Geochemistry of diagenesis of sapropel sediments of small lakes in Southern West Siberia and Eastern Baikal

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Abstract. Organogenic sediments (sapropels) in lakes are characterized by a recovery type of diagenesis, during which organic compounds are decomposed, the chemical composition of the pore waters is modified, and authigenic minerals (first of all, pyrite) are formed. Pyrolysis data indicate that organic matter undergoes radical transformatons already in the uppermost sapropel layers, and the composition of this organic matter is principally different from the composition of the organic matter of the its producers. The sapropels contain kerogen, whose macromolecular structure starts to develop during the very early stages of diagenesis, in the horizon of unconsolidated sediment (0–5 cm). The main role in the diagenetic transformations of organic matter in sediments is played by various physiological groups of microorganisms, first of all, heterotrophic, which amonifying, and sulfatereducing bacteria.

Keywords: geochemistry, diagenesis, organic matter, sulfate reduction, pore waters

Insufficient knowledge of the diagenesis of sediments of continental water bodies in general, and of small lakes in Siberia in particular, makes this problem extremely topical both in theoretical and practical aspects. This led the authors of this publication to launch in 2011 a study of freshwater diagenesis. This led the authors of this publication to launch in 2011 a study of freshwater diagenesis. This study was financially supported by the Russian Foundation for Basic Research, project N 11-05-00655 “Diagenesis of Lacustrine and Bog Sediments in the Piedmont-Plain Zone of the Eastern Baikal Shore and Forest–Steppe Zone of West Siberia”. The methodological approaches applied in studying the geochemistry of diagenesis of oceanic and marine sediments [1, 6] were utilized by the authors in studies of small lakes in different climatic zones in Siberia.

Freshwater diagenesis was investigated in typical small lakes (Bol’shie Toroki and Minzelinskoe) in southern West Siberia and the Eastern Baikal area (Kokotel’, Dukhovoe, and Ochki), whose bottom sediments are sapropel (Fig. 1). According to N.V. Korde’s definition, sapropel is thin-structure continental sediment containing much organic matter, certain concentrations of inorganic components of biogenic nature, and foreign mineral admixtures [3]

Our research was carried out using materials collected during the 2011–2013 fieldwork. The long cores of undisturbed sediments were obtained by vibrodrilling (with a Livingstone piston corer) the bottoms of lakes to the depths of the bedrock: Bol’shie Toroki (1.8 m), Minzelinskoe (5 m), Ochki (4.5 m), Dukhovoe (7 m), and Kokotel’ (14 m). We collected samples of the surface lacustrine and entrapped water and of primary producers of organic matter (plankton and macrophytes.

According to their contents of organic matter and the chemical composition of their mineral constituents, the bottom sediments of the lakes are classified into two sedimentary complexes, which are correlated with the geographic settings of the water bodies. The first sedimentary complex comprises high-ash mineral-organic sapropels of the calcareous type (Table 1), which are formed in sedimentation basins of lakes in southern West Siberia. In contrast to this complex, the other one is composed of carbonate-free low-ash sapropels of organo-mineral and organic types, which are formed in lakes in the Eastern Baikal area [4].

Table 1. Types of lacustrine sapropels [3], their major-component composition (average data per absolutely dry weight, %), and producers of the organic matter (OM)

Sapropel type, its thickness, m	Lake	OM producers	Ash content	SiO_2	CaO	OM	C_{org}
Mineral-organic sapropels							
Calcareous, 4,2	Minzelinskoe	Macrophytes	70	5.6	30.5	30	14.8
Calcareous–siliceous, 1.4	Bol'shie Toroki	Macrophytes	64	27.2	12.5	36	14.3
Organo-mineral sapropels							
Siliceous, 14,5	Kokotel	Phytoplankton	41	26.0	1.3	59	26.0
Organic sapropels							
Low-siliceous, 1.8	Dukhovoe	Phytoplankton	29	15.3	1.2	71	38.7
Low-siliceous, 2.7	Ochki	Phytoplankton	23	14.6	0.5	77	25.8

Major Trends and Relations in the Transformations of Organic Matter during Diagenesis

Redox potential (Eh) of the sediments. The uppermost (0–5 cm) horizon of sediments in the lakes was determined to be characterized by oxidized or weakly reduced conditions with Eh from +10 (Lake Kotokel') to –3 mV (Lake Bol'shie Toroki). Farther down the sediment thickness, the Eh values rapidly become negative, vary from –76 (Lake Kotokel') to –260 mV (lakes Bol'shie Toroki and Minzelinskoe), and characterize a recovery environment.

