

ARSENOPYRITE FROM THE LOW-SULPHIDATION
SEDEFICHE AU-AG DEPOSIT, EASTERN RHODOPES:
MINERAL ASSOCIATION AND GOLD POTENTIAL

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Abstract

The Sedefche Au-Ag deposit is located in the eastern Rhodopes, Bulgaria and is part of the Zvezdel-Pcheloyad ore field. The deposit is of low-sulphidation epithermal type, hosted in Oligocene highly silicified intermediate volcanic tuffs, which lie above shallow marine sediments of organogenic limestones. The orebody has stratiform shape partly outcropping onto the surface.

The ore mineralization is represented by small crystals and fine grained aggregates of sulphides (mainly pyrite, arsenopyrite, marcasite, chalcopyrite, galena, sphalerite) and associated sulphosalts (tetrahedrite, pyrargyrite, freibergite, and miargyrite) within matrix of quartz, formed in several stages of deposition.

Gold in the deposit is detected in significant amounts in bulk ore samples, while native gold (a single < 1 µm gold nugget) and gold-bearing phases were sporadically discovered. The form of gold presence in the deposit is nevertheless debatable.

Using combined SEM-EDS, EPMA and LA-ICP-MS approach, the highest concentrations of gold have been established in the arsenopyrite – the gold content there is up to hundredfold higher than in other ore minerals being potential concentrators of gold such as pyrite, marcasite and chalcopyrite. The presence of gold in arsenopyrite predominantly as nanoparticles, irregularly disseminated in the crystals as clusters of inclusions is suggested.

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Key words: “invisible gold”, nanoparticles, arsenopyrite, low-sulphidation epithermal type, LA-ICP-MS

Introduction. The Sedefche Au-Ag deposit is located in the eastern Rhodopes, between the towns of Momchilgrad and Krumovgrad, south Bulgaria. It has been known since late-Antiquity when it has been mined for its silver content. The increasing prices and demands for precious metals in recent years have promoted interest and further exploration of these resources. The silver in the deposit mostly occurs as proper silver-bearing mineral phases (sulphides, sulphosalts, and native silver as well). The gold in the deposit is much more elusive. Although it has been detected in significant amounts in bulk samples, native gold and gold-bearing phases have not been discovered until recent years and the form of its presence in the deposit has long remained unknown. A microscopic ($< 1 \mu\text{m}$) gold nugget has been observed in polished samples of artificially extracted heavy mineral fraction from the Sedefche ores [1]. LA-ICP-MS study on the trace element incorporation in the sulphide minerals from the deposit revealed that gold preferably is accommodated by arsenopyrite and to a lesser extent by pyrite. The present study reports mineralogical and geochemical properties of the arsenopyrite.

Geological background. The Sedefche deposit is considered a part of the Zvezdel-Pcheloyad ore field [2]. The metamorphic basement in the region is presented by the marble and amphibolite rocks from the Krumovitsa lithotectonic Unit [3,4] covered by Oligocene organogenic limestones (*coquina/coquinite*), consisting of debris of mollusc shells, formed in a shallow marine environment. The latter are overlain by basic to intermediate volcanic materials also of Oligocene age (andesitobasalts to andesites; pyroclastics and epiclastics) of the Zvezdel volcanic complex [3,4], dominated by intermediate tuffs in the Sedefche area.

The Sedefche deposit is a low-sulphidation epithermal deposit, hosted in the intermediate volcanic tuffs. The orebody has stratiform shape and corresponds to highly silicified areas in the tuffs. Its upper parts outcrop near the surface [5–7]. The rocks laying stratigraphically below the tuffs (limestones and metamorphites) do not contain any ore mineralization. From structural and tectonic standpoint, the duct and source of the ore-bearing hydrothermal fluids is debatable, but most likely connected to the nearby system of Zvezdel paleovolcano. The ore mineralization is represented by microscopic crystals and fine grained aggregates of sulphides (mainly pyrite, marcasite, chalcopyrite, arsenopyrite, galena, sphalerite) and sulphosalts (tetrahedrite, pyrargyrite, freibergite and miargyrite) within matrix of quartz [8]. The crystal size of the ore minerals very rarely exceeds $100 \mu\text{m}$, usually up to $30\text{--}40 \mu\text{m}$ or less.

