NEW DATA ON MINERALOGY OF DEPOSITS OF PLUTONOGENIC GOLD–QUARTZ FORMATION IN THE NORTHERN CENTRAL KAZAKHSTAN. PART I

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The formation history of mineralogy of plutonogenic gold-quartz deposits of the Stepnyak group in the Northern Central Kazakhstan is discussed. Mineral facies referred to the depth of the deposit formation; mineralogical features of ore shoots, nature of ore-bearing fluids, white micas, quartz, carbonates, scheelite, pyrite, arsenopyrite, pyrrhotite, gersdorffite, sphalerite, berthierite, argentotennantite, argentotetrahedrite, roshchinite, bismuth tellurides and sulfotellurides, mattagamite, Co-bearing frohbergite and melonite, montbrayite, calaverite, sylvanite, petzite, petzite-hessite solid solution, and hessite are reported. The deposition sequence from Au to Ag tellurides and affinity for Te: Co > Fe, Ni > Bi, Sb > Pb > Ag, Hg > Au, Cu are improved.
10 figures, 8 tables, 60 references.
Keywords: scheelite, mattagamite, frohbergite, melonite, montbrayite, calaverite, krennerite, sylvanite, petzite-hessite solid solution, affinity to Te.

Despite many reviews, current state of geology causes genetic typification of gold deposits. One of the ways is the detailed study of specific gold formations, and separate gold provinces and deposits.

Hydrothermal gold deposits are frequently referred to the three formations on the basis of the formating depth: (1) shallow (with abundant sulfides, low-fineness gold, Ag sulfosalts), (2) medium (with moderate sulfides and relatively low-fineness gold), and (3) deep (low sulfides with high-fineness gold) (Petrovskaya *et al.*, 1976). This conventional in our country classification is not up to the recent geological standards. For example, many deep-seated deposits are enriched in sulfides; low-sulfide deposits with high-fineness gold are abundant among shallow deposits; some deposits with features typical of shallow deposits were formed at the depth of 1.5 – 2 km; the deposits with features characteristic of deep-seated deposits were formed at the same depth. The classification of hydrothermal gold deposits on the basis of host rocks (many US researchers) or basic formations (groups of large-volume deposits of sulfide ores) is unconvincing. The classifications of Lindgren (1933), Schneiderhöhn (1941), Bilibin (1947), Ramdohr (1980), Smirnov (1982), and similar classifications of Ivensen and Levin (1975), and Spiridonov (1995; 2010) taking into account geological features of gold deposits and in particular magmatic rocks to which mineralization is related are better argued. Hydrothermal plutonogenic formations of folded areas, volcanogenic formations of folded areas, arcs, and mid-oceanic ridges, volcano-plutonogenic formations, and amagmatic formations are distinguished on the basis of type of magmatic rocks, which immediately predated or accompanied gold mineralization.

Plutonogenic hydrothermal gold-quartz formation. The deposits of the plutonogenic gold-quartz beresite-listvenite formation are paragenetically related to tonalite-granodiorite-plagiogranite, adamellite, and monzonite-granite intrusive complexes of folded areas. These deposits are formed in closed system under elevated pressure (P). The P value is determined by the top of hydrothermal system located close to the roof of intrusives or slightly above. The lowest pressure estimated from fluid inclusions (FI) in the early quartz and carbonates of the ores ranges from 0.3 to 0.6 kbar (Spiridonov, 1995; Trumbull *et al.*, 1996) that corresponds to the shallowest formation depth of 1 to 1.5 km; the highest values reach 3.5 – 4 kbar (cca. 12 – 15 km) (Spiridonov, 1995; Hagemann and Brown, 1996; Mishra and Panigrahi, 1999; Jia *et al.*, 2000). The P values higher than 4 kbar correspond to the metamorphosed ore. The Early Archean to Cenozoic plutonogenic gold deposits were formed under relatively stable pressure at gradual temperature decreasing. Subtle (to disappearance) vertical geochemical and mineralogical zoning is typical (Smith, 1948; Naz'mova *et al.*, 1978; Spiridonov, 1995). Long vertical extension of gold mineralization is typical: 4.5 km, cca. 5 km taking into account erosion level at Kolar, India; cca. 3 km at Moro Velho, Brazil; cca. 2.5 km at Ashanti, Ghana; cca. 2 km at dozen deposits in Canada, Africa, Australia, and Kazakhstan.

North Kazakhstan gold province. The North Kazakhstan gold province localized in the western Caledonian megablock of the Northern Central Kazakhstan (Bogdanov, 1959, 1965; Shul'ga and Bulygo, 1969; Geology...,

1971) comprises Stepnyak megasinclinorium (East-Kokchetav depression) and adjacent regions. In the western megablock, granitoids and metamorphic sequences with the Proterozoic granitic gneiss domes are abundant (Spiridonov, 1982_1); ultramafic rocks and olistostrome sequences are less common; and gold mineralization is mainly plutonogenic. The Proterozoic metamorphic sequences form "granitic layer" of the Earth crust of the region that underlays in places the Archean granulite layer according to xenoliths in the Stepnyak pluton. The outlines of the ancient continental mass are marked by the chains of zircon and rutile paleoplacers hosted in the Late Riphean to Vendian quartzite-sandstone in the Kokchetav, Ishke-Ulmes, and Erementau Rises (Shlygin, 1962; Spriridonov, 1987_1, 1991). At the Caledonian stage, the Earth crust of the region was substantially altered. For example, in the Kokchetav Rise (middle massif) the Zerinda granodiorite-adamellite batholith with $^{86}Sr/^{87}Sr = 0.703_5$ – (Shatagin, 1994) that is age and formation analogue of the Krykkuduk Complex of the Stepnyak Depression was arisen among metamorphic sequences with $^{86}Sr/^{87}Sr =$ 0.716.

In the eastern Maikain megablock, there are numerous ultramafic bodies and olistostrome sequences; granitoids are few; gold mineralization is referred to the massive-sulfide type (Geology..., 1971); this area is developed on the crust of ocean type.

The Caledonian Stepnyak megasinclinorium comprises the Stepnyak and Selety depressions (sinclinorium) and Ishke-Ulmes Rise (anticlinorium) (Shul'ga and Bulygo, 1969). Gold deposits are located within these structures close to the boundaries between them. As all over the world (Nesbitt, 1988), mesothermal gold-quartz deposits of the Stepnyak group are hosted in the upper part of continental crust within the zone of brittle deformation above isotherm 400°C.

Gold deposits of the Stepnyak group

Why this group of plutonogenic gold deposits is of the greatest interest? Because these deposits are located in non-linear folded area and are not affected post-ore tectonization and metamorphism; they are located in the Caledonian folded structures. Here, there are extremely shallow to highly deep-seated coeval deposits, which are unusual in Mezo-Cenozoic and Pre-Paleozoic folded areas. All crucial deposits are opened by mines and deep drill holes because unlike Uzbekistan, no giant gold deposits were found here. In addition, mineralogy and geology of these deposits are studied in detail including geological, petrographic, geochemical, and mineralogical survey of 1:4000 to 1:1000 at Stepnyak down to 300 m below surface (Spiridonov, 1986), and Bestyube and Zholymbet down to 600 m (Spiridonov *et al*., 1986_1); 3D geological, geophysical, mineralogical and geochemical survey of 1:25,000 to 1:10,000 in the Aksu ore field including deposits Kvartsitovye Gorki, North and South Aksu, and Budennovsk down to 900 m below surface (Spiridonov *et al*., 2002).

Geological setting of the deposits. The largest Stepnyak-group deposit Bestyube is located at the joint of the Ishke-Ulmes anticlinotium and Selety sinclunorium. Large deposits Zholymbet, Kvartsitovye Gorki, and Aksu are located at the joint of the Stepnyak sinclinorium and Ishke-Ulmes anticlinorium in the zone of meridional transregional Omsk-Tselinograd deep fault, it was transected by the NW-trending faults for example the Atansor Fault and others. Large deposits are spatially related to the smallest intrusions of granodiorite formation and are distal from large intrusions.

The major Caledonian gold deposits in North Kazakhstan are related to small intrusions of the Stepnyak type, which were referred to the Stepnyak Complex (post-batholite formation of small gold-bearing diorite intrusions) (Bilibin, 1945) that is younger than the Krykkuduk Complex (tonalite-granodiorite formation). Recently it was proved that the Stepnyak-type intrusions and major gold deposits are the products of the Late Ordovician Krykkuduk Complex (Spiridonov, 1968, 1986, 1995; Spridonov *et al*., 1986_1, 1986_3, 2002). Small gold-bearing intrusions and dykes to which the deposits are paragenetically related belong to the inversion stepnyakite-tonalite-granodiorite formation with the age of 445±5 Ma. Low and poor-sulfide deposits of the Stepnyak group Bestyube, Zholymbet, Kvartsitovye Gorki, Stepnyak, and Aksu belonging to the Late Ordovician plutonogenic gold-quartz formation with the age of 445 ± 3 – 5 Ma are opened by mines down to 450 – 1100 m below surface and drill holes, down to 1200 – 1700 m. Other types of hydrothermal-metasomatic formations are rather developed at these deposits. There is a negative correlation between size of ore-bearing intrusion and related ore concentration that indicates deep-seated source of gold (Spiridonov, 1995).

