

Speciation of Noble Metals and Conditions of Their Concentration in Massive Sulfide Ores of the Urals

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Abstract—The distribution of noble metals has been studied in ores and sulfide concentrates from the Gai, Uchaly, Uzel'ga, Aleksandrinsky, Degtyarsk, and Saf'yanovka deposits. The ores, technological products, and hand-picked monofractions were analyzed with INAA; PGE were determined with kinetic and chromatographic methods after their preliminary chemical separation. The ultraheavy fractions from Au-rich samples were used for examining minerals of noble metals. Phase relations and compositions of ore minerals were studied with an X-ray microprobe and electron microscope equipped with an energy dispersive X-ray analyzer. Gold is associated largely with Fe and Cu minerals (pyrite, chalcopyrite, fahlore) and has been detected as an admixture in Pb, Bi, and Ag tellurides. Pyrite—the major mineral of massive sulfide ores—is the main gold concentrator (up to 20 ppm, ~1 ppm on average). As follows from the results of rational analysis, the concentration of finely dispersed gold in sulfide ores from the studied deposits ranges from 0.8 to 5.0 ppm, i.e., is less than the bulk Au content in the respective samples (0.93–21.2 ppm). Formation conditions of Au-enriched massive sulfide ores were estimated from the homogenization temperature of fluid inclusions in minerals and on the basis of the electrum–argentite–pyrite–sphalerite and electrum–hessite geothermometers, taking into account the sulfur and tellurium fugacities. The appearance of visible gold and tellurides in ores is caused by recrystallization of their fine-grained intergrowths with ore-forming minerals and, likely, by release of isomorphic admixtures contained in sulfides during epigenetic hydrothermal alteration.

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INTRODUCTION

Massive sulfide deposits are important sources of nonferrous and noble metals and some rare elements, providing 40% of the world's output of silver and 5% of gold. Approximate estimates of the world's resources of noble metals contained in massive sulfide deposits exceed 4000 t Au and 100000 t Ag; more than 40% of these resources are contained in deposits of the former Soviet Union, which are localized mainly in Russia and Kazakhstan. Many large massive sulfide deposits initially contained more than 100 t Au and 2000 t Ag; the greatest amount (>330 t Au) has been mined at the Horn deposit in Canada. The question remains open of why most of the deposits contain only ~1 g/t Au, whereas the Au grade in others is as high as 2–3 g/t (Eremin et al., 2000; Huston, 2000). The Urals is among the world's largest provinces with respect to gold and silver resources related to massive sulfide deposits. Nonetheless, the spatial distribution and chemical speciation of Au and Ag in ores have been considered only fragmentarily (Maslennikov and Zaikov, 1998; Petrovskaya, 1973; Salikhov et al., 2003).

The intensification of ore processing in the last decades aggravated the problem of gold recovery. While Cu and Zn are recovered into concentrates almost completely (75–85% of the bulk in ore), the total output of gold into the copper and zinc concentrates reaches only 20–50%. The problem of recovery of by-product gold is especially acute for the Uchaly Mining and Concentrating Works, where 75–80% of Au and >50% of Ag are lost by processing of ores derived from the Uchaly, Uzel'ga, Molodezhny, and Talgan deposits because, as at most deposits in the Urals, the visible gold amounts only to 15–50% and this percentage is mainly due to fine intergrowths with sulfides and microinclusions therein. The total loss of unrecoverable gold in pyrite concentrate and tailings is estimated at 11–12 t Au a year.

Gold occurs in massive sulfide ores as its own minerals and dispersed in sulfides. The Au minerals are represented by native gold, tellurides, and less abundant compounds of Au and Ag. The epigenetic origin of free gold was emphasized by Berengilova et al. (1973), Eremin et al. (2000), Ismagilov and Ismagilova (1978), Maslennikov (1940), Novgorodova (1983), Petrovskaya (1973), Plaksin et al. (1940), and Pshenichny (1976), to name only a few authors. Invisible (finely dispersed,

submicroscopic) gold in sulfides commonly is predominant; however, it remains unclear whether this gold is incorporated into the sulfide lattice or occurs as microinclusions (Larocque et al., 1995; Novgorodova, 1983; Pshenichny et al., 1999).

In this paper, we present the results of an investigation concerning the distribution of noble metals in ores and sulfide concentrates of the Urals' largest Gai deposit, as well as Uchaly, Uzel'ga, Degtyarsk, and Saf'yanovka deposits belonging to the Ural (copper-zinc) type of massive sulfide deposits and of the medium-size Aleksandrinsky deposit, which is close to the Baimak (copper-zinc-gold-barite) type. Data on other deposits of the southern and central Urals are given for comparative purposes.

RESEARCH METHODS

Samples of massive sulfide ores collected in the course of mapping of underground workings and open pits and documentation of cores from deep boreholes were examined under a microscope with a special emphasis on the orebody segments enriched in gold. The ores, technological products, and hand-picked monofractions of minerals were analyzed with INAA. Platinum group elements (PGE) were determined in ultraheavy sulfide concentrates of Au-rich ore using direct kinetic and chromatographic methods with preliminary chemical separation of the total PGE sum. To identify minerals of noble metals, the ultraheavy fractions were separated from large (0.5–1.0 kg) samples in which elevated Au contents had been established by preliminary analysis (Laverov et al., 1997).

The samples, freed from sludge, were divided with electromagnetic separators and heavy liquids; after washing out of grain-size fractions from +0.06 to –0.1 and –0.06 mm in water and bromoform, the obtained ultraheavy concentrate was used for preparation of specimens afterwards analyzed with a microprobe. The Au and Ag contents in individual grains of ore minerals and the compositions of gold and silver minerals were analyzed with a Camebax SX-50 microprobe (exposure at each point was increased up to 100 s and the detection limit reached 0.005 wt %, correspondingly) and with a JSM-5300 electron microscope equipped with a Link ISIS-10000 energy dispersive analyzer. More than 150 grains of native gold and hundreds of grains of other minerals were analyzed.

The speciation of gold in sulfide ores, including the presence of structurally bound species, may be detected with aid of some modern physical methods (Cabri et al., 2000; Simon et al., 1999) that are not available in Russia. To estimate possible gold species in sulfides approximately, we used the results of so-called rational (phase) analysis, commonly applied to the assessment of technological properties of Au-bearing ores in domestic practice. This analysis was performed at the Unipromed Institute for representative large technolog-

ical samples. The method is based on the different chemical resistance of gold species associated with sulfides and silicates (Lodeishchikov, 1968). Relatively coarse free gold is recovered from ore by amalgamation; fine native gold in tiny intergrowths with sulfides is recovered by cyanide leaching; and finely dispersed (largely structurally bound) "hard" gold is also recovered from sulfides by cyanide leaching, with the residue insoluble in cyanide being additionally decomposed in nitric acid.

This technique of estimation of gold species has obvious restrictions because the degree of chemical extraction of gold is controlled not only by its mineral species and grain size but also by the different availability of submicroscopic gold for contacting with a chemical reagent, in particular, due to inhomogeneities of sulfide and silicate hosts, including pores, microfractures, and lattice defects.

To determine the physicochemical formation conditions of Au-bearing mineral assemblages, we took into account the homogenization temperature of fluid inclusions in minerals (analysts V.Yu. Prokof'ev and V.S. Karpukhina). Experimental and theoretical data on the stability of telluride-bearing mineral assemblages and estimates of sulfur and tellurium fugacities pertaining to the formation of these minerals also were involved in the consideration. To interpret the physicochemical formation conditions of native gold, we used the results of experimental studies of gold-silver alloys (Gammons and Williams-Jones, 1995; Shikazono, 1985; Vaughan and Craig, 1978). The composition of these alloys is characterized by the atomic fraction of silver:

$$N_{Ag} = Ag/(Ag + Au).$$

The inverse value of fineness of gold (thousandth weight parts of pure Au in native gold) is commonly used as a characteristic of gold in ore (Petrovskaya, 1973).

The temperature of mineral formation in most samples was determined with the electrom-argentite-pyrite-sphalerite geothermometer (Shikazono, 1985). Argentite appears as a thin film on the surface of Au-Ag alloys at a certain $\log f_{S_2}$ value at the given temperature; this film induces the so-called loss of electrom luster. It is practically impossible to observe such a film with optical methods in natural samples. An increase in Ag content along margins of native gold combined with the appearance of sulfur recorded in microprobe profiles serves as indirect evidence for an outer argentite film.

We also used arsenopyrite thermo- and fugometry based on the As content in arsenopyrite brought into equilibrium with pyrite, pyrrhotite, and other sulfides (Bortnikov, 1993; Scott, 1984). The temperature and sulfur fugacity were found graphically from intersections of As isopleths in arsenopyrite with lines of pyrite-pyrrhotite and pyrite-arsenopyrite equilibria

plotted on the $\log f_{S_2}$ - T diagram that demonstrates phase relations in the Fe-As-S system (Kretschmar and Scott, 1976). In calculating atomic As contents, Ni and Co concentrations were added to Fe and Sb was added to As (Vaughan and Craig, 1978).

The tellurium fugacity was determined with the electrum-hessite geothermometer and from consideration of the phase relations in the Au-Ag-Te system (Bortnikov et al., 1988). The tellurium fugacity was also estimated from the equilibrium of galena with altaite, the most abundant telluride in ores of the studied deposits (Moloshag et al., 2002). The temperature and the sulfur fugacity also were assessed with other mineralogical thermo- and fugometers.

MASSIVE SULFIDE DEPOSITS OF THE URALS: AN OVERVIEW

Almost all large massive sulfide deposits of the Urals are clustered in the Magnitogorsk Megazone (Fig. 1). The Degtyarsk and Saf'yarovka deposits, which are situated far to the north, are related to the tectonic fragments of this megazone (Prokin and Buslaev, 1999). The massive sulfide orebodies are hosted in the Middle Devonian rocks of the island-arc basalt-rhyolite association that underwent greenstone alteration. The orebodies commonly reside in the upper part of rhyolitic-rhyodacitic lava member and occasionally in extrusions, which are directly overlain by basaltic andesite or by thin-bedded volcanomictic rocks and sporadically associated limestones, in turn, overlapped by a thick pile of basaltic andesite. The silicic lava and tuff in the lying wall of the massive sulfide lens were affected by hydrothermal quartz-sericite-pyrite alteration and cut by quartz \pm carbonate veinlets that bear sulfides; pyrite and chalcopyrite are the most abundant. The orebodies are composed of prevalent (up to 90 vol %) pyrite, sphalerite, and chalcopyrite; fahlore and galena are second in abundance; pyrrhotite and magnetite are present at some deposits. Quartz is the major gangue mineral; sericite, chlorite, barite, and albite are notable also. Bedded pyrite ore with lean sphalerite and chalcopyrite mineralization commonly occurs as relics. The main bodies are composed of massive and brecciated ores. Compact banded ore occurs as small lenses and near-contact fault-line zones of large sulfide ore ribbons and sheetlike bodies.

The Gai Deposit

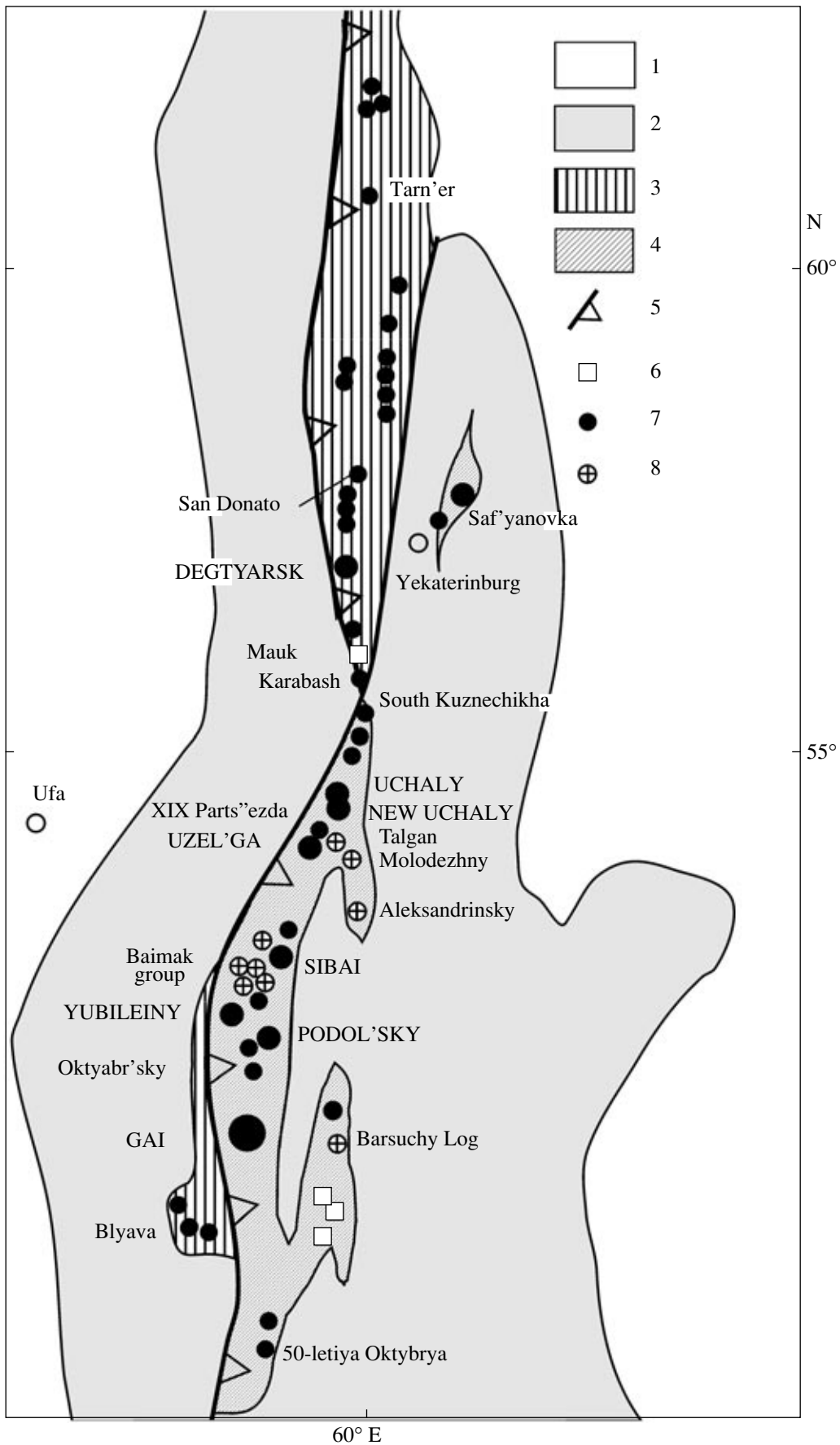
The Urals' largest and one of the world's largest deposits, the Gai deposit comprises a series of closely spaced steeply dipping lenticular orebodies that extend for a distance from 40 m to a few hundred meters (up to 1300 m) down the dip. Their thickness is measured in tens of meters and reaches 150 m in bulges. The orebodies make up a near-meridional sheetlike ore zone about 300 m thick (maximum thickness 600–800 m). The ore zone extends for 3.7 km along the strike and for

more than 1.7 km down the dip, remaining not contoured at a depth. The deposit is mined by three open pits (only one is in operation now) and crossed by a deep mine, which is currently developed at levels of 685–940 m; 140 Mt of ore (less than one-third of the ultimate reserves) have been mined to date. The reserves in-place, together with the exhausted ore, amount to ~9 Mt of Zn and Cu (Zn : Cu = 0.4). The average Au grade is 1.15 g/t (0.5–30 g/t) and the average Ag grade, 14 g/t. The mine produces about 2 t of gold per year in copper and zinc concentrates (Gai..., 2004). The sum recovery of noble metals into copper and zinc concentrates is 55% Au and 65% Ag, including 42% Au and 53% Ag recovered into copper concentrate. The highest Au grade of copper concentrate is 4–7 g/t Au, and the highest Ag grade of zinc concentrate is 80–100 g/t; 20% Au and 15% Ag are lost in pyrite concentrate; losses in tailings amount to 25% Au and 20% Ag.

According to the microprobe results, the highest Au contents are established in galena (0.2–0.4 ppm Au against 0.10–0.15 wt % Ag). The highest Ag contents (0.16–0.55 wt %) are detected in bornite (>0.4 wt % in most samples). The Au content in bornite is appreciable (up to 0.17 wt % and >0.1 wt % in half of samples). Au and Ag contents in sphalerite, pyrite, and chalcopyrite are low (<0.01 wt %). Fahlore in association with native gold is distinguished by extremely low Ag contents (0.05–0.16 wt %), which may drop below the detection limit.

The Uchaly Deposit

This is a large deposit that consists of a single nearly vertical and thick (up to 150 m in bulges) lens of high-grade Cu-Zn ore that extends for 1.2 km in the meridional direction and for 1.3 km down the dip. The deposit has been studied in detail and serves as a reference massive sulfide deposit of the Ural type (Mineral..., 1994). The deposit is severely deformed; the massive copper-zinc ore is sharply predominant. The primary, rhythmically bedded and brecciated ores are retained only as local relics. Gneissose ore and small folds occur in postmineral fault zones, especially at contacts of the ore lens and at its pinchouts. About 75% of 120 Mt of ore (Cu : Zn : Pb = 1 : 3.46 : 0.14) have been mined to date. The Au grade in the ore is ~1.4 g/t, locally increasing to 3–4 g/t (6–20 g/t in particular hand specimens). The Ag grade in the ore is 8–30 g/t, occasionally reaching 100 g/t. The recovery of gold and silver into copper, zinc, and pyrite concentrates approximately amounts to 14, 8, and 50 wt % and 26, 15, and 37 wt %, respectively. The zinc concentrate is enriched in noble metals to the greatest degree (4 g/t Au and 150 g/t Ag). The copper concentrate contains 2.5 g/t Au and 90 g/t Ag, and the pyrite concentrate, 1.5 g/t Au and 25 g/t Ag; noble metals are not recovered from the pyrite concentrate. The crude copper contains as much as 86 g/t Au and more than 1560 g/t Ag. According to the results of



phase analysis, the free gold content is only 13–15%; gold mostly occurs as tiny intergrowths with sulfides, which are not opened by grinding of ore (95% of the fraction is <0.074 mm). The Au content in sphalerite is 1.3 ppm on average and may reach 3 ppm; the Ag content is 20–75 ppm. Pyrite contains 1.2 ppm Au (up to 1.6 ppm) and 9.5 ppm Ag (up to 30 ppm). The lowest Au content (1 ppm) was established in chalcopyrite, which contains 10–20 ppm Ag.

