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Geochemical barriers in oligotrophic peat bog (Western Siberia)

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ABSTRACT

Peat bogs play an important role in the functioning of the biogeochemical cycles of the chemical elements that are connected to climatological and environmental changes, at least at the regional level. For several decades, this has made the issue of wetland evolution of particular interest among the scientific community worldwide. A number of authors have studied different aspects of wetland geochemistry and evolution: the chemical composition of bog water and peat, including nutrient dynamics, bog vegetation, hydrological characteristics, and the mineralogical composition of peat. However, some issues remained insufficiently studied, including the distribution of chemical elements in peat deposits and, particularly, the causes of the formation of some minerals in the peat deposits. To research these issues, we estimated the geochemical conditions of the formation of some minerals in the oligotrophic pine-shrub-sphagnum bog and adjacent area (part of the Vasyugan Swamp, Western Siberia) in the winter period of 2017 and 2018. It was revealed that there were no less than two complex geochemical barriers in the peat deposit. These barriers correspond to changes in advective and diffusion flows and result in the accumulation of Fe and some other chemical elements in the peat deposit. The upper complex geochemical barrier of redox, sulfide, and sorption type is located approximately at a depth of 0.40–1.25 m. The bottom barrier, which is the combination of complex geochemical barrier of alkaline and sorption type with mechanical barrier, are located at the bottom layer of the peat deposit, at a depth of 2.25–2.50 m. Accumulation of substances in the upper geochemical barrier is always less significant than in the bottom barrier. Therefore, the probability of detecting high concentrations of various substances is very high in the bottom part of the peat deposit, the organomineral sediments, and the upper part of the underlying mineral ground.

1. Introduction

During the last decade, there has been a sustainable interest in wetlands because of their interconnection with climate conditions and obvious benefit for paleoreconstructions and development of a climate change scenario [Avis et al., 2011; Cooper et al., 2017; Fischer et al., 2008]. Among the wetlands, peat bogs play an important role in the functioning of the biogeochemical cycles of the chemical elements that are connected to climatological and environmental changes, at least at the regional level. The role of peat bogs is particularly important in West Siberia within the Ob River Basin because more than a third of this territory is occupied by peatlands, including bogs. In many small river catchments, the area of the peatlands exceeds 50% [Liss et al., 2001; Minayeva et al., 2006]; and the square of the peatlands in the Taiga zone is increasing, with an average rate of peat vertical growth of about 1 mm/year [Pologova and Lapshina, 2002]. Furthermore, in the course of the rise and evolution of peatlands, the removal of some substances and the accumulation of others increase. Substances distributed in a certain way to the depth of peatlands and horizontally within the area of river basins, and their distribution are reflected in conditions of coal formation [Liss et al., 2001]. This determines the relevance of studying the origin and evolution of the chemical and mineralogical composition of peat bogs in the Taiga zone of Western Siberia as one of the largest wetlands in the world.

A comprehensive review of research on various aspects of the peatland development and characteristics of peat and peatland water in the last century is given in [Shotyk,1988]. It should also be noted a number of relatively recent research devoted to the formation, origin, and fate of mineral inclusions in peat [Cabala et al., 2013; Le Roux et al., 2006; López-Buendía et al., 2007; Zaccone et al., 2013]. Basically, in these

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Abbreviations: OMS, organomineral sediments; HHC, hummock–hollow complex; ICP-MS, inductively coupled plasma mass spectrometry; REE, rare-earth elements; SI, saturation indice; PPD, potassium permanganate demand; EC, electric conductivity.

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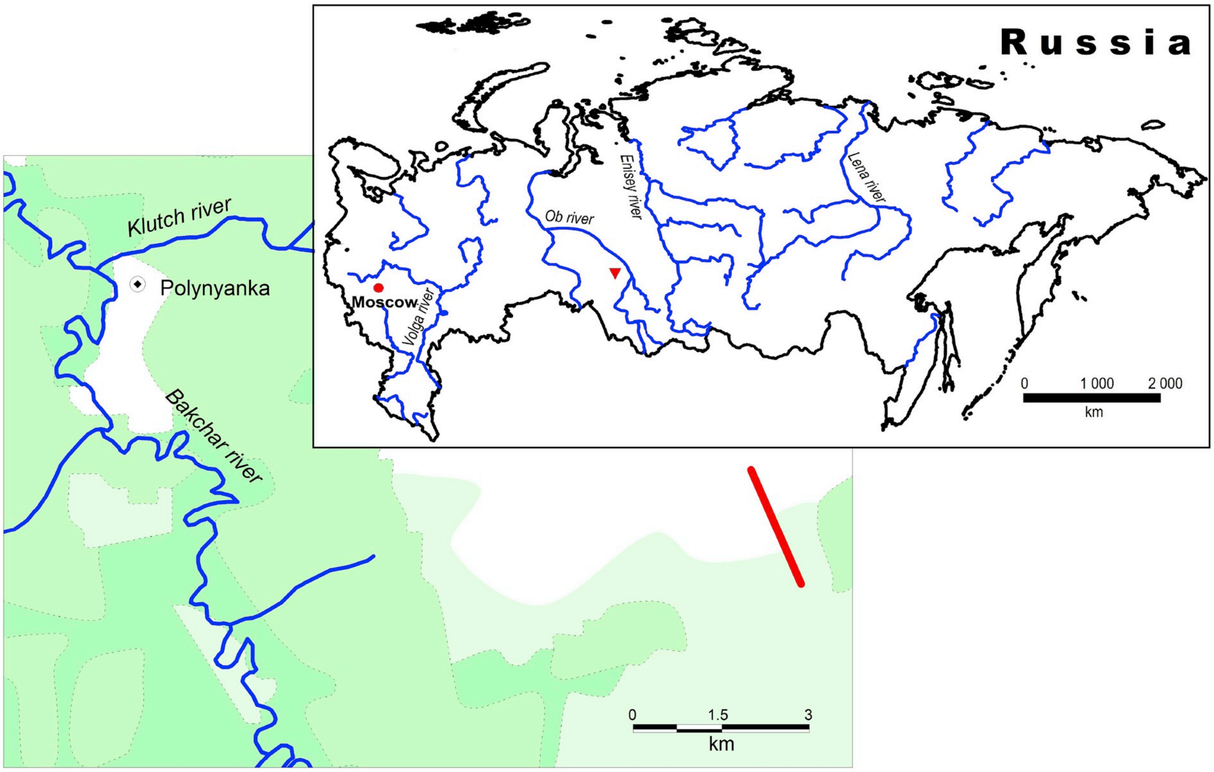

Fig. 1. Scheme of the study area located in the eastern part of the Vasyugan Swamp
The red line is the profile of the research points. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

studies, the authors focused on the importance of the atmospheric deposition of mineral particles. Only Cabala et al. (2013) and López-Buendía et al. (2007) paid attention to influence of water-rock-organic matter system on the formation of minerals in a peat deposit as in research of Chagué-Goff et al. (1996), where the geochemistry of bogs was considered as comprehensive process affected by complex of factors.