Characteristics of plutonogenic gold-quartz formation. The ore formation comprises quartz and carbonate-quartz veins and stockworks, mineralized berisitized and listvenitized rocks including skarns and breccias of erupted hydrothermal pipe-like bodies. The structure of the deposits ranges from simple (occasional veins and lenticular stockworks) to very complex (numerous systems of ore veins, stockwork zones, and mineralized metasomatites). All deposits are root; compression and related low-amplitude gapping faults are typical; and multi-system fracture structures are common. Fractures filled by ore veins are shear with overfault movement along them. The main ore veins frequently proceed along dykes of microdiorite and spessartite. Ore stockworks occur both at contacts and within dyke-type intrusions and dykes of granitoid porphyries, within erupted hydrothermal breccias, in tectonized and listvenitized areas of skarns, and along high-amplitude feathering faults of the deep-seated Tselinograd Fault. The high angle branches of this fault are important feature of the Kvartsitovye Gorki structure. Wedges of the Paleoproterozoic and Riphean metamorphic rocks and blocks of Vendian and Cambrian terrigenous rocks and black shales occur in these faults cutting Ordovician sediments.

Like famous Kalgoorlie, at Kvartsitovye Gorki, gold mineralization is nearly complete hosted in hard rocks, which are positioners of fractures (cherty rock-phtanite at Kvartsitovye Gorki and doleritic gabbro at Kalgoorlie); adjacent black shales, carbonaceous mudstones, and siltstones host poor ores.

The reserves of the deposits do not depend on the structure. Stockwork- and mineralized metasomatites deposits contain cca. 2/3 of gold reserves; vein deposits contain cca. 1/3 of the reserves. The deposits are relatively small in area ($< 2 \times 2$ km) and extend down to > 0.5 to > 2 km.

Forming processes of gold-quartz formation. This formation is resulted from the beresitization-listvenitization process that is medium-temperature CO_2 metasomatism (Korzhinsky, 1953; Zaraisky, 1989) one of the latest stages of post-intrusion hydrothermal activity (Spiridonov, 1995). Beresite and listvenite contain *n*.10 ppb of Au everywhere as compared with a few ppb of Au in primary rocks that unambiguously indicates introduction of Au by the beresitezied fluid (like As, Sb, Ag, and Te; for example the concentration of Hg in primary rocks is < 0.04 ppb, whereas in beresite, it ranges from 0.06 to 0.17 ppb and higher). The highest PT parameters of ore deposition are 375°C, 3.3 kbar; salinity of $NaCl$-KCl-$MgCl_2$ fluid is 17 wt.% NaCl equiv., concentration of CO_2 and CH_4 is 7 and 2.5 mole/kg of solution, respectively (Spiridonov, 1992; Spiridonov *et al.*, 2002). Cogenetic H_2O-CO_2 and CO_2-H_2O inclusions in quartz, carbonate, and scheelite and inclusions of liquid CO_2 indicate that the ore deposition was accompanied by fluid immiscibility, boiling, and outgassing with tectonic movements. Substantial part of CO_2 incorporated into carbonates of beresite, listvenite, and ore veins. In the ore veins hosted in intrusive rocks, liquid CO_2 in the inclusions from quartz and scheelite is nearly pure, whereas that from ore bodies hosted in sedimentary sequences contains admixture of methane. According to the study of individual fluid inclusions, the highest concentration of CH_4 is 2.5 mole/kg of solution at Bestyube. Cogenetic inclusions with methane and light and medium bitumen (reason for orange-red color of scheelite) in quartz, scheelite, and carbonates indicate a migration of hydrocarbons into fracture zones that was resulted in concentrated deposition of gold. H_2S played the same role: quartz and carbonates of some deposits contain inclusions with liquid H_2S.

Weak acid (H_2CO_3) gold-bearing hydrothermal fluids with low fO_2 and fS_2 leached SiO_2, Fe, Cu, Zn, Pb, Ni, Co, and W from ore-hosting and underlying sequences, but not Mn and Mo. The ores are depleted in Mn, Ba, and Mo, and extremely poor in F, Sn, Ge, Be. Light hydrocarbons (methane) and bitumen, which migrated into fracture zones at the process of pre-ore acid metasomatism, provided the concentrated gold precipitation. The richest ores (> 2 kg/t Au) including mineralized black shales contain less than 20 ppm of Pt and Pd.

It used to be substantial part of gold in the ores is "dissolved" in sulfide minerals. Calculation showed that even in pyrite-bearing black shales at Kvarysitovye Gorki with veinlet-impregnated mineralization, 80 to 90% of Au occur as native species (Spiridonov *et al.*, 1986_3). This value is close to 100% in the rich ores at Kvartsitovye Gorki and other ores of low-sulfide deposits of the Stepnyak group.

Gold-bearing bodies of any type are composed of the following assemblages: relict minerals, scheelite-quartz (± chlorite, carbonate, sericite, graphitoid) (375 – 305°C, usually 330 – 315°C); early sulfides (pyrite, arsenopyrite ± pyrrhotite) (290 – 270°C); carbonate-polysulfide (As-rich pyite, arsenopyrite, sphalerite, galena, pyrrhotite, cubanite, bornite, bournonite, tennantite, tetrahedrite) (270 – 210°C); economic (gold ± sulfides and complex sulfides of Pb, Sb, Ag, and Bi or tellurides of Bi, Pb, Ag, Ni, Fe-Co, Au-Ag, and Au) (210 – 155°C). The Late Ordovician post gold ore antimony mineralization was identified at some deposits. The

Table 1. **Mineralogical types of the Stepnyak-group deposits in composition of economic mineral formation**

Facies of formation depth of deposit	Estimated depth of formation	Economic mineral formation	Deposit
Hypabyssal	~1 km	Gold-stibnite-Ag sulfosalt	Kvartsitovye Gorki IV
	~1 – 2 km	Gold-galena-Ag sulfosalt	Kvartsitovye Gorki I
	~2 – 3 km	Gold-galena-sulfoantimonide	Bestyube
Mesoabyssal	~3 – 7 km	Gold-galena-sulfoantimonide with tellurides	Budenovsk
			Karaul-Tyube
			Stepnyak
			East Zholymbet
Abyssal	~7 – >10 km	Gold-galena-telluride to gold-telluride	Zhana-Tyube
			Zgolymbet
			South Aksu
			North Aksu

minerals of early scheelite-quartz assemblage containing inclusions with liquid CO_2 precipitated from the CO_2-rich NaCl-KCl-$MgCl_2$ solutions with salinity of 9 – 17 wt.% NaCl equiv. The minerals of carbonate-polysulfide and economic assemblage precipitated from the solutions of the same composition with salinity of 2 – 11 wt.% NaCl equiv., more frequent 4 – 9 wt.% NaCl equiv.; liquid CO_2 was not found in inclusions; this indicates that the minerals were deposited at fluid outgassing with loss of CO_2 that could be resulted in increasing pH of the solutions and one of the reason of gold precipitation. The minerals of carbonate-polysulfide and economic assemblages are developed metasomatically. The gold grade in ore bodies and wall rocks metasomatites is caused by minerals of economic assemblage usually formed at 190 – 170°C. Therefore, the deposits are related to the small intrusions and dykes of the same age, because they had time for cooling to the required temperature. Otherwise, gold is scattered!

Depth facies of the deposits. According to geological data, the deposits were formed at the depth of 1 to 10 km and deeper. These plutonogenic deposits originated in relatively close system at the background of gradual temperature decreasing that caused stable composition of ores and ore minerals along vertical extension of particular deposits and fractionation of ore matter depending on the formation depth of the deposits. As the depth increases, content of Sb, Hg, and Tl decreases, whereas that of Te and W and the Au/Ag, Te/Se (from 1 – 2 to 100 – 3000), and Au/Hg (from 1 to 200 – 6500) values increase. Mineralogical type determined by the mineralogy of economic assemblage corresponds to the depth facies (Table 1): hypabyssal facies (P and T at the start of mineral formation are 0.3 – 0.9 kbar and 310 – 305°C; C_{CO_2} 2 – 2.5 mole/kg of solution) – gold-Ag sulfosalts-stibnite with α-amalgam of gold and gold-galena-sulfoantimonide; mesoabyssal facies (1.0 – 1.8 kbar and 330 – 315°C; C_{CO_2} 2.5 – 4.5 mole/kg of solution) – gold-galena-sulfoantimonide and gold-galena with tellurides; and abyssal facies (2.1 – 3.6 kbar and 375 – 325°C; C_{CO_2} 4 – 7 mole/kg of solution) – gold-galena-telluride and gold-telluride (Spiridonov, 1985, 1992, 1995, 2010). Telluride minerals at the deep-seated deposits are probably caused by the higher dissociation temperature of H_2Te, whereas stability of the latter is lower than that of H_2S. Width and intensity of halos of Hg strongly differ: from hundred meters and 0.*n*–*n* ppm at the hypabyssal deposits to a few meters and 0.0*n* ppm at the abyssal deposits.

The pressure is a function not only of the formation depth. However, the general increase of fluid pressure from gold-stibnite through gold-galena to gold telluride deposits of the Late Ordovician gold-quartz formation of the Northern Central Kazakhstan is evident. Thermobaric gradient at the deposits of this formation is specific cca. 9.5 bar/degree.

Mineralogical and geochemical zoning of the deposits. Poor vertical mineralogical and geochemical zoning was identified at all deposits (Naz'mova *et al.*, 1978; Spiridonov, 1995). Nevertheless, the economic mineralization is localized in the central part because the process of ore deposition is centripetal. The Au/Ag, Pb/Zn, and Te/Se values decrease toward margins of orebodies and deposits. At certain deposits as depth increases, content of Sb, Hg, Ag decreases, whereas that of Bi and W, and Au/Ag (vein Yanvarskaya at South Aksu from 2.1 to 3.3), Au/Hg, and As/Sb values increase; halos of Sb and Hg become narrow; gold fineness increases while concentration of Hg in gold decreases; and concentration of Hg, Cd, and Se in sphalerite drops. Vein zones at the upper levels of the deposits are enriched in Sb-bearing minerals, whereas at the lower levels those are enriched in arsenopyrite and scheelite.

