Occurrence modes of As, Sb, Te, Bi, Ag in sulfide assemblages of gold deposits of the Urals

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Abstract. Review of occurrence modes of trace toxic elements ("potential pollutants") in ores from large gold deposits (the Urals) of different genetic types is presented. Mineral forms of these elements as well as their presence in main minerals from gold-bearing sulfide assemblages according to SEM, EPMA, INAA, ICP-MS and LA-ICP-MS are demonstrated.

1. Introduction
At the present time, great attention is paid to the complex use of precious and non-ferrous metals ores, both in Russia and abroad. Besides the main components the gold deposits contain copper, arsenic, antimony, lead, zinc, tungsten, uranium, mercury, bismuth, thallium, selenium, tellurium, etc. Some of these elements have the commercial interest but other are ”potential pollutants”. During ore processing the “pollutants” fall into waste and represent the risk to the environment and health [1, 2]. The importance of the present study is due to the sharply increased in recent years demands for comprehensive utilization of raw and the environmental protection from the effects of toxic industrial waste. It is necessary to study the modes of these elements occurrence in the ore, and their variability in different physical states and the possibility of changes in the technological cycle of ore processing.

2. Materials
The Urals is the oldest (266 years) gold-mine province of Russia [3] where about 60 million tons of sulfide-bearing tailings (gravity separation and flotation) are accumulated. Objects of this study are large gold deposits of different genetic types – Berezovsk (Au), Svetlinsk (Au-Te) and Vorontsovsk (Au-As-Hg). The comparative characteristics of the studied deposits are given in table 1.

3. Methods
Determination of the occurrence modes of potentially harmful elements in the gold ores was studied using complex of methods. Proper mineral forms of these elements were identified by optical and scanning electron microscopy and were investigated using an electron-probe microanalysis (EPMA). Contents of the trace elements in monomineral probes of the main sulfides from gold assemblages were examined by instrumental neutron activation analysis (INAA) and by mass-spectrometry with inductively coupled plasma (ICP-MS). Contents of trace elements in gold-bearing pyrite were determined by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) firstly done for the gold deposits of the Urals. All investigations have been carried out in IGEM RAS, while the LA-ICP-MS was studied also in LabMaTer at the Université du Québec à Chicoutimi (Canada).
Table 1. Characteristics of studied gold deposits

| Deposit, region | Vorontsovsk, North Urals | Berezovsk, Middle Urals | Svetlinsk, South Ural |
|----------------|--------------------------|-------------------------|------------------------|
| Host rocks     | Volcanic-sedimentary (S2-D1) | Volcanic-sedimentary (O-S), gabbro, serpentine, granite | Metamorphosed volcano-sedimentary rocks (D-C) |
| Geochemical type | Au-As-Hg | Au | Au-Te |
| Ore bodies     | Vein-disseminated zones; rare veinlets | Veins | Vein-disseminated zones; veins |
| Wall rock alteration | Propilite, quartz-seritsite, argillizite, jasperoid | Berezite, listvenite | Quartz-biotite (with amphi-bole), quartz-biotite-sericite |
| Stage of mineral formation | Arsenopyrite-pyrite→Pyrite-realar→Sulfosalt-polymetallic→Polymetallic | Ankerite-quartz→Pyrite-quartz→Polymetallic→Carbonate | Quartz-pyrite→Au-Te-polymetallic→Quartz-carbonate-sulfide |
| Au reserves (CAu) | ~60 t (2.8 g/t) | 350 t (2.4 g/t) | ~80 t (1.8-2.8 g/t) |

4. Results and Discussion

Studied chemical elements occur as invisible form in common sulfides as proper minerals (table 2).

a. Arsenic

Mineral forms of As have been found in all studied deposits (table 2) but on the Vorontsovsk deposit its are widespread and the most typical. On the Vorontsovsk deposit arsenopyrite predominates and it contains 10-1018 ppm Au (INAA data), realgar and orpiment being also common. Minerals of tennantite-tetrahedrite series occur on all studied deposits (figure 1). Ratio As/(As+Sb+Bi) ranges from 0.1 to 1 (Vorontsovsk), from 0.04 to 0.07 (Svetlinsk) and from 0.52 to 1 (Berezovsk). According to data LA-ICP-MS pyrite of the Vorontsovsk deposit contains 5.6-12710 ppm of As (figure 2).

