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# Gold and silver in a system of sulfide tailings. Part 2: Reprecipitation on natural peat



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## ABSTRACT

More than eighty years of mining at the Novo–Ursk Au-bearing sulfide field (Kemerovo region, Russia) have produced a mixed natural–industrial system "wastes–gold-bearing acid mine drainage (AMD) waters–peat". The behavior of Au, Ag and related elements in the system "wastes–AMD" is described in Part 1 of our study (Myagkaya et al. 2016) where we discuss interaction between the gold-bearing mine drainage waters and peat. This interaction leads to rapid accumulation of Ca, Fe, Mn, Ba, Cu, Zn, Se, Au, Ag, Hg, Pb to concentrations exceeding those in cyanidation wastes (especially, Cu, Zn, Se, Hg, and Pb). The contents of Au (about 5 ppm on average, locally as high as 155 ppm) and Ag (average about 11.2 ppm, locally up to 560 ppm) in peat are above the lowest economic values. These results provide clues to technologies for both generation of secondary gold (silver) deposits at existing or planned tailings and immobilization of toxic elements.

Gold is accumulated in peat by a series of processes (reduction of ion gold to elemental form, sorption by complexation, biochemical reactions, etc.). This secondary gold is mostly chemically bound and invisible and a minor part is nanoparticulate (from tens of nm to 1.5–4 µm particles; with 7.5–53‰ Cu); it coexists with barite, secondary pyrite, tiemannite, Hg and Zn sulfides. Silver becomes redeposited in peat as silver-bearing sulfides and selenides. The presence of fossil bacterial fragments points to microbially mediated physicochemical processes leading to sulfide and gold mineralization by sulfate reduction and biosorption. Formation of abundant gold and mercury minerals may be due primarily to microbial activity.

Peat in the area of the Ursk tailings is actually a prototype of coalbeds. Therefore, the mineralogical and geochemical patterns of gold and silver reprecipitation on organic matter, and the respective Au and Ag enrichment, provide insights into the early history of gold mineralization in coal.

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## 1. Introduction

Dumped sulfide wastes (tailings) of the ore cyanide process and products of their alteration (acid mine drainage (AMD) and ochreous precipitates) cause large-scale pollution of the surrounding areas, which arouses special interest to the problem (e.g. Nordstrom and Alpers, 1999; Jung, 2001; Blowes et al., 2003; Al et al., 2006; Dold et al., 2009; Equeenuddin et al., 2010; Sarmiento et al., 2011; Carbone et al., 2013; Lghoul et al., 2014). Publications known to date refer to the formation of tailings and contamination trains, as well as to their chemistry, physics, mineralogy, and related microbiota (Alpers et al., 1994; Jambor, 1994; Ritchie, 1994; Bigham et al., 1996; Nordstrom, 2000; Dold and Fontbote, 2002; Descostes et al., 2004; Druschel et al., 2004; Gleisner et al., 2006; Marescotti et al., 2012; Auld et al., 2013; Sun et al., 2013). Most studies of tailings focus on the behavior of heavy metals and toxic elements (As, Hg, etc.) (Boulet and Larocque, 1998; Lazareva et al., 2002; Al et al., 2006; Roychoudhury and Starke, 2006; Gustaytis et al., 2010, 2013; Shcherbakova et al., 2010; Equeenuddin et al., 2013; Lusilao-Makiese et al., 2013; Rieuwerts et al., 2014).

However, the behavior of gold in tailings remains little explored, though its high mobility is known from studies of surface (Vlassopoulos and Wood, 1990; Vlassopoulos et al., 1990) and ground waters that drain sulfide ores (Andrade et al., 1991; Benedetti and Boulegue, 1991; Cidu et al., 1995; Dutova et al., 2006), gold deposits and laterites around them (Mann, 1984; Stoffregen, 1986; Bowell, 1992; Reith and McPhail, 2007; Kalinin et al., 2009; Fairbrother et al., 2012 et al.). The available data on Au concentrations in solids (wastes and bottom sediments) and in waters that react with gold-bearing material are sporadic, though there are some works on gold speciation (Bortnikova et al., 1996; Leybourne et al., 2000; Al et al., 2006; Roychoudhury and Starke, 2006; Naumova et al., 2013; Myagkaya et al., 2013).

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Gold transported in streams is commonly dissolved or particulate. Dissolved gold is bound in Cl- and S-bearing, OH, cyanide, or mixed complexes (Stoffregen, 1986; Vlassopoulos and Wood, 1990; Andrade et al., 1991; Benedetti and Boulegue, 1991; Tossell, 1996; Leybourne et al., 2000; Dutova et al., 2006; Xia, 2008; Ta et al., 2014). Particulate gold results from sorption on mineral particles (Sarkar et al., 1999) or on amorphous iron hydroxides (Benedetti and Boulegue, 1991; Ran et al., 2002), complexation with humic and fulvic acids (Baker, 1978; Vlassopoulos et al., 1990; Baranova et al., 1991; Bowell et al., 1993a,b; Wood, 1996), and formation of Au<sup>°</sup> colloids (Ong and Swanson, 1969; Avramenko et al., 2012). Gold migration in industrial and natural waters was investigated as a case study of a heterogeneous contamination train around the tailings of the Novo-Ursk pyrite deposit in the Kemerovo region (southwestern Siberia, Russia) (Myagkaya et al., 2013). Particulate gold in natural waters not affected by acid mine drainage (AMD) was found out to be about an order of magnitude more abundant than dissolved Au (0.007 ppb against 0.0006 ppb) (Myagkaya et al., 2016). Similar patterns were reported from other mining areas in Russia (Radomskaya et al., 2005). The dissolved species transforms into particulate gold away from the ore source due to breakdown of gold complexes and the ensuing sorption on suspended particles. Such behavior of gold was described in surface waters that drain an old gold mine in France (Benedetti and Boulegue, 1991) and gossan tailings in Canada (Leybourne et al., 2000).

Formation of chemically reprecipitated secondary metallic gold of an unusual morphology is also known from natural and manmade supergene systems (Vasconcelos and Kyle, 1991; Lawrance and Griffin, 1994; Novgorodova, 2004; Hough et al., 2011; Fairbrother et al., 2012; Reith et al., 2012; Zhmodik et al., 2012; Naumova et al., 2013) and experimental systems representing biogeochemical conditions in fluvial environment of Au placers (Shuster and Southam, 2015). Nanometer (1 to 100 nm) secondary gold was found as thin porous crusts, reniform aggregates, or fine dust (Osovetsky, 2012). Nanoparticles of supergene gold were observed in mining wastes at a placer gold deposit in the Urals (Naumova et al., 2013). Gold forms in superficial conditions by erosion and chemical weathering of gold-bearing material; additionally, the process can be mediated by metabolism of microorganisms widespread in sulfide oxide zones (Baker and Banfield, 2003; Druschel et al., 2004; Xie et al., 2009; Auld et al., 2013). Bacteria that oxidize iron, sulfur, and thiosulfate complexes, as well as sulfate-reducing bacteria, contribute to all stages of gold formation, from destabilization of Ausulfide material to bio-accumulation and precipitation (Korobushkina and Korobushkin, 1998; Lengke and Southam, 2005, 2006; Reith and McPhail, 2007; Reith et al., 2007; Southam et al., 2009).

Natural organic materials, such as peat and coal, are good sorbents and can act as geochemical barriers for different elements (Sobolewski, 1999; Brown et al., 2000; Koivula et al., 2009; Parviainen et al., 2014), including precious metals (Varshal et al., 1996; Radomskii et al., 2009; Kuimova et al., 2012; Radomskaya et al., 2015). Peat that bears extremely high concentrations of gold (0.6 to 16 ppb, locally to 160 ppb Au) was discovered in the southeastern West Siberian plate by Arbuzov et al. (2006). The sources required to produce gold concentrations exceeding the bulk crust average (1.8 ppb) (Taylor and McLennan, 1985) may correspond to gold deposits in the West Siberian plate (Arbuzov et al., 2006), while peatland deposits are known to be a coal-forming environment (Peng et al., 1999; Orem and Finkelman, 2003; Seredin, 2007). Coal can store high concentrations of gold and PGE minerals (Baruah et al., 1998; Dai et al., 2003; Sorokin et al., 2013) and has been considered an unconventional source of noble metal mineralization (Sorokin et al., 2012).

