Speciation of Chemical Elements in the Waters of the Herberz Historical Mine, Karelia, Russia: Thermodynamic Calculations and Fractionation

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Abstract—The speciation of chemical elements in the waters and its dependence on the dissolved organic matter were studied by a complex of methods, involving thermodynamic calculations and experimental fractionation. The waters were studied at the abandoned and flooded Herberz Mine in the Pitkäranta district, Karelia, Russia. The regional natural waters are typically highly humified. In combination with the unique metallogeny of the rocks, this makes the mine suitable for solving the formulated problems. The eastern shaft of the Herberz Mine was sampled to a depth of 20 m to trance the changes induced by changes in the redox conditions. One of the geochemical characteristics of the waters is their relatively high concentrations of trace elements and a low salinity (TDS, total dissolved solids). All water samples from the Herberz Mine contain elevated concentrations of Zn, Fe, Mn, Cu, Ni, As, and W. Experimental fractionation and thermodynamic simulations of the speciation of chemical elements led us to identify metals whose accumulation most strongly depends on organic matter (OM). Both methods have demonstrated that U, Th, Cu, Ni, and Y show a high chemical affinity to OM. Metals (Cd and Fe) weakly bonded to the functional groups of natural OM, with the predominance of electrostatic bonding and a higher proportion of carboxyl bonds, are most susceptible to transformations with changes in geochemical conditions.

Keywords: heavy metals, organic matter, NICA-Donnan model, experimental data, abandoned mine, fulvic acids, humic acids

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INTRODUCTION

Abandoned historical mines provide unique opportunities of studying long-term interaction between rocks and waters in supergene processes. The long exposure of the dumps and stagnant hydrody-namic regimes in flooded mines allow us to assess the environmental impacts of the mining operations long after the mines were abandoned: to study the super-genic transformations of the ores and estimate the roles of the various factors affecting the natural water chemistry at the mining sites. It is worth mentioning that the harmful impacts of abandoned mines are widespread both in Russia and elsewhere and are actively studied (Yurkevich et al., 2023; Aykol et al., 2003; Wang et al., 2019).

Natural organic matter (OM) occurring in waters at mining sites notably modifies the geochemistry of these waters. Studies with the application of a wide spectrum of techniques (e.g., Dinu, 2018; Dinu and Baranov, 2022; Moiseenko, 2017) have shown that OM can differently affect the accumulation of behavior of various chemical elements in natural waters. Moreover, an important role in this process is played by the characteristics of the organic compounds, which depend, in turn, on several factors, such as the landscape-climatic parameters of the territory. Keen interest in the problem of the effects of OM contents on the behaviors of toxic elements in natural waters (Moiseenko et al., 2021) reflects the pressing character of this problem. Waters in the North are typically highly humified, and this makes the northern Ladoga region, with its unique metallogeny, highly suitable for studying how OM affects the behaviors of chemical elements in natural waters. The abandoned Herberz mine in the Pitkäranta district, Karelia, was chosen for this study in attempt of the comprehensive evaluation of the effects of organic matter on the chemical com-



Fig. 1. Location map of the study area and mines and a photo of the eastern shaft of the Herberz historical mine (prepared using materials at https://d-maps.com/carte.php?num car=67018&lang=ru).

position of waters at the site of the mine, which is characterized by a stagnant hydrodynamic regime, with the application of thermodynamic simulations and experimental fractionation of species of chemical elements.

HISTORICAL OVERVIEW

The Herberz Mine is one of the historical industrial facilities of the so-called Mining Road (Shchiptsov et al., 2014), which extended from the town of Petrozavodsk on Lake Onega across the northern Ladoga territory to the town of Kuopio in Finland. The study area belongs to the so-called New Ore Field, which lies 1.5–2 km east of Pitkäranta (Fig. 1). The New Ore Field comprised the Herberz I, Herberz II, and Valkealampi mines, with the latter nowadays caved in and thus not accessible any more for studying. The Herberz I Mine is one of the best preserved mines and has a status of a historical-cultural heritage monument of Karelia. The well-preserved dumps of this mine attract attention of geologists thanks to the diversity of the minerals. The Herberz I Mine is located not far from the town of Pitkäranta, is thus readily accessible, and attracts many tourists.

The mine was named after B. Herzberz, one of the owners of Ladoga Joint Venture. Ores were produced by the Herberz I and Herberz II mines (Trüstedt, 1907; Shchiptsov et al., 2014). Herberz I operated from 1896 through 1903 and has produced 31 300 t magnetite ore. Two vertical mine shafts were sunk at a distance of 33 m from each other and reached depths of 33 m (western shaft) and 57 m (eastern one). The orebody 0.5–1.5 m thick was encountered in them at depths of 28 and 43 m, respectively. Ore was produced at three levels by drifts at depths of 18, 25, and 30 m, which

were driven on both sides of the Easternmost Shaft along the strike of the orebody. The Herberz II Mine is located 550 m southwest of the eastern shaft. It has produced 619 tonnes magnetite ore in 1899–1900. The depth of the shaft is 25 m.

Starting in 1897, ore from the mines of the New Ore Field was delivered via a cableway to the Ristioja processing plant south of the town of Pitkäranta.

Nowadays all Herberz underground mines are flooded. Collapse sinks were formed above the lined shafts, and loose ground creeps. Water level in the Herberz I shaft reaches the fifth timber-work level from the top. The upper timber-works of the Herberz II mine shaft are destroyed by creeping ground in the west. Nevertheless, the mine waters can be sampled, and their samples were collected in 2021–2023 by a research team.

GEOLOGY OF THE STUDY AREA

The study area is constrained within the Raahe– Ladoga junction zone of the Karelian craton and Svecofennian orogen. The oldest regional geological structures are domes (AR_2-PR_1) , which consist mostly of granite-gneisses. The domes are framed by metavolcanic–metasedimentary rocks of the Sortavala Group (PR_1) : marbles that are locally replaced by pyroxene and garnet skarns, amphibolites, and graphite-bearing quartz–feldspar–biotite schists. They are overlain by mica schists of the Pitkäranta Group. Orogenesis at 1.8 Ga resulted in that the granite-gneiss domes were remobilized and the surrounding rocks acquired conformable structures.