The Uzel'ga Deposit

This deposit is comparable in reserves with the Uchaly deposit; Zn : Cu = 2.5. The ore zone extends for 2 km in the NNW direction and consists of an echelon arranged orebodies. The orebodies are large and thick gently dipping lenses, commonly with obtuse endings. Orebodies are 300 × 500 m in size and 100–170 m thick in swells. The orebodies are hosted in a large paleovolcanic edifice composed of the basalt–rhyolite rock association and localized at two hypsometric levels: 130–180 m (orebodies 1, 5, 6, and 9) and 420–640 m (orebodies 2–4, 7, and 8) 300–350 m above each other. The orebodies of the lower level, first of all, Orebody 4 and the adjacent small Orebody 3 are mined currently; orebodies 2 and 7 are being developed for mining.

The massive ore amounts to 90% of reserves at this deposit. The ore is characterized by a high grade of Ag ranging from 10 to 50 g/t (32 g/t on average and 150–550 g/t as maximal contents). The Au grade is 0.5–2.5 g/t, attaining 10–12 g/t in particular samples. These figures provide for the profitable exploitation of this deposit at Zn and Cu grades moderate for underground mining. High concentrations of As (0.3–0.6 wt % and up to 3.5 wt % in ore at the upper level), Te (50–100 ppm), and Hg (15–25 ppm on average and 0.01–900 ppm as a range) are noted. The Cu–Zn ore at the northern flank of Orebody 4 and the ore from Orebody 3 are distinguished by elevated Au and Ag grades (2–4 g/t, occasionally 10–23 g/t and as high as 230–550 g/t, respectively). The zinc and especially copper and pyrite ores elsewhere at this deposit are enriched in gold to a lesser extent.

The average Au content in pyrite is 1.0–2.5 ppm (0.2–20 ppm); the Ag content is 24 ppm. According to the INAA results, pyrite III with the highest Au content (16–20 ppm) is enriched in Ag (130–150 ppm) and Se (0.01–0.02 wt %). The Au–Hg–Se, Au–Ag–Sb, and Au–Ag–Sb–Hg assemblages of microelements are recognized in the samples of pyrite III with high (6–11 ppm) Au contents. A microadmixture of Au–Se ± Ag is detected in pyrite III at elevated Au contents of 4–6 ppm. The strong positive correlation between Au and Ag in

pyrite III (the strongest in comparison with any other pair of elements), together with a rather high dispersion of contents, indicates that gold occurs here as electrum nanoparticles; the aforementioned assemblages of elements show that Au compounds with Sb, Se, and Hg also are present as nano-inclusions. A less strong (in comparison with the Au–Ag pair) but significant positive correlation between Ag and Sb suggests that Ag–tetrahedrite nano-inclusions may occur in pyrite III. The Au content in colloform and kidney-shaped pyrite I (5.5–11 ppm) is higher than in the common grained pyrite II. According to the microprobe results, the As and Ag contents in the kidney-shaped pyrite I attain 1.35 and 0.2 wt %, respectively, against <0.2 wt % As and <0.01 wt % Ag in the associated fine-grained pyrite II. Chalcopyrite contains 1.8 ppm Au and 42 ppm Ag, respectively; Au ranges from 1.5 to 3.0 ppm and Ag, from 0.5 to 18.6 ppm. Au, Ag, As, and Hg are typical admixtures in chalcopyrite II at the highest Au content; at a high Au content (4–6 ppm), the assemblage Au–Hg–Se is characteristic. Sphalerite contains 1.6 ppm Au and 135 ppm Ag, on average. The ordinary Au contents are 1.5–4.5 ppm (the entire range is 0.10–10.6 ppm); the Au–Ag–Sb–Hg assemblage is noted in the Au-richest sphalerite III. An elevated Au content (1.8–10.6 ppm) in sphalerite III is noted when this mineral is saturated with emulsion-like chalcopyrite microinclusions. The relatively homogeneous grains contain only 0.3–3.0 ppm Au. Hence, most gold is incorporated into chalcopyrite inclusions. According to the INAA results, pyrrotite is characterized by the lowest Au content (0.19–1.35 ppm). The microprobe detected Au in galena I (0.05–0.20 wt %); this mineral also contains 0.01–0.12 wt % Ag, 0.03–0.14 wt % Pd, and ~0.1 wt % Hg with a maximum Hg content at 0.25 wt %, i.e., only slightly above the detection limit of the microprobe.

Fahlore is the main concentrator of silver at this deposit (Table 1). The Ag content in tennantite from the upper level of the deposit (Orebody 5) is 0.1–0.6 wt % (0.4 wt % on the average). Tennantite from the lower ore-bearing level (orebodies 3 and 4) only rarely contains more than 0.2 wt % Ag. Tennantite enriched in Ag (0.2–0.5 wt %) and, commonly, in Hg (up to 1–2 wt %) occurs only near contacts of basic dikes and in the superimposed fault zones. Tennantite with the highest Sb content (largely at the lower level) is characterized by a low Ag content, while fahlore with Sb/(Sb + As) = 0.2–0.5 is enriched in Ag (0.5–0.6 wt %). Sporadic tennantite grains enriched in Te (up to 8.89 wt %) and Ag (up to 8.14 wt %) (Table 1) that occur within large pyrite crystals are not larger than a few micrometers in size and are accompanied by rounded nano-inclusions of native silver. The silver minerals (hessite, petzite,

Fig. 1. Index map of massive sulfide deposits in the Urals. (1) West Siberian and East European platforms; (2) folded complexes of the Urals; (3) Tagil Megazone (Upper Ordovician–Lower Silurian); (4) Magnitogorsk Megazone (Middle Devonian); (5) Main Ural Fault; (6–8) large, medium, and some small deposits are shown by symbols of different size from large to small: (6) Cyprus type, (7) Ural type (Cu–Zn), (8) Baimak type (Cu–Zn–Au–Ba).

Table 1. Chemical composition (wt %) of fahlore from massive sulfide deposits of the Urals (results of microprobe and energy dispersive X-ray analyses)

No.	Sample	Ag	Bi	Hg	Fe	Cu	Zn	As	Sb	Te	Se	S	Total
Uzel'ga deposit													
1	104-14	8.14	–	–	5.39	32.81	3.33	8.13	1.60	8.21	–	30.79	98.41
2	104-14	2.45	–	–	5.84	35.83	3.39	11.02	2.82	8.89	–	28.33	98.59
3	5466-12	0.36	–	0.07	1.5	42.33	7.63	14.11	9.22	–	–	25.99	100.78
4	5466-12	0.27	–	0.05	2.23	42.57	7.21	16.13	4.96	–	–	26.28	99.38
5	5466-12	0.25	–	0.09	1.22	42.1	7.73	14.06	9.47	–	–	25.68	100.26
6	Uz-51	0.14	–	0.05	1.83	43.47	7.55	17.33	2.71	–	–	27.72	100.61
7	Uz-61	0.12	–	0.21	0.37	35.79	8.86	2.48	26.32	–	–	24.21	98.03
8	Uz-32	0.1	–	–	1.81	42.47	8.07	18.13	0.85	–	–	29.22	100.55
9	104-14	0.09	–	–	0.84	42.98	7.11	19.78	1.43	0.61	–	26.95	99.79
10	2267	–	–	–	1.33	43.00	7.38	15.07	5.25	–	–	27.62	100.05
11	104-14	–	–	–	0.86	43.09	7.31	20.13	1.52	0.51	–	26.77	100.19
12	104-14	–	–	0.13	0.63	41.14	5.57	11.61	9.86	3.99	0.14	26.17	99.24
13	2267	–	–	0.22	1.97	40.81	6.78	17.55	3.57	0.24	–	28.52	99.74
14	104-14	–	–	–	4.87	37.65	5.49	13.91	2.83	4.50	–	29.99	99.24
Aleksandrinsky deposit													
15	6025/179.5	0.07	0.11	0.08	0.27	43.07	7.74	18.66	2.26	–	–	27.48	99.74
16	6031/173.5	0.04	0.71	0.19	0.68	42.91	7.64	19.07	0.36	0.42	0.12	27.26	99.4
17	6025/191.7	–	0.76	–	1.04	40.70	7.38	16.48	4.44	0.75	0.13	27.33	99.01
18	6031/180	–	0.11	–	0.12	43.30	7.16	17.62	2.63	1.10	–	27.28	99.32
19	6025/186.5	–	1.72	0.11	0.91	42.28	7.16	17.88	0.48	1.43	–	27.06	99.03
20	6025/186.5	0.04	1.36	–	1.19	42.07	7.01	17.05	0.65	2.48	0.11	27.21	99.17
21	6025/186.5	–	0.56	–	0.20	42.52	7.93	17.46	0.47	2.81	0.09	27.40	99.44
22	6025/186.5	0.04	3.23	0.09	1.03	41.55	7.08	15.28	1.11	4.27	–	26.70	100.38
23	6025/191.7	–	6.78	0.09	1.71	40.98	5.92	12.0	0.95	5.13	0.09	26.34	99.99
Degtyarsk deposit													
24	D-2-5	0.22	0.15	–	4.34	41.67	4.04	18.84	1.72	0.08	0.07	28.58	99.79
25	D-2-5	0.09	–	–	3.81	41.39	4.51	19.03	1.55	–	0.11	28.3	98.91
26	D-1-3	–	0.28	–	5.07	41.3	3.74	18.61	2.68	0.03	0.1	28.43	100.2
27	D-1-3	–	0.44	–	4.6	42.29	3.66	19.37	1.62	–	0.19	28.27	100.4
28	D-2-3	–	–	–	3.94	42.42	3.9	19.68	1.06	–	0.06	28.63	99.9
29	D-2-3	–	–	–	4	42.37	3.86	19.85	1.17	–	0.15	28.19	99.73
30	D-2-3	0.05	0.07	–	4.16	42.45	4.22	19.89	1.09	0.03	0.07	28.21	100.3
31	D-2-3	0.25	–	–	3.42	39.09	5.34	9.24	16.63	–	0.11	26.75	101.2

Note: Additional contents of elements, wt %. No. 10: 0.38 Pd; no. 24: 0.08 Cd; no. 25: 0.12 Cd; no. 28: 0.17 Au, 0.04 Cd; no. 29: 0.13 Au, 0.14 Cd; no. 30: 0.17 Au; no. 31: 0.16 Cd.

Here and in Tables 2–7, a dash denotes not detected and a blank denotes not analyzed.

krennerite, stützite, native gold and silver, and electrum) are inferior in the total Ag balance.

The ore at the northwestern flank of Orebody 4, the largest, is enriched in Ag and Au and bears high-grade telluride mineralization. Altaite and hessite are the most abundant tellurides. Altaite is identified as very fine emulsion-like disseminations and very thin veinlets in

pyrite and chalcopyrite, 1–5 µm in thickness, as well as larger euhedral grains 200–300 µm in size (Fig. 2a) with admixtures of Se, Ag, Au, and Hg (Table 2). Petzite occurs as intergrowths mainly with galena I (Fig. 2b) and fahlore I and as euhedral crystals (Fig. 2c). Segregations of hypidiomorphic hessite around small euhedral pyrite crystals are occasionally associated with galena I and altaite. Coloradoite (Hg telluride), very

rare at other massive sulfide deposits, is often observed in the ore. Sporadic grains of native tellurium, silver, and rhenium were detected in the ore of this deposit (Vikentyev et al., 2004). The native tellurium is probably rather abundant, but the very fine disseminations in pyrite grains, 2–3 μm or less in size, make its optical identification difficult.

The Aleksandrinsky Deposit

This is a small deposit that contains high-grade ore with a total Cu + Zn grade of 10 wt % (Zn \geq Cu). Three orebodies (1, 4, and 5) are delineated; 90% of reserves are contained in Orebody 1. The massive and disseminated copper and copper–zinc ores are predominant in Orebody 1; pyrite and disseminated zinc ore with Zn/Cu \sim 1.0–1.5 are second in importance. Massive barite–copper–zinc and barite–zinc ores occur in Orebody 5, which is localized eastward along the strike in the opposite side of the fault. Massive barite–base-metal ore (Cu–Zn–Pb–Ba) occurs sporadically. The thickness of the orebody is 1–18 m (up to 25 m locally); it extends for 440 m along the strike and for 300 m down the dip. The orebodies are largely gently dipping and conformable with host rocks. Orebody 1 dips to the east and southeast at angles of 10°–30° at the upper levels, with the dip angle increasing to 60° at the lower levels. Orebody 5 dips to the south at angles of 50°–70°, extends for 320 m along the strike and for 250 m down the dip, and has a thickness of 2–10 m.

Gold and silver are distributed in Orebody 1, a major one, nonuniformly, and their grades are generally higher than at the deposit as a whole. The highest Au grades (0.5–10.5, commonly 2–3 g/t) are established in massive, bornite-bearing copper and copper–zinc massive sulfide ores; bornite-free ore has a grade of 0.5–8.0, commonly 1–3 g/t Au. The ore of the hanging wall of Orebody 1 is richer in gold than the ore in the lying wall (Vikent'ev et al., 2000). The Ag grade of the massive bornite-bearing copper and copper–zinc massive sulfide ores varies from 10 to 110 g/t (largely 40–60 g/t). Other ore types contain 10–90 g/t Ag (largely 20–40 g/t). The average Ag grade in the copper ore of Orebody 1 is 50 g/t (15–67 g/t). The Au and Ag grades in Orebody 5 are 1.2 and 32 g/t, respectively. According to the results of microprobe analysis (Ag contents in pyrite and chalcopyrite were also determined with laser spectroscopy), the main economic minerals that are concentrators of noble metals are as follows: sphalerite II (<0.02–0.12 wt % Au, <0.02–0.24 wt % Ag), bornite (<0.02–0.07 wt % Au, 0.10–0.27 wt % Ag), and chalcopyrite II (<0.02–0.09 wt % Au, 0.001–0.09 wt % Ag). The main losses of gold in the course of ore processing are related to pyrite (<0.005–0.022 wt % Au and 0.001–0.005 or even up to 0.008 wt % Ag). Fahlore I (Table 1) is represented by tennantite with elevated concentrations of Bi (up to 7 wt %) and Te (up to 5 wt %); the mineral contains <0.02–0.09 wt % Ag and up to 0.11 wt % Hg. An admixture of Ag was detected in galena I (<0.02–

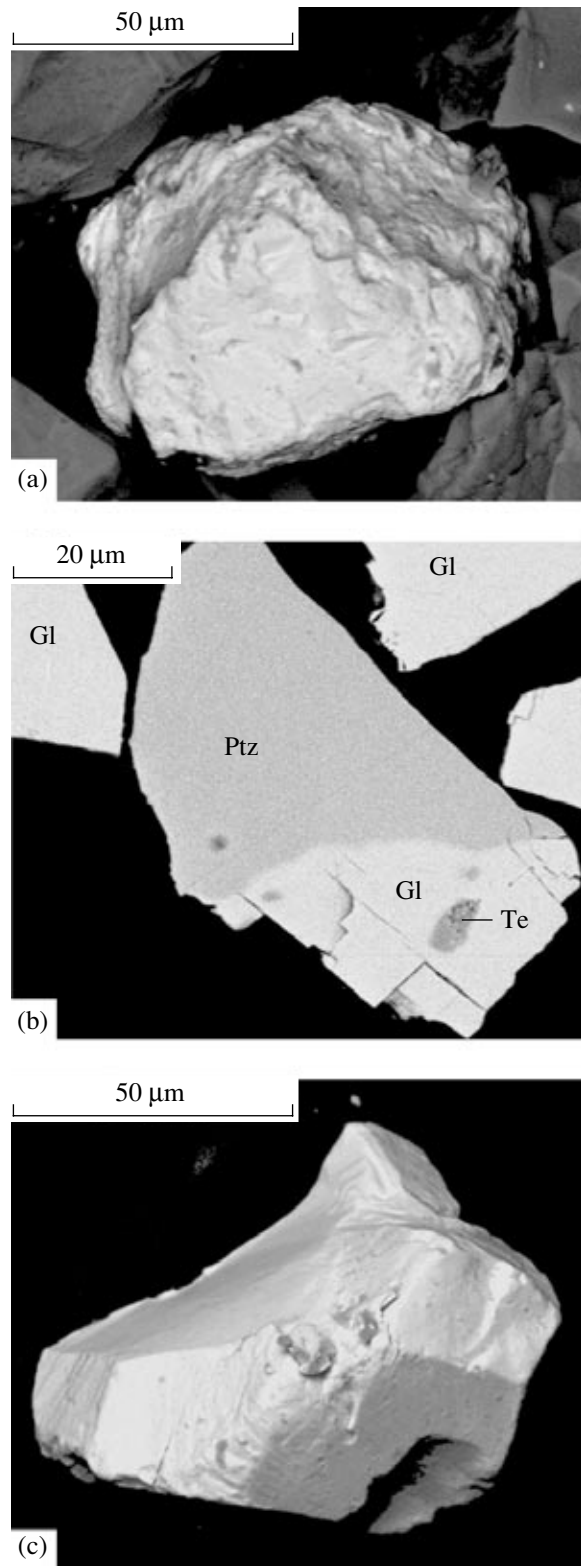


Fig. 2. Telluride grains in massive sulfide ore. (a) Euhedral altaite crystal with rounded faces; (b) xenomorphic petzite (Ptz) grain intergrown with galena (Gl) and native tellurium (Te); (c) petzite grain from the Uzel'ga deposit, SEM microphotographs.