Figure 1. Minerals of As, Sb, Te, Ag in ores of Svetlinsk (a), Vorontzovsk (b) and Berezovsk (c) deposits. Q – quartz, Cp – chalcopyrite.

b. Antimony

The most common mineral form of Sb in all studied deposits is tennantite-tetrahedrite. On the Vorontsovsk deposit sulfides of Sb, sulfoantimonides of Pb, Cu, Mn, Fe and sulfosalts of Tl-(Hg)-Sb,As are present in the ores (table 2). Neutron activation analysis revealed antimony in pyrite (0.5-367 ppm), As-pyrite (19.5 ppm - 3.8 wt %), arsenopyrite (50.7-678 ppm) and sphalerite (1-63 ppm) from the Vorontsovsk deposit, as well as in pyrite (5-1147 ppm) and galena (3 ppm – 4 wt %) from the Berezovsk deposit. Pyrite from altered rocks of both deposits has the lower concentrations of antimony - 1.7-21.2 and 12.49-4 ppm for Vorontsovsk and Berezovsk deposits, respectively. Pyrite of the Vorontsovsk deposit contains 0.01-350 ppm of Sb (LA-ICP-MS) (figure 2).

c. Bismuth

The most common mineral form of Bi in all studied deposits is tennantite-tetrahedrite. On the Vorontsovsk deposit sulfides of Sb, sulfoantimonides of Pb, Cu, Mn, Fe and sulfosalts of Tl-(Hg)-Sb,As are present in the ores (table 2). Neutron activation analysis revealed antimony in pyrite (0.5-367 ppm), As-pyrite (19.5 ppm - 3.8 wt %), arsenopyrite (50.7-678 ppm) and sphalerite (1-63 ppm) from the Vorontsovsk deposit, as well as in pyrite (5-1147 ppm) and galena (3 ppm – 4 wt %) from the Berezovsk deposit. Pyrite from altered rocks of both deposits has the lower concentrations of antimony - 1.7-21.2 and 12.49-4 ppm for Vorontsovsk and Berezovsk deposits, respectively. Pyrite of the Vorontsovsk deposit contains 0.01-350 ppm of Sb (LA-ICP-MS) (figure 2).

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**Table 2.** Mineral forms of trace elements for gold deposits of the Urals (data of authors and [4])

|                | Vorontsovsk | Berezovsk                  | Svetlinsk                     |
|----------------|-------------|----------------------------|-------------------------------|
| **As**         | Arsenopyrite FeAsS, löllingite FeAs2, orpiment As2S3, realgar AsS, tennantite Cu12As4S13, tennantite-tetrahedrite Cu12(As, Sb)4S13, routhierite TIHgAsS3, aktashite Cu6Hg3As4S12, native As, pierrotite Ti2(Sb,As)6S17, geocronite Pb14(Sb,As)6S23 | Tennantite Cu12As4S13, tennantite-tetrahedrite Cu12(As, Sb)4S13, arsenopyrite FeAsS, gersdorffite NiAsS, löllingite FeAs2, native As, pierrotite Ti2(Sb,As)6S17 | Löllingite FeAs2 |
| **Te**         | Coloradoite HgTe, hessite Ag2Te | Hessite Ag2Te, tetradyminite Bi2Te2S | NiTe2, frohbergite FeTe, altaite PbTe, calaverite AuTe2, sylvanite AuAgTe4, krennerite (Au,Ag)Te2, petzite AuAg3Te2, hessite Ag2Te, tsunmoite BiTe, tellurantimonite Sb2Te3, volynskite AgBiTe2, tetradyminite Bi2Te2S |
| **Sb**         | Tetrahedrite-tennantite Cu12(Sb,As)4S13, klerite Sb2S3, stibnite Pb5Sb4S11, jamesonite PbCuSbS3, geocronite Pb14(Sb,As)6S23 | Tetrahedrite-tennantite Cu12(Sb,As)4S13, bournonite PbCuSbS3, livingstonite HgSb4S8 | Tetrahedrite Cu12Sb4S13, tellurantimonite Sb2Te3 |
| **Bi**         | Aikinite Cu3BiS3, wittichenite Aikinite CuPbBiS3, cosalite Pb2Bi2S5, tetradyminite Bi2Te2S, bismuthinite Bi2S3, Cu3BiS3, matildite AgBiS2, emplectite CuBi2S, galenobismutite PbBi2S4 | Tsumoite BiTe, volynskite AgBiTe2, tetradyminite Bi2Te2S | Electrum AuAg, sylvanite AuAgTe4, krennerite (Au,Ag)Te2, petzite AuAg3Te2, hessite Ag2Te, volynskite AgBiTe2 |
| **Ag**         | Hessite Ag2Te, electrum AuAg, kustelite Ag3Au | Native silver Ag, electrum AuAg, acanthite Ag2S | Native silver Ag, electrum AuAg, acanthite Ag2S |
| **Hg**         | Aktashite Cu6Hg3As4S12, cinnabar HGs, routhierite TIHgAsS3, coloradoite HgTe | Cinnabar HGs, livingstonite HgSb4S8 |

