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Gold and silver in ores of Kadjaran copper-porphyry deposit (southern Armenia)

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ABSTRACT

The results of the study of the distribution of gold and silver in the main sulfide minerals of the Kadjaran mine of the copper-molybdenum-porphyry formation are presented. The regularity of the behavior of gold and silver was revealed and a forecast estimate of the gold-silver content of the lower horizons of the deposit was given. Gold and silver are unevenly distributed in the vertical range of horizons 2175-1965 m (above sea level). At the upper horizons (above the 2175 horizon), Au and Ag show selective accumulation in chalcopyrite, at the lower horizons (2150-2050 m), in addition to chalcopyrite, they also accumulate in pyrite and molybdenum; moreover, with depth (2050-1985m), the storage capacity of molybdenum and chalcopyrite continues to increase. A significant enrichment of the lower horizons of the deposit (below the horizon of 1965 m) with Au and Ag is unexpected, since their contents are largely limited by concentrations of copper ores, the ratio of which to molybdenum steadily decreases with depth. The studies carried out on distribution of Au and Ag in the main industrial sulfides of Kadjaran copper-molybdenum deposit made it possible to single out the main patterns of their distribution.

Keywords: Armenia; gold; silver; ore; Kadjaran copper-porphyry deposit.

INTRODUCTION

Recent publications have been dedicated to the identification of geodynamic settings in the Southern Armenia (Zangezur ore district), which are associated with the formation of copper-molybdenum-porphyry deposits of Zangezur ore district (Figure 1), the issue of epithermal nature of gold on Kadjaran deposit (Hovakimyan et al., 2015, 2016a, 2016b, 2019) and the time of its deposition relative to the copper-molybdenum-porphyry system (Moritz et al., 2016).

In copper-porphyry and gold-copper-porphyry deposits gold has been shown to be epithermal and formed at subvolcanic levels (Sillitoe, 1993; Krivtsov et al., 1985; Korobeinikov et al., 2003). However, for copper-molybdenum-porphyry deposits, such as the Kadjaran copper-molybdenum deposit, lack of direct observational data over the vertical range of mineralization does not allow for a definite assessment of how the gold formed.

This article, written on the basis of unpublished analytical data by Karamyan (1981-1986) and Tayan (1986-2010) on the grades of gold and silver in basic sulfides (molybdenite, chalcopyrite, pyrite, sphalerite, galenite and bornite as a supergene mineral) of the deposit, as well as the data of the authors, aims to give an idea of the patterns of distribution of gold and silver in the ores of Kadjaran stockwork and help clarify the place of gold in the copper-

