

## **Precious metal and telluride mineralogy of large volcanic-hosted massive sulfide deposits in the Urals**

**I. V. Vikentyev**

Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, Moscow, Russia

Received March 13, 2005; revised version accepted March 15, 2006  
Published online June 14, 2006; © Springer-Verlag 2006  
Editorial handling: N. J. Cook

### **Summary**

The study focuses on the mode of occurrence of Au, Ag and Te in ores of the Gaisk, Safyanovsk, Uzelginsk and other volcanic-hosted massive sulfide (VHMS) deposits in the Russian Urals. Minerals containing these elements routinely form fine inclusions within common sulfides (pyrite, chalcopyrite and sphalerite). Gold is mostly concentrated as 'invisible' gold within pyrite and chalcopyrite at concentrations of 1–20 ppm. Silver mainly occurs substituted in tennantite (0.1–6 wt.% Ag). In the early stages of mineralization, gold is concentrated into solid solution within the sulfides and does not form discrete minerals. Mineral parageneses identified in the VHMS deposits that contain discrete gold- and gold-bearing minerals, including native gold, other native elements, various tellurides and tennantite, were formed only in the latest stages of mineralization. Secondary hydrothermal stages and local metamorphism of sulfide ores resulted in redistribution of base and precious metals, refining of the common sulfides, the appearance of submicroscopic and microscopic inclusions of Au–Ag alloys (fineness 0.440–0.975) and segregation of trace elements into new, discrete minerals. The latter include Au and Ag compounds combined with Te, Se, Bi and S. Numerous tellurides (altaite, hessite, stützite, petzite, krennerite etc.) are found in the massive sulfide ores of the Urals and appear to be major carriers of gold and PGE in VHMS ores.

### **Introduction**

Globally, reserves of by-product gold in massive sulfide ores exceed 4000 t, and account for around 5% of current annual world gold production. The Uralian orogen is one of the largest single ore belts in the world and contains about 2 billion t of ore reserves, with 70 million tons (MT) of non-ferrous metals in volcanic-hosted

massive sulfide (VHMS) deposits. The belt is comparable with the Iberian Pyrite Belt in terms of total ore reserves, but contains more gold.

From 114 VHMS deposits in the Urals, 41 have been mined to exhaustion and 20 deposits are currently under exploitation: the large Gaisk, Uchaly, Sibai, Uzelginsk, Safyanvsk and Jubileynoye deposits, and the medium-sized Levikha, Mauk, Talgansk, Molodezhnoye, Alexandrinsk, Oktyabrsk, Tash-Tau, Balta-Tau, Maisk, Barsuchii Log, Dzhusinsk, Yaman-Kasy, Letneye and Osenneye deposits. In terms of total reserves of associated, by-product Au, the Uralian province occupies a dominant position among massive sulfide ore provinces in the world. To date, more than 50% of Uralian gold is produced as a by-product from VHMS ores; each deposit contains reserves of 20 to 500 t of gold. The increasing volumes of massive sulfide ores processed annually (currently 13–15 Mt p.a.) has aggravated the problem of poor gold recovery. A loss of 50–80% of the gold to the pyrite concentrate and tailings can amount to a loss of as much as 10–12 t of Au each year in the Urals. The scale of the problem can be underlined by the fact that 75 t gold is contained in the tailings dump of the Uchaly plant alone. The distribution and mineralogy of not only gold, but also of tellurium, selenium, silver and PGE, which may form mineral compounds with gold, in the Uralian VHMS ores are poorly understood, despite the economic importance of the deposits of this large ore belt. Native gold in Uralian massive sulfide ores was first established in 1936 (Yushko, 1936), yet its distribution is still insufficiently studied, due to its low abundance in many ores.

### Samples and analytical methods

Our study of the mode of occurrence of Au, Ag and Te was based on open pit and underground mapping and sampling of drillcore, concentrates and tailings of the major Uralian mines. We have focused on ores from five giant VHMS deposits: Safyanovsk (non-deformed); Uzelginsk (altered by late hydrothermal processes); and Gaisk, Degtyarsk and Uchaly (intensely deformed), but we have also compared the distribution of noble metals and the composition of native gold in a number of other deposits. Ore samples were mainly taken from the Au-rich zones of the studied deposits. Concentrations of Au, Ag, base and rare metals were determined in bulk samples using instrumental neutron activation analysis (INAA), and in some case, also by inductively-coupled plasma mass spectroscopy (ICP-MS). In addition, sulfide separates, 20–50 mg in weight, were handpicked under a binocular microscope to ensure >90% purity, and were analyzed by INAA. Measurements of induced activity were carried out with a gamma spectrometer with an accuracy of  $\pm 0.1$  ppm for Au and 2–5 ppm for Sb, Co, As, Ag, Cd, Se and Te. In order to detect precious metal minerals in massive sulfide ores, we separated ultra-heavy fractions, using bromoform, elutriation and hydroseparation, from (100 g) samples with particularly elevated Au contents. Ore concentrates were prepared as thin and polished sections. The compositions of native gold, tellurides and other ore minerals were studied on a Camebax SX-50 electron probe microanalyzer (EPMA), with 100 second count times for PGE and Au concentrations in sulfides and tellurides, with detection limits of 0.002 to 0.005 wt.%, and a JSM-5300 electron microscope equipped with a LINK ISIS energy-dispersive spectrometer (EDS). The routine accuracy of the microprobe and EDS analyses was  $\pm 0.02$  wt.%. In most cases,

contents of Au, Ag and PGE in bulk ores and mineral concentrates, as determined by INAA and chemical analysis, are given in g/t (mg/t for PGE) but the microanalytical data for concentrations in specific sulfide minerals, as determined by microprobe or INAA, are given in ppm (or wt.% in the case of EPMA). Formation conditions for the Au-bearing mineral assemblages were estimated on the basis of the electrum-sphalerite (*Shikazono*, 1985) and arsenopyrite geothermometers (*Scott*, 1983), and from fluid inclusion data. Tellurium fugacity was estimated on the basis of observed paragenetic assemblages, experimental data for telluride mineral stabilities (*Affi et al.*, 1988) and the empirical equation of *Bortnikov et al.* (1988).

### Regional setting

Most of the Uralian ore deposits are located within the main greenstone belt of the Urals, the Tagil-Magnitogorsk Trough, which stretches longitudinally for 2000 km along longitude 60° E (*Prokin and Buslaev*, 1999; *Puchkov*, 1997). The trough, previously referred to as the active margin of the East European craton, is filled by arc-related, mainly femic, volcanic complexes of Ordovician-Early Carboniferous age. Formation of volcanogenic massive sulfide deposits mostly relates to sodium rhyolite-basalt complexes corresponding to the primitive arc stages of the Lower Silurian (Tagil Megazone) and Lower-Middle Devonian (Magnitogorsk Megazone).

World-class deposits with 3–10 MT of (Cu + Zn) reserves are located within the Magnitogorsk Megazone (Fig. 1). They can be classified as *Uralian* (Cu–Zn-pyritic) type and contain ores with  $Cu \geq Zn$  (Gaisk, Sibai, Degtyarsk, Jubileinoe, Podolsk, Safyanovsk), or as  $Zn > Cu$  type (Uchaly, Novo-Uchaly and Uzelginsk). These nine large deposits contain more than 65% of the known bulk initial base metal reserves in the Urals. Eight of the deposits contain >100 t Au and >1000 t Ag. A few small deposits of the Magnitogorsk Megazone are classified as *Bajmak* (Au-pyritic) type: Balta-Tau, Tash-Tau, Maisk and Uvarjzh. Ores of these deposits are enriched in Cu, Zn, Pb, Ba, Au and Ag. These deposits are interpreted as analogues of Kuroko-type deposits (*Prokin and Buslaev*, 1999; *Zaykov et al.*, 2001). *Cyprus* type deposits occur within basaltic pillow lava hosted ophiolitic rocks and are small and rather rare (Letneye and Osenneye in the Dombarovsk region, Mauk in the Karabash region).

### Ore geochemistry

In most of the VHMS deposits, massive sulfide ores predominate, with only subordinate amount of disseminated ores (commonly 10–20 vol.% of the total). Gold, Ag and Te are relatively uniformly distributed in the massive sulfide ores (Figs. 2 and 3). Gold contents in ores commonly range from 0.1–0.5 g/t (Cyprus type), 1–2 g/t (Uralian type) and 2–5 g/t (Bajmak type), but can reach 15–90 g/t in the Au-rich zones of deposits of the Uralian and Bajmak types. The dominant Cu–Zn massive ores are enriched in Au (1–2 g/t), but single commodity Zn- and Cu- massive ores have rather lower Au concentrations (0.5–1 g/t), except for the bornite-bearing Cu-ores (2–3 g/t Au). Not uncommonly, Cu–Zn ores with a Au content of 1.5–2 g/t or more are characterized by high concentrations of Pb, Ba, Ag, Te, Se,