In the Mesoproterozoic at 1547–1530 Ma (Neymark et al., 1994; Amelin et al., 1997), the metamor-



Fig. 2. Geological map of the area of the Herberz Mine and geological profile across this territory (modified after Trüstedt, 1907). (1) Granite-gneisses; (2) granites; (3) actinolite schists; (4) amphibolite schists; (5) mica schists; (6) marble-replacement skarns; (7) loose rocks; (8) lake; (9) rivers and streams; (10) lines of the profiles; (11) mine shafts; (12) faults.

phic rocks were intruded by granites of the Salmi anorthosite—rapakivigranite complex (ARGC). According to (Dukhovskii et al., 1994), the top of the granites in the area of the "New Ore Field" occurs at a depth of a few hundred meters. Trüstedt (1907) pointed out that the Herberz II Mine exposed an apophysis of greisenized granite. Many researchers are prone to believe that the skarns and greisens with Sn—Fe—base metal mineralization that was deposited in them were formed in relation to the emplacement of the Salmi ARGC (Larin, 2011).

The "New Ore Field" occurs in the southeastern surroundings of the Pitkäranta (Koirinoja–Pitkäranta) gneiss-granite dome. All historical mining works in the Pitkäranta area are constrained within the skarnified marbles of the Sortavala Group that envelop gneiss-granite domes. The Sortavala Group is made up in this area of two carbonate-rich layers (lower and upper ones) and an amphibolite strata in between. The Herberz I and II mines developed the upper and lower carbonate units, respectively (Fig. 2).

The study area includes no bedrock outcrops, because the bedrocks are everywhere overlain by loose Quaternary sediments. The mineralogy and petrography of the rocks at the mine can be studied only in material found in the mining dumps. The mineralogy of the rocks was studied to interpret relations between concentrations of components in the waters and in the rocks.

SAMPLING PROCEDURE AND STUDY METHODS

Natural waters were sampled in the mine shafts of the Herberz Mine by a research team during the 2021, 2022, and 2023 fieldwork. Nine water samples were taken: P1 and P2 were taken from a depth of 2 m and from the surface water layer of the eastern shaft of Herberz I in 2021; samples 22-01 and 22-02 were from the western shaft of Herberz I, from depths of 0.5 and 3 m, respectively; 22-03 is from the Herberz II Mine (collected in 2022); and 23-61–23-64 originated from Herberz I, depths 0.2, 5, 10, and 20 m, respectively, and were taken in 2023. Samples from various depths were taken using a bathometer. In addition, typical rocks were collected at the dumps during the fieldwork.

When sampling the waters, pH, Eh, conductivity (HM Digital), dissolved oxygen content (WaterLiner WDO-64 oxymeter), and temperature were determined at various depths. The temperature of the water and its conductivity were measured in 2023 in the east-

ern shaft of Herberz I at a depth of 20 m using a Solinst 3001 levelogger. Preparatorily to analysis for chemical elements and ion chromatography, the samples were filtered through nylon membranes with 0.45- μ m pores into clean Falcon test tubes 15 mL in volume.

The components of the carbonate system and organic matter were analyzed in samples stored in 300-mL bottles, which had been washed three times with the studied water before water samples were poured into them.

The samples collected during the 2021 and 2022 fieldwork were analyzed for Ca, Mg, Na, K, Fe, Al, and S by AES-ICP on an iCAP 6500 DUO (Thermo Scientific) plasma spectrometer (analyst I.N. Gormyak), for trace elements by MS-ICP on an X-series 2 (Thermo Scientific) quadrupole mass spectrometer (analyst D.N. Dogadkin), and for anions by ion chromatography on a Dionex ICS-6000 (analyst A.A. Dolgonosov). The samples collected in 2023 were analyzed for ions by capillary electrophoresis on a Kapel 205 (analyst V.N. Kolotygina), AES-ICP, and MS-ICP

(V.K. Karandashev). Concentrations of HCO_3^- were determined by potentiometric titration on an Expert-001 (Econics-Expert) high-precision analyzer according to the State Standard GOST 31957-2012 (analyst A.S. Toropov). Dissolved organic carbon (DOC) was analyzed by oxidation by $K_2Cr_2O_7$ and spectrophotometry on a Shimadzu UV-1900i. The calibration and recalculation of the results into organic carbon were conducted using glucose oxalic acid standard reference samples. Proportions of fulvic and humic acids (FA and HA, respectively) were determined upon preconcentrating on a XAD-8 and subdividing the eluate at pH 2 with subsequent analysis for DOC (Konyshev et al., 2021).

To evaluate how much element *x* is enriched in the waters relative to the rocks, we calculated its accumulation coefficient, as proposed by A.I. Perelman (1989),

$$K_x = (m_x \times 100)/(an_x),$$
 (1)

where m_x is the concentration (mg/L) of element x in the water, a is the total concentration (mg/L) of mineral compounds dissolved in the water, and n_x is the concentration (wt %) of element x in the rock. The composition of the rock is assumed as corresponding to the average concentration of chemical elements in the upper continental crust (Grigor'ev, 2009).

The method applied to evaluate the tetrad effect is based on evaluating the deviation of the measured REE concentrations of the central members of a tetrad to the value calculated by interpolating from the concentrations of the first and last elements of the tetrad (Irber, 1999)

$$T_{i} = \left[\left(C_{2cn} / \left(C_{1cn}^{2/3} C_{4cn}^{1/3} \right) \right] \right] / \left[C_{3cn} / \left(C_{1cn}^{1/3} C_{4cn}^{2/3} \right) \right]^{0.5}, \quad (2)$$

$$TE_{1,3,4} = (T_1 \times T_3 \times T_4)^{1/3}$$
(3)

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where T_i is tetrad *i*; C_n is the number of the element in the tetrad, from 1 through 4; C_{cn} is the chondrite-normalized concentration of the element; and TE_n is the integral tetrad effect.

The speciation of elements, with regard to OM, in the analyzed waters were calculated with the Visual Minteq software, using the NICA-Donnan model. The model assumes that OM is of macromolecular nature, i.e., it contains several charged functional groups. The NICA-Donnan model is a combination of a description of the isotherm of nonideal competitive adsorption (NICA) on a heterogeneous material in combination with the Donnan electrostatic model, which describes electrostatic interactions between ions and humic matter. The distributions of ions between two phases in the above submodels are controlled by Donnan equilibrium. It is assumed that the amount of a bonded cation in the NICA submodel is in equilibrium with the concentration of this cation in Donnan phase. A detailed description of the NICA-Donnan model and critical compilation of experimental data on bonding of metals with humic matter used in the current version of Visual Minteq is presented in (Milne et al., 2003). It is pertinent to mention that the NICA-Donnan model assumes an interaction with 1:1 stoichiometry of the newly formed complexes. The speciation of chemical elements in the studied natural waters was numerically simulated for samples P1, P2, 22-01, 22-02, and 22-03.