Table 2. Chemical composition (wt %) of tellurides and some rare minerals from massive sulfide deposits of the Urals (results of microprobe and energy dispersive X-ray analyses)

No.	Sample	Mineral	Ag	Au	Pb	Hg	Bi	Fe	Cu	Zn	Sb	Te	Se	S	Total
Uzel'ga deposit															
1	2266	Petzite	39.43	25.29	–	–	–	–	–	–	–	35	–	–	99.72
2	2267	"	40.39	22.54	–	–	–	–	–	–	–	35.48	–	–	98.41
3	2267	"	42.4	24.13	–	–	–	–	–	–	–	34.74	–	–	101.27
4	2266	"	43.78	23.37	–	–	–	–	–	–	–	30.21	0.49	–	97.85
5	2266	"	46.6	19.98	–	–	–	–	–	–	–	35.5	–	–	102.08
6	104-14	Stützite	55.52	–	–	0.20	–	0.38	–	0.73	–	40.62	0.10	–	97.55
7	104-14	"	57.61	–	–	0.18	–	0.20	–	0.37	–	41.44	0.08	–	99.88
8	104-14	"	58.07	–	–	0.14	–	0.19	–	0.15	–	41.52	0.05	–	100.12
9	104-14	"	59.63	–	–	–	–	0.20	–	0.70	–	40.59	–	–	101.12
10	104-14	Hessite	60.70	–	–	0.26	–	0.63	–	0.16	–	39.24	–	–	100.99
11	104-14	"	61.65	–	–	0.17	–	0.14	–	0.27	–	37.85	0.09	–	100.17
12	2266	"	61.73	–	–	–	–	0.96	–	2.28	–	33.56	–	–	98.53
13	2268	"	63.88	–	–	0.02	–	–	–	–	–	35.22	–	–	99.12
14	2267	Altaite	–	–	58.92	–	–	2.35	–	–	–	37.60	0.34	–	99.21
15	2266	"	0.06	–	59.03	0.02	–	–	–	–	–	38.17	0.09	–	97.36
16	2267	"	–	–	59.42	0.07	–	0.61	–	–	–	37.79	0.21	–	98.1
17	2266	"	0.02	–	60.07	0.08	–	–	–	–	–	37.97	0.08	–	98.22
18	2267	"	0.36	0.14	60.15	0.52	–	0.59	–	–	–	38.83	0.04	–	100.63
19	2267	"	0.03	–	60.30	0.06	–	–	–	–	–	38.34	0.07	–	98.80
20	2267	"	0.02	–	61.54	0.05	–	–	–	–	–	38.29	0.05	–	99.97
21	2267	Native tellurium	–	0.19	–	0.18	–	1.20	–	–	–	99.84	0.22	–	101.63
22	2267	Coloradoite	0.37	–	–	59.94	–	–	–	–	–	38.99	–	–	99.64
Gai deposit															
23	29656	Muthmannite	13.90	38.13	–	–	–	–	0.59	–	–	46.67	–	–	99.28
24	29656	Calaverite	–	42.39	–	–	–	–	–	–	–	55.59	–	–	97.98
25	29656	"	0.65	43.47	–	–	–	–	–	–	–	54.86	–	–	98.98
26	29656	"	2.12	44.77	–	–	–	–	–	–	–	53.97	–	–	100.86
27	29656	"	–	46.91	–	–	–	–	–	–	–	55.98	–	–	102.89
28	29656	Montbrayite	0.98	47.76	–	–	–	–	0.96	–	–	46.82	–	–	98.01
29	29656	Altaite	–	–	60.49	–	–	–	–	–	–	39.08	–	–	99.56
30	29656	Coloradoite	4.24	–	–	60.99	–	–	–	–	–	36.75	–	–	101.98
31	29656	Mineral X	48.12	–	30.08	–	–	–	1.98	1.26	–	0.86	–	15.78	98.08
Saf'yanovka deposit															
32	2149/126	Tetradymite	–	–	–	–	57.76	–	0.23	–	0.19	35.59	0.90	–	99.09
33	2149/126	"	–	–	–	–	56.67	–	0.52	–	0.15	35.48	0.81	–	98.28
34	2149/126	"	0.11	–	–	0.12	56.29	–	0.45	–	0.23	35.42	0.90	–	97.87
35	2149/126	"	–	0.14	–	–	58.05	0.07	0.11	–	0.14	36.04	0.98	4.30	99.83
36	2149/126	"	–	–	–	–	57.92	0.11	0.23	–	0.15	36.25	1.07	4.20	99.93
37	2149/126	Wittichenite	1.78	–	0.70	0.19	41.99	0.45	32.15	2.13	0.09	0.27	1.02	18.87	99.79
38	2149/126	Aikinite	–	0.05	36.79	–	32.58	0.11	11.20	–	–	–	0.44	17.14	98.31
39	2149/126	"	0.05	–	36.54	–	34.21	–	11.10	0.05	–	–	0.32	16.69	98.96
40	2149/126	Hessite	60.89	0.16	0.09	–	–	–	0.15	–	0.21	37.33	–	–	98.97

Note: Additional contents of elements, wt %. No. 22: 0.34 Sb; no. 28: 1.48 As; no. 32: 0.12 Pd; no. 33: 0.26 Pt; no. 37: 0.15 Pt; no. 40: 0.14 Pt.

0.07 wt %). Most of the gold and silver gets into the copper concentrate (~2–3 g/t Au and 150–250 g/t Ag), which also contains ~0.1–0.2 wt % As and 100–200 ppm Te. In contrast to the concentrates produced at the Uchaly Mining and Concentrating Works and derived from the ore of the Uchaly and Uzel'ga deposits, the zinc concentrate from the Aleksandrinsky deposit is less enriched in silver and especially in gold; however, the rough zinc concentrate contains >10 g/t Au along with high contents of Ba (~1 wt %), As (~0.3 wt %), Sb (400–500 ppm), and Te (100–150 ppm).

The Degtyarsk Deposit

The deposit was in operation in 1914–1994. The single, almost vertical sheetlike lode extends for more than 5 km along the strike and 650 m down the dip, having a thickness of 5–10 m. In swells (ore columns), the thickness increases by 10–15 times and attains 120 m in the central column. The lode was folded and pulled apart as boudins. The sharply predominant massive and banded ores are represented by copper, copper–zinc, and pyrite types. The host rocks were metamorphosed under conditions of the lower greenschist facies. The pyrite content decreases toward the flanks of the ore lode and with depth, whereas sphalerite and chalcopyrite contents increase in the same direction along with quartz and barite. The average grades are 1.3% Cu, 2.7% Zn, 1.0–1.2 g/t Au, and 10–30 g/t Ag; the average Zn : Cu ratio is 1.4.

The ore, largely studied at the lower pinchout of the lode, is enriched in Zn, Au, Ag, and Sb. According to the results of microprobe analysis with a prolonged exposure, the highest Au contents are established in fahlore I (0.02–0.22 wt %), galena I (<0.02–0.17 wt %), and sphalerite II (<0.02–0.14 wt %). Such high Au contents and their wide scatter may testify to the presence of optically invisible nano-inclusions of Au minerals, first of all, of native gold. The Ag content amounts to <0.02–0.03 wt % in pyrite III and chalcopyrite II, <0.02–0.05 wt % in sphalerite II, <0.02–0.25 wt % (mainly >0.10 wt %) in fahlore I, and 0.06–0.20 wt % in galena I. In the copper massive sulfide ore, gold is largely related to sphalerite II, and silver, to galena I. In the high-grade Cu–Zn ore, elevated Au contents have been established by microprobe in galena I, whereas silver concentrates in fahlore I (Table 1). Fahlore reveals elevated Au and Ag contents in both ore types. By processing of marketable ore with Au and Ag grades of 1 and 23.5 g/t, respectively, these metals are distributed by middlings as follows (ppm): 3.6 and 145 in the copper concentrate, 2 and 153 in the zinc concentrate, and 0.8 and 1.0 in the pyrite concentrate and tailings. The crude copper contains ~50 g/t Au.

The San Donato Deposit

This medium-size deposit is situated in the southern part of the Tagil Megazone of the Urals and consists of a series of near-meridional steeply dipping lenses and

ribbons of massive and less abundant stringer–disseminated copper–zinc ores. The ore lenses are 1–30 m thick and extend for 150 m along the strike and for 600 m down the dip. The ore lodes are severely folded and sheared. In comparison with most of the studied deposits except the Aleksandrinsky deposit, the ore is enriched in chalcopyrite and sphalerite. Fahlore, bornite, and galena are second in abundance; chalcocite, enargite, cubanite, pyrrhotite, valleriite, arsenopyrite, magnetite, hematite, native gold, calaverite, tetradymite, altaite, and hessite are rare minerals. No Au (<0.02 wt %) has been detected in fahlore and pyrite coexisting with native gold, whereas fahlore contains rather much Ag (0.45 wt %). A high Hg content (0.25 wt %) was detected in pyrite.

The Saf'yanovka Deposit

This large deposit consists of two parts. In the northern part, with high-grade ore at a depth from 20 to 300 m, the massive sulfide ore occurs as a thick, wedge-shaped lode that comprises several orebodies. The southern part of the deposit is tectonically overlapped by the Rezh serpentinite melange. The massive ore occurs as a discontinuous chain of lenticular lodes, conformable with host rocks, varying in thickness from one to a few tens of meters. Ore ribbons that lie at three levels within the depth interval from 190 to 400 m gently dip to the south and pinch out after a short distance. A significant percentage of reserves is contained in stockwork ore with high-grade but thin pyrite–chalcopyrite veins. The massive copper, copper–zinc, and pyrite ores are inferior in reserves. Steeply dipping ore shoots (zones of stringer–disseminated ore markedly enriched in chalcopyrite) extend along the boundary between massive and stockwork ores in the northern lode (Yazeva et al., 1991). The ore shoots vary in thickness from decimeters to 20 m and contain tellurides and other rare minerals. Down to a depth of 265 m, the deposit will be mined by an open pit, and an underground mine will be sunk to a depth of 500 m. The ore is metamorphosed extremely weakly and is relatively enriched in noble metals: the ordinary ore contains 1–2 g/t and the grade locally increases to 2.6 g/t; the Ag grade is 20–60 g/t (up to 400 g/t) with a maximum in the copper massive sulfide ore. In general, the copper–zinc massive sulfide ore is enriched in Au and Ag to the greatest extent, with approximately equal proportions of both noble metals in sulfides (ppm): 2.5 and 150 in chalcopyrite, 1.5 and 140 in sphalerite, and 1.9 and 80 in pyrite. Fahlore is appreciably enriched in Ag, up to 6 wt %. Tellurides of noble metals occur in the ore. The highest Au admixture is detected in tetradymite (up to 1.16 wt %) and hessite (up to 1.35 wt %) (Moloshag et al., 2002). The considerable amount of tellurides in the absence of fahlore in the ore shoots at the Saf'yanovka deposit is accounted for by a low As content in the ore; the results of analyses of composite samples from the ore shoots yielded 145 ppm As in compar-

ison with 2320 ppm in the massive sulfide ore elsewhere. The difference in contents of other admixtures is much less: 5.7 and 9.2 ppm Te, 35.7 and 41.9 ppm Bi, and 47.2 and 59.0 ppm Ag, respectively (Koroteev et al., 1997). Aikinite CuPbBiS_3 and wittichenite Cu_3BiS_3 were found in the ore enriched in gold (Table 2).

Thus, as follows from the above overview, the Au and Ag grades of copper and copper-zinc ores from deposits of the Ural type proper (Gai, Uchaly, Uzel'ga, Saf'yanovka, etc.) are 0.5–15 and 10–50 g/t, respectively. At all deposits, sporadic values of 7–15 and even 90 g/t Au and 100–600 g/t Ag are noted in ordinary and composite samples taken at intervals of 10 m. In these cases, the ore is characterized by elevated Ba, Te, As, and occasionally Hg and Se contents (the Uzel'ga deposit). As a rule, such enrichment is detected at the pinchouts of gently and steeply dipping ore lodes, in the zones of brecciated ore, and at the contacts of dikes within massive ore. The aforementioned anomalously high contents stand out against the background of general enrichment of ore in gold up to 2.0–2.5 g/t. This is commonly a massive, copper-zinc ore composed of the late mineral assemblages: pyrite III + chalcopyrite II + sphalerite II + fahllore I + galena I ± bornite and low-abundant veined chalcopyrite III + sphalerite III + fahllore II + galena II + quartz II + barite. The local areas of such base-metal or barite-base-metal massive sulfide ores at deposits of the Ural type are close to the ordinary ore at small deposits of the Baimak type with higher grades of lead and barite and 2–3 (up to 20–30) g/t Au, as noted at the Bakrtau, Tashtau, and Aleksandrinsky deposits (Yushko, 1936).

The copper and zinc concentrates as products of processing of massive sulfide ores are appreciably enriched in noble metals; however, in some cases, their Au grades are higher than the grade of ore only by 20–30%. The Au contents in ores are correlated more closely with Cu than with Zn, and most gold is recovered by metallurgical processing of copper concentrates. The Uchaly Mining and Concentrating Works—one of the Russian monopolists in production of Zn and Ag concentrates—is the only exception. The Au content in zinc concentrate produced by the Uchaly Works is higher than in the copper concentrate produced there.

SPECIATION OF GOLD IN MASSIVE SULFIDE ORES OF THE URALS

The aforementioned INAA results show that the monomineral fractions of practically all sulfides except pyrrhotite may be enriched in gold to a considerable extent (up to 20 ppm). Likely, it is not accidental that the colloform and kidney-shaped pyrite with small chalcopyrite inclusions is richer in gold than the euhedral pyrite without inclusions. Elevated Au contents also are detected in sphalerite that hosts the fine emulsion-like disseminations of chalcopyrite. The wide scatter of Au contents in sulfides indicates the extremely nonuniform distribution of this element.

The bulk of orebodies at the massive sulfide deposits in the Urals is composed of fine-grained, densely impregnated, up to massive sulfide ore that contains 1–2 g/t Au; native gold, tellurides, and other gold minerals are observed extremely rarely. The native gold is identified under a microscope only in samples of relatively high-grade copper-zinc ore with a grade not lower than 2–3 g/t Au.

According to the data obtained by rational analysis, the concentration of finely dispersed gold in sulfide ore of the Gai deposit varies from 0.90 to 2.60 ppm; this interval is much narrower than the range of bulk Au contents in the respective samples (2.16–21.2 ppm). The same may be said about the ore from the San Donato deposit, where the finely dispersed gold in sulfides amounts to 0.86–5.0 ppm, while the bulk contents are 1.08–19.2 ppm Au. The content of finely dispersed gold in ore of the Saf'yanovka deposit is 0.8–1.6 ppm and, in one sample, 0.16 ppm against the bulk Au content of 0.93–1.83 ppm and, in one sample, 0.19 ppm Au. These values are somewhat lower than in the ore from the Gai deposit, whereas the relative amount of fine gold at the Saf'yanovka deposit is much higher. A high content of finely dispersed gold (0.93–2.9 ppm) has been established in the Voroshilovsky Lode at the Karabash deposit, and a maximum value of 5 ppm, at the San Donato deposit. In general, in the ore with ordinary Au contents (0.2–3.0 ppm), the prevalent percentage of Au (35.4–87.0%) is represented by finely dispersed gold presumably bound in sulfides. The contribution of native gold (free and intergrown with sulfides and silicates) varies from 2 to 90% (Fig. 3). If the high-grade technological samples that contain 7.9–21.2 ppm Au are omitted, this contribution falls to 2–64%. Thus, the relative amount of native gold in massive sulfide ores is directly correlated with the bulk Au content (Fig. 4).

