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Complex argentopentlandite-mackinawite inclusions in chalcopyrite: A solid state exsolution mechanism

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Abstract. According to almost all the existing reports, the scarce mineral argentopentlandite is typically found as fine inclusions in chalcopyrite, very often associated with mackinawite. The last finding in the Bulgarian Rhodope Mountains, revealed well developed regularities, that could explain the insistence of this assemblage to appear. Argentopentlandite is represented by fine octahedral crystals, all parallel to each other within one and the same chalcopyrite grain and with their crystallographic axes parallel to these of chalcopyrite. Almost inevitably it forms complex regular twins with mackinawite, after the twin law: Agp (001)[100] // Mcw (001)[110]. The assemblage is easily produced during a solid-state atom rearangement in the common cubic closest packing of S atoms. The slightly reduced volume of mackinawite (according to chalcopyrite) produces local contraction zone, facilitating the movement of larger Ag atoms, thus providing best nucleation points for argentopentlandite, that with its slight volume excess in its turn compensates the overall volume discrepancy. This "symbiosis" forms the complex argentopentlandite-mackinawite oriented inclusion. Thus the existence of mackinawite is considered determinative for the argentopentlandite nucleation. Probably some other coherent exsolutions with smaller volume (e.g. greigite or pentlandite) can play similar role.

Key words: argentopentlandite, mackinawite, chalcopyrite, topotaxy, exsolution

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Резюме. Според почти всички досегашни публикации, типичната форма на проявление на редкия минерал аргентопентландит е като фини включения в халкопирит, почти винаги заедно с макиноуит. Последната находка в Родопите разкри добре изразени закономерности в срастванията между двата минерала, които биха могли да обяснят постоянството в тяхното съвместно проявление. Аргентопентландитът е представен от дребни октаедрични кристали, ориентирани взаимно паралелно в едно и също халкопиритово зърно. Техните кристалографски оси са разположени успоредно на съответните оси при халкопирита. Почти винаги той образува сложни закономерни срастванияс макиноуит по закон на срастване: Agp (001)[100] // Mcw (001)[110]. Асоциацията би могла лесно да се образува при пренарежданае на металните атоми в една обща кубична опаковка от S атоми. Известният обемен дефицит на макиноуита спрямо халкопиритовата структура създава локална зона на свиване, облегчаваща придвижването на относително големия Ag атом към нея и по този начин предоставя подходящо място за образуване на аргентопентландитови зародиши, които със своя малко по-голям обем, на свой ред компенсират обемните несъответствия. Тази "симбиоза" води до образуването на ориентираните сложни включения. Така наличието на макиноуит играе определена улесняваща роля в образуването на аргентопентландита. Вероятно и други ориентирани отсмесвания с по-малък обем (като грейгит и пентландит) могат да играят такава роля.

Ключови думи: аргентопентландит, макиноуит, халкопирит, топотаксия, отсмесване

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Introduction

The scarce mineral argentopentlandite, first found in Sudbury, Canada (Michener, 1940) and recognized as a distinct mineral species in 1977, is currently known from only a few occurrences. Further developments, establishing the mineral formula, structure and phase relations of argentopentlandite are due to: Scott and Gasparrini (1973); Hall and Stewart (1973); Rudashevskii et al. (1977) and Groves and Hall (1978). Additional argentopentlandite descriptions for the Canadian deposits Sudbury, Falkonbridge and Bird River give Scott and Gasparrini (1973), Karpenkov et al. (1973), Cabri and Laflamme (1976) and Imai et al. (1975). The few other reports are as follows: Shishkin et al. (1971) from Talnach, Octiabrskoe and Hovu-Aksi in Russia and Kazachstan; Vuorelainen et al. (1972) - in seven Finnish deposits; Mariko et al. (1973) from Kamaishi mine, Japan; Groves and Hall (1978) from Mount Windarra, Australia; Mposkos (1983) from Koronuda, Greece; Yakovlev and Pachomovskiy (1982), Balabanin (1984) and Abzalova and Polejaeva (1987) from the Kola peninsula; Benvenuti (1991) from Bottino, Italy; Kojonen (1993) from Kelokorpi, Finland; Kontny et al. (1994) from Oberpfalz, Germany and Morales-Ruano and Fenoll Hach-Ali (1996) from El Harcon, Spain. Synthetic analogues of argentopentlandite are known from the work of Knop et al. (1965).

