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GEOLOGY

Role of Microorganisms in the Supergene Transformation of Polymetallic Ores and the Formation of Biogeochemical Anomalies of Noble Metals in Deposits of Transbaikalia

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Sulfide and sulfide–oxide ores of silver–lead–zinc deposits (Tarbagatai, Mykert-Sanzheev, and Dovatka) of the Dzhida–Vitim base metal belt confined to the Paleozoic–Mesozoic Uda–Vitim rift zone are characterized by high contents of Ag (up to 2990 g/t), platinum group metals (up to 12.3–74.6 g/t), and Au (up to 1.2 g/t) [1]. Oxidized ores are more enriched in noble metals than primary ores. It has also been established that, relative to incinerated samples of undecomposed wood, wood ash of decayed stumps of pine and larch growing above orebodies of the Mykert-Sanzheev deposit are characterized by the highest concentrations of Ag, Au, Pt, and Pd [2, 3]. For example, wood ash of decayed stumps, old crust, and decayed pine cone in the Mykert-Sanzheev deposit area is characterized by anomalously high concentrations of Ag (3000 g/t), Pt (5 g/t), Ru (230 mg/t), Au (190 mg/t), and Pd (60 mg/t), which are comparable with their concentrations in sphalerite–galena ores.

Phytotissue samples of extinct and artificially decayed wood contain opal, chalcedony, quartz, hydromica, fluorite, magnetite, iron and manganese oxides, marcasite, pyrite, pyrrhotite, galena, sphalerite, arsenopyrite, cerargyrite, and native gold [4]. Pt and Pd were supplied to plants from a depth 1.5–3.5 m below the day surface in the eluvium horizon (oxidation zone) of orebodies [3]. Oxidized sphalerite–galena ores contain particles of native platinum (up to 8 μm in size) and Os-iridium. The oxidation zone in the loose sedimentary section is distinguished by high contents of the following elements (mg/t): Pt (20–500), Pd (5–60), Ir (up to 60–120), Rh (up to 40–60), and Ru (20–40). The zone is also enriched in Au (up to 0.4–0.8 g/t in the clay fraction) and Ag (up to 800 g/t). According to [4], the development of intense biogeochemical anomalies of native metals is related to the formation of native metals (microbiolites) in the course of ageing and dying of plant cells. This process is accompanied by the concentration of Ag, Au, and PGE due to the self-purification of phytotissues and the formation of respective minerals during the evaporation of solutions. However, this model is inconsistent with experimental data on K^+ and Ca^+, suggesting a drastic decrease in the contents of cations in exudates of plant roots devoid of the nutrient medium [5].

The results of our experimental works made it possible to substantiate the bacterial nature of the concentration of Ag, Au, and PGE biogeochemical anomalies discussed above and elucidate the role of microorganisms in the transformation of primary ores in oxidation zones in the Mykert-Sanzheev and Dovatka deposits.

Depending on the degree of tectonic reworking of quartz–sulfide orebodies, the root-inhabited section of the ore oxidation zone in the Mykert-Sanzheev deposit contains 5–50% of supergene minerals. The relict association of primary ore minerals is represented by galena, sphalerite, pyrite, chalcopyrite, silver sulfosalts (pyrargyrite and matildite), bismuthite, albandine, pyrrhotite, ilmenite, rutile, magnetite, and native gold. Fine particles (10–15 μm) of native gold make up a sparse dissemination in quartz at its contact with chalcopyrite–pyrite–galena aggregates. The supergene mineral associa-