**Tellurium**

Tellurides are typical for the Svetlinsk deposit (table 2, figure 1); native gold (fineness 873-948) is closely associated with them in quartz-sulfide veins. Tellurides of Ni, Fe, Pb, Bi, Sb, Ag and Au were identified in the ore assemblages. Tellurium is present in galena (147-977 ppm) and pyrite (64.4 ppm) of the Berezovsk deposit according to INAA. Pyrite of the Vorontsovsk deposit contains 1.64-76.5 ppm of Te (LA-ICP-MS) (figure 2).
e. Silver
Main Ag minerals are tellurides of silver, whereas the Au-Ag alloys, native silver and silver sulfide are occasionally found (table 2). Silver is a constant impurity in tennantite-tetrahedrite minerals and galena. Native gold always contains silver (EPMA, wt %): 1.4-14 and 9.3-26.7 for early and late generation of native gold in the Berezovsk deposit, respectively; 10.7-21.2 for the Svetlinsk deposit. On the Vorontsovsk deposit besides of native gold (7.1-30 wt% Ag) electrum (44.2-48 wt% Ag) and kustelote (69.6-77.5 wt% Ag) are found. According to EPMA tennantite-tetrahedrite minerals contain Ag up to 0.9 wt% (Berezovsk), 1.9-4.5 wt% (Svetlinsk) and up to 22.5 wt% (Vorontsovsk). Sulfides of the Berezovsk deposit are enriched of Ag: in pyrite 9.2-260.6 ppm (INAA) and 1.2-62.5 ppm (ICP-MS); in chalcopyrite 67.2-75 ppm (ICP-MS) and up to 0.18 wt% (EPMA); in galena 0.1-0.4 wt% (EPMA) and 639 ppm-2.5 wt% (INAA); in tennantite-tetrahedrite 0-0.89 wt% (EPMA) and 1062-3212 ppm (INAA).

f. Other elements
Mercury determines the geochemical type of Vorontsovsk deposit. In addition to its proper mineral forms (table 2) mercury is constantly present in native gold (up to 5 wt%) of this deposit as well as in sphalerite (up to 21 wt%) and tennantite-tetrahedrite (up to 0.21 wt% [4]).

Figure 2. Distribution of Au, As, Sb, Bi, Te and Ag in pyrite from Vorontzovsk deposit

5. Conclusion
High concentrations of chemical elements - "potentially polluting substances" - were found in the ores of gold deposits of the Urals. The proper minerals of these elements and disseminated form in the main sulfides are demonstrated. The results of the present study should be considered when selecting technological scheme of gold ore processing for reducing the risk of potential environmental problems.

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