Three successive stages of ore mineralization (quartz-sulphide – $300\text{--}260^\circ\text{C}$, quartz-chalcedony-sulphosalt – $255\text{--}175^\circ\text{C}$, and carbonate – $290\text{--}90^\circ\text{C}$), with different mineral associations, where galena-sphalerite, pyrrhotite-arsenopyrite, sulphosalt and carbonate are mainly outlined by previous authors [2,9,10]. Sphe-

rutiles of native arsenic are established at the very late ore-mineralization process under 150 °C marking the low S-activity of the fluids [11].

Materials and methods. Polished ore samples were studied by polarized reflected-light microscope Meiji 9430 and Leica DM750P in order to select representative mineral relationships and suitable crystals for further analytical procedures. Rare sulphide crystals with size larger than 50 µm were preferred for the LA-ICP-MS study, assuming that the laser beam diameter would be at least 30 µm.

SEM-EDS analyses were conducted with JEOL JSM-6010 PLUS/LA (at UMG “St. Ivan Rilski”, Sofia) prior to electron-microprobe JEOL JXA-8200 WDS at Montanuniversität (Leoben, Austria) by using natural and synthetic standards.

The LA-ICP-MS investigations were done with Perkin-Elmer SCIEX ELAN DRC-e and LA New Wave Research UP-193; $\lambda = 193$ nm; laser Ar-F; diameter of the laser beam – 30 µm at the Geological Institute of the Bulgarian Academy of Sciences. Mass 1 was used as external standard in recalculation of the trace element incorporation.

Although arsenopyrite is commonly encountered in Sedefche deposit, it is represented mostly by μ -sized crystals and aggregates. Larger crystals (≥ 40 –50 µm), suitable for investigation by LA-ICP-MS method are used. Two samples containing the largest arsenopyrite crystals and aggregates were selected.

Results. Stages of mineralization in the Sedefche Au-Ag deposit. According to the observed mineral relationships and textural diversity of the studied ore samples, several successive mineral associations are distinguished in the Sedefche deposit discussed below (Fig. 1).

Quartz-arsenopyrite association is the earliest and formed at the highest temperature. It is characterized by intense silicification of the host tuffs and formation of euhedral 1st generation arsenopyrite. It is represented as elongated (along the *c*-axis, Fig. 2a) prismatic to needle-like crystals or as their rhombic cross-sections (normal to the *c*-axis) hosted in quartz. Their length rarely exceeds 50 µm. Generally, this early arsenopyrite crystals associate with pyrite, sphalerite and tetrahedrite (Fig. 2b) and occasionally crystals contain inclusions of early miargyrite (Fig. 2c). The euhedral arsenopyrite is often intersected and overlapped by pyrite which was later turned into marcasite (Fig. 2d).

Quartz formation accompanies all subsequent ore associations (till the calcite one). Late quartz veinlets frequently intersect earlier arsenopyrite.

Quartz-pyrite association is scarcely developed in the studied samples. Pyrite appears as euhedral or subeuhedral single crystals or aggregates often overgrown by later-precipitated ore minerals (such as sphalerite) hosted in quartz. The mineral is affected and partially overprinted and converted into marcasite due to late ore-forming processes in the deposit.

Pyrite was chemically studied by combination of EPMA and LA-ICP-MS for major and trace elements. Typically, it contains small but constant quantity of