The saturation indexes (SI) were also calculated with Visual Minteq. The SI, were calculated with regard to complexation reactions, including those with OM, and redox reactions for multivalent elements. SI were calculated by Eq. (4)

$$SI = \log IAP / K_{SP}.$$
 (4)

where IAP is the product of ion activities, and K_{SP} is the constant of the solubility product of the mineral. Negative SI values mean saturation, and near-zero values correspond to equilibrium between the solution and mineral. The calculations were conducted for all possible phases of the O, H, C, Cl, S, Ca, Mg, Na, K, Fe, Mn, Co, Ni, Cu, Zn, Ba, Pb, Th, and U system, but the indexes presented below pertain to minerals that were in equilibrium or close to it. The starting composition of the solution was specified in the form of ions (for major elements) and elements (for trace elements). The acidity and redox state were specified as pH and Eh according to the field measurements. The calculations were carried out based on data on the field measurements of the water temperature. The saturation index was calculated for all samples.

The speciation of elements in the natural waters was experimentally studied as illustrated by the flowprocess chart in Fig. 3, using the sequential fractionation of the hydrophobic component of the natural OM (of dominantly humic nature), positively and negative charged particles. To experimentally study in



Fig. 3. Flow-process chart of the fractionation of element species found in the natural waters.

detail the metal species bonded to organic matter, fractionation was carried out with samples of the surface mine waters (samples P2 and 22-01). The water (100-250 mL) was subsequently passed through cartridges with DAX-8 nonpolar adsorbing agent to get rid of the humic constituent of the natural OM, then through DOWEX 50W-X8 cation-exchange resin, and then through DOWEX 1x8 anion-exchange resin. The resins and cartridges with an adsorbing agent had been preparatorily washed, and the purity of the eluants was controlled in compliance with the protocol (Guggenberger, 1994). The cartridge with a nonpolar adsorbent was preliminarily activated with methanol.

In addition, a set of replicate experiments was conducted at pH 2 to assess the proportion of metals strongly bonded to OM. The pH values were adjusted using HCl and NaOH solutions. The relative concentration of a species in the experiments was evaluated from the difference between the concentrations in the fractions and their ratios to the total concentration in fraction F0. If the differences between the fractions were statistically false or suspect (only for ionexchange resins), then the resins after the experiments were washed with a small volume of 10 M HNO₃, the eluate was analyzed for concentrations of the elements, and the mass balance was calculated. The totals of the fractions, with regard to the mass-balance data, varied in the experiments from 87 to 107%. We used reactants of the classification *for ultratrace analysis* and Milli-Q Millipore (<1 µg/L DOC), 18.2 MΩ/cm deionized water. The mass spectrometry of the solutions after fractionation was carried out on a PlasmaQuant MS Elite. The accuracy of the measurements was assessed by the introduced–found method, using ICP-MS-68 standard solutions High Purity Standards, with the introduction of an additive into the same samples as a matrix within the range of 50–200% of the actual concentration of the element in the samples. The yield of the additive was 89 to 106%.

The main characteristics of the colloids were determined by methods of photon correlation spectroscopy on a Malvern Nano ZS. The concentration and average hydrodynamic *z*-diameter were calculated by the algorithm of multimodal analysis by the method of non-negative least squares (NNLS) based on the dynamic light scattering with a narrow-band He–Ne laser (633 nm) and radiation scattering to 90°. The zeta potential was calculated from the electrophoretic mobility with the Helmholtz–Smoluchowski equation.

Rock samples from the dumps were utilized to manufacture sections to study by optical and scanning-electron microscopy. The mineralogy of the rocks was examined under a Tescan MIRA 3 electron microscope equipped with an X-MAX system for local EDS analysis of the chemical composition of minerals.

RESULTS

Mineralogy of the Rocks

The rocks sampled at dumps of the Herberz Mine are skarns that developed by replacing marbles. The skarnified rocks at this deposit belong to the following four types, with gradual transitions between them:

(1) Ore like type, with magnetite (no less than 80%) and subordinate amounts of phlogopite, chalcopyrite, and carbonate relics;

(2) garnet-pyroxene skarn with a lower content of magnetite and higher contents of carbonates (up to 20-30%) and with chalcopyrite and relicts of carbonates;

(3) same but containing visible fluorite;

(4) weakly skarnified marble, which is dominated by carbonates.

Inasmuch as the percentages of minerals in the rocks have not been determined when the mine operated, and material available from the dumps fail to provide representative information, such estimates can ne done only qualitatively. The rocks consist of

• oxides: magnetite, unidentifiable uranium oxides, and scheelite;

• phosphates: fluorapatite (2–2.7 wt % F);

• fluorides: fluorite;

• carbonates: dolomite (containing up to 3 wt % MnO) and calcite (containing up to 0.2 wt % Fe);

• silicates: phlogopite, serpentine-group minerals, epidote-group minerals, chlorite-group minerals, andradite-grossular garnet, and pyroxene (mostly diopside);

• sulfides: chalcopyrite, pyrite, sphalerite, and (according to Trüstedt, 1907) galena.

It is worth mentioning that, according to literature data, ores from the "New Ore Field" were different from those from the "Old Ore Field" in containing less sulfides and no cassiterite (Trüstedt, 1907).

Chemical Composition of the Natural Waters

The Herberz mine shafts are now flooded, and available for sampling. Figure 4 represents the field measurements and the variations in the physicochemical parameters of the waters with depth. The observed range of the pH variations is 6.33 to 8.2, and hence, the waters can be classified into different types from weakly acidic to weakly alkaline (Fig. 4). In all shafts, Eh notably decreases with depth from positive or small negative values (42 to -9 mV), which correspond to transitional redox parameters of the waters, to -172 mV, i.e., reduced parameters of the waters. The variations in the redox conditions with depth are likely controlled primarily by the decrease in the concentration of dissolved oxygen, which is the main potential-controlling component of surface natural waters. The dissolved oxygen content in the waters changes most contrastingly in the surface water layer 0-0.5 m, gradually decreasing to about 2 mg/L. The exception was water from the Herberz II Mine, in which dissolved oxygen content monotonously increased from 2.8 to 3.7 within the depth range of 0.5-2.75 m. The variations in the parameters with depths are most vividly demonstrated by the measurements in 2023 in the eastern shaft of Herberz I to a depth of 20 m (Fig. 4b).

The temperature of the water also decreased with depth to below 5° C at a depth of approximately 4.5 m and then did not change with depth (Fig. 4b). It should be stressed that the situation with the other mine shafts in which the measurements were conducted was analogous.

