

## GOLD AND PGE IN MASSIVE SULFIDE ORE OF THE UZELGINSK DEPOSIT, SOUTHERN URALS, RUSSIA

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### ABSTRACT

The Uzelginsk deposit in the southern Urals, in Russia, is an example of a weakly altered classical massive sulfide deposit of the Uralian type. Pyritic Cu–Zn ore contains gold in two main modes: so-called “invisible” gold in sulfides, and mineral forms represented by native gold and tellurides. Gold and PGE concentrations in sulfides from the Uzelginsk deposit have been determined by instrumental neutron-activation analysis (INAA) and wet-chemical analysis with chromatographic and ICP–MS determinations in parallel. Most of the gold occurs invisibly in pyrite and in chalcopyrite, and ranges from 0.7 to 20 ppm and from 1 to 18 ppm, respectively. Sphalerite bearing fine-grained emulsion-like inclusions of chalcopyrite contains 1.8 to 10.6 ppm Au. The gold content of pure grains of sphalerite, as detected by INAA, is between 0.3 and 3 ppm. Tennantite is the main host of Ag; low-iron tennantite (0.1–0.6 wt.% Ag) is the dominant variety, whereas Ag-bearing tennantite (up to 8.4 wt. % Ag) is scarce. Considerable PGE enrichment (up to 354 ppb Pt, 1220 ppb Pd and 707 ppb Rh) was determined in heavy-mineral concentrates from Au-rich mineralization above the quite low levels of PGE background in the ore. Metamorphism of sulfide ores resulted in the redistribution of non-ferrous and precious metals and the formation of submicrometric inclusions of Au–Ag alloy and Au compounds with Te, Se, S, As, Sb and Hg. Some PGE are hosted by pyrite and may be sent to the tailings during processing; the remainder was deposited from a hydrothermal fluid during metamorphism and enriched the products of the latest paragenesis. Sulfide precipitation is shown to have occurred under conditions favorable for the incorporation of gold in solid solution in these minerals at high temperature (250–380°C). The paragenesis of native metals (gold, silver, tellurium and rhenium), tellurides and sulfosalts was formed at the latest stage of the hydrothermal processes, at 165–190°C.

*Keywords:* massive sulfide ore, gold, silver, platinum-group elements, Uzelginsk deposit, Southern Urals, Russia.

### SOMMAIRE

Le gisement de Uzelginsk, dans le secteur sud des Ourales, en Russie, est un exemple d'un amas classique de sulfures massifs à faible degré d'altération de type Ouralien. Dans le minerai pyritique à Cu–Zn, l'or se présente de deux façons, soit l'or dit “invisible”, dans les sulfures, et l'or dans une expression minéralogique, par exemple l'or natif ou sous forme de tellurures. Les concentrations de l'or et des éléments du groupe du platine (EGP) dans les sulfures de ce gisement ont été établies par activation neutronique et par analyses par voie humide, avec déterminations chromatographiques et par ICP–MS en parallèle. La plupart de l'or est invisible dans la pyrite et la chalcopyrite, entre 0.7 et 20 ppm, et entre 1 et 18 ppm, respectivement. La sphalérite montrant une émulsion d'inclusions très fines de chalcopyrite contient entre 1.8 et 10.6 ppm Au. La teneur en or de la sphalérite pure, telle que détectée par activation neutronique, se situe entre 0.3 et 3 ppm. La tennantite serait l'hôte principal de l'argent; la tennantite à faible teneur en fer (0.1–0.6% Ag, poids) est la variante dominante, tandis que la tennantite riche en Ag (jusqu'à 8.4%) est rare. Nous signalons un enrichissement notable en EGP (jusqu'à 354 ppb Pt, 1220 ppb Pd et 707 ppb Rh) dans les concentrés de minéraux lourds des zones minéralisées en or, par rapport aux seuils assez faibles des EGP dans le minerai en général. Le métamorphisme du minerai sulfuré a causé la redistribution des métaux autres que le fer, en particulier les métaux précieux, et la formation d'inclusions submicrométriques d'un alliage Au–Ag et de composés de l'or impliquant Te, Se, S, As, Sb et Hg. Certains des EGP piégés dans la pyrite sont donc répartis dans les rejets au cours du traitement; le reste de la fraction EGP a été précipité par le fluide hydrothermal lors du métamorphisme, et a enrichi les produits de la paragenèse tardive. La précipitation des sulfures a eu lieu à des conditions favorables à l'incorporation de l'or en solution solide dans ces minéraux, à une température relativement élevée, entre 250° et 380°C. L'association des métaux natifs (or, argent, tellure, rhénium), des tellurures et des sulfosels marque le stade ultime des processus hydrothermaux, entre 165° et 190°C.

(Traduit par la Rédaction)

*Mots-clés:* minerai de sulfures massifs, or, argent, éléments du groupe du platine, gisement d'Uzelginsk, Ourales du Sud, Russie.

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## INTRODUCTION

Volcanogenic massive sulfide (VMS) deposits currently provide 5% of the global production of gold and 40% of that of silver. There are seven giant VMS deposits in the Urals, each with Au reserves exceeding 100 tonnes, six of them containing more than 2000 tonnes of Ag reserves. The discovery of the largest deposits and a new VMS region in the Urals in the third quarter of the past century place this area in a leading position with respect to reserves of copper, zinc and associated gold, comparable only with those in the Iberian Pyritic Belt. Currently, half of the Uralian gold is produced from sulfide ores hosted by giant VMS Cu–Zn–Au–Ag deposits, with gold reserves in the range of 50–500 t. World-class deposits with a total (Cu + Zn) reserve of 3–10 Mt belong to the Uralian or Cu–Zn–pyritic type and contain ores with  $\text{Cu} \geq \text{Zn}$  (Gai, Sibai, Degtyar, Jubileynoe, Podolsk, Saf'yanovka) or  $\text{Zn} > \text{Cu}$  (Uchalinsk and Uzelginsk). A few small deposits seem to be analogues of the Kuroko type; they are classified as of Bajmak or Au–pyrite type (Alexandrinsk, Bakrtau, Baltatau, Tashtau, Maysk) (Prokin & Buslaev 1999). Ores of massive sulfide deposits associated with volcanic rocks of the Urals contain gold grades commonly ranging from 1 to 2 g/t (Uralian type) and from 2 to 5 g/t (Bajmak type), but can amount from 15 to 90 g/t. The increasing amount (now 18 billion tonnes per year) of processed ores has aggravated the problem of gold recovery: whereas copper and zinc are recovered in concentrates almost completely (75–85%), integrated recovery of gold in copper and zinc concentrates ranges from 20–25% (Uchaly) up to 55–30% (Gai). Loss of gold in the pyrite concentrate and tailings can amount to several tonnes for each of the large Ural mines (Uchaly, Gai, Sibai), making a total of 10–12 tonnes annually, as much as twice the Au recovered from massive sulfide ores. Gold occurs in the sulfide ore in two principal modes: 1) as free particles and inclusions of minerals with size of 1–200  $\mu\text{m}$  (free gold and tellurides, more rarely other compounds with As, Bi, S and Sn), and 2) invisible (refractory, submicroscopic) gold (Cabri *et al.* 2000b, Chrissyoulis & Cabri 1990, Genkin *et al.* 1998). The second mode predominates in VMS ores, but its nature has not been established in these deposits. The factors that favor the precipitation of gold in either invisible or mineral modes remain unclear. In this article, we focus on the distribution and relationship of structurally bound noble metals, including the platinum-group elements (PGE), in sulfides and as their own discrete mineral phases.

## GEOLOGICAL SETTING

Uzelginsk (54°07'N, 59°20'E) is one of the eight largest massive sulfide deposits of the Urals (Fig. 1). The ore-bearing structure is weakly deformed, and the deposit is considered to be typical of the Uralian type of

massive sulfide deposits (Prokin & Buslaev 1999). The so-called Magnitogorsk trough formed on the active margin of the Eastern European Craton, comprising ensimatic arc-related complexes of Ordovician to early Carboniferous age (Baranov *et al.* 1988). Numerous subvertical subvolcanic diabase and gabbroic dykes of various ages ( $D_2$ ,  $D_{3fr}$ ,  $C_1$ ) cut these volcanic complexes.

The orebodies are hosted by locally altered felsic rocks ( $D_{2e-gv_1}$ ). Thick piles of explosive breccias constitute the hanging wall of the ore lenses at the lower level; there are agglomerate and psephite breccias with lava or tuff as a matrix. Orebodies have the form of thick gently pitching lenses whose terminations wedge out at high angles. The total extent of a mining zone is 2 km (Fig. 2). The bodies range from 50 to 170 m in thickness and are located on two hypsometric levels, 130–380 m (bodies numbered 1, 5, 6, 9) and 420–640 m (bodies numbered 2–4, 7, 8) at distances of 300–350 m from each other. The large paleovolcanic structure is reminiscent of a stratovolcano.