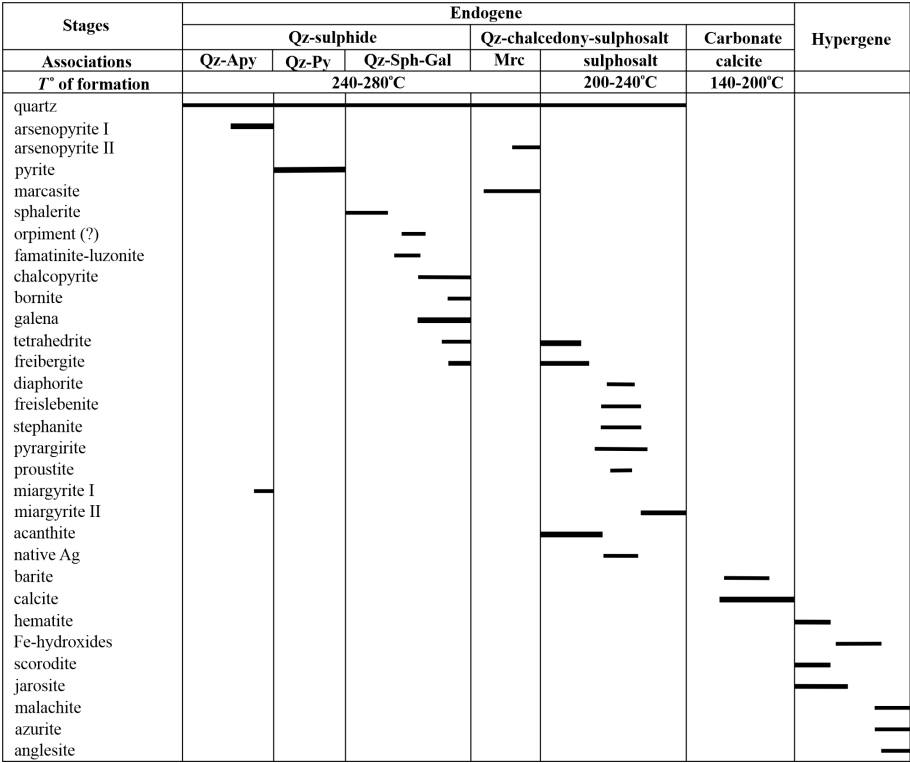


Fig. 1. Paragenetic sequence of the mineral formation in the Sedefche Au-Ag deposits (modified after [12, 13])

As. In cases of pyrite/marcasite transformation, As-content is not detected [12], but instead it hosts μm -sized standalone phases (inclusions) of 2nd generation arsenopyrite. The formation of secondary arsenopyrite could be triggered by the released arsenic during the conversion of pyrite to marcasite. Due to their small sizes (less than $10\text{ }\mu\text{m}$), these arsenopyrite inclusions have not been thoroughly compositionally investigated and their Au-bearing potential is unknown. Based on the metal contents in the original As-bearing pyrite ($0.19\text{--}4.54\text{ ppm}$), gold incorporation in 2nd generation arsenopyrite is probably insignificant [13].

Quartz-sphalerite-galena association is widespread in the investigated samples and has abundant and various mineral composition. The main ore mineral is sphalerite, forming single subeuhedral crystals in quartz matrix, frequently observed in association with other ore minerals. Earlier-formed arsenopyrite and pyrite are commonly enclosed within this sphalerite. Often it contains inclusions of galena with irregular shape and exsolutions of chalcopyrite. The latter can be classified as 1st generation, while at a later stage 2nd generation of chalcopyrite veinlets were formed intersecting and overgrowing earlier pyrite, marcasite and sphalerite. As a result of decomposition of solid solution, bornite exsolutions have been formed scarcely within the 2nd generation chalcopyrite veinlets.

Formation of some earlier sulphosalt minerals is assigned with this stage. The occurrence of famatinite-luzonite has been established as inclusions in sphalerite. The final ore forming impulses are connected with deposition of other sulphosalt minerals such as tetrahedrite observed as veinlets and/or haloes around sphalerite and or chalcopyrite. Compositionally, the studied members of famatinite-luzonite are not silver-bearing, whereas tetrahedrite-tennantite series have clearly expressed Ag-bearing potential.

Marcasite association is characterized by the recrystallization of primary pyrite into marcasite. Pseudomorphoses of marcasite after pyrite crystals and aggregates are typical, preserving the initial pyrite habit and shapes. The mineral transformation is clearly visible under microscope due to well defined anisotropy in crossed polarizing light. Marcasite also appears as colloform aggregates with radial or concentric internal structure. The colloform marcasite envelops early-formed minerals such as sphalerite.

According to the chemical data, the composition of marcasite barely deviates from the theoretical stoichiometry. Sometimes in marcasite can be encountered some microscopic inclusions of second generation arsenopyrite. A probable explanation is connected with formation during recrystallization of As-bearing pyrite into “clean” marcasite, containing arsenopyrite inclusions. In other words, the arsenic presented in the primary pyrite separated from the FeS_2 and formed distinct inclusions as an independent phase of arsenopyrite (FeAsS). The Au-bearing potential of this 2nd generation arsenopyrite is uncertain due to the small size ($<10\text{ }\mu\text{m}$) as it was discussed above.

