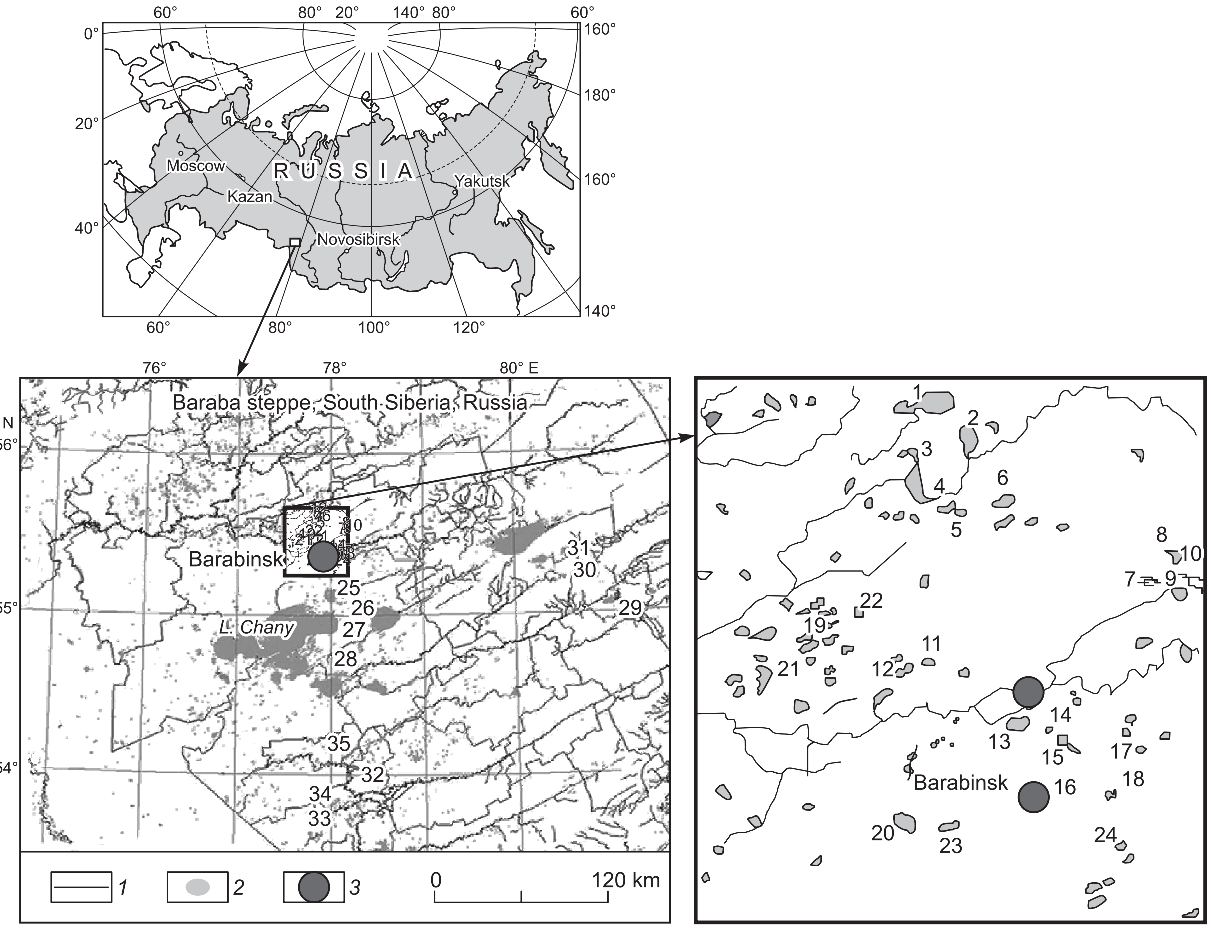

Fig. 1. Schematic map of the studied lakes: 1, Barchin; 2, Kambala; 3, Kazatovo; 4, Kayly; 5, Bergul'; 6, Yargol'; 7, Syetok; 8, Bol'shoi Kurgan; 9, Bil'gen; 10, Sarybulak; 11, Zhiloe-K; 12, Mostovoe; 13, Bol'shie Kayly; 14, Peshchanoe; 15, Chistoe; 16, Bugristoe; 17, Verhnee; 18, Nizhnee; 19, Tsybovo; 20, Goldobinskoe; 21, Mangazerka; 22, Krugloe; 23, Shubinskoe; 24, Novaya Opushka; 25, Dolgoe; 26, Zhiloe; 27, Bo'shaya Chicha; 28, Malaya Chicha; 29, Itkul'; 30, Kankul'; 31, Kachkul'nya; 32, Kuklei; 33, Krotovaya Lyaga; 34, Kusgan; 35, Melkoe. *1*, rivers; *2*, lakes; *3*, explored lakes.

phology and phase composition of bottom sediment samples of various classes were studied using a TESCAN MIRA 3 scanning electron microscope equipped with an OXFORD XMAX 450+ energy spectrometer (SEM).

The organic matter group composition was determined by the method of sequential extraction according to technique adapted from (Yudina et al., 1998; Krivonos, 2012; Strus, 2015). Preliminary dried and crushed sapropel samples were treated with 0.05 N HCl to remove Ca^{2+} ions (CAR) (Taran et al., 2018). Then water-soluble compounds (WS) were extracted from the decalcified air-dry samples by boiling in water for 5 h at a sample/solvent ratio of 1/100. Bitumens (BM) were extracted then by ethanol-benzene mixture (1:1) in Soxhlet (extraction) apparatus. Humic compounds (HA + FA) were extracted by treating with a 0.1 N NaOH solution at 20–25 °C for 24 h and subsequent additional extraction with 0.02 N NaOH at 80 °C. The alkali-free residue was used to extract easily hydrolyzed compounds (HP) (hemicelluloses and nitrogen-bearing compounds) by double treating with 2% HCl at 90°C for 2.5 h. The residue was washed, dried, and treated with 80% H_2SO_4 for 2.5 h to extract hydrolysis-resistant compounds (HR) (cellulose) and then boiled with 5% H_2SO_4 for 5 h at a ratio of 1:100. The residue was a nonhydrolysable substances (NHS).