Specifically for the Ob River Basin, including the area of the Vasyugan Swamp, peatland geochemistry and evolution were studied by Kharanzhevskaya et al. (2011), Kharanzhevskaya and Sinyutkina (2017), Maloletko et al. (2018), Schipper et al. (2007), who investigated the chemical composition of bog water, bog vegetation, and hydrological characteristics and their interconnection. The chemical and mineralogical composition of the peats was studied by Arbuzov et al. (2018), Preiss et al. (2010), Savichev et al. (2018), Veretennikova (2015). Team of researchers [Minayeva et al., 2006; Pologova and Lapshina, 2002] was focused on the accumulation of nutrients within the Vasyugan Swamp. However, a number of issues remained, including the distribution of chemical elements in peat deposits and, particularly, the causes of the formation of some minerals in the peat deposits (e.g., phosphates rich in rare-earth elements (REE)).

At present, the dominant point of view considering the evolution and functioning of peatlands is atmospheric mass transfer of mineral aerosols (atmospheric dust deposition) and prevalence of detrital material in peat deposits, at least for an upper part of cross section, ignoring or even denying influence of water solution [Le Roux et al., 2006; Sapkota et al., 2007; Shotyk, 1988, 1996; Steinmann and Shotyk, 1997; Zaccone et al., 2012, 2013]. However, this hypothesis explains only part of the revealed patterns in the behavior of chemical elements and the distribution of minerals in bog ecosystems. In the current research, we attempt to expand the understanding of the functioning and evolution of peatlands considering another way of the accumulation of chemical elements and the formation of minerals from the standpoint of the water–rock–organic matter interaction. For this purpose, we studied chemical and mineralogical composition of peat, organomineral sediments (OMS), and underlying mineral ground in the oligotrophic peat bog and adjacent areas using appropriate methods for chemical analysis of aqueous and acid extracts (including ICP-MS), scanning electron microscopy and X-Ray diffraction for analysis of mineralogical composition, and methods of equilibrium thermodynamics and mathematical statistics to reveal patterns of the distribution and accumulation of chemical elements and mineral inclusions in the oligotrophic peat bog cross section.

2. Study area and methodology

This research was carried out in the eastern part of one of the largest wetlands in the world, the Vasyugan Swamp, Western Siberia (Fig. 1). The study area is located on the watershed of two small rivers, the Klyuch River and the Gavrilovka River, which are parts of the Klyuch–Bakchar–Chaya–Ob and Gavrilovka–Iksa–Chaya–Ob river systems. The study area presents an association of oligotrophic pine-shrub-sphagnum bog (later referred to as "ryam", which is the local term for oligotrophic sphagnum-shrub bog with stunted (0.4–0.5 m) pines, which are present as ridges within wide expanses of patterned peatland complexes [Verhoeven et al., 2006; Walter and Breckle, 1989]) with a mesotrophic pine-shrub peatland on the border of a boggy forest (later referred to as the "mesotrophic margin") and with a hummock–hollow complex (HHC). The average depth of the peat deposit is 1.95 m, with a maximum depth of 5.3 m [Peat deposits of the Tomsk region ..., 1998]. The study area includes a raised bog, a transitional bog, a fen, and a mixed bog. The average peat decomposition degree is 22%, the ash content of the peat is 6%, and the peat moisture is 90.1%.

The Vasyugan Swamp is at the junction of two geological structures: the West Siberian Plate and the Altai–Sayan folded area. The area under study is situated within a plate that consists of a lower Precambrian and Paleozoic folded basement and an upper Meso-Cenozoic sedimentary cover with a 2.0–2.5 km thickness [Sidorenko et al., 1967; Orlov et al., 2000]. Paleogene-Neogene lacustrine-alluvial gray-colored sands, siltstones, and clays form the upper part of the sedimentary cover underlying the peat deposits.

Our methodology included the following: (1) sampling and chemical analysis of the peat, OMS (sediments with an organic substance content of 15–50% of the total dry weight [GOST 21123-85, 1985]), and mineral ground; (2) calculation of the hydraulic properties (i.e., hydraulic conductivity coefficient k_w of the organic sediments and the mineral ground, the filtration velocity v, and the dispersion coefficient), accounting for both molecular diffusion and hydrodynamic dispersion D; (3) calculation of the saturation indices (SI) for aqueous extracts relative to a number of minerals and organomineral compounds; and (4) statistical analysis of the data obtained.

The samples of the peat, OMS, and mineral ground were collected at the end of the low-water winter period in 2017 and 2018. On March 23, 2017, the peat was sampled within the ryam (56.961°N, 82.515°E; peat deposit depth: 2.50 m). On March 30, 2018, samples were taken along the profile located approximately perpendicularly to the bog margin (Fig. 1): (a) mineral ground in a boggy forest (56.919°N, 82.708°E) at a depth of 0.00–0.10 m, (b) a mesotrophic margin (56.923°N, 82.705°E) with a peat deposit depth of 1.6 m, (c) a ryam (56.928°N, 82.700°E) with a peat deposit depth of 3.75 m, and (d) a hummock (56.937°N, 82.698°E) and hollow (56.939°N, 82.698°E) complex with a peat deposit depth of 3.60 and 3.70 m, respectively. Samples from the peat deposit were collected each 25 cm using peat type drill according to the methodology given in [GOST 5396-77, 1988]. Drilling was carried out to the depth of the mineral ground inclusive. In March 2018, samples were collected selectively to control changes in the composition of the peat, OMS, mineral ground at the key depths targeted after research carried out in 2017. At these depths, according to previous studies, changes in the filtration properties and/or chemical composition was revealed. Samples were placed in double plastic bags. A label made of laminated paper was inserted between the bags. The samples were delivered to the laboratory for 5 h after sampling. Measured bog water level during the sampling was about 0.20–0.40 m from the bog surface that corresponds to the data of the other authors for surrounding areas [Ivanov, 1975, Kharanzhevskaya and Sinyutkina, 2017].

The samples were analyzed at the Basic Research Laboratory of Hydrogeochemistry of Tomsk Polytechnic University (TPU). The chemical composition of the aqueous and acid extracts from the peat, the OMS, and the mineral ground was analyzed. Air-dried samples were powdered in a porcelain vessel.

In order to analyze the aqueous extracts of the sediments, a 50–100 g sample was mixed with nonionized water at a ratio of 1: 10 for 3 min, followed by centrifugation for 5 min. In order to analyze the acid extracts of the sediments, a 0.2–0.5 g sample mixed with 3 mL of nitric acid was placed into a polyethylene test tube, which was then heated in a microwave for 10 min, avoiding its boiling.

The pH and electric conductivity (EC) values of the aqueous extracts were measured using potentiometry (Anion-7051, Infraspak-Analit, Russia); potassium permanganate demand (PPD) was measured by titrimetry with potassium permanganate solution; nitrite was measured using spectrophotometer KFK-2 (ZOMZ-Plus, Russia). In both of the aqueous and acid extracts, the concentrations of other chemical elements were measured using inductively coupled plasma mass spectrometry (NexION 300D; PerkinElmer, USA).