Although the geochemistry of coal-hosted gold has been largely studied, there remains controversy as to the sources and mechanisms of metal enrichment of coal (epigenetic or syngenetic processes) (Seredin and Finkelman, 2008; Sorokin et al., 2012). However, organic matter has been accepted to be an active concentrator of noble metals and related elements (Ong and Swanson, 1969; Bowell et al., 1993b; Wood, 1996; Varshal et al., 1996; Ran et al., 2002; Avramenko et al., 2012; Radomskaya et al., 2015). There are different processes gold may undergo while interacting with organic matter:

- (1) sorption caused by complexation of ion gold with oxygenbearing (carboxyl and phenol) groups in organic matter, in which humic acids act as precipitation barriers for noble metals (Baranova et al., 1991; Varshal et al., 2000). Gold and organics can form strong complexes only provided that the organic ligands contain sulfur and nitrogen (Vlassopoulos et al., 1990);
- (2) reduction of ion gold by dissolved organic compounds and its further stabilization by organic molecules (Ong and Swanson, 1969). According to data on kinetics of Au sorption on humic acids (HA) in the system HA–Au(III) Avramenko et al. (2012), Au<sup>3+</sup> can reduce to Au°, which is commonly colloidal and precipitates slowly. In these cases, humic material causes a stabilizing effect that prevents coagulation (Avramenko et al., 2012);
- (3) bioaccumulation playing an important role in the formation of gold nanoparticles (e.g., Lengke and Southam, 2006; Reith et al., 2007; Southam et al., 2009; Das et al., 2012; Brugger et al., 2013; Yin et al., 2014). Namely, biosorption may increase gold concentration in brown coal at the stage of peat deposition or in the zone of degradation and impoundment of coal deposits. Sorption is possible at pH from 2 to 9 and is mediated mainly by hydroxyl and carboxyl groups in the walls of bacterial cells. Au<sup>3+</sup> reduces to Au<sup>°</sup> and becomes adsorbed on cell surfaces. Biogenic metallic gold that forms in peat is remarkable by the presence of Cu impurity in the absence of Ag (Kuimova et al., 2012).

Interaction between noble metals and organic matter observed in experiments leads to gold and silver sorption on peat by ion exchange and subsequent incorporation of the functional group atoms of the sorbent into the internal sphere of the noble metal complex. As a result, the sorption equilibrium sets up for a long time and nanoparticles of reduced gold contain metal impurities, specifically, copper. Interaction of noble metals with peat does not stop at the sorption stage but continues till metals reduce to nanometer particles which then form aggregates (Radomskaya et al., 2015).

These processes may occur either during peat deposition or during later deposition and degradation of coal. However, accumulation of Au mostly occurs in the early history of deposits (Varshal et al., 2000) at the account of sorption on humic acids by complexation. The reason is that diagenesis of humic material destroys the chemical bonds of ligands, which decreases the sorption capacity. The latter may result also from increase in C and decrease in H, N, S, O and P, especially oxygen (Radomskii et al., 2009). Therefore, redistribution of elements becomes possible in the presence of disseminated noble metals, sulfides, selenides, and other authigenic minerals, while authigenic sulfides can adsorb gold as well. Complexation and reduction appear to act jointly (Bowell et al., 1993a,b). Experimental modeling of gold accumulation in peat and brown coal shows that reduction and complexation of ion gold by humic acids are possible in peat which comprises ligands capable of both reaction types. The prevalence of this or that mechanism depends on pH and amount of dissolved gold: reduced Au occurs as spherical particles upon the surfaces of humic acids at pH = 6-7 while particles of diverse morphologies (spherical, lamellar, etc.), with Cu and Zn impurities, form at lower pH (3) (Kuimova et al., 2011).

This study is important in two aspects. First it deals with disposal sites of cyanide wastes which are numerous worldwide and store unrecovered useful components being potential sources of manmade mineral deposits. Second, it sheds light on the behavior of gold in the conditions of tailings still remaining poorly understood. The study consists of two parts, where we discuss gold and silver migration in waters of an AMD creek and a natural river it flows into (Myagkaya et al., 2016) and reprecipitation of gold on a biogeochemical barrier of natural peat exposed to prolonged interaction with wastes and AMD (this paper).

The fate of noble metals is considered together with that of other elements that form secondary phases associated with native gold and with silver minerals.

The system "organic matter–gold-bearing solution" is another focus of our work having implications for the genesis of coal and black shale. Formation of coal and black shale deposits has been described by several models (e.g., Nemerov et al., 2010; Large et al., 2011). The "organic matter–gold-bearing water" system, and in situ interaction of its components, can be considered in terms of biological and geochemical controls upon preliminary sorption of metals on carbonaceous matter, and is a prototype of coal and black shale deposits.

## 2. Study area

The Ursk tailings site is located at 54°27′11.03″ N, 85°24′09.76″ E in Ursk Village (Fig. 1) within the Ur ore field in the northern Salair Ridge (Altai-Sayan mountains, Siberia). The site has been mined for more than eighty years and stores cyanide wastes of pyritic and auriferous complex ores of the Novo–Ursk deposit. The ore mineralogy includes pyrite (FeS<sub>2</sub>), sphalerite (ZnS), chalcopyrite (CuFeS<sub>2</sub>), galena (PbS), arsenopyrite (FeAsS), fahlore (tennantite Cu<sub>3</sub>AsS<sub>3</sub>), cinnabar ( $\alpha$ -HgS), as well as quartz (SiO<sub>2</sub>), barite (BaSO<sub>4</sub>), calcite (CaCO<sub>3</sub>), chlorite-group minerals ((Mg, Fe)<sub>3</sub>(Si, Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·(Mg, Fe)<sub>3</sub>(OH)<sub>6</sub>), sericite (KAl<sub>2</sub>(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>2</sub>), albite (Na[AlSi<sub>3</sub>O<sub>8</sub>]), graphite (C), rutile (TiO<sub>2</sub>), and fluorite (CaF<sub>2</sub>), with Au and Ag ranges 0.7–4 ppm and 16.5–29.65 ppm, respectively (Myagkaya et al., 2013, 2016).



**Fig. 1.** Sketch map of Ursk tailings site. Legend: 1 = forests; 2 = residential areas; 3 = flooded quarry; 4 = gangue dump; 5, 6 = tailings: wastes I (5) and II (6); 7 = proximal zone of dispersion train composed of shed wastes I; 8 = proximal zone of dispersion train composed of shed wastes I; 8 = proximal zone of dispersion train composed of shed wastes I; 9-12 = middle zone of train (shed wastes I and II); 13 = main AMD creek; 14 = pond; 15 = distal zone of train; 16 = intercalated wastes I and II; 17 = boundaries of train zones; 18 = sampling sites of trenches and depth profiles; 19 = lateral sampling sites.

The Ursk tailings are dumped as two 10–12 m high piles of primary ore (wastes I) and ore from the gold-bearing weathering profile (wastes II), in the upper part of a natural ravine; nearby there are a flooded quarry and a gangue dump (Fig. 1). Wastes I consist mainly of barite (15%), pyrite (35%), and quartz (20%), while pyrite and barite make the heavy fraction. Pyrite preserves inclusions of other opaque minerals: galena, chalcopyrite, bornite (Cu<sub>5</sub>FeS<sub>4</sub>), arsenopyrite, sphalerite, tennantite, altaite (PbTe), geffroyite (Ag,Cu,Fe)<sub>9</sub>(Se,S)<sub>8</sub>, and mercury telluride. We encountered metallic gold of 910‰ fineness (with 28.6‰ Cu and 61.4‰ Ag impurities) only once, as inclusion in pyrite. Barite encloses naumannite (Ag<sub>2</sub>Se) and mercury selenide with significant amounts of Ag and S: Hg<sub>0.8</sub>Ag<sub>0.2</sub>Se<sub>0.7</sub>S<sub>0.3</sub> (Myagkaya et al., 2016).

Wastes II contain barite, pyrite, quartz, gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) and goethite ( $\alpha$ -FeOOH), as well as aluminosilicate minerals: muscovite, albite, minor chlorite, and trace microcline (K[AlSi<sub>3</sub>O<sub>8</sub>]). Compared to wastes I, they bear smaller percentages of barite and pyrite (4% and 9%, respectively) and more abundant quartz (60%) and jarosite (KFe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>). As for chemistry, wastes I have larger Fe, Cu, Zn, Se, Sr, Cd, Te, Ba, Hg and Pb, while wastes II are richer in Na, Mg, Al, Si, K, Ca, Ti and Rb (Table 1). Residual Au and Ag are generally lower in wastes II (0.26 and 13 ppm) than in wastes I (0.5 ppm and 18 ppm), respectively (Table 1). Their contents in pyrite monofraction are quite low as well (0.5 ppm Au and 4.5 ppm Ag).

