

# **Mineral Composition and Origin of the Stratiform Polymetallic Ore Deposits in the Balkanides Compared with the Stratiform Lead-Zinc Deposits of the Alps**

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## **Abstract**

Data are given on the geotectonic position, enclosing rocks, dolomitization, mineral composition and succession of mineral formation in the stratiform polymetallic deposits (of the "Sedmochislenitsi" type) in the Balkanides. Specific features indicative of their epigenetic origin are pointed out.

## **Introduction**

Bed-like ore deposits in Bulgaria are found in the Balkanide region only in a small area of about  $30 \times 25$  km. They differ to a certain extent from the known bed-like lead-zinc deposits elsewhere in the world and in the Eastern Alps in particular, owing mainly to the considerable content of copper, arsenic, silver, and partially of cobalt, nickel and bismuth. Consequently they are defined as polymetallic. One of their typical features is that they are formed by two kinds of sulphide mineralizations — a lead-zinc and a lead-copper one (with silver, arsenic and bismuth). While the former mineralization is encountered in calcareous rocks of Middle Triassic age only, the lead-copper one is found almost uniformly and has identical specific features both in the same calcareous rocks, as well as in calcareous sandstones and phyllitoid rocks of Lower Triassic, Lower Jurassic and Paleozoic age. That is why these deposits were described separately as the "Sedmochislenitsi" type of deposits as early as 1961. They form a part of the Eastern Mediterranean Ore Province of Petrascheck (1963).

## **Geotectonic position of the ore deposits**

The western part of the Balkanide structural zone where the ore deposits under consideration are localized is formed by the Berkovitsa block-anticlinorium structure built up of a Paleozoic core and Mesozoic mantle. From north and south this structure is bound by large deep faults of an old age, known as the Stara Planina frontal strip and Sub-Balkan

fault respectively (E. Bončev, 1961). They are complex fault zones causing the formation of additional folded structures and horizontal dislocations (along the bed surfaces). The vertical displacement along the Stara planina frontal strip is about 4.000 m, and that along the Sub-Balkan fault over 1.500 m (E. Bončev, Tronkov).

The ore deposits under consideration are spatially distributed following these two structures (Fig. 1) forming distinct ore-bearing zones (Minčeva-Stefanova, 1962). The deposits in the region of the Stara planina frontal strip in particular are linked with a pair of conjugated fault systems (the Vratsa and the Sokolez zones), the middle part of the structure being raised horst-like. The ore deposits in the region of the Sub-Balkan fault are linked with a system of parallel fold upthrusts because of which several subzones are distinguished in the corresponding ore zone (the Izremez zone). There is a distinct direct proportional dependence between the degree of shifting along the faults and the intensity of mineralizations.

A typical feature of the geologic relations of the individual ore deposits is that they are localized in synclines in places where faults of the main system (in the direction of  $120^{\circ}$ — $90^{\circ}$ ) are cut by oblique or transverse faults of a lower order. In some places the ore deposits in the calcareous rocks are bound by Carboniferous aleurolithes forming a narrow band as a consequence of the fault displacements. The displaced part of the same calcareous rocks on the other side of this band does not contain any ore (Minčeva-Stefanova, 1961, 1965).

### Enclosing rocks

The ore deposits are embedded mainly in Anisian calcareous sediments, partially in the calcareous interbeds of the Rötian rocks or in Lower Triassic or Lower Jurassic sandstones, but only in those with a calcareous cement (for example, in the Izremez zone). Along the boundaries of such sediments with Paleozoic phyllites as well as with Carboniferous calcareous aleurolithes some inconsiderable ore deposits are also localized in the latter two kinds of rocks.

Anisian sediments are chiefly limestones and to a certain extent dolomites which are relatively more frequently found in the Lower Anisian levels (Tronkov, 1960). In general, the calcareous beds alternate with fine clay-marly intercalations with a thickness usually of fractions of a millimeter.