The ash content of the peat was calculated as the difference between the weights of dry peat, which has been dried up at 105°C, and the mineral part of the peat, which was obtained after combustion at 450°C for 12 h. The mineral inclusions of the peat and the mineralogical composition of the underlying ground and soil were analyzed at TPU using scanning electron microscopy (TESCAN VEGA3 SBU, TESCAN-UK Ltd., United Kingdom, with a prefix OXFORD X-Max 50, Oxford Instruments NanoAnalysis, United Kingdom). In order to analyze the mineral inclusions, we used dry samples. A thin layer of each sample was fixed to a double-sided 9 mm carbon tab placed on an aluminum stub, and then it was carbon-coated (15 nm) prior to the analysis. These prepared samples were studied using a scanning electron microscope with an accelerating voltage of 20 kV, a specimen current of 12 nA, and a spot diameter of approximately 2 μm [Rudmin et al., 2018]. The authors also used X-Ray diffraction for analysis of the peat, the OMS and the mineral ground mineralogical composition, which was performed at the Institute of Geology and Mineralogy of the Siberian Branch of the Russian Academy of Sciences using the automated diffractometer DRON-4 (CuKα emission, graphite monochromator). The bulk samples that are powdered nonoriented aggregates without separation into a fraction was analyzed. The diffraction patterns were scanned in the 2θ interval of 3–65°, with a step of 0.05° and a scan time of 4 s.

The characteristics of the hydraulic properties were defined as follows:

$$D = D_0 + \lambda * v, \tag{1}$$

$$v \approx k_w \cdot \left(1 + \frac{h_k + h_a}{L}\right), \tag{2}$$

$$k_{w\ (peat)} = k_{f\ (peat)} * ((w - w_0)/(w_1 - w_0))^{3.5}, \tag{3}$$

$$k_{f(peat)} = \frac{k_a \cdot k_1}{(z + k_2)^{k_3}}, \tag{4}$$

$$k_{w\ (ground)} = k_{f\ (ground)} * (w/w_s)^b, \tag{5}$$

where z is a coordinate on the vertical axis (the depth of the sediments); v is the filtration velocity; D is the dispersion coefficient; D_0 is the molecular diffusion coefficient; λ is the dispersivity factor; k_f and k_w are the coefficients of the filtration and hydraulic conductivity; L is the length of the infiltration zone; h_k is the height of the capillary rise; h_a is the runoff depth; w is the peat moisture at peat depth z; w_0 is the inherent moisture; w_s is the porosity; k_a is the factor of peat anisotropic properties; and k_1, k_2, k_3 are empirical factors, b is empirical coefficient taking into account the effect of soil moisture on the ratio of hydraulic conductivity and filtration [Gusev and Nasonova, 2010; Ivanov, 1975; Lishtvan et al., 1989; Savichev, 2015]. The hydraulic conductivity coefficient (k_w) of organic and mineral sediments, filtration velocity (v) and dispersion coefficient (D) account for both molecular diffusion and hydrodynamic dispersion.

Information regarding the parameters λ (0.0025), w_0 (0.53), w_1 (0.96), k_a (0.626), k_1 (82.659), k_2 (1), and k_3 (3.244) and the calculation methodology are given in [Savichev, 2015]. The parameters of formula (5) are accepted according to [Gusev and Nasonova, 2010]. The value of h_k is assumed to be equal to 0.5 m [Ivanov, 1975], and the value of h_a is equal to 0.485 m (the mean value at the Bakchar meteorological station).

The SI (see Eq. (6)) of the aqueous extracts with respect to the number of minerals and organomineral compounds are calculated on the basis of the thermodynamic constants using the Davis equation for determining the activity coefficients of dissolved ions:

$$SI = \lg(IAP) - \lg K_{sp}, \tag{6}$$

where IAP is the product of dissolved ions' activities and K_{sp} is an equilibrium constant. A negative SI value indicates potential undersaturation, whereas a positive one indicates saturation of solution with a mineral.

Statistical analysis (correlation and regression) of the data obtained were performed using MS Excel (Microsoft Corp., USA) at a significance level value of 5%. The correlation was assumed to be significant under the following condition:

$$|r| > 2 \cdot \frac{1 - r^2}{\sqrt{N - 1}}, \tag{7}$$

Table 1
Physicochemical characteristics of the aqueous and acid extracts from the peats, the OMS and the mineral ground in various intrabog ecosystems (March 2018).

Characteristics	Type of extracts	Hummock of HHC		Hollow of HHC	Ryam					Mesotrophic margin		Forest
		OMS 3.60–3.75 m	Mineral ground 3.90–4.00 m	Mineral ground 3.80–3.90 m	Peat 0.00–0.25 m	Peat 0.75–1.00 m	Peat 1.75–2.00 m	Peat 2.75–3.00 m	Mineral ground 4.25–4.50 m	OMS 1.60–1.75 m	Mineral ground 1.75–1.85 m	Soil 0.00–0.10 m
k_w, m/sec	–	$5.46\cdot10^{-7}$	$2.05\cdot10^{-9}$	$4.04\cdot10^{-10}$	$9.73\cdot10^{-3}$	$2.30\cdot10^{-5}$	$2.06\cdot10^{-7}$	$8.77\cdot10^{-8}$	$2.89\cdot10^{-10}$	$6.79\cdot10^{-9}$	$2.05\cdot10^{-9}$	$5.90\cdot10^{-2}$
pH	aqueous	7.97	8.40	8.40	4.24	4.42	5.39	5.77	8.26	6.86	7.84	7.20
EC, μS/cm	water	198.4	141.1	163.7	57.2	58.3	42.2	57.8	185.4	74.5	121.8	184.4
mg/kg												
Ca	aqueous	50280.9	40884.5	36529.7	2002.7	3217.5	22415.8	23997.8	34900.0	10113.2	33233.5	21898.3
	acid	34389.0	51568.6	38118.1	1716.5	1931.3	18759.6	23922.1	32857.4	9709.0	12143.5	9172.3
Mg	aqueous	2999.0	3006.6	3904.9	590.5	368.6	933.3	1050.7	2448.3	3827.6	4501.4	2282.3
	acid	5003.5	5952.3	7693.0	534.6	427.9	848.5	1156.0	4861.2	5933.6	7727.3	1198.0
Na	aqueous	73.6	73.4	88.4	88.4	42.8	30.6	23.5	66.7	57.6	79.5	223.6
	acid	101.9	136.2	140.3	46.2	36.2	23.9	20.1	111.4	88.9	112.1	133.3
K	aqueous	564.2	703.2	930.7	490.8	134.8	102.9	70.6	1113.2	577.9	706.4	2023.5
	acid	1207.3	1115.1	1634.1	123.9	93.2	107.0	65.3	2260.4	1477.7	1626.7	1008.1
S	aqueous	195.0	339.3	426.6	1003.5	1060.4	2637.3	3289.6	159.4	444.7	525.2	5702.1
	acid	230.8	733.3	282.4	1157.6	938.5	2247.0	3141.8	400.6	556.8	463.9	2063.0
Si	aqueous	1100.3	1131.0	1310.7	176.2	121.4	197.4	149.5	1099.6	898.8	987.4	606.4
	acid	1556.9	1864.8	1816.3	398.7	179.1	103.1	98.7	3139.4	1765.4	3140.8	1024.2
P	aqueous	337.8	298.0	362.4	400.0	254.8	424.8	400.7	334.0	287.5	212.3	2404.9
	acid	474.0	418.9	421.2	235.0	215.2	418.3	421.5	425.9	382.9	412.4	1302.1
Al	aqueous	6627.1	6347.8	6306.7	706.1	548.9	1275.6	1009.0	4807.8	8263.8	5792.2	2693.3
	acid	10788.6	9135.5	11496.2	699.5	418.1	1181.4	803.3	8578.8	13952.9	14649.5	1443.1
Fe	aqueous	8062.6	9013.8	13017.8	992.5	621.2	2566.6	2670.2	14262.7	8707.4	7265.7	15212.0
	acid	13431.9	13499.3	24088.1	873.8	611.8	2242.5	2882.2	19493.9	14839.0	17350.3	7135.6
Ti	aqueous	6.73	6.92	8.75	11.96	9.28	21.67	13.32	6.49	4.67	4.79	29.40
	acid	17.46	18.78	22.50	13.73	8.60	22.04	16.07	25.27	14.71	24.89	17.44
Pb	aqueous	9.92	10.42	12.23	9.96	0.66	0.64	0.66	11.89	11.85	9.89	24.19
	acid	12.74	12.37	11.92	6.62	2.60	0.75	0.48	13.22	13.34	13.97	11.17
Ba	aqueous	138.1	139.9	142.7	12.2	20.6	42.3	33.8	118.5	151.6	150.4	89.9
	acid	146.4	147.3	142.3	9.1	7.3	17.9	35.3	121.6	142.3	171.8	41.2
La	aqueous	11.003	11.335	12.999	0.369	0.239	0.508	0.454	11.724	13.904	11.890	3.374
	acid	15.172	13.878	14.510	0.370	0.198	0.646	0.430	14.637	16.290	18.976	1.760
Ce	aqueous	25.441	25.961	29.521	0.727	0.527	1.144	0.980	27.796	31.350	29.094	6.776
	acid	35.732	29.284	32.395	0.779	0.408	1.426	0.908	34.150	37.467	43.104	3.162
Sm	aqueous	2.743	2.652	2.949	0.075	0.050	0.127	0.095	2.582	3.063	2.687	0.590
	acid	3.289	3.126	3.146	0.077	0.044	0.141	0.088	3.390	3.462	4.161	0.320
U	aqueous	0.967	0.735	0.712	0.044	0.038	0.111	1.253	0.395	0.604	0.641	0.313
	acid	1.173	1.005	1.219	0.047	0.028	0.141	1.826	0.585	0.829	1.121	0.154
Sn	aqueous	0.005	0.008	0.010	0.191	0.065	0.056	0.043	0.011	0.015	0.042	0.668
	acid	0.027	0.019	0.013	0.084	0.035	0.034	0.032	0.020	0.034	0.014	0.163
Ag	aqueous	0.046	0.076	0.070	0.338	0.059	0.052	0.043	0.046	0.048	0.045	0.141
	acid	0.021	0.028	0.026	0.034	0.046	0.010	0.006	0.032	0.045	0.072	0.042

