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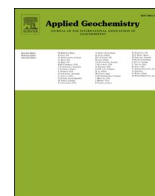
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## Biogeochemistry and element speciation in sapropel from freshwater Lake Dukhovoe (East Baikal region, Russia)

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### ABSTRACT

This paper presents results of biogeochemical investigation of the Holocene organic-rich sapropelic sediments of Lake Dukhovoe situated not far from the Baikal. The main source of organic matter in Lake Dukhovoe is phytoplankton, which serves as a biogeochemical barrier where elements are accumulated from water and then buried in the bottom sediments. Microorganisms (e.g., bacteria, micromycete and actinomycetes) play significant role in decomposition of organic matter and formation of organic-mineral complexes in four distinguished types of sapropels: organic, organic-mineral, mineral-organic and mineral. Diagenetic transformations of the Lake Dukhovoe sapropels under influence of mechanical, biochemical, microbiological and physicochemical processes lead to transformation of element speciation. A boundary between oxidizing and reducing diagenesis conditions is at the depth of 167 cm in the sapropel core. Change of the conditions forms geochemical barrier in bottom sediments and control the formation of secondary phases (organic-mineral complexes, diatomite, framboidal pyrite, vivianite, carbonates, etc.) as well as processes of accumulation and leaching of chemical elements. Additionally, high contents of Fe, Mn, Cu, Zn, Pb, Cd, and Mo in the upper 10 cm of the sapropel might have been caused by forest fires and anthropogenic factors. The fact of marcasite formation in the stomatocysts of Chrysophyte algae (golden algae) is new and was established for the first time. Based on the results and geochemical equilibrium modelling, the stomatocysts of Chrysophyte algae can be considered as a microreactor for iron sulfide formation.

### 1. Introduction

Sapropels are biogenic unconsolidated sediments accumulating mainly in lakes of the Earth humid regions and in some seas, for example, Mediterranean and Black. Sapropel contains a significant amount of organic matter, mainly residues of aquatic organisms (phyto- and zooplankton, benthos and macrophytes), as well as inorganic substances of biogenic origin and mineral impurities being run off from catchment area. Formation of sapropel is influenced by mechanical, physicochemical, biochemical and microbiological processes.

Sapropels are an important object of scientific study and are investigating in two main fields: 1) fundamental - paleoclimatic

reconstructions, geochemical and biogeochemical studies (Potonie, 1920; Korde, 1960; Lukashev et al., 1971; Volkov and Fomina, 1971; Passier et al., 1999; Largin and Shadrin, 1989; Knicker and Hatcher, 2001; Emeis and Weissert, 2009; Bezrukova et al., 2011; Leonova et al., 2011, 2015; Melenevskii et al., 2011; Moller et al., 2012; Krivonogov et al., 2012a; Dirksen and Meijer, 2020; Ignatavicius et al., 2022); and 2) practical - use in agriculture, balneotherapy, construction and industry (Lishtvan and Lopatko, 1976; Shtin, 2005; Plaksin and Krivonosov, 2007; Topachevsky, 2011; Kurzo et al., 2012; Leonova et al., 2014; Patent N2336253, RU et al., 2008; Patent N2414430 et al., 2011; Patent N2414961 RU et al., 2011; Patent N2428195 et al., 2011). Some scientists assume that sapropel was a material to form carbonaceous

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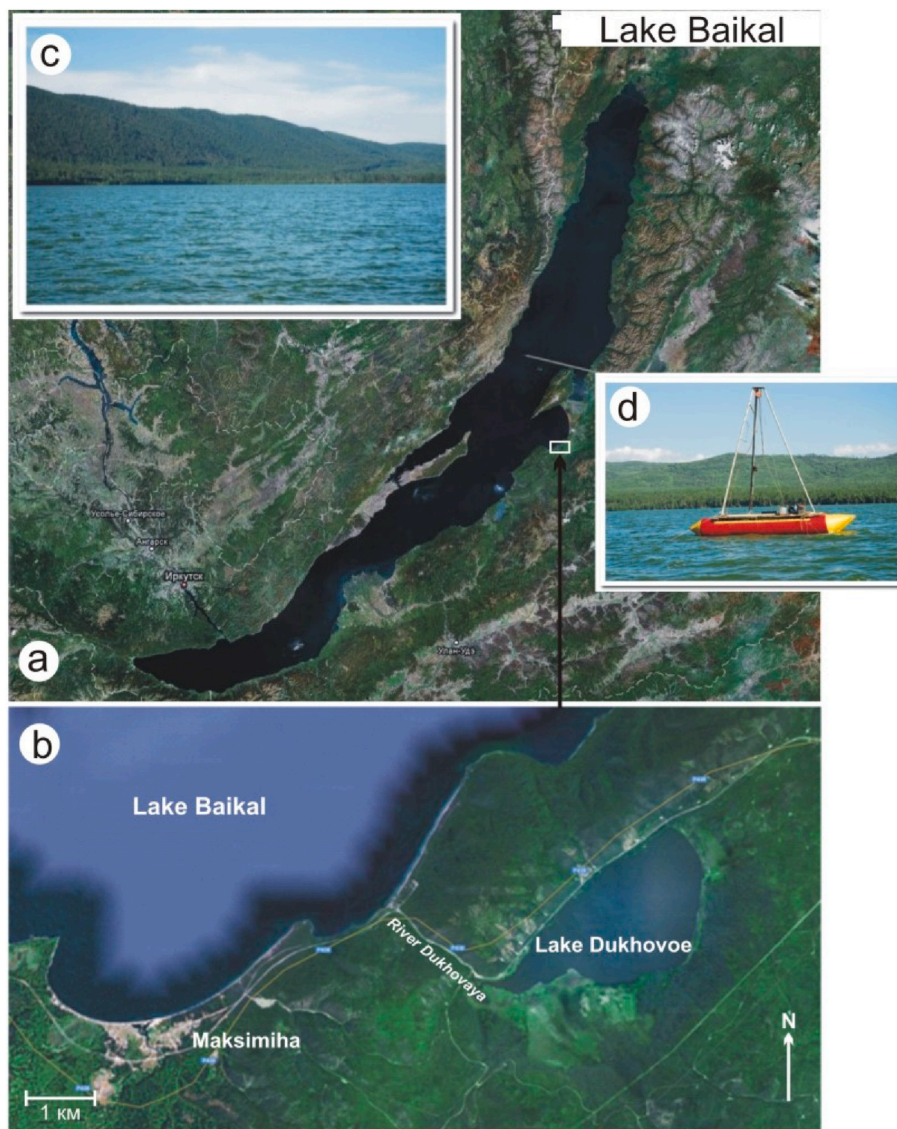


Fig. 1. Location of Lake Dukhovoe: a) satellite image of Lake Baikal from Google Maps; b) satellite image of Lake Dukhovoe; c) photo of Lake Dukhovoe; d) photo of a drilling unit.

sedimentary rocks such as black shales, pyroschists, Paleozoic mat coals, and sapropelic clays (Poplavko et al., 1978; Vine and Tourtelot, 1970; Yudovich and Ketris, 2002; Zalesskii, 1916, 1928).

Most previous works have focused on the investigation of marine sapropels (e.g., Volkov and Sevastyanov, 1968; Pruyssers et al., 1993; Passier et al., 1999; Cramp and Sullivan, 1999; Emeis and Weissert, 2009; Gallego-Torres et al., 2010; Dean and Arthur, 2011; Moller et al., 2012; Dirksen and Meijer, 2020) or large freshwater lakes such as Siberian Lake Baikal (Vihristuk, 1980; Mizandrontseva, 1990; Granina, 2008; Muller et al., 2005). Sapropels of small freshwater lakes of this region were not investigated in detail; researchers mainly paid attention to paleoclimatic aspects (Korde, 1968; Blyakharchuk, 2003; Khazina, 2006; Shichi et al., 2009; Tarasov et al., 2009; Ishiwatari et al., 2009; Bezrukova et al., 2008, 2011). Geochemical and biogeochemical aspects of the diagenesis of small lakes are still not clearly understood.

The main goal of this work is the complex biogeochemical investigation of sapropel from Lake Dukhovoe (East Baikal region, Russia). We illustrate and discuss a number of biogeochemical and geochemical questions e.g., element speciations which are very important in understanding element accumulation and migration; and role of living matter in the sapropel formation.

## 2. Description of the study area, materials and methods

Lake Dukhovoe (53°18' N, 108°53' E) is situated not far from the south-eastern shore of the Baikal Lake near the Maksimiha Village (Fig. 1). The lake occupies a depression between forehills of the Ulan-Burgasy Range and an uplifted intermediate tectonic step of the Baikal shore which is only two km wide. The lake surface has altitude of 514 m above the sea level and 95 m above the level of the Baikal. Lake Dukhovoe is 2.5 km long and 1.6 km wide, and its depth reaches 2.8 m (average depth 2.3 m). There are no large streams flowed into the lake; several creeks gather surficial waters from ca. 40 km<sup>2</sup> catchment. Small Dukhovaya River flows out of Dukhovoe Lake and falls into the Baikal. Therefore, the lake is fed mainly by atmospheric transport (e.g. precipitation, aerosols and dusts), run off from catchment area and possibly by sulphate groundwaters that are present in this region (Vetrov and Kuznetsova, 1997; Khodzher, 2005; Granina, 2008).