Distribution of microorganisms in the vertical sections of the sediments. Our data on the layer by layer distribution of various physiological groups of microorganisms (heterotrophic, nitrifying, ammonifying, iron-oxidizing, and sulfate-reducing) over the vertical sections of the lacustrine sapropel indicate that their maximum numbers occur in the upper sapropel horizons, in which (in the so-called active layer of sediment) labile components of the organic matter are destructed under the effect of the microorganisms (Table 2).

Transformation of organic matter during early diagenesis. Analysis of the pyrograms (chromatographic spectra of the pyrolysis products) of the sediments provides an insight into the composition of organic matter during diagenesis (Fig. 2). The pyrograms show characteristic peaks: high-temperature (500°C), which indicate that the sediments contain macromolecular aliphatic structures, kerogen, which is organic matter significantly transformed under anaerobic conditions, and gently sloped low-temperature peaks (300–400°C), which correspond to labile components of protein–carbohydrate compounds. Data of pyrolysis indicate that organic matter undergoes profound transformations already in the uppermost layers of the sapropels and is remarkably different in composition from the sapropel-forming organisms (producers of the organic matter): macrophytes and plankton.

Table 2. Abundances of various physiological groups of microorganisms in bottom sediments in colony-forming units per gram (CFU/g) × 15^5

Horizon of sediments, cm	Physiological groups of microorganisms CFU/g × 10^5			
	TAM	heterotrophic	sulfate-reducing	ammonifying
Lake Bol'shie Toroki				
5	2970	29.2	3.5	14.5
35	2490	20.9	5.0	11.9
115	2300	26.4	7.0	7.7
Lake Minzelinskoe				
5	406.7	337.0	Не определяли	16.7
45	124.9	56.6		8.3
105	109.5	23.3		6.1
225	34.5	15.7		5.6
Lake Dukhovoe				
5	6.3	3.0	0.009	2.0
70	4.2	0.2	0.014	0.1
115	2.1	0.3	0.218	0.2

TAM is the total abundance of microorganisms.

Comparative analysis of the pirograms of the primary producers and the sapropel indicates that the sapropel (already in its uppermost 5-cm horizon) contains no labile protein–carbohydrate compounds (low-tem- perature peaks at ~330^0 C), which are typical of the primary producers, but contains kerogen (high-tem- perature peaks at ~500^0 C), which is organic matter significantly transformed under anaerobic conditions . This indicates that the decomposition of organic mat- ter in the sediments (and the synthesis of kerogen) start already in the uppermost layers of the sapropel during the earliest diagenesis. At further sedimenta- tion, deeper levels of the sapropel contain only highly stable organic matter, which is further decomposed very slowly.

Biogenic elements in the pore waters. Pore waters are determined to be transformed during early diagenesis of sapropel sediments in the lakes, and this leads to an increase in the concentration of mineral modes of organic matter (HCO_3^-, NH_4^+, HPO_4^{2-}). This elucidates the mechanism of anaerobic oxidation of organic matter by microorganisms. The decrease in the concentration SO_4^{2-} in the pore waters down the vertical sections of the sediments reflects the process of sulfate reduction SO_4^{2-} because of reduction $SO_4^{2-}$with the participation of sulfate-reducing bacteria. Thereby the decrease in the concentrations SO_4^{2-} down the vertical sections of sediments in the lakes in southern West Siberia is much more significant than in the western Baikal area, which indicates that sulfate reduction in more intense in the sapropels of the former lakes. This can depend on both the composition of the organic matter (its availability for the sulfate reducers) and the bulk concentrations of sulfates in the pore waters (their main source is the surface waters of the lakes). Our results do not contradict literature data, according to which the main process responsible for changes in the chemical composition of entrapped waters during diagenesis is bacterial sulfate reduction [1, 7, 8, 10].

