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Geochemistry and Mineralogy of Organic-Mineral Bottom Sediment of Small Lakes in the Middle Mountains of the Russian Altai: A Case Study of the Chibitka Lake System

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Abstract: The article introduces the first geochemical and mineralogical data regarding the organic-mineral bottom sediment in the small middle mountain lakes (Chibitka Lake system, Russian Altai). The lacustrine sediments are sapropel and mineral silt, which are formed in the nival type of lithogenesis (cryolithogenesis). Sapropel is categorized into three types based on ash content (A, %): organic-mineral (42–46), mineral-organic (66), and mineralized (81) and primarily belongs to the silicon class and macrophytic species. The bottom sediment geochemistry is impacted by cryolithogenesis processes, reflecting the composition of the soil-forming substrate and the soils within the catchment area. Based on an initial assessment of heavy metals (mg/kg) – Cd (0.044–0.159), Pb (7–34), Hg (0.047–0.197), trace elements (mg/kg) – Cu (26–71), Mn (0.03–0.04), Cr (56–83), Co (7–13), Ni (34–52), technogenic ^{137}Cs (32–154 Bq/kg) and the total effective specific activity of natural radionuclides (A_c – 5.5–14.8 Bq/kg), sapropels belong to the first class of suitability in accordance with GOST (the Russian interstate system of technical standards). The presence of authigenic low-Mg calcite, gypsum, and halite has been identified in the bottom sediment of freshwater Lake Biryuzovoe. The formation of these minerals is a result of various factors influenced by the cryolithogenesis, such as shallow depth, ice thickness, cryogenic concentration, and HCO_3–Ca water composition with a high SO_4 content.

Keywords: sapropel, small lakes, nival type of lithogenesis, authigenic minerals, Russian Altai.

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Research Article

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Introduction

The Altai Mountains comprise a mountain system in the southern region of Western Siberia and Central Asia on the border of Russia, Mongolia, China and Kazakhstan. This system consists of both high and mid-mountain ranges, which are separated by deep river valleys and expansive intramountain basins. There are approximately 7000 lakes, possessing a water surface area of 600 km^2.

Lakes are the ultimate reservoirs of runoff and their bottom sediments become natural archives for reconstructing the history of the lake and its catchment area. Small lakes also function as modern natural laboratories, influenced by both natural and anthropogenic agents, with a close interplay between biotic and abiotic factors [*Last and Ginn*, 2005; *Ovdina et al.*, 2020; *Solotchina et al.*, 2021].

Contemporary researches on lakes in the Altai Mountains and other mid- and high-altitude systems focus mostly on biota activity, hydrology, and climate paleoreconstructions. However, the geochemistry and mineralogy of the sedimentary process are not often considered in detail [*Ran et al.*, 2015; *Rudaya et al.*, 2009].

Lacustrine sediments as well are a prospective mineral resource. Moreover, the studying of small lakes serves the important geoecological purpose of establishing scientific principles for the sustainable utilization, conservation, and regulation of water resources [*Slukovskii and Dauvalter*, 2020; *Vincevica-Gaile and Stankevica*, 2017].

For the first time we have established that, the bottom sediments of the Chibitka Lake system are sapropel and mineral silt. Sapropel (gyttja, dy) is an organic-mineral bottom sediment formed under anaerobic conditions as a result of chemical, biochemical, microbiological and mechanical processes from the remains of biota, organic and mineral impurities [*Stein*, 2016; *Strakhovenko et al.*, 2019].

Sapropel exemplify a renewable resource of non-metallic minerals, thus enabling their extraction and processing in the long term. The examination of the geochemistry and mineralogy of sapropels is imperative for further assessment of raw materials [*Shtin*, 2005; *Strakhovenko et al.*, 2019]. The customary utilization of sapropel is associated with agriculture as easily accessible fertilizer, containing a wide array of organic substances [*Sartakov et al.*, 2019]. By additional intricate processing, sapropel can be used in fields such as metallurgy, medicine, ecology, and so on [*Shtin*, 2005; *Vincevica-Gaile and Stankevica*, 2017].

According to *Strakhov* [1960], there are four main types of lithogenesis – humid, arid, nival and volcanogenic-sedimentary. The humid type correlates with the zone of intensive sapropel accumulation in the taiga and forest-steppe landscape [*Shtin*, 2005]. The examples are numerous small lakes of the Vasyugan plain and the Baraba lowland [*Ovdina et al.*, 2020]. Under these conditions, the bottom sediment can accumulate in various proportions through biogenic, chemogenic, and physical processes. In the arid type, brackish sapropel and mineral silt are most common type of bottom sediment [*Shtin*, 2005]. For example, they are in small salt and soda lakes of the Kulunda plain [*Ovdina et al.*, 2023].

The climate in the Altai Mountains is sharply continental with short, hot summers and long, cold winters. Harsh conditions lead to nival type of lithogenesis (cryolithogenesis), where ice within rocks causes unique permafrost-related phenomena like solifluction, thermokarst, and so on. Sedimentary matter is mobilized, coarse-grained deposits accumulate, and rocks crush to siltstone dimension due to physical and cryogenic weathering. These processes result in rocks and sediments composed of over 95% clastic material, with reduced biogenic and chemogenic activity. High- and mid-mountain permafrost areas are classified as azonal territories with weak sapropel accumulation [*Shtin*, 2005].

The work aims to establish the first data on the geochemical and mineral composition of bottom sediment formed in small lakes within the Chibitka Lake system under cryolithogenesis conditions and give a primary assessment of sapropel raw materials.

Material and Methods

Object of Research

The object of the study is the Chibitka Lake system located within the Chibitka River valley in the Sorlukol depression at the junction of the Aigulak and Kurai ranges. The study focuses on five small (up to 10 km^2), shallow (up to 10 m) lakes (Figure 1, Table 1). The research area belongs to a mid-mountain landscape with mountainous gray and brown forest soils, and mountain-taiga and subtaiga forests in a zone of permafrost distribution [*Fedak et al.*, 2011].