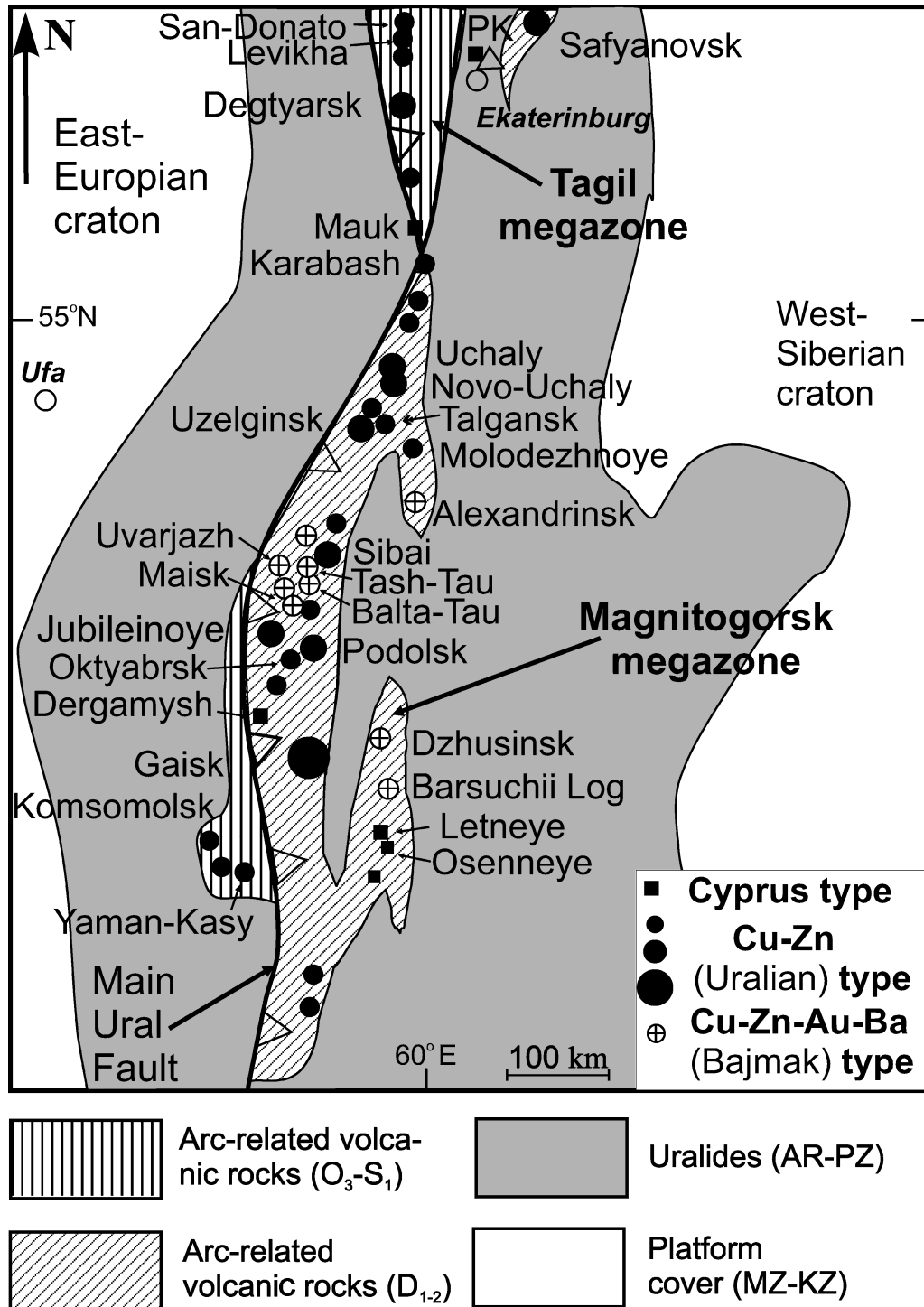


Fig. 1. Schematic tectonic map of South Urals and position of VHMS deposits. PK – Pyshminsk-Kljuchevsk deposit; triangle – Berezovsk gold vein deposit

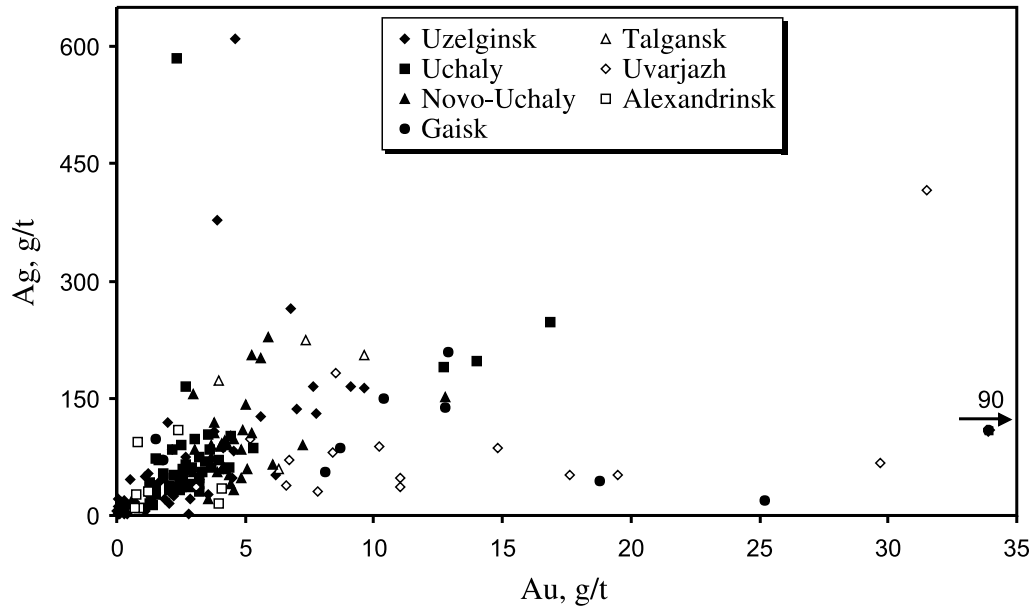


Fig. 2. Plot of Au vs. Ag (INAA data) for ores from VHMS deposits of the Urals

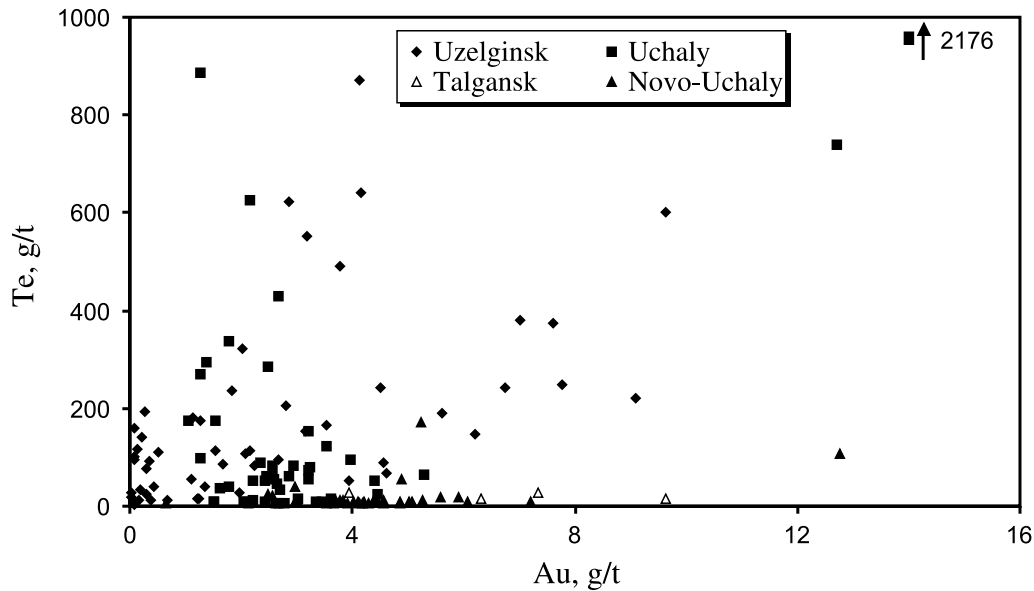


Fig. 3. Plot of Au vs. Te (INAA data) for ores from VHMS deposits of the Uchaly region (South Urals)

As and/or Sb. Contents of other elements are typically in the following ranges: Ag from 5–50 g/t (rarely up to 600 g/t), Pt from 1–100 mg/t (up to 1200 mg/t), Pd from 1–50 mg/t (up to 340 mg/t), Te from 10–100 g/t (up to 2300 g/t), Se from 20–100 g/t (up to 450 g/t), As from 10–1000 g/t (up to 6100 g/t), and Sb from 1–100 g/t (up to 3900 g/t).

### **Ore mineralogy and Au, Ag, PGE and Te distributions**

Pyrite is the dominant mineral in the ores (40–90 vol.%), but chalcopyrite and sphalerite are the major economic minerals (typically 1–10 vol.%, sometimes up to 30 vol.%). Tennantite-tetrahedrite (usually tennantite) and galena are common (0.2–1, up to 15 vol.%, and 0.1–0.5, up to 2 vol.%, respectively). Bornite, digenite, galena, pyrrhotite, marcasite, magnetite and hematite are notable in some deposits (Table 1). The Au–Ag parageneses are mainly composed of Ag-bearing tennantite, Ag-bearing galena, bornite, various tellurides (altaite, hessite, stützite, coloradoite, petzite and others), Ag-sulfides (acanthite, argentite, petrovskaita, argentopentlandite, stromeyerite, jalpaite and mckinstryite), sulfotellurides (tetradymite) and Bi-sulfosalts (aikinite, wittichenite, cosalite), native elements and alloys (Au–Ag, Ag, Te). These parageneses are irregularly distributed within the orebodies and generally relate to zones affected by late hydrothermal processes (e.g., *Vikentyev et al., 2004*).