Upper levels of many ore veins are enriched in tetrahedrite and gold, intermediate levels are enriched in tennantite, and lower levels are enriched in chalcopyrite. Early mineral aggregates are retained frequently at the margins of orebodies. The study of early mineral aggregates allowed determination of distribution of berthierite (replaced pyrrhotite), chalcostibite (replaced chalcopyrite), and zinkenite (replaced galena) in the economic ores at Kvartsitovye Gorki.

Mineralogical facies of ores in the composition of ore-hosting environment. Mineralogical facies of ores and metasomatites are resulted from the composition of ore-hosting environment and concentration of sulfur in it (Spiridonov, 1998). This relationship is shown in the content of carbonates, chlorite, pyrrhotite (and its composition), Cu, Co, and Ni minerals, and formations of sulfosalts and tellurides. The orebodies hosted in black shales are enriched in carbonaceous matter, S, As, and Se. The ores hosted in basic rocks contain pyrrhotite, ilmenite, Ni and Co minerals, and are enriched in Cu minerals (chalcopyrite, bornite, cubanite, fahlores, bournonite) with Cu content reaching 1 – 2% that is economic. The orebodies hosted in granitoids contain galena and Pb sulfosalts. The orebodies hosted in Na gabbros, quartz diorite, tonalite, and plagiogranite are poor in Bi (Spiridonov, 1985, 1998). The ores hosted in potassium granitoid adamellite are enriched in Bi (Spiridonov, 1982_2; Spiridonov *et al*., 2002).

Mineralogical and geochemical signs for gold ore shoots. Substantial part of gold reserves is concentrated in ore shoots. The ore shoots are spatially related to intraore brecciation. Vein quartz and carbonates within the shoots contain appreciable methane, bitumen, and graphitoid, while grains of gold are larger than those in common ores. The ore shoots especially their upper parts are enriched in Ag and Hg relative to Au: at Kvartsitovye Gorki I, the mean Au/Ag and Au/Hg value in the common ores is 0.8 and 1.5, respectively; in the ore shoots it is 0.5 and 0.7; and in the upper parts of the ore shoots this value is 0.2 – 0.3 and 0.5 – 0.6, respectively. Mineralogical signs of the ore shoots at the hypabyssal deposits are stibnite, Pb-Sb and Ag-Pb-Sb sulfides, Hg-bearing gold, and graphitoid; negative signs are pyrrhotite, chalcopyrite, cubanite, and bornite. Positive signs at the mesoabyssal deposits are complex Pb-Sb and Ag-Pb-Sb sulfides, tetrahedrite, tellurides, and graphitoid; those at the abyssal deposits are tellurides, fahlores, pyrrhotite, and bornite.

Nature of ore-forming fluids. Oxygen isotopic composition of scheelite, the mineral that is stable for epigenetic isotopic exchange, is nearly uniform at the Stepnyak-group deposits: $\delta^{18}O = +4 \div +6‰$ SMOW. Like oxygen and carbon isotopic composition of carbonates from ore veins, it testifies to deep metamorphic nature of H_2O-CO_2 fluids, which accompanied the formation of inversion stepnyakite-tonalite-granodiorite formation (Spiridonov, 1995).

Mineralogy of the Stepnyak-group deposits

Light micas of beresite, listvenite, and quartz veins. Light micas of the shallow deposits are predominantly phengite, whereas at the deeper deposits these are muscovite. Both are extremely poor in F and NH_4^+.

At Kvartsitovye Gorki, beresite and ores replacing cherty rocks with admixture of ultramafic ash contain green phengite, aluminoseladonite $2M_1$ with 1 – 2 wt.% Cr; beresite-quartzite replacing V-bearing carbonaceous cherty rocks contains phengite with 1 – 1.5 wt.% V; beresite replacing cherty and carbonaceous shales with kaolinite contains pyrophyllite along with phengite. Yellowish pyrophyllite at Kvartsitovye Gorki contains 0.4 – 0.6 wt.% Fe; according to the X-ray diffraction data, it is monoclinic pyrophyllite (Table 2). Occasional aggregate pseudomorphs composed of fine flaky muscovite – phengite with 4 – 9 wt.% Ba and 1 – 2 wt.% Na and less frequent paragonite with 1 – 2 wt.% Ba after plates of barite occur in beresite-quartzite replacing jasper-like rock at Kvartsitovye Gorki.

Chlorites of beresite, listvenite, and quartz veins. Chlorites are abundant in listvenite replacing basic rocks and carbonate-quartz veins hosted in them (Zhana-Tyube, South Aksu, Kvartsitovye Gorki) and less common in beresite and quartz veins hosted in them. According to electron microprobe and X-ray diffraction data, green ripidolite is the most abundant. Corundophyllite is more frequent at the deeper deposits. Al-poor Fe-rich diabantite (Al 0.8 – 1.1 apfu) (low-temperature) occurs in the outer zones of beresite and listvenite zonal aureoles; sheridanite and clinochlore are developed in the intermediate zones; and Al-rich ripidolite (Al 1.3 – 1.6 apfu) (medium-temperature) is common in the inner zones. Therefore, ore-bearing fluids reacted with cooled rocks. Pyrrhotite and/or ilmenite and less frequently rutile are associated with chlorites at the deeper deposits, whereas pyrrhotite or anatase are associated minerals at the shallower deposits.

Carbonates of beresite, listvenite, and quartz veins. Fe-rich dolomite is predominant at

Table 2. ***X-ray powder diffraction data of monoclinic pyrophyllite from Kavartsitovye Gorki IV (pit Flangovaya, level -270 m)***

hkl	I/I_1	*d*, Å	*hkl*	I/I_1	*d*, Å
001	30	18.4	134	4	2.163
002	39	9.20	20-6	5	2.149
004	40	4.60	222	5	2.088
020	18	4.46	13-6	5	2.063
110	16	4.43	028	2	2.046
021	14	4.395	136	3	1.896
111	11	4.178	20-8	1	1.870
022	9	4.020	0.0.10	12	1.840
006	100	3.065	31-2	1	1.692
20-2	9	2.563	150	2	1.688
200	10	2.548	24-2	2	1.685
13-2	10	2.536	240	2	1.679
132	12	2.422	310	4	1.668
20-4	12	2.416	334	5	1.646
202	2	2.352	152	5	1.642
13-4	2	2.340	2.0-10	6	1.630
008	6	2.299	1.1.10	2	1.609

Notes: Diffractometer DRON 1.5; Co radiation. Analyst E.M. Spiridonov.

the ultrahypabyssal Kvartsitovye Gorki; siderite associated with Fe-rich pyrrhotite is frequently associated with it.

The ferrodolomite-ankerite-dolomite series is common at the hypabyssal deposits. In metasomatites and ores of the less deep Central location of the Bestyube deposit, the cation variations in carbonates of beresite and listvenite are $Ca_{50}Mg_{16\text{-}44}Fe_{6\text{-}32}Mn_{1\text{-}3}$, average $Ca_{50}Mg_{35}Fe_{13}Mn_2$; and in gold-bearing veins these are $Ca_{50}Mg_{24\text{-}46}Fe_{4\text{-}24}Mn_{1\text{-}4}$, and $Ca_{50}Mg_{37}Fe_{11}Mn_2$, respectively. In metasomatites and ores of the slightly deeper West location of Bestyube, carbonates are Fe- and Mn-poorer; compositional variations of beresite and listvenite carbonates are $Ca_{50}Mg_{26\text{-}44}Fe_{6\text{-}24}Mn_{0\text{-}3}$, average $Ca_{50}Mg_{37}Fe_{12}Mn_1$; in gold-bearing veins these are $Ca_{50}Mg_{24\text{-}44}Fe_{5\text{-}24}Mn_{0\text{-}2}$, and $Ca_{50}Mg_{38}Fe_{11}Mn_1$, respectively. Vertical zoning in the chemical composition of carbonates was established at Bestyube: direct zoning in the composition of dolomite from beresite and listvenite (the Fe/(Fe+Mg) value increases upward) and reverse zoning in the composition of dolomite from ore veins. The combination of beresite with ferrodolomite and gold-bearing veins with low-Fe dolomite testifies to insignificant erosion level of hypabyssal plutonogenic deposits (Spiridonov *et al.*, 1995_1). The absence of calcite distinguishes the Bestyube beresite from classic beresite column (Zaraisky, 1989). The evolution of the carbonate-polysulfide formation at Bestyube is following: Fe-rich dolomite (Fe/(Fe+Mg) value 0.49–0.19) → Fe-rich dolomite (0.34–0.15) + arsenopyrite → dolomite (0.20–0.16) + chalcopyrite + galena → dolomite + bournonite + jamesonite → dolomite (0.18–0.09) + tetrahedrite + boulangerite.

Calcite is common together with dolomite and Fe-rich dolomite at the mesoabyssal deposits. Calcite is predominant in the metasomatites and ores at the abyssal deposits. Carbonates from listvenite replacing magnesian skarn at the South Aksu deposit are specific: matrix is calcite, inclusions are dolomite (after fassaite) and magnesite (after forsterite).

All types of carbonates in the gold-quartz formation are Mn-poor.

Vein quartz. Milky quartz contains numerous minute inclusions of low-saline aqueous solutions and liquid CO_2. These inclusions cause milky color of quartz. According to ESR data, the content Al centers in vein quartz corresponds to 13–24 ppm of isomorphic Al; concentration of isomorphic Ti and Ge does not exceed 1 ppm and 0.1 ppm, respectively. These feature is resulted from low temperature of quartz formation involving moderate acidic fluid poor in F.

