





# NEW DATA ON THE MINERAL AND GEOCHEMICAL COMPOSITION OF BOTTOM SEDIMENTS IN THE TANATAR SODA LAKES (KULUNDA PLAIN, RUSSIA)

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**Abstract:** The lakes of the Kulunda plain have long attracted the attention of researchers. A detailed geochemical testing of a chain of four small soda lakes of the Tanatar group allowed answering a number of questions. We used a complex of modern methods of mineralogy and geochemistry to update and add new data on the main phases of bottom sediments. The studied lakes have a pH  $\geq 8$  and a TDS of 2.1–41.5 g/L and a soda water composition. It has been established that over the past  $\sim 100$  years there has been no change in the mineral composition of bottom sediments. The main phases of the bottom sediments consist of intermediate and high-Mg calcite and Ca-excess dolomite. Magnesite is presented only as a small impurity. The formation and accumulation of these minerals occur throughout the core of bottom sediments. According to received data, a change in the hydrological regime of the catchment area was established. The feeding regime of the lakes has been changed because of the drying up of the Rublevaya River.

**Keywords:** small soda lakes, bottom sediments, high-magnesium carbonates, Ca-excess dolomite, Tanatar lakes, Kulunda plain

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## Introduction

Historically, researchers have focused on bigger water bodies like oceans, seas and large lakes. Data of the ILEC World Lake Database [*International Lake Environment Committee Foundation (ILEC)*, 1999] shows that researchers around the world are still most interested in large lakes. The study of small inland lakes is getting more relevant according to the works from various fields of science [*Bartosiewicz et al.*, 2015; *Borzenko*, 2020; *Galbarczyk-Gqsiorowska et al.*, 2009; *Strakhovenko et al.*, 2014; *Zheng*, 2014].

Small lakes are open systems where is a clear relationship between sedimentation process and physical, chemical, geographical, and climatic conditions. Each component of the lake (water, sediments, soils, soil-forming substrate and biota) is connected to each other and is a subject to anthropogenic impact. The geochemical and mineral compositions of bottom sediments reflect the lake environment and the interplay of various factors inside and outside the reservoir. It makes lakes informative and important objects of research [*Hammer*, 1986; *Solotchina et al.*, 2019; *Stankevica et al.*, 2020; *Strakhovenko et al.*, 2014].

In the south of Western Siberia, the lake area percentage averages  $\sim 2\%$  [*Izmailova and Korneenkova*, 2020]. Lakes are mainly small according to the classification by [*Ivanov*, 1948], shallow (up to 3–5 m deep) and drainless [*Savchenko*, 1997].

The water composition of the small lakes in the south of Western Siberia varies from bicarbonate magnesium-calcium freshwater (in the north, taiga zone) to sodium chloride brines (in the south, the steppe zone and the ribbon forest subzone). The meridional (from north to south) change in the ionic composition and total dissolved solids (TDS) of

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water is complicated by the presence of numerous small lakes with a bicarbonate-sodium (soda) water composition and an increased pH ( $> 8$ ) [Kolpakova et al., 2016; Savchenko, 1997; Strakhov, 1951; Strakhovenko et al., 2019]. The influence of climatic and landscape conditions leads to a complex factors affecting on soda lakes water. It determines a wide range of the TDS in lake waters [Kurnakov, 1935; Sorokin et al., 2015]. The Kulunda lakes take place in a cryoarid climate and are the only example of ultrahaline soda lakes in Russia [Sapozhnikov et al., 2016].

For over 100 years, researchers in various fields of science have been interested in the group of Tanatar soda lakes, especially, Rublevo–Demkino–Tanatar-4–Tanatar-6. The 1930s can be considered as a certain frontier, when large-scale soil science, geomorphological, limnological, and biological and other studies began in 1931–1933 by the Kulunda expedition of the USSR Academy of Sciences for soda deposit exploration [Kurnakov, 1935]. The obtained results formed the work basis of many researchers, and many of the results are still relevant.

Further, it is worth noting the work of [Nikol'skaya, 1961]. In 1949–1954, she studied in detail the hydrochemistry of rivers and lakes of the Kulunda steppe, considered the issues of the salt formation in lakes and its relationship with the water composition and soil-forming processes [Nikol'skaya, 1961]. Her work presents data on the composition and physical and chemical parameters of water for more than 100 lakes, including the group of Tanatar soda lakes. In the bottom sediments of soda lakes, along with trona, mirabilite, halite, etc., calcium and magnesium carbonates were noted.

In the 1940–50s, the first data on the model system of soda lakes Rublevo–Demkino–Tanatar-4–Tanatar-6 of the Tanatar group were obtained by [Strakhov, 1951]. This lakes system considered as "natural laboratory" in which metamorphism of water of the same composition occurred under natural conditions. At that time, it gave new ideas about soda continental reservoirs and the processes occurring in them.

The first data on carbonate paragenesis in the sediments of soda lakes of the Tanatar group were obtained [Strakhov, 1951]. The study was both from an experimental point of view (experiments on the deposition of carbonate minerals from solutions corresponding to the waters of the studied lakes) and from the empirical (studies of sediments and lake water samples). The carbonate paragenesis in the sediments of soda lakes consisted of authigenic calcite, dolomite, and brucite (?). Along with carbonate minerals, Mg-silicates of the sepiolite-kerolite type were determined in the main phase of the bottom sediments. The obtained amount of magnesium silicates ranged from 3–4 to 22–24% of the total sediment [Strakhov, 1951].

Modern works on the Kulunda soda lakes are related to biodiversity and the functioning of microbial communities of aquatic and terrestrial systems and hydrology. Despite the extreme conditions in soda lakes, their inhabitants are characterized by high productivity and biological diversity [Kompantseva et al., 2009; Samylina et al., 2014; Sapozhnikov et al., 2016; Sorokin et al., 2015; Zavarzin and Zhilina, 2000]. However, the geochemistry and mineralogy of the sedimentary process is considered in a number of works, including the authors of this study [Gas'kova et al., 2017; Lebedeva (Verba) et al., 2008; Ovdina et al., 2020].