Most of the available descriptions are unanimous on one point: argentopentlandite is invariably found as fine inclusions in chalcopyrite. Although other possibilities are also considered in some cases, most authors accept the solid-state exsolution from chalcopyrite or ISS as the most probable way of forming argentopentlandite. The last find in the Rhodope Mts., Bulgaria, (Kerestedjian, 1997) reveals also regular relationships among argentopentlandite, mackinawite and chalcopyrite. These relationships provide a clue to the understanding of a common genetic mechanism, producing the whole observed assemblage during a solid-state transformation of an ISS. It is the scope of this paper.

Observed mineralogical and crystallographic relationships

The assemblage found in the Rhodope Mountains comprises chalcopyrite, pyrrhotite and sphalerite unevenly distributed in the amphibolites of the Chepelare suit of the Rhodopean metamorphic complex. The sulphides are sometimes accumulated in fine cracks or veinlets, but mostly they are found as small nests or single grains in the host rock. Argentopentlandite, mackinawite and rarely Bi-Te sulphides are only represented as tiny inclusions in chalcopyrite. Sphalerite also is found in chalcopyrite as typical stars. In very few instances tiny lamellae of cubanite also are observed in the chalcopyrite.

Argentopentlandite is represented by isotropic, pale-reddish-brown, bornite-like, euhedral to subhedral grains, few micrometers in size. Its chemical composition, determined by electron microprobe analyses (Kerestedjian, 1997) is: Fe 36.12, Ni 20.69, Ag 11.90, S 31.36, Σ 100.07 (wt.%, mean of three analyses), with calculated formula $Fe_{5.29}Ni_{2.88}Ag_{0.90}S_{8.00}$. The slight Ag deficit suggests some Ag insufficiency in the environment.

Mackinawite occurs as abundant tiny inclusions of thin lamellar or irregular shape in the chalcopyrite. A high Ni content, up to 8 wt.% (Fe/Ni atomic ratio about 7) was determined by microprobe analyses. As previously reported (Vaughan, 1969; Borishanskaya et al., 1981), Ni is a common component of mackinawite and the limits of its substitution reach 18-22 wt.%.

Chalcopyrite occurs as anhedral homogeneous grains, few millimeters in size, with nearly stoichiometric composition. Trace amounts of

Ni (0.10 wt.%) and Ag (0.26 wt.%) were detected.

Orientation relationships

Most grains of argentopentlandite are represented by square or acute-angled cross-sections parallel to each other within certain chalcopyrite grain. The same pattern was also reported in previous works (Karpenkov et al., 1973; Scott, Gasparrini, 1973; Groves, Hall, 1978). Although all the observations are made in two-dimensional polished sections, the comparison between large number of differently oriented sections allowed us to use three-dimensional terms for description. In these terms, most argentopentlandite inclusions are simple octahedra, in some cases with very small cubic faces. This observation is also consistent with its Fm$\bar{3}$m or P$\bar{4}$3m space group, strong [110] PBC directions and the weak bond [111] directions in its crystal structure, producing the well-known octahedral cleavage of pentlandite. This cleavage can be observed parallel to the section edges (see e.g. Fig. 1 of Scott and Gasparini, 1973).