Aphanitic and hypidiomorphic-granular textures are predominant in the ores. There are spherulitic and radial textures within kidney-shaped aggregates; the rhythmic zoning of pyrite is commonly marked by bands or fine inclusions of chalcopyrite, sphalerite or tennantite. Framboidal, metaglobular pyrite may be found. Cataclastic textures commonly occur in pyrite grains, and the clasts are cemented by calcite or secondary copper minerals without regeneration along the cracks. Analysis of the ore fabrics demonstrates a very low-grade postdepositional metamorphism (Vikentyev & Karpukhina 2000). Recrystallization occurs within narrow, steep and subvertical zones along contacts of orebodies as well as near contacts with diabase dikes.

## SAMPLES AND ANALYTICAL METHODS

Our study is based on the results of mineralogical mapping of the deposit, supplemented by detailed trenching and drill-core sampling. Mineralogical observations were carried out on polished sections, as well as on sulfide and heavy-mineral concentrates. Electron-microprobe analyses were carried out with a Cameca MS-46 and a Camebax SX-50 electron-probe micro-analyzers (EPMA), as well as with a JSM-5300 scanning electron microscope with an energy-dispersion spectrometer (EDS), and a Link-ISIS detector at the Institute of Geology of Ore Deposits, Mineralogy, Petrography and Geochemistry (IGEM), Russian Academy of Sciences, Moscow. Mineral compositions were determined at an accelerating voltage of 20 kV, with a beam 1  $\mu\text{m}$  in diameter, 20 nA and 10 s counting time. Analyses at 20 kV, 100 s and 100 nA were done for the determination of PGE and Au admixtures in minerals. The increased contents of silver in reniform pyrite were measured by EPMA at 20 kV, 100 nA and 200 s counting time. For standards, we used the pure metals Cu, Ni,

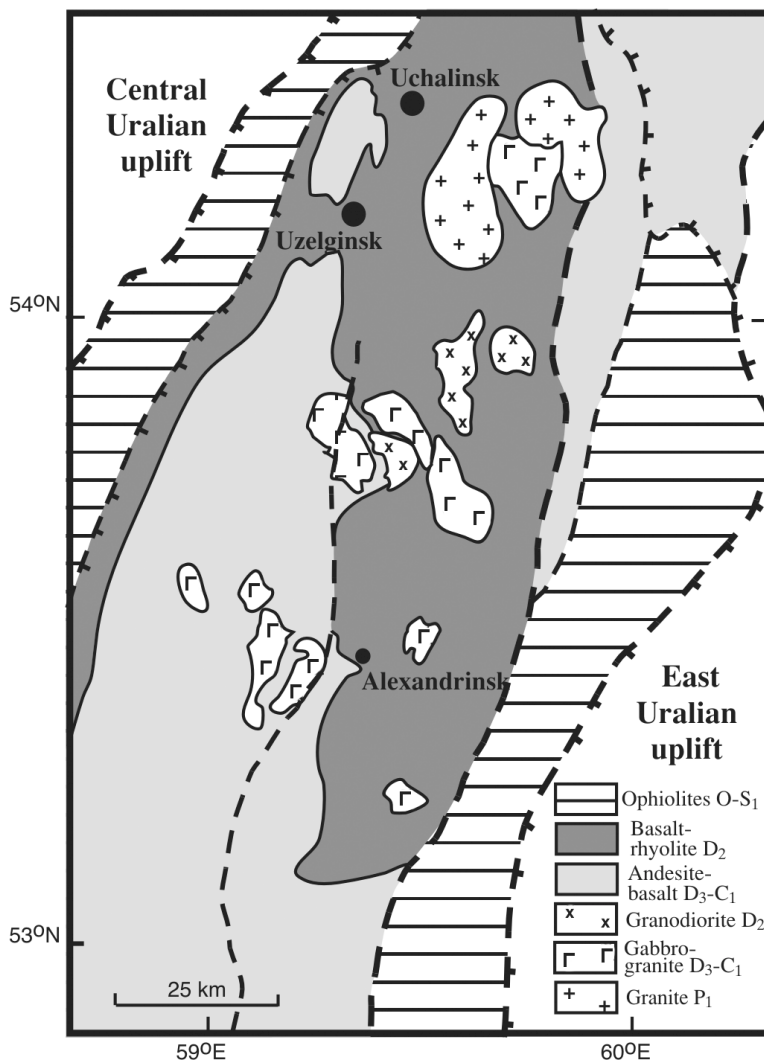


FIG. 1. Schematic geological map of the South Urals region.

Co, Au, Ag, Bi, Sb, Te, Se, and Ge, and the synthetic compounds  $\text{FeS}_2$ ,  $\text{ZnS}$ ,  $\text{HgTe}$ ,  $\text{InAs}$ ,  $\text{PbS}$ , and  $\text{CdS}$ . The concentrations of Au, Ag, base and rare metals in bulk samples and hand-made mineral concentrates were determined by instrumental neutron-activation analysis (INAA). The contents of PGE in 2–5 g of bulk samples, sulfide and ultra-heavy-mineral concentrates were determined by wet-chemical analysis with chromatographic and ICP-MS (IGEM RAS) determinations in parallel. The detection limits for the chromatographic method (ppm) are: Pt 0.02, Pd 0.01, Rh 0.001, Ir 0.002; for the ICP-MS method, they are: Pt 0.002, Pd 0.002, Rh 0.0005, Ru 0.0002, Ir 0.0005.

#### ORE GEOCHEMISTRY

The reserves of the Uzelginsk deposit at the beginning of 2000 were about 84 million tonnes with an average Cu content of 1.36 wt.% and 3.4% Zn, corresponding to about 1.140 million tonnes of copper and 2.850 million tonnes of Zn. The Cu–Zn ore is the prevailing type, with routine average contents: 1–1.5 wt.% Cu, 2.5–5% Zn, 1.8 ppm Au, 35 ppm Ag (Fig. 3). Massive ores make up about 90% of the reserves. The distinguishing features of the ores are: Hg enrichment (up to 900 ppm, routinely 14–25 ppm) and elevated As contents (ranging from 0.1 to 3.5 wt.%). Tellurium and in-

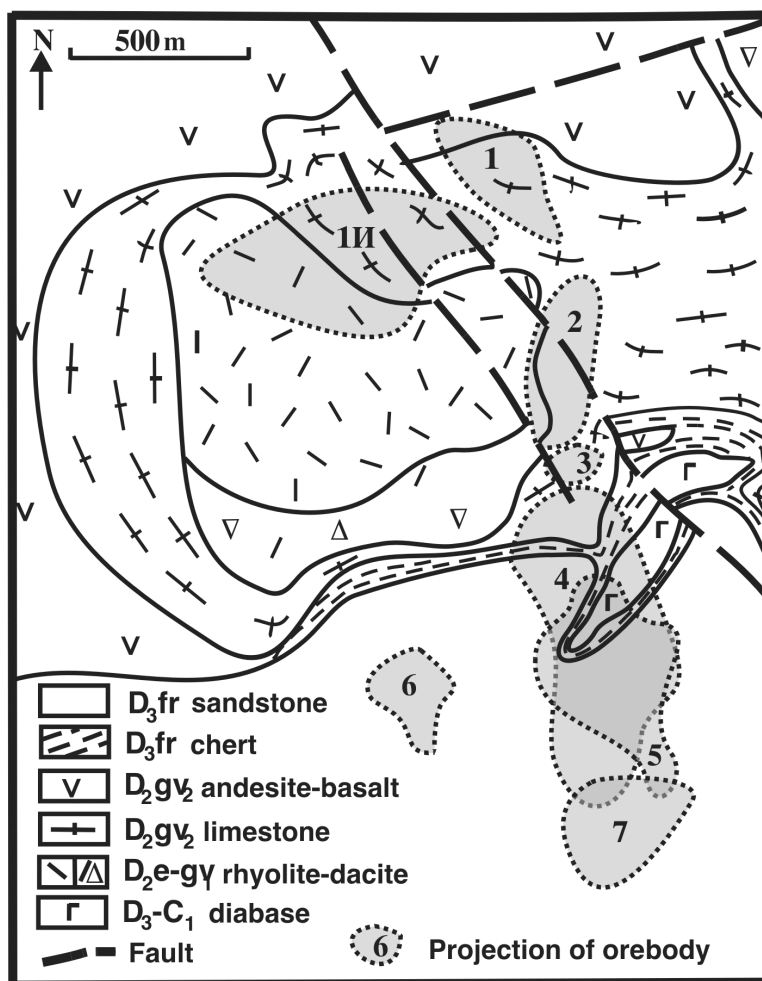


FIG. 2. Geological map of the Uzelginsk deposit.

dium contents range from 10 to 100 ppm and from 5 to 10 ppm, respectively.

