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Argentopentlandite $(Fe, Ni)_{8+x}Ag_{1-x}S_8$ from Kamilski Dol — a new mineral species for Bulgaria

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Абстракт. В слабо впръслечно орудени амфиболити от района на рудопроявление Камилски дол, Ивайловградско беше установен за първи път в страната редкият минерал аргентопентландит. Той е представен от дребни (до 10 μm), идиоморфни до хипидиоморфни включения в халкопирит. По цвят (червеникаво-розов), твърдост и оптическа анизотропност, както и по липсата на вътрешни рефлекси и цепителност минералът силно наподобява борнит, с който лесно може да бъде сбъркан. Съставът му по данни от рентгенов микроанализ е: Fe — 36.12; Ni — 20.69; Ag — 11.90; S — 31.36 тегл. %, съответстващ на формулата: $(Fe_{5.3}Ni_{2.9})_{8.2}Ag_{0.9}S_8$.

Съотношенията Fe/Ni и Me/S при наблюдавания Ag дефицит напълно потвърждават кристалохимичната прогноза, базираща се на компенсативно заместване на атоми в структурата.

Key words: argentopentlandite, chrystal chemistry, microprobe analyses, Kamilski dol, Bulgaria

Introduction

A hydrothermal mineralization of rich chemical and mineral composition, occurs in the Kamilski Dol area, Ivailovgrad district, Bulgaria, where the scarce mineral species argentopentlandite is first recorded in the country.

First data of Ag-bearing pentlandite come from Michener's doctoral thesis (1940) on the Sudbury mineralization in Canada. The few further reports are as follows: Шишкин и др. (1971) from Talnach, Octiabrskoe and Hovu-Aksi in Kazachstan; Vuorelainen et al. (1972) — in seven Finnish deposits; Mariko et al. (1973) from Kamaishi mine, Japan; Groves & Hall (1977) from Mount Windarra, Australia; Benvenuti (1991) from Bottino, Italy, and Morales-Ruano&Fenoll Hach-Ali(1994) from El Harcon, Spain. Additional argentopentlandite descriptions for the Canadian deposits Sudbury, Falkonbridge and Bird river give Scott & Gasparrini (1973), Карпенков и др. (1973), Cabri & Laflamme (1976) and Imai et al. (1975). On the basis of analyses known up to date Scott &Gasparrini (1973) propose the generalized formula $(Fe,Ni)_{8+x}Ag_{1-x}S_8$ for the mineral. This formula reflects Shiskin's (1971) suggestion, that Ag atoms in the mineral occupy specific structure sites and hence it should be considered as a separate mineral species. This suggestion was proved in 1973 by Hall & Stewart, who first determined argentopentlandite structure — space group Fm3m, a_0=10.521(3), Z=4, with Ag atoms occupying octahedral 4b sites exclusively and (Fe, Ni) at tetrahedral 32f sites. Proved structure, together with the relatively narrow field of compositional variations are the evidence for the IMA new minerals commission to recognize the phase as an individual mineral species with the name argentopentlandite, based on the proposal of Рудашевский и др. (1977) supported also by S. D. Scott.

Synthetic analogues of argentopentlandite are known from the work of Knop et al. (1965). The phase relations in the system Ag-Fe-Ni-S are studied in detail by Mandziuk & Scott (1977). This work also represents a crystallochemical explanation of the variations in Me/S, (Fe+Ni)/Ag and Fe/Ni ratios of the mineral. Alternative, structural explanation of the most common ratio Fe/Ni≅5/3 give Groves & Hall (1977) supposing that Fe occupies two 4e and one 12i site, while Ni atoms fill the other 12i, thus decreasing the symmetry to P43m, hardly distinguishable from Fm3m by the means of x-ray analysis.

Geological setting

The Kamilski Dol area consists of various metamorphic rocks — gneisses, gneissoschists, schists, marbles, amphibolites, calcoschists, aplitoid leptinites, Fe-bearing quartzites etc., putting together the Chepelare formation (Kozhoukharov, 1992). Different in composition and geological position ore mineralizations are represented in the region. Despite Mankov's (1987) opinion, connecting all mineralizations in the area to one and the same hydrothermal process, most geological facts point, that some conform to the schistosity ores are pre- or intrametamorphic (Драгов и др., 1987), while the cutting mineralizations are postmetamorphic, of supposed Palaeogene age. Their genetic connection to the medium or acid volcanism from the nearby Madjarovo ore field is probable.