Sulfate Reduction and Sulfur Geochemistry at Early Diagenesi. As is known from the literature, the main process resulting in the synthesis of all intermediate and final sulfur compounds in modern bottom sediments is the microbiological reduction of sulfates by a group of anaerobic microorganisms: sulfate-reducing bacteria [1, 2, 9]. In the Siberian lakes discussed herein, sulfate reduction is the most intense in lower horizons of the sediments and is less intense in their uppermost horizons. At bacterial reduction of sulfates, the SO_4^{2-}concentration and Eh simultaneously decrease, and the contents of reduced sulfur species increase. The total alkalinity of the entrapped waters (mostly carbonate and hydrocarbonate ions) also increases with depth. The low sulfate concentrations in the lacustrine waters hamper sulfate reduction, and the major source of the sulfates is the entrapped waters of the sediments. The pore waters inherit their SO_4^{2-}mostly from the bottom waters. Because of this, sulfate concentrations in pore waters in the upper horizons of the sediments are close to sulfate concentrations in the lacustrine waters.

Fe Geochemistry at Early Diagenesis. Using X-ray diffraction techniques, we have determined that the most widely spread Fe minerals of the sapropel sediments of the lakes are sulfides (pyrite), more rare ones are oxides (goethite) and sulfates (jarosite), and even more rare Fe minerals are phosphates (vivianite) and carbonates (siderite) [5]. Pyrite is the most widely spread authigenic diagenetic mineral of the sapropels (Fig. 3), and its contents (according to data recalculated to reduced sulfur) vary from 0.2 to 2.3 wt %, provided that all sulfur occurs in the form of FeS_2. Pyrite is most often found in lacustrine sediments as framboids, which are spherical or oval aggregates ranging from 10 to 30 μm across (mostly 20 μm). They consist of pyrite crystals no larger than ~1 μm: Lake Bol’shie Toroki (horizon 140–150 cm, Fig. 3b) and Lake Kokotel’ (horizon 40 cm, Fig. 3c). It is interesting that individual pyrite crystals are formed in Lake Dukhovoe in smooth spherical capsules, which are cysts of yellow-green algae (Chrysophyceae).Throughout the whole vertical section of the sapropel, pyrite is found exclusively in the cysts as individual crystals or accumulations of two to six crystals (Fig. 3d).

Conclusion

According to our data, all of the lakes are characterized by a reduced type of diagenesis, when organic matter is destructed with the participation of microorganisms, the chemical composition of the pore waters is modified, and authigenic minerals (first of all, pyrite) are formed.

Pyrolysis data indicate that organic matter is deeply transformed already in the uppermost horizons of the sapropel sediments, and its composition is notably different from that of the producers of organic matter – macrophytes and plankton.

It was determined that pore waters are modified in the course of early diagenesis of sapropel sediments in the lakes. These transformations lead to an increase in the contents of mineral modes of organic matter (HCO_3^-, NH_4^+, HPO_4^{2-}). and this highlights the mechanism of anaerobic oxidation of organic matter by microorganisms. The decrease in the SO_4^{2-} concentrations in the entrapped waters down the vertical section of the sediments reflects the process of sulfate reduction: the reduction of with the participation of sulfate-reducing bacteria.

The sediments of all of the lakes, except only Lake Ochki, were determined to contain authigenic (diagenetic) pyrite, which is a typical mineral of most modern reduced sediments. Comparative analysis shows that sapropels in lakes in southern West Siberia generally contain more reduced Fe species and pyrite than lakes in the eastern Baikal area do, and this may reflect more intense sulfate reduction processes in the West Siberian lakes.

