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A case of pyrite-küstelite intergrowth in Popsko deposit, Eastern Rhodopes

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Abstract. An exotic küstelite-pyrite mirmecitic intergrowth was found in the base metal ores of Popsko deposit, Eastern Rhodopes, Bulgaria. Its existence puts a number of genetic questions. The most probable forming mechanism is an eutectoid decomposition of an unstable noncoherent ISS in the system Au-Ag-Fe-S. The hypothesis rises the necessity of investigation of the phase relations in this system.

Key words: küstelite, pyrite, integrowth, Popsko deposit, Rhodopes

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В полиметалното орудяване на находище Попско (Източни Родопи, България) беше установен случай на закономерно мирмекитоподобно срастване между кюстелит и пирит. Неговото съществуване поставя редица генетични въпроси. Най-вероятният механизъм на образуване е евтектоиден разпад на нестабилен некохерентен междинен твърд разтвор в системата Au-Ag-Fe-S. Хипотезата сочи необходимостта от изследване на фазовите отношения в тази система.

Ключови думи: кюстелит, пирит, срастване, находище Попско, Родопи

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Introduction

Mineralogical studies of the ores from the Popsko hydrothermal deposit, Eastern Rhodope region, revealed an exotic pyrite-küstelite mirmecitic intergrowth. Although such kind of structure may reflect a number of different genetic mechanisms, the one possible — dissolution from an ISS is worth to be considered in connection with the possible miscibility in the system Au-Ag-Fe-S.

Geological setting

The Popsko deposit is located about 30 km NE of the town of Krumovgrad and 30 km north of the frontier with Greece within the East-Rhodopian metallogenic region at the border of the East Rhodopian Paleogene depression. The region comprises Pre-Tertiary metamorphic rocks of the Rhodope massif and Oligocene magmatic rocks.

The metamorphic series consist of biotite- and two-mica gneisses, amphibolites, marble lenses, schists and migmatites. This succession is cross-cut by an intrusion with monzonitoidic composition and volcanic rocks of rhyolites and trachyrhyolites.

The Popsko deposit is spatially and genetically associated with the Oligocene magmatism (Boyanov, Mavroudchiev, 1961). The isotopic ratio of Pb in galena points to a model age of the deposit of 32±7 Ma (Amov et al., 1985). The K/Ar dating of a rhyolite dike there points to 27.5 Ma (Lilov et al., 1987). This age corresponds to the Late Eocene-Early Oligocene boundary.

The gold - base metal mineralization occurs within hydrothermal quartz-carbonate veins which fill north-north-east trending fissures (0-20°).

The quartz-carbonate veins are characterized by several textural varieties (massive, brecciated, cross-cutting), which are usually mixed. According to textural relationship the paragenetic sequence can be described by five successive mineral parageneses 1) pyrite-chalcopyrite; 2) base metal; 3) sulphosalts; 4) baryte; 5) late base metal.

Sulfosalts paragenesis, containing the considered pyrite-küstelite intergrowth, includes arsenopyrite and abundant silver minerals — electrum, küstelite, acanthite, proustite, pearceite.

Characteristics of the pyrite-küstelite intergrowth

The pyrite-küstelite intergrowth was found as an irregular grain 50 × 80 mm in association with acanthite, sphalerite, galena, chalcopyrite and pearceite within quartz gangue. The intergrowth is in direct contact with all these minerals excluding galena (Plate Ia).

The intergrowth consists of two optically different phases observed in the polished section. The light one has a relative reflection comparable to that of native silver. The second one is yellowish and significantly darker than the first one.

The fine texture of the grain can be described with the term mirmecitic in its clearly morphological meaning. The light phase is noticed to originate from several centres and goes further with steadily increasing the grain size from less than 1 mm close to these centres, to about 5 mm at the rim. The development of the light phase follows some sort of branching at its derivation from these centres (Plate Ib). The dark phase fills up the space between the grains of the light one.

The chemistry of the two optically distinguished phases was investigated by EDS electron-microprobe analyses on JEOL JSM 35 CF, with Tracor Northern TN-2000 analyzing system. Due to the strong photochemical decomposition encountered under the electron beam (and even under normal light microscope), different analytical conditions had to be tried. Best results (totals closer to 100 %) were obtained at 20 kV and beam diameter of 3 mm. The standards used were: pure metals for AuL_α, AgL_α, CuK_α and FeK_α; chalcopyrite for SK_α. Acquisition times for all elements were 100 s.