The mineral composition of the cutting mineralizations include: arsenopyrite, pyrite, chalcopyrite with mackinawite, sphalerite, marcasite, cobaltite, bismuthinite, galena, native gold, as well as still undetermined Bi-Te sulfides. Submicroscopic mixtures of Cu-Pb-Ag Bi-sulfosalts are also typical. Mankov et al. (1984) and Мънков (1987) describe in addition tetradymite, aikinite, cosalite, native Bi and Te, maldonite, clausthalite, ikunolite, laitakarite, cubanite, stannite, smythite and eskebornite in the same mineralization.

The argentopentlandite was found in slightly mineralized amphibolites from the Golemia Dol locality. The lack of well developed cutting structures immediately connected to the concrete samples may enforce the idea of metamorphic genesis for the mineral, but the existence of Bi-Te sulfides, always connected with cutting mineralizations in the region, makes this possibility improbable.

Mineralogical features

Mineral assemblage

The argentopentlandite is represented by tiny (up to 10 µm) euhedral to semieuhedral inclusions in chalcopyrite, together with mackinawite, represented as a network of fine lamellae situated in three mutually perpendicular planes. Almost all argentopentlandite grains are in regular intergrowth relations with mackinawite. The unidentified Bi-Te sulfides are also represented as inclusions in chalcopyrite. Additional pyrhotite, sphalerite and supergene minerals can be found in separate grains. Late, fine marcasite grains can sporadically be found close to holes and cracks in chalcopyrite.

Optical features

Mineral's optical features fully correspond to those described by cited authors. Its color is reddish pink in fresh polished samples, getting slightly darker with oxidation. Anisotropic effects, internal reflections or fracturing were not observed. Its hardness and reflectivity are close to that of the chalcopyrite host. Based on the complex of optical features the mineral is hardly distinguishable from bornite, and can be easily omitted during a routine diagnostics.

Composition

The small grain dimensions of the examined argentopentlandite established the X-ray microanalysis as the only possible method for determining the composition. The equipment used was an electron microprobe JEOL 773 with added ORTEC's energy dispersion analysis SYSTEM 5000. Even with this highly local method the grain dimensions caused certain problems. The first series of 20 analyses, carried out under standard sulfide analysis conditions, invariably showed certain copper contents. The fact that the copper contents varied significantly even within the limits of one and the same grain suggested that it is due to the influence of the chalcopyrite matrix. This influence could not be avoided during computation, as chalcopyrite affected not only Cu but also Fe and S. That is why measures have been taken for decreasing the generating area of secondary electron emission, namely — decreasing the applied current and the sample's dead time. The first four analyses listed in the following Table 1 belong to one and the same grain and were performed at decreasing current and dead time values, until no copper was detected any more. Final values were — 193 nA and 10 µs. Remaining parameters were: accelerating voltage — 20 kV, impulse counting time — 100 s. Chalcopyrite of known composition was used for Fe and S standard. Ag and Ni were compared to pure metals. The atomic number, absorption and luminescence correction routine was ORTEC's SPRINT 5.00. Once the final analysis conditions were fixed, two more grains were analyzed, that showed practically identical results and were considered to represent the true mineral composition.

Mean values of the last three analyses were used in formula estimations, given in Table 2.

The final formula estimated on 8 atoms basis at 0.1 atom precision is: $(Fe_{5.3}Ni_{2.9})_{8.2}Ag_{0.9}S_8$.

Table 1
Microprobe analyses of the Kamilski Dol argentopentlandite: 1a-d — one and the same grain at decreasing sample current and dead time - down to 193 nA and 10ms respectively; 2-3 — other grains at listed conditions

Таблица 1
Микросондови анализи на аргентопентландита от Камилски Дол: 1a-d — едно и също зърно при намаляващ ток и мъртво време на образеца, до стойности 193 nA и 10ms съответно; 2-3 — други зърна при тези условия на анализа

wt.% for analysis No	1a	1b	1c	1d	2	3
Fe	36.37	35.60	36.79	36.16	35.99	36.21
Ni	20.27	19.69	20.04	20.73	20.50	20.85
Ag	11.79	12.02	11.66	11.95	11.96	11.80
S	30.77	31.18	31.24	31.34	31.17	31.56
Cu	0.83	0.65	0.60	-	-	-
Total	100.03	99.14	100.33	100.18	99.62	100.42

