Selenium, tellurium and precious metal mineralogy in Uchalinsk copper-zinc-pyritic district, the Urals

I Vikentev
Institute of geology of ore deposits, petrography, mineralogy and geochemistry (IGEM), Russian Academy of Sciences, Moscow, Russia

E-mail: viken@igem.ru

Abstract. During processing the most of Au, Ag, Se, Te, Pb, Bi, Sb, Hg as well as notable part of Cu, Zn and Cd fail for tailings and became heavy metal pollutants. Modes of occurrence of Au, Ag, Te and Se covers two giant VMS deposits: Uchaly (intensively deformed) and Uzelginsk (altered by late hydrothermal processes) as well as middle-sized Molodezn and West Ozern deposits (nondeformed) have been studied. Mineral forms of these elements as well as their presence in disperse mode in common ore minerals (pyrite, chalcopyrite, sphalerite) have been studied using SEM, EPMA, INAA, ICP-MS and LA-ICP-MS.

1. Introduction
The Urals stretching longitudinally over 2000 km represents the largest ore belt containing about 2 billion tones of massive sulfide reserves with 70 MT of non-ferrous metals in volcanogenic massive sulfide deposits (VMS deposits). Major non-ferrous metal output in the Urals are cooper, zinc, gold and silver producing from ores of 18 small and 6 large VMS deposits [1]. The increasing amount of processed ores of VMS deposits (25 million tones per year) has aggravated a problem of gold recovery [2]. Loss of gold in the pyritic concentrate and tailings can amount from 13 to 15 tones annually (for example, by now reserves of gold at tailing dump of Uchaly plant range 80 t). Up to a half of primary silver contained in ore is also lost in the tailings.

Ores of VMS deposits of the Urals are characterized by multicomponent composition but only a small part of trace elements is extracted: 10-20% of primary quantities of Se, Te, Co, Ni; 15-40% Au, Tl, In, Ga, Hg; 30-60% Ag and 80% Cd contained in ore. Lead, antimony and arsenic are not extracted. During processing the most of these elements as well as notable part of Cu, Zn fails for tailings and become pollutants (heavy metals plus arsenic) [3]. Se and Te are very toxic elements and they usually occur as admixtures in sulfide ore in VMS deposits. Nevertheless modes of occurrence of these and other trace elements (the most of them are toxic elements) in VMS deposits are left unclear. There is only total agreement that they are dispersed over the common sulfides of ore (pyrite, chalcopyrite, sphalerite). There is rare exception – a few papers deal with telluride mineralogy of some VMS deposits of the Urals [2,4]. It is also important to know the ways of potential pollutants during processing and smelting [3,5]. In this connection it is especially vital to study the mode of occurrence of the toxic trace elements in ores and ore minerals.

Geological and geochemical overview. The most of VMS deposits are located on the east slope of the Urals within the Main greenstone belt of the Urals – Tagil-Magnitogorsk megazone [1,6] and there are the most of ore dressing plants and smelters in this megazone. VMS deposits of the Urals associate with transitional from tholeiitic to calc-alkaline Na-bimodal rhyolite-basalt series [1]. According to the
modern genetic model their formation was related to shallow chamber of acidic magma resulted from
differentiation of mantle-derived basalt [7]. Specific features of VMS deposits of the Urals are the
following: (1) large dimension: nine deposits involve 80-480 Mt of ore and 3-10 Mt of (Cu+Zn)
reserves – these nine deposits totally contain more than 65% of the bulk initial base metal reserves of
the Urals; (2) seven deposits contain 120-500 t of associated gold; (3) ore bodies are usually lens-like
or lenticular; (4) massive sulfide ores predominate with subordinate amount of disseminated ores; (5)
grade of metamorphism varies from zeolite to amphibolite facies [1,2]. World-class deposits are
located within Magnitogorsk megazone, they belong to Uralian (or Cu-Zn-pyritic) type (major one for
the Urals), which can be divided on two subtypes: Cu>>Zn and Zn>>Cu. Gold and silver are unevenly
distributed in massive sulfide ores [2,8]. Gold content in ores commonly ranges about 1 ppm, in some
bodies it amounts 3-5 ppm and very rarely single samples with 70-90 ppm Au can be found.
Common Ag contents are measured 10-30 ppm (up to 600 ppm).

