



## Modes of occurrence of rare earth elements in peat from Western Siberia

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### ABSTRACT

Selective leaching of rare earth elements (REE) from peat samples from Western Siberia indicates unanticipated modes of occurrence. It has been determined that from 40 to 80% of the total REE in the peat is accounted for in the hydrolyzable and water-soluble substances, 10–30% of the REE is concentrated in humic acids. Minerals in peat play a minor role in the accumulation of REE. In general, no > 25% of REE is accounted for in mineral association. Among the mineral forms of REE in peat, clastogenic phosphates (monazite, xenotime, crandallite group) and zircon are the dominant hosts. REE are distributed in different phases of the peat: the water-soluble and hydrolyzable substances are relatively enriched in light REE, and humic substances are enriched in heavy REE.

### 1. Introduction

The modes of occurrence of chemical elements in peat are important indicators of deposit formation and the nature of low temperature geochemical processes. They are also useful for determining the accumulation conditions of trace elements in coals resulting from the peats.

Unlike coals, the modes of occurrence of rare earth elements (REE) in peat have not been studied extensively. Existing information is rare and is generally related to the upper part of peat deposits, which is called the peat-forming or active layer. In this horizon active processes of the organic matter transformation occur, including bacterial activity. Oxygen is present in sufficient quantity and therefore the environment is oxidative, unlike the whole peat deposit (Rakovsky and Pigulevskaya, 1978; Shotyk, 1992; Savichev, 2015; Savichev et al., 2016).

In contrast to the peats, the modes of occurrence of REE have been studied in detail in soils of different composition, including waterlogged soils (Mihajlovic et al., 2014; Davranche et al., 2016). The results of the soil research are often applied to peat as the soils can be considered as peat analogues. However, the physical-chemical properties of the lower peat-forming layers differ considerably from soils of any composition, including waterlogged soils (wetland and paddy soils). The main differences between soils and the lower peat layers are the anaerobic regimes with low oxygen activity, high concentrations of organic substances and low microbial activity in the peatlands. Unlike soils, metals in peatlands are present in the reduced state, often in the native mode (Smieja-Król et al., 2010). In soils, individual REE can oxidize to the

4+ valence state and form Ce/Ce\* anomalies (Cao et al., 2001; Compton et al., 2003; Davranche et al., 2016), where Ce\* is a theoretical mean Ce content, calculated from the La and Pr (Vodyanitskii, 2012). Within the oxidizing environment in soils, Ce (III) is oxidized to Ce (IV) and is easily hydrolyzed when co-depositing with Fe hydroxides. In the upper part of podzolic soils a negative Ce/Ce\* anomaly is formed which is caused by Ce (IV) loss of dissolved complexes with OH<sup>-</sup> и CO<sub>3</sub><sup>2-</sup>. Below, in the podzolic horizon a positive Ce/Ce\* anomaly is formed, which is associated with Ce sorption on Fe hydroxides. In peat deposits, even in the upper peat-forming layer such anomalies have not been found. The Ce/Ce\* anomalies, found in peat, are not caused by REE fractionation in a peat bog, but by the composition features of the mineral matter entering into the bog. The majority of the mineral matter enters from the adjacent dry lands. Usually, this is the mineral soil immediately outside of the peat deposit. Therefore, the ratio of individual REE in peat will correspond to the composition of the initial dry land soils.

The research on REE in peat had long been limited by their low concentrations and the absence of analytical methods with detection limits in the range of 0.1–0.01 ppm. The problem of studying their modes of occurrence in peat is not only due to the difficulty in recognizing the different modes of occurrence, but also to the necessity of determining the ratio of the different REE forms. There is limited information on the REE modes of occurrence in peat (Arbutov and Ershov, 2007). In the research of Smieja-Król et al. (2010) the authors showed that in the upper part of the peat deposit some of the REE

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phosphates were present together with other lithogenic minerals. However, in an ombrotrophic bog in Germany a fast dissolution of the fluorapatite was observed in the upper zone of the peatland, indicating its weak stability in the peat-forming process (Le Roux et al., 2006). The decomposition of other minerals was also observed in the peat-forming layer (Bennett et al., 1991; Le Roux et al., 2006; Smieja-Król et al., 2010). Therefore, an essential part of the REE passes into mobile forms with the formation of organic complexes (Davranche et al., 2011) or into autigenic minerals.

This work represents an attempt to provide general data on the modes of occurrence of REE for different peat deposits of Western Siberia. Considering that the upland (oligotrophic) peatlands prevail among these deposits, an assessment of the dissolution of REE-containing minerals during the peat-forming process can be provided.

### 1.1. Description of sampling sites

Modes of occurrence of REE were studied in eight peat deposits of Western Siberia.

REE occur in peats which have formed in different geological-geochemical environments. Thus, we studied peat deposits from typical upland peat (the deposits Poludenovskoe, Vasyuganskoe-22, Uginskoe, Aigarovo, and Kolpashevskoe), lowland peat (Gusevskoe), and transitional peat (Vasyuganskoe-5, Berezovaya Griva) (Fig. 1). In Western Siberia the peat deposits are formed in such conditions that in a deposit with one prevailing peat type other peat types can also be found. Numerous publications give detailed descriptions of the studied deposits and conditions of their formation (For example: Ivanova and Novikova, 1976; Inisheva et al., 1995; etc.).

The peat bearing Western-Siberian basin is quite large and is comparable to the largest coal basin in the world – the Tungusky Basin. The source area of terrigenous matter for the peat accumulation in the basin is geochemically varied, but, due to long-term transportation, the detrital material becomes homogenized and the composition of peat is generally quite homogeneous. The underlying deposits are represented by clay and sand-siltstone sequences. The essential regional features of the peat accumulation in the southwestern part of the Western-Siberian plate are the substantial differences in the composition of the underlying ground on the right-bank and left-bank of the Ob River. Light

permeable ground of sand-siltstone composition are spread within the Ob-Enisey interfluvial area (the deposits Poludenovskoe, Berezovaya Griva and Kolpashevskoe), whereas heavy clay and clay-carbonates are spread within the Ob-Irtysh interfluvial area (the deposits Vasyuganskoe-5, Vasyuganskoe-22, Uginskoe, Aigarovo, Gusevskoe).