The site is drained by a natural creek which has turned into an acid mine drainage (AMD) stream flowing 0.7 km further into the Ur River (an Inya tributary). The AMD waters have pH = 1.9, Eh = 655 mV, TDS  $\leq 4.8$  g/L, and a sulfate composition with SO<sub>4</sub><sup>2-</sup> reaching 3600 ppm, quite high enrichments of Al (>26 ppm) and Fe (780 ppm) and minor Cl (13 ppm). The contents of other elements are: 2.5 ppm Cu, 11 ppm Zn, 110 ppb Pb, 630 ppb As, 440 ppb Se, 28 ppb Te, 11.4 ppb Hg, 18 ppb Cd (Table 2) and 1239 ppb SREE. The concentrations of gold and silver in the AMD waters near the tailings depend on season and range within 0.2–1.2 ppb Au and 0.01 to 0.3 ppb Ag; away

Table 1

Average values, ranges an	d standard	deviations (	SD) of	element	contents	in taili	ngs
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Element	Units	Wastes I	SD	Wastes II	SD	Ν
Ν	wt.%	< 0.05	n.d.	< 0.05	n.d.	
С	wt.%	0.03/0.025-0.05	0.014	0.3/0.025-0.9	0.5	2
Н	wt.%	0.2/0.05-0.4	0.18	0.4/0.3-0.6	0.15	С
S	wt.%	26/22-29	3.5	1.4/0.6-1.9	0.7	
Na <sub>2</sub> O	%	< 0.001	n.d.	0.36/0.001-0.6	0.2	
MgO	%	< 0.001	n.d.	0.1/0.001-0.3	0.13	
$Al_2O_3$	%	0.56/0.33-0.76	0.15	4.1/2-6	1.4	
SiO <sub>2</sub>	%	16/6-23	5.9	58/26-70.3	17	
$P_2O_5$	%	< 0.001	n.d.	< 0.001	n.d.	
K <sub>2</sub> O	%	0.09/0.04-0.17	0.04	0.53/0.2-0.9	0.21	6
CaO	%	0.05/0.001-0.11	0.04	0.3/0.14-0.54	0.18	
TiO <sub>2</sub>	%	0.14/0.1-0.18	0.03	0.3/0.18-0.46	0.09	
MnO	%	< 0.001	n.d.	< 0.001	n.d.	
Fe <sub>2</sub> O <sub>3</sub>	%	27/12.4-35	7.3	9.4/4.4-18.3	4.6	
LOI	%	19/7-24	6	5.4/2.5-8.6	2.52	
Cu	ppm	290/134-443	107	100/49.3-193	47.6	
Zn	ppm	286/51-591	173	160/96-204	37	
Se	ppm	159/81-322	73	107/52-166	35	
Rb	ppm	17.8/12.2-24	5	34.8/19-54	10.2	
Sr	%	0.09/0.05-0.17	0.04	0.07/0.03-0.16	0.04	
Mo	ppm	6.3/2.8-11	2.6	5.6/2.2-7.9	2.1	
Cd	ppm	1.36/0.3-2.82	0.74	0.37/0.14-0.84	0.25	
Sn	ppm	13/6.5-25.6	6	5.5/0.98-11	3	9
Sb	ppm	247/163-336	56	154.4/47.5-334	85.4	
Te	ppm	21.7/14.2-32	5.3	15/3.5-27	7	
Ba	%	23.7/11.4-40	10	13/3.2-39	10.3	
Hg	ppm	75/33-106	25.3	36/16-71	19	
Pb	ppm	2867/1700-4100	929	2000/1100-2700	487	
Ag	ppm	18/11-25	4.9	13/8.2-21	5.4	
Au	ppm	0.5/0.21-0.71	0.19	0.26/0.13-0.49	0.15	

Note: N is the number of samples; wastes I are wastes of processed primary ore; wastes II are weathered gold-bearing wastes; *n.d.* is no data; LOI is loss on ignition; and B.D.L. is below detection limit. Data were reported in (Myagkaya et al., 2016).

Table 2AMD water chemistry.

Elements	Units	AMD	Element	Units	AMD
pН		1.9	Te	ppb	28
Eh	mV	655	Ι	ppb	25
02	ppm	< 0.2	Cs	ppb	0.2
TDS	g/L	4.8	Ba	ppb	10
TOC	ppm	14	La	ppb	190
Na <sup>+</sup>	ppm	17	Ce	ppb	470
$Mg^{2+}$	ppm	100	Pr	ppb	61
K <sup>+</sup>	ppm	0.9	Nd	ppb	260
Ca <sup>2+</sup>	ppm	190	Sm	ppb	61
HCO <sup>3</sup>	ppm	4.2	Eu	ppb	17
$SO_{4}^{2-}$	ppm	3600	Gd	ppb	55
Cl	ppm	13	Tb	ppb	8
Al	ppm	>26	Dy	ppb	47
Si	ppm	57	Но	ppb	9.3
Р	ppm	1	Er	ppb	28
Ti	ppm	0.41	Tm	ppb	4
V	ppm	0.06	Yb	ppb	25
Cr	ppm	0.11	Lu	ppb	3.5
Mn	ppm	17	Au	ppb	1.2
Fe	ppm	780	Hg	ppb	11.4
Cu	ppm	2.5	Pb	ppb	110
Zn	ppm	11	Th	ppb	21
As	ppb	630	U	ppb	24
Se	ppb	440			
Br	ppb	140			
Rb	ppb	12			
Sr	ppb	590			
Mo	ppb	6.7			
Ag	ppb	0.3			
Cd	ppb	18			
Sn	ppb	0.04			
Sb	ppb	0.7			

Note: Data were obtained by ICP-MS on an *Agilent Technologies* Agilent 7500 quadrupole ICP-MS spectrometer and reported in (Myagkaya et al., 2016).

from the tailings, they decrease to 0.003 ppb Au and 0.008 ppb Ag, while pH increases. The same patterns are observed in most of elements coexisting with gold and silver. The chemistry of AMD and local natural

waters was mainly characterized in Part 1 of the study (Myagkaya et al., 2016). Estimating the sorption capacity of plants (water hyacinth) as to elements from the AMD and surface waters of the Ursk site allowed identifying candidates for phytomining (Romanova et al., 2016), and active sorption was inferred only for Ag and Ba among the analyzed elements of Ag, Ba, Cd, Mo, and Pb.

The wastes remain unfixed and are exposed to rainfall and floods, being thus shed to a natural swampy peat ravine where peat has been in permanent interaction with AMD waters and wastes. The material shed from the tailings undergoes hydraulic sorting, with coarser sand fractions settling near the discharge point and finer silt fractions carried away to longer distances. The related dispersion train of elements and particles can be divided conventionally into a proximal (Fig. 1, Legend # 7-8), middle (Fig. 1, Legend # 9-12) and distal (Fig. 1, Legend # 15) grain size zones located, respectively, at short (60 m), medium (130 m) and long (600 m) distances from the tailings (Gustaytis et al., 2010; Shcherbakova et al., 2010). Most of the peatland burnt by AMD is located within the intermediate zone, where remnant peat mounds of sedge and cane, and half-degraded tree stumps rise above the surface. This zone comprises two isolated topographically different domains (Fig. 1), with mostly wastes I and II in the west and east, respectively. The eastern part is perennially flooded by AMD waters and abounds in tree stumps and mounds.

The material shed from the pile of wastes I (Fig. 1, trenches 1–3; Fig. 2a) makes thin layers lying over peat between sedge and cane mounds and is partly flooded by AMD waters. The buried peat occupies the greatest part of the section. The contents of secondary Fe(III) in the zone are the lowest.

Peat that contacts wastes II (Fig. 1, trenches 4–6; Fig. 2b) is impregnated with drainage waters and is covered with a thick layer of secondary Fe(III) compounds which impart ochreous-yellow, brown, or locally pink colors to the peat. The surfaces of peat and wastes in ephemeral streams are often covered and cemented with Fe(III) crusts (Myagkaya et al., 2016). Being originally deposited on the surface, they likely have been buried under the material shed later from the waste piles.



**Fig. 2.** Depth profiles of dispersion train, with examples of four typical trenches (element contents are in ppm), and vertical patterns of gold and silver; a – trench 1 from zone covered with wastes I; b – trench 2 from zone covered with wastes II; c – trench 3 from zone of intercalated wastes I and II; d – trench 4 from distal zone of dispersion train. Colors in sketches are close to natural soil colors. Legend: 1 = peat; 2 = ochreous Fe(III) precipitates; 3 = punctuated peat lenses; 4 = coarse clastic sediments; 5 = sand; 6 = sand and mud; 7 = mud.

The dispersion train part within the perennial AMD creek consists of peat and alternating wastes I and II shed from both piles (Fig. 1, trench 7; Fig. 2c). Peat mounds are locally buried under 20 cm of wastes; the material of wastes encloses layers of siliciclastic sediments.