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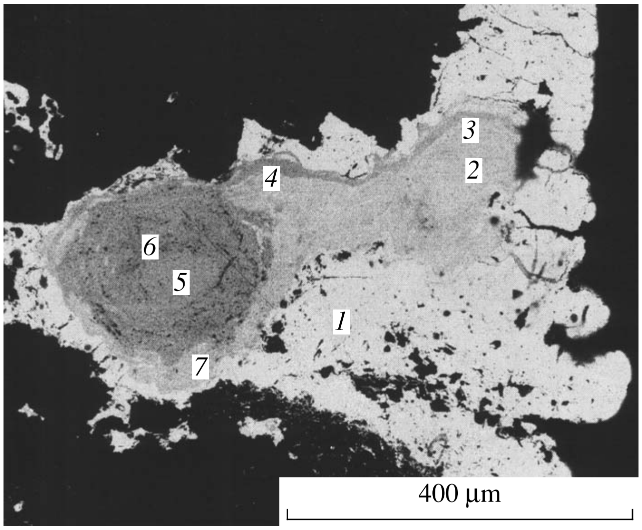

Fig. 1. Concentric-zonal organomineral aggregate from oxidized base metal sulfide ores of the Mykert-Sanzheev deposit. The structure includes discontinuous rings composed of remains of bacterial colonies (black inclusions) and segregations of cerargyrite and chloraluminite. Minerals: (*1*) cerussite, (*2*) argentite with galena, (*3*) cerargyrite, (*4*) argentite with admixture of galena, cerargyrite, and chloraluminite, (*5*) argentite, cerargyrite, and chloraluminite, (*6*) cerargyrite, argentite, and chloraluminite, (*7*) argentite with admixture of galena.

tion includes cerussite, anglesite, hematite, limonite, pyrolusite, covellite, zincite, chalcocite, malachite, calcite, siderite, magnesite, apatite, fluorite, hydromica, iron sulfates, argentite, cerargyrite, vanadates (mottramite and tangeite), chloraluminite, native silver and its alloys with Mo and Pb ($Mo_{0.2}Ag_{0.8}$; $Mo_{0.21}Pb_{0.4}Ag_{0.65}$), native platinum, and Os-iridium.

In contrast to primary ores of the Mykert-Sanzheev deposit, primary ores of the Dovatka deposit are enriched in magnetite. With respect to its content, the ores can be divided into the sphalerite–magnetite, magnetite–sphalerite (with galena), and sphalerite–galena (with magnetite) varieties. Secondary and accessory minerals are represented by chalcopyrite, pyrrhotite, marcasite, pyrite, stannite, löllingite, tetrahedrite, bournonite, silver sulfosalts, and native gold. The association of oxidized ores (the oxidation zone is developed to a depth of 20 m) includes martite, hematite, limonite, covellite, smithsonite, pyrolusite, manganite, jarosite, plumbojarosite, copper carbonates, and native silver. It is known that microbiological processes play a significant role in transformations of hypogene sulfide minerals in oxidation zones of base metal deposits [6, 7]. Processes of oxidation are particularly intense under the influence of autotrophic thionine bacteria, in particular, *Thiobacillus ferrooxidans.* In the course of the bacterial oxidation of sulfides, native metals and rare metals situated in the fine-dispersed and/or isomorphous form are transferred to the solution.

Study of samples of oxidized ores from the Mykert-Sanzheev deposit revealed that secondary silver minerals make up a rhythmic-banded structure around oval galena grains. Such galena-based aggregates include oncolite-shaped concentric-zonal organomineral coatings (Fig. 1). They are composed of cerargyrite, argentite, chloraluminite, and spherical (coccoid) or less common rod-shaped segregations of extinct bacteria. Analogous microstructures were obtained in experiments with oxidation of galena and its transformation into anglesite with the help of *Thioparus* subsp. *antimoniticum*, which can oxidize the reduced sulfur compounds at pH = 6–8 [7]. However, the oxidation zone in our case is characterized by pH = 2–6 and the abundance of Fe. Such a zone could be formed only with the active participation of sulfur-oxidizing bacteria, such as *T. ferrooxidans.* Indeed, we found sulfur-oxidizing bacteria of the *Thiobacillus* group in accumulator cultures obtained from biochemical soil samples taken above oxidation zones of orebodies (Table 1). They are represented by gram-negative mobile rods 0.5 × 1.0 µm in size.