Another important feature is the increasing role of upland peat formations among the deposits from south to north from the forest-steppe landscape zone to the sub-taiga and taiga zones. About 60% of the peat deposits in Western Siberia are represented by upland peat with the degree of decomposition of about 18% and ash yield of about 5%. Of the rest, 40% of the resources are transitional and lowland peat types with the degree of decomposition of about 29% and 43% and ash yield of 7.2% and 15.6%, correspondently (Inisheva et al., 1995).

The studied peatlands have lower ash-yield than the mean value in the region ranging from 1 to 3% and higher in rare cases. REE concentrations and ash yield in the peat samples are shown in Table 1.

Lowland and transitional peatlands also have low-ash yields, generally not exceeding 10%. Such low-ash yields for the lowland and transitional peat is explained by the wide area of the peat accumulation with poor relief, which limits the input of water borne terrigenous matter from mountain margins. Aerosol dust input of mineral matter into the peat deposits is also limited by great distances from the rock-weathering regions. A humid, cold climate does not favor chemogenic mineral formation in the bogs.

The sampling of the peatlands of different types was done with a peat borer through the whole depth of the deposit. The peat samples were collected with intervals ranging from 2 to 50 cm. The depth of peat deposits in Western Siberia usually ranges from 2 to 4 m on average, rarely reaching 10–12 m (Arbuzov et al., 2009). For the research on the modes of occurrence of REE in peat, from one to seven samples were taken within each deposit. Samples from Vasyuganskoe-5, Vasyuganskoe-22 and Aigarovo deposit were taken to estimate the variability of modes of occurrence in relation to deposit type (upland, transitional, lowland), distance from dry land, degree of decomposition of organic matter, ash yield, and other characteristics. Botanic composition, ash yield, degree of decomposition of organic matter, and concentrations of trace elements were determined for each sample. The samples all have quite low concentrations of REE, which are partly a result of low-ash yield. The sum of the seven REE in the peat ash ranges

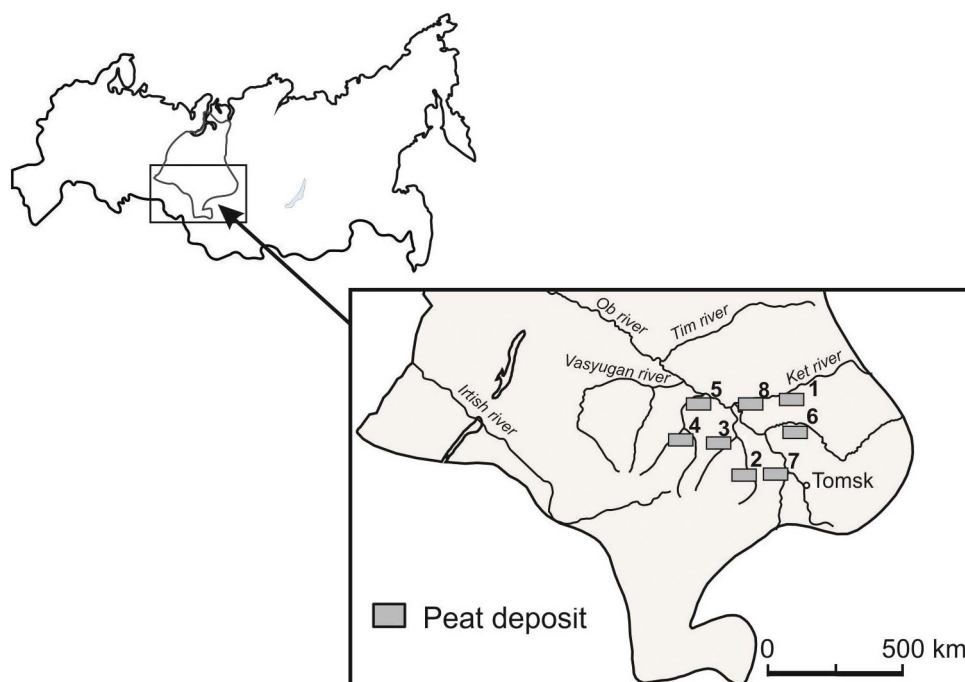


Fig. 1. Locations of the studied peat deposits in Western Siberia Basin.

1 – Poludenovskoe, 2 – Vasyuganskoe-5, 3 – Vasyuganskoe-22, 4 – Uginskoe, 5 – Aigarovo, 6 – Berezovaya Griva, 7 – Gusevskoe, 8 – Kolpashevskoe.

