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AN UNCOMMON METAMORPHIC Cr-Ba-Fe-Cu DEPOSIT FROM THE BUSOVACA DISTRICT, CENTRAL BOSNIA

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ABSTRACT

The metamorphic deposit occurs at the contact with a metabasite, conformable with the surrounding Upper Silurian-Lower Devonian metasediments. The ore deposit is stratified. The millimeter-scale mineral banding and the grain size contrasts between layers are well preserved. The main minerals are siderite, albite, quartz, magnetite, pyrite, significant constituents are hyalophane, Mn-ankerite and chromian-spinel. The authors relate the Cr-spinel to the detrital chromite, and other metals by convecting hydrothermal fluids. The regional metamorphism caused alkali-metasomatism, recrystallization and formation of porphyroblasts. In the Paleocene/Eocene time tension-fractures were filled by big crystals of quartz and hyalophane cutting the metamorphic deposit.

INTRODUCTION

The Mid-Bosnian Ore Mountains belong to the Dinaric system of Yugoslavia. They comprise a triangular region with the surface area of 3.000 sq. km. The length amounts to cca 90 km, the average width to 35 km. The Busovača region is situated on the north-eastern part of this triangle (Fig. 1).

The oldest and the most widespread rocks in Central Bosnia are the Silurian metamorphites whose affiliation was determined on the basis of the superposition in relation to the paleontologically well documented overlying Devonian carbonate complex (ŽIVANOVIĆ, 1975, 1979). The deepest horizons of the schists belong eventually to the Ordovician. The sedimentation in Silurian time was relatively calm, most often there were sediments of deeper sea. At the end of the Silurian and the beginning of the Lower Devonian time a shallowing of the sea began as did the formation of isolated limestones lenses.

The existence of Gedinian and Siegenian in Central Bosnia was determined for the first time in the platy limestones, NE of Gornji Vakuf (ŽIVANOVIĆ, 1975) on the basis of abundant faune of Corals, Bryozoa and Stromatoporida, and of the lower part of the Emsian (earlier conceived by KATZER, 1925 as Carboniferous and Lower Permian).

In the Emsian and during the Middle Devonian time a shallowing of the sea took place and deposition of the reef facies began. The Upper Devonian fossils were found locally.