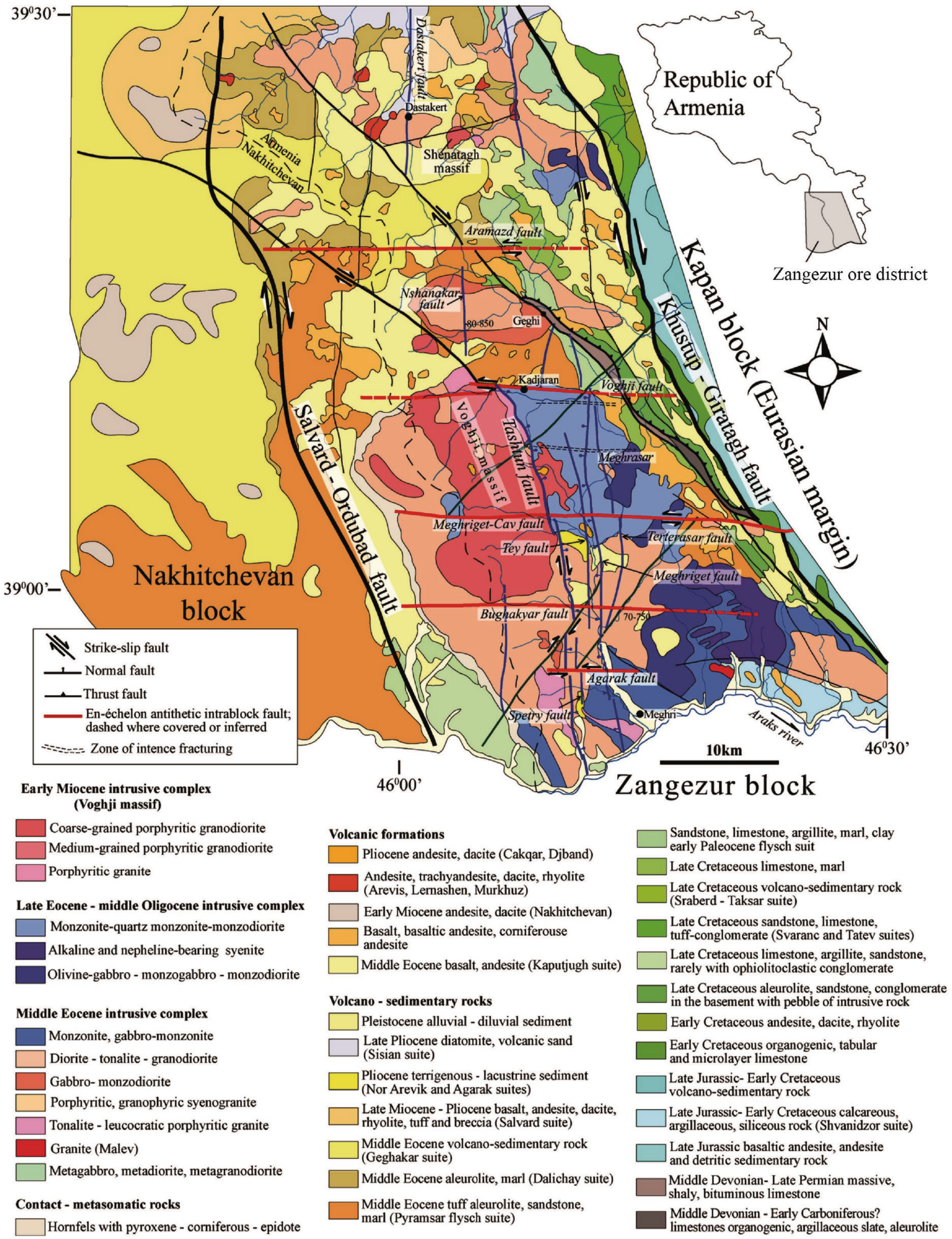

Figure 1. Geological map of the Zangezur ore district (modified by Djrbashyan and Tayan, 2008).

molybdenum-porphyry system. Information about gold mineralization of ore deposits of copper-molybdenum-porphyry formations of Armenia in connection with the conditions of secrecy regarding the complex of noble, rare and dispersed elements dictated under the Soviet system, had not been reflected in the scientific literature for a long time. Summarizing previous studies on distribution of rare and noble elements in the ore formations of the Armenian SSR under the guidance of Maghakyan (1972) showed that gold and silver are unevenly distributed not only on the individual deposits of copper-molybdenum formation, but also in ore concentrates of different stages; chalcopyrite and bornite. The zone of secondary sulfide enrichment-covellite, chalcocite, bornite, was isolated in separate areas under the oxidation zone and worked out at the end of the last century. Therefore, the content of Au in bornite is given according to the data of researchers (Akmaeva et al., 1981). were singled out as industrial mineral-carriers. It was recommended to organize the extraction of noble metals from copper concentrates. Practical value of Agarak and Kadjaran deposits with respect to noble metals, despite the small amounts of gold and silver, was justified by large reserves of copper ores in which they were contained.

Reserves of copper-molybdenum ores of the Kadjaran deposit, as well as the accompanying elements, were reaffirmed repeatedly. Information available in literature on gold and silver mineralization of the ores of Kadjaran copper-molybdenum-porphyry deposit referred to the upper horizons of the Central site (Maghakyan et al., 1972; Pharamazyan, 1974; Pidjyan, 1975; Karamyan, 1978; Akmaeva et al., 1981). During the operation of the open pit the North-Eastern Myakan and Shlorkut sites were put into processing, which differ primarily in intensity and morphological type of mineralization, as well as in material composition of ores and, correspondingly, the satellite-elements accompanying them. General calculation of reserves for Central, North-Eastern, Myakan and Shlorkut sites (all sites are now within the boundaries of the open pit.), according to conditions (standards) of 1959, established by the USSR State Committee for Reserves, was based on average grades of gold in the ore - 0.085 g/t, silver - 3.137g/t (Zilman et al., 1962).

The average annual production of noble metals on the Central site being developed during that period was stable, deviations were observed only towards large indicators, and that was associated with the enrichment of the upper horizons of the deposit by supergene bornite. According to the general calculation in 1985 (Aghamiryan et al., 1985), combining all sites into a single stockwork, conditions (standards) of gold dropped to 0.027 g/t, silver - to 1.58 g/t, with the outcrop of Au in copper concentrate - 2.6 g/t, Ag - 44 g/t.

However, according to Aloyan, in the ores of Kadjaran deposit, within the contour of the first mining, 49 t of gold and 2749 t of silver are concentrated, and besides, the grade of the latter is 1.3 times higher than the reserves of silver counted on all gold ore deposits of Armenia as a whole (Aloyan et al., 2003). According to the latest recalculation of reserves as of 01.01.2007 (Shekhyan et al., 2007) in the ores of the stockwork, calculated by categories B+C_1, reserves of gold make 59 t, of silver - 3314.07 t, with the predicted output of Au in copper concentrate - 3,5g/t, Ag - 75g/t.

GEOLOGICAL STRUCTURE OF KADJARAN DEPOSIT

Detailed geological research on Kadjaran deposit since it was recommended for exploration by Grushev in 1929, are associated with the names of Rusakov, Movsesyan, Mkrtchyan, Maghakyan, Sahakyan, Kazhdan, Pack, Isayenko, Arevshatyan, Pidjyan, Pharamazyan, Hakobyan, Karamyan, Tayan, as well as exploration geologists and mining geologists such Zilmann, Isakhanyan and many others. The stockwork of copper-molybdenum ores of Kadjaran deposit is localized in monzonites of the hanging (eastern) wall of Tashtun Fault and is extended in the submeridional direction for 6.5 km, with the width of about 2 km (Shekhyan et al., 2007). The fault runs through the contact plane of porphyritic granitoids of the Lower Miocene (Tayan, 1969) with Early Oligocene monzonites (Melkonyan et al., 2013; Melkonyan et al., 2014; Rezeau et al., 2014, 2015; Moritz et al., 2015; Moritz et al., 2016). The zones of nevadite and polyphyric granodiorite-porphyries restrict the deposit ores from the eastern flank. Megaphyric granodiorite-porphyries of Early Miocene within the territory of the deposit they have sub-latitudinal and north-western strike (Figure 2), controlling the mineralization and being traced both in monzonites, and in porphyritic granitoids (Harutyunyan et al., 2002). In addition to them, within the deposit itself, rather extended dykes of kersantites and minettes of north-eastern strike occur (Arevshatyan, 1961). Based on the study of age relationships between various paragenetic associations of minerals, 10 stages of mineralization were established (Karamyan and Faramazyan 1960). The main minerals are manifested by several generations, which are clearly established by their structural and crystallographic features, the qualitative and quantitative composition of trace elements (Re, Se, Te, etc.). In each subsequent stage, the continuity of the mineral composition is outlined.