Sulphosalt association represents the latest ore assemblage and is characterized by formation of quartz and numerous Ag-bearing sulphides and sulphosalts [8], such as acanthite, tetrahedrite, freibergite, stephanite, pyrargyrite, proustite, miargyrite, diaphorite, and freieslebenite. Rare native silver has also been reported [10,14]. The majority of these sulphosalts are Sb-rich varieties, although As-rich sulphosalts are also present. Microscopic exsolutions of proustite in pyrargyrite [14] are rarely observed.

The tetrahedrite-tennantite series formed during the quartz-sphalerite-galena stage, has negligible Ag-content, while the members of tetrahedrite-freibergite series formed during the sulphosalt stage contain significant amounts of Ag and have high Ag-bearing potential. The majority of these Ag-bearing sulphosalt minerals appear as anhedral veinlets and aggregates with irregular shape, hosted in quartz. Generally, they intersect earlier ore minerals, such as marcasitized pyrite.

Calcite association corresponds to the latest hydrothermal mineralization in the deposit and represents the post-ore-forming endogenous stage, which consists almost entirely of calcite with some accompanying barite.

Arsenopyrite mineral features and chemical composition. Arsenopyrite from the quartz-arsenopyrite paragenesis (1st generation) is widespread min-

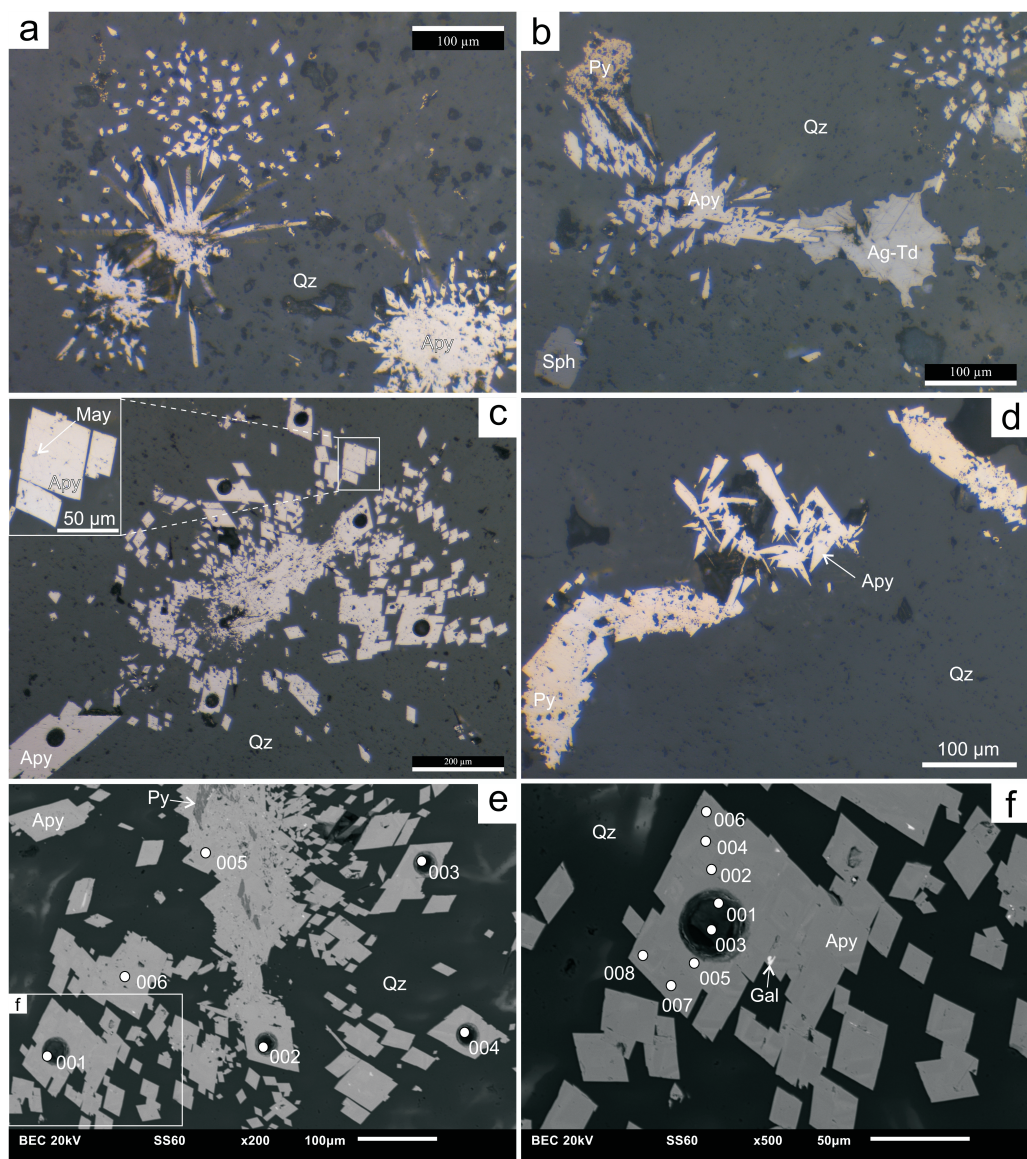


Fig. 2. Reflected light and BSE images of arsenopyrite crystals and its association: a) Clusters of arsenopyrite with rhombic cross-section and “star-like” radial aggregates; b) Arsenopyrite association with pyrite, sphalerite and tetrahedrite; c) Some of the largest single-crystals of arsenopyrite, encountered in the investigated samples. In one of these arsenopyrites can be seen a miniature inclusion of miargyrite 1st generation; d) Rhombic and needle-like arsenopyrite crystals, deposited in quartz matrix. The euhedral arsenopyrite is intersected and replaced by pyrite which was later transformed into marcasite; e) Euhedral arsenopyrite crystals with analytical points; f) Detail from e) showing slight crystal inhomogeneity. Abbreviations: Apy – arsenopyrite; Gal – galena; Sph – sphalerite; May – miargyrite; Ag-Td – silver-bearing tetrahedrite; Qz – quartz