Native gold forms grains and aggregates with sizes of about 2–50, up to 150  $\mu\text{m}$ ; larger grains are rare. In some cases, as shown in Fig. 4, native gold is inhomogeneous and contains emulsion-like inclusions of altaite. Fineness of native gold ranges from 0.500 to 0.975 in the metamorphosed deposits, and from 0.440 to 0.920 in the non- or slightly-deformed deposits (Fig. 5). Compositions of native gold of VHMS deposits of the Urals cluster close to  $\text{Au}_3\text{Ag}$ ,  $\text{Au}_2\text{Ag}$  and  $\text{Au}_3\text{Ag}_2$  (*Vikentyev, 2003*). Admixtures (in wt.%) of Pt attain up to 2.23, Pd up to 0.85, Te up to 1.17, Hg up to 0.89, Fe up to 0.5 and Se up to 0.49. Contents of all elements are highest in native gold from the unaltered deposits. Native gold from markedly metamorphosed deposits generally has lower contents of all elements except Ag and Cu (0.1–0.2 wt.%), below EPMA detection limits in many cases. Copper is the only element that appears to be present in electrum from the metamorphosed ores at high concentrations (up to 5 wt.%). An inverse correlation between the Au content is noted between electrum composition and the Fe content in the associated sphalerite. This trend may relate to an increase in fluid  $f\text{S}_2$ , or a decrease of sphalerite crystallization temperature, as mineralization proceeds. The role of  $f\text{S}_2$  is more substantial, as an increase promotes  $\text{Ag}_2\text{S}$  stability relative to electrum and leads to crystallization of higher-Au electrum (*Gammons and Williams-Jones, 1995*; *Shikazono and Shimizu, 1987*).

Large gold flakes, 100–1000  $\mu\text{m}$  in size, locally even more, are found in those deposits which have suffered significant metamorphic overprinting (Gaik, Degtyarsk, Karabash and San-Donato). In the non- or weakly deformed deposits (Uzelginsk, Uchaly, Molodezhnoye, Alexandrinsk and Safyanovsk), native gold is only rarely observed as small (5–25  $\mu\text{m}$ ) grains (*Vikentyev et al., 2004*; *Zaykov et al., 2001*). Larger grains (up to 150  $\mu\text{m}$ ) are only detected in areas characterized by superposition of late hydrothermal processes (recrystallized ores) and veinlets consisting of quartz + sulfide  $\pm$  barite  $\pm$  tennantite. The appearance of gold minerals is evidently related to release of solid solution gold from sulfides during recrystallization, as well as the coarsening of submicroscopic grains of native gold grains during epigenetic hydrothermal alteration.

Numerous telluride minerals occur in the massive sulfide ores (Table 1, Fig. 6). These include altaite, coloradoite, tellurobismuthite and a number of Au–Ag tellurides: hessite, stützite, empressite, petzite, krennerite, sylvanite, calaverite,

Table 1. *Ore mineralogy of massive sulfide deposits in volcanic complexes of the Uralts (including Moloshag et al., 2002; Zaykov et al., 2001)*

Age, geodynamic environment	Type of deposits; elements	Magmatic complexes	Main minerals	Common minerals	Rare minerals	Very rare minerals	Examples of deposits
O <sub>3</sub> -S <sub>1</sub> <sub>1</sub> oceanic spreading	Cu-Co-pyritic (Cyprus type): Cu (Co)	Tholeiite-basalt	Pyrite, chalcopyrite, pyrrhotite	Pentlandite, cubanite, magnetite*, ilmenite	Sphalerite, cobaltite, millerite, arsenopyrite, hematite, Ni-troilite, molybdenite, linnaeite, vallerite, mackinawite	Native gold, argentopentlandite, melonite, hessite, tellurobismuthite, coloradoite, siegenite	Pyshminskok, Klyucheensk, Dergamyshsk
S <sub>1</sub> <sub>2</sub> primitive island arc	Cu-Zn-pyritic (Uralian type): Cu ≥ Zn (Au, Ag)	Sodium rhyolite-basalt	Pyrite, chalcopyrite, sphalerite	Arsenopyrite, tennantite, marcassite	Galena, bornite, cubanite, magnetite, coloradoite, altaite, tellurobismuthite	Native gold, hessite, stützite, sylvanite, goldfeldite, volynskite, native tellurium, persite, siegenite	San-Donato, Levikha, Komsomolsk, Yaman-Kasy
D <sub>1e</sub> back-arc spreading	Cu-Co-pyritic (Cyprus type) Cu (Zn, Co)	Tholeiite-basalt	Pyrite, chalcopyrite	Sphalerite, pyrrhotite, magnetite, hematite	Tennantite, marcassite, pentlandite, cubanite	Native gold, altaite	Letneye, Osenneye Mauk
D <sub>1e</sub> -D <sub>2gv1</sub> primitive island arc	Cu-Zn-pyritic (Uralian type): 1) Cu ≥ Zn (Au, Ag) 2) Zn > Cu (Au, Ag)	Sodium rhyolite-basalt	Pyrite, chalcopyrite, sphalerite	Pyrrhotite*, tennantite*, bornite*, covellite*, magnetite*, hematite, arsenopyrite, galena	Altaite, coloradoite, hessite, rucklidgeite, stützite, native tellurium, tetradymite, tellurobismuthite, enargite, digenite, cubanite, pentlandite, native gold, germanite, mawsonite, stannoidite, jalpaite, molybdenite	Petzite, sylvanite, krennerite, calaverite, montbrayite, empresseite, muthmanite, volynskite, mckinstryite, aikinite, stromeyerite, betekhtinite, petrovskite, petrovskite	1) Gaisk, Sibai Degtyarsk, Safyanovsk, Jubileinoe, Podolsk, Molodezhnoye, Talgansk, Oktyabrsk 2) Uchaly, Uzelginsk, Novo-Uchaly

(continued)

Table 1 (*continued*)

Age, geodynamic environment	Type of deposits; elements	Magmatic complexes	Main minerals	Common minerals	Rare minerals	Very rare minerals	Examples of deposits
Cu–Zn–barite-pyritic				Tennantite, galena, bornite	Covellite, chalcocite, anilite	native silver, acanthite, argentite, wittichenite, reinierite, bismuthine, native bismuth, colusite, cosalite	Alexandrinsk
				Galena, tennantite, magnetite	Bornite, pyrrhotite, arsenopyrite	Native gold, <b>altaite</b> , stromeyerite, reinierite	Barsuchii Log, Dzhusinsk
				Tennantite*, bornite*, pyrrhotite, covellite	Native gold, <b>hessite</b> , chalcocite, germanite, molybdenite	Germanite, jalpaite, stromeyerite, argentite, küstelite, native silver	Tash-Tau, Balta-Tau, Maisk, Uvarjazh
Cu–Zn–Pb–Au–pyritic		Potassium–sodium andesite-dacite	Pyrite, chalcopyrite, sphalerite, galena				

