Authigenic Carbonates in the Water–Biota–Bottom Sediments' System of Small Lakes (South of Western Siberia)

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Abstract: We studied 46 small, drainless lakes in various landscape types: The sub-taiga (Vasyugan plain), forest–steppe (Baraba lowland), and steppe and subzone of ribbon forests (Kulunda plain). Sampling of lake components (sediments, water, and biota) was performed. The materials were analyzed via a combination of modern analytical methods (atomic absorption spectroscopy, X-ray fluorescence, scanning electron microscopy and X-ray diffractometry). It was found that in the south of Western Siberia, lakes with a bicarbonate-sodium water composition are widespread against the background of general landscape zoning. This composition contributes to the abundant growth of biota in the lakes, which leads to the processes of authigenic carbonate formation from calcite–dolomite series and aragonite on geochemical barriers, i.e., drifting biota–water, submerged biota–water, and water–bottom sediments against a background of terrigenous demolition and organic matter accumulation. The article shows the differences in the composition and structure of low-temperature carbonate minerals formed on various geochemical barriers. It was found that low-magnesium calcite and aragonite are the most common authigenic carbonates in small lakes in the south of Western Siberia and are formed on all three geochemical barriers in lakes. High-magnesium calcites and Ca-excess dolomites are formed only at the water–bottom sediment barrier in lakes with HCO_3–Na and Cl–HCO_3–Na water composition at pH > 9 and with a total dissolved solids > 3 $g \cdot L^{-1}$ (in some lakes of HCO_3-Na composition with a TDS < 3 $g \cdot L^{-1}$ and pH > 9).

Keywords: authigenic minerals; calcite–dolomite carbonates; aragonite; small lakes; Western Siberia

1. Introduction

One of the characteristics of Western Siberia is the extensive system of lake basins. There are more than 20,000 lakes in the south of its territory alone. Most of them are small and have an area of less than 10 km^2 [1,2]. Small lakes are more severely affected by environmental changes than large reservoirs, which is reflected in their sedimentary records. Bottom sediments contain information about the behavior of elements in the processes of modern sedimentation, e.g., in the patterns of their distribution and concentration in different landscape settings in conditions of increasing anthropogenic influence. The occurrence and development of small lakes is directly related to the formation of terrain and changes in natural and climatic conditions. The study of sedimentation processes in small lakes has shown that there is a certain set of factors that affects the sediment's geochemical composition [3–10]. The hallmark of each lake is the composition of the water, bedrock, and soil of the catchment area, the sediments and biota, and the life processes which occur both in the lake itself and the corresponding coastal zone. The substance that makes up the bottom sediment has different origins: Allogeneic (introduced from the catchment area) and authigenic (formed directly in the lake). Thus, the bottom sediments of lakes consist of terrigenous, chemogenic, biochemogenic, and biogenic material.

The influence of the biota contained in the water body on bottom sediment formation, especially carbonate, has been noted in work by a number of scientists [11–19]. The biogeochemical aspect of sedimentary processes and processes of carbonation still attract the attention of researchers; however, because of the complexity of the research objects, many issues remain open to discussion. One of the problems is to identify the mechanism of modern dolomite formation in lakes and the factors that influence this process. It should be noted that not enough attention is paid to small inland reservoirs, despite the fact that mineralized and saline lakes of semiarid and arid zones make up a fifth of all inland lakes [20–25]. However, in a number of studies by Siberian scientists [4,22,26,27], the issues of carbonate formation on the water–bottom interface in small lakes of the Tazheran steppe (the Baikal region, Eastern Siberia) were considered. As a result of the conducted research, it was found that Mg-calcites, Ca-excess dolomites, and aragonite predominate among the carbonate minerals. Similar studies have also been conducted in a number of areas of Western Siberia (the south of the Vasyugan plain, the Baraba lowland, and the Kulunda plain), where carbonates are formed in lake sediments [5,6,24].

The aim of this work was to determine the carbonate-mineral formation factors in the water–biota–bottom sediments' system of small lakes in the south of Western Siberia. The process of authigenic carbonate formation was considered in various landscape types of the region. The main focus of the study was the peculiarities of the carbonate-forming process on geochemical barriers in lakes, i.e., drifting biota–water, submerged biota–water, and water–bottom sediments.

2. Materials and Methods

2.1. Materials

The objects of study were small lakes (with an area under 10 km^2, and a depth up to 5 m), located within areas of sub-taiga (Vasyugan plain), forest–steppe (Baraba lowland), steppe (Kulunda plain), and the ribbon forests' subzone (Kulunda plain), using values of total dissolved solids (TDS), from freshwater to brine, according to the classification by A. M. Ovchinnikov [28]. The selection of objects was carried out along the meridian from north to south, covering several landscape types (Figure 1).
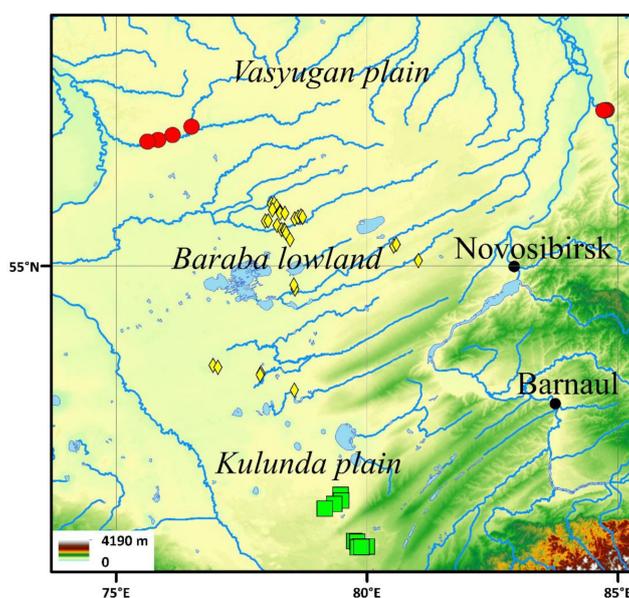

Figure 1. The layout of the studied small lakes in the south of Western Siberia. Symbols: Red circle—the Vasyugan plain lakes, yellow rhomb—the Baraba lowland lakes, green square—the Kulunda plain lakes.

The territory of the south of Western Siberia has its own climatic features. It is located at the intersection of climatic regions and is exposed to the most diverse air masses—The southern Central

Asian and Northern polar. This fact determines the continentality and aridity of the climate, which is expressed in a large variability of atmospheric pressure, temperature, humidity, and other meteorological elements both daily and annually. Each landscape type has its own local characteristics but, in general, hot dry summers and cold winters are typical. Precipitation is low: 230–350 mm to 500 mm per year. The main sources of lake nutrition are meltwater, rainwater, and groundwater, while strong winds accelerate the evaporation of moisture from the surface of snow cover and water areas. The period of lake-ice cover lasts on average 7–9 months, with a short period of melting (up to 1–2 weeks).

All the studied lakes were grouped into lake systems (Table S1: Studied lakes (territories, landscapes, and lake systems)). Lake systems contain lakes that are located compactly in the same landscape and climatic conditions and have a single or similar catchment area and water sources. This allowed us to consider the physical, chemical, geochemical, and mineral features of the small lakes, both within the same landscape type, and in comparison with lakes of different landscape types. The lake systems in this work are called by the name of the nearest settlement.

There are the Kyshtovskaya and Samus'kaya lake systems in the West Siberian sub-taiga landscape (Vasyugan plain). The lakes of this zone belong to the Vasyugan relict system of lakes [29].

The Baraba lowland lakes, located in the West Siberian forest–steppe landscape, belong to the Om'-Ichan hillock-hollow system of lakes, which is a part of the Ob'-Irtysh interfluve [29]. There are the Gzhatskaya, Bergul'skaya, Novokievskaya, Kuibyshevskaya, Barabinskaya, Chulymskaya, Zdvinskaya, Karasukskaya, and Terengulskaya lake systems.

The Mikhailovskaya and Petukhovskaya systems belong to the lakes of the Kulunda plain (the West Siberian and Kazakhstan dry steppe). Lakes of the ribbon forests' subzone are divided into two systems: Salty lakes of ribbon forests and slightly salted lakes of ribbon forests [29].

Field and analytical studies have shown that the bottom sediments of small lakes in the south of Western Siberia are organic–mineral silts (sapropels and mineral silts), differing in the ratio of organic and mineral components (ash content) and chemical composition. The genesis features and diverse composition determine the classifications and characteristics of organic–mineral silts (sapropels). There are types depending on the ash content and classes according to the Si/Ca ratio, as well as the dominant primary products, i.e., planktonic, macrophytic, and mixed. Mineral silts are the bottom sediments with an ash content higher than 85% [30,31].