We have applied the principle of conducting a detailed study of a single lake within the context of an entire lake system. The lakes are located close to each other and share similar landscape, geological, and geochemical features. This approach allows us to understand how the mineral and geochemical compositions vary within and among the lake systems and individual lakes themselves.

The bottom sediments are massive texture sapropel and mineral silt. There is no seasonal layering in sediments. Occasionally there are remnants of macrophytes and small mollusk shells (Figure 2). We have observed brown-green, brown, and black color of the bottom sediments. Sometimes they have a faint odor of H_2S. The formation of the

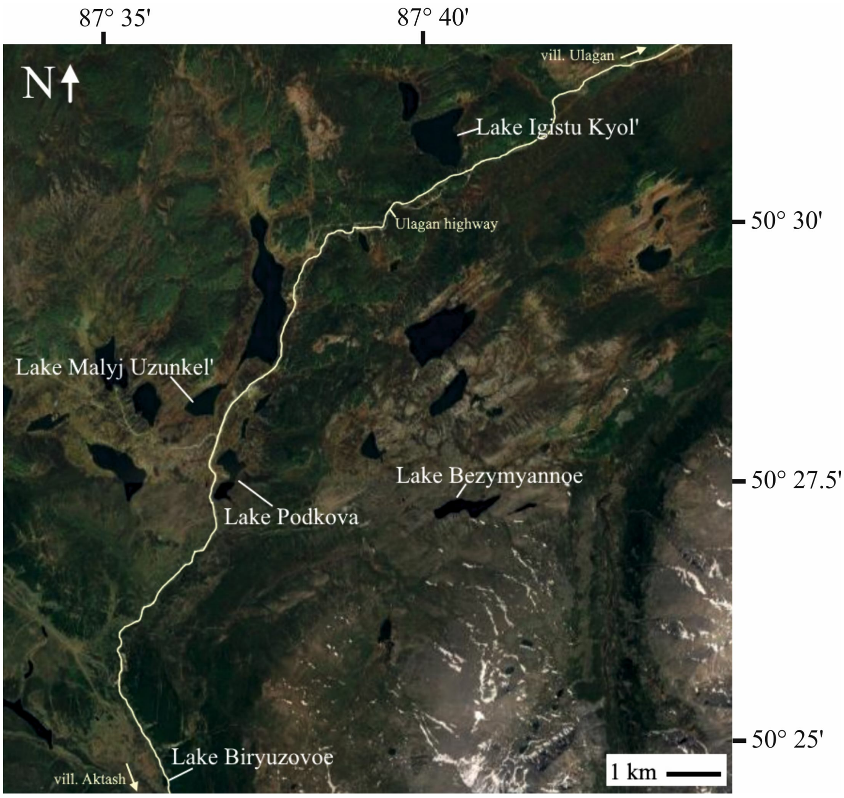

Figure 1. The layout of the studied small lakes of the Chibitka Lake system (Russian Altai) on the Google Earth image scheme.

Table 1. The samples quantity and general data on the Chibitka Lake system

Lake	Location		Altitude a. s. l., m	Bottom sediments	Core depth, cm	Soil-forming substrate	Soil	Water	Water depth, m
	N	E							
Bezymyannoe	50.4544	87.6785	2147	20	110	2	3	3	
Podkova	50.459282	87.617	1972	26	260	2	3	3	1.5
Malyj Uzunkel'	50.471043	87.6096	1991	19	110	2	3	3	2.1
Igistu Kyol'	50.514132	87.6715	1924	14	70	2	3	3	3.5
Biryuzovoe	50.409081	87.5996	1826	17 (2011)	90	2	9	3	9
				20 (2023)	97	—	—	4	
				26 (2023)	123				
Total				142		10	21	19	

lacustrine sediments starts at the water-bottom sediment boundary with the accumulation of a dense suspension that then transitions into the liquid sapropel with moisture content of 98–99%. The sediment becomes denser and drier by the lower layers with a moisture content around 70–75%.

Methods

Prior to selecting the testing point, we conducted preliminary studies on the lake bottom relief using the Garmin ECHOMAP Plus 62CM echo sounder. Bottom sediment sampling (142 samples) was carried out in the center of the lake from the PVC boat "Stormline Adventure" (South Korea) using a cylindrical sampler ($\varnothing = 82$ mm, $L = 120$ cm) with a vacuum seal (Taifun RPA, Russia). Cylindrical sampler allowed us to collect 7 stratigraphic sediment cores and keep the water-bottom sediment boundary undisturbed. The

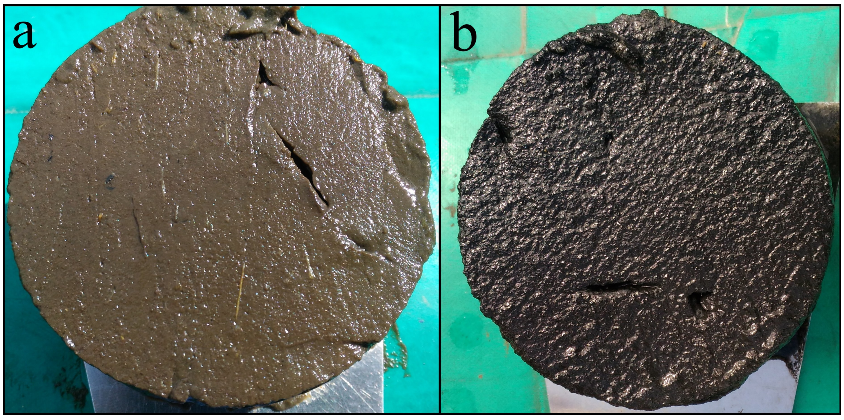

Figure 2. Bottom sediments core section of Lakes (a) Malyj Uzunkel' – brown-green sapropel with filamentous remnants of macrophytes and (b) Biryuzovoe – black fatty sapropel with shells of small mollusks.

bottom sediment cores were tested in 5 cm thick layers. The 19 water samples were taken in the center of the lake. Values of the water pH were recorded *in situ* using an ANION-7000 portable liquid analyzer (Biomer, Russia).