The lake is surrounded by the taiga forest composed of Siberian and Scotch pine, Siberian fir, spruce and larch. The forest closely approaches the lake on the steep western bank and is separated by a narrow belt of reeds and in places sphagnum and green mosses bog on the lowland eastern bank. A silted near-shore part of the lake is overgrown by

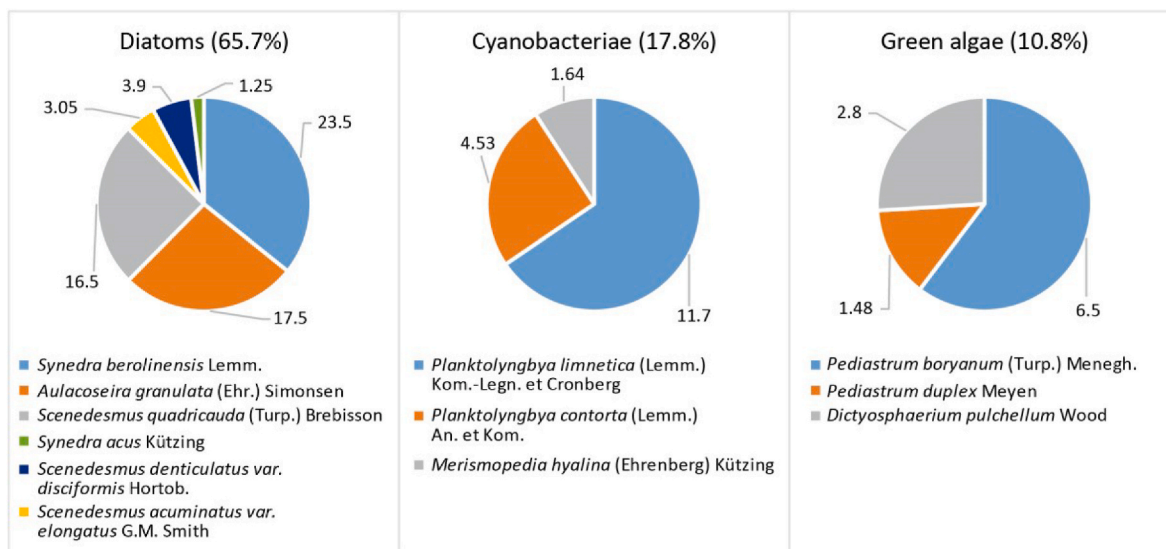


Fig. 2. Phytoplankton composition of Lake Dukhovoe. The data were provided by Dr. E.G. Sorokovikova from the Limnological Institute SB RAS (Irkutsk, Russia).

submerged macrophytes. The climate is temperate continental with the average annual temperature  $-0.7^{\circ}\text{C}$  ( $-23^{\circ}\text{C}$  - in January and  $+18^{\circ}\text{C}$  - in July). Annual precipitation is about 400–500 mm.

The lake water was tested in the field. Its temperature, pH, and Eh were measured by the Ionomer-4151 (Novosibirsk, Russia) device. Concentration of dissolved oxygen was measured by the MERCK tester (Germany). The unfiltered lake water was divided in two subsamples: 1) the unacidified subsample for analysis of anions and cations; 2) the acidified subsample with  $\text{HNO}_3$  for the elemental analysis. Plankton was gathered with a  $73\ \mu\text{m}$  Juday net, which prevents intake of terrigenous suspension. The etching was made to a depth of 1–2 m with special care against touching the bottom sediments. After removal of water through a paper filter, the samples were weighed and dried. Part of each sample was conserved in formalin to determine the plankton species and a proportion of the dominant ones (Abakumov, 1983).

A continuous undisturbed 6 m long and 7.5 cm in diameter core was collected by a Livingston-type vibro-corer in the central part of the lake. The core was split lengthwise in two halves used for different analyses. For geochemistry, liquid and solid samples were taken from 10 cm fragments of the core. Pore waters were extracted from these samples at pressures of 10–15 MPa using a manually operated laboratory press. The solid residues were then hermetically sealed in polyethylene bags and stored at low temperature in refrigerator. The sediment pore water samples were filtered through a  $0.45\ \mu\text{m}$  membrane filter and then divided in two subsamples. First subsample was acidified to  $\text{pH} < 2$  using concentrated ultra-pure  $\text{HNO}_3$  and was used for the elemental analysis. Second subsample, which was not acidified, retained in amber-plastic containers with minimal headspace and then was used for ion analysis. The surface lake water and sediment pore water compositions as well as the transformation of the sediment pore water in the sediment of Lake Dukhovoe was discussed in details in the previous publication (Maltsev et al., 2014).

In order to investigate element speciation in solid samples, we used a modified sequential extraction procedure for samples enriched by organic matter (Bogush et al., 2012), a variation of classic sequential extraction technique of Tessier et al. (1979) applicable for soil. The procedure includes the following steps: (1) water-soluble fraction ( $\text{H}_2\text{O}$ ,  $V = 20\ \text{ml}$ ,  $T = 25^{\circ}\text{C}$ ,  $t = 1\ \text{h}$ ); (2) exchangeable fraction (1 M  $\text{NH}_4\text{OAc}$ ,  $\text{pH} 7$ ,  $V = 20\ \text{ml}$ ,  $T = 25^{\circ}\text{C}$ ,  $t = 1\ \text{h}$ ); (3) carbonate fraction (elements associated with carbonates, 1 M  $\text{NH}_4\text{OAc}$  buffered by  $\text{HOAc}$  to  $\text{pH} 5$ ,  $V = 20\ \text{ml}$ ,  $T = 25^{\circ}\text{C}$ ,  $t = 5\ \text{h}$ ); (4) oxidizable (30%  $\text{H}_2\text{O}_2$ ,  $V = 20\ \text{ml}$ , leave the mixture over night, then on sand bath for 2–3 h); (5) reducible fraction (elements associated with Fe/Mn oxides, 2 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25%  $\text{HOAc}$ ,

$V = 20\ \text{ml}$ ,  $\text{pH} 2$ ,  $T = 96^{\circ}\text{C}$ ,  $t = 6\ \text{h}$ ); and (6) residual fraction (acid digestion:  $\text{HF}\text{--}\text{HNO}_3\text{--}\text{HClO}_4\text{--}\text{HCl}$ ). After each stage of the extraction, the residue was rinsed in 10 ml of distilled water and centrifuged. All fraction samples were filtered through a  $0.45\ \mu\text{m}$  membrane filter.

The laboratory research was carried out at the Analytical Centre of the Institute of Geology and Mineralogy of Siberian Branch of Russian Academy of Sciences, Novosibirsk. Bulk and trace elements were analysed in all fraction samples from the sequential extraction procedure using AAC, ICP-OES and ICP-MS. The certified reference material (CRM) of Baikal silt BIL-1 (Govindaraju, 1994) was used for control in the elemental analysis. In the solid samples of sapropel, total nitrogen, carbon, hydrogen and sulfur were determined using a CHNS analyser. X-ray diffraction analysis (XRD; DRON-3M powder diffractometer using filtered  $\text{CuK}\alpha$ -radiation) was used to characterize the crystalline phases of the sapropel. The database of the International Centre for Diffraction Data (ICDD) was used for their identification. The morphology and microstructure of sapropel were investigated by SEM on TESCAN MIRA 3 LMU and LEO 1430VP high-performance, variable pressure analytical scanning electron microscope. Energy-dispersive X-ray spectroscopy (Oxford Instrument X-Max 80 EDS-system) was used for microanalysis of the solid phases viewed by SEM.

Radiocarbon dating of the sediments was performed in the Institute of geology and mineralogy SB RAS by the scintillation method. The remanent carbon activity was measured on the QUANTULUS-1220 liquid scintillation counter. The ages were calculated based on the 5570 years  $^{14}\text{C}$  half-life. We did not apply any correction for the radiocarbon fractionation, as the total organic carbon of plant origin was measured in the samples. Further calibrations were made with a help of the CALIB 7.1 at <http://calib.org> (Reimer et al., 2013).

Characterisation of microbial communities (microbial detection and enumeration) was investigated using the culture-dependent technique including inoculation of suspension of bottom sediments (1 g/100 ml water) onto selective agar media using limit dilution method (Konratyeva et al., 2000). The number of colonies was expressed in terms of colony-forming units (CFU/g). The abundance of viable heterotrophic bacteria (HB) and ammonifying bacteria (AMB) was determined on diluted fish-peptone agar (FPA:10) and undiluted FPA, respectively. Nitrifying microorganisms (NM), assimilating ammonium nitrogen, were incubated on starch-ammonia agar (SAA): soluble starch = 10 g/L,  $(\text{NH}_4)_2\text{SO}_4$  - 2 g/L;  $\text{K}_2\text{HPO}_4$  - 1 g/L;  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$  - 1 g/L,  $\text{NaCl}$  - 1 g/L,  $\text{CaCO}_3$  - 3 g/L, agar - 15 g/L. The phenol-resistant and phenol-oxidizing bacteria (PRB/POB) were determined on a mineral medium with the following composition:  $\text{KNO}_3$  - 1 g/L,  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$  - 0.2 g/L;  $\text{K}_2\text{HPO}_4$  -



**Table 1**

The C/N, C/P and N/P ratios for the surface layer of Lake Dukhovoe and literature data for plankton, submerged and terrestrial plants, and wood tissues.

Reference	C/N	C/P	N/P
<b>Surface layer of sapropel from Lake Dukhovoe</b>			
Authors' data	8.0	120	15
<b>Plankton</b>			
Redfield et al. (1963)	6.6	106	16
Healey and Hendzel (1980)	8.3–14.6	129–258	22
Duarte (1992)	5–15	30–200	5–15
Burkhardt et al. (1999)	5–10	50–120	–
<b>Submerged and terrestrial plants</b>			
Ruttenberg and Goni (1997)	20–100	300–1300	–
<b>Wood tissues</b>			
Ruttenberg and Goni (1997)	100–1000	>1300	–

1 g/L; NaCl - 1 g/L, phenol - 1 g/L, agar - 20 g/L. The sulphate-reducing bacteria (SRB) were determined on a Morris's agar medium with the following composition: fish nutrient agar - 35 g/L; peptone - 1 g/L; NaCl - 0.5 g/L; CH<sub>3</sub>COOPb - 1 g/L; agar-agar - 20 g/L (Gerhardt, 1981). The denitrifying bacteria (DNB) were determined on a synthetic media of Gil'taya (Gorlenko et al., 1977).