During the fieldwork, samples of phyto- and zooplankton were taken, macrophyte production was investigated, and experiments on the study of phytoplankton primary production, composition determination and settling lake suspension abundance were carried out (using the method of sedimentation traps). Physical, chemical and hydrological indicators were measured simultaneously: water depth, transparency, color, temperature, concentration of dissolved oxygen in water (by the titrimetric method), and biochemical consumption of oxygen per five days (BOD_5). The methods for selection and procession of hydrobiological samples can also be found in previously published papers (Yermolaeva et al., 2016).

The authors have the largest database on analytical characteristics of organomineral bottom sediments of the Baraba Lowland, obtained during field studies and generalizations of literature data published before 2018. Based on the mineralogical-geochemical and biogenetic approaches, the authors have classified the studied organomineral bottom sediments. According to ash content, bottom sediments are divided into four **types**: *organogenic* type with ash content of up to 30%; *organomineralized* type (30–50% of ash); *mineral-organogenic* type (50–70%) and *mineralized* type (70–85%). Bottom sediments with ash content higher than 85% are classified as *mineral silt* (Shtin, 2005). All types of organomineral bottom sediments, except the organogenic one, are divided into three **classes** according to the Si/Ca ratio: *siliceous* (Si > Ca); *calcium* (Ca > Si), *and mixed* (Si ~ Ca). The elemental and group composition of organomineral bottom sediments autochthonous organic matter is greatly influenced by the predominance of aquatic organisms of different groups in the lakes (phyto-, bacterio- and zooplankton or macrophytes). Organomineral bottom sediments are divided into *plankton*, *macrophyte* and *plankton-macrophyte* sediments based on the dominating organism groups by biomass.

RESULTS

Characteristic of lake waters and watershed areas. Intensive accumulation of soluble salts occurs in the semiarid zones of the Baraba Lowland forest steppe and steppe. Therefore, the lake waters composition corresponds to the entire salinity spectrum from freshwater to brines in these territories. The lakes differ in the degree of water mineralization, pH value, dissolved oxygen content in water, concentration of organic matter (by BOD_5), hydrocarbons, sulfates, nitrates and phosphates. Since the studied lakes are shallow, they do not lack light and nutrients. According to the main ions content, waters of these lakes are mainly hydrocarbonate Mg–Na or hydrocarbonate Na (Fig. 2). Waters of the studied lakes are alkaline, with pH values ranging from 8.1 (Lake Bol'shoe Kazatovo) to 10 (Lake Zhiloe-K). According to the value of total salinity, lake waters are mostly fresh (from 0.2 to 0.6 g/l). Several lakes (Lakes Tsybovo, Chistoe, Zhiloe) with total salinity from 1 to 3 g/l are brackish, and one lake is saline (Lake Peshchanoe) (3.3 g/l). It is necessary to note correlation of the Eh and pH values for lake waters, which is explained by similar hydrogeological conditions. The Eh value of water in all studied lakes is positive and relatively high from 287 mV (Lake Chistoe) to 375 mV (Lake Kazatovo). This indicates the oxidizing conditions. The oxygen content is quite high and varies from 9.7 mg/l in Lake Kambala to 6.5 mg/l in Lake Bugristoe. According to analytical data and publications, element concentrations in studied lake waters are generally lower than their distribution in the hydrosphere (Yaroshevskii, 2004), and they are at the level set for the Northern lakes of Eurasia by trace elements (Reimann and Caritat, 1998). The lake waters are enriched with a group of elements, which are usually found in the form of suspension and/or they are suspended in water (Al, Fe, Mn, Cu, Zn). Carbon and phosphorus contents in these lakes are higher than those in the hydrosphere (Fig. 3).

The soil-forming rocks are represented by lake-alluvial and subaerial loess-like sediments, mainly of silt granulometric composition with varying salinity degrees. Since the soil-forming substrate is represented over the entire territory by loess-like loams with prevailing quartz and feldspars, when high-sodium rocks are weathered, waters acquire sodium composition. The catchment areas have common geo-

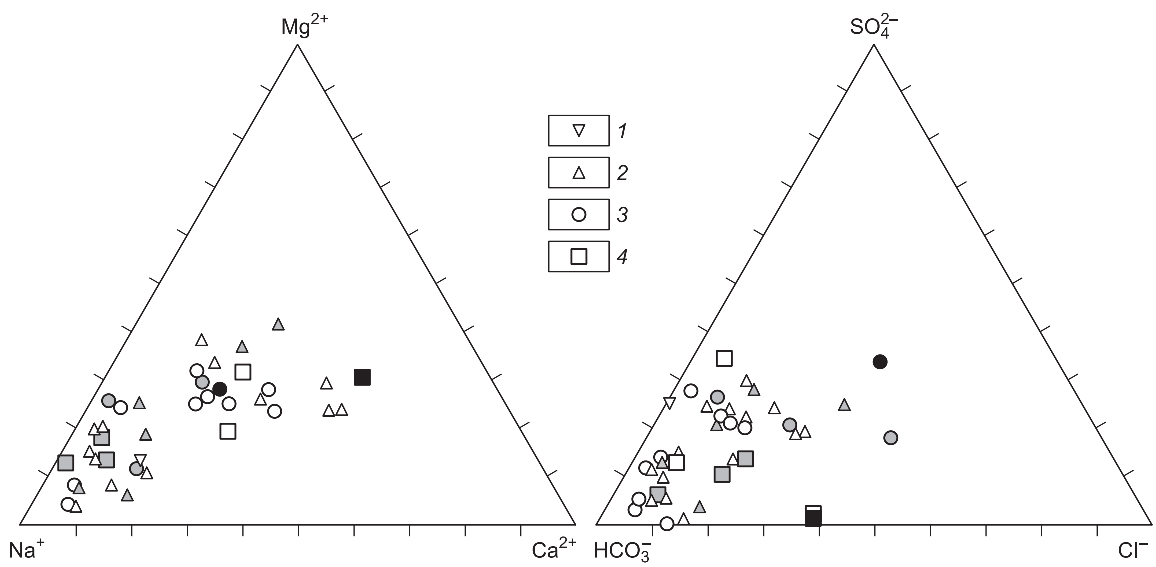

Fig. 2. Diagrams of the cationic and anionic composition of the waters of the studied lakes taking into account their water mineralization in comparison with the type of organomineral deposits formed in the lake. Total mineralization of lake waters: light signs, <1 g/l; gray signs, 1.1–3.0 g/l; black signs, >3 g/l. Organomineral deposits, type: *1*, *organogenic* type with ash content of up to 30%; *2*, *organomineralized* type (30–50% of ash); *3*, *mineral-organogenic* type (50–70%), *4*, *mineralized* one (70–85%).