Scheelite. Scheelite is a typical mineral of plutonogenic gold-quartz deposits, because W is mobile at beresitization. Scheelite occurs as nests up to 40 cm across in vein quartz. Average content of scheelite in the Zholymbet gold-quartz veins is 0.5 vol.% sometimes up to 5 vol.% (Spiridonov *et al.*, 1986_1).

The reddish orange color of scheelite (Fig. 1) is caused by microinclusions of bitumen (up to 0.5 wt.%). The superimposed gold mineralization results in elimination of bitumen and gradual disappearance of color (Fig. 2). In the gold-rich quartz veins, scheellite poorly differs from quartz. The color of scheelite is indicator of gold grade.

The feature of scheelite is abundant Eu, whose amount sometimes higher than that of other lanthanides. For example, scheelite in one specimen from the Stepnyak gold field contains, ppm: 153 Eu, 99 Ce, 58 La, and 37 Nd. According to spectroscopic study, more than 90% Eu is Eu^{2+} that corresponds to reductive environment of gold deposition. Average contents of trace elements in scheelite of variable facies of depth deposits: hypabyssal (Bestyube ore field, 10 analyses) – mesoabyssal (Stepnyak ore field, 8 analyses) – abyssal (Zholymbet ore field, 15 analyses), are different, ppm: Sr 7050–3200–650; Mo 3–152–240; Y 22–231–275; total *REE* 122–619–1016; La 12–47–65; Ce 20–52–127; Nd 18–152–240;

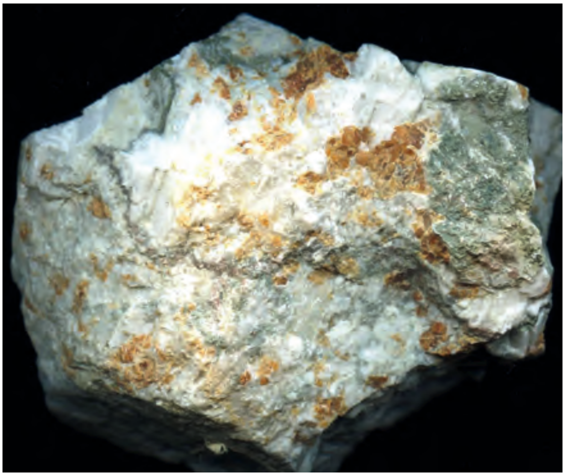


Fig. 1. Impregnation of bright colored scheelite in calcite-quartz vein. 103 × 84 mm. Central location of the Zholymbet deposit.
Fig. 2. Pockets of light scheelite within gold-bearing quartz vein. 77 × 77 mm. Central location of the Bestyube deposit.

Sm 25 – 98 – 150; Eu 26 – 59 – 103; Gd 10 – 76 – 120; Dy 5 – 52 – 94; Ho 1 – 14 – 26; Er 2 – 11 – 20 and Yb 2 – 12 – 21 (Spiridonov *et al.*, 1998). Thus, the contents of Sr, Mo, Eu, Y, Nd, Sm, and Gd in scheelite could be indicators of the formation depth of Au deposits. The indicative Sr/Mo value in scheelite decreases from higher than 2000 in hypabyssal through cca. 20 in mesoabyssal to 3 – 6 in abyssal gold deposits.

Early sulfides – pyrite, arsenopyrite, and pyrrhotite, of beresite, listvenite, and carbonate-quartz veins. As a rule, pyrite is stoichiometric with p-type conduction. Its crystals reach 35 mm in size, commonly, less than 10 mm. Pyrite is extremely irregular distributed in quartz veins. For example, in many long veins of 50 – 120 cm thick at the Bestyube deposit, segments up to 40 – 60 m in length with the content of pyrite ranging from trace to 0.5% alternate with segments up to 2.5 m in length nearly completely composed of coarse-crystalline pyrite and the content of Au lower than 1 – 3 g/t; therefore no any such nests were mined.

Pyrite is usually accompanied by minor S-rich arsenopyrite overgrowing crystal of pyrite. In beresite and listvenite replacing black shales, and also quartz veins, and beresite replacing dykes of granitoid porphyry hosted in these rocks, contents of pyrite and arsenopyrite are approximately equal; arsenopyrite is frequently predominant (Fig. 3a). At the East location of the Bestyube deposit, crystals of arsenopyrite reaches 13 mm in size; usual size is less than 3 mm. The crystals of arsenopyrite are fine-zoned with the variable S/As value: rims are enriched in S (direct zoning). S-rich arsenopyrite with the S/As value 1.08 to 1.10 are abundant at the most deposits. Arsenopyrite with reverse zoning occurs at Kvartsitovye Gorki; rims of the crystals are enriched in As and contain up to 0.4 – 1 wt.% Sb.

In the ore veins and listvenite hosted in mafic rocks – quartz gabbro and gabbro-anorthosite (Central location of Zholymbet), magnesian skarn (South Aksu), olivine basalt (Kvartsitovye Gorki), and its tuff (Zhana-Tyube), Fe-rich pyrrhotite frequently associated with cubanite and ilmenite is found together or instead of pyrite (Spiridonov *et al.*, 1974; Spiridonov and Shapur Khamid, 1978). Fine-lamellar intergrowths of pyrrhotite of variable composition (from Fe_9S_{10} to $Fe_{16}S_{17}$), and texture of Fe-rich pyrrhotite exsolved to troilite FeS and monoclinic pyrrhotite Fe_7S_8 are observed in quartz-chlorite-calcite veins and listvenite at South Aksu and Zhana-Tyube. The composition of Fe-rich pyrrhotite associated with siderite, cubanite and magnetite in listvenite at the western flank of Kvartsitovye Gorki ranges from Fe_8S_9 to $Fe_{20}S_{21}$, average $Fe_{11}S_{12}$. The composition of pyrrhotite in the chlorite-calcite-quartz veins and listvenite at the Central location of Zholymbet ranges from Fe_9S_{10} to $Fe_{10}S_{11}$.

Pyrite of carbonate-polysulfide assemblage. Pyrite is fine crystalline nonstoichiometric with p-type conduction; it is precipitant of Au. The mineral occurs as fine-grained split spherulitic aggregates with 4 – 9 wt.% As and 1 – 5 wt.% Sb in metasomatites and small quartz veins at hypabyssal Kvartsitovye Gorki. At the deeper deposits, it contains cca. 0.5 wt.% As; in association with gersdorffite, it contains up to 2 wt.% Ni and 1 wt.% Co.

Arsenopyrite of carbonate-polysulfide assemblage. Usually, it is p-type conduction enriched in S; the mineral is a good precipitant of Au. In the mineralized metasomatites and small quartz veins at Kvartsitovye Gorki, arsenopyrite occurs as aggregates of fine crystals with reverse zoning (Fig. 3b).

Gersdorffite of carbonate-polysulfide assemblage. Fine zonal crystals of gersdorffite are associated with late pyrite and chalcopyrite in the ore veins and listvenite hosted in basic rocks at Zholymbet, South Aksu, and Kvartsitovye Gorki. Usually they are located in the rims of chalcopyrite grains. The composition of gersdorffite corresponds to the formula $(Ni_{0.56-0.97}Fe_{0.07-0.31}Co_{0.01-0.04}Cu_{0.01-0.03})_{0.97-1.08}As_{0.98-1.09}S_{0.88-0.97}$. The cores of its crystals are enriched in Ni, while rims are enriched in Fe. Some crystals are rimmed by Ni-bearing arsenopyrite $(Ni_{0.15}Fe_{0.89}Co_{0.01}Cu_{0.03})_{1.07}As_{1.03}S_{0.90}$.

Pyrrhotite of carbonate-polysulfide assemblage occurs as metasomatic inclusions in the crystals of pyrite. Compositionally, it is S-rich stable monoclinic pyrrhotite Fe_7S_8. This pyrrhotite is easily replaced by gold creating false impression of gold inclusions in pyrite.

Sphalerite of carbonate-polysulfide assemblage is common mineral; size of its nests reaches 15 cm, but usually it occurs as fine impregnation. Not less than three generations are distinguished everywhere: (1) early dark brown to black $(Zn_{0.82-0.90}Fe_{0.10-0.18})S$ with cca. 0.05 wt.% Cd, (2) later brown $(Zn_{0.94-0.96}Fe_{0.04-0.06})S$ with cca. 0.2 wt.% Cd, and (3) the latest light brown $(Zn_{0.96-0.98}Fe_{0.02-0.04})S$ with cca. 0.3–0.4 wt.% Cd. Early sphalerite from abyssal South Aksu contains 100–200 ppm In and traces of Hg and Se. At hypabyssal Kvatsitovye Gorki, this mineral is In-free; it contains Hg and Se: in late sphalerite content of these elements reaches 0.6–1 and 0.4 wt.%, respectively.

Sulfides and complex sulfides of Pb and Sb. The ores of the ultrahypabyssal Kvartsitovye Gorki are enriched in Sb. Stibnite is abundant in economic assemblage, where the earlier minerals with reactive Fe, Cu, and Pb are absent. Mn-free berthierite after pyrrhotite, jamesonite after pyrrhotite and galena, zinkenite after galena, bournonite after chalcopyrite and galena, chalcostibite and tetrahedrite after chalcopyrite and bornite, and chalcostibite and pyrite after cubanite were resulted from the Sb-bearing fluids affected these minerals. Therefore, pyrrhotite, chalcopyrite, bornite, and cubanite are absent in the ore shoots at Kvartsitovye Gorki. In some places of the shoots, the content of berthierite is comparable with that of stibnite (Fig. 4), while in the other places, zinkenite, jamesonite, or Ag-tetrahedrite are abundant.