The data on metal contents in the industrial concentrates permit estimates of losses in noble metals at various stages of processing (Table 1). Most unliberated gold accumulates in the final tailings and zinc flotation tailings, containing from 1 to 2 ppm of Au. From a third up to half of the silver is lost to the tailings.

#### PGE GEOCHEMISTRY

Ores of VMS deposits usually show low contents of platinum-group elements, yet selective PGE enrichment of some ore types or mineral associations has been noted (Dobrovolskaya & Distler 1998, Pan & Xie 2001). The results of PGE determination in concentrates and tail-

ings of the Uzelginsk deposit are given in Table 2. The PGE contents in most of the ore samples at Uzelginsk are at or below analytical detection limits. Some processing concentrates are characterized by increased PGE content. The maximum contents are found in zinc flotation tailings (sample 49-4 with Pt up to 188 ppb, Pd up to 318 ppb, Rh up to 21 ppb), consisting mainly of pyrite (more than 90 vol.%) with minor amounts of chalcopyrite and gangue minerals. These tailings are characterized by slightly increased contents of cobalt associated with pyrite. The elevated contents of Pt and Pd (up to 193 and 240 ppb, respectively) are also established in the final tails of the same sample. Ore from this sample is enriched in PGE also, though ore composition is typical and contents of other minor elements are slightly lower in comparison with other samples of

this study. The Pd/Pt value in the pyrite-rich technological products ranged from 1:15 to 7:1. PGE enrichment, particularly of Pd, is observed in other zinc tailings.

The highest concentration of PGE was found in ultra-heavy-mineral concentrates of ores rich in Au. These ultra-heavy-mineral concentrates, 0.028 g and 0.041 g in weight, were obtained by repeatedly washing in bromoform 50 g samples with initial contents of 22.8 and 11.1 ppm Au, respectively. The concentrates consist of pyrite (about 25 vol.%), galena (20%), altaite (20%), hessite (15%), petzite (5%), native gold (10%), with minor amounts of native tellurium and sulfides of base metals. The contents of PGE in the second sample exceed 2 ppm, and palladium is present at twice the concentration of platinum (Table 2). Up to 707 ppb of Rh was detected in one of these ultra-heavy-mineral concentrates. Ru is below the detection limit in both samples. Significant PGE enrichment in these concentrates may be connected to both tellurides and native gold. Assuming that such concentrates include the total PGE of ore, the initial content was estimated to be about 13 ppb, which corresponds well to the real PGE concentration in the ore.

ORE MINERALOGY

Pyrite is the dominant mineral of the ores (40–90 vol.%). Chalcopyrite and sphalerite are the major economic minerals (1–10, up to 30 vol.%). Tennantite is a common mineral in the lower-level orebodies (0.1–1 vol.%) and is widespread in the upper-level sulfide lenses (0.5–5 vol.%). Galena occurs widely, but in smaller quantities (0.1–0.5 vol.%). Pyrrhotite is abundant in the axial zone of the southern parts of the largest orebody of the deposit (body 4). Bornite, arsenopyrite, magnetite, marcasite, hematite, ilmenite, hessite,

stützite, petzite, altaite, coloradoite, molybdenite, sylvanite, tellurobismutite, native gold and tellurium are rare. Quartz, carbonates (calcite, ankerite, dolomite, siderite), white mica, chlorite and barite predominate among the gangue minerals; fluorite, andradite, epidote, zoisite, apatite and gypsum are rare.

The major morphological varieties of pyrite are kidney-shaped and euhedral grains. The euhedral variety ranges in size from tens of micrometers up to 5 mm; it is characterized by a zonal structure and is full of mineral inclusions. Kidney-shaped or reniform pyrite is characterized by elevated contents of arsenic (up to 1.35 wt.%), silver and nickel within distinct concentric zones (Table 3). Gold was not detected in these grains (detec-

TABLE 2. THE CONCENTRATION OF PLATINUM-GROUP ELEMENTS IN ORE AND PRODUCTS OF PROCESSING OF THE MASSIVE SULFIDE ORES, UZELGINSK DEPOSIT, RUSSIA

sample type	Pt	Pd	Rh	Ru	Ir	Pt/Pd
49-1 ore	45	35	7	0.2	-	1.29
49-2 Cu-Zn conc.	12	11	-	0.4	-	1.09
49-3 Cu conc.	4.5	5	21	3	-	0.90
49-4 Zn tails	188	318	16	6	0.35	0.59
49-5 Zn conc.	25	15	14	5	0.35	1.67
49-6 tails	193	240	4.8	0.25	-	0.80
55a ore	13	7	2	-	-	1.86
55b tails	4.5	7	3.2	-	-	0.64
55c Zn tails	23	1.5	3.2	-	-	15.33
55d Cu-Py conc.	3	4.5	9.2	-	-	0.67
55e Zn conc.	5	1	9	-	-	5.00
55f Cu conc.	25	10	8	-	-	2.50
55g Cu head	2	5	4.7	-	-	0.40
56a ore	1	4	5	-	-	0.25
56b tails	2.5	18	0.7	-	-	0.14
56c Zn tails	1.2	4.5	2.8	-	-	0.27
56d Zn conc.	1	1.8	6.8	-	-	0.56
56e Cu conc.	4	17	-	-	-	0.24
2267 Ultra-heavy conc.	375	804	-	-	1.8	0.47
2268 Ultra-heavy conc.	354	1220	707	-	-	0.29

The concentrations, quoted in ppb, were established by ICP-MS analysis; - below the detection limit.

TABLE 3. CHEMICAL COMPOSITION OF PYRITE IN THE MASSIVE SULFIDE ORES, UZELGINSK DEPOSIT, RUSSIA

N	As	S	Ag	Fe	Ni	Cu	Zn
<b>Reniform pyrite</b>							
1	0.3	53.17	0.199	46.4	0.04	0.03	-
2	1.05	52.22	-	46.12	-	0.07	0.3
3	0.26	52.66	0.027	47.19	0.02	0.08	0.04
4	1.35	51.48	-	46.16	0.06	0.32	0.22
5	0.25	53.2	-	46.3	-	0.09	0.81
6	0.63	53.44	-	45.61	0.05	0.07	-
<b>Euhedral pyrite</b>							
7	-	53.05	-	47.19	0.02	-	0.06
8	-	52.9	-	47.02	0.02	-	0.02
9	-	52.92	-	47.18	-	-	0.03
10	-	53.41	-	46.65	0.08	0.02	0.29
11	-	53.45	-	46.33	-	-	0.14
12	-	53.65	-	46.19	0.162	-	0.05
13	-	53.6	-	46.12	0.1	-	0.17
14	0.19	53.74	-	46.09	-	-	0.11
15	0.16	53.81	-	45.74	0.05	0.08	0.23
Limit of detection	0.02	0.046	0.016	0.045	0.02	0.02	0.03

The data are reported in wt.% and were established by electron-microprobe analysis.

TABLE 1. THE CONCENTRATION OF SELECTED METALS IN ORE AND PRODUCTS OF PROCESSING OF THE MASSIVE SULFIDE ORES, UZELGINSK DEPOSIT, RUSSIA

Sample	Co	As	Se	Ag	Cd	Sb	Te	Au	Hg
49-1 ore	13	1797	32	37	157	98	74	2.756	80
49-2 Cu-Zn conc.	13	2792	41	34		257	172	3.417	95
49-3 Cu conc.	8	3555	45	41		393	144	3.317	96
49-4 Zn tails	18	1825	30	32		78	103	3.202	35
49-5 Zn conc.	5	703	83			107	120	3.917	271
49-6 tails	13	1483	23	25		61	69	2.294	24
55a ore	123	851	88	51	130	63	251	2.739	92
55b tails	106	793	68	24	30	152	1.816		26
55c Zn tails	140	704	101	46	29	33	414	2.648	64
55d Cu-Py conc.	224	1273	135	97	382	101	1239	6.447	164
55e Zn conc.	26	261		116	1496	144	411	4.865	502
55f Cu conc.	122	1414	158	101	143	337	298	4.557	210
55g Cu head	78	454	165	79	195	96	201	3.130	185
56a ore	66	1272	79	37	87	128	234	1.857	114
56b tails	57	1121	69	13		34	102	1.258	24
56c Zn tails	67	1270	75	39		65	260	2.345	76
56d Cu conc.	76	642	91	208	1859	285	1231	4.902	708
56e Cu conc.	64	3960	118	128	275	1895	637	3.444	687
56f Cu head	41	1180	132	117	231	431	713	4.170	933

The concentrations, reported in ppm, were established by instrumental neutron-activation analyses. Blank: not determined.

