Crystal habit of Ag-, Sb- and Bi-bearing galena from the Pb-Zn ore deposits in the Rhodope Mountains

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Abstract. Despite of the enormous information on the contents of minor and trace elements in galena from many ore deposits and regions, the relationship between mineral chemistry and crystal morphology of galena crystals is not well understood. To obtain such information representative and well-characterized natural mineral samples were examined. The materials descend from some Tertiary hydrothermal vein and metasomatic skarn-ore Pb-Zn deposits of the Rhodope Mts. in Bulgaria, mainly from the major Madan and Laki ore districts (deposits of Mogilata, Ossikovo, Gradishte, Petrovitsa, Strashimir, Jourkovo, Kenan Dere, etc.), and from some other deposits.

Galena crystals of varied morphologies are formed by open-space crystallization in the ore veins, as also in the cavities of altered and locally dissolved skarns. In all crystals both cubic $a\{100\}$ and octahedral $o\{111\}$ faces are developed, in different proportions, determining cubic, octahedral and cubic-octahedral crystal habits. About 40 samples were chemically analysed through ICP AES and AAS methods for Ag, Bi, Sb and Te, which are the most important minor elements in galena. Ag and Sb were found in all samples in variable amounts, mainly in the ranges 10-1000 ppm for Ag, and 70-600 ppm for Sb. Bi is nearly fully absent in some deposits, like Mogilata and Ossikovo, but is of elevated and irregular content in other. Highest values were found for samples from Strashimir, Laikov Choukar and Gradishte, in the range 100-2500 ppm. In smaller amounts are presented Te (0-77 ppm) and Tl (0-7 ppm).

All crystals of octahedral and cubic-octahedral habit belong to the early generation of galena, deposited at rather high temperature (>300°C). They contain increased amounts of Bi and Ag (+ Sb), most likely in solid solution, which suggests that Bi plays important role in stabilizing the octahedral faces. In the PbS structure they are kinked K-faces, in contrast to the cubic flat F-faces, growing through a layered mechanism. The crystals of cubic habit contain Ag + Sb, with only traces of Bi (always bellow 30-40 ppm).

All morphological varieties of definite habit have similar amounts of minor elements: Ag + Sb for crystals of cubic habit (polyhedral crystals, as also hopper, platy-skeletal and tabular crystals, penetration twins, filaments, whiskers and negative crystals), Bi with some Ag and Sb, for galena of prevailing octahedral habit (polyhedral crystals, thin and skeletal $\{111\}$ twins). Inclusions of different Pb-Ag-Bi-Sb phases sometimes occur in galena, mostly as later, lower temperature nano-sized exsolution products, only rarely reaching larger size.

Key words: Galena, crystal habit, crystal morphology, exsolutions, Ag-Bi-Sb-Te admixtures

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Introduction

Galena as a principal mineral component in the ores of the lead-zinc deposits, is a subject of intensive and versatile mineralogical and geochemical investigations. Very often it contains increased amounts of minor and trace elements, interesting from crystallochemical and genetic point of view, being of significance to the geological and mining practice, as well. Enormous analytical material has been obtained till now for ores of various mines and prospects. However, information about the possible relationships between the mineral chemistry and the crystal morphology of the examined galena samples is nearly absent, although it can be an important and informative genetic indicator.

The aim of this study is to put the question for the relationships between the chemical admixtures and the crystal habit and variable morphologies of galena crystals, through observation on representative natural mineral samples.
**Geological settings and materials**

The studied materials descend from some Tertiary hydrothermal ore deposits of the Rhodope Mountains which are an important part of the Alpine-Carpathian-Balkan province of the Alpine-Himalayan metallogenic belt. During the last century the deposits of the Rhodope region, and especially those from the ore districts of Madan, Laki, Zvezdel, Ardino, Madjarovo and Spahievo, were objects of intensive prospecting and exploitation in numerous underground mines, some of which are still operating.

The Pb-Zn ore deposits in the Central Rhodopes include both vein and metasomatic ore bodies, enclosed in the high-grade metamorphic rocks of the Rhodope massif (migmatized gneisses and granito-gneisses, biotite gneisses, amphibolites, mica-shists and layers of marbles), and partly in the overlying Paleogene sediments (Kolkovski et al., 1996, 2000). Four main ore districts related to separate hydrothermal ore-forming systems are known: Madan, Laki, Davidkovo, and Ardino.