**Table 1**  
Ash yield and REE content in dry peat samples.

№	Deposit	Sample	A <sup>d</sup> , %	Elements content, ppm							ΣREE	ΣREE <sub>as</sub>	La/Yb
				La	Ce	Sm	Eu	Tb	Yb	Lu			
1	Poludenovskoe	679-2 (H)	1.4	0.75	2.5	0.14	0.069	0.012	0.048	0.018	3.5	253	15.6
2	Vasyuganskoe-5	397-1 (H)	1.9	1.45	2.9	0.18	0.061	0.019	0.081	0.012	4.7	247	17.9
3		397-2 (T)	4.0	1.55	4.1	0.25	0.07	0.082	0.16	0.025	6.2	156	9.7
4		397-3 (T)	5.1	1.59	3.9	0.24	0.07	0.058	0.12	0.016	6.0	118	13.3
5		397-4 (T)	7.2	1.67	4.4	0.27	0.11	0.066	0.15	0.023	6.7	93	11.1
6		397-5 (H)	3.3	1.13	3.0	0.19	0.06	0.041	0.085	0.016	4.5	137	13.3
7		397-6 (T)	7.1	2.14	5.5	0.38	0.11	0.096	0.19	0.029	8.4	119	11.3
8		397-7 (H)	1.5	1.05	2.5	0.17	0.05	0.024	0.10	0.019	3.9	261	10.5
9	Vasyuganskoe-22	397-9 (H)	1.3	1.04	2.4	0.24	0.05	0.031	0.11	0.023	3.9	300	9.5
10		397-9-1 (H)	2.0	0.73	1.74	0.12	0.057	0.014	0.049	0.014	2.7	136	14.9
11		397-11 (L)	4.3	0.95	2.48	0.18	0.085	0.015	0.15	0.026	3.9	90	6.3
12	Uginskoe	397-18 (H)	1.3	0.54	1.0	0.08	0.01	0.035	0.075	0.010	1.8	135	7.2
13	Aigarovo	496-1B (H)	1.5	0.73	1.75	0.14	0.007	0.017	0.080	0.010	2.7	182	9.1
14		496-2B (H)	1.3	0.71	1.41	0.14	0.033	0.030	0.061	0.010	2.4	184	11.6
15		496-3B (H)	2	1.36	3.19	0.25	0.072	0.019	0.13	0.021	5.0	252	10.5
16		496-1H (H)	2.8	1.96	5.85	0.49	0.11	0.11	0.18	0.030	8.7	312	10.9
17		496-2H (H)	2.6	1.72	3.78	0.34	0.076	0.051	0.17	0.028	6.2	237	10.1
18		496-3H (H)	10.9	3.88	9.6	0.88	0.16	0.12	0.45	0.064	15.2	139	8.6
19	Berezovaya	817-5 (T)	5.6	5.6	11.7	1.13	0.33	0.13	0.29	0.056	19.2	344	19.3
20	Gusevskoe	902-6 (L)	8.3	1.29	1.24	0.16	0.11	0.017	0.11	0.019	2.9	35	11.7
21	Kolpashvskoe	542-2 (H)	6.4	3.15	6.97	0.89	0.18	0.10	0.27	0.037	11.6	181	11.7

Note: \* – peat type: H – upland, T – transitional, L – lowland, A<sup>d</sup>, % – Ash yield in %, ΣREE – content of the sum of La, Ce, Sm, Eu, Tb, Yb, Lu in peat, ppm, ΣREE<sub>as</sub> – content of the sum of La, Ce, Sm, Eu, Tb, Yb, Lu in peat ash, ppm.

from 35 to 340 ppm comparable with the mean values for the coal ash (Ketris and Yudovich, 2009). The range in concentration of individual REE is generally a factor of 10 but for Eu it is 47. The La/Yb ratio is generally quite moderate and close to the mean value in continental crust - 13.0 (Taylor and McLennan, 1985), but in single samples it is as high as 19.3 or as low as 6.3 (Table 1).

## 1.2. Analytical procedures

Traditionally, the modes of occurrence of elements in peat, as well as in soils, are investigated by sequential chemical extraction methods. One of the basic methods is a 5-stage scheme first extracting ion-exchangeable and acid-soluble elements, followed by extraction of reduced and oxidized phases, resulting in an undissolved residue. Such a method was developed by Tessier et al. (1979). There are some modifications of this scheme (Outola et al., 2009; Virtanen et al., 2013).

In this research on peats the modes of occurrence of the REE were studied using a range of analytical methods. Because the ratios of mineral and organic modes of occurrence, as well as the ratio of different organic forms, are important for the interpretation of the accumulation conditions and redistribution of REE in coals, the authors developed a scheme based on the standard method of the peat separation into different organic and inorganic phases.

The composition of peat was studied by sequential leaching of bitumen, water-soluble, and hydrolysable substances (WSS and HS), as well as extraction of humic acids (HA), fulvic acids (FA) and lignin-cellulose residue (LCR) following the Instorf procedure (Lishtvan and Korol', 1975). These four leachates and the residue are herein referred as phases. Twenty-one peat samples from eight peat deposits were subjected to this selective leaching procedure. Bitumen was extracted from the raw samples by benzene and ethanol-toluene solution. The residue was treated with 4% HCl for 5 h in a water bath to extract water-soluble substances and hydrolysable substances. The insoluble residue was exposed to 0.1 N NaOH in a water bath for 1 h at 100 °C. The residue was treated three times with a solution of Na-humates. Addition of HCl, causing substitution of Na<sup>+</sup> by H<sup>+</sup>, results in the precipitation of humic acids. Fulvic acids thus remain in the solution. The solution was evaporated for further study. A part of the selective leaching products at each step was used to measure the concentrations

of REE and another part was ashed at 800 °C for the determination of ash yield. The concentration of REE in each phase of the humic substances was found as the difference between the concentration in the sample before it was leached and the concentration in the insoluble residue, for each step along the leaching pathway. REE concentrations were directly determined in single samples of humic acids and bitumens.

Lanthanum, Ce, Sm, Eu, Tb, Yb, and Lu concentrations were determined in all phases of the peat and balance calculations were performed. The peat and each residue after each sequential extraction were analyzed by instrumental neutron activation analysis (INAA) at the nuclear-geochemical laboratory of the Department of Geoecology and Geochemistry of Tomsk Polytechnic University (TPU, Russia; analyst Sudyko A.F.). The irradiation of samples was carried out with the neutron research reactor IRT-T in the Physical-Technical Institute of TPU. The weight of each INAA sample ranged from 100 mg to 200 mg. Quality control was done parallel to the study of the original sample and its residue obtained by ashing the sample at 800 °C, as well as through the use of standard reference samples (BIL, ZUK-1) (Sudyko, 2016).

Mineral hosts of REE micron and nanometer dimensions in some samples of dry peat were studied at the International Innovation Scientific-Educational Center "Uranium Geology", Department of Geoecology and Geochemistry of TPU. A Hitachi S-3400 N scanning electron microscope with a BrukerXFlash 4010 energy dispersive spectrometer was used. The technique allowed visualizing and identifying mineral forms of micron and nanometer dimensions as well as determining their elemental composition.

