GEOCHEMISTRY, MINERALOGY AND PETROLOGY • SOFIA
ГЕОХИМИЯ, МИНЕРАЛОГИЯ И ПЕТРОЛОГИЯ • СОФИЯ
2006, **44**, 1-18.

Two crystallographically different types of skeletal galena associated with colloform sphalerite

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Abstract. Skeletal "knitted" galena crystals (*gestrickte Bleiglanze*) enclosed in banded colloform sphalerite of *Schalenblende* type are known from many low-temperature sulphide Pb-Zn deposits. The former studies established the cryptocrystalline to fibrous structure, fine depositional banding and low-Fe content of this sphalerite. Controversial opinions about its genesis and about the galena inclusions are developed. However, up to now, the real crystal morphology of the skeletal galena, its relationships with the colloform sphalerite and the origin of their specific intergrowth textures have not been characterised well with modern microscopic and SEM methods. Two crystallographically different skeletal types of galena were distinguished in this study.

1st type, here denoted as {111}<001>, consists of numerous fine (0.05-1 mm) octahedral microcrystal sub-individuals, stacked in parallel orientation along the four-fold axes. Such very delicate branched three-dimensional single-crystal skeletal forms reach several cm (even up to 10 cm) in length. Branches of first, second and third order are detected. The dendrites are entirely encrusted of colloform fine-banded sphalerite, often with remaining open gaps between the separate branches. Skeletal galena of this type was found in the ores of carbonate-hosted Pb-Zn deposits, especially these in the Silesian-Cracow region in Poland (Olkusz, Trzebionka, etc.), Moresnet region in Belgium and Aachen region in Germany (Eschbroich, Schmalgraf), Pine Point in Canada, etc.

2nd type skeletal galena, {100}<111>, consists of fine (< 0.5 mm) cubic microcrystal sub-individuals stacked along the three-fold axes. Such skeletal forms reaching several mm in length, were observed within platy transparent barite crystals, and are located only in their apex parts which are directed to the open druse cavities. This galena associates also with scarce colloform fine-spherulitic sphalerite. Such crystals were found as late formations in the Erma Reka vein Pb-Zn deposit of the Madan ore district, South Bulgaria.

It is suggested that the skeletal galena crystals arose by fast growth in open space from low-temperature (200-100°C) fluids at diffusion-controlled regime and restricted nucleation. The associated colloform fine-banded and low-Fe sphalerite is composed of fine-fibrous <111> microcrystals formed at high supersaturation and abundant nucleation soon after the galena. The extremely non-equilibrium interfaces of the gentle galena skeletal crystals have been preserved intact by the overgrowing sphalerite (in the first case), or barite (in the second case).

Keywords: galena, sphalerite, skeletal-dendritic crystals, colloform texture, crystal growth

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Радостина Атанасова, Иван К. Бонев. Два кристалографски различни типа скелетен галенит, асоцииращ с коломорфен сфалерит

Резюме. Скелетни "плетени" галенитови кристали ("gestrickte Bleiglanze"), обхванати от финослоест коломорфен сфалерит (тип Schallenblende), са известни от редица нискотемпературни сулфидни Pb-Zn находища. Предхождащите изследвания установяват криптокристалния до влакнест строеж, фината зоналност и ниското желязно съдържание на този сфалерит, като са изказани противоречиви мнения за генезиса му, както и за включения галенит. Досега реалната кристална морфология на скелетния галенит, взаимоотношенията му с коломорфния сфалерит и произходът на техните специфични текстури на прорастване не са характеризирани с модерни микроскопски и СЕМ методи. В настоящото изследване се установяват два кристалографски различни типа скелетен галенит.

Първият тип галенитови скелети, означени като {111}<001>, са съставени от множество фини (0,05-1 mm) октаедрични микрокристални субиндивиди, развити в паралелна ориентировка по посока на четворната ос. Тези тримерно разклонени изящни монокристални скелетни форми достигат на дължина до няколко cm (дори 10 cm). Наблюдават се разклонения от първи, втори и трети порядък. Дендритовидните скелети са изцяло обраснати от финослоест коломорфен сфалерит, като често между отделните разклонения се наблюдават незапълнени открити празнини. Скелетен галенит от този тип е представен в рудите на Pb-Zn находища в карбонатни скали от Силезийско-Краковския район в Полша (Олкуш, Тржебионка и др.), района Мореснет в Белгия и района Аахен в Германия (Ешбройх, Шмалграф), Пайн Пойнт в Канада, и др.

Вторият тип галенитови скелети, {100}<111>, са съставени от фини (<0,5 mm) кубични микрокристални субиндивиди, паралелно развити по посока на тройната ос. Тези скелетни форми, достигащи на дължина до няколко mm, се наблюдават в плочести, прозрачни баритови кристали и са разположени само в техните върхови части, издаващи се към друзовите празнини. Галенитът асоциира и с оскъдно представен коломорфен финосферолитов сфалерит. Тези кристали бяха установени в образци от късните минерализации на жилното Pb-Zn находище Ерма река от Маданския руден район, Южна България.

Счита се, че галенитовите скелетни кристали са формирани чрез бърз растеж в свободно пространство от нискотемпературни (200-100^{o}C) разтвори, при дифузионен режим и ограничено зародишеобразуване. Асоцииращият финослоест и нискожелезен сфалерит е съставен от фино-иглести <111> микрокристали, образувани при повишено пресищане и голям брой зародиши, скоро след формирането на галенита. Извънредно неравновесните интерфейсни повърхности на фините галенитови скелети са напълно запазени от обрастващия ги сфалерит (в първия случай) или барит (във втория случай).

Introduction

Skeletal galena crystals included in banded colloform sphalerite of *Schalenblende* type form specific reticulate "knitted" ore textures known as *gestrickte Bleiglanze*. Such textures have been found in many low-temperature carbonate-hosted Pb-Zn deposits, especially these from the Aachen region in Germany and Moresnet region in Belgium (Ehrenberg, 1930, 1931; Kutina, 1952; Ramdohr, 1955), the deposits of Silesian-Cracow region in Poland (Haranczyk, 1959, 1962; Gorecka, 1996; Leach et al., 1996; Viets et al., 1996, etc.), deposits of the Mississippi Valley type (MVT) in USA and Pine Point in Canada (Roedder, 1968; Fowler, L'Heureux, 1996), etc. Similar ore textures have been described also from Pb-Zn deposits in W. Stara Planina Mt., Bulgaria (Minčeva-Stefanova, 1961), in the Caucasian Pb-Zn deposits Tators (Radkevich, 1966) and Kvaissa (Zhabin, 1984) and others. In rare cases similar reticulate galena crystals have been observed included in barite (Chebotarev, 1966).

Controversial opinions about the origin of the colloform aggregates exist. Rogers (1917) proposed this term for "rounded, more or less spherical, forms assumed by colloidal and metacolloidal substances in open space". The concept of the colloidal origin was summarised by Ramdohr (1955, 1980), Betekhtin et al. (1958) and is accepted by many authors. It is assumed that the viscous gel masses are bounded by spherical interfaces with minimum surface energy as a result of the action of surface tension. Thus, the fine banding is interpreted as depositional feature, and the radial-fibrous structure as a result of later recrystallisation process.

Roedder (1968) provided decisive observations and argumentation for the non-colloidal crystallisation origin of the colloform textures, especially studying colloform sphalerite aggregates from Pine Point and some classic European and American Zn-Pb deposits. Zhabin (1984) considered the colloform sphalerite and skeletal galena from the Kvaissa deposit a result of direct crystallisation from hydrothermal solutions, and not from gels. Fowler and L'Heureux (1996) concluded that sphalerite-galena aggregates are indicative of far-from-equilibrium crystallisation in which the branching nature of the galena is consistent with diffusion limited growth. Thus, *colloform* now is mostly accepted as descriptive, morphological not as genetical term, in contrast to the term *metacolloid*, indicative of proved colloidal origin.