In the largest Madan district, main ore-controlling role plays a system of large, up to 10-15 km long, NNW trending subvertical zones which include well-mineralized ore veins. The skarn-ore bodies are located in the marble horizons along the veins. The replacement ores are inserted in the contours of the primary skarn bodies and follow their complex morphology.

Three main stages of hydrothermal deposition in the ore-forming system are observed (Bonev, 2002): skarn stage, with deposition of pre-ore infiltration marble-hosted exoskars of highly Mn-rich clinopyroxenes; main ore stage, presented by quartz, pyrite, sphalerite, early galena, and some minor sulphides, formed at rather high T and accompanied by acid alteration of the gneissic rocks and skarns, with formation of retrograde post-skarn Mn silicates and carbonates; and late, post-ore lower-T (260-200°C) stage with deposition of carbonates, quartz and chalcedony, barite, scarce sulphides including late galena and sulphosalts.

The mineralogical, fluid inclusion and stable isotope studies suggest that the main ore deposition took place at rather high-temperature (350-330-280°C), and low pressure (~100 bar), from low-concentrated (4-5 wt.% salinity) Cl-Na-K fluids. Solutions are slightly acidic (pH 6.5) and of reduction character (Fe^{2+} and Mn^{2+}). Ore deposition is realized by intensive fluid/rock interaction with the embedding gneisses and early skarns, under the strong control of the fracture network. Boiling of solutions is important as well (Bonev, Piperov, 1977).

In the very similar but some smaller Laki district the ore veins are meridional to NNE oriented and skarn-ore bodies are located in one available marble horizon. The Davidkovo district, in the central part of the area, has only vein deposits of different orientation, whereas in the smallest Ardino district only metasomatic ore bodies are known, controlled by smaller W-E faults without economic vein mineralization.

The ore mineralizations in the Eastern Rhodopes are of vein type. The main ore districts: Madjarovo, Zvezdel-Pcheloyad, Spahievo, are closely related to the Tertiary volcanism. The ore veins are enclosed mainly in the volcanic rocks, partly also and in the metamorphic basement. They have been formed at some lower temperatures (270-180°C) but have similar mineral composition of quartz, galena, sphalerite, pyrite, carbonates, minor other sulphides and sulphosalts.

An overview on the knowledge about the mineralogy and metallogeny of the hydrothermal mineralization in the Rhodope Massif was presented in the monograph *The Lead-Zinc Deposits in Bulgaria* (Dimitrov, 1988), in the reviews of Kolkovski et al. (1996, 2000), also by Bonev (2002), and recently by Marchev et al. (2005), and others.
Previous data

The chemical composition of galena from different ore districts and deposits has been studied by numerous authors. Though obtained by different methods and precision, their data give a general picture about the ore mineralizations in the area.

For the Madan ore district, the largest in the Rhodope Massif, analytical data about the trace-elements in ore minerals and especially in galena have been presented by Bogdanov (1960) and Dimitrov (1963), furthermore by Kirov and Minčeva-Stefanova (1962) for the Borieva deposit, by Minčeva-Stefanova and Gorova (1965) for Gradishte, by Eskenazy et al. (1971) for the deposits of the Spolouka - Laikov Choukar fault, by Eskenazy et al. (1979) for Murzyan and the deposits of the Karaaliev Dol - Petrovitsa fault, by Kolkovski et al. (1983) for the Golyam Palas - Ribnitsa fault, by Gadjeva (1983) for the Erma River area, etc. A summary of more than 550 analyses, characterizing galena from the main deposits in Madan district was given by Kolkovski et al. (1996, 2000). The most important additional components in galena are silver, antimony and bismuth, their content varying in the ranges: 300-1200 ppm (Ag), 130-1410 ppm (Sb), 0-2300 ppm (Bi). Ag and Sb are relatively uniformly presented in all deposits, and their average contents for the district, according to these authors, are the same, about 660 ppm. However, the distribution of Bi in galena is rather irregular, mainly concentrated in several deposits: Spolouka, Strashimir, Laikov Choukar, Kroushev Dol, Borieva, Gradishte, Petrovitsa, Golyam Palas. Kolkovski et al. (1996) considered, that these deposits form a Bi-enriched zone, situated below the upper Ag-Sb enriched zone, and followed in depth by a sulphideless zone of barren quartz, thus outlining a vertical dome-like zoning of the ore mineralization. Some other trace-elements which are in lower concentration are: Te (between 0 and 80 ppm), Se (4-87 ppm), Cd (10-64 ppm), Tl (0-10 ppm), Mo (0-2 ppm), Mn (20-300 ppm), Cu (50-100 ppm), and some Zn (when excluding some single extreme results, connected most probably with admixtures of other rare sulphide minerals). Sn, Ni, Co were found only occasionally as traces.