2. Materials
We will focus on Uchalinsk copper-zinc-pyritic district [7,8,9], which contains significant metal
reserves in three large and ten medium-sized VMS deposits (figure 1): 435 Mt non-ferrous metals ore,
including 5.7 Mt of Cu, 12 Mt of Zn, 1.2 Mt of Pb, 635 t of Au and 11.1 Kt of Ag. VMS deposits of
the district are belong to Zn-dominated subtype of Uralian type. Specific feature of the deposits of this
region is the most “rich” geochemistry of trace elements with enrichment of Au, Ag, Pb, Se, Te, Sb,
As, Sn and Cd being compared with other ore districts of the Urals [10]. Ore bodies comprise large
bodies of massive sulfide ores. In some case (Uchaly, Uzelginsk) their thickness can reach 120-150 m.

Figure 1. Scheme of Uchalinsk region (South Urals)
1 – ophiolites O–S1; (2,3) – island arc basalt- hyolite D2 (2) and andesite-basalt, basalt-trachyte
complexes D3–C1, some limestone C1t (3); 4 – ranodiorite, plagiogranite (D2–D3fr); 5,6 – gabbro-
granite series D3fm–C1t1 (5) and C1 (6); 7 – ranite P1; 8 – fault; 9 – overthrust; 10 – VMS deposit
(black – large, grey – small and medium-sized)
3. Methods
The distribution of chemical elements has been studied for bulk samples of ores as well as for sulfide concentrates. The contents of Au, Ag, and base metals and some rare elements (Co, Ni, Se, Te, As, Sb, Cd, Hg, Ba) were examined by instrumental neutron activation analysis (INAA). PGE contents in 2-5g bulk samples, sulfide and ultra heavy concentrates were measured by wet-chemical analysis with preconcentration of sum of PGE and following ICP-MS determination. Laser ablation (LA) ICP-MS (IGEM RAS and LabMaTer at the Université du Québec à Chicoutimi) has been used for trace element analysis of sulfides from the Uchaly and Uzelginsk deposit. Microprobe analyses were carried out using an electron-probe microanalyser (EPMA) and a scanning electron microscope.

4. Results and Discussion

Geochemistry. There is broad variation of trace element contents in VMS ores (table 1, figure 2). Gold content in ores commonly ranges 1-1.5 ppm but in Au-rich zones of deposits can amount 5-20 ppm of Au. Silver content in ores ranges 5-100 ppm (up to 1000-3000 ppm) (figure 3). Cu-Zn ores with high Au content usually bear high concentrations of Pb, Ba, As, Sb and Ag, for some deposits (Uzelginsk) – Au-bearing ore is also enriched in Hg, Se and Te trace elements. Maximums of ΣPGE in VMS ore (0.5-0.6 ppm) are usually corresponding to high Te contents (250-1300 ppm) [11]. During processing the most of trace elements containing in ore of the deposits aren’t extracted (Au, Ag, Pt, Pd, Pb, Se, Te, Sb, As, Sn, Co, Ni and Hg) and many of them (Pb, Se, Te, Sb, As, Co, Ni and Hg) become pollutants (heavy metals and As together with sulfur dioxide, Fe, Cu, Zn, Cd) (see also [3]).

| Element | Common contents | Maximum | Element | Common contents | Maximum |
|---------|-----------------|---------|---------|-----------------|---------|
| Au      | 1-2             | 16.8    | Hg      | 10-100          | 1500    |
| Ag      | 5-50            | 2990    | Sb      | 50-500          | 7250    |
| Se      | 20-100          | 1324    | As      | 1000-5000       | 23650   |
| Te      | 20-150          | 3650    | Pb      | 1000-5000       | 25564   |

Figure 2. Te, Se, Ag and Au contents in VMS ores of Uchalinsk ore district

Selenium, tellurium and precious metal mineralogy. Pyrite, chalcopyrite and sphalerite are dominant ore minerals. Tennantite is a common mineral in most of the VMS deposits (0.1-1 vol%) while galena and bornite occur locally in smaller quantities. The ore samples which are anomalous in terms of gold concentration are mainly composed of tennantite, tennantite-tetrahedrite, galena, bornite with subordinated tellurides, sulfotellurides (tetradymite), Ag-sulfurals, Bi-sulfosalts (aikinite,
wittichenite), Au-Ag-sulfides (petrovskaite, uyttenbogaardtite), native elements and alloys (native gold, native silver, electrum Au-Ag, native tellurium).