This set of analytical procedures allowed us to assess REE chemical forms and concentration mechanism in peat with high reliability.

## 2. Results and discussion

The existence of coals in which the REE concentrations in the ash are as high as 0.2–1.0 % (Kronberg et al., 1987; Seredin, 1991; Hower et al., 1999; Seredin, 2001; Mardon and Hower, 2004; Goodarzi et al., 2006; Seredin and Finkelman, 2008; Seredin and Dai, 2012; Seredin et al., 2013; Dai et al., 2010, 2014, 2016; Arbutov et al., 2003, 2014; Arbutov and Ershov, 2007) commonly with the average concentration

of REE in the coal ash of 300–400 ppm, assumes the presence of REE-bearing phases such as mineral or organic compounds. Studies show that the ratio of different elemental modes of occurrence can vary greatly in the process of coalification (Arbutov and Ershov, 2007; Arbutov et al., 2012). Thus, it is reasonable to try to understand the accumulation conditions and modes of REE occurrence in the early stage of coal formation – the stage of peat accumulation.

The REE concentrations are usually much lower in the northern Eurasia modern peats than in coals, even though the REE concentrations in the peat ash are often comparable with the coal ash (Bernatonis et al., 2002; Arbutov et al., 2009; Mezhibor et al., 2013). Peat bogs are known in Finland in which the light REE (LREE: La, Ce, Pr, Nd, and Sm) sum in the peat ash exceeds 0.1% on average, and in some areas the sum of the LREE can be up to 0.5% (Yliruokanen and Lehto, 1995). REE concentration is lower in the underlying granites and gneisses than in the peat and almost an order of magnitude lower than in the peat ash. For instance, in the Rapakivi granite the La, Ce, and Nd concentrations were reported to be 128, 270 and 100 ppm respectively. Their concentrations in the peat ash in separate horizons are as high as 1268, 2598, and 1766 ppm, respectively (Yliruokanen and Lehto, 1995). With certain assumptions (such as difference in climate conditions and vegetation composition), modern peat bogs of the northern hemisphere can be considered as examples of precursors of coal. Thus the origin of REE distribution in modern peat deposits can be taken as representative for ancient peat bogs.

The results obtained from the selective extraction of the 21 peat samples indicate that the main hosts of the REE in peat are the water-soluble and hydrolysable substances (Tables 2, 3), which account for 36 to 68 % of the total REE concentration in the samples, on average more than 50% for both upland and lowland peat (Table 2).

These data substantially differ from the results of the investigations of waterlogged soils. Sequential extractions that are performed on soil wetlands generally show, regardless of the leaching protocol, that REEs dominate in the residual fraction, followed by the reducible and the oxidizable fraction, with the exchangeable fraction being very low (Leybourne and Johannesson, 2008; Pédrot et al., 2008; Davranche et al., 2011; Mihajlovic et al., 2014). This indicates a substantial change of the modes of REE occurrence during the transition from the formation of wetland and peatland soils to the buried peat deposit.

Weak HCl, used to extract hydrolysable substances, readily dissolves sulfates and carbonates, as well as some ferrous aluminosilicates without affecting pyrite (Gulyaeva and Itkina, 1974). Experiments show that the treatment of peat by weak 4% HCl dissolves and carries into solution amino acids in addition to other organic compounds such as: (aspartic acid (63% of their content is leached from the peat), glycine (60% leached), and methionine (59% leached) (Rakovsky and Pigulevskaya, 1978). Other amino acids are cleaved under more severe conditions. Amino acids and amino polyacids may form insoluble anionic type chelate complexes with REE. This feature is widely used in the technological processing of REE (Mikhailichenko et al., 1987; Singh et al., 2006). These complexes can be considered as one of the possible

**Table 2**  
REE in the phases of upland and lowland peat, calculated %.

Phase	Phase share, %	La	Ce	Sm	Eu	Yb	Lu	Average
Upland peat (14 samples)								
Bitumen	4.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1
WSS and HS	45.7	58.1	59.5	59.1	57.6	44.5	42.7	53.7
Humic acids	31.9	11.2	9.1	11.4	18.3	18.7	19.0	14.6
Residue	18.3	30.9	31.7	29.5	24.1	37.8	39.3	32.2
Lowland and transitional peat (7 samples)								
Bitumen	4.0	1.8	2.0	1.7	1.3	2.7	1.6	1.8
WSS and HS	33.6	55.3	58.2	58.8	63.0	51.0	43.9	55.0
Humic Acids	42.5	21.1	21.8	22.9	16.6	27.8	32.2	23.7
Residue	15.2	19.3	18.6	12.5	18.4	18.7	21.4	18.2

**Table 3**  
REE in the phases of upland peat of the Aigarovo deposit, calculated %.

Phase	Phase share, %	La	Ce	Sm	Eu	Yb	Lu	Average
Low-decomposition upland peat (3 samples)								
Bitumen	3.7	2.7	2.2	3.1	0.7	1.7	0.1	1.8
WSS and HS	50.1	51.5	51.1	51.3	58.8	36.1	37.7	47.7
Humic acid	31.2	9.6	8.9	10.5	10.3	15.0	16.7	11.8
Residue	15.0	36.2	37.8	35.1	30.2	47.2	45.5	38.7
High-decomposition upland peat (3 samples)								
Bitumen	5.8	4.0	3.9	3.5	1.9	3.6	4.2	3.5
WSS and HS	34.0	68.0	66.0	62.1	62.6	56.0	53.3	61.3
Humic acid	43.4	4.4	6.3	11.1	10.1	12.7	12.8	9.6
Residue	16.8	23.6	23.7	23.3	25.4	27.7	29.7	25.6

modes of REE in the water-soluble and hydrolysable substances in peat. Glycine or aspartic acids are good complexing agents, often used for the chromatographic separation of REE (Hnatejko et al., 2000). Thus, REE may be present not only in ionic form or in the form of chloride complexes in the water-soluble and hydrolysable substances, but also as complexes with organic compounds such as amino acids involved in the formation of fulvic and then humic acids.

