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# Sedimentation and Accumulation of Elements in the Vydrino Peat Bog (Southern Baikal Region)

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**Abstract**—The evolution of peat deposits of the Vydrino bog (southern Baikal region) and concentration of elements in them are discussed. The bog peat massif more than 4 m in thickness formed mostly during the Holocene. The beginning of peat formation dates back to the late Allerød (13.1 ka). At present, the Vydrino bog is a biogeocoenosis of the high-moor type with a transitional peat deposit. We have established that the bog nonuniformly accumulated chemical elements during its formation. Concentration of Pb, Sn, Cd, Zn, and Sb in recent vegetation and in the upper layer of the peat bog is mainly due to forest fires and anthropogenic air pollution. The anomalous enrichment of peat with Zn and Cu in the Early Holocene (12.1–8.8 ka) horizons proceeded through the periodic inflow of thermal groundwater into the bottom part of the peat deposit. Authigenic Zn and Cu sulfides formed on the inner membrane of the cell wall of sphagnum moss. Geochemical modeling has shown that Zn and Cu sulfides can form abiotically.

*Keywords:* peat bog, concentration of elements, genesis, rate of peat accumulation, pigment profile, geochemical modeling, Holocene, East Siberia

## INTRODUCTION

It is commonly known that peat can accumulate various chemical elements (Shotyk et al., 2001; Bernatonis et al., 2002; Ezupenok, 2003; Arbuzov et al., 2004; Mezhibor, 2009; etc.). Regular input of atmospheric dust and anthropogenic aerosol precipitations leads to enrichment of upper peat intervals, which makes it possible to estimate atmospheric presence of multiple chemical elements today and in the past (Shotyk et al., 1998). The chemical composition of dust is primarily defined by local weathering and soil formation products delivered into the atmosphere via wind erosion, although it may carry traces of more distant geological processes as well (Bolikhovskaya, 1995). The amount of dust deposited in peatlands depends significantly on natural-landscape conditions and anthropogenic activity in the area (Lukashev, 1971). Chemical elements in the form of both soluble and insoluble compounds are carried to the bog surface via atmospheric drift. Soluble compounds are primarily a part of rain precipitations (Khodzher, 2005). Insoluble compounds of chemical elements arrive in the form of clayey-silt fractions of minerals. The researchers use the data on microelement concentration in top intervals of peat deposits to assess environmental pollution and trace the sources of anthropogenic activity, as well as its intensity (Shotyk, 2002; Orru and Orru, 2006; de Vleeschouwer et al., 2007). For example, the study of highmoor peat bogs in Tomsk Oblast by Mezhibor (2009) showed that they accumulated chemical elements, such as Sb, Co, Cr, Au, and U, as a result of anthropogenic atmospheric pollution. Pollution sources were as follows: combustion of coal from the Kuznetsk Basin at state district power plants in Seversk and Tomsk (Arbuzov et al., 2000); petrochemical production facilities in the Northern industrial hub (Yazikov, 2006); and emissions of the Siberian Chemical Combine (Rikhvanov, 1997).

Silamikele et al. (2011) studied an ombrotrophic highmoor bog in Latvia and demonstrated that Cd, Co, Ni, Cu, Zn, and Pb were concentrated in surface intervals of the peat bog, whereas bottom intervals accumulated Ca, Mg, Fe, Mn, Cu, Ni, As, and Cr. Bernatonis et al. (2002) studied the Great Vasyugan Mire and found that various chemical ele-

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ments (Na, Ca, Ba, Fe, Co, Cr, Au, Hg, Sb, Se, Br, La, Ce, Sm, Eu, Hf, Th) may concentrate in wetland vegetation and peat. Sources of increased concentrations of chemical elements are as follows: (1) natural and industry-related aerosols; (2) transient dust; (3) groundwater; (4) underlying and rim rocks.

Some researchers identify certain distribution regularities for chemical elements along peat deposit profiles (Arkhipov et al., 1997, 2000; Bernatonis and Arkhipov, 2000; Arbuzov et al., 2004). According to Bernatonis et al. (2002), near-surface layers of peat bogs (up to 0.5 m) are enriched with multiple chemical elements, then the contents of almost all elements are reduced to their minimums at depths of 0.5–1.0, and then smoothly increase to their maximums towards the bottom of the deposit. Arbuzov et al. (2004) note that increased Au concentrations are associated with surface and bottom layers of peat deposits. Vertical distribution of chemical elements may be affected by variations in climate and environmental conditions (composition of feeding waters, specific features of water migration), as well as microbiological activity. A number of authors present several possible causes for increased concentrations of chemical elements in surface intervals of highmoor peat bogs, which are as follows: (1) surface layer represents a redox and alkaline-acid sorption barrier for atmospheric precipitations; (2) evaporative barrier forms as a result of seasonal draining of peat bogs (lower bog water level); (3) the surface living layer of the peat bog may accumulate some chemical elements due to the absorption capacity of root systems of peat-forming plants (Bernatonis and Arkhipov, 2000; Bernatonis et al., 2002). The same authors also found that bottom peat layers are often enriched with certain chemical elements due to the effect of the underlying bed, while being depleted of biophilic elements.

Bernatonis and Arkhipov (2000) note the increased microelement contents in drained peat bogs due to accelerated mineralization of organic matter as a result of improved aeration of the deposit. In addition, Bernatonis et al. (2002) found that accumulation of chemical elements by plants does not always depend on water-mineral feeding conditions. For instance, accumulation of most chemical elements in moss (Fe, Co, Ag, Hg, Sb, Sc, La, Sm, Eu, Hf, Th) is barrier-free. Some researchers consider the presence of significant amounts of humus compounds with high absorption capacities to be the key factor affecting metal accumulation in peat (Gondar et al., 2005; Zaccone et al., 2007, 2008, 2009).

In general, we may state that, despite the vast evidence of accumulation of chemical elements in peat deposits, specific mechanisms of the process are still poorly researched, along with the role of organic matter and the problems regarding forms of chemical elements in peat. The data presented above were primarily obtained in western regions, i.e., Europe and West Siberia.

The goal of the present paper is to investigate the evolution history and specific features of concentration of chemical elements, in particular Zn and Cu, in peat deposit profiles using Vydrino bog in Southern Baikal region in East Siberia as an example.

## RESEARCH OBJECTIVE

Mountains of the Baikal region are formed by strongly faulted Archean and Proterozoic metamorphic schists, limestones, quartzites, gneisses, and intrusive granites. Granitoids and associated pegmatites forming bedding-parallel veins are rather common in the Southern Baikal region. Paleogene–Quaternary deposits have high thicknesses in intermountain basins and in the Tankhoi stage of the southern coast of Baikal. Upper Pleistocene–Holocene deposits form low terraces of Baikal, as well as the glacial, alluvial, and deluvial–proluvial structures of piedmont plains (Kislov, 2009).

The research subject, i.e., the Vydrino bog, is located on the Tankhoi plain. It is a narrow (2–5 km) piedmont strip between the northern scarp of the Khamar-Daban ridge and Lake Baikal, which extends from the Khara-Murin River in the west to the town of Babushkin in the east. The plain is drained by a large number of rivers and streams, covered by a taiga-type forest of birch, pine, spruce, fir, and cedar trees, and is partially stagnant. Climatic conditions are rather mild compared to other continental Siberian regions. Total annual precipitation reaches up to 900 mm, the maximum being observed in summer months; winters are relatively warm, but snowy, with the snow depths reaching 1 m; summers are fairly cool. Relatively mild climate and significant moisture content are explained by physical and geographical features, i.e., the presence of a high mountain ridge, which collects moisture, and Lake Baikal, which warms the territory. The climate has a significant effect on hydrochemistry of rivers and lakes, as it defines low water mineralization in the maximum water content period, while snowmelt waters cause a sharp decrease in mineralization in spring (Kozneeva and Rusenek…, 2001; Leonova et al., 2015).

