

**CHARACTERISTICS OF DISTRIBUTION OF ARSENIC  
IN KADJARAN DEPOSIT ORES**

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Ore-geochemical profile of deposit of copper-molybdenum-porphyry type is determined not only by concentration levels of profiling metals, but also by the nature of distribution of secondary metals accompanying them. In the copper-molybdenum stockwork of Kadjaran deposit (the absolute elevation of the upper rim of industrial ores is 2300m, of the lower one - 1450m) average depth interval of the horizons is identified - 2005-1965m, enriched in As; with background content of arsenic 0.005% in some sites, the contents of As reach 0.1-0.3%. The copper-arsenic sulfosalts both in the upper and lower horizons (traced to the horizon of 1840m) are observed in associations of quartz-molybdenite, quartz-molybdenite-chalcocopyrite, quartz-pyritic and quartz-polymetallic stages, i.e. in all ore stages of the deposit. Vertical mineralogical zonality of deposition of arsenic sulfosalts to the depth is manifested by the replacement of enargite-luzonite containing mineral parageneses with tennantite containing ones.

**Keywords:** copper-molybdenum–porphyry deposits, zonality, arsenic, enargite, luzonite, tennantite.

**Introduction:** Researches of copper-molybdenum-porphyry deposits of Zangezur ore district (ZOD) in recent years are mostly related to their distribution by age and composition of ore-bearing intrusions, identifying the geodynamic environment of their formation, as well as isotopy of ores and igneous rocks (Мелконян и др., 2014; Hovakimyan et al., 2015, 2016, 2018, Moritz et al., 2015, 2016; Rezeau et al., 2015; Rezeau, 2017). Less attention is paid to the characteristics of material composition of ores, which in the deposits of copper-molybdenum porphyry type of Zangezur ore district are characterized by the analogous set of secondary metals (Мовсесян, Исаенко, 1974; Пиджян, 1975; Карамян, 1978; Карапетян, 1982), in varying degrees of prevalence. Meanwhile, it is particularly the features of distribution of both profiling and secondary metals in the ores of stockwork must determine the ore-geochemical profile of the deposit and contribute to the construction of its mineralogical and geochemical model.

As far as possible, this gap has been filled by research in recent years

(Арутюнян, Оганесян, 2018). The material accumulated over the years of continuous detailed study of ores of Kadjaran deposit on the study of features of distribution of not only basic sulphides of deposits of copper-molybdenum-porphury type – chalcopyrite and molybdenite, but also the accompanying minerals – pyrite, galena, sphalerite, and many others, among which no small place is occupied by copper-arsenic sulfosalts, allows summarizing the data, highlighting the characteristic features of distribution of As over the vertical span of copper-molybdenum mineralization.

***Mineralogy of arsenic ores.*** The beginning of the study of mineral composition of ores of Kadjaran deposit was laid in the first half of the last century in connection with their industrial development and solution of a number of technological issues. The first study of ore mineralogy of the deposit was carried out by P.M. Zamyatin and I.N. Chirkov (1937), somewhat later they were continued by S.A. Movsesyan (1941) and Z.V. Rupasova (1942). Later, detailed studies were carried out by I.G. Magakyan (1954, 1970), M.P. Isayenko (1964, 1966), G.O. Pijyan (1960, 1975), E.A. Hakobyan (1960), A.S. Haramazyan (1958, 1974), R.N. Zaryan (1964), S.A. Movsesyan (1969), K.A. Karamyanyan (1960, 1978, 1981). In addition to the description of individual minerals (the researches recorded more than 70 mineral types), study of material composition of basic and secondary sulphides of the deposit, the development features of minerals of oxidation zone and of secondary sulfide enrichment were also studied (Акопян, 1960; Мовсесян, 1941; Мовсесян, Исаенко, 1974; Мкртчян и др., 1969; Фарамазян, 1974; Пиджян, 1975; Карамян, 1978, 1981).