Notes: k_w – coefficient of hydraulic conductivity.
EC – electrical conductivity.

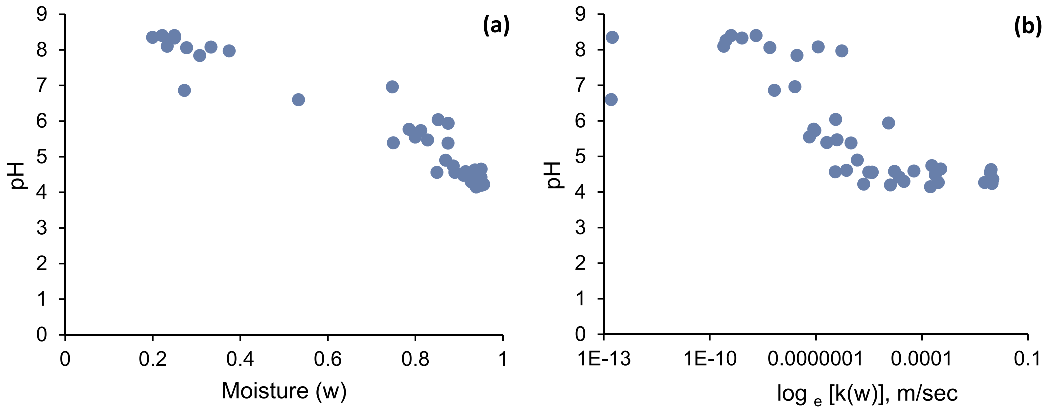

Fig. 2. Relationship between the pH of the aqueous extracts and moisture (a) and the coefficient of hydraulic conductivity (b) of the peats, the OMS, and the mineral ground.
Legend: k(w) is the coefficient of hydraulic conductivity.

where r is the correlation factor and N is the number of samples.

Regression dependence was taken to be significant, provided that regression coefficients modulo two times exceed the error of their calculation, with the correlation ratio $R^2 > 0.36$.

3. Results and discussion

The mineralogical composition of the OMS and mineral ground includes quartz (whose content varies from 35.6 to 49.8%, with an average of 42.4%), plagioclase (whose content varies from 8.1 to 14.1%, with an average of 11.8%), potassium feldspar (whose content varies from 4.6 to 15.3%, with an average of 9.3%), illite and chlorite (whose average values are 5.1 and 9.0%, respectively), and calcite (Appendix A). At the mesotrophic margin, the presence of calcite is noted; in other intrabog ecosystems, the average content of calcite is 8.7% [Rudmin et al., 2018].

Mineral inclusions in peats include Fe hydroxides (oxides), REE-rich phosphates, pyrite, galena, sphalerite, chalcopyrite, stibnite, barite, calcite, dolomite, quartz, ilmenite, and a number of other minerals [Rudmin et al., 2018].

In general, the pH and specific electrical conductivity values in the aqueous extracts and the concentrations of a wide range of chemical elements (i.e., Li, Na, Mg, Si, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Ge, As, Se, Rb, Sr, Y, Zr, Pd, Cd, Cs, Nd, Sm, Gd, Dy, Ho, Hf, Pb, Bi, and Th) in the acid extracts decrease in the following order: mineral ground → OMS → peat (Table 1, Table B.1). However, an inverse relationship (i.e., the concentrations increase in the following direction: mineral ground → OMS → peat) exists for B, Ag, Sn, Sb, and W. It should be noted that the highest concentrations in the peat are established for S, Cl, Zn, Br, Mo, and Ta. The highest concentrations in the OMS were found to be for Be, Al, P, Ti, Ga, Nb, In, Ba, La, Ce, Pr, Eu, Tb, Er, Tm, Yb, Lu, Tl, and U [Savichev et al., 2018].

The concentrations of the majority of the elements in the aqueous extracts are interconnected with the ones in the acid extracts, except for Ti, Zn, Br, Nb, Ag, Te, Cs, and Ta. The correlation factors change from 0.53 to 0.58 for K, Tl and Hf to 0.98–0.99 for Li, Sc, Y, Mo, Cd, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, W, and Th (Appendix C).

In accordance with the changes in the concentrations of the acid extracts with the depth of the peat deposit, we subdivided the chemical elements into three groups. The first group includes elements with a rather steady increase in their concentrations from the upper layer of the peat deposit to the bottom mineral ground and/or a strongly pronounced maximum in the mineral ground (e.g., Al, Ca, Fe, Mg, Cr, Mn, Ce, La, Sm, and Zr). The second group includes elements with a well-pronounced maximum in the upper layer peat deposit and the bottom part of the organic and mineral sediments (Na, K, Ti, Pb, Sb, Sn, and Si). The third group includes elements with all other types of distributions (e.g., S, P, and U) (Table 1, Table B.2).