The extremely bireflectant and anisotropic inclusions of mackinawite clearly belong to three distinct groups of optical and crystallographic orientations. Its (001) lamellae take three mutually perpendicular orientations, which are perpendicular to the three crystallographic axes of chalcopyrite, respectively. Two of these orientations (perpendicular to the chalcopyrite two-fold axes) are crystallographicaly identical. In polished sections perpendicular to these axes, the two orientations of mackinawite show maximum anisotropic effects, whereas the third group is in quasi-isotropic position. These relations were first explained by Bonev (1975, 1976) and were also observed by Kouvo et al. (1963, Fig. 1), where square "tetragonal iron sulphide" (mackinawite) crystals grow in an uniform orientation on chalcopyrite surface, along with a neighboring sphalerite star.

Because the chalcopyrite does not have crystal faces developed, sphalerite stars and also mackinawite lamellae, which always obey strict crystallographic rules in their orientation with respect to chalcopyrite host (Bonev, 1974; Bonev, Radulova, 1994), as well as polysynthetic twin lamellae (112) of chalcopyrite, were used to identify the mutual orientation of argentopentlandite and chalcopyrite. It was found that the directions of all three crystallographic axes for both minerals coincide. Schematic representation of the observed mineral relations is given on the following Fig. 1.

Argentopentlandite was almost exclusively found intergrown with mackinawite

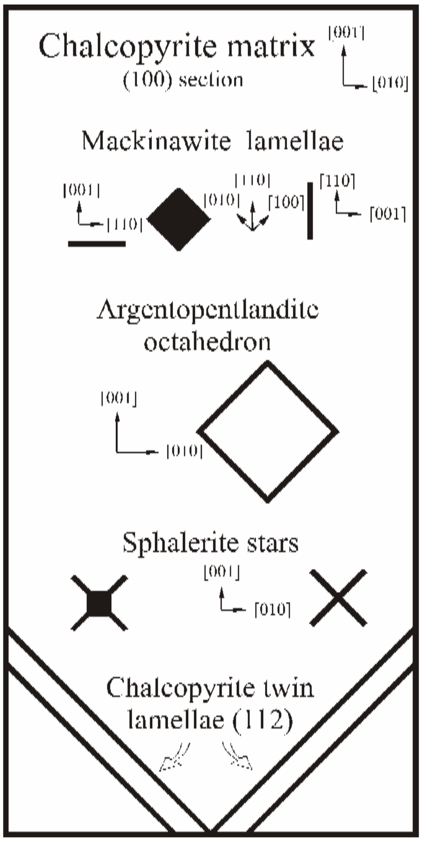

Fig. 1. Mutual orientation of mineral inclusions and chalcopyrite twin lamellae in chalcopyrite matrix
Фиг. 1. Взаимна ориентация на минералните