Common copper-molybdenum ores, currently developed on Kadjaran deposit are represented by rare thin veins and predominantly, by zones of veining with the capacity up to the first meters, often with localization of mineral associations of different time stages; the proportion of disseminated mineralization is 10% (Мкртчян и др., 1969; Карамян, Фарамазян, 1960; Мовсесян, Исаенко, 1974; Пиджян, 1975). Exploitation work is carried out below the oxidation surface (Акопян, 1960; Мовсесян, Исаенко, 1974; Пиджян, 1975), in the distribution zone of sulfide ores, represented not only by chalcopyrites and molybdenites of basic industrial stages, but also by the minerals sufficiently widespread on the deposit. These include pyrite, galena, sphalerite, tellurides, native gold, silver and many others, and among others arsenic minerals, which are undesirable component of commercial copper concentrates.

Presence of enargite was observed in the ores of quartz-chalcopyrite-molybdenite, quartz-chalcopyrite, quartz-pyritic and quartz-sphalerite-galenic stages (Мкртчян и др., 1969; Фарамазян, 1974; Карамян, 1978, 1981). Enargite was noticed by G.O. Pijyan (1975) also in paragenetic associations of quartz-molybdenite stage. The amount of enargite in the veinlets of different composition ranges within 0.05-0.2%, size of grains is – 0.05-0.5mm; most of all enargite together with luzonite are spread in the veinlets of quartz-chalcopyrite stage (Мкртчян и др., 1969; Фарамазян, 1974). In the upper horizons enargite was observed in single grains (Фарамазян, 1974). Copper-arsenic sulfosalts in the form of thin monomineral veinlets, rarely with quartz,

cross segregations of chalcopyrite, rarely of pyrite, sphalerite, sometimes of molybdenite; enargite also occurs in the form of reactionary fringes, accrued on segregations of chalcopyrite (Фарамазян, 1974). Luzonite grain size is 0.05-0.1mm, their relict form in the enargite grains allowed the researchers to assume that enargite represents product of luzonite transformation. Tennantite like enargite, occurs in all stages of mineralization, depositing at the end of ore deposition. A reactionary replacement of enargite by tennantite is often observed (Карамян, 1972; Фарамазян, 1974; Мовсесян, Исаенко, 1974; Пиджян, 1975; Карамян, 1978, 1981). Tennantite grain size ranges within 0.1-0.2mm. S.A.Movsesyan and M.P.Isayenko (1974) noted intensive replacement of enargite and luzonite by tennantite at a depth of 300-400 m from the surface.

***Distribution of arsenic in the ores of stockwork.*** Close association of copper-arsenic sulfosalts with chalcopyrite conditions their transition during flotation together with chalcopyrite into copper concentrate with average content of 0.5% (Агамирян и др., 1985). Exceeding of these contents in copper concentrates in 1990 made it necessary to single out on the deposit the sites with content of As in the ores of 0.1-1% and mapping them (Таян и др., 1991). It should be noted that before that in the ores of overlying horizons the contents of arsenic up to 0.1% were rarely observed (Фарамазян, 1974). When drawing up single-element maps (Таян и др., 1991) it was considered appropriate to single out 5 classes of As contents: 0.005%; 0.005-0.05%; 0.05-0.15%; 0.15-0.30%, and >0.30%. The data on the As content in ores were summarized by us according to the general plan of the mine 1: 2000, which combines 3 horizons of the deposit - 2005, 1985, 1965m (fig.1).

The scheme of distribution of arsenic drafted by us illustrated the prevailing development of ores of the first class contents – 0.005 %. The ores exceeding these contents were located within the fields of the first class by local islets. The largest contrasting anomaly with an area of about 1200m<sup>2</sup>, represented by thickening of isolines, reflecting 3-4 classes of contents, was observed in the northern part of the deposit and had a sublatitudinally elongated shape; to the east it was traced by two branches of the northeastern direction. Less contrasting anomalies to the south of this zone, represented by 2-3 classes of contents, and occupying small areas up to 600m<sup>2</sup>, were also characterized by elongation in the sublatitudinal, less often in the northeastern direction.