The following series were formed in the ores of the deeper deposits Bestyube and Stepnyak as affected by the Sb-bearing fluids: in acidic rocks (plagiogranite, arcose) – primary galena → boulangerite + galena → boulangerite + semseyite → jamesonite + zinkenite; in medium rocks (quartz diorite, tonalite, polymictic rocks) – primary chalcopyrite + galena I → bournonite + tennantite-tetrahedrite I → tetrahedrite II + galena II ± boulangerite → Ag-tetrahedrite III + jamesonite; and in mafic rocks (greywacke, gabbroic) – primary chalcopyrite → tennantite-tetrahedrite I → tetrahedrite II → Ag-tetrahedrite III. The Pb/Cu value determined by the composition of host environment did not evolve unlike minerals of Pb and Cu.

Small amount of tetrahedrite replacing chalcopyrite was formed in the ores of the deepest Zholymbet and Aksu as affected by the Sb-bearing solutions.

Complex sulfides of Pb and Bi. The ores of the Ishke-Ulmes deposit are skarn that is listvenitized and contains superimposed veinlet-disseminated Au mineralization. The deposit is related to the Seletinsky intrusion of potassium granitoid – adamellite, and therefore is enriched in Bi. The aikinite-group mineral gladite, $CuPbBi_5S_9$, is abundant in the ores; size of its grains reaches 9 mm (Spiridonov, 1982_2).

The fahlores-group minerals. The fahlores-group minerals are named according to (Spiri-

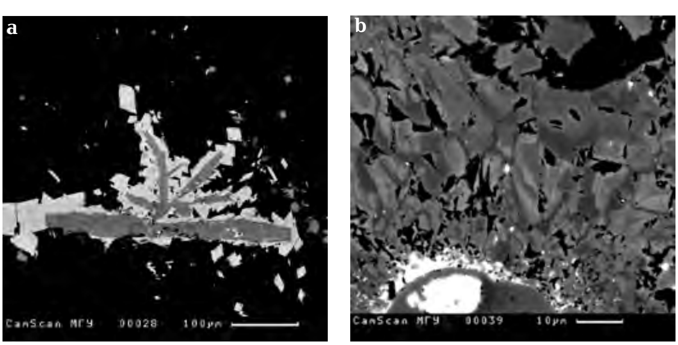


Fig. 3. Back-scattered electron images of arsenopyrite from Kvartsitovye Gorki:
(a) rims and isolated crystals of arsenopyrite (light gray) around lamellae of pyrite (gray) in listvenite, pyrite probably replaced lamellae of pyrrhotite;
(b) aggregate of fine complexly zoned crystals of arsenopyrite whose rims are enriched in As (lighter); spherulite of pyrite penetrated by late jamesonite at the bottom of image.

donov, 1984). Fahlores $(Cu^{1+},Ag,Tl)_{10}(Zn,Fe,Cu^{2+},Hg,Cd)_2(As,Sb,Bi,Te)_4(S,Se)_{13}$ are sensitive indicators of ore genesis; these minerals are the major carries of Ag and Hg at many hydrothermal deposits. Sb/(As+Sb) and $Cu^{2+}/(Zn+Fe+Cu^{2+}+Hg+Cd)$ values are their characteristics. Fahlores of the economic assemblage are of the great interest. These are poor in Te and Bi and have the low $Cu^{2+}/(Zn+Fe+Cu^{2+}+Hg+Cd)$ value. The crystals are smooth zoned everywhere (Spiridonov *et al.*, 2009).

Zn-rich As-tetrahedrite and Sb-tennantite containing up to 5 wt.% Ag are the early generations at the ultrahypabyssal Kvartsitovye Gorki. At the shallowest Kvartsitovye Gorki IV, these minerals contain, wt.%: up to 7 Hg, 0.9 Se, 0.4 Cd, and 0.2 Tl. Evolution of ore-forming process resulted in the decreasing Hg concentration in fahlores; Hg fractionated into Hg-rich gold. The later generation of fahlores is As-poor freibergite (Ag-tetrahedrite containing up to 25 wt.% Ag); argentotetrahedrite poor in As and containing trace Hg is the latest (Spiridonov, 1984, 1987_2; Filimonov and Spiridonov, 2005). All these fahlores are associated with the minerals enriched in Sb: from stibnite, zinkenite, and jamesonite to andorite, roshchenite, and miargyrite.

In the deeper orebody at Kvartsitovye Gorki I, content of Ag increases, while the Sb/(As+Sb) value decreases from the early to late fahlores; the latest generation is Sb-argentotennantite and As-argentotetrahedrite (up to 39 wt.% Ag) (Spiridonov *et al.*, 1986_2; Spiridonov, 1987_2).

At Bestyube and mesoabyssal Stepnyak, Budenovsk, and East Zholymbet, the early generation of fahlores is Zn-rich tetrahedrite and tennantite containing < 1.5 wt.% Hg and up to 3 wt.% Ag; the late generation is tetrahedrite (up to 10 wt.% Ag) and occasional freibergite (up to 21 wt.% Ag and 1 wt.% Cd) (Spiridonov *et al.*, 1996, 2002, 2009). At abyssal Zholymbet and Aksu, fahlores are Fe-rich tennantite and tetrahedrite poor in Ag (< 0.5 wt.%) and Hg (< 0.01 wt.%) (Spiridonov, 1985). Thus, the composition of fahlores of the economic formation at the plutonogenic gold deposits is additional criterion of the formation depth of deposit.

Ag and Sb sulfides and complex sulfides. The ores of ultrahypabyssal Kvartsitovye Gorki are enriched in Ag and Sb. The economic assemblage contains a series of minerals with conventional increasing content of Ag: freibergite (Ag-tetrahedrite) → andorite $AgPbSb_3S_6$ → roshchinite $Ag_{19}Pb_{10}Sb_{51}S_{96}$ → miargyrite $AgSbS_2$ (Spiridonov *et al.*, 1990, 2002; Spiridonov, 2010) and latest rare pyrargyrite Ag_3SbS_3 → argentite Ag_2S. The andorite-group minerals Me_5S_6, or $Me_{20}S_{24}$, andorite in the first place, are developed at many hydrothermal deposits enriched in Ag and Sb (Sveshnikova, 1975; Moëlo, 1983; Moëlo *et al.*, 1989). Roshchinite, specific mineral of the andorite group associated with andorite is the feature of plutonogenic hypabyssal Kvartsitovye Gorki (Fig. 5). The composition of roshchinite $(Ag,Cu)_{19}Pb_{10}(Sb,As)_{51}S_{96}$ (Fig. 6) registers special conditions of late stage ore deposition at Kvartsitovye Gorki IV: abundant Sb and Ag and relative deficiency of Pb. The structure of roshchinite differs from that of the other andorite-group members and is particular type (Fig. 7).

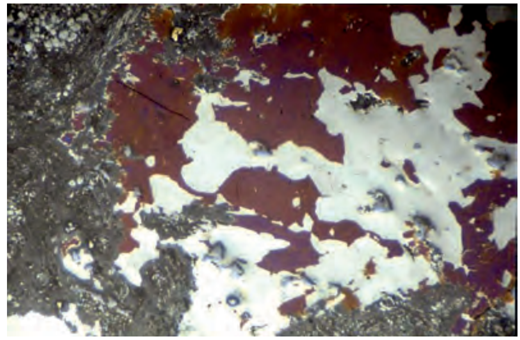


Fig. 4. Photomicrograph of aggregate of berthierite (coated by red film resulted from of air etching) and antimonite (light) in listvenite, Kvartsitovye Gorki IV. Width of image 6 mm. Reflected plane polarized light.

The Bestyube and Stepnyak ores contain few owyheeite $Ag_3Pb_{10}Sb_{11}S_{28}$. Ag-Sb sulfosalts are absent at the deeper deposits.

Tellurides. According to uniform association of tellurides and native gold, these were resulted from the reaction of Au-Te-bearing solutions with the early minerals in ore veins. For example, in the pyrrhotite-rich ores of Zhana-Tyube hosted in basic rocks, numerous metacrysts of frohbergite with inclusions of gold are enclosed in pyrrhotite (Fig. 8a). The probable reaction is: $2FeS + Au_{fluid} + 2Te_{fluid} \rightarrow FeTe_2$ (frohbergite) $+ Au + FeS_2$. In this case, almost the whole Te incorporated into frohbergite, therefore native gold was developed rather than gold tellurides. In the pyrrhotite-free quartz veins hosted in silicic rocks at Zhana-Tyube, frohbergite and melonite are absent. Native gold is also absent in these veins, because all Au incorporated into tellurides.

Tellurobismuthite, Sb-rich tellubismuthite, and other Bi tellurides. The intergrowths of native gold and Bi tellurides, which are tellurobismuthite and/or tetradymite, are the most abundant; the intergrowths with tsumoite and

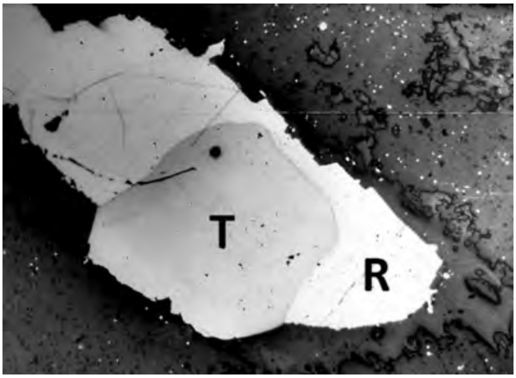


Fig. 5. Photomicrograph of intergrowth of roshchinite (R) and Ag-tetrahedrite (T) in carbonate nest within quartz vein, Kvartsitovye Gorki IV. Width of image 3 mm. Reflected plane polarized light.

other tellurides are less frequent. Like all over the world, Bi tellurides at the Stepnyak-group deposits contain admixture of Pb and trace Sb (Spiridonov *et al*., 1978_2), because Sb incorporated into the earlier fahlores.