включения и халкопиритовите двойникови ламели в халкопиритова матрица

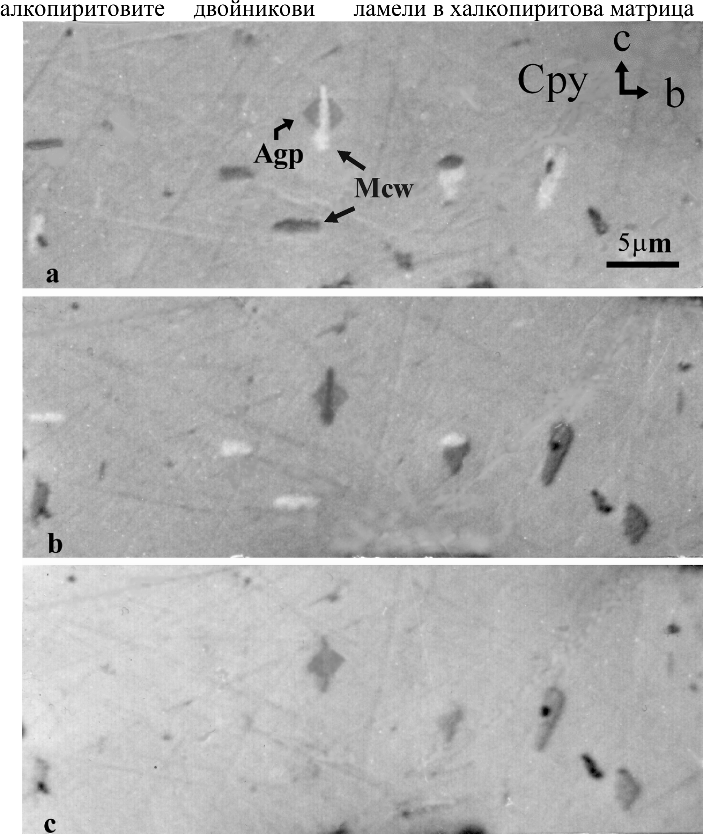

Fig. 2. Argentopentlandite-mackinawite (Agp-Mcw) regular intergrowths in chalcopyrite (Cpy) matrix. Polarizing microscope, 3 different polarizing directions (subfigures a, b and c) of one and the same area

Фиг. 2. Закономерни аргентопентландит-макиноуитови (Agp-Mcw) срастванияв халкопиритова (Cpy) матрица. Поляризирана светлина, 3 различни посоки на поляризация (подфигури a, b и c) в една и съща област на образеца

lamellae forming diagonal (according to square argentopentlandite crosscuts) “mustaches” (Figs. 2, 3).

Summarized topotaxic (endotaxic) relations of the inclusions in chalcopyrite matrix are:

Argentopentlandite (100)[001] // chalcopyrite (100)[001];

Mackinawite (001)[110] // chalcopyrite (001)[010] - (the case on the left in Fig. 1);

Mackinawite (001)[110] // chalcopyrite (100)[001] and (010)[001] - (next two on the right in Fig. 1).

Attempting to explain the unusual “mustache” intergrowth and the reasons producing it almost without exception, we had to look for some specific features in the structures and crystal chemistry of the minerals involved.

Topological similarity of the structures

All three minerals can be represented with the same cubic closest-packing of S atoms. Only the nature and position of metallic atoms differ among these minerals (Fig. 4). In the case of *mackinawite* Fe atoms form completely filled and completely empty alternating (001) layers of FeS_4 tetrahedra. In the case of *argentopentlandite* Fe and Ni distribution gives rise to 8-member clusters of MeS_4 tetrahedra, alternating in all translational directions with AgS_6 octahedra.

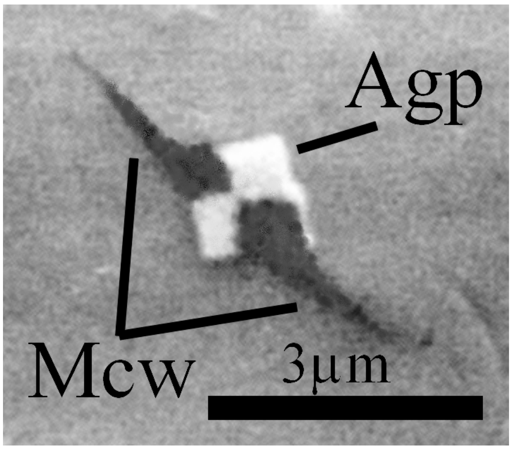

Fig. 3. Typical “mustache” intergrowth. SEM, 35 kV
Фиг. 3. Типични срастваиия "с мустаци". SEM, 35 kV

For better comparison with argento-pentlandite and in order to leave the array of S atoms placed on the unit-cell edges (as in the two other structures), chalcopyrite is shown translated -1/4, 1/4, 1/8 from the conventional representation.

The cubic argentopentlandite cell was divided into subcell elements with tetragonal symmetry, so as to be directly comparable to chalcopyrite. These elements can fill the entire argentopentlandite space by shifting each second subcell in both *a* and *b* directions by 1/2 *c* (Fig. 5).