The article used materials collected from fieldwork in 2012–2018, performed as part of a combined expedition with the institutes of the Siberian branch of the Russian Academy of Sciences: Institute for Water and Environmental Problems, Institute of Soil Science and Agrochemistry, and Institute of Catalysis.

Bottom sediment sampling (942 samples) was carried out from the catamaran with a cylindrical sampler (diameter 82 mm, length 120 cm) with a vacuum seal (Taifun Research and Production Association, Russia). Sampling using a cylindrical sampler allowed collecting stratigraphic undisturbed sediment cores. The sampling site was selected far from settlements or at the maximum distance from them. The sampling point was located in the central part of the lake. The core of bottom sediments was tested in layers with a step of 3 or 5 cm, to a depth of 50 to 250 cm. Each sample was numbered according to the number in order and packed in a plastic bag. The sediment was weighed after sampling, then dried to an air-dry state, first in the field, then in the laboratory (at room temperature for further determination of mercury content or in a laboratory drying cabinet (LOIP LF 240/300-VS1, Laboratory equipment and devices, Saint Petersburg, Russia) at 50 °C for determination of major and trace elements.

Water samples for all analyses were taken in the center of the lake. When sampling, bottles of 1 and 0.5 L (plastic bottles for determining the major and trace element composition) and 0.33 L (glass bottles for determining the content of mercury) were used. Water samples for the trace elements composition and Hg were preserved with 0.1 H nitric acid.

Soil samples were taken by pressing a metal ring with a diameter of 82 mm and a height of 50 mm to the depth of the entire soil section. All soil samples were dried and weighed according to the method for bottom sediments.

In addition, samples of water (201), aquatic biota (38), and soil (137) were taken and analyzed. Physical and chemical variables of water and bottom sediments material were recorded in situ (pH-Eh, TDS) using an ANION-7000 portable liquid analyzer (Biomer, Novosibirsk, Russia).

2.2. Methods

Analytical studies of the lake components were conducted in the Analytical Center for multi-elemental and isotope research SB RAS and in the Laboratory of Geochemistry of Noble and Rare elements of the Institute of Geology and Mineralogy SB RAS, Novosibirsk.

Major and trace elements were determined via atomic absorption using a Solaar M6 instrument equipped with a Zeeman and deuterium background corrector (Thermo Electron, Waltham, MA, USA). Two versions of atomic absorption were used: Flame atomization (acetylene-air and nitrous oxide-acetylene) to quantify the content of a wide range of chemical elements, the content of which in the samples was > 0.0001 mass%, and electrothermal atomization for the quantitative determination of lower contents (less than 0.000001 mass%). Atomic absorption determination allowed us to identify: Li, Rb, Cs, Na, K, Sr, Ba, Al, Ca, Mg, Fe, Mn, Ti, V, Cr, Ni, Co, Cu, Zn, Pb, Mo, Be, Cd, Sb, and As. For analysis, certified atomic absorption spectroscopy methods were used, which are included in the State Register or methods developed in the Laboratory of Geochemistry of Noble and Rare elements of the Institute of Geology and Mineralogy SB RAS, Novosibirsk. The laboratory has a bank of standard samples (domestic and foreign) of more than 40 items that were used in the analysis. Standard samples of the appropriate composition were analyzed with each batch of samples, which allowed us to control the accuracy of the analysis. The laboratory regularly participates in the Interlaboratory comparison tests. Interlaboratory comparison tests results confirmed a high quality assessment of atomic absorption analysis. The detection limits of various trace elements are shown in (Table 1). The procedure for preparing samples for analysis depended on the type of substance being tested.

Table 1. Detection limits of trace elements by atomic absorption method.

Element	Soil, Bottom Sediments, $(g \cdot t^{-1})$	Biota, $(mg \cdot kg^{-1})$	Water, $(\mu g \cdot L^{-1})$
Hg	0.01	0.01	0.02
Sb	0.2	0.03	0.1
Cd	0.015	0.001	0.005
Pb	6.0	0.1	0.1
Ni	7.5	0.1	0.1
Co	5.0	0.03	0.1
Cu	2.5	1.0	0.1
Cr	7.5	0.5	10
Zn	0.5	0.1	1.0
Ba	12.0	5.0	10
Be	0.5	0.2	0.01
Mn	5.0	2.0	2.0
Mg	2.5	1.0	-

The major element composition was determined by X-ray fluorescence analysis (ARL-9900-XP, Applied Research Laboratories, Austin, TX, USA). X-ray fluorescence analysis was performed from fused tablets: The analyzed sample was dried at 105 °C for 1.5 h to determine the hygroscopic humidity. Then it calcined at 960 °C for 2.5 h to determine the mass loss during calcination and then mixed with a fluxing agent (66.67% lithium tetraborate, 32.83% lithium metaborate, and 0.5% lithium bromide) in a ratio of 1:9 (the total weight of the mixture was 5 g). The mixture was melted in platinum crucibles in an induction furnace Lifumat-2.0-Ox (Linn High Therm, Hirschbach, Germany). To check the correctness

of the analysis, the following state standard samples of rock composition were used: MU-1, MU-3, MU-4, SA-1, SCHT-1, SCHT-2, SDO-1, SDU-1, SG-1A, SG-2, SG-3. SGS1, SGS2, SGS-1, SGS-5, GSM-2, GSM-3, SI-1, SI-2, SMS-1, SMS-2, SUP-1, ST-1.

The sample morphology and phase and elemental compositions were determined using a scanning electron microscope, MIRA 3 TESCAN (Tescan, Brno-Kohoutovice, Czech Republic). The current modification of the equipment used a Si (Li) energetic detector (OXFORD, Oxford Instruments, Abingdon, UK). The method allowed quantitative chemical analysis to be carried out on microvolumes. The INCA Energy 300 program (Labspec 5) was used for quantitative chemical analysis with reference standards (2145 definitions of mineral compositions). All microphotographs presented in this work were taken using the SEM MIRA 3 TESCAN.

X-ray diffractometry (XRD) was used to determine sample mineral composition (ARLX'TRA, Thermo Fisher Scientific (Ecublens) SARL, Waltham, MA, USA) (emission CuKα).

For phase analysis, the samples were scanned in a range from 2° to 65° (2Θ) with a step of 0.05°; the scanning time at the point was 3 s. For studying the XRD profiles of the sediment carbonate component, scanning was carried out in the range from 28° to 32° (2Θ) with the same step, but a longer scanning time (15 s). The differential diagnostics of low-temperature calcite–dolomite carbonates presented certain difficulties due to their high dispersion (crystallite sizes < 10 μm). XRD analysis was performed using the most intense reflections of hkl = 104 in the area of angles 28–32° 2Θ CuKα for trigonal carbonates. The values of the d_{104} interplane distances ranged from 3.036 Å (calcite) to 2.887 Å (stoichiometric dolomite) and served as a magnesium measure of the carbonate minerals.

Magnesium-calcites were divided into three groups according to the d_{104} value:

(1) Low-magnesium calcites with a $MgCO_3$ content in the structure of <4–5 mol. % (3.036 Å > d_{104} > 3.020 Å),

(2) Intermediate-magnesium calcites with 5–18 mol. % $MgCO_3$ in the structure (3.02 Å > d_{104} > 2.98 Å), and

(3) High-magnesium calcites with 30–43 mol. % $MgCO_3$ (2.94 Å > d_{104} > 2.91 Å).

Ca-excess dolomites, in the structure of which the excess of $CaCO_3$ can reach 7 mol. % with respect to stoichiometric dolomite, are characterized by the values of d_{104} from 2.910 to 2.887 Å (Figure 2).
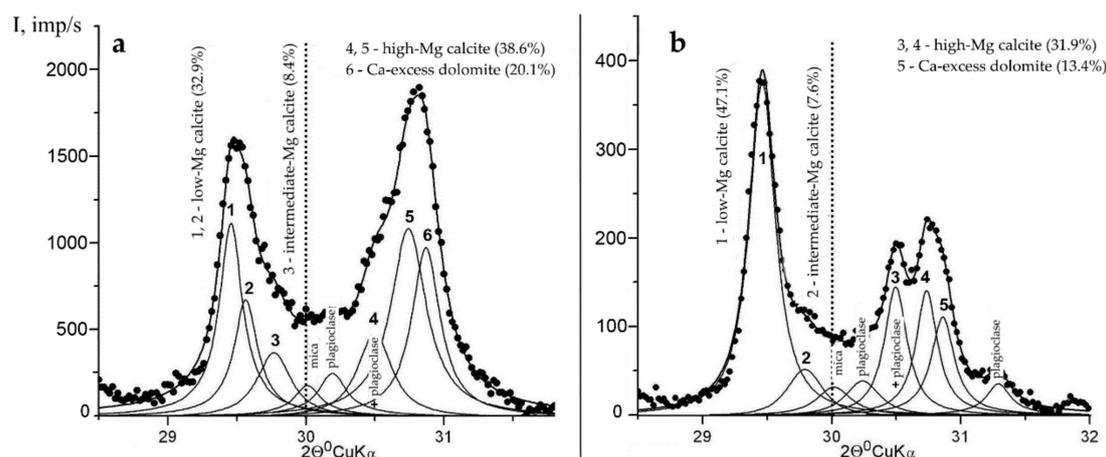

Figure 2. Practical application of the modeling complex XRD-profiles' method of low-temperature carbonates in lacustrine sediments. Experimental profiles—dotted line, model profiles (individual and total)—solid line. The total content of carbonates in the sample was assumed to be 100%.