The dolomite areas in the calcareous rocks increase in direct proportion to the intensity of the mineralization.

In some deposits like Rakov dol (Fig. 1) where the stratigraphic profile is built up of Paleozoic phyllites and of the sediments of Lower Triassic and Lower Jurassic age (with a normal sedimentation absence of Middle Triassic sediments), the ore mineralizations spread over the entire stratigraphic profile. They are concentrated along the interformational surfaces and begin from pronounced faults.

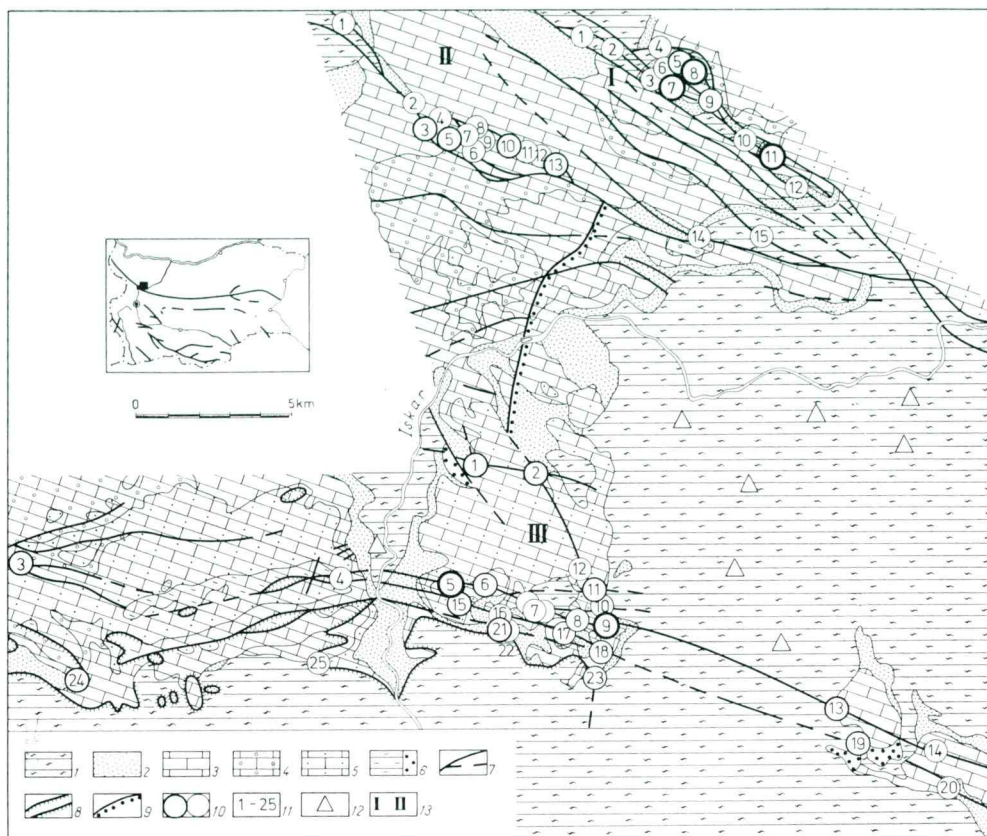


Fig. 1. Geologic map showing the region of ore deposits of the "Sedmochislenitsi" type according to Tronkov, D., Nikolaev, Gr., Stoinov, S., the author, et al.

