MORPHOGENETIC TYPES OF ORE BODIES, ORE TEXTURES AND CRYSTALLIZATION MECHANISMS IN THE HYDROTHERMAL MADAN DEPOSITS, CENTRAL RHODOPES

Vassileva R. D., Atanassova R., Bonev I.K.

*Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev str. 24, Sofia 1113, Bulgaria; rosivas@geology.bas.bg*

**Abstract:** In the Madan Pb-Zn deposits three morphogenetic types of ore bodies are recognized – steep simple veins and complex disseminated stockworks, as well as gently sloping marble-hosted skarn-ore bodies. Their formation is structurally controlled by the ore-controlling fault systems, and lithological variety of the host Rhodope metamorphic complex. The replacement ore bodies reveal complex morphology according to the number, thickness and position of the host marble layers, shifts along the fault structures and local physicochemical parameters. Among the well presented morphological types – bed-like, mushroom-like, columnar or irregular, single or multilayered replacement bodies occur. The ore textures are indicative for crystallization in open space or metasomatic growth in solid state. Infill ore textures like cutting veinlets, layered textures, druses, crustifications and breccias are formed by crystallization in open space. Typical for the vein and stockwork mineralization, they are observed as well as in the dissolution cavities formed by “hydrothermal karst” in the replacement ore bodies. In the latter, characteristic are the textural varieties inherited by the primary skarns in the processes of alteration and overprinting. Radiate and spherulitic, concentric, conical, massive, porous, rhythmic-banded textures typically occur. Ore impregnations and nests, pseudomorphs and interstitial formations complete the textural diversity. Certain zonal distribution in the minerals and textural characteristics is determined. The main mechanisms of ore deposition include boiling, intensive fluid/rock interaction, retrograde alteration of skarns performed generally by convection and diffusion.

**Key words:** vein and replacement ore bodies, mineral textures, crystallization mechanisms, Madan Pb-Zn deposits, Central Rhodopes

1. Introduction

Skarn deposits, especially those in which sulphide minerals dominate, may have set of indicative textures that record useful information on primary and overprinting processes. Understanding the mineral textures and their paragenetic implications is the basis for all ore deposits studies (Ciobanu and Cook, 2004). The knowledge of ore bodies’ morphology, ore textures, factors determining the ore deposition, and mechanisms of crystallization is fundamental to unraveling the genesis of an ore deposit, which in turn allows exploration and mining geologists to build their conceptual models of the deposits (Taylor, 2009).

Base metal vein and metasomatic sulphide ores are a major part of the economically important Tertiary (~30 Ma) mineral province of the Central Rhodopes, especially in the large Madan ore district. The ore-bearing skarns are part of the economically important vein and replacement deposits of Bulgaria. The replacement ore bodies are preferably hosted in early manganian skarns, which in turn were affected by vein-related hydrothermal replacement of marble interbeds between high-grade gneisses (Bonev, 2003). The Madan deposits comprise the largest region producing Pb-Zn ores in Bulgaria. They are and among the largest Pb-Zn deposits of particular type associated with Mn-rich skarns (Einaudi et al., 1981). Some of the most spectacular and imposing mineral polyhedral crystals of galena, sphalerite and chalcopyrite and their aggregates from the hydrothermal Madan deposits are well known worldwide (Kostov and Kostov, 1999). This contribution presents generalized information about the features of the vein, stockwork and replacement ore bodies and characteristic types of textures as well as the factors controlling the ore deposition in the Madan district.
2. Geological Background

The Madan Pb-Zn deposits are hosted in the high-grade metamorphic Rodope massif (Dimov et al., 2000; Vassileva et al., 2005). The lower part of the massif is composed of migmatised gneisses in the core of the Central Rhodope dome. The upper, overtrusted parts, Madan and Startsevo allochthones, developed in the western and eastern slopes of the dome, are composed of gneisses, amphibolites, mica-schists and marbles (Kolkovski et al., 1996). One to three marble horizons are known in the different parts of the area, hosting the metasomatic skarn-ore mineralization. Four main ore districts are known: Madan, Laki, Davidkovo, and Ardino (Fig. 1a). The slightly sloping marble-hosted skarn-ore bodies are related to systems of steep to subvertical ore-bearing faults with no visible direct link to magmatic rocks. In the largest Madan district, the main ore-controlling system is controlled by large, up to 10-15 km long, NNW trending subvertical zones which include well-mineralized veins. The skarn-ore bodies are located in the three available marble horizons along the veins. The marbles are white, massive, fine- or medium-grained, composed almost entirely of calcite, with insignificant amounts of MgO, MnO and FeO. The replacement ores are included into the contours of the primary skarn bodies and follow their complex morphology.