The authigenic carbonates and, accordingly, carbonate sediments in water bodies are an important source of information for the paleoclimate reconstruction and have been a topic of discussion for many years [Chagas et al., 2016; Deelman, 2011; Fussmann et al., 2020; Kelts and Hsü, 1978; Last et al., 2012; Solotchin et al., 2017; Strakhovenko et al., 2015]. The beginning of an integrated approach to the minerals study as an object of interaction between different (litho-, hydro-, bio-, etc.) geospheres was laid back in the first half of the 20th century in the works of [Vernadsky, 1927]. In the modern scientific world, the direct connection of the minerals formation with the physical, chemical and climatic conditions of the environment has already been irrefutably proved. In this regard, the mineral and, accordingly, the geochemical composition of the lacustrine bottom sediments can be used as a reliable highlighter of natural environment changes.



The work aims to identify the features of the mineral and geochemical composition of bottom sediments in the model lakes of the Tanatar system (Demkino–Rublevo–Tanatar-4–Tanatar-6) and to assess the environmental changes over the past ~ 100 years.

## Material and Methods

### *Subject and Objects of Research*

The object of the study is a system of four small lakes (area  $\leq 10$  km<sup>2</sup>, depth  $\leq 5$  m): Tanatar-6, Tanatar-4, Demkino and Rublevo (Figure 1). The study area (southwest of the Kulunda plain) belongs to the subboreal continental group and is an accumulative lowland plain. This is a regional scale alluvial fan. Its topography consist of parallel-elongated hill ranges and valleys between them. Sandy deposits constitute hills and valley bottoms. Because of it, there are ribbon forests grow on bands of sandy soil. There is a local redistribution of moisture and easily soluble salts. They flow from hill ranges into the space between them, where lakes are located due to the landscape features (parallel-elongated hill ranges 40–60 m high, 0.2 to 2 km wide and depressions of the northeastern extension).

The bottom sediments of the studied small lakes are organic-mineral bottom sediments (sapropel). The texture of sediment is massive, finely lumpy, and nutty-lumpy. Sometimes there are remnants of macrophytes and algae. The color of bottom sediments can be different: bluish-green, olive, tobacco-green, brown, and black. Bottom sediments have a strong smell of hydrogen sulfide. High density is a characteristic of the lower horizons. The moisture content (from top to bottom) varies from 98 to 70%. In all the studied lakes at the water–bottom sediment boundary, a dense suspension is formed, similar to fluffy layer [Lein *et al.*, 2011], gradually turning into liquid sapropel; the humidity of which is 98–99% [Strakhovenko *et al.*, 2014].



**Figure 1.** The layout of the studied Tanatar soda lake system: 1 – Tanatar-6; 2 – Tanatar-4; 3 – Demkino; 4 – Rublevo based on Yandex Maps. Yellow circles – sampling points of bottom sediments and water; pink star – the Mikhailovsky Chemical Reagents Plant.

We classified the sapropels in types by [Korde, 1969] and in classes and species (Table 1) according to [Strakhovenko *et al.*, 2014] based on mineral, geochemical and biological data.

The Lake Tanatar-4 sapropel is a planktonic species by the sort of dominant primary production that adds organic matter. Sapropel of Lakes Rublevo and Demkino is a planktonic-macrophytic species. In all the aforementioned lakes, sapropel belongs to the calcium class according to the Si/Ca ratio and to the mineral-organic type according to ash content. Sapropel of Lake Tanatar-6 also is a planktonic species, but it belongs to the

silicon class ( $\text{Si} > \text{Ca}$ ). Ash content in Lake Tanatar-6 sapropel is quite high, and it belongs to the mineralized type.

**Table 1.** Classification of the studied small soda lakes sapropel by types, classes and species

Type	Ash content (%)	Class	Species	Lake
mineral-organic	50–70	calcium	planktonic, planktonic-macrophytic	Tanatar-4, Rublevo, Demkino
mineralized	70–85	silicon	planktonic	Tanatar-6

### Methods

Fieldwork was conducted in 2015 and 2019. Bottom sediment sampling (51 sample) (Table 2) was carried out in the center of the lake from the rubber boat using a cylindrical sampler (diameter 82 mm, length 120 cm) with a vacuum seal (Taifun Research and Production Association, Russia). Using a cylindrical sampler allowed us to collect stratigraphic sediment cores and keep the water-bottom sediment boundary undisturbed. The core of bottom sediments was tested in layers that were 5 cm thick to a depth up to 75 cm.

**Table 2.** Number of bottom sediment and water samples, core (cm) and water (m) depth

Lake	Bottom sediments samples	Core depth, cm	Water samples	Water depth, m
Tanatar-6	11	55	4	0.8
Tanatar-4	12	60	4	1.7
Rublevo	15	75	4	1.5
Demkino	13	65	4	1.5
Spring-1 (near Tanatar)	–	–	3	–
Spring-2 (near Rublevo)	–	–	3	–

The water samples (22) (Table 2) were taken in the center of the lake. We used plastic bottles of 1 and 0.5 L for determining the major and trace element composition, and 0.33 L glass bottles for determining the content of mercury. Physical and chemical variables of water were recorded *in situ* (pH, TDS) using an ANION-7000 portable liquid analyzer (Biomer, Novosibirsk, Russia).

Analytical studies of the lake components were conducted in the Analytical Center for multi-elemental and isotope research 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). The major element composition was determined by X-ray fluorescence analysis (ARL-9900-XP, Applied Research Laboratories, Austin, TX, USA). The sample morphology, phase and elemental composition were determined using a scanning electron microscopy (SEM) (Mira 3 Tescan, Tescan, Brno-Kohoutovice, Czech Republic). The INCA Energy 300 program (Labspec 5) was used for quantitative chemical analysis with reference standards.