However, up to now the real morphology of skeletal-dendritic crystals of galena, their relationships with colloform sphalerite or other including matrix, and the origin of these specific intergrowths have not been precisely characterised with modern microscopic and SEM methods. This study is aimed to give such characterisation. Typical samples from representative low-temperature carbonate-hosted and some vein Pb-Zn deposits were investigated.

We distinguished two crystallographic different types of skeletal galena, which we denoted as {111}<001> and {100}<111> (Fig. 1). These peculiar galena crystals closely associate with colloform sphalerite, and in the second case also with crystals of barite.

Occurrences and studied materials

The investigated sphalerite-galena samples originate mainly from the carbonate-hosted sulphide Zn-Pb deposits of the Silesian-Cracow area (Olkusz, Trzebionka and Pomorzany mines) in Poland, from Moresnet in Belgium and Aachen (Eschbroich mine) in Germany, Raibl, Italy, etc. Skeletal galena in barite was found in the Erma Reka Pb-Zn vein deposit, Madan ore district, Bulgaria.

The zinc and lead mineralisations from the Silesian-Cracow region are embedded mainly in Triassic carbonate limestone-dolomitic rocks and especially in the metasomatic ore-bearing dolomites and have been studied by many authors (Haranczyk, 1959, 1962; Sass-Gustkiewicz et al., 1982; Dzulynski, Sass-Gustkiewicz, 1993; Gorecka, 1993, 1996; Kozlowski, 1995; Leach et al., 1996; Sass-Gustkiewicz, 1997, and others). The ore bodies are metasomatic lenticular zones or

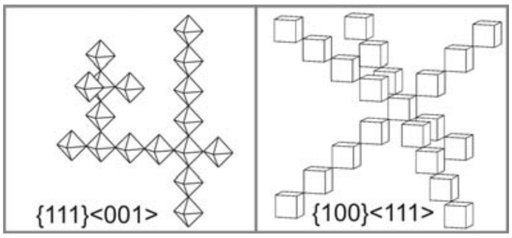

Fig. 1. Idealised scheme of the two types crystallographic different skeletal-dendritic forms of galena: 1^{st} type, {111}<001>, composed of octahedral microcrystal sub-individuals in parallel orientation, stacked along the four-fold axes; 2^{nd} type, {100}<111>, formed by parallel cubic sub-individuals, stacked along the three-fold axes

Фиг. 1. Идеализирана схема на двата вида галенитови скелети: I тип, {111}<001>, съставени от октаедрични микрокристални суб-индивиди в паралелна ориентировка, развити по посока на четворните оси; II тип, {100}<111>, изградени от кубични субиндивиди, паралелно развити по посока на тройните оси на галенита nests, ore fillings of steep fissures and caverns of hydrothermal karst, brecciated zones, etc.

Sphalerite occurs in granular, fibrous or colloform varieties. The colloform sphalerite texture of *Schalenblende* type consists of alternating bands of fine- to cryptocrystalline, fibrous, or granular forms. Sometimes wurtzite also occurs. Galena appears as crystals and druses or as skeletal forms within the colloform masses. It was established that this light sphalerite is nearly Fe-free but contains some Cd (up to 1.5 wt.%). Pyrite, marcasite and a few other minerals also occur in these ores. Similar geological characteristics have and the long ago abandoned mines of the Moresnet-Aachen region, near the Belgium-Germany border, etc.

The Tertiary vein and replacement Pb-Zn deposits from the Madan ore district are embedded in the rocks of the Rhodopian metamorphic complex: gneisses, amphibolites and marbles (Kolkovski, Manev, 1998). The ore mineralization is controlled by several steep ore faults, more branched in the southern part, where the Erma Reka deposit is situated. Metasomatic skarn-ore beds are enclosed in the marble horizons.

The earliest mineralization stage of Mn-pyroxene skarns developed only in marbles, has been followed by the main productive high-temperature (350-300°C) ore stage of galena, coarse-grained brown sphalerite, pyrite, chalcopyrite, quartz and carbonates, and then by a late lower-temperature (220-150°C) quartz-carbonate stage with some sulphides and barite. Large crystals of low-iron (<1 wt.%) light brown or yellow sphalerite of this late stage sometimes occur in the ore veins of Erma Reka (Gadjeva, 1983; Kolkovski, Dobrev, 2000; Bonev, Kouzmanov, 2002). Close related to them but much rarer are small druses of barite crystals with inclusions of skeletal galena and colloform sphalerite, which were investigated in this work. Barite overgrows milky quartz and large-crystal sphalerite.

Methods

The mineral relationships in galena-bearing aggregates were studied by stereomicroscopic and microscopic observations in reflected and transmitted light. Hand specimens, polished slabs and doubly polished plates were investigated. Cathodoluminescence and fluorescence images of fine banded colloform sphalerite were obtained in the Cathodoluminescence Laboratory of the University of Bern. Crystal morphology and textural peculiarities of galena aggregates were examined by scanning electron microscopy by using SEM Philips-515 device in the Central Laboratory of Mineralogy and Crystallography of the Bulgarian Academy of Sciences. The morphological analysis and interpretations of SEM images were made by SHAPE Software (Dowty, 1980). Crystal orientation of sphalerite individuals was determined by X-ray techniques using rotation and divergent KVK cameras. Chemical analyses were performed by JEOL Superprobe-733 electron-probe microanalyser equipped with EDS ORTEC-5000 system at the Geological Institute of the Bulgarian Academy of Sciences.

1st type skeletal galena: {111}<001>

This type skeletal galena is entirely included in fine-banded colloform botryoidal sphalerite of *Schallenblende* type from the carbonate-hosted Zn-Pb ore deposits. The observations ascertained that the dendrite-like galena skeletons consist of numerous octahedral microcrystal sub-individuals stacked along their four-fold axes (or close to them) in parallel orientation with transverse branches of second and third order (Fig. 1).

The crystallographic characteristic of galena forms can be especially well observed on broken surfaces of sphalerite-galena hand samples from Olkusz (Fig. 2a) and Moresnet