In the Ur valley, in the distal zone farthest from the tailings (Fig. 1, trenches 8–9; Fig. 2d), the shed wastes are interlayered with organic remnants and peat, while the upper section consists mostly of sand. The zone is free from mounds, and the wastes lie over limestones of the dredge dump.

## 3. Materials and methods

## 3.1. Collection and preparation of samples

In the course of field trips, we sampled shed wastes, peat mounds interacting with wastes, and peat buried under the wastes. The samples were collected continuously depthward from walls of 0.6 m deep trenches, with regard to visible zoning, layer by layer. Sampling was from several areas in the contamination train (Fig. 1): (1) a zone covered with shed wastes I at different distances till 130 m (trench 1–3); (2) a zone opposite the pile of wastes II at three points of the ephemeral AMD stream (trench 4), in its vicinity (trench 5) and away from it in the flooded area (trench 6); (3) a zone of layered wastes of both types near the main AMD channel (trench 7); (4) the most distal part of the train (about 0.6–1 km away from the tailings), where the wastes are intercalated with plant remnants and peat (trenches 8–9).

In order to reveal the Au and Ag distribution patterns, the wastes and the peat on their interface were sampled from small cuts (no deeper than 20 cm). Altogether 210 samples were collected at sites spaced at 15–20 m (Fig. 1).

#### 3.2. Laboratory investigations

The contents of major elements in peat were determined by wholerock X-ray fluorescence spectroscopy (XRF) in pellets made in the following way. The samples were dried at 105 °C for 1 h, ignited at 1000 °C for 2.5 h, and then mixed with a flux consisting of 66.67% lithium tetraborate, 32.83% lithium metaborate, and 0.5% lithium bromide, at 1:9 (total weight of the mixture 5 g). The mixture was fused in Pt crucibles, in a *Linn High Therm Gmbh* Lifumat-2.0-Ox induction furnace. The analysis was performed on an *ARL*-9900-*XP* X-ray spectrometer (Applied Research Laboratories, Switzerland). See Table 3 for the concentration ranges of individual elements and their relative errors. The lower bound, about the limit of detection but with a smaller confidence interval, was used as the detection limit.

The carbon contents in the samples were determined by the CHNS elemental analysis on an *EvroVector* Euro EA 3000 analyzer (Italy), using the combustion/gas chromatography techniques. The analysis was by catalytic combustion followed by packed column gas

Table 3
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Parameters	for	X-rav	fluorescence	analysis	(%)
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Oxides	Measured range, wt.%	Relative error*
Na <sub>2</sub> O	0.04–15	28-3.5
MgO	0.05-45	30-1.7
$Al_2O_3$	0.01-100	30-1.1
SiO <sub>2</sub>	0.01-100	30-0.7
$P_2O_5$	0.01-2	21-4.3
K <sub>2</sub> O	0.01-10	30-3.5
CaO	0.01-100	30-1.2
TiO <sub>2</sub>	0.01-100	27-0.8
MnO	0.01-2	24-3.4
Fe <sub>2</sub> O <sub>3</sub>	0.01-100	30-0.7
BaO	0.005-0.5	30-16
LOI	0.2–50	11-1.4

Note: \* for lower and upper bounds of element contents, respectively; LOI = loss on ignition.

chromatographic separation with thermal conductivity detection (using a single TCD). The analytical accuracy was 0.3–0.5%, at the range of measured concentrations from 1.5 to 95%.

The element contents in peat were determined and compared by the atomic absorption spectroscopy (AAS) and X-ray fluorescence analysis with synchrotron radiation (SR-XRF). The AAS analysis was performed using a Thermo Electron Corporation *Solar M6* spectrometer with a Zeeman and deuterium background correction system (USA), to an accuracy of  $\pm$  10–30 relative % at p = 0.95 confidence probability, with the ranges of measured concentrations listed in Table 4 (M-MVI-80-2008, 2008). The analyses were checked against certified standards of SPSS-3 (sod-podzol silt soil), RES-3 (red earth soil), and TCS-3 (typical black earth (chernozem) soil). Each fifth sample was run in duplicate.

Total mercury in pore waters was analyzed by gold amalgamation with cold vapor AAS, on a 3030B *Perkin–Elmer* spectrometer (USA), with an MHS-20 mercury-hydrate detector. The detection limit was 0.01–0.02 ppb, and the analytical accuracy was 35%. The method was tested at the laboratory of the US National Bureau of Standards (Kovalev et al., 1998).

The SR-XRF analysis was performed on a VEPP-3 spectrometer operated at 15 to 50 keV. Samples were prepared as 30 mg compressed pellets, 5–6 mm in diameter, and analyzed to an accuracy of  $\pm$  30% relative to the absolute abundance (for detection limits see Table 4).

The contents of Au and Ag were determined at a certified laboratory of the Institute of Geology and Mineralogy (Novosibirsk) following the procedures from (MVI NSAM N 237-S, 2006; MVI NSAM N 130-S, 2006) modified after the method by Tsimbalist (1984) which was specially designed for evaluation of ultra-trace Ag and Au contents  $(n \cdot 10^{-6} - n \cdot 10^{-8})$ . According to the procedure, preconcentrated elements were extracted into the organic phase and the elements in the extract were analyzed by AAS. Subsample solids (1 g) were acid digested. The analyses were checked against certified standards of GBO-3 gold-bearing ore and BSL-1 (black shale), used with each set of samples. Each third sample was run in duplicate. For silver analysis, samples were digested in aqua regia and HCl, and the solution with silver was sprayed (atomized) in flame to assess the absorption of radiation by free silver atoms. Silver present in contents below 10 ppm was extracted by isopropylamine before flame atomization (MVI NSAM N 130-S, 2006). The samples analyzed for gold were likewise digested in aqua regia and HCl but after being annealed in a muffel furnace at 650 °C (MVI NSAM N 237-S, 2006). The element that was transferred to the acid solution was extracted by toluene solutions of organic sulfides. The extracts were analyzed by flame AAS on a Perkin-Elmer

Table 4

Ranges of element contents ()	ppm)	measured by	r flame AAS	S and S	SR-XRF
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Element	Ranges of element contents				
	AAS	SR-XRF			
Cu	From 1 to $5 \cdot 10^3$	2–5			
Zn	From 1 to $5 \cdot 10^3$	2-5			
Se	From 1 to $1 \cdot 10^3$	0.3-1			
Rb	n.d.	0.1-0.5			
Sr	From 5 to $5 \cdot 10^3$	0.1-0.5			
Мо	n.d.	0.5-3			
Ag	From 0.2 to $2 \cdot 10^3$	0.5-3			
Cd	From 0.05 to 5 · 10 <sup>3</sup>	0.5-3			
Sn	n.d.	0.5-3			
Sb	n.d.	0.5-3			
Те	n.d.	0.5-3			
Ba	From 5 to $5 \cdot 10^3$	10-15			
Au	From 0.1 to 20	n.d.			
Hg	0.01–0.02 ppb	0.5-3			
As	From 0.05 to 5 · 10 <sup>3</sup>	0.3-1			
Pb	From 1 to $5 \cdot 10^3$	0.5-3			

Note: n.d. = not determined.

3030 B spectrometer (USA) and a Thermo Electron Corporation *Solar M6* photometer (USA). Each third sample was run in duplicate. The analytical accuracy was from 16 to 59% for gold and 5–59% for silver, at the p = 0.95 confidence depending on the Au and Ag contents (from 0.1 to 20 ppm Au and 0.2 to 2·10<sup>3</sup> ppm Ag, respectively).

Scanning electron microscopy (SEM) was applied to study the morphology of particles and to identify separate particles. The instrument was a *TESCAN MIRA3* LMU (Czech Republic) scanning electron microscope with an *INCA Energy* 450 + microanalyzer based on the Oxford Instruments *NanoAnalysis X-MAX* 80 (UK) system, with an optical resolution of 1 nm. The operation conditions were: 15 mm working distance, 20 keV acceleration voltage, and 1.5 nA beam current. The contents of elements in mineral grains smaller than the beam spot (many particles <1  $\mu$ m and porous aggregates) were estimated from relative contents of major elements subtracting the elements of the host mineral. Minerals in wastes and sediments were studied by powder X-ray diffraction (XRD) on a *DRON-4* diffractometer operated at 40 kV and 24 mA, with CuK- $\alpha$  radiaton.

## 4. Results

## 4.1. Peat chemistry

The material of peat mounds within the contamination train bears less carbon than that of buried peat, irrespective of the type of wastes it interacts with (Table 5), and thus may be more strongly degraded by AMD waters. Compared to the wastes, peat has greater enrichments in Na<sub>2</sub>O, MgO, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, CaO, and MnO, as well as Zn (to 7270 ppm), Se (to 6060 ppm), Ag (to 560 ppm), Au (to 155 ppm), and Hg (to 11,730 ppm) (Tables 1, 5). Thus, it acts as a concentrator and an active biogeochemial barrier for elements (Brown et al., 2000; Arbuzov et al., 2006; Koivula et al., 2009; Parviainen et al., 2014).

