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Abstract. The article examines the structure and composition of mineral-organic formations within the hypergenesis zone of Berezitovy deposit (the Amur region). The detailed study has shown that these recent formations are represented by algae identified as *Trentepohlia jolithus* (Linnaeus) Wallroth. The process of macro and micro element accumulation in these formations is likely to have a complex sediment-chemogenic-organogenic nature and results from the flow of the suspended and dissolved substances formed within the hypergenesis zone of sulphide ores. It is also assumed that some elements accumulated in the formations were previously absorbed by algae from the mineralized water environment.

1. Introduction
In hypergenesis zone of sulphide ore deposits, the original sulphide minerals exposed to the atmosphere and hydrosphere are intensively dissolved due to various sulphurous processes, which, in its turn, results in the development of geochemical anomalies in the element-rich water environments. The recent studies aimed to analyze the element concentration in water environments within the hypergenesis zone of sulphide ore deposits have shown that metal content in acid waters can be extremely high, several times exceeding natural background values [1, 2, 3, 4]. In addition, formation of acid and high-mineralized water systems characterized by complex hydrochemisty is always accompanied by the processes of authigenic mineral formation [5], which leads to formation of sulphate, aluminium fluoride and other complex minerals [6].

2. Materials and methods

2.1 Research object
The research was carried out in Berezitovy gold-polymetallic deposit, the Amur River region (Figure 1), located within the Selenga-Stanovoy terrane [7]. The deposit consists of two joined, steeply dipping and hopper-shaped fluid-explosive bodies identified within the Paleozoic granitoids [8]. These bodies are composed of tourmaline-garnet-quartz-muscovite metasomatites which carry stringer-porphyry sulphide mineralization of primarily pyrite, pyrrhotite, false galenite, and galena composition [8]. The concentrations of macro- and microelements have been identified in granites, ore-bearing

metasomatites, surface and ground waters of the ore field [7, 8]. The conducted research has revealed that acid (pH 3.0–4.5) sulphate waters with total salt content up to 10 g/l are the basic reason for anomalously high metal content in surface waters [1].

The hydrochemical study of the surface waters in the Konstantinovsky streamlet, within the head of which Berezitovy deposit is located, has revealed abundant mineral-organic formations recently occurred across the whole valley of the streamlet due to the action of acid sulphate waters. This can be explained by the fact that such formations have not been identified in other water streams, beyond the zone of action within Berezitovy ore field. The mineral-organic formations cause development of significant number of dark-brown and reddish-brown crusts on the surface of block deluvial streamlet deposits up to 1-2 mm in thickness (Figure 2). The crusts are of fragile and loose texture. Most of them contain fine-grained filamentous aggregates of white and light-grey colors. The upper layer is a thin film composed of dark-brown aggregates. The crusts do not dissolve in water.

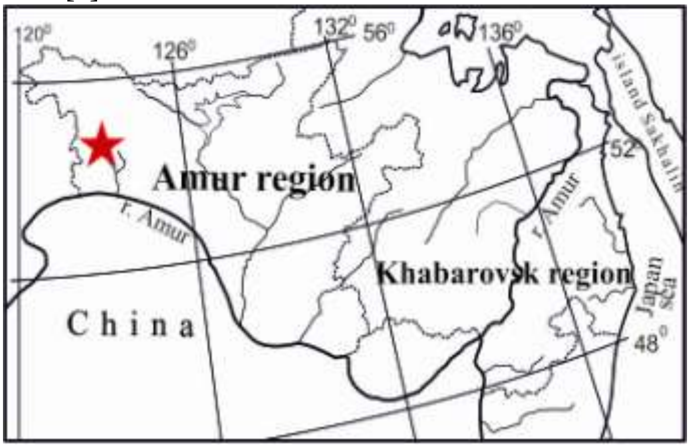


Figure 1. Location map of the study area.