X-ray diffractometry (XRD) was used to determine sample mineral composition (ARLX'TRA, Thermo Fisher Scientific (Ecublens) SARM, Waltham, MA, USA) (emission  $\text{CuK}\alpha$ ). For phase analysis, the samples were scanned in a range from  $2^\circ$  to  $65^\circ$  ( $2\theta$ ) with a step of  $0.05^\circ$ ; 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  $28^\circ$  to  $32^\circ$  ( $2\theta$ ) 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  $< 10 \mu\text{m}$ ). XRD analysis was performed using the most

intense reflections of  $hkl = 104$  in the area of angles  $28\text{--}32^\circ$   $2\Theta$   $\text{CuK}\alpha$  for trigonal carbonates. The values of the  $d_{104}$  interplane distances ranged from  $3.036 \text{ \AA}$  (calcite) to  $2.887 \text{ \AA}$  (stoichiometric dolomite) and are as a magnesium measure of the carbonate minerals.

Magnesium-calcites were divided into three groups according to the  $d_{104}$  value: *low-magnesium calcites* with a  $\text{MgCO}_3$  content in the structure of  $< 4\text{--}5 \text{ mol. \%}$  ( $3.036 \text{ \AA} > d_{104} > 3.020 \text{ \AA}$ ); *intermediate-magnesium calcites* with  $5\text{--}18 \text{ mol. \%}$   $\text{MgCO}_3$  in the structure ( $3.02 \text{ \AA} > d_{104} > 2.98 \text{ \AA}$ ), and *high-magnesium calcites* with  $30\text{--}43 \text{ mol. \%}$   $\text{MgCO}_3$  ( $2.94 \text{ \AA} > d_{104} > 2.91 \text{ \AA}$ ). *Ca-excess dolomites*, in the structure of which the excess of  $\text{CaCO}_3$  can reach  $7 \text{ mol. \%}$  in relation to stoichiometric dolomite, are characterized by the values of  $d_{104}$  from  $2.910$  to  $2.887 \text{ \AA}$  [Ovdina et al., 2020; Solotchina and Solotchkin, 2014].

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 [Ovdina et al., 2020; Solotchina and Solotchkin, 2014]. The convergence of the experimental and simulated profiles is estimated as the standard deviation of the intensity at the calculated point of the model profile. The applicability of the model is described by the following expression:  $R = \sum_{i=1}^N (I_{\text{calc}}(2\Theta_i) - I_{\text{obs}}(2\Theta_i))^2$ , where  $N$  is the number of the point at which the model is calculated,  $I_{\text{calc}}$  is the calculated intensity and  $I_{\text{obs}}$  is the observed (experimental) one at the point

The calculation of the water chemical composition was carried out using the formula by [Kurlov, 1928], which is used to express the chemical composition of water. Anions and cations with a content of more than  $10 \text{ mg-eq\%}$  are introduced into the formula. The name of the chemical type of water involves anions and cations with a content of  $25 \text{ mg-eq\%}$  (for mineral waters from  $20 \text{ mg-eq\%}$ ). The name of the water composition is given in increasing order of the anions and cations content.

## Results and Discussion

### Composition, Physical and Chemical Features of Lakes Water

According to physical and chemical features in the considered chain of lakes, the waters are soda, alkaline, and have a wide range of TDS (g/L). From Lake Rublevo to Lake Tanatar-6, there is an increase in pH and TDS (Table 3). The water samples taken in 2015 and 2019 did not differ.

The composition of modern lake waters varies from  $\text{HCO}_3\text{--Mg--Na}$  (Lakes Rublevo and Demkino) through  $\text{HCO}_3\text{--Na}$  (Tanatar-4) to  $\text{HCO}_3\text{--Cl--Na}$  (Tanatar-6) (Table 3). From Lake Rublevo to Lake Tanatar-6, in the anionic composition  $\text{HCO}_3^-$  is partially replaced by  $\text{Cl}^-$ , and in the cationic composition  $\text{Na}^+$  begins to prevail, while  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions significantly reduced. As the value of TDS increases, the value of  $\text{Ca/Mg}_{\text{water}}$  in the water decreases.

The data obtained by [Nikol'skaya, 1961] after water sampling in 1949 and calculated by us according to the Kurlov formula [Kurlov, 1928] are shown in (Table 3). Comparison of these data with the authors' data for 2015 shows that the value of TDS in all lakes has increased 2–4 times over 66 years. The content of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions has decreased to varying degrees, as well as  $\text{Ca/Mg}_{\text{water}}$ . For Lake Tanatar-6, the significant decrease in  $\text{Ca/Mg}$  in water was noted from 3.6 to 0.1 when the composition of lake water almost unchanged.

We also studied the water of two springs (self-discharge), Spring-1 (near Tanatar) and Spring-2 (near Rublevo) located near the lakes Tanatar-6 and Rublevo (Table 3). There are differences in composition and physical and chemical parameters of the springs' water compared to lakes' water. The springs' water characterizes the composition of groundwater feeding lakes. Water of the Spring-1 (Tanatar) is  $\text{HCO}_3\text{--Ca--Na}$ , fresh, pH 7.8. Water of the Spring-2 (Rublevo) is  $\text{HCO}_3\text{--Na--Ca}$ , fresh, pH 7.5.