chemical characteristics of soils, grouped and calculated for each class of sapropel. According to the obtained data, the content of humus compounds in the upper part of the studied soils profile varies widely. Even within the same catchment area, the degree of their humus content varies from the low (0.9%) to the high (8.3%) ones. The minimal amount of humus substances is found in the meadow-swamp humus soil (Lake Zhiloe-K), and the maximum is in gray forest typical soil (Lake Bol'shie Kayly). The studied soils have high water permeability, low water-lifting capacity and moisture capacity. There are carbonates mycelium almost everywhere in the soil profiles (from 22 to 0.6%), and they are especially abundant in the lower soil horizons.

Mineral and geochemical composition of organomineral bottom sediments. All selected samples of bottom sediments are bluish-green or tobacco-brown. They have high viscosity (mainly in the lower horizons) and homogenized massive or walnut-shelled texture. Sometimes there are remains of vegetation. Humidity varies from 98 to 70% in a cross-section.

Eight lakes with different types of biogenetic formation and class of organomineral bottom sediments have been selected for studying the detailed relationship between the organic and mineral parts of sediment: Kachkul'nya, Barchin, Peshchanoe, Bol'shie Kayly, Yargol', Kambala, Maloe Minzelinskoe, and Tsybovo (Table 1).

The lakes with calcium and mixed class of bottom sediments are mesotrophic and mesotrophic-eutrophic water reservoirs with dominating biomass of cyanobacteria (in terms of phytoplankton development). Most likely, calcification of cyanobacteria and submerged hydrophytes is associated with plant photosynthesis, which changes not only the gas regime, but also the carbonate equilibrium towards formation of hardly soluble calcium salts on the plants surface (Lukina and Smirnova, 1988; Bilan and Usov, 2001). Cyanobacteria are not utilized in the food chain, and, withering away together with emophytes, they enrich bottom sediments with calcium. Border and flood-plain types of overgrowth characterize the lakes of this type with predominance of air-aquatic vegetation, represented by *Phragmites australis* (Cav.) Trin ex Steud.) and *Typha angustifolia* L.

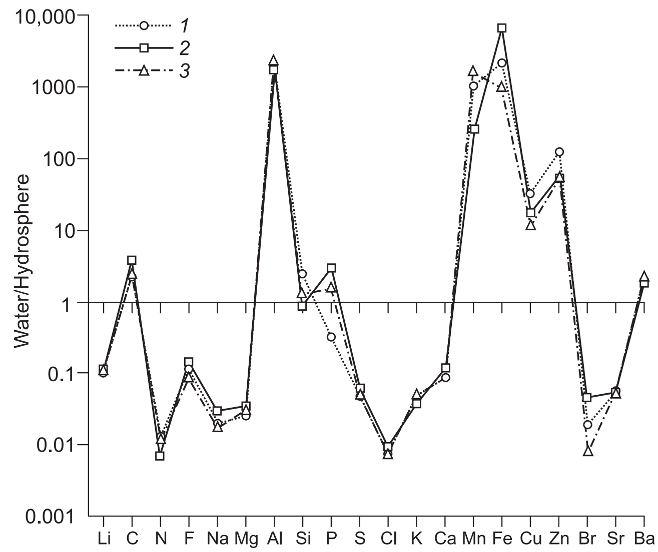

Fig. 3. Multielement average range of element contents in waters of lakes, grouped according to the classes of organomineral sediments, normalized to the content of elements in the hydrosphere (Yaroshevskii, 2004).

communities with overgrowth area from 10 to 85%. Air-aquatic plants make a significant contribution of Ca to bottom sediments. The reed has the greatest ability to accumulate Ca (Schoelynk et al., 2010). According to a number of researchers (Grishantseva et al., 2010; Gashkina et al., 2012), the above-ground organs of reed contain from 4.9 to 15 mg/g dry weight of calcium. The biomass amount generated by reed communities during the period of maximum development in these lakes is on average 1284 g/m^2 in dry weight. Based on this, from 6.3 to 19.2 g/m^2 calcium precipitates into bottom sediments annually from reed decomposition. Zooplankton of lakes with a calcium sediment type is mainly represented by small filtering *Cladocera*. Typically, *Bosmina longirostris* (Müller) and *Chydorus sphaericus* (Müller) dominate. Zooplankton production is 66,200–190,000 mg/m^3 per year.