Symbols: 1 Paleozoic rocks, 2 Lower Triassic sediments, 3 and 4 Middle and Upper Triassic sediments, 5 Jurassic sediments, 6 Cretaceous sediments and Quaternary overburden, 7 Main faults, 8 Line of thrusting, 9 Flexure, 10 Ore deposits, 11 Names of the ore deposits (I — 1 Pärvi rupi, 2 Vtori rupi, 3 Leštaco, 4 Široko lice, 5 Studenite korita, 6 Strašnata voda, 7 Sedmochislenitsi — old mine, 8 Sedmochislenitsi — new mine, 9 Gladna, 10 Borov kamäk, 11 Plakalnitsa, 12 Kalaminata; II — 1 Dolna bjala rečka, 2 Debel rät, 3 Mäžo, 4 Anatema, 5 Baličün preslap, 6 and 7 Ravno kamäk, 8 Gärloto, 9 Gladna, 10 Borov kamäk, 11 Plakalnitsa, 12 Kalaminata; II — 1 dolna bjala rečka, 15 Meča bara; III — 1 Veneza, 2 Lakatnik, 3 Brese, 4 Sassele, 5 "Hristo Botev", 6 Kollbišteto, 7 Košuški vräh, 8 Bakära, 9 Izremez — old mine, 10 Zapačiza, 11 Rakov dol, 12 Svärdelo, 13 Rogo, 14 Gradište, 15 Sabačevce, 16 Bresovo bärdo, 17 Metleva padina, 18 Trite kladenci, 19 Osenovlak, 20 Gabrovniza, 21 Stamenova korija, 22 Taninata, 23 Ravno ussoe, 24 "Otečestvo", 25 Perovo), 12 Barite deposits of Alpine age, 13 Ore-bearing zones: I — Vratsa-, II — Sokolez- and III — Izremez zone

### Form of the ore bodies

The ore bodies are predominantly bed-like ore lenses up to or about 50 m long, and varying from 1 to 8 m in thickness. Bed-like ore bodies up to 360 m and rarely up to 500 m long and of varying thickness, 2 m average, are also found. In the places of intersection of larger faults the

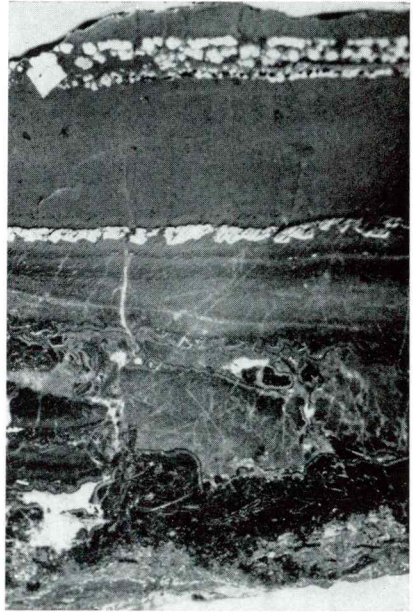


Fig. 2. Banded texture (case 2) of galena-sphalerite mineralization, transitional to brecciated texture. Some of the bands formed by subparallel blind veinlets of galena metacrysts. Scale 10:1

ore bodies are placed one above the other and form a kind of ore shoot. Impersistent ore veins of small thickness are found very rarely.

In the Anisian sediments especially the mineralizations are spread over the entire profile. It is typical, however, that the lead-zinc ore bodies are found usually in the upper levels of the Anisian complex; only at places of considerable fault displacements they occur in lower levels. Copper-lead ore bodies begin from the base of the Anisian complex and spread vertically almost throughout it, the corresponding mineral occurrences being superimposed on the lead-zinc ones.

#### Ore textures

The following ore textures are frequent: massive, brecciated, partially cockade, banded, veinlet and impregnation textures (Minčeva-Stefanova, 1965).

*The massive texture* is typical of the fine-grained metasomatic mineralization represented most often by sphalerite and dolomite metacrysts as well as of nest-like assemblages of massive sulphide aggregates amid the carbonate and sandstone, partially phyllitoid rocks.

*The brecciated texture* is formed as a result of the cementation of mineralized or ore-free rock fragments with sulphide and carbonate minerals on one hand and, on the other, as a consequence of metasomatic replacement of re-sedimentary breccia in which the fragments and the cement are replaced in various degrees because of the differences in the contents of calcareous, dolomitic and marly constituents (Minčeva-Stefanova, 1965).