2.2 Research methods

The samples of the mineral-organic crusts were taken from the middle part of the Konstantinovsky streamlet (area of exploratory adit № 2) during three years under various climatic conditions of the summer months. The chemical and microelemental composition was studied on the basis of plasma spectrometry using quadrupole plasma mass spectrometer Agilent 7500 series. In order to identify mineral phases in the crust composition, infrared spectroscopy, X-ray diffraction analysis, and scanning electron microscopy were applied. Infrared absorption spectrum of the samples were recorded by the multifunctional infrared Fourier spectrometer Nicolet 6700 (Termotechno, USA) over the frequency range of 4000-50 cm. The morphological study of mineral aggregates was carried out using analytical scanning electron microscopy, precisely, microscope JSM 6490 equipped with energy dispersive x-ray spectroscopy INCA Energy 350. X-ray diffraction meter (XRD) MiniFlex II manufactured by RIGAKU (Japan) was used for X-ray diffraction analysis. In order to identify the species of algae, light microscopes «Axioskop 40» (Zeiss, lens 40x/0.65 and 100x/1.25 oil) and «Alphaphot–2 YS–2» (Nikon, lens 40x/0.65 and 100x/1.25 oil) were applied. The species of algae were identified in accordance with the procedure proposed by N.A. Moshkova and M.M. Gollerbakh [10]. All studies were carried out on the basis of the Center for Elemental and Isotopic Analysis, Far East Geological Institute (FEGY), Far East Branch of Russian

Figure 2. The recent mineral-organic formations on the surface of the Konstantinovsky streamlet block deluvial deposits.

Academy of Science and Institute of Biology and Soil, Far East Branch of Russian Academy of Science (Vladivostok).

3. Geochemistry of mineral-organic formations

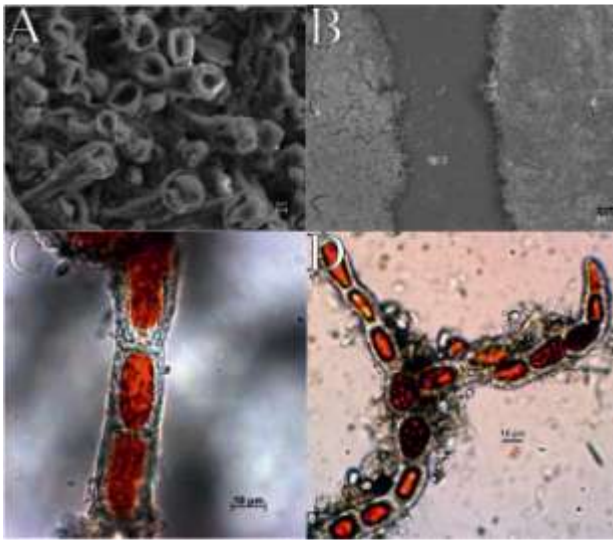
3.1 Formation composition

As initially proposed, the studied crusts were formed as the result of the recent autogenic mineralization. They are basically composed of iron oxide and iron hydroxide formed during chemogenic precipitation from the ore waters. As a rule, such aggregates are well represented in the zone of oxidized sulphide ores. However, the detailed study of the crusts sampled from the Konstantinovsky streamlet has shown that they have more complex mineral-organic origin.

3.2 Biological studies

The crusts analysis by means of scanning electron microscopy has revealed that most of light-grey aggregates are composed of microsponge elongated organic formations of complex structure (Figure 3). More detailed analysis gives grounds to believe that these recently formed aggregates are represented by green algae known as *Trentepohlia jolithus* (Linnaeus) Wallroth (class Ulvophyceae, order Trentepohliales, family Trentepohliaceae) [10]. *T. jolithus* forms thick mats or tussocks 1-2 mm in thickness which are rust colored when wet. As they dry, they dim and turn to dusty-vinous or greyish-green. The tussock fibers abundantly and randomly ramify. The cells are of elliptical and cylindrical shape, slightly tighten near the traverse septums. Cell thickness ranges between 14–27.5 μm, the length - 25–45 μm. The cell membranes are thick and obliquely laminated (figure 3). It is the first time when *T. jolithus* was found in the south of the Russian Far East [9, 11].

Having porous structure, crust organic formations contain a large number of fine-grained mineral granules. Mineral aggregates are composed of hypogene rock-forming minerals, ore, and secondary recently-formed minerals found within the deposit.



A, B – morphology of organic formations (scanning electron microscope EVO-50XVP light microscope); C – thallus fragment, D – lamination of cell membrane (light microscope).

Figure 3. Trentepohlia jolithus.

3.3 Mineral composition

The infrared spectroscopy results have shown that hydromica, kaolinite, quartz, and goethite are the basic minerals that compose the crusts. Based on the X-ray diffraction analysis of heat-treated crusts (at 1100 C$^{\circ}$), the presence of quartz, plagioclase, muscovite (1M and 2M), biotite, and hematite in the crusts has been identified.

Based on the X-ray microanalysis carried out by means of energy dispersive x-ray spectroscopy INCA Energy 350, the following single aggregates (not more than 10-20 μm in size) of hypogene minerals have been identified: melanterite, plumbojarosite, zinc- melanterite, and halloysite.