The Vydrino bog (51°29′39″ N, 104°52′48″ E) is located within the Baikal biosphere reserve on a terminal moraine bar 30 m above the Baikal level at the water divide of the Vydrinaya and Pereemnaya Rivers (Fig. 1). Moraine deposits are represented by sand, loam, broken stone, gravel, poorly-rounded pebble, boulders, and isolated gneiss blocks. They are present at the basement of the peat deposit as well.

The bog occupies one of multiple depressions at the moraine surface and is characterized by primarily atmospheric feeding. Groundwater level is not linked to the water surface of Lake Ochki located 100 m to the south from the Vydrino bog and separated from it by a 3 m high upland ridge. Nitric, methane, and acidulous water discharges are present in the neighborhood of the Vydrino bog (Galazii, 1993). Deep heat flows in the Vydrino area have temperatures of about 75 °C.

The Vydrino bog is classified as a highmoor bog with ledum-sedge-sphagnum plant association also including dwarf birches and rare suppressed pines. The surface of the

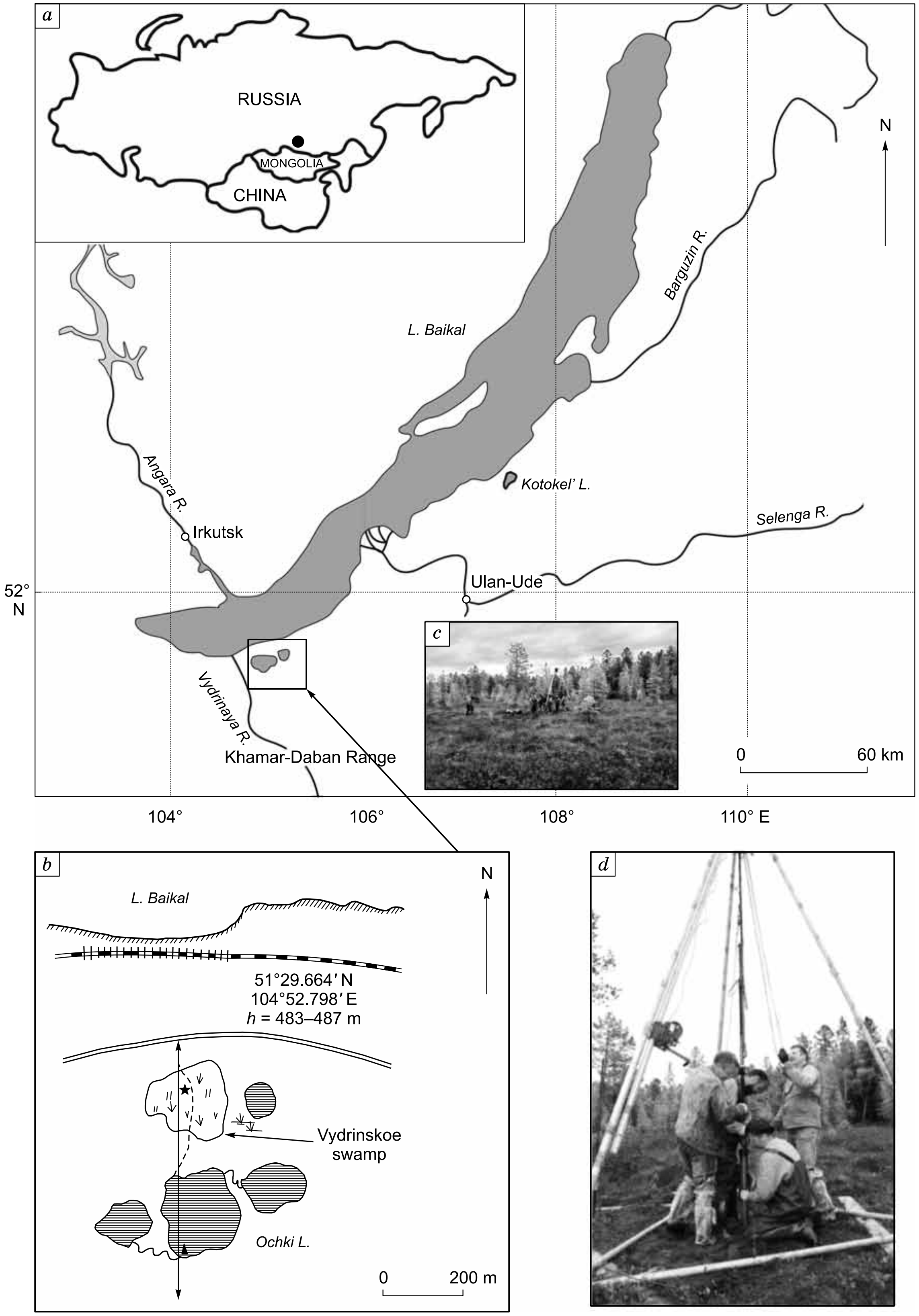

**Fig. 1.** Vydrino bog location. *a*, Vydrino bog location; *b*, diagram of the Vydrino bog location plotted by V.A. Krasnobaev; *c*, Vydrino bog; *d*, drilling site at the Vydrino peat bog.

**Table 1.** The Vydrino bog: vegetation description

| Plant species | Abundance | |
|---|---|---|
| | Braun-Blanquet | Drude |
| A (tree layer) | | |
| *Betula platyphylla* Sukacz. | 1 | sol. |
| *Pinus sibirica* Du Tour | + | un. |
| *Abies sibirica* Ledeb. | + | un. |
| *Picea obovata* Ledeb. | + | un. |
| B (brush layer) | | |
| *Betula nana subsp. rotundifolia* (Spach) Malysch. | 2a | cop.1 |
| C (shrub–grass layer) | | |
| *Ledum palustre* L. | 3 | cop. 2 |
| *Andromeda polifolia* L. | 2a | cop. 1 |
| *Chamaedaphne calyculate* (L.) Moench | 1 | sp. |
| *Vaccinium uliginosum* L. | + | un. |
| *Oxycoccus palustris* Pers. | 2b | |
| *Oxycoccus microcarpus* Turcz. ex Rupr. | + | un. |
| *Rubus chamaemorus* L. | 3 | cop. 2 |
| *Carex pauciflora* Lightf. | 4 | cop. 3 |
| *Eriophorum vaginatum* L. | 2a | cop. 1 |
| D (moss layer) | | |
| Knobs | | |
| *Sphagnum fuscum* (Schimp.) Klinggr. | 4 | cop. 3 |
| *Sphagnum magellanicum* Brid. | 4 | cop. 3 |
| *Polytrichum strictum* Brid. | 1 | cop. 1 |
| Basins | | |
| *Sphagnum capillifolium* (Ehrh.) Hedw. | 2a | cop. 1 |
| *Sphagnum magellanicum* Brid. | 2b | sp. |
| Hollow | | |
| *Sphagnum fallax* (Klinggr.) Klinggr. | 5 | soc. |

Note. The bog plant association is described by S.G. Kazanovskii (Siberian Institute of Plant Physiology and Biochemistry, SB RAS). Braun-Blanquet scale: + – < 1%, 1, 1–5%, 2a, 5–15%, 2b, 15–25%, 3, 25–50%, 4, 50–75%, 5, >75%. Drude scale: un., unicum (unique), sol., solitorius (very rare), sp., sparsae (sparse, rare plants), cop. 1, copiosae (quite common), cop. 2, common, cop. 3, very common, soc., socialis (absolute prevalence of the plant, close canopy).

bog massif displays knob and basin microtopography. The data describing the vegetation cover according to Braun-Blanquet system and representing abundance values based on two scales (Braun-Blanquet and Drude) are presented in Table 1. The tree layer is poorly expressed with its density not exceeding 0.1.