The ore-bearing systems of the stockwork have a regular arrangement. In the west of the ore field near the Tashtun fault, a mainly northwestern system of ore-bearing faults with a strike azimuth of 320^0 is developed; as they move eastward, ore-bearing faults acquire a sub-latitudinal protrusion with a dip of NE 30-60^0. Still further to the east, mineralized faults strike northeast, dipping NW. The

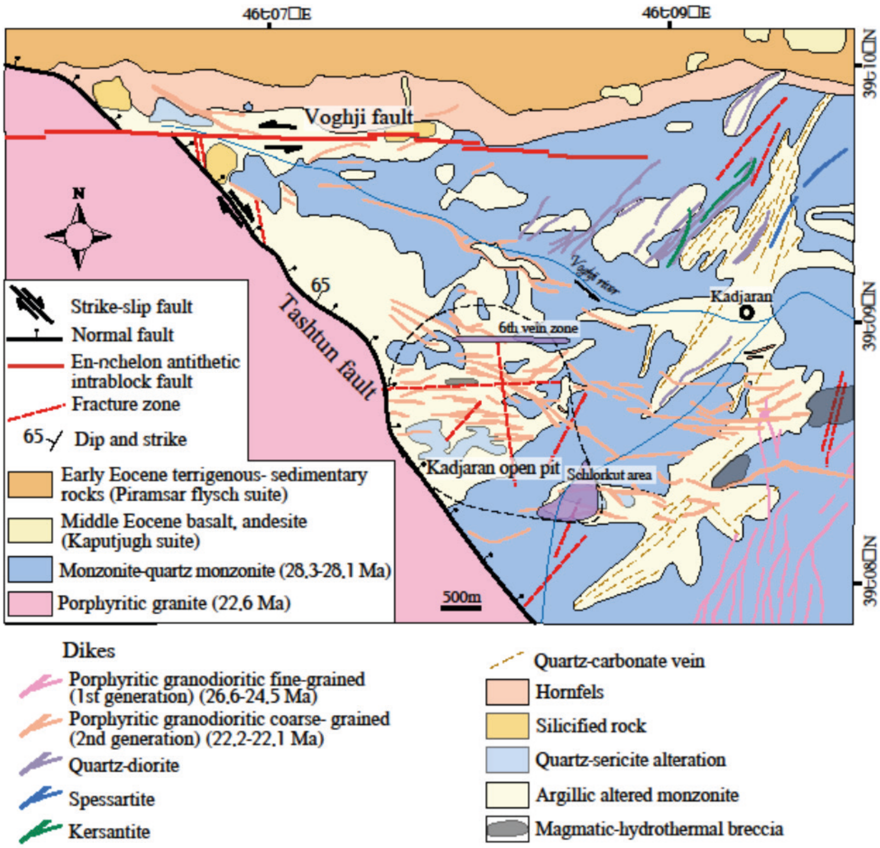

Figure 2. Geological map of the Kadjaran copper-porphyry deposit (after Tayan et al., 2006, modified by Hovakimyan et al., 2019).

veinlets that form the main industrial type of mineralization are represented by thin formations from a millimeter to 3-5 cm, traced up to several meters. The intensity of development of veining and the spatial combination of productive stages of mineralization determine the presence within the stockwork of areas enriched in copper and molybdenum. Vein mineralization is of subordinate importance. Against the background of the prevailing vein-disseminated mineralization, separate quartz-sulfide veins stand out, of which the most powerful up to 4m and extended up to 500m quartz-molybdenite vein can be traced along the dip for 200 m. A characteristic feature of the vein is the overlay of late-stage mineralization.

The ore stockwork is formed by streak-veined and ingrained formations of quartz-magnetite, quartz-feldspar, quartz-molybdenite, quartz-chalcopyrite-molybdenite, quartz-chalcopyrite, quartz-pyrite, quartz-polymetallic stages; the following quartz-carbonate, chalcedony, anhydrite-gypsum is barren (Karamyan and Pharamazyan, 1960; Mkrtchyan et al., 1969).

The copper-molybdenum mineralization at intersections of megaphyric granodiorite-porphyries, as well as the chronometric studies of sericites in circum-ore rocks of economic stages of mineralization were attributed to the Lower Miocene (Movsesyan, 1941; Mkrtchyan et al., 1969; Pidjyan, 1975; Karamyan, 1978).

More than 80 mineral species have been identified at the deposit. Molybdenite and chalcopyrite are of industrial value. The main minerals are manifested by several generations, which are clearly established by their structural and crystallographic features, the qualitative and quantitative composition of trace elements (Re, Se, Te, etc.). Pyrite, bornite, bismuthine, copper-bismuth minerals, enargite, sphalerite, galena appear in a number of ore-bearing stages of mineralization and periods of the most intensive development are outlined for these minerals.