In addition, the characteristic features of the changes of chemical compositions in the aqueous and acid extracts from the peat within different ecosystems should also be noted. One of these features is the increase of the electrical conductivity of the aqueous extracts and the increase of the concentrations of some chemical elements in the acid extracts (e.g., Na and Cl) with a decrease in the coefficients of hydraulic conductivity k_w and/or standard uncertainty of their distribution δ_A ($\delta_A \approx \frac{\sigma}{\sqrt{N}}$, where σ is the standard deviation and N is the number of samples). The pH values of the aqueous extracts increase with the decrease of peat moisture w (Fig. 2). Another important characteristic is the direct relationship between the pH values of the aqueous extracts and the concentrations of some chemical elements (Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, etc.) in the acid extracts (Tables 1 and 2).

The highest content of CO_2 is found in the upper layer of the peat deposit (Table B.1), where an initial accumulation of organic debris and its decomposition in the presence of oxygen occur. The highest concentration of NO_2^- in the aqueous extract at a depth of 1.25–1.75 m (Fig. 3), as well as the increase of the content of S in the acid extracts (Table B.2), denotes sharply limited oxygen access at this depth.

Aqueous extracts are generally oversaturated with quartz throughout the peat deposit depth and undersaturated with primary aluminosilicates; thus, water can dissolve aluminosilicates if there is available matter. These aforementioned conditions are typical not only for the underlying mineral ground but also for the active layer of the peat deposit, which receives atmospheric aerosols and decomposed products of bog vegetation. This fact is confirmed by the increase of the aqueous extract saturation of mica and plagioclases at a depth of 0.00–0.25 m (Table D.1), as well as the increase of the Si concentration in the acid extracts (Table B.2) at the bottom part of the active horizon of the peat (at a depth of 0.25–0.50 m).

The nature and degree of interaction among the concentrations of chemical elements in the aqueous extracts and mineral particles demonstrate the strong influence of organic matter both directly, owing to the formation of poorly soluble compounds of humic acids with metals [Ephraim and Allard, 1997; Kraynov et al., 2004], and indirectly, through the release of CO_2, which is associated with the shift of the carbonate equilibrium toward the precipitation of calcite. Furthermore, decomposition of organic matter by bacteria is accompanied by the formation of reducing conditions in the peat deposit [Savichev et al., 2019]. Such conditions lead to the formation of sulfide minerals; in particular, pyrite, sphalerite, galena, and barite inclusions are noted at different depths of the inert horizon of the peat deposit, as confirmed both by our own data [Rudmin et al., 2018] and by the researches of other authors [López-Buendía et al., 2007].

Studying the changes of the chemical composition of the extracts, we

Table 2
Average physicochemical characteristics of the acid and aqueous extracts from the peats in various intrabog ecosystems.

Characteristic	Hummock of HHC		Hollow of HHC		Ryam		Mesotrophic margin	
	A	δ_A	A	δ_A	A	δ_A	A	δ_A
N	7		5		16		4	
k_w, m/sec	$8.81 \cdot 10^{-4}$	$8.50 \cdot 10^{-4}$	$2.11 \cdot 10^{-3}$	$2.03 \cdot 10^{-3}$	$1.22 \cdot 10^{-3}$	$8.02 \cdot 10^{-4}$	$2.21 \cdot 10^{-3}$	$2.14 \cdot 10^{-3}$
in aqueous extracts								
pH	4.85	0.40	4.42	0.07	4.96	0.14	5.46	0.49
EC, μS/cm	98.8	38.0	63.1	8.1	62.8	4.5	40.7	6.6
in acid extracts, mg/kg								
Na	63.2	9.2	39.1	4.7	51.2	7.7	47.2	13.6
Mg	1107.6	559.2	484.9	12.0	624.2	73.6	2089.2	1086.7
Al	2611.5	1499.3	784.0	129.5	845.5	159.1	4132.0	2950.2
Si	492.9	137.9	246.2	76.3	361.1	74.8	874.5	729.9
P	293.2	53.2	218.3	9.5	354.8	33.1	621.3	36.8
S	1209.6	196.3	1223.6	176.6	1964.6	178.8	1908.5	175.8
Cl	437.0	71.0	446.0	35.1	1165.8	209.4	241.9	42.8
K	266.5	157.1	64.8	8.5	124.9	36.5	441.5	205.4
Ca	8453.4	4161.6	2586.4	240.6	10893.0	2478.4	11592.6	2896.6
Sc	0.753	0.479	0.181	0.046	0.235	0.032	0.783	0.645
Ti	15.386	1.546	15.215	3.139	15.091	1.554	16.688	2.783
V	6.939	3.794	1.909	0.487	2.794	0.892	9.559	5.924
Cr	5.954	3.294	1.949	0.484	2.096	0.356	7.810	5.283
Mn	76.767	27.785	45.017	8.828	93.317	15.464	156.330	12.306
Fe	3314.0	2007.5	591.2	152.0	2301.3	512.0	5381.7	2667.1
Co	2.351	1.551	0.374	0.042	1.509	0.403	3.778	2.017
Ni	7.144	4.535	1.235	0.192	3.234	1.096	9.689	6.617
Cu	6.361	2.914	1.788	0.462	3.468	0.893	7.823	4.824
Zn	77.697	35.214	46.432	18.090	30.396	7.167	30.369	6.114
Ga	1.042	0.648	0.263	0.074	0.296	0.060	1.269	0.906
Ge	0.043	0.019	0.018	0.004	0.020	0.003	0.045	0.016
As	1.440	0.394	1.095	0.601	2.296	0.426	4.491	0.505
Se	0.477	0.163	0.303	0.047	0.518	0.064	0.517	0.143
Br	18.427	2.387	26.355	1.687	32.797	5.738	17.265	4.493
Rb	1.509	0.919	0.255	0.028	0.432	0.101	2.073	1.142
Sr	49.115	23.681	16.663	2.133	71.243	16.085	110.874	36.993
Y	2.020	1.420	0.307	0.056	0.513	0.198	2.760	2.169
Zr	2.455	1.473	0.502	0.212	0.676	0.234	3.131	2.323
Nb	0.115	0.039	0.058	0.017	0.068	0.009	0.160	0.085
Mo	0.294	0.068	0.268	0.020	1.046	0.147	3.246	0.907
Pd	0.015	0.009	0.003	0.001	0.003	0.001	0.016	0.013
Ag	0.032	0.008	0.063	0.022	0.169	0.137	0.015	0.004
Cd	0.132	0.029	0.116	0.041	0.090	0.018	0.167	0.036
In	0.005	0.002	0.003	0.002	0.002	0.001	0.005	0.003
Sn	0.060	0.015	0.085	0.056	0.074	0.026	0.105	0.032
Sb	0.161	0.030	0.147	0.068	0.112	0.023	0.161	0.064
Te	0.009	0.002	0.011	0.003	0.008	0.002	0.012	0.004
Cs	0.142	0.075	0.044	0.017	0.066	0.010	0.187	0.075
Ba	40.082	19.953	13.286	1.685	26.502	5.169	54.166	25.166
La	2.612	1.875	0.399	0.070	0.643	0.239	3.603	2.890
Ce	5.988	4.366	0.841	0.153	1.343	0.508	8.137	6.499
Pr	0.671	0.485	0.097	0.020	0.158	0.060	0.911	0.728
Nd	2.670	1.927	0.387	0.076	0.623	0.241	3.662	2.931
Sm	0.575	0.417	0.091	0.020	0.132	0.052	0.778	0.622
Eu	0.131	0.092	0.020	0.004	0.033	0.012	0.178	0.138
Gd	0.593	0.427	0.088	0.016	0.141	0.056	0.834	0.673
Tb	0.081	0.058	0.013	0.002	0.019	0.008	0.114	0.091
Dy	0.427	0.308	0.066	0.013	0.104	0.041	0.588	0.467
Ho	0.077	0.055	0.012	0.002	0.019	0.007	0.104	0.082
Er	0.207	0.150	0.031	0.007	0.049	0.020	0.284	0.228
Tm	0.029	0.021	0.004	0.001	0.007	0.003	0.039	0.031
Yb	0.176	0.128	0.025	0.005	0.040	0.017	0.250	0.201
Lu	0.025	0.018	0.004	0.001	0.006	0.002	0.034	0.027
Hf	0.103	0.059	0.023	0.010	0.019	0.005	0.118	0.079
Ta	0.029	0.010	0.012	0.003	0.016	0.003	0.018	0.004
W	0.039	0.011	0.031	0.014	0.030	0.007	0.035	0.006
Tl	0.021	0.011	0.006	0.001	0.013	0.003	0.037	0.014
Pb	4.170	1.697	3.408	2.110	2.928	1.076	5.706	1.943
Bi	0.053	0.018	0.037	0.023	0.027	0.007	0.064	0.021
Th	0.647	0.558	0.025	0.013	0.116	0.042	0.624	0.604
U	1.613	1.249	0.055	0.003	0.437	0.195	1.403	1.318