Botanical analysis of peat intervals performed at the Siberian Institute of Plant Physiology and Biochemistry of the Siberian Branch of the Russian Academy of Sciences showed that peat deposits of the Vydrino bog are divided into five significantly different intervals as follows:

0–40 cm—sphagnum peat with small amounts of shrub and grass residue.

40–180 cm—peat with primarily grass or shrub–grass composition with small amounts of tree and shrub residues.

180–220 cm—peat with prevalence of green moss residue and small amounts of shrub and grass residue.

220–360 cm—woody peat with grass peat interlayers.

360–440 cm—sheet peat with variable composition. Thin interlayers with prevalence of either tree or grass residues, along with sphagnum and occasionally hypnum moss residues may be identified. Peat interlayers with mixed composition, i.e., tree–grass, tree–hypnum, tree–sphagnum, and grass–tree–sphagnum peat are encountered as well.

Bog waters have very low contents of principal ions: $SO_4^{2-}$—2.86 mg/l, $Cl^-$—0.42 mg/l, $NO_3^-$—0.24 mg/l, $NO_2^-$—0.031 mg/l, $PO_4^{3-}$—0.007 mg/l, $NH_4^+$—2.53 mg/l, $Ca^{2+}$—0.6 mg/l, $Mg^{2+}$—0.26 mg/l, $Na^+$—0.37 mg/l, $K^+$—0.11 mg/l, $Fe_{tot}$—0.41 mg/l. According to the classification proposed by O.A. Alekin (1970), bog waters belong to calcium group of the sulfate class. These are sweet (mineralization of 7.4 mg/l), acid waters (pH of 4.02) with high organic matter content (dispersed organic matter of 10 mgC/l). Biochemical oxygen demand is 2.6 mgO/l, and chemical oxygen demand is 74 mgO/l.

## MATERIALS AND METHODS

The peat deposit structure was studied by vibration drilling using the modified Livingston sampler. A continuous 5 m long core column of 7.5 cm in diameter was collected from the central part of the Vydrino bog. The thickness of the peat deposit was 4.5 m. This drilling technique made it possible to breach through the whole peat deposit and penetrate the underlying rocks. The core was extracted from the sampler, its preliminary description was obtained, and then the whole sample was wrapped in polyethylene and placed in plastic cases to deliver it to the laboratory in an undisturbed state.

The chemical composition of bog waters was studied by capillary electrophoresis (Kapel 103-R system) at the analytical laboratory of the Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences. Peat deposit core samples were cut into 2-cm fragments and dried following the moisture content and density measurements. Ash content was determined at 450 °C.

The deposit age was controlled by six radiocarbon ages presented in Table 2. Six 6-cm core fragments were used for dating, with no additional core material from these intervals available for other analytical studies. Residual $^{14}$C activity was analyzed using QUANTULUS-1220 system (V.S. Sobolev Institute of Geology and Mineralogy of the Siberian Branch of the Russian Academy of Sciences, analyst L.A. Orlova). Calibration of radiocarbon dates and their conversion into calendar years were performed using the OxCal 4.2 software. Peat accumulation rate was calculated based on calibrated dates (Table 2).

Contents of chemical elements in peat were determined by instrumental neutron activation analysis (INAA) and mass spectrometry with inductively coupled plasma (ICP-MS) using an ELEMENT mass spectrometer. X-ray fluorescence with synchrotron radiation (XFA-SR) was also performed using a VEPP-3 accelerator at the Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences capable of analyzing biogenic matter without preliminary ignition (Baryshev et al., 1986). Atomic absorption and X-ray spectrum analysis were performed for peat samples pre-ignited at 450 °C. However, we cannot be completely certain that all chemical elements were preserved in the ignited samples (Karyakin and Gribovskaya, 1979). Nondestructive INAA and XFA-SR were required for the adjustment of the analytical data. The mineral matrix composition in some peat intervals was identified via X-ray fluorescence using an ARL-9900-XP spectrometer.

Qualitative and quantitative composition of photosynthetic pigments (pheopigments) preserved in peat deposits of the Vydrino bog were studied using the technique from (Klimin and Sirotskii, 2005). Contents of demetallized chlorophyll derivatives *a*, *b*, and *c* (pheophytins) and total carotenoid content were determined in individual layers. Pigment ratio (PR), i.e., the relation between carotenoids and pheophytin *a*, and pigment index (PI), i.e., the relation between the sum of all pigments and pheophytin *a*, were calculated. Pigment profile of the peat deposit, ash content data (ignition at 450 °C), and radiocarbon dating results were used to reconstruct the evolution of the bog.

Geochemical modeling of chemical element concentrations in peat was performed using the Selektor-S software system (Karpov et al., 1997; Chudnenko, 2010). The Selektor-S system uses the algorithm based on Gibbs free energy minimization. The theoretical framework of physical-chemical modeling includes equilibrium conditions in heterogeneous multicomponent systems with constraints represented by linear mass balance equations (Chudnenko, 2010).

## RESULTS AND DISCUSSION

**Evolution of the bog.** The results of distribution investigation of qualitative and quantitative composition of the preserved photosynthetic pigment derivatives and ash content values along the Vydrino peat bog profile are presented in Fig. 2. Gaps at certain depths correspond to the samples collected for radiocarbon analysis. The age model, which demonstrates deposition rate variations, is shown in Fig. 3.

Bog formation at the drilling point started on mineral substrate with ash content of 95.7–87.9%. The beginning of peat formation at depths of 440–446 cm is dated to 13.1 calibrated thousand years ago (Fig. 3).

**Table 2.** Radiocarbon analysis results for samples from the Vydrino peat bog

| Interval, cm | Lab index | $^{14}$C age, years | Calendar age, years |
|---|---|---|---|
| 50–56 | COAH-7693 | 2520 ± 75 | 2470–2690 |
| 100–106 | COAH-7694 | 4415 ± 95 | 4920–5200 |
| 200–206 | COAH-7695 | 6120 ± 120 | 6850–7150 |
| 300–306 | COAH-7696 | 7590 ± 140 | 8250–8550 |
| 400–406 | COAH-7697 | 8510 ± 130 | 9340–9680 |
| 440–446 | COAH-7698 | 11,260 ± 180 | 12,930–13290 |