It is well known that many of the deposits especially in the Madan district besides the coarse-grained ore aggregates contain well-formed crystals of ore and gangue minerals. The space necessary for their crystallization includes the open voids and cracks in the ore-controlling strike-slip faults, and also the cavities of ‘hydrothermal karst’ formed by local dissolution of the altered skarns. Such crystals and crystal druses, especially also of galena (Fig. 1), often of unique quality and beauty are exposed in leading world mineralogical museums and private collections. It is strange that all vast analytical material obtained for galena from the Rhodope deposits gives no any information about its crystal morphology. Rarely is mentioned only, that galena crystals in some deposits commonly have cube and octahedron shapes.

Data on morphology of galena crystals from Gradishte have been presented by Minčeva-Stefanova and Gorova (1965). The increased Bi content in some samples of early galena from the deeper parts of the deposit they explained with admixtures of Bi mineral (cosalite) having no influence on the galena habit. Bonev (1980) studied crystal morphology of galena from the deposits of the Central Rhodopes in details. He recorded that Bi plays important role in stabilizing the octahedral faces and \{111\} twinning in galena crystals, but gives no analytical data.

The Laki ore district is very similar though and of smaller scale. Stoinova (1962) gave information about galena. Atanassov and Eskenazy (1965) and Radonova et al. (1976) gave the chemical information about galena in the Madjarovo district. As main typomorphic elements for galena they marked Ag, correlated
Fig. 1a) Druse of numerous cubic galena crystals, 19.5 cm wide. The Mogilata deposit. b) Giant octahedral galena crystals with thick jagged growth layers on their large \{111\} faces. The smaller rough cubic faces contain irregular deep pits. 20 cm in width. Petrovitsa
with Bi or Sb. Galena from the Ardino skarn-polymetallic deposit according to Bonev (1991) is in subordinate amount as compared to sphalerite, but is Ag- and Bi-bearing. Earlier, skeletal galena from the Zvezdel-Galenit deposits was studied by Bonev and Gorova (1972).

**Results**

The content of Ag, Sb, Bi and Te, partly and Tl, in representative galena crystals with diverse crystal morphology were examined through chemical methods (ICP AES, AAS) and some analytical results are presented in Table 1. The materials studied originate predominantly from the Madan ore district, in addition of some typical samples from Laki, Madjarovo and other districts. For comparison, in Table 1 are included and the mean values of these elements for the single deposits, as determined by Kolkovski et al. (1996). In addition, electron microprobe analyses were used to obtain chemical information about some microcrystals and about the chemical homogeneity of some studied materials.

In nearly all crystals from the studied deposits both cubic \(a\{100\}\) and octahedral \(o\{111\}\) faces are developed, though in different proportions. As in many other deposits, \(d\{110\}\) forms are rare. Following Kalb and Koch (1929), Obenauer (1932), Kostov and Kostov (1999), three main habit types for galena can be differentiated:

- **Cubic**, with large cubic faces \(a\{100\}\), and only small triangle \(o\) truncations of the crystal apices (Figs. 1a, 2a);
- **Octahedral**, with prevailing octahedral faces \(o\{111\}\) of ditrigonal or hexagonal shape and small, but always presented diagonally oriented quadratic cubic faces truncating the crystal tips (Figs. 1b, 4a); and
- **Cubo-octahedral** or octahedral-cubic, the intermediate habit in which the both \(o\) and \(a\) forms are nearly equal \((a \approx o)\), the opposite \(o\) faces of triangle shape being touched at their tips, surrounding the diagonally oriented quadratic \(a\) faces.

In addition to the normal well-shaped polyhedral galena crystals, various cases of complicated and skeletal crystal morphology were also observed, discussed by Bonev and Gorova (1972) and Bonev (1980, 1993).

