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Diagenetic transformation of sapropel from Lake Dukhovoe (East Baikal region, Russia)

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Abstract

The chemical and microbiological composition of sapropel was investigated in the 7 m Holocene sediment core of Lake Dukhovoe. Sapropel is mainly formed from phytoplankton. Heterotrophic bacteria play the main role in the decomposition of organic matter in this sapropel, with the formation of organic-mineral complexes. A reducing type of diagenesis was established in the sapropel. Processes of sapropel transformation under the influence of mechanical, biochemical, microbiological, and physicochemical processes lead to the formation of geochemical barriers and new phases (organic-mineral complexes, diatomite, pyrite inside the cyst of *Chrysophyceae,* framboidal pyrite, vivianite, carbonates, etc.), as well as the accumulation and leaching of elements.

1. Introduction

Almost 90 years ago, Vladimir Ivanovich Vernadsky, who was an outstanding Russian scientist, philosopher, social leader and a founder of geochemistry, hydrochemistry, biogeochemistry and radiogeology, created the holistic doctrine of the Biosphere where he demonstrated the primacy of life as a geological force. He wrote: “Living matter is a small part of the Biosphere, but it plays an exceptional role in geological processes associated with the transformation of the face of our planet” [1]. Vernadsky's

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law [2] states that "Migration of chemical elements in the biosphere is carried out either through the direct participation of living matter (biogenic migration) or in an environment whose geochemical properties (O_2, CO_2, H_2, etc.) are controlled by living matter, either now occupying the given system or which has operated in the biosphere during geological history".

In this work we would like to consider role of living matter and nonliving organic matter in element migration on example of sapropel. Sapropel is an unconsolidated dark-coloured sedimentary deposit enriched in organic matter. Sapropel is formed from residues of aquatic organisms (plankton, benthos, aquatic vegetation) as well as from organic and mineral substances run off from catchment area under influence of mechanical, biochemical, microbiological and physicochemical processes. The diagenetic transformation of sapropel from oceans and seas [3 - 11] as well as of the freshwater Lake Baikal [12 -14] was widely investigated as distinguished from small freshwater continental lakes with organogenic type of sedimentation [15 - 17]. The purpose of this work is to investigate some aspects of sapropel diagenetic transformation in Lake Duhovoe (Southern Baikal region, Russia), presenting the importance of living and organic matter in elements migration.

2. Description of the studied area, materials and methods

Lake Dukhovoe (coordinates: 53°18' N, 108°53' E, 2.5 km of length, 1.6 km of width and a maximum depth of 2.8 m) is situated near the village of Maksimiha at the East Baikal region (Fig. 1). The sapropel thickness of Lake Dukhovoe is about 7 m. The Duhovaya River outflows from Lake Duhovoe and inflows into Lake Baikal. The 7 m core of sapropel was sampled by high-frequency drilling. Liquid and

Figure 1. Satellite image of investigated area (from Google Maps)

solid samples were sampled every 10 cm from this core. The temperature, pH, and Eh of the water samples were measured in the field using an Ionomer-4151 (Novosibirsk, Russia). Concentration of dissolved oxygen was measured in the water samples in the field using the MERCK test (Germany). Pore waters were extracted from solid samples at pressures of 10-15 MPa using a manual laboratory press. The solid samples were then hermetically sealed in polyethylene bags and stored in a room with environmental control or in a refrigerator. Surface and pore water samples were filtered through a 0.45 μm membrane filter and then divided in two subsamples. A first subsample was acidified to pH 2 using concentrated HNO_3 prior to elemental analysis. A second subsample, which was not acidified, was used for ion analysis. Analyses were undertaken at the Analytical Center of the Institute of Geology and

Mineralogy of the Siberian Branch of the Russian Academy of Sciences. The unacidified water subsamples were analysed by ion chromatography to determine the concentrations of anions (SO_4^{2-}, Cl^-, NO_3^-, F^-), cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), and HCO_3^- was determined by titrimetric analysis. Bulk and trace elements were analysed in the acidified subsamples by AAC, ICP-OES and ICP-MS. The solid samples were studied by powder X-ray diffraction. The total nitrogen, carbon, hydrogen and sulfur are determined using a CHNS analyzer. The morphology of solid samples is investigated by scanning electron microscope SEM. Energy-dispersive X-ray spectroscopy was used for microanalysis of the solid phases viewed by SEM. Additionally, modified sequential extraction technique [18] was used in this study in order to investigate element species in sapropel.