Ultraheavy concentrates 0.028 and 0.041 g in weight were obtained from two 100-g samples of ore from the Uzel'ga deposit quartered from 3-kg samples containing 22.8 and 11.1 ppm Au, respectively. The heavy fractions consist largely of pyrite (25 vol %), galena (20 vol %), altaite (20 vol %), hessite (15 vol %), petzite (5 vol %), and native gold (10 vol %) with secondary amounts of native tellurium and sulfides of base metals. High PGE contents have been established in the ultraheavy fractions (Table 3). In all samples, the Ru content was below the detection limit of the chromatographic method (0.02 ppm). In the second sample, the bulk PGE content was 2.3 ppm, and 707 ppb falling on Rh. PGE in these concentrates may be related to tellurides and sulfotellurides or native gold. A similar ultraheavy concentrate, consisting by 80 vol % of native gold of high fineness with an admixture of galena and tellurides, was separated from a sample of ore at the Gai deposit. This ultraheavy fraction contained 73.4 ppm Au as determined with AAS at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences (RAS), or 90 ppm as determined with a fire assay at the Gai Mining and

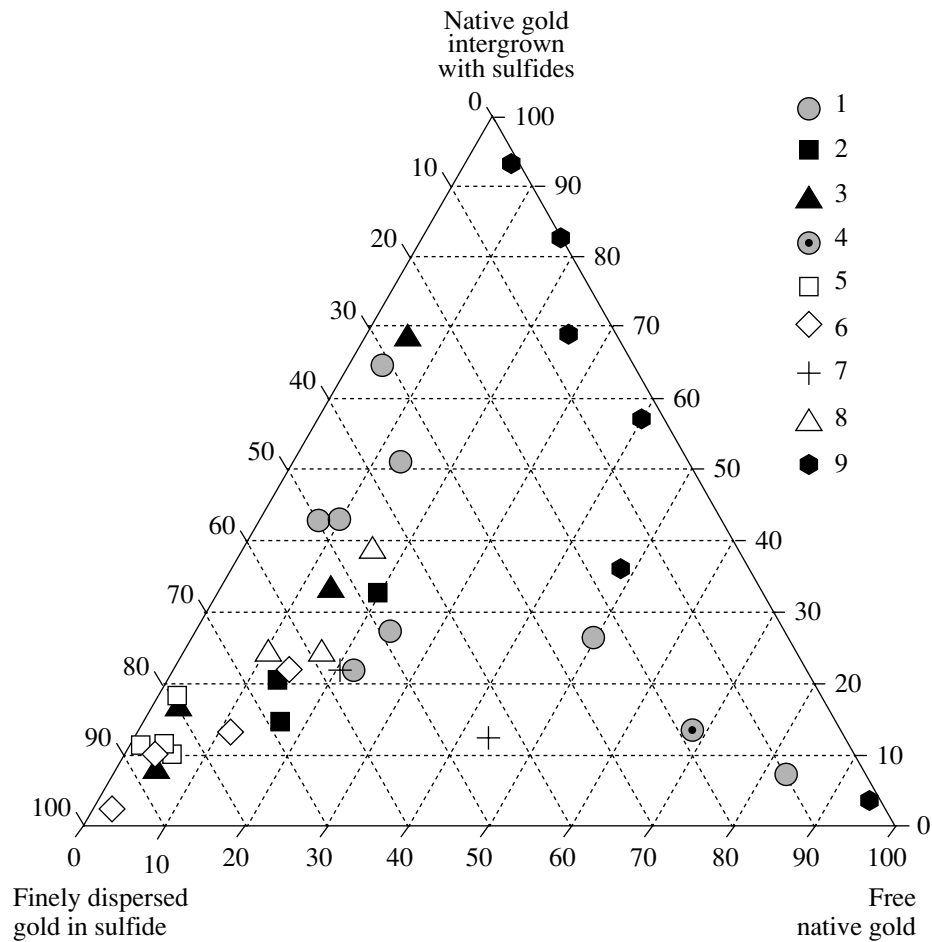


Fig. 3. Speciation of gold in ores from massive sulfide deposits of the Urals (results of rational analysis). Deposits: (1) Gai, (2) Karabash, (3) San Donato, (4) Barsuchy Log, (5) Saf'yanovka, (6) Uchaly, (7) XIX Parts'ezd, (8) Blyava, (9) Berezovsky (Murzin et al., 1999). The strongly metamorphosed deposits are designated by filled symbols, and unmetamorphosed and slightly metamorphosed deposits, by open symbols.

Concentrating Works; 150 ppb Pt, 1800 ppb Pd, and 100 ppb Ru were detected in the ultraheavy concentrate (Table 3). The elevated PGE contents are related to the impurities in native gold; thereby, it cannot be ruled out that the lower Pt and Rh contents in this sample are caused by the lower contents of tellurides.

In a first approximation, the native gold from massive sulfide deposits may be regarded as a series of continuous Au–Ag solid solutions from $Au_{0.98}Ag_{0.02}$ to $Au_{0.60}Ag_{0.40}$. Compositions with a higher percentage of Ag are extremely rare; the copper admixture does not

exceed 3 wt %. Admixtures of Hg, Bi, and Sb are significantly lower in concentration than Cu. It should be noted that the Au–Ag alloys are often named electrum in the international literature (e.g., Huston, 2000), in contrast to Russian authors (Petrovskaya et al., 1973).

The native gold from the Gai deposit (Table 4) is distinguished from that at the other Ural deposits by elevated Au contents that reach 97.3 wt %, with most samples containing more than 75 wt % Au; the native gold 770–840 fine contains 0.2–0.9 wt % Hg. Some grains contain as much as 0.17 wt % Pd and up to

Table 3. PGE contents (ppb) in ultraheavy concentrates of Au-bearing ores from the massive sulfide deposits (results of chromatographic analysis), modified after Vikentyev et al. (2004)

Deposit	Sample	Pt	Pd	Rh	Ru	Ir	Pt/Pd
Gai	29656	150	1800	–	100	–	0.08
Uzel'ga	2267	375	804	–	–	1.8	0.47
"	2268	354	1220	707	–	–	0.29

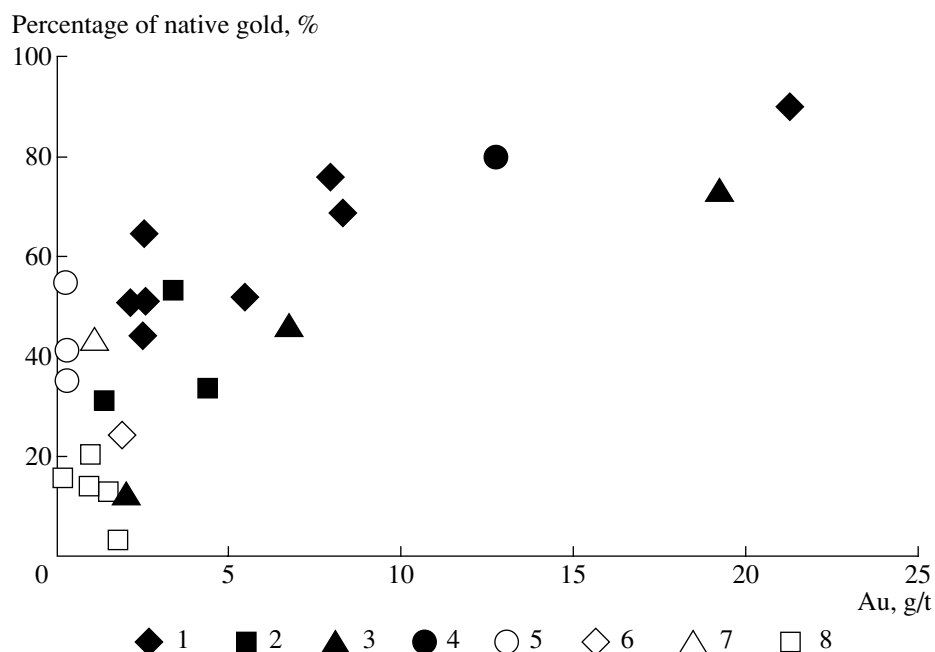


Fig. 4. Percentage of native gold (free gold + intergrowths with sulfides as estimated from rational analysis) versus the bulk Au content in ore. Strongly metamorphosed deposits (filled symbols): (1) Gai, (2) Voroshilovsky, (3) San Donato, (4) Barsuchy Log; slightly metamorphosed deposits (open symbols): (5) Blyava, (6) Uchaly, (7) XIX Parts'ezd, (8) Saf'yanovka.

0.2 wt % Pt. Admixtures of siderophile elements (Cr, Ni, and Co) are detected in the native gold containing >92 wt % Au. Native gold grains from the Gai deposit are characterized by large size and elevated concentrations in particular orebodies and at margins of large sulfide lenses (up to 90 ppm in composite samples). The native gold most often occurs as discrete xenomorphic grains along the contacts between chalcopyrite, fahlore, and bornite (Fig. 5) and occasionally makes up intergrowths with other minerals of noble metals, mainly tellurides. The gold of the highest fineness is associated with coloradoite, tetrahedrite, and altaite. In some cases, the grains of native gold have a rim with still higher fineness; the Au content in the outer rims is higher by a few weight percent. The Au and Ag tellurides at the Gai deposit include altaite, hessite, and tellurobismuthite; single grains of calaverite, petzite, muthmannite, and montbrayite, all previously unknown at this deposit, have been identified (Table 2). These minerals commonly occur in the pyrite–chalcopyrite and sphalerite–chalcopyrite ores as xenomorphic grains intergrown with pyrite, chalcopyrite, sphalerite, galena, and fahlore; isolated euhedral grains as large as 50 μm with smoothed faces are also noted. A mineral grain of about 10 μm in size, the chemical composition of which is recalculated to PbAg_3S_3 , was detected as an intergrowth with gold of high fineness, coloradoite, tetrahedrite, and altaite (Fig. 6).

Hessite, calaverite, native gold, and electrum are known in the ore of the Uchaly deposit. Petrovskaitite—an extremely rare Au–Ag sulfide—has been identified as a rim a few μm thick that coats a grain of electrum

550 fine, $\sim 20 \mu\text{m}$ in size (Fig. 7a). The composition of this rim is close to petrovskaitite with approximately equal amounts of Au and S and recalculated to $\text{Ag}_3\text{Au}_2\text{S}_2$. No Se admixture was detected. Similar Au–Ag sulfides— AgAuS and $(\text{Ag}, \text{Au})_2(\text{S}, \text{Se})$ —have been established at the Alfa and Yakutsky gold deposits, where they were formed under conditions of a high sulfur activity 10^{-10} – 10^{-6} (Nekrasov et al., 1988; Samusikov et al., 2002).

Petzite has been identified in ore from the Uzel'ga deposit as very fine grains in galena and chalcopyrite; this mineral also occasionally occurs here as larger grains that reach 200 μm in size (Fig. 2c). Native gold ~ 800 fine (670–870) is extremely rare in the ore of this deposit and found as clusters of euhedral grains, rims that grow over pyrite, and xenomorphic aggregates (Figs. 7b, 7c). Xenomorphic grains of native gold as large as 150 μm contain emulsion-like disseminations of altaite (Fig. 7d) and exhibit a myrmekite structure of mutual intergrowing. The predominant size of gold grains is 10–20 μm ; some grains reach 150 μm in size. The most frequent impurities in the native gold include Te (up to 1.06 wt %), Fe (up to 0.42 wt %), Se (up to 0.27 wt %), and less abundant Hg (up to 0.30 wt %); Pd (up to 0.85 wt %) and Pt (up to 2.23 wt %) are detected sporadically.

Only sporadic grains of native gold 685–800 fine are noted in ore of the Aleksandrinsky deposit. Native gold from the San Donato deposit is characterized by the widest scattering of fineness from 540 to 585 with frequency maximums at 650–690 and 770–790.

Table 4. Chemical composition (wt %) of native gold from massive sulfide deposits of the Urals (results of microprobe and energy dispersive X-ray analyses)

No.	Sample	Au	Ag	Cu	Fe	Hg	Te	Se	Pd	Pt	As	Total
Gai deposit												
1	29457	66.53	32.81	—	—	—	—	—	—	—	—	99.34
2	29656	74.64	24.83	—	—	—	—	—	—	—	—	99.48
3	29457	76.57	22.13	—	—	—	—	—	—	—	—	98.70
4	523/76	77.93	19.37	1.53	—	0.27	0.09	—	—	0.18	—	99.37
5	754/3	78.77	21.01	0.44	—	—	0.06	—	0.03	—	—	100.31
6	523/76	79.10	19.38	—	—	0.52	—	—	—	—	—	99.0
7	523/76	79.37	18.87	0.36	—	0.89	0.03	—	—	—	0.13	99.65
8	523/76	79.59	18.51	—	—	0.61	0.08	—	—	—	—	98.79
9	754/1	81.60	16.56	0.74	—	—	—	—	—	—	0.08	98.98
10	754/1	81.81	17.64	0.15	—	—	—	—	0.10	—	—	99.7
11	754/1	82.14	16.96	0.08	—	—	0.06	—	—	—	0.04	99.28
12	754/1	82.40	17.45	0.30	—	—	0.05	—	—	—	—	100.2
13	754/1	83.57	15.94	0.18	—	0.13	—	—	—	0.20	—	100.02
14	754/3	84.41	14.04	1.15	—	0.09	—	—	0.17	0.17	—	100.03
15	29656	86.60	13.74	—	—	—	—	—	—	—	—	100.34
16	754/3	87.43	12.06	0.49	—	—	0.15	—	0.09	—	—	100.22
17	29656	88.52	10.65	—	—	—	—	—	—	—	—	99.17
18	29656	90.22	9.75	—	—	—	—	—	—	—	—	99.98
19	29656	91.55	11.45	—	—	—	—	—	—	—	—	103.00
20	29656	92.12	8.36	—	—	—	—	—	—	—	—	100.48
21	29656	93.39	6.15	—	—	—	—	—	—	—	—	99.53
22	29656	93.94	6.73	—	—	—	—	—	—	—	—	100.67
23	29656	94.01	7.86	—	—	—	—	—	0.66	—	—	101.87
24	29656	94.24	7.77	—	—	—	—	—	—	—	—	102.01
25	29656	97.32	2.56	—	—	—	—	—	—	—	—	99.87
San Donato deposit												
26	715	58.31	39.45	0.59	—	0.09	0.11	—	—	—	—	98.55
27	1524	63.75	30.70	4.85	—	0.06	—	0.11	0.06	0.09	0.06	99.68
28	1524	64.82	32.62	2.03	—	—	0.08	—	—	—	—	99.55
29	1524	66.20	33.31	0.68	—	—	—	—	—	—	—	100.19
Saf'yanovka deposit												
30	S-7-4	86.91	11.88	—	—	0.74	—	—	—	—	—	99.53
31	S-7-4	87.18	12.10	—	—	—	—	—	—	—	—	99.28
32	S-7-4	87.59	12.03	—	—	0.14	—	—	0.10	—	—	99.86
Uchaly deposit												
33	228-2	55.76	43.71	—	—	—	—	—	—	—	—	99.47
Uzel'ga deposit												
34	104-14	81.17	16.86	—	—	0.07	3.01	0.05	—	—	—	101.16
35	104-14	81.89	16.76	—	0.13	—	0.38	—	—	—	—	99.16
36	104-14	81.96	17.37	—	0.22	0.10	—	—	—	—	—	99.65
37	104-14	82.20	17.66	—	0.13	0.13	0.10	—	—	—	—	100.22
38	104-14	82.42	17.52	—	0.50	—	—	—	—	—	—	100.44
39	2266	82.74	17.28	—	—	—	0.53	—	—	—	—	100.55
40	2266	82.83	16.70	—	0.33	—	—	—	—	—	—	99.86
41	2266	83.21	14.96	—	0.31	—	—	—	—	—	—	98.48
42	104-14	83.55	14.45	—	—	0.30	0.20	—	—	—	—	98.50
43	2268	83.77	15.54	—	0.42	—	—	0.21	—	—	—	99.94
44	2268	84.16	15.67	—	—	—	0.68	—	—	—	—	100.51
45	2268	85.93	14.47	—	—	—	—	—	—	—	—	100.40
46	2267	86.60	13.56	—	—	—	—	—	—	—	—	100.16
47	2267	86.97	13.26	—	—	—	—	—	—	—	—	100.23
48	2268	86.45	15.16	—	0.15	—	—	—	—	—	—	101.76
49	2267	87.35	13.23	—	0.23	—	—	—	—	—	—	100.81

Note: Additional contents of elements, wt %. No. 24: 0.4 Cr; no. 20: 0.32 Ni; no. 22: 0.31 Co; no. 25: 0.31 Ni; no. 23: 0.26 Cr, 0.4 Co, 0.28 Ni.

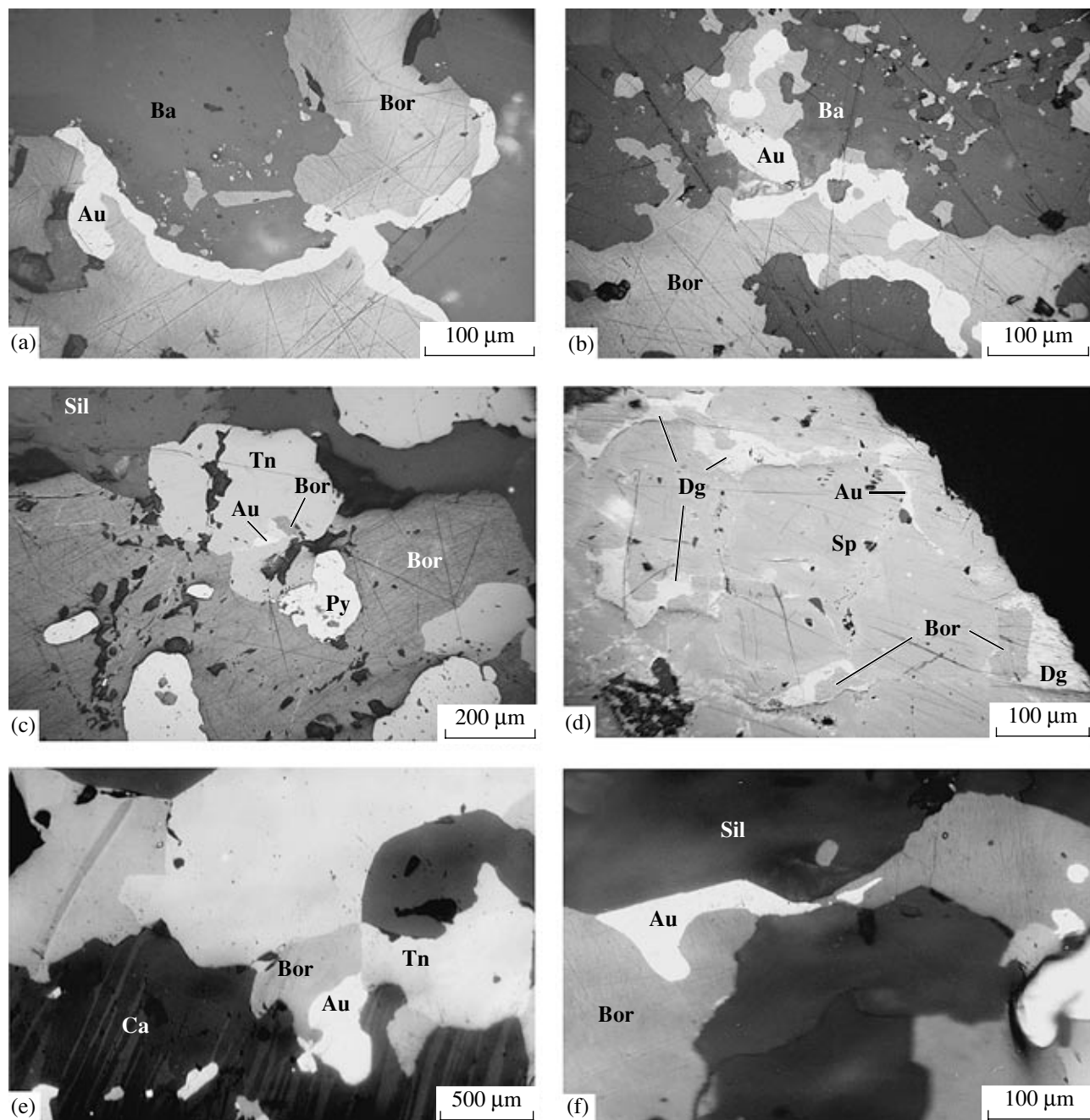


Fig. 5. Native gold grains in ore of the Gai deposit in polished sections examined in reflected light. (a) Rims of native gold (Au) at the bornite (Bor)–barite (Ba) boundary, sample 754-3; (b) rims and xenomorphic gold grains at the boundary of a bornite (Bor) inclusion in barite (Ba), sample 754; (c) microintergrowth of gold, pyrite (Py), and bornite (Bor) within a tennantite (Tn) grain, Sil is a silicate grain, sample 754; (d) gold (Au) in association with digenite (Dg) and bornite (Bor) makes up a veinlet in sphalerite (Sp), sample 501/74; (e) large gold grain at the contact between bornite (Bor) and tennantite (Tn) with carbonate (Ca), sample 754-1; (f) xenomorphic gold at the boundary between bornite (Bor) and silicate (Sil), sample 754-3.