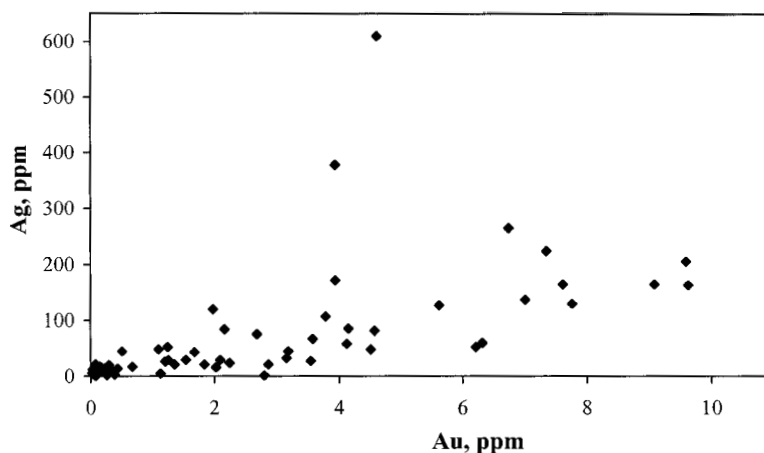


FIG. 3. Levels of concentration of Au and Ag in massive sulfide ore from zones enriched in gold in the Uzelginsk deposit (INAA data).

tion limit: 0.02 wt.%). Euhedral pyrite is depleted in both As and Ag.

Monomineralic fractions were prepared for determination of the Au content in these types of pyrite and other sulfides also. The INAA data show that pyrite is more enriched in Au (routinely 1.0–2.5, up to 20 ppm) compared with the other ore-forming minerals (chalcopyrite, sphalerite, pyrrhotite) (Fig. 4). Gold enrichment in reniform pyrite (5.5–20 ppm), usually containing chalcopyrite inclusions, was found. Gold-bearing pyrite with maximum Au contents (16–20 ppm) also has high contents of Ag (130–150 ppm) and Se (150–220 ppm). Pyrite with 6–11 ppm Au contains the following trace elements: Ag–As, Ag–Hg–Se, Au–Ag–Sb, Au–Ag–Sb–Hg. Tellurides, native tellurium and tennantite together with the main sulfides were detected as micro-inclusions in pyrite. Fine rounded micro-inclusions of native silver, less than 0.5  $\mu\text{m}$  in size, were found within a 2  $\mu\text{m}$  grain of Te-rich argentiferous tennantite (see below, Fig. 9c) under the electron microscope in a large grain of recrystallized kidney-shaped pyrite. This example suggests the possibility of the presence of both invisible silver and nano-inclusions of other Ag minerals within pyrite.

Sphalerite contains the usual amounts of Fe, within the ranges 0.3–0.6 wt.% (rarely up to 5.2 wt.%), 0.02–0.55 wt.% Cu (up to 4.9%), 0.02–0.4 wt.% Cd (up to 0.84%), and 0.6 wt.% Hg (94 analyses by EPMA). The positive correlation (coefficient of correlation 0.77) between Fe and Cu in sphalerite probably testifies to the presence of fine emulsion-type inclusions of chalcopyrite (“chalcopyrite disease”), considering the high content of Cu and known low solubility of copper in sphalerite (Brett 1964). Monomineralic fractions of sphalerite contain commonly 1.5–4.5 ppm Au. The

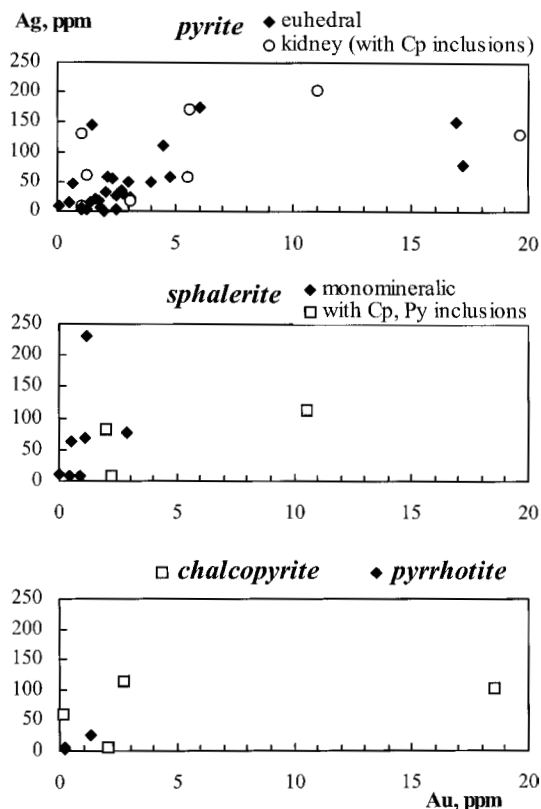


FIG. 4. Au and Ag contents in sulfides determined by INAA.

highest Au contents occur in sphalerite with the emulsion-like inclusions of chalcopyrite (1.8–10.6 ppm) as compared with the usual 0.9–3 ppm of gold in sphalerite without chalcopyrite inclusions. Tiny inclusions of gold-bearing chalcopyrite in sphalerite are considered to be responsible for most of the gold in the latter mineral. Gold-bearing sphalerite is characterized by trace amounts of Au–Ag–Sb–Hg, as determined by INAA for the monomineralic fractions.

The gold content of chalcopyrite averages 1.5–3 ppm (total range 1–18.6 ppm) by INAA. The most Au-enriched chalcopyrite contains 18.6 ppm Au, and is also rich in Ag, As and Hg, whereas that with 4–6 ppm Au is enriched with Hg and Se only.

A positive correlation between gold and silver in sulfides and at the same time a high dispersion of the contents seem to reflect the occurrence of some fraction of the gold as micro-inclusions of native gold and Au–Ag alloy. Elevated contents of other components (S, Sb, As, Hg, Te, Se) in some gold-bearing sulfide grains can account for the occurrence of other Au and Ag minerals. The presence of thin inclusions of tennantite–tetrahedrite (Ag–Sb–Hg-bearing in sphalerite and Ag–As–Hg-bearing in chalcopyrite) along contacts of grains of sulfides and inside the grains cannot be ruled out, considering that inclusions of such minerals were observed in pyrite.

The dominant variety of tennantite–tetrahedrite from more than 200 analyses is a low-iron tennantite (0.05–0.4 wt.% Ag by EPMA and EDS) (Table 4). The grains of tennantite are routinely anhedral in relation to other sulfides, forming fine poikilitic intergrowths with chalcopyrite, sphalerite and galena. In some cases, tennantite replaces separate zones of pyrite. High-Sb tennantite and tetrahedrite grains are commonly heterogeneous, with a mosaic internal texture or regular growth-zoning. The Ag content in tennantite from the upper-level ores

ranges from 0.1 to 0.6 wt.% (average 0.4 wt.% of Ag), whereas tennantite from the lower levels rarely contains more than 0.2 wt.% Ag. The largest concentration of Ag (0.2–0.5 wt.%) and Hg (up to 1–2 wt.%) in tennantite of the lower orebodies (bodies 3, 4) was found near contacts with mafic dikes and near the east end of orebody 4, where a subvertical shear-zone encounters massive ores. Among unusual trace elements, Se (0.14 wt.%), Pd (0.38 wt.% in one grain), Hg (0.05–0.3 wt.%) and Te (from 0.2 up to 4.5 wt.%) were found in some grains. Argentiferous tennantite within reniform pyrite from native gold-bearing association is extremely rich in Te (more than 8 wt.%) and Fe and depleted in Zn (Table 4, anal. 1, 2).

The composition of galena is characterized by low contents of trace elements close to the detection limits of the microanalyzer. Trace elements found are Se (0.1–0.2 wt.%, uniform), Te (0.1–0.14 wt.%), Au (0.05–0.2 wt.%), Pd (up to 0.14 wt.%) and Hg (near 0.1 wt.%, maximum: 0.25 wt.%).

#### RARE MINERALS OF THE GOLD-BEARING PARAGENESIS

The association of minerals enriched in Au and Ag mainly consists of argentiferous tennantite, Ag-bearing galena, bornite, various tellurides and native elements. Occurrences of this association are irregularly distributed within orebodies, coinciding with maximal development of the latest hydrothermal processes. They form fine disseminations and veinlets superimposed on the background of the earlier insignificantly metamorphosed mineral associations. Ore with this mineralization is characterized by high contents of gold and silver (up to 23 and 610 ppm, respectively). Native gold and gold minerals occur in samples whose Au content in ore is higher than 3–5 ppm.