Besides them, anomalies of arsenic of small area, of the same intensity, oriented in the submeridional direction were distinguished. The research allowed evaluating the contamination of the deposit ores by arsenic. According to recommendations given upon completion of the work two operational units were identified in the northeastern part of the deposit, enriched in copper-arsenic sulfosalts with contents of As >0.05% with sites of enrichment up to 0.3%. It was estimated that with proper ore blending with the prevailing distribution of ores with classes of contents less than 0.05%, these contents do not have a significant impact on the quality of copper concentrates and do not exceed the contents of As up to 0.3% acceptable in them (Таян и др., 1991).

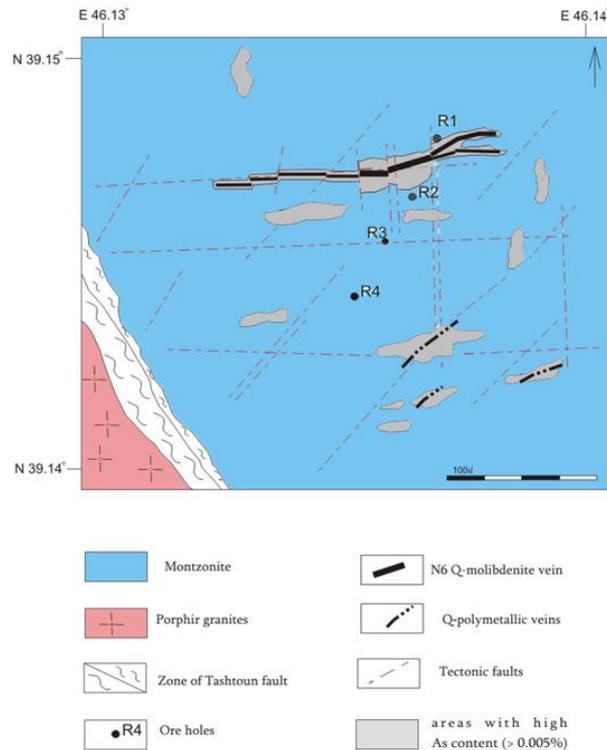


Fig.1. Generalised 3 horizon schematic map of arsenic anomalies for Kadjaran open pit (in WGS 84 coordinate system)

Geological interpretation of sublatitudinal anomaly of arsenic of the northern section showed that it is tied to the longest – up to 800m and deepest quartz-molybdenite vein N6 on the deposit (traced to the horizon of 1840m) (Мкртчян и др., 1969); both in terms of the area and of the intensity, an increase of anomalies is observed from west to east, with fixation of sites of vein expansion. Increase eastward in the vein mass of spotty and nested segregations of chalcopyrite, pyrite, sphalerite and galena, quite often veinlets, along with black fine-grained cryptocrystalline quartz of brecciated structure, in which fragments of white quartz with molybdenite are observed, speaks of sequential fragmentation and «grouting» of the early mineral associations by the later ones (Мкртчян и др., 1969). The nature of the halo of arsenic anomaly, accompanying the formation of the vein and its branches all over, suggests that metal deposition occurred from one and the same solution when reopening the latitudinally oriented localizing structure, complicated in the eastern part by the structures of northeastern strike.

Relatively contrasting anomalies of As, recorded to the south of the 6th vein, are associated with the areas of intensive veining of quartz-chalcopyrite and quartz-molybdenite-chalcopyrite stages. In addition to them, anomalies close to quartz-polymetallic veins are also observed, that is mainly observed on the southeastern flank of the deposit.