Determination of age of the deposit of molybdenites by spectrographic Re-Os method, confirmed the Lower Miocene age of mineralization -23.5±1.2 Ma (Pharamazyan., 1974). Later determinations (26.43-27.2 ±0.11 Ma according to 4 molybdenites) allowed the authors to single out the Oligocene stage of mineralization (Moritz et al., 2013, 2015, 2016), which was contrary to the actual geological data given by many researchers

(Movsesyan, 1941; Mkrtchyan et al., 1969; Movsesyan et al., 1974; Pidjyan, 1975; Karamyan, 1978).

The stockwork is characterized by non-uniform structure; laterally copper in relation to molybdenum mineralization "is pushed" to the periphery, which is particularly clearly observed in the eastern direction of Tashtun Fault. In the same direction, an increase in thickness of quartz-polymetallic veins is observed. Linearly extended zones are distinguished inside the stockwork with streak-ingrained mineralization enriched by copper (Mkrtchyan et al., 1969; Karamyan, 1978). The vertical zonality is expressed in a successive increase of molybdenum and decrease in grade of copper with increasing depth. On the upper horizons the ratio of their grades was 9:1-7:1 (2175-2085 m horizons, above sea level), it decreases to 5-4.8:1 with the depth (2040-1965 m horizons above sea level) (Tayan et al., 2003). Quartz-polymetallic veins with the thickness of up to 1.2 m on the south-eastern flank are traced to the horizon of 1900 m.

In 1970s, a dyke body of oligoclase-quartz-diorite composition was detected within the Central site on the horizon of 2130 m (Pashkov et al., 1975; Shipulin et al., 1975) or quartz syenite-porphyry (Karamyan et al., 1976), which was characterized by saturation with clastic material (a large amount of clastic material of host rocks) and being impregnated with microcrystalline pyrite (from a later hydrothermal event). Features of the mineral composition of the dike made it possible to attribute this formation to eruptive-breccia bodies of the hypabyssal level of formation (Tayan et al., 2002). The formation time of breccias of Central site by the presence in them of ore clasts of quartz-molybdenite stage and their intersection, as well as the breccia body itself, by quartz-chalcopyritic streaks, was attributed to the interval between quartz-molybdenite and quartz-chalcopyritic stages.

Gold and silver in the stockwork ores

Until the 70s the data on grade of gold and silver in concentrates of copper and molybdenum, as well as in ore minerals were based on the results of fire assay, and later of atomic absorption and spectrochemical analyses. It was believed that gold and silver of Kadjaran deposit mainly occur in form of fine-dispersed inclusions in sulfides (Figure 3 a,b) or the smallest segregations of tellurides of quartz-polymetallic stage - hessite, petzite, krennerite (Maghakyan et al., 1972; Pharamazyan, 1974; Pidjyan, 1975; Karamyan, 1978).

Native gold outside the oxidation zone (Pidjyan, 1960), according to Pharamazyan (1958, 1974) was observed in the ores of quartz-pyrite and quartz-polymetallic stages of mineralization. Pidjyan revealed native gold also in the composition of quartz-chalcopyrite stage (1975). Later Karamyan revealed native gold in the ores of all major mineral associations; small segregations of gold up to 5μm in size were found out in ores of quartz-molybdenite-chalcopyrite stage in close intergrowth not only with chalcopyrite, but also with enargite; in quartz-chalcopyrite ores - in interstices of grains of chalcopyrite and gray copper ore; in quartz-pyrite ores - in form of inclusions up to 10μm in fields of pyrite; in the ores of quartz-polymetallic stage in intergrowths with pyrite, sphalerite, chalcopyrite, gray copper ores and most of all with galena (Akmaeva et al., 1981). Thus, gold was observed in all stages of mineralization with the exception of quartz-molybdenite one.

Native silver was observed by Pidjyan (1975) as part of mineral associations of quartz-pyrite, quartz-chalcopyrite and quartz-polymetallic stages. To the presence of silver in the composition of quartz-molybdenite-chalcopyrite stage testified its high grades in concentrated copper of that stage (Pharamazyan, 1974).