Notes: N – number of samples.
A – mean value; δ_A – standard uncertainty.
k_w – coefficient of hydraulic conductivity.
EC – electrical conductivity.

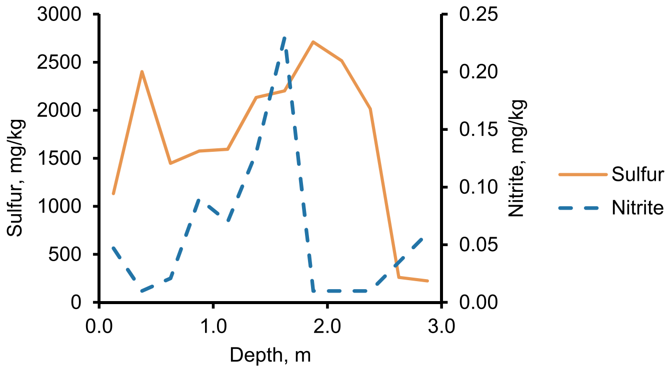

Fig. 3. Changes of the nitrite content in the aqueous extracts and the sulfur content in the acid extracts from the peats, the OMS and the mineral ground within the ryam with depth (March 2017).

paid special attention to the concentrations of Ca, Fe, Al, and Ce within the ryam. This was done because the precipitation of Ca from solution as calcite indicates a considerable increase in the pH and leads to the precipitation of the hydroxides of some other metals. Similarly, the precipitation of poorly soluble compounds of Ca and humic acids provokes the precipitation of other chemical elements. The accumulation of Fe in bog ecosystems prevails over its removal beyond the ecosystem, which makes Fe a characteristic component of bog water and peat chemical composition. Fe precipitates from the aquatic environment both within oxidizing (e.g., hydroxide barrier) and within reducing (e.g., sulfide barrier) geochemical barriers. At the same time, sorption of Fe occurs on the surface of colloidal and suspended Fe particles. As for Al, most of the minerals in peats and in the mineral ground of dry land and the main part of bogs contain Al as part of their structure. Accordingly, the fluctuations of the Al content in peats and bog water obviously reflect the origin of the chemical composition of a bog ecosystem. Finally, Ce, as well as a number of other REEs, is found in the extracts from the peat and the mineral ground. The mineral inclusions in the peat were defined as monazite [Rudmin et al., 2018]. The nearest ore occurrence with monazite is the Tuganskoye zircon-ilmenite ore deposit [Rikhvanov et al., 2001], which is located more than 100 km to the east of the study area. The flow of particles from the Tuganskoye zircon-ilmenite ore deposit to the Vasyugan Swamp seems to be impossible over such a distance. Moreover, these objects are separated by two large rivers (the Ob River and the Tom River). This suggests that the concentrations of Ca, Fe, and Al in the aqueous and acid extracts reflect the general mineralogical and geochemical characteristics of bog ecosystems, whereas the concentration of Ce determines the specifics of the accumulation of trace elements.

The analysis of the data obtained showed that the highest Ca content within the ryam is noted in the acid extracts from the OMS (Table B.2), where the calcite content can reach levels up to 10.1% [Rudmin et al., 2018] and the SI of calcite and compounds with humic acids in the aqueous extract reach the maximum values (Table D.1). The highest Fe content within the ryam is found in the acid extracts from the bottom layer of the peat (at a depth of 2.25–2.50 m) and from the mineral ground (2.75–3.00 m; Table B.2), where illite, ilmenite, and a number of other Fe-containing minerals are present in addition to the Fe hydroxides (oxides) [Rudmin et al., 2018]. The highest content of Al within the ryam is found in the acid extracts from the OMS and the mineral ground. A high Al content is also found in the upper active layer of the peat deposit comparable to the values from the bottom layer of the peat (Table B.2). Furthermore, the content of illite sharply increases (up to 6.5% [Rudmin et al., 2018]) simultaneously with the Al content. This likely indicates the intensification of the formation of Al-containing