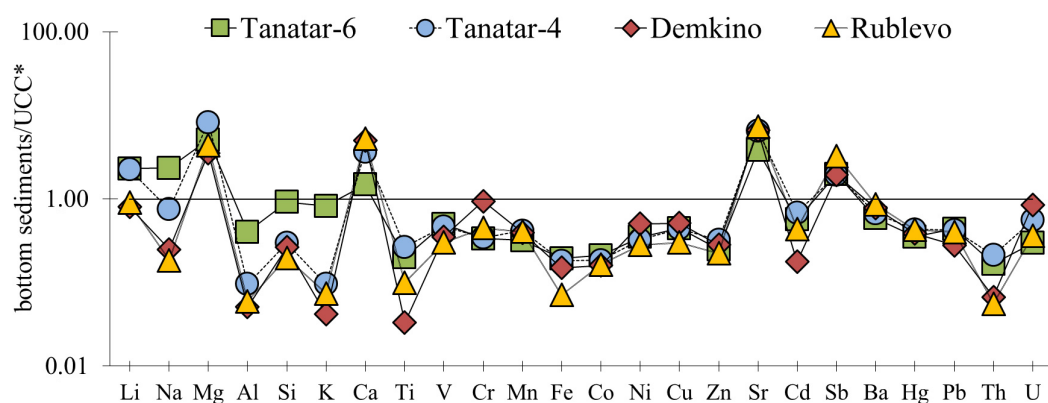
**Table 3.** Water composition, physical and chemical parameters of small soda lakes of the Tanatar system (and springs near Lakes Tanatar-6 and Rublevo) by authors' data (for 2015) and [Nikol'skaya, 1961] (for 1949)

Lake	pH	TDS, g/L	Water composition	Ca/Mg <sub>water</sub>	TDS, g/L	Water composition	Ca/Mg <sub>water</sub>
Author's data (2015)					[Nikol'skaya, 1961] (1949)		
Tanatar-6	9.8	41.5	Cl 56 HCO <sub>3</sub> 32 [SO <sub>4</sub> 12] Na 100	0.1	9.2	Cl 57 HCO <sub>3</sub> 31 [SO <sub>4</sub> 12] Na 93 [Ca 5]	3.6
Tanatar-4	9.5	9.0	HCO <sub>3</sub> 82 [Cl 15] Na 93 [Mg 6]	0.1	4.4	HCO <sub>3</sub> 54 Cl 39 [SO <sub>4</sub> 7] Na 93 [Mg 6]	0.4
Demkino	9.0	2.1	HCO <sub>3</sub> 89 [Cl 9] Na 66 Mg 30	0.2	1.5	HCO <sub>3</sub> 84 [Cl 13] Na 61 Mg 26 [Ca 13]	0.8
Rublevo	9.1	2.6	HCO <sub>3</sub> 94 [Cl 5] Na 67 Mg 29	0.2	1.2	HCO <sub>3</sub> 81 [Cl 15] Na 62 Mg 26 [Ca 12]	0.8
Bych'e	–	–	–	–	4.0	SO <sub>4</sub> 51 HCO <sub>3</sub> 34 [Cl 15] Na 84 [Mg 15]	0.2
Zolotoe	–	–	–	–	2.2	HCO <sub>3</sub> 92 Na 75 [Mg 22]	0.2
Spring-1 (near Tanatar)	7.8	0.4	HCO <sub>3</sub> 82 [SO <sub>4</sub> 11 Cl 7] Na 64 Ca 33	16.7	–	–	–
Spring-2 (near Rublevo)	7.5	0.5	HCO <sub>3</sub> 97 Ca 56 Na 40	3.2	–	–	–

Note: pH – *in situ* measurements during fieldwork, TDS (g/L) – calculation according to the Kurlov formula [Kurlov, 1928]

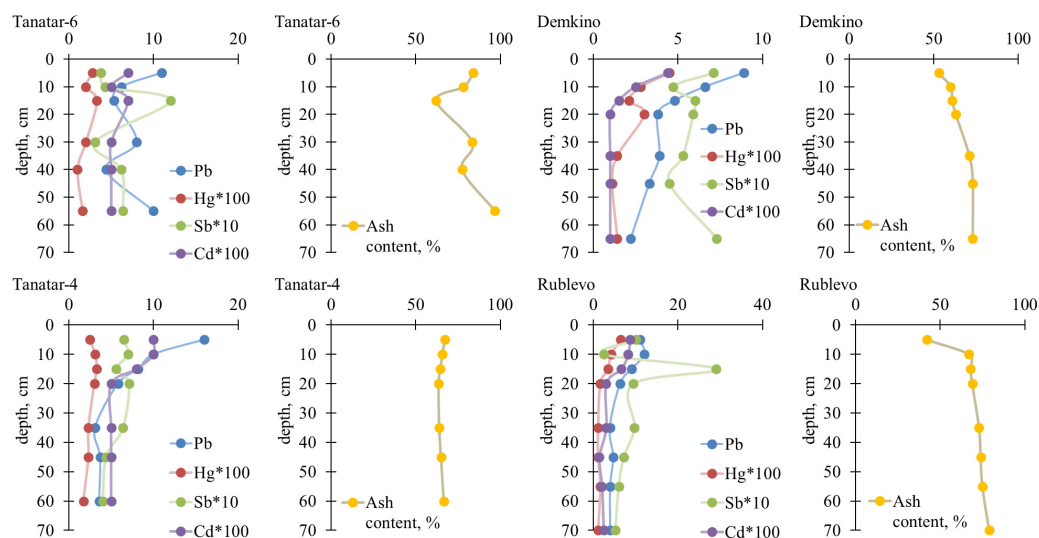
#### Geochemistry and Mineralogy of Bottom Sediments

The average elements concentrations in the lacustrine sediments were compared to the elements' concentrations in the upper continental crust, according to [Wedepohl, 1995]. A comparison showed increased concentrations of Ca, Mg (major elements) and Sr (trace elements) in all studied lakes (Figure 2). The cause is accumulation of authigenic carbonates in the bottom sediments. Depletion of other trace elements is due to the dilution effect of sediments by carbonates and organic matter. This has also been shown to be the case for the south of Western Siberia [Ovdina et al., 2020].

**Figure 2.** The multi-element spectrum of the studied elements (averaged values) in the bottom sediments of the Tanatar soda lake system normalized to the elements' concentrations in the upper continental crust according to [Wedepohl, 1995].