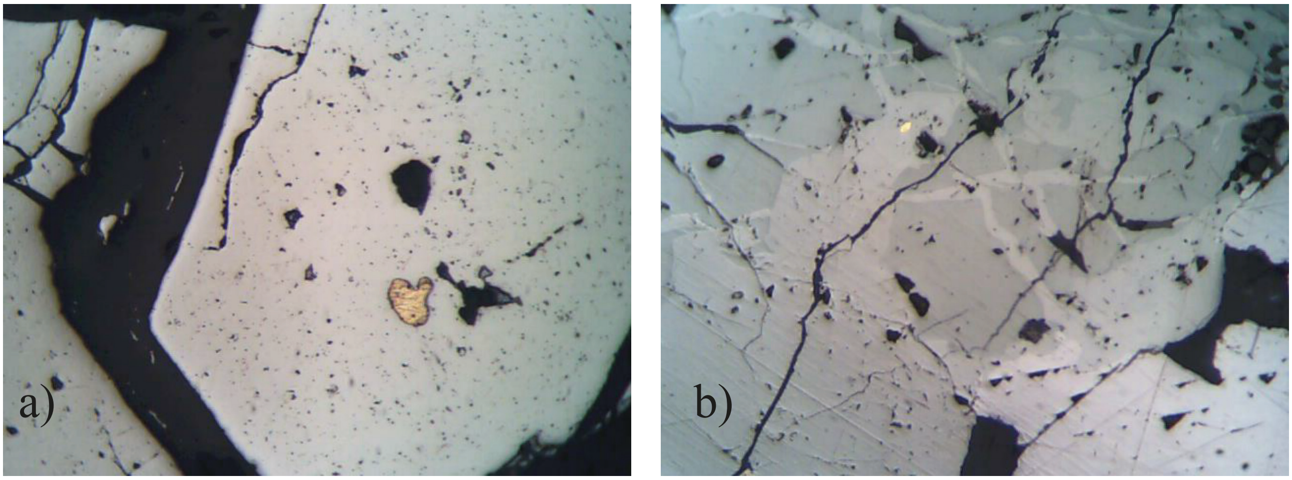

Figure 3. a) gold in pyrite. Magnification x500; b) gold in fahlore. Magnification x500.

METHODS AND MATERIALS

The authors (with S. Akmaeva) analyzed the average monthly samples of the enrichment products of molybdenum and copper concentrates for gold and silver. The data of the assay analysis of the enrichment plant of the Kajaran Mining and Processing Plant were used, which were rechecked by a number of laboratories- the laboratory of the Geographical Administration of the Armenian SSR, the Metallurgical Laboratory of Armniprotsvetmet, the laboratories of the Zangezur and Alaverdi mining plants. According to these studies, Au in copper concentrates is 1.68 g/t (total 92 samples), Ag - 44.71 (total 54 samples); in molybdenum concentrate, the content of Au is 0.71 g/t (total 47 samples), Ag - 22.45 g/t (total 29 samples).

In order to determine the gold content in the ore and to understand the minerals-carriers of precious metals, this group of authors involved analyzes performed by the Bronitsky expedition of the IMGRE (Moscow).

The sensitivity of gold determination was 0.005 g/t (ppm). The average gold content according to the results of analysis of samples of pure minerals (Table 1) was calculated from the results of atomic absorption analysis of 19 samples (Akmaeva et al., 1981).

Revealing the nature of distribution of Au and Ag in the most common minerals of the deposit in the interval of 2150-2050 m horizons (above sea level) was conducted by mono-mineral selections from the collection of Karamyan. The explorations covered the Central and North-Eastern sites of the deposit (Table 3).

RESULTS

Lack of gold was observed in pure samples of molybdenite and low grades of silver up to 2 g/t. Notable grades of Au in molybdenum concentrates on average of 0.71g/t, (22.45 g/t Ag; 47 samples defined), with its absence in mono-minerals, were associated with admixture of flotation-active minerals as galenite and tellurides.

Unusual enrichment of ore clast molybdenites by gold was observed - up to 0.6 g/t (Table 2) with extremely low grades of Ag. The Shlorkut explosive-breccia bodies differ from the eruptive formations of the Central area in the development of several types of cementing matrix with the predominant development of a hydrothermal-

Table 1. Grades of Au and Ag (g/t) in Sulfides of Kadjaran Deposit (averaged over the ore deposit, Akmaeva et al., 1981).

	Au		Ag		
		Average		Average	Number of Samples
Molybdenite	not detected traces	-	1.6-2.4	1.92	5
Chalcopyrite	traces 5.2	2.43	4.6-34	17.5	6
Pyrite	not detected 1.0	0.45	not detected 3.2	1.8	4
Sphalerite	1.6	1.6	132.0	132.0	1
Galenite	0-1.2	0.7	401-620	495.5	3
Bornite	45.0	45.0	409.1	409.1	1

Table 2. Grades of Gold and Silver (g/t) in Sulfides of Explosive-Breccia Formations.

	Central Site									Shlorkut Site				
	Molybdenite						Pyrite			Molybdenite				
Sample N	14	17	19	20	23	24	12	16	22	27	28	29	30	31
Au	0.299	0.334	0.30	0.217	0.623	0.428	-	0.06	-	0.276	0.648	0.700	0.599	0.400
Ag	-	-	-	0.120	0.008	-	-	-	-	0.006	-	-	-	-

Note: The data of microprobe determination, conducted in the Department of Marine Geology of IFREMER, Brest and France, with the assistance of Professor Rodger Hekinyan.

Table 3. Grades of Au and Ag (g/t) in Ore Minerals of Kadjaran deposit (2150-2050 m horizons).