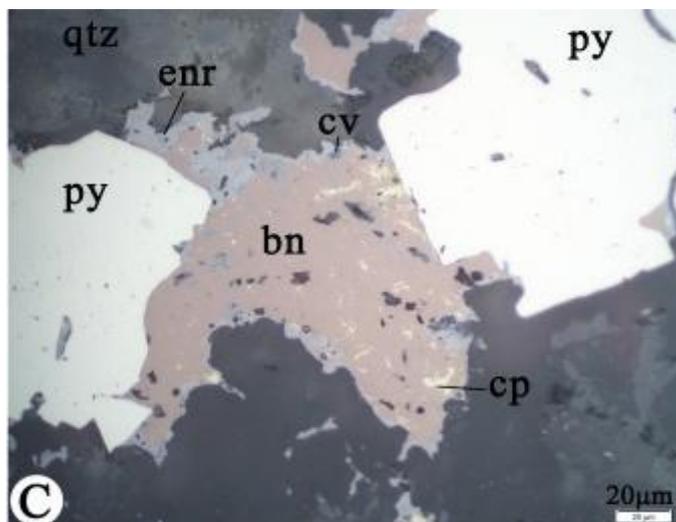


Fig.2. Numerous relics of chalcopyrite in the field of bornite testify to the metasomatic formation of the latter and displacement of arsenic component to the periphery.

Association of enargite with chalcosine, bornite and covellite in bakelites of copper concentrates, in addition to assessing the quality of concentrates, contributed to the identification of associative links of arsenic with other minerals except chalcopyrite (Таян и др., 1991). This allowed linking small anomalies of arsenic with zones of limonitization, developing in areas of steeply dipping meridional faults. In the absence in the zone of supergenesis of clearly defined zone of secondary sulfide enrichment (Акопян, 1960; Мовсесян, Исаенко, 1974; Фарамазян, 1974), development of minerals of secondary sulfide enrichment along fractures was observed by researchers up to the depth of 200m (Акопян, 1960; Пиджян, 1975). According to our research the minerals of secondary sulfide enrichment zone were traced up to the horizon of 1965m (fig.2).

Quantitative distribution of As in monomineral fractions of chalcopyrite, molybdenite, pyrite, selected from the horizons enriched by arsenic, is illustrated in fig.3. The average contents are shown in the table 1. It should be noted the difficulty of comparability of diverse analysis of arsenic, carried out in different years by laboratories with various technological and analytical equipment.

Table 1.

Distribution of arsenic in basic sulphides of Kadjaran deposit

Minerals	Number of samples	X	S	V
Chalcopyrite	18	0.13	0.16	123
Molybdenite	25	0.01	0.007	70
Pyrite	16	0.0348	0.037	106

Note: X – arithmetical mean; S – standard deviation; V – coefficient of variation

In molybdenites the contents of As range within 0.008-0.018%; in the most part of molybdenites hundredths of a percent of As are observed (fig.3).

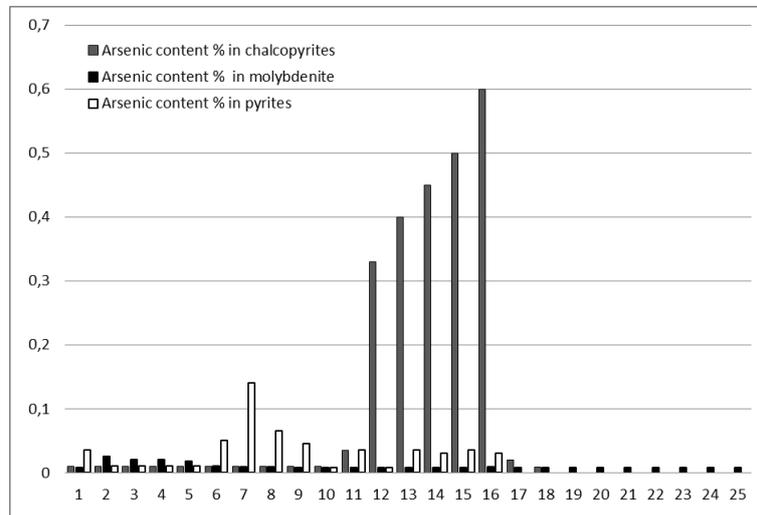


Fig.3. The nature of distribution of arsenic in chalcopyrites, molybdenites and pyrites (in %).