eral in the deposit. It appears as well shaped euhedral crystals (rhombic or needle-like, depending on their orientation) or aggregates (star-like clusters) of such crystals, radiating from and filling in cavities in quartz formed in the earliest hydrothermal stages. The individual single crystals of arsenopyrite, although numerous, are of small μm -size and the majority of them are $\leq 30 \mu\text{m}$. Arsenopyrite crystals with sizes $\sim 50 \mu\text{m}$ are rare.

Slight inhomogeneity and zonal structures due to Fe:As:S compositional variation have been detected in these arsenopyrites using BSEI observations (Fig. 2e, f). According to WDS-EPMA analyses, Fe in the mineral varies between 30.6–36.3 mass%, S is 18.3–22.8 mass%, whereas As is 41.07–51.1 mass%. Sporadic presence of Sb (up to 2.7 mass%) is also detected. Additionally, some trace elements have been measured – Au – 0.12, Cu – 0.04, Co – 0.06 mass%, but their incorporation is almost at the detection limit. A representative crystal chemical composition ($\text{Fe}_{1.06}\text{As}_{0.98}\text{S}_{0.96}$) corresponding to the EPMA data is introduced.

According to the LA-ICP-MS analyses of trace elements signatures, the 1st generation arsenopyrite is the principal endogenous mineral revealing significant gold incorporation (up to 361 ppm) in the deposit (Fig. 3). The chemical composition of the mineral is additionally characterized by increased content of Sb (21276 ppm), Cu (1494 ppm), Ag (380 ppm), Pb (323 ppm), Se (54 ppm), Mn (48 ppm), Zn (37 ppm), and negligible amount of Tl (9 ppm).

As a counterpoint of the arsenopyrite the content of Au in the studied pyrite is generally low and inconstant with single points reaching up to 195 ppm, As (26698 ppm), Sb (5893 ppm), Mn (1710 ppm), Pb (949 ppm), Ag (903 ppm), Cu (548 ppm), Tl (367 ppm), Cr (83 ppm), Co (35 ppm), Ni (21 ppm).

The content of Au in marcasite is close to the detection limit. Furthermore, As (6643 ppm), Sb (4800 ppm), Mn (769 ppm), Ag (533 ppm), Pb (432 ppm), Tl (421 ppm), Cu (323 ppm), Zn (107 ppm), Cr (54 ppm), and Co (20 ppm) are incorporated in the mineral.

