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GEOCHEMISTRY

Mineralogical and Geochemical Features of a Peat Deposit in the Eutrophic Obskoye Fen under Anthropogenic Load (Western Siberia)

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Abstract—The chemical composition and mineral inclusions in peats and the underlying soils of the eutrophic Obskoye fen (Western Siberia, Tomsk Region) are studied. The basic pattern of a change in the mineralogical and geochemical conditions at depth consists in domination of hydroxides on top of the peat deposit and sulfides at the bottom. The geochemical reduction barrier is formed at the bottom of the peat deposit. Its functioning is related to increased concentrations of U and Hg. The markedly pronounced influence exerted by sewage discharge is associated with an increase in the Na concentration in acid extracts from peats and additional accumulation of the mixture of suspended, colloidal, and dissolved forms of some metals in the boggy environment.

Keywords: mineralogical and geochemical conditions, anthropogenic impact, Obskoye fen, Western Siberia

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The chemical composition of peats is an important characteristic that to a significant extent determines the areas of their use in the thermal power industry, agriculture, and the chemical industry. The mineral composition is also of great importance, especially when peats are used in the power industry. All this underlies the consistant interest in mineralogical and geochemical studies of wetland ecosystems, including those in Western Siberia, one of the boggiest regions in the world. The purpose of this work is to determine the changes in the mineralogical and geochemical conditions of functioning of the eutrophic valley bog in the watershed area of the Ob River under conditions of long-term sewage discharge.

Taking this into consideration, we selected our study object, the Obskoye fen, which contains segments with different degrees and characteristics of the anthropogenic load. The Obskoye fen is situated on the territory of Tomsk Region on the left bank of the Ob River valley from the settlement of Kozhevnikovo in the south to the settlement of Ishtan in the north as a band 1.5–7.0 km wide and 104 km long. It contains fen peat deposits with an average thickness of 3.2 m up to a maximum of 6 m. The geobotanical conditions and the chemical composition of the bog waters were characterized in detail in [1, 2]. The site under a markedly pronounced anthropogenic impact is located near the settlement of Mel'nikovo, the administrative center of the Shegar District of Tomsk Region, where residential sewage waters have been discharged for several decades. The geographical coordinates of the observation point (I) at this site are 56°5520′ N, 84°1033′ E; it is found 0.75 m from the sewage outlet. The point for studying the conventionally background state (II) is located to the south of the settlements of Mel'nikovo and Nashchekovo, approximately 6.3 km up along the slope of the Ob River at the point with the geographical coordinates 56°5154′ N, 84°0263′ E. The depth of the peat hole at point II (background) is 4 m. The sampling was done by intervals, every 0.25 m, including the sampling of organo-mineral deposits (OMD) on the interval of 4.00–4.25 m and the sampling of mineral soil (clay loam) on the intervals 4.25–4.50, 4.50–4.75, and 4.75–5.00 m. At point I, the peat samples were selected down to only 3 m. The examination procedure was described in [3, 4].

For both sites of the Obskoye fen, the methods of scanning electron microscopy and XRD analysis were used to detect about 20 mineral phases in the peat and basal deposits. All mineral phases identified are grouped by origin into detrital (supplied) and authigenic (newly formed or in situ). The detrital phases

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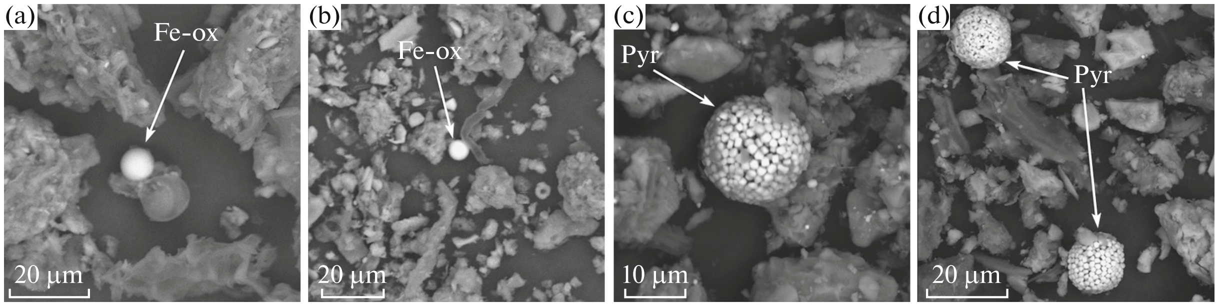