According to the obtained results, the light phase is to be defined as küstelite (Table 1). The small amount of Fe there is most probably due to analytical errors coming up from the insufficient grain sizes, but its actual existence can not be entirely excluded, as minor amounts of Fe are common in natural AuAg alloys and even significant values are reported by Boyle (1979).

Three bulk area analyses at 35, 100 and 100 mm^2 areas differing in the mirmecitic grain size show the approximate composition — $Ag_{29-33}Au_{28-29}Fe_{21-24}S_{15-20}$ (Table 1).These analyses were done in connection with the hypothesis of dissolution from ISS, believed to roughly approach in composition these values.

The dark phase — pyrite (Table 1) always shows minor quantities of Au and Ag. Some part of these results is definitely due to the restricted grain sizes and hence the probability of matrix influence, but we are uncertain to link all of these impurities to analytical errors only, as far as minor Au and Ag are commonly reported in this mineral (Cook, Chryssoulis, 1990). Moreover, a good quality analysis of large pyrite grain in direct contact with the investigated intergrowth also showed comparable amounts of Au and Ag (Table 1).

Table 1

Microprobe analyses (wt. %) of küstelite, pyrite and bulk areas of the intergrowth

Таблица 1

Електронно-микросондови анализи (тегл. %) на кюстелит, пирит и валов състав на площи от срастъка

Mineral	Au	Ag	Fe	Cu	S	Total
Küstelite (light phase)	51.20	31.01	3.15			85.36
	54.39	35.63	2.90			92.50
	52.77	36.64	1.00	1.02		91.42
Pyrite (dark phase)	12.77	10.28	34.53		41.67	99.25
	2.24	5.69	38.70		47.73	94.37
Pyrite separate grain	6.06	3.96	41.78	0.71	44.92	98.40
Bulk analyses- 35 μm^2	55.35	34.46	11.79		4.69	106.29
100 μm^2	50.40	29.14	12.17		5.91	97.61
100 μm^2	50.49	32.80	10.49		5.39	99.17

Realizing that the extremely difficult analytical conditions (small grain sizes together with photochemical decomposition) add significant uncertainty to our results, we also tried some semiquantitive methods to ensure the case.

Plate IIb represents a 12 mm characteristic X-ray profile scan through the grain represented on Plate IIa. The result is two reciprocal groups of parallel curves — Fe-S and Au-Ag respectively, that confirm the existence of two separate phases with the respective composition.

Discussion

Concerning the genesis of the observed phenomenon puts more questions than answers. The only genetic clue in this case is the fine mirmecitic texture. However, following Ramdohr (1975) we should stress that a number of different genetic mechanisms may be responsible for almost one and the same textural result: fast skeletal growth of one phase in another liquid or solid one; eutectoid crystallization from binary or polynary melt; decomposition of unstable intermediate solid solution (ISS); recovery of cracks in cataclased grains; nucleation from mixed gel solutions.

PLATE I

a. Pyrite-küstelite intergrowth in association with acanthite, pearceite, sphalerite, galena and chalcopyrite within quartz gangue

b. Backscattered electron image, illustrating nucleation and branching from several centers

ТАБЛИЦА I

a. Пирит-кюстелитов срастък в асоциация с акантит, пирсеит, сфалерит, галенит и халкопирит в кварцова основна маса

b. Електронно-микроскопско изображение на срастъка, илюстриращо нуклеация и разклоняване от няколко центъра