Native gold 685–800 fine at the Saf'yanovka deposit occurs as grains 5–25 μm in size, mainly in the ore enriched in Zn. The gold is observed beyond the telluride-bearing zone in the younger disseminated copper–zinc ore at the periphery of the main ore zone or in local areas of massive Cu–Zn ore enriched in galena but free of tellurides. One large (200 μm) gold grain 870–880 fine was found in the supraore gravelstone (Table 4).

In general, a wide range of native gold compositions is established for each deposit. In the total selection of analyses, two compositions are predominant: Au_3Ag , as insisted by Nekrasov (1991), and Au_2Ag , as was suggested by Petrovskaya (1973).

The largest grains of native gold (100–1000 μm or larger) are found at the deposits that experienced strong dynamometamorphism (Gai, Degtyarsk, Karabash, and

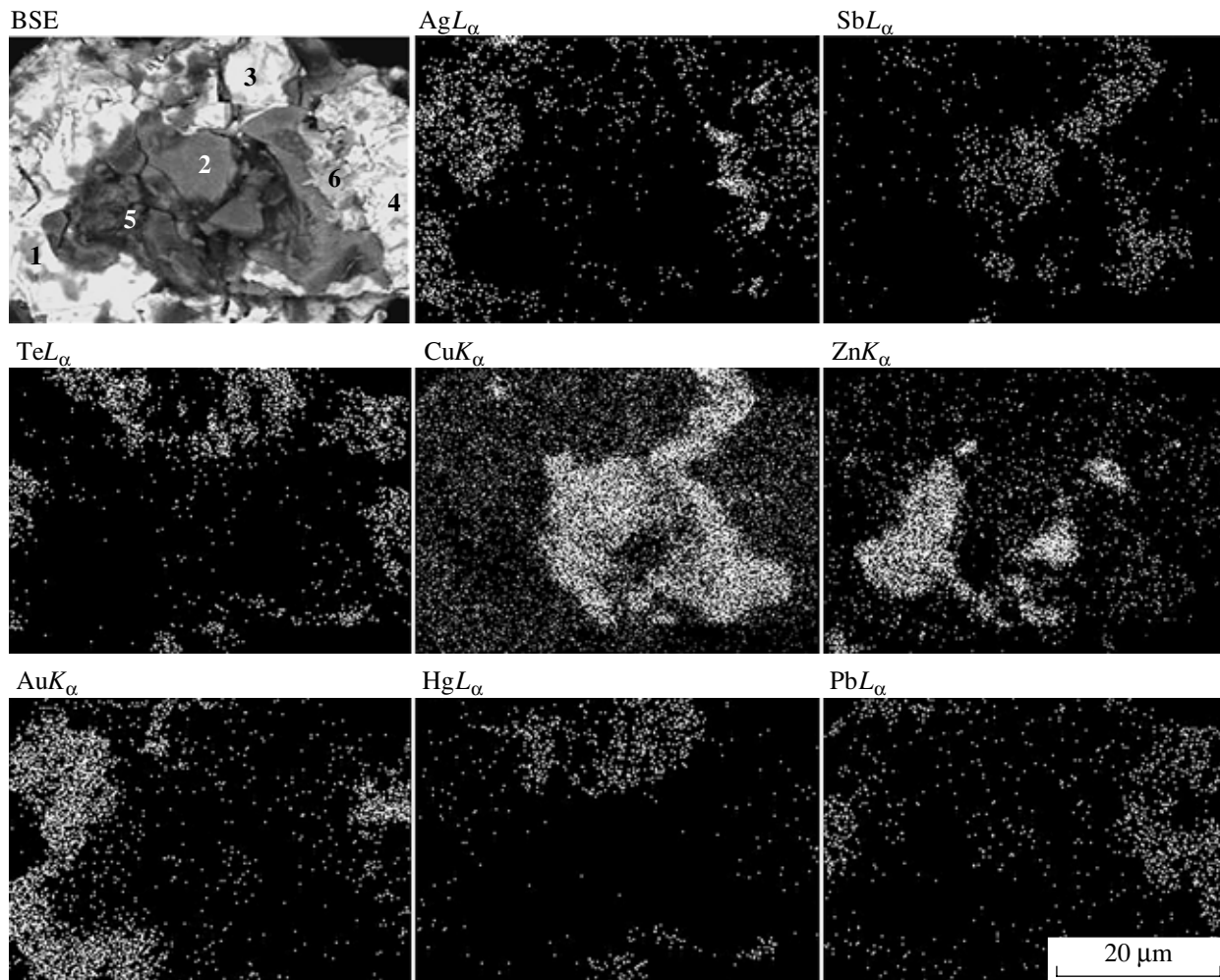


Fig. 6. Intergrowth of (1) highly fine-grained native gold with (2) fahlore, (3) coloradoite, (4) altaite, (5) sphalerite, and (6) a phase of composition PbAg_3S_3 at the Gai deposit. BSE image and images in characteristic X-ray irradiation AgL_α , CuK_α , HgL_α , SbL_α , TeL_α , AuL_α , PbL_α , and ZnK_α .

San Donato). In moderately and slightly metamorphosed ore (the Uzel'ga, Uchaly, Molodezhny, Aleksandrinsky, and Saf'yanovka deposits), native gold grains are rare and small (commonly $<25 \mu\text{m}$). Larger grains appear in zones of superimposed hydrothermal alteration that gave rise to the formation of recrystallized base-metal ore (the northern part of Orebody 4 and Orebody 3 at the Uzel'ga deposit) and in quartz-sulfide and barite-sulfide veinlets. Native gold is distributed nonuniformly as a constituent of various mineral assemblages.

MINERAL ASSEMBLAGES OF Au-BEARING MASSIVE SULFIDE ORES

The mineral assemblages with elevated Au content (commonly with visible native gold) in bornite, chalcopyrite, and pyrrhotite ore facies and subfacies are compositionally variable. The subfacies are recognized on the basis of a series of As minerals consecutively

replacing one another: loellingite \rightarrow arsenopyrite \rightarrow fahlore \rightarrow enargite. In the course of the microscopic study, special attention was paid to the relationships between the above-mentioned index minerals of Fe and Cu (bornite, chalcopyrite, and pyrrhotite) and As with minerals of noble metals (Figs. 5, 8). The relationships between arsenopyrite, on the one hand, and fahlore and chalcopyrite, on the other hand, are particularly important for the chalcopyrite facies because the visible gold is mostly associated with fahlore and chalcopyrite. Arsenopyrite is a key mineral in the mineral assemblages of massive sulfide deposits as a source of information on temperature and sulfur fugacity (Bortnikov, 1993). Arsenopyrite occurs in the ores that pertain to pyrrhotite and partly chalcopyrite facies. Under conditions of chalcopyrite facies, arsenopyrite is stable at a relatively low sulfur fugacity and is replaced with fahlore when the sulfur fugacity increases and the temperature drops. If arsenopyrite and chalcopyrite do not show reaction relationships, the arsenopyrite grains are euhedral and represent various sections of the pseudor-

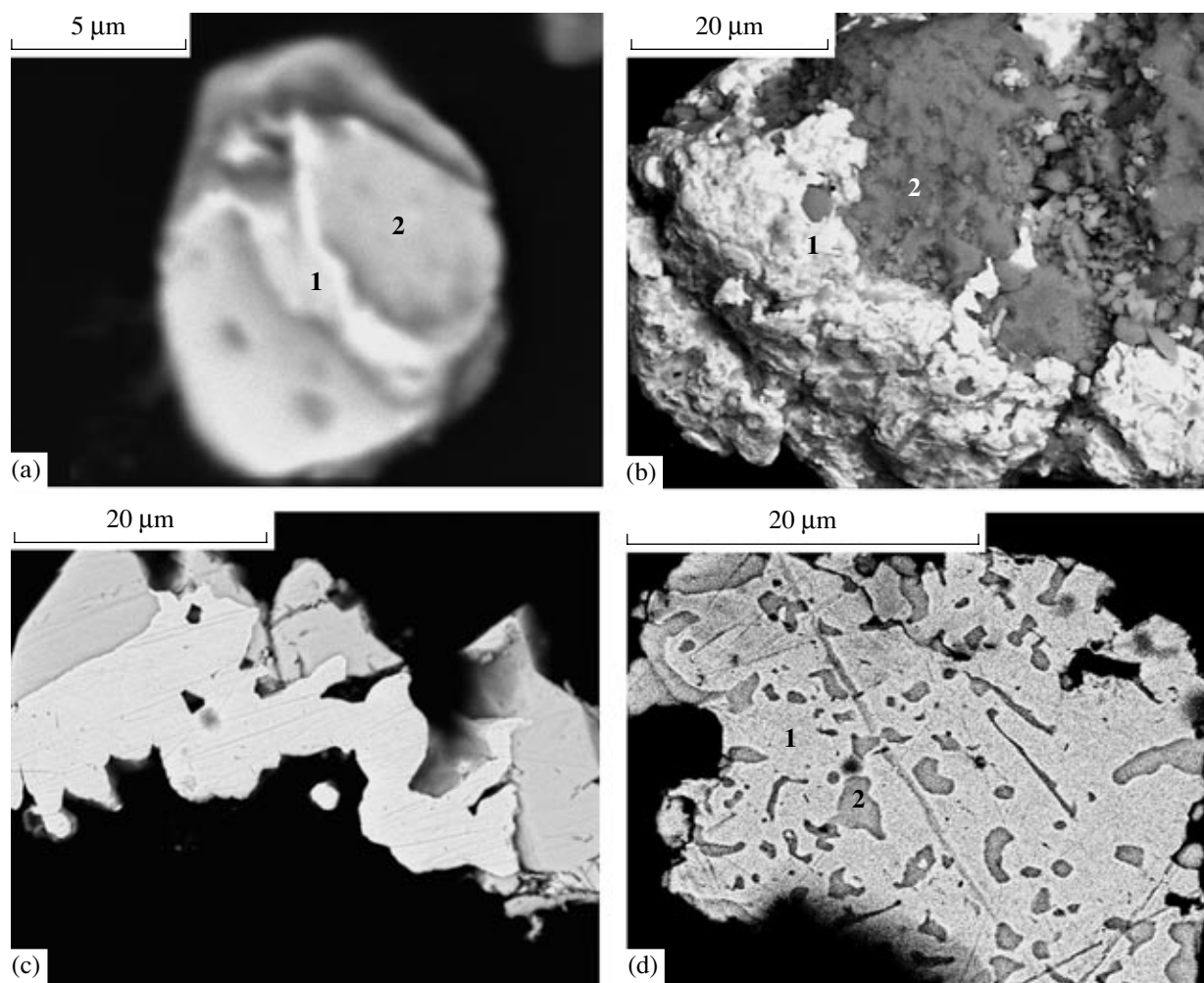
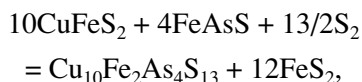


Fig. 7. Native gold grains in massive sulfide ore in SEM images. (a) (1) Native gold grain and (2) petrovskaite rims in concentrate from the Uchal'y deposit; (b) native gold rimming an aggregate of fine-grained pyrite in concentrate from the Uzel'ga deposit; (c) intergrowth of fine-grained subhedral gold in a polished epoxy tablet, the Uzel'ga deposit; (d) myrmekite-like intergrowth of native gold and altaite in a polished section, the Uzel'ga deposit.

hombic habit of this mineral (Fig. 8). The replacement of arsenopyrite with fahlore begins with the formation of thin fahlore films at the surface of arsenopyrite (Figs. 8b, 8d); further, fahlore penetrates deeper into the grain along fractures. The process is completed by the formation of the ferrous fahlore end member $\text{Cu}_{10}\text{Fe}_2\text{As}_4\text{S}_{13}$ according to the reaction



as has been shown for mineral assemblages at the Uzel'ga deposit. Such a reaction product is confirmed by the compositions of arsenopyrite, fahlore, and pyrite (Table 5). The unaltered arsenopyrite grains in this sample contain Ni and Co admixtures, which are also detected in the newly formed pyrite. At the same time, the pyrite grains that make up the bulk of this sample are free of the above impurities. Fahlore is represented by ferrous tennantite. Note that the fahlore grains, which are devoid of relict inclusions of arsenopyrite

and do not intergrow with this mineral, are enriched in zinc (Table 5).

This tennantite variety is also found at other deposits and commonly occurs in samples taken from areas where arsenopyrite is replaced with fahlore. We calculated this reaction and plotted the line of the respective equilibrium constant on the $\log f_{\text{S}_2}$ versus T diagram. Because no thermochemical data are available for fahlore, we were obliged to resort to the approximate method of mixed components (Vaughan and Craig, 1978). In qualitative terms, the results of our calculations are consistent with the data obtained by Seal et al. (1990) on the basis of the same approximate method.

The arsenopyrite grains that do not undergo replacement with fahlore and demonstrate structural equilibrium with other sulfides are distinguished by insignificant Ni, Co, and Sb admixtures, and this makes possible to apply the arsenopyrite geothermometer to estimation of the formation temperature (Table 6).

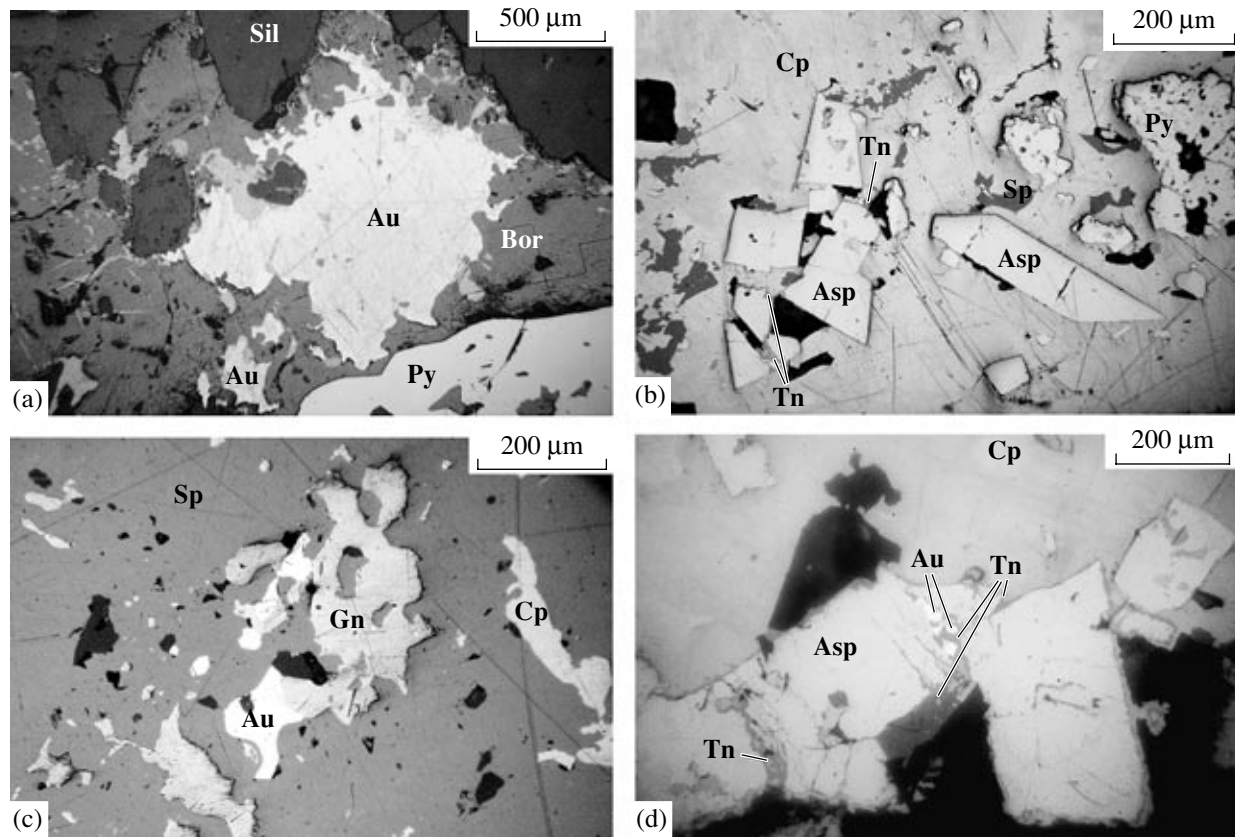


Fig. 8. Native gold grains in ore of the San Donato deposit in a polished section examined in reflected light. (a) Large gold grain (Au) in bornite (Bor), sample 1184-i; (b) tennantite (Tn) as replacement rims and veinlets in arsenopyrite (Asp), sample 1077-i; (c) small gold grains and chalcopyrite (Cp) and galena (Gn) disseminations in sphalerite (Sp), sample 715-i; (d) small gold grains within tennantite replacement rims and veinlets in arsenopyrite, sample 1077-i.