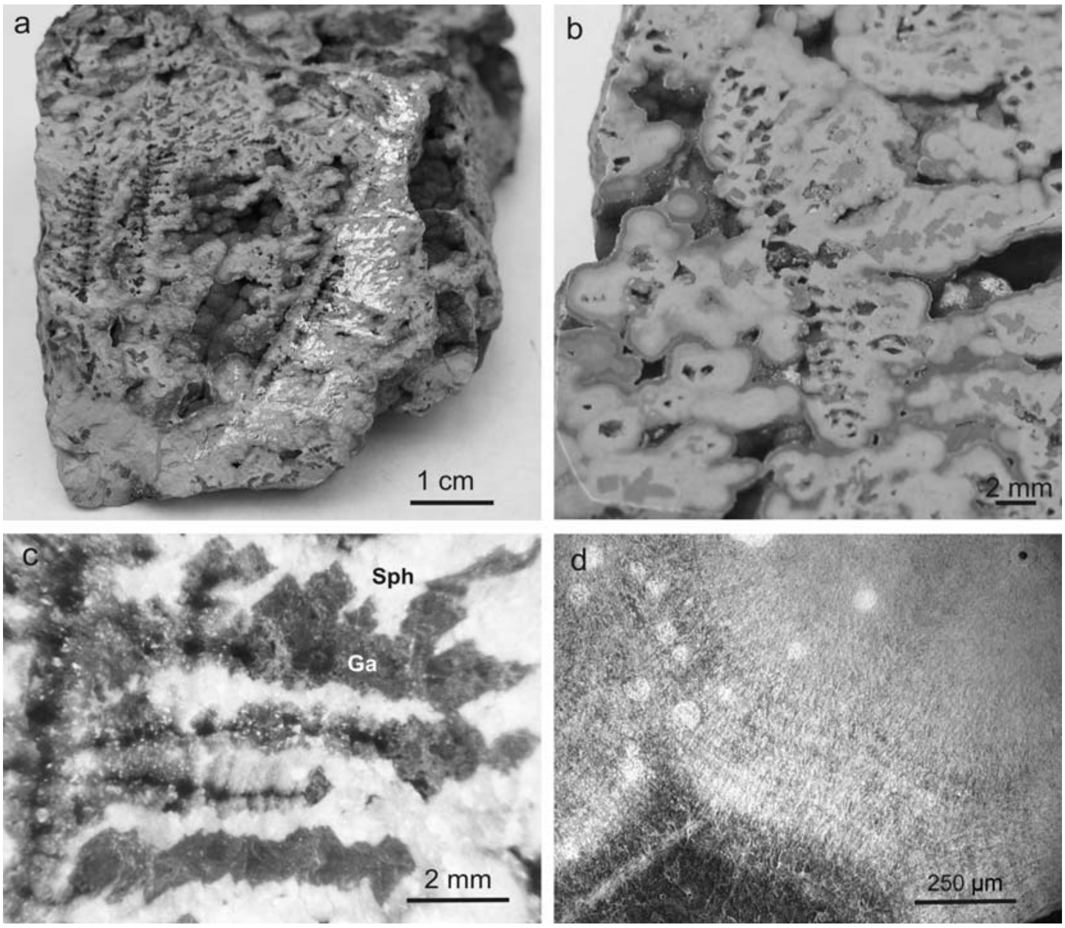

Fig. 2. Dendritic-skeletal galena encrusted by colloform sphalerite (grey). Cavernous specimen from Olkusz mine, Poland: a) the white dendrite form on the right side of the sample is the shining cleavage surface of a single galena crystal, when the black dendrites on left reveals the negative forms of dissolved galena; b) sphalerite encrustations (grey) over skeletal galena (dark grey), parts of which (black) are negative forms of leached galena; an enlarged polished section of a); c) detail of a): relationships between galena (Ga) and sphalerite (Sph) crust; d) fluorescence microphotograph revealing the fine-banded and radial-fibrous structure of sphalerite

Фиг. 2. Скелетен галенит, обраснат от коломорфен сфалерит (сив), с незапълнени интерстициални пространства (сиво-черни). Кавернозен образец от Олкуш, Полша: a) дендритовидното образувание разкрито в дясно представлява блестяща бяла цепителна повърхност на единичен галенитов монокристал, докато контрастно черните форми вляво са негативни празнини от разтваряне на такъв кристал; b) отношения между скелетния галенит (сив), кората от сфалерит (светло сив) и празнинките от разтваряне на галенита (черни) - полирана плоскост от a); c) детайл от a) показващ отношенията на галенит (Ga) и сфалерит (Sph); d) флуоресцентна микрофотография, разкриваща финослоестия и радиално-лъчест строеж на сфалерита

(Fig. 3a). At oblique illumination, all (100) cleavage planes of the branches of a single crystal galena dendrite in such samples show uniform coherent shining reflections. This concerns not only to the central stem, but also and to all branches and numerous minute blebs scattered around, which is strong evidence of the single crystal orientation of all these grains.

At higher magnification it is clearly seen, that the composing microcrystals have parallel quadratic outlines, and the cleavage steps (001):(010) on them are in the two diagonal (45º) positions, along the main elongation of branches, which undoubtedly demonstrate the octahedral shape of such a crystal (Fig. 2b,c). In samples from Olkusz, the size of the sub-individuals is from 0.25 to 1 mm (in some peripheral dendritic parts and larger), when in Moresnet this size is smaller (<0.2 mm). One single-crystal 3D-dendrite of galena occupies considerable space, often reaching up to several (5-6 and even 10) cm in length. Thus, e.g., one 6-7 cm large hand specimen can contain only one or two such reticulate galena crystals (Figs. 2a, 3a). After the classification of Shafranovsky (1961) these skeletal forms of galena belong to the cubic vertex forms.

The routine observations on polished sections of such samples under reflection microscope can not decide definitely the question on attachment of the neighbour isotropic blebs to one and the same galena crystal. This especially concerns areas with disseminated minute galena grains in sections removed from the dendrite axes (e.g. Fig. 3c-f).

The reticulate galena in the studied samples is entirely encrusted by fine-banded colloform sphalerite, which preserves uniform thickness along all skeletal parts (Fig. 3c-e). The sphalerite bands from Olkusz are yellow to dark yellow in colour and have a thin peripheral light-brown zone. This sphalerite contains very low Fe (0.08 wt.%) and up to 0.2-0.74 wt.% Cd, which is in accordance with the data of Viets et al. (1996) and Mayer and Sass-Gustkiewich (1997). In Moresnet the bands are yellow to brown, and contain 0.4-0.7 wt.% Fe, 0.15-0.25 wt.% Cd, and some (0.2 wt.%) As. The sphalerite crust in the samples reaches to 1-2 mm thickness, being thinner in Moresnet. The chemical composition of galena is close to the stoichiometric, with small admixtures of As or Sb, as known (Viets et al., 1996; Mayer, Sass-Gustkiewich, 1997).

The thin sections in plane-polarised light show that sphalerite has fine-fibrous radiate texture with fibres oriented perpendicular to the banding and coarser to the periphery. Such texture is well revealed on the cathodo-luminescence microphotographs (Figs. 2d and 3c-d), and at partly crossed nicols (Fig. 3e). In more details, the radial-fibrous texture is seen by SEM studies on broken cross-sections (Fig. 4a-d). The rather uneven single fibres (of μm thickness) often display longitudinal cleavage planes. The intersecting edges of these {110} sphalerite cleavages have radial orientation, thus indicating [111] fibre elongation (Fig. 4d). This was confirmed by rotation X-ray diffraction patterns.

The space around the encrusted branched galena-sphalerite aggregates is not completely filled and open gaps with different shape often remain (Figs. 2a,b, 3a,b and 6). The outer surfaces of the gaps are covered by the euhedral fibre terminations of sphalerite, bounded by dodecahedral *d*{110} and small tetrahedral *o*{111} faces.

The colloform mass from Olkusz on places includes and small nearly white sphalerite spherulites, up to 0.5 mm in diameter (Fig. 5a,b), with fine-concentric and radial-fibrous structure. They are nearly Fe-free, with up to 0.74 wt.% Cd. The fibres have skeletal development and consist of micron-sized crystal particles with elongated interstitial gaps (Fig. 5b-d). The outer darker zones are coarser grained, terminating again by {110} and small transverse tetrahedral {111} faces (Fig. 5e,f).

Dissolution processes affect the galena grains included in banded sphalerite from Olkusz. Some parts of the galena skeletons are