A high content of Sb relative to the upper continental crust was found in the sediments of the studied lakes (Figure 2). According to the configuration graphs of the Sb, Pb, Cd, Hg and ash content (%) distribution (Figure 3), a separate distribution of Sb is traced along the

core. The ash content in the bottom sediments increases as the depth increases (Figure 3). Both natural and anthropogenic factors can be associated with this aspect. Sb can enter the bottom sediments of lakes with eolian material: sandstorms are characteristic of the territory [Gavshin et al., 1999], which can transport eolian material over long distances, and more than 10 polymetallic ore deposits of Ore Altai are located within a radius of ~100 km. A possible anthropogenic source may be the Mikhailovsky Chemical Reagents Plant, which is located in 6 km from the studied lakes in vil. Malinovoe ozero and the highway of regional significance 01K-21 (Rubtsovsk–Uglovskoye–Mikhailovskoye) of the Altai Territory (Figure 1).

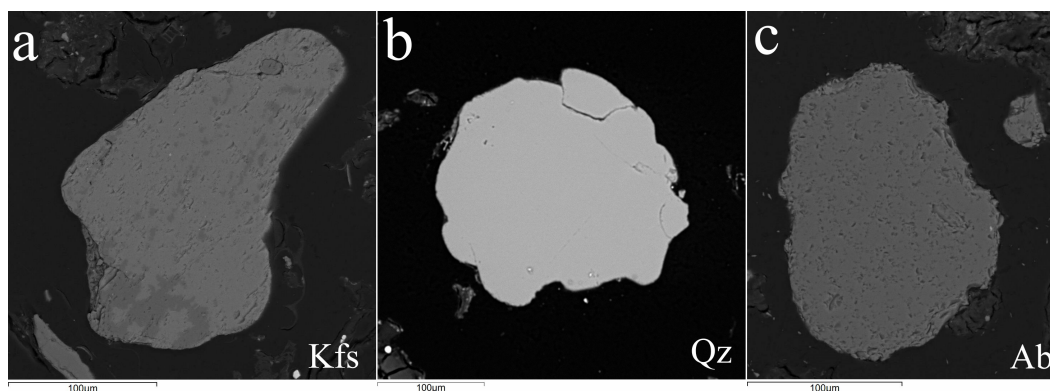


**Figure 3.** Configuration charts of vertical distribution of Sb, Pb, Cd, Hg and ash content (%) in the bottom sediments of the studied lakes.

The terrigenous component is represented as sharp-angled clastic forms and well-rounded grains of eolian origin (Figure 4) [Gavshin et al., 1999; Strakhovenko et al., 2014].

It is found that the Ca/Mg ratio decreases in the upper horizon (0–20) of the sediments in all the studied lakes (Figure 5) due to a decrease in the content of Mg, while Ca is  $\pm$  constant.

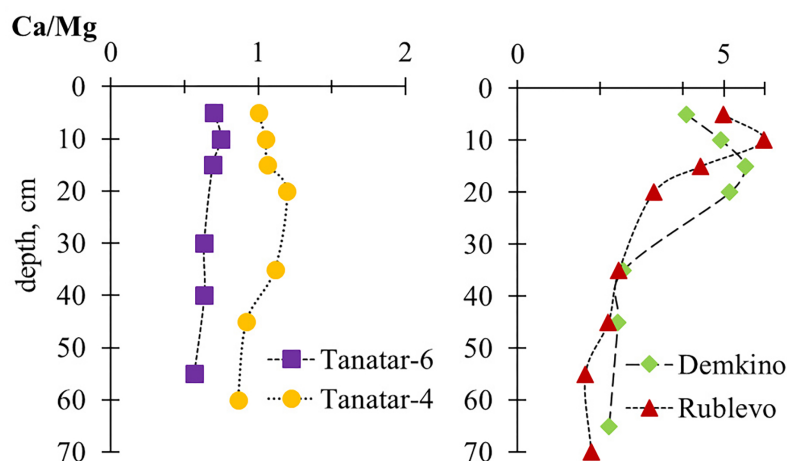
A decrease in Mg content up the core is noted at a depth of 15–20 cm. The sedimentation rate for small lakes in southern Siberia is 0.35 cm per year, according to [Strakhovenko et al., 2010]. Comparison of the Ca/Mg distribution and the sedimentation rate shown that the moment of change in the Mg accumulation is around 1950–1960. We considered possible changes in the feeding of lakes to explain the behavior of magnesium. One of



**Figure 4.** Photos of terrigenous component of bottom sediments. a – potassium feldspar (Kfs), b – quartz (Qz), c – albite (Ab) (SEM MIRA 3 TESCAN, BSE).



the sources in the number of works [Kurnakov, 1935; Nikol'skaya, 1961; Strakhov, 1951] was noted the Rublevaya River. Its source was near Lakes Bychye and Zolotoe (to the northeast of the Tanatar lakes), and the mouth on the southeast shore of Lake Demkino. The river was temporary and flowed only in spring. Presumably, the river water inherited the composition of Lakes Bychye and Zolotoe waters and could be an additional source of Mg. This is confirmed by the Ca/Mg ratio in the waters of Lakes Bychye and Zolotoe, which was 0.2 (Table 3). Now, the Rublevaya River has not been established either in fact or according to satellite images.



**Figure 5.** Vertical distribution of Ca/Mg in the sediments of the studied lakes.

According to [Kharlamova, 2019], the trends of annual precipitation and moisture coefficients are negative for almost the entire territory of the forest-steppe and steppe regions of Kulunda in the Altai Territory during the almost 50-year period of 1966–2012. It could lead to the drying up of the river and the disappearance of an additional and significant source of Mg in the lakes of the Tanatar group because the composition of groundwater (spring waters) does not contain Mg (Table 3).

The modern authigenic component of the water-bottom sediment boundary in the considered lakes mainly consists of high-Mg-Cal – Ca–Dol carbonates series, quartz, feldspar, calcite, and dolomite. Disordered smectite, aragonite, magnesite, chlorite, siderite, mica are impurities (Table 4, Figure 6). In all studied lakes, carbonates of the high-Mg-Cal – Ca–Dol series are formed and preserved throughout the core of bottom sediments (Table 4).