Soil sampling (21) was carried out at the most informative points. A continuous ring sampling scheme ($\varnothing = 82$ mm, $L = 50$ mm) was used in the upper 30 cm. Then, sampling continued along the genetic horizons: (A) the humus-accumulative horizon, (B) mineral subsurface horizon, and (C) soil-forming substrate.

Bottom sediments and soil sample preparation included weighing after collection, followed by drying the samples during the fieldwork to an air-dry state. Then further drying was either in the laboratory under room temperature conditions for Hg content determination or in a drying cabinet (LOIP LF 240/300-VS1, Russia, with the TS87B basic control module) set to 50 °C. The samples were thoroughly mixed and reweighed, and then ground for analysis from a standardized volume sample.

Analytical studies of the lake components were conducted in the Analytical Center for multi-elemental and isotope research SB RAS, Novosibirsk, Russia.

The ash content (A, %) of bottom sediments was studied by calcining 50 g of the sample at 550 °C. Ash content is the mass of solid inorganic residue formed after complete combustion of a combustible substance under certain conditions. The ash content allows a qualitative assessment of the organic and mineral matter content in the sample.

Major and trace elements were determined via atomic absorption using a Solaar M6 instrument equipped with a Zeeman and deuterium background corrector (Thermo Electron, USA). The major element composition was determined by X-ray fluorescence analysis (ARL-9900-XP, Applied Research Laboratories, USA). The total Hg content in the sediments and soil samples was determined according to the accredited methodology M 03-09-2013 using the RA-915M analyzer with RP-91S attachment (Lumex, Russia). The sample morphology and elemental composition were determined using a scanning electron microscopy (SEM) (Mira 3 Tescan, Tescan, Czech Republic). The INCA Energy 300 program (Labspec 5) was used for quantitative chemical analysis with reference standards.

The bottom sediments were analyzed using a "shashka"-type tablets, made of epoxy resin ($\varnothing = 2$ cm, $H = 0.5$ cm) via method, developed by [*Malikov*, 1984]. The process involves filling a sample of sediment with epoxy resin to form compact tablets, followed by polishing with diamond pastes to achieve a perfectly flat surface.

X-Ray Powder Diffraction was used to determine mineral composition (ARL X'TRA, Thermo Fisher Scientific (Ecublens) SARL, USA) (emission Cu$K\alpha$). A detailed description of the calcite-dolomite series carbonates determination is given in [*Ovdina et al.*, 2023; *Solotchina et al.*, 2021]. Determination of the natural (^{232}Th, ^{238}U, ^{40}K) and technogenic (^{137}Cs) radionuclides was carried out by gamma-spectrometric method on a well coaxial detector made of ultrapure germanium (HPGe) with a preamplifier and a low-background cryostat EGPC 192-P21/SHF 00-30A-CLF-FA (Eurisys Mesures, France). The identification of the main cations and anions of water composition was carried out using liquid ion chromatography (HPLC-10AVp, Shimadzu, Japan).

The expression of the water chemical composition was carried out using the formula by *Kurlov* [1928]. The principle of the formula is the image of the ions contained in water in descending order in the form of a pseudo-fraction, in the numerator of which anions are written, and in the denominator – cations (Table 2). Anions and cations with a content of more than 10 mg-eq% are introduced into the formula. The water chemical composition is defined by anions and cations in increasing order, with a content of more than 25 mg-eq%.

Results

The water composition of the Chibitka Lake System

The waters in the lakes are ultra-fresh (< 0.1 g/L) and fresh (0.1–0.2 g/L). The pH of the water ranges from neutral (7.4) to alkaline (8.9) (Table 2). The water transparency is ranging from 1.2 to 4 m. The oxygen concentration in the water is ranging from 6.20 to 7.90 mg/dm^3. The slight increase of total dissolved solids (TDS) value is accompanied by an increase in pH and the Ca content in the lake water. Among the three lakes, Malyj Uzunkel', Igistu Kyol', and Podkova, the water has a $HCO_3-Ca-Na$ composition. Lake Bezymyannoe has a HCO_3-Na (soda) composition, while Lake Biryuzovoe has a HCO_3-Ca composition with the highest content of Ca, SO_4 and HCO_3 among the considered lakes (Table 2).

The sampling of near-bottom water and analysis of trace element content were not conducted due to our previous research indicating that the composition of lake water has a limited impact on the composition of lacustrine sediments. The key factors are the composition of soil and soil-forming substrate in the catchment, composition of the dominant gross primary production, and anthropogenic activity [*Strakhovenko et al.*, 2019].

Table 2. TDS (g/L), pH and water composition of the Chibitka Lake system

Lake	pH*	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	TDS**	Water composition**
			mg/L			%		(g/L)	
Bezymyannoe	7.4	23.2	0.6	0.8	2.4	0.6	12	0.04	HCO_3 92 / Na 77 [Ca 16]
Malyj Uzunkel’	7.9	42.1	0.7	0.3	6.5	1.2	12	0.1	HCO_3 96 / Na 60 Ca 31
Igistu Kyol’	7.8	45.7	0.7	1.7	8.6	2.0	19	0.1	HCO_3 93 / Na 60 Ca 29 [Mg 11]
Podkova	8.9	59.8	0.5	1.8	13.0	2.8	22	0.1	HCO_3 95 / Na 53 Ca 34 [Mg 12]
Biryuzovoe	8.4	165.9	0.7	7.5	36.0	10.4	18	0.2	HCO_3 94 / Ca 52 [Mg 25 Na 24]

Note. *The pH was measured during fieldwork. **The TDS (g/L) and formula of water composition are expressed by *Kurlov* [1928].