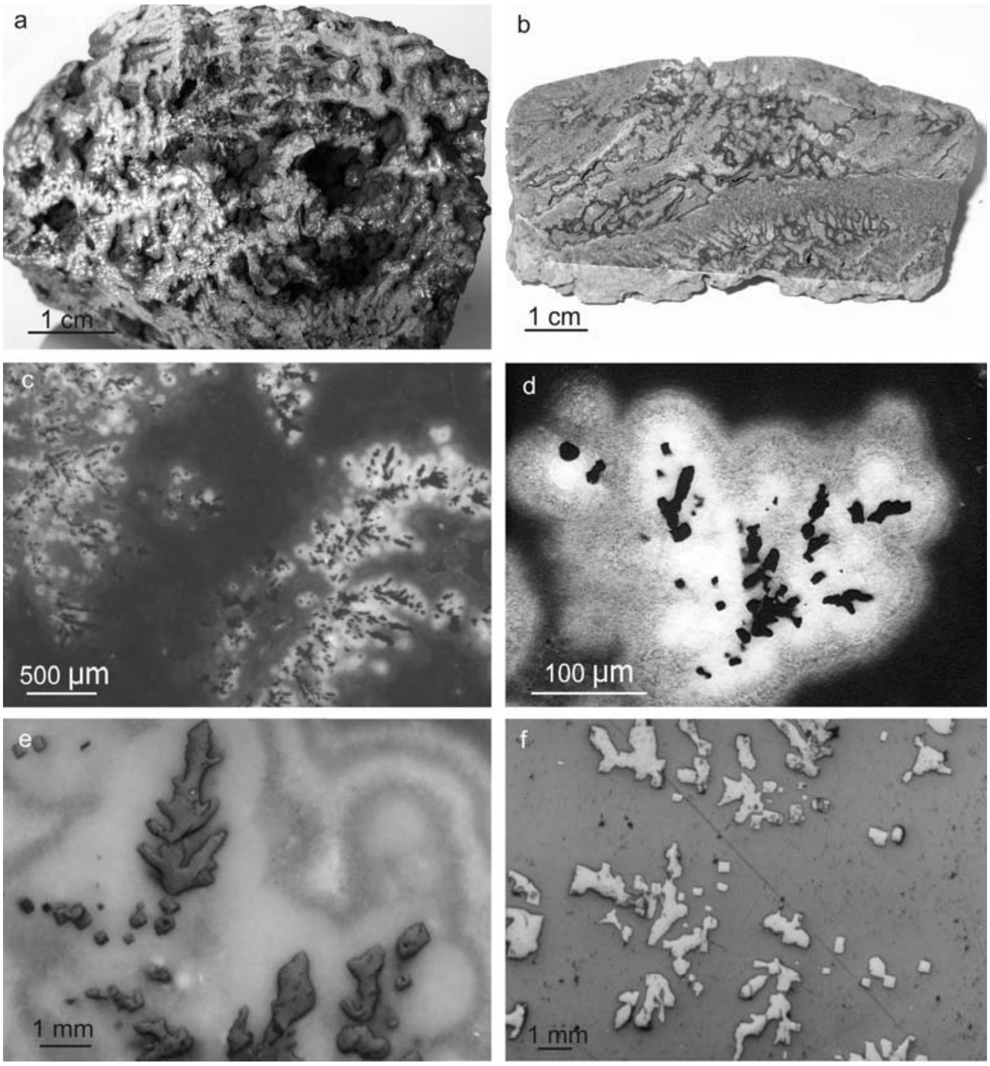

Fig. 3. Dendritic galena-sphalerite aggregates from Moresnet, Belgium: a) in broken surface with clearly shining cross-shaped branches of a galena single crystal, and b) in polished section; c-f) microphotographs from polished sections in random orientation and far from the dendrite stem: c-d) cathodoluminescense images revealing the sphalerite banded structure; e-f) pictures under reflected light at partly crossed nicols, in e), and at parallel nicols, in f)

Фиг. 3. Дендритни галенит-сфалеритови агрегати от Мореснет, Белгия: а) с блестящи кръстовидни разклонения на монокристален галенитов скелет, видими в отцепена плоскост, и b) в полирана повърхност; c-f) микрофотографии от неориентирани сечения, отдалечени от дендритната ос: c-d) катодолуминесцентни изображения, показващи слоестата структура на сфалерита; e-f) изображения в отразена светлина - при частично кръстосани николи в е), и при паралелни николи в f)

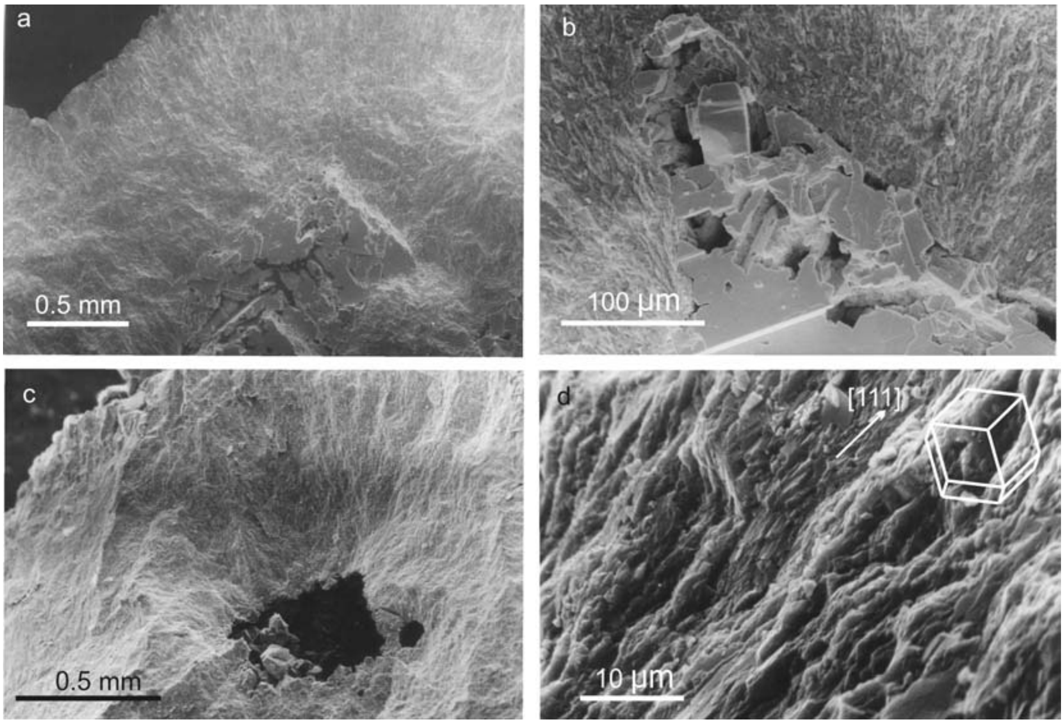

Fig. 4. SEM microphotographs illustrating the radiate-fibrous structure of the sphalerite crust covering the galena skeletons. Olkuzs, Poland. The enclosed galena is partly (in a and b), or entirely (in c) dissolved, leaving negative open gaps (black); in d) (a detail of c) the sphalerite intersecting {110} cleavages indicate the [111] elongation of the sphalerite fibres

Фиг. 4. SEM микрофотографии, показващи радиално-влакнестата структура на сфалеритовата кора, покриваща галенитовите скелети. Олкуш, Полша. Галенитовите включения са частично (при a и b) или напълно (при c) разтворени, оставяйки открити празнини (черни); при d) (детайл от c), пресичащите се цепителни плоскости на сфалерита {110} указват посоката на влакната: по [111]

partially corroded, along their boundaries and in their interior, as seen even in hand specimens (Fig. 2a,b), and especially well by SEM (Fig. 4a-c). On places, parts of the dendritic forms are entirely leached and only negative octahedral open gaps of completely removed former galena microcrystals are preserved (Fig. 4c). A thin band of the last darker sphalerite often covers also and the gaps of dissolved galena, which proves the hypogene nature of the process. The skeletal galena from Moresnet is only slightly affected by similar dissolution.

Examined in doubly polished sections by transmitted light the radial grains composing the coarser outer sphalerite bands show internal fine growth zoning of sharp crystal faces, similar to those, documented by Roedder (1968).

The investigations on the fluid regime in the discussed carbonate-hosted deposits (Roedder, 1984; Kozlowski, 1995; Kozlowski et al., 1996, etc.) established low-*T* (158-100-80°C and even lower) conditions, aqueous hydrocarbon-bearing Na-Ca-Cl solutions of moderate to high salinity and complex origin.