Decomposition of the extended diffraction maxima, which had a complex configuration and represented a superposition of several peaks of carbonate phases with different Mg contents in the structure, into individual peaks using the Pearson VII function allowed us to establish the position and integral intensity of each peak and obtain quantitative ratios of carbonates [4,32].

3. Results

3.1. Biota Contribution in Small Lakes (the South of Western Siberia)

The sources of autochthonous organic matter in the studied lakes were primary producers (phytoplankton and macrophytes), as well as consumers and decomposers (zoo- and bacterioplankton). Primary producers (phytoplankton, phytoperifiton, phytobenthos, and macrophytes) in the reservoir during photosynthesis create organic matter that is processed in the food chain and enters the bottom sediments. All subsequent stages after photosynthesis are stages of mineralization and destruction [33]. The interaction of the production and destruction of organic matter ultimately determines, along with other factors, the parameters of the bottom sediments. In a collaborative article with biologists [34], the fluxes of organic compounds (organic carbon, nitrogen, and phosphorus) and the contribution of phytoplankton with regard for its grazing by zooplankton, zooplankton, and macrophytes were calculated for small lakes in south of Western Siberia. It is reasonable to expect that organic matter in the sapropel of lakes should contain compounds found in the plankton biomass (proteins, lipids, and polysaccharides), as well as the components of the biomass of the higher plants. However, the autochthonous organic matter was significantly modified while recycled in the "microbial loop", and this notably affected the final forms of compounds coming to the sapropel. The significant biogenic contribution to the organic matter flow into the bottom sediments of small lakes in the south of Western Siberia was considered circumstantially in various papers [33–35].

3.2. Water Composition in Small Lakes (the South of Western Siberia)

The water TDS of the studied lakes varies significantly from freshwater and brackish, found in all landscape types, to brines in the steppe landscape. In areas with a humid climate (Vasyugan plain), ultra-fresh and freshwater are mainly formed as a result of excess moisture, as well as the migration of easily soluble salts and soil formation products to lower soil horizons. In the zones of the semiarid and arid climate of forest–steppe and dry steppe (Baraba lowland, Kulunda plain), more intensive accumulation of easily soluble salts occurs, and water in a full range of salinity is formed, from fresh to brine. The water chemical composition in the studied lakes is mainly bicarbonate with variations in the cationic composition of Ca–Na–Mg. It forms because of the water transformation caused by evaporation and winter cryogeochemical processes (Figure 3).
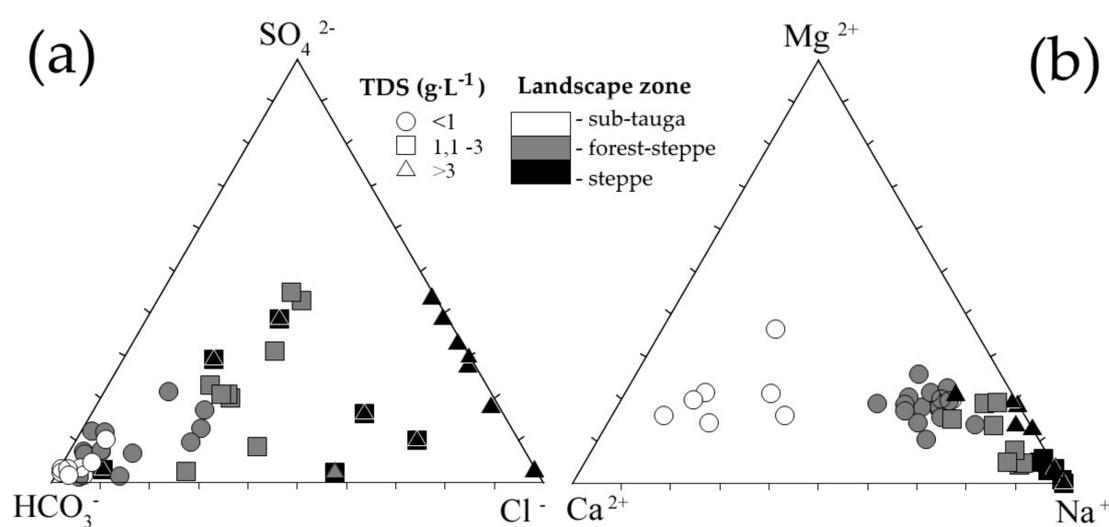

Figure 3. Ferre Triangle of lake water composition, taking into account the total dissolved solids' (TDS) values and landscape type. (**a**) anionic composition of water, (**b**) cationic composition of water.

The waters are mostly alkaline (pH > 8), with the exception of some sub-taiga lakes (pH 6.3–6.7). The Eh indicator of water in all lakes is positive and changes within the range of 287–375 mV regardless of the landscape. The content of oxygen dissolved in water in most lakes is quite high and varies from 134% (11.47 mg·L^{-1}) to 72% (6.29 mg·L^{-1}), and only in some lakes is it significantly lower (<50%), which is explained by the active processes of organic matter destruction occurring during bottom sediment formation.

3.3. Bottom Sediments in Small Lakes (the South of Western Siberia)

Lacustrine bottom sediments are organic–mineral silts (sapropels and mineral silts) with an ash content of 45–94% with a massive, small-lumpy, nutty-lumpy texture. Sometimes there are the remains of vegetation. The color of the bottom sediments is bluish-green, tobacco-green to black. There is often a strong smell of hydrogen sulfide. The sediments have a high viscosity (mainly in the lower horizons). Humidity throughout the depth of the core varies from 98% to 70%.

Regardless of the landscape type, most lakes are characterized by the organic–mineral (ash content 30–50%) and mineral–organic (ash content 50–70%) types of sapropel. The distribution of sapropel classes (Si/Ca ratio) among all the considered lakes is uneven. Lakes with a silicon-class sediment predominate. Most lakes are mixed in terms of the dominant production type. Features of the composition and genesis of bottom sediments of various classes are considered in detail in [35].

The major and trace element composition of small lakes' bottom sediments in the south of Western Siberia has been studied. The concentration of trace elements occurs mainly because of the minerals of the terrigenous component of deposits: Quartz, feldspar, and mica. A significant role also belongs to the dark-colored minerals contained in the fragments of rocks from the catchment areas (epidote, hornblende, actinolite, cummingtonite, and accessory minerals: Ilmenite, rutile, titanite, magnetite, hematite, zircon, monocyte, etc.), represented as sharp-angled, unpolished, clastic forms, and well-rounded grains of eolian origin [3,29,36].

Comparison of the element concentrations in the lacustrine bottom sediments of various landscapes in the south of Western Siberia with the composition of the upper continental crust showed accumulation of Ca, Mg, Sr, Ni, Cu, Cd, and Sb during modern sedimentation and depletion of K, Al, Si, Ti, Th, and Ba, as well as Fe, Co (Figure 4). The depletion of elements, including Na, K, and Al, is caused by the effect of the dilution of the sediment by carbonates and organic matter. A detailed description of the mineral composition of the small lakes' bottom sediments in the south of Western Siberia is discussed below.
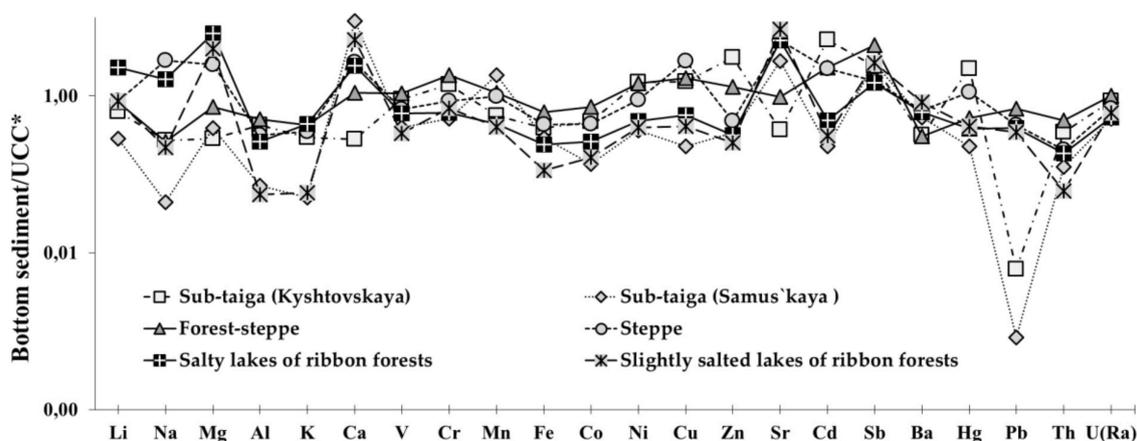

Figure 4. The multi-element spectrum of the average values of the studied elements for bottom sediments of lake systems in the south of Western Siberia normalized to the values of the upper continental crust concentrations according to Wedepohl, K.H. [37].