\* Sometimes – main mineral; bold – Te minerals



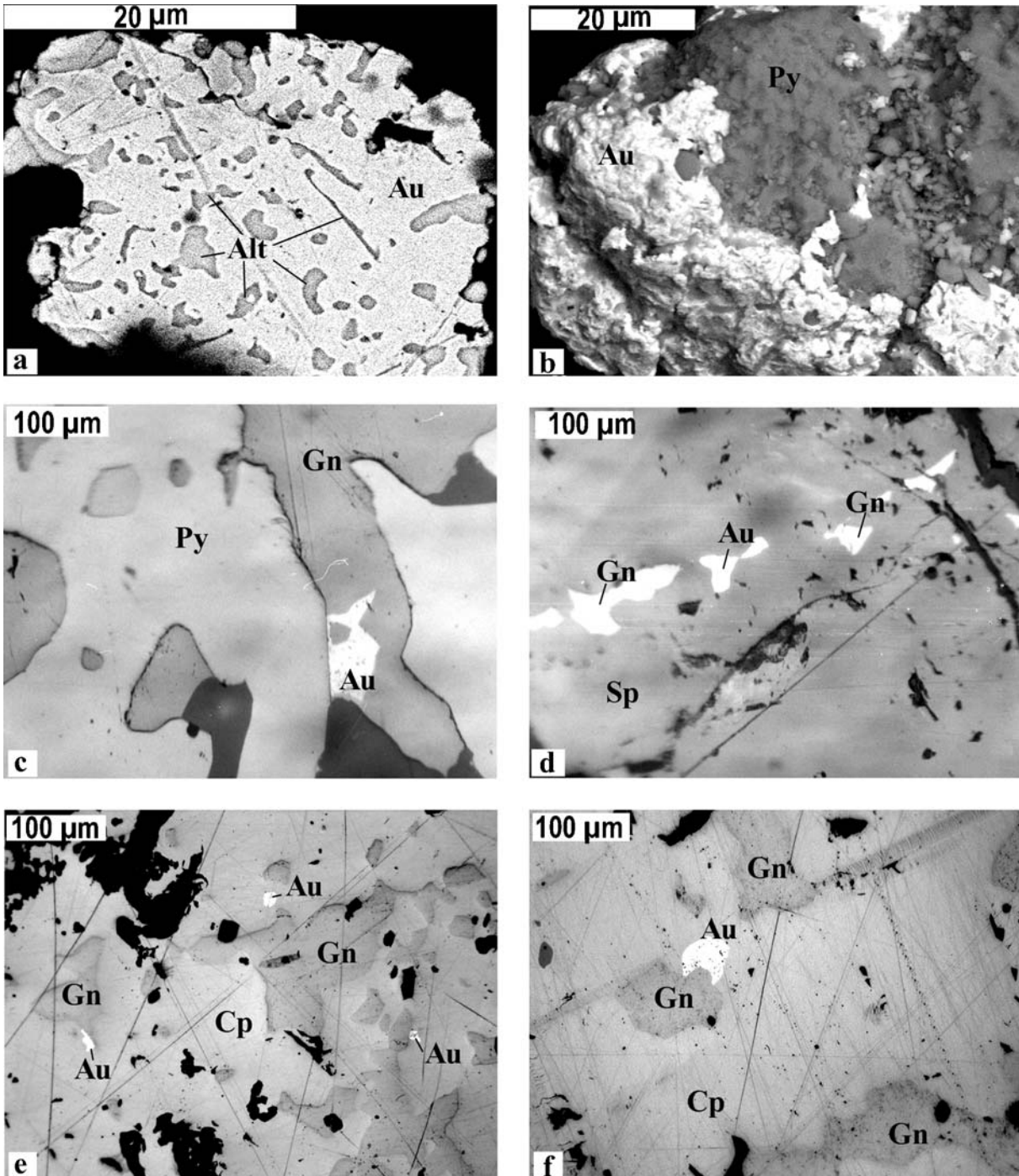


Fig. 4. Native gold from ores and heavy sulfide concentrate of gold-rich VHMS ores. Back-scattered electron images (a and b, Uzelginsk deposit) and reflected light photomicrograph (c–f, San-Donato deposit). a – Intergrowths of native gold (Au) and altaite (Alt); b – aggregate of pyrite (Py) surrounded by xenomorphic gold; c – native gold in quartz-galena (Gn) veinlet cutting coarse pyrite (with irregular inclusions of chalcopyrite); d – echelon-like inclusions of native gold and galena in sphalerite (Sp); e, f – sub-rounded inclusions of native gold within chalcopyrite-galena intergrowth

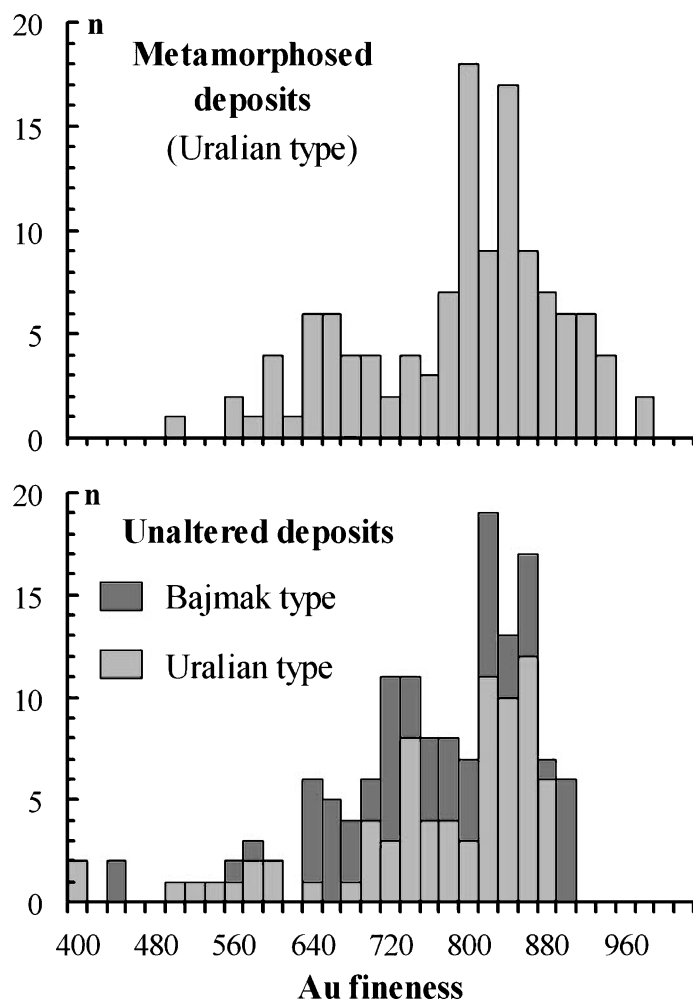


Fig. 5. Gold fineness of native gold and Au–Ag alloys in ores of VHMS deposits of the Urals, (electron microprobe data)

volynskite, muthmannite and montbrayite. The tellurides are routinely found in Cu- (but not when bornite is present) and Cu–Zn ores, and are associated with chalcopyrite, tennantite-tetrahedrite and galena; pyrrhotite-bearing ores carry only minor amounts of tellurides (*Moloshag et al., 2002*).

Discrete Au-, Ag- and Te-minerals routinely form fine inclusions (1–50  $\mu\text{m}$ , occasionally up to 150  $\mu\text{m}$ ; larger grains are very rare) inside pyrite, chalcopyrite and sphalerite. Gold-Ag alloys, altaite, hessite and tetradyomite are relatively common, native tellurium, Au- and Au–Ag-tellurides, native silver, Ag- and Au–Ag-sulfides (acanthite, argentite, petrovskaita and others) are rare. Many of these tellurides contain solid solution gold: altaite – up to 5.2 wt.%, coloradoite – up to 4.2 wt.%, hessite – up to 1.4 wt.% and tetradyomite – up to 1.2 wt.% (Table 2). Such Au concentrations are much higher than found in the common sulfides (e.g., *Cook and Chryssoulis, 1990*; *Chryssoulis and Grammatikopoulos, 2003*). Admixtures of Se were found in tetradyomite (up to 2.8 wt.%), altaite (up to 0.86 wt.%) and tellurobismuthite (up to 0.85 wt.%). Significant traces of PGE were found in some

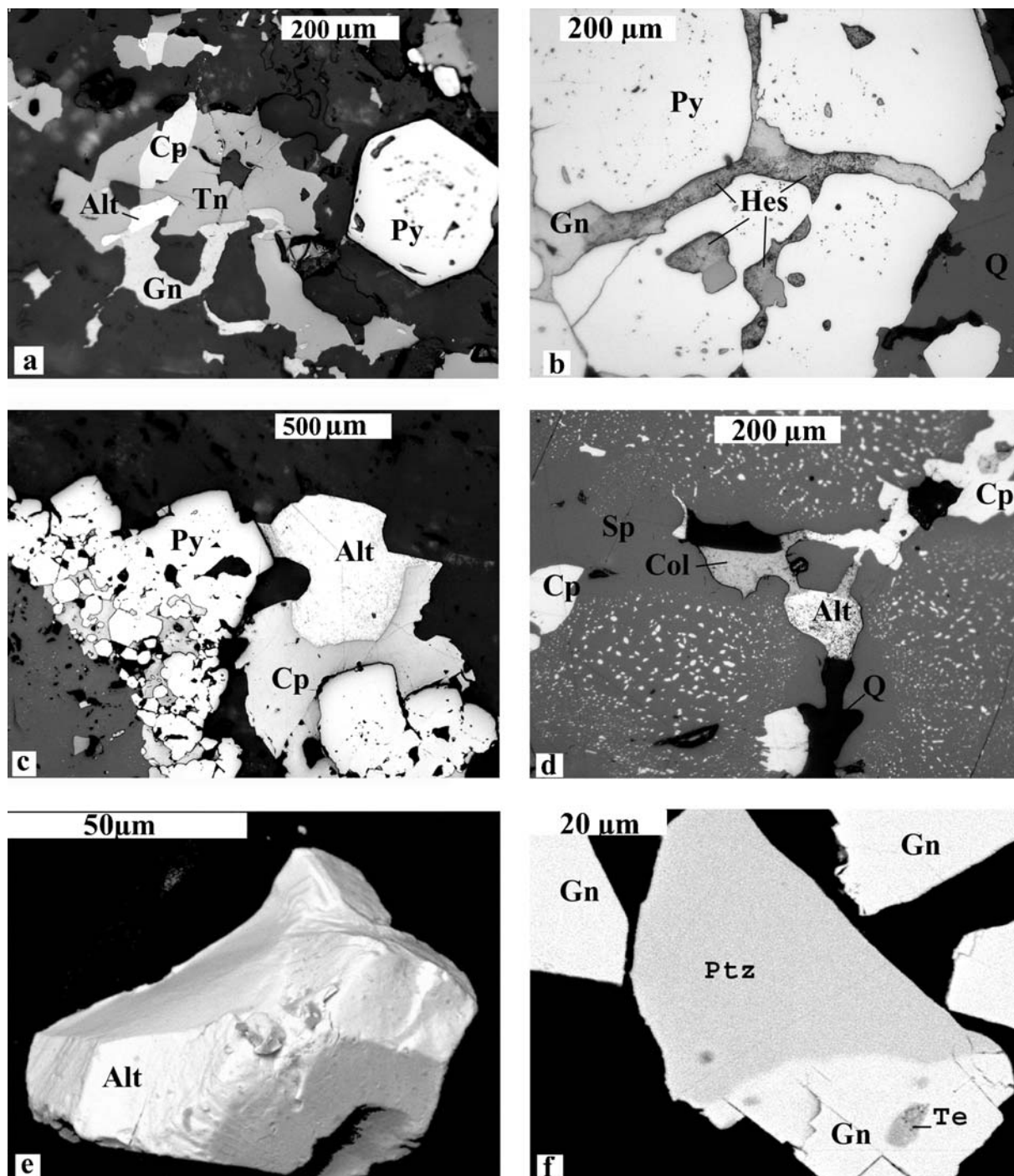


Fig. 6. Intergrowths of Te minerals and common sulfides of massive and semi-massive Cu-Zn ores of Uzelginsk deposit. Photomicrographs of telluride minerals in polished sections (a-d) and SEM images of heavy concentrates (e and f). a – altaite, galena and tennantite (Tn) close to an idiomorphic pyrite crystal; b – hessite (Hs)-galena veinlets in pyrite; c – large grain of altaite associated with chalcopyrite and pyrite; d – altaite and coloradoite (Col) of quartz-chalcopyrite veinlets in coarse-grained sphalerite; e – idiomorphic smooth crystal of altaite; f – intergrowths of petzite (Ptz) and native tellurium (Te) with galena