More stable distribution of arsenic was observed in the upper horizons by A.S.Pharamazyan (1974), moreover, in molybdenites of different generations – 0.01-0.03%. Chalcopyrites and pyrites of the mentioned horizons in comparison with the data of A.S. Pharamazyan (1974) show relative enrichment in As: chalcopyrites – 0.01 – 0.60% (0.01-0.3% acc. to A.S. Pharamazyan), pyrites – 0.01-0.14% (0.01-0.1%) wherein, both in chalcopyrites and in pyrites As is mostly represented by hundredths of a percent.

The study of the mineral composition of ores has shown that already from the horizon of 1935m in copper-molybdenum ores enargite is much less frequently observed, while tennantite occurs more often, as it was noted in earlier studies (Мовсесян, Исаенко, 1974).

A similar replacement of the near-surface associations with enargite-luzonite in the lower horizons with tennantite containing ones is described on the copper-porphyry gold bearing deposit of El Salvador in Chile, however in polymetallic Cp-Py-Sl-Gl associations (Einaudi et al., 2003). If in the upper horizons in Kadjaran copper-molybdenum and polymetallic ores along the edges of granular aggregates or individual crystals of enargite replacing chalcopyrite, a thin rim of tennantite is observed, then in the lower horizons the role of tennantite increases significantly.

Starting from the horizon of 1975m primary tennantite is observed in the association with chalcopyrite, not containing relics of foreign minerals, which forms more or less idiomorphic grains 0.1-0.2mm in size. The primary tennantite is also observed in chalcopyrite-molybdenite ores of the 6th quartz-molybdenite vein in the horizon of 1840m (fig.4).

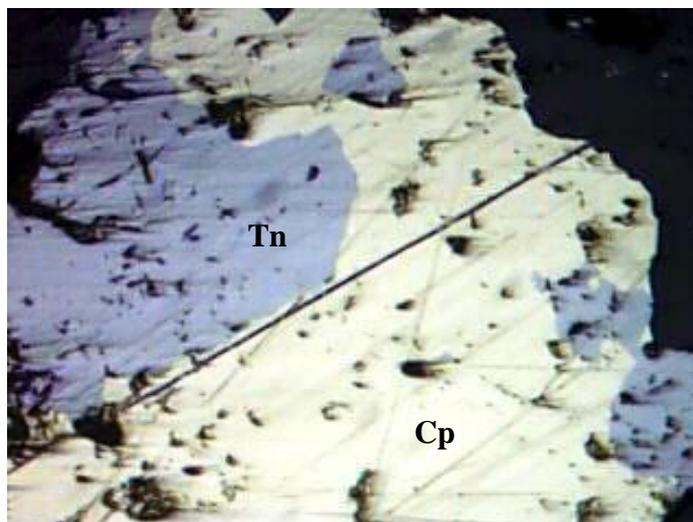


Fig.4. Phenocryst of chalcopyrite (Cp) with tennantite (Tn). x 400. Quartz-molybdenite 6th vein. Horizon of 1840m.

### Discussion and conclusions

Copper-arsenic sulfosalts are typical of the deposits of Cu-porphyry type ( $Cu/Mo = 180-300$ ) of Western Mediterranean segment of Tethys-Eurasian metallogenic belt (Buchim, Zlatitsa-Plavitsa Majdanpek, Veliki Krivel, Bor, Asarel, Medet, etc.), and they are less typical of deposits of Eastern Mediterranean segment. In the ores of Cu-Mo porphyry deposits – Kadjaran, Agarak, Lichk, Aygedzor, Hankasar, Dastakert, Hankavan of Tsaghkunk-Zangezur zone of the Lesser Caucasus, of central part of Tethys-Eurasian metallogenic belt the presence of arsenic was observed by many researchers (Мовсисян, Исаенко, 1974; Пиджян, 1975; Карамян, 1978; Карапетян, 1982 и др.).