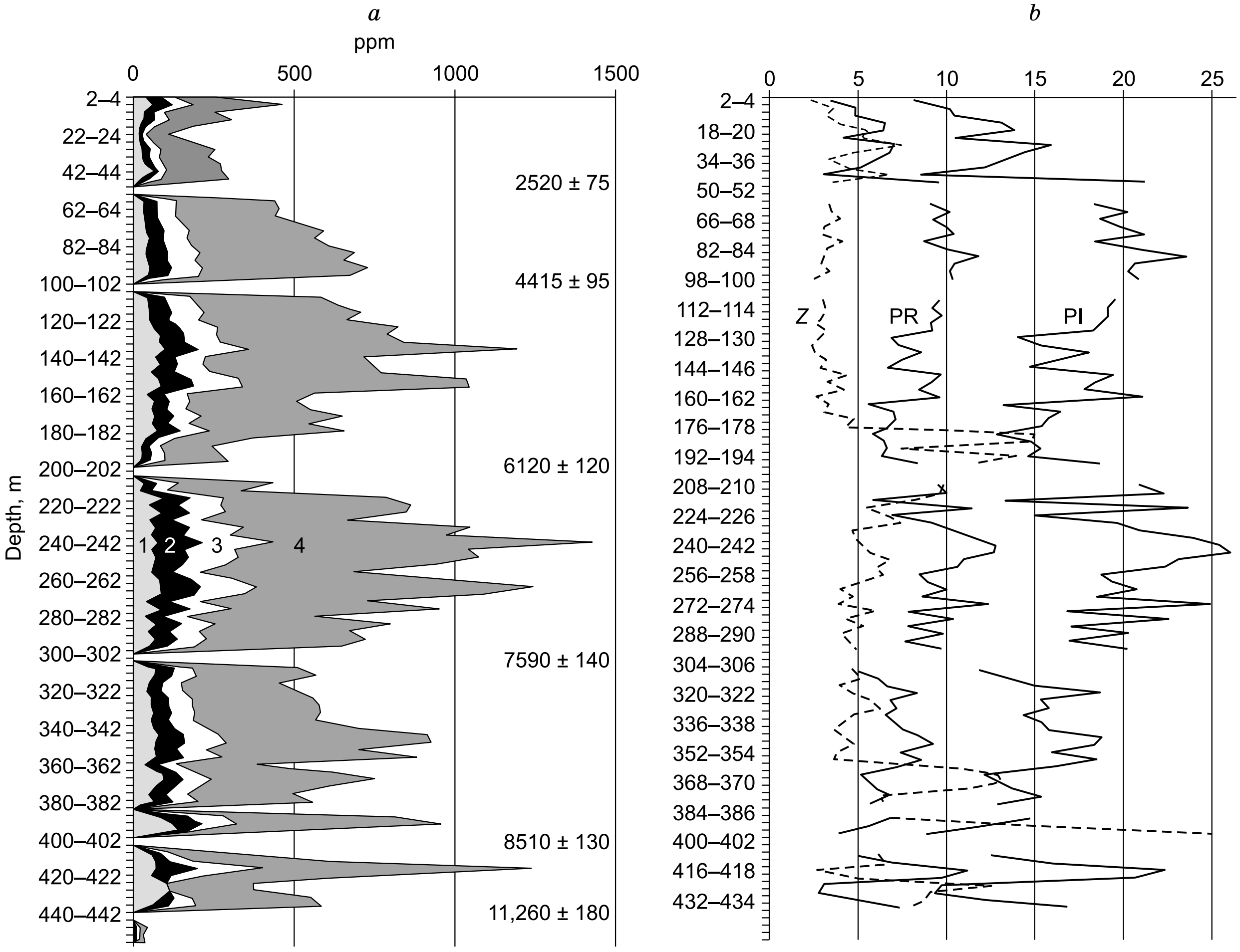

**Fig. 2.** Description of the Vydrino peat deposit section. *a*, Pigment profile; *b*, ash content of deposits and pigment ratios. 1, pheophytin *a*; 2, pheophytin *b*; 3, pheophytin *c*; 4, carotenoids; 2520 ± 75, radiocarbon age; Z, ash content, %; PR, pigment ratio; PI, pigment index.

The period of 13.1–9.5 calibrated thousand years ago corresponds to peat soil accumulation at average rate of 0.11 mm a year. Pigment distribution (Fig. 2*a*) illustrates several climatic fluctuations in this period. Here, we can see two pronounced pigment maximums corresponding to instances of warming. They are separated by a deep minimum characterized by the absence of pheophytins *b* and *c*. These pigment complexes indicate cold and wet conditions (Klimin et al., 2013), which is reflected by minimums of PR and PI and a slight increase in ash content (Fig. 2*b*). Unfortunately, identification of these climatic fluctuations, which should also include cooling following the second instance of warming, is complicated, since it has been much more than 4 similar fluctuations in 3.6 thousand years from the late Allerød age to the middle Boreal period of the Holocene. The lower 40–50 cm of the peat deposit was formed under unstable water conditions, which is confirmed by diversity and frequent variations in the pit's botanical composition in the interval of 440–360 cm. This layer also demonstrates a high probability of significant gaps in deposition.

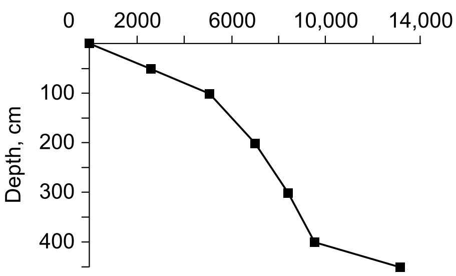

**Fig. 3.** Age model of the Vydrino bog.

The peat deposit in the interval of 400–100 cm was accumulated at much higher rate of 0.52–0.9 mm a year from the middle Boreal to the early Subboreal period of the Holocene. Climatic fluctuations discovered by researchers in various regions of Eurasia in these periods can be clearly seen in the pigment profile (Fig. 2*a*) (Kind, 1974; Khotinsky, 1977, 1987; etc.). For instance, gradual warming in the second half of the Boreal period was followed by cooling at the Boreal-Atlantic boundary. In general, the warming matches with the system of pigment maximums in the plot in the interval of 398–340 cm. Peat deposition primarily the tree residue type started in the bog in the end of this warming period. The fragment of the pigment diagram in the interval of 340–280 cm characterizes a rather significant cooling in the early Atlantic period of the Holocene at about 8.4 calibrated thousand years ago, which continued for about 500 years. It is indicated in the diagram by the minimum pigment content (Fig. 2*a*) and low values of their relations (Fig. 2*b*).

Some authors extrapolate the following warming over the whole Atlantic period (8.9–5.7 calibrated thousand years ago) with heat climax at about 5500–5000 radiocarbon years ago (6.3–5.8 calibrated thousand years ago). However, other researchers show that this period was not that uniformly warm. For example, Mikishin and Gvozdeva (1996) present the data on several heat waves in Sakhalin Island, the first of them passing 7200 radiocarbon years ago (8.0 calibrated thousand years ago), according to the authors. Its climax is possibly reflected in Fig. 2 by the pigment maximum and very high PR and PI values at the depth of 240–242 cm.

The period of 7000 to 6000 radiocarbon years ago (7.8–6.8 calibrated thousand years ago) is identified as a middle-Atlantic cooling (Khotinsky, 1987). A significant decrease in photosynthetic pigment derivatives preserved in peat layers is observed in the interval of 220–180 cm in the studied section, which indicates a rather deep cooling at about 7.8 calibrated thousand years ago. This layer displays sharp variations in peat deposition features, i.e., when ash content in peat increases sharply and significantly (by three times, from 5 to 15%) (Fig. 2*b*), peat composition changes from tree-type to primarily green moss-type, which is usually considered the result of fires. Peat accumulation rate in the interval of 242–200 cm 8.0–7.0 calibrated thousand years ago was 0.38 mm a year (Fig. 3). Since the underlying peat formed during the warming of 8.4–8.0 calibrated thousand years ago accumulated at the average rate of 1.55 mm a year, it becomes clear that the warming was followed by a sharp decrease in peat accumulation rate. A similar situation was described earlier for the Gur bog massif in the Lower Amur region 2300 km to the east of the Vydrino bog (Klimin and Sirotskii, 2005; Klimin et al., 2007). It is found that there was a lengthy gap of up to 1000 years in peat formation in the Gur bog from 7200 to 6100 radiocarbon years ago (8.0–6.9 calibrated thousand years ago).