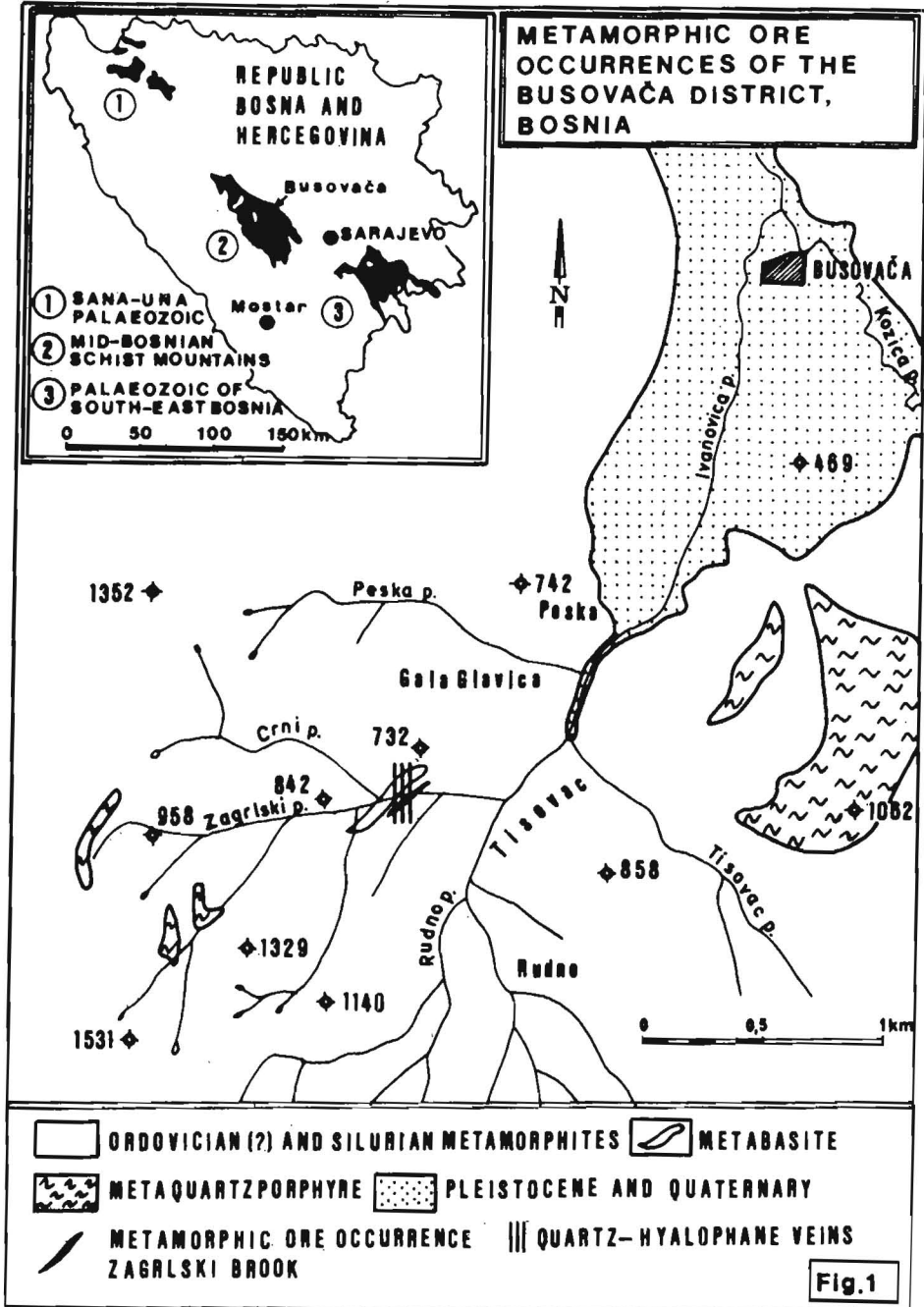
The Lower Carboniferous is developed only in some parts of Central Bosnia which were covered by sea. At that time, uplifting began in connection with orogeny and related magmatic activity. Dry land phase existed between the Middle Carboniferous and the Upper Permian time.

The Upper Permian dry land-lagoonal deposits lie unconformably on the older Palaeozoic rocks.

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The succession continued with the Lower and Middle Triassic deposits.

The oldest known magmatic cycle is probably the Upper Silurian-Lower Devonian basic and intermediary magmatic phase. Actinolite-epidote schists, albite-chlorite-epidote schists, tremolite schists, amphibolite schists are metamorphic products of that period.

As the following phase, effusions and subvolcanic intrusions of quartz-porphyry (less keratophyre) lavas took place mostly in the period between the Middle Carboniferous and the Upper Permian times. These rocks are leucocratic acid effusive rocks of the granite group of aplite-granite magma (JURKOVIĆ and MAJER, 1954). These rocks are seldom massive, but are strongly schistose and metamorphosed under various degrees of metamorphism. The direction of schistosity is almost always in conformity with the direction of schistosity of the surrounding sedimentary rocks. Under the higher grades of metamorphism the igneous character of these rocks disappears very often completely, and today we have to consider them as metamorphic sericite-chlorite-quartz schists.

Analysis of foliation, cleavage, lineation and fractures indicate that this Palaeozoic complex has been folded in at least two phases. The basic structural forms in the oldest members of Palaeozoic were formed in the older phase of folding, followed by magmatic activity. Further affection of the Palaeozoic schists and the dynamometamorphism of magmatites took place in the younger phase.