Galena and fahlores are unstable as affected by Au-Te-bearing fluids. The relationship of galena and replacing altaite PbTe indicates intensity of such affect. In the most ore veins of Zholymbet and South Aksu, galena is predominant. In some veins enriched in gold, altaite is predominant; in the same veins, Sb-rich tellurobismuthite is developed rather than usual tellurobismuthite; the former contains Sb that is product of fahlore decomposition. This is Sb-rich tellurobismuthite of South Aksu containing up to 8 wt.% Sb (Table 3). The ores of the small but very gold-rich Zhana-Tyube deposit is distinguished by abundant tellurides including Sb-rich tellurobismuthite (up to 11 wt.% Sb, Table 4), absence of galena and fahlores, and presence of late arsenopyrite associated with tellurides. These distinctions are caused by effect of abundant Au-Te-bearing solutions. Galena was replaced by altaite and fahlores were replaced by Sb-rich tellurobismuthite, chalcopyrite, and arsenopyrite: $PbS + Cu_{10}Fe_2SbAs_3S_{13} + 13FeS + 7Te_{fluid} + 3Bi_{fluid} \rightarrow PbTe + 2(Bi_{1.5}Sb_{0.5})_2Te_3 + 3FeAsS + 10CuFeS_2 + 2FeS_2$.

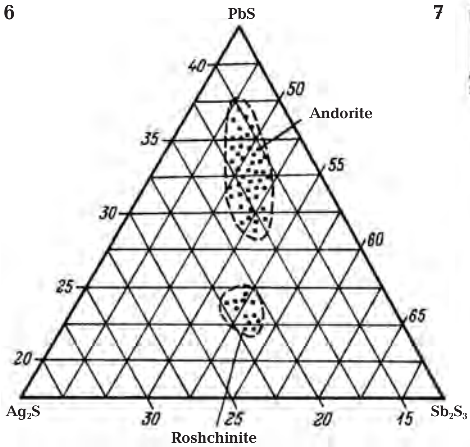
The South Aksu orebodies hosted in intrusive rocks poor in S predominantly contain tellurides – tellurobismuthite, tsumoite, and others. Polymineralic clusters of tellurides were found in them: earlier pilsenite Bi_3Te_2 and wehrlite Bi_4Te_3, later tsumoite Bi_2Te_2, then tellurobismuthite Bi_2Te_3, and the latest sulfotelluride – tetradymite Bi_2Te_2S (Table 5). In the South Aksu orebodies hosted in hornfels after black shales enriched in S, tetradymite is predominant.

Fe-Co-Ni tellurides – frohbergite, mattagamite, and melonite. According to Veits *et al*. (1971), N.P. Krikunova found frohbergite in the Zhana-Tyube ores for the first time. The author of this article has established that in some places of chalcopyrite-pyrrhotite-chlorite-calcite-quartz veins hosted in listvenitized melanobasaltic tuffs with limestone cement the content of frohbergite reaches 1 – 3 vol.% and frohbergite enriched in Co has been identified (Spiridonov *et al*., 1974, 1978_1). This mineral is stoichiometric in composition; admixtures are, wt.%: up to 0.5 Sb and Se, up to 0.2 – 1 Ni, and 0.0*n* Co, Cu, Ag,and Au.

The zoned crystals of frohbergite are frequent in the Zhana-Tyube ores. Co-rich frohbergite $(Fe_{0.6-0.5}Co_{0.4-0.5})Te_2$ is in the cores of these crystals. Occasionally, in the cores of these crystals content of Co is higher than that of Fe; these small places with the composition $(Fe_{0.48-0.49}Co_{0.52-0.51})Te_2$ correspond to mattagamite. This is the first finding of mattagamite at the plutonogenic gold deposits. Intermediate zones of the zoned crystals are composed of frohbergite with 1 – 6 wt.% Co. Sometimes, the zones of Co-bearing frohbergite alternate with the zones of Co-free frohbergite. The composition of rims corresponds to frohbergite with 0.0*n* wt.% Co. The composition of minerals of the mattagamite-frohbergite series is given in Table 6 and Fig. 8b.

Melonite and associated altaite were identified in the Zholymbet ores (Borishanskya, 1952; Naz'mova *et al*., 1978). According to Veits *et al*. (1971), in the ores of Zhana-Tybe, N.P. Krikunova found melonite for the first time. The author of this paper has established abundant melonite in the pyrrhotite ores of Zhana-Tyube and Co-rich melonite in these ores. The size of nests of melonite intergrown with frohbergite reaches 6 mm. Melonite and Co-bearing frohbergite paragenese from Zhana-Tyube contains traces of Co; the isolated grains of melonite contain 0.5 wt.% Co as usual, occasionally up to 5.5 wt.% Co. Co-rich melonite occurs as crystal cores; also it contains up to 3 wt.% Fe (Table. 7; Fig. 8b). Thus, the affinity of Co for Te is higher than that of Fe and Ni for Te.

Au-Ag tellurides – montbrayite, calaverite, krennerite, sylvanite, and others. Montbrayite, $Au_2(Te,Sb,Pb,Bi)_3$, rare early telluride occurs in the pyrrhotite ores with melonite, frohbergite, and high-fineness gold (Zhana-Tyube, South Aksu, Central location of Zholymbet). It contains up to, wt.%: 3 Ag, 0.5 Cu, 1.5 Sb, and 4.5 Pb (Table 8). Calaverite, $AuTe_2$ is relatively



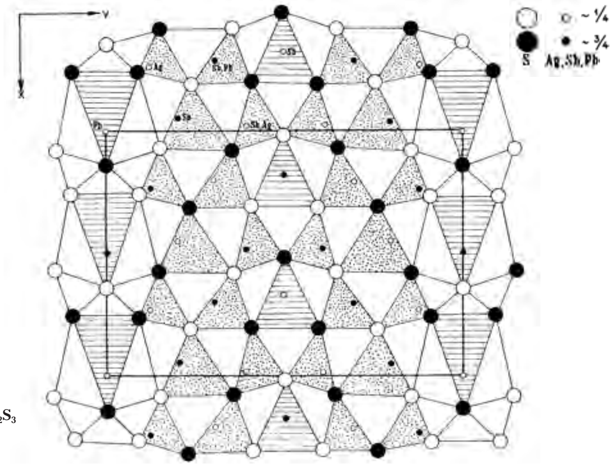


Fig. 6. Ternary diagram $Ag_2S - Sb_2S_3 - PbS$ with the compositional fields of roshchinite from Kvartsitovye Gorki (author data), andorite (Sveshnikova, 1975; Moëlo, 1983; Moëlo et al., 1989).
Fig. 7. Crystal structure of roshchinite projected onto axis c according to I.V. Petrova.

rare early telluride in the central parts and deep levels of gold veins and stockworks. The mineral is associated with high-fineness gold (970 – 992), altaite, and melonite (Zholymbet), extremely high-finenness gold (990 – 1000) and tellurobismuthite (North Aksu), and tsumoite (South Aksu). It contains, wt.%: from traces to 3 (usually < 0.5) Ag, cca. 0.5 Se, and 0.0*n* Hg, Sb, Cu, and Bi. The extremely high-fineness gold in the North Aksu ores is evidently caused by cogenetic calaverite in the same formation (Table 8) that incorporated residual Ag from the ore-bearing fluids.

Krennerite, $Au_3(Au,Ag,Cu)Te_8$, is common relatively early telluride is developed in the central parts and deep levels of ore veins and stockworks. At Zhana-Tyube, it is the third most important Au carrier; the mineral is abundant in the pyrrhotite ores, where it commonly occurs within frohbergite enclosed in pyrrhotite (Fig. 9a) or as clusters with frohbergite in pyrrhotite (Fig. 9b); native gold or petzite are frequently observed with these minerals. Krennerite is also abundant in the pyrite-quartz veins at Zhana-Tyube, where it forms small intergrowth with altaite, petzite, and Sb-rich tellurobismuthite. The composition of krennerite ranges from $AuTe_2$ до Au_3AgTe_8; the content of Ag varies from 0.5 to 6.5 wt.%, usually 3 – 5 wt.%. The mineral contains 0.*n* wt.% Sb and 0.0*n* wt.% Hg and Cu. Krennerite replacing bornite at the Central location of Zholymbet contains up to 1.5 – 2 wt.% Cu. The mineral is frequently cogenetic with high-fineness gold (945 – 960) (Spiridonov, 1985). In the Zhana-Tyube pyrite-quartz ores it is replaced by sylvanite.

Petzite, $AuAg_3Te_2$, is common telluride with the garnet-type structure (Shapur Khamid *et al.*, 1978). In the pyrrhotite ores with frohbergite it is intimately associated with krennerite; the compromise growth surfaces are between these minerals. The fineness of gold in this formation is 930 – 880. In the frohbergite-free pyrite ores, petzite is associated with sylvanite and altaite. Petzite is stoichiometric in composition; admixture of Hg 0.0*n* – 0.*n* wt.% is typical. The composition of petzite at Zhana-Tyube corresponds to

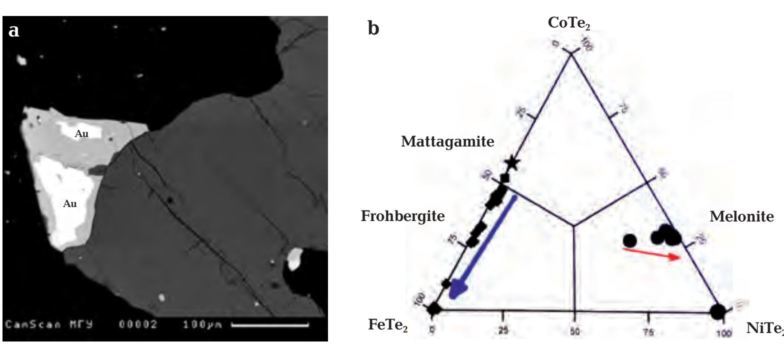


Fig. 8. Ditellurdes of Zhana-Tyube:
(a) back-scattered electron image of metacryst of frohbergite (gray) with inclusions of gold (Au), matrix is composed pyrrhotite (dark gray), vein quartz is black;
(b) the composition of Fe-Co-Ni ditellurides (arrows indicate the compositional evolution of zoned crystals of frohbergite and melonite).