As it is well-known (Kostov, Kostov, 1999), in the cubic, \(Fm\overline{3}m\), structure of galena of NaCl type, the dense-packed compensated \\{100\}\ faces comprising both Pb and S atoms, contain two important periodic bond chain PBC vectors in \(<100>\) directions, and are flat F-faces, belonging to the equilibrium forms, and growing slowly according to a layer-by-layer mechanism. The \\{110\}\ are stepped S-faces with one PBC vector, and the \\{111\}, without such vectors, are kinked K-faces. The \\{111\}\ faces constituted of non-compensated alternating Pb- and S-slices require no nucleation and grow very fast. They may become important habit faces when other interfering factors (e.g., supersaturation or specific impurities) retard their growth.

**Galena with cubic habit**

The cubic habit of galena is prevailing in the most deposits in the area, Mogilata and Ossikovo being the most representative between them. Often, the polyhedral crystals of uniform size and bounding overgrow the walls of some open cavities forming crystal druses (Fig. 1a). Usually, the size of crystals is about 1-2 cm. Sometimes, and particularly in some deposits (Fabrika, Gradishte, Kenan Dere, Jourkovo) galena crystals reached 10 and even 15 cm. Unique giant crystals, were discovered long ago in the ore vein of the Golyam Palas mine, one of them reaching 34 cm, size not known for galena (!). Penetration twins along \\{111\}\ are developed in some crystals, with protrusion of their pyramidal twinned parts over the cubic faces.

**Skeletal** shapes are not rare. The beginning of skeletal growth is marked by
Fig. 2. Galena crystals of cubic habit: a) Large crystals with thick growth layers. The surface concavities indicate the location of enormous (mm-sized) fluid inclusions - negative crystals within galena. Mogilata; b) Large (100) tabular crystals. Mogilata; c) Skeletal box-like crystal constituted by thin plates along the three mutually perpendicular {100} planes. Mogilata; d) Large skeletal crystals with slight superficial corrosion. Mogilata; e) Large cubic crystals partly autoepitaxically overgrown by later {100} platy crystals. Ossikovo; f) Large cubic crystal autoepitaxically overgrown by small cubic crystals. Kenan Dere
Table 1. Contents of Ag, Bi, Sb, Te and Tl in selected galena crystals with typical morphology

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<th>Deposit</th>
<th>Sample No</th>
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<th>Sb ppm</th>
<th>Te ppm</th>
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forming of concave depressions in the central parts of the crystal faces and predominant development of the edges and corners (Fig. 2a). In the consequent stage hopper crystals arise developed along the four-fold axes and bounded by stepped cubic faces (Fig 2d). Such are known from Zvezdel-Galenit, Mogilata and other deposits. Another remarkable type of skeletal forms are the box-like crystals from Mogilata and Ossikovo, built up by thin (< 1 mm) \{100\} platelets developed along the three mutually perpendicular cubic planes (Fig. 2c). Sometimes they can reach up to 4-5 cm in size. Thicker, up to several mm, and up to 3-4 cm wide single tabular crystals (Fig. 2b) bounded only by cubic faces, were found within the layers of hydrothermal clays (kaolinite, etc.) filling the bottom parts of some druse cavities in Mogilata and Ossikovo.

Skeletal-dendritic crystal shapes are known from the Erma Reka deposit, mostly included in barite (Atanassova, Bonev, 2006). These peculiar skeletons denoted as \{100\}<111> type, consist of numerous fine (< 0.5 mm) cubic microcrystals stacked along the three-fold axes (Fig. 3a). Very strange are and the rare highly non-equilibrium galena filamentary microcrystals and straight and kinked whiskers (Fig. 3b) of µm width, found in Mogilata and Gradishte (Bonev, 1993).
Especially interesting and important are the macroscopic fluid inclusions of mm-size (Bonev, 1977) formed as negative crystals within many crystals, and often revealed as small concavities of plastic deformation on the galena crystal faces (Fig. 2a).

In some favourable cases from the altered carbonatized skarns in the Kroushev Dol and Ossikovo deposits it was possible to separate isolated metasomatic crystals of galena. Their SEM examination proved that they have well-formed skeletal stepped-like surfaces bounded entirely by oscillating cubic faces (to be published).

As shown, all described here polyhedral crystals and peculiar more complex formations of galena are bounded in general by cubic faces. The systematic chemical analyses (Table 1) established that the principal minor components in them are Ag and Sb. Bi, when found, is in a very low content, usually below 10-15 ppm. The average values characterizing these deposits are of the same order.