Mackinawite was assigned an unconventional face-centered cell, corresponding to a rotation of 45° around *c* axis. Some authors (Kostov, Minčeva-Stefanova, 1981) accept this cell choice, with respective cell parameters *a* 5.2, *c* 10.04. Thus, two mackinawite cells could

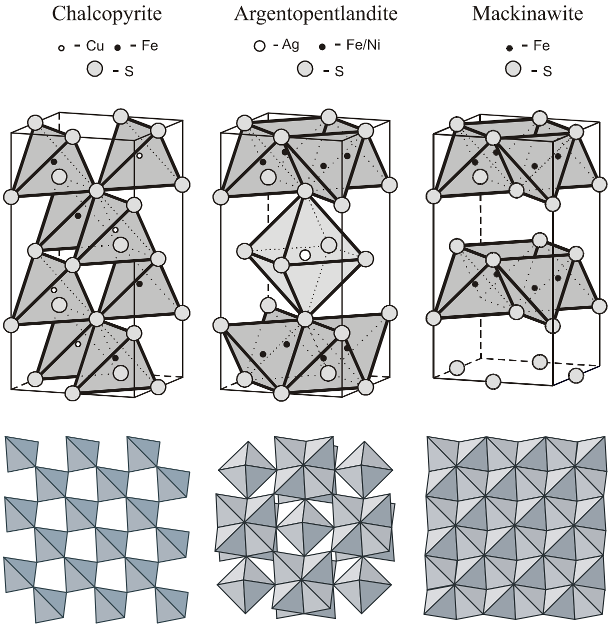

Fig. 4. Comparison between the three focused structures. Argentopentlandite is shown with just a tetragonal subcell element. The way it relates to the complete structure is shown on Fig. 5. Lower part of the figure shows the principal (001) layer filling for all three structures
Фиг. 4. Сравнение между трите разглеждани структури. Аргентопентландитът е показан само с един тетрагонален субклетъчен елемент. Начинът по който този елемент се отнася към цялостната му структура е показан на фиг. 5. Долната част на фигурата показва запълването на слоевете (001) за всеки от трите минерала

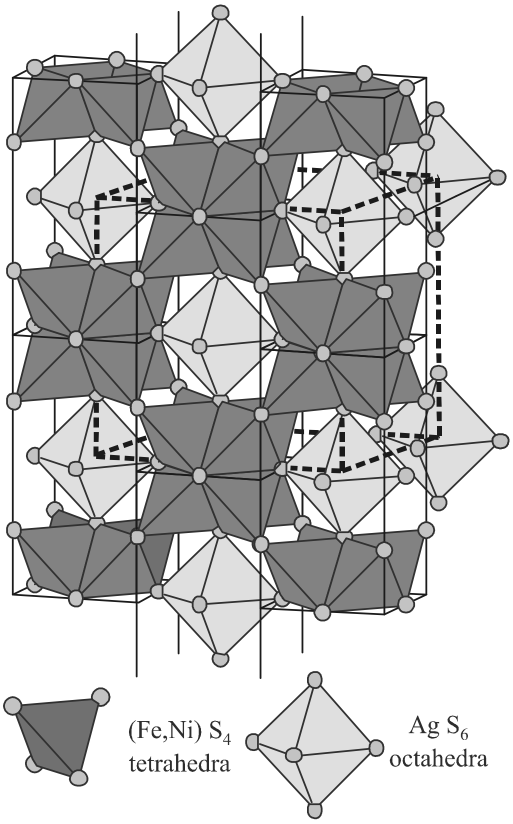

Fig. 5. Argentopentlandite structure, represented as a construction of the tetragonal subcell elements on Fig. 4. Just a front slice of the structure is shown to avoid figure overwhleming. The regular cubic cell is shown dashed

Фиг. 5. Аргентопентландиова структура, представена като конструкция от тетрагоналните субклетъчни елементи, показани на фиг. 4. За да се избегне претрупване на фигурата е показана само предната част на структурата. Цялостната кубична структура е оконтурена с пунктир

fit in one chalcopyrite unit cell, or one tetragonal argentopentlandite subcell element.

We must stress, that unconventional representations do not apply to the general crystallographic features of the minerals concerned and are only introduced for comparison purposes.