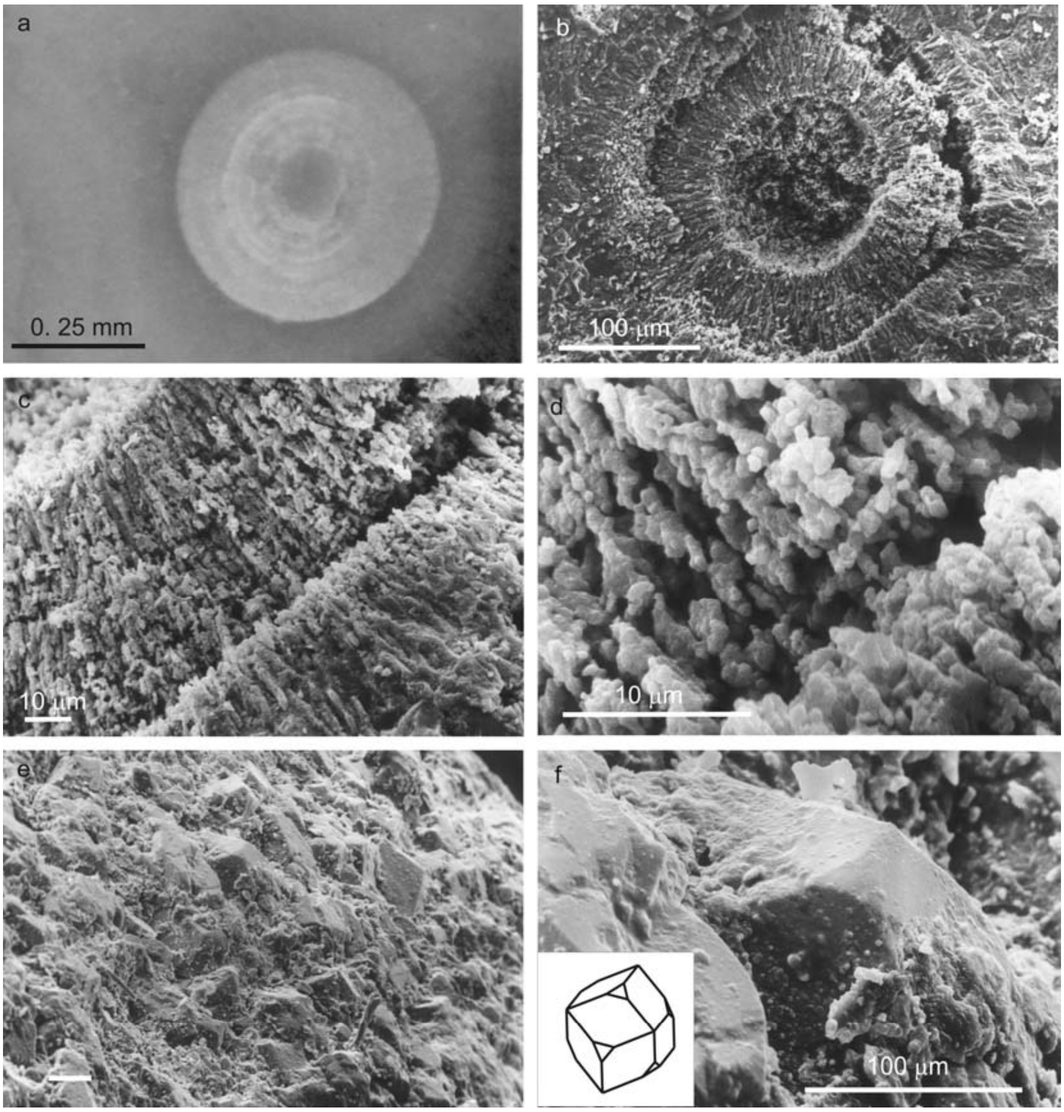

Fig. 5. Microphotographs of radial-fibrous and porous micro-spherulite of sphalerite included in colloform sphalerite. Olkusz, Poland: a) in polished section under reflected light, partly crossed nicols; b-d) SEM images on a broken surface at increasing magnifications, and e-f) on the outer surface of the spherulite formed by microcrystals: {110} + {111}

Фиг. 5. Микрофотографии на радиално-лъчест порьозен сферолитов сфалерит, включен в масата на коломорфния агрегат. Олкуш, Полша: а) полиран шлиф в отразена светлина при непълно кръстосани николи; b-d) SEM изображения на отцепена повърхност при нарастващи увеличения, и e-f) на външната повърхност на сферолита, съставена от микрокристали: {110} + {111}

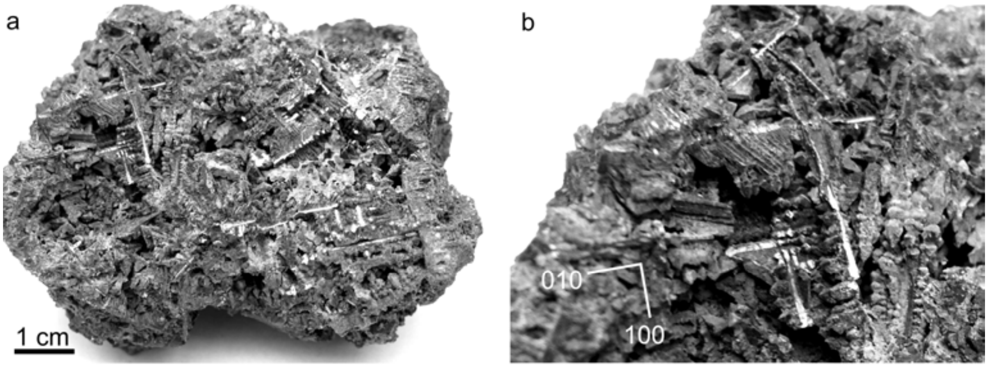

Fig. 6. Cavernous aggregate of cruciform dendrites of galena covered by thin layers of colloform sphalerite. The single dendrites of {111}<001> type are composed of parallel octahedral microcrystals, stacked along the main four-fold axes: a) overview, b) details. Schmalgraf, Moresnet-Aachen region. Mineralogical Museum of the Sofia University, sample N 238

Фиг. 6. Кавернозен агрегат от кръстовидни галенитови дендрити, покрити с тънък слой от коломорфен сфалерит. Монокристалните дендрити от {111}<001> тип са съставени от паралелни октаедрични микрокристали, нарастващи по посоките на четворните оси: а) обзор, b) детайли. Шмалграф, Мореснет-Аахенски район. Минералогически музей на Софийския университет, образец № 238

The discussed here relationships of reticulate galena and colloform sphalerite are observed and in other similar deposits, e.g. Raibl, Trzebionka and Pomorzany. In a similar sample of unknown deposit described by Kormilizyn (1966), the space between the branched forms is filled by later calcite. The presented photos clearly show that the skeletal morphology of galena is identical with the described here, although it was interpreted as a network of straight linear <100> bars.

Interesting is the case from Moresnet-Aachen region (Welkenraed deposit) described by Ehrenberg (1930). The dendritic galena there is dominating mineral, covered by very thin (~1 mm) band of colloform sphalerite. It is argued that the dendrite axes are not the cubic zones but [010], [301] and [103], owing to twinning along (310) and (201) planes. In a nearly identical museum sample from Schmalgraf of the same district (Fig. 6a,b), we found undoubtedly, that the cruciform dendrites are developed only along their four-fold <100> axes. The longitudinal cleavage steps on the shining cleavage surfaces and the parallel rows of stacked octahedral microcrystals clearly express the normal cubic symmetry of galena (Fig. 1), without signs of twinning. Ramdohr (1955, his Fig. 405, after Ehrenberg), for the same case from Eschbroich at Aachen mentioned that the galena skeletons consist of needles following mostly the cube edges, but sometimes and other directions.

In some of the Mississippi Valley type deposits and especially in Pine Point, as reported by Lasmanis (1989), elongated skeletal crystals of galena of herringbone shape and up to 10 cm long can be easily removed from the sphalerite matrix.