The enrichment factors (EF) of plankton and of the sapropel top layer (0–2 cm) were calculated as the element concentrations normalized to the average concentrations of Sc, geochemically inert rare-earth elements, and to the analogous average ratio in shales (Li, 1991) by the formula:

$$EF = (X_i/X_{Sc})_{sample} / (Y_i/Y_{Sc})_{shale}$$

where X<sub>i sample</sub> - content of the ith chemical element in the sample; X<sub>Sc sample</sub> - content of Sc in the sample; Y<sub>i shale</sub> - content of the ith chemical element in shale; and Y<sub>Sc shale</sub> - content of Sc in shale. This formula is in compliance with the approach of (Shotyk et al., 1996).

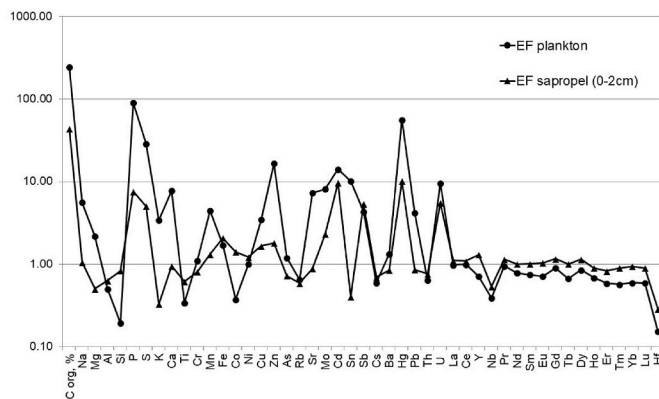
Geochemical equilibrium modelling, performed by SELECTOR-C software (Karpov, 1981; Karpov et al., 1997), was used in order to understand if iron sulphide can be formed in cyst (stomatocysts) of Chrysophyte algae (*Chrysophyceae*) under aging condition. The calculation algorithm of the SELECTOR-C software is based on the minimization of the Gibbs free energy. The theoretical fundamentals of physicochemical modelling include the equilibrium conditions in heterogeneous multicomponent systems with restrictions in the form of linear mass balance equations (Chudnenko, 2010).

### 3. Results and discussion

#### 3.1. Biota of Lake Dukhovoe

Environmental conditions of Lake Dukhovoe (shallowness, lack of water oxygen and temperature stratification) are favourable for active phytoplankton growth. The phytoplankton is dominated by green algae, cyanobacteria and diatoms (Fig. 2). The dominated species of diatoms are *Synedra berolinensis*, *Aylacoseira granulata* and *Scenedesmus quadricauda*, cyanobacteria *Planktolyngbya limnetica* and green algae *Pediastrum boryanum* (Fig. 2). Phytoplankton is not exposed to significant change with depth due to the shallowness of the lake. As, Lake Dukhovoe is impoverished in higher aquatic plants and zooplankton (Leonova and Bobrov, 2012), phytoplankton can be considered as the main producer of the sapropel forming organic matter. Its autochthonous planktonic origin is additionally evidenced by similarity of the total organic carbon concentrations in the phytoplankton (21 wt%) and in the topmost layer of the sapropel (22 wt%).

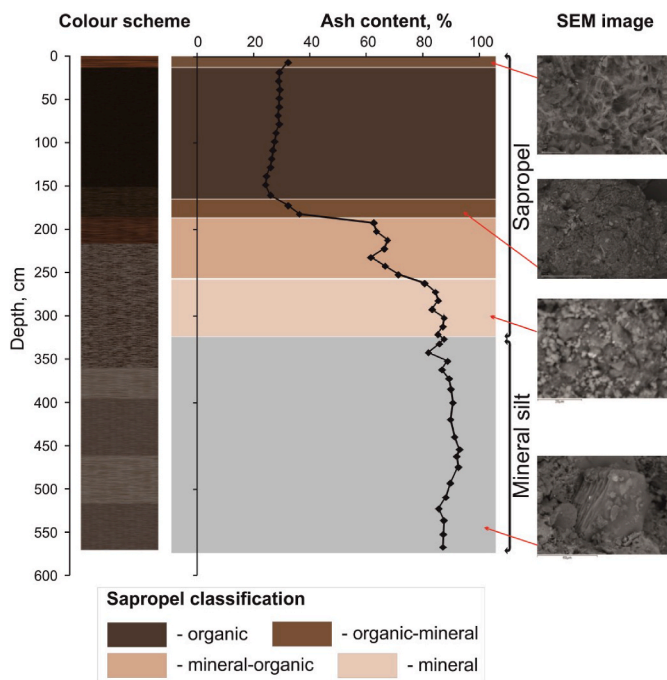
The C, N, P inter-ratios which reflect differences in the biochemical composition of present organisms can be also used to explain origin of



**Fig. 3.** Enrichment factors of elements in plankton and in the top layer of sapropel.

organic matter of bottom sediments (Vinogradov, 1944, Table 1). It is well known that higher aquatic and terrestrial vegetation is depleted in nitrogen and has the C/N ratio varying from 20 to 100 (Table 1; Skopintsev, 1950; Ruttenberg and Goni, 1997). The C/N ratio of plankton ranges from 5.0 to 15 (Redfield, 1934; Harvey, 1948; Redfield et al., 1963; Healey and Hendzel, 1980; Duarte, 1992; Burkhardt et al., 1999), for example, plankton of Lake Baikal shows the C/N ratio around 10 (Votintsev, 1961). The C/N ratio of wood tissues is in the range of 100–1000 (Ruttenberg and Goni, 1997). In Lake Dukhovoe, the topmost layer of sapropel showed the C/N, C/P and N/P ratios inherent to plankton (Table 1).

Fig. 3 shows the enrichment factors (EF) of elements in the plankton and the top layer of sapropel which give geochemical characterisation of modern aquatic ecosystem and the atmosphere above it. Plankton is enriched with major biologically required elements (C org, P, S, Na, K, Ca, Mg, Fe, and Mn), and such elements as Zn, Cu, Cd, Pb, Mo, Sn, As, Sb, Hg, and U, which clearly highlight an anthropogenic impact. Zn, Cu, Mo, and Cd are biologically important elements (e.g. trace metal nutrients) which participate in physiological and biochemical processes in phytoplankton, and like major nutrients, can be uptaken intracellularly by specialized transport proteins on the cytoplasmic membrane of algal cells (Lane et al., 2005; Sunda, 2012). Pb, Sn, As, Sb, Hg, and U are abiogenic elements and are not essential for phytoplankton; however, they can be adsorbed on the surface of phytoplankton, passively/actively absorbed, and sequestered inside phytoplankton (e.g. toxic form of element can be enzymatically and/or intracellularly converted to a less toxic form; complexing of metal ions with excreted metabolites; precipitation of insoluble metal complexes; etc.) (Gonzalez-Davila, 1995). Phytoplankton can assimilate dissolved species (free aqua-ions and inorganic complexes) of elements (Budnikov, 1998; Linnik and Nabivanets, 1983, 1986; Bruland and Lohan, 2004), that probably be present in the lake water (Maltsev et al., 2014). The role of phytoplankton in the accumulation of elements were also ephasised in the previously published works (Monin and Lisitsyn, 1983; Gonzalez-Davila, 1995; Dotsenko and Mikhailenko, 2019). Therefore, plankton can be considered as a biogeochemical barrier where some elements are accumulating. Comparison of the EFs of the plankton and the sapropel top layer shows their similar enrichment by Corg, P, S, Fe, Cu, Zn, Mo, Cd, Sb, Hg, and U. This regularity is in agreement with the “model of direct inheritance” (Yudovich and Ketris, 1990). However, such elements as K, Na, Ca, Mg and Pb and to a certain degree P, S, Cu and Zn are depleted in the top sapropel layer due to their leaching from the plankton detritus during sedimentation. The depletion in Rare Earth Elements (REEs) and Hf, which are known to be indifferent to the biogenic accumulation, was observed in the plankton and the top layer of sapropel.



**Fig. 4.** The Lake Dukhovoe sediment layers colour scheme (left column), loss on ignition graph and classification (central part) and scanning electronic microscope (SEM) images of the sediments (right column). The sediment layers: 0–220 cm - dark brown highly watered unconsolidated organic-rich sapropel. The sediment has reddish tinge at the top and bottom of the layer; 220–360 cm - gray-brown compacted silt with smoky-blue tinge; 360–393 cm - bluish-gray silt; 393–460 cm - dark gray clay; 460–520 cm - bluish-gray silt; 520–574 cm - sandy clay. Classification of lake sapropelic sediments based on the amount of the ignition residue (Korde, 1960): 1) organic (up to 30%); 2) organic-mineral (30–50%); 3) mineral-organic (50–70%); 4) mineral (70–85%). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

### 3.2. Sediments of Lake Dukhovoe

#### 3.2.1. Stratigraphy and classification

The 6 m long sediment core from Lake Dukhovoe has layered structure and consists of heterogeneous substances (Fig. 4); however, origin of the layers and sedimentologically important boundaries are not obvious. When packing immediately after drilling, the sediments were blackish in the upper 200 cm and greenish to brownish below which indicates the reducible conditions. Atmospheric oxidation changed the colors according to the color scheme of the core photographed in the lab (left column in Fig. 4 and the description in the figure caption). In general, the drilled sediments include two parts: sapropelic in the interval of 0–220 cm and silty and clayey 220–574 cm.