Geochemical composition of the soil-forming substrate and the soils of the Chibitka Lake System

There is a similarity in element distribution among the catchments soil-forming substrates of the studied lakes (Figure 3a) according to the average element content graphs in comparison with Post-Archean Australian Shale (PAAS) [*Taylor and McLennan*, 1985]. This allows data to be compared and leads to a common reference point, which is also used by researchers in various water reservoir studies [*Dubinin*, 2004].

The soil-forming substrate of nearly all the catchments exhibit a marginally increased concentration of Na and Ca. The increased concentration of Ca, Sr, Cd and Hg is distinct to the catchment of Lake Biryuzovoe.

The distribution of the average element concentrations in the catchment soils (Figure 3b) mirrors the composition of the soil-forming substrate (a slight increase in Na and Ca) (Figure 3a). Catchment soils of Lake Biryuzovoe and Lake Bezymyannoe are characterized by a slight Cd increase. The Hg content in the catchment soils of the all lakes is slightly increased, except for Lake Podkova.

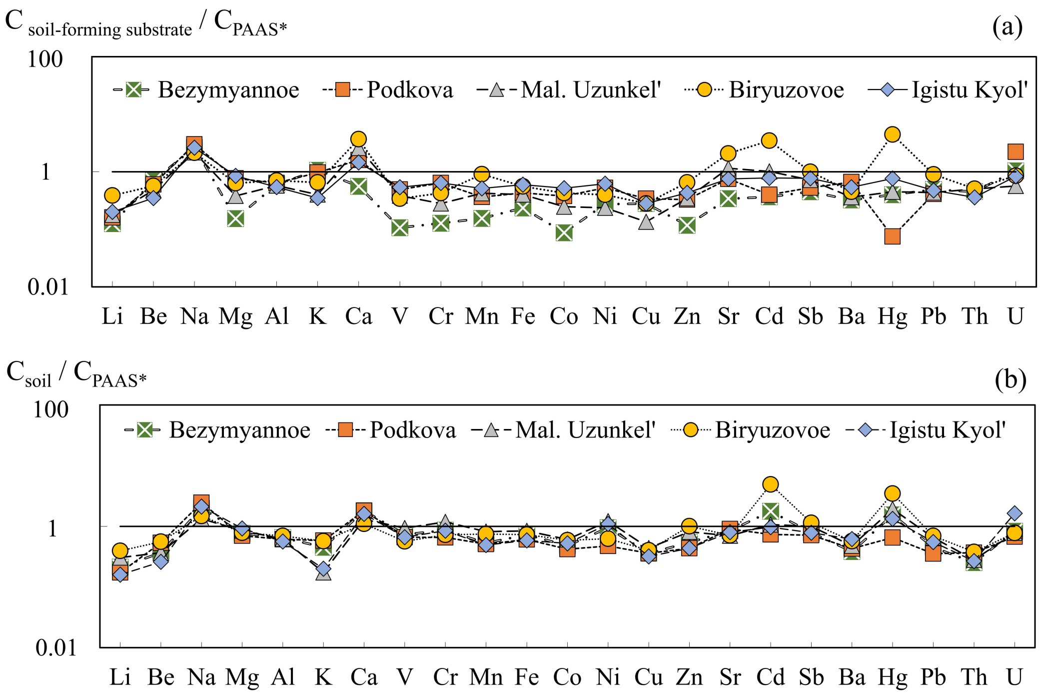

Figure 3. The distribution graph of the average element contents normalized to PAAS [*Taylor and McLennan*, 1985] in (a) soil-forming substrates and (b) catchment soils of the Chibitka Lake system.

The classification of the Chibitka Lake System bottom sediments

The genesis of sapropels, their diverse geochemical composition, and physical properties, determine the variety of their classifications. We classified sapropels into four types (Table 3), according to ash content (A, %) by [*Korde*, 1960]: *organic* (up to 30%), *organic-mineral* (30–50%), *mineral-organic* (50–70%) and *mineralized* (70–85%). Bottom sediments with ash content more than 85% are *mineral silts*. Based on the Si/Ca ratio as on the most informative major elements for lacustrine bottom sediments of Western Siberia, we divided the sediments into three classes: *silicon* (Si > Ca), *calcium* (Ca > Si) and *intermediate* (Si ≈ Ca) [*Strakhovenko et al.*, 2019].

Table 3. Classification of the Chibitka Lake System bottom sediments by types, classes and species

Lake	Type	A, %*	Class	Species
Podkova	organic-mineral	42	silicon	macrophytic
Malyj Uzunkel’		46		
Bezymyannoe	mineral-organic	66		
Biryuzovoe	mineralized	81	intermediate	
Igistu Kyol’	mineral silt	86	silicon	

Note. *A% – ash content.

The elemental and group composition of autochthonous organic matter is greatly influenced by the dominant groups of aquatic organisms (or gross primary production – GPP) in lakes, including phyto-, bacterio- and zooplankton as well as macrophytes. A high level of GPP in a lake indicates an increased amount of organic matter, which is significant for describing the material composition of bottom sediments. Therefore, according to the GPP, we distinguish between *planktonic*, *macrophytic*, and *mixed* species, as described in [*Strakhovenko et al.*, 2019]. For this study, we used the data on GPP from [*Zarubina and Fetter*, 2022].

The lakes are oligotrophic, with a low concentration of biogens (BOD_5 0.15–1.25 mgO_2/dm^3). The main primary producers of organic matter, except phytoplankton, are macrophytes (mainly pondweed, hornwort and parrot's-feather). The lakes are characterized by a very low value of the GPP of phytoplankton (0.09–0.19 mgO_2/L/h) and a wide range of GPP values for macrophytes (0.74–26.7 mgO_2/dm^3/h). The rate of organic matter destruction in all lakes is much lower than the rate of production, but both are still very low [*Zarubina and Fetter*, 2022].