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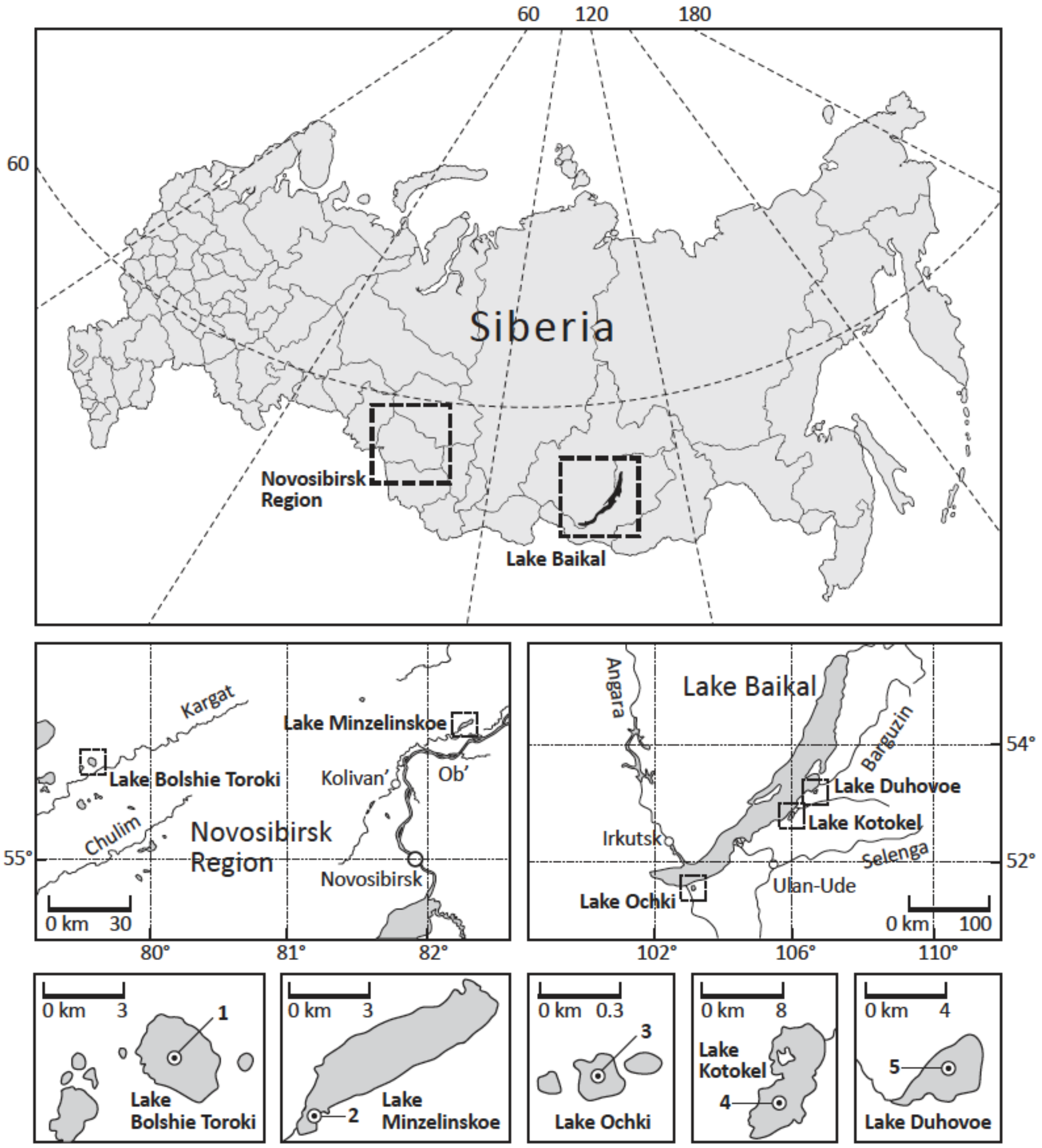

Fig. 1. Overview map of study areas. 1, 2, 3, 4, 5 – points of drilling of sapropel deposits of lakes.