The La/Yb ratios and data on REE found in the various phases (Tables 4 and 5) indicate the preferential accumulation of LREE (La, Ce) in the water-soluble and hydrolysable substances. Table 4 represents upland peat of different decomposition extent. It is seen that in the more decomposed peat the value of La/Yb is higher in the WSS and HS phase. Lowland peat is generally more decomposed than upland peat, which is illustrated in Table 5. Consequently, La/Yb in the WSS and HS phase of the lowland peat is higher than in the upland peat. These are mobile forms of the elements that can be considered as potential material for the formation of mineral and organic-mineral complexes in the process of coalification.

The important role of low-molecular organic acids in the REE transportation in boreal stream waters was described by Andersson et al. (2006). Two different colloidal carrier phases, different in size and chemical composition were identified with flow field-flow fractionation chromatography. A small (3 nm) organic-rich phase and a larger (12 nm) iron-rich phase could be detected. Small organic compounds were determined to be low molecular organic acids. In the opinion of authors (Andersson et al., 2006), these phases may be responsible for the increase of REE in the water during the flooding period. It was found that these organic acids were enriched in LREE. High-molecular colloids extracted from the same water were enriched in heavy and light REE in comparison with the mineral suspended matter. All these data correspond well with the results that we obtained.

It is important to note that experimental studies of the REE sorption by humic acids and xylene of brown coals did not show selective accumulation of heavy REE in relation to light REE (Eskenazy and Chakarova, 1995; Eskenazy, 1999). They both are accumulated proportionally. The study of humic acids of brown coals of different



**Table 4**  
Average REE concentrations and La/Yb ratios in the phases of upland peat of Aygarovo deposit.

Phase	Phase share, %	Elements content, ppm						La/Yb
		La	Ce	Sm	Eu	Yb	Lu	
Low-decomposition upland peat (3 samples)								
Raw peat	100	0.89	1.94	0.17	0.048	0.10	0.014	8.9
Bitumen	3.7	< 0.05	< 0.05	< 0.01	< 0.01	< 0.01	< 0.005	
WSS and HS	50.1	1.0	2.4	0.19	0.065	0.09	0.011	11.1
Humic acid	31.2	0.25	0.34	0.05	0.015	0.06	0.007	4.3
Residue	15.0	2.1	4.4	0.38	0.084	0.31	0.044	6.7
High-decomposition upland peat (3 samples)								
Raw peat	100	2.7	6.3	0.55	0.13	0.29	0.042	9.3
Bitumen	5.8	< 0.05	< 0.05	< 0.01	< 0.01	< 0.01	< 0.005	
WSS and HS	34.0	6.4	14.0	1.0	0.26	0.34	0.067	14.5
Humic acid	43.4	0.26	0.86	0.16	0.027	0.085	0.011	3.0
Residue	16.8	3.8	9.1	0.71	0.20	0.51	0.076	7.6

deposits of Siberia also shows close La/Yb values for the initial coal and for the extracted humic acids (Arbutov and Ershov, 2007). From these data we can suppose that during the coalification the condensation of low-molecular organic acids with high-molecular humic acids occurs followed by the formation of brown-coal humic acids.

The residual yield (insoluble residue) is relatively uniform (15.2–18.3%) for different peatlands. The insoluble residue is composed of lignin, cellulose, mineral substances and other organic substances insoluble in HCl and NaOH such as humins. It ensues from the balance calculations that no > 30–40% of the REE-bearing minerals are resistant to the effects of weak (4%) hydrochloric acid in peat (Tables 2, 3).

The studied upland and lowland peat varied in the REE distribution in the phases. Despite the higher ash yield in the lowland peat compared with the upland peat (in this case 4–10% for lowland peat and 1.3–2.8% for the upland peat), the organic-mineral residue of the upland peat carries a significantly larger proportion of REE compared with the insoluble residue of the lowland and transitional peat. The upland peat residual phase contains 32.2% of the REE on average and in the lowland peat only 21.7% (Table 2). This indicates a subordinate role of REE-bearing minerals in the upland peats. It is clearly seen by the low-decomposition of some upland peat and higher decomposition of some upland peat within the same deposit with similar composition of underlying sequences (Table 3). The differences in the peatland source area are offset in this case: the influence of different source areas of terrigenous matter is minor and the composition of the mineral matter entering the peatland is more homogenous.

According to these data, even if we assume that all the REE in the residual phases are in minerals, the mineral substances of peat do not account for > 40% of the total REE. Calculations show that in the

residual phase accounts for < 20% of the REE in the more mineralized lowland peat, the REE concentration is distinguished by no > 1.5-fold (Tables 4 and 5). The calculations also illustrate the secondary importance (subordinate role) of the mineral matter in the concentration of REE in peat. Electron microscopy analysis of peat revealed only a few minerals, which are all of micron dimensions containing REE (Fig. 2).

Some stable mineral phases (monazite, xenotime, zircon, minerals of the crandallite group) may have initial clastogenic origin. The presence of separate fine rare-earth minerals in the modern peat supports this conclusion (Fig. 2).

Smieja-Król et al. (2010) noted the presence of REE phosphates without indicating specific mineral forms in a peatland of Upper Silesia below the peat-forming layer. Whereas Le Roux et al. (2006) observed the fast dissolution of fluorapatite in the upper zone of an ombrotrophic bog in Germany indicating weak stability in the peat-forming process. Probably, a part of the initially clastogenic REE minerals was destroyed in the aggressive moor environment enriched by organic acids releasing the REE to change their mode of occurrence, enriching the organic matter in REE. The probability of such mechanisms of REE redistribution in peatlands is indicated by both observations of the change of lithogenic minerals contents in the vertical profile of peatlands and the results of experiments. For example, the experiments of Bogolyubova et al. (1971) showed that in the acidic and reducing peat environment even montmorillonite is quickly transformed into kaolinite, changing its structure and losing Fe, Mg, and Ca.

