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Geochemistry of iron in organogenic water of Western Siberia, Russia

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Abstract

In the central part of Western Siberia a study of the chemical composition of bog water was conducted. Bog water contains high concentrations of iron and organic matter. By means of thermodynamic methods were calculate the equilibrium of bog water with the major minerals. It was shown, that bog water is in equilibrium with kaolinite, vivianite, α-apatite. Primary aluminium minerals are undersaturated and release iron and other elements, to which a bog water are not at equilibrium and which is dissolve actively.

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Keywords: Western Siberia, The Vasyugan bog, organogenic water, the sources of iron ;

1. Introduction

Western Siberia is characterized of high waterlogging, where the bogs are occupy about 70 % of area. Besides, here is location the largest bog in the world – The Vasyugan bog. These features are playing a significant role in formation of organogenic type of natural waters here [1] which also is characterized by high contents of iron.

In Western Siberia, Fe-containing waters are widespread and form a province. From the depth of 10 m (from 2 m in bogs), groundwater is everywhere enriched with Fe (at concentrations often reaching 30–40 mg/l) [2].

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Bog water hydraulically interacts with groundwater (the bog water is a temporary perched groundwater [3]) therefore, on this article we are researched just a bog water, groundwater were researched earlier[9].

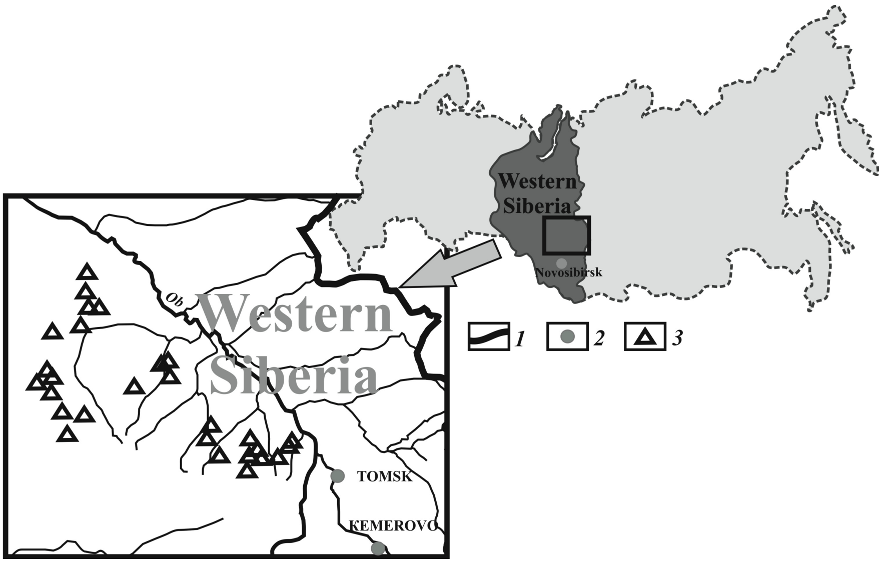

Fig. 1. Arrangement of sampling in natural water: 1 – border of Western Siberia, 2 – city, 3 – selection of bog water, 4 – line of profile of peat deposits

47 samples of bog water were collected (Fig. 1). Water samples were analyzed in the Basic Research Hydrochemical Laboratory, Tomsk Polytechnic University, registered in the System of Analytical Laboratories, GosStandard of Russia, and in the Laboratory of Georesources and Environment Toulouse, National Center Scientific Research, France.

Typical analyzes of non-filtered bog water described in detail in previous studies [4-6] are shown in Table 1.

The study area is lowland, heavily swamped territory, composed of Neogene–Quaternary deposits up to 350 m in thickness. The upper part of the section of those deposits in the major portion of the territory is represented by peat layers up to 8 m in thickness (Fig. 2). The Neogene–Quaternary deposits are underlain by sand–clay Paleogene deposits 200–400 m in thickness, overlying Upper Cretaceous deposits up to 600 m in thickness [4]

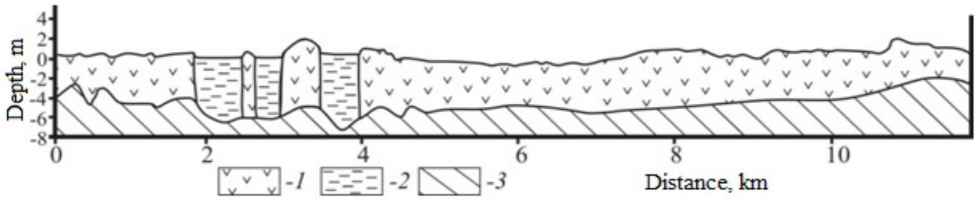

Fig. 2. Profile of peat deposits in an area in The Vasyugan bog (according to [7]): 1 – peat; 2 – water; 3 – mineral base.