Diatoms, whose valves contain silicon, compose a significant proportion of phytoplankton in lakes with a siliceous bottom sediments class. The lakes of this class are

Table 1. Geographic coordinates of lakes, classification of organomineral sediments in the lake by type and class

Lake	Coordinates		Ash	Type of organomineral sediments	Class
	N	E			
Barchin	55º41´990	78º09´370	40	Organomineralized plankton-macrophyte	Calcium
Peshchanoe	55º24´326	78º20´868	40	Organomineralized plankton-macrophyte	Calcium
Maloe Minzelinskoe	55º34´390	83º16´070	45	Organomineralized macrophyte	Mixed (Si ~ Ca)
Kachkul'nya	55º14´528	80º34´791	17	Organogenic macrophyte	Siliceous
Kambala	55º40´733	78º11´234	56	Mineral-organogenic plankton-macrophyte	Siliceous
Tsybovo	55º30´673	77º58´808	48	Mineral-organogenic plankton-macrophyte	Siliceous
Bol'shie Kayly	55º25´193	78º17´356	40	Organomineralized plankton-macrophyte	Mixed (Si ~ Ca)
Yargol'	55º36´078	78º21´550	34	Organomineralized macrophyte	Mixed (Si ~ Ca)

divided into two groups by vegetation type: lakes with border and massive-overgrown or floodplain types of vegetation. Air-aquatic vegetation (*Phragmites australis, Typha angustifolia* L.) dominates in the lakes with border overgrowth in the littoral zone with colonization area of up to 15%. Reed can accumulate in its aerial organs of up to 14 mg Si/g of dry weight during the growing season (Grishantseva et al., 2010; Schoelynk et al., 2010). The phytomass amount (in dry weight) formed by reeds reaches on average of 1133 g/m^2 per year in this group of lakes. Therefore, when reed decomposes in the littoral zone of lakes, up to 15.9 g/m^2 of Si can be supplied to bottom sediments per year. The main part of water area is overgrown with hydrotophytes (up to 40–70%) in the group of lakes with massive-overgrown overgrowing type. The communities of *Ceratophyllum demersum* L., *Potamogeton pectinatus* L., *P. perfoliatus* L. and *P. macrocarpus* Dobroch., *Stratiotes aloides* L., *Myriophyllum sibiricum* Kom. dominate here. The phytomass amount formed by air-aquatic vegetation is 934–2419 g/m^2. And phytomass formed by hydrotophytes is from 8 to 752 g/m^2. According to (Schoelynk et al., 2010), hydrotophytes contain Si from 7 to 28 mg/g of dry weight. The maximum content of Si is noted in *Ceratophyllum demersum* L., *Myriophyllum sibiricum* Kom. and *Potamogeton pectinatus* L., *P. perfoliatus* L., *P. macrocarpus* Dobroch. Thus, each year up to 34.9 g/m^2 of Si is supplied to lacustrine bottom sediments at decomposition of reed, *Ceratophyllum demersum* L. supplies up to 6.1 g/m^2, and clasping-leaved pondweed supplies up to 0.2 g/m^2. The basis of the branch crustacean's complex of zooplankton is formed by *Cerodaphnia quadrangula* (Müller), *Daphnia longispina* Müller, *Daphnia pulex* (De Geer). in lakes of siliceous sapropel type. Zooplankton production is up to 950,000 mg/m^3 year.

The element composition (CHNOS) of organic matter and macrocomposition of the mineral part of organomineral bottom sediments are shown in Table 2. The composition of bottom sediments differs in Si and Ca concentrations from lake to lake, which determine the sediment class. The contents of other major elements vary in a narrow range. The differences in these element contents between different classes of the organomineral bottom sediments from are similar to those within the same class.

The atomic absorption method has been used to study the content of trace elements in samples of various organomineral bottom sediments (Table 3). Trace elements concentrations in bottom sediments of different classes are basically comparable. The cases of trace elements depletion (Lakes Kachkul'nya, Barchin) are associated with the effect of sediment impoverishment with organic matter or carbonates.

The studies using X-ray analysis and SEM revealed similar composition of terrigenous fraction of organomineral bottom sediments in all lakes. This fraction is represented by slightly rounded or acute-angled grains and aggregates of mineral grains: quartz, feldspar (albite, oligoclase, andesine, microcline), mica (muscovite, biotite, illite), and chlorite. The authigenic fraction of organomineral bottom sediments is formed mainly of the following minerals: pyrite, calcite of various magnesia degrees, amorphous silica (which later crystallizes into quartz), and aragonite. However, the mineral content ratios differ for different lakes, and some bottom sediments of these lakes do not contain the listed minerals. Diffractograms for organomineral bottom sediments of all lakes have a pronounced large halo with a maximum in the range of 20 °CuK_α. The amorphous halo intensity correlates with the organic carbon content and/or concentration of diatom valves (amorphous silica).

Group composition of bottom sediments organic matter. The group composition of organic matter is determined by the method of sequential extraction using technique adapted from (Yudina et al., 1998; Krivonos, 2012; Strus, 2015) (Table 4). The following fractions were isolated: carbonates, soluble in cold dilute HCl (CAR); substances, soluble in boiling water (WS); bitumens, extractable with an ethanol-benzene mixture (BM); humic substances (HS), including fulvic (FA) and humic (HA) acids; substances, easily hydrolyzed (in dilute hydrochloric acid) (HP); substances, hardly hydrolyzed (in concentrated sulfuric acid) (HR), and nonhydrolysable residue (NHS), which may contain

Table 2. Chemical composition (wt.%) of organic matter and mineral part of bottom sediments

Lake	Ash	C	H	O	N	S	SiO_2	AL_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3
Calcium class bottom sediments															
Barchin	40	14	2.0	11	1.2	1.9	11.2	1.7	1.0	1.4	20	0.3	0.3	0.2	3.0
Peshchanoe	40	19	2.2	16	1.4	1.4	15.4	4.1	2.4	1.9	15	0.8	0.5	0.2	4.1
Maloe Minzelinskoe	45	25	3.2	16	2.1	0.5	11.2	1.7	2.2	0.7	22	0.2	0.2	0.6	2.1
Siliceous class bottom sediments															
Kachkul'nya	17	36	4.2	27	2.5	3.8	7.2	1.2	0.8	1.4	3	0.3	0.2	0.1	1.8
Kambala	56	12	1.6	12	0.8	1.0	37.5	6.8	3.6	1.3	3	0.5	1.2	0.2	1.2
Tsybovo	48	16	1.9	10	1.4	1.4	32.5	6.5	2.9	1.6	3	0.6	1.2	0.3	1.3
Mixed class (Si ~ Ca) bottom sediments															
Bol'shie Kayly	40	20	2.6	12	1.6	1.4	22.9	4.5	2.4	1.2	6	0.9	0.7	0.5	1.5
Yargol'	34	23	3.0	18	2.1	1.6	27.0	6.5	2.3	0.8	7	1.4	1.8	0.9	3.8

