Redistribution of elements between wastes and organic-bearing material in the dispersion train of gold-bearing sulfide tailings: Part I. Geochemistry and mineralogy

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HIGHLIGHTS

- Organic-bearing material interacting with high-sulfide wastes accumulates Cu, Zn, Se, Cd, Ag, Au, Hg.
- High contents of Zn, Se, and Hg reside in sulfides and selenides, which form sheaths on microbial cells.
- Average gold content in organic-bearing material is 10–30 g/t and locally reaches 345 g/t.

GRAPHICAL ABSTRACT
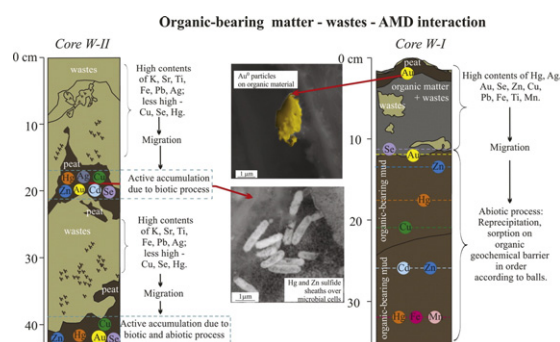
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ABSTRACT

Migration and redistribution of elements during prolonged interaction of cyanide wastes with the underlying natural organic-bearing material have been studied in two ~40 cm deep cores that sample primary ores and their weathering profile (wastes I and II, respectively) in the dispersion train of gold-bearing sulfide tailings in Siberia. Analytical results of SR-XRF, whole-rock XRF, AAS, CHNS, and SEM measurements of core samples show high K, Sr, Ti, and Fe enrichments and correlation of P_2O_5 and Mn with LOI and C_{org}. Organic material interlayered or mixed with the wastes accumulates Cu, Zn, Se, Cd, Ag, Au, and Hg. The peat that contacts wastes II bears up to 3 wt.% Zn, 1000 g/t Se, 100 g/t Cd, and 8000 g/t Hg. New phases of Zn and Hg sulfides and Hg selenides occur as abundant sheaths over bacterial cells suggesting microbial mediation in sorption of elements. Organic-bearing material in the cores contains 10–30 g/t Au in 2–5 cm thick intervals, both within and outside the intervals rich in sulfides and selenides. Most of gold is invisible but reaches 345 g/t and forms 50 nm to 1.5 μm Au^0 particles in a thin 2–3 cm interval of organic remnants mixed with wastes I. Vertical and lateral infiltration of AMD waters in peat and oxidative dissolution of wastes within the dispersion train of the Ursk tailings lead to redistribution of elements and their accumulation by combined physical (material's permeability, direction AMD), chemical (complexing, sorption by organic matter and Fe(III) hydroxides) and biochemical (metabolism of sulfate-reducing bacteria) processes. The accumulated elements form secondary sulfates, and Hg and Zn

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selenides. The results provide insights into accumulation of elements in the early history of coal and black shale deposits and have implications for remediation of polluted areas and for secondary enrichment technologies.

1. Introduction

Tailings left by mining and ore processing are sources of pollution as oxidation of sulfides exposed to free oxygen access leads to the formation of acidic sulfate solutions (Blowes et al., 2003; Favas et al., 2016) with high concentrations of potentially toxic elements such as Fe, Cu, Zn, Pb, Hg, Cd, As, etc. (Lazareva et al., 2002; Rieuwerts et al., 2014; Kwon et al., 2015). Particulate and dissolved elements carried off the tailings by streams and wind form extensive geochemical trains (Sarmiento et al., 2011; Huang et al., 2016). However, besides being a source of pollution and hazard (Sima et al., 2011), wastes containing unrecovered useful components may become a source of manmade mineral deposits (Bortnikova et al., 1996; Makarov and Talalay, 2012; Kirillov et al., 2016). Specifically, peat within the contamination trains of sulfide cyanide wastes can accumulate as much as 155 g/t Au and 560 g/t Ag (Myagkaya et al., 2013, 2016a, 2016b).

In this respect, interaction of acid mine drainage (AMD) waters and wastes with organic material (Parviainen et al., 2014) is worth special attention because peat, plant detritus, or living matter can act as a natural sorption and reduction barrier for many elements (Arbuzov et al., 2006; Lourie and Gjengedal, 2011). Organic matter can take up elements by various physical, chemical, and biological processes, such as settling, filtration, adsorption, precipitation, co-precipitation into insoluble compounds, ion exchange, etc. Thus, it is a perfect sorbent for AMD purification (Brown et al., 2000; Sheoran and Sheoran, 2006; Chen et al., 2016). However, organic matter can release the adsorbed metals in the case of oxidation (Tipping et al., 2003).

Under limited oxygen access and high moisture, natural organic matter is known to capture heavy metals (Fe, Cu, Zn, Cd, Hg, Pb) from sulfate AMD by microbially mediated sulfate reduction, which leads to formation of secondary sulfides of metals and oxidation of organic matter (Brown and Macqueen, 1985; Spratt et al., 1987; Sheoran and Sheoran, 2006). Similar reactions can occur with Se that forms selenite anions, elementary Se, selenides (Oremland et al., 1990; Lusa et al., 2015; Nancharaiah and Lens, 2015), and Se organic compounds (Masscheleyn and Patrick, 1993).