TABLE 4. REPRESENTATIVE COMPOSITIONS OF TENNANTITE–TETRAHEDRITE FROM Au-BEARING ASSOCIATION IN THE MASSIVE SULFIDE ORES, UZELGINSK DEPOSIT, RUSSIA

	Ag	Pd	Hg	Fe	Cu	Zn	As	Sb	Te	Se	S	SUM
104-14* wt.%	8.14	-	-	5.39	32.81	3.33	8.13	1.60	8.21	-	30.79	98.41
104-14*	2.45	-	-	5.84	35.83	3.39	11.02	2.82	8.89	-	28.33	98.59
5466-142	0.36	-	0.07	1.5	42.33	7.63	14.11	9.22	-	-	25.99	100.78
5466-142	0.27	-	0.05	2.23	42.57	7.21	16.13	4.96	-	-	26.28	99.38
5466-142	0.25	-	0.09	1.22	42.1	7.73	14.06	9.47	-	-	25.68	100.26
UZ-51	0.14	-	0.05	1.83	43.47	7.55	17.33	2.71	-	-	27.72	100.61
UZ-61	0.12	-	0.21	0.37	35.79	8.86	2.48	26.32	-	-	24.21	98.03
UZ-32d	0.1	-	-	1.81	42.47	8.07	18.13	0.85	-	-	29.22	100.55
104-14	0.09	-	-	0.84	42.98	7.11	19.78	1.43	0.61	-	26.95	99.79
2267*	-	0.38	-	1.35	43.00	7.38	15.07	5.25	-	-	27.62	100.05
104-14	-	-	-	0.86	43.09	7.31	20.13	1.52	0.51	-	26.77	100.19
104-14*	-	-	0.13	0.63	41.14	5.57	11.61	9.86	3.99	0.14	26.17	99.24
2267*	-	-	0.22	1.97	40.81	6.78	17.55	3.57	0.24	-	28.52	99.74
104-14*	-	-	-	4.87	37.65	5.49	13.91	2.83	4.50	-	29.99	99.24

\* established by energy-dispersion analysis; the others: established by electron-microprobe analysis. -: Below the limit of detection. Blank: not analyzed.

Native gold forms grains and aggregates of about 10–50  $\mu\text{m}$ , and up to 150  $\mu\text{m}$  (Fig. 5a), whereas grains of less than 2  $\mu\text{m}$  are rare. Intergrowths of gold crystals with indistinct intergrain seams appear to be the most widespread, but separate single grains are common as well. In some cases, crystals of native gold have a cubo-octahedral habit, with smooth edges and rough a surfaces (Figs. 5b, 6b). The distinct idiomorphic isometric habit of crystals with smooth surfaces was established by electron microscope observation of ultra-heavy-mineral concentrates. Native gold with a xenomorphic shape forms a rim around aggregates of fine-grained and medium-grained pyrite (Figs. 5c, d). Platy gold represents intergrowths of numerous xenomorphic crystals of gold; deformed, bent and squeezed grains commonly have replicas of matrix minerals and in some cases contain inclusions of galena and altaite (Figs. 5e, f). Native gold and altaite can form symplectitic structures, in which large (up to 150  $\mu\text{m}$ ) grains of native gold contain fine irregular inclusions of altaite (Fig. 6). Considering that grains of both minerals are idiomorphic, such an intergrowth (Fig. 6a) is considered to be due to simultaneous growth in relatively free space; it is not an exsolution-induced texture. The fineness of native gold ranges from 772 to 870 (Table 5, Fig. 7). The Ag content varies from 13.23 to 19.2 wt.%, and incorporation (in wt.%) of Te (up to 3.01), Hg (up to 0.3), Fe (0.5) and Se (0.27) was found.

Petzite is less abundant; it forms large idiomorphic crystals up to 200  $\mu\text{m}$  in size with smooth round edges (Fig. 8a). It forms an intergrowth with galena and occurs as fine inclusions in galena and chalcopyrite. Selenium is the only trace element found in petzite (single occurrence, 0.49 wt.%, Table 6).

TABLE 5. CHEMICAL COMPOSITION OF NATIVE GOLD IN THE MASSIVE SULFIDE ORES, UZELGINSK DEPOSIT, RUSSIA

N	Au	Ag	Hg	Fe	Te	Se	SUM
1	81.17	16.86	0.07	-	3.01	0.05	101.16
2	81.89	16.76	-	0.13	0.38	-	99.16
3	81.96	17.37	0.10	0.22	-	-	99.65
4	82.20	17.66	0.13	0.13	0.10	-	100.22
5	82.27	18.47	-	0.31	-	-	101.05
6	82.42	17.52	-	0.50	-	-	100.44
7	82.74	17.28	-	-	0.53	-	100.55
8	82.83	16.70	-	0.33	-	-	99.86
9	82.39	14.89	-	-	0.14	-	97.42
10*	82.99	13.91	-	-	1.06	0.21	98.17
11	83.01	15.77	-	-	-	-	98.78
12*	83.14	13.28	-	0.27	0.84	0.27	97.80
13*	83.21	14.96	-	0.31	-	-	98.48
14	83.55	14.45	0.30	-	0.20	-	98.50
15*	83.77	15.54	-	0.42	-	0.21	99.94
16*	84.16	15.67	-	-	0.68	-	100.51
17*	85.93	14.47	-	-	-	-	100.40
18	86.60	13.56	-	-	-	-	100.16
19	86.97	13.26	-	-	-	-	100.23
20*	86.45	15.16	-	0.15	-	-	101.76
21*	87.35	13.23	-	0.23	-	-	100.81

The compositions were established by energy-dispersion analysis (\*) or by electron-microprobe analysis (the others), and are quoted in wt.%.

Among rare minerals, altaite and hessite are the most abundant (Table 6). Altaite forms fine emulsion-like inclusions and veinlets 1–5  $\mu\text{m}$  in size within pyrite and chalcopyrite, coarse octahedral idiomorphic smooth crystals (Fig. 8b) 20–200  $\mu\text{m}$  in size and, as recorded above, symplectitic inclusions in native gold (Fig. 6a). Several trace elements, *e.g.*, Fe, Se, Ag, Au and Hg, were detected (Table 6).

Hessite forms intergrowths mainly with galena and tennantite. Coarse round aggregates of hypidiomorphic hessite with small inclusions of pyrite and galena are widely developed in ores. Hessite, altaite, tennantite, galena and chalcopyrite form numerous veinlets cutting barite-sulfide ore. Stützite was found in galena-tennantite veinlets together with coloradoite and altaite (Table 6).

Coloradoite forms rare xenomorphic inclusions in pyrite 1–2 to 100  $\mu\text{m}$  in size (Figs. 8c, d) and also occurs in the veinlet mentioned above.

Native tellurium (Fig. 9a) is abundant. It commonly forms fine inclusions within pyrite up to 2–3  $\mu\text{m}$  in size or less, which are difficult to identify optically. Trace amounts of Au, Hg, Fe, and Se were detected.

Native silver forms small spherical grains of a porous nature in sulfide ore (Fig. 9b), and also spherical inclusions approximately 100 nm in size in argentiferous tennantite (Fig. 9c) hosted by a reniform aggregate of pyrite grains.

A grain of pure native rhenium 5  $\mu\text{m}$  across (Fig. 9d) was found in the ultra-heavy-mineral concentrate. No trace elements were detected in the micro-analysis.

TABLE 6. COMPOSITION OF TELLURIUM MINERALS IN THE MASSIVE SULFIDE ORES, UZELGINSK DEPOSIT, RUSSIA

Sample	Mineral	Ag	Au	Pb	Hg	Fe	Zn	Tc	Se	SUM
2266	Petzite	39.43	25.29	-	-	-	-	35.0	-	99.72
-	-	40.39	22.54	-	-	-	-	35.48	-	98.41
-	-	42.4	24.13	-	-	-	-	34.74	-	101.27
-	-	43.78	23.37	-	-	-	-	30.21	0.49	97.85
-	-	46.6	19.98	-	-	-	-	35.5	-	102.08
7	Stützite	55.52	-	-	0.20	0.38	0.73	40.62	0.10	97.55
6	-	57.61	-	-	0.18	0.20	0.37	41.44	0.08	99.88
8	-	58.07	-	-	0.14	0.19	0.15	41.52	0.05	100.12
27	-	59.63	-	-	0.00	0.20	0.70	40.59	-	101.12
16	Hessite	60.70	-	-	0.26	0.63	0.16	39.24	-	100.99
5	-	61.65	-	-	0.17	0.14	0.27	37.85	0.09	100.17
2266	-	61.73	-	-	-	0.96	2.28	33.56	-	98.53
2268*	-	63.88	-	-	0.02	-	-	35.22	-	99.12
23	Altaite	-	-	58.92	-	2.35	-	37.60	0.34	99.21
-	-	0.06	-	59.03	0.02	-	-	38.17	0.09	97.36
17	-	-	-	59.42	0.07	0.61	-	37.79	0.21	98.1
-	-	0.02	-	60.07	0.08	-	-	37.97	0.08	98.22
15	-	0.36	0.14	60.15	0.52	0.59	-	38.83	0.04	100.63
-	-	0.03	-	60.30	0.06	-	-	38.34	0.07	98.80
-	-	0.02	-	61.54	0.05	-	-	38.29	0.05	99.97
2267*	Native tellurium	-	0.19	-	0.18	1.20	-	99.84	0.22	101.63
2267*	Coloradoite	0.37	-	-	59.94	-	-	38.99	-	99.64

Coloradoite also contains 0.34 wt.% Sb. The compositions were established by energy-dispersion analysis (\*) or by electron-microprobe analysis (the others), and are quoted in wt.%. -: Below the limit of detection.