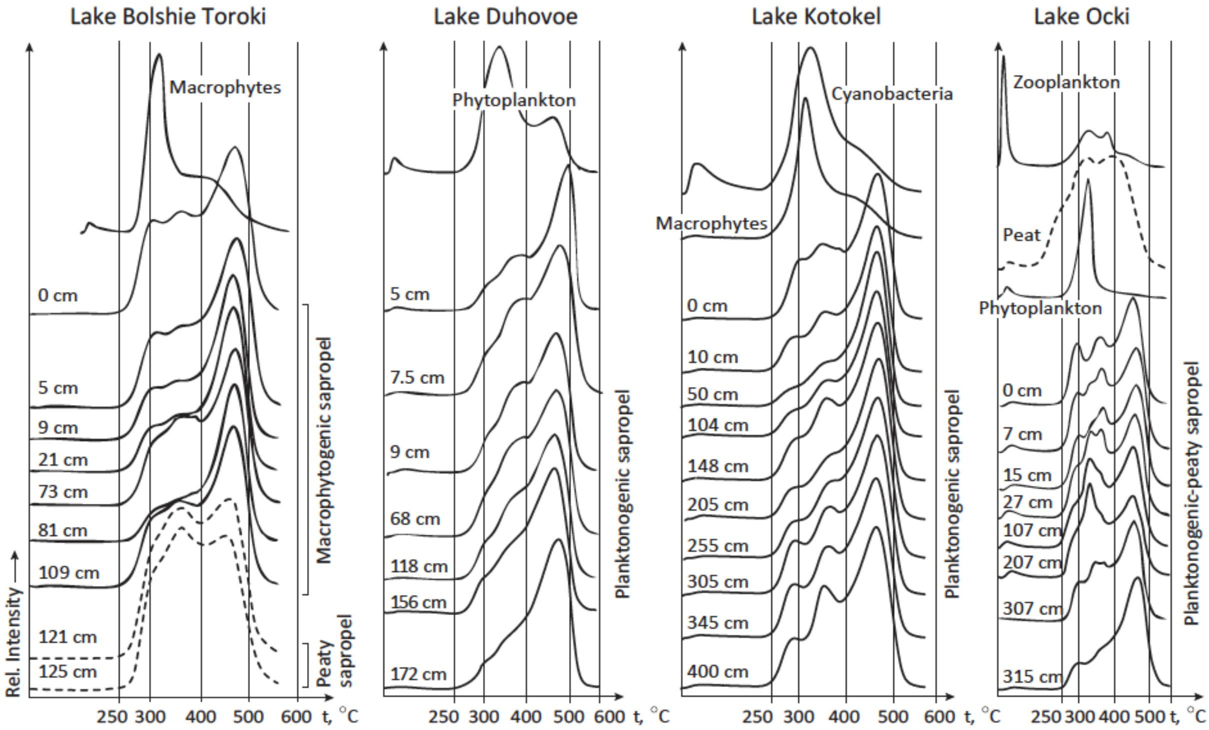

Fig. 2. Pyrograms of producers of organic matter and sediments of the lakes of Great Toroki (A), Dukhovoye (B) and Points (C). BUT - unconsolidated sediment (0–2 cm). Rel. Intensity - the rate of release of a substance per unit of time at a given temperature.

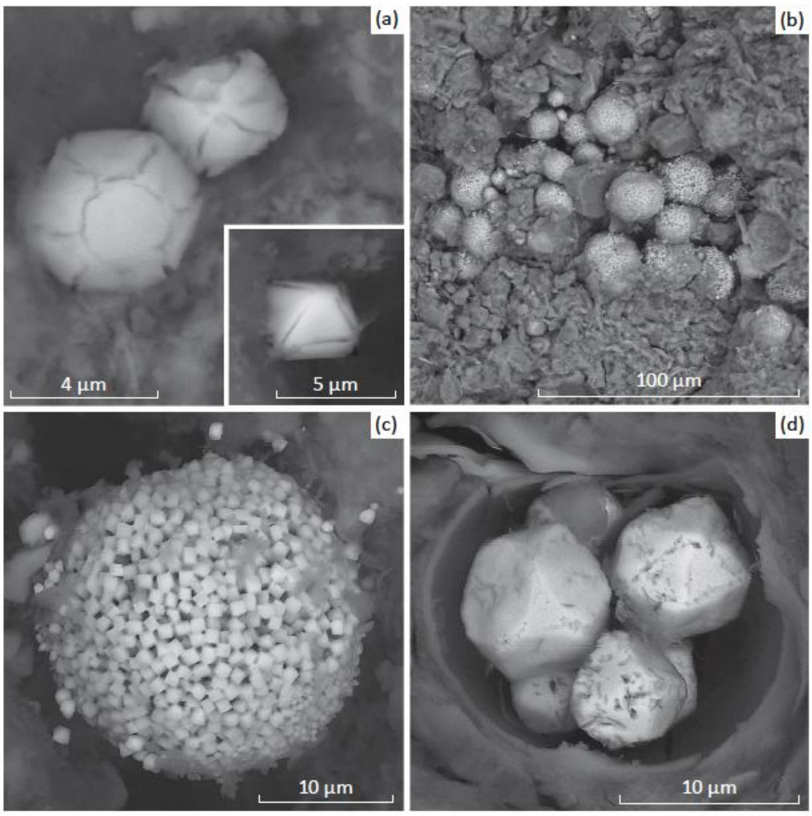

Fig. 3. SEM images (taken together with Dr. E.M. Lazareva of the Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences) of pyrite (a), (d) crystals and (b), (c) framboids from various horizons of sediments in (a, b) Lake Bol’shie Toroki, (horizons 0–2 and 140–150 cm, respectively), (c) Lake Kokotel’ (horizon 40 cm), (d) Lake Dukhovoe (135 cm) (pyrite crystals hosted in alga cysts).

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