Table 2. *Maximum gold contents in rare minerals of massive sulfide ores of the Urals (electron microprobe data)*

Mineral	Formula	Au, wt.%
Altaite	PbTe	5.2
Coloradoite	HgTe	4.2
Hessite	Ag <sub>2</sub> Te	1.4
Tetradymite	Bi <sub>2</sub> Te <sub>2</sub> S	1.2
Rucklidgeite	(Bi,Pb) <sub>3</sub> Te <sub>4</sub>	0.91
Argentite	Ag <sub>2</sub> S	0.73
Empressite	AgTe	0.57
Tellurobismuthite	Bi <sub>2</sub> Te <sub>3</sub>	0.54
Native tellurium	Te	0.2
Aikinite	CuPbBiS <sub>3</sub>	0.05
Stützite	Ag <sub>5-x</sub> Te <sub>3</sub>	0.00
Wittichenite	Cu <sub>3</sub> BiS <sub>3</sub>	0.00

tellurides from Au-enriched ores (Vikentyev et al., 2002). These include petzite (up to 1.55 wt.% Pt), hessite (up to 0.66 wt.% Pt, 1.24 wt.% Pd), coloradoite (up to 0.75 wt.% Pd), altaite (up to 0.30 wt.% Pt, 0.14 wt.% Pd) and tetradymite (up to 0.26 wt.% Pt, 0.12 wt.% Pd), as well as native tellurium (up to 0.75 wt.% Pd). These data indicate that tellurides appear to be major carriers of Au, Ag and PGE in some VHMS deposits of the Urals. Native gold and other gold minerals are, not unexpectedly, most commonly observed in ore with Au contents higher than 3 g/t.

Gold and tellurium are mostly concentrated in pyrite and chalcopyrite (1–20 ppm Au and 10–100 ppm Te; Table 3). INAA determinations identified 0.1–2.5 ppm Au and 5–60 ppm Ag in euhedral pyrite, the dominant ore mineral. Gold and Ag concentrations in colloform As-bearing pyrite are 5.5–20 ppm Au (INAA) and 0.01–0.20 wt.% Ag, respectively. Arsenic concentrations of 0.25–1.35 wt.% As were determined by EPMA in this pyrite type, in which fine inclusions of chalcopyrite are abundant. The euhedral pyrite that coexists with As-bearing pyrite is characterized by concentrations of Au, Ag, and As about an order of magnitude lower (Vikentyev et al., 2004). Tellurides, native tellurium, tennantite-tetrahedrite and base metal sulfides are observed as microinclusions in the recrystallized pyrite.

Table 3. *Maximum Au, Ag, Te, Se contents in common minerals of massive sulfide ores of the Urals*

Method	Mineral	Au, wt.%	Ag, wt.%	Te, wt.%	Se, wt.%
INAA*	Pyrite	0.0022	0.020	0.058	0.052
	Chalcopyrite	0.0019	0.010	0.066	0.031
	Sphalerite	0.0011	0.023	0.024	0.047
	Pyrrhotite	0.0001	0.002	0.046	0.036
EPMA	Tennantite-Tetrahedrite	6.0	8.14	8.89	0.20
	Galena	0.41	0.34	0.14	1.36
	Bornite	0.17	0.55	0.07	0.11

\* Analyses of handpicked sulfide separates, 50 mg in weight

Gold contents in chalcopyrite average 1.5–3 ppm (full range 1–18.6 ppm Au); 10–100 ppm Ag is also determined. The sphalerite that hosts fine emulsion-like inclusions of chalcopyrite contains 1.8 to 10.6 ppm Au. Gold contents in inclusion-free sphalerite are determined to be just 0.3 to 3 ppm. Therefore, the tiny chalcopyrite inclusions in sphalerite are considered to be Au-bearing and thus responsible for the majority of the Au in sphalerite (Vikentyev et al., 2004). EPMA data indicates that galena is characterized by admixtures of Au (0.05–0.41 wt.%), Ag (0.01–0.34 wt.%), Pd (up to 0.14 wt.%), Pt (up to 0.24 wt.%), Se (0.1–0.2 wt.%), Te (0.1–0.14 wt.%) and Hg (near 0.1 wt.%, up to 0.25 wt.%). Some precious metals occur in bornite (0.02–0.27 wt.% Au, according to the EPMA data).

Silver and Te also occur substituted into fahlore. A low-Fe tennantite (0.1–0.5 wt.% Ag, 0.02–0.2 wt.% Te) is the dominant variety; Ag-tennantite (up to 8.4 wt.% Ag), Te-tennantite (up to 8.9 wt.% Te) and Te-bearing tennantite-tetrahedrite (up to 4 wt.% Te) are scarce.

Among the abundant ore minerals in Uralian VHMS deposits, tennantite-tetrahedrite and galena are the major concentrators of PGE. Tennantite contains up to 0.26 wt.% Pt and 0.38 wt.% Pd, while galena contains up to 0.24 wt.% Pt and 0.14 wt.% Pd. The highest PGE concentrations in any mineral were found in native gold (Vikentyev et al., 2002). Concentrations of up to 0.85 wt.% Pd and 2.23 wt.% Pt were determined. The highest PGE concentrations were consequently found in a series of ultra-heavy ore concentrates rich in free native gold. These concentrates were prepared from 50 g ore samples with initial contents of 22.8 and 11.1 g/t gold (Uzelginsk) and 90 g/t gold (Gaisk). The Uzelginsk ultra-heavy concentrates consist of pyrite (ca. 25 vol.%), galena (20 vol.%), altaite (20 vol.%), hessite (15 vol.%), petzite (5 vol.%) and native gold (10 vol.%), with minor amounts of native tellurium, base metal sulfides and tennantite-tetrahedrite. PGE contents in one of the Uzelginsk concentrates exceed 2.3 g/t (Pt + Pd + Rh): 354 mg/t Pt, 1220 mg/t Pd and 707 mg/t Rh. Concentrations of 375 mg/t Pt and 804 mg/t Pd were detected in another ultra heavy concentrate (Vikentyev et al., 2004). Significant PGE enrichment in these concentrates may be related to the presence of both tellurides and native gold. The ultra-heavy concentrate produced from the Gaisk ore mostly consists of native gold (80 vol.%) with minor amounts of galena and tellurides and contains 150 mg/t Pt, 1800 mg/t Pd and 100 mg/t Ru. In this sample, elevated PGE contents relate to their presence as impurities in native gold.

### **Gold behavior during ore processing and modes of gold occurrence**

In most of Uralian processing plants, milling of VHMS ores is undertaken without primary gravitational separation. The Au contents in the Cu- and Zn-flotation concentrates are commonly 20–50% higher than those in raw ores and range between 1.5 and 6 g/t. The two- to three-fold increase in Au content in the concentrates is accompanied by an increase in Ag content (2–5 fold), Te (1.5–6, up to 100 fold), Hg (2–6 fold), occasionally Sb (1.5–2 fold), Se (~1.5 fold), and As (2–3 fold). This suggests that precious metals occur as tellurides and native metals/alloys, possibly as admixtures in As-pyrite and tennantite, and also as inclusions of mineral compounds with S and Se such as petrovskaitite.



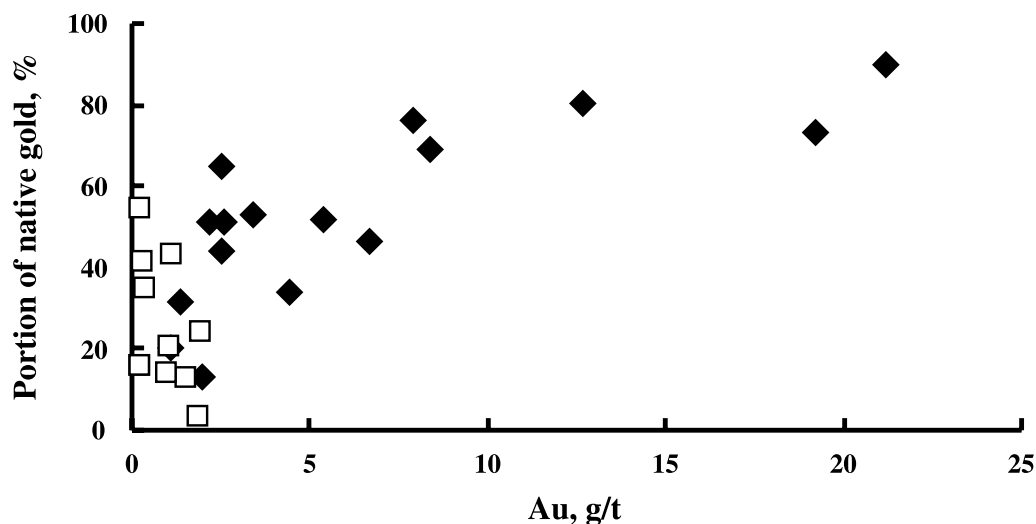


Fig. 8. Relationship between the portion of 'native gold' in massive sulfide ore (data of step-by-step autoclave leaching) and bulk gold concentration in this ore (fire assay) for VHMS deposits of the Urals. Solid diamonds – metamorphosed deposits; open squares – unaltered deposits

joints, lattice dislocations) within the host sulfides which largely influence reactivity and thus exposure of the sub- $\mu\text{m}$ -size inclusions of native gold and other Au-bearing trace minerals to the chemical reagent.