The reduced exoskarns consist of radiate aggregates of the highly manganoan clinopyroxenes belonging to the hedenbergite-johannsenite series. The retrograde alteration of these skarns leads to the formation of manganoan silicates (pyroxenoids, amphiboles, manganilvaite, chamosites, andraditic garnets) and carbonate minerals (Vassileva and Bonev, 2003) in the process of lowering the temperature and pH of the hydrothermal solutions, which favors the precipitation of rich Pb-Zn ores.

3. Hydrothermal mineralization

Three main mineralization stages have been divided on the basis of temporal and spatial mineral relationships and microthermomtermy study on fluid inclusions (Vassileva et al., 2009a and references therein).

3.1 Skarn stage

The earliest stage is connected with the formation of distal infiltration exoskarns in the marble layers, composed by highly manganoan clinopyroxenes...
and later overprinted by manganese pyroxenoids. Temporally, these skarns are clearly pre-ore, without any primary sulphide formation. The skarns exhibit well expressed zonation defined by the different Mn/Fe ratio across lateral and vertical direction (Vassileva, 2004). In comparison to the other skarn types (Meinert et al., 2005), manganese skarns are formed at relatively lower temperatures. According to Vassileva et al. (2009a) the Th of fluid inclusions is 420-400°C.

3.2. Main ore stage
The sulphide mineralization is uniform in both the veins and the metasomatic ore bodies. Galena, sphalerite, pyrite andchalcopyrite are the main ore minerals, deposited in three main ore parageneses: quartz-pyreite, quartz-galena and quartz-sphalerite-galena. Subordinate ore minerals are arsenopyrite, tennantite-tetrahedrite, pyrrhotite and sulphosalts of Ag and Bi. The formation of sulphide paragenesis according to the fluid inclusion data is relatively high T: 350-300-280°C (Kolkovski et al., 1996; Kostova et al., 2004; Kotseva et al., 2008; Vassileva et al., 2009a). The major sulphide deposition in replacement bodies is utilized and coincides with the retrograde alteration after the manganese clinopyroxenoses (Vassileva and Bonev, 2003). The acid wallrock alteration in the silicate rocks is of quartz-sericite type.

3.3. Late post-ore stage
Deposition of late gangue minerals includes carbonates, quartz andchalcedony, barite, etc., with few scarce sulphides and sulphosalts within T interval 260-180°C (Bonev and Kouzmanov, 2002; Vassileva et al., 2009a). The stage is contemporaneous with intensive inter-ore tectonic movements, leading to complex morphology of the ore bodies.

Physical chemistry of the hydrothermal fluids was obtained by detailed fluid inclusion studies in ore minerals (Piperov et al., 1977; Bonev and Kouzmanov, 2002) and quartz, calcite, barite etc. (Kostova et al., 2004; Kotseva et al., 2008; Vassileva et al., 2009a). The ore-precipitating fluid is diluted, slightly acid (pH near 6.5) and reducing (Fe 2+ and Mn2+) to form horse-tail-like structures (Kolkovski et al., 1996). The vein infilling is composed by intergrowth of quartz-sulphide mineralizations. Sometimes, the ores reveal banded (layered) structure. In such cases the separate bands have different mineral composition, deposited one after another in the open space. The quantity of galena often prevails that of sphalerite, defining the Pb/Zn ratio of 1.2-2.0. Large base metal veins are representative for the deposits of Strashimir, Spoluka, Kroushev Dol, Pshenichishte, Shoumachevski Dol, Shadiitsa, Goliam Palas.