2. Chemistry of bog water

Studying bog water chemistry (Table 1) has shown that it is acid or weakly acid (especially in raised and transitional bogs) or nearly neutral (lowland bogs), ultrafresh and fresh with total mineralization varying from 12 to 385 mg/l. The bog water is also high in Fe, reaching, according to some data, 85 mg/l [8]. The concentrations of Cl- and SO_4^{2-} are low, while the concentrations of NO_3, PO_4, and NH_4 are, conversely, higher than in fresh water [4, 9].

The research water is rich of dissolved organic matter, whose total concentration sometimes is far in excess of total mineral salts, as is especially common in raised bogs. Converted to DOC, its amount varies from 12 to 165 mg/l and accounts for 78% of the total mineral matter. An increase in mineralization and pH is accompanied by a decrease in DOC (Fig. 3). According to the calculation data, fulvic acids dominate among organic compounds (the share in terms of DOC varies from 25 to 95%), humid acids on second place and compound about 5–20%.

The concentration of NH^{4+} in bog water varies from 0.5 to 15.6 (with a mean of 3.7) mg/l. The measured values of Eh in some samples vary from –0.4 to+0.1 V. Thus, anoxic gley environment dominates in bog water.

Table 1. Characteristics and chemistry of some types of bog water, mg/l (dash means no data available).

Component	Raised bogs			Transitional bogs			Lowland bogs		
	min	max	mean	min	max	mean	min	max	mean
pH	3,6	4,8	4,0	4,2	5,6	5,2	6,0	7,2	6,6
HCO_3^-	0,5	11,8	4,6	5,0	30,5	13,8	37,0	220,0	128,3
SO_4^{2-}	0,3	11,0	5,0	0,5	9,2	3,0	2,0	31,0	10,9
Cl^-	0,6	29,9	4,8	3,5	28,4	12,3	1,2	21,3	9,2
Ca^{2+}	0,5	6,2	2,6	2,0	20,0	11,8	14,0	156,8	60,8
Mg^{2+}	0,1	4,0	1,1	0,3	48,8	12,3	1,2	12,0	7,7
Na^+	0,1	11,0	2,2	0,1	8,6	2,4	1,0	6,1	3,4
K^+	0,1	2,3	0,8	0,1	1,0	0,5	0,2	2,0	0,1
NH_4^+	0,5	15,6	2,5	1,6	7,8	4,8	1,2	3,7	2,1
NO_3^-	0,2	5,2	0,8	0,1	3,1	0,8	0,3	6,9	2,3
DOC	39,0	165,0	73,3	17,0	120,0	59,4	12,0	31,0	21,8
FA[1]	10,1	95,1	46,1	13,6	61,2	39,0	6,0	25,8	12,7
HA[2]	1,7	21,7	10,6	3,0	17,3	6,2	1,3	11,6	7,1
Fe_{tot}	0,2	4,8	2,2	0,4	17,5	4,5	0,4	2,3	1,4
Fe^{2+}	0,1	3,2	2,0	0,1	12,7	3,8	0,1	1,6	0,9
Al^{3+}	0,05	1,17	0,27	0,05	0,56	0,15	0,05	0,21	0,09
TDS[3]	12	71	26	57,0	122,0	79,7	77,0	385,0	226,5
number of samples	23			13			11		