THE GEOLOGY OF THE BUSOVAČA REGION ITSELF (Fig. 1)

According to ŽIVANOVIĆ, SOFILJ, and MILOJEVIĆ (1967) the metamorphic complex in the Busovača region is built chiefly of chlorite-muscovite-quartz schists as the most widespread ones, then of quartz sericite schists, locally quartz-graphite schists and limited intercalations (lenses) of subarcose and subgraywacke metasandstones, with limited occurrences of amphibole-tremolite schists and tremolite-sericite schists. The clastic series is interpreted as Silurian, and in the higher horizons as Lower and Middle Devonian.

Ribboned (striped) structures of the schists occur dominantly in the lower part of the geological column whereas in the upper part of the column, the structure disappears and foliation dominates. A pelitic series with a little psammitic components, and very rare occurrences of basites, later intruded by rhyolites, is the protolith of the whole series.

This region is characterized by the divergent folding, with the fold axis NE-SW perpendicularly to the common NW-SE axis of the Dinaric folding. The stratification as structural element is almost always transposed in foliation. The metamorphism destroyed the primary structure and stratification.

The Variscan tectonics shaped the Silurian, Devonian and the Lower Carboniferous strata as well as some rhyolitic masses which belong to the earliest phases of rhyolitic magmatic activity. The main orogenic phase is immediately after the Lower Carboniferous: an intermediate variscan tension phase caused emplacement of rhyolites in the SW-NE directions.

MAJER, LUGOVIĆ, and TRUBELJA (1991) have proved recently that the metamorphics in the region of Busovača were formed chiefly under low grade metamorphism at 350-450°C and intermediate pressure of 3 to 5 kbars, locally under 5 kbars. Paragenesis of the para- and orthometamorphics is simple and monotonous: quartz, white mica, rarely phengite-muscovite with less than 10 mole % of celadonite and paragonite components, then iron-bearing ripidolite chlorite, poor with Mg, with transition to pseudothuringite, locally in ripidolite-pinochlorite, chloritoid with high content of Al and Fe, low content of Mn (3.3 to 7.0 mole %), and Mg (less than 8 mole %, exceptionally with 23 to 26 mole %), actinolite and baroisite with elevated ribeckite (crossite) component.

ORE OCCURRENCE

KATZER (1910) reported the first impregnations of magnetite and pyrite north of the village Gola Glavica, on the southern bank of the Zagradje (Zagrl-

ski, or Crni) brook and on the location at Peska. DIVLJAN and SIMIĆ (1954) and DIVLJAN (1954) discovered and described some almost vertical quartz-hyalophane veins cutting the schists, impregnated with calcite, siderite, magnetite, pyrite and chalcopyrite in the valley of the Crni (Zagrlski) brook. JURKOVIĆ (1956) and SIMIĆ (1956) investigated microscopically the magnetite-chalcopyrite occurrence in the Zagrlski (Crni) brook and defined it as metamorphosed (Jurković) and high hydrothermal (Simić). JURKOVIĆ (1956, 1957) defined the quartz-hyalophane veins as "Alpine type" veins.

Particular minerals or the specific characteristics of the veins have been described: as hyalophane by BARIĆ (1955, 1961, 1969, 1972), ARSENIJEVIĆ (1960), ROY (1965), GAY and ROY (1968), ZEBEC and ZAGORŠČAK (1985), ZEBEC (1987/88): as anhydrite by BARIĆ (1971/72), as quartz by BARIĆ (1969) and VARIČAK (1971, 1976): as anatase by ZEBEC (1980/81): as apatite by ZEBEC and ZAGORŠČAK (1983): as albite by ZEBEC and BERMANEC (1985), and as rutile and hematite by BERMANEC and ZEBEC (1987).

The mineralization in the Zagrlski brook is adjacent to a bigger, elongated, outcrop of metabasite consisting of muscovite, quartz, chlorite and green amphibole, appearing to be conformable with the surrounding schists. According to TRUBELJA and SIJARIĆ (1970), a narrow zone of at most one meter thick, characterized by alternation of two types of schists, separates the metabasite from the metapelites. A dark colored biotite-chlorite-ankerite schist with accessory albite, muscovite, quartz, actinolite, epidote, magnetite, pyrite alternates with the brighter colored albite-chlorite schist with variable subordinate amounts of biotite, epidote, pyrite, quartz and magnetite. Locally, the accessory minerals, especially magnetite and pyrite accumulate forming zones enriched with opaque minerals. The structure of these two schists is heteroblastic-porphyroblastic.