Fig. 1. The SEM images of authigenic mineral phases: (a, b) iron oxides and hydroxides (Fe-ox) with a spherical shape in the upper layers; (c, d) pyrite (Pyr) framboids in the bottom layers of the peat deposit.

include the following: quartz, feldspars, micas, ilmenite, rutile, magnetite, zircon, monazite, xenotime, cheralite, apatite, and bismuthine. The authigenic minerals (Fig. 1) are represented by iron oxides and hydroxides, pyrite, siderite, galena, barite, acanthite, native silver, and some other minerals. Such mineral phases were found in a peat deposit of the Vasyugan Bog [3–5]. The distribution of mineral phases over the organic particles is nonuniform in the section of the peat deposit at point II. On top of the peat deposit (0.00–2.75 m), iron oxides and hydroxides with a spherical shape (microspheroids) from 0.5 to 10 μm in size are dominant among the authigenic minerals (Figs. 1a, 1b). The detrital minerals in the upper layers of the section are dominated by quartz, fedlspars, micas, ilmenite, magnetite, zircon, and rutile. In the bottom part of the deposit (2.75–4.50 m), there is a noticeable increase in content of pyrite framboids (Figs. 1c, 1d), which represent an aggregated cluster of pyrite microcrystallites up to 0.5–1.2 μm in size. In sandy loams underlying the fen (at a depth of 4.5–5.0 m), the relative share of pyrite gradually decreases at the same set of detrital minerals. The composition of mineral inclusions in the peat at the contaminated site of the Obskoye fen is similar to that in the background site except for the decreased amount of framboidal pyrite and the much greater amount of magnetite (intervals 0.00–0.50 and 1.50–1.75 m) and siderite and barite (1.50–1.75 m), as well as the presence of such fragmentary minerals rare as cheralite and bismuthine at point I.

The acid extracts from the mineral soil against the background segment of the Obskoye fen have higher concentrations of Li, Be, Mg, Al, Si, K, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, Rb, Y, Zr, Pd, Ag, Cd, In, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Tl, Pb, Bi, and Th, while the peat extracts have greater contents of Mo, Rh, Sb, I, W, and Ir. In addition, the dispersion of the concentrations of Mo, Rh, Sn, Sb, I, Ba, W, Re, Ir, and U is much greater in the peats. The concentration of U rather sharply increases in the peat deposit in the depth range of 2.25–3.25 m, i.e., in the layer where the hydroxide specialization changes to a sulfide one in the composition of mineral iron forms.

The comparison of the chemical composition of the acid extracts from the peats at points I and II showed that, in the contaminated site of the fen, there are greater average contents of Li, Be, Na, Mg, Al, Si, K, Ti, V, Cr, Fe, Co, Ni, Cu, Ga, Ge, Rb, Y, Zr, Nb, Pd, Ag, Cd, In, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Tl, Pb, Bi, and Th, with the maximum concentrations of these elements (except for Na, Ti, Fe, Rb, Y, Nb, and Ba) from the background site being recorded for the underlying mineral soils. The higher contents of these elements in the peats of the contaminated site may be caused by the high dustiness of the Obskoye fen territory near Mel'nikovo, rather than by the sewage discharge. As for the rest of the elements, Na mostly shows the most evident relationship with the flows and is characterized by typical changes in the depth of the peat deposit: (1) in the depth range of 0–1 m, the average content is 101 mg/kg at the background site and 989 mg/kg at the contaminated site; (2) in the depth range of 1–2 m, it is 82 mg/kg at the background site and 331 mg/kg at the contaminated site; (3) in the depth range of 2–3 m, it is 83 mg/kg at the background site and 169 mg/kg at the contaminated site. Na concentrations are usually elevated in sewage waters, as is the case near Mel'nikovo [2]. Judging by a rather sharp decrease in the Na concentrations in the depths of the peat deposit at the contaminated site, the maximum impact of the sewage discharge is observed in the top meter-deep layer, which is quite noticeable, down to 2 m.