Authigenic minerals containing REE have not yet been found in peat. However their formation is quite possible. There are phosphates (vivianite), carbonates (siderite, calcite), sulfides (pyrite, galena, etc.), sulfate (barite, gypsum), and other minerals known in peat deposits (Kalaitzidis et al., 2002) that can contain REE.

**Table 5**  
Average regional REE concentrations and La/Yb ratios in the phases of upland and lowland peat.

Phase	Phase share, %	Elements content, ppm						La/Yb
		La	Ce	Sm	Eu	Yb	Lu	
Upland peat (14 samples)								
Raw peat	100	1.1	2.6	0.21	0.08	0.11	0.018	10.4
Bitumen	3.0	< 0.05	< 0.05	< 0.01	< 0.01	< 0.01	< 0.005	
WSS and HS	47.7	1.6	3.7	0.29	0.10	0.13	0.027	12.2
Humic acid	29.8	0.68	1.29	0.09	0.10	0.09	0.015	7.4
Residue	19.5	1.66	3.82	0.28	0.074	0.20	0.033	8.3
Lowland peat (7 samples)								
Raw peat	100	2.2	5.1	0.47	0.13	0.22	0.090	10.5
Bitumen	4.0	< 0.05	< 0.05	< 0.01	< 0.01	< 0.01	< 0.005	
WSS and HS	35.0	4.1	10.9	0.93	0.25	0.31	0.12	13.5
Humic acid	45.0	0.80	1.75	0.18	0.05	0.12	0.067	6.5
Residue	16.0	2.6	7.0	0.44	0.15	0.32	0.079	8.1

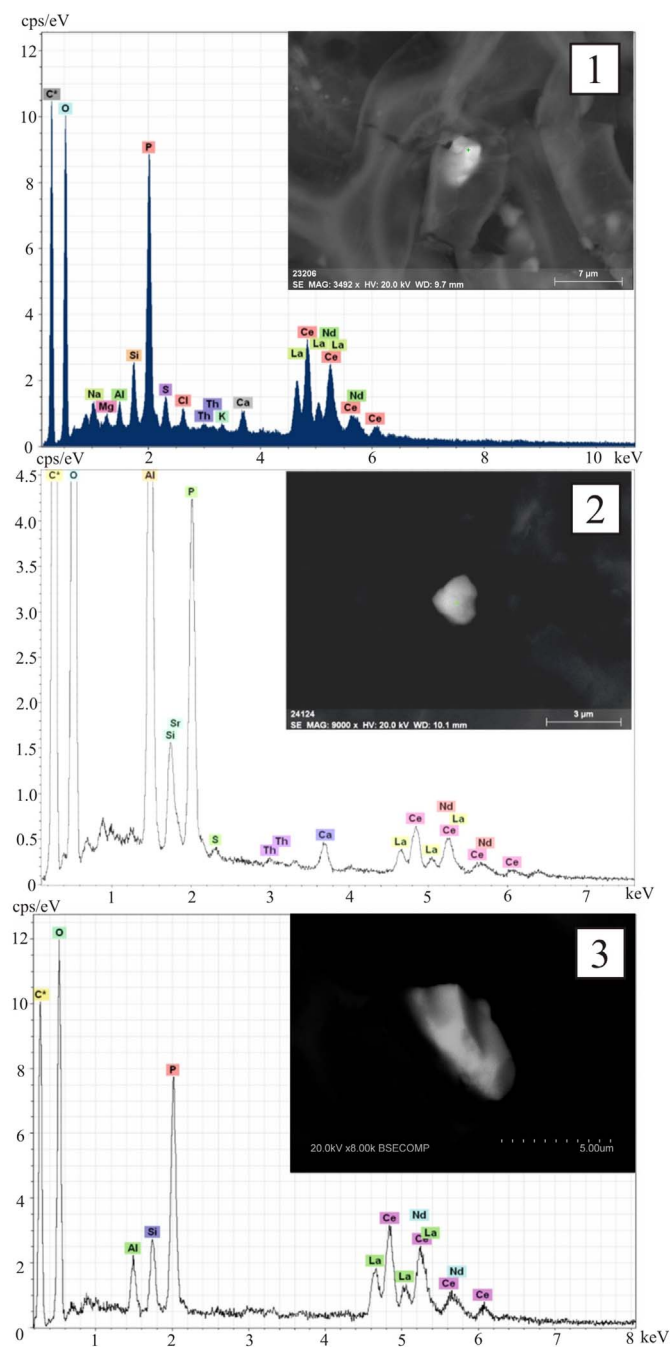


Fig. 2. Minerals of rare earth elements in peat and their element composition. 1 – monazite; 2 – goyazite; 3– kularite (Ce, Nd, La, Eu)[PO<sub>4</sub>].

Formation conditions of peat deposits, especially the formation of low-ash upland peat, are unfavorable for the accumulation of heavy minerals by placer deposits formation from water streams. Fine REE minerals can enter the peatlands in the form of aerosol dust and fine suspended matter (Smieja-Król et al., 2010; Talovskaya et al., 2015, 2017). A substantial input of REE in a paleo-peatland by this mechanism was not evident in our samples.