[1]Fulvic acids; [2]Humid acids; [3]Total Dissolved Solids

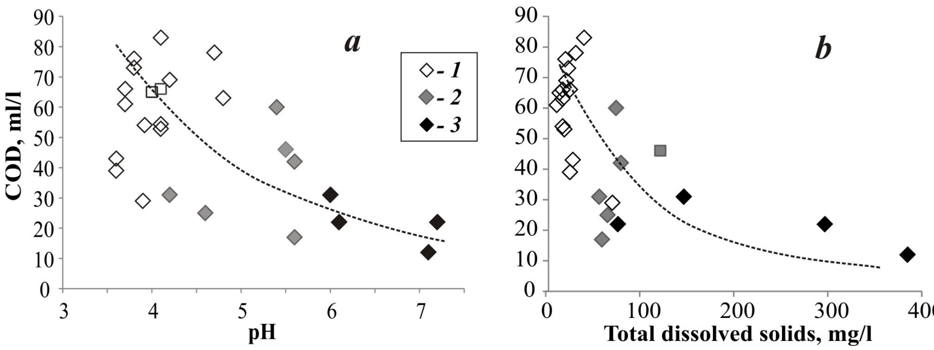

Fig. 3. Dependence of DOC by (a) pH and (b) total salts in bog water: 1 – raised; 2 – transitional; 3 – lowland bogs.

The total concentration of Fe in bog water varies from 0.5 to 17.5 (with a mean of 3) mg/l. The concentration of Fe, as well as all macroelements tended increase from raised to lowland bogs, except for organic matter (OM), which showed an inverse trend. According to the calculations, in the overwhelming majority of cases, Fe^{2+} dominates over Fe^{3+}, though the difference is not significant. At the same time, the amounts of $Fe^{3+}$and Fe^{2+} in raised bogs were comparable.

3. Equilibrium of organogenic water with major rock minerals

Equilibriums between natural waters and minerals were calculated using HydroGeo software complex, based on minimizing Gibbs energy [10].

First, forms of migration of Fe^{2+} and Fe^{3+} in water were calculated. As known from experiments [11-13], Fe shows highest affinity to complex formation with organic matter among all metals, this feature contributing to the retention and accumulation of Fe in water [14-17]

The results of calculation forms of migration of iron in groundwater are given in Table 2.

As can be seen from data in Table 2, complex Fe^{2+} compounds dominate in bog water, where their share can reach 50%. An increase in pH is accompanied by an increase in the share of carbonate forms of $Fe(HCO_3)_2^0$ and $FeHCO_3^+$ (with a total of 26%). The share of other migration forms, i.e., $FeCO_3^0$, $FeSO_4^0$, $FeHSO_4^+$, $Fe(FA)_2^{2-}$, $FeCl^+$, $FeOH^+$ at highest pH, never exceeds 2%.

Table 2. The prevailing forms of migration of Fe in groundwater by the results of physicochemical modeling, % of initial ion concentration (the top number is the minimal and maximal values, the bottom number is mean value).

Major ion	Forms of migration					
	Fe^{2+}	$Fe(HCO_3)^0_2$	$FeHCO_3^+$	$FeCO^0_3$	$FeSO^0_4$	FeFA
Fe^{2+}	50,1–97,1 76,7	0,1–16,6 2,2	0,1–9,5 2,2	0,1–0,9 0,1	0,1–0,8 0,4	2,0–47,4 17,5
Major ion	Forms of migration					
	Fe^{3+}	$FeHA^+$	$FeFA^+$	$FeOH^{2+}$	$Fe(OH)_2^+$	$Fe(OH)^0_3$
Fe^{3+}	0,1–0,8 0,15	0,1–15,8 2,7	0,1–26,4 4,0	0,1–23,0 6,2	39,4–95,9 79,5	0,1–52,7 7,5

Dominating among forms of Fe^{3+} are hydroxocomplexes of $Fe(OH)^{2+}$ (39–96%) and, at lower pH values, $FeOH_2^+$ (23%). The share of $Fe(OH)_3^0$ abruptly increases in weakly alkaline waters (50%). Organomineral complexes $FeHA^+$, $FeFA^+$, and $Fe(FA)_2^-$ rank second in terms of significance (at a total of 30–40%).