The Au-content in sphalerite is also close to the detection limit. The chemical composition of the mineral is supplemented by significant incorporation of Fe (up to 44755 ppm), Cu (3810 ppm), Cd (2779 ppm), Mn (2029 ppm), Ag (1583 ppm), Ga (169 ppm), and In (50 ppm).

Scarcely detected trace elements in chalcopyrite are Zn (up to 1158 ppm), Ni (209 ppm), and Ag (112 ppm). The Au-content is under the detection limit. Pyrargyrite also shows limited trace element incorporation with up to 29 ppm Au, As (up to 68649 ppm) and Tl (65 ppm).

Discussion and concluding remarks. Arsenopyrite from Sedefche Au-Ag deposit contains significant amounts of gold – the highest among all ore minerals in the deposit, which were subjected to LA-ICP-MS investigations.

The presence of that gold is most likely as nanoparticles, irregularly disseminated within the arsenopyrite crystals as clusters of inclusions – a colloidal system in solid state “crystalosol”, as suggested previously [15]. According to

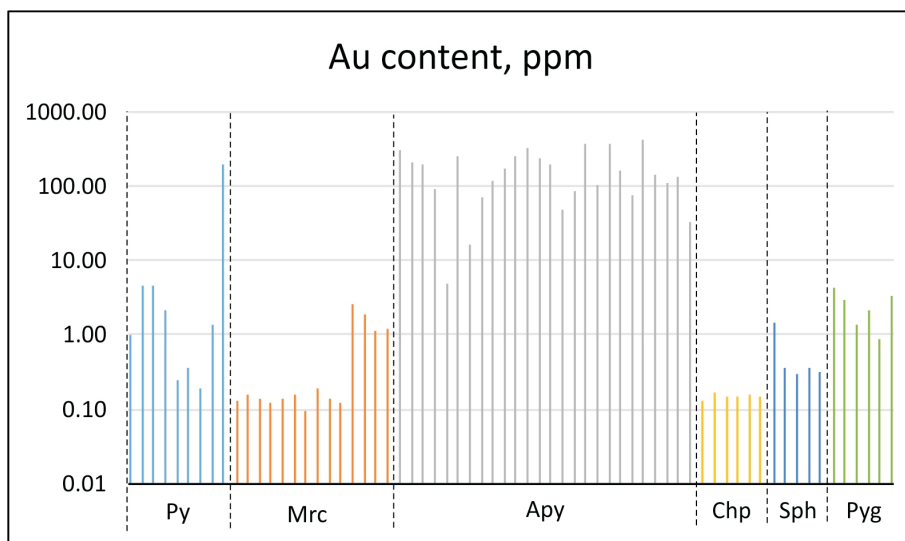


Fig. 3. Comparison of gold content in arsenopyrite, pyrite, marcasite, chalcopyrite, sphalerite, and pyrargirite from Au-Ag Sedefche deposit, determined by LA-ICP-MS. Abbreviations: Apy – arsenopyrite; Chp – chalcopyrite; Sph – sphalerite; Py – pyrite; Mrc – marcasite; Pyg – pyrargirite

[16] and the references therein, arsenopyrite typically has a higher gold content compared to pyrite, and the gold content of arsenian pyrites generally increases relatively with the arsenic. A significant portion of this gold is presented as “invisible”, (particles $< 0.1 \mu\text{m}$), and numerous studies have indicated that this gold occurs either as submicroscopic metallic particles or is incorporated as “chemically bound” gold. Recently, the presence of nanoparticles in the hydrothermal fluids has been increasingly commented in the scientific literature, as an alternative to the traditional model for the transport of metals through ligands (e.g., chloride- and bisulphide-bearing) in ore-forming fluids [17]. In the case of Sedefche Au-Ag deposit the support of this suggestion can be based on the following principal evidence: although the flat ablation profiles, correspond to isomorphic incorporation of gold in arsenopyrite, the results of the LA-ICP-MS analyses show increased but also very highly variable (by factor of almost 70) values of the gold content. If that gold was part of the crystal lattice of the mineral, its distribution would have been much more uniform. According to several studies [18,19], the gold may be incorporated in arsenopyrite through mechanism of bonding with As. Even though such way of gold substitution within the arsenopyrite lattice cannot be completely excluded, it is certainly much less prevalent in the studied samples, because of the lack of clear Au/As compositional correlation.

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