Table 3. Average content of microelements (mg/kg) in organomineral sediments of lakes

Lake	Li	V	Cr	Mn	Co	Ni	Cu	Zn	Sr	Cd	Ba	Hg	Pb	Th
Salcium class bottom sediments														
Barchin	7	14	19	975	3	9	9	36	716	0.13	144	0.03	4	1.0
Peshchanoe	7	17	48	615	3	10	14	43	834	0.09	142	0.06	8	4.7
Maloe Minzelinskoe	4	12	39	275	4	19	10	38	398	0.23	182	0.03	42	1.3
Siliceous class bottom sediments														
Kachkul'nya	24	13	20	319	4	9	13	29	282	0.14	67	0.03	6	0.8
Kambala	14	48	52	462	8	28	26	64	138	0.24	51	0.03	8	5.4
Tsybovo	13	48	58	532	8	28	23	85	242	0.45	210	0.04	13	6.6
Mixed class (Si ~ Ca) bottom sediments														
Bol'shie Kayly	9	33	89	455	5	21	31	77	258	0.27	190	0.12	10	6.7
Yargol'	8	36	33	483	6	18	15	57	116	0.21	53	0.01	5	4.0

Table 4. Groups of organic compounds in the organic matter of sapropel from lakes

Sampling site (lake)	Class of sapropel	Compounds soluble in 0.05 N HCl, wt.%	Water-soluble compounds, wt.%	Bitumens, wt.%	Humic compounds, wt.%		Hydrolysis prone compounds, wt.%	Hydrolysis resistant compounds, wt.%	Nonhydrolyzable residue, %
					FA	HA			
Macrophyte									
Yargol'	Mixed	20.5	4.3	4.1	12.2	9.3	9.6	1.7	39
Minzelinskoe	Mixed	39.1	5.8	1.7	7.7	5.2	20.1	0.9	20
Kachkul'nya	Siliceous	3.2	7.2	5.3	1.1	2.9	12.5	9	60
Plankton-macrophyte									
Bol'shie Kayly	Mixed	8.9	4.6	4.5	2.2	18.6	14.9	17.4	29
Kambala	Siliceous	15.1	6.7	4.9	13.3	19.1	2.9	0.3	38
Tsybovo	Siliceous	5.4	6.2	4.6	2.1	20.0	6.3	3.9	39
Barchin	Calcium	44.6	3.5	2.2	7.1	3.1	12.6	0.15	28
Peshchanoe	Calcium	4.1	8.4	4.3	1.1	2.4	61.2	1.2	17

both high molecular organics (lignin) and inorganic substances (quartz, feldspar, etc.). The predominant content of calcite fraction, as expected, was found in the organomineral bottom sediments of the calcite class (Lakes Barchin, Peshchanoe, and Minzelinskoe). The contents of water-soluble and bitumen fractions for all organomineral bottom sediments were low (3.5–8.4 and 1.7–5.3%, respectively). The contents of fulvic and humic acids varied in the wider ranges from 1.1 to 13.3 and from 2.4 to 20.0%, respectively. Moreover, for plankton-macrophyte organomineral sediments, the amount of humic acids exceeded significantly the amount of fulvic acids, except Lake Barchin. No correlations were found for the content of easily hydrolyzed in dilute hydrochloric acid compounds (from 2.9–14.9%) for organomineral bottom sediments of different types and classes. The sapropel of Lake Peshchanoe containing 61.2% easily hydrolyzed compounds is exception. The highest contribution of hardly hydrolyzed in concentrated sulfuric acid substances was found in the bottom sediments of Lake Bol'shie Kayly (17.4%). The fractions of hardly hydrolyzed substances in other organomineral bottom sediments were close in values and varied in a narrow range of 0.9–3.9%. The fractions of nonhydrolysable residue for organomineral sediments of different types and classes varied from 17 to 39%. The sediment of the Lake Kachkul'nya (NHS 60%) formed mainly by reeds and similar in elemental composition to lignin (Taran et al., 2018) was the exception.

The **silicon class** of organomineral bottom sediments is characterized by the presence of significant amounts of diatom valves (amorphous silica) (Lake Peshchanoe, up to 35% of the total weight of bottom sediments) (Fig. 4*a*, *b*). Pseudomorphs of SiO_2 over the macromass of macrophytes (Lake Yargol', up to 46% of the bottom sediments total mass) occur everywhere (Fig. 4*c*). Detrital quartz is also found in the total mineral mass of all lakes along with chalcedony globules of different genesis (Fig. 4*d*, *e*).

Pyrite is the second most common authigenic mineral in bottom sediments of all lakes, but not in quantity (Fig. 5). Bottom sediment samples analysis by scanning electron microscopy (SEM) showed that pyrite is present in all lakes in the form of individual crystals, groups of crystals of octahedral, cubic, pentagonal dodecahedron, and sometimes cubic octahedral habitus (Fig. 5*a*), ranging in size from 1 to 2 µm, and framboids of no larger than 0.01 mm. Pyrite framboids

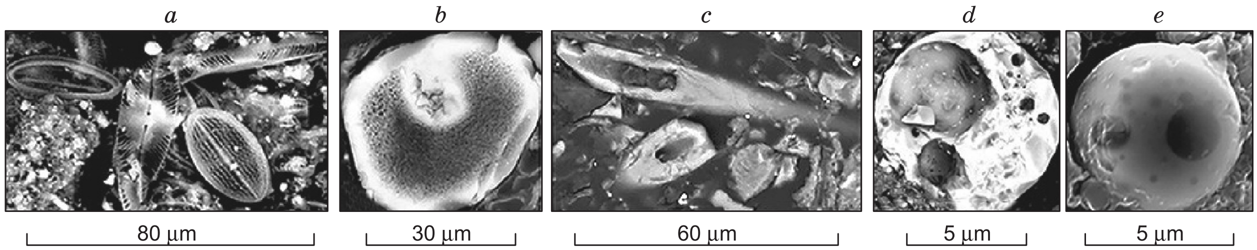

Fig. 4. Electron microscopic images (SEM). *a*, *b*, Leaves of diatoms consisting of SiO_2 (*a*, L. Kambala, *b*, L. Peshchanoe; *c*, SiO_2 in the pseudomorph mortmass macrophytes (L. Yargol'); *d*, *e*, globules from SiO_2 having different genesis (*d*, L. Bol'shie Kayly, *e*, L. Sarybulak).