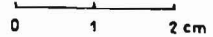
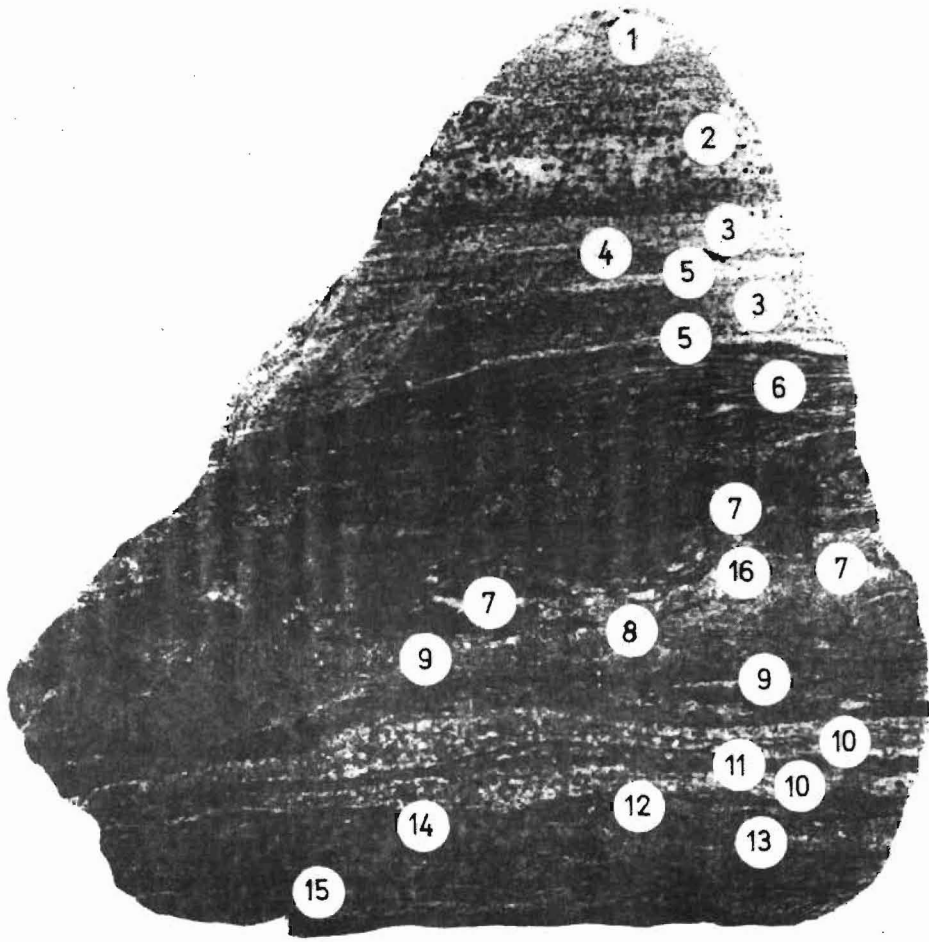
We present the results of the investigation of the above mentioned zone on both sides of the Zagrlski brook where this zone was thinner, but very well opened, containing a section, 15 to 30 cm thick, built up of fresh and compact banded ore.

The banded mineralization is essentially a rhythmical sequence consisting of a set of parallel or subparallel bands (0,5-5 cm thick) having alternating layers that differ in color, texture, structure and in mineral composition. The mineralization consists primarily of alternating layers of variable amounts of ore and gangue minerals. The composition of individual layers ranges from about one mineral to approximately equal amounts of several minerals. The grain-size of individual layers varies from ten micrometers to 1-3 mm big of porphyroblasts and xenoblasts of pyrite and magnetite. Dark colored bands consisting predominantly of opaque minerals alternate with brighter ones of gangue minerals. Grain-size contrasts between layers are preserved and very finely formed laminae show no sign of homogenization. Individual beds thicken and thin, the middle section of the vertical profile shows soft sediment deformation-microfolding, microfolds, pressure-shadows, cross-beddings).