Bottom sediments of Lakes Podkova and Malyj Uzunkel' are organic-mineral silicon sapropel. Bottom sediment of Lake Bezymyannoe is mineral-organic silicon sapropel. Sapropel of Lake Biryuzovoe belongs to mineralized type and intermediate class. Bottom sediment of Lake Igistu Kyol' is mineral silt of silicon class (Table 3). Bottom sediments of all lakes belong to the macrophytic species by gross primary production. There is no organic sapropel among the bottom sediments of the Chibitka Lake system

Geochemical composition of the Chibitka Lake System bottom sediments

The distribution of average elements concentrations in the bottom sediments has a similar configuration and shows the absence of significant differences between lakes and as well between sapropels of different types and classes formed in them (Figure 4, Table 4).

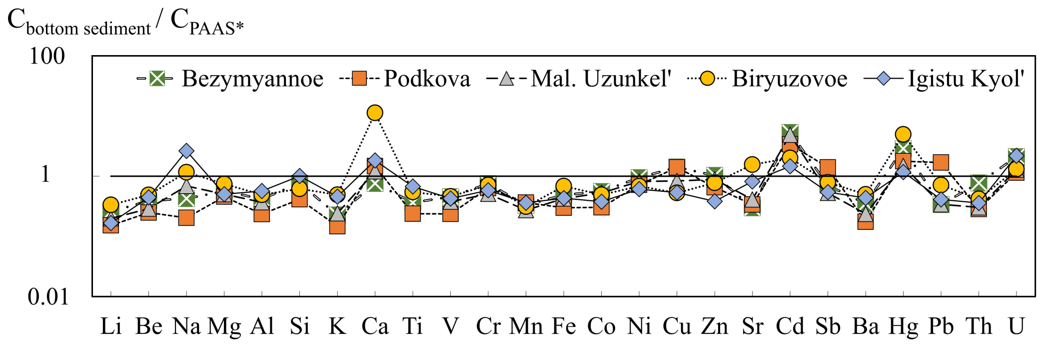

Figure 4. The distribution graph of the average element contents normalized by PAAS [*Taylor and McLennan*, 1985] in the bottom sediments of the Chibitka Lake system.

All lakes are characterized by a slightly increased content of Cd and Hg in the bottom sediments, which reflects the composition of soils and soil-forming substrate (Figure 3). On the contrary, slightly increased Na content characterize only bottom sediment of Lake Igistu Kyol'. The highest content of Ca and Sr is observed in the bottom sediment of Lake Biryuzovoe (Figure 4, Table 4).

To utilize sapropel in various sectors according to [*GOST R 54000-2010*, 2012], the raw materials must correspond to radiation and hygiene standards for natural (^{238}U, ^{232}Th, and ^{40}K) and artificial (^{137}Cs) radioactivity. This is achieved by calculating the total effective specific activity (A_c) of natural radionuclides using the following formula:

$A_c = A_U \cdot 3.4 \times 10^{-7} + 1.31 A_{Th} + 0.085 A_K$ (Bq/kg) [*Rikhvanov*, 2009], where A_U, A_{Th}, A_K represent the specific activities of respective radioisotopes. Moreover, the total activity of ^{137}Cs ($\Sigma^{137}Cs$) must also be evaluated (Table 4).

Table 4. The major and trace elements content (mean ± s. d.) in the Chibitka Lake System bottom sediments

Lake	Bezymyannoe	Podkova	Mal. Uzunkel'	Igistu Kyol'	Biryuzovoe
%					
Ca	0.8 ± 0.1	1.5 ± 0.1	1.2 ± 0.2	1.8 ± 0.2	11.3 ± 8.1
Mg	0.7 ± 0.1	0.6 ± 0.1	0.7 ± 0.1	0.7 ± 0.2	1.0 ± 0.3
Na	0.4 ± 0.1	0.2 ± 0.02	0.6 ± 0.1	2.4 ± 0.8	1.0 ± 0.6
K	0.7 ± 0.1	0.5 ± 0.04	0.7 ± 0.1	1.4 ± 0.4	1.5 ± 0.7
Si	22.7 ± 1.0	12.2 ± 2.1	—	29.8 ± 4.2	18.0 ± 7.5
Al	4.2 ± 0.4	2.4 ± 0.5	3.7 ± 0.4	5.7 ± 1.1	4.9 ± 2.2
Fe	2.5 ± 0.8	1.5 ± 0.1	2.2 ± 0.5	2.2 ± 0.2	3.5 ± 0.7
mg/kg					
Li	19 ±4	12 ± 2	15 ± 2	13 ± 4	25 ± 12
Be	1.2 ± 0.4	0.7 ± 0.1	0.9 ± 0.2	1.3 ± 0.5	1.5 ± 0.6
Ti	0.2 ± 0.02	0.1 ± 0.02	—	0.4 ± 0.03	0.3 ± 0.1
V	68 ± 17	35 ± 12	57 ± 3	64 ± 10	69 ± 30
Cr	83 ± 12	70 ± 6	56 ± 9	64 ± 15	79 ± 27
Mn	0.04 ± 0.01	0.04 ± 0.03	0.03 ± 0.01	0.04 ± 0.01	0.03 ± 0.01
Co	13 ± 1	7 ± 1	12 ± 1	9 ± 1	11 ± 4
Ni	52 ± 7	40 ± 3	45 ± 8	34 ± 11	38 ± 19
Cu	71 ± 8	70 ± 12	42 ± 2	27 ± 11	26 ± 11
Zn	88 ± 23	56 ± 15	75 ± 11	32 ± 8	66 ± 19
Sr	60 ± 4	68 ± 3	82 ± 15	164 ± 38	313 ± 123
Cd	0.159 ± 0.106	0.102 ± 0.059	0.146 ± 0.074	0.044 ± 0.022	0.060 ± 0.023
Sb	1.0 ± 0.5	2.0 ± 1.7	0.7 ± 0.2	0.8 ± 0.2	1.1 ± 0.6
Ba	228 ± 32	114 ± 29	154 ± 60	284 ± 74	325 ± 96
Hg	0.115 ± 0.016	0.071 ± 0.023	0.059 ± 0.023	0.047 ± 0.025	0.197 ± 0.111
Pb	7 ± 3	34 ± 52	7 ± 2	8 ± 5	14 ± 11
Bq/kg					
^{232}Th	11.3 ± 1.4	4.2 ± 0.7	4.5 ± 0.8	5.2 ± 1.3	6.1 ± 2.4
^{238}U	6.5 ± 2.2	3.6 ± 1.9	4.0 ± 2.0	6.8 ± 6.5	4.1 ± 0.8
^{40}K	0.6 ± 0.1	0.3 ± 0.1	0.5 ± 0.1	1.2 ± 0.4	1.3 ± 0.6
Σ^{137}Cs	137	60	38	165	99
A_c	14.8	5.5	5.9	7.0	8.2