Another similar case of fine-branched galena ("corallites") overgrown by crust of light sphalerite, was described by Zhabin (1994) from the Kadaya Pb-Zn deposit in Eastern Zabaikalie, Russia. Although these skeletons are considered as special cubic forms, in fact they do not differ from the octahedral vertex forms described here (Fig. 1), with the same longitudinal and cross <100>

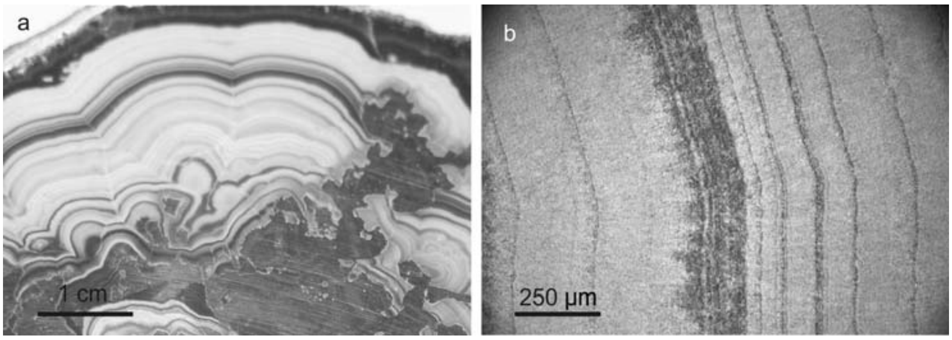

Fig. 7. a) Polished surface of colloform sphalerite with inclusions of skeletal galena from Pomorzany, Poland; b) fluorescence microphotograph showing the fine banded and radiate-fibrous structure of sphalerite

Фиг. 7. a) Полирана повърхност на коломорфен сфалерит с включения от скелетен галенит. Поморжани, Полша; b) флуоресцентна микрофотография, разкриваща фино-ивичестата и радиално-влакнеста структура на сфалерита

cleavage steps, but with more rounded outlines.

Some colloform sphalerites containing galena inclusions differ from the described here cases. Their botryoidal aggregates are rather thicker, up to 5-10 cm or more, and both the galena dendritic crystals and sphalerite fibres are radially oriented normal to the bands (Fig. 7a,b). Such textures are known from the same environment, e.g. in Moresnet-Aachen deposits (e.g. Kutina, 1952), Pomorzany and Olkusz (Haranczyk, 1962; Gorecka, 1996; Leach et al., 1996), Pine Point (Roedder, 1968, Fowler, L'Hereux, 1996).

2nd type skeletal galena: {100}<111>

The second crystallographic type skeletal galena crystals were observed in druses of barite crystals from the Erma Reka deposit, Madan Pb-Zn ore district, Bulgaria.

The large, up to 2-3 cm wide and 3 mm thick transparent crystals of barite belong to the platy prismatic habit type spread in the district (Terziev, Hissina, 1963). They are bounded by well-developed faces of pinacoid *c*{001} and vertical rhombic prism *m*{210}, with small faces of pinacoids *a*{100} and *b*{010}, and prisms *d*{101} and *o*{011} (structural setting). Numerous small (~0.5 mm) cubic galena crystals are embedded in 1 or 2 internal growth zones of the barite crystals (Fig. 8a,b). Some of the galena cubes have slightly protruded corners, indicating initial transition to skeletal growth. Well-developed dendritic skeletons are observed within some barite crystals, located on their apex parts directed to the open druse cavity, thus being in a favourable position (Fig. 8a,b). These dendritic forms are composed of euhedral cubic microcrystal sub-individuals, stacked approximately along the 3-fold [111] galena axes (Figs. 1, 8a-d). They can be classified as octahedral vertex forms after Shafranovsky (1961).

Scarce fine spherulites of sphalerite, 0.1 to 1.5 mm in diameter, are observed together with galena. They are included in barite crystals or are deposited on their surfaces. Studies by optical, cathodoluminescence and SEM microscopy reveal their banded and radial-fibrous inner structure (Fig. 9e). The outer surfaces of spherulites display numerous microcrystals, faced by dodecahedral faces (Fig. 9b-d). It is interesting that such fine fibrous crust covers and some associated large sphalerite crystals, as continuation of their growth by splitting to numerous parallel

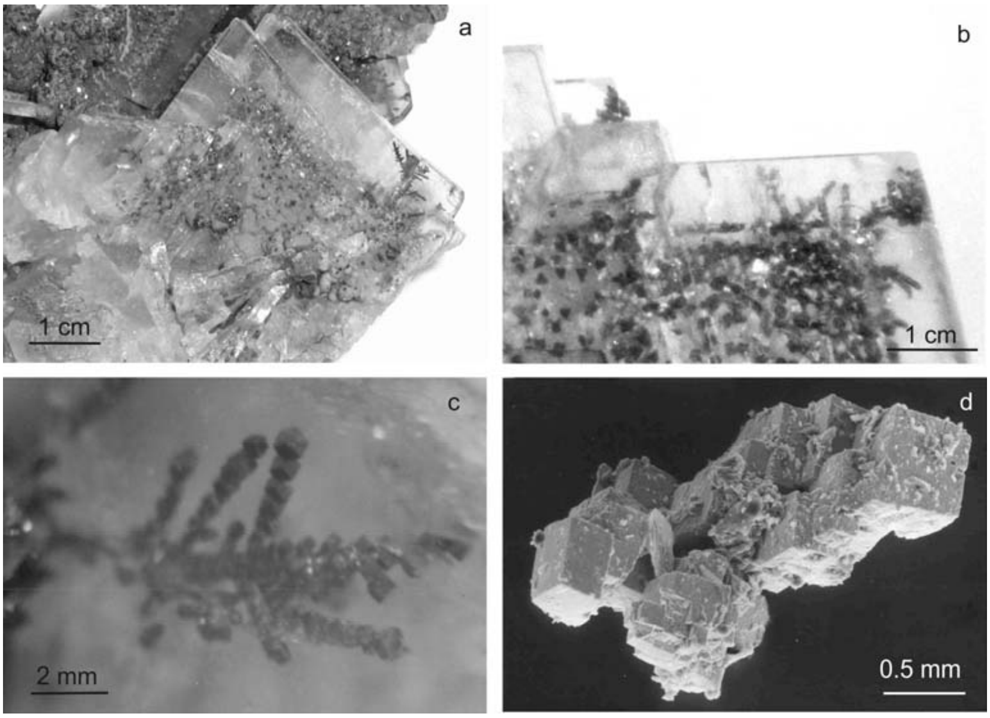

Fig. 8. Skeletal galena of 2[nd] type, {100}<111>, from Erma Reka, Bulgaria: a-b) numerous galena microcrystals (black), which are embedded in transparent platy barite outlining its internal growth zones. Only a few of them located on the apex parts of barite continued growing as dendritic-skeletal galena forms; c-d) morphology of the galena dendrites composed of small cubes, stacked approximately along their three-fold axes; microscopic image within barite (c) and SEM image of an extracted dendritic branch (d)

Фиг. 8. Скелетен галенит от II тип, {100}<111>: a-b) многобройни галенитови кристалчета включени в прозрачните баритови кристали очертават техните вътрешни растежни зони. Само някои от тях, намиращи се във върховите части на барита, продължават разрастването си като дендритно скелетни форми на галенита; c-d) морфология на дендритните форми, съставени от подредени по тройните оси кубични кристалчета; микроскопска снимка в барита (c), и СЕМ снимка на отделено галенитово клонче (d)

crystals (Fig. 9a), such as known for the "coated diamonds". A few small cubic galena crystals occur over spherulites. The fibrous sphalerite is nearly Fe-free and contains some Sb (0.25-0.70 wt.%), not found in the large earlier sphalerite crystals.