Dimensional relationships

The following structure data were used to evaluate the dimensional relationships between the minerals (in Å and at ambient T):

- Chalcopyrite, I$\bar{4}$2d, *a* 5.289, *c* 10.423, Z = 4, *V* 291.568 Å^3 (Hall, Stewart, 1973a);
- Argentopentlandite, Fm$\bar{3}$m or P$\bar{4}$3m, *a* 10.52 (determined for our material from the diagram of Mandziuk & Scott 1977, for the measured Fe/Ni = 1.837, and Ag = 0.9 at.%), Z = 4, *V* 1164.253 Å^3;
- Mackinawite, P4/nmm, *a* 3.676, *c* 5.032, Z = 2, *V* 67.997 Å^3 (Kouvo et al., 1963, for material with several % Ni; Taylor, Finger, 1970), [110] = 5.199.

The estimations for the linear and volume discrepancies of the three considered structures are given in the following Table 1.

Discussion

Exsolutions from ISS

According to the classical papers of Cabri (1973) and Sugaki et al. (1975), an Intermediate Solid Solution (ISS) is formed at high temperature conditions instead of chalcopyrite. It can remain stable down to 300°C (or lower) even in equilibrium with chalcopyrite. This ISS has a sphalerite-like cubic structure with a cell parameter slightly greater than that of chalcopyrite, *a* 5.4 Å and is metal-rich, compared to chalcopyrite. Its metal content can often comprise also metals other then Cu and Fe (Ni is a typical example). On slow cooling, a process of coherent exsolution of one or more phases takes place. The formation of stable metal-excess phases (like pentlandite) and monosulphides (like pyrrhotite and mackinawite) leads the rest of the solid solution to the chemical composition of chalcopyrite, thus permitting its transformation to chalcopyrite by ordering Cu and Fe in the respective tetrahedral positions.

Keeping in mind the growth of metal excess-phases, in the case of silver-bearing ISS

Table 1. *Dimensional discrepancies between the chalcopyrite matrix and the oriented inclusions of argentopentlandite and mackinawite for the coincing directions*

Таблица 1. *Метрично несъответсвие между халкопиритовата матрица и ориентираните включения от аргентопентландит и макиноуит за съответните съвпадащи посоки*

Cpy	[100], [010]	[001]	Δ V
Agp	[100], [010] -0.54%	[001] 0.94	-0.17%
Mcw 1	[110] -1.70%	[001] -3.44%	-6.71%
Mcw 2	[001] -4.86%	[110] -0.24%	-6.71%

argentopentlandite is most likely to form. The process is considered to evolve as follows:

An Ag atom takes the octahedral 4b position in the center of the cubic ISS unit cell. This fact has the following consequences:

1. It prevents the occupancy of the immediately neighboring tetrahedral positions. The Fe, Ni and Cu from these places are shifted to next closest possible tetrahedral positions (32f).
2. It prevents also the occupancy of the im mediately neighboring octahedral positions, thus allowing next Ag atom to take position not closer than the second next octahedral one. This gives rise to the $Fm\bar{3}m$ symmetry of the mineral.
3. Both these phenomena are due to the relatively high effective covalent radius of the Ag in octahedral coordination (1.15 Å, compared to that of Fe – 0.63, Cu – 0.57 and Ni – 0.55 in tetrahedral coordination). Also the strong antibonding t_{2g} orbitals of octahedrally coordinated Ag play a role.
4. Ni^{10} atoms are preferably captured in 32f sites (instead of Cu^{11}), following the electroneutrality rule:

$Ag^{11}+1/2\ Fe^{8} = 3/2\ Ni^{10}$, assuming that Ag = 1 apfu (Mandziuk, Scott, 1977). Superscripts represent the number of outer shell electrons.