Table 3. **Chemical composition (wt.%) of zoned Sb-bearing tellurobismuthite (anal. 1 – 3) from vein Yanvarskaya and Pb-Sb-bearing tellurobismuthite (anal. 4 – 6) from intergrowths with gold enclosed in pyrite of vein Vesennyaya, South Aksu deposit**

Comp.	1	2	3	4	5	6
	core	intermediate	rim			
Bi	41.86	47.71	50.59	46.05	46.13	42.64
Sb	7.60	3.20	1.65	1.62	1.66	1.36
Pb	b.d.l.	b.d.l.	b.d.l.	3.49	4.88	6.97
Cu	b.d.l.	b.d.l.	b.d.l.	0.12	b.d.l.	b.d.l.
Ag	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.17	0.15
Au	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.44	0.41
Te	49.62	49.65	48.93	47.71	47.37	46.48
Se	b.d.l.	b.d.l.	следы	b.d.l.	b.d.l.	b.d.l.
S	0.65	b.d.l.	b.d.l.	b.d.l.	0.47	0.32
Total	99.73	100.56	101.17	98.99	101.13	100.43
	Atoms per formula unit					
Bi	1.49	1.78	1.89	1.76	1.70	1.62
Sb	0.46	0.20	0.11	0.11	0.11	0.09
Pb	–	–	–	0.13	0.18	0.27
Cu	–	–	–	0.01	–	–
Ag	–	–	–	–	0.01	0.01
Au	–	–	–	–	0.02	0.02
Total	1.96	1.98	2.00	2.01	2.02	2.01
Te	2.89	3.02	3.00	2.99	2.87	2.89
S	0.15	–	–	–	0.11	0.10
Total	3.04	3.02	3.00	2.99	2.98	2.99

Notes: Cameca SX-50 electron microprobe, analyst E.M. Spiridonov. Here and after, b.d.l. denotes that the content of the element is below detection limits.

the formula $(Au_{0.98\text{-}1.02}Ag_{2.96\text{-}3.01}Hg_{0\text{-}0.01})_4(Te_{1.98\text{-}2.00}Sb_{0.01\text{-}0.02}Bi_{0\text{-}0.01}Se_{0\text{-}0.01})_2$.

Sylvanite, $Au(Ag,Au)Te_4$, is abundant late telluride; it is the major carrier of Au in ores at Zhana-Tyube. In the stockworks and veins of the deep Central location at Zholymbet, the mineral is developed down to 1450 m below surface. At Zhana-Tyube, sylvanite occurs in the gold-free quartz veins; the size of its nests reaches up to 6 cm; the mineral is associated with altaite, Sb-rich tellurobismuthite (Fig. 9c), and occasionally with frohbergite (Fig. 9d); its formula is $(Au_{1.00\text{-}1.03}Ag_{0.94\text{-}0.98}Cu_{0.01}Hg_{0\text{-}0.01})_{1.97\text{-}2}(Te_{3.97\text{-}4.00}Sb_{0.02\text{-}0.03}Se_{0\text{-}0.01})_{4\text{-}4.03}$ (Spiridonov *et al.*, 1976). The mineral uniformly contains cca. 0.1 wt.% Hg. Sylvanite at South Aksu replacing cubanite contains up to 1 wt.% Cu. Copper content in sylvanite from Zhana-Tyube is cca. 0.5 wt.%; the replaced fahlores were source for Cu. Thus, it is evident that there is natural solid solution series sylvanite $AuAgTe_4$ – kostovite $AuCuTe_4$. At the Central, South, and North locations of Zholymbet and South Aksu, sylvanite is associated with native gold of moderate fineness (910 – 890). The composition of sylvanite from plutonogenic gold deposits in North Kazakhstan corresponds to the formula $AuAgTe_4$ that is consistent with the formation temperature below 200°C according to diagram reported by Cabri (1965). Sylvanite is replaced by petzite and hessite (Fig. 10a).

Table 4. **Chemical composition (wt.%) of Sb-bearing tellurobismuthite from pyrrhotite ores of the Zhana-Tyube deposit**

Comp.	7	8	9	10	11
Bi	42.04	41.14	37.99	36.56	35.90
Sb	7.50	8.80	8.94	10.14	10.95
Pb	0.21	0.01	0.02	0.08	0.14
Ag	0.17	0.43	0.41	0.66	0. 61
Te	49.91	52.33	50.41	50.32	50.26
Se	0.12	traces	0.04	0.11	0.09
Total	99.95	102.71	97.81	97.87	97.97
	Atoms per formula unit				
Bi	1.53	1.44	1.39	1.32	1.29
Sb	0.47	0.53	0.56	0.63	0.68
Pb	0.01	–	–	–	0.01
Ag	0.01	0.03	0.03	0.05	0.04
Total	2.02	2.00	1.98	2.00	2.02
Te	2.97	3.00	3.02	2.99	2.97
Se	0.01	–	–	0.01	0.01
Total	2.98	3.00	3.02	3.00	2.98

Notes: Cameca SX-50 electron microprobe, analyst N.N. Kononkova.

Table 5. **Chemical composition (wt.%) of Bi tellurides in zoned intergrowth: wehrlite (core) (anal. 12) – pilsenite (anal. 13) – tsumoite (anal. 14) – tellurobismuthite (anal. 15) – tetradymite (rim) (anal. 16), vein Yanvarskaya, South Aksu deposit**

Comp.	12	13	14	15	16
Bi	69.87	67.21	63.30	50.75	57.82
Sb	0.46	0.46	0.45	1.50	0475
Te	27.73	30.62	36.21	46.71	35.56
S	0.14	0.14	0.15	0.07	4.66
Total	98.20	98.24	101.11	99.12	98.51
	Atoms per formula unit				
Bi	2.99	3.95	2.01	1.94	1.96
Sb	0.03	0.05	0.03	0.10	0.03
Total	3.02	4.00	2.04	2.04	1.99
Te	1.94	2.95	1.93	2.94	1.98
S	0.04	0.05	0.03	0.02	1.03
Total	1.98	3.00	1.96	2.96	3.01

Notes: Cameca SX-50 electron microprobe, analyst E.M. Spiridonov. Contents of Pb, Hg, Ag, Cu, Au, and Se are below detection limits.

Table 6. **Chemical composition (wt.%) of zoned crystals of mattagamite (anal. 17) – Co-bearing frohbergite – frohbergite from pyrrhotite ores at the Zhana-Tyube deposit**

Comp.	17	18	19	20	21	22	23	24	25
	core	intermediate	rim	core	intermediate	rim	core	intermediate	rim
Fe	8.57	16.10	17.97	12.28	13.07	18.05	17.79	11.03	17.91
Co	9.80	2.12	0.09	6.05	5.10	0.12	0.61	7.50	0.05
Ni	b.d.l.	0.37	3.21	–	b.d.l.	0.19	b.d.l.	0.01	0.07
Cu	b.d.l.	0.11	0.08	–	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.09
Te	81.53	81.88	81.79	81.52	81.69	82.01	82.05	81.41	82.07
Sb	0.21	0.15	0.19	0.11	0.17	b.d.l.	0.08	0.18	0.10
Bi	b.d.l.	0.14	0.11	b.d.l.	0.14	b.d.l.	b.d.l.	0.14	b.d.l.
Se	b.d.l.	0.10	0.03	0.22	0.11	0.06	0.09	0.11	0.10
Total	100.11	100.56	100.30	100.24	100.28	100.53	100.62	100.45	100.28
Atoms per formula unit									
Fe	0.48	0.89	1.00	0.68	0.73	0.995	0.98	0.62	0.99
Co	0.52	0.11	0.01	0.32	0.27	0.005	0.03	0.39	0.01
Ni	–	–	–	–	–	0.01	–	–	–
Total	1.00	1.00	1.01	1.00	1.00	1.01	1.01	1.01	1.00
Te	1.99	1.98	1.99	1.99	1.99	1.985	1.99	1.98	1.995
Sb	0.01	0.01	–	–	0.005	–	–	0.01	–
Se	–	0.01	–	0.01	0.005	0.005	–	–	0.005
Total	2.00	2.00	1.99	2.00	2.00	1.99	1.99	1.99	2.000

Notes: A Cameca SX-50 electron microprobe, analyst N.N. Korotaeva.

Table 7. **Chemical composition (wt.%) of zoned (anal. 26–29) and unzoned (anal. 30–32) crystals of melonite from pyrrhotite ores of the Zhana-Tyube deposit**

Comp.	26	27	28	29	30	31	32
	core	inter-mediate	inter-mediate	rim			
Ni	12.72	13.27	10.67	17.97	18.38	18.41	18.14
Co	5.08	5.07	4.71	0.31	b.d.l.	b.d.l.	b.d.l.
Fe	0.89	0.37	3.21	0.19	0.02	0.01	0.07
Cu	b.d.l.	0.11	0.08	b.d.l.	0.01	b.d.l.	0.09
Te	81.32	81.29	81.42	80.98	80.17	80.19	80.27
Sb	0.06	0.10	0.09	0.41	0.35	0.39	0.50
Bi	b.d.l.	0.05	0.07	b.d.l.	b.d.l.	0.06	0.04
Se	0.05	0.03	0.06	b.d.l.	0.11	0.09	0.12
Total	100.12	100.29	100.31	99.86	99.04	99.15	99.23
Atoms per formula unit							
Ni	0.68	0.71	0.57	0.965	0.995	0.995	0.98
Co	0.27	0.27	0.25	0.015	–	–	–
Fe	0.05	0.02	0.18	0.01	–	–	0.005
Cu	–	0.01	0.005	–	–	–	0.005
Total	1.00	1.01	1.005	0.99	0.995	0.995	0.99
Te	2.00	1.99	1.995	2.00	1.99	1.99	1.995
Sb	–	–	–	0.01	0.01	0.01	0.01
Se	–	–	–	–	0.005	0.005	0.005
Total	2.00	1.99	1.995	2.01	2.005	2.005	2.01

Notes: A Cameca SX-50 electron microprobe, analyst N.N. Korotaeva.