Stockwork zones are closely spatially connected to the veins, characteristic for the relatively deeper levels of the deposits, where the steep ore-bearing faults are marked by strong alteration of the gneisses. Large areas of intensive water/rock interaction around the fault zones determine the unclear contacts between the stockworks and the embedding rocks. The irregularly-shaped discordant ore mineralization is presented as disseminated thin sulphide veins and veinlets, impregnations and breccias. Their width is 1-2 to 10 m, rarely up to 20 m and up to 1-2 km in length. The Pb/Zn ratio of 0.8-1 is characteristic. Stockworks are typical for the deposits of Ribnitsa, Stratiev Kamuk, Pechinsko, Enyovche.

Rich replacement skarn-ore bodies are formed at the intersections of the ore-bearing faults with certain marble layers by the way of infiltration-driven metasomatism. The main minerals are sphalerite, galena, pyrite, johannsenite, rhodonite, carbonates and Pb isotope ratios of galena are $^{206}$Pb/$^{204}$Pb 18.68-18.75; $^{207}$Pb/$^{204}$Pb 15.66-15.70; $^{208}$Pb/$^{204}$Pb 38.86-39.05 (Marchev and Moritz 2006).

4. Morphogenetic types of ore bodies
The main morphogenetic types of ore bodies in the Madan Pb-Zn deposits can be subdivided into: simple ore veins, complex stockwork systems and replacement bodies. These types often co-exist in one deposit, showing close connection and transitions from one type to another (Fig. 1b, Vassileva et al., 2009b).

Veins comprise regularly-shaped, simple, single, steeply-dipping mineralized bodies, parts of the ore-bearing NNW fault zones. Their thickness varies between 20-40 cm and 1-2 m to several meters, sometimes tens of meters. The contacts with the embedding gneissic rocks are sharp, often clearly tectonic. Appophyses are common, generally joining the main vein in depth. The upper parts of the veins are often splitting to form horse-tail-like structures (Kolkovski et al., 1996). The vein infilling is composed by intergrowth of quartz-sulphide mineralizations. Sometimes, the ores reveal banded (layered) structure. In such cases the separate bands have different mineral composition, deposited one after another in the open space. The quantity of galena often prevails that of sphalerite, defining the Pb/Zn ratio of 1.2-2.0. Large base metal veins are representative for the deposits of Strashimir, Spoluka, Kroushev Dol, Pshenichishte, Shoumachevski Dol, Shadiitsa, Goliam Palas.

Stockwork zones are closely spatially connected to the veins, characteristic for the relatively deeper levels of the deposits, where the steep ore-bearing faults are marked by strong alteration of the gneisses. Large areas of intensive water/rock interaction around the fault zones determine the unclear contacts between the stockworks and the embedding rocks. The irregularly-shaped discordant ore mineralization is presented as disseminated thin sulphide veins and veinlets, impregnations and breccias. Their width is 1-2 to 10 m, rarely up to 20 m and up to 1-2 km in length. The Pb/Zn ratio of 0.8-1 is characteristic. Stockworks are typical for the deposits of Ribnitsa, Stratiev Kamuk, Pechinsko, Enyovche.
and quartz. The general width of the bodies is 30-60 m, sometimes even more. Their thickness depends on the host layer thickness reaching 4-5m, rarely 20-25 m.

Several morphological types skarn-ore bodies have been observed: single and multi-layered beds and ledges with a complex shape, column- and mushroom-like in cross section ore bodies within thick (15-20 m) or several thin marble horizons. These bodies are developed around large single or sub-parallel adjacent veins, or around non-mineralized faults (Vassileva et al., 2009b).

The variable morphology, size and mineralogical characteristics of the skarn-related ore bodies are controlled by a complex of lithological and structural factors: number, thickness, and position of the host marbles layers; number, size and position of the ore-controlling faults; shifts along the controlling faults, etc.