The method of the sequential leaching of bitumen, water-soluble, and hydrolysable substances (WSS and HS), as well as extraction of humic acids (HA), and fulvic acids (FA) supposes the concentrating of mineral matter in the residual phase of the peat. In this case, the REE minerals, determined in the residual phase, are not sufficient to account for even a small part of the total REE present in the residual phase of the peat. It can be supposed that a part of the REE is concentrated in the

residual material in the insoluble humins. This assumption is founded on the reduced La/Yb ratio in this phase compared to that of the raw peat. The ratio drops sharply in humic and fulvic acids and to a lesser extent in the residual material. Mixing of organic (low La/Yb) and mineral (high La/Yb) forms of REE probably take place in the residual material. Taking into account the La/Yb ratio for the mineral matter equal to its ratio in the upper continental crust as 12.8 (Grigor'ev, 2003), it is possible to roughly calculate the share of the mineral component in the total REE balance in the residual peat material. This is, on average, 17% for the upland peat and 25% for the lowland peat (Table 5), 28% and 47%, respectively, for the peat with small and high decomposition degree in the Aygarovo deposit. The uncertainty of the calculation is due to the complexity of the La/Yb ratio choice for the initial mineral substance. The proportion of minerals in the total balance of REE in the residual material does not exceed 65% even in the case of the present La/Yb ratio in the raw peat. The proportion of minerals is not higher than 25% including the full share of that phase in the total REE balance for the peats of Western Siberia.

It is significant that in the peat sample enriched in REE from the Berezovaya Griva deposit (Table 1), only 3–6% of the total REE amount is concentrated in the residual material (Table 6). The main part of the REE is accumulated in the water-soluble and hydrolysable substances. Elements can enter into the emerging humate complexes or authigenic minerals in the process of diagenesis due to changes in the peat composition. Thus, these data support a secondary role of REE mineral modes of occurrence in peat.

Macromolecular humic acids (humic and fulvic acids) in the peat do not play a major role in the concentration of REE in contrast to the geochemically-close elements scandium and thorium which are complexed by humic and fulvic acids (Arbuзов et al., 2012, 2015). The proportion of total REE associated with humic and fulvic acids may be as high as 50% in rare cases, but typically ranges only from 10 to 20% (Tables 2 and 3). The heavy REE (Yb, Lu) accumulate in humic acids more than the light REE. This is evidenced by a larger percentage of the heavy REE output in a given phase and low La/Yb ratio in humic acids. The La/Yb ratio in peat as a whole is close to the Clarke (mean concentration) value, indicating a predominantly clastic input of REE to the peat. Dissolution and partial redistribution of REE occur directly in the peat. The heavy REE are mostly concentrated in humic and fulvic acids and light ones in the water-soluble phase and hydrolysable substances. This is demonstrated by the La/Yb ratio and is especially clearly seen in the Aygarovo peat (Table 4). When the value of the La/Yb ratio is about 9 in the raw peat, it is 18.6 for the lowland peat and 11.1 for the upland peat in the WSS and HS phases, and 3.0 and 4.3, respectively, in the HA phase. Even smaller values of La/Yb characterize some types of fulvic acids. Although humic substances in the peat samples are neither hosts nor carriers of REE, heavy REE selectively accumulate in the HA phase. Yb and Lu concentrations in the humic acid ash are 2–8-times higher than in the raw peat ash (Table 7). The ash of humic acids is strongly enriched by Ce and Tb in the Gusevskoe high-ash peat deposit. The

Table 6  
REE in the phases of lowland peat, calculated %.

Phase	Phase share, %	La	Ce	Sm	Eu	Yb	Lu
817-5 (Berezovaya Griva)							
Raw peat	100	100	100	100	100	100	100
Bitumen	3.1	0.1	0.1	0.4	0.3	0.1	0.1
WSS and HS	46.0	79.4	90.1	91.3	82.7	73.2	74.4
HA	35.6	5.1	4.0	5.1	7.0	20.5	21.2
Residue	15.3	5.4	5.8	3.2	10.0	5.7	4.3
542-2 (Kolpashevskoe)							
Raw peat	100	100	100	100	100	100	100
Bitumen	4.5	1.2	0.5	3.5	4.5	1.2	1.4
WSS and HS	44.4	77.1	78.6	84.6	74.7	60.2	61.3
HA	38.1	11.9	9.6	5.8	11.9	27.0	30.8
Residue	13.0	9.8	11.3	6.1	8.8	11.6	6.5

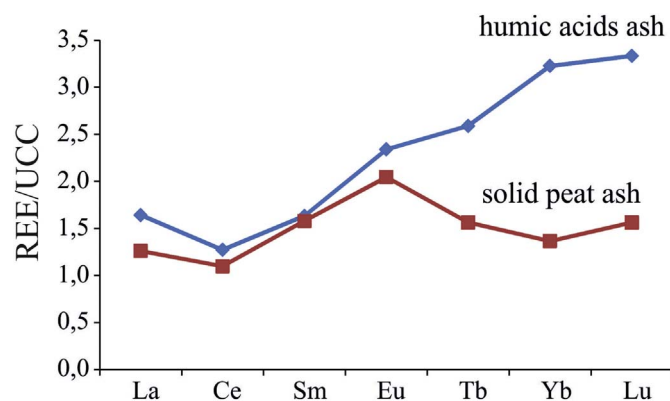
**Table 7**  
REE content in the raw peat ash and extracted humic acids of ash samples.