Calcite–dolomite carbonates and aragonite are widely distributed among modern authigenic minerals in small lakes in the south of Western Siberia. Siderite, rhodochrosite, and magnesite are occasionally found in subordinate quantities. The formation of authigenic carbonate minerals occurs at geochemical barriers: Drifting biota–water (cyanobacterial mats, macrophytes/algae drifting on the water surface), submerged biota–water (submerged macrophytes and/or algae), and water–bottom sediments.

Carbonate formation on the geochemical barriers drifting biota–water and submerged biota–water can be seen with the naked eye. Mineral formation occurs directly on and under cyanobacterial mats, on the surface of submerged algae, and underwater parts of macrophytes. The size of individual formations reaches 30–50 µm, and their clusters 0.5–1 cm. They can be spread over the entire surface of cyanobacterial mats and/or submerged biota. At the water–bottom sediment boundary, the size of individual formations does not exceed 20–30 µm, and their clusters are about 100–150 µm, which can be observed using SEM.

Authigenic aragonite and low-magnesium calcite are the main minerals of the drifting biota–water and submerged biota–water borders in Lake Linevo. At the same time, authigenic carbonate mineralization occurs at the water–bottom sediment boundary. The formed carbonates complement the carbonates that move from the drifting biota–water and submerged biota–water borders and, without dissolving, are buried in the sediment (Figure 5).

Figure 5. Diffractograms of Lake Linevo carbonate minerals (Kyshtovskaya system, Vasyugan plain) formed on geochemical barriers: Water–bottom sediments (black color) and submerged biota–water (gray color).

4. Discussion

The full salinity range of the lake waters is due to the surface features of the Baraba lowland and the Kulunda plain. The territory is characterized by the presence of a strictly parallel, north-eastern stretch of alternating hillocks and hollows in which there are numerous small and large lakes, swamps, and drylands. Under the conditions of structural and geological control, there is a local redistribution of moisture and easily soluble salts: Their flow is from the hillocks to the inter-hillocks spaces [31]. It is established that the known meridional change in the ionic composition and TDS of waters in the south of Western Siberia from north to south (from the sub-taiga to the dry steppe zone) is complicated by the presence of a large number of small lakes with a bicarbonate-sodium (soda) water composition.

It is known that soda water, which is found in the considered landscape types, contributes to the abundant development of biota [12,38]. The development of biota of various species (cyanobacterial mats, macrophytes/algae drifting on the water surface, submerged macrophytes and/or algae) in turn leads to the processes of the biomineralization, biorecovery, biosorption, and bioaccumulation processes (their difference is schematically explained in [39]). New complexes are formed in solution, local pH and Eh conditions are changing, and biominerals appear. The influence of different biota types was considered, for example, in the works [15,40–43].

Lakes of all of the landscape types were grouped according to the value of TDS. The first group was made up of freshwater lakes (TDS < 1 g·L^{-1}). The composition of water was mainly bicarbonate-sodium. Bottom sediments were sapropels mainly characterized by the mineral–organic type of the calcium class. Less common sapropels were the organic–mineral and mineralized types. Authigenic minerals were single grains (~60 μm) and clusters of grains of low-magnesium calcite and aragonite (Figure 5).

The second group was made up of brackish lakes (TDS 1.1–3 g·L^{-1}). The main composition of water was bicarbonate-sodium with a significant content of Cl^- and/or SO_4^{2-}. Bottom sediments were similar in composition to the first group. However, in the authigenic part of the bottom sediment, increased values of intermediate- and high-Mg calcites were found with a subordinate amount of low-Mg calcite (Figure 5).

The third group was made up of salt lakes (TDS 3.1–10 g·L^{-1}) and brines (TDS > 50 g·L^{-1}). Bottom sediments were a mineralized type of sapropel and mineral silts. In lakes with a composition of water characterized by sodium bicarbonate, grains of high-magnesium calcite and Ca-excess dolomite were precipitated. Calcite, low-magnesium calcite, and aggregations of aragonite grains (3–5 μm) were formed in lakes with sodium-chloride brines (Figure 5).

The Ca-excess dolomite formation in lacustrine sediments was of particular interest. It should be emphasized that the mixed, layered structure of Ca-excess dolomite was closer to the structure of high-Mg calcite than the structure of dolomite sensu stricto [32]. The generally accepted opinion is that the Ca-excess dolomite is a so-called "protodolomite", i.e., a transitional metastable phase that occurs at the early stages of dolomite formation, and does not arrive to crystal-chemical confirmation, at least in normal P-T conditions.

Authigenic Ca-excess dolomite is an extreme member of the Ca–Mg series of anhydrous carbonates and has a different genesis than stoichiometric dolomite [44]. Variations in CaO and MgO content in Ca-dolomite are shown in the range of 10–15%-eq relative to stoichiometric dolomite (Figure 6). In our case, we can trace the entire spectrum of calcite–dolomite series' carbonates formed in small lakes in the south of Western Siberia from low-magnesium calcites to Ca-excess dolomites.

Living organisms, in accordance with their physiological characteristics, have the ability to use chemical elements from the environment to form the skeleton, and include them in enzymes and the cycle of substances in the process of photosynthesis, etc. [15,45]. It was found that at the drifting biota–water and submerged biota–water borders, authigenic minerals form thin films on the primary skeleton of algae (pseudomorphoses by filaments and cells of microorganisms) (Figure 7b). The films consist of fine-grained aragonite and/or calcite and are formed during the life of algae in lakes of all the studied landscape types and in a wide variety of TDS values.