**Galena with octahedral and cubic-octahedral habit**

As already mentioned, the galena crystals of prevailing octahedral habit are known only from several deposits. Nevertheless, the morphology of these crystals is also variable and deserves attention. Always, in one and the same druse cavity the polyhedral crystals of this habit have uniform proportion of the cubic to octahedral forms, often with marked prevailing of the octahedral faces (Figs. 1b, 4a), which are distinguished with their ditrigonal or hexagonal shapes. No crystals of cubic habit can be found together, evidently due to differences in the crystallization conditions. Remarkable is that the octahedral faces of galena always have rough sometimes wavy surface, in contrast to the fine-layered smooth cubic faces. Clearly, this is a consequence of the different character of these two faces: (100) are flat (F) and (111) are kinked (K) faces. It is interesting, that in many cases the octahedral
Fig. 4. Various galena crystals of octahedral habit: a) Large octahedral crystal. Yuzhna Petrovitsa; b) Quartz druse with single cubo-octahedral galena crystals of skeletal development. Golyam Palas; c) Platy galena (111) twin of skeletal development and beginning corrosion. Kroushev Dol; d) Skeletal accretion of several parallel (111) twin plates. Kroushev Dol; e) Large octahedral-cubic crystals autoepitaxically overgrown by small later cubes. Strashimir; f) SEM image of the skeletal-octahedral interface of a metasomatic galena crystal separated from the embracing altered hedenbergite skarn. Ardino
galena crystals are very large, up to 5 cm and wider, reaching even 10-15 cm (Fig. 1b). Very thick growth layers with jagged fronts are observed on their octahedral faces.

Sometimes skeletal forms of cubo-octahedral galena crystals occur, as well (Fig. 4b). It them, skeletal depressions occupy the undeveloped central areas on both types of faces, octahedral and cubic.

Very interesting are the twinned platy crystals of galena, well presented in Kroushev Dol, Strashimir-Nadezhda, Shoumachevski Dol, etc. Such single plates (Fig. 4c) are developed along a twin (111) plane, being up to several cm wide and several mm thick. They have hexagonal outlines and rough skeletal surface formed by smaller triangle crystal subindividuals in two antiparallel positions. Remarkable are the skeletal twins, composed of several twinned platelets in parallel position forming spatial comb-like frameworks (Fig. 4d). These impressive peculiar crystal formations with shining surface from the Kroushev Dol deposit sometimes reach up to 10 cm length.

In a rare case, from the Ardino deposit it was possible to detach from the altered pyroxene skarn and metasomatic crystals of galena. The SEM examination established peculiar skeletal development of their interfaces (Fig. 4f) formed only by pure octahedral crystal faces. As it is known (Bonev, 1991), galena from this deposit is enriched in Ag, Bi, Te and Se, when Sb is always in low concentration.

It was found, that all such galena crystals of octahedral habit contain increased Bi content (Table 1) exceeding 100 ppm and reaching up to 2500 ppm. The analysed for comparison classical (as known from Khetchikov, 1958) octahedral bismuthian galena from Tetyukhe/Dalnegorsk contains 8700 ppm Bi.

Autoepitaxic relationships in galena

Occasionally, the early large galena crystals have been overgrown authoepitaxically by smaller crystals of later galena generation. In some cases such overgrowths following previous dissolution of galena has character of regeneration of the crystal forms. Two characteristic cases were observed:
- Overgrowth of large early cubic crystals by numerous smaller also cubic crystals (Figs. 2e, f).
- Overgrowth of large early octahedral-cubic crystals by numerous smaller cubic crystals (Fig. 4e). On the original (111) faces the late crystals obtained pyramidal shape, when on the (100) faces form nearly continuous overgrown platelets, continuing there growth and outsiders, as inclined overhangs around the octahedral faces.

In the first case the Bi content changes from 15 to 40 ppm (Kenan Dere, analyses 34 and 35 in Table 1), when in the second case it changes from 530 to 33 ppm (Strashimir, analyses 23 and 24 in Table 1).

Discussion

The chemical determinations (Table 1) confirmed that Ag, Sb and Bi are the most important minor elements and have uneven distribution in the studied galena. Ag and Sb were found in all samples in variable amounts, mainly in the ranges 10-1000 ppm for Ag, and 70-600 ppm for Sb. Some higher values probably are due to contamination with foreign phases. Especially interesting is Bi which is absent or only in traces in some deposits, like Mogilata and Ossikovo, but of elevated and irregular amounts in others. Highest values were found for samples from Strashimir, Laikov Choukar, Gradishte (in the range 100-2500 ppm), in accordance with the previous chemical determinations of Kolkovski et al. (1996). In smaller amount are Te (0-77 ppm) and Tl (0-7 ppm). The other trace-elements (As, Se, Sn, Mo, was not determined now because of their low content and insignificant role for morphology.