Ash content (middle column in Fig. 4) indicates content of the organic matter in the sediments. According to the classification basing on proportion of ash content (Korde, 1960; see caption for Fig. 4), the sediments are organic and organic-mineral in the upper 187 cm, mineral-organic in the 187–260 cm interval and mineral below.

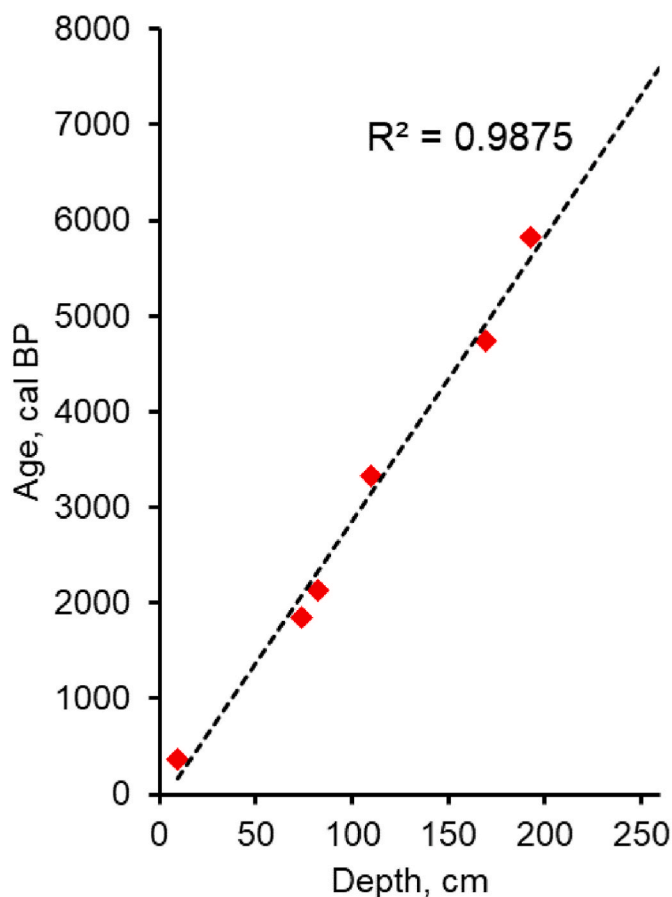
In the sapropelic part of the sediments the organic matter mostly originates from phytoplankton (see Section 3.1). Green algae seemingly are its main source. The diatom frustules and their residues are observable in the sapropel and are absent in the mineral part of the core. Kurzo et al. (2012) outlined that this type of sapropel can be used as a component of drilling fluids, healing mud, soil improver, animal feed additive, and fertilizer. The organic matter holds huge amount of water, content of which is about 95% in the upper 2 m; then it gradually decreases to 10% towards the bottom of the core.

Radiocarbon dates were obtained for the organic-rich part of the core

**Table 2**

Results of radiocarbon dating of the Lake Dukhovoe sediments and their calibrated ages.

Sampling interval, cm	<sup>14</sup> C age, yrs	Calibrated age interval	Calib. age median probability
7–11	280 ± 40	282–465	370
57–62	710 ± 35	638–704	668
71–76	1905 ± 45	1725–1944	1849
80–85	2140 ± 45	1998–2306	2130
108–112	3120 ± 45	3219–3413	3334
167–172	4220 ± 50	4608–4863	4739
190–195	5090 ± 65	5661–5941	5821



**Fig. 5.** Age to depth plot for the upper 260 cm of the Lake Dukhovoe core based on the calibrated radiocarbon dates. Red rhombuses show the reliable dates. Dashed line shows the trend line used as the age model. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

in the interval of 0–200 cm (Table 2). Samples collected from the lower part of the core contained small amount of the organic matter below requirements of the applied dating method. According to the age-depth plot (Fig. 5), the calibrated dates fit the reliably approximating linear trend except of the date from the depth of 57–62 cm which, by unknown reason, is considerably younger and should be excluded from the set as a mistake. The trend line indicates the 5.5 ka BP age for the boundary between the organic rich and mineral-organic layers at 187 cm depth and 7.7 ka BP for the boundary between the mineral-organic and mineral layers at 260 cm depth and the age approaches 10 ka BP in the depth

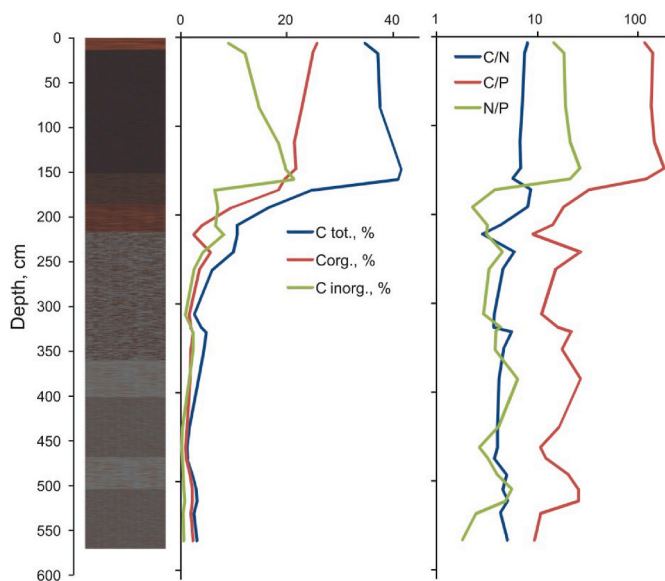


Fig. 6. Distribution of carbon and variations in the C/N, C/P and N/P ratio within the sediment of Lake Dukhovoe.

of 325 cm. Therefore, the age data for the Dukhovoe Lake coincide the literature data about accumulation of sapropels in modern lakes during the Holocene (Khazina, 2006; Bezrukova et al., 2008, 2011; Blyakharchuk, 2003; Krivonogov et al., 2012a, 2012b). Lake Dukhovoe was formed on a mineral substrate in a humid and warm climate (Bezrukova et al., 2008, 2011; Shichi et al., 2009). We suggest that the bottom of the lake sediment is at the 325 cm boundary (Maltsev et al., 2014) as it shows considerable changes in the sorting of the sediment matrix (Fig. 4). During the entire Atlantic period of 6–9 ka BP, predominantly mineral sediments were accumulated in the lake. The 325–260 cm interval can be considering as the basal layer representing the early stage of the lake evolution lacked of biogenic sedimentation. These deposits are composed of illite, chlorite, plagioclase, and quartz; accessory minerals are K-feldspar and amphibole. It is known (Sklyarov et al., 2008), that the predominance of illite in the mineral composition of sediments in this region is a characteristic of a warm and humid climate. Further, there was an accumulation of mineral-organic sediments in the 187–260 cm, which were replaced by organic-mineral sediments (172–187 cm) about 5 ka BP. The mineral composition of organic-mineral sediments does not differ from the underlying mineral-organic sediments, the only difference is the presence of gypsum in trace amounts and a significant decrease in the ash content (Fig. 4). The last ~5 ka BP is characterized by sustained conditions of sedimentogenesis throughout the entire length of sapropel formation in the interval of 0–172 cm, as evidenced by a homogeneous mineral composition and fairly consistent ash content throughout the depth of the section. The organic sediments are composed of mica (very disordered), chlorite, plagioclase, and quartz; accessory minerals are K-feldspar and amphibole. The above 260–187 and 187–0 cm intervals both having diatoms and showing a step-like increase of the amount of the organic matter represent further biota-rich stages of the lake history. There was an increase in the continentality of the climate, climatic cooling, and a decrease in atmospheric moisture (aridization trend) in the region for the time period of 4.5–6.5 ka BP (Tarasov et al., 2009). Then later 4.5 ka BP, temperate cold climate, close to the modern climate, was dominated (Tarasov et al., 2009). The decrease in climate humidity led to a decrease in the level of lake water, an increase of the bioproductivity of the lake ecosystem, the accumulation of organogenic sediments, and change in the mineral composition, to the predominance of mica over all other minerals and the disappearance of illite. Approximately 0.7 ka BP, there was a trend towards an increase in the

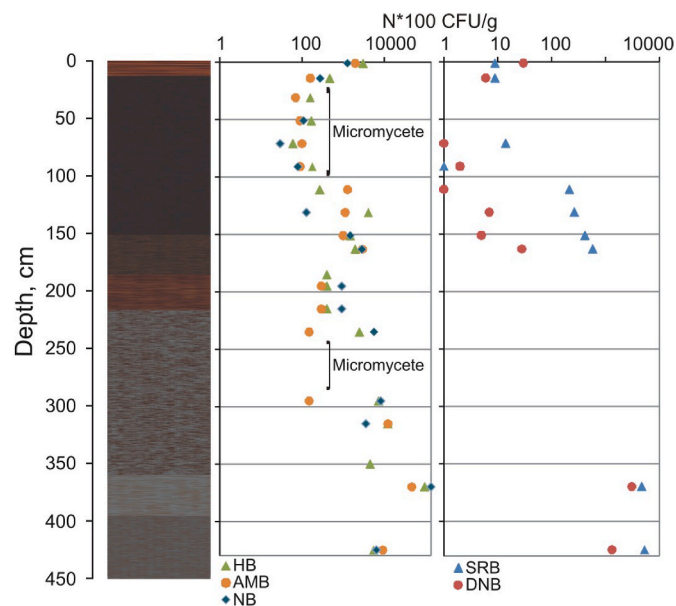


Fig. 7. Distribution of total cell concentrations of microbial populations in the sediment of Lake Dukhovoe. N - total cell concentration (CFU/g); HB - heterotrophic bacteria; AMB - ammonifying bacteria, NB - nitrifying bacteria, SRB - sulphate-reducing bacteria, DNB - denitrifying bacteria.

level of lake waters, expressed in a slight increase in ash and quartz contents, which may indicate an increase in the input of terrigenous components into the lake through the surface runoff and atmospheric transport. The sedimentation rate in Lake Dukhovoe averages to 0.3 mm per year.