Another possible way of carbonates being formed is through mineral deposition, which results from the concentration of individual elements when living matter creates specific local pH and Eh conditions during photosynthesis. In addition to aragonite (Figure 7a), new formations of magnesium sulfates (Figure 7b) or magnesium carbonates (Figure 7c,d) were found in the composition of thin films on the primary framework of algae. The formation of primary magnesium minerals may be due to the presence of Mg^{2+} in the center of the chlorophyll molecule. It is known that photosynthetic organisms, while extracting carbon dioxide dissolved in water, shift the pH to alkaline values and thereby stimulate the deposition of carbonates.
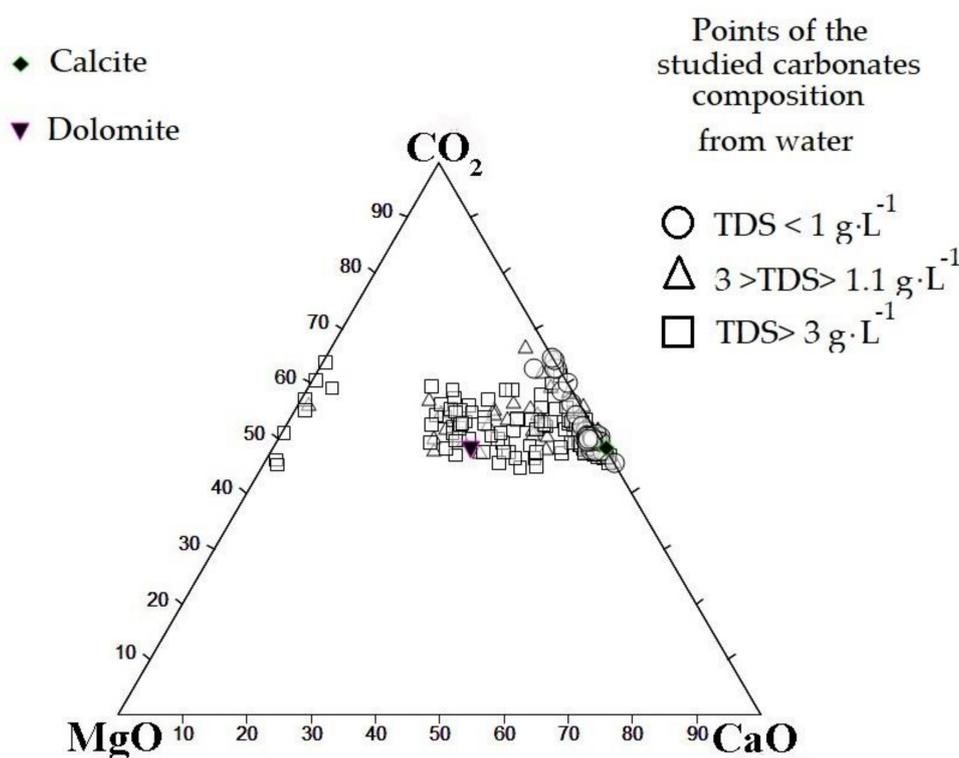
Figure 6. Ferre Triangle of calcite–dolomite series' carbonate (%-eq) composition formed in small lakes in the south of Western Siberia taking into account the value of TDS (g·L^{-1}). The composition of calcite (rhombus) and dolomite (inverted triangle) corresponds to the theoretical formula.
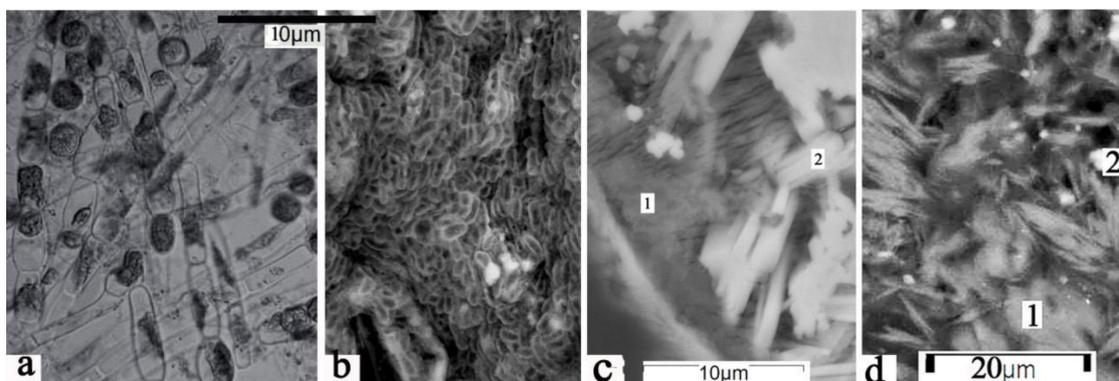

Figure 7. Microphotographs of authigenic minerals at the drifting biota–water and submerged biota–water borders: (**a**) Photo of *Ctenocladus circinnatus Borz* (Lake Petukhovo) [46]; (**b**) mineral films (Mg-sulfate) on the surface of the algobacterial colony (Lake Petukhovo); (**c**) mineral films (Mg-carbonate) on the surface of the algobacterial colony (Lake Urmannoe) and their replacement by carbonates: 1—$MgCO_3$, 2—$CaCO_3$; (**d**) 1—$MgCO_3$-substituted algobacterial colony (Lake Tanatar—6), 2—$CaCO_3$.

Anaerobic decomposition of the initial sedimentary organic matter produces gases (CO_2, H_2S, NH_3, etc.) through a large amount of bacterial activity in the first centimeters of bottom sediments. It contributes to the dissolution and disappearance of magnesium sulfates and carbonates, as well as aragonite partially, followed by biochemogenic deposition of calcite (Figure 8a,b) and high-magnesium calcite of various morphologies (Figure 8c) in lakes from fresh to brines. Aggregates of low-magnesium calcite and calcite are among the most common authigenic minerals in small lakes in the south of Western Siberia (Figure 8d).
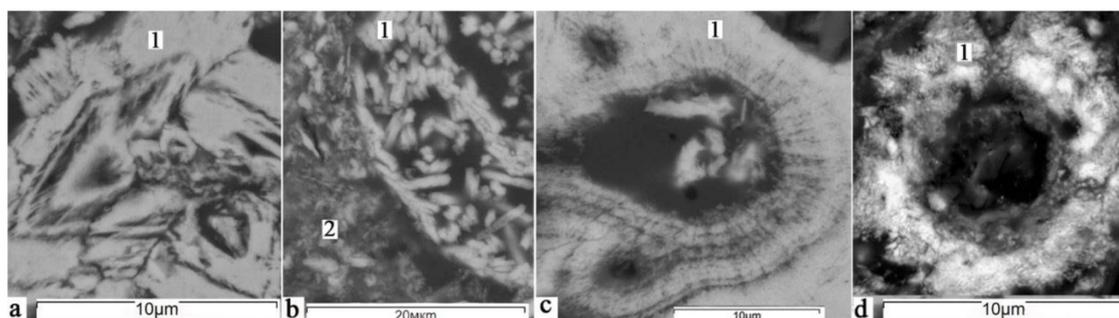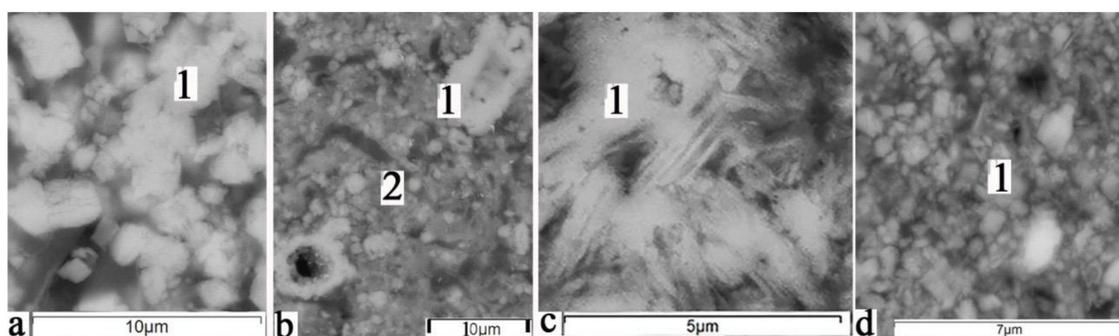
Figure 8. Microphotographs of authigenic carbonates at the water–bottom boundary. Calcite (a,b) and low-magnesium calcite (c,d): (**a**) Rhombohedral crystals of different sizes (Lake Danilovo), 1—$CaCO_3$; (**b**) 1—dendrite aggregates (presumably the fusion of thin scalenohedral crystals) and 2—their replacement by low-magnesium calcite; (**c**) zonal–concentric formations of low-magnesium calcite (Lake Karbalyk); (**d**) pseudomorphoses of low-magnesium calcite on the remains of macrophytes (Lake Peschanoe).

Chemogenic Ca-excess dolomites with different calcium contents (Figure 9a,b) and high-magnesium calcites (Figure 9c,d) are deposited mainly at the water–bottom sediment boundary in lakes with bicarbonate-sodium (soda) and chloride–bicarbonate–sodium water compositions with a TDS $> 3g \cdot L^{-1}$ and pH > 9. Biochemogenic high-magnesium calcites and Ca-excess dolomites are deposited at the water–bottom sediment boundary in lakes with a bicarbonate-sodium (soda) water composition with a TDS $< 3g \cdot L^{-1}$ and pH > 9.

Figure 9. Microphotographs of authigenic carbonates at the water–bottom boundary. Ca-excess dolomite (a,b) and high-magnesium calcite (c,d): (**a**) Rhombohedral crystals of various sizes (Lake Tanatar—4), 1—Ca-excess dolomite; (**b**) 1—fouling of thin rhombohedral crystals of Ca-excess dolomite around terrigenous grains and mortmass, 2—grains of high-magnesium calcite (Lake Rublevo); (**c**)—intergrowth of thin scalenohedral crystals of high-magnesium calcite (Lake Tanatar-6); (**d**)—micrograins of high-magnesium calcite (Lake Petukhovo).

Variations in the carbonates' composition, in turn, correlate with the values of TDS, pH, and water composition. In lakes of HCO_3–Mg–Na water composition (TDS 2.1–2.6 $g \cdot L^{-1}$), carbonates are characterized by high-magnesium calcite and Ca-excess dolomite. In lakes of a HCO_3–Na and HCO_3–Cl–Na water composition, (TDS 9, 41.5 $g \cdot L^{-1}$) carbonates are characterized by Ca-excess dolomites (Table 2).

In lakes of a Cl–HCO_3–Na, Cl–Mg–Na, and Cl–Na composition (TDS 52.3–54.2 $g \cdot L^{-1}$), the main carbonate was Ca-dolomite (Table 2). For all the above-mentioned lakes, the pH of water varied in the range 9.0–9.6. In lakes of a Cl–Na composition, such as Lake Malinovoe, aragonite was formed (TDS = 396.6 $g \cdot L^{-1}$, pH 7.6). In Lake Krasnovishnevoe (TDS = 297.3 $g \cdot L^{-1}$, pH 7.7), there were only low levels of calcite impurities.