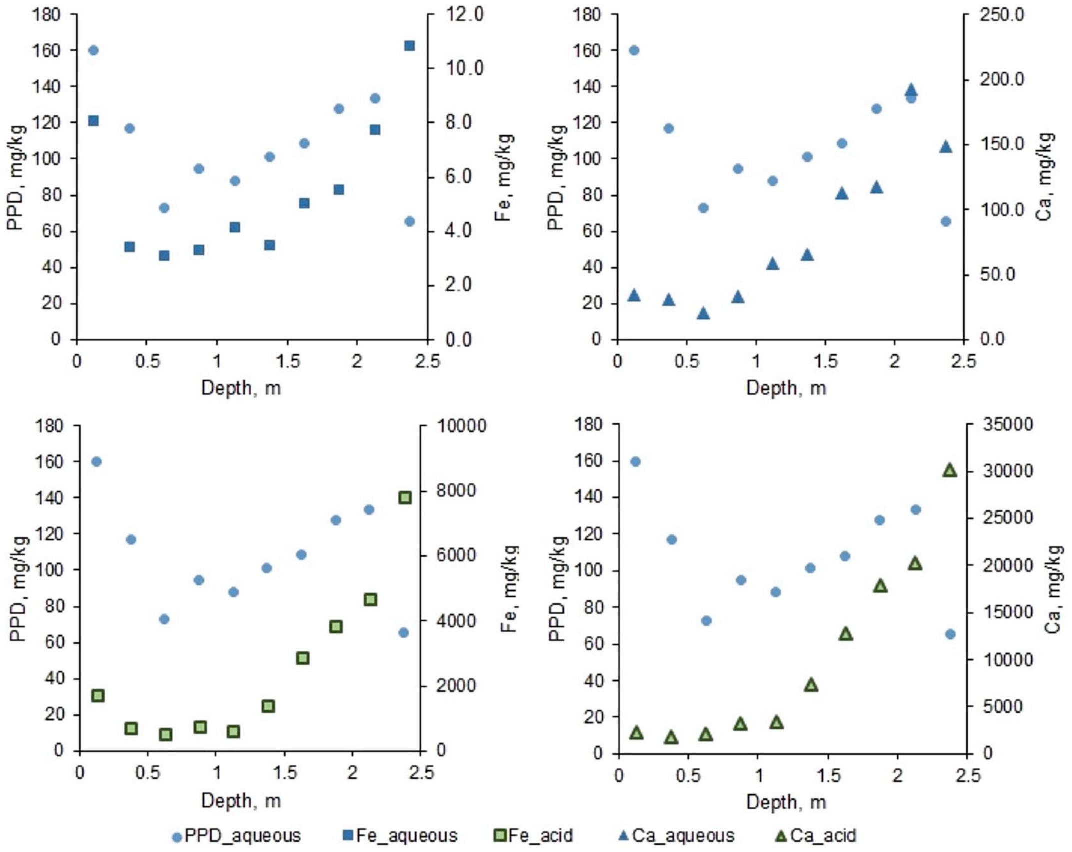

Fig. 4. Changes in the concentrations of Ca and Fe in the aqueous and acid extracts and potassium permanganate demand (PPD) of the aqueous extracts from the peat within the ryam with depth (March 2017).

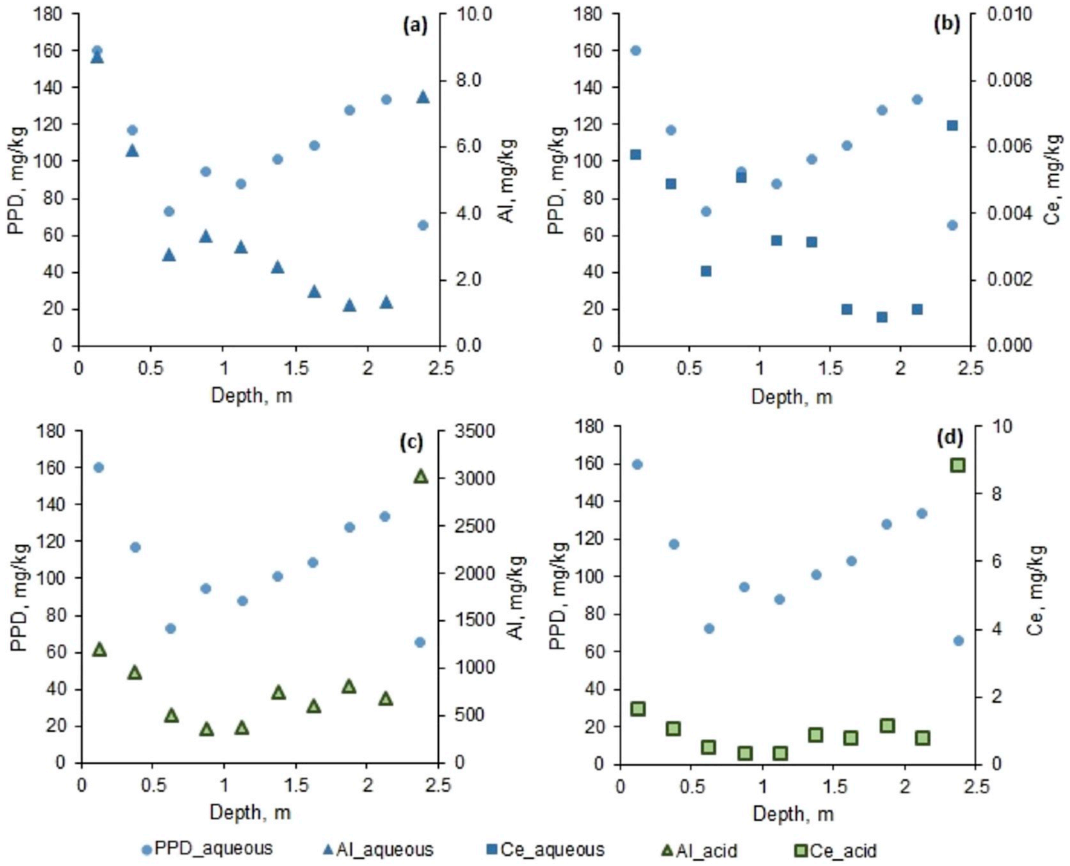

Fig. 5. Changes in the concentrations of Al and Ce in the aqueous and acid extracts and potassium permanganate demand (PPD) of the aqueous extracts from the peat within the ryam with depth (March 2017).

colloids. The highest Ce content within the ryam is noted in the acid extracts from the OMS and the mineral ground (Table B.2) probably owing to the prevalence of sorption and coprecipitation of Ce on Fe and phosphorus compounds.

The following relationship was found for the concentrations of the elements in the aqueous and acid extracts. The concentrations of Ca and Fe in the aqueous and acid extracts from the peat increase with the value of potassium permanganate demand (PPD) of the aqueous extracts (Fig. 4), as well as the concentrations of Al and Ce in the acid extracts (Fig. 5 c, d), whereas the content of Al and Ce in the aqueous extracts decreases in the samples with a higher PPD (Fig. 5 a, b). An inverse relationship was noted for the concentrations of Fe and Ce in both the acid and aqueous extracts and the content of P in the aqueous extracts. The concentration of S analyzed in the acid extracts is in direct proportion with the content of Fe analyzed in the aqueous extracts (Appendix B).

These aforementioned observations show that the noticeable effect of advective transfer on the distribution of chemical elements is manifested mainly at depths up to 1.00–1.25 m, below which reducing conditions likely prevail according to the sharp increase in the total content of sulfur in the acid extracts [Savichev et al., 2019], as proven by previous research [Inisheva et al., 2003; Savicheva and Inisheva, 2000]. Fluctuations in the water level in the bog are usually within the limits of the depth of 0.20–0.40 m, which allows approximating the boundaries of the complex redox, sulfide, and sorption (hydroxide) barrier in the peat deposit at depths of 0.40–1.25 m. This complex geochemical barrier affects the content of Fe and S in the acid extracts, which is in correspondence with data reported by [Damman, 1978].

Another barrier, which is complex geochemical barrier, combines the features of alkaline barrier of carbonate and hydrolytic type and sorption barrier (sorption of hydroxides, clay minerals, and carbonates). It occurs at the bottom part of the peat deposit and corresponds to a relatively sharp decrease of the filtration properties of the peat at a depth of 2.25–2.50 m along with a sharp increase in the pH values. Thus, between the peat deposit and the mineral ground within the main part of the bog, not only advective but also diffusion transport of substances noticeably decreases. In this case, the dissolution–precipitation and sorption–desorption processes affect the concentrations of the chemical

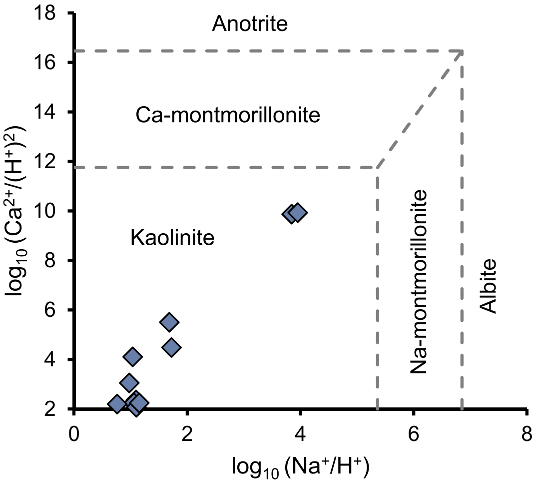

Fig. 6. Diagram of the HCl–H_2O–Al_2O_3–CO_2–CaO–SiO_2–Na_2O system with the data of the chemical composition of the aqueous extracts from the peat, the OMS, and the mineral ground (at 25°C, $\log_{10}(H_4SiO_4) = -3.5$, $P_{CO2} = 101.5$ Pa).