Thermodynamic calculations of the equilibrium of water with different carbonate (Fig. 4) and aluminosilicate minerals showed all water to be not in equilibrium with primary minerals of water-bearing rocks: feldspars, muscovite, biotite, pyroxene, hornblende, epidote, peach, and many others. Therefore, minerals of the first group, which are unstable under such conditions, rapidly dissolve and, thus, serve as a source of not only Fe, but also Ca, Mg, Na, K, Si, Al, etc.

Bog water, which show high acidity and low salinity, are not saturated with respect to calcite (Fig. 4). Only water of bog, which show relatively high mineralization (lowland bogs) and higher pH values because of their low OM content, are close to equilibrium with calcites.

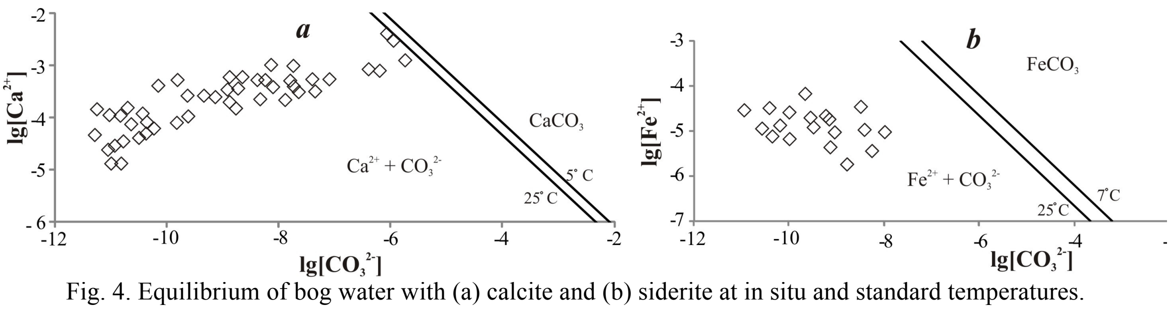

Fig. 4. Equilibrium of bog water with (a) calcite and (b) siderite at in situ and standard temperatures.

The bog water of The Vasyugan Bog is mostly saturated or close to saturation with vivianite (Fig. 5*a*). Analysis of data has shown that the degree of equilibrium in this case is primarily determined by Fe^{2+} concentration—saturation is commonly attained at Fe^{2+} concentration greater than 1 mg/l.

Equilibriums with crystalline α-apatite were calculated using thermodynamic data from [10]. The constant of reaction is 10^{-29}.69 at 25°C. Water in The Vasyugan Bog is oversaturated with respect to apatite (Fig. 5*b*), even if the value of the constant are out of date. Therefore, in bog water, in a reduction (gley) geochemical environment, at relatively low pH and higher concentrations of PO_4^{3-}, equilibrium forms not only with siderite, but also with vivianite and apatite.

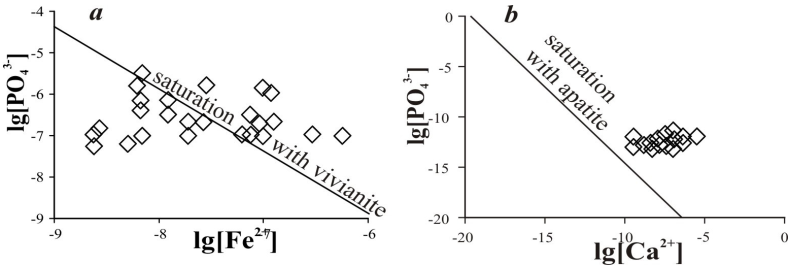

Fig. 5. Equilibrium of water of The Vasyugan Bog with (a) vivianite and (b) α-apatite.

The source of Fe in bog water in the region is aluminosilicate rocks, though this source is indirect, because Fe first concentrates in plants (groundwater–plants–bog water). The presence of a large amount of OM facilitates the accumulation of Fe^{3+} and Fe^{2+} in the form of organomineral complexes. In addition to primary aluminosilicate rocks, bog water, because of its low salinity and pH, as well as high OM concentrations, remain also not in equilibrium with calcite and siderite, which ensures their higher ability to concentrate this element compared with underlying water.