Mackinawite exsolution as well as the transformation of the ISS into chalcopyrite take place at the same time. All these changes start when the temperature drops down, which turns the excess crystal energy into a driving force for transformation, but keep going only while the temperature is still high enough to provide kinetic energy for overriding energetic barriers for atom repositioning. Clark (1966) shows that the low stability limit of pure mackinawite (~ 135°C) increases markedly with the substitution of Fe by Ni (and Co). For such nickeloan mackinawite this temperature reaches 200-250°C (Vaughan, 1969; Borishanskaya et al., 1981). The estimations about the stability range of argentopentlandite (Mandziuk, Scott, 1977) are similar. Thus, we consider that the studied complex mackinawite-argentopentlandite intergrowths are exsolved from high-T Ag- and Ni-containing ISS at temperatures of about 200°C.

Induced growth

The presence of Ag and Ni in the initial ISS is not an obligatory part of the hypothesis. These elements may probably be also provided by external (later) hydrothermal fluids, over the interval 300-200°C, while chalcopyrite still allows some metal rearangement, thus being "transparent" for external metal ions, causing argentopentlandite nucleation. Hence, externally induced growth of argentopentlandite is possible, but the nucleation and growth mechanism further on, should be the same as above.

Volume discrepancies

As seen on Table 1, linear discrepancies in the unit-cell dimensions of all three structures are small (below 5%). Nevertheless, volume discrepancies need due consideration.

Compared to the chalcopyrite matrix, *mackinawite* inclusions have notably smaller unit-cell volume: -6.7%. Since volume discrepancies are prominently anisotropic, this discrepancy becomes even more significant along [001] (perpendicular to the dense (001) layers).

Argentopentlandite inclusions are almost identical to chalcopyrite in cell volume (discrepancy –0.17%) at normal temperature. Considering the extreme thermal expansion values of pentlandite-like structures, however,

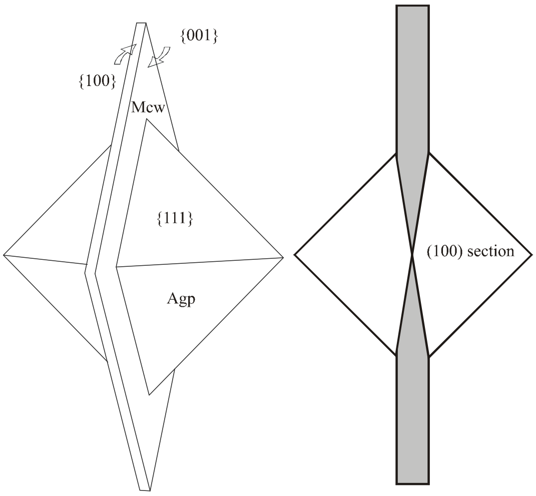

Fig. 6. Three dimensional and cross section models of the regular intergrowth between argentopentlandite and mackinawite: Agp (001)[110] // Mcw (001)[100]

Фиг. 6. Закономерен аргентопентландит-макиноуитов срастък: Agp (001)[110] // Mcw (001)[100], представен триизмерно и в пререз

significantly higher volume discrepancy may be expected for the time of formation of argentopentlandite.

As shown by Rajamani and Prewitt (1975) for the pentlandite from Frood Mine, its linear thermal expansion at 200°C is 1.2%, while for chalcopyrite it is 0.195 along *a* and 0.136% along *c* (Raduluova, Bonev – unpublished data). Although no direct data exist for argentopentlandite, considering its similarity to normal pentlandite, enhanced volume discrepancy, causing lattice strain (thus energetic difficulties) should be expected for its formation in chalcopyrite at higher temperatures.

The special role of mackinawite

Described relations can explain the observed specific coupled growth of argentopentlandite and mackinawite. Due to their smaller unit-cell volume, the growth of mackinawite inclusions creates a contraction zone in their immediate surrounding, thus facilitating the diffusion of larger Ag atoms. Structurally similar mackinawite surface becomes the best place for the heterogeneous and heterotaxic nucleation of argentopentlandite, thus overriding the higher energetic barrier for standalone nucleation. Further growth of the two-phase inclusion follows with structurally controlled shaping for each mineral – isometric, octahedral for argentopentlandite and thin platy for mackinawite.