The *banded textures* are of several varieties, formed in different ways:

1. As a result of the rhythmical deposition of the colloform aggregates of sulphide minerals: sphalerite (Schalenblende type) and melnikovite-pyrite as well as marcasite and bravoites in subparallel fractures, situated close together in the carbonate rocks.
2. By replacement of the carbonate substance in beds of banded textures (Fig. 2). In this case the ore texture inherits the texture of the enclosing rock as is the case described for one of the brecciated textures.
3. As a result of the displacement of the front of metasomatism. In this case the bands are undulating and are frequently found amid the massive sphalerite mineralization (Fig. 3).

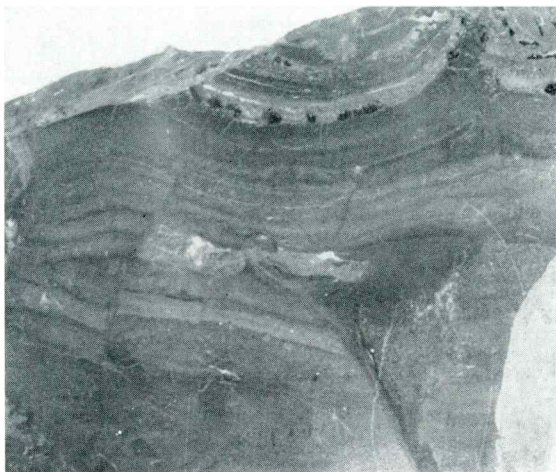


Fig. 3. Banded texture (case 3) in massive metasomatic sphalerite. Galena metacrysts developed in some of the bands or as veinlets cutting the bands. Scale 1:1

The *veinlet texture* is more frequently found in the primary (Fig. 4) and secondary dolomites and is typical of the mineralizations amid the sandstones and phyllites.

The *impregnation texture* is widespread among mineralizations in all kinds of enclosing rocks, except in phyllites.

### **Mineral composition, types of sulphide mineralizations and mineral parageneses**

The minerals of the ore deposits in the Balkanides under consideration can be divided into the following groups:

1. Main minerals — sphalerite, galena, pyrite, chalcopryite, dolomite, calcite;
2. Subordinate — tennantite, bornite, chalcocite, marcasite, quartz, barite;
3. Rare — arsenopyrite, wurtzite, carrollite, siegenite, bravoite ( $\text{Fe,Co,NiS}_2$ ), cobalt pyrite, nickel pyrite, nickel cathierite, stromeyerite, pearceite, unknown silver-arsenic mineral, acanthite, silver  $\alpha$ -amalgam, freieslebenite?, dyscrasite?, pyrargyrite, miargyrite, stephanite, polybasite,

tetrahedrite, wittichenite, cobalt smithsonite, ullmanite, cinnabar, celestite, gypsum, fluorite, dickite, kaolinite, and others.

Among the secondary minerals, the following are established: hydrozincite, smithsonite, cerussite, calcite, aragonite, azurite, malachite, cupro-zincite, rosasite, aurichalcite, barite, gypsum, anglesite, unidentified copper sulphates, mimetesite, tyrolite, zinc olivenite, strashimirite, adamite, cupro-adamites, conichalcite, native copper, chalcocite and others.

The iron content of sphalerite is low, about 1 per cent. This mineral in the form of fine-grained and colloform aggregates respectively, is analogous with the sphalerite from Bleiberg-Kreuth (Schroll, 1953) in its content of admixture elements. Arsenic, thallium, silver and antimony are established in galena, and arsenic, silver, thallium and selenium in pyrite. The presence of silver, mercury, germanium and bismuth is typical of the main and subordinate copper minerals. All these elements except for germanium so far have been found in their own minerals.

All above mentioned minerals always contain certain amounts of cobalt and nickel, the presence of which is due to the minerals of cobalt and nickel (from the bravoite and linneite groups) closely admixed in the ores.