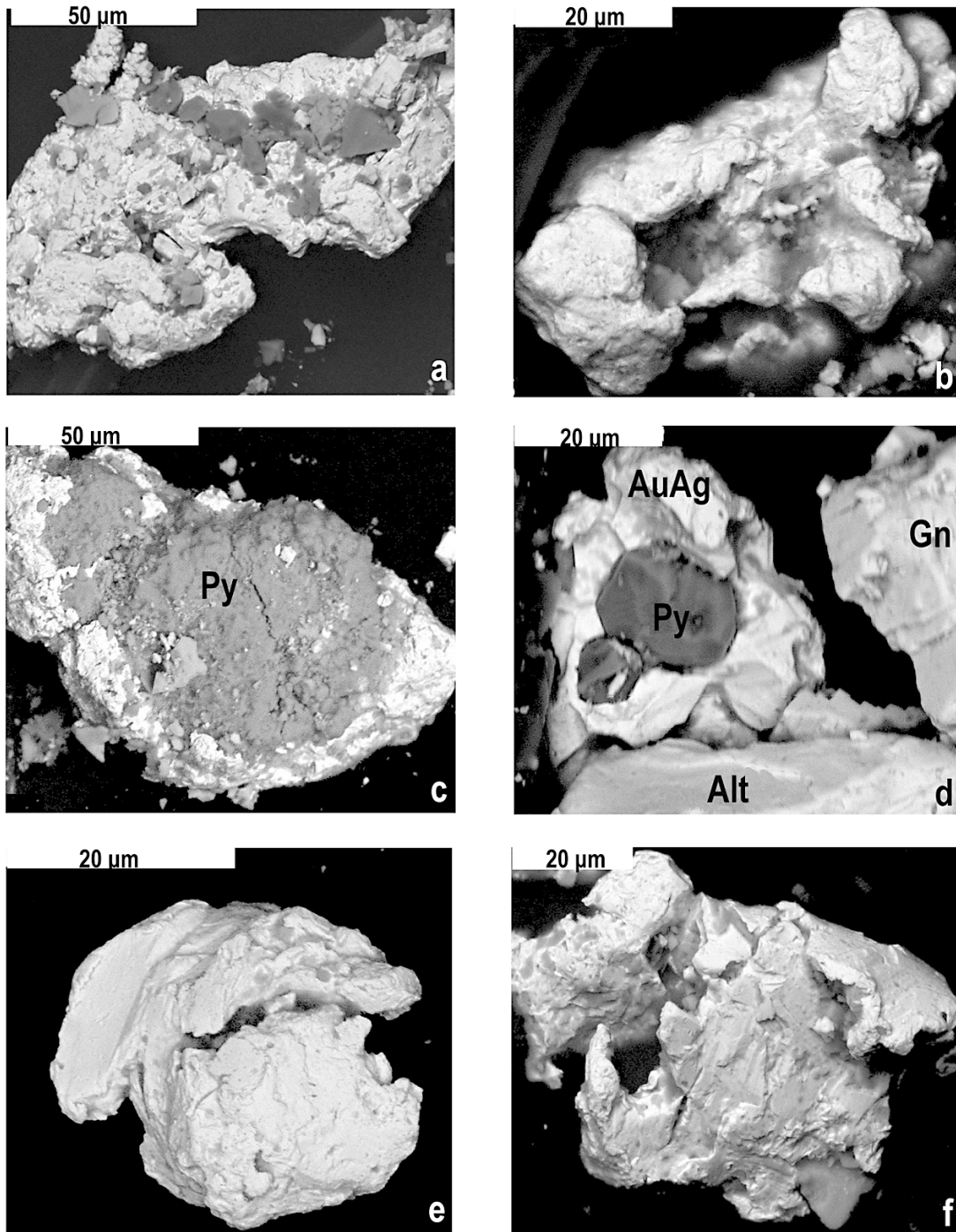


FIG. 5. Native gold from heavy mineral concentrates (SEM). a) Coarse aggregates of xenomorphic habit. b) Idiomorphic smooth crystals. c) Aggregate of pyrite (Py) surrounded by xenomorphic gold. d) Smooth crystals of pyrite surrounded by native gold. e, f) Morphology of xenomorphic aggregates, with casts of associated minerals.

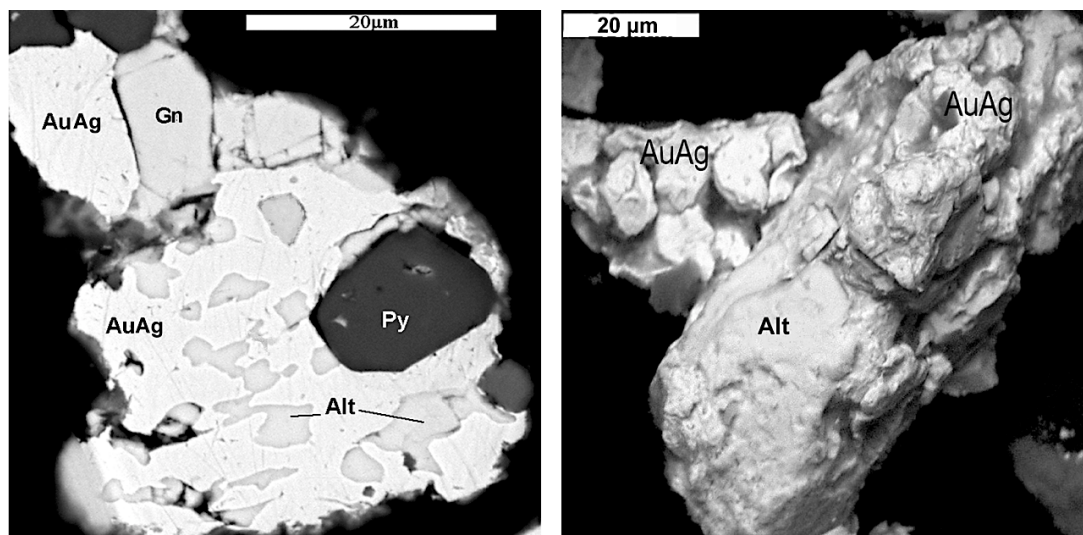


FIG. 6. Intergrowths of native gold and altaite (SEM). a) Polished grains. b) Heavy-mineral concentrate. Alt: altaite, Py: pyrite, Gn: galena.

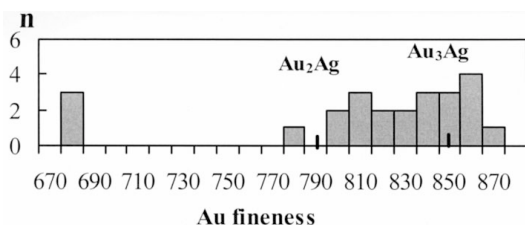


FIG. 7. Gold fineness in Uzelginsk ores (EPMA and EDS data).

#### PARAMETERS OF ORE DEPOSITION

The conditions of mineralization were established by the study of fluid inclusions in opaque minerals of unmetamorphosed and recrystallized ores (Vikentyev & Karpukhina 2000). Fluid inclusions were studied to determine their temperature of homogenization ( $T_h$ ) with an accuracy of  $\pm 2^\circ\text{C}$ . Salinity was obtained from a measured melting point of ice with an accuracy of  $\pm 0.2^\circ\text{C}$ , and the eutectic temperature is known with an accuracy of  $\pm 1.5^\circ\text{C}$ . The pressure was estimated from  $\text{CO}_2$  phases and PVT data.

Primary inclusions in quartz, barite and carbonates from the orebody are liquid-rich. The observed temperature reflects the extent of transformation of the epigenetic ore. The temperature of homogenization of inclusions in fine-grained ore with colloform relics is lower ( $137\text{--}200^\circ\text{C}$ ) than in recrystallized coarse-grained ore ( $200\text{--}300^\circ\text{C}$ ) and vein-type ore, whose inclusions

have homogenization temperatures in the range of  $270\text{--}378^\circ\text{C}$ . For minerals hosted by altered rocks, the  $T_h$  of fluid inclusions ranges from  $140$  to  $335^\circ\text{C}$ . The dominant temperature of ore deposition was  $150\text{--}200^\circ\text{C}$  (up to  $300^\circ\text{C}$ ) for the orebodies of the upper level, and  $250\text{--}300^\circ\text{C}$  (up to  $378^\circ\text{C}$ ) for the lower level.