3.4 Chemical and micro element composition

Chemical analysis of mineral-organic formations (table1) shows that they are composed mainly of silicon oxide, aluminum, and iron. The percentage of carbonates themselves is rather small. The mineral-organic formations are characterized by high loss-on-ignition values. This fact proves the leading role of organic compounds in their composition. High concentrations of ore elements (Zn, Pb, Cu, As and Cd) are identified in the micro element composition of the crusts. This is a characteristic feature of the contaminated surface water, the Konstantinovsky streamlet [1].

It is noteworthy that the concentrations of micro elements in crust samples collected at different time periods and places across the streamlet are rather constant (table 1).

Table 1. Chemical and micro element composition of the recent mineral-organic formations found in the Konstantinovsky streamlet (Berezitovy deposit).

Elements	Sampling years		
	2009	2010	2011
SiO_2 (mas. %)	17.71	23.05	19.32
TiO_2	0.22	0.31	0.25
AI_2O_3	6.09	7.80	6.96
Fe_2O_3 (tot.)	2.52	3.07	2.81
MnO	0.06	0.09	0.07
MgO	0.60	0.71	0.66
CaO	0.68	0.91	0.80
K_2O	1.54	1.91	1.73
Na_2O	0.79	1.03	0.89
P_2O_5	0.15	0.20	0.16
loi[a]	69.50	60.42	65.85
Total	99.87	99.51	99.50
Li (g/t)	6.16	7.54	6.70
Be	0.44	0.64	0.62
Sc	3.09	4.03	3.62
V	21.50	28.30	23.90
Cr	15.10	18,52	17.01
Co	3.60	4.21	3.99
Ni	8.70	11.50	10.50
Rb	67.65	80.98	75.47
Sr	106.22	137.40	118.33
Y	8.70	11.90	10.00
Nb	4.51	6.32	5.27
Cs	2.25	2.48	2.44
Ba	286.30	386.40	327.20
Hf	0.45	0.60	0.49
Ga	7.00	8.94	8.12
Mo	4.02	5.14	5.08
Sn	1.18	1.43	1.26
W	4.13	5.72	5.53
Cu	85.70	87.90	84.00
As	66.60	51.04	50.46
Pb	526.10	796.50	608.70
Zn	726.20	998.70	860.70
Ag	3.56	4.15	3.74
Cd	3.58	4.74	3.72
Th	6.76	8.56	7.61
U	3.09	2.80	3.07

[a.] loi – loss-on-ignition. Determination of element concentration in water samples was carried out by ISP-MS Agilent 7500 (by M. G. Blokhin, E. V. Elovskiy).

This proves the fact that being a basic constituent of mineral-organic formations, algae can significantly contribute to the concentration of elements absorbing them from the Konstantinovsky streamlet.

4. Results and discussion

Thus, it can be stated that the recent mineral-organic crusts found in the Konstantinovsky streamlet are composed mainly of organic formations (supposedly, algae) which were favorable for accumulation of fine-grained minerals suspended, finely dispersed, and dissolved in the surface water of the streamlet. Inorganic material identified in the crusts is a complex combination of chemically and physically weathered host rocks and ores. The area where mineral-organic formations were found is confined to the zone of acid sulphide surface waters of the Konstantinovsky streamlet characterized by high concentrations of heavy metals [4].

The processes of micro element accumulation in biologicals have been previously studied. It has been stated that some types of water plants such as algae and macrophytes are capable of accumulating definite chemical elements including toxic heavy metals [12]. The level of element concentration is basically dependent on hydrochemical composition of water environment and severity of water contamination with heavy metals. Therefore, it is possible to conclude that the organic formations, i.e. algae, found in the Konstantinovsky streamlet significantly contribute to minimizing the impact of contaminated mining runoffs on the environment.

5. Conclusion

The recent mineral-organic aggregates, widely-spread within the valley of the Konstantinovsky streamlet, formed under the impact of acid ore waters of Berezitovy deposit. The process of macro and micro element accumulation in these formations is likely to have a complex sediment-chemogenic-organogenic nature and is the result of the flow of the suspended and dissolved substances formed within the hypergenesis zone of sulphide ores. It is also assumed that some elements accumulated in the formations were previously absorbed by algae from the mineralized water environment.

The specific mineral-organic formations, firstly found in the Russian Far East and confined to the area of the surface waters contaminated with the products of the sulphide ore hypergenesis zone, can be regarded as a new indicator of geo-ecological condition of modern technogenic landscapes.

Acknowledgments

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