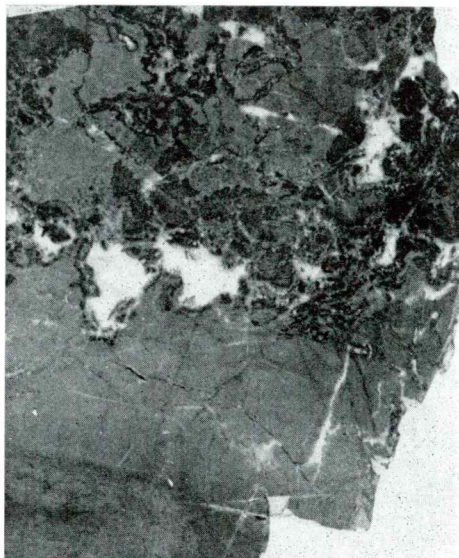


Fig. 4. Veinlet texture in part brecciated, of the sphalerite (schalenblende) in primary dolomite. Scale 1:1

The detailed studies of the mineral composition and of the age and paragenetic relationships of the individual minerals show that the mineralizations under consideration are formed by two kinds of sulphide minerals — lead-zinc (galena-sphalerite) and lead-copper (galena-tennantite-chalcopyrite). They are considered as products of two large and complicated ore-forming stages, the lead-copper one being later (Minčeva-Stefanova, 1961, 1962). Each of them is characterized by several

mineral parageneses whose successive deposition within each stage reflects a definite geochemical evolution of the corresponding mineral-forming solutions.

The lead-zinc mineralization consists of the following mineral parageneses (according to the order of deposition):

1. Paragenesis of pre-ore dolomitization (found only occasionally), represented by dolomite, pyrite and calcite.

2. Pyrite paragenesis — with pyrite, marcasite, bravoites and dolomite.

3. Dolomite-sphalerite paragenesis — with dolomite, sphalerite, arsenopyrite, pyrite and galena. It determines to a great extent the zinc mineralization in the deposits. It has a massive texture and is deposited metasomatically amid the pure limestones. At first dolomite metacrysts are formed, followed by the fine-grained sphalerite replacing in varying degrees the remains of the calcareous rocks between dolomite rhombohedra (Fig. 5). Galena metacrysts surrounded by pyrite grow on these two minerals.

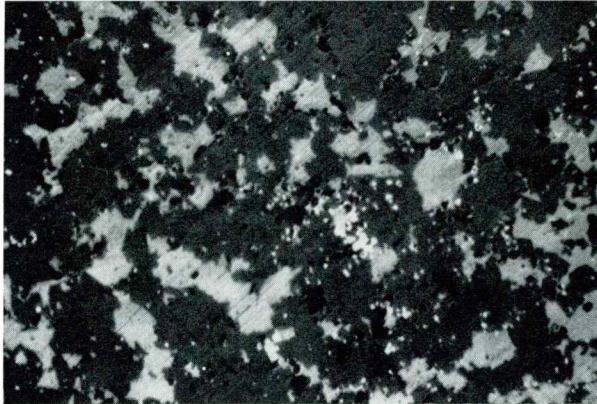


Fig. 5. Sphalerite-dolomite mineralization represented by dolomite rhombohedral crystals and fine-grained sphalerite metasomatically replacing the limestones. Along the borders of the two minerals there are pyrite-bravoite aggregates. Scale 63:1

4. Galena-sphalerite paragenesis with sphalerite (small-grained and Schalenblende type), galena, pyrite (metasomatic and melnikovite-pyrite type), marcasite, bravoite, wurtzite, arsenopyrite. The deposition of this paragenesis begins after intensive crushing and cracking of the enclosing sediments which determine also the high supersaturation of the solutions (Fig. 6).

5. Galena paragenesis consisting of galena, sphalerite, pyrite and dolomite. It is deposited in numerous veinlets cross-cutting and parallel to the beds (Fig. 2). There are clear indications that sphalerite, pyrite and dolomite are redeposited on account of the earlier parageneses.