Mineral composition of the Chibitka Lake System bottom sediments

We used X-ray diffraction analysis (Table 5) and SEM to study the mineralogy of the lacustrine sediments. The mineral composition over the entire bottom sediments core in all the lakes consists of mostly terrigenous minerals (Table 5, Figure 5) – quartz, plagioclase, potassium feldspar, micas, chlorite (mainly Mg-chlorite), amphibole, disordered smectite, epidote, and magnetite. The X-ray amorphous component is present in all samples in different quantity. It is related both to the fine-grained material of bottom sediments and to the biogenic component – diatoms (SiO_{2bio}) (Figure 5).

We found authigenic low-Mg calcite (Table 5, Figure 6, 7) which is formed in the upper horizons of Lake Biryuzovoe bottom sediments while the terrigenous mineral composition prevails in the lower horizons with small calcite admixture (Table 5).

Table 5. The main mineral composition of the Chibitka Lake System bottom sediments according to the X-Ray Powder Diffraction

Lake	Depth, cm	Mineral composition
Bezymyannoe		Qz, Ab, Ms, Mg-Chl, Hbl, Ilt-Sme
Podkova		Qz, An_{50-70}, Ms, Fe-Chl, Hbl, Kfs, disordered Sme
Igistu Kyol'		Qz, Ab, An_{10-30}, Ms, Hbl, Mg-Chl, impurities of Kfs, Py
Biryuzovoe	0–10	Cal, impurities of Qz, Ab, An_{10-30}, Ms, Py
	65–75	Qz, Ab, An_{10-30}, Ms, Fe-Chl, Kfs, Hbl

Note. Qz – Quartz, Ab – Albite, An_{10-30} – Oligoclase, An_{50-70} – Labradorite, Ms – muscovite, Chl – chlorite, Hbl – Hornblende, Kfs – potassium feldspar, Sme – smectite, Ilt-Sme – Illite- smectite, Py – pyrite, Cal – Calcite.

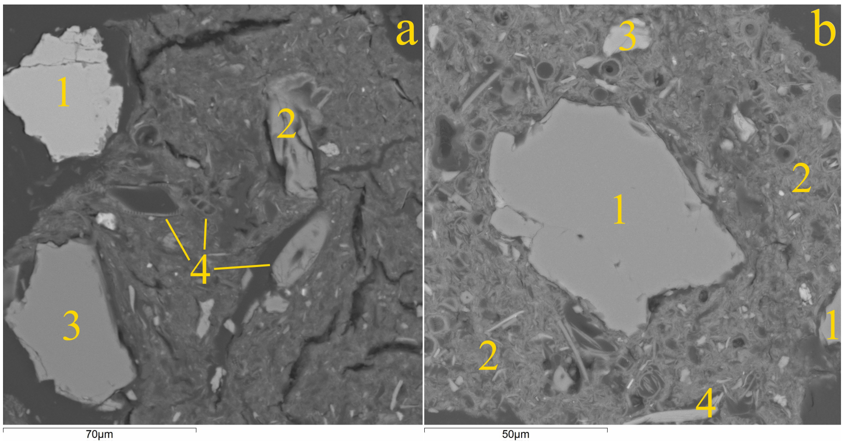

Figure 5. Photo SEM using BSE (Mira 3 Tescan) of terrigenous and biogenic components in bottom sediments of (a) Lake Podkova – (1) plagioclase (An $_{50-70}$), (2) Fe-chlorite, (3) quartz, (4) diatom shells (SiO_{2bio}); (b) Lake Bezymyannoe – (1) quartz in the mass of (2) diatom shells (SiO_{2bio}), (3) albite, (4) muscovite.

Firstly, numerous outgrowths and crusts of carbonates were observed on rounded and sharp-angled rock fragments at the water – bottom sediment boundary with the naked eye (Figure 6a). Further, with a more detailed study on SEM, we established that such crust consists of authigenic low-Mg-calcite (Figure 6b).

In the upper horizons (0–5 cm) of the Lake Biryuzovoe sediments, low-Mg calcite has a variety of shapes. It can be found in irregular shapes (Figure 7a), as small scalenohedral, rhombohedral and case crystals (Figure 7b), and in the form of "curd"-like mass (Figure 7c).

In the upper part of Lake Biryuzovoe core, we found gypsum nodules (Figure 8a) with a radially radiant structure and halite crystals (Figure 8b, Table 5).

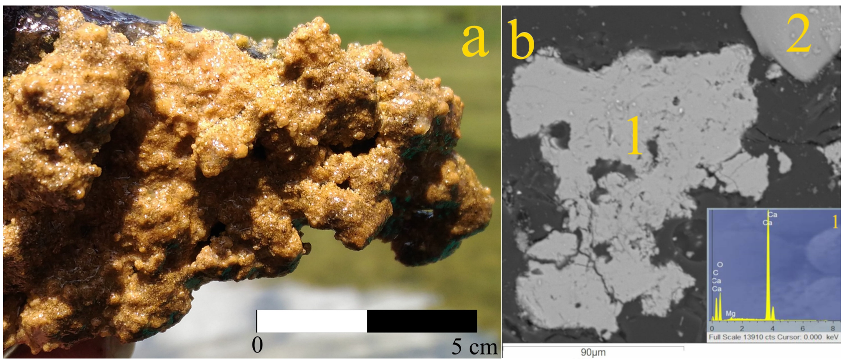

Figure 6. (a) Photo of a carbonate crust on a rock fragment from Lake Biryuzovoe and (b) photo SEM using BSE (Mira 3 Tescan) of low-Mg calcite (1), of which the crust consists, (2) quartz.