Gold was mostly concentrated in pyrite and chalcopyrite (1-20 ppm Au in the mode of "invisible" gold). Main trace toxic elements (Se, Te, As, Hg) occur in common sulfides (table 2) as well as Se is host by galena (up to 0.45 wt %, EPMA), pyrrhotite (up to 343 ppm, INAA), tellurobismuthite (up to 0.69-0.85 wt %, EPMA) and petzite (up to 0.02-0.49 wt %, EPMA). Selenium can be rarely found in pyrite and other common sulfides as tiny inclusions of clausthalite PbSe and galena-clausthalite Pb2SeS (Uchaly, West-Ozern deposits) and kawazulite-tetradymite Bi2Te1.9(Se0.57-0.65S0.3-0.26) (Molodezhn deposit). Tellurides, native tellurium, Au-Ag alloys, tennantite-tetrahedrite together with main sulfides are detected as microinclusions in pyrite [2]. A positive correlation between Au and Ag in ore and a high dispersion of the contents seems to reflect the occurrence of Au-Ag alloys (see figure 2). The similar tendency occurs for contents of Au and Ag in pyrite: pyrites with high Au content usually bear high concentrations of silver and tellurium trace elements, that can be related with tiny inclusions of Au-Ag alloys, Au-tellurides and Te-bearing (up to 8.9 wt % Te) tennattite-tetrahedrite in pyrite (figure 3).

Table 2. Trace element contents (ppm, INAA) in common sulfides of deposits of Uchalinsk district

| Mineral      | Au     | Ag    | Se    | Te    | As   | Hg    |
|--------------|--------|-------|-------|-------|------|-------|
| Pyrite       | 0.21-17.11 | 4-326 | 2-511 | <4-583 | <1-5600 (up to 2.3 wt %) | 0.1-1257 |
| Chalcopyrite | 0.4-0.15 | 1-6   | 7-313 | 1-314 | <1-33 (up to 0.3 wt %) | 0.2-792 |
| Sphalerite   | no data | no data | <6-471 | 28-1367 | <1 | 40-581 |

Figure 3. Trace elements in pyrites (INAA)

In the Uchaly deposit the bulk of Au and Ag occurs in a dispersed form in sulfides – sphalerite, pyrite and chalcopyrite. Important hosts of Au and Ag are native gold, sulfides (petrovskaite, argentite), tellurides (hessite, empressite, calaverite) and sulfosalts of silver (Ag-tetrahedrite, Ag-tennattite-tetrahedrite with 7-8 wt % Ag and pirseit) (figure 4). Native gold is extremely rare, size from 5 to 30 microns (up to 150 μm), usually low-grade with the composition range from Au0.69Ag0.31 to Au0.34Ag0.59Hg0.1. Mercury-bearing native gold (11.3 wt. % Hg) was also found rarely.

In the Uzelginsk deposit neutron-activation analysis found Au enrichment up to 22 ppm as well as elevated Ag and As in reniform pyrite. The euhedral pyrite associated with this variety is characterized by an order of magnitude lower concentrations of Au, Ag and As [8]. Native gold (up to 200 μm) occurs in recrystallized ores of lower ore level (ore bodies 3 and 4) in association with Au-Ag and Ag tellurides (petzite, hessite, stützite). In some case grains of native gold is inhomogeneous and contains emulsion-like inclusions of altaite [8].
Silver mainly occurs as isomorphic component of tennantite-tetrahedrite. Low-iron tennantite (0.1-0.5 wt.% Ag) is dominant variety; Ag-tennantite (up to 8.4 wt % Ag), Ag-tennantite-tetrahedrite (7-8 wt % Ag) and Ag-tetrahedrite (8-11 wt % Ag) are scarce [2,8]. In addition, up to 0.14 Se (wt%, EPMA), 0.38 Pd, 0.05-0.3 Hg and 0.2-4.5 Te were found in tennattite-tetrahedrite from the Uzelginsk deposit. Positive correlation of Ag, Sb and As in pyrites is seems to related to tiny inclusions of Ag-tetrahedrite and tennantite-tetrahedrite occurring in pyrites (see figure 3). In some case tennattite-tetrahedrite is enriched in gold (up to 6 wt %).

Proper minerals of Au, Ag and Te routinely form fine submicron inclusions inside of common sulfides of the ores: sphalerite, chalcopyrite and pyrite. A lot of tellurides occurs in massive sulfide ores: these are altaite, coloradoite, tellurobismuthite and tellurides of gold and silver [2,8]. Tellurides of gold and silver include hessite, stützite, empressite, petzite, krennerite and sylvanite. Some tellurides bear gold admixture (as solid solution) especially altaite (up to 5.2 wt % Au), coloradoite (up to 4.2 wt % Au), hessite (up to 1.4 wt % Au) and tetradymite (up to 1.2 wt % Au), with gold content being much more than that in sulfides may be due to more metallic character of chemical bond in tellurides. Apparently, it is the presence of small inclusions of Au-Ag tellurides (and other tellurides with appreciable admixture of Au) in pyrite causes a significant correlation of gold and tellurium in the composition of the pyrite. In this way tellurides are a major carrier of gold and silver in VMS deposits of the Urals.