The total dissolved solids (TDS) of the waters increased with depth, likely because of the longer interaction time of the waters with rocks. According to their TDS, all of the waters are fresh. The waters in the surface layer contain the lowest TDS, 68 mg/L on average, in all of the sampled shafts. TDS increases with depth: 81 mg/L is the average value at a depth of 2-3 m, and 138 mg/L is the average at a depth of 20 m.

Chemically, the waters are hydrocarbonate calcium-magnesium (Fig. 5). The strongly dominant ion is hydrocarbonate. The cation composition of the waters are more diverse: the dominant cation is calcium, the magnesium concentrations is 20%-equiv/L and higher, and the samples collected during the 2023 fieldwork contain elevated sodium concentrations, up to 30%-equiv. in a sample from a depth of 20 m.

The trace-element composition of the waters makes it possible to distinguish their types according to the ore elements in these waters (see Supplementary Table 1). First of all, these are Fe, Zn, and Cu. Iron concentrations in a sample from greater depths are higher, whereas the zinc and copper concentrations show opposite tendencies. It is most likely that Fe, Cu, and Zn are transferred into the natural waters at the oxidative dissolution of sulfide minerals (pyrite, sphalerite, and chalcopyrite) contained in the rocks. A discernible increase in concentration was also found for Pb, U, and Th. In addition to these elements, an increase in concentrations above the geochemical background was found for Al, V, Cr, Co, As, Rb, Sr, and Mo. The geochemical background values were assumed according to data on surface waters in the Northwestern Federal Territory of Russia and some territories in Finland and Norway (State..., 2007). The trace-element composition of the waters is discussed below in more detail using the accumulation coefficients (Fig. 6), because the absolute concentrations of trace elements are very low, and the found relations and trends can be more conveniently demonstrated using normalized values.

According to calculations, most elements in the discussed natural waters are characterized by intermediate accumulation (Ca, Mg, Na, Li, Mn, Zn, As, Sr,



Fig. 4. Variations in the physicochemical parameters of waters at the Herberz Mine with depth for samples taken in (a) 2021–2022 and (b) 2023. Data on the shafts: (1) Herberz I, western; (2) Herberz II; (3) Herberz I, eastern (2021); (4) Herberz I, eastern (2023).

Y, and W), and a smaller group of elements is characterized by weak accumulation (Si, V, Co, Ni, Rb, and Ba). Some elements belong to different accumulation group in the various samples. The only element that is strongly enriched in the waters is sulfur (except only the sample from a depth of 20 m). In addition to it, the profile of sample 23-64 shows Ti and Co as elements with the lowest K_x and W as an element whose K_x is the greatest. It is also worth mentioning that the profile of elements at Site 22-03 differs from those of all other water samples by values for Li, Y, Pb, U, and Th. This sample was taken from the Herberz II Mine, which is located at a certain distance from Herberz I, and the reason for these differences seems to the differences in the composition of the rocks with which the waters interact. The elemental composition of Site 22-03 suggests the absence of drainage, or insignificant drainage, for the rocks enriched in Li, Pb, Th, and U, which serve as the sources of these elements for the waters of the other mines, or otherwise, the absence of the inflow of groundwater with such an elemental profile. The water at this site contains a higher concentration of the sulfate ion. The differences in the hydrogeochemical composition parameters of the drained rocks for the groups of Herberz I Mine and those of Herberz II are also confirmed by the differences in the configurations of the REE patterns and the contrasting differences between the Eu (Eu/Eu*) anomalies (Fig. 7). The shapes of the individual REE patterns of the samples from different depths of water in the same shaft are almost identical, but the total concentrations of this group of elements differ. The normalized La/Lu ratio (the slope of the REE pattern) also varies from 2.6 to



Fig. 5. Piper diagram for the natural waters of the Herberz historical mine. Data on the shafts: (1) Herberz I, eastern; (2) Herberz I, western; (3) Herberz II.



Fig. 6. Accumulation coefficients for some elements in the waters of the Herberz historical mine. Data on: (1) sample P2; (2) sample 22-01, (3) sample 22-03, (4) sample 23-64; (5) geochemical background (*State...*, 2007).

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Fig. 7. REE patterns of the natural waters of the Herberz Mine. Data on: (1) Herberz I, eastern (average of data on 2021–2023), (2) Herberz I, western (average on data on 2022); (3) Herberz II (2022).

3.8 in samples from the group of mines Herberz I and about 7.1 for the water from the Herberz II Mine.

The chondrite-normalized (McDonough and Sun, 1995) REE patterns of the water samples (Fig. 7) show a W-type tetrad effect (Irber, 1999). This effect is typically shown by algae, seawater, and groundwaters (Masuda and Ikeuchi, 1979). Because of the inaccuracy of ICP-MS analysis, the integral tetrad effect calculated according to (Irber, 1999) for tetrads 1, 3, and 4 for W-type is significant if $TE_{1, 3, 4} \le 0.9$ (Yasnygina and Rasskazov, 2008). However, none of the water samples does meet this requirement. Inasmuch as the intensity of this effect in aqueous solutions is related to complexation (Kawabe and 1992; Kawabe et al., 1999; Kawabe, 1999), and REE show strong affinity to OM (Tang and Johannsson, 2003), the tetrad effect should likely be stronger if OM is more intensely introduced into the waters of the mine.

Remote-sensing data indicate that the conductivity increases with depth, i.e., TDS increases, and its increase is associated with an increase in the concentrations of major and trace elements. Because of this, the accumulation coefficients for the samples collected in 2023 are closely similar (Fig. 6).

The accumulation coefficients calculated for the background values (Fig. 6) at the points of major ele-

ments and usually slightly higher than the values calculated for mine waters and are, conversely, lower for trace elements. This is best seen for Al, Fe, Zn, U, and Th and can also be detected for Co and As. This comparison confirms that the natural waters contain elevated concentrations of ore elements. However, no such relations were obtained for Cu and Ni, which is explained by the high background concentrations of these elements, which are, in turn, caused by high concentrations of these metals in natural waters in the areas of the Severonickel and Pechenganickel smelter facilities, with these areas also included in the calculations of the background.

It is worth mentioning that the accumulation of chemical elements in the natural waters results from interaction between these waters and rocks of the mine and is controlled by saturation with respect to minerals and by complexation. These processes are discussed below.

Saturation Indexes

Among the mineral discussed herein, the most interesting ones are Fe-bearing phases (Table 1). Hematite and magnetite are the most stable Fe phases, and their calculated saturation is caused by the equilibrium approach applied in these calculations. Under

Mineral	Sample								
	22-01	22-02	22-03	P1	P2	23-61	23-62	23-63	23-64
Calcite	-5.5	-2.5	-2.5	-1.9	-2.3	-0.8	-0.9	-0.6	-0.2
Cerussite	-7.9	-4.3	-6.2	-4.6	-16.0	-4.6	-5.0	-4.8	-4.7
$Fe(OH)_2(c)$	-4.2	-4.7	-4.5	-3.5	-4.7	-1.3	-1.9	-0.8	-0.5
Ferrihydrite	-2.7	-6.1	-4.4	-2.5	-2.0	0.4	-0.1	0.9	0.4
Goethite	0.0	-3.0	-1.3	0.7	1.1	3.5	3.0	4.1	3.6
Hematite	2.5	-3.6	-0.3	3.7	4.5	9.4	8.4	10.4	9.5
Lepidocrocite	-0.8	-3.2	-1.6	0.6	0.8	3.4	2.9	4.0	3.5
Maghemite	-5.3	-10.1	-6.9	-2.5	-2.1	3.1	2.1	4.3	3.4
Magnesite	-7.0	-3.6	-3.7	-2.8	-3.4	-1.8	-1.8	-1.5	-1.0
Magnetite	6.3	-1.1	2.5	7.2	7.1	15.2	13.7	16.7	16.1
Rhodochrosite	-5.2	-2.1	-2.1	-1.3	-2.1	-0.2	-0.3	0.0	0.5
Siderite	-4.3	-1.2	-1.3	-0.4	-1.6	0.5	0.0	0.8	1.4
Smithsonite	-5.9	-3.1	-3.2	-2.6	-2.4	-0.8	-0.8	-0.5	-0.3
Witherite	-9.0	-5.9	-5.8	-5.5	-5.8	-4.2	-4.2	-4.0	-3.5
Zincite	-4.5	-6.3	-5.9	-5.4	-5.0	-2.5	-2.4	-2.0	-2.0

 Table 1. Saturation indexes for minerals calculated for the natural waters of the Herberz Mine

other natural climatic conditions, secondary hematite can sometimes be formed (Sracek, 2015), but the secondary phases in our situation are obviously goethite, ferrihydrite, and lepidocrocite. At greater depths, where the Fe(II) content is likely higher than at the surface, the water is close to saturation with respect to the phase $Fe(OH)_2$ and is saturated with siderite. In addition to siderite, the waters at deeper levels are saturated with rhodochrosite. The water samples taken at greater depths have higher saturation indexes for carbonate minerals (calcite, magnesite, Cerussite, smithsonite, and witherite) than the surface water, which is likely explained by the higher concentrations of the metals and carbonate ion at greater depths.

Speciation of Chemical Elements in the Natural Waters

The distributions of the discussed chemical elements between their species are discussed with regard to the concentrations of organic acids of various type, the bonding types, and the total concentrations of the elements. The model deals with two types of bonds (phenol and carboxyl) and metal interactions with a Donnan-type gel phase.

The following groups of elements can be distinguished according to the speciation of these elements. The largest group comprises chemical elements whose dominant species (85-96%) are simple ionic compounds, and the second most abundant type (3-7%) of species is organic species in a Donnan phase. Other types of bonds with organic matter and sulfate and carbonate species account for approximately 1% of the total concentrations of the elements in the analyzed waters. This group of elements comprises Ca, Mg, Mn, Sr, Zn, Ba, Co, and Cd (Table 2). The table reports the minimum and maximum concentrations (in %) of the species calculated relative to the concentrations of the chemical elements.

A similar distribution between species is shown by Ni and Fe(II). Their dominant species are also simple ionic compounds: 71-76 and 75-89% for Ni and Fe(II), respectively. These elements are characterized by a higher percentage of organic complexes. The Donnan phase makes up 3-6% of the total concentrations of these metals. The concentrations of the fulvate complexes with carboxyl-type bonds are higher: 36% on average for Ni and 13% for Fe.

The dominant Fe(III) species are those with humic and phenolic types of bonds: 78-94%. Note that the rest of Fe(III) belongs to the group of organic complexes: fulvate, mostly with carboxylic bonds.

Pb, Cu, V, U, and Th also typically occur only as organic complexes, mostly phenolic, i.e., with stronger binding. Fulvate complexes with a phenolic-type bonds account for up to 100% U, up to 76% Cu, 93% Pb, 94% V, and 100% Th. Another widespread speciation type of Cu and Pb is fulvate with carboxylic (weaker) bonds.

Y typically occurs as carbonate (up to 64%) and simple ionic (up to 28%) species, and Donnan phases compose up to 31% Y. The strongly dominant Cs species are simple ionic. The dominant Be, Al, Ti, and Sn species are hydroxylic ones.

In considering the speciation of chemical elements with regard to the contents of organic matter, the fol-

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Са			Ba	Th			
Ca ²⁺	91-96	Ba ²⁺	91-96	ThFA(phen)	100		
CaSO ₄	1-2	BaSO ₄	0-1	l	J		
CaHCO ₃ ⁺	0-1	BaHCO ₃ ⁺	0-1	UO ₂ HA(phen)	100		
CaD	3-7	BaD	3–7	Y	[
Mg			Ni	Y ³⁺	16-28		
Mg ²⁺	91–96	Ni ²⁺	71–76	YOH ²⁺	0-1		
MgCl	0-1	NiSO ₄	0-1	YSO_4^+	1-5		
MgSO ₄	0-1	NiCO ₃ $0-1$ $Y(CO_3)_2^-$		$Y(CO_3)_2^-$	0-2		
$MgHCO_3^+$	0-1	NiHCO ₃ ⁺	0-3	YCO ₃ ⁺	34-64		
MgD	3-7	NiD	4—6	YHCO ₃ ²⁺	2-3		
N	In	NiFA(carb)	6-10	YD	16-31		
Mn ²⁺	87–94	NiFA(phen) 2–88		Cs			
MnSO ₄	0-1	NiHA(carb)	1-4	Cs ⁺	100		
MnHCO ₃ ⁺	1	NiHA(phen)	0-5	Мо			
MnCO ₃	0-1	Fo	e(II)	MoO ₄ ²⁻	85-89		
MnD	3-7	Fe ²⁺	75-89	MgMoO ₄	5-10		
MnFA(carb)	1-3	FeSO ₄	0-2	CaMoO ₄	5-6		
S	Sr	FeHCO ₃ ⁺	FeHCO ₃ ⁺ 0–1		W		
Sr ²⁺	90-93	FeD	3—6	WO_4^{2-}	85-89		
SrSO ₄	1-2	FeFA(carb)	7—17	MgWO ₄	5-10		
SrHCO ₃	1	FeHA(phen)	0-1	CaWO ₄	5-6		
SrD	3-7	Fe(III)		Be			
C	Co	FeFA(carb)	5-20	Be ²⁺	0-3		
Co ²⁺	84–91	FeFA(phen)	1-2	Be(OH) ₂	96-100		
CoSO ₄	0-1	FeHA(carb)	1	Ti			
CoHCO ₃ ⁺	2-5	FeHA(phen)	78–94	Ti(OH) ₄	100		
CoD	3-7	Pb		Sn			
CoFA(carb)	2-3	Pb ²⁺	0-1	$\operatorname{Sn}(\operatorname{OH})_{6}^{2-}$	99		
CoHA(carb)	0-1	PbFA(carb)	4-8	A	1		
Zn		PbFA(phen) 83–93		AlOH ²⁺	1-2		
Zn ²⁺	85-93	PbHa(carb)	1-6	$Al(OH)_2^+$	2-17		
ZnSO ₄	0-2	PbHA(phen)	1-3	Al(OH) ₃	1-18		
ZnCO ₃	0-1		Cu		2-35		
ZnHCO ₃ ⁺	1-2	CuFA(carb)	13–29	$Al_2(OH)_2CO_3^{2+}$	4-58		
ZnD	3-7	CuFA(phen)	49–76	AlFA(phen)	27-48		

Table 2. Speciation of metals (% for each element) in the natural waters of the Herberz Mine

Table 2. (Contd.)

ZnHA(carb)	0-2	CuHA(carb)	1–6	AlHA(phen)	1-4
ZnHA(phen)	0-2	CuHA(phen)	6-16	As(V)	
Cd		V	/	HAsO ₄ ²⁻	20-42
Cd^{2+}	87	VOFA(carb)	0-1	$H_2AsO_4^-$	58-80
$CdCl^+$	1	VOFA(phen)	83–94	As(III)	
$CdHCO_3^+$	1	VOHA(carb)	1-4	H ₃ AsO ₃	100
CdD	3	VOHA(phen)	4		
CdFA(carb)	7				

D is a Donnan-type phase. The table lists complexes whose concentrations are higher than 1%.

lowing phases can be distinguished. The Donnan-type phase accumulates mostly the following elements (percentage values in parentheses correspond to the Donnan-type phase): Ca (54-66%) > Mg (23-30%) > Fe (8-13%) > Na (1%) > Mn (1%).

The following sequences can be distinguished in the distribution of fulvic and humic species with bonds of different type: for FA with carboxylic type of bonds, Fe > Ca > Mg > Mn > Cd > Al > Cu; for FA with phenolic-type bonds, Al > V > Cu > Pb > Th > U; for HA carboxylic-type bonds, Fe > Mg > Ca > Al > Mn > Zn > Cd > Cu; and for HA with phenolic-type bonds, Al > Fe > Mg > Cu > Zn > Cd > V. In spite of their strong affinity to organic matter, Pb, Cu, U, Th, Y, V, and Ni bind only a small fraction of their active sites with HA and FA.

The Visual Minteq database of the stability constants of organic complexes contains no data on Be, Mo, W, Ti, and Sn. The speciation of these elements is not diverse: Ti, Sn, and Be occur mostly as hydroxyl-complexes, and W and Mo typically form anionic species.

Fractionation of Organic Species of Elements in Natural Waters

The ambiguity of interpreting thermodynamic calculation data when predicting transformations in the geochemical parameters of an environment and changes in the mobility of a wide spectrum of pollutant elements poses a challenge in bridging this gap with experimental data.

Our initial idea was to select a method for the fractionation OM in natural waters to maximize the isolation of the main functional groups of humic compounds with different affinity to bind elements (carboxylic and phenolic) in order to assess to compatibility of the calculated and experimental data. However, due to the specifics of the NICA-Donnan model itself and to complications of the selective fractionation of carboxylic and phenolic groups, another fractionation method of OM into hydrophobic and hydrophilic subfractions and the subsequent subdivision of the hydrophilic fraction according to the charge was taken as a basis. The same fractionation protocol was additionally carried out in for acidic solutions (pH 2). It is known that the humic part of natural OM can be subjected to conformational changes in different pH values and salt concentrations in the solution. In low pH, some of the functional groups of the humic molecules are inactivated because of the more compact hydrophobic skeleton, and the contribution of hydrogen bonds increases. Geochemical changes at the allochthonous OM destruction brought to the mine shafts can change acidic balance in such water bodies. The acidification of boreal surface waters significantly alters both the nature of their OM and the bioavailability of this OM (Moiseenko, 2017; Aleshina, 2024). The distribution of organic species of metals in acidic waters can be observed as a strictly conservative scenario of changes in a geochemical environment for the possible assessment of the fraction of metals weakly bonded to OM.

Analysis of the distribution of organically-bound species in neutral and acidified waters (Fig. 8) allowed us to categorize the chemical elements into several groups. Group 1 consist of metals that are strongly bonded to organic macromolecules and do not experience any significant changes (or only slight changes) in their percentage when extracted with hydrophobic OM. In order of decreasing percentage of metal bonded to humic matter, these metals are arranged as follows: Ni > Tl > Ti > As > W > Be > Co. Identified as a group 2 comprises metals whose percentages bonded to humic compounds drastically decrease with the shift to pH 2. As pointed out above, a change in the pH leads to the release of weakly bonded and surfaceadsorbed organo-mineral metal species into solution, which makes it possible to likely distinguish between strongly and weakly bonded species. The latter are U, Al, Cu, Cd, Y, REE, and Th. It is assumed that this fraction of the elements was weakly (electrostatically) bonded to OM or was associated with colloids of Fe and Mn (oxi)hydroxides, which dissolved with decreased pH and ceased to operate as a retaining SIDKINA et al.



Fig. 8. Distribution of the species of various elements in the natural waters of Herberz Mine according to fractionation data. Upper rows: distributions at the original near-neutral pH values, lower rows: same at pH 2. (1) Bound to humic compounds (hydrophobic OM); (2) positively charged species; (3) negatively charged species; (4) electrically neutral (zero-charge) species.

phase. Dominantly ionic species are typical of alkaliearth elements (Mg, Ca, Sr, and Ba) and Cs. The migration of multiple-charge elements mostly in anionic complex is typical of Mo, W, and Sn, and additionally to U in acidic waters.

About 45% Fe can be removed with an anionexchange resin from the waters, and this fraction increase to 70% in acidified water with pH 2. This may be explained by nonselectivity of unpolar resins like DAX-8 in the retention of organomineral colloids, which are an important phase of Fe transport in natural waters. However, this phase could be additionally retained by the anion exchange resin, and this effect strengthens at pH 2. The anion exchanger can likely retain in acidic waters much such elements as Ca, Mg, Cu, and Cd. A high percentage of anionic Fe species was found in riverine waters in a cold and humid climate (Aleshina et al., 2024). These authors hypothesized that the anionic complexes of allochthonous OM are dominant, because the percentage of anionic species positively correlates with the aromaticity of the isolated anionic subfractions. In our experiments, the organic species were dominated by nonhumic OM and also, perhaps, by colloids. (Supplementary Table 2). The acidification of the water leads to a six- to eight-fold decrease in the percentage of organic species of uranium. The most likely uranium species in near-neutral solutions is dissolved triple negatively charged uranylcarbonate complexes or uranyl-carbonates adsorbed on mineral colloids; the uranyl-carbonates are coordinate in the sphere by two or three carbonate ions, which ensure a strong enough bond to resist the repelling forces between the surface and anion (Jo et al., 2018).

The likely uranium species in acidified solutions may be uranyl cations, uranyl hydroxo complexes, and compounds bonded to fulvic acids. Because the dominantly aromatic body of the OM was removed at fractionation before, the remained OM fractions in the solution mostly belong to aliphatic complexes. Uranium was partly retained in a cationic form on the cation exchange resin, and the rest was distributed between the uncharged particles in the anion exchanger. The ability of anion-exchange resin to retain colloid- and subcolloid-sized particles has already been discussed in the literature (Wiercik, 2024).

It is difficult to interpret in more detail interactions between metals and the hydrophilic part of the dissolved OM (protein-like and hydrocarbon components, low-molecular carboxylic acids, and many other compounds) without any accurate their identification in the fractions, also because it is not possible to separate the ionic and organic molecules retained in the ion exchange resins, and also because of the presence of natural colloids. Experimental protocol for OM fractionation was the first attempt for the estimation of metal-OM bond in a given metallogenic profile of the studied area. We are going to continue these studies and are eager to improve the techniques for the separation of natural OM subfractions. Although these studies place high demands on the applied analytical techniques, more rigorous analysis of the characteristics of the individual fractions will not later give extrapolations back to the entire system. A more representative experimental dataset should allow for more realistic approximations of the ecologically hazardous elements behavior in water-mineral-OM systems.

DISCUSSION

When analyzing the geochemistry of natural waters at the Herberz Mine, it should be emphasized that these waters contain elevated concentrations of the ore elements and higher TDS. Similar trends, with some changes in concentrations of some chemical elements, have been identifies at other mines in the Pitkäranta area (e.g., Konyshev et al., 2021; Sidkina et al., 2024), indicating a regional rather than local nature of these trends. The geochemical specifics of the waters is due to their interaction with the rocks containing elevated concentrations of ore elements. The minerals concentrating these elements in this area are mainly sulfides: chalcopyrite, pyrite, sphalerite, and also galena according to (Trüstedt, 1907). All analyzed water samples from the Herberz Mine, as a rule, contain higher concentrations of Zn, Fe, Mn, Cu, Ni, As, and W. Detailed studies of natural waters at the Herberz II Mine, located far away from the Herberz I Mine, have shown that concentrations of Li, Pb, Th, U (Fig. 6), as well as in REE and Y (Fig. 7) differ. These differences may be explained by the fact that the mines developed different rock units (Fig. 2), and, consequently, the rocks interacted with waters of different chemistry.

Sampling the water using a bathometer in 2023 from the shaft of the Herberz II Mine allowed us to obtain the first data on variations in the water composition with depth. These values indicate that concentrations of most of the analyzed elements increase with depth (Supplementary Table 1), as also does the conductivity (Fig. 4b). The increase in the concentrations are likely explained by the more extensive interaction times between the waters and rocks. We think that the waters drained the mine shafts were provided by atmospheric precipitation, i.e., the upper water layers are systematically diluted with new portion of precipitation, whereas the waters at deeper levels occur in a stagnant regime, interacting with the rocks for a longer time, and are thus able to accumulate higher concentrations of chemical elements. Moreover, the *in situ* results indicate that the water temperature decreases with depth (to 5° C at a depth of 4.5 m and below). A higher solubility of carbonates at lower temperatures may be one of the reasons for the higher concentrations of hydrocarbonate compared to those in the surface water layers.

The natural waters typically contain OM, which forms complexes with metals and cause their accumulation in the solution. This is most clearly discernible in the behavior of Fe. The high stability of Fe(III) complexes with OM results in Fe accumulation in natural waters and hampers the formation of secondary minerals. In the absence of OM under oxidizing conditions, Fe precipitates as (hydro)oxides and is practically not retained in the solution (Krainov et al., 2012).

Although the influence of humic compounds on the element behavior in natural waters has been assessed and reviewed by several researchers (Vega and Weng, 2013), the approaches proposed to elucidate relations between metals and natural ligands were neither enough selective nor comprehensive (Yang et al., 2021).

Among many studies of this kind, interest is attracted first of all to experimental studies that proposed to develop methods of physical and chemical fractionation, as well as the study mechanisms for complex of metals with OM, also determine complexation and adsorption constants. Another avenue of the research is a data-driven approach that make it possible to model (predict) the elements speciation using of specialized software, such as PHREEQC, HCh, WATEQ4F, Visual Minteq, Geocheq, HydroGeo (Merkel et al., 2005; Lepokurova et al., 2022; Lipatnikova and Grichuk, 2011; Gogoi et al., 2016; Kolpakova et al., 2018). Fewer works applied these approaches together to heavy metals (Dinu and Shkinev, 2020), alkali-earth elements (Cai et al., 2024), redox-active elements (Zhang et al., 2021), and radionuclides (Toropov et al., 2020).

As mentioned above, binding of metals with humic acids is strongly affected not only by the ionic strength and their diversity of these waters but also their pH and Eh, along with the structure and origin of the presence OM. All these aspects are taken into account in both experimental and computational studies. Both approaches have their own advantages and disadvantages.

To quantitatively evaluate the metal species distribution associated to dissolved OM, the Non-Ideal Competitive Adsorption (NICA) model has been described based on extensive experimental studies, coupled to the Donnan model to consider nonspecific (electrostatic) interactions (Kinniburgh et al., 1999). The model assumes that a dominant role in complexation is played by certain functional groups of organic acids, and the chemical heterogeneity of the OM can be described using a given number of specific constants for proton affinity. This model considers only the bimodal distribution of the binding sites, which are conveniently subdivided into types according to high and low affinity to a proton. With regard to the diversity of the functional groups of humic matter, phenolic groups are believed to be highly specific ("strong") sites, whereas the carboxylic groups are regarded as weak specific. This is recognized in the literature despite the fact that they overlap in a bimodal distribution, and both phenolic and carboxylic groups can act as either strong or weak binding sites (Koopal et al., 2005, 2020).

An advantage of the NICA-Donnan model is that the calculation apparatus of its NICA part is able to consider the effects of pH, ionic strength, and competition of ions, and the parameters of the Donnan nonspecific interactions are not sensitive to the difference of the size and spatial geometry of humic macromolecules. Practice has shown that the NICA-Donnan model can well describe experimental data, including competitions of ions, and can be applied in combination with spectroscopic measurements (Fan et al., 2022; Zhang et al., 2021).

Results of thermodynamic calculations by the NICA-Donnan model for the interactions between metals and dissolved OM are variably consistent with real occurrences. The more different the structural and size parameters of the pool of the organic macromolecules in the samples from those tested experimentally and built into the model by its authors (Kinniburgh et al., 1999), the less definite is the calculated speciation of elements bonded to OM. A drawbacks of the NICA-Donnan model is its parameter of ion-specific nonideality n_{ii} because of its insensitivity to the stoichiometry of complexes of metals with functional groups (Koopal et al., 2020). Also, the NICA-Donnan model deals only with the multidentate metal binding with either several carboxyl groups or several phenol ones. Although heterocomplexation with both carboxyl and phenol groups also occur in nature, they are not considered in the model. No constants are available so far for binding with sulfur- and nitrogen-bearing ligands of humic compounds, which can also contribute to complexation. Another disadvantage of the model is also the oversimplified procedure for electrostatic interaction (in the Donnan part of the model), which does not consider ion competitions, diffusion charge compensation, and chemical and electrostatic heterogeneity. However, according to (Brunn, 2010) these parameters are not comprehensively derived in any of the models.

A reasonably accurate interpretation of experimental data on the fractionation of organic species of elements (Fig. 8) should take into account the specifics of the behavior of the elements and dissolved OM at the separation of individual fractions both between one another and when interacting with the surface of the ion exchange resins and adsorbents. The occurrence of a colloid phase should also be taken into consideration. At naturally occurring pH values, it is most probable that the solution contains a Fe (oxi)hydroxide colloid phase coated with a film of humic compounds (Mal'kovskii and Pek, 2009; Liao et al., 2017). At neutral pH, humic acids are notably more ionized, make up fiber-shaped structures, and thus maximize the interaction surface area (Alvarez-Puebla, Garrido, 2005; Lan et al., 2022). Metal binding with natural OM is controlled by several mechanisms: electrostatic interactions, complexation with HA and FA functional groups, and ion exchange with and adsorption on organo-mineral colloids (surface complexation). A pH decrease to 2 induces the following processes: Fe (oxi)hydroxide colloids dissolve, and humic molecules are restyled rearranged into more compact droplet-shaped or spherical structures (Lan et al., 2022; Yang et al., 2021). This strengthens the hydrophobic nature of the organic macromolecules and enhances the contribution of the hydrogen bonds. Also, the particles become coarser, their average hydrodynamic diameter extends outside the range of particle size assumed by IUPAC for colloid parameters, and the charge of the particles decreases (Supplementary Table 2). The contribution of electrostatic interactions drastically decreases. Because of the protonation of active sites of the macromolecules and strengthening of intra- and intermolecular repulsion, metals weakly bound to dissolved OM pass in solution into the ionic form or could recaptured by organic colloids (Cai et al., 2024). Strongly bonded with humic compounds species are preserved. The zeta-potential of colloids in the waters retained a negative charge during acidification, and hence, these colloids could be retained by anion-exchange resin.

The results of comparison of the calculation and experimental data on the migration of elements in the form of organic species are schematically generalized in Fig. 9.

The problem of comparing data on the modeling of organic species of elements and their experimental determination remains largely philosophical and fall into the dichotomy of approaches to studying the properties of nature and the structure of organic matter: "modeling the measurable or measuring the modelable" (Elliott, 1996; Brunn, 2010). None of the experimental fractionation methods is able to produce a consistent, well-defined, and systematic pool of natural OM that can be accurately described by any thermodynamic model.

CONCLUSIONS

In our study, we determined that waters at the historical Herberz Mine are hydrocarbonate calcium– magnesium, with elevated concentrations of the sulfate ion in some samples. One of the principally important geochemical features of the waters is their relatively high concentrations of trace elements, first of all, ore ones, at a low TDS values, a feature that is



Fig. 9. Schematic illustration of the distribution of the studied elements between organic species: (a) model results, (b) based on fractionation experiments.

explained by the interaction of the waters with host rocks. Concentrations of chemical elements, both major and trace, in the waters in the eastern shaft of the Herberz Mine increase with depth. All analyzed samples of natural waters from this mine contain elevated concentrations of Zn, Fe, Mn, Cu, Ni, As, and W. The sources of these elements are rocks of the mine, which contain, according to our and literature data, such phases as pyrite, chalcopyrite, sphalerite, scheelite, and these minerals contain admixtures.

The alterations of the rocks during the mining (of magnetite ore) and stripping operations, crushing, dumping, and other anthropogenic impacts resulted in an increase in the rock/water ratios and, hence, in more active accumulation of chemical elements in the natural waters.

The undersaturation of the surface waters of the mine shafts with most of minerals found in rocks of the mine and the high contents of OM in these waters (with OM serving as a complexation agent for some metals) are the main factors that control the chemical composition of the waters. The inflow of allochthonous OM should facilitate accumulation of the waters and REE and ore elements.

Experimental fractionation and thermodynamic modeling of the speciation of chemical elements in the waters allowed us to identify metals whose accumulation in the waters most strongly depends on OM. Both

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methods demonstrate the generally high affinity of OM to U and Th, as well as to Cu and Ni in the near-neutral ultrafresh waters with high TOC concentrations.

Metals weakly bonded to the functional groups of OM, with the dominance of electrostatic bonds (Donnan phase) and a high percentage of nonspecific adsorption sites (carboxyl groups), including several ore elements, are most susceptible to transformations at changing geochemical conditions. When the waters become more acidic (decreasing pH), inorganic colloids start to play a more important role in transporting Mg, Fe, Ca, Cu, and Cd. Bonds of Ni, Co, Be, and Tl with natural organic ligands are shown to be highly stable.

Based on experimental studies conducted according to the proposed protocol along with thermodynamic calculations of the speciation of the elements, led us to better understanding of the migration of a wide range of elements. This is crucial for development of a reasonably accurate long-term assessment of the environmental impacts of mining operations.

SUPPLEMENTARY INFORMATION

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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