Intense biogeochemical anomalies of noble metals above ore zones are related to wood plants subject to ageing and decay up to the point of their extinction and transformation into the humic substrate. In order to study the nature of such anomalies, we carried out microbiological, mineralogical, and geochemical investigation of samples of pine (*Pinus silvestris*) and larch (*Larix dahurica*). The results showed that the wood bacterial community is dominated by organotrophs (proteolytes, cellulose-decomposing bacteria, and others) that exploit a wide range of organic compounds (organic acids, alcohols, carbohydrates, and aromatic compounds) for processes of constructive and energetic exchange. The population of sulfur-oxidizing bacteria is significantly smaller (their characteristics are given below). Sulfur-reducing bacteria are rare (Table 1).

The accumulator culture was prepared from wood samples of decayed stumps and underlying soil at the Dovatka deposit. The culture contained not only the physiological groups of microorganisms mentioned above, but also filiform forms of bacteria similar to *Callionella* (10^2 cells/ml). Gram-negative cells in the forms of vibrions similar to *Desulfovibrio* were also present.

In order to detect and identify biogenic minerals, we took a special phytotissue sample (12 kg in weight) from the decayed core of pine stump in the Sanzheevka sector. We omitted the wood material of the saw cut zone that could be contaminated with the eolian dust. After the washing and removal of wood fragments subjected to weak bacterial decomposition, the heavy concentrate of the sample was investigated under X-ray and electron microscopes. We recognized calcite, dolomite, an unidentified mineral of the isomorphous lazulite–scorzalite series, tachyhydrite, aluminite, sigloite, calcium hydrosilicates, and native gold. Gold particles, 1.1–2.3 µm long and 0.4–0.75 µm thick (Fig. 2), con-

Table 1. Population of bacteria in wood plants and soil beneath orebodies of the Mykert-Sanzheev and Dovatka base metal deposits with native metals

Characteristics of samples	Population of bacteria (cells/ml)		
	organotrophs	sulfur-oxidizing	sulfur-reducing
Mykert-Sanzheev deposit			
Soil beneath pines (5)	$\frac{3.4 \cdot 10^5–5 \cdot 10^7}{3.53 \cdot 10^7}$	$\frac{10–9.4 \cdot 10^3}{3.2 \cdot 10^3}$	n.d.
Roots of decayed pine stumps (1)	$4.6 \cdot 10^7$	$1 \cdot 10^3$	n. d.
Crust of decayed pine stumps (1)	$9.6 \cdot 10^7$	43	n. d.
Wood of decayed pine stumps (2)	$\frac{1.1 \cdot 10^6–6 \cdot 10^6}{3.35 \cdot 10^6}$	$\frac{34–100}{67}$	n. d.
Crust of pine (3)	$\frac{3 \cdot 10^5–1.5 \cdot 10^7}{7.3 \cdot 10^6}$	$\frac{0.0–10}{3.3}$	n. d.
Upper layer of wood of intensely decayed larch stumps (1)	$1.5 \cdot 10^6$	0	n. d.
The same, inner crust (1)	$1.31 \cdot 10^6$	100	n. d.
Dovatka deposit			
Soil beneath larch (2)	$\frac{0.5 \cdot 10^7–2.8 \cdot 10^7}{1.65 \cdot 10^7}$	$\frac{2.7 \cdot 10^3–3 \cdot 10^3}{2.85 \cdot 10^3}$	$\frac{12–100}{56}$
Crust of decayed larch stumps (1)	$9.6 \cdot 10^7$	$1 \cdot 10^3$	14
Wood of decayed larch stumps (2)	$\frac{8 \cdot 10^5–8.8 \cdot 10^5}{8.4 \cdot 10^5}$	$1 \cdot 10^3$	n.d.