Data obtained by Bonev and Kouzmanov (2002) from study of primary fluid inclusions in such low-Fe sphalerite show temperature range *Th* 220-200^{o}C and relatively low salinity of fluids (<5-6 wt.% NaCl equiv.), and 185-160^{o}C (for the secondary inclusions). Similar data (220-150^{o}C) were obtained and by Krasteva and Gadjeva (1986). In the samples studied here we obtained for the earlier sphalerite and for the closely following it barite similar temperatures - about 200°C

The skeletal crystals from Erma Reka are similar to those described by Chebotarev (1966) from the Pistaly locality, Uzbekistan, which are included in coarse-grained barite mass. This dendritic galena there also consists

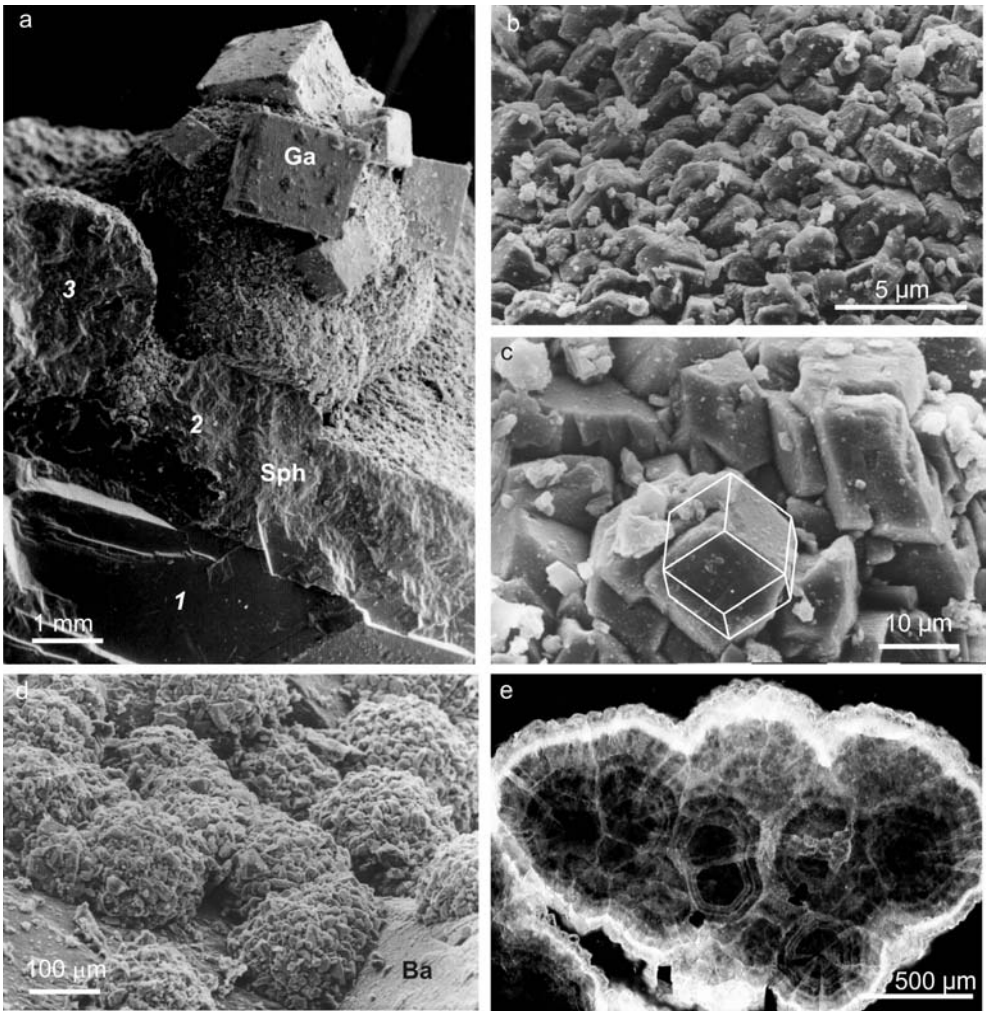

Fig. 9. SEM microphotographs of the colloform sphalerite associated with skeletal galena. Erma Reka, Bulgaria: a) sequences in the sphalerite (Sph) formation: *1*) upper part of a large-crystal of early sphalerite with (110) cleavage planes, *2*) overgrowing fine-fibrous crust formed by the crystal splitting, *3*) late spherulitic sphalerite associated with small galena (Ga) cubes; b) and c) surface morphology of the sphalerite crust, composed of numerous subparallel crystals, and d) surface of the spherulites over barite crystals (Ba); e) cathodoluminescence picture of a cross section of the fine-banded spherulitic sphalerite

Фиг. 9. SEM микрофотографии на коломорфния сфалерит, асоцииращ със скелетен галенит. Ерма река, България: a) последователност при формирането на сфалерита (Sph): *1*) горна част на кристал от ранен сфалерит с цепителни плоскости по (110), *2*) финовлакнеста кристална кора, нарастваща върху кристала-подложка чрез разцепване, *3*) късен сферолитов сфалерит, обраснат от галенитови (Ga) кубични кристалчета; b) и c) финокристална повърхност на сфалеритовата кора, и d) на сферолитите, върху баритови кристали (Ba); e) катодолуминесцентно изображение на финослоистия сферолитов сфалерит of small uniform mainly cubic crystals stacked along the <111> axes, but due to intensive oxidation galena is replaced by cerussite. Another case of intergrowth of skeletal galena with barite from the Pomorzany mine was shortly reported by Sass-Gustkiewicz (1996).

Discussion

According to Ramdohr (1955, 1980), Betekhtin et al. (1958), Lebedev (1965), etc. the skeletal galena crystals included in colloform banded sphalerite arose by recrystallisation of complex sulphide gels, in which especially important is considered the strong crystallisation power of galena. A list of criteria for colloidal origin proposed in the literature was given and critically reviewed by Roedder (1968). The most important features of the colloform textures are considered: spherical forms, syneresis cracks, concentric banding and radial structures, and the colloidal state is accepted as a necessary intermediary during their formation. Roedder (1968) approved that the colloform sphalerite grew directly as aggregates of continuously euhedral crystals projecting into the ore fluid.

Important for understanding the mechanisms and the sequence of formation of skeletal galena of these two different types are some of their crystallographic features and relationships with the enclosing minerals, as summarised in Figs. 10 and 11.

1st type: {111}<001>, Fig. 10

The galena skeletons are perfectly developed dendritic crystals composed of numerous stacked microcrystals. These delicate 3D-branched single crystals reach significant dimensions occupying large volumes of the ore.

- The fine, exceptionally mechanically unstable galena crystals are perfectly preserved without any distortions.
- The reticulate galena crystals are entirely overgrown by fine banded sphalerite crust of uniform thickness.
- The radial fibres composing the sphalerite crust are normal to the surface of the covered skeletal branches, and terminate by sharp euhedral crystal faces, not by smooth spherically-rounded surface (as noted yet by Roedder, 1968).

All these features indicate that the fine skeletal galena crystals were growing in open space, nondisturbed by outer influences, before to be encrusted by colloform sphalerite. As generally acknowledged, the growth of dendritic crystal is a diffusion-limited process (Chernov, 1980; Müller-Krumbhaar, 1987; Glicksman, Marsh, 1993, etc.).

The very fine-grained sphalerite aggregates characterise growth from highly supersaturated solutions far from the equilibrium (e.g. Fowler, L'Heureux, 1996). The growth of reticulate galena was realised also in such environment, in a chemical diffusion field, but from restricted number of nuclei and before the burst of nucleation of sphalerite. The growth of galena was rather fast process, since its high-energetic skeletal forms could not be equilibrated, remaining fossilised into the colloform sphalerite. The sphalerite deposition started from the available galena surfaces and only some isolated growth centres produced the randomly scattered microspherulites.

The exhausting of PbS can lead to undersaturation of fluids and local dissolution of galena. Sometimes the edges of skeletal forms are rounded before their encrustation by sphalerite (as shown by Haranczyk, 1959).