The contribution of submicroscopic inclusions of native gold and structurally-bound gold ('invisible gold') to the bulk gold concentration is most dramatic in the case of the non-deformed VHMS deposits of the Urals (Fig. 7). The proportion of visible gold minerals (chiefly native gold) as gold carriers is accordingly much higher in those massive sulfide ores which have been metamorphosed. The contribution of native gold to the overall gold balance for the Uralian VHMS deposits ranges broadly from 2% to as much as 90%, but if technological samples exceptionally enriched in Au (7.9–21.2 g/t) are excluded, the maximum contribution is only 53% (Fig. 8). These data indicate that the major part (45–90%) of gold in the common VHMS ores (0.2–3 g/t Au) is incorporated in sulfides as 'invisible gold'. The inference is that the loss of precious metals, particularly Au, during ore dressing is essentially caused by the only subordinate role of easily extractable ('visible') gold in the majority of the Uralian VHMS deposits.

## Discussion

In sulfide ores, gold is present in the following forms: the first type is as 'invisible' (finely-dispersed and submicroscopic) gold in sulfides. Whether this is present as structurally-bound gold (solid solution in sulfide lattice) or as (invisible) micro-inclusions, remains the subject of debate (e.g., *Bortnikov et al., 2003; Pals et al., 2003*). The second type is found as a late generation of 'free' Au-bearing mineral segregations (generally native gold, tellurides, and lesser amounts of common other compounds of Au) typically varying from 1 to 100  $\mu\text{m}$  in size (*Huston et al., 1992; Leistel et al., 1998; Vikentyev, 2003*).

The strong positive correlation between Au and Ag contents in sulfides analyzed by INAA, as well as the broad variation in the Au and Ag contents in sulfides from Au-rich zones of the deposits, seem to reflect the occurrence of some part of the gold as microinclusions of both native gold and Au–Ag alloys. The elevated contents of other components (Sb, As, Hg, Te, Se) in some Au-bearing sulfides testify, however, to the occurrence of other Au and Ag compounds. Elevated Au concentrations in pyrite in Uralian VHMS deposits correlate with high As contents, a feature common with other gold-sulfide deposits (e.g., *Fleet and Mumin, 1997; Simon et al., 1999a, b; Pals et al., 2003*) and are concordant with data showing high As contents in gold-bearing FeS<sub>2</sub> (both pyrite and marcasite) in present-day seafloor ores (*Bortnikov et al., 2003*).

Several competitive mechanisms have been suggested for the incorporation of Au in pyrite (and arsenian pyrite) as ‘invisible gold’: (1) Submicroscopic inclusions of native gold (e.g., *Genkin et al., 1998; Pals et al., 2003*), Au-telluride (*Pals et al., 2003*) or Au-bearing arsenopyrite (*Simon et al., 1999a*); (2) Structurally-bound, via a coupled substitution mechanism (*Cook and Chryssoulis, 1990*), a compound AuAsS or (Au, As)S<sub>2</sub> (*Arehart et al., 1993*); chemisorption of gold onto growth surfaces of pyrite crystal (*Fleet and Mumin, 1997*), as Au<sup>0</sup> (*Knipe et al., 1992; Simon et al., 1999a, b*), as Au<sup>+</sup> with subsequent reduction to Au<sup>0</sup> (*Scaini et al., 1998*); as Au<sup>+</sup> within Au(HS)<sup>0</sup> complex (*Widder and Seward, 2002*); as Au<sup>+</sup> in a vacant cation site (Au<sup>+</sup><sub>py</sub>) (*Simon et al., 1999a; Tauson, 1999*) and Au<sup>+</sup> as Au<sub>2</sub>S clusters (*Simon et al., 1999a*), or by adsorption of Au<sup>+</sup> in modes of Fe(SAs)–Au(HS)<sup>0</sup> or Fe(SAs)–Au<sub>2</sub>S<sup>0</sup> complexes (*Simon et al., 1999b*); as Au<sup>+</sup> in Fe(SAs)–Au(HTe)<sup>0</sup> or Fe(SAs)–Au<sub>2</sub>Te<sup>0</sup> complexes (*Pals et al., 2003*). It is difficult to establish which of these mechanisms takes place, but on the hypothesis that S<sub>2</sub><sup>2-</sup> is replaced by (AsS)<sup>3-</sup> in arsenian pyrite, and Au<sup>+</sup> replaces Fe<sup>2+</sup>, a process of gold reduction from Au-bearing As-pyrite with a theoretical formula FeAu(AsS) can be expressed by: FeAu(AsS) + H<sub>2</sub>S = Au<sub>(cr)</sub> + FeS<sub>2</sub> + As<sup>-</sup> + H<sub>2</sub>. Gold could be transferred to the visible state as a result of sulfide recrystallization and migration of As from pyrite to form tennantite, a mineral typical of the late parageneses especially at upper levels of hydrothermal ore system. H<sub>2</sub>S may be generated by desulfidation of pyrite to pyrrhotite (FeS<sub>2</sub> + H<sub>2</sub> + 2ē = FeS + H<sub>2</sub>S), since clearly secondary pyrrhotite ores make up large proportions of the central, internal part of the largest orebody (no. 4) in the Uzelginsk deposit (lower ore level), as well as in the root zones of other VHMS deposits (*Prokin and Buslaev, 1999*).

There is a general evolutionary trend for massive sulfide deposition, in which parameters change with time. In general, the hydrothermal fluids evolve from high-temperature, acidic, reduced solutions towards low-temperature, weakly acidic and near-neutral and oxidized solutions. Evolutionary trends in sulfide deposits of the Urals are also expressed in space, from the lower to upper levels and from the center to the peripheries of the ore lenses. On the basis of current knowledge (e.g., *Hannington et al., 1986; Huston et al., 1992; Zotov et al., 1985*) and most recent experimental determinations of gold and silver solubilities (*Tagirov et al., 2005*, and references therein), it is believed that AuCl<sub>2</sub><sup>-</sup>, AuOH<sup>0</sup>, AuCl<sub>2</sub><sup>-</sup>, AgCl<sup>0</sup> complexes are the main species controlling precious metal transport in volcanic-derived hydrothermal fluids during early high-temperature stages of submarine mineralization. The AuCl<sub>2</sub><sup>-</sup> complex is, however, the dominant species in high-temperature



chloride-rich acidic solutions ( $t \geq 350^\circ\text{C}$ ,  $\text{pH} < 3$ ). The relative role of  $\text{AuOH}^0$ ,  $\text{AuHS}^0$ , and  $\text{AgHS}^0$  will increase as mineralization progresses, and the main species controlling gold and silver transport in lower-temperature and near-neutral solutions are  $\text{Au}(\text{HS})^{2-}$  and  $\text{AuHS}^0$ , in the case of gold, and  $\text{AgCl}^{2-}$  and  $\text{Ag}(\text{HS})^{2-}$ , in the case of silver.

Early Au-bearing mineral parageneses consist of dominant Fe-sulfides and chalcopyrite, sometimes with subordinate magnetite and rare Co-Ni minerals. They occur mainly in the root and lowest levels of Urals VHMS deposits – in most cases more closely spatially related to shallow acid magmatic bodies. In the early stages of ore mineralization at higher temperatures ( $380^\circ\text{C}$ – $300^\circ\text{C}$ ) favorable for deposition of Cu-rich pyrite ores and relatively high  $f\text{Te}_2$  and low  $f\text{S}_2$ , gold deposition results from increase in pH (neutralization of solution) or drop in temperature (Huston, 2000). Co-precipitation of sulfides and gold may occur because the reactions that lead to destabilization of chloride complexes of Au and base metals are similar (Huston and Large, 1989). Decrease in the solubility of Au and Ag and the subsequent deposition of precious metals occurred during mixing of metal-bearing solutions with  $\text{CO}_2$ -rich fluids (Palyanova et al., 1995).

Gold is concentrated in sulfides as ‘invisible’ gold (mostly within the mineral lattice) and does not form discrete Au-minerals. Primary sulfide precipitation was shown to have occurred under conditions favorable for incorporation of the gold into pyrite and chalcopyrite during the high temperature ( $250^\circ\text{C}$ – $380^\circ\text{C}$ ) stages of ore deposition (Bortnikov et al., 2003). Gold in hydrothermal sulfide edifices in present-day oceanic settings (non-metamorphosed analogues of Paleozoic VHMS ores) is primarily confined to solid solution within Fe-(Cu)-sulfides, as well as fine-grained dissemination of Au-bearing chalcopyrite in sphalerite; free gold is atypical in these modern seafloor massive sulfide ores. Native gold can precipitate when the temperature decreases to  $150^\circ\text{C}$ – $200^\circ\text{C}$  (Bortnikov et al., 2003). The latter conditions correspond to late (low-temperature) stages of ore recrystallization.