For definite elements (Ca, Mn, As, Sr, Mo, Rh, W, and Re) or their dispersions (B, S, Ca, Mn, Sr, Mo, Rh, W, Re, Hg, and U), the highest values of the average concentrations were recorded at the background site, rather than at the contaminated one. Correlation analysis made it possible to reveal the statistically significant relationships between the U concentrations and the pyrite content (the correlation coefficient is 0.64) and the relationship between C_{ac} with a pH value of water extracts (0.59). This suggests that, in certain layers of the peat deposit, the enhanced concentrations of definite elements, including Hg and U, can be related not only to the impact of some concentrated sources, e.g., a sewage discharge or leaching of the underlying soils), but also to the functioning of geochemical barriers. In particular, a rather sharp increase in the Hg concentrations (up to 0.4 mg/kg) at the background site is confined to the layer of 1.75–2.00 m, and in the U concentrations (up to 10.9–12.5 mg/kg), to the layer of 2.50–3.25 m. This increase, according to [6], is attributed to the reduction barrier and the activity of sulfate-reducing bacteria. The average content of the latter is 20 mln c/mL in the layer of 0.00–1.75 m and 37.6 mln c/mL in the layer of 2.75–4.00 m; while the count is 60 mln c/mL in the layer of 2.50–3.25 m.

In many cases, correlation analysis did not permit us to establish statistically significant relationships between the mineralogical, geochemical, and microbiological indicators, which is explained by the opposite direction and irreversibility (or weak reversibility) of some processes in the peat bog. In particular, mercury accumulation is likely to cause a sharp decrease in the number of sulfate-reducing bacteria, which nonlinearly affects the U content. The possible influence of the composition and concentrations of organic acids should not be left unmentioned. According to [7], the maximum molecular weights for humic acids (HA), consisting primarily of branched aliphatic chains with the dominant aminoacid, alcohol, alkyl, and carbon fragments, can be recorded in the upper part of the peat deposit. Consequently, deeper into the soil, there may be a higher content of the low-molecular HA fraction. Taking into account that most metals form low-soluble compounds with humic acids [6], this cannot but affect the change in their concentrations in the acid extracts in the depths of the peat deposit. This study may help specify the mechanism of HA transport and transformation in the Ob River flow from the upper reaches to the Gulf of Ob [8] in terms of estimating the potential contribution of the Obskoye fen to the signal integrated by HA.

Thus, the following main results have been obtained: (1) the main pattern of the change in the mineralogical and geochemical conditions by depth is the dominance of hydroxide mineral forms and sulfide forms on the top and at the bottom of the peat deposit, respectively; (2) a geochemical reduction barrier the functioning of which determines the enhanced concentrations of U and Hg is formed at the bottom of the eutrophic Obskoye fen; (3) the markedly pronounced impact of sewage discharges consists in an increase in Na contents in acid extracts from the peats; (4) the anthropogenic load is also manifested in the changing composition of authigenic minerals formed in the peats (e.g., in the formation of siderite and barite) and in the additional accumulation of a mixture of suspended, colloidal, and dissolved forms of some metals in the boggy environment, which would most likely have produced mineral forms under natural conditions; and (5) an indirect but quite noticeable anthropogenic impact may be caused by the higher dust load on the fen near the settlements.

The results of studying the mineralogical and geochemical conditions in the Obskoye fen, which were integrated with the results of studying the Vasyugan Bogs [3–5], may help specify the ecological role of the bogs in the formation of the geochemical signal of the Ob River flow under the current anthropogenic load, as well as in the interpretation of the paleoconditions on the "dry" shelf of the Kara Sea prior to the onset of the Holocene transgression.

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