Note: In Tables 1 and 2, the number of samples is given in parentheses. (n.d.) Not detected.

tain tiny inclusions of cerargyrite and carnallite (Fig. 3). The energy-dispersive spectrum of the biomorphic oval particle (4.4 μm in diameter) revealed an aggregate of acanthite, cerargyrite, and siliceous matter.

Data on the SES analysis (Table 2) are consistent with results of the investigation of the mineral composition of the phytotissue sample of wood analyzed in our work and [4]. The wood was subjected to bacterial decomposition. The mineral and elemental compositions of products of the oxidation zone of base metal ores are surprisingly similar to those of the phytotissue sample from the microbially altered wood plant with the root feeding system in these zones. Hence, the microbially altered biomass of woods growing above oxidation zones of orebodies serves as a natural continuation, i.e., subaerial part of the system. Moreover, one can clearly see vertical zonality in the distribution of minerals (greater diversity of the mineral composition at upper levels) that is typical of supergene zone profiles at many silver deposits [8].

Thus, the materials presented in our work clearly indicate the crucial role of bacteria in the formation of oxidation zones and biogeochemical anomalies at Au- and PGM-bearing silver–base metal deposits. Moreover, one can also see a clear "division of labor" between various physiological groups of the bacterial community. For example, leaching of Ag, Au, and PGE from primary sulfide and oxide–sulfide ores in the

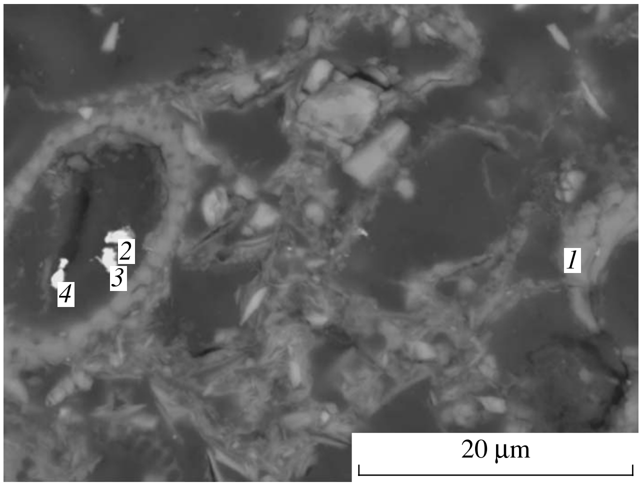

Fig. 2. Gold particles (*1–4*) in the phytotissue sample of a decayed core of a pine stump (Mykert-Sanzheev deposit).