Two main types of fluids were distinguished: (1) potassium bicarbonate – chloride and (2) sodium chloride (modified seawater). Salinity ranges from 1 to 10.7 wt.% NaCl equiv., being usually 2–3 times higher than that of seawater. Fluid (1) is distributed in ore and altered rocks associated with high-temperature zones, whereas fluid (2) occurs on flank zones, characterized by a lower temperature. Fluid 1 can be interpreted as juvenile in terms of its composition and spatial distribution. The  $\text{H}_2\text{O}\text{--}\text{CO}_2$ -bearing fluid inclusions are found in a wide zone below orebodies of the upper level, extending to a depth of 500 m. The pressure values for the Uzelginsk deposit appear to be in the range of 0.6–1.0 kbar. Evidence of boiling of the hydrothermal solution was found in the host rocks. According to argentian gold – sphalerite geothermometry (Shikazono 1985), the crystallization of native gold in association with tennantite and chalcocopyrite occurred over the range  $165\text{--}190^\circ\text{C}$ , with  $10^{-15.5} < f(\text{S}_2) < 10^{-14.3}$  and  $f(\text{O}_2) \approx 10^{-27.5}$ .

#### DISCUSSION

Gold and silver are relatively uniformly distributed in the massive sulfide ores of the Urals (average values for the deposits 0.5–1.5 ppm of Au, 10–50 ppm of Ag),

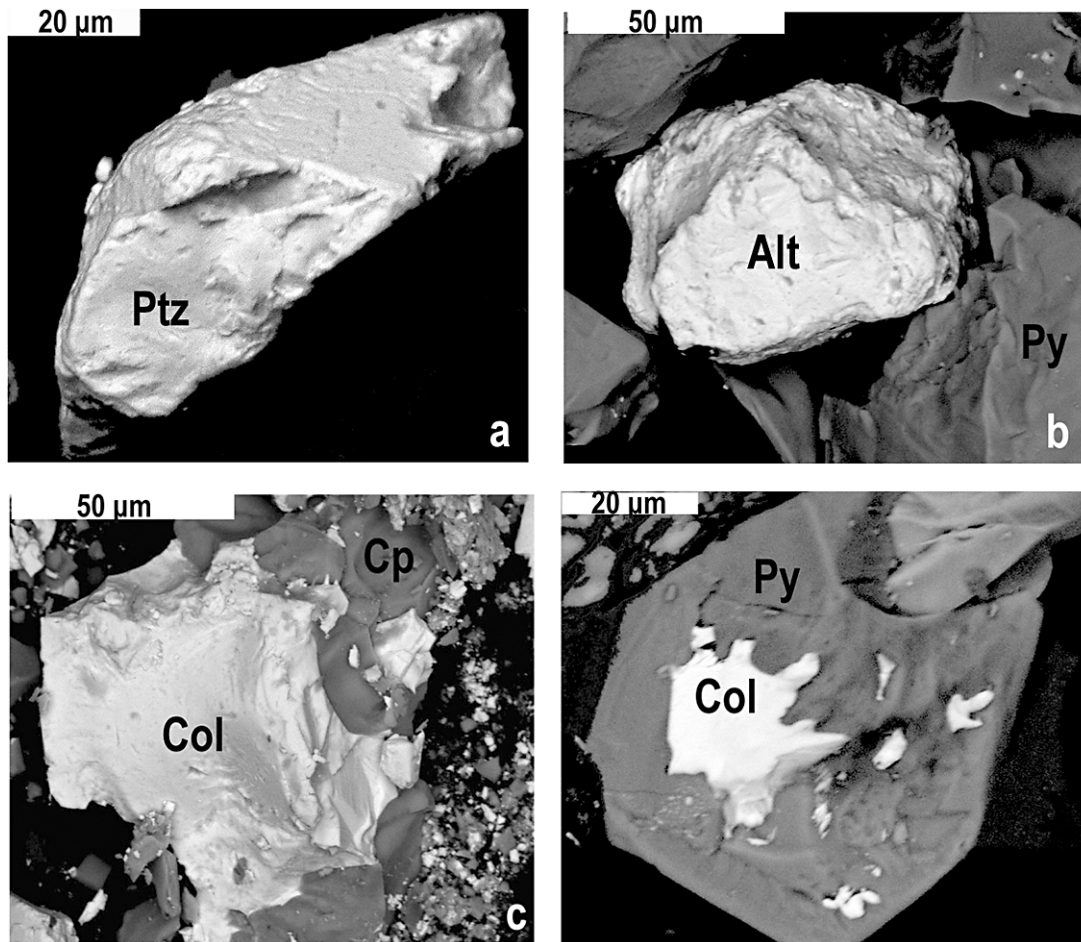


FIG. 8. SEM photographs of tellurides from heavy-mineral concentrates. a) Idiomorphic crystal of petzite (Ptz). b) Idiomorphic smooth crystal of altaite (Alt). c) Grain of coloradoite (Col) with chalcopyrite. d) Xenomorphic grains of coloradoite within pyrite crystal.

but local enrichments occur (up to 10–90 ppm of Au and up to 150–600 ppm of Ag). Most (50–90%) of the gold in the common VMS ores (0.5–2 ppm Au) is incorporated in the sulfides in the form of “invisible” gold, such that Au is sent to the tailings, mainly with the pyrite. Milling of VMS ores proceeds without primary gravity separation at the most of Uralian concentrating plants. The Au contents in the flotation Cu and Zn concentrates are commonly 20–30% more than in the ores and range from 1.5 to 3 (rarely up to 5) ppm. Most of the unliberated gold accumulates in pyrite concentrates and tailings containing 1–1.3 ppm of Au. Silver occurs mainly as a solid solution in minerals of the tennantite–tetrahedrite series. From a third up to a half of the silver also is lost to the tailings. Thus most of Au, Ag, Pb, Se, Te, As, Hg, Bi, and Sb, as well as a notable part of Cu,

Zn and Cd, form part of the tailings and may appear as heavy-metal pollutants.

Investigators of Uralian VMS deposits have pointed to the late superimposed character of coarse-grained native gold (*e.g.*, Novgorodova *et al.* 1977). The paragenetic associations with high-fineness native gold can have different compositions of minerals depending on the temperature of reworking and on the geochemical characteristics of the ore. Geochemical specialization and enrichment in specific trace elements are related to peculiarities of ore composition which, as shown for massive sulfide deposits (Ohmoto 1996), are in turn determined by the composition of the ore-bearing magma. A possible cause for the formation of a late paragenesis with coarse gold is regional metamorphism with redistribution of metals.

Most of the gold in unaltered modern oceanic sulfides is invisible (Cabri *et al.* 2000a), and observations of visible particles of gold are extremely rare (Hannington *et al.* 1995). Studies of sulfides from many gold and some VMS deposits show that chemically bound gold plays a significant role in the total budget of this metal in ores. It is concentrated in solid solution in sulfides at the early stages of mineralization (Bortnikov *et al.* 2003, Chrissoulis & Cabri 1990, Genkin *et al.* 1998, Larocque

*et al.* 1995). However, the linkage between formation of a post-ore paragenesis of noble metals and metamorphism is difficult to reconcile with the ubiquity of such associations in various unmetamorphosed deposits (Huston 2000). Development of late hydrothermal associations and redistribution of dispersed trace and noble elements have been established in particular for the young, weakly altered VMS deposits of Japan (Ohmoto & Skinner 1983). The high incidence of late noble-metal-bearing parageneses over a large number