The average peat accumulation rate in the interval of 200–100 cm in the Vydrino peat bog is 0.52 mm a year. At depths above 180 cm, peat is primarily represented by grass and shrub residues with insignificant amounts of tree and brush residues. A peat layer possibly formed during the latest warming in the Atlantic period of the Holocene is observed in the middle part of this interval (at the depth of 158–152 cm). Lower pigment contents and sharp decrease in PR and PI values in the layers above make it possible to assume that peat layers at 150–140 and 134–128 cm were formed during two instances of cooling at the Atlantic-Subboreal boundary of the Holocene dated at 4900 and 4600 radiocarbon years (Khotinsky, 1977) or 5.7 and 5.4 calibrated thousand years ago.

The analysis of the data describing the upper 1 m of the Vydrino peat deposit section makes it possible to identify some of its formation features. The lower part of the deposit in the interval of 100-40 cm is primarily represented by grass or shrub–grass peat, in which thin interlayers with occasionally high sphagnum moss residues (up to 40–50% and above) appear starting from the depth of 70 cm. Sphagnum moss residues prevail in the upper 35 cm of the peat deposit, at times reaching 90–95%, which allows us to state that the highmoor development stage of the bog started about 2.0 calibrated thousand years ago.

Ash content values in the lower part of the deposit fall within range of 2.5–4.0%, which usually corresponds to highmoor peat deposits. However, here we do not observe neither prevalence of sphagnum mosses, which are an essential element of highmoor plant cover, nor sometimes even their mere presence in the botanical composition. Ash content variation range increases in the overlying sphagnum peat up to 2.3–7.5%, and two pronounced maximums are observed at depths of 42–44 and 26–28 cm (Fig. 2*b*).

Extremely low peat growth rate of slightly above 0.2 mm a year in the upper 1 m is noteworthy as it is strongly atypical for a mesotrophic bog in transition to its oligotrophic stage. It is known from the literature (Neishtadt, 1957; etc.) that in the last 5000 years Eurasian highmoor peat bogs have accumulated peat layers, which are much thicker than 1 m and reach 2–3 m and more.

The distribution of photosynthetic pigment derivatives in the upper 1 m of peat deposits, namely a sharp decrease in their amounts (Fig. 2*a*) does not match the significant climatic fluctuations identified in the considered period. In addition, small amounts of pigments in the upper 40 cm of the deposit contradict with normal values for highmoor peat, which usually preserves a significantly higher amounts of pigments, than transient or lowmoor peat (Klimin et al., 2013).

Since this part of the diagram is explicitly shortened and fragmentary, its interpretation is complicated. The fragmentary character is possibly explained by natural causes, namely specific features of autonomous development of the peat body when bog growth is slowed down due to lack of moisture at the elevated topography or similar factors. It is confirmed by a slight increase in ash content at the uppermost part of the section (Fig. 2*b*), which may be associated with peat decomposition processes that occur when aeration of the active layer of bog deposits occasionally improves.

Thus, the Vydrino bog, which is a typical highmoor bog biogeocenosis with a transient peat deposit, is currently at the development stage that may be described as climax or near-climax. The further evolution of the bog will depend on the type of environmental variations. If water feeding of the bog massif does not improve, the parameters of the upper peat layers will change inevitably and significantly towards higher decomposition up to destruction. However, if water feeding of the massif improves, it may stimulate the revival of peat formation, which has almost stopped.

Overall, ash content in peat (2.5–7.5%) matches that for normal transient peat, except for the layer at 180–220 cm (Pyavchenko, 1972). The amount of extracted pigments in some peat layers below 120 cm is rather high at over 800 µg/g of peat, which better matches with Far Eastern and European highmoor peat types (Klimin and Sirotskii, 2014). However, the fact that pigment parameters of peat in the Baikal region are poorly researched should be taken into account.

**Distribution type of some chemical elements in the peat deposit profile.** Peat color changes from light brown to dark brown towards the bottom of the section, which is linked to peat decomposition increasing with depth. TOC in peat varies across the section from 29 to 39%. Peat density is rather low (<0.2 g/cm$^3$) at depths down to 448 cm, and it increases from their downwards reaching 1.5 g/cm$^3$ at 455 cm. Ash content is low throughout most of the peat deposit (Fig. 2*b*). Increase in ash content is observed in some intervals of the upper, middle, and especially lower part of the peat deposit indicating an increase in the lithogenic component.

The composition of the ash component is presented in Table 3 for the plant cover sample, two peat samples (active bog layer at 2–4 cm and 98–100 cm), and two samples from the underlying mineral layer below peat. Principal elements of the ash component of the plant cover are as follows: Si, Ca, Mn, S, Mg, K, Na, Fe, and P. They account for 71% of the ash residue in the form of oxides.

The active bog layer is enriched with Ca, Mg, K, Mn, Fe, and S. Compared to the plant cover, this interval has higher contents of lithogenic elements, such as Si, Al, and Ti. The underlying peat layer (98–100 cm) displays much lower contents of biogenic and similar or slightly higher contents of lithogenic elements for similar ash content values. The intervals corresponding to the mineral bed of the bog massif, and therefore characterized with high ash content, have radically different composition of chemical elements from peat intervals, first of all in terms of contents of lithogenic and biogenic components.

The plant cover and the upper layer of the peat deposit include larger amounts of Pb, Sn, and Cd (Table 3), which, according to the studies (Wiersma and Davidson, 1986), fall into 'anomalous enrichment' category of elements in aerosols mostly due to forest fires and anthropogenic air pollution. Their amounts however decrease rather rapidly down the profile.

The distribution of concentrations of certain elements (K, Ca, Fe, Zn, and Cu) across the peat deposit section is shown in Fig. 4. The active layer with thickness of several tens of centimeters displays increased contents of multiple elements. Mechanical redistribution of mineral matter, water circulation, and migration of elements occur in this layer. It forms a redox and alkaline-acid sorption barrier for percolating atmospheric precipitations; the surface of the deposit becomes an evaporative barrier during the seasonal draining of the peat bog as a result of lowering groundwater level. It should be noted that Zn and Cu contents increase significantly in lower intervals of the peat deposit, and Zn content also increases in the upper intervals, where sphagnum moss prevails.

**Specific features of Cu and Zn concentrations in peat in the Vydrino bog.** It was mentioned earlier (Bobrov et al., 2011) that anomalous concentrations of Cu and Zn up to 500–600 ppm on a dry basis were discovered in the peat deposit of the Vydrino bog in the ancient and early Holocene intervals (360–440 cm) formed 11,300–8100 radiocarbon years ago or 12.1–8.8 or calibrated thousand years ago (Fig. 4). Concentrations of these elements significantly exceed the respective abundance values in the Earth's crust (Zn = 50–70 ppm; Cu = 14–100 ppm (Vinogradov, 1956; 1962; Taylor, 1964; Wedepohl, 1995), soils (Zn = 50 ppm; Cu = 20 ppm (Vinogradov, 1957), and clayey schists (Zn = 93 ppm; Cu = 45 ppm (Li, 1991).

The data obtained for the peat deposit interval of 360–440 cm associated with anomalous copper and zinc concentrations are presented in Fig. 5. As can be seen from Fig. 5*a* these elements are distributed differently both in terms of contents, as Zn concentrations are usually above those of Cu, and the number of maximums, with 3 for the former and 5 for the latter element.

To explain what causes this behavior, we may use the data on climatic conditions at the time of deposit formation and botanical composition of peat.