#### Table 5

## 4.2. Peat mineralogy

Peat in the swampy ravine is mainly X-ray amorphous, especially that of mounds (Fig. 3a, green line), and bears high contents of organic matter. Prominent peaks are from jarosite, goethite, and gypsum. Other possible phases are schwertmannite ( $FeO(OH)_{0.8}(SO_4)_{0.2} \cdot nH_2O$ ) and ferrihydrite ( $Fe_4O_5(OH)_2 \cdot 2.5H_2O$ ) (Bigham, 1994), as well as very low percentages of quartz and barite and some amounts of layered clay minerals (illite; ( $K_{0.75}(H_3O)_{0.25}$ )Al<sub>2</sub>(Si<sub>3</sub>Al)O<sub>10</sub>(( $H_2O)_{0.75}(OH)_{0.25}$ )<sub>2</sub>). Similar mineralogy is observed in peat buried under wastes II and impregnated with AMD waters (Fig. 3a, black line). It contains very small or trace amounts of primary minerals (quartz, barite, muscovite, albite, microcline), but the percentages of secondary minerals (jarosite, goethite, and gypsum) are higher than in the mound samples.

Locally, notable amounts of pyrite coexisting with schwertmannite and layered clay minerals (smectite group minerals and kaolinite  $Al_4[Si_4O_{10}](OH)_8]$ ), was found in peat lying under wastes II (Fig. 3b, gray line; Fig. 4e). Aluminosilicate clay minerals may precipitate from pore and AMD waters saturated with Al and Si (Table 2), as it was reported for coal (Jambor, 1994) and sulfide (Valente and Gomes, 2009) wastes. Samples from the peat/wastes interface contain abundant gypsum and goethite, a significant amount of jarosite (Fig. 3b, brown line), as well as quartz, plagioclase, and barite (Fig. 3b, brown line), which are primary minerals existing in the wastes.

Secondary minerals include Fe(III) compounds (ochreous precipitates) which often impregnate plant remnants and occur as concentric encrustations or spherical particles (Fig. 4a). They are commonly found in oxide zone wastes and consist of goethite ( $\alpha$ -FeOOH), ferrihydrite (Fe<sub>4</sub>O<sub>5</sub>(OH)<sub>2</sub>·2.5H<sub>2</sub>O), lepidocrocite ( $\gamma$ -FeOOH), jarosite (KFe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>), schwertmannite (FeO(OH)<sub>0.8</sub>(SO<sub>4</sub>)<sub>0.2</sub>·nH<sub>2</sub>O), hydrogoethite, etc. (Jambor, 1994; Bigham, 1994, Bigham et al., 1996; Marescotti et al., 2012).

Jarosite exists among X-ray amorphous Fe(III) compounds as separate granular aggregates of (Fig. 4b) rhombohedrons  $(1-3 \mu m)$ . Jarosite group minerals form in low-pH (pH < 3) environments, at a high

Element	Units	Peat I	SD	Peat II	SD	Peat III	SD
С	wt.%	11/2.4-36.7	10.5	16.8/0.8-26	8.8	20.1/4.3-33.5	10.7
Na <sub>2</sub> O	%	0.78/0.15-1.56	0.43	0.4/0.1-1.15	0.3	0.8/0.13-1.4	0.5
MgO	%	0.43/0.1-1.2	0.36	0.37/0.19-0.73	0.18	0.62/0.3-0.9	0.2
$Al_2O_3$	%	4.9/1.1-11.5	3.3	4.8/3-8.2	1.7	6.8/4.5-11.8	2.2
SiO <sub>2</sub>	%	39.1/8.7-60.2	16.5	26/10.3-47.5	12.7	15.5/8-21.5	6
$P_2O_5$	%	0.26/0.15-0.6	0.16	0.14/0.06-0.21	0.04	0.28/0.17-0.43	0.12
K <sub>2</sub> O	%	0.97/0.22-1.8	0.5	0.67/0.36-1.28	0.3	1.1/0.17-1.6	0.53
CaO	%	0.64/0.13-1.8	0.55	0.85/0.31-2.7	0.7	0.6/0.18-1.25	0.3
TiO <sub>2</sub>	%	0.52/0.12-0.8	0.21	0.35/0.12-0.6	0.19	0.17/0.1-0.22	0.06
MnO	%	0.02/0.004-0.04	0.01	0.02/0.01-0.03	0.01	0.09/0.02-0.25	0.09
Fe <sub>2</sub> O <sub>3</sub>	%	9/5-15.8	3.3	13.5/4.4-38.1	10.5	5.4/3.8-7.4	1.3
LOI	%	34.6/12.2-83	24	46.1/15.2-66	17.7	65/57-76	7.3
Cu	ppm	216/95-334	81	220/48-455	136	266/47-531	169
Zn	ppm	193/34-395	95	578/162-1343	443	403/47-7270	169
Se	ppm	341/129-560	129	2073/234-6059	1934	91/23-263	83
Rb	ppm	306/197-435	88	127/26-285	88	n/d	n/d
Sr	%	214/29-448	149	346/182-645	148	124/63-176	29
Мо	ppm	4.7/3.4-5.8	1.2	5.8/1.7-12.4	4	n/d	n/d
Cd	ppm	0.3/0.25-0.55	0.11	0.8/0.34-1.36	0.5	0.6/0.25-1.9	0.57
Sn	ppm	2.6/1.12-3.9	1.04	4.2/1.5-7	2.3	n/d	n/d
Sb	ppm	76.6/4.2-136	50.6	85.2/18.9-171	62.4	n/d	n/d
Те	ppm	9.8/6.1-16.3	4.2	7.4/1.8-15.8	4.8	n/d	n/d
Ba	%	1.1/0.3-1.56	0.53	1.5/0.7-4.27	1.2	n/d	n/d
Hg	ppm	43/29-62	13	300/48-11,730	272	14,717/707-2480	939
As	ppm	238/99-550	162	232/100-300	79	68/8-210	59
Pb	ppm	975/124-2000	557	1160/170-3300	1050	239/20-590	167
Ag	ppm	8.5/0.75-58	6.2	7/1.7-560	5.6	0.57/0.2-5.2	0.52
Au	ppm	17/3.7-32	10.3	30/13-155	28	11/0.26-27	10
n		7		8		10	

Note: Peat-1 is surface peat layer at the interface with wastes I; peat-2 is surface peat layer at the interface with wastes II; peat-3 is peat buried about 0.6 m below shed mixed wastes (wastes I + wastes II). LOI is loss on ignition; n is number of samples.



**Fig. 3.** X-ray spectra for (a) green line refers to a peat mound on contact with wastes II (trench 6, interval 6–1, 17 ppm Au), black line refers to peat impregnated with AMD waters from impoundment (flooded wastes II): sampling site 41 of geochemical surveys, 155 ppm Au); (b) gray line refers to peat buried under wastes II (trench 6, interval 6–5, 18 ppm Au) and (b) brown line refers to peat from train part flooded with AMD waters: sampling site 44 of geochemical surveys, 80 ppm Au). Legend: Sh = schwertmannite, ferrihydrite, Gy = gypsum, Bar = barite.

reduction potential (above 0.8 V), as a result of  $[FeHSO_4]^{2+}$  hydrolysis upon iron sulfide oxidation; the reactions may be also mediated by thionic bacteria. At late stages of oxidation, iron hydroxide may substitute for jarosite (Bigham, 1994; Gas'kova et al., 2007). Coexistence of iron hydroxides and jarosite in a sample is evidence of local Eh-pH variations.

Gypsum occurs mostly as tabular or acicular crystals, up to  $600 \ \mu m$  long and  $300-400 \ \mu m$  wide, (Fig. 4c) or their aggregates. Otherwise, it

may form parallel or radiated fibrous segregations in the mixture of hydroxides and Fe(III) sulfates.

Primary barite brought into peat from wastes occurs as fragments with pitted surfaces cut along cleavage planes. Authigenic barite most often forms druses of platy crystals (Fig. 4d) or fills voids in organic matter. It may precipitate when the system reaches saturation or upon the redox barrier, as in the case of saproperls (van Os et al., 1991).



Fig. 4. SEM images of minerals in peat. a: concentric encrustation and spherical particles of ochreous precipitates (Fe(III) and Al(III) compounds); b: granular aggregates of rhombohedral K-Na-jarosite crystals; c: coarse gypsum crystals (gyp) with barite (bar); d: a druse of tabular barite crystals; e: octahedral microcrystals and a framboid of pyrite; f: sphalerite in organic matter.