Table 2
Mean analytical results and formula values for the investigated argentopentlandite

Таблица 2
Усреднени аналитични резултати и формулни параметри на изследвания аргентопентландит

	wt. %	At.% norm.	ratio	Coefficient
Fe	36.12	30.98	Fe/Ni=1.834	5.29
Ni	20.69	16.89		2.88
Ag	11.90	5.29		0.90
S	31.36	46.85	Me/S=1.135	8.00
Total	100.07			

Discussion

Argentopentlandite's ideal stoichiometric composition, determined on the basis of addition-ommition replacement in normal pentlandite is $Fe_5Ni_3AgS_8$. This is also the composition of the most stable phase (DTA data of Mandziuk & Scott, 1977), as well as the most common composition in nature. The general formula for preserving electroneutrality at pentlandite ratio Me/S = 9/8 is:

$$(1-x)Ag^{11} + (0.5 - x/2)Fe^{8} = (1.5 - 1.5x)Ni^{10},$$

where x is the value of the Ag deficit to 1 atom.

However, the phase relations in the system Fe-Ni-Ag-S (Mandziuk & Scott, 1977) point out that the mineral can still be stable at Me/S ratios from 1.10 to 1.145, as well as at Ag deficit (Ag<1). The authors mentioned above relate the phenomenon to possible addition — omission effects in some tetrahedral sites, free in stoichiometric case. The crystallochemical forecast (Rajamani & Prewitt, 1973) for the Me/S — Fe/Ni relation in argentopentlandite with stoichiometric Ag (Ag=1) is given in Fig. 1 with heavy line. It is clear from the last equation, that the curve in case of Ag deficit should be parallel to this but situated higher. The curve corresponding to the Ag deficit of our sample (dashed line in Fig. 1) was determined in point X at Me/S=9/8. It is evident from this figure that investigated sample's composition coincides precisely with its theoretical presumption.

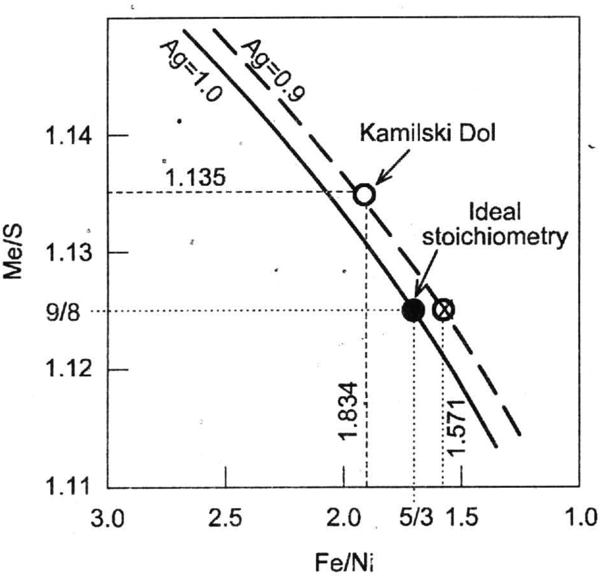

Fig. 1. Position of the investigated argentopentlandite (open circle), according to the crystallochemical relation Me/S — Fe/Ni (Rajamani & Prewitt, 1973)

Фиг. 1. Положение на изследвания аргентопентландит (празно кръгче) по отношение на кристалохимичната зависимост Me/S — Fe/Ni (Rajamani & Prewitt, 1973)

The Kamilski Dol finding is typical also in genetic respect. As in all known cases it is included in chalcopyrite and its coexistence with mackinawite is characteristic. Up to 1994 the mineral has been connected to basic and ultrabasic rocks exclusively. However, the El Harcon finding in Spain (Ruano-Morales & Fenoll Hach-Ali, 1994) showed that acid volcanism can also cause its deposition. The El Harcon environment is very close to that found in Kamilski Dol. In our case the acid volcanism of the nearby Madjarovo region can be the possible cause for it. Both assemblages contain Ag and Pb bearing Bi-sulphosalts. In both cases the mineral is deposited in amphibolites at some distance from the main hydrothermal mineralizations, that is also characteristic in other cases as well (Groves & Hall, 1977). A possible explanation for this behavior can be that solutions derived from acid magmas need some alteration that transfusion through basic or ultrabasic rocks provides to enable argentopentlandite deposition.

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