are the spherical aggregates ranging in size from 2 to 80 µm of close-packed microcrystals that have a rounded shape at the initial stage of formation (Fig. 5*b*), which is further transformed into the octahedral or cubic shape (Fig. 5*c*), with the sizes of up to 2 µm. The composition of pyrite corresponds usually to its formula, sometimes Mn is present as an impurity (<1%); in framboids of the initial stage of formation, water is present in the amount of up to 3%. The presence of pyrite and its amount in bottom sediments does not depend on total mineralization of water, its ion composition and sapropel genesis.

Pseudomorphous aggregates formations over the plant detritus of calcitic or low-Mg calcite composition (Lakes Barchin, Maloe Menzelinskoe), zonal-concentric formations of low-Mg calcite (Lakes Peshchanoe, Barchin), and numerous fragments of aragonite shells are most common for organomineral bottom sediments of the **calcium class.** The fragments of aragonite composition shells are present in different quantities in bottom sediments of all investigated lakes.

Organomineral bottom sediments of the **mixed class** are characterized by formation of pseudomorphs of amorphous silica over *Stratiotes aloides L.* (Lake Yargol') and pseudomorphs of low-Mg calcite in the macrophyte mortmass (reed), which is one of the dominants of the coastal-aquatic plant communities of the studied lakes group (Lake Bol'shie Kayly).

DISCUSSION

Changes in the ionic composition and values of total mineralization of lake waters in the south of Western Siberia from north to south (from the southern taiga zone to the steppe landscape zone) correspond generally to the well-known latitudinal zonality (Perel'man, 1982). However, a large number of small lakes are located on the territory of the Baraba Lowland; water composition in these lakes is hydrocarbonate-sodium and deviates significantly from the patterns of latitudinal zonality because it is caused by the processes of water interaction with soils and rocks of the watershed territories.

The situation is complicated by the contribution of biogenic processes to formation of both water and bottom sediment compositions. Although, there are no obvious correlations between the organic substance groups depending on the class and amount of organic matter as it was discussed in the previous section. However, some differences in elemental (CHNSO) and organic organomineral bottom sediments have been found differing by the type of biological contribution to their formation. Organomineral bottom sediments of all studied lakes in which the total organic matter content varies from 87% (Lake Kachkul'nya) to 44% (Lake Kambala) are classified according to the type of biological contribution to their formation. The study of dependence between the H/C and O/C ratio, the value of primary production

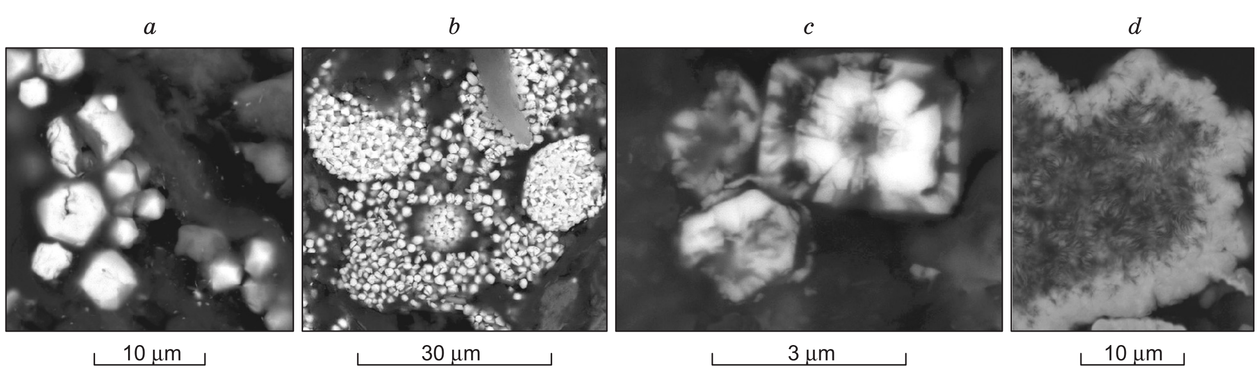

Fig. 5. Electron microscopic images (SEM). *a*, Individual crystals of the pentagon dodecahedral habitus in the bottom sediments of L. Barchin; *b*, framboidal pyrite and some individuals rounded crystals of pyrite in bottom sediments of L. Peshchanoe; *c*, recrystallization of pyrite framboids into metacrystal of cubic habitus in bottom sediments of L. Kambala; *d*, pseudomorphosis of pyrite in the mortmass of macrophytes in bottom sediments of L. Peshchanoe.

of macrophytes, phyto- and zooplankton, and precipitated lake suspension showed (by the sedimentation traps) that organomineral bottom sediments of Lakes Kachkul'nya, Yargol', Maloe Menzelinskoe are mainly formed by macrophytes, and their elemental composition is close to lignin. Organomineral bottom sediments of Lakes Barchin and Peshchanoe are predominantly planktonic in origin with predominance of phytoplankton, and in terms of their component composition they have an intermediate position between peptides and lignins.