Native gold comprises grains and aggregates with size from first to 200 micrometers. In weakly transformed ore deposits of Uchalinsk ore district, native gold is observed as rare tiny grains (up to 20 μm). Larger grains (up to 200 μm) are detected in recrystallized ores and within late quartz+sulfide-barite-tennantite veinlets. Evidently, the appearance of gold minerals was mainly related to the release of isomorphous Au from sulfides as well as coarsening of tiny ("invisible") native gold grains during epigenetic hydrothermal alterations.

The sulfide precipitation occurred under conditions favourable for the incorporation of isomorphic gold into pyrite, chalcopyrite and sphalerite+chalcopyrite during high temperature stages of ore genesis [2]. Parageneses of native metals (Au-Ag alloys, native Te), tellurides and sulfosalts were mainly formed at the latest stage of hydrothermal process at below 200°C as well as during low grade metamorphism due to refining of the common sulfides and segregation of rare elements as well as coarsening of tiny gold grains [2,8].

PGE do not form proper minerals in VMS ores of the Urals. According to LA-ICP-MS data admixtures of Au, Ag and PGE in pyrite range between (ppm): 0.03-0.2 Pd, 0.04-0.26 Rh for Uchaly deposit [11] The LA-ICP-MS method has been used for trace element analysis of sulfides from the Uchaly and Uzelginsk deposits. The bulk of the PGE and gold occur invisibly in pyrite and chalcopyrite. Their contents range from ~0.01-42.8 ppm Au, 0.03-0.2 ppm Pd and 0.02-0.25 Rh ppm. The PGE enrichment (ppb, up to 1220 Pd, 375 Pt and 707 Rh for the Uzelginsk deposits) was established [8] in ultra heavy concentrates from Au rich ores.
5. Conclusion
There are broad variations of Se, Te, Au, Ag, Pt, Pd contents in VMS ores (but usually below 0.1 ppm for Pd and Pt). The bulk of the gold and PGE occur invisibly in pyrite and chalcopyrite with predomination of Au.

Tellurides appear to be major carriers of gold and silver (and probable Pt+Pd) in VMS deposits of the Urals – along with native gold. Tennantite-tetrahedrite is also important host of Au, Ag and Pt+Pd in VMS deposits.

Visible segregations of native gold (~1 μm or more) and tellurides appear in massive sulfide ores as a result of recrystallization during late (mainly low-temperature) hydrothermal processes and low-grade metamorphism.

During processing the most of pyrite, pyrrhotite, tennantite-tetrahedrite and galena bearing a major part of Pb, Se, Te, Co, Sb, As, Hg as well as notable part of Cu, Zn and Cd fails for tailings and became pollutants (heavy metals and As together with sulfur dioxide, Fe, Cu, Zn, Cd).

Mineralogical study of the VMS deposits may clarify the mode of occurrence of trace toxic elements in ore and in such way it can help to optimize ore processing with output of additional quantity of noble metals as well as to prevent the pollution of environment by toxic elements and make the process of mining and dressing of ore of VMS deposits more green to keep the nature for future generations.

This work was supported by Russian Science Foundation (Project 14-17-00693).

References
[1] Prokin V A and Buslaev F P 1999 Ore Geol. Rev. 14 1
[2] Vikentyev I V 2006 Mineral. Petrol. 87 305
[3] Shafigullina G T and Udachin V N 2009 Prospect and Protection Miner. Res. 1 60
[4] Maslennikov V V et al 2013 Mineral. Petrol. 107 67
[5] Udachin V et al 2003 J. Sustainable Dev. 11 133
[6] Puchkov V N 2013 Miner. Petrol. 107 3
[7] Karpukhina V S et al 2013 Geol. Ore Dep. 55 125
[8] Vikentyev I V et al 2004 Can. Mineral. 42 651
[9] Vikent'ev I V et al 2000 Geol. Ore Dep. 42 221
[10] Vikentyev I V et al 2013 Volcanic-hosted massive sulfide deposits of the Urals, Russia: Evidence for a magmatic contribution of metals and fluid Proc. 12th Bien. SGA Meet. 1526
[11] Vikentyev I V et al 2014 PGE in minerals of volcanogenic massive sulfide deposits of the Urals: ore geochemistry and first LA-ICP-MS data Abs. 12th Int. Platinum Symp. 326