A lateral primary zoning is characteristic for the pyroxene skarn bodies with Mn/Fe ratio increasing towards the metasomatic front with the marbles. In distal parts often almost pure johannsenite occurs (Fig. 1c). Rhodonite, appearing in the outermost zone is always a later reaction product after johannsenite. More complex is the secondary zoning, due to retrograde alterations of skarns and sulphide overprinting with variable mineralogical, quantitative and textural relationships. Since the Mn-members of the hedenbergite-johannsenite series are considerably more stable in the sulphidation environment, the Fe-containing skarn pyroxenes in the proximal zones, along the veins, are nearly fully replaced by rich sulphide ores, whereas in the distal outermost zones the highly-Mn pyroxenes and rhodonite often remain unchanged. In some cases manganilvaite also occurs. In this way the generalized mineral zonation considering the textural diversity in the skarn-ore bodies is: ore vein - massive sulphide ore - banded ore - altered skarn with scarce sulphide impregnations – unaltered Mn pyroxene skarn - marble (Fig. 1c).

A general trend of vertical zoning in skarn mineralization may be outlined, with respect to the pyroxene/pyroxenoide relationships. At the upper mine levels (elevation 1000-900 m) rhodonite is intensively presented, in rare cases even prevailing over johannsenite. At mean levels (800-500 m) it is subordinate but still well preserved; while at deeper levels (< 400 m) it is sporadic or missing, sometimes being replaced by wollastonite. Bustamite, manganilvaite (Bonev et al., 2005) and andradite are locally developed, mostly in the proximal areas of some skarn bodies.

5. Textures of the mineral aggregates

The ore mineralization in most of the Madan deposits is practically uniform, and is represented by galena, sphalerite, pyrite and chalcopyrite. The studied textural characteristics are also applicable to the other ore districts in Central Rhodopes.

The remarkable variety of ore textures in the deposits of Madan district is indicative for the mode and local conditions of deposition: open space filling or replacement and like in all natural systems also the interweaving exists in some degree.

5.1. Crystallization in open space

Important and widespread ore textures are formed during the processes of crystallization in open spaces forming cutting veinlets, layered textures, druses, crustifications and breccias (Fig. 2a, b). The infill textures occur in the vein and stockwork mineralization, as well as in the replacement ore bodies, especially presented in the dissolution cavities formed by “hydrothermal karst” processes. The veins and veinlets with different mineral composition (quartz, sulphides and carbonates) are formed under similar processes with open space crystallization under structural tectonic control. Ore breccias are recognized as fragments of earlier sulphide mineralization contained within later carbonate cement.

“Hydrothermal karst”. The massive, coarse-grained metasomatic sulphide ores are characterized by high porosity. A system of open space cavities are often developed within the skarn bodies as a result of selective dissolution mainly of the carbonates formed by the retrograde metasomatic processes. It includes: uniform isometric pores of mm-size; concentric shell-like concave and convex vugs, result of replacement and dissolution of concentric-zoned primary pyroxene aggregates (Fig. 2c); radial and cone-like vugs of selective dissolution of carbonates, large flat cavities, roughly following the primary bedding of marbles; large isometric and irregular cavities reaching up to several m in size. Other textures connected with the cav- erns and vugs of the “hydrothermal karst” are gravitational, crustifications, bottom clays, druses and geodes. Performing a system of channelways for fluids the “hydrothermal karst” is favourable space for direct open space druse crystallization of sulphide minerals, carbonates and quartz.
Rare peculiar textures. In rare cases sphalerite and galena stalactites and tube-like textures can be observed, as well as ore ‘sands’ (loose grainy pyrite). Also, bilateral epitaxic (Fig. 2d) and autoepitaxic overgrowths and other mutual relationships are typical for the metasomatic textures.

Dissolution forms. Locally, selective natural dissolution of main sulphides and gangue minerals occurs (Atanassova 2009). Rounded corrosion surfaces resulting from the processes of hydrothermal dissolution are typical for single or twinned galena and sphalerite crystals. The predominantly oval faces and edges of large cubo-octahedral galena crystals (Fig. 2e), solid inclusions in paragenetic quartz crystals and post-dissolution deposition of hydrothermal minerals (calcite, quartz, chalcopyrite, tetrahedrite and others) are clear evidence that the final state of the sulphide surfaces is accomplished by natural dissolution process.

Sometimes “open cuts” from previous thin-platy calcite in quartz crystals are observed, characteristic for the crystallization in open space.