According to [Strakhov, 1951], a significant proportion of magnesian silicates of the sepiolite  $(\text{Mg}_4(\text{Si}_6\text{O}_{15})(\text{OH})_2 \cdot 6\text{H}_2\text{O})$  – kerolite  $(\text{Mg},\text{Ni})_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  ( $n \sim 1$ ) type was found in the bottom sediments of Lakes Tanatar-4 and Rublevo (Table 4). However, the authors of this study did not establish them either by XRD (Figure 6) or by SEM (Figure 7, 8). In addition, according to the geochemical composition of bottom sediments, there is no accumulation of Ni (Figure 2), which could be assumed during the formation of kerolite. The Ni content is lower or corresponds to the background values (10 mg/kg) in the bottom sediments of this area. There are no outcrops of ultrabasic rocks on the studied territory, and the parent rocks are Upper Pleistocene pebble gravel beds, sands, silts, siltstones, clays.

In order to specify the composition of modern bottom sediments, we used additional studies by XRD and SEM methods. Modeling of experimental XRD profiles of carbonates in the range of  $d_{104}$  peaks was included in a more detailed study on Lakes Tanatar-4 and Rublevo (Figure 6).

The total modeled profiles (solid line) are in agreement with the experimental ones (dotted line). The diffraction peaks of individual phases are described by Pearson VII function. The modeling approach ensures a reliable differential identification of the entire

set of present carbonate minerals and determination of their quantitative ratios. The total content of carbonates in the sample is taken equal to 100%.

Modeling of experimental XRD profiles of carbonates reflected the results of X-ray diffractometry (XRD), clarified the percentage of high-magnesian carbonates and Ca-excess dolomite, and confirmed the absence of magnesium silicates in the main phase of modern bottom sediments of the studied lakes.

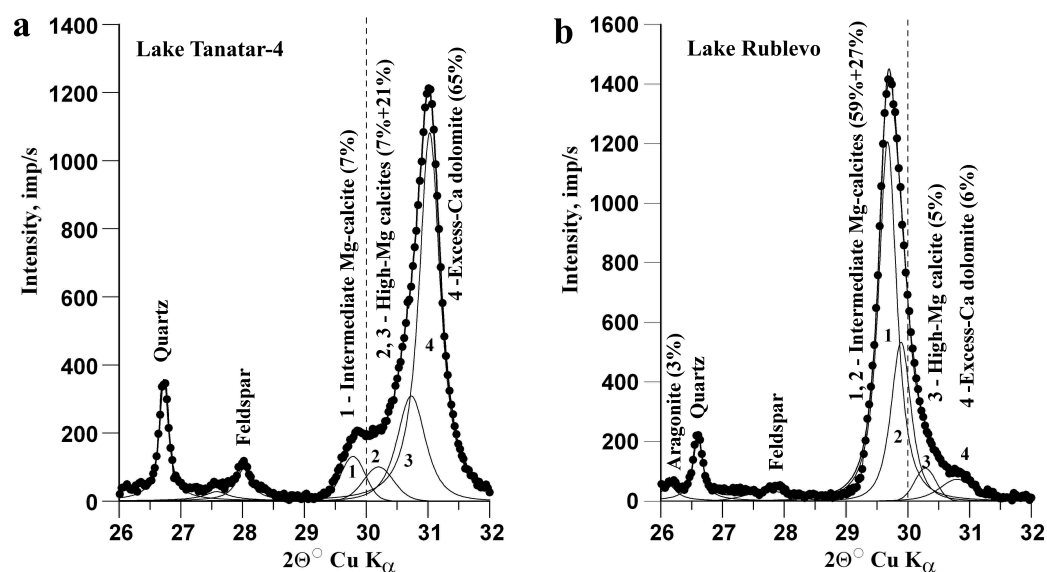
At high TDS ( $> 9$  g/L) and pH ( $> 9.5$ ), Ca-excess dolomite prevails in the main phase of bottom sediments in lakes Tanatar-6 and Tanatar-4 (Table 4). This is again confirmed by the data obtained using SEM (Figure 6a, 7). The CaO/MgO ratio in bottom sediments is 0.7 and 0.9, respectively.

In Demkino and Rublevo lakes, the TDS and pH in water are similar (TDS = 2.1–2.6 g/L, pH  $\approx 9.0$ ) (Table 4). High-Mg calcite, intermediate-Mg calcite and Ca-excess dolomite dominate in the main phase of bottom sediments (Figure 6b, 8). The CaO/MgO ratio in the bottom sediments is 3.8 and 5.9, respectively.