Table 8. **Chemical composition (wt.%) of tellurides intergrown with gold: Pb-bearing montbrayite (anal. 33–34) from vein Yanvarskaya, South Aksu deposit and calaverite (anal. 35–38) from vein Pologaya, North Aksu deposit**

Comp.	33	34	35	36	37	38
Au	46.75	44.95	44.11	43.74	43.59	45.21
Ag	3.13	3.32	0.10	0.22	0.17	0.16
Cu	traces	traces	traces	traces	traces	traces
Hg	traces	traces	traces	traces	traces	traces
Te	45.00	44.75	56.03	55.44	56.22	56.65
Se	b.d.l.	b.d.l.	0.57	0.69	0.58	0.48
Sb	1.41	1.69	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Pb	4.41	4.45	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Total	100.70	99.17	100.81	100.09	100.56	102.50
Atoms per formula unit						
Au	1.82	1.77	1.00	1.00	0.99	1.01
Ag	0.22	0.24	0.01	0.01	0.01	0.01
Total	2.04	2.01	1.01	1.01	1.00	1.02
Te	2.71	2.72	1.96	1.95	1.97	1.95
Se	–	–	0.03	0.04	0.03	0.03
Sb	0.09	0.10	–	–	–	–
Pb	0.16	0.17	–	–	–	–
Total	2.96	2.99	1.99	1.99	2.00	1.98

Notes: Cameca SX-50 electron microprobe, analyst E.M. Spiridonov. Contents of Fe, Bi,and S are below detection limits.

Fine-grained clusters of petzite and hessite with pattern typical of exsolution texture (Fig. 10b) are common in the Zhana-Tyube ores. Obviously, these are products of petzite-hessite exsolution. The average composition of the solid solution series is $(Ag_{1.54-1.69}\,Au_{0.31-0.46}Cu_{0-0.01})_2(Te_{0.99}Sb_{0-0.01}Bi_{0-0.01})_1$. These clusters overgrow grains of sylvanite, krennerite, and frohbergite and in turn are overgrown by homogeneous (without exsolution texture) petzite, hessite,

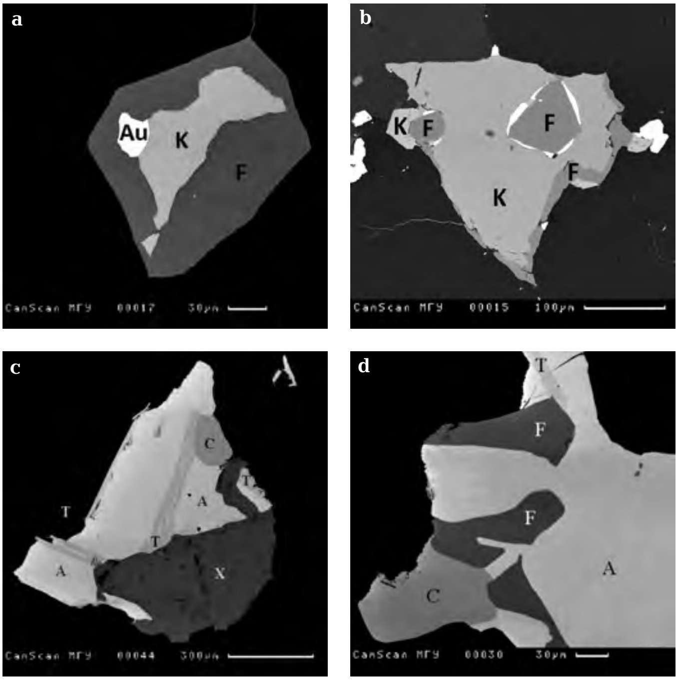


Fig. 9. Back-scattered electron images of intergrowths of tellurides from the Zhana-Tyube ores:
(a, b) metasomatic krennerite (K), frohbergite (F), and gold (white) enclosed in pyrrhotite,
(c) altaite (A) with lamellae of Sb-rich tellurobismuthite (T) and sylvanite (C) corrode chalcopyrite (X),
(d) intergrowth of sylvanite (C), altaite (A), frohbergite (F) and tellurobismuthite (T). Vein quartz is black.

and Ag-rich gold with fineness 860 – 840 (Fig. 10b).

Hessite, Ag_2Te, the latest abundant telluride, occurs as isolated aggregates and intergrowths with tellurobismuthite and altaite (Fig. 10c); overgrowth and replacement rims on sylvanite and petzite, and metasomatic inclusions in pyrite, chalcopyrite, and pyrrhotite. Aggregates of hessite are mosaic of tiny grains, which are resulted from recrystallization of twins of polymorphic transition cubic → monoclinic hessite. The composition of hessite from Zhana-Tyube complies with the formula $(Ag_{1.99-2.00}Au_{0-0.01}\ Cu_{0-0.01})_{2-2.01}(Te_{0.98-1.00}Sb_{0-0.01})_{0.99-1}$, that corresponds to low formation temperature. Ag-rich gold with fineness 780 – 810 is occasionally associated with hessite.

Thus, the succession of Au-Ag telluride deposition is following: early substantially Au tellurides (montbrayite → calaverite → krennerite), later Au-Ag tellurides (sylvanite, petzite), and the latest Ag tellurides (hessite).

Tellurides as indicators of deposit zoning. Au-Ag tellurides indicate zoning of orebodies: Au-rich tellurides (calaverite, krennerite) are predominant in the central parts and at the depth; Au-Ag tellurides (sylvanite and petzite) are developed in outer zones; and Ag-dominated tellurides (hessite and petzite-hessite solid solution) occur at the margins.

The contrast types of ores at Zhana-Tyube, which are pyrite ores hosted in silicic rocks and pyrrhotite-rich ores hosted in basic rocks contain approximately equal amounts of Au, Ag, Te. Mineral species of these elements drastically differ. Frohbergite is the major telluride in pyrrhotite ores; krennerite and petzite are minor; their quantitative relationship is close to 5:1:1 ($5FeTe_2 + Au_3AgTe_8 + AuAg_3Te_2$, i.e., the relationship of elements is 20Te:4Au:4Ag). Altaite and sylvanite are the major tellurides in pyrite ores; their amounts are nearly equal ($4PbTe + 4AuAgTe_4$, i.e., the relationship of the elements is the same 20Te:4Au:4Ag). The Zhana-Tyube deposit exemplifies mineralogical zoning of ores in the composition of host environment.

Affinity of chemical elements for Te. According to natural paragenes, the affinity for Te is following: Co > Fe, Ni > Bi, Sb > Pb > Ag, Hg > Au, Cu.

Native gold and its nanostructural characteristics as well as supergene species will be described in the second article devoted to the deposits of this group.

Acknowledgements

G.N. Naz'mova, Yu.S. Shalaev, and N.F. Sokolova are thanked for discussion of problems of formation of gold deposits in the Northern Central Kazakhstan; N.N. Korotaeva and N.N. Kononkova are thanked for the high-quality back-scattered electron images and chemical

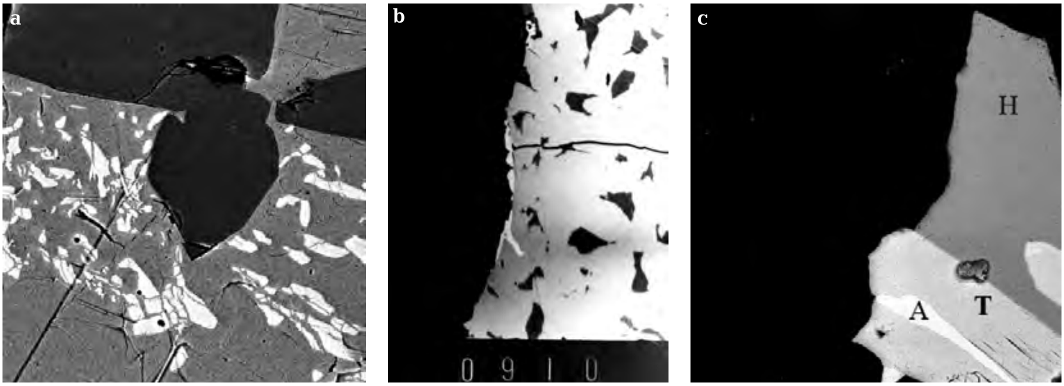


Fig. 10. Back-scattered electron images of aggregates of tellurides from quartz veins of Zhana-Tyube: (a) relics of sylvanite (white) enclosed in petzite (light gray); they are replaced by hessite (gray); (b) intergrowths of petzite (matrix) and hessite (exsolution bodies) rimmed by Ag-rich gold (white) in vein quartz, width of image 80 μm, (c) intergrowth of hessite (H), altaite (A), and Sb-rich tellurobismuthite (T) in vein quartz (black).

data obtained with electron microprobe at the laboratories of Geological Faculty, Moscow State University.

This study has been supported by the Russian Foundation for Basic Research (project no. 13-05-00839).

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