### 3.2.2. Carbon and other biologically important elements in the sediments

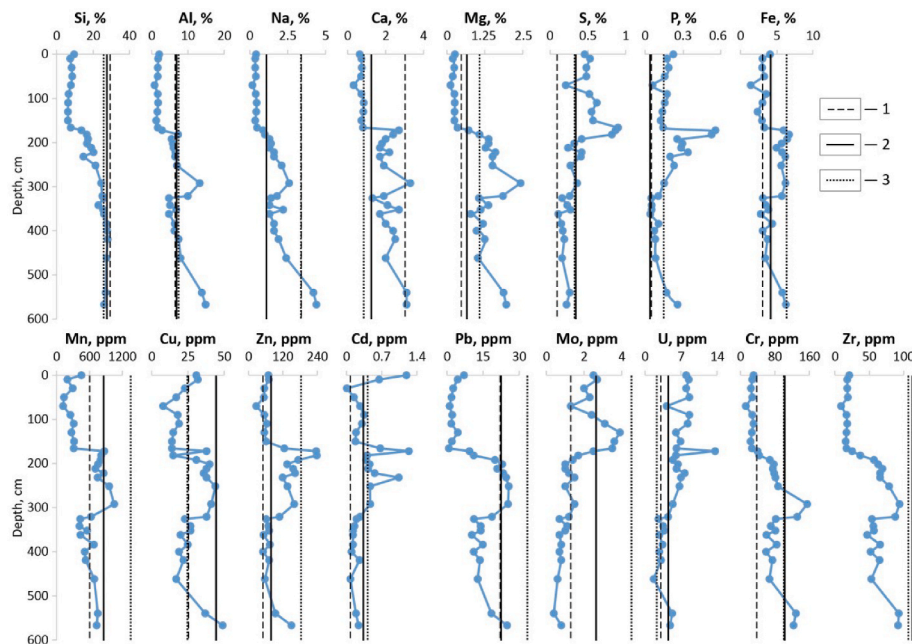
The content of organic carbon is high (up to 22 wt%) at the top sediment layers, sharply reducing in the interval of 170–190 cm and then smoothly decreasing to 2% with depth (Fig. 6). Concentrations of organic and inorganic carbon are similar in the lower mineral and mineral-organic parts of the core and considerably divorce in the upper part above the 170 cm depth: organic carbon rises upon the inorganic one.

As it was mentioned above, the C, N, and P inter-ratios help us to identify genesis of the organic matter in the sediments through proportions of terrestrial and lacustrine organic matter. The ratios considerably range along the core: C/N from 3.6 to 8.1, C/P from 9 to 110, and N/P from 3 to 21. A sizeable increase of values occurs near the sapropel boundary at ca. 180 cm. The C/N, C/P and N/P ratios correlate well with those ratios identified for plankton (Redfield, 1934; Harvey, 1948; Votintsev, 1961; Redfield et al., 1963; Healey and Hendzel, 1980; Duarte, 1992; Burkhardt et al., 1999). Therefore, plankton can be considered as a main source of organic matter of the Lake Dukhovoe sapropel. In the mineral part of the lake sediments, the C/N, C/P and N/P ratios indicate difference between organic and mineral sedimentation, which lacked organic part can be due to a release of C as carbon dioxide and bicarbonate (precipitated to carbonates), a release of N as nitrate and P as phosphate phases. The values of  $C_{tot}$ ,  $C_{org}$ ,  $C_{inorg}$  and the ratios C/N, C/P, N/P increase from the bottom upwards to the top horizons of bottom sediments (Fig. 6).

### 3.2.3. Microorganisms

Fig. 7 shows distribution of total cell concentrations (TCC) of microbial populations in the Lake Dukhovoe sediments. The distributions of heterotrophic bacteria (HB), ammonifying bacteria (AMB) and nitrifying bacteria (NB) are quite similar generally showing gradual increase of their TCC with depth. The bacterial TCC are low in the 30–90 cm





**Fig. 8.** Distribution of the total element concentrations in the sediments of Lake Dukhovoe. 1 - Upper Continental Crust (Taylor and McLennan, 1995); 2 - Shale (Li, 1991); 3 - Oceanic pelagic clays (Li, 1991).

interval as micromycetes and actinomycetes are dominant there; the proportion changes to the bottom of the sapropel layer. High concentrations of heterotrophic bacteria as well as micromycetes and actinomycetes in the upper part of the sapropel indicate intensive transformation of the organic matter and the dominance of filamentous forms of microorganisms (fungi and actinomycetes) can be explained by presence of a hardly decomposable organic matter. Heterotrophic bacteria require organic compounds as a carbon source and have been indicated as the main decomposers of organic matter in the aquatic sediments with the most of the heterotrophic bacteria activity occurred in the upper sediment layers (den Hayer and Kalff, 1998; Wetzel, 2001). Although, depending on the sapropel composition and geochemical environments, these microorganisms can form complex assemblages consisting of many taxonomic groups. The contents of sulphate-reducing bacteria (SRB) and denitrifying bacteria (DNB) are low in the upper part of the sapropel and considerably increases downcore (Fig. 7). Those bacteria usually dominate in easily decomposable organic substances.

Distribution of ammonifying, nitrifying and denitrifying bacteria, participating in the nitrogen cycle (Hayatsu et al., 2008; Kirchner, 2018) reveals stages of organic matter decomposition. For instance, ammonifying bacteria are involved in the first stage of decomposition of nitrogen-bearing organic matter. The main products of the ammonifying bacteria activity are ammonium ions and carbon dioxide (Kirchner, 2018). Then AMB give place to nitrifying bacteria involving in sequential nitrification accompanied by oxidation of the nitrogen ions to nitrites and then to nitrates (Kim and Gadd, 2008). At anaerobic condition, denitrifying bacteria are involved to denitrification as a part of the nitrogen cycle, where these bacteria utilize nitrate and produce nitrogen through a series of intermediate gaseous nitrogen oxide products (Bothe et al., 2006). Nitrogen is formed at the final stage of the nitrogen cycle and can also be metabolized by nitrogen-fixing microorganisms, or simply released to the atmosphere. The increase of TCC of the sulphate-reducing and denitrifying bacteria with depth in the Lake Dukhovoe sapropel reflects changes in intensity of anaerobic denitrification and sulphate reduction. The dependence of the intensity of sulphate reduction processes on the degree of destruction and availability of organic matter is well described in the literature (Trudinger et al., 1972; Zehnder and Brock, 1980; Mitterer, 2010), where it is shown that sulphate-reducing bacteria are able to utilize only relatively low

molecular weight organic matter such as acetate, lactate, volatile fatty acids, and pyruvate. Therefore, in natural environments, sulphate reduction requires preliminary partial degradation of complex organic molecules by oxidative and enzymatic reactions catalyzed by other microorganisms, for example, heterotrophs.

#### 3.2.4. Total element concentration

The total element concentrations in the sapropel and mineral silt of Lake Dukhovoe are summarised in Fig. 8 along with the average element concentrations in the Earth Crust, shale and oceanic pelagic clays (Taylor and McLennan, 1995; Li, 1991).

The Si concentration in the Lake Dukhovoe sediments decreases from the top to the depth of 166 cm and then gradually increases bottomward. The Si concentration in the sapropel does not exceed the average element concentrations of the Earth Crust, shale and oceanic pelagic clays (Taylor and McLennan, 1995; Li, 1991). The distributions of Al, Na, Ca, Mg, Zr, and Cr along the core are similar to Si. Their concentrations are quite constant in the 0–166 cm interval and then they increase to the bottom forming several maxima. The similar distribution of lithophile elements in the sapropel indicate that they are mostly from a terrigenous source. Fe and Mn concentrate at the top (0–10 cm), middle (172–321 cm) and bottom (540–567 cm) parts of the sediment section. S and P are considerably enriched in the sapropel, their concentrations exceed the average element concentrations in the Earth Crust, shale and oceanic pelagic clays (Taylor and McLennan, 1995; Li, 1991). The highest S and P concentrations are found in the layer of 168–182 cm. P is one of the main biologically required element which participate in physiological process in phytoplankton (Bristow et al., 2017). S is a biologically important for synthesis of polypeptides, proteins, and enzymes in phytoplankton. As discussed above, phytoplankton can be considered as a main source of sapropel forming organic matter and also some biologically required and important elements such as P and S in the Lake Dukhovoe sapropel. U and Mo have similar distribution and are also enriched in the sapropel. The U concentration exceeds the average element concentrations in the Earth Crust, shale and oceanic pelagic clays as well. U can be accumulated by phytoplankton as was discussed in Section 3.1. Strakhovenko et al. (2014) also identified U accumulation in the sapropel sediments of small lakes in the Ob'–Irtys interfluvium. The distributions of Zn, Cd, Pb, and Cu concentrations are similar. These elements are enriched in the upper 10



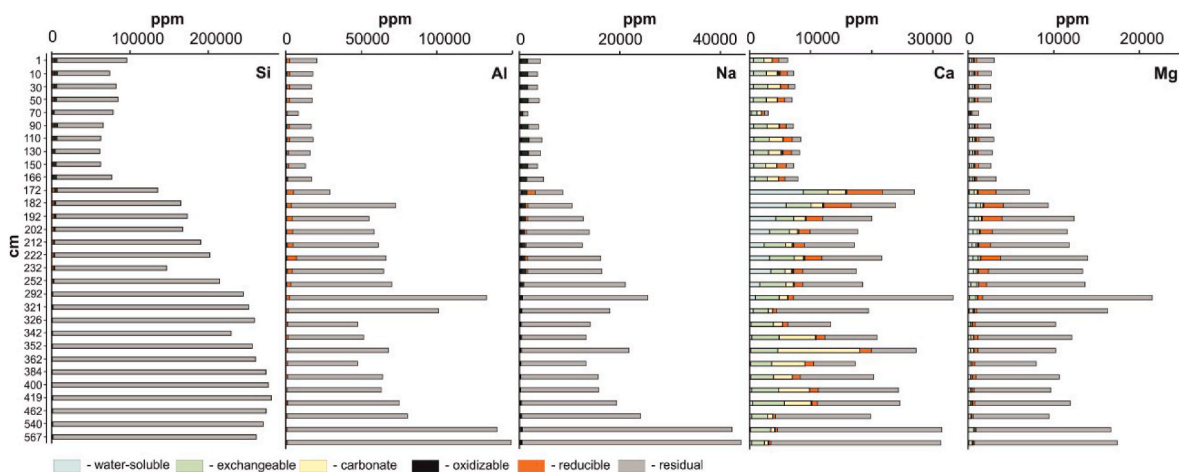


Fig. 9. Si, Al, Na, Ca, Mg speciation within the sediment of Lake Dukhovoe.