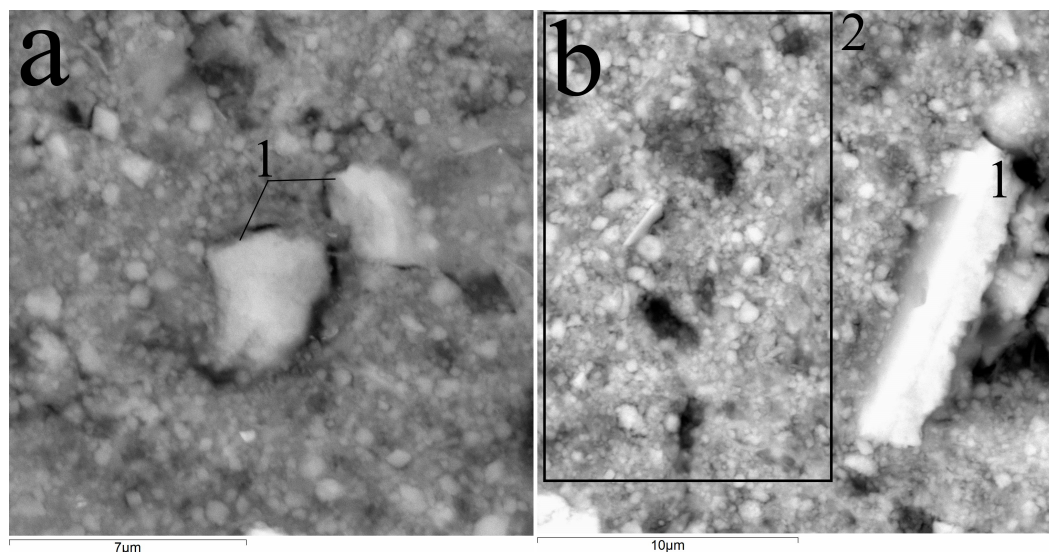
It should be noted that Mg-silicates were determined not in fact, but by calculations based on the definitions of macro- and microscopic methods of micaceous sericite-like mineral in bottom sediments and the establishment of a hydromica type peak by thermogravimetry [Strakhov, 1951]. The results showed that a lot of MgO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> remained after calculating the dolomite and calcite content (using CaO, MgO and CO<sub>2</sub>). So further calculation was done for silicates or aluminosilicates. Even after recalculation, in most cases there was either an excess of MgO, or it was not enough to saturate the entire SiO<sub>2</sub>. In this case, it was assumed that there was excess magnesium hydroxide in the form of brucite (?).

According to [Strakhov, 1951], bottom sediments of the Tanatar lake group contain only calcite and dolomite within carbonates. However, when describing experimental data on the salts' deposition from solutions corresponding in composition to the lakes waters, there was a "certain admixture" of MgCO<sub>3</sub> in calcite.

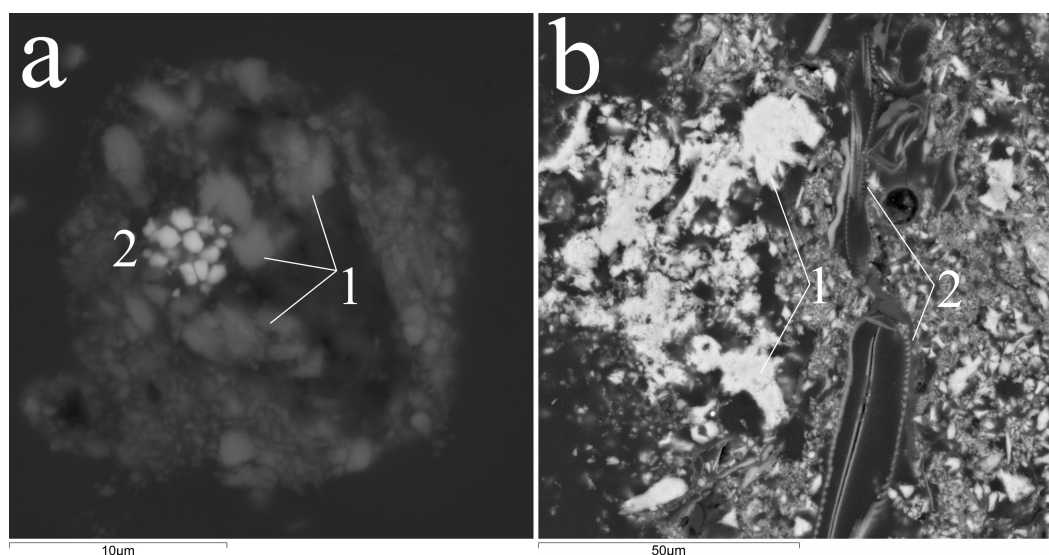
Our modern data show that carbonates in the main phase of the bottom sediment are intermediate-Mg calcite (from 5–18 mol.% MgCO<sub>3</sub> in the structure), high-Mg calcite (with 30–43 mol.% MgCO<sub>3</sub>) and Ca-dolomite (excess CaCO<sub>3</sub> up to 7 mol.% relative to stoichiometric dolomite). This aspect explains the excess of MgO in the calculations of the bottom sediments mineral composition by [Strakhov, 1951]. As well as the presence of



**Figure 6.** Results of experimental XRD profiles modeling of carbonates in the range of  $d_{104}$  peaks: (a) – Lake Tanatar-4, (b) – Lake Rublevo.



**Figure 7.** Photos of high-Mg carbonates in bottom sediments of Lake Tanatar-4, depth 0–5 cm: (a) – Ca-dolomite grains in small-lumpy bulk (mixture) having the composition of high-Mg calcite, Ca-excess dolomite, trona; (b) 1 – plagioclase, 2 – small-lumpy bulk (mixture) having the composition of high-Mg calcite, Ca-excess dolomite, trona (SEM MIRA 3 TESCAN, BSE).



**Figure 8.** Photos of high-Mg carbonates in bottom sediments of Lake Rublevo, depth 0–5 cm, (a) 1 – high-Mg calcite; 2 – cluster of pyrite crystals; (b) 1 – high-Mg calcite, 2 – shells of diatoms ( $\text{SiO}_{2\text{bio}}$ ) (SEM MIRA 3 TESCAN, BSE).

magnesite in the form of a small impurity (Table 4) in the bottom sediments of the studied lakes can introduce MgO.