The principal maximums for Cu (430–432 cm, 504 ppm) and Zn (426–428 cm, 618 ppm) in the lowermost part of the section do not match, but both of them are confined to peat layers formed under cold conditions. Minimum contents of these elements located above at 422–424 cm (Cu) and 418–

**Table 3.** Composition of the ash component of plants, peat, and underlying rocks across the Vydrino peat deposit section

| Target, depth, cm | Ash content, % | Si | Al, | Fe | Ca | Mg | K | Na | Mn | Ti | P | S | Ba | Pb | Sn | Cd | Sb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | | | | | | | | | | | | | ppm | | | |
| Plant cover | N/A | 11 | 0.23 | 1.6 | 10.7 | 2.9 | 2.2 | 1.7 | 9.1 | 0.006 | 0.96 | 2.3 | 0.11 | 270 | 66 | 9.0 | 2.6 |
| 2–4 | 2.35 | 20 | 3.0 | 1.7 | 7.0 | 2.5 | 2.5 | 0.82 | 0.88 | 0.23 | 0.43 | 1.8 | 0.16 | 220 | 29 | 6.6 | 6.7 |
| 100 | 2.59 | 18 | 4.4 | 0.49 | 1.3 | 0.58 | 0.88 | 0.51 | 0.0077 | 0.52 | 0.52 | 0.012 | 0.063 | 65 | 6.6 | 0.96 | 2.4 |
| 450–452 | 91.77 | 31 | 3.8 | 0.99 | 1.2 | 0.82 | 0.92 | 0.96 | 0.039 | 0.38 | 0.041 | 0.024 | 0.054 | 18 | <0.01 | 0.2 | 0.47 |
| 458–460 | 95.69 | 34 | 3.6 | 0.88 | 1.1 | 0.55 | 0.86 | 0.91 | 0.062 | 0.25 | 0.028 | 0.02 | 0.063 | <0.01 | <0.01 | <0.01 | <0.01 |

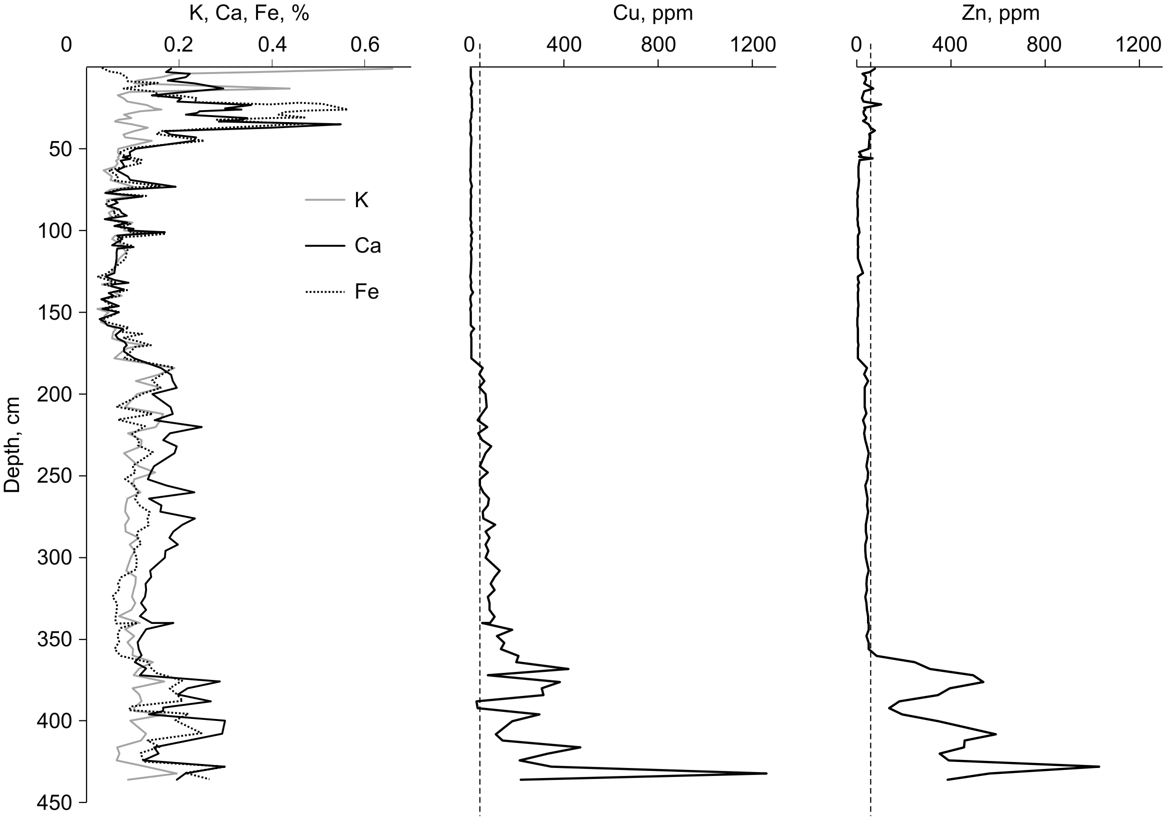

**Fig. 4.** Distributions of K, Ca, Fe, Cu, and Zn contents across the peat deposit section. Red dashed line indicates abundance values in the Earth's crust.

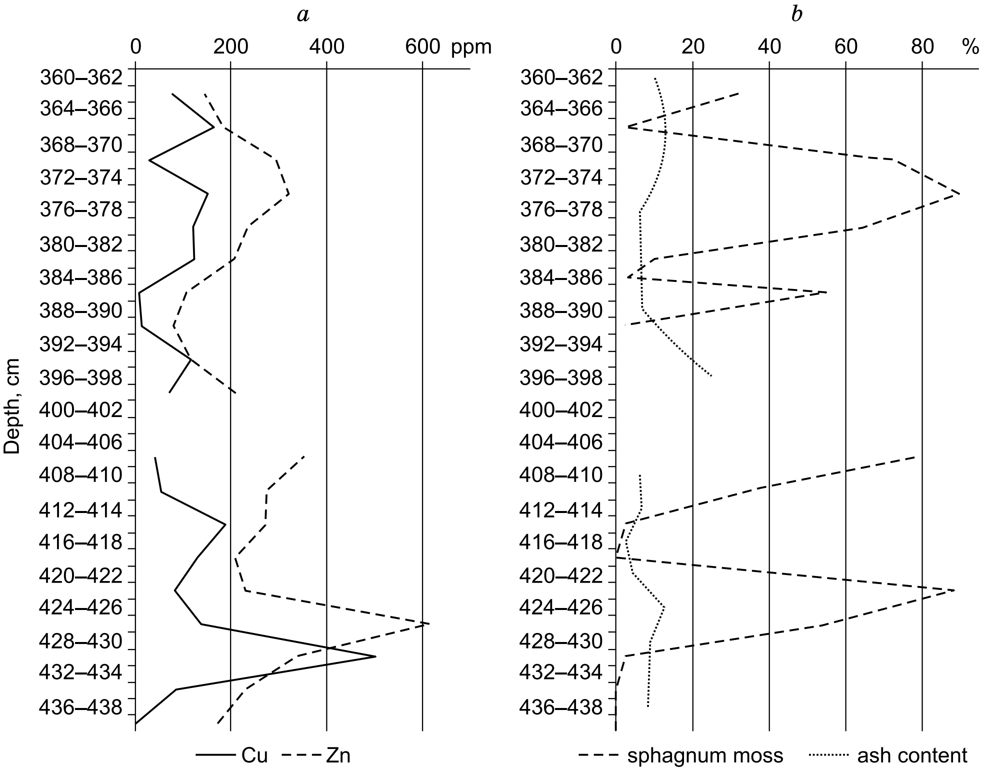

**Fig. 5.** Distributions of Cu and Zn contents (*a*) and changes in ash content and sphagnum moss residue (*b*) in the anomalous concentration zone in peat deposit profiles in the Vydrino bog.

420 cm (Zn) are, on the contrary, associated with a significant warming. It was shown earlier that these warming and cooling periods appear impossible to identify.