Table 2. Comparison of physical and chemical parameters and water composition of small lakes in the south of Western Siberia with the results of X-ray diffractometry (XRD).

Lake	TDS, g·L^{-1}	Ph	Water Composition	Mineral Composition
Demkino	1	9.0	bicarbonate magnesium-sodium, fresh	Main phase high-Mg-Cal, impurity smectite
Rublevo	1.5	9.1	bicarbonate magnesium-sodium, saltish	Main phase high-Mg-Cal, Ca-Dol, impurity smectite, Qtz, KFsp
Tanatar-4	9.0	9.5	bicarbonate sodium, salt	Main phase Ca-Dol, impurity high-Mg-Cal, disordered smectite, Qtz
Tanatar -6	41.5	9.8	bicarbonate-chloride sodium, brine	Main phase Qtz, Pl, Ca-Dol, Cal, halite, impurity KFsp, trona, disordered smectite
Petukhovo (ribbon forests)	52.3	9.8	chloride- bicarbonate sodium, brine	Main phase Ca-Dol, Qtz, impurity Cal, halite, Pl, disordered smectite and illite-smectite, trona, KFsp
Petukhovo (steppe)	54.2	9.5	chloride magnesium-sodium, brine	Main phase Qtz, Pl, Ca-Dol, impurity Ca-Dol, KFsp
Jodnoe	177	9.6	chloride sodium, brine	Main phase NaCl, Ca-Dol, Cal, Qtz, impurity thenardite
Krasnovishnevoe	297.3	7.7	chloride sodium, brine	Main phase Qtz, NaCl, impurity Pl, KFsp, gypsum, small impurity Cal
Malinovoe	396.6	7.6	chloride sodium, ultrabrine	Main phase NaCl, aragonite, impurity Qtz, Pl, Cal, Ca-Dol

High-Mg-Cal—high-magnesium calcite; Ca-Dol—Ca-excess dolomite; Cal—calcite; Qtz—quartz; KFsp—potassium feldspar; Pl—plagioclase.

The Al/Ca ratio is the best representation in terms of showing the correlation between the allogenic and authigenic parts of small lake sediments through the distribution of elements along the core. Aluminum demonstrates the amount of terrigenous fraction in the sediment and calcium shows mainly authigenic fraction. Silicon, being a rock-forming element, in this case, cannot be used to characterize the terrigenous component, because there is a large number of diatoms in the lacustrine bottom sediments. In general, the small lakes studied are characterized by a higher content of Ca in the upper horizons of bottom sediments, which is associated with the formation of authigenic calcite–dolomite carbonates on the geochemical barriers (Figure 10). This is evidence of a hot and dry climate in the summer and a long period of lake-ice cover, possibly even complete freezing in the winter. As a result, the supersaturation boundaries of the solution are reached, and favorable conditions for the formation of calcite–dolomite series' carbonates arise.
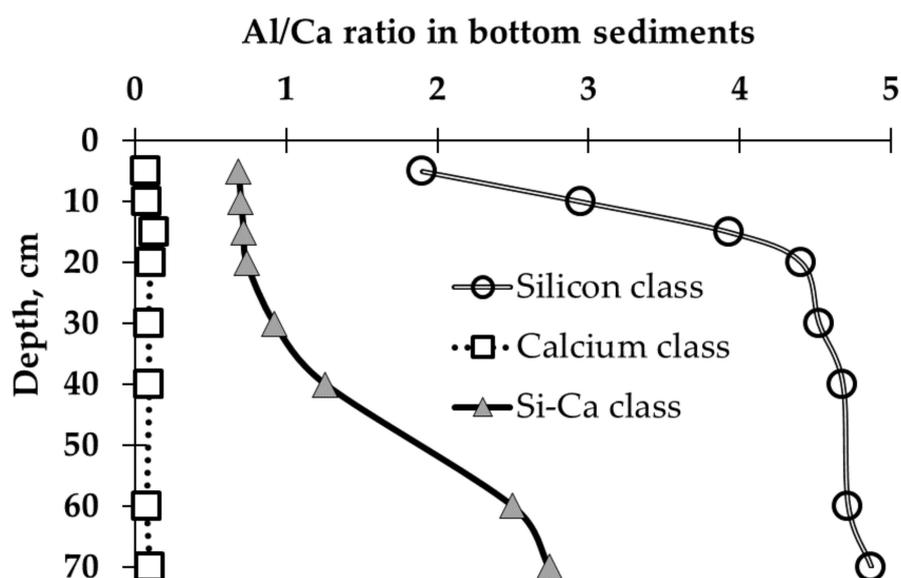

Figure 10. Vertical distribution of the Al/Ca ratio by depth for silicon, calcium, and mixed classes of bottom sediments of small lakes in the south of Western Siberia.

Cryogenic mineral formation is when the temperature decreases and the amount of unfrozen water decreases, respectively, causing the concentration of salts in it to increase. As the solution reaches eutectic points, salt crystallization begins. In multicomponent systems, such as natural waters, the eutectic points may shift slightly in one direction or another as compared with the empirical data for simple systems, but the sequence of salt precipitation is usually preserved [47].

Significant changes in TDS even occur during the summer period in lakes Rublevo and Demkino (Kulunda plain). For these lakes, it was found that in June, the TDS value was 0.77 and 0.93 $g \cdot L^{-1}$, and then in August, it was 1.5 and 1 $g \cdot L^{-1}$, respectively. Fluctuations in the physical–chemical parameters were associated with landscape–climatic characteristics, such as shallow lake depths (up to 3 m), wind mixing, the absence of the thermocline in lakes, and the presence of reducing conditions at the water–bottom sediments' boundary, as evidenced by the formation of framboidal pyrite since the first centimeters of sediments (Figure 11). High water pH is not only the result of organic matter decomposition in the lakes, the soil and rocks of the catchment area also play a significant role.
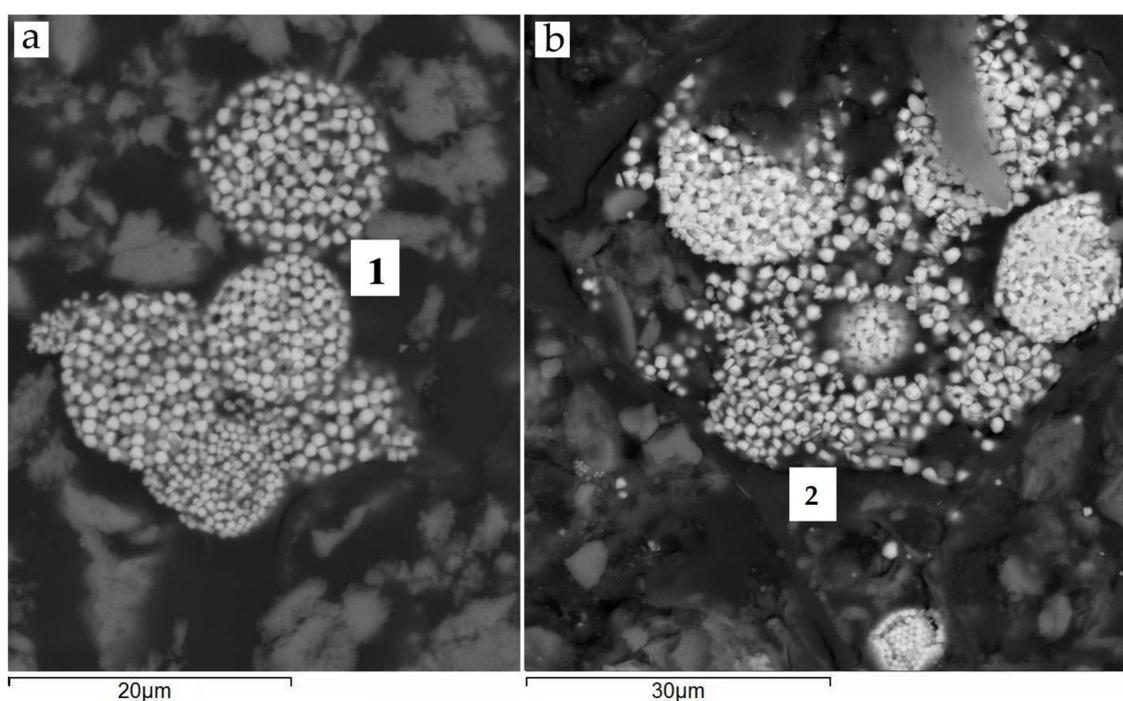

Figure 11. (**a**) Lake Karbalyk (1)—framboidal pyrite from the depth of 0–5 cm of the bottom sediments. (**b**) Lake Kukley (2)—framboidal pyrite and a cluster of pyrite crystals from the depth of 0–5 cm of the bottom sediments.