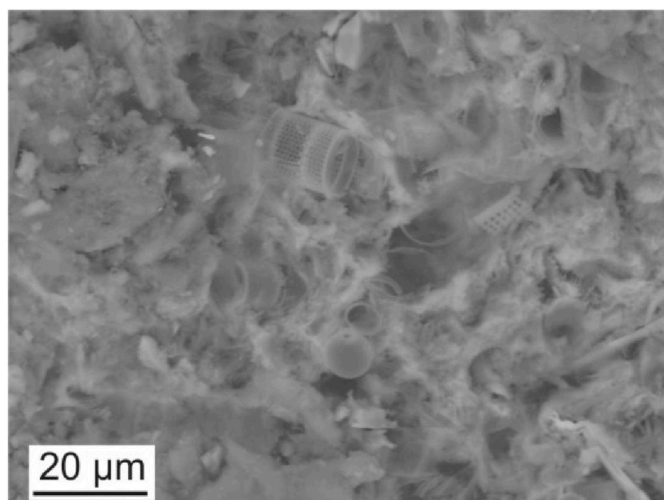


Fig. 10. Debris of diatoms (SEM image) in the upper layers of the Lake Dukhovoe sapropel.

cm which can be explained by forest fires and technogenic pollution (Vetrov and Kuznetsova, 1997; Obolkin et al., 2004; Khodzher, 2005; Voronin, 2005; Granina, 2008). Additionally, high concentrations of Zn, Cd, Pb, and Cu occur in the 170–320 cm interval and (excluding Cd) at the bottom of the sediment section.

3.2.5. Element speciation

Si, Al, Mg and Na are mainly stored in the mineral part (terrigenous clastic materials) of the lake sediments, e.g. in chlorite, plagioclase, quartz, K-feldspar, and amphibole that are present in the sediment core; illite - below 172 cm; and mica (very disordered) – above 172 cm (see section 3.2.1; Fig. 9). In the sediment interval of 0–260 cm, some part of Si can be biogenic due to presence of diatom frustules and debris which consist of amorphous silica (Fig. 10). Also, in the upper layers, Si and Na are associated with the organic matter, for example, present in the tissues of microorganisms, and forming organic-mineral complex (e.g., amorphous Si - organic matter) (Fig. 9). Ca is presented in different forms such as water-soluble, exchangeable, carbonate, associates with organic matter, and residual. Ca can be both biogenic (mainly in upper layers) and terrigenous (mainly below 2 m – high content of residual form). Gypsum was identified in the depth of 172–187 cm that is consistent with data from sequential extraction procedure.

P is enriched in the sapropel and is mainly present as authigenic phosphates (Fig. 11; see section 3.2.2). Also, some P is associated with

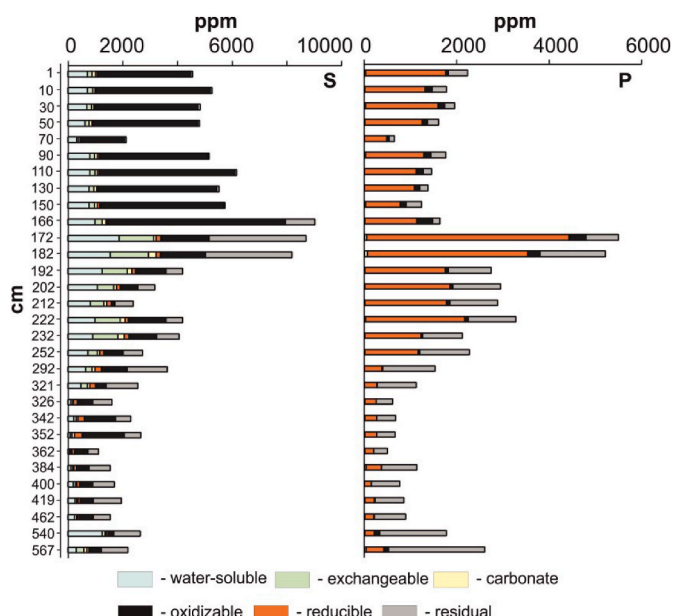


Fig. 11. S and P speciation within the sediment of Lake Dukhovoe.

the organic matter, especially in the upper 2 m of the sediments, where P is present as a constituent element in the organic matter (e.g. residues of biota such as phytoplankton (see section 3.1)). Mineralization of the organic matter causes release of phosphorus, which then is accumulating in authigenic P-bearing minerals, such as powder-like vivianite (Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·8(H<sub>2</sub>O)) (in the interval 166–187 cm), formed under reducing conditions (Fig. 12). Kurzo et al. (2012) also identified vivianite formation in the sapropel of the Lake Pribylovichi (Belarus). The P accumulation in sapropel makes it a valuable raw material to produce fertilizers (Kurzo et al., 2012).

S is concentrated in the sapropel and is presented in different forms: water-soluble and exchangeable (mainly gypsum), oxidizable (associated with organic matter and some sulfides), and residual (sulfides) (Fig. 11). In the upper layers (0–166 cm), S is mainly presented as an essential constituent of biomass (e.g. residues of phytoplankton that is enriched with major biologically required elements including S (see section 3.1 and Fig. 3)). Mineralization of the organic matter causes release of S, which then is accumulated as gypsum. Gypsum was identified by XRD in the layer of 172–187 cm, that is correlated with results from the sequential extraction procedure for S and Ca (Figs. 9 and 11). Maltsev et al. (2014) showed that the pore water from the upper layers

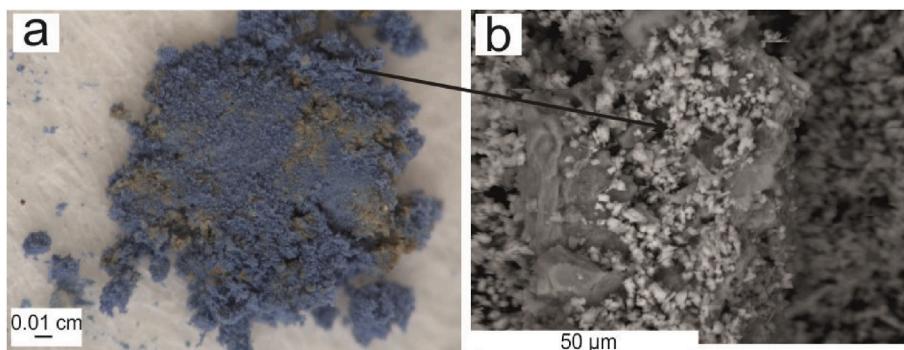


Fig. 12. Powder-like vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$ ) from the interval of 166–187 cm: a) image under binocular; b) SEM image.