The analysis of the results obtained from the systematic studies on galena crystals of well-characterized diverse morphology (Table 1, Fig. 5) is indicative and allow to find definite correlation between the chemistry and
In an early paper Khetchikov (1958) reported that galena crystals with dominant platy morphology along the octahedral faces from the Tetyukhe deposit in the Far East contain up to 2 wt.% Bi (and inclusions of galenobismutite), whereas in the cubic crystals Bi is much lower. Some later, Marshall and Joensuu (1961) for samples from the Mississippi Valley, and Blackburn and Schwendeman (1977) for samples from different replacement and cavity fillings deposits, do not found causal relationship between crystal habit an the concentration of trace elements in galena.

Many authors have examined the crystallochemical relationships of Ag, Sb and Bi with galena, as experimentally, so also in various natural cases, which show large diversity and often remaining not fully understood. In a comprehensive review Foord and Shawe (1989) have discussed these

![Fig. 5](image_url) Fig. 5. Triangular plot showing the atomic relations between Ag, Sb and Bi in analysed galena crystals of different habit
problems, and there can be find detailed and exhaustive references and commentaries. Usually the affinity between Ag and galena is explained by the coupled substitution $\text{Ag}^+ + \text{Sb}^{3+} (\text{Bi}^{3+}) \leftrightarrow 2\text{Pb}^{2+}$. The experimental studies found that above 220°C there is a complete solid solution series between PbS and AgBiS$_2$ (matildite). For the PbS and AgSbS$_2$ such solubility exists at high $T$ (<500°C), and is much lower at 300°C, less than 4 mol.% (and <2 mol.% at 200°C) (Nenasheva, 1975; Hoda, Chang, 1975; Åmcoff, 1976; Chang et al., 1988, etc.). No connection with the morphology of crystals was established or discussed.

All galena crystals of octahedral habit studied here, belong to the early generation of the mineral, deposited at rather high-$T$ (>300-330°C), so the increased contents of Bi and Ag in them suggest for a solid solution substitution of Pb in galena. Neither reflected-light microscopy, nor the high-magnification and high-contrast BSE imaging gave evidence for existence of non-homogeneities on a µm scale also in galena with highest Bi content. The accuracy of powder X-ray determinations is also not sufficient for explaining the form of such not high-concentrated admixtures in galena. However, by using of other techniques, such indications could be expected. Thus, on high-magnification electron microscopy photographs of cellulose replicas from one of these galena samples numerous sub-micron inclusions of regular crystal orientation (Figs. 6a, b) were observed. In the first case, these are elongated inclusions oriented along three (most probably <110>) directions, and in the second, oriented inclusions are of two kinds, one of larger size (0.3/0.15 µm) and one of much smaller size, of length below 50 nm. The detailed study of these relationships requires applying of high-resolution transmission electron microscopy (HRTEM) combined with analytical electron microscopy techniques and is an aim for specialized future studies. Evidently, it concerns to post-deposition exsolutions from the solid-solutions of AgBiS$_2$ and AgSbS$_2$ or Ag(Bi,Sb)S$_2$ for which is known that their low-temperature crystal forms (matildite, miargirite, and aramayoite, respectively) have different monoclinic crystal structures (Kostov, Minčeva-Stefanova, 1982). It is probable, that in the Bi- and Sb-bearing galena such phases form and other modulated domains of different kinds.

So, it can be assumed, that the habit type of the galena crystals is controlled to a great extent by the chemistry of the fluids, and the presence of definite minor elements like Bi and Sb, whereas the morphological modification and development depends mainly from the specific physical changes during the crystallization process ($T$ and supersaturation, diffusion, convection, etc.). The inclusions of different Pb-Ag-Bi-Sb and other phases are mostly later unmixing products, reaching sometimes enough larger size (e.g., Khetchikov, 1958; Czamanske, Hall, 1976; Ramdohr, 1980; Sveshnikova, 1981; Foord, Shawe, 1989; Sharp, Buseck, 1993; Lueth et al., 2000; and others), in some high-Bi galenas even causing octahedral parting.