Our researches have been devoted to the study of nature of distribution of As in the ores of Kadjaran copper-molybdenum deposit to the depth, which allowed identifying the main features of its manifestation.

1. In vertical section of copper-molybdenum ores As is distributed unevenly; the near surface horizons rich in copper mineralization are depleted in As, and the identified interval of the horizons – 2005-1965m, enriched in As, is the average part in depth (the upper edge of industrial ores is 2300m, the lower one is 1450m). Copper-arsenic sulfosalts are observed in the mineral associations of all ore stages of Kadjaran deposit – quartz-molybdenite, quartz-molybdenite-chalcopyritic, quartz-chalcopyritic, quartz-pyritic, quartz-polymetallic, as noted by some researchers, only with predominant deposition in quartz-chalcopyritic stage (Акопян, 1960; Мкртчян и др., 1969; Фарамазян, 1974; Мовсисян, Исаенко, 1974; Пиджян, 1975).

It is interesting that in the scheme of generalized ore zoning of deposits of Cu -porphyry type (Sillitoe, 1993, 2010; Кривцов и др. 1986; Einaudi et al.,

2003), arsenic sulfosalts gravitate to the apical part of the ore system and are common in chalcopyrite-pyrite-hematite and galena-sphalerite-chalcopyrite-pyritic associations.

2. With background content of As 0.005%, local sites with contents of As 0.1-0.5%, are confined to the areas of intense manifestations of the stages not only productive on Cu, but also to the veins of quartz-polymetallic composition, which allows suggesting unlike the previous researchers (Мкртчян и др., 1969; Фарамазян, 1974) that a considerable part of copper-arsenic sulfosalts is in the mineral associations of this stage. No significant concentrations of arsenic in the upper horizons of 2145-2040m of Kadjaran deposit with great development of copper mineralization  $Cu/Mo = 6.5-8.3$ , compared to lower horizons, where  $Cu/Mo = 5.0-4.4$  (Таян и др., 2003), indicates the absence of correlations between migratory activities of Cu and As in ascending solutions.

3. The assumption of the vertical mineralogical zoning of deposition of arsenic sulfosalts in the ores of Kadjaran stockwork (Мовсесян, Исаенко, 1974) is completely confirmed by our researches. Up to 60-80m from the surface (stockwork of copper-molybdenum ores is traced from 2300 to 1450m) enargite and luzonite occur in rare grains in mineral associations with prevailing chalcopyrite; in the range of the horizons of 2200-2150m increase of the contents of enargite-luzonite is observed and tennantite appears; the prevailing role of tennantite among copper-arsenic sulfosalts is traced from the horizon of 1935m.

Deposition of luzonite, enargite and tennantite in the mentioned sequence during each ore stage (quartz-molybdenite-chalcopyritic, quartz-pyritic and quartz-polymetallic) speaks of a gradual replacement of oxidative conditions by reducing ones; displacement of enargite-luzonite association by tennantite to the depth testify to the more rapid increase in the recovery potential of ore formation environment in comparison with the upper horizons.

4. Between the basic sulfides of the deposit – molybdenite, chalcopyrite and pyrite, As is unevenly distributed. It is significant that even the highest contents of As in pyrites of Kadjaran deposit – 1400g/t do not exceed its average contents in pyrites of deposits of gold polymetallic formation of Zangezur Ore District – 5097 g/t (Таян и др., 2005), that allows moving out pyrite from the standpoint of formational analysis as mineral-indicator (Григорян, Ляхович, 2000) when assessing the geochemical anomalies.