In some thick colloform aggregates as these from Pine Point (Roedder, 1968; Fowler, L'Heureux, 1996) acicular galena crystals are synchronous with the radial sphalerite fibres. In other cases, as from Kvaissa in the Caucasus (Zhabin, 1984), and Pomorzany (Fig. 7a,b, see also Viets et al., 1996: Fig. 4), rather thick but still skeletal forms of galena are enclosed in sphalerite following its radiating texture. Similar is the case from Schmalgraf-Moresnet described by Kutina (1952, e.g. his Figs. 8 and 9),

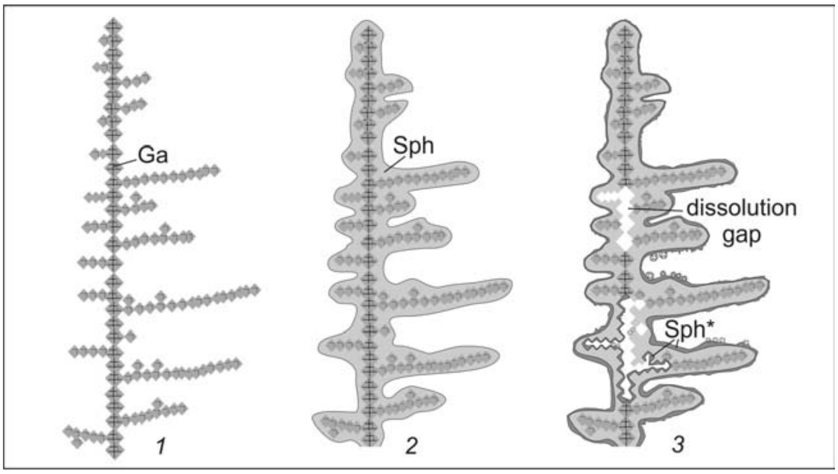

Fig. 10. Growth sequence in formation of galena-sphalerite (Ga/Sph) intergrowths of the type {111}<001>: *1)* growing of dendritic-skeletal galena, *2)* incrustation by banded sphalerite, *3)* partial dissolution of galena with arising of negative forms (white) and deposition of a thin peripheral darker layer of sphalerite (Sph*). A scheme

Фиг. 10. Схема на растежната последователност при образуване на галенит-сфалеритовите (Ga/Sph) сраствания: *1)* бърз растеж на дендритно-скелетния галенит от тип {111}<001>, *2)* обрастване от ивичест сфалерит, *3)* частично разтваряне на галенита с възникване на негативни форми и последващо отлагане на тънък периферен слой от по-тъмен сфалерит (Sph*)

where the separate branches of skeletal galena (again of {111}<001> type) also have the same radial orientation as the fibrous sphalerite. The proposed metasomatic origin of galena along radial syneresis cracks in gels is not realistic.

2^nd^ type: {100}<111>, Fig. 11

The second type skeletal galena, {100}<111>, found in Erma Reka, is included in barite crystals and associates with scarce spherulitic sphalerite.

- In an earlier moment numerous galena microcrystals were deposited on the outer barite crystal surfaces (Fig. 8a,b). Some of them show elements of initial skeletal growth (the elongated tips). Only a few galena crystal-nuclei situated around the crystal corners of barite and directed to the open druse cavity, survived (Fig. 8a,b). From their favourable position towards the feeding environment they developed several branches (Fig. 8a-d), extended along their crystal apexes. Similar case of directed growth of filamentary pyrite, included in large calcite crystals is described by Bonev et al. (2005).
- All other galena crystals remain undeveloped and became completely enclosed in the next growth zone of the faster growing barite crystals. The position and morphology of dendritic galena indicates diffusion-controlled regime of crystal growth, like in the 1st case. The dendritic branches that continue their growth nearly simultaneously with barite usually also remain included in its crystals.
- The presence of sphalerite spherulites and fibrous crusts on the earlier sphalerite crystals are indicative for sudden increase of ZnS supersaturation, which probably enhanced the diffusional resistance in the fluid.

The morphology and development of these two different types dendritic forms is predestined by the habit type of the polyhedral

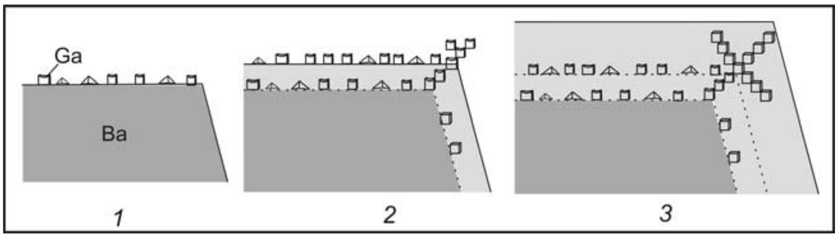

Fig. 11. Growth sequences in formation of galena-barite (Ga/Ba) intergrowths: *1)* deposition of galena crystals on the barite growth surface, *2)* and *3)* dendritic growth {111}<001> of galena nuclei located in favourable position on the barite corners. A scheme

Фиг. 11. Схема на растежната последователност при образуване на галенит-баритовите (Ga/Ba) сраствания: *1)* отлагане на галенитови кристалчета върху повърхността на барита, *2)* и *3)* дендритен растеж на галенитови зародишни кристали от тип {100}<111>, разположени в благоприятна позиция

crystals in the two differing environments. As it is known (Kalb, Koch, 1929; Obenauer, 1932; Kostov, Kostov, 1999), galena in the low-temperature carbonate-hosted deposits associated with sphalerite, marcasite and carbonates occurs preferably in octahedral habit and such is the case with the studied here materials. For the higher-temperature deposits in association with bulk quartz, the main galena habit is cubic, which is the case of Erma Reka and the Madan vein deposits. So, the directed growth at the corners of different seeds creates diverse dendritic morphology.

The results from galena synthesis proved the skeletal crystallisation of galena in viscous media at diffusional regime. Lebedev (1965) examined the diagenetic changes in mixed highly supersaturated PbS-ZnS gel solutions. After gradual stratification for 1.5 years, in their final stage they formed 3 zones: upper zone of fine-globular sphalerite, intermediate mixed zone, and bottom black spongy zone of dendritic-skeletal galena crystals very similar to the described here 1st type skeletons.

Garcia-Ruiz (1986) investigated growth behaviour of PbS single crystals, formed within silica-gel media. A morphological evolution from dendritic to hopper and polyhedral crystals with equilibrium cubic forms was established in a rather short time (~ 40 days).

Conclusions

Two crystallographically different types of dendritic-skeletal galena associated with colloform sphalerite are established.

- 1st type: {111}<001>, found in the low-temperature carbonate hosted Zn-Pb deposits of the Upper Silesian-Cracow, Moresnet-Aachen and other similar regions. The dendritic skeletons of galena, reaching up to 10 cm in length, are composed of parallel octahedral microcrystals stacked along the four-fold axes. They are encrusted by thin uniform crust of colloform, low-Fe banded sphalerite with radial-fibrous structure.
- 2nd type: {100}<111>, found as a late mineralisation of the Erma Reka vein high-temperature Pb-Zn deposit, Madan district. The dendritic skeletons of galena are composed of cubic microcrystals stacked along the three-fold axes, in association with spherulites of colloform sphalerite. They are included in large-crystal barite and are located on their corners directed to the feeding environment.

The obtained mineralogical data are indicative that skeletal galena was arisen by fast growth in open space, from restricted number of nuclei, in supersaturated low-temperature stagnant fluids at diffusion-controlled regime. The associated fine-banded low-Fe sphalerite composed of fine-fibrous along <111> crystals formed at higher super-saturation and intensive nucleation. The extremely non-equilibrium interfaces of galena skeletal crystals are preserved intact by overgrowing sphalerite (in the first case) or barite (in the second case).

Acknowledgements: The authors are thankful for donated samples to Prof. Czeslaw Haranczyk, Prof. Tatyana Schadlun, Prof. Zurab Othmezuri, Dr. Yotso Yanev and Dr. G. Chebotarev. Important information was obtained and from samples of the Mineralogical Museum of the Sofia University with the assistance of Dr. Vassilka Mladenova and Dr. Vsevolod Kurchatov. Thanks are due also to Prof. Karl Ramseyer for the cathodoluminescence images, to Zvetoslav Iliev for microprobe analyses, and to Dr. Michail Tarassov and Luchezar Petrov for some of the SEM photographs. This study is part of the project NZ-1307, sponsored by the Bulgarian National Science Foundation.

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Accepted April 03, 2006
Приета на 03. 04. 2006 г.