In all the lakes, framboidal pyrite forms, starting from the first centimeters of the bottom sediments and throughout the entire depth of the sediment core, indicating the restoration conditions for the lacustrine sediment environment.

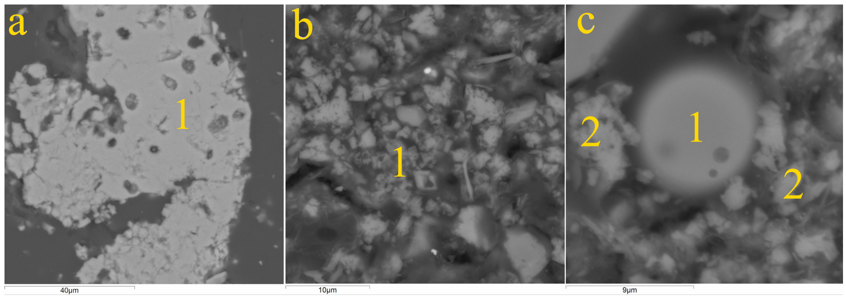

Figure 7. Photo SEM using BSE (Mira 3 Tescan) of authigenic low-Mg calcite in the bottom sediments of Lake Biryuzovoe (0–5 cm): (a) aggregates of irregular shape (1); (b) small scalenohedral, rhombohedral and case crystals (1); (c) diatom cyst (1) in the bulk of "curd"-like low-Mg calcite (2).

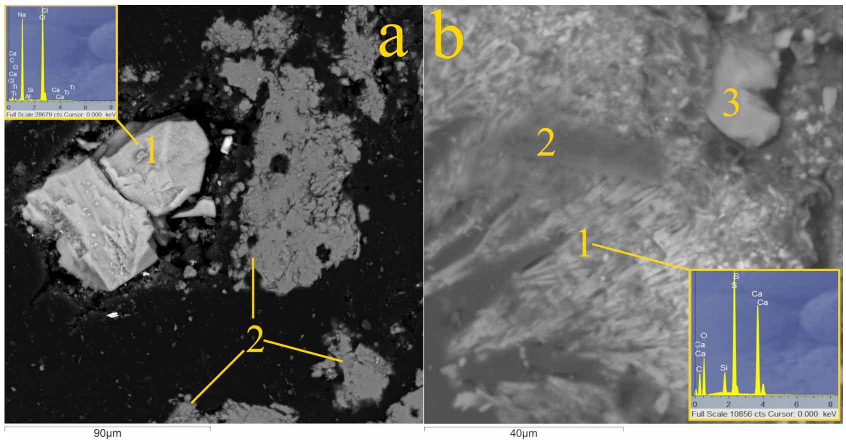

Figure 8. Photo SEM using BSE (Mira 3 Tescan) of (a) halite (1) and low-Mg calcite (2) from a carbonate crust in 0–5 cm bottom sediments of Lake Biryuzovoe; (b) radially radiant structure of gypsum (1), diatoms (2) and quartz (3).

Discussion

The composition of lake waters (HCO_3-Ca, $HCO_3-Ca-Na$ and HCO_3-Na) is consistent with data for the mid-mountain region of the Altai Mountains [*Fedak et al.*, 2011]. The lakes feed mainly from atmospheric precipitation, as well as the groundwater supply. Lake waters are HCO_3-Ca (among the carbonate rocks) or HCO_3 $-Mg$ or $-Na$ (among the igneous rocks). The composition of the lake waters also correlates with our data on increased Na and Ca content in the composition of soil-forming substrates and the soils in the catchment area (Figure 3). The reflection of the chemical composition of catchment rocks on lake water composition can be observed in many mountain lakes. For example, this is discussed in a review paper on European mountain lakes [*Camarero et al.*, 2009].

It is worth noting that the composition of Lake Biryuzovoe water correlates with the composition of the spring ($HCO_3-(SO_4)-Mg-Ca$), which is located 1 km away from the lake on the eastern side of the Chibitka River valley along the Kadrinsky regional fault. Modern travertines are formed from this spring [*Kokh et al.*, 2018]. We assume that the aqueous fluid that feeds the aforementioned spring also enters Lake Biryuzovoe via the Kadrinsky fault zone, contributing to the composition of the lake water and further assisting in the formation of low−Mg calcite and gypsum.

Using the example of the Chibitka Lake system, we observe a direct inheritance of the geochemical composition of bottom sediments during the redeposition of physical and cryoweathering products and destruction of catchment areas rocks and soils without significant change. The average geochemical composition of the bottom sediments almost completely coincides with the composition of the soils and soil-forming substrate (Figure 9). The catchment of Lake Biryuzovoe is characterized by an increased Hg content associated with the Kurai mercury zone where the lake is located [*Fedak et al.*, 2011]. Possible additional anthropogenic impact may be related to the proximity of the Aktash Mining and Metallurgical Enterprise (Hg).

Despite the increased concentrations of potentially toxic elements (Cd and Hg) in some individual samples, the average concentrations by the bottom sediments section are at the maximum permissible concentration for sapropels [*GOST R 54000-2010*, 2012]. The minimum concentrations of Cd and Hg are established in mineral silt of Lake Igistu Kyol'. According to our data (Table 4) and values in the [*GOST R 54000-2010*, 2012], the sapropels are classified as belonging to the First class of suitability (Cd < 3, Pb < 50, Hg < 1.0 mg/kg). In addition, the concentrations of other trace elements (Table 4), the content of which should be taken into account, are also within the First class of suitability for sapropel (Cu <100, Mn <500, Cr <100, Co <20 and Ni <50 mg/kg). The presence of heavy (Cd, Pb, Hg) and other metals in bottom sediments often reflects the natural geochemical background of the catchment area, emphasizing the role of underlying geology in sediment composition as demonstrated for other lacustrine systems [*Gregorauskiené and Kadūnas*, 2000].