Table 3
Statistically significant correlation factors between the contents of minerals and chemical elements in the aqueous and acid extracts (March 2018).

Chemical element	Smectite		Kaolinite		Chlorite	
	Aqueous extracts	Acid extracts	Aqueous extracts	Acid extracts	Aqueous extracts	Acid extracts
Na	–	0.67	–	0.66	–	–
Mg	0.90	0.95	0.59	0.74	0.61	0.65
Al	0.97	0.97	0.50	0.57	0.79	0.75
Si	0.89	0.75	0.72	0.76	0.69	0.73
P	–	–	–	–	–	–
S	−0.68	−0.76	–	−0.51	−0.60	−0.62
Cl	−0.69	–	−0.49	–	−0.61	–
K	–	0.76	–	0.67	–	0.68
Ca	0.57	0.52	0.57	0.65	0.52	–
Ti	−0.71	–	–	0.67	−0.64	–
Cr	0.97	0.98	0.57	0.66	0.79	0.77
Fe	–	0.85	0.49	0.74	–	0.58
Ag	–	–	–	–	–	–
Sn	−0.49	−0.54	–	–	–	–
Ba	0.93	0.96	0.61	0.67	0.74	0.79
La	0.96	0.96	0.65	0.66	0.78	0.81
Ce	0.96	0.96	0.66	0.63	0.79	0.82
Sm	0.97	0.95	0.64	0.68	0.79	0.82
Pb	–	0.81	–	0.56	–	0.72
U	–	0.51	–	–	–	–

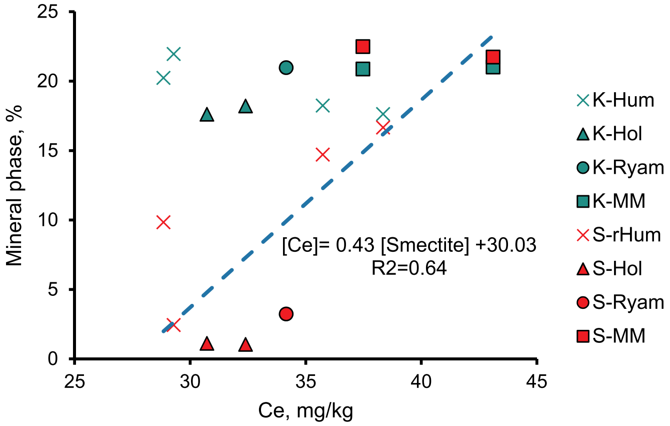

Fig. 7. Concentration of Ce in the acid extracts versus the content of kaolinite and smectite in a clay fraction.
Legend: The content of kaolinite (K) and smectite (S) within the different parts of the bog: the hummock of the hummock-hollow complex – K-Hum and S-Hum; the hollow of the hummock-hollow complex – K-Hol and S-Hol; the ryam – K-Ryam and S-Ryam; the mesotrophic margin – K-MM and S-MM.

elements in the acid and aqueous extracts. Consequently, both the complex geochemical and the mechanical barriers are at the bottom part of the peat deposit [Savichev et al., 2019].

The mechanical barrier exists because of a decrease in the filtration coefficients of the bottom mineral ground and the formation of modern secondary minerals at the bottom part of the peat deposit. The direct relationship between the ratio D/v and SI confirms this statement. The correlation factor between D/v and SI of carbonates, quartz, and a number of aluminosilicates varies from 0.71 to 0.86 (Table D.2). Along with the precipitation of calcite from an aqueous solution, the formation of kaolinite and the transformation of minerals of the smectite group that are present in the bottom mineral ground, dry lands, and atmospheric aerosols play an important role in the formation of the mechanical barrier [Timofeyev and Bogolyubova, 1999]. The saturation of the aqueous extracts to secondary aluminosilicates (Fig. 6) confirms the capability of this process.

Montmorillonite and other minerals of the smectite group have a higher sorption capacity compared to minerals of the kaolinite group. This is why minerals of the smectite group have stronger relationships with a set of elements (Table 3). Therefore, the transformation of the minerals of the smectite group in the intrabog ecosystem provides the increase of the concentrations of chemical elements (Ca, Na, etc.) that accumulated at the boundary between the organic and mineral sediments. The distribution of Ce in the OMS and the underlying loam (mineral ground) within the different intrabog ecosystems confirms this statement (Fig. 7).

4. Conclusions

The functioning of two complex geochemical barriers that are connected with rather sharp changes in the filtration properties of sediments conforms to the distribution of the chemical elements in the aqueous and acid extracts from the peat, the OMS, and the mineral ground. The upper complex geochemical barrier of redox, sulfide, and sorption type (sorption of hydroxides) is located approximately at a depth of 0.40–1.25 m and corresponds to the substantial decrease of oxygen concentration and the rate of advective flow of substances to the depth of the peat deposit. The bottom barrier is the combination of complex geochemical barrier that joins the features of alkaline (carbonate and hydrolytic) barrier and sorption barrier (sorption of hydroxides, clays, and carbonates) with mechanical barrier. It is located at the bottom layer of the peat deposit (at a depth of 2.25–2.50 m) and is characterized by additional deterioration of the filtration properties of the sediments and of the diffusion flow.

As a result, the upper barrier provokes the formation of Fe oxides and REE-rich phosphates in the peat deposit. Among others, there is local precipitation of clay minerals and sulfides of Fe and some other metals (e.g., barite) within the geochemical gradient between areas with oxidizing and reducing (oxygen-free) conditions. Owing to the bottom barrier, the intensity of formation and/or accumulation of clay minerals increases. This results in the accumulation of the substances entering (though in a small amount) both from above with an atmospheric aerosol and from underlying horizons at the stage of the existence of eutrophic bogs. Besides, autotrophic sulfate reduction and methane formation in the absence of dissolved oxygen in free bog water lead to an increase in the pH values and the precipitation of calcite and hydroxides of some metals from solution.

The abovementioned processes proceed in rather thin layers. This limits the opportunity to use generalized characteristics of peat bogs (e.g., the average values of chemical element concentrations, pH, ash content, etc.) for detailed evaluations of the mineral and geochemical conditions in peat deposits. Besides, the barriers' borders are variable because of both the changes in the water exchange in the peat bog and its evolution. In particular, the borders of the barrier in the upper horizon change as a result of the long-term fluctuations of the atmospheric precipitation amount, due to the growth or degradation of a peat deposit, or in response to a peat type change as a result of the transformation of organic substances. Taking into account all of this, the accumulation of substances in the upper layer of the peat deposit (upper geochemical barrier) is always less significant compared to the accumulation in the bottom barrier. The role of the bottom barrier increases during bog evolution. Therefore, the probability of detecting high concentrations of various substances is very high in the bottom part of the peat deposit, the OMS, and the upper part of the underlying mineral ground.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2019.104519.

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