Four copper content maximums located up the profile have close values, but none of them exceeds 200 ppm. Given the pigment profile parameters of the peat deposit (Fig. 2), Cu content growth in cool climatic periods is the common feature of these maximums.

The second maximum of Zn content possibly matches with the peat deposit present in the 6 cm block used for dating of the deposits, which produced radiocarbon age of 8510 ± 130 years or 9.3 calibrated thousand years, which corresponds to the beginning of the second half of the Boreal period of Holocene. The third maximum for Zn at 374–376 cm is the only one that matched with the maximum for Cu. Both maximums for Zn exceed 300 ppm, which is 1.5–3 times as high as copper content in four upper maximums. Almost all minimums for both elements are associated with peat layers formed during periods of warming.

Many authors noted that microelement contents (Mn, Fe, Pb, Zn, Cd, Co, and Cr) in moss peat may be several dozen times higher than their abundance values (Dobrovolskii, 1983; Dobrodeev, 1990; Moskovchenko, 2006). It can be seen from Fig. 5*b* that sphagnum moss contents in the considered peat deposit interval shows significant variations. When we compare it to Cu and Zn distributions, it becomes clear that most copper content maximums coincide with minimum contents of sphagnum moss residue. There is only one layer (374–376 cm), in which local maximum for copper coincides with the maximum for moss. Meanwhile, the behavior of zinc is slightly different. For instance, the deepest maximum peak for this element corresponds to a rather high content of sphagnum moss residue in peat. The second maximum for Zn is also associated with the ascending branch of sphagnum moss content. The third maximum matches with the local maximum of sphagnum moss residue, which is followed by a gradual decrease in Zn content.

The investigation of mineral forms of Zn and Cu in peat showed the presence of these elements inside sphagnum plant cells in the form of micron-sized authigenic crystals (Fig. 6). The crystals are mainly represented by copper and zinc sulfides. Sizes of individual crystals are below 3 μm.

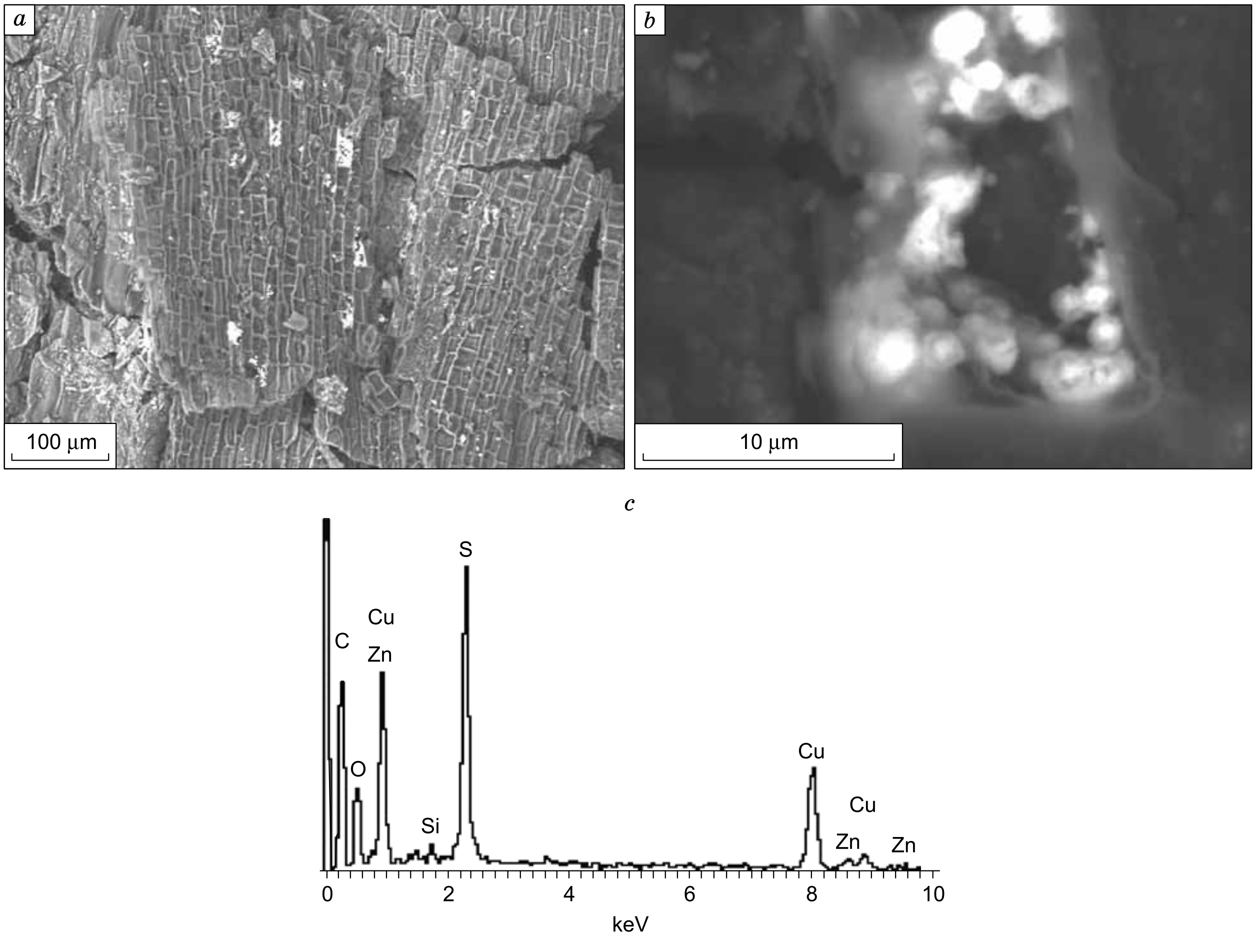

**Fig. 6.** Copper and zinc sulfide formation inside a sphagnum cell (Bobrov et al., 2011). *a*, SEM-image of sphagnum with numerous Cu and Zn single crystals; *b*, SEM-image of a sphagnum cell, in which Cu and Zn sulfides are generated; *c*, energy dispersive spectrum for Cu sulfide microcrystals with added Zn.

Copper and zinc sulfides are deposited on inner membranes of plant cell walls consisting of organic matter with presence of Ca, Si, S, Fe, and Al. Active forms of Zn and Cu are most likely delivered into plant substrates via deep thermal water feeding, whose presence is confirmed by relatively high water temperatures in Lake Ochki and its chemical composition (Bobrov et al., 2010). The assumption of a currently active deepwater source in the specific case of Vydrino bog is based on observations of daily air temperatures, which in June 2009 did not exceed 15 °C, whereas water temperature in the lake was at least 23–25 °C. The data on discharges of nitric and methane thermal waters with temperatures of 75 °C in the tectonic fault zone along the (northern) flank of the Khamar-Daban Ridge (Vydrino bog location) were described in the (Galizii, 1993).

The plant cover and its moss component in particular is capable of absorbing groundwater and accumulating chemical elements. Several possible ways of sulfide formation are suggested because sorption centers or sulfide crystallization centers may form on non-uniform surfaces of plant cell walls. Adsorption at the cellular membrane may be both physical and chemical due to the presence of negatively charged anion groups, such as $PO_4^{3-}$, $COO^-$, $HS^-$, and $OH^-$, in the cellular wall. Copper and zinc are deposited in the form of sulfides under certain conditions, which in the present case means reductive conditions, for example, provided by organic matter decomposition or activity of sulfate-reducing bacteria. When a cell loses water (aging, dying, draining, etc.), some chemical elements may be accumulated in local areas, where supersaturation of the solution with certain minerals, i.e., copper and zinc sulfides in our case, may occur at some point. Sulfate-reducing bacteria, whose quantities increase sharply in lower intervals (360–440 cm) of the peat deposit may play a major part in Cu and Zn sulfide formation.