Peat contains abundant sulfides, especially framboidal pyrite (Fig. 4e) existing as 30  $\mu$ m spherical aggregates of 0.1 to 0.5  $\mu$ m microcrystals. The origin of this pyrite is controversial: it may result either from metabolism of sulfate-reducing bacteria and HS substitution for organic spherical particles (Love, 1957), or from recrystallization of aqueous sulfide gels and slow alteration of greygite (Fe<sub>3</sub>S<sub>4</sub>) (Wilkin and Barnes, 1997); or, it may be due to a combination of both biotic and abiotic processes (Wang et al., 2013).

Sphalerite existing as fine  $(0.5-1 \ \mu\text{m})$  equant grains covers plant remnants (Fig. 4f), together with barite. Precipitates of Zn and Cu sulfides, similar in composition and shapes, fill membranes in peat plant remnants (Bobrov et al., 2011). Some sphalerite grains contain impurities of Hg (31 wt.%: Zn<sub>0.7</sub>Hg<sub>0.3</sub>S). There is a solid solution series between sphalerite and metacinnabarite (HgS), while Hg impurity in sphalerite may reach 38 wt.% (Vasil'ev, 2011).

Mercury minerals are widespread in peat around the Ursk tailings and occur as  $5-10 \mu m$ , often less than  $2 \mu m$  segregations of selenides, sulfides, and intermediate varieties (Fig. 5).

Mercury selenides have been classified as tiemannite HgSe (Fig. 5a–c) on the basis of Hg/Se ratios (from 17.5/7.5 to 58/20.2 wt.%, which corresponds to 0.08/0.09 and 0.29/0.26 apfu, respectively) (Mineralogy database, webmineral). Evidence of supergene tiemannite

has appeared only recently. Tiemannite in a natural weathering profile was first reported from the Gay massive sulfide deposit in the Urals (Sergeev et al., 1994). Supergene phases were later found also in other pyrite deposits of the Urals (West-Ozerny, Dzhusy, and Yubileiny) (Belogub et al., 2003, 2008), as well as in the Amur and Verkhnyaya Arsha fields of brown iron ore (Southern Urals) (Blinov, 2015). Actually, tiemannite must be very rare due to low contents of Se in primary ore (Belogub et al., 2003, 2008), but selenides may form more often than sulfides because they have larger stability fields and require lower activity of H<sub>2</sub>Se relative to H<sub>2</sub>S in oxidizing conditions (Belogub, 2009). The mineral occurs in peat impregnated with iron hydroxides and among silicified cells of microorganisms. Most tiemannite crystals are hollow tubes (Fig. 5a) or spherules (Fig. 5b) varying in size from tens of nanometers to 3–5  $\mu$ m; tiemannite coexists with silver iodide.

Some mercury sulfides are small equant particles free from any impurity found in organic matter together with ochreous precipitates. They include the varieties of cinnabar ( $\alpha$ -HgS), a primary ore mineral at the Novo–Ursk deposit, and metacinnabarite ( $\beta$ -HgS). The latter forms in Hg-bearing deposits near the surface at low temperature and occurs as thin films on cinnabar, the two varieties having different microstructures (Mineralogy database, webmineral). It is hard to reliably identify the mineral of such a small grain size, but it appears to be





metacinnabarite, which is the most probable candidate to form in this supergene environment.

Other Hg sulfides bear the impurities of Se, Zn, and Cu (Fig. 5d); metacinnabarite may contain Se, Zn, Fe and Mn (Godovikov, 1983). Depending on their concentration, the phases may include guadalcazarite (Zn = 4.23%, Se = 1.08%), onofrite (Se = 4.58–8.40%, Zn = 0.54–1.30%, Mn = 0.69%) and leviglianite (Zn = 2.17%, Fe = 0.52%) (Vasil'ev, 2011). Cu–Zn and S pyrite ores commonly contain much Se which is either present as isostructural impurity in sulfide or form solid solutions with the latter (Ivanov, 1996). Recent reports mention the sphalerite (ZnS) – metacinnabarite (HgS) and metacinnabarite – tiemannite (HgSe) solid solution series rather than separate phases (Vasil'ev, 2011). In this respect, peat at the site of the Ursk tailings contains intermediate members of the series.

The third group of mercury sulfides includes those with Zn, Cu, Se, Ag, I, and Cl (Fig. 5e–i), which are too small to discriminate between isomorphic impurities and fine segregations. The minerals exist as single crystals (Fig. 5e), aggregates, or encrustations on plant remnants (Fig. 5g). The particle sizes vary from 100 nm to 2–3 µm. Some fine mercury sulfide particles coat plant remnants or locally form sheaths on bacterial cells (Fig. 5h). Traces of microbial activity are evident in fossil silicified remnants of microorganisms.

Spherical pyrite concretions (possibly framboids) and mercury sulfides were detected in the anoxic environment of a microbial community at the pool bottom of the Zavarzin Hot Spring (Uzon Caldera, Kamchatka, Russia) (Rozanov et al., 2014). Mercury sulfides found in peat may owe their origin to metabolism of sulfate-reducing bacteria which reduce S and immobilize Hg in sulfides. Such reactions, known for the case of mercury sulfides formation by sulfate-reducing bacteria  $(Hg^{2+} \rightarrow CH_3Hg^+ + H_2S \rightarrow (CH_3Hg)_2S \rightarrow (CH_3)_2Hg + HgS (Weber et al., 1998))$ , occur in anoxic conditions at pH from 4.5 to 8, in the presence of  $H_2S_{gas}$ , which forms from  $SO_4^{2-}$  by biological transformation



Fig. 7. Gold fineness as a function of Cu contents.

(Craig, 1980). These very conditions exist in the peat around the Ursk tailings. Furthermore, Se is biologically active, and is an important nutrient for some microorganisms (Umysová et al., 2009). There were reports of microbial precipitation and reduction of Se to selenides (Herbel et al., 2003), including HgSe (Jiang et al., 2012). Tiemannite was discovered even in liver of marine mammals (Lailson-Brito et al., 2012). By analogy with Hg sulfides, Hg selenides may form by a similar process.

Submicron-scale particles of metallic gold are extremely rare, restricted to peat organic matter that contacts wastes II flooded by AMD waters. The gold coexists with secondary minerals: Fe(III) hydroxides and sulfates, K-jarosite, framboidal pyrite, or druse-like barite pseudomorphs after plant remnants (Fig. 6a). Gold particles are as small as <1.5  $\mu$ m, rarely reaching 4  $\mu$ m (Fig. 6), and are either single or aggregated. They are most often flaky (Fig. 6b, c), like typical supergene gold



Fig. 6. SEM images of native gold in peat. a: pure gold in peat among secondary barite (bar), pyrite (pyr), and ochreous precipitates of Fe(III) compounds (Fe-hdr); b: submicron-scale particle of pure gold; c: flaky particle of Cu-being gold; d: aggregate of flaky particles of Cu-Ag-being gold.

(Southam et al., 2009; Zhmodik et al., 2012), or are aggregates of flaky particles (Fig. 6d). The gold fineness is 947–1000‰ (Fig. 7), with Cu being main impurity (to 1.2 wt.% or from 7.5 to 53‰). The Cu content is within the limit (3 wt.%) known for secondary gold (Kucha, 1995). A few particles contain up to 11 wt.% Ag and 6 wt.% Cu.

The possibility for gold of high fineness to form in supergene environments was proven long ago (Lawrance and Griffin, 1994; Hough et al., 2011). Cu-bearing gold was found in magmatic ore systems (Novgorodova and Tsepin, 1976; Murzin et al., 2009), as well as in coalbeds where it contained Zn impurity (Sorokin et al., 2009). Unusual (spherical, lamellar, etc.) nanoparticles of secondary gold with Co and Zn precipitated on peat by microbial mediation were observed in experiments (Kuimova et al., 2011). Gold with Cu impurities found in brown coal resulted from reduction by fungi at the stage of peat deposition (Kuimova et al., 2012). Bioaccumulation of Cu-bearing gold by sulfate-reducing bacteria was also reported by Lengke and Southam (2005,



**Fig. 8.** Distribution of Au and Ag in solid particles of dispersion train and their preliminary statistics. a: Ag in wastes; b: Ag in peat; c: Au in wastes; d: Au in peat. Legend: 1 = forests; 2 = residential areas; 3 = wastes I; 4 = wastes I; 5 = proximal zone of dispersion train composed of shed wastes I; 6, 7 = distal zone of dispersion train; 8 = main AMD stream; 9 = sampling sites (circle sizes are proportional to concentrations); 10\* = range of contents (ppm); 11\* = scale of highest contents (ppm). Sizes of circles are proportional to concentrations (the largest ones corresponding to peaks).