6. Three carbonate, mainly dolomitic, parageneses with which the lead-zinc mineralization generally comes to an end. Barite, quartz, cleio-phane, galena, calcite, cobalt smithsonite, and sporadically fluorite participate in them together with the medium-grained dolomite. The minerals fill veinlets and numerous nests and can be considered as a manifestation of a post-ore dolomitization subsequent to the lead-zinc mineralization.

The mineralizations described are cross-cut (Fig. 7) or brecciated by the minerals of the next lead-copper mineralization. It is formed by the following mineral parageneses:

1. Bornite-chalcopyrite-galena in which considerable amounts of tennantite and subordinate amounts of carrollite, siegenite, pearceite, sphalerite, arsenopyrite, pyrite, dolomite and quartz also occur. The most considerable deposition of lead-copper ores is connected with this paragenesis. Though rarely, barite is deposited at its beginning.

2. Two silver-bearing parageneses deposited in numerous veinlets consisting jointly of bornite, chalcopyrite, galena, stromeyerite, silver-antimony sulfosalts\*, pearceite, acanthite, silver  $\alpha$ -amalgam\*, chalcocite, neodigenite, tetrahedrite, wittichenite\*, cinnabar\*, barite, celestite\*, calcite and others.

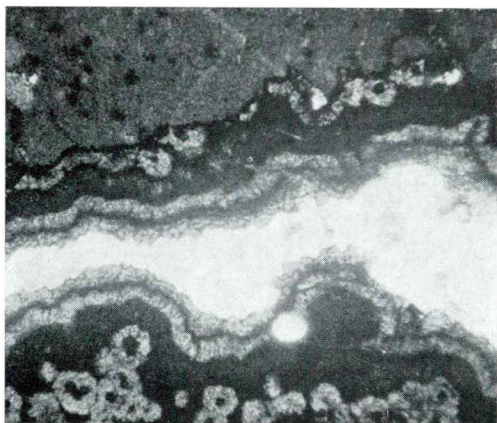


Fig. 6. Schalenblende deposited in crevices of primary dolomite. In the latter sphalerite impregnations. Scale 40:1

The amount of dolomite gradually decreases in the later parageneses. In the latest parageneses the relative amount of calcite increases.

The intergrowths of dolomite crystals with sulphide minerals as well as the specific features of ore textures clearly show that the sulphide deposition in the carbonate rocks is accompanied by a secondary dolomitization. As a result, the limestones in which the metasomatic processes have been most intensive, have changed into dolomites.

There is a distinct vertical zoning of both kinds of ore mineralizations. The following zones are developed from bottom to top in the lead-zinc mineralization: 1. pyrite-sphalerite; 2. sphalerite; 3. galena-sphalerite; and 4. predominantly galena zone.

\* These minerals are described by V. Atanassov (1964, 1971).



The lead-copper mineralization shows the following zoning (from bottom to top) regardless of whether it is deposited in calcareous or sandstone rocks: 1. bornite zone; 2. chalcopyrite-tennantite zone; 3. chalcopyrite-galena with tennantite; and 4. galena zone with small amounts of chalcopyrite and tennantite.



Fig. 7. Quartz-tennantite-chalcopyrite veinlet cutting the sphalerite-dolomite mineralization. Scale 40:1

#### Isotopic composition of lead

The isotopic composition of lead from the ore mineralization in the Balkanides under consideration varies greatly (Minčeva-Stefanova, Amov, 1966, 1969). Some of the values obtained correspond to the isotopic composition of lead from the young (Tertiary) mineral deposits in Bulgaria while others, the larger part, are intermediate compared to the values of isotopic composition of lead from the Tertiary and from the Young Paleozoic ore deposits in Bulgaria.