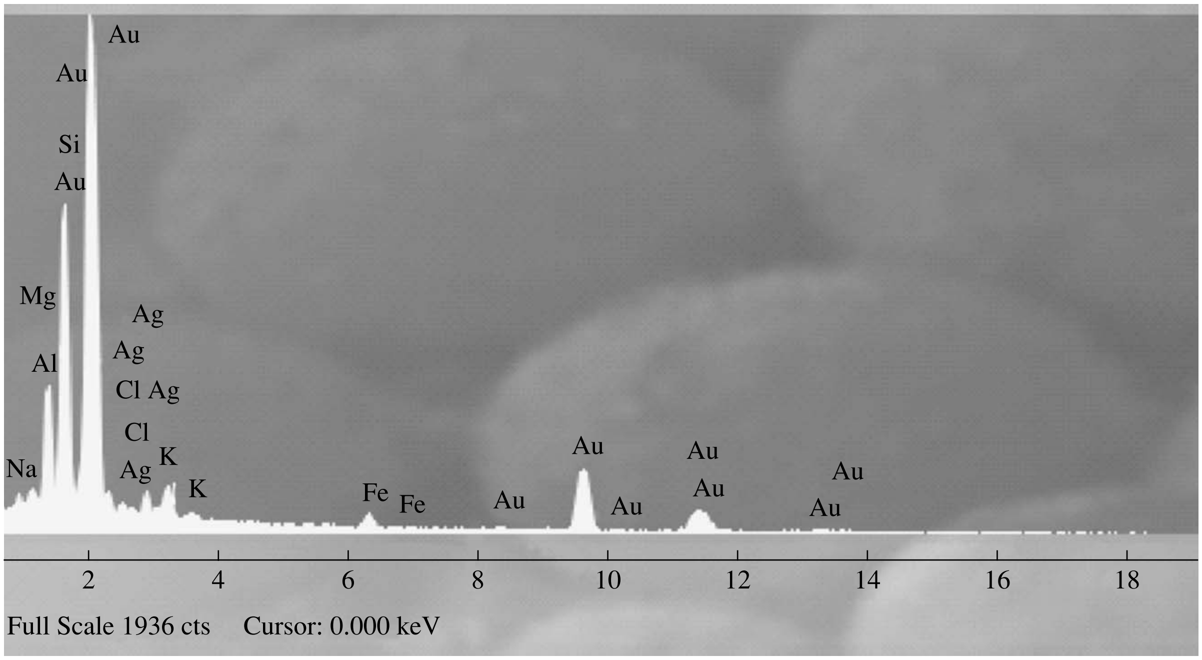

Fig. 3. Energy-dispersive spectrum of native gold in the phytotissue sample (see Fig. 2).

leaching subzone of the oxidation zone was mainly accomplished by the sulfur-oxidizing thionic bacteria. This process was accompanied by the formation of mobile (colloidal and ionic) complexes of these metals. Heterocoagulation (colloidal-biogenic aggregation [9]) and the subsequent deposition of fine-dispersed native noble metals inside the cells of microorganisms, secondary sulfides, and halogenides in the secondary enrichment subzone of the oxidation zone was probably accomplished by Fe-accumulating and S-reducing bacteria [10]. The dissolved compounds of noble and other metals in the leaching subzone were consumed by living trees and distributed in phytotissues more or less uniformly (i.e., without considerable differentiation of their contents). The contrast redistribution of ore minerals, which are concentrated in living plant tissues and transported to the subaerial organs of trees together with water, is related to the activity of organotrophic bacteria (protolytes, cellulolytes, aminolytes, and others). Decomposition of wood owing to this activity promotes the hydrolysis of polymers and the formation of various products (organic acids, low-molecular organic matter, hydrogen peroxide, CO_2, H_2S, H_2, CH_4, and others). The medium thus formed is favorable for the vital activity of bacteria of other physiological groups (sulfate-reducers, spore bacteria, iron bacteria, and so on). These bacteria actively absorb compounds of noble metals and other ore elements to form ore microfossils

Table 2. Contents of noble metals and arsenic in wood plant and soil developed above orebodies of the Mykert-Sanzheev and Dovatka deposits (the samples were dried at room temperature and analyzed by the SES method)

Characteristics of samples	Ag, g/t	Au, mg/t	Pt, mg/t	Pd, mg/t	As, g/t
Mykert-Sanzheev deposit					
Soil beneath pines (4)	0.27–⩾10.0	0.0–700	*n* impulses, high background	0.0–50	0.0–10
Roots of decayed pine stumps (1)	⩾10.0	n. d.	<1000	n. d.	n. d.
Wood and crust of decayed pine stumps (3)	0.114–⩾10.0	100–500	0.0–<1000	n. d.	n. d.
Slightly decayed pine cone (3)	0.0–⩾10.0	0.0–120	0.0–<1000	n. d.	n. d.
Wood of decayed birch stumps (1)	1.268	120	n. d.	n. d.	n. d.
Wood of decayed larch stumps (4)	0.03–0.314	0.0–20	n. d.	n. d.	0.0–10
Dovatka deposit					
Soil beneath larch (2)	0.502–0.82	n. d.	n. d.	n. d.	n. d.

Note: (n.d.) Not detected.

and organomineral aggregates. Such newly formed material includes various sulfates, carbonates, phosphates, vanadates, halogens, hydromicas, and silica minerals.

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