The vertical distribution of the individual ore and gangue minerals along the profile of the ore deposit, perpendicular on the bedding planes is presented in Fig. 2. It is the result of a detailed investigation of the sixteen samples submitted to the X-ray diffraction powder, microscopic analyses of the thin and polished sections as well different methods of chemical analyses.

The established paragenesis is arranged in decreasing amounts as follows: siderite, quartz, albite, magnetite, pyrite, Mn-ankerite, hyalophane, magnetite with cores of chromian-spinel rimmed by ferritchromit, chalcopyrite, muscovite, chromian chlorite, biotite, enargite, siegenite, millerite, bornite, idaite (?), martite, zircon, tourmaline, apatite, ilmenite, leucoxene, silver, gold.

In the upper part of the vertical profile (samples 1 to 5), the main gangue minerals are quartz, siderite and albite in relatively equal abundance



Zagrlski brook, Busovača, Bosnia

Vertical section through the metamorphic deposit showing the distribution of ore and gangue minerals. **Symbols:** q=quartz; si=siderite, ab=albite; hy=hyalophane, ank=ankerite; mu=muscovite; mt=magnetite; py=pyrite; cp=chalcopyrite; sp=magnetite with Cr-spinel cores; en=enargite. **Encircled numbers** represent the analyzed ore samples (X-ray powder diffraction; microscopical analyses in polarized light; chemical analyses)

No 1 = q ab si mt (py) (mu) No 2 = si ab mt (py) (q) No 3 = ab si q No 4 = ab si q mt (py) (hy) No 5 = q ab si mt No 6 = si mt q sp py (ab) (ank) No 7 = si ank mt q (ab) (py) (hy) No 8 = ank py si q mt sp (ab) No 9 = si ank mt (ab) (q) (py) No 10 = ab si hy py (mt) No 11 = si mt hy sp ab No 12 = si mt sp (py) (ab) (ank) No 13 = ank si py mt sp (cp) (en) (ab) (q) No 14 = si py q mt (sp) (ab) (cp) (en) (ank) No 15 = si mt q (py) (sp) (ab) No 16 = ank (q) (si) (mt). In the parentheses are accessories.

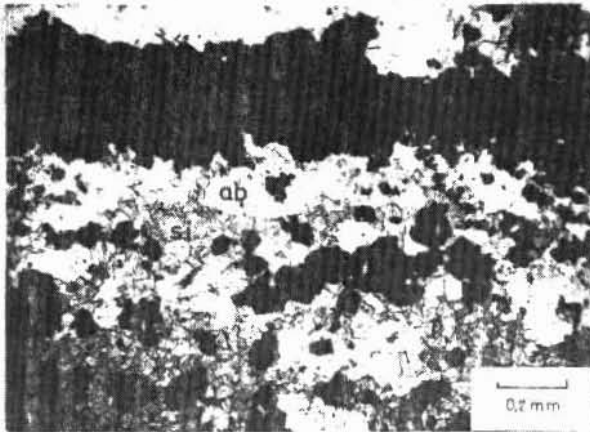
excepting sample 2. Magnetite is the main ore mineral, pyrite is subordinate, chalcopyrite is only an accessory mineral. Magnetite without chromian-spinel cores is mainly coarse-grained (0,5-3 mm). In the middle part of the profile, (samples 6 to 9) siderite and quartz are the main gangue minerals, fine-grained magnetite with many chromian-spinel cores and pyrite are the main ore minerals. Chalcopyrite is found more often than in the upper part of the profile. This section is characterized by numerous lense-shaped or irregular nests of the manganian ankerite and in places with hyalophane. In the lower part of the profile (samples 10 to 15), very thin layers of coarse-grained, often idioblastic pyrite and magnetite with numerous chromian-spinel cores dominate. The siderite is dominant gangue mineral, quartz and albite are subordinate. In sample 13, next to siderite, Mn