A significant amount of the visible native gold is related to the fahlore segregations. With the onset of replacement of arsenopyrite with fahlore, tiny native gold inclusions appear in the latter mineral (Fig. 8d). If fahlore is the only mineral of arsenic (fahlore subfacies), native gold often occurs as syngenetic rounded inclusions therein. Even insignificant postmineral displacements result in stretching of these inclusions, which are transformed into veinlets and chains of grains. Native gold, commonly in association with galena, fills small fractures that cut fahlore grains. It is hardly probable that such veinlets crystallized directly from solution. In this case, they would extend beyond the boundaries of fahlore grains and penetrate into other sulfides. Most likely, the gold in the massive sulfide deposits is closely related to minerals of arsenic, as has been described previously for gold deposits.

In the pyrrhotite and pyrrhotite-bearing ores at the Uzel'ga, Mauk, Tarn'er, and 50-letiya Oktyabrya deposits, arsenopyrite is in equilibrium with pyrite and pyrrhotite. The compositions of arsenopyrite and pyrrhotite grains serve as a basis for estimation of temperature and sulfur fugacity under conditions of pyrrhotite facies. Arsenopyrite grains, especially in stringer-dis-

seminated ore, often exhibit a distinctly expressed euhedral habit.

Native gold is detected in the ore of pyrrhotite facies much less frequently in comparison with pyrrhotite-free ore. Visible native gold was found only at the Tarn'er deposit (Table 7) as inclusions in sphalerite, chalcopyrite, and pyrrhotite. In contrast to the native gold from ores of chalcopyrite and bornite facies, its composition is close to electrum: the $Ag/(Ag + Au)$ ratio varies from 0.4627 to 0.5020, indicating a low sulfur fugacity during its crystallization in pyrrhotite ore (Vaughan and Craig, 1978). Galena, Ag and Bi sulfosalts, pyrrargyrite, cosalite, and molybdenite are noted in the pyrrhotite ore together with native gold (*Copper Massive Sulfide...*, 1988). Native gold was not detected at the 50-letiya Oktyabrya deposit; native bismuth and bismuthine were identified in a similar mineral assemblage instead of gold (Table 7). Native gold was also not found in telluride-bearing pyrrhotite ore at the Mauk deposit or in Orebody 4 at the Uzel'ga deposit.

Galena is frequently associated with native gold along with fahlore. Galena—the major lead mineral—is stable in all of the studied mineral assemblages of the massive sulfide ores; thereby, the amount of galena var-

Table 5. Chemical composition (wt %) of minerals related to the replacement of arsenopyrite with fahlore (microprobe results). The Uzel'ga deposit, sample 212/78 from the collection of F.P. Buslaev

Mineral	Arsenopyrite		Pyrite			Tennantite		
Cu						42.36	41.90	42.48
Ag						0.07	0.09	0.09
Zn						0.43	0.39	4.83
S	19.87	19.58	54.18	53.71	52.17	28.57	28.93	28.55
Fe	34.32	34.14	46.29	46.07	47.23	7.15	7.20	4.42
Co	0.17	0.17	0.13	0.13	0.00			
Ni	0.16	0.16	0.11	0.11	0.00			
As	45.29	45.56	0.49	0.56	0.00	22.19	23.07	22.02
Sb	0.37	0.36	0.00	0.16	0.00	0.57	0.35	0.32
Total	100.18	99.97	101.01	99.45	99.41*	101.34	101.73	102.71*
As, at %	32.74	33.58						
$T, ^\circ\text{C}$	470	500						
$\log f_{\text{S}_2}$	-5.3	-4.5						

* Compositions of the grains unrelated to the replacement are indicated by an asterisk.

ies within a wide range. The high plasticity of galena in comparison with other sulfides probably promoted its association with native gold.

The estimates of temperature and sulfur fugacity obtained for mineral associations of the studied deposits (Tables 5, 6, 8) are summarized in Tables 9 and 10 and shown in Fig. 9a. As follows from these data, a considerable portion of the Au-rich massive sulfide ores (2–3 g/t Au, native gold is often detected) was formed at an elevated sulfur fugacity that only slightly deviates from the values of the chalcopyrite–bornite equilibrium.

At each temperature, the ore enriched in gold relative to the ordinary ore (~1 g/t Au) was formed at a sulfur fugacity one to two orders of magnitude higher. The $\log f_{\text{S}_2}$ values vary in most of the studied mineral assemblages from -12 to -5, ranging overall from -16 to -3. The temperature is quite variable: $T = 150\text{--}360^\circ\text{C}$ for the fahlore-bearing bornite assemblage, $130\text{--}450^\circ\text{C}$ for the fahlore-bearing chalcopyrite assemblage, and $250\text{--}520^\circ\text{C}$ for the arsenopyrite assemblage.

The Au-rich (~2–3 g/t Au) deposits are not numerous and, as a rule, are small. They are localized largely in the Baimak district (Tashtau, Baldatau, Bakrtau, Maisky, Uvaryazhsky, etc.). The deposits with an Au grade of ~2 g/t are also close to the former in many attributes, including the enrichment in Pb and Ba and small reserves. Such deposits are known in the southern Uchaly–Aleksandrinsky zone (Talga, Molodezhny, Aleksandrinsky). The spatial separation of these deposits from those with ordinary Au grade (~1 g/t) allows us to suggest that a source enriched in gold is an important prerequisite of deposition of Au-rich ore. A mafic magma chamber and, especially, its final rhyodacitic

derivatives may serve as such a source. Rhyodacitic melt crystallizes as stocks at a shallow depth. Many deposits in the Baimak district are hosted in these stocks. Voluminous primary syngenetic sulfide ores with ordinary Au grade (~1 g/t) most likely provided the local enrichment of the Ural-type deposits in gold up to 90 g/t.

The highest Au contents are related to the bornite-bearing massive sulfide ore (bornite facies). Gold grains as large as a few millimeters are found in this ore. The visible gold in the bornite ore mostly occurs as inclusions and thin veinlets in tennantite, galena, and less frequently sphalerite and bornite. When barite pockets or indistinct stockwork zones are delineated in the bornite ore, the native gold often concentrates precisely in these areas rather than in massive bornite ore. In this case, gold also occurs as inclusions in tennantite, galena, sphalerite, and bornite and makes up intergrowths with these minerals.

The variation in gold fineness and N_{Ag} value is controlled by sulfur fugacity to a greater extent than by temperature. This is seen from the variation in Fe content in sphalerite coexisting with native gold (Table 8, Fig. 10). Like the native gold composition, the Fe content in sphalerite is determined by the relationship between temperature and sulfur fugacity. Pressure was not taken into account in calculations because, according to geological data, the depth of massive sulfide ore deposition was not greater than 3 km, so that the lithostatic pressure was lower than 1 kbar. Such pressure does not change the equilibrium constants of solid-phase reactions markedly (Vaughan and Craig, 1978).

Table 6. Chemical composition of arsenopyrite, wt % (microprobe results) and estimates of temperature and sulfur fugacity

Deposit	Sample	Element content, wt %						Total	As, at %	T, °C	log f_{S_2}
		S	Fe	Co	Ni	As	Sb				
Chalcopyrite facies											
Uz	212/78-1	19.87	34.32	0.17	0.16	45.29	0.37	100.18	32.74	470	-5.3
	212/78-2	19.58	34.14	0.17	0.16	45.56	0.36	99.97	33.58	500	-4.5
	328/78	20.67	34.67	0.36	0.51	45.18	0.12	101.51	32.01	450	-5.6
	3/78	21.94	35.69	0.08	0.08	42.20	0.15	100.14	29.79	350	-8.5
	313/78	19.74	34.35	1.02	0.10	46.14	0.30	101.65	32.97	490	-4.7
	323/78	22.08	35.20	0.07	0.09	43.37	–	100.81	30.46	360	-7.8
	321/78-1	21.83	35.40	0.09	0.11	42.57	–	100.00	30.12	365	-8.0
	321/78-2	19.11	35.20	0.09	0.11	46.67	–	101.18	33.62	515	-4.3
	319/78	20.18	34.52	0.10	0.10	45.33	–	100.23	32.60	470	-5.4
	343/78	19.32	34.33	0.10	0.09	46.05	–	99.89	33.49	510	-4.3
D	144/79	20.66	34.01	0.03	0.06	42.55	–	97.31	31.18	385	-7.4
	145/79	21.12	34.90	0.04	0.05	43.88	–	99.99	31.40	420	-6.15
	146/79	20.38	33.22	0.04	0.05	42.16	–	95.87	31.38	420	-6.15
	67/79	21.06	34.34	0.04	0.05	41.74	–	97.23	30.46	425	-6.1
	180/79	20.63	34.61	0.04	0.04	43.27	–	98.59	31.38	420	-6.15
	47/79	20.94	34.22	0.03	0.05	42.93	–	98.17	31.16	380	-7.5
	193/79	20.43	34.74	0.10	0.07	42.44	–	97.78	31.03	405	-6.5
	65/67	20.52	33.87	0.03	0.07	42.17	–	96.66	31.11	380	-7.5
K	15/82	21.01	34.48	0.04	0.10	44.14	0.06	99.83	31.61	420	-6.2
	16/82	20.96	34.49	0.07	0.08	43.15	0.06	98.81	31.16	405	-6.3
SD	I-1249	21.39	34.70	0.16	0.17	43.73	0.29	100.44	31.17	400	-6.6
	I-1247	21.24	34.76	0.04	0.07	44.52	0.07	100.70	31.61	430	-6.0
	I-1367	21.43	34.34	–	–	43.55	–	99.32	31.17	410	-6.3
	I-1115	21.40	35.21	0.06	0.08	44.06	0.06	100.86	31.16	410	-6.3
	I-1124	21.41	35.92	–	0.10	43.03	0.37	100.83	30.54	380	-7.2
	I-1213	20.73	34.30	0.03	0.03	40.43	–	95.54	29.97	360	-7.65
BL	0175	21.17	35.45	0.04	0.04	44.58	–	101.27	31.46	415	-6.15
S	2151/212.2	19.96	29.37	4.16	1.96	46.61	–	102.06	33.19	515	-4.3
	2151/212.2	20.58	32.30	1.47	1.37	45.34	0.17	101.23	32.27	520	-4.2
Pyrrhotite facies											
T	1050/331.2	19.84	34.12	0.09	0.09	45.12	0.16	99.42	32.96	470	-5.0
50-letiya	96	21.08	34.86	0.11	0.22	43.52	–	99.79	30.76	370	-8.1
	110	21.11	34.56	0.28	0.28	45.18	–	101.41	31.91	425	-6.7
	114	21.34	34.53	0.11	0.13	43.37	–	99.48	31.01	370	-8.1
	116	20.82	34.71	0.27	0.11	44.36	–	100.27	31.76	430	-6.7

Note: Deposits (here and in Table 8): (K) Karabash, (BL) Barsuchy Log, (Uz) Uzel'ga, (Okt) Oktyabr'sky, (D) Degtyarsk, (G) Gai, (SD) San Donato, (M) Molodezhny, (50-let) 50-letiya Oktyabrya, (S) Saf'yanovka, (YK) South Kuznechikha.

Tellurides, including calaverite, krennerite, petzite, sylvanite, muthmannite, and montbrayite, are important gold minerals in ore. This is confirmed by elevated Au and Ag contents precisely in those segments of orebodies at the Gai and Uzel'ga deposits where tellurides

have been identified. The distribution of tellurides within orebodies is controlled by collective recrystallization and fractionation. Like native gold, tellurides crystallize together with chalcopyrite, galena, sphalerite, and tennantite. The hardness of these minerals is

Table 7. Chemical composition (wt %) of native gold and rare minerals from massive sulfide ore of pyrrhotite facies (microprobe results)

Element	Tarn'er deposit			50-letiya Oktyabrya deposit		
	native gold			cosalite	native bismuth	Bi ₂ S ₃
	1030/32	1060/160.4	1514/508.3	1001/110.2	T-112	T-112
Au	63.14	68.57	66.72	0.01	0.01	0.01
Ag	34.86	30.71	31.47	0.01	0.01	0.01
Cu	0.01	0.01	0.01	1.87	0.12	0.01
Bi	0.57	0.63	0.72	46.16	98.54	81.09
Pb	–	–	–	41.05	0.01	0.01
Hg	0.83	0.84	0.90	0.36	0.01	0.52
Cd	0.01	0.01	0.01	0.01	0.01	–
Sb	–	–	–	–	–	–
S	–	–	–	15.37	0.01	17.27
Te	0.01	0.01	0.09	0.01		0.01
Fe	–	–	–	0.01	0.01	0.01
Total	99.44	100.79	99.94	104.86	98.73	98.96
Ag/(Ag + Au)	0.5020	0.4499	0.4627			

lower than that of pyrite, which is a brittle mineral predominant in volume. Therefore, the above minerals are more subject to ductile deformation and accompanying dissolution under pressure and redeposition. In this connection, tellurides are confined to the upper portions of orebodies or to their lenticular tectonic fragments, as noted at the Gai, Karabash, and other deposits. The postmineral modification of disseminated and stockwork ores leads to the formation of orebodies or their segments enriched in chalcopyrite and tellurides. The high-grade copper ore at the Saf'yanovka deposit serves as an example (Yazeva et al., 1991).

Tellurides are associated with chalcopyrite, fahlore, and galena at the Gai, Karabash, Uzel'ga, Sibai, Degtyarsk, and other deposits. Fahlore amounts to 3–5% of the total sulfide volume and contains as much as a few weight percent Te. According to the microprobe results, the highest Te content in fahlore attains 2.18 wt % at the Gai deposit, 5.13 wt % at the Aleksandrinsky deposit, and 8.89 wt % at the Uzel'ga deposit. Native gold occasionally also contains a Te admixture (as much as 4.86 wt % at the Uzel'ga deposit). Appreciable Te contents were noted in arsenopyrite (up to 0.86 wt %) and galena (up to 0.28 wt %). The Te contents in other minerals are much lower. The wide abundance of tellurides in the stringer–disseminated ore and ore shoots at the Saf'yanovka deposit is related to recrystallization of fahlore and its subsequent replacement with minerals of the enargite–famatinitite series accompanied by the release of an isomorphous Te admixture from fahlore. At the Gai deposit, where enargite is unknown, inclusions

of tellurides and native gold in tennantite are a common phenomenon.

The association of tellurides with goldfieldite, native gold, and native tellurium in ore of the Yaman-Kasy massive sulfide deposit (Maslennikov, 1999) deserves attention. Like other deposits of the Mednogorsk ore district in the southern Urals, this deposit was affected by metamorphism to a lesser extent. Well-preserved mineralized fauna (remains of vestimentifera, brachiopods, etc.) has been found here, as well as bitumen and other organic substances in ore. The specific attributes of ore at this deposit testify to its genetic affinity to sulfide occurrences of modern submarine hydrothermal springs (Zaikov et al., 1995).

At the Saf'yanovka deposit, native gold has been detected only in the disseminated copper–zinc ore at the periphery of the main ore zone and in the massive Cu–Zn ore enriched in galena and fahlore. The same is true of the Karabash deposit, where calaverite and other tellurides are extremely rare in association with native gold. When native gold occurs together with tellurides, the latter are most frequently represented by hessite. We did not identify tellurides in Au-bearing ores at the San Donato and Degtyarsk deposits.