To test the possibility of copper and zinc sulfide formation within plant cells in process of water loss in absence of bacteria, geochemical modeling was used. Bog water composition was used for the model. Organic matter in the system was defined as carbon. After that, water was gradually removed from the initial composition (Fig. 7).

The modeling results showed that, if the chemical composition of bog waters is used as represented by hydrochemical analysis, then the pH calculated at the first iteration is approximately 8.0, which generates reductive conditions (Eh = 0.32V). Organic matter (introduced in the model as $C_{org}$) cannot be completely dissolved in this system. Thus, solid organic matter is generated in the equilibrium state (Fig. 6). Bornite ($Cu_5FeS_4$) is present in the equilibrium state at initial iterations. When 700 g of water remain, hydroxylapatite and covellite are generated (CuS). Chalcopyrite ($CuFeS_2$) may be generated at final stages, when 150 g of the water solution remains. Calcite ($CaCO_3$) is generated, and sphalerite (ZnS) traces appear at the evaporation stage corresponding to 100 g of water. When less than 300 mg of water remains, the gas phase represented by hydrogen sulfide, methane, and nitrogen is generated, while hydroxylapatite, covellite, solid carbon, calcite, magnesite, sphalerite, and pyrite co-exist in the equilibrium state. At this stage, pH of the solution reaches 7, although the overall alkalinity of the environment increases.

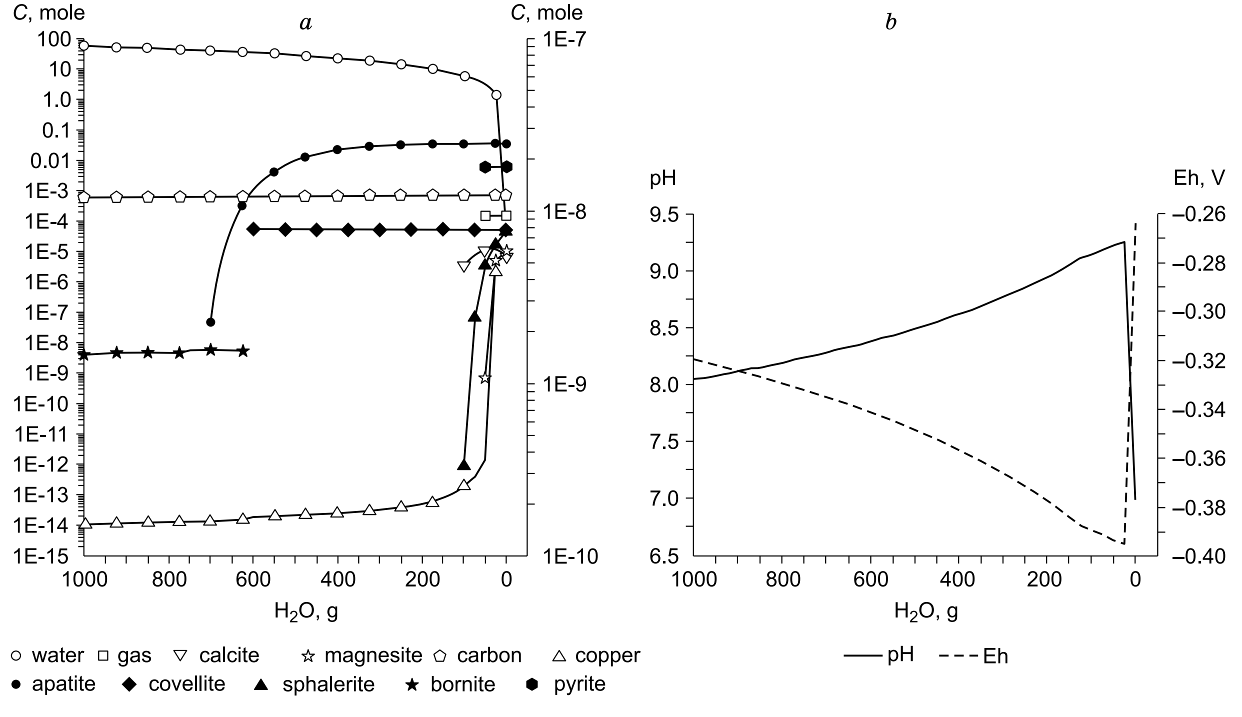

**Fig. 7.** Geochemical modeling of plant cell aging.

## CONCLUSIONS

The bog massif with peat deposits with thicknesses over 4 m was mostly formed in the Holocene. The beginning of peat formation is attributed to the late Allerød age (13.1 calibrated thousand years ago). The Vydrino bog is a highmoor biogeocenosis, although its peat deposit is of transient type. The average peat accumulation rate at the initial bog formation stage (the first 3.6 thousand years) was low (0.11 mm per year), with peat-like and later peat soil developing in the depression. A much higher peat accumulation rates are observed in the overlying peat: 0.90 mm a year at 4–3 m, 0.71 mm a year at 3–2 m, and 0.52 mm a year at 2–1 m. The peat growth rate in the upper 1 m of the deposit is rather low (approximately 0.2 mm per year). The peat accumulation rate variations reflect the natural bog development from lowmoor to highmoor type. Low peat accumulation rates in the upper part of the deposit are explained by the climax state of the bog, i.e., insufficient moisture content.

The plant cover and the upper layer of the peat deposit accumulate Pb, Sn, Cd, Zn, and Sb. Sources of increased concentrations of chemical elements include transient dust, natural and industry-related aerosols, which agrees with numerous data in the literature.

Anomalous peat enrichment with zinc and copper in ancient and early Holocene intervals formed 11,300–8100 radiocarbon years ago or 12.1–8.8 calibrated thousand years ago is linked to the regular inflow of thermal groundwater to the lower part of the peat deposit profile. Here, a gradual decrease in Zn content at its maximums from the bottom to the top of the profile is noteworthy, since it may indicate additional enrichment of peat layers in the lower part of the deposit with zinc during repeated rises of thermal groundwater. Lengthy and discontinuous peat deposit formation at the initial stage directly indicated by significant changes in botanical composition, low peat accumulation rates, and pigment parameter values is among the possible causes of peat enrichment with microelements in the lower part.

Maximums of abnormally high Zn contents are associated with peat layers formed under cold or cool conditions. Two minimums of Zn content match with peat layers formed under warm conditions. Copper demonstrates similar behavior, although its maximums are slightly lower than those for Zn. The first principal maximum is associated with the peat layer formed under cold conditions. The second maximum coincides with the very beginning of cooling following a significant warming. The three remaining maximums correspond to cool conditions. Minimums of Cu are mostly located in peat layers formed under warm conditions. Fuzzy distribution regularities for Zn and Cu may be explained in multiple ways, for example, by the fragmentary character of the lower part of the deposit associated with lengthy gaps in peat accumulation or differences in solubility products between sulfides of these elements.

Formation of fine-dispersed zinc and copper sulfides may possibly be a highly common phenomenon for bogs in piedmont plains, where (hydrothermal) groundwater with sulfate composition and increased contents of metals becomes an additional source of these elements, along with atmospheric drift. Authigenic Zn and Cu sulfides are formed at inner membranes of cellular walls of sphagnum moss. According to geochemical modeling, it was shown that Zn and Cu sulfides may form abiotically. However, the presence of sulfate-reducing bacteria in the lower intervals of the peat deposit leaves the possibility for biochemical sulfide formation. A combination of physical-chemical and biochemical processes appears to be a possible source of Zn and Cu sulfide formation in this situation.

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