Characteristic differences in the chemical composition of the biochemogenic component of the lake sediments fraction with different classes of sapropel deposits are, owing to the processes of modern authigenic mineral formation, occurring with active participation of microorganisms. In the total mineral mass of all lakes, chalcedony formed from amorphous silica of diatom valves and phytomorphosis over macrophytes adds to detrital quartz and silicates. Minerals formation during the life of algae can give thin membranes over the primary framework of algae, consisting of fine-grained calcite, low-Mg calcite, sometimes aragonite, and pyrite. Most often pyrite forms framboids and/or individual crystals of different habits. As it is known, Fe^{3+} is reduced due to microbiological processes of organic matter decomposition. Anaerobic microorganisms can oxidize H_2S producing sulfur in boarder environment section conditions (Potekhina, 2005). Sulfur obtained by oxidation of H_2S is colloform. Colloids coagulation leads to formation of the characteristic framboidal pyrite, regardless of further pyrite formation due to the microbiological or chemogenic process (Belogub, 2009). Chemogenic formation of carbonates in freshwater is impossible. However photosynthetic organisms cause precipitation of dissolved carbonates by extracting carbon dioxide dissolved in water and changing pH of the environment in the alkaline direction. CO_2, H_2S, NH_3, etc. are emitted during anaerobic destruction of the original organic matter of silts as a result of bacteria and fungi vital activity that live in the bottom part and surface layers of bottom sediments in large quantities. This contributes to chemical precipitation of calcite-dolomite carbonates in lakes with soda water composition. Aragonite and calcite accumulate in all lakes with different type of water.

The cluster analysis of geochemical and biological analytical data was carried out to specify the contribution of various organisms and their metabolic products to formation of the bottom sediments mineral matter. The following parameters were used: ash content, content of macro- and microelements in organomineral sediments, elemental and group composition of organic matter, products (organic carbon (C_{org}, gC/m^2·year), nitrogen (N_{org}, gN/m^2·year) and phosphorus (P, gP/m^2·year)) of phytoplankton, macrophytes and nonmineralized production and excretion of zooplankton. The cluster analysis use allows us to single out the groups of objects based on the correlation parameters from the entire set of considered features and evaluate the correlation of both individual pairs of objects and the entire groups (Davis, 1986). The Q-type cluster analysis divided the sample of organomineral bottom sediments into three groups, which mainly correspond to the biogenetic type of sediment formation. Three main groups with positive internal connections with a negative correlation factor between the groups were distinguished as a result of cluster analysis of the R-type, which reveals correlations between the given parameters (Fig. 6). The samples of sediments were treated with a 0.05N solution of hydrochloric acid to remove calcium carbonate while studying the group composition of organic matter of organomineral bottom sediments by the method of sequential extraction. The calcium fraction obtained in this way has strong positive correlation with Ca and carbonatophile elements (Sr, Mg, Mn) as it was expected. In addition, significant correlation of the calcium group with the production of phytoplankton and fulvic acids (whose formation is mainly contributed by microorganisms) indicates the biochemogenic and biogenic carbonates genesis. Macrophytes are the most important primary producers of organic matter in water reservoirs. This explains high correlation of macrophyte production with the contents of C, H, N and O in organomineral bottom sediments. The main components of macrophyte biomass are polysaccharides (cellulose, hemicellulose) and lignin. Therefore, high concentrations of substances, easily hydrolyzed in dilute hydrochloric acid (hemicellulose hydrolysis products) and nonhydrolysable residue (mainly lignin) are characteristic of macrophytogenic organomineral bottom sediments. In general, the amount of nonhydrolysable residue differs in all samples. This residue consists mainly of mineral matter in planktonogenic sediment. Separation of nonhydrolysable residue indicates the combined effect of several factors. If the connection of U with substances, easily hydrolyzed in diluted hydrochloric acid, can be explained by the known fact of uranium sorption by organic matter, then high positive correlation of nonhydrolysable residue with S and Li requires further research. The relative content of bitumen for lakes on average ranges from 2.5 to 5.3%. According to literary data, it indicates the syngenetic nature of bitumen (Ivanova et al., 2014). Hardly hydrolyzed in concentrated sulfuric acid substances are found in significant amounts only in macrophytogenic bottom sediments. The main component of hardly hydrolyzed substances is cellulose. It is indicated by high positive correlation between hardly hydrolyzed substances and elemental composition of nonmineralized products biomass. We should note that nonmineralized products and excretion of zooplankton are also closely related to some metals (Hg, Cu, Zn, etc.). Their selective accumulation by zooplankton was noted by us earlier (Polukhina et al., 1998; Ermolaeva et al., 2000). In addition, correlation between the quantitative characteristics of zooplankton and phosphorus compounds was clearly demonstrated before, since it is the filter feeders and detritophages (*Cladocera* and *Diaptomidae* groups) that determine the main flow of phosphorus to bottom sediments,