The pyrrhotite ore is distinguished by a lesser amount of tellurides, probably owing to the lower fugacity of tellurium. As a result, sulfides and sulfosalts are the leading mineral species of Ag, Pb, and Bi. The 50-letiya Oktyabrya deposit is interesting in this regard. Bismuthine and native bismuth were identified here in the absence of Bi tellurides under conditions of pyrrhotite facies. This is also confirmed by findings of cosalite

Table 8. Results of electrum–sphalerite thermometry of massive sulfide deposits

Deposit	Sample	N _{Ag}	X _{FeS}	T, °C	log f _{S₂}	Sample	N _{Ag}	X _{FeS}	T, °C	log f _{S₂}
Bornite–fahlore subfacies										
G	501/74	0.245	0.0010	280	−7.2	536/78-1	0.244	0.0009	278	−7.2
	502/76-1	0.162	0.0020	364	−4.3	536/78-2	0.248	0.0009	276	−7.4
	502/76-2	0.206	0.0020	330	−5.6	536/78-3	0.199	0.0009	306	−6.0
	502/76-3	0.229	0.0020	316	−6.2	507/77	0.271	0.0012	272	−7.8
K	M-193	0.174	0.0010	340	−3.0					
SD	1184	0.334	0.0038	280	−8.4	1184/c	0.325	0.0038	285	−8.2
	1184/a	0.253	0.0038	326	−6.4	1184/d	0.276	0.0038	312	−7.0
	1184/b	0.301	0.0038	298	−7.6					
Chalcopyrite–fahlore subfacies										
G	2017/63.5	0.190	0.0012	368	−3.9	543/79	0.274	0.0021	304	−7.1
	4023/295	0.510	0.0322	297	−9.8	019	0.235	0.0347	446	−4.2
	4023/295	0.510	0.0353	301	−9.7	East-1	0.265	0.0149	378	−5.6
	551/78	0.421	0.0081	283	−9.3	2316/3d	0.468	0.0485	326	−8.8
	548/78	0.248	0.0095	369	−5.6	2316/3d	0.468	0.0292	306	−9.3
	625/79	0.238	0.0159	409	−4.7					
K	K 16/82	0.145	0.0388	543	−1.8					
SD	1115	0.314	0.0280	376	−6.2	1124	0.492	0.0394	296	−9.7
	1114-1a	0.352	0.0327	373	−6.5	1269	0.485	0.0301	288	−9.8
	1114-1b	0.333	0.0327	373	−6.6	1269	0.485	0.0301	290	−9.8
	1114-1c	0.342	0.0327	372	−6.5	1028	0.262	0.0374	429	−4.8
	1114-3	0.346	0.0264	354	−6.9	715	0.547	0.0395	273	−10.8
	1201	0.472	0.0386	305	−9.3	808	0.546	0.0567	288	−10.4
	1425 V	0.469	0.0015	193	−12.6	1215	0.452	0.0127	269	−10.0
	1073	0.418	0.0466	341	−7.9	1295	0.610	0.0265	236	−12.4
	716	0.266	0.0372	431	−4.8	1370	0.492	0.0603	315	−9.2
	900	0.510	0.0502	299	−9.8					
D	46/79	0.523	0.0226	279	−10.4	145/79	0.337	0.0272	372	−6.5
	140/79	0.352	0.0095	320	−7.7	190/79	0.317	0.0095	338	−6.9
S	2182/133.4	0.615	0.0420	269	−11.5	2091/128.9	0.516	0.0051	232	−11.7
	2182/133.4	0.554	0.0420	289	−10.4	P30/535.0	0.447	0.0014	151	−16.4
	2182/133.4	0.601	0.0420	274	−11.2	P19/161.0	0.304	0.0060	327	−7.0
Uz	232/78	0.47	0.0272	165	−15.5	232/78	0.470	0.0016	190	−14.3
Okt	0625	0.332	0.0022	279	−8.40	0625-2	0.332	0.0016	268	−8.65
BL	175	0.307	0.0121	354	−6.50	B-1	0.341	0.0073	316	−7.66
SK	SK-1a	0.268	0.0094	366	−5.83	SK-1b	0.268	0.0094	365	−5.84

Pb₂Bi₂S₅ at the Tarn'er deposit (Table 7) and pyrrhgyrite Ag₃SbS₃ (*Massive Sulfide Deposits...*, 1988). Similar relationships have been established at the massive sulfide deposits of the Rudny Altai, where the amount of Pb, Bi, and Ag sulfosalts increases and the content of tellurides decreases with increasing pyrrhotite content (Pokrovskaya, 1982). As follows from the data presented above, tellurides become unstable in the process

of metamorphism of massive sulfide ores pertaining to pyrrhotite facies. As a result, tellurium must be removed to the low-temperature zones of ore-forming systems. This suggestion is supported by findings of tellurides in the only slightly metamorphosed ore at the Yaman-Kasy deposit.

Our data on the Te fugacity are given in Table 11. The Te fugacity for ore samples taken from the Gai and

Table 9. Formation conditions of Au-bearing ores at massive sulfide deposits in the southern and central Urals, modified after Moloshag et al. (2000)

Deposit	Assemblage	T, °C	log f _{S₂}	log f _{O₂}	Method
Uzel'ga	FC	130–370			I
	FC	165–190	–15.5...–14.3	–27.5*	II
	A	<250–515	<–12...–4.3	–26.5*	III
Aleksandrinsky	FB	160–360	–12...–8**	–35...–28**	I
Gai	FB	272–364	–8.4...–4.3	–3.9...–3.7*	II
	FC	297–446	–9.8...–3.9		II
Degtyarsk	FC	210–295			I
	FC	279–372	–10.4...–6.5		II
	A	465			I
	A	380–425	–7.5...–6.1		III
San Donato	FB	280–340	–8.4...–3.0		II
	FC	193–431	–12.6...–4.8		II
	A	360–430	–7.7...–6.0		III
Saf'yanovka	FC	151–327	–16.4...–7.0		II
	A	515–520*	–4.3...–4.2*		III

Note: Mineral assemblages: (FB) fahlore–bornite, (FC) fahlore–chalcopyrite, (A) arsenopyrite. Methods: (I) homogenization of fluid inclusions; (II) electrum–sphalerite and (III) arsenopyrite geothermometers.

* Single determinations.

** Approximate estimates.

Table 10. Mineral assemblages and temperature of sulfide deposition at the massive sulfide deposits of the Urals

Facies	Assemblage	Tipomorphic minerals	Main accessory minerals	T, °C
Bornite	Enargite–digenite	Py, sp, dg, ba	Bt, str, jal, mc, (Au, Ag)	150–230
	Fahlore	Py, bn, sp, fl, ba ± gn	Mw, col, ger, st, (Au, Ag)	150–300
Chalcopyrite	Enargite	Py, cp, en	(Au, Ag), alt	180–300
	Fahlore	Py, cp, sp, fl ± hem, gn	Au, Ag, and Bi tellurides; Ag and Bi sulfotellurides; alt; Te; (Au, Ag)	180–370
Pyrrhotite	Arsenopyrite	Py, cp, sp, asp ± mt	Au, Ag, and Bi tellurides; (Au, Ag)	250–500
	Arsenopyrite	Py, po, cp, sp ± mt, asp	Cb, pn, Bi and Ag tellurides, mo, bs, Bi, (Au, Ag)	<250–560
	Loellingite	Py, po, cp, sp, löl ± mt		480–660

Note: Abbreviations of minerals (here and in Table 11): (py) pyrite, (bn) bornite, (cp) chalcopyrite, (en) enargite, (po) pyrrhotite, (asp) arsenopyrite, (dg) digenite, (mt) magnetite, (hem) hematite, (löl) loellingite, (pn) pentlandite, (cb) cubanite, (fl) fahlore, (ba) barite, (gn) galena, (Au, Ag) native gold, (cv) calaverite, (alt) altaite, (mo) molybdenite, (Te) native tellurium, (Bi) native bismuth, (bt) betekhtinite, (bs) bismuthine, (mc) mckinstyrite, (mw) mawsonite, (str) stromeyerite, (st) stannoidite, (col) colusite, (ger) germanite, (val) valleriite, (jal) jalpaite, (hes) hessite.

Oktyabr'sky deposits, where hessite is associated with native gold, was calculated using the formula proposed by Bortnikov et al. (1988) at a temperature that was measured with the electrum–sphalerite thermometer. The Te fugacity for the sample from the Voroshilovsky deposit was estimated on the basis of arsenopyrite geothermometry. The pyrite–pyrrhotite solvus was used to determine temperature and sulfur fugacity at the Mauk deposit.

The values of Te fugacity and temperature were plotted on the diagram of phase relations in the Au–Ag–Te system (Bortnikov et al., 1988). In most samples, the data points fall into the field of coexisting hessite and native gold (Fig. 9b), in agreement with microscopic examinations. The data points of the samples that contain Au tellurides also fall into the field hessite + native gold. Both native gold and Au tellurides, as well as galena and altaite, are contained in ore assemblages at

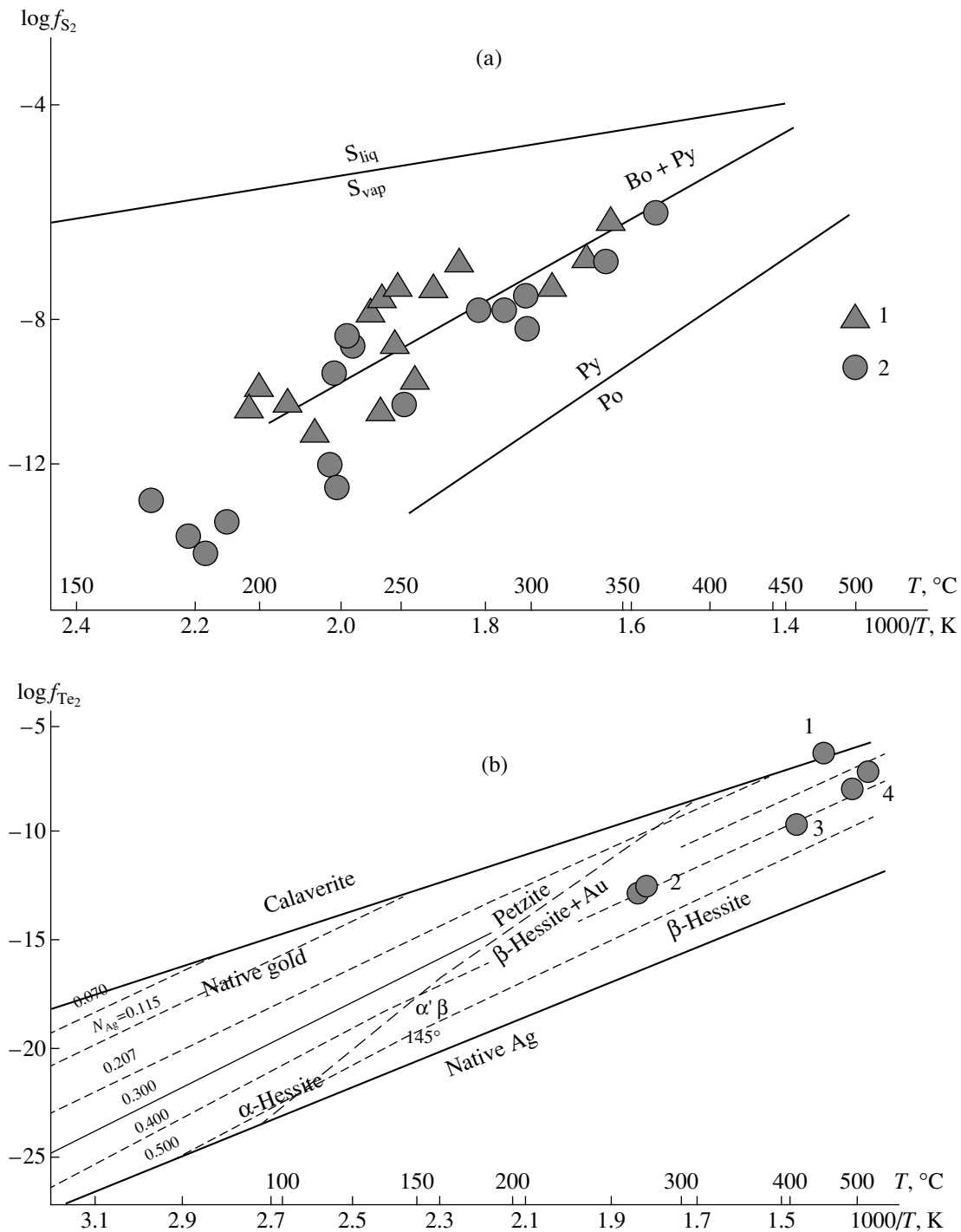


Fig. 9. Formation conditions of Au-bearing mineral assemblages at massive sulfide deposits of the Urals. (a) Results of electron-sphalerite thermometry. Mineral assemblages: (1) bornite–fahlore, (2) chalcopyrite–fahlore. (Py) pyrite, (Po) pyrrhotite, (Cp) chalcocopyrite, (Bo) bornite, (S_{liq}) liquid sulfur, (S_{vap}) sulfur vapor. (b) Te fugacity values for Au-rich mineral assemblages plotted on the diagram of calaverite, hessite, and native gold stability (Bortnikov et al., 1988). Points 1–4 are the parameters presented in Table 11 for ore mineral associations at the (1) Gai, (2) Oktyabr'sky, (3) Karabash, and (4) Mauk deposits.

most deposits. These mineral assemblages and findings of coloradoite, hessite, stützite, and occasional native tellurium and silver make it possible to specify the f_{Te_2} values on the basis of paragenetic diagrams (Afifi et al.,

1988; Cabri, 1965) and the obtained f_{S_2} and temperature estimates. At the predominant temperature of mineral formation of $\sim 300^{\circ}\text{C}$, $\log f_{\text{Te}_2}$ varies from -16 to -6 . The Te fugacity gradually drops with falling tem-

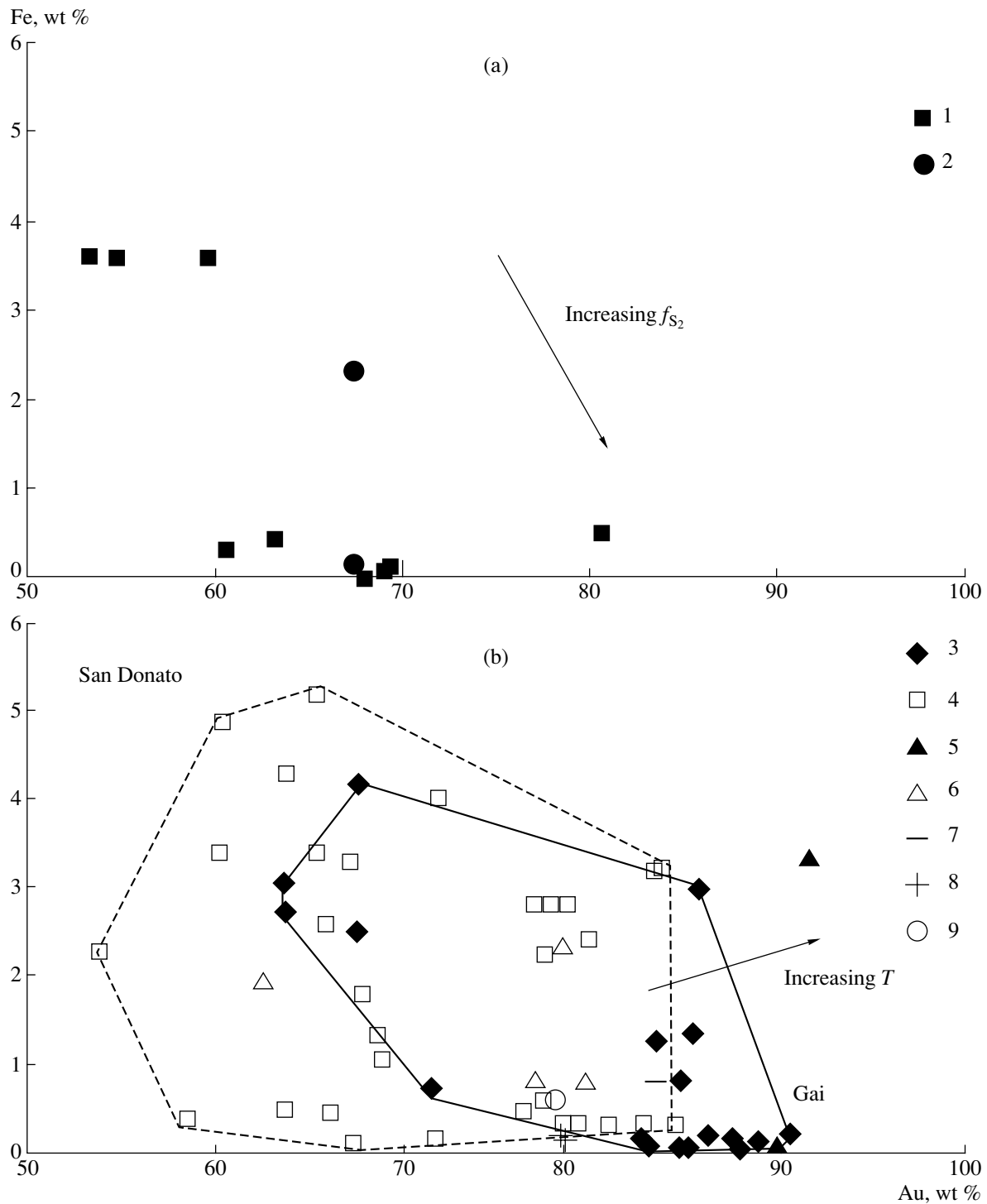


Fig. 10. Fe content in sphalerite versus Au content in the coexisting native gold in massive sulfide ores of the central and southern Urals. (a) Slightly metamorphosed deposits: (1) Saf'yanovka, (2) Uzel'ga; (b) strongly metamorphosed deposits: (3) Gai, (4) San Donato, (5) Karabash, (6) Degtyarsk, (7) South Kuznechikha, (8) Oktyabr'sky, (9) Barsuchy Log.

perature of mineral formation and at 100°C $\log f_{\text{Te}_2}$ is within the range from -20 to -15 .

Most of the samples with estimated temperature and sulfur fugacity are devoid of optically visible tellurides,

and the main mass of tellurium probably is incorporated into the lattices of fahlore and galena. Keeping in mind the problems arising in optical identification of very small Ag telluride grains, it cannot be ruled out that hessite and petzite occur in a greater number of

Table 11. Calculated tellurium fugacity

Deposit	Sample	T , °C	1000/ T K	$\log f_{S_2}$	$\log f_{Te_2}$	Assemblage
Gai	019	446	1.39	-4.2	-6.93	cv + hes + (Au,Ag)
Oktyabr'sky	0625	279	1.81	-8.40	-12.39	hes + (Au,Ag)
	0625-2	268	1.85	-8.65	-12.77	"
Karabash	K 16/82	405	1.47	-6.3	-10.0	"
Mauk	368/105.5	510	1.27	-4.9	-8.4	"
		480	1.33	-5.2	-9.3	"

samples that characterize the Au-bearing ores formed under conditions of chalcopyrite facies.

DISCUSSION

It has been established that elevated concentrations of gold are typical of the copper–zinc ore; gold is incorporated preferentially into chalcopyrite and fahlore rather than into sphalerite as the major economic mineral of zinc. This correlation is consistent with recent data on the distribution of gold in modern massive sulfide deposits in oceans (Bortnikov et al., 2003). At the same time, the elevated Au content in Zn-bearing (Cu–Zn) ore in comparison with copper ore and the close spatial localization of maximum Au and Zn concentrations within orebodies probably are related to the joint deposition of Au and Zn at the late stage of the hydrothermal process. In the respective mineral assemblages, gold is related to its own mineral species and to minerals of Cu, Fe, and Te.