Mackinawite in its turn may benefit from the coupled growth with argentopentlandite, because the overall discrepancy in volume in respect to the chalcopyrite matrix is thus diminished. Perhaps this is why mackinawite lamellae intergrown with argentopentlandite are larger than the others.

If the “symbiotic” relations of the two minerals start as early as the nucleation stage, induction boundaries are formed to give rise to the typical regular intergrowth as shown in Fig. 6, explaining the photographs above (Figs. 2 and 3).

Significance of the described relations

An important question is to what extent the described exsolution mechanism is of general significance. According to literature references, the argentopentlandite-chalcopyrite connection is permanent, unlike the argentopentlandite-mackinawite relation, for which the information is insufficient.

Two papers with detailed descriptions of the inclusions are of interest in this respect:

1. In the quartz-sulphide ores of Lega Dembi gold deposit in Ethiopia, Cook and Ciobanu (2001, and personal comm.) have observed uniformly oriented, composite inclusions of argentopentlandite + Ni-Co-rich greigite. Greigite forms a system of thin, regularly oriented lamellae in argentopentlandite. Greigite ($FeFe_2S_4$) as a densely-packed cubic thiospinel (Fd3m) has a cell edge of 9.88 Å, dimensionally close to that of chalcopyrite. However, in a parallel-axial orientation the discrepancies are -6.6% along a_{cp} , and -5.2% along c_{cp} . Evidently, greigite can compensate the volume excess of argentopentlandite (according to chalcopyrite matrix) even better than mackinawite. Moreover greigite itself can be a product of topotaxic transformation of mackinawite, as shown by Lennie et al. (1997).

2. Another similar case is described by Yakovlev et al. (1981) in the Cu-Ni deposits of the Cola Peninsula, Russia. Argentopentlandite inclusions in a chalcopyrite matrix contain a regular network of thin lamellae of normal pentlandite. In this case the pentlandite with *a* 10.03 Å has again a lower volume according to argentopentlandite (linear discrepancy is -4.7%). According to chalcopyrite the linear discrepancies are: -5.18% along a_{cp} and -3.77% along c_{cp}.

It seems obvious, that in both cases above, as well as in the case of mackinawite described here, the local strain, created by the negative linear dimensional discrepancies of coexisting phases according to the chalcopyrite matrix, play a significant role, facilitating the argentopentlandite growth. Thus, argentopentlandite tends to grow preferably together with other phases (iron sulphides), having smaller cell volume and mackinawite is just one possible case.

Visualization of the observed phenomena

Represented mineral relations are hard to observe. The optical properties of the three minerals are pretty different, but the very small size of the grains forces the observer to the technical limits of quality imaging. The electron microscope, on the contrary, provides the required magnification, but the atomic contrast that it deals with is too small for the considered set of minerals. The overall net atomic weight for the three minerals is as follows: chalcopyrite – 21.75; mackinawite – 21.00; argentopentlandite – 22.88. This very small difference makes the minerals almost indistinguishable, unless very high accelerating voltage (35kV or more) is applied in combination with the highest contrast values.

Conclusions

1. Argentopentlandite is typically formed on cooling of an ISS, producing chalcopyrite with regularly exsolved inclusions.
2. If Ag and Ni exist in the ISS, the high structural and metric similarity is very likely to produce argentopentlandite.
3. The formation of argentopentlandite benefits from earlier or simmultaneous deposition of mackinawite, and appears in typical regular intergrowths with it.
4. Oriented inclusions of other phases, like greigite and pentlandite can play a similar role, as well.

The proposed model is applicable for a case of ISS deposition, starting at relatively high temperatures (well over 300 ˚C) as can be expected in contact metasomatic, high metamorphic or pretty high temperature hydrothermal environments. It does not exclude the possibility for other argentopentlandite forming mechanisms.

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