PLATE II

a. Portion of the pyrite-küstelite intergrowth with profile line

b. Profiles in characteristic X-rays — Au, Ag, Fe, S

ТАБЛИЦА II

a. Част от пирит-кюстелитовия срастък с профилна линия

b. Профили в характеристично лъчение - Au, Ag, Fe, S

PLATE I ТАБЛИЦА I

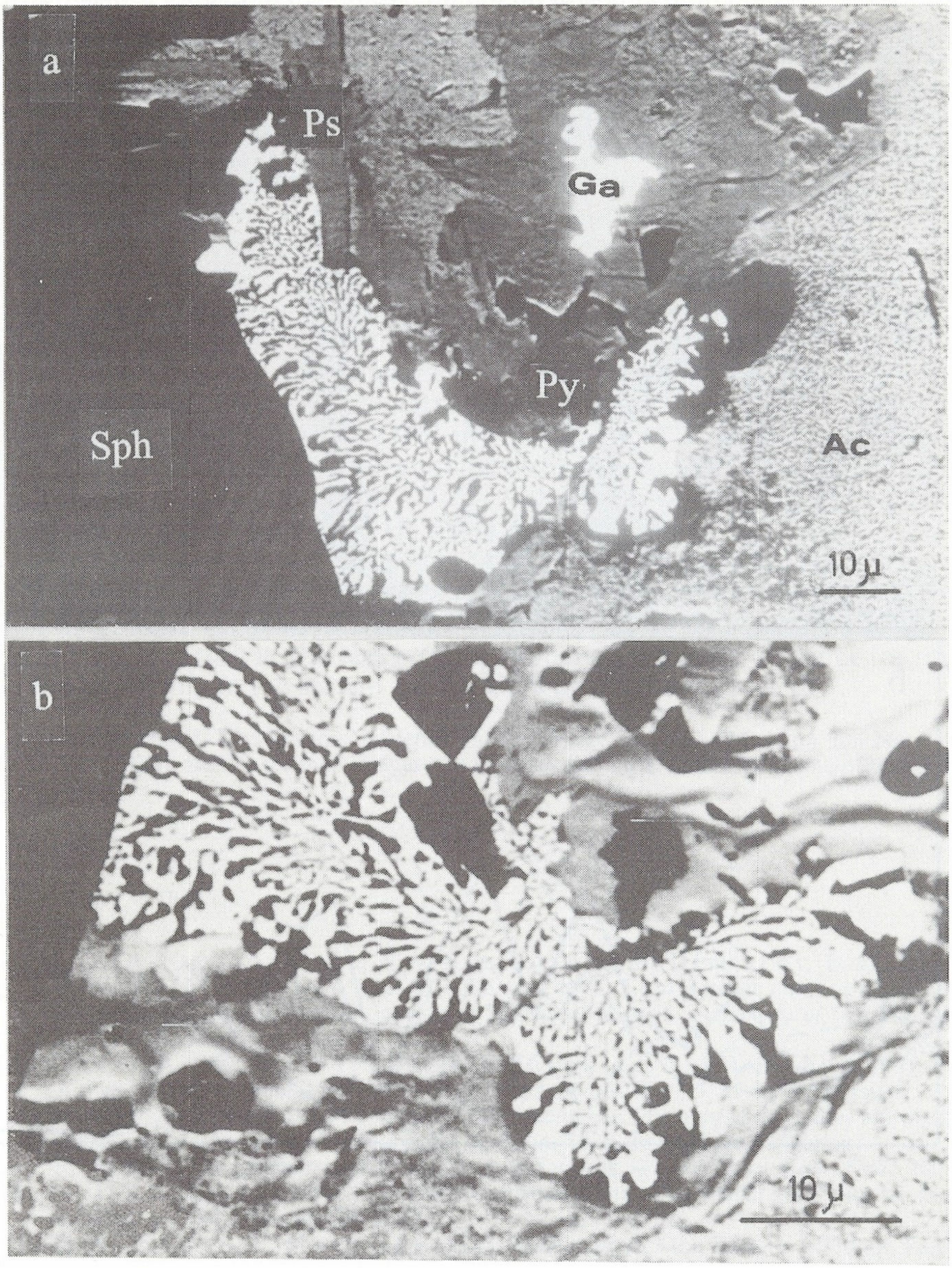
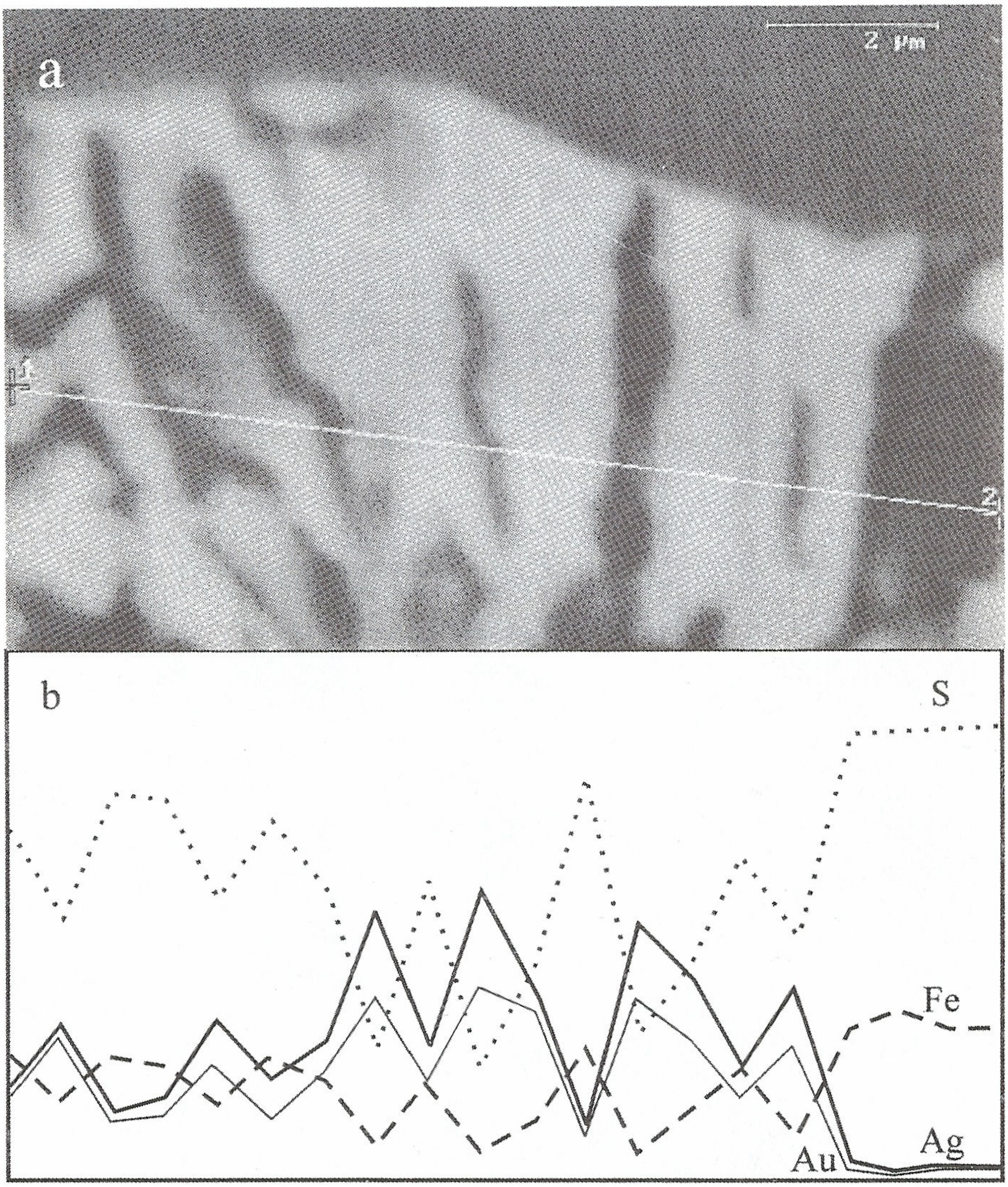