It is suggested that invisible, finely dispersed gold is an important species in the studied deposits. Such gold largely is related to chalcopyrite and pyrite, while silver is associated with fahlore, sphalerite, chalcopyrite, and occasionally bornite. The fire assay results for ores and concentrates and the balance of gold distribution in minerals indicate that pyrite is the major mineral concentrator of gold in massive sulfide ores (Chanturiya and Bocharov, 2001) with an ordinary Au grade of ~1 g/t. The concentration of the finely dispersed admixture of Au in sulfides, assessed in Russian nonferrous metallurgy by making use of rational analysis, amounts to 0.8–5.0 ppm and is much lower than the range of Au contents in the respective samples (0.93–21.2 ppm).

Based on these results, one may suggest that the critical limit of concentration of finely dispersed gold in massive sulfide ore is close to 5 ppm. This estimate is even higher than the limit that constrains incorporation of gold in the lattice of pyrite at $T = 500^\circ\text{C}$ and $P = 1$ kbar (3 ± 1 ppm). At these parameters, the isomorphous capacity of sulfide is higher than at $T = 250\text{--}350^\circ\text{C}$ typical of massive sulfide ore formation (Tauson, 1999; Tauson and Kravtsova, 2002).

The content of structurally bound Au estimated for the natural pyrite from the gold deposits formed at 300–350°C is only 0.12 ppm against 40–97 ppm bulk Au content in four selections of 14–19 pyrite crystals; 0.24 ppm against 18–104 ppm bulk Au content in six selections of 14–18 pyrite crystals; and 0.34 ppm against 2–22 ppm bulk Au content in five selections of 17–20 pyrite crystals from metasomatic rocks. Thus, the mass percentage of isomorphous gold amounts only to 0.5–5.0% of the bulk Au content in pyrite (Tauson and Kravtsova, 2002). These authors have established an inverse correlation between the Au content in pyrite (from results of fire assay) and the size of gold grains. A similar result has been obtained with the more local method of secondary ion mass spectroscopy (SIMS) (Spry and Thieben, 2000). Thereby, the maximum concentration of invisible gold in pyrite was estimated at 1.18 ppm. These data allow us to suggest that the prevalent percentage of finely dispersed gold in sulfides from the Ural deposits is due to rather uniformly distributed nanosized (<0.5 μm) disseminations of gold minerals, mainly native gold, rather than to a solid solution of Au in pyrite.

The SIMS results indicate that the anomalously high contents of invisible gold in pyrite are correlated with the highest As contents (Chryssoulis and Grammatikopoulos, 2003; Pals et al., 2001). It remains ambiguous how As can be incorporated in the pyrite structure (Fleet and Mumin, 1997). It is assumed that the arsenian pyrite contains thin (10–15 Å) layers of marcasite or arsenopyrite that concentrate arsenic (Simon et al., 1999). Furthermore, the results of X-ray absorption near-edge spectroscopy (XANES) have shown that arsenic in As-bearing pyrite occupies a site similar to its site in arsenopyrite, making up AsS^{-2} pairs (Simon et al., 1999). The deep profiling of the Au-rich pyrite from the Emperor epithermal deposit (as high as 11 kg/t Au) with the SIMS method revealed still finer gold of submicrometer dimension and Te minerals <0.1 μm in size together with invisible gold (Pals et al., 2001). Thereby, the Au content in pyrite is correlated positively not only with arsenic but also with tellurium. The authors of the cited publication partly account for this correlation by the presence of inclusions of an Au–Te mineral, for example, calaverite. Native gold or elec-

trum and tellurides (sylvanite, krennerite, calaverite, and petzite) are the prevalent mineral species of visible gold at this deposit. The same has been established at the Ural deposits. In general, the same Au and Ag tellurides (hessite, stützite, sylvanite, calaverite, krennerite, petzite, and montbrayite), along with other minerals of this group (altaite, coloradoite, empressite, tellurobismuthite, tetradymite, rucklidgeite, and pilsenite), occur at both the large gold-sulfide-quartz and the massive sulfide deposits (Konstantinov et al., 2000; Shackleton et al., 2003). The study of sulfides from porphyry copper deposits with the SIMS technique (Kesler et al., 2002) has shown that invisible gold accumulates both in chalcopyrite (0.05–1.4 ppm; 0.08 and 0.10 ppm as averages for two deposits) and pyrite (0.05–2.5 ppm; 0.19 and 0.50 ppm as averages for two deposits). Our data are consistent with these results and demonstrate an equal or somewhat higher Au content in pyrite in comparison with chalcopyrite at massive sulfide deposits, although these minerals were deposited at a lower temperature than in porphyry copper systems.

Elevated gold concentrations were revealed in ore with relict colloform structure at the Aleksandrinsky deposit (Vikent'ev et al., 2000) and at the Uzel'ga deposit (Vikentyev et al., 2004); such structure is especially characteristic of arsenian pyrite. Gold could replace Fe in the lattice of As-bearing pyrite and then pass to the metallic state due to the recrystallization of ore and removal of As from pyrite and its subsequent fixing in fahlore at the final stage of mineral formation.

The indications of the secondary hydrothermal and synmetamorphic redistribution of gold with its removal from ore-forming sulfides and enlargement of native gold grains come into conflict with the idea of enrichment of syngenetic sulfide bodies in the veined gold related to the late orogenic gold-ore systems. This idea was set forth by many researchers and synthesized by Groves et al. (2003).

The small but Au-rich deposits clustered in the Baik district are related to the specific ore-bearing basalt-rhyolite complexes and closely associated with subvolcanic rhyodacitic domes.

The study of ore minerals from massive sulfide ores of the Urals has shown that in some cases gold accumulates as an admixture in Pb, Bi, and Ag tellurides and in pyrite, chalcopyrite, sphalerite, galena, and fahlore. Altaite is the most abundant telluride, containing <0.02–5.2 wt % Au, 0.1–1.0 wt % Ag, up to 0.3 wt % Pt, and up to 0.14 wt % Pd. Hessite and stützite also occur at some deposits in appreciable amounts; they contain as much as 1.35 wt % Au, 1.24 wt % Pd, and 0.66 wt % Pt. Coloradoite contains as much as 0.4 wt % Ag and 0.75 wt % Pd. Other Au and Ag tellurides (sylvanite, calaverite, krennerite, petzite, muthmannite, and montbrayite) are extremely rare. Other Te minerals (empressite, tellurobismuthite, tetradymite, rucklidgeite, and pilsenite) occur sporadically and contain

gold in amounts close to the microprobe detection limit (0.02 wt %). Tellurides are hosted only in ores devoid of bornite (Moloshag et al., 2002). Occasional findings of hessite in bornite ore at the massive sulfide deposits do not contradict this tendency because, in these circumstances, hessite is a younger mineral superimposed with respect to bornite (Kachalovskaya and Khromova, 1970). This tendency is also observed at gold deposits (Kovalenker et al., 1990).

The metallicity of chemical bonds is expressed in tellurides more distinctly than in sulfides (Batsanov, 1971). In this regard, the higher concentration of an isomorphous structural admixture of gold in tellurides than in sulfides becomes understandable. The phase M-Te-Au diagrams, where M is Bi, Pb, and other metals, demonstrate that Au solid solutions may exist in tellurides (Cabri, 1973; Markham, 1960). Crystallization of tellurides is more typical of the final stages of mineral formation, when, on the one hand, the activity of Te in hydrothermal fluid is increased, while, on the other hand, bornite, sphalerite, and galena crystallize. The isomorphous capacity of these minerals with respect to tellurium is insignificant and inferior to that of pyrite and chalcopyrite, which dominate at the early stage of mineral formation.

One of the factors controlling the appearance of visible grains of native gold and tellurides in ore is its reworking by epigenetic processes that gave rise to the recrystallization and enlargement of ore-forming mineral grains. In most cases, such recrystallization was related to superimposed metamorphism (Eremin et al., 2000; Pshenichny, 1976; Yarosh, 1973).

The possibility of enlargement of gold and its transition from submicroscopic (<0.2 μm) to visible species as a result of metamorphism was suggested for the Ural massive sulfide deposits by Kreiter (1948). First, he noted that only visible microscopic gold occurs at the deposits of the central Urals, whereas, at the Blyava, New Sibai, and other deposits of the southern Urals, the gold is largely submicroscopic. Second, he recalled the technique of recovery of "hard" (difficult to recover) gold by heating (sometimes multiply) to 300–850°C; thereby, the gold is enlarged and becomes visible and readily recoverable (Bürg, 1930). The mechanism of this process remained unclear and was defined as a self-purification of pyrite lattice (Bürg, 1935).

The native gold composition at the massive sulfide deposits of the Urals varies widely with a scatter that attains a few tens of weight percent at some deposits. The mosaic structure of the native gold has been confirmed, and it was established that impurities concentrate at the margins of grains or micromosaic blocks. Ag and S admixtures were detected within a film ~6–7 μm thick that coats native gold grains (argentite Ag_2S ?) irrespective of the composition of the quartz or sulfide grains that adjoin the native gold (Novgorodova et al., 1977).

The increasing fineness of gold is accompanied by decreasing Fe content in the coexisting sphalerite

(Fig. 10), probably, owing to the growth of f_{S_2} in fluid (Barton and Skinner, 1979). The increasing f_{S_2} raises the stability of Ag_2S in comparison with electrum and ensures crystallization of gold with a higher fineness (Shikasono and Shimuzu, 1987), in accordance with thermodynamic calculations (Gammons and Williams-Jones, 1995). An increase in pH and a temperature drop lead to the formation of electrum with a higher Ag content (Huston et al., 1992). The native gold composition also depends on Au and Ag activities in ore-bearing fluid.

The enrichment in Au of native gold from slightly to severely metamorphosed deposits in the Urals most likely is caused by growth of the temperature of massive sulfide ore transformation. This statement is consistent with experimental data on an increase in fineness of gold inclusions in pyrite under hydrothermal conditions ($T = 300^\circ\text{C}$ and $P = 500$ bar) that provide for removal of excess Ag into solution (Laptev et al., 2002). The increase in grade of metamorphism affecting the ore at the Ural deposits not only changes the composition of native gold but also raises its concentration in ore relative to Ag, Pb, and Ba as more mobile elements. The Au and Ag contents in sphalerite, chalcopyrite, and pyrite decrease (Vikent'ev et al., 2000).

Most mineral assemblages in the Au-bearing massive sulfide ore were formed at relatively low and medium temperatures and at a relatively high sulfur fugacity. Irrespective of the formation temperature of gold-bearing mineral assemblages, which do not even contain bornite, the values of these parameters plotted on the $\log f_{S_2} - T$ diagram are clustered close to the line of the solid-phase sulfidation: $\text{chalcopyrite} + \text{sulfur}_{\text{gas}} = \text{bornite} + \text{pyrite}$.

The native gold in the ore at massive sulfide deposits of the Urals is observable also against a relatively low bulk Au grade of ore, probably, as a result of low-temperature recrystallization, which is expressed also in the appearance of luminescent sphalerite. This process leads to development of a block microstructure of pyrite and is accompanied by formation of coarse-grained and porphyroclastic structures. The enlargement of grains is noted for all ore minerals and accompanied by the release of impurities. The collective recrystallization promotes enlargement of native gold grains, especially in bornite-bearing ore, which was formed at a sulfur fugacity higher than that on the replacement of chalcopyrite with bornite.

The sulfide hydrothermal mounds in modern oceans are composed of unmetamorphosed fine-grained ore close in composition to the ore at massive sulfide deposits located on continents. Gold in the oceanic ore occurs largely as an isomorphic admixture in pyrite, marcasite, and chalcopyrite (Bortnikov et al., 2003). SIMS microprobing has shown that the high Au contents in sphalerite grains are provided largely by fine disseminations of Au-bearing chalcopyrite. The gold is

enlarged by submarine oxidation of ore with formation of native gold grains 1–5 μm in size (occasionally as large as 18 μm). Primary fine-grained (0.5–2.0 μm) gold also is deposited within pipes of black smokers, emphasizing the boundaries between zones of contrasting composition and structure (Murphy and Meyer, 1998). Segregations of native gold as large as 30 μm in unusual association with sphalerite; chalcopyrite; galena; pyrite; and Cu, Pb, As, and Sb sulfosalts have been found in veinlets of amorphous silica that cut volcanics (Petersen et al., 2002). The thermodynamic conditions of gold incorporation into sulfides as Au^{+1} ($AuS_{0.5}$ -sulfide solid solution) show that a relatively high temperature (250–350 $^\circ\text{C}$) promotes the entering of gold into the sulfide structure (Bortnikov et al., 2003). Therefore, chemically bound invisible gold in sulfides may be the major species at the early, high-temperature stages of ore formation. Native gold most likely arises at a lower temperature of 150–200 $^\circ\text{C}$ as a result of subsequent recrystallization.

The depletion of the major ore-forming sulfides in gold, along with loss of the colloform structure of pyrite during metamorphism, and the enlargement of native gold grains with increasing intensity of postmineral transformation of massive sulfide deposits in the Urals are controlled by the same process of ore recrystallization. This statement is supported by the study of unmetamorphosed ore deposited at modern black smokers. In the primary ore unaffected by postmineral tectonic deformation, the gold is invisible and presumably structurally bound. Finely dispersed gold is also predominant in the slightly metamorphosed deposits of the Urals in combination with sporadic grains of native gold and tellurides. The relative amount of the gold finely dispersed in sulfides decreases in the intensely recrystallized ore of tectonically deformed deposits, whereas the amount of native gold and the dimensions of native gold grains increase markedly. It should be emphasized that the problem concerning actual Au speciation of invisible gold dispersed in sulfides remains unsettled with the current status of laboratory equipment in Russia.

CONCLUSIONS

(1) The temperature and the sulfur fugacity that characterize formation conditions of mineral assemblages with native gold and Au and Ag tellurides at the massive sulfide deposits in the Urals were estimated with the electrum–argentite–sphalerite–pyrite, arsenopyrite, and pyrite–pyrrhotite mineralogical geothermometers and by study of fluid inclusions. The evolution of gold ore mineralization has been traced for bornite, chalcopyrite, and pyrrhotite ore facies and subfacies. The subfacies are classified on the basis of arsenic minerals consecutively replacing one another: loellingite \rightarrow arsenopyrite \rightarrow fahllore \rightarrow enargite. The following values of temperature and sulfur fugacity correspond to

the ore facies: 150–360°C and 10^{-3} – 10^{-13} atm, bornite facies; 180–500°C and 10^{-7} – 10^{-14} atm, chalcopyrite facies; and 250–640°C and $10^{-1.4}$ – $10^{-12.7}$ atm, pyrrhotite facies.

(2) The formation conditions of ore with elevated Au grades (2–3 g/t) were markedly distinguished from those of ore with ordinary Au grade (~1 g/t). The sulfur fugacity required for formation of Au-enriched ore was one to two orders of magnitude higher at the same temperature. The visible native gold grains largely were formed as a result of ore recrystallization at relatively low and medium temperatures and at a relatively high sulfur fugacity close to the chalcopyrite–bornite equilibrium.

(3) Minerals new for the Urals have been identified in the ores enriched in gold: calaverite, petzite, muthmannite, and montbrayite at the Gai deposit; wittichenite and aikinite at the Saf'yanovka deposit; Te-tennantite, Ag-tennantite, native tellurium and rhenium, petzite, and stützite at the Uzel'ga deposit; Bi-tennantite at the Aleksandrinsky deposit; and petrovskaite at the Uchaly deposit.

(4) Finely dispersed gold dominates at the slightly metamorphosed massive sulfide deposits, where it amounts to 95% of bulk Au content in the ore. This gold probably is represented by uniformly distributed nanosized disseminations of native gold (Au–Ag alloys) in pyrite and chalcopyrite. In ores of the Gai and other moderately and strongly metamorphosed deposits, gold occurs as visible grains of its own minerals and as an admixture in sulfides and tellurides of other metals. These minerals are intergrown with chalcopyrite, fahllore, and bornite. The relative amount of visible gold minerals with predominance of native gold (mainly Au_3Ag and Au_2Ag alloys) and tellurides increases with the intensity of metamorphism and tectonic deformation of sulfide lodes.

(5) The crystallization of the visible native gold is related to the enlargement of its fine-grained intergrowths with ore-forming minerals and to the release of finely dispersed gold from sulfides affected by epigenetic hydrothermal alteration and involved in collective recrystallization. When arsenopyrite is replaced with fahllore, the gold initially contained in the latter is released with formation of separate mineral phase, e.g., as small droplike grains of native gold within fahllore in the severely metamorphosed ores at the Gai and Karabash deposits.

(6) The Au content in colloform As-bearing pyrite is higher than in euhedral pyrite crystals. This implies that gold in the recrystallized ore could partly replace Fe in the lattice of arsenian pyrite, as takes place at gold deposits. The transition of gold into the visible state is caused by the recrystallization of early pyrite and removal of As from sulfide ore and its fixation in tennantite, typical of the final mineral assemblages.

(7) Fahlore, which occupies 3–5 % of ore volume and contains 0.1–0.2 wt % Ag (occasionally up to 8 wt %), serves as the major concentrator of silver in ore. The silver contained in chalcopyrite, sphalerite, and pyrite also contributes to the total balance. The role of silver minerals (hessite, petzite, krennerite, stützite, native gold and silver, electrum) is insignificant.

(8) Submicroscopic native gold as inclusions and intergrowths with sulfides is the predominant mineral species of free gold. These intergrowths are not opened by grinding, while some amount of relatively coarse free gold turns out to be overground. All this leads to the loss of most gold. To augment the gold recovery, special gravitational and flotation regimes that prevent overgrinding of brittle and soft minerals of noble metals should be applied to the processing of particularly high-grade ore with a high percentage of free gold.

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