Fig. 2. Macro photographs of representative mineral textures from the Pb-Zn Madan deposits. a – galena-sphalerite druse; b – tetrahedrite crust over hydrothermally dissolved galena; c – peculiar concentric-zoned shell-like texture, resulting from “hydrothermal karst” after primary pyroxene aggregates; d – bilateral epitaxic growth of quartz over thin-platy calcite; e – dissolution forms of cubo-octahedral galena crystals; f – radiate skarn pyroxene-rhodonite aggregates; g – galena-sphalerite aggregate, inheriting the radial pyroxene texture; h – nests of manganelvaitic, galena and sphalerite, carbonates and quartz in skarns; i – massive rhythmic-banded texture composed by galena and sphalerite in carbonate matrix; j – porous sphalerite and pyrite aposkarn rhythmites; k – conical, coral-like late fibrous Fe-Mn dolomite; l – pyrite pseudomorphs after altered skarns, with interstitial quartz. Scale bars refer to 2 cm.
5.2. Metasomatic textures

The replacement skarn ore bodies are connected with the processes of metasomatic crystallization, where alteration and overprinting of primary textures are observed. The overprinting textures are typical for the process of ore deposition in the main sulphide stage in the Madan base metal deposits. The skarn clinopyroxenes in the marbles form radiate-columnar and spherulitic textures (Fig. 2f), which are complicated during the subsequent alteration and overprinting of the ore minerals. Most alteration minerals (manganoan fine-fibrous amphiboles; pyroxenoids) exhibit an incredible degree of textural inheritance from their host pyroxenes.

Pyroxenoids, sulphides and carbonates formed by metasomatic crystallization in anisotropic medium with inheritance of skarn textural features occur as radiate (Fig. 2g) and spherulite aggregates with concentric-zoned and conical textures. The main sulphides are observed as massive, porous and banded aggregates, as well as ore impregnations and nests (Fig. 2h). Typical for the replacement bodies are the rhythmic-banded, massive and vuggy textural varieties (Fig. 2i, j) resulting from periodic crystallization in quasi-isotropic medium (Bonev 2001). Peculiar conical, coral-like textures are formed in anisotropic medium with inheritance of skarn features (Fig. 2k). A rare case of metasomatic pyrite {100} euhedral crystals and tabular (100) galena is connected with crystallization in soft clay matrix. Also, elongated, skeletal and angular interstitial mineral formations are characteristic. Crystal and aggregates pseudomorphs after primary pyroxenes are often developed (e.g. rhenodite, sulphides, Fig. 2l, carbonates and quartz).

6. Mechanisms and factors of ore deposition

The ore deposition in the hydrothermal system is a result of several physicochemical mechanisms of neutralization of acid fluids, which transport the metals as highly-soluble chloride complexes. This neutralization is achieved specifically in the different morphogenetic types of ore bodies (Bonev et al., 2000). Boiling of solutions in the upper parts of the open space favoring the ore deposition. The metal transport is accomplished by chloride complexes stable in acid conditions and destructed by their neutralization after fluid/rock interaction.

7. Discussion and conclusions

The ore bodies in the Madan Pb-Zn deposits, Central Rhodopes, comprises two types of steeply dipping zones, simple ore veins, and mineralized stockwork zones, as well as sloping bed-like and irregular replacement bodies. Marble-hosted manganese skarns are a favorable environment for deposition of high-grade metasomatic ores accompanying large ore veins. Fault and fracture structures are decisive factor controlling both, the ways of movement of ascending fluids, and arising of open space favoring the ore deposition.

The variety of the mineral specimens is determined not by variety in the mineral composition, but by the different textures and morphology of the crystals and aggregates, due to combination of local physicochemical processes and crystallization mechanisms. The metasomatic ore textures often inherit the textural pattern of the skarns. Part of the ores is deposited by free drusy crystallization in open cavities of post-skarn “hydrothermal karst”. The highly variable external and internal morphology of crystals also reflects the crystallization conditions and their temporal changes. The complex
history of ores in the Madan deposits includes two main crystallization mechanisms: 1. metasomatic growth in solid medium realized by solid-state topotactic ion-exchange reactions or reconstructive dissolution/precipitation processes; and 2. crystallization in open space.

Acknowledgements
This study is partly supported by 2009-2010 World Federation of Scientists Scholarship; DO1-904 MON and the SCOPES project IZ73Z0-128089.

References