Stages of Mineralization	Minerals	Num. of anal.	Au			Ag		
			X	S	V	X	S	V
Quartz-magnetite	Magnetite	31	0.016	0.019	118.7	2.09	5.36	256.4
Quartz-molybdenite	Molybdenite	10	0.080	0.070	87.0	3.49	2.60	74.5
Quartz-molybdenite-chalcopyrite	Molybdenite	29	0.320	0.030	93.7	4.14	4.81	116.2
	Chalcopyrite	29	1.920	1.490	77.6	23.90	27.56	115.3
Quartz-chalcopyrite	Chalcopyrite	8	2.100	1.600	76.2	22.90	25.30	110.5
Quartz-pyritic	Pyrite	39	1.200	0.61	50.8	13.10	16.10	123.0
Quartz-sphalerite - galenitic	Sphalerite	3	6.360			69.25		
	Galenite	5	4.280			394.70		

Note: X - average grade; s - root-mean-square deviation; V - coefficient of variation (chemical laboratory of IGS AS of the Armenian SSR, atomic absorption method, made by J. Melikyan).

metasomatic chlorite aggregate. Since the ore clasts of breccia bodies could not be captured above the formation level of breccias (2100-2130 m above sea level), it turned out that the gold grade in molybdenites of quartz-molybdenite stage increases with the depth, and the silver grade significantly reduces until complete disappearance. It raised certain doubts about the reliability of the data. At the same time, enrichment of Au was revealed also in explosive-breccia bodies of Shlorkut site; in the in molybdenites of hydrothermal-chlorite matrix of explosions cementing the, grades of Au varied within 0.3-0.7 g/t, (0.0-0.006 g/t Ag). For comparison, grades of Au in the ores of the upper horizons of the deposit, including the oxidation zone average 0.08 g/t.

In that depth interval (2150-2050m - upper horizons) gold and silver are extremely unevenly distributed in ore minerals (Table 3). The root-mean-square deviation of gold grades closest to the average grade of the element, and coefficients of variation of Au in minerals reveal dispersion from 50.8 to 118.7. The latter value characterizes the distribution of gold in magnetites at its minimal grade. In sulfides the dispersion of grades of Au is much less (V=50.8-93.7). The coefficients of variation of chalcopyrites of different stages vary slightly despite the fact that chalcopyrites of quartz-chalcopyritic stage are more enriched in Au (2.10 g/t) in comparison with chalcopyrites of quartz-molybdenite-chalcopyritic stage (1.92 g/t). The same can be said about molybdenites. Gold is most invariably distributed in pyrites. The coefficient of variation of Au in pyrites 50.8 (Table 3) indicates its fairly stable distribution in the mineral; while in other minerals it is represented by large values. Characteristically, for VAg, the coefficient of variation in pyrites is 123.

Grade of silver in minerals shows more significant dispersion (V=70-256.4), and besides, the greatest values of coefficient of variation are typical for magnetites at the average grade of 2.1 g/t. A relatively low V of Ag is typical for molybdenites of quartz-molybdenite stage (V=70). The root-mean-square deviation of Ag exceeds the average values of grades of the element except for molybdenites of quartz-molybdenite stage. Chalcopyrites of different stages both by the average grades of Ag, and by the statistic parameters of its distribution are almost identical. The pyrites of that depth interval with significant dispersion of grades are characterized by greater accumulation of silver (13.1 g/t) compared to the grades of Ag in pyrites of the upper horizons. The interval of 2050-1985 m horizons is covered by fewer samples. Since the average grades, as well as the statistic parameters of distribution of noble metals in sulfides of various paragenetic associations - chalcopyrites and molybdenites, did not reveal significant discrepancies, they were combined in the same samples (Table 4).

The coefficient of variation of grades of noble elements in sulfides detects insignificant dispersion, which is mostly typical for silver (V_{Ag}=32-47) and to a lesser extent, for gold (V_{Au}=43-55). The root-mean-square deviations are much lower than the average grades, which is observed both for Au and Ag. The average grade of Au in molybdenites (1.1 g/t), and at a significant excess in comparison with the molybdenites of the upper horizons they are characterized by its more monotonous distribution (V=43); furthermore, the absence of gold-free molybdenites is characteristic. The sampling does not include the data of microprobe analysis of molybdenites of ingrained type. Grade of Au in molybdenites forming

Table 4. Grades of Au and Ag (g/t) in Sulfides of Kadjaran Deposit for 2050-1985 m Horizons.

Stages of Mineralization	Minerals	N. of anal.	Au			Ag		
			X	S	V	X	S	V
Quartz-molybdenite and Quartz-molybdenite-chalcopyrite	Molybdenite	19	1.10	0.470	43.0	5.3	2.5	47.0
Quartz-molybdenite-Chalcopyrite and Quartz-chalcopyrite	Chalcopyrite	15	2.170	1.150	52.0	32.80	11.80	35.9
Quartz-pyritic	Pyrite	11	0.780	0.430	55.0	8.50	2.70	32.0
Quartz-magnetite	Magnetite	31	0.016	0.019	118.7	2.09	5.36	256.4
Quartz-molybdenite	Molybdenite	10	0.080	0.070	87.0	3.49	2.60	74.5
Quartz-molybdenite-chalcopyrite	Molybdenite	29	0.320	0.030	93.7	4.14	4.81	116.2
	Chalcopyrite	29	1.920	1.490	77.6	23.90	27.56	115.3
Quartz-chalcopyrite	Chalcopyrite	8	2.100	1.600	76.2	22.90	25.30	110.5
Quartz-pyritic	Pyrite	39	1.200	0.610	50.8	13.10	16.10	123.0
Quartz-sphalerite -galenitic	Sphalerite	3	6.360			69.25		
	Galenite	5	4.280			394.70		

Note: Chemical laboratory of IGS NAS RA, method of atomic absorption, analyst - A. Apresyan.