During the middle and latest stages of hydrothermal processes in VHMS deposits of the Urals, as temperature decreases from  $300^\circ\text{C}$  to  $\sim 150^\circ\text{C}$ , mineral assemblages mainly composed of pyrite-chalcopyrite-sphalerite + tennantite-tetrahedrite  $\pm$  galena  $\pm$  barite are deposited (e.g., Prokin and Buslaev, 1999). Elevated Au and Ag concentrations in Cu–Zn and barite-polymetallic ores were considered to have resulted from deposition of Au and Ag, together with common sulfides, sulfosalts and barite, at relatively low-temperature conditions. Deposition of Au occurred during oscillations of redox conditions (Bortnikov et al., 2003), oxidation or increase in pH increase during mixing of weakly acidic fluid with ambient sea water (Hannington et al., 1986), as a response to a drop in the  $\text{H}_2\text{S}$  concentration in the ore-forming fluid due to either its incorporation into precipitated sulfides (Huston and Large, 1989) or boiling and consequent transfer of  $\text{H}_2\text{S}$  into the vapor phase as pressure decreases, or due to a decrease of concentrations of  $\text{S}^{2-}$  (for gold) and  $\text{Cl}^-$  (for silver) caused by dilution of solutions due to mixing with seawater.

Bornite-bearing ores crystallize at high  $f\text{S}_2$  and barite-bearing ones indicate oxidizing conditions. An increase in  $f\text{O}_2$  causes transition of  $\text{Te}^{2+}$  to  $\text{Te}^{4+}$  and leads to incorporation of Te in tennantite (up to 9 wt.%) and tennantite-tetrahedrite (up to 4 wt.%). These Te-bearing minerals occur in barite-polymetallic ores in Bajmak-type deposits and a few of Uralian type that are enriched in Pb, Ba and

Au; Table 1). The parageneses containing native metals (Au, Ag, Te), tellurides and sulfosalts in the Uralian VHMS deposits were formed during the latest stages of mineralization (usually syn-metamorphic) at temperatures of 200 °C–130 °C, due to recrystallization and refining of the common sulfides (mainly chalcopyrite and pyrite), segregation of rare elements and coarsening of tiny gold grains. As a result of these processes, the Au and Ag contents in pyrite, chalcopyrite and sphalerite decrease as metamorphism increases from zeolite to lower greenschist facies. In contrast, tennantite-tetrahedrite and galena, typical minerals in the late assemblages, display the opposite trend (Vikentyev et al., 2000). Gold contents in pyrite and chalcopyrite from the metamorphosed deposits are low (0.1–0.5 ppm, INAA) compared to the non-deformed deposits (average 1–2 ppm).

Metamorphism of sulfide ores is thus considered to contribute to the redistribution of base and precious metals, with the resulting formation of microscopic inclusions of Au–Ag alloys, native tellurium, as well as compounds of Au, Ag, Pb, Bi, Hg with Te, Se, S, Sn, As and Sb. The possibility of gold grain coarsening involving transformation from submicroscopic (<0.2 µm) to visible scales during metamorphism was first suggested by Kreiter (1948), who compared the mineralogy of weakly metamorphosed orebodies of the Southern Urals (with very rare visible native gold) with strongly metamorphosed deposits of the Middle Urals that contain visible coarse gold. The vital role played by synmetamorphic recrystallization for coarsening of gold grains and increase of the proportion of free gold is proven by the following evidence: (i) the inverse correlation between Au and Ag contents in the major sulfides with increase in metamorphic grade; (ii) the Au content of colloform pyrite that exceeds that in euhedral pyrite (cf. Huston, 2000) and (iii) the more widespread presence of coarse inclusions of native gold in the metamorphosed deposits.

Crystallization temperatures varied from 380 °C to 150 °C and  $\log fS_2$  ranges from –12 to –5 in the majority of the studied associations (Moloshag et al., 2002; Vikentyev et al., 2004). Under such conditions, the formation of bornite + tennantite-tetrahedrite and chalcopyrite + tennantite-tetrahedrite paragenetic associations is most typical. For each temperature, the sulfur fugacity required for formation of these Au-rich ores was one to two orders of magnitude higher than for ores with ‘normal’ Au contents of approximately 1 g/t. Good examples of such features are seen in the slightly-deformed Alexandrinsk (2–3 g/t Au) and Uzelginsk (1 g/t Au) deposits, as well as in deposits only metamorphosed at the sub-greenschist facies: Gaisk (2 g/t Au in rich ore), San-Donato and Degtyarsk (both  $\leq 1$  g/t Au) deposits (Vikentyev, 2003). Bornite-bearing ores occur in some VHMS deposits of the Urals (Gaisk, Alexandrinsk, Molodezhnoye) and crystallized at  $fS_2$  conditions above the chalcopyrite-bornite equilibrium line. These are extremely enriched in gold (2–20 g/t, up to 90 g/t) and often bear large gold inclusions. This gold is considered to be chemically-bound gold released from pyrite and bornite. Pyrrhotite-dominant ores, where  $\log fS_2$  conditions of crystallization are lowest, bear only low gold concentrations ( $\leq 0.5$  g/t Au).

Data on the stability of telluride minerals (Afifi et al., 1988; Cabri, 1965; Moloshag et al., 2002; Zhang and Spry, 1994) and estimation of  $fTe_2$  on the basis of empirical equations (Bortnikov et al., 1988) suggest that the studied mineral associations mainly fall into the hessite-native gold field in the  $\log fTe_2 - \log fS_2$

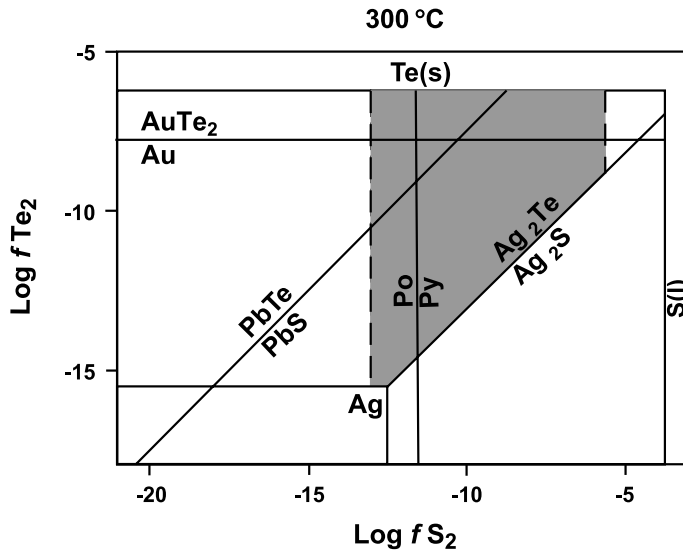


Fig. 9. Stability of sulfides and tellurides in Uralian VHMS deposits as a function of  $fS_2$  and  $fTe_2$  (after data from *Moloshag et al.*, 2002; *Shackleton et al.*, 2003; *Vikentyev*, 2003)

diagram (Fig. 9) at  $\log fTe_2$  between  $-16$  and  $-6$  at  $300\text{ }^\circ\text{C}$  and between  $-21$  and  $-13$  at  $150\text{ }^\circ\text{C}$ . Tellurium may be transported from the magma in a gas phase and deposition of Te-minerals may result from condensation of  $H_2Te_{(g)}$  or  $Te_{2(g)}$  into hydrothermal solution (*Cooke and McPhail*, 2001).

Elevated contents of Pt and Pd in various minerals presumably reflect isomorphous substitution of large ions (Au, Ag and Pb). Preferential PGE accumulation has been found in native gold, tellurides, and tennantite-tetrahedrite, all minerals with complete (or partial) metallic bonding. All these minerals typically exhibit broad fields of solid solution (Te for Bi and Sb, As for Sb, Au for Ag, Cu for Ag, Pb for Bi etc.). The presence of detectable PGE in native gold, as well as PGE and Au enrichment in tellurides and tennantite, indicates possible co-precipitation of these elements from hydrothermal fluids. It is important to keep in mind that the stability fields of Pt and Pd tellurides in  $\log fO_2 - pH$  diagrams overlap those of Au and Ag tellurides (*Mountain and Wood*, 1988; *Zhang and Spry*, 1994).

The geochemical behavior of Au, Ag and Te during synvolcanic deposition of pyritic ores on and below the ocean floor, and corresponding enrichment of the primary sulfide ores, as well during metamorphic regeneration, is directly analogous to their behavior in other sulfide-bearing ore-forming systems (porphyry Cu deposits, Cu-skarns, orogenic gold, epithermal  $Au \pm Ag$  deposits etc.). Later phases of mineralization, synmetamorphic deformation and recrystallization caused the appearance of secondary assemblages of visible gold (Au–Ag alloys), tellurides and a number of discrete minerals of Bi, Sb and Sn.

## Conclusions

Conditions of elevated  $fS_2$  (near or above the chalcopyrite-bornite equilibrium line) are favorable for crystallization of ore with higher Au content (1–3 g/t and higher).

Under such conditions, bornite + tennantite-tetrahedrite and chalcopyrite + tennantite-tetrahedrite assemblages are most typical. Invisible, finely-dispersed gold in the major ore-forming sulfides is the dominant form of gold in the studied deposits. Because large amounts of the gold in the run-of-the-mill VHMS ores (Au <3 g/t) are incorporated as 'invisible' gold in sulfides, gold is generally lost to the tailings. Visible segregations of gold (~1 µm or more) and tellurides formed in massive sulfide ores during recrystallization resulting from late (low-temperature) hydrothermal processes and low-grade metamorphism at prehnite-pumpellyite – greenschist facies. These processes lead to coarsening of gold grains as a result of selective recrystallization and an increase in the proportion of free gold (native gold and subordinated Au–Ag-tellurides). Tellurides appear to be major carriers, alongside native gold, of gold, silver and PGE in VHMS deposits of the Urals.