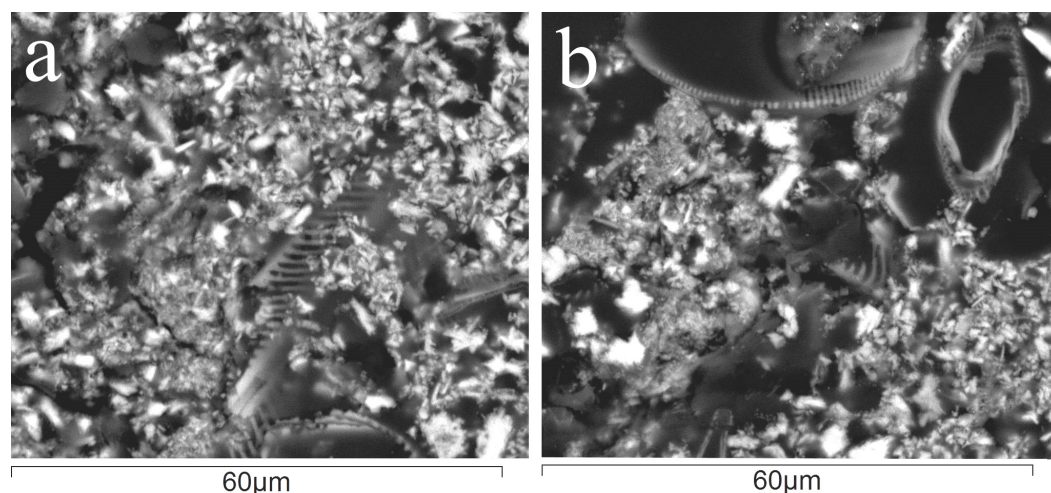
The content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the bottom sediments of small lakes in the south of Western Siberia corresponds to the composition of the terrigenous component (mainly quartz, feldspar and mica). Additionally, the  $\text{SiO}_2$  content is controlled by the presence of a significant amount of biogenic  $\text{SiO}_2$  in sapropel deposits. Biogenic  $\text{SiO}_2$  ( $\text{SiO}_2\text{nH}_2\text{O}$ ) is usually composed of diatom shells (Figure 8b, 9) and macrophyte remains. This explains the excess of  $\text{SiO}_2$  obtained during the calculations by the [Strakhov, 1951].

**Table 4.** X-ray diffractometry (XRD) results of small soda lakes bottom sediments (Tanatar system) by authors' data and data of optical, wet chemical methods, X-ray and part of thermal research by [Strakhov, 1951]

Lake	TDS, g/L	CaO/MgO <sub>bs</sub>	Mineral composition	Salinity, %	CaO/MgO <sub>bs</sub>	Mineral composition
Authors' data				[Strakhov, 1951]		
Tanatar-6	41.5	0.7	<b>0–5 cm</b> <u>Main phase</u> Qz, Pl, <i>Ca-Dol</i> , <i>Dol</i> , <i>Cal</i> , Hal, <u>impurity</u> Kfs, trona, disordered smectite; <u>small impurity</u> mica, chlorite, siderite	–	–	–
			<b>50–55 cm</b> <u>Main phase</u> Qz, Pl, <u>impurity</u> Kfs, <i>Dol</i> , Hal, <u>small impurity</u> disordered smectite, trona, <i>Cal</i> , mica, chlorite, kaolinite, siderite			
Tanatar-4	9.0	0.9	<b>0–5 cm</b> <u>Main phase</u> <i>Ca-Dol</i> , <u>impurity</u> <i>high-Mg-Cal</i> , disordered smectite, Qz; <u>small impurity</u> Pl, goethite, <u>traces</u> chlorite, siderite, mica	1	0.94	<u>Main phase</u> <i>Dol</i> , <i>Mg-silicates</i> ; <u>impurity</u> <i>Cal</i>
			<b>55–60 cm</b> <u>Main phase</u> <i>Ca-Dol</i> , <u>impurity</u> <i>high-Mg-Cal</i> , disordered smectite, <u>small impurity</u> Qz, Pl, <u>traces</u> siderite, goethite, chlorite			
Demkino	2.1	3.8	<b>0–5 cm</b> <u>Main phase</u> <i>high-Mg-Cal</i> , <u>small impurity</u> Qz, <u>traces</u> Pl, Kfs, aragonite, disordered smectite (?), a lot of X-ray amorphous component	–	–	–
			<b>60–65 cm</b> <u>Main phase</u> <i>high-Mg-Cal</i> – <i>Ca-Dol carbonates series</i> , <u>impurity</u> smectite, <u>small impurity</u> Qz, <u>traces</u> Pl			
Rublevo	2.6	5.9	<b>0–5 cm</b> <u>Main phase</u> <i>intermediate-Mg-Cal</i> , <i>Ca-Dol</i> , <u>small impurity</u> Qz, magnesite? a lot of X-ray amorphous component	0.3	1.72	<u>Main phase</u> <i>Cal</i> ; <u>impurity</u> <i>Dol</i> , <i>Mg-silicates</i>
			<b>75–82 cm</b> <u>Main phase</u> <i>high-Mg-Cal</i> – <i>Ca-Dol carbonates series</i> ; <u>impurity</u> smectite, Qz; <u>traces</u> Pl, Kfs			

Note: High-Mg-Cal – high-magnesium calcite; Ca-Dol – Ca-excess dolomite; Dol – dolomite; Cal – calcite; Qz – quartz; Kfs – potassium feldspar; Pl – plagioclase; Hal – halite. Almost all minerals have a low degree of crystallinity.





**Figure 9.** Photos of diatom shells in small-lumpy bulk having the composition of high-Mg calcite (SEM MIRA 3 TESCAN, BSE).

### Conclusion

The results obtained on the geochemical and mineral composition of bottom sediments in the model lakes of the Tanatar group (Demkino-Rublevo-Tanatar-4-Tanatar-6) allowed us to draw a number of conclusions:

1. Over the past 100 years, a change in the hydrological regime of lake feeding has been revealed in the catchment area (drying up of the Rublevaya River feeding the lakes under study). It has changed the nature of Mg accumulation in the upper horizons of bottom sediments. In addition, there has been a  $TDS_{water}$  increase in lakes by 2 to 4 times;
2. Throughout the core depth, the mineral composition of the authigenic component does not change and is represented by carbonates of the Cal–Dol series (high–Mg Cal, Ca–excess Dol). It has been established that Mg-containing minerals are represented by carbonates, while Mg-silicates of the sepiolite-kerolite type in the bottom sediment have not been established;
3. The results obtained can be further used for detailed complex paleoreconstructions of the climate.

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