Samples	Elements content, ppm							La/Yb
	La	Ce	Sm	Eu	Tb	Yb	Lu	
Kolpashevskoe field 542-2								
Raw peat ash	49.2	108.9	13.9	2.9	1.5	4.2	0.57	11.7
Humic acids ash	72.3	109.7	7.8	< 0.2	2.3	12.8	1.61	5.6
Concentration coefficient	1.5	1.0	0.6	0.03	1.5	3.1	2.8	
Aygarovo field 496-3B								
Raw peat ash	37.8	83.4	6.1	1.7	0.7	3.4	0.5	11.1
Humic acids ash	48.2	90.4	8.5	2.3	1.3	6.8	1.0	7.1
Concentration coefficient	1.3	1.1	1.4	1.3	1.7	2.0	1.9	
Aygarovo field 496-2H								
Raw peat ash	58.8	101	10.4	2.2	1.3	4.3	0.96	13.7
Humic acids ash	64.9	79	14.8	2.8	2.5	12.7	2.5	5.1
Concentration coefficient	1.1	0.8	1.4	1.2	1.9	3.0	2.6	
Vasyuganskoe field 397-9								
Raw peat ash	31.2	62.7	4.8	1.5	0.69	2.5	0.49	12.5
Humic acids ash	71.2	115	11.9	3.2	1.1	10.3	2.61	6.9
Concentration coefficient	2.3	1.8	2.5	2.1	1.6	4.1	5.3	
Gusevskoe field 902								
Raw peat ash	12.4	8.8	0.8	1.3	0.21	1.3	0.18	9.3
Humic acids ash	55.3	99.8	2.8	6.2	3.5	10.8	1.5	5.1
Concentration coefficient	4.5	11.3	3.5	4.8	16.8	8.1	8.2	
Average for peat deposits								
Raw peat ash	37.8	70.2	7.1	1.8	1.0	3.0	0.5	12.4
Humic acids ash	52.5	92.8	9.3	2.9	2.2	10.0	1.6	5.3
Concentration coefficient	1.4	1.3	1.3	1.9	2.1	3.3	3.0	

Note: concentration coefficient – the ratio of the elements content in the humic acids ashes to the raw peat samples.

concentration ratios of individual REE for the samples range from 1.2 to 3.7 on average in the humic acids ash relative to the raw peat ash (Table 7).

According to the research carried out by Purrett et al. (2007), natural humic acids in stream waters may have REE normalized to mean contents in the continental crust, UCC) patterns of two types: HREE enrichment and MREE (Sm, Eu, Gd, Tb, Dy-Ho) enrichment. In our case, the normalized graphs of REE in the ash of humic acids, extracted from the peat show HREE enrichment (Fig. 3), whereas the REE normalized patterns for the ash of the same peat have MREE enrichment.



**Fig. 3.** REE patterns for a solid peat ash and peat humic acids ash from the Western Siberia (Russia) normalized to the mean contents in the continental crust (UCC) (Taylor and McLennan, 1985).

Fig. 3 showing of normalized REE contents in the peat ash and humic acid ash is similar to graphs for solid peat and dissolved humic acids from peat deposits of France (Auterives, 2007; Davranche et al., 2016). The enrichment of humic acids by heavy REE corresponds well with the high yield of LREE and MREE in the easy hydrolyzed and water-soluble substances. Therefore, the fractionation of REE has taken place in the peat. We may infer from the data that HREE form stronger bonds with high-molecular humic acids and pass into the hydrolyzable and water-soluble substances to a lesser degree than other REE, further enriching the alkaline extract of humic acids.

A weakly pronounced tendency distinguishes the increase of both light and heavy REE in humic acids with increasing ash yield in the raw peat. Humic substances output increases with the degree of decomposition and hence with the ash yield of peat. Climate has a great influence on the humic substances formation according to Timofeev and Bogolyubova (1999). The process of water-soluble and hydrolysable substances condensation and the synthesis of fulvic and then humic acids are accelerated in tropical and subtropical climates. Therefore, we can assume that the role of humic substances formed in the warmer climates of ancient peat bogs in the accumulation of REE was significantly higher than in that of modern analogues.

According to experimental and field research of Nakada et al. (2016), the accumulation of REE in humic acids predominately occurs due to complexation by carboxyl groups. The decrease in the amount of carboxyl groups when heating the humic acids is accompanied by a proportional decrease in REE.

Thus, selective laboratory leaching of REE from peat samples revealed that the bulk of the elements concentrated in the water-soluble and hydrolysable substances and, to a lesser extent, in the insoluble residue and humic substances. From 40 to 80% of the total content of REE in the peat is accounted for by the hydrolyzable and water-soluble substances. 10–30% of the REE is concentrated in humic acids. The insoluble residue contains no > 30–40% of the REE. Mineral matter in peats plays a secondary role in the accumulation of REE. In general, no > 25% of the REE is accounted for by minerals. Among the mineral hosts of the REE in peats are phosphates (such as monazite, xenotime, crandallite) and zircon.

The water-soluble and hydrolyzable substances are relatively enriched with light REE, and humic substances are enriched with heavy REE. REE output to the residual material is the lowest in the REE-enriched peats. This indicates that the role of REE minerals in low and high-ash peat is secondary in the peat accumulation stage. Predominance of organic forms of the REE is probable and physical adsorption on clay minerals is also possible.

These data show that at the peat stage there is a REE differentiation in different phases of the organic substance. This factor needs to be taken into account when using peat extracts as fillers in the animal nutrition. According to scientific studies, the selective REE concentration in food may lead to different diseases (Panichev, 2015).

### 3. Conclusion

During peat formation, REE are generally concentrated in the water-soluble and hydrolyzable substances, probably predominately associated with low-molecular acids and in a subordinate quantity in the humic substances with a total of > 60–80% of the REE. In the leached residue of the peat, REE can be partly present in the organic matter as a part of insoluble NaOH humines. Thus, mobile modes of occurrence of REE prevail in the peat-formation stage. Minerals do not play a significant role in the accumulation of REE in peat, even if they are present in the form of stable REE-bearing minerals (e.g. monazite, xenotime, zircon). Light and heavy REE were separated in the peat phases. The water-soluble and hydrolyzable substances are relatively enriched in light REE and humic substances are enriched in heavy REE.

The modes of occurrence of REE in peat testify to the leading role of hydrogenic mechanisms for their concentration in coal. Without

reference to a source of input (clastogenic material, colloids and dissolved substances) in a peat formation basin, REE pass essentially into mobile forms in the active acid environment of the peat and are finally accumulated in the organic matter. Further, the processes of peat maturation and coalification, accompanying by the temperature increase, lead to the REE release from the organic matter and formation of autigenic minerals. The role of organic modes of occurrence of REE in peat should be taken into account while developing the technologies for peat use. Especially it is important when using different peat extracts as fillers for animal nutrition.

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