4. Conclusion

In the central part of Western Siberia is widespread organogenic water. By the chemical composition bog water is acid or weakly acid (especially in raised and transitional bogs) or nearly neutral (lowland bogs). ultrafresh and fresh with total mineralization varying from 12 to 385 mg/l. The maximum content of iron in the bog water is 17,5 mg/l by our data, but by the data another author's – 85 mg/l. The concentration of Fe, as well as all macroelements tended increase from raised to lowland bogs, except for organic matter. In bog water iron migrates mainly into the ionic form (Fe2 +) or a complex with organic compounds. An increase in pH is accompanied by an increase in the share of carbonate forms and hydro complexes. By thermodynamic calculations, bog water in equilibrium with kaolinite, vivianite and apatite, with all other minerals - not in equilibrium. The source of Fe in bog water in the region, as well as in groundwater [9], is aluminosilicate rocks, though this source is indirect, because Fe first concentrates in plants.

5. Acknowlegements

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6. References

1. Bulakh, A.G., Bulakh, K.G. Physicochemical Properties of Minerals and Components of Hydrothermal Solutions. Leningrad: Nedra, 1978 p.
2. Rasskazov, N.M., Major features of bog water chemistry: Case study of southeastern part of the Western Siberia, Izv. TPU, 2005, N 4, pp. 55–58.
3. Vernadsky V.I. Histiry of natural water. Moscow: Nauka, 2003. 751 p.
4. Ivanova, I.S., Lepokurova, O.E., and Shvartsev, S.L., Iron-containing water in Tomsk province, Razved. Okhr. Nedr, 2010, N 11, pp. 58–62.

5. Rasskazov, N.M., Major features of swamp water chemistry: Case study of southeastern part of the Western Siberia, Izvestiya TPU, 2005, N 4, pp. 55–58.

6. Shvartsev, S.L. Hydrogeochemistry of Hypergenesis Zone, Moscow: Nedra, 1998.

7. Lapshina, E.D., and Mul'diyarov, E.Ya., Major stages of development of Great Vasyugan Bog, Great Vasyugan Bog: Current State and Development Processes, Tomsk: Institut Optiki atmosfery SO RAN, 2002, pp. 36–44.

8. Ermashova, N.A., Hydrogeochemical features and formation conditions of fresh groundwater in Ob–Chulym interfluve, Siberia Geography Issues, Tomsk, 1979, pp. 95–109.

9. Ivanova I.S., Lepokurovaa O.E., Pokrovsky O.S., Shvartsev S.L. Geochemistry of iron in fresh groundwater of the Sredneobskoy basin (Russia), Procedia Earth and Planetary Science, N 7, 2013. pp.385–388.

10. Garrels, R.M., Christ, C.L. Solutions, Minerals, and Equilibria, Harper & Row, New York, 1965.

11. Dinu, M.I., Comparison of complexing ability of Fulvic and humic acids in the aquatic environment with iron and zinc ions, Water Resources, 2010, vol. 37, N 1, pp. 65–69.

12. Lapin, I.A., Krasyukov, V.N. The role of humic substances in the processes of complex formation and migration of metals in natural waters, Water Resources, 1986, N 1, pp. 134–143.

13. Moiseenko, T.I., Dinu, M.I., Gashkina, N.A., Metal speciation in natural waters and metal complexing with humic matter, Doklady Akademii Nauk, 2012, vol. 442, part 2, pp. 267–271.

14. Dalva M., Moore T.R. Sources and sinks of dissolved organic carbon in a forested swams catchment biogeochemistry, Biogeochemistry, 1991, N 15, pp. 1–19.

15. Fritsch E., Allard Th. Benedetti M.F. Organic complexation and translocation of ferric iron in podzols of the Negro River watershed. Separation of secondary Fe species from Al species, Geochim. Et Cosmochim. Acta, 2009, V. 73, N 17, pp. 1813–1825.

16. Fujii M., Ito H., Rose A.L. etc. Superoxide-mediated Fe(II) formation from organically complexed Fe(III) in coastal waters, Geochim. Et Cosmochim. Acta, 2008, V. 72, N 24, pp. 6079–6089.

17. Pham N., Waite D. Oxygenation of Fe(II) in natural waters revisited: Kinetic modeling approaches, rate constant estimation and the importance of various reaction pathways, Geochim. Et Cosmochim. Acta, 2008, V. 72, N 15, pp. 3616–3630.