Mechanisms responsible for accumulation of precious metals remain poorly understood. Several suggested possibilities for gold are reduction of ion gold by dissolved organic compounds and its further stabilization by a layer of organic molecules (Avramenko et al., 2012); sorption by Au^+ complexing with functional groups of organic compounds (Radomskaya et al., 2015); or biosorption (Kuimova et al., 2012), all producing Au^0 particles. Silver inseparably co-occurs with gold and may participate in ion exchange and formation of Ag-organic complexes (Mousavi et al., 2015; Kleja et al., 2016).

The role of organic matter and microorganisms in accumulation of Au, Ag, PGE, REE, Ge, U, Ta, Nb, and other elements in various geological settings has been largely discussed (Arbuzov et al., 2006; Reith et al., 2013; Han et al., 2015; Dai et al., 2016; Fuchs et al., 2016; Shuster et al., 2016). However, these processes are hard to model and observe in the field, for several reasons: carbonization of organic matter with age; low concentrations of target elements in natural systems; necessity of studying systems as a whole rather than their individual components; time limitations on laboratory studies of natural processes; complexity of modeling real natural systems; strict requirements to analytical resolution and sensitivity, etc. Knowledge of wastes-organic matter interactions is crucial to many fields of science and technology. It can provide clues to mechanisms that drive accumulation of elements in zones of supergenesis and can help modeling such processes for heavy and precious metals in fossil organic systems such as coal or

black shale. Also this knowledge has implications for technologies of secondary enrichment and creating manmade deposits by increasing locally the concentrations of useful components. As well as, it can make basis for remediation of territories contaminated by tailings (Chen et al., 2016).

This study addresses mineralogical and geochemical redistribution of multiple elements in the system "organic matter-sulfide-bearing wastes" with an example of two cores composed of cyanide wastes and buried organic-bearing mud from the dispersion train of the Ursk sulfide tailings (West Siberia, Russia). Several methods (high-resolution SR-XRF scanning, whole-rock XRF, AAS, CHNS, and SEM) are applied jointly to analyze the behavior and speciation of elements along the two cores with implications for mechanisms by which toxic and precious components precipitate on organic barriers. This is the first attempt to gain a comprehensive perspective of processes that govern the behavior of precious metals and toxic elements, as well as rock- and ore-forming components. This paper reports the first part of the study, with a special focus on sites where the precious and toxic elements reach the highest concentrations in the cores of wastes and organic-bearing material. The second part of the study concerning speciation of elements investigated by sequential extraction techniques will be the subject of the following publication with a tentative title *Redistribution of Elements between Wastes and Organic-Bearing Material in the Dispersion Train of Gold-Bearing Sulfide Tailings: Part II. Speciation of Elements*.

2. Ursk tailings site

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, southwestern Siberia, Russia). 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 Ursk tailings have been dumped in two 10–12 m high piles of primary ore (wastes I) and its 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%). Pyrite preserves inclusions of other opaque minerals: galena, chalcopyrite, bornite (Cu_5FeS_4), arsenopyrite, sphalerite, tennantite, altaite (PbTe), geffroyite ($(Ag,Cu,Fe)_9(Se,S)_8$), and mercury telluride. Barite encloses naumannite (Ag_2Se) and mercury selenide with significant amounts of Ag and S: $Hg_{0.8}Ag_{0.2}Se_{0.7}S_{0.3}$ (Gustaytis et al., 2010; Shcherbakova et al., 2010; Myagkaya et al., 2016a, 2016b).

Wastes II contain barite, pyrite, quartz, gypsum ($CaSO_4·2H_2O$) and goethite (α-FeOOH), as well as aluminosilicate minerals: muscovite, albite, minor chlorite, and trace microcline ($K(AlSi_3O_8)$). Compared to wastes I, they bear smaller percentages of barite and pyrite (4% and 9%, respectively) but more abundant quartz (60%) and jarosite ($KFe_3(OH)_6(SO_4)_2$). As for chemistry, wastes I have higher Fe, Cu, Zn, Se, Sr, Cd, Te, Ba, Hg and Pb contents, while wastes II are richer in Na, Mg, Al, Si, K, Ca, Ti and Rb. Residual Au and Ag concentrations are generally lower in wastes II (0.26 and 13 g/t) than in wastes I (0.5 g/t and 18 g/t), respectively.

The wastes remain unfixed and are exposed to rainfall and floods, being thus shed to the natural swampy peat ravine where peat has been in permanent interaction with acid mine drainage (AMD) waters and wastes. The site is drained by a natural creek which has turned into an AMD stream flowing 0.7 km further into the Ur River. The AMD waters have pH = 1.9, Eh = 655 mV, TDS ≤ 4.8 g/L, and a sulfate chemistry with SO_4^{2-} reaching 3600 mg/L, quite high enrichments of