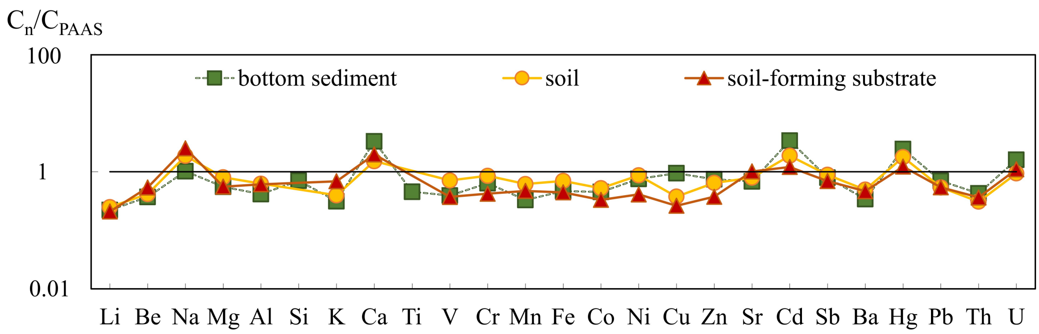

Figure 9. The distribution graph of the average element contents normalized by PAAS [*Taylor and McLennan*, 1985] in the bottom sediments, soils and soil-forming substrate of the Chibitka lake system.

The A_c for bottom sediments varies from 5.5 to 14.8 Bq/kg (Table 4) and does not exceed the standard of 300 Bq/kg [*GOST R 54000-2010*, 2012]. Values of ^{137}Cs specific activity (up to 112 Bq/kg) were determined only in the upper horizons of the bottom sediments in Lakes Igistu Kyol' and Bezymyannoe. However, despite the values for the entire sapropel deposits in all studied lakes are within the standard range. The total specific activity of ^{137}Cs varies from 32 to 154 Bq/kg. The ^{137}Cs vertical distribution gradually decreases towards zero values to a depth 15 to 20 cm. This distribution is linked to the removal of ^{137}Cs from the catchment area through soil particles entering the lakes. Such horizons can be diluted with a material with a low specific activity of ^{137}Cs or completely removed [*Strakhovenko et al.*, 2022].

The noteworthy aspect is the increased concentration of Ca in the bottom sediments of Lake Biryuzovoe. Analytical studies have shown that Ca is mainly located in low-Mg calcite (Figure 6, 7). Low-Mg calcite, calcite and aragonite are among the most common authigenic minerals of small lakes in the south of Western Siberia and their formation in most cases in the zones of humid and arid sedimentogenesis is associated with biochemogenic processes [*Ovdina et al.*, 2020]. In general, low-Mg calcite (and other carbonates, including dolomite), are extremely common all over the World, in lacustrine and marine sediments [*Fussmann et al.*, 2020; *Last and Ginn*, 2005].

The subzero and moderately low temperatures in areas within nival lithogenesis impede chemical processes and organism activity in water reservoirs. Fluctuations in physical and chemical parameters are associated with the landscape and climatic features, the altitude above sea level, the shallow depth of the lakes (up to 10 m), wind mixing of water, the absence of thermocline, as well as the presence of restorative conditions, as evidenced by the formation of framboidal pyrite (Figure 9). Prolonged water freezing leads to water supersaturation, when the TDS increases by two or more times. The degree of TDS and cryogenic concentration during ice cover growth is heavily influenced by reservoir depth and ice thickness [*Smits et al.*, 2021]. The HCO_3–Ca composition of lake waters with a sufficiently high content of SO_4 ion also plays an important role (Table 2) in the process of cryogenic mineral formation. Prolonged freezing of lake water and bottom sediment leads to the concentration of dissolved salts in unfrozen water, as a result of which, among authigenic minerals not only low-Mg calcite is formed in bottom sediments in the ultra-fresh Lake Biryuzovoe, but also gypsum nodules, and sometimes even small halite crystals (Figure 8).

Conclusion

Despite the nival type of lithogenesis and oligotrophy of lakes, organic-mineral bottom sediments of different types and classes are formed in lakes of the Chibitka system, Russian Altai. The classification of sapropels based on geochemical composition, ash content and gross primary production is the first step to determine the development of scientific foundations for the rational use of the studied sapropel. We determined three sapropels types with ash content from 42 to 81%, silicon and mixed classes, and macrophytic species. Lake Igistu Kyol' has mineral silt (A>85%) with the same characteristics.

The geochemical composition of lake sapropels is closely related to the composition of the soils and the soil-forming rocks of the catchment area due to physical and cryogenic weathering. The content of potentially toxic elements (mg/kg) – Pb (7–34), Cd (0.044–0.159) and Hg (0.047–0.197), as well as other trace elements (mg/kg) – Cu (26–71), Mn (0.03–0.04), Cr (56–83), Co (7–13), Ni (34–52), are within the First class of suitability for sapropel according to GOST standards. The total effective specific activity of natural radionuclides A_c (5.5–14.8 Bq/kg) is extremely low and does not exceed 300 Bq/kg. The ^{137}Cs content in some sediment horizons is increased (up to 112 Bq/kg); however, the thickness of such horizons does not exceed 15 cm and the values for the entire sapropel deposits in all studied lakes are within the standard range.

The mineralogy of the bottom sediments is a feature of the nival lithogenesis. For most of the studied lakes, physical and cryogenic weathering determines the mineral composition of bottom sediments, mainly composed of terrigenous material. Only in freshwater Lake Biryuzovoe there are authigenic low-Mg calcite, gypsum and halite found. The formation of these minerals is directly related to the nival type of lithogenesis due to a variety of factors, the main of which are landscape and climatic features, small lake depth (up to 10 m), ice thickness, TDS increase under the ice, cryogenic concentration and the HCO_3–Ca composition of lake water with a sufficiently high content of SO_4.

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