### Acknowledgements

The author wishes to thank N. Bortnikov, V. Moloshag, V. Murzin and M. Judovskaya for help and fruitful discussions. This manuscript has benefited significantly from the careful comments, constructive criticism, and editorial handling by N. J. Cook. Analyses were performed by A. Mokhov (JSM-5300 + LINK ISIS), A. Tsepin (EPMA) and A. Kerzin (INAA). The study was supported by the Russian Foundation for Basic Research (grant 04-05-65040), the Earth Science Brunch of Russian Academy of Sciences (Nanoparticles project) and the Russian Science Support Foundation.

### References

- Afifi AM, Kelly WS, Essene EJ* (1988) Phase relations among tellurides, sulfides, and oxides. I. Thermodynamic data and calculated equilibria. *Econ Geol* 83: 377–394
- Arehart GB, Chryssoulis SL, Kesler SE* (1993) Gold and arsenic in iron sulfides from sediment-hosted micron gold deposits: Implications for depositional processes. *Econ Geol* 88: 171–185
- Bortnikov NS, Kramer H, Genkin AD, Krapiva LYa, Santa-Crus M* (1988) Parageneses of gold–silver tellurides in gold deposit Florensy (Cuba). *Geol Ore Deposits* 30: 49–61 (in Russian)
- Bortnikov NS, Cabri L, Vikentyev IV, Tagirov BR, McMahan G, Bogdanov YuA, Stavrova OO* (2003) Invisible gold in sulfides of modern sulfide edifices. *Geol Ore Deposits* 45: 232–245
- Cabri LJ* (1965) Phase relations in the Ag–Au–Te systems and their mineralogical significance. *Econ Geol* 60: 1569–1606
- Chryssoulis SL, Grammatikopoulos TA* (2003) Forms of gold. In: *Eliopoulos DG et al., Mineral exploration and sustainable development*, Millpress, pp 961–964
- Cook NJ, Chryssoulis SL* (1990) Concentration of “invisible” gold in the common sulfides. *Can Mineral* 28: 1–16
- Cooke DR, McPhail DC* (2001) Epithermal Au–Ag–Te mineralization, Acupan, Baguio district, Philippines; numerical simulations of mineral deposition. *Econ Geol* 96: 109–132
- Fleet M, Mumin AH* (1997) Gold-bearing arsenian pyrite and marcasite and arsenopyrite from Carlin Trend gold deposits and laboratory synthesis. *Am Mineral* 82: 182–193
- Gammons CH, Williams-Jones AE* (1995) The solubility of Au–Ag alloy + AgCl in HCl/NaCl solutions at 300 °C: New data on the stability of Au (I) chloride complexes in hydrothermal fluids. *Geochim Cosmochim Acta* 59: 3453–3468

- Genkin AD, Bortnikov NS, Cabri LJ, Wagner FE, Safonov JuG, McMahon G, Kerzin AL (1998) A multidisciplinary study of invisible gold in arsenopyrite from four mesothermal gold deposits in Siberia, Russian Federation. *Econ Geol* 93: 463–487
- Hannington M, Peter JM, Scott SD (1986) Gold in sea-floor polymetallic sulfide. *Econ Geol* 81: 1867–1883
- Huston DL (2000) Gold in volcanic-hosted massive sulfide deposits: distribution, genesis, and exploration. *Rev Econ Geol* 13: 401–426
- Huston DL, Bottrill RS, Creeman RA, Zaw K, Ramsden TR, Rand SW, Gemmell JB, Jablonski W, Sie SH, Large RR (1992) Geological and geochemical controls on the mineralogy and grain size of gold-bearing phases, Eastern Australian volcanic-hosted massive sulfide deposits. *Econ Geol* 87: 542–563
- Huston DL, Large RR (1989) A chemical model for the concentration of gold in volcanogenic massive sulfide deposits. *Ore Geol Rev* 4: 171–200
- Knipe SW, Foster RP, Stanley CJ (1992) Role of sulfide surfaces in sorption of precious metals from hydrothermal fluids. *Trans Inst Mining Metall Sect B* 101: B83–B88
- Kreiter VM (1948) Gold particle dimensions in sulfide deposits as feature of post-ore metamorphism. *Izv Akad Nauk SSSR, ser Geol* 1: 159–162 (in Russian)
- Leistel JM, Marcoux E, Deschamps Y, Joubert M (1998) Antithetic behaviour of gold in the volcanogenic massive sulfide deposits of the Iberian Pyrite Belt. *Mineral Deposita* 33: 82–97
- Lodeishikov VV (1999) Technology of gold and silver extraction from refractory ores. Irkutsk. IRGIREDMET, 342 p (in Russian)
- Moloshag VP, Vikentyev IV, Grabezhev AI, Gulyaeva TY (2002) Tellurides of massive sulfide deposits of the Urals. *Proc Zavaritsky Inst Geol Geochem UB RAS*: 189–195 (in Russian)
- Mountain BW, Wood SA (1988) Chemical controls of the solubility, transport, and deposition of platinum and palladium in hydrothermal solutions: A thermodynamic approach. *Econ Geol* 83: 493–510
- Pals DW, Spry PG, Chryssoulis S (2003) Invisible gold and tellurium in arsenic-rich pyrite from the Emperor gold deposit, Fiji: Implications for gold distribution and deposition. *Econ Geol* 98: 479–493
- Palyanova GA, Shironosova GP, Kolonin GR (1995) Modelling of gold behavior in hydrothermal complex fluid with gas component. *Proc 8 Int Symp Water-Rock Interact*, pp 819–823
- Prokin VA, Buslaev FP (1999) Massive copper-zinc sulfide deposits in the Urals. *Ore Geol Rev* 14: 1–69
- Puchkov VN (1997) Structure and geodynamics of the Uralian orogen. In: *Burg JP, Ford M* (eds), *Orogeny through time*. *Geol Soc London Spec Publ* 121: 201–236
- Scott SD (1983) Chemical behaviour of sphalerite and arsenopyrite in hydrothermal and metamorphic environments. *Mineral Mag* 47: 427–435
- Scaini MJ, Bancroft GM, Knipe SW (1998) Reactions of aqueous Au<sup>1+</sup> sulfide species with pyrite as a function of pH and temperature. *Am Mineral* 83: 316–322
- Shackleton JM, Spry PG, Bateman R (2003) Telluride mineralogy of the Golden Mile deposit, Kalgoorlie, Western Australia. *Can Mineral* 41: 1503–1524
- Shikazono N (1985) A comparison of temperatures estimated from the electrum-sphalerite-pyrite-argentite assemblage and filling temperatures of fluid inclusions from epithermal Au–Ag vein-type deposits in Japan. *Econ Geol* 80: 1415–1424
- Shikazono N, Shimizu M (1987) The Ag/Au ratio of native gold and electrum and the geochemical environment of gold vein deposits in Japan. *Mineral Deposita* 22: 309–314
- Simon G, Hyang H, Penner-Hanh JE, Kesler SE, Kao L-S (1999a) Oxidation state of gold and arsenic in gold-bearing arsenian pyrite. *Am Mineral* 84: 1071–1079

- Simon G, Kesler SE, Chryssoulis S* (1999b) Geochemistry and textures of gold-bearing arsenian pyrite, Twin Greeks, Nevada: Implications for deposition of gold in Carlin-type deposits. *Econ Geol* 94: 405–422
- Tagirov B, Salvi S, Schott J, Baranova NN* (2005) Experimental study of gold-hydrosulfide complexing at 350–500 °C, 500 and 1000 bars using mineral buffers. *Geochim Cosmochim Acta* 69: 2119–2129
- Tauson VL* (1999) Gold solubility in the common gold-bearing minerals: Experimental evaluation and application to pyrite. *Eur J Mineral* 11: 937–947
- Vikentyev IV* (2003) Composition of native gold in massive sulfide ores of the Urals. *Dokl Earth Sci* 393A: 1284–1288
- Vikentyev IV, Belenkaya YuA, Ageev BI* (2000) Alexandrinsk pyrite-polymetallic deposit in the Urals. *Geol Ore Deposits* 42: 248–274
- Vikentyev IV, Moloshag VP, Yudovskaya MA, Eremin NI* (2002) Platinum group elements in ores of massive sulfide deposits of the Urals. *Dokl Earth Sci* 385: 488–492
- Vikentyev IV, Yudovskaya MA, Mokhov AV, Kerzin AL, Tsepin AI* (2004) Gold and PGE in massive sulfide ore of the Uzelginsk deposit, Southern Urals, Russia. *Can Mineral* 42: 651–665
- Widler AM, Seward TM* (2002) The adsorption of gold(I) hydrosulfide complexes by iron sulfide surfaces. *Geochim Cosmochim Acta* 66: 385–402
- Yushko SA* (1936) About mineralogical form of gold and its assemblages in pyritic ores of the Urals. *Izv Akad Nauk SSSR, ser Geol* (2–3): 436–440 (in Russian)
- Zaykov VV, Maslennikov VV, Zaykova EV, Herrington R* (2001) Ore-formation and ore-facies analyses of massive sulfide deposits of the Urals paleocean. *IMin, UB RAS, Miass*: 315 p (in Russian)
- Zhang X, Spry PG* (1994) Calculated stability of aqueous tellurium species, calaverite and hessite at elevated temperatures. *Econ Geol* 89: 1152–1166
- Zotov AV, Baranova NN, Daryna TG, Bannykh LN, Kolotov VP* (1985) The stability of  $\text{AuOH}^0_{\text{sol}}$  in water at 300–500 °C and 500–1500 atm. *Geochem Intern* 22: 156–161

Author's address: *I. V. Vikentyev* (e-mail: viken@igem.ru), Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences (IGEM RAS), 35 Staromonetny per., Moscow 119017, Russia