PLATE II ТАБЛИЦА II



Considering described specifics of the observed fine texture we tend to accept the hypothesis of eutectoid decomposition of an unstable noncoherent ISS with composition in the system Au-Ag-Fe-S. Such ISS is not actually known but we consider it probable as far as a number of minerals are known in closely related ternary systems: Ag-Fe-S — argentopyrite ($AgFe_2S_3$), sternbergite ($AgFe_2S_3$), argyropyrite ($Ag_2Fe_7S_{11}$), freisite ($Ag_2Fe_5S_8$); Ag-Au-S — uytenbogaardtite (Ag_3AuS_2), liujinyinite (Ag_3AuS_2), petrovskaite (AuAg(S,Se)), lenaite ($AgFeS_2$) (Amuzinsky et al., 1995). Moreover, minor miscibility between these ternary systems is indicated by the common reports of Au- and Ag-bearing pyrites (including also this study).

Taking into account the melting points of the constituents, one should expect extremely high forming temperatures for such solid solution, but a probable eutectic relations can significantly decrease this temperature down to completely acceptable for the hydrothermal process values. The associated mineral assemblage indicates temperature range up to 250°C. Even stating that this solid solution is formed at higher temperatures in the earlier stages, temperatures over 350—400°C are unlikely.

It should be stated, however, that the possibility of contemporary nucleation from mixed polynary gel still remains probable. Such solutions can keep components dissolved down to temperatures of 100 °C and are known to form aggregates very similar in shape to those observed (Ramdohr, 1975).

Other more exotic hypothesis may refer to küstelite dendrites, starting their growth from several centres, interpreted in the former consideration as exsolution nucleation centres. Later pyrite fills up the space between dendritic branches.

Whatever the truth is, the observed phenomenon is a good evidence for investigating the miscibility in the system Au-Ag-Fe-S on synthetic grounds.

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