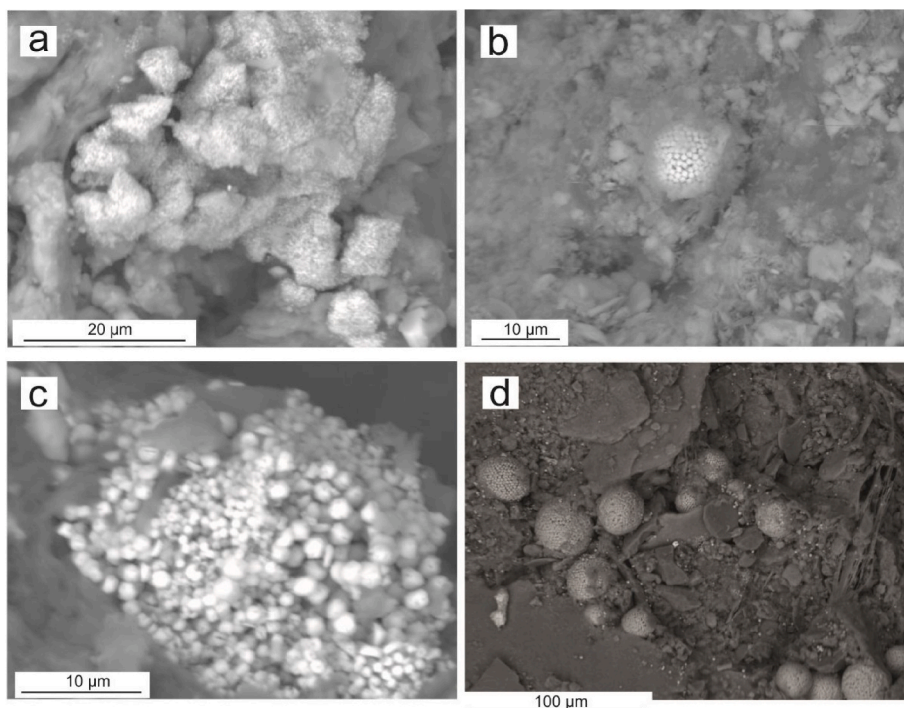


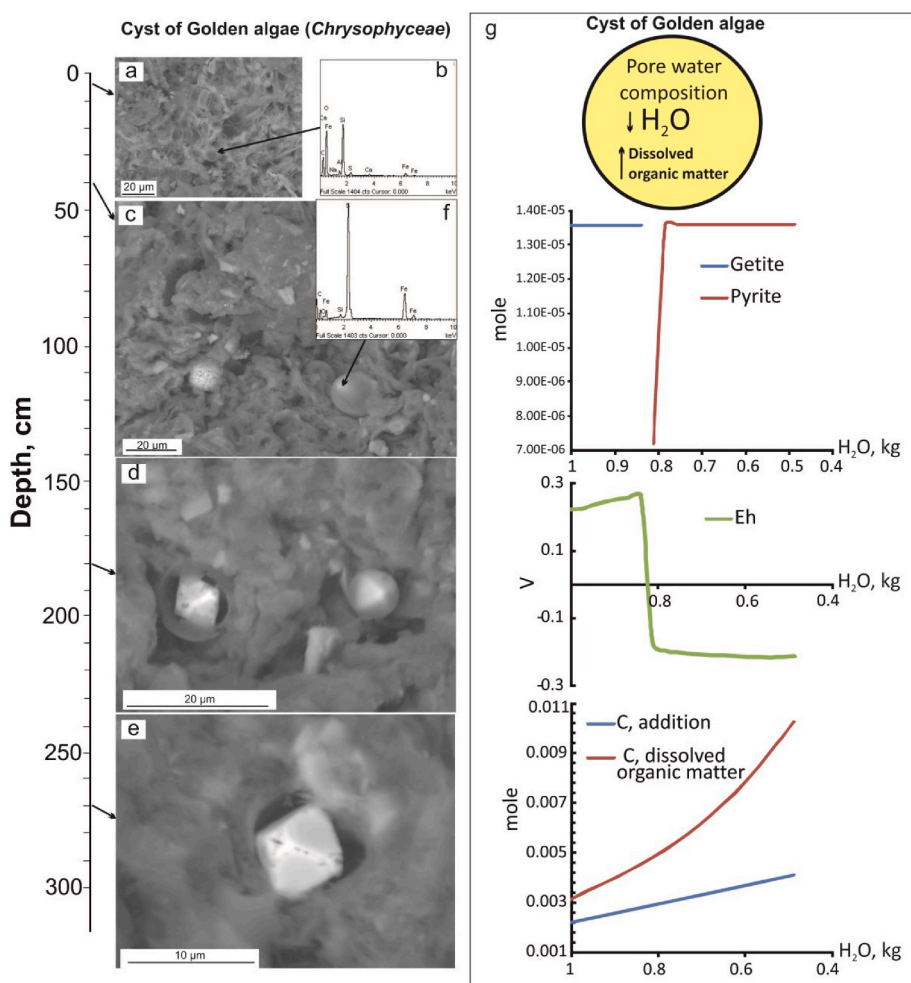
Fig. 13. Fe-bearing phases within the sediment of Lake Dukhovoe: a) SEM image of Fe oxy-hydroxides in the organic matter (0–50 cm); b) SEM image of framboidal pyrite in the organic matter (166–172 cm); c) SEM image of framboidal pyrite in the organic matter (172–200 cm); d) SEM image of framboidal pyrite below 200 cm.

( $\text{HCO}_3\text{-SO}_4\text{-Ca-Mg-Na}$  type) transformed to the  $\text{SO}_4\text{-HCO}_3\text{-Ca-Mg}$  and even to  $\text{SO}_4\text{-Ca-Mg}$  types in the lower layers of the organic sapropel. The transformation in the porewater composition in sapropel is due to diagenetic processes such as decomposition of the sapropel matrix (e.g. physicochemical and biological processes) and release of elements from sapropel to the pore water. Significant concentration of sulphate ions in the sapropel pore water comparing to the lake water most likely is associated with intensive decomposition of organic-mineral substances (e.g., decomposition of organic matter) and possible input of sulphate-bearing ground waters which are present in this area (Granina, 2008). The role of sulfides increases with depth, mainly below 166 cm, where framboidal pyrite is common (Fig. 13).

Fe is mainly presented in form of oxy-hydroxides and associates with the organic matter in the upper layers; lower, in the reduction zone, framboidal pyrite is abundant (Fig. 13). The content of iron sulfides such as pyrite, identified by SEM, increases with depth which is also confirmed by distribution and speciation of S in the sapropel: 90% of S are concentrated in sulfides (Fig. 11).

We established a very interesting and unique fact of biomineral formation in the sapropel of Lake Duchovoe. The octahedral crystals of

iron sulfide (probably marcasite) with a size about 5–15 μm were identified in the plain spherical capsules (Fig. 14). These capsules are the cysts (stomatocysts) of Chrysophyte algae (*Chrysophyceae*), also known as golden algae, which is spherical with smooth siliceous structure and the wall of the cyst consists of Al, Ca, S, Fe, and Na as impurities (Fig. 14a&b). Chrysophyte algae, belonged to *Chrysophyceae* and *Synurophyceae* classes (Yang et al., 2012; Škaloud et al., 2013), inhabit mainly in fresh oligotrophic water and may be used as indicators of changes in water quality and for paleoecological studies (Cronberg, 1986; Betts-Piper et al., 2004; Kristiansen, 2005; Firsova et al., 2008; Bai et al., 2021). Chrysophyte algae produces siliceous resting stages called stomatocysts (Piatek and Piatek, 2014). Many works concerning the investigation of Chrysophyte algae are about morphology, diversity, ultrastructure and taxonomy (Sandgren et al., 1995; Wilkinson et al., 2001; Piatek and Piatek, 2014) but not many relate to biomineralization. Only some aspects of biomineralization in the Chrysophyte were investigated, for example, silica deposits in stomatocysts, iron and manganese mineralized material occurred in the brown-colored stalks of *Anthophysa Vegetans*, the brown-colored loricae of pseudokephyrion pseudospiral, the gelatinous holdfasts of phaeothamnion articulate and



**Fig. 14.** Formation of marcasite in the cyst of Golden algae (*Chrysophyceae*): a) SEM image of the spherical cyst of Golden algae; b) EDS spectrum of elemental composition of the cyst; c) SEM image of a small crystal of marcasite in the cyst of Golden algae; d) SEM image of a single marcasite crystal in the cyst of Golden algae; e) SEM image of a marcasite crystal in the remaining of the cyst of Golden algae; f) EDS spectrum of elemental composition of marcasite; g) geochemical equilibrium modelling of the iron sulfide formation in the cysts of Golden algae under aging condition. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

calcareous deposits (Preisig, 1986 and 1994; Leadbeater and Barker, 1995; Sandgren et al., 1995). The cyst of golden algae from the sapropel of Lake Duchovoe has a single pore which can be sealed by an organic plug containing little or no silica. *Chrysophyceae* stomatocysts are abundant in the sapropel of Lake Dukhovoe in the upper 2 m. Only one well crystallized octahedral crystal of iron sulfide was formed inside the cyst and occupied the whole space (Fig. 14c, d, f). Moreover, crystal of iron sulfide began to form in the cyst in the top layers of the sapropel where there is an oxidizable condition which is unusual for iron sulfide formation. Also, sulphate-reducing bacteria, which play important role in iron sulfide formation (particularly in bottom layers of the Lake Dukhovoe sapropel), were detected in low content in the upper part of the sapropel (Fig. 7). It could be considered that the cyst of Chrysophyte algae is a “microreactor” in which favourable conditions for iron sulfide formation are created. Fig. 14d shows that the cysts are destroyed under pressure and changing physicochemical condition within the depth and marcasite crystals are released in the environment. Also, it is quite important, that in the bottom layers under reducible condition we observed only framboidal pyrite which mainly induced by sulphate-reducing bacteria (Duverger et al., 2020) dominated at the bottom of the sapropel (Fig. 7).

More detailed interpretations of the iron sulfide formation in the cysts of Chrysophyte algae under aging condition were made possible using geochemical equilibrium modelling with SELECTOR-C software (Karpov, 1981; Karpov et al., 1997) (Fig. 14g). The following input data and condition were used for a simple model: 1) pore water composition from the upper layers of the sapropel was used for inside cyst solution; 2) simulation of aging process - dewatering process (e.g., gradual decrease

of water content) and organic matter mineralization inside the cyst (e.g., gradual increase of organic matter content ( $\text{CH}_2\text{O}$  from 0.0008 to 0.0015 mol)). It was shown, that Eh sharply changed from oxidizable to reducible under dewatering at about 18%. Getite was formed under oxidizable condition but pyrite started forming under reducible condition.

The trace elements, such as Zn, Pb and U, are also enriched in the sapropel (Fig. 15). The high concentrations of Cd, Cu, Pb, Mo, and Zn in the upper 2 cm layer of the sapropel can be explained by environmental pollution from the nearby road. Cu is mainly associated with the organic matter in the upper 167 cm. Zn is presented in different forms such as water-soluble, exchangeable, carbonate and associates with the organic matter and sulfides. Also, Pb is presented in the carbonate fraction in several layers as cerussite ( $\text{PbCO}_3$ ) and/or anglesite ( $\text{PbSO}_4$ ). Content of the sulfide species for Cu, Zn and Pb increases with depth where SRB are also dominated and can play an important role for the formation of metal sulfides. U prevails in carbonate species and is associated with the organic matter in the upper 167 cm interval, lower a portion of the U phosphate species increases.