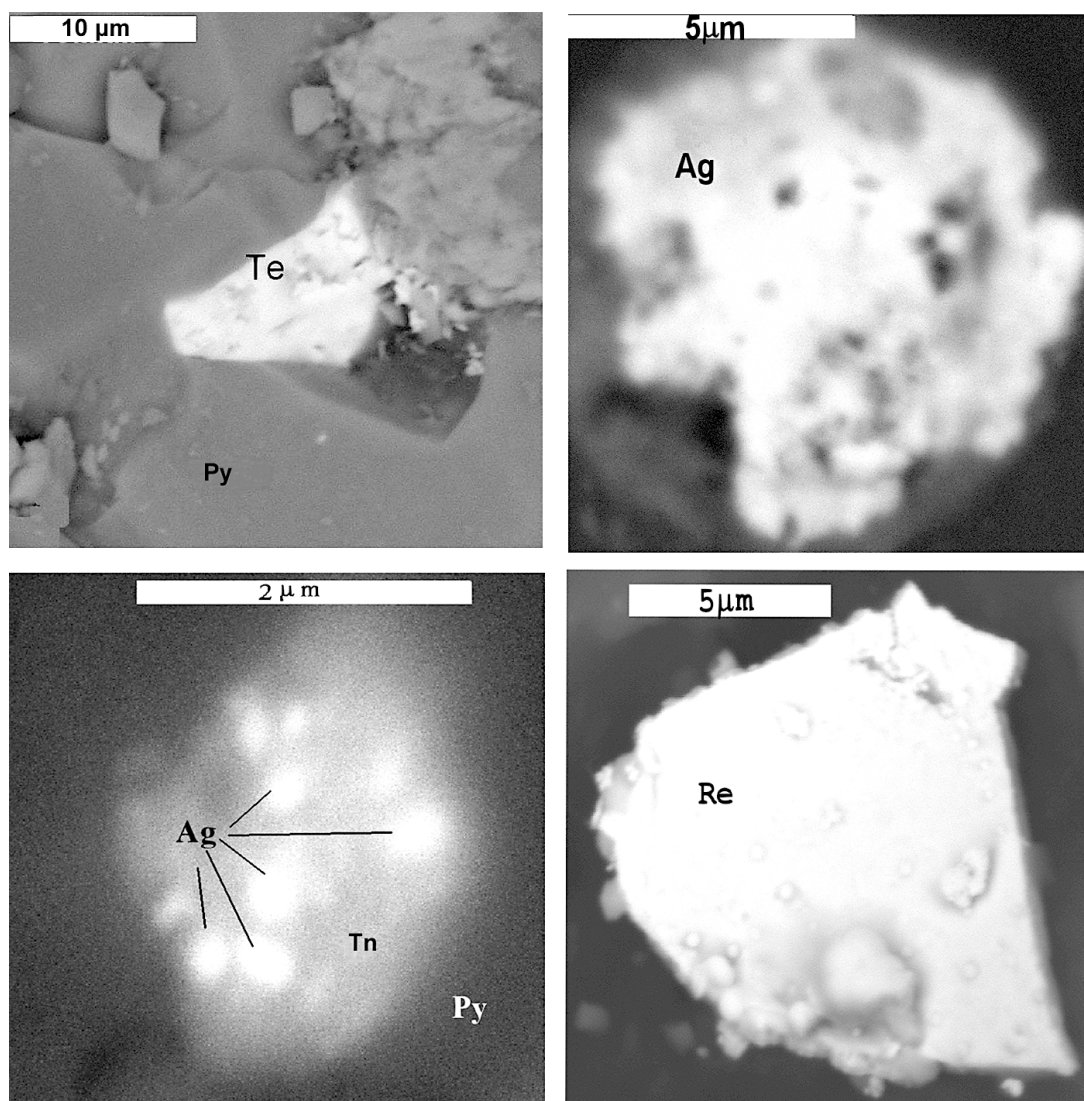


FIG. 9. Native elements encountered in the Uzelginsk ore (polished sections, SEM). a) Native tellurium (Te) in pyrite (Py). b) Rounded grain of porous native silver. c) Globules of native silver within tennantite grains (Tn) in reniform pyrite (Py). d) Native rhenium.

of VMS deposits suggests that its formation is a regular stage of their hydrothermal evolution.

Thermodynamic calculations reveal that fluid equilibrated with sulfide gold-rich ores at 275 to 350°C is undersaturated by an order of 0.7 to 1.0, relatively to Au<sub>S</sub> (Bortnikov *et al.* 2003), which suggests that gold deposited under these conditions is “invisible” gold, in solid solution within sulfides. Precipitation of metallic gold probably occurs below 250°C. Ores enriched in metallic gold can be deposited from 200° to 150°C. These conditions are attained at the latest stage of ore formation by infiltration of fluid through a sulfide body (Bortnikov *et al.* 2003). This stage is quite distinct, and its occurrence is confined to the fissured and permeable zones, where veins and disseminations of reprecipitated minerals accompany the concentration of certain trace elements. This paragenesis in ore of the Uzelginsk deposit contains various native metals (gold, silver, tellurium and rhenium); these metals remain largely dispersed in sulfide minerals, however, because the remobilization process was not pervasive. The presence of large amounts of structurally bound components leads to important losses during ore processing.

Structurally bound gold may be a major mode of gold occurrence in sulfide–gold and VMS deposits (Chryssoulis & Cabri 1990, Cook & Chryssoulis 1990, Genkin *et al.* 1998, Marion *et al.* 1991) in pyrite and other sulfides, and in modern submarine sulfide mounds (Cabri *et al.* 2000a, Bortnikov *et al.* 2003), in Fe sulfides (up to 31.6 ppm) and Cu–Fe sulfides (up to 9.3 ppm). Usually, the high Au content in pyrite correlates with a high As content, with the following maximum values for Au and As, respectively: 1400 ppm and 9.6 wt.% (Fleet *et al.* 1993), 4000 ppm and 13 wt.% (Fleet & Mumin 1997, Hofstra & Cline 2000, Simon *et al.* 1999), 11057 ppm and 16.6 wt.% (Pals *et al.* 2001). Increased As contents (up to 1.35 wt.%) have been also found in the gold-bearing (up to 20 ppm) reniform pyrite in the Uzelginsk deposit.

Cabri *et al.* (2000a) have shown that the highest concentration of invisible gold occurs in pyrite from a sphalerite-rich sample of modern massive ores, and that Au associated with sphalerite is actually in the chalcopyrite that occurs as micro-inclusions in the sphalerite. In the case of Uzelginsk ores, the Au contents in sphalerite with emulsion-like inclusions of chalcopyrite are noticeably greater than those in inclusion-free sphalerite.

Because the PGE contents in VMS ore are quite low, the remobilization process does not concentrate them sufficiently to form discrete mineral phases, unlike the other trace elements (Sb, As, Te, Ag, Au, Hg). However, PGE enrichment is established for ultra-heavy-mineral concentrates consisting of tellurides, galena and native gold, indicating that PGE have been mobile and could be redistributed together with gold and tellurium by the same late processes. The level of total PGE concentration in massive sulfide ore, as well as that of the other trace elements, are inherited from their initial dis-

tribution in the parent ore-bearing magma. VMS deposits connected with felsic or intermediate rocks, depleted in PGE, are potentially poor sources of PGE, unlike the Uralian type confined to felsic volcanic rocks, which are in fact differentiates of mafic magmas. In the case of several world-class VMS deposits, the elevated concentrations of the PGE are considered to reflect the influence of superimposed metamorphic processes (Pan & Xie 2001). In addition, the extreme fractionation of PGE and Au has been considered to result from the differential solubility of transporting complexes of these elements. Significant fractionation of PGE and gold has not been observed in Uzelginsk ore; moreover, the increased content of Pt in concentrates of ultra-heavy minerals corresponds to an increased content of Pd and Rh, which suggests a common mechanism of their redistribution.

Experimental data show that invisible gold is expelled from host sulfides during heating and is partitioned into fluid and other sulfides and arsenides (*e.g.*, Bürg 1930). Mountain & Wood (1988), Wood *et al.* (1992) and Zhang & Spry (1994) have found in their experiments that parameters of solubility, migration and deposition of hydrosulfide and ammonium complexes are relatively similar for Au, Pt and Pd. The solubility of Au as a bisulfide complex is more likely in environments of massive sulfide ore, being three orders higher than that of Pt and Pd (Gammons & Williams-Jones 1997). Gold is extremely soluble at high temperatures and migrates easily as a chloride complex also. The higher solubility of Au than PGE in hydrothermal fluids and its interaction with a large number of different complexing agents allow for more significant accumulation of gold (Wood 2002).

The fields of stability for platinum and palladium tellurides overlap those for gold and silver tellurides on the  $f(\text{O}_2)$ –pH diagram. Mineralogical data suggest that Pt and Pd are able to precipitate as tellurides, arsenides, *etc.*, and the presence of such elements as Se, Te, As, Sb in solution can lead to sufficient PGE enrichment even in environments unsaturated in PGE. The possibility of PGE impurity in tellurides is confirmed by observations of melonite with 0.4–1.8 wt.% Pd in massive sulfide ore of the Pyshminsko–Kluchevskoe deposit, Middle Urals (Eremin *et al.* 1997). The suggestion of a link between the formation of tellurides, native gold and PGE is not new. Zvyaginzev (1936) documented elevated contents of the PGE in altaite and native gold from recrystallized coarse-grained ore from the Rudny Altai VMS deposits (Republic of Kazakhstan, currently). Those data were obtained by wet-chemical analyses, with a total PGE content in some monomineralic fractions of altaite and native gold (up to 10 ppm Pt, 60 ppm Pd, 2 ppm Rh and 2 ppm Ir). If the simultaneous accumulation of PGE and gold could be confirmed with further investigations, it would allow consideration of the conditions for their joint concentration in mineral-processing products of pyritic ore.

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