impregnation along the granodiorite-porphyritic dyke of North-Eastern site on the horizon of 2025m near explosive body, according to two determinations is 0.55-0.6 g/t, Ag - 0 and 0.047 g/t; in molybdenite of lamprophyric dyke of Shlorkut site, the grade of Au is 0.52 g/t, and Ag is 0.005 g/t. The pyrite of that depth interval reveals slightly lowered gold grades (0.78 g/t) compared with the pyrite of the upper horizons (1.20 g/t). At the same time, at almost equal values of root-mean-square deviation of Au in molybdenite and pyrite, the dispersion of coefficient of variation in the latter is a little higher, which indicates a significant excess over the average values. The average grade of gold in chalcopyrite of that depth interval (2.17 g/t) is somewhat higher as compared with its grades in chalcopyrites of the upper horizons (1.92 and 2.10 g/t), but dispersion of grades is less significant: the coefficient of variation is 52 (Table 3). Silver in molybdenite is characterized by a relatively low grade (5.3 g/t) with the coefficient of variation 47, exceeding this parameter for chalcopyrite and pyrite. The low values of coefficient of variation of grades of Ag in chalcopyrites (V=35.9) and in pyrites (V=32), indicate a steady distribution of the metal in those sulfides. The accumulation trend of gold in molybdenites with the depth is confirmed by the data for 1965m horizon, the molybdenites of which are characterized by more elevated grades of Au from 1.33 g/t to 2.67g/t, amounting to an average of 1.40 g/t (n=7). They are characterized by lowered grades of Ag from 1.66-4.98 g/t, on average 2.63 g/t.

Available data on grades of noble metals in the average annual copper concentrates since 1985 are quite variable. Low grades of noble metals in copper concentrates of Au 0.1-0.5 g/t, and Ag 15-35 g/t, net years (1990-1999), characterized by a well-known decrease in the plant productivity, for the most part, are related to the direction of expansion of the open pit. In all cases with the progress of the open pit in the eastern direction, where copper and polymetallic ores are concentrated, increase in grades of noble metals is observed in copper concentrates, which is reflected in monthly indicators: Au=4.5-5 g/t; Ag=45-76 g/t.

DISCUSSION

Review of published materials on the deposits of copper- porphyry, gold-copper-porphyry and copper-molybdenum-porphyry formations showed that in the ores of the latter type the average grades of gold are most often within 0.005-0.01 g/t, rarely reaching 0.03 g/t (Krivtsov et al., 1985, Korobeinikov et al., 2003), which is quite comparable to the average grade of Au 0.027 g/t on Kadjaran deposit. Mineralogical studies showed that the main volume of noble metals, as for the deposits of copper-porphyry type is concentrated in the form of finely dispersed gold in copper sulfides of the deposit - bornite and chalcopyrite (Pharamazyan, 1974; Pidjyan, 1975; Karamyan, 1978; Akmaeva et al., 1981). This was confirmed by the balance of grades of Au, to a lesser extent of Ag, in copper concentrates and enrichment tailings (Akmaeva et al., 1981).

Analysis of statistical parameters of distribution of gold and silver in the main industrial mineral-carrier-chalcopyrite on the upper horizons (2175-2075 m) indicates the irregularity of their distribution not only in minerals of different stages, but also in chalcopyrites of the same paragenetic association. The coefficient of variation of gold in chalcopyrites of quartz-molybdenite-chalcopyritic stage V_{Au}=77.6, with the average grade of Au - 1.9 g/t, V_{Ag}=115.3 with the grade of Ag - 23.9 g/t. In chalcopyrites of quartz-chalcopyritic stage V_{Au}=76.2, with the average grade of Au - 2.1 g/t, V_{Ag}=110.5, with the average grade of Ag - 22.9 g/t. There is a tendency to smoothing the heterogeneity of distribution of noble metals in chalcopyrites with the depth. Thus, in the interval of 2085-1985 m horizons the coefficient of variation V_{Au}=52, Au - 2.17 g/t, V_{Ag}=35.9, with the average grade of Ag - 32.8 g/t.

The irregularity in distribution of Au, to a lesser extent of Ag, is also observed in molybdenites of different stages: zero values on the upper horizons in the interval of 2175-2075m horizons are replaced by minimal grades with significant dispersion of statistic parameters. Thus, in molybdenites of quartz-molybdenite stage with V_{Au}=87.5 the grade of Au is 0.08 g/t, with V_{Ag}=74.5 the grade of Ag is 3.49 g/t. In molybdenites of quartz-molybdenite-chalcopyritic stage of the same level with V_{Au}=93.7 the grade of Au is 0.32 g/t, with V_{Ag}=116.2 the grade of Ag is 4.14 g/t. Molybdenites of 2050-1985 m horizons are characterized by more monotonous distribution of noble elements: V_{Au}=43, grade of Au - 1.1 g/t, V_{Ag}=47, Ag - 5.3 g/t. On the 1965 m horizon the average grade of Au is 1.4 g/t.

In pyrites in the interval of 2175-2075m horizons, V_{Au}= 50.8, Au - 1.20 g/t, V_{Ag}=123, Ag - 13.1 g/t. In the interval of 2050-1965m horizons V_{Au}=55, Au - 0.78 g/t, V_{Ag}=32 with the average grade of Ag - 8.5 g/t.