Morphologically very interesting are the "knitted" galena crystals (gestrickte Bleiglanze) enclosed in banded colloform sphalerite (Schalenblende) known from many low-temperature stratiform lead-zinc deposits like in the Mississippi Valley and Upper Sylesian-Crakow regions. It was shown (Ramdohr, 1980; Atanassova, Bonev, 2006) that these skeletal formations consist of octahedral microcrystals. Outstanding galena polyhedral crystals with cubic and sometimes with octahedral habit and museum-quality are known from these type deposits (Lasmanis, 1989). Arsenic instead of Bi is an important trace-element in these deposits, and it is not excluded that it plays a habit-modifying role.

Interesting data have been obtained in experiments of hydrothermal crystallization of galena, though not always the information presented is enough to interpret the results. Two approaches have been applied. In the first one, PbS was used as source of metal and S in stoichiometric ratio. By means of temperature gradients it was redeposited through the
transporting water solutions mainly of chloride composition. Thus, Badikov and Godovikov (1966) have produced isometric and skeletal-hopper cubic crystals, and Czamanske and Rye (1974) isometric cubic galena crystals. But, in solutions with NH₄I the last authors obtained fine galena dendrites composed of minute octahedrons stacked along the fourfold-axes, together with some new formed PbI. Most probably, in this and other similar cases the disturbance of the Pb/S stoichiometry caused deficit of one of the components (here Pb) and thus retarded the growth of the {111} faces composed of alternating Pb and S layers. Streitel (1970) in similar experiments with NH₄Cl solutions also obtained two different results: cubic crystals in inert titanium ampoules, and octahedral crystals together with pyrrhotite, in iron ampoules. In the last case, coupling of some S with available iron in the new-formed pyrrhotite, disturbed the stoichiometry (Pb>S). In chloride medium Garcia-Ruiz (1986) also crystallized in gels skeletal and hopper-like crystals of cubic habit.

The second approach uses different sources for Pb and S and the strong stoichiometry was not attained. Daryussina and Distler (1965) starting from Pb acetate, thiourea and KOH at low T have produced minute, very thin (111) PbS plates growing by layered and mosaic mechanisms and reaching up to 10 µm in size. In a similar way Sunagawa and Endo (1971) produced micrometer-sized cubo-octahedral skeletal galena crystals with concave faces. However, such experiments realized in very restricted experimental volumes can not be directly applied to the natural reactions usually realized in open hydrothermal systems of much larger volumes.

Supersaturation of solutions is usually considered as another important factor. Thus, for most halide crystals of NaCl-type structure experimental crystallization at high supersaturation shows {111} as prevailing habit. Aoki (1979) explains this with the important role of the linkage vectors of coordination polyhedra, which for this structure are <110>. Thus, {111} faces with three such vectors are determined as the habit form. Aoki applies this approach to crystals of galena, but for this case there are no experimental confirmations.

Galena crystals with varying morphology (not always crystallographically clearly defined) were prepared and in other recent experimental works (e.g., Ni et al., 2007; Wang et al., 2007) but they are not directly applicable to the
natural conditions and for evaluating the influence of admixtures on crystal habit.

Conclusions

The perceived correlation between the Bi content (together with Ag + Sb) and development of octahedral habit suggests the important modifying role of Bi in stabilizing the octahedral faces of galena. For the cubic habit characteristic are Ag + Sb admixtures, at absence or very low Bi content. The examined Bi-bearing galenas are relatively high-temperature, which agrees with the experimental data for arising of such solid solutions. The non-stoichiometry in fluids with deviations in the Pb/S ratio may also contribute to development of \{111\} faces, as known from some experiments.

In general, the habit \(a:o\) ratio of galena crystals reflects except the basic crystal structure, also the chemical control of the solutions: main and minor components, esp. Bi, Sb and Ag, also pH, etc. (at defined 7) leading to development of the kinked octahedral faces.

The morphological variations in crystals of definite habit, with appearance except of polyhedral also of skeletal, dendritic and tabular shapes, twins, filamentary crystals, whiskers, and negative crystals, depend on the deviation from the equilibrium, and thus reflect the physical control of the crystallization determined by the supersaturation, diffusion, direction of the convective flows, etc.

The habit changes observed in a deposit \((o\to a\ or\ a\to a)\) characterize the evolution in the solutions with development of the ore-forming process during the geological time, and not of a portion of solutions in a restricted space.

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