3. Results and discussion

It is observed that phytoplankton (*Chlorophyta* – 16 species, *Cyanophyta* – 9 species, *Bacillariophyta* – 8 species and *Chrysophyceae* – 3 species) growths rapidly in shallow Lake Dukhovoe. In the sapropel core, the substance becomes more homogeneous towards the bottom layers. In the top layers we can observe individual species of plankton that are not visible at the bottom layers. Also there is color variation of the core material: dark brown in 1-180 cm, reddish-brown in 180-320 cm and grayish-brown in 320-600 cm. The moisture content of sapropel is about 95% in the upper 2 m. Similar concentrations of total organic carbon in the phytoplankton (21%) and in the upper layer of sapropel (22%) show that sapropel is mainly formed from phytoplankton. Total organic carbon was high (22-27%) at 0-180 cm interval, sharply reduced at 200 cm and then smoothly decreased up to 2% with depth. Concentrations of C, N and H decreased with depth indicating organic matter distraction and transformation in sapropel. In contrast, Si content increased with depth in sapropel. The ratio of organic carbon and nitrogen reflects differences in biochemical composition of present organisms and allows us to consider the genesis of organic substance. It is known, that the higher water and land vegetation is poor in nitrogen and has high C/N=20-40. In comparison, C/N ratio is 5.5-7.0 for phytoplankton. The C/N ratio in sapropel of the Lake Dukhovoe varies from 5.7 to 8.7, showing that phytoplankton plays a main role in sapropel formation.

The surface water of Lake Dukhovoe is HCO_3–Ca–Mg-Na type. HCO_3-SO_4-Ca-Mg-Na pore water type from the upper layers of sapropel core was changed to SO_4-HCO_3-Ca-Mg and SO_4-Ca-Mg ones at the lower layers. Population of heterotrophic bacteria was high at 0-270 cm interval and then smoothly decreased with depth. This correlate to carbon distribution and indicated in intensive process of organic matter decomposition at the layers enriched in organic matter. The activity of sulfate-reducing, ammonifying and denitrifying bacterias increased with depth. There are three complex geochemical barriers in the sapropel core:1) at 95-160 cm depth where there were changes in pH (6.2–7.1), Eh (311-270 mV) and decrease in concentration of SO_4^{-2} (from 270 to 170 ppm) in pore water; 2) at 200-320 cm where pH decreased (up to 4), Eh increased (up to 400 mV), Fe hydroxide precipitated and concentration of some elements (Ca, Zn, Cu, Cd, etc.) and SO_4^{2-} in pore water increased; 3) at 330-400 cm where pH sharply increased to 10 with Eh reduction up to 150 mV and framboidal pyrite formation increased.

The content of iron sulfides such as pyrite (SEM and XRD) increased with depth that is also confirmed by S distribution and S species (up to 90 % of sulfide species) in sapropel. It is significant, that crystals of pyrite with size about 5-10 μm were formed only in the cysts of Chrysophyte algae (*Chrysophyceae*) at the upper 2 m where oxidizing condition was observed. It could be supposed that cyst of Chrysophyte algae is a microreactor in which favorable conditions for formation of iron sulfides were created. Below 2 m formation of framboidal pyrite at reducing condition occurs. Vivianite ($Fe_3(PO_4)_2 \cdot 8(H_2O)$) precipitated at the surface of organic matter at the depth below 2 m and formation of organic-mineral complexes that can adsorb elements is observed. Some elements like Cu, Zn and Pb were accumulated in sapropel. Cu was mainly retained by organic matter (up to 80%). Pb was extracted in the reducible fraction, suggesting that Pb precipitated with iron oxyhydroxides. Also lead was present in the carbonate fraction in some layers, i.e. as cerussite ($PbCO_3$) and/or anglesite ($PbSO_4$).

Finally, sapropel from Lake Dukhovoe is mainly formed from phytoplankton. Heterotrophic bacteria plays main role in decomposition of organic matter in this sapropel. Significant transformation of organic matter, i.e. decomposition of phytoplankton with formation of organic-mineral complexes, was observed. The reducing type of diagenesis was established in this sapropel. The processes of sapropel transformation under influence of mechanical, biochemical, microbiological, and physicochemical processes lead to formation of geochemical barriers and new phases, accumulation and leaching elements.

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