The average distribution parameters of Au, as well as its content in chalcopyrites, both in the quartz-molybdenite-chalcopyrite and quartz-chalcopyrite stages, almost do not differ from each other. That is, the uneven distribution of Au in chalcopyrite within one stage is the same as from stage to stage. The coefficient of variation of Ag for chalcopyrites of both stages is quite high - 110-115 Molybdenites of the same stages differ significantly both in terms of Au content, which in molybdenites of the quartz-molybdenite-chalcopyrite stage is 0.32 g/t higher than in molybdenites of the quartz-molybdenite stage 0 08 g/t with comparable coefficients of variation V - 93.7 and 87.

These are actual data, which are confirmed by the content of Au and Ag in molybdenum and copper concentrates of the Kadjaran plant.

The studies carried out on distribution of Au and Ag in the main industrial sulfides of Kadjaran copper-molybdenum deposit made it possible to single out the main patterns of their distribution. Considerable dispersion of statistic parameters of distribution of noble metals in common sulfide ore minerals, perhaps, is due to irregularity of sampling points both for the horizons and the sites of the deposit; the investigations cover a great range of depth, the main part of molybdenites characterize the western flank of the deposit, whereas the chalcopyrites - the Central and North-Eastern sites. Deposition of copper-molybdenum stockwork ores took place in the temperature range of 420-250 °C (Hovakimyan et al., 2015, 2016 a,b) at the hypabyssal depth level. This is established by the fact of a breakthrough of molybdenum ores by intra-mineralization dike, the hypabyssal level of formation of which has been established on the basis of a number of mineralogical criteria (Tayan et al., 2002; Harutyunyan et al., 2004). The biotite of the dike, in terms of its magnesium and titanium content, is close to the low-pressure region of biotites of moderately magnesian high-titanium compositions (Bachinski, 1984). The parameter Al^{YI} - 0.160-0.165 is the indicator of depth crystallization. The biotites of the intra-mineralization dike in this parameter indicate deeper conditions of crystallization relative to porphyritic granites of the Miocene (Arutyunyan and Mnatsakanyan, 2007). The mentioned conditions of localization of ores with the nature of distribution of noble metals in sulfides reflect the particularity of formation of ore-metasomatic column of copper-molybdenum-porphyry type, in which there is no place for gold ore mineralization of epithermal type.

Stockwork ores are localized in the near-dome part of Late Oligocene monzonites of the mesoabyssal level without going beyond it, overlaying Oligocene granodiorite porphyries and kersantites cutting them. Mineralization is represented mainly by vein-disseminated formations of quartz-molybdenite, quartz-molybdenite-chalcopyrite and quartz-chalcopyrite stages; quartz-pyrite and quartz-polymetallic stages are manifested to a very small extent. Gold plays a cross-cutting role in the ore process; its insignificant contents are noted in magnetites, the earliest stage, forming lenticular accumulations and quartz-magnetite veins on near-surface horizons, and also sometimes observed in molybdenites of early stages. Moreover, in the near-surface horizons, its content is extremely insignificant, with a depth in the range of 2050-1985 m, the distribution is more stable at an average content of 1.1 g/t, the same is noted for chalcopyrite. Obviously, in this depth interval, the physicochemical conditions of deposition from solutions are quite stable.

At the same time, judging by the data in Table 4, for molybdenites of different stages - quartz-molybdenite and quartz-molybdenite-chalcopyrite, the physicochemical conditions differ significantly, while they do not have a decisive effect on the deposition of gold in chalcopyrite. The role of molibenite as a gold concentrator and features of its selective accumulation are considered. The total effect of which processes caused this accumulation is a big question.

CONCLUSIONS

1. Gold and silver, judging by their distribution in sulfides, are unevenly distributed in the vertical range of 2175-1965 m horizons. On the upper horizons (above the 2175 m horizon) Au and Ag show selective accumulation in chalcopyrite (Akmaeva et al., 1981), on the lower horizons (2150-2050 m), in addition to chalcopyrite, they also accumulate in pyrite and molybdenite; and besides, the accumulation capacity of molybdenite and chalcopyrite keeps growing with depth (2050-1985 m). A stable decrease in the statistical parameters in the same direction allows us to assert that the observed distribution of Au and Ag is regular and the geochemical connections of those elements with chalcopyrite recorded in the upper layer are not a constant characteristic of the deposit ores.

2. The presence of Au in ore forming fluid from the beginning of productive stages is evidenced by its elevated grades in "deep" molybdenites of quartz-molybdenite stage, and the patterns of distribution of Au and Ag in sulfides point to the restriction of migratory mobility of noble metals in solutions as they move towards the present-day surface. However, the nature of the behavior of Au and Ag in sulfides reflects a gradual increase in the role of Au, to a lesser extent of Ag in ore forming solutions not only with depth, but also with time, from early stages to the late ones. This is also indicated by the enrichment molybdenite by Au of hydrothermal matrix of explosive breccias, the formation time of which is associated with post-productive stages of mineralization (Harutyunjan et al., 2004).

3. Significant enrichment with ore minerals of the lower horizons of the stockwork (below the 1965 m horizon) by Au and Ag is unexpected because (with the same, if not less development of minerals of quartz-polymetallic stage) their grades are largely limited by the concentrations of copper ores, the ratio of which to molybdenum ones steadily decreases with depth. However, a steady increase of grades of Au and Ag in molybdenites with depth along with a decrease in the values of statistical parameters in the same direction suggests that this trend is sustainable, and the increasing gold mineralization of molybdenite up to 1.4 g/t of Au (average for the 1965 m horizon) allows it to be considered as a mineral-carrier already from the horizon of 2050 m.

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