As a result, even with the TDS from 0.77 to 1.5 $g \cdot L^{-1}$ in different periods, high-magnesium calcites and Ca-excess dolomites were formed in lakes Rublevo and Demkino along the entire depth of the bottom sediment core (Table 3). It should be noted that all the minerals had a low degree of crystallinity. A significant amount of X-ray amorphous component was found on diffractograms, and this may not only be due the presence of organic matter.

The landscape features of the study area promote the burial of carbonate minerals in bottom sediments-lakes are located in the same azonal landscape (eolian) [29]. The eolian fraction being introduced into the bottom sediments was considered in [36], using the example of "black dust storms" typical of the steppe of the south of Western Siberia. Plowing of virgin lands in the 1960s (flat, unpaved territories) increased the eolian component in bottom sediments. It, in turn, contributes to the burial of authigenic minerals in organic–mineral silts, and now, because of the flat-low terrain and climate of the territory, and particularly in the winter and spring period, the eolian component's "hurricane-like" demolition heavily affects the lakes.

Table 3. Bottom sediment mineral composition of small lakes Rublevo and Demkino (Kulunda plain).

Lake	Depth (cm)	Mineral Composition
Rublevo	0–5	Main phase high-Mg-Cal, small impurity Qtz, Ca-Dol, magnesite; and a lot of X-ray amorphous component
	75–82	Main phase carbonates series high-Mg-Cal – Ca-Dol, impurity smectite, Qtz
Demkino	0–5	Main phase high-Mg-Cal, small impurity Qtz; and a lot of X-ray amorphous component
	60–65	Main phase carbonates series high-Mg-Cal – Ca-Dol, impurity smectite

High-Mg-Cal—high-magnesium calcite; Ca-Dol—Ca-excess dolomite; Qtz—quartz.

Thus, in the autumn–winter period, small lakes in the south of Western Siberia with a depth of 3–5 m are covered with ice up to 1.5 m thick, which significantly increases the TDS of unfrozen water under the ice, since the volume of water decreases several times. As a result of a long period of ice covering (7–9 months), eolian material accumulates on the lake ice surface and during the spring–summer melting period, it is released into the lake. This leads to carbonate mineral burial in the bottom sediments.

5. Conclusions

In the small, drainless lakes of the south of Western Siberia, in all the landscapes studied, calcite–dolomite carbonate series' minerals and aragonite are formed on geochemical barriers: Drifting biota–water (cyanobacterial mats, macrophytes/algae drifting on the water surface), submerged biota–water (submerged macrophytes and/or algae), and water–bottom sediments.

The wide distribution of bicarbonate-sodium waters in the south of Western Siberia breaks the general zoning of lake waters in the considered landscapes and contributes to the abundant development of biota of various species. It, in turn, leads to the processes of concentration and redistribution of substances, as well as to local changes in the environment in the water body.

The shallow depth (up to 5 m) of lakes, the sharply continental climate, the mainly subzero temperatures, and the ice and snow cover contribute to a significant cryogenic effect, which influences authigenic mineral formation in the small lakes. Water metamorphization contributes to consistent precipitation of minerals corresponding to water freezing. Ice and snow cover together with the flat landscape and extremely diverse air masses contribute to the accumulation of eolian material in the lake area. When the ice and snow cover melts, this material is released into the lake and leads to authigenic mineral burial in the bottom sediments.

Minerals formed during the life of aquatic biota at the drifting biota–water and submerged biota–water borders form thin films on the primary framework of algae. They consist of sulfates and/or carbonates of magnesium. In this case, the magnesium ion in the chlorophyll molecule becomes the seed for the process of carbonation. Mineral aggregates are formed consisting of fine-grained aragonite, carbonates, and/or magnesium sulfates.

Biochemogenic low-magnesium calcite, calcite, and aragonite are formed in lakes with TDS from ultra-fresh to brine (from <0.2 to 400 g·L^{-1}), mainly at the drifting biota–water and submerged biota–water borders. Chemogenic calcite is deposited in sodium-chloride brines mainly at the water–bottom sediment boundary.

Chemogenic high-magnesium calcites and Ca-excess dolomites are deposited at the water–bottom sediment boundary in lakes with bicarbonate-sodium (soda) and chloride-bicarbonate-sodium water compositions with TDS > 3 g L^{-1} and pH >9.

Biochemogenic high-magnesium calcites and Ca-excess dolomites are deposited at the water–bottom sediment boundary in lakes with a bicarbonate–sodium (soda) water composition with TDS < 3 g L^{-1} and pH > 9 as a result of changes in physical and chemical conditions due to a combination of landscape, geochemical, and biogenic factors.

References

1. Bejrom, S.; Vasil'ev, I.; Gadzhiev, I. *Natural Resources of the Novosibirsk Region*; Nauka: Novosibirsk, Russia, 1986; p. 215. (In Russian)

2. Shtin, S. *Lake Sapropels and the Basics of Their Integrated Development*; MISIS National University of Science and Technology "MISIS": Moscow, Russia, 2005; p. 373. (In Russian)

3. Strakhovenko, V.D.; Taran, O.P.; Ermolaeva, N.I. Geochemical characteristics of the sapropel sediments of small lakes in the Ob'-Irtysh interfluve. *Russ. Geol. Geophys.* **2014**, *55*, 1160–1169. [CrossRef]

4. Solotchina, E.P.; Sklyarov, E.V.; Strakhovenko, V.D.; Solotchin, P.A.; Sklyarova, O.A. Mineralogy and crystal chemistry of carbonates in modern sediments of shallow lakes of Olkhon area (Baikal region). *Dokl. Earth Sci.* **2015**, *461*, 394–400. [CrossRef]

5. Solotchina, E.P.; Kuzmin, M.I.; Solotchin, P.A.; Maltsev, A.E.; Leonova, G.A.; Danilenko, I.V. Authigenic carbonates from Holocene sediments of Lake Itkul (south of West Siberia) as indicators of climate changes. *Dokl. Earth Sci.* **2019**, *487*, 745–750. [CrossRef]

6. Zhdanova, A.N.; Solotchina, E.P.; Krivonogov, S.K.; Solotchin, P.A. Mineral composition of the sediments of Lake Malye Chany as an indicator of Holocene climate changes (southern West Siberia). *Russ. Geol. Geophys.* **2019**, *60*, 1163–1174. [CrossRef]

7. Borzenko, S.V.; Shvartsev, S.L. Chemical composition of salt lakes in East Transbaikalia (Russia). *J. Appl. Geochem.* **2019**, *103*, 72–84. [CrossRef]

8. Last, W.M.; Ginn, F.M. Saline systems of the Great Plains of western Canada: An overview of the limnogeology and paleolimnology. *Saline Syst.* **2005**, *1*, 1–38. [CrossRef] [PubMed]

9. Hammer, U.T. *Saline Lake Ecosystems of the World*; Dr. W. Junk Publishers: Dordrecht, The Netherlands, 1986; p. 616.

10. Stankevica, K.; Vincevica-Gaile, Z.; Klavins, M.; Kalnina, L.; Stivrins, N.; Grudzinska, I.; Kaup, E. Accumulation of metals and changes in composition of freshwater lake organic sediments during the Holocene. *Chem. Geol.* **2020**, *539*, 119502. [CrossRef]

11. Strakhov, N. On the classification of sediments of modern seas and lakes of low mineralization. *Izvestiya USSR AS* **1953**, *3*, 59–65. (In Russian)

12. Vernadskii, V. *Geochemistry and the Biosphere*; Synergetic Press: Santa Fe, NM, USA, 2007; p. 480.

13. Leeder, M. *Sedimentology: Process and Products*; George Allen & Unwin: London, UK, 1982; p. 344.

14. Berner, R.A.; Westrich, J.T.; Graber, R.; Smith, J.; Martens, C.S. Inhibition of aragonite precipitation from supersaturated seawater; a laboratory and field study. *Am. J. Sci.* **1978**, *278*, 816–837. [CrossRef]

15. Kuznetsov, V. Petrography and origin of dolomite in carbonate deposits in various paleoclimates. *Carbonates Evaporites* **1999**, *14*, 125–137.