#### Discussion of the genesis of ore deposits

The geotectonic position of the stratiform deposits under consideration showing a definite structure control of their localization as well as the presence of two kinds of ore mineralizations with definite age relationships, indicate the epigenetic origin of the ore deposits. The form of ore bodies has been controlled by the bedding of the enclosing rocks and by the differences of their chemical composition as well as by the presence of faults and fractures subparallel to the beds. Those ore textures which imitate a syn-sedimentary sulphide deposition are actually sedimentary textures of the enclosing rocks inherited during metasomatic replacement. The fact that the lead-copper mineralization is identical in degree and composition both in calcareous rocks and in sandstones shows the controlling role of the carbonate sediments in the deposition of metals, and of zinc in particular, from very low temperature solutions connected with a favourable change of pH of the solutions after their infiltration into the carbonate rocks.

There are no outcrops of young igneous rocks nor manifestations of Triassic volcanism in the region of ore deposits. However, there are quartz-diorite dikes to the east of this region in its immediate vicinity which (judging by the rock outcrops) cut through Neocomian sediments also.

All above considerations make it feasible to connect the genesis of the ore deposits with a young (Eocene?) hydrothermal activity which has also caused an extraction of mobilized metals from the Paleozoic basement (Minčeva-Stefanova, 1966).

### **Comparison with the stratiform lead-zinc deposits in the Alps**

The features of the lead-zinc mineralization of the stratiform deposits in the Balkanides which have been pointed out are indicative of a definite resemblance to the lead-zinc mineralization representing the stratiform deposits in the Eastern Alps. The typical, although small, content of cobalt and nickel in the lead-zinc mineralization in the Balkanides is indicative of specific geochemical peculiarities of the corresponding metallogenic region while the practical absence of fluorite in them is a difference connected with the possibilities of enrichment of the ore-bearing solutions with fluorine before the mineral deposition because of which this difference cannot be of any particular genetic importance. On the basis of the ore textures and sequences of the mineral formation described by various authors for the stratiform lead-zinc deposits in the Alps (Schroll, 1953; Duhovnik, 1967 and others), regardless of the tendencies in the interpretation of the origin of the mineralizations, a general analogy can be found between these deposits and the lead-zinc mineralization in the Balkanide deposits. In both geotectonic regions the mineralizations considered have a poor metal and mineral composition.

The basic difference between these deposits is certainly the superimposed lead-copper mineralization in the Balkanide deposits which is now characterized by a varied metal and mineral composition. Its formation cannot be attributed to an ore-forming activity having taken place after a period which is very long in comparison with the period of formation of the lead-zinc mineralization. The place of deposition of the two kinds of sulphide mineralizations in calcareous rocks is one and the same everywhere because of which they should be considered as products of a single but complex ore-forming activity. The distinct connection of the later mineralization with rupture movements of a higher order is indicative of an inflow of solutions from deeper parts of a corresponding magma source or of the earth crust in general.

The very occurrence of this mineralization in the Balkanides might also be used as an indication that the rupture movements in this geostructural zone have been more prolonged in time and stronger as a factor.

The data on the occurrence of a "mixed" lead in the deposits under consideration both in the Alps (Schroll, 1965) and in the Balkanides (Minčeva-Stefanova, Amov, 1965, 1969) are indicative of an extraction of mobilized metals from older deposits and from older rocks in general. All specific features mentioned can be logically explained in

the light of the conceptions of formation of generated magma and generated ore-bearing solutions in the earth crust during the tectonic stresses (Kostov, 1968 and others, q. v.). Depending on the depth at which the solutions are formed, their composition will vary owing to the crystallochemical segregation of the elements in the earth crust (Kostov, 1968).

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### SUMMARY

The stratiform polymetallic ore deposits in the Balkanides occur in the Western Balkan Mountains along two large and complex faults delineating the Berkovitz block-anticlinorium from north and south. The individual ore deposits are located in synclinal folds where the main faults are cut by transverse or oblique faults. The intensity of mineralization is controlled by the amount of fault movements.

The enclosing rocks are calcareous sediments of Anisian and partially of Rötian age. Although infrequently, country rocks are also calcareous sandstones of Lower Triassic and Lower Jurassic ages as well as Paleozoic phyllite and calcareous siltstone in some places.