Gold is concentrated in the depth of 2–3.5 m (18–51 mg/t) and is mainly presented in the native state (70–85%). Also, 1–3  $\mu\text{m}$  micro-particles of native gold were found in the sapropel. Minor portion of Au is associated with the organic matter or/and sulfide (20–30%) and with iron hydroxide (2–5%).

#### 4. Conclusions

Our study revealed the biogeochemical features of Lake Dukhovoe



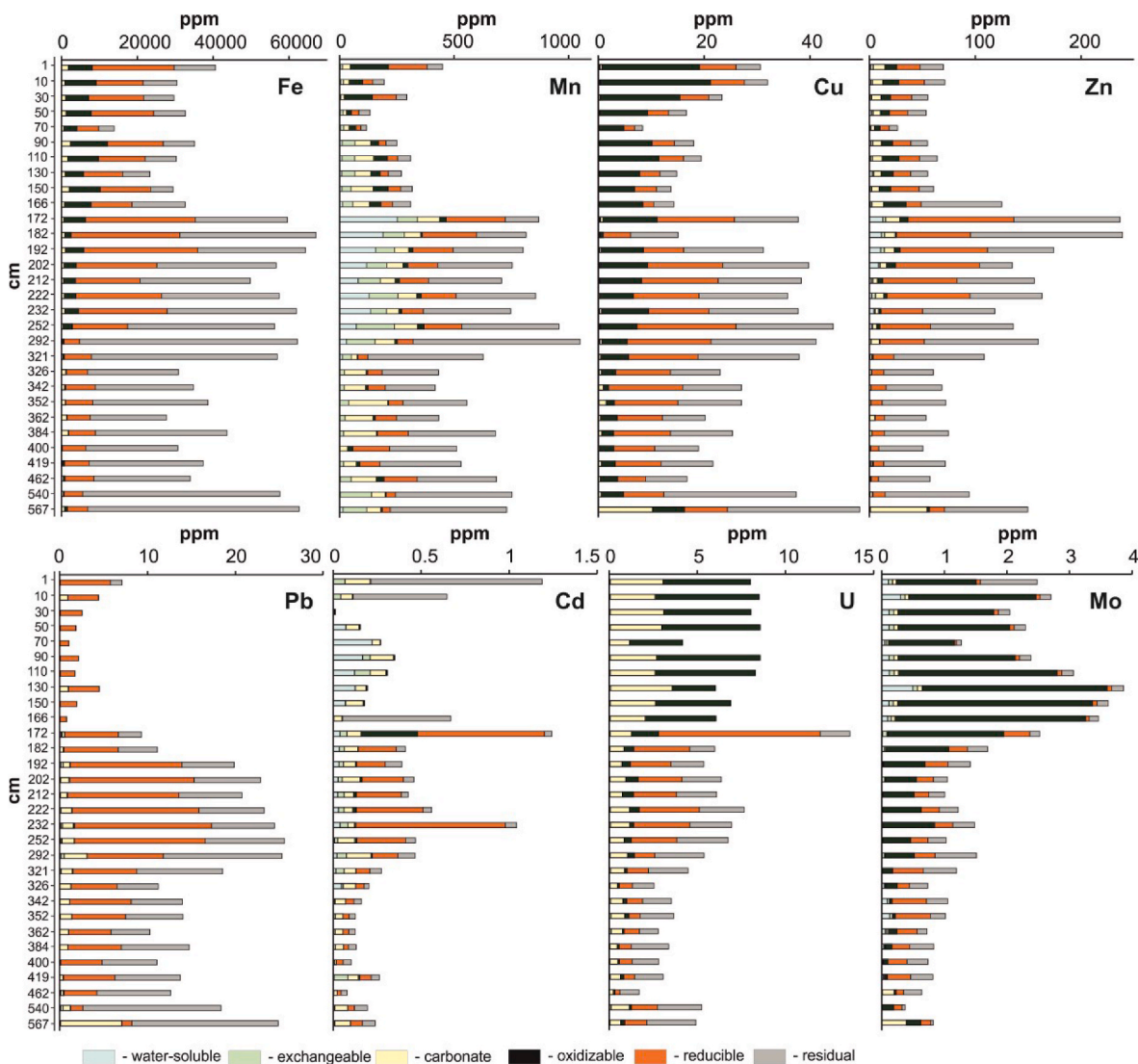


Fig. 15. Fe, Mn, Cu, Zn, Pb, Cd, U, Mo speciation within the sediment of Lake Dukhovoe.

biota and sediments, and resulted in the following peculiarities and regularities of the chemical elements distribution, speciation and interaction.

1. Phytoplankton is the main source of organic matter for the Lake Dukhovoe sapropel and has several biogeochemical functions: transport, concentration and barrier for the elements, as described by Vernadsky (1965), and acts as a significant factor of the lake environment. Phytoplankton can be considered as a biogeochemical barrier where major and trace elements can be accumulated. The enrichment factors of C org, P, S, Fe, Cu, Zn, Mo, Cd, Sb, Hg, and U for the plankton and the top 2 cm layer of sapropel are in agreement with the “model of direct inheritance” proposed by Yudovich and Ketris (1990).
2. Lake Dukhovoe with sapropel sediments was formed on a mineral substrate in a humid and warm climate about 10 ka BP in the depth of 325 cm. The sapropelic sediments was classified as: organic and organic-mineral sapropel in the upper 187 cm; mineral-organic sapropel in the 187–260 cm interval; and mineral below 260 cm.
3. The oxidation and reduction environment and corresponding types of diagenesis are inherent to the sapropel above and below the depth of 167 cm, respectively. The oxidation process is characteristic of the following lake and sediment properties: 1) shallow 2–3 m deep lake;

- 2) high, about 90%, watering of the sapropel; 3) high, +310 V, Eh of the pore water of the top layers; 4) abundant aerobic heterotrophic ammonifying and nitrifying bacteria; 5) abundant micromycetes; 6) formation of indicative solid phases, e.g., Fe oxide/hydroxide. The reduction process is characteristic of the following sediment properties: 1) abundant anaerobic denitrifying and sulphate-reducing bacteria; 2) formation of indicative solid phases, e.g., sulphides and vivianite.
4. Microorganisms such as bacteria, micromycete and actinomycetes play significant role in decomposition of organic matter (mainly originated from phytoplankton) of sapropel, formation of organic-mineral complexes and in circulation of chemical elements in the sapropel. The total cell concentration of the sulphate-reducing and denitrifying bacteria increases with depth and reflects the intensity of anaerobic denitrification and sulphate reduction.
5. Various mechanical, microbiological, and physicochemical processes in the sapropel lead to the formation of the geochemical barriers. The most important barrier, where S, P, Fe, Mn, Cu, Zn, Pb, Cd, and U are enriched, occurs in the horizon of 172–182 cm and performs transition from oxidation to reduction.
6. Si, Al, Mg and Na are mainly stored in the mineral part (terrigenous clastic materials) of the lake sediments, e.g. in chlorite, illite, mica, plagioclase, quartz, K-feldspar, and amphibole. Some part of Si in the



sapropel can be biogenic due to presence of diatom frustules and debris which consist of amorphous silica. Also, in the upper layers, Si and Na are associated with the organic matter, for example, tissues of microorganisms, and in the form of organic-mineral complex (e.g., amorphous Si - organic matter).

- The contents of Fe, Mn, Cu, Zn, Pb, Cd, and Mo are high in the upper 10 cm layer accumulated during the last 280 years which can be resulted from the environmental pollution. The sources of pollution are motor transport and forest fires in the last 100 years and forest fires in the earlier times.
- P, S and Fe are biologically required elements for phytoplankton and are inreached in it. Therefore, P, S, and Fe are biogenic elements in the sapropel. Mineralization (mainly microbiological) of the sapropel organic matter causes release of those elements, which then are accumulated as sulfides (e.g. marcasite, framboidal pyrite); sulphates (e.g. gypsum); Fe oxy-hydroxides; and authigenic P-bearing minerals, such as powder-like vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$ ) in different sapropel layers.
- Cu, U, and Mo are mainly associated with the organic matter. Zn is presented in different forms such as water-soluble, exchangeable, carbonate, associates with organic matter and sulfides. Pb was mainly extracted in the reducible fraction, suggesting that Pb precipitated with iron oxy-hydroxides. The role of sulfide species for Cu, Zn and Pb increases with depth. U prevails in carbonate form and is associated with organic matter in the upper 170 cm, below a portion of the U phosphate species increases. Gold was concentrated at the depth of 2–3.5 m (18–51 mg/t) and is mainly in native state.
- The fact of marcasite formation in the stomatocysts of Chrysophyte algae (golden algae) is new and was established for the first time. Based on the results and geochemical equilibrium modelling, the stomatocysts of Chrysophyte algae can be considered as a micro-reactor for iron sulfide formation.

#### CRedit author statement

Bogush A.A.: conceptualization, methodology, investigation, elemental speciation, writing and original draft preparation; Leonova G. A.: sampling, investigation, reviewing; Krivonogov S.K.: radiocarbon dating analysis, reviewing and editing; Bychinsky V.A.: modelling; Bobrov V.A.: investigation, reviewing and editing; Maltsev A.E.: sampling, investigation; Tikhova V.D.: CHNS analyser, investigation; Mir-shnichenko L.V.: XRD analysis, investigation; Kondratyeva L.M.: characterisation of microbial communities, investigation; Kuzmina A.E.: phytoplankton composition, investigation.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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