16. Kholodov, V. *Geochemistry of the Sedimentary Process*; Publishing House GEOSGEOS: Moscow, Russia, 2006; p. 608. (In Russian)

17. Wittkop, C.A.; Teranes, J.L.; Dean, W.E.; Guilderson, T.P. A lacustrine carbonate record of holocene seasonality and climate. *Geology* **2009**, *37*, 695–698. [CrossRef]

18. Solotchina, E.P.; Sklyarov, E.V.; Solotchin, P.A.; Vologina, E.G.; Stolpovskaya, V.N.; Sklyarova, O.A.; Ukhova, N.N. Reconstruction of the Holocene climate based on a carbonate sedimentary record from shallow saline Lake Verkhnee Beloe (western Transbaikalia). *Russ. Geol. Geophys.* **2012**, *53*, 1351–1365. [CrossRef]

19. Last, F.M.; Last, W.M.; Halden, N.M. Modern and late Holocene dolomite formation: Manito Lake, Saskatchewan, Canada. *Sediment. Geol.* **2012**, *281*, 222–237. [CrossRef]

20. Lee, C. Controls on organic carbon preservation: The use of stratified water bodies to compare intrinsic rates of decomposition in oxic and anoxic systems. *Geochim. Cosmochim. Acta* **1992**, *56*, 3323–3335. [CrossRef]

21. Frey, K.E.; McClelland, J.W. Impacts of permafrost degradation on arctic river biogeochemistry. *Hydrol. Process.* **2009**, *23*, 169–182. [CrossRef]

22. Sklyarov, E.V.; Solotchina, E.P.; Vologina, E.G.; Izokh, O.P.; Kulagina, N.V.; Orlova, L.A.; Sklyarova, O.A.; Solotchin, P.A.; Stolpovskaya, V.N.; Ukhova, N.N. Holocene climate history of the Western Baikal region: Carbonate sedimentary record of Kholbo-Nur Lake. *Dokl. Earth Sci.* **2010**, *431*, 490–496. [CrossRef]

23. Audry, S.; Pokrovsky, O.S.; Shirokova, L.S.; Kirpotin, S.N.; Dupré, B. Organic matter mineralization and trace element post-depositional redistribution in Western Siberia thermokarst lake sediments. *Biogeosciences* **2011**, *8*, 3341–3358. [CrossRef]

24. Gas'kova, O.L.; Strakhovenko, V.D.; Ovdina, E.A. Composition of brines and mineral zoning of the bottom sediments of soda lakes in the Kulunda steppe (West Siberia). *Russ. Geol. Geophys.* **2017**, *58*, 1199–1210. [CrossRef]

25. Mandal, S.K.; Ray, R.; González, A.G.; Mavromatis, V.; Pokrovsky, O.S.; Jana, T.K. State of rare earth elements in the sediment and their bioaccumulation by mangroves: A case study in pristine islands of Indian Sundarban. *Environ. Sci. Pollut. Res.* **2019**, *26*, 9146–9160. [CrossRef]

26. Solotchina, E.P.; Sklyarov, E.V.; Vologina, E.G.; Solotchin, P.A.; Stolpovskaya, V.N.; Sklyarova, O.A.; Izokh, O.P.; Ukhova, N.N. Climatic signals in the holocene carbonate sedimentary record of Namshi-Nur lake, West Baikal Region. *Dokl. Earth Sci.* **2011**, *436*, 295–300. [CrossRef]

27. Strakhovenko, V.D.; Solotchina, E.P.; Vosel', Y.S.; Solotchin, P.A. Geochemical factors for endogenic mineral formation in the bottom sediments of the Tazheran lakes (Baikal area). *Russ. Geol. Geophys.* **2015**, *56*, 1437–1450. [CrossRef]

28. Ovchinnikov, A. *Hydrogeochemistry*; Nedra: Moscow, Russia, 1970; p. 200. (In Russian)

29. Klochko, A.A.; Romanovskaya, M.A. *National Atlas of Russia Vol. 2. Nature and the Environment*; Federal State Unitary Enterprise GOSGISCENTER: Moscow, Russia, 2004; p. 495. (In Russian)

30. Korde, N. *Biostratigraphy and Typology of Russian Sapropels*; Publishing house of the USSR Academy of Sciences: Moscow, Russia, 1969; p. 219. (In Russian)

31. Strakhovenko, V.D.; Roslyakov, N.A.; Syso, A.I.; Ermolaeva, N.I.; Zarubina, E.Y.; Taran, O.P.; Puzanov, A.V. Hydrochemical characteristic of sapropels in Novosibirsk oblast. *Water Resour.* **2016**, *43*, 539–545. [CrossRef]

32. Solotchina, E.P.; Solotchin, P.A. Composition and structure of low-temperature natural carbonates of the calcite-dolomite series. *J. Struct. Chem.* **2014**, *55*, 779–785. [CrossRef]

33. Yermolaeva, N.I.; Zarubina, E.Y.; Romanov, R.E.; Leonova, G.A.; Puzanov, A.V. Hydrobiological conditions of sapropel formation in lakes in the south of Western Siberia. *Water Resour.* **2016**, *43*, 129–140. [CrossRef]

34. Taran, O.P.; Boltenkov, V.V.; Ermolaeva, N.I.; Zarubina, E.Y.; Delii, I.V.; Romanov, R.E.; Strakhovenko, V.D. Relations between the chemical composition of organic matter in lacustrine ecosystems and the genesis of their sapropel. *Geochem. Int.* **2018**, *56*, 256–265. [CrossRef]

35. Strakhovenko, V.D.; Ovdina, E.A.; Malov, G.I.; Yermolaeva, N.I.; Zarubina, E.Y.; Taran, O.P.; Boltenkov, V.V. Genesis of organomineral deposits in lakes of the central part of the Baraba Lowland (south of West Siberia). *Russ. Geol. Geophys* **2019**, *60*, 978–989. [CrossRef]

36. Gavshin, V.M.; Scherbov, B.L.; Melgunov, M.S.; Strakhovenko, V.D.; Bobrov, V.A.; Tsibulchik, V.M. [137]Cs and ^{210}Pb in lake sediments of the Steppe Altai as indicators of the dynamics of the anthropogenic changes in the geochemical background during the XX century. *Russ. Geol. Geophys.* **1999**, *40*, 1331–1341. (In Russian)

37. Wedepohl, K.H. The composition of the continental crust. *Geochim. Cosmochim. Acta* **1995**, *59*, 1217–1232. [CrossRef]

38. Zavarzin, G.A. Epicontinental soda waters as inferred relict biotopes of terrestrial biota formation. *Microbiology* **1993**, *62*, 789–800. (In Russian)

39. Newsome, L.; Morris, K.; Lloyd, J.R. The biogeochemistry and bioremediation of uranium and other priority radionuclides. *Chem. Geol.* **2014**, *363*, 164–184. [CrossRef]

40. Shirokova, L.S.; Mavromatis, V.; Bundeleva, I.; Pokrovsky, O.S.; Benezeth, P.; Pearce, C.; Oelkers, E.H. Using Mg isotopes to trace cyanobacterially mediated magnesium carbonate precipitation in alkaline lakes. *Aquat. Geochem.* **2013**, *19*, 1–24. [CrossRef]

41. Sanz-Montero, M.E.; Rodriguez-Aranda, J.P. Silicate bioweathering and biomineralization in lacustrine microbialites: Ancient analogues from the Miocene Duero Basin, Spain. *Geol. Mag.* **2009**, *146*, 527–539. [CrossRef]

42. Samylina, O.S.; Zaytseva, L.V.; Sinetova, M.A. Participation of algal-bacterial community in the formation of modern stromatolites in Cock Soda Lake, Altai Region. *Paleontol. J.* **2016**, *50*, 635–645. [CrossRef]

43. Holmer, M.; Storkholm, P. Sulphate reduction and sulphur cycling in lake sediments: A review. *Freshw. Biol.* **2001**, *46*, 431–451. [CrossRef]

44. Deelman, J.C. *Low-Temperature Formation of Dolomite and Magnesite*; Compact Disc Publications: Eindhoven, The Netherlands, 2011; p. 512.

45. Pokrovsky, O.S. Laboratory synthesis of calcium and magnesium carbonates: Factors controlling the formation of magnesian calcites in natural waters. *Lithol. Miner. Resour.* **1996**, *5*, 531–540. (In Russian)

46. Sapozhnikov, Ph.V.; Kalinina, O.Yu.; Nikitin, M.A.; Samylina, O.S. Cenoses of phototrophic algae of ultrasaline lakes in the Kulunda steppe (Altai krai, Russian Federation). *Oceanology* **2016**, *56*, 95–106. [CrossRef]

47. Gas'kova, O.L.; Solotchina, E.P.; Sklyarova, O.A. Reconstruction of solution chemistry evolution based on the sedimentary record of salt lakes in the Olkhon region. *Russ. Geol. Geophys* **2011**, *52*, 548–554. [CrossRef]