2006). Experiments demonstrate that nanoparticulate gold produced by sorption on peat may bear Cu just because of multiple stages in the process (ion exchange and incorporation of the sorbent functional group into the noble metal complex) leading to prolonged sorption equilibration (Radomskaya et al., 2015).

#### 4.3. Vertical patterns of gold and silver

Gold and silver have different vertical patterns in the contamination train around the tailings (Fig. 2). Silver is quite uniformly distributed, in both wastes and peat, though there are local highs at sites where wastes II are mixed with peat (Fig. 2c, trench 7, samples 7–2, 7–3) and lows away from the tailings where mud is mixed with organics and covered with ochreous precipitates (Fig. 2d, trench 8, samples 8–4).

Unlike silver, the distribution of gold is uneven (Fig. 2). Gold concentrations are especially high in peat at its interface with wastes: 4 to 20 times higher than in wastes, in all trenches (Fig. 2a, b, trenches 1 and 6, respectively) except for the most distant zone (Fig. 2d, trench 8). The gold contents in buried peat are lower but still high (to 0.5 ppm).

The patterns of both Au and Ag differ as a function of distance from the tailings, which is evident in depth profiles and in lateral distribution.

#### 4.4. Lateral patterns of gold and silver

The lateral distribution of gold and silver in peat and wastes was mapped using preliminary statistics of geochemical data (with the  $\chi^2$ criterion, or chi-square test for goodness of fit). The maps of concentration isolines were compiled without spikes (both extremely high and low values) which were replaced by sample maximums (minimums). The sites of peak concentrations are marked by largest circles in Fig. 8.

#### 4.4.1. Ag and Au in wastes

The lateral distribution of Ag in the shed wastes is relatively uniform (Fig. 8a): mean contents (13 ppm) are close to the median (12 ppm) and to the contents in tailings (Table 1). Within the contamination train, there are several sites with high Ag enrichment (Fig. 8a): near the pile of wastes I (to 28 ppm); near the pile of wastes II (16–20 ppm); at short distances from the tailings, where the wastes of two types are intercalated and drained by the AMD waters (to 24 ppm). High enrichment in the latter case is associated with inclusions of Agbearing minerals in pyrite and barite (Myagkaya et al., 2016), which precipitate in greater abundance according to hydraulic sorting, as well as with Ag isomorphic impurity in jarosite (Dill, 2001) having large percentages in wastes II.

The distribution of gold is likewise uniform (Fig. 8c), mostly within the range 0.1–1.3 ppm. The mean contents in wastes I and II are 0.53 ppm and 0.7 ppm, respectively, and are lower (0.38–0.45 ppm) near both piles. In the dumps of wastes I and wastes II the contents are, respectively, 0.5 ppm and 0.26 ppm. The gold contents are high (up to 3.8 ppm) in 10% of the sample and are distributed randomly over the train. Higher values more often fall within the AMD stream and the areas it floods, at medium distances from the tailings (Fig. 8c). This pattern is consistent with mineralogical data of low Au° contents in the wastes (Myagkaya et al., 2016).

## 4.4.2. Ag and Au in peat

Mean Ag (11.2 ppm) in peat within the dispersion train is slightly lower than in the shed wastes (Fig. 8a, b). The difference may result from preferable Ag reprecipitation in wastes upon oxidation leaching. However, the silver contents in peat are locally notably above the mean, indicating that the enrichment does occur but the required conditions realize only locally. The high-Ag sites are distributed in different ways in wastes and peat. The distribution is quite uniform near and away from the piles. Silver in peat is especially high opposite the pile of wastes II flooded by AMD waters (Fig. 8b). The highest value of



Fig. 9. Au and Ag enrichment of peat over wastes, where \* denotes extremely high contents (logarithmic scale).

560 ppm Ag is due to Ag and silver iodide impurities in Se-bearing Hg sulfides.

The lateral distribution of gold in peat is very uneven (Fig. 8d), the contents varying from 0.18 to 155 ppm Au, being most often between 0.18 and 19 ppm. The arithmetic mean for this range (5 ppm) is ten times greater than the mean for the wastes (0.56 ppm). The Au concentrations in peat are the highest near the tailings, unlike those in wastes which are higher in the intermediate zone. There are three main sites of high Au: (1) interface of wastes I and II near the tailings and the main AMD channel (mean 7 ppm, 40 ppm the highest); (2) boundary between the proximal and middle zones of the train, far from the tailings, where the two types of wastes are intercalated and drained by the main AMD stream (mean 13 ppm); (3) eastern protrusion of the intermediate zone flooded by AMD waters and buried under wastes II (Fig. 8d), where most of the mounds are located (mean 32 ppm). This is the area where extremely high Au concentrations (40 to 155 ppm) were recorded.

Thus the peat around the Ursk tailings concentrates much more gold than wastes (Fig. 9); the logarithmic coefficient of gold concentration from AMD waters is LogCC ~4 for mean values of Au in peat and an order of magnitude higher with extremely high contents taken into account (Fig. 10). Gold in wastes II must be more mobile, and thus more easily escapes to become entrained with waters and accumulated in peat, while the AMD-affected area is bio-geochemically favorable for Au° precipitation. The contents of silver in wastes and peat are similar



Fig. 10. Sorption of elements (logarithmic concentration coefficient (LgCC)) from AMD waters on peat.

on average, but are locally very high in peat. The respective concentration coefficient LogCC of silver the peat takes from AMD waters is 5 for the mean Ag contents and about ten times higher for all values including the peaks (Figs. 9, 10).

As for the behavior of other elements in the system "sulfide wastes– AMD waters–peat" (Figs. 9, 10), peat concentrates much Hg, Ba, K, Pb and Se from AMD waters (Fig. 10). Compared with wastes, peat is more strongly enriched in Cu, Ca, Zn, Mn, Hg (Fig. 9) but contains less Ba, Pb, Na, K, Al, and Mg. The difference may be due to low solubility of barite, low mobility of Pb, and higher contents of clay minerals in wastes than in peat.

## 5. Discussion

Summing up the two parts of our study on the behavior of gold and silver in the system of sulfide tailings (this paper and (Myagkaya et al., 2016)) with the example of the Ursk gold-bearing high-sulfide tailings, we suggest a model for migration of noble metals in supergene environments. The model explains all stages of the process from oxidation leaching of primary ore to redistribution of elements in the dispersion train around the tailings.

The tailings consist of primary ore and ore from the gold-bearing weathering profile (cyanidation wastes I and II, respectively), with remnant 0.5 ppm Au and 18 ppm Ag in the former. Metallic gold is rare and has been found only once so far. Most gold is invisible (Cook and Chryssoulis, 1990; Kalinin et al., 2009; Kovalev et al., 2011; Zhmodik et al., 2012; Tauson et al., 2014) being disseminated in sulfides, adsorbed on solid particles, etc. Silver is present as impurity in minerals preserved as inclusions in pyrite (chalcopyrite, telluride, and Hg selenide), as well as in its proper minerals (geffroyite and naumannite). Wastes II store less gold and silver (0.26 ppm Au and 13 ppm Ag). Gold in this material may be adsorbed on grain surfaces of layered clay minerals and Fe(III) compounds, etc.; Ag may be as isomorphic impurity in jarosite (Dill, 2001).

As a result of oxidation leaching, elements (Al, Fe, Cu, Zn, Pb, As, Se, Te, Hg, Cd, REE, etc.) are mobilized and transferred to the solution (Myagkaya et al., 2016). Gold and silver, which are mobile in supergene environments (Bowell, 1992; Dutova et al., 2006; Reith and McPhail, 2007, etc.), likewise become leached: in AMD waters, dissolved Au and Ag concentrations reach 0.2–1.2 and 0.1–0.3 ppb, respectively, and decrease to 0.003 ppb Au and 0.008 ppb Ag away from the tailings. This trend is common to most other elements coexisting with noble metals (Myagkaya et al., 2016). Proceeding from published evidence of gold speciation and transport (Mann, 1984; Benedetti and Boulegue, 1991; Radomskaya et al., 2005; Xia, 2008; Ta et al., 2014), we infer that gold ion complexes present in the solution break down away from the tailings under the effect of high pH, while solid particles that precipitated on the bottom of the AMD creek (Mironov et al., 1989; Leybourne et al., 2000) adsorb elements, including gold and silver. Sorption of metal cations is especially active in the conditions of high pH and precipitation of iron hydroxides (Seal and Hammarstrom, 2003). Silver, present as isomorphic impurity in alunite-jarosite group minerals (Menchetti and Sabelli, 1976; Rattray et al., 1996; Dill, 2001) existing as suspended particles (Myagkaya et al., 2016), is likewise mostly suspended in all solutions we analyzed. Thus, there are three stages of gold migration in a surface stream: (1) oxidation leaching from wastes and transport by AMD waters, (2) change from dissolved Au to suspended particles away from the tailings, and (3) precipitation to sediments. Silver becomes dissolved and transported with suspended matter.