The nature of distribution of arsenic along the vertical section of copper-molybdenum ores together with mineralogical zoning of deposition of copper-arsenic sulfosalts vertically, is one of the most important characteristics, which reflects the ore-geochemical profile of Kadjaran copper-molybdenum deposit. Further research will show according to the uniformity of the material composition of ores to what extent it may be extended to the other copper-molybdenum-porphyry deposits of Tsaghkunk-Zangezur zone.

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**ՄԿՆԴԵՂԻ ՏԵՂԱԲԱՇԽՄԱՆ ԱՌԱՆՁՆԱՀԱՏԿՈՒԹՅՈՒՆՆԵՐԸ  
ՔԱԶԱՐԱՆԻ ՀԱՆՔԱՎԱՅՐԻ ՀԱՆՔԱՔԱՐԵՐՈՒՄ**

**Հարությունյան Մ.Ա., Հովհաննիսյան Ա.Ե., Մաղաքյան Ն.Ի.,  
Հովակիմյան Ս.Է., Միրադեղյան Վ.Վ.**

**Ամփոփում**

Պղինձ-մոլիբդեն պորֆիրային տիպի հանքավայրերի հանքաքանակ-երկրաքիմիական պրոֆիլը որոշվում է ոչ միայն պրոֆիլացնող մետաղների կոնցենտրացիայի մակարդակով, այլ նաև նրանց ուղեկցող երկրորդական մետաղների տեղաբաշխման առանձնահատկություններով: Քաջարանի հանքավայրի պղինձ-մոլիբդենայի շտոքվերկում (արդյունաբերական հանքայնացման վերին սահմանը 2300մ բացարձակ բարձրություն, ներքինը՝ 1450մ) առանձնացված է միջին խորության հորիզոնների միջակայք՝ 2005-1965մ՝ հարստացված մկնդեղով, որտեղ մկնդեղը ունի 0,005% ֆոնային արժեքները, բայց առանձին տեղամասերում մկնդեղի արժեքները հասնում են մինչև 0.1-0.3%: Վերին հորիզոններից սկսած մինչև ուսումնասիրված 1840մ հորիզոնը, պղինձ-մկնդեղային սուլֆոաղերը հանդիպում են քվարց-մոլիբդենիտային, քվարց-մոլիբդենիտ-խալկոպիրիտային, քվարց-պիրիտային, քվարց-բազմամետաղային ստադիաներում, այսինքն հանքավայրի բոլոր հանքային ստադիաներում: Մկնդեղային սուլֆոաղերի նստեցման միներալոգիական ուղղահայաց գոտիականությունը, ըստ խորության, արտահայտվում է էնարգիտ-լյուցոնիտ պարունակող միներալների պարագենեզիսի հերթափոխով տենանտիտ պարունակողներով:

**ОСОБЕННОСТИ РАСПРЕДЕЛЕНИЯ МЫШЬЯКА В РУДАХ  
КАДЖАРАНСКОГО МЕСТОРОЖДЕНИЯ**

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**Резюме**

Рудно-геохимический профиль месторождения медно-молибден-порфирового типа определяется не только уровнями концентрации профилирующих металлов, но и характером распределения сопутствующих им второстепенных металлов. В медно-молибденовом штокверке Каджаранского месторождения (абсолютная отметка верхней кромки промышленных руд 2300м, нижней 1450м) выделен средний по глубинности интервал горизонтов 2005-1965м обогащенный As; при фоновом содержании мышьяка 0,005% на отдельных участках, содержания As достигают 0,1-0,3%. Медно-мышьяковые сульфосоли как на верхних, так и нижних горизонтах (прослежены до горизонта 1840м) отмечаются в ассоциациях кварц-молибденитовой, кварц-молибденит-халькопиритовой, кварц-пиритовой и кварц-полиметаллической стадий, т. е. во всех рудных стадий месторождения. Вертикальная минералогическая зональность отложения мышьяковых сульфосолей с глубиной проявляется сменой энаргит-люционит содержащих минеральных парагенезисов на теннантит содержащие.