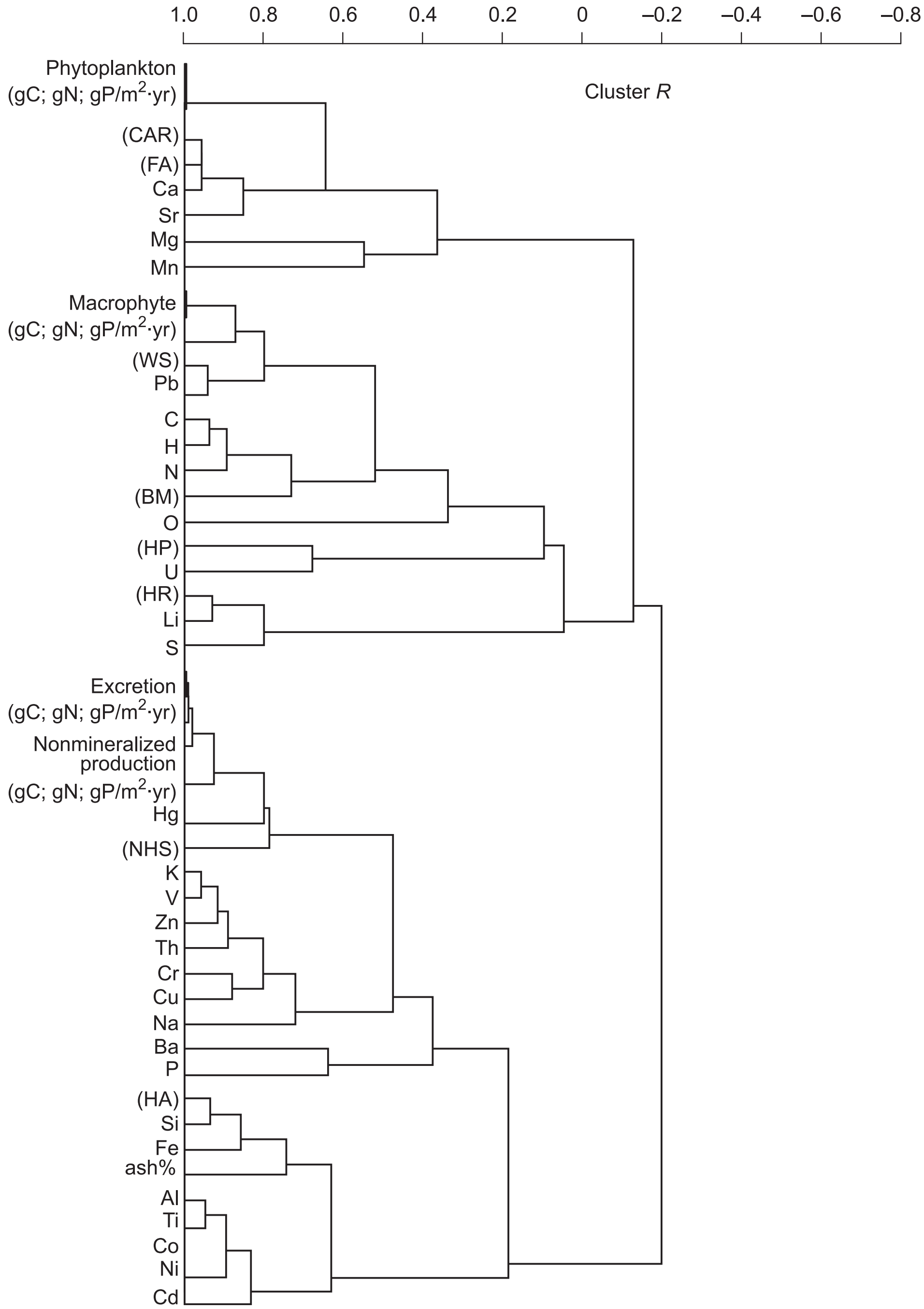

Fig. 6. R-type cluster analysis dendrogram, where the following parameters were used: ash content, content of macro- and microelements in organomineral sediments (Si, Ca, Na, K, Al, Mg, Fe, Ti, P, Mn, Sr, Ba, Pb, Cd, Li, V, Cu, Zn, Co, Ni, Cr, Hg, U, Th); elemental (C, N, H, O, S) and group composition of organic matter (carbonates sapropel samples were treated with 0.05 N HCl to remove Ca^{2+} ions (CAR); water-soluble compounds (WS) were extracted from the decalcified air-dry samples by boiling in water for 5 h at a sample/solvent ratio of 1/100; bitumen (BM) was extracted then by ethanol-benzene mixture (1:1) in Soxhlet's (extraction) apparatus; humic compounds (HA + FA) were extracted by treating with 0.1 N NaOH solution at 20–25 °C for 24 h and subsequent additional extraction with 0.02 N NaOH at 80 °C; the alkali-free residue was used to extract easily hydrolyzed compounds (HP) (hemicelluloses and nitrogen-bearing compounds) by double treating with 2% HCl at 90 °C for 2.5 h; the residue was washed, dried, and treated with 80% H_2SO_4 for 2.5 h to extract hydrolysis-resistant compounds (HR) (cellulose) and then boiled with 5% H_2SO_4 for 5 h at a ratio of 1:100; the residue was a nonhydrolysable substance (NHS)); products (organic carbon (C_{org}, gC/m^2·year), nitrogen (N_{org}, gN/m^2·year) and phosphorus (P, gP/m^2·year)) of phytoplankton, macrophytes and nonmineralized production and excretion of zooplankton.

"canning" it in their pellets (Strakhovenko et al., 2014). The amount of humic acid in the lacustrine bottom sediments varies within very wide limits and significantly exceeds the content of all other components. The close positive relationship of bitumen with Si, Fe, and ash content indicates a polygenic source of silicon and iron. On the one hand, these are the minerals of terrigenous fraction (micas, quartz, etc.). On the other hand, according to (Orlov, 1993; Mayer, 1994a; Vermeer and Koopal, 1998) humic acids are found in nature both in dissolved form and immobilized on mineral surfaces (iron oxides and hydroxides, silicon and aluminum-containing minerals), acting as a natural modifier, i.e., complexes of humic acids with mineral particles form an organomineral buffer of suspended matter in aquatic ecosystems.

According to (Mayer, 1994b), maximal adsorption of humic substances is tens and hundreds of grams per kilogram of mineral. For example, the content of natural organic matter is 1 mg C_{org}/m^2 in ocean bottom sediments. Correlation of Al, Ti, Cd, Ni, Co with ash indicates that this subgroup of elements has an allochtonic origin, i.e., brought from the catchment area.

CONCLUSIONS

Summarizing the data on distribution of the studied elements in bottom sediments of lakes with consideration of sediment class and type, it can be argued that a fundamental role in the formation of the geochemical and mineral composition of small lakes bottom sediments is played by complex natural processes, determined mainly by combination of azonal factors: the formation of sedimentation material in the lake catchment area depending on relief, geology, soil and vegetation cover, as well as human activities; formation of authigenic organic and mineral matter as a result of biological, biochemical and physicochemical processes; precipitation of a complex mixture of allochthonous and autochthonous matter on the lake bottom, occurring under prolonged freeze-up conditions (under anaerobic conditions).

We determined that organomineral bottom sediments of various classes and biogenetic types of formation differ both in relative concentrations of the main elements (Si, Ca, C, O) and in the content of the main groups of organic matter. The direct effect of organic matter transformation on the mineral composition of bottom sediments has been revealed. The content of other elements varies in a narrow range, and the differences in the content of elements between organomineral bottom sediments of different types and classes are comparable with similar differences within one class.

The results obtained can be useful in developing recommendations for the use of sapropel deposits both in agriculture and animal husbandry and when considering them as promising raw materials for other sectors of the national economy.

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