The calcareous rocks in the regions of ore deposits are mainly dolomites. The participation of limestones increases rapidly with the distance from the mineralized areas. Sulphide formation is accompanied by dolomite resulted from secondary dolomitization. The intensity of this process depends on the degree of mineralization and the amount of primary dolomites in the calcareous complex.

The ore bodies are most frequently elongated lenses, lying one above the other at some places. Ore veins occur only occasionally.

The ore deposits are of two kinds — a lead-zinc one and a lead-copper one overlying the former.

The lead-zinc deposit is of metasomatic origin. The fissures and cavities have been filled later. The ore is represented by fine grained light-coloured sphalerite, schalenblende, pyrite, marcasite, galena, small amounts of arsenopyrite, bravoite  $[(\text{Fe}, \text{Co}, \text{Ni})\text{S}_2]$ , and sporadic Ag-Sb-sulfosalts. The lead-copper deposit is represented by one main bornite-tennantite-chalcopyrite-galena paragenesis with pearceite. The latest deposits are veinlets of several sulphide parageneses of silver, bismuth and mercury minerals and others. Cobalt and nickel also occur in the form of bravoite (in the Pb-Zn deposit) and of minerals of the linneite group or as sulphoarsenides (in the Pb-Cu deposit).

Dolomite and, to a lesser extent, barite, quartz and calcite are typical gangue minerals. Celestite and gypsum occur sporadically. Barite forms considerable masses in some deposits, but only in the initial stages of the Pb-Cu mineralization.

According to its mineral composition and its complex manner and features of deposition, the lead-zinc mineralization of the stratiform poly-metallic deposits in the Balkanides is analogous to that of the stratiform ore deposits in the Alps (despite the absence of celestite and fluorite). The main difference of the ore deposits under consideration is the presence of lead-copper ore in the Balkanides marked by a complicated geochemical evolution.

A significant genetic peculiarity of the ore deposits in the Balkanides is the occurrence of the lead-zinc minerals in calcareous rocks only, while the lead-copper ones are found in all kinds of country rocks.

## DISCUSSION

*Duhovnik:* Haben Sie die Schwefelisotopenanalysen durchgeführt?

*Minčeva:* Leider noch nicht, wir werden es aber versuchen. Herr R e n t z s c h aus Freiberg hat sich auch mit diesen Problemen beschäftigt, und zwar am Beispiel unserer Lagerstätten. Er hat festgestellt, daß die Schwefelisotopenzusammensetzung variiert und daß das leichtere Schwefelisotop in größerer Menge vorkommt. Ich kann die Tatsache noch nicht interpretieren, er selbst hat aber einen Vergleich mit den Vererzungen vom Freiburger Typ gemacht.

*Duhovnik:* Ich möchte noch wissen, ob irgendein Unterschied im Schwefelisotopengehalt zwischen Kupferkies und Bleiglanz besteht.

*Minčeva:* Herr R e n t z s c h hat leider die Kupferminerale nicht untersucht, nur Pyrit, Galenit und Sphalerit. Wir hoffen, diese Analysen in einigen Jahren selbst ausführen zu können.

*Maucher:* Keine Frage, aber eine kleine Antwort. In Lagerstätten einheitlicher Entstehung, wo die einzelnen Mineralien sicher einem Bildungsgang entsprechen, ist die Schwefelisotopenzusammensetzung in Bleiglanz, Zinkblende, Kupferkies und Pyrit, die gleichartig und gleichalterig entstanden sind, nicht dieselbe. Ein Unterschied dazwischen würde nichts genetisches besagen.

*Duhovnik:* Das weiß ich. Aber wie groß sind diese Unterschiede? Denn wir haben auch Schwefelisotope bei uns untersucht und haben gefunden, daß auch bei demselben Mineral in derselben Lagerstätte kleine Unterschiede in der Schwefelisotopenzusammensetzung vorkommen, die von der Tiefe der Mineralisation abhängig sind.