The natural peatbog in the swampy ravine downstream of the Ursk tailings is exposed to the effect of Au-bearing acid mine drainage waters and wastes II shed form the piles. Being a biogeochemical barrier (Varshal et al., 1996; Wood, 1996; Brown et al., 2000; Koivula et al., 2009; Kuimova et al., 2011; Parviainen et al., 2014), peat accumulates a broad range of elements, judging by the concentrations of Zn (to

7270 ppm), Se (to 6060 ppm), Ag (to 560 ppm), Au (to 155 ppm), and Hg (to 11,730 ppm) which are higher in peat than in the wastes (to 160–286 ppm Zn, 107–159 ppm Se, 13–18 ppm Ag, 0.26–0.5 ppm Au, and 36–75 ppm Hg).

Comparing the mineralogy of peat in the dispersion train with the vertical and lateral patterns of gold, we suggest gold concentration either in anoxic or oxygenated conditions. The anoxic (reduced) setting occurs in peat itself, which may accumulate gold by two mechanisms that can act in "organic matter-noble metals" systems (Ong and Swanson, 1969; Bowell, 1992; Bowell et al., 1993a,b; Varshal et al., 2000; Kuimova et al., 2011, 2012; Avramenko et al., 2012). One mechanism is accumulation by organic matter due to (i) reduction of ion gold by dissolved organic compounds and its further stabilization by organic molecules (Ong and Swanson, 1969; Avramenko et al., 2012) or (ii) sorption as a result of Au<sup>+</sup> complexation with organic ligands (Varshal et al., 2000). However, the sorption capacity of organic matter decreases upon degradation of peat as the chemical bonds of humic acid groups break down. In this case, gold becomes redistributed with the formation of fine Au particles and sulfides (Varshal et al., 2000). By binding with fulvic acids, gold becomes more mobile (Bowell, 1992; Bowell et al., 1993a, b), which is recorded in the presence of supergene sulfides in peat within the train (pyrite, sphalerite, metacinnabarite).

On the other hand, the secondary minerals mentioned above indicate a possibility of microbially mediated reprecipitation of gold. The framboidal morphology of pyrite and nanometer particles of sphalerite result from reduction of sulfate, which is known to be part of metabolism in bacteria (Craig, 1980; Weber et al., 1998; Belogub, 2009; Bobrov et al., 2011; Perelomov et al., 2013; Wang et al., 2013). We also observed Se-bearing sulfide substitutions for bacterial cells coexisting with fossil cell remnants. This provides additional proof that microorganisms can act as a biogeochemical barrier and thus play a critical role in precipitation of minerals. Selenium, a biologically active element, is a nutrient for some bacteria (Umysová et al., 2009). Sulfate-reducing bacteria can destabilize gold(I)-thiosulfate complex  $(AuS_2O_3)^{3-}$  and precipitate nanoparticulate elemental gold by creating localized barriers where Au<sup>+</sup> mobilized from the gold-thiosulfate complexes in AMD and pore waters reduces to Au° while sulfates reduce to sulfides (Lengke and Southam, 2006). Redistribution of gold in the anoxic environment may produce extremely high Au concentrations reaching 80 ppm without formation of elemental gold, at the account of invisible gold which remains disseminated in authigenic sulfides. Gold is known to be sulfophilic and able of accumulating on the barriers of diagenetic iron sulfides (Korobushkina and Korobushkin, 1998; Lengke and Southam, 2006).

The oxygenated environment favors precipitation of Fe<sup>3+</sup> compounds (X-ray amorphous mixed compounds of Fe hydroxides and sulfates and crystalline K and Na-K-jarosite) that cover organic remnants, as well as precipitation of elemental gold. Coexistence of goethite and jarosite (Bigham, 1994; Gas'kova et al., 2007) with the sulfides (see above) attests to chemical contrasts in the environment, with local redox barriers. Bio-accumulation of gold is possible also in oxygenated conditions which are favorable for some microorganisms, e.g., Acidithiobacillus thiooxidans (Blowes et al., 2003; Lengke and Southam, 2005). Biotic precipitation of gold is also indicated by the presence of Cu impurity in gold particles (Kuimova et al., 2012), which we observed in the analyses. The model of gold precipitation mediated by thiosulfate-oxidizing Acidithiobacillus thiooxidans in an oxygenated environment (Lengke and Southam, 2005) implies that microorganisms use gold-bearing complexes as an energy source and oxidize them to sulfate in the course of metabolism; thereby sulfate is brought to the cell surface while Au° precipitates as colloidal particles inside the cells and on the surface. Gold colloids may exist in cells in the presence of the gold-thiosulfate complex breaking down to Au<sup>+</sup> and  $S_2O_3^{2-}$ . Bacteria reduce Au<sup>+</sup> to Au<sup>°</sup> in order to mitigate its toxic effect, while thiosulphate becomes again oxidized to sulfate. This model provides quite a reasonable explanation for gold bio-accumulation

upon local redox barriers around the Ursk tailings. Note that the occurrence of Au° does not correlate with high or abnormal gold contents. Furthermore, panning of waste and peat samples does not increase contents of gold, which thus occurs mostly in invisible form in the dispersion train of the Ursk tailings.

## 6. Conclusions

Mining at the Novo–Ursk deposit since the 1940s has produced a mixed natural–industrial system "wastes–gold-bearing AMD–peat", which makes a model of a technogenic mineral deposit. The system undergoes several basic processes.

- (1) Sulfides in cyanidation wastes stored in piles on the surface are exposed to moisture and air oxygen and their oxidative leaching produces acid mine drainage (AMD) with high Fe, Al, Cu, Zn, Se, Ba, Sr, Cd, Te, Hg, and Ag enrichments. As sulfides decompose, they release Au which has eluded extraction during ore processing (Myagkaya et al., 2016).
- (2) Interaction between gold-bearing acid mine drainage waters and peat in the dispersion trains of sulfide-bearing tailings leads to accumulation of very high (sometimes extreme) contents of silver and especially gold in organic matter. Peat within the dispersion train of tailings contains 11.2 ppm Ag and 5 ppm Au on average. The concentrations of gold and silver are the highest (155 ppm Au and 560 ppm Ag) in the flooded part of the train where living bacteria are especially abundant, judging by cell remnants and mineral pesudomorphs making sheaths over bacterial cells.
- (3) Mean contents of Au in peat are ten times higher than in wastes (the maximum being two orders of magnitude higher). Thus, the Ursk tailings simulate technogenic mineralization, and its conditions prompt how secondary gold can be obtained technologically from the existing tailings.

In addition to gold and silver, peat also accumulates potentially toxic elements (Cu, Zn, Se, Hg, Pb), especially mercury. Thus, the reported processes provide clues to technologies for immobilization of these elements.

- (4) AMD-peat interaction leads to generation of new elemental gold. This secondary gold either is chemically bound and invisible or occurs as nanometer particles (from tens of nm to  $1.5-4 \mu$ m). Not only gold reprecipitates on peat but also most of elements dissolved in AMD (Na, Mg, Al, Si, K, Ca, Ba, Sr, Fe, Ni, Al, Cu, Zn, Pb, Hg, Ag, etc.). Their reprecipitation produces secondary phases, such as iron hydroxides, jarosite, clay minerals, gypsum, framboidal pyrite, tiemannite, Hg and Zn sulfides, and barite; among these, gold coexists directly with secondary pyrite, tiemannite, Hg and Zn sulfides, and barite. Silver reprecipitates on peat as silver-bearing sulfides and selenides. The presence of fossil bacterial cells indicates that physicochemical processes can be microbially mediated and lead to sulfide and gold mineralization by sulfate reduction and biosorption.
- (5) Accumulation of noble metals results from several complex processes, especially, reduction of ion gold to elemental Au, sorption by complexation, microbially mediated chemical reactions, etc. Microbial activity may be responsible for high contents of gold and Hg minerals. Additional studies are required to identify the species in such communities, as a basis for investigation of element-specific strains of potential value for biotechnological uses.
- (6) Peat in the area of the Ursk tailings is actually a prototype of coalbeds. Therefore, the mineralogical and geochemical patterns of gold and silver reprecipitation on organic matter, and the respective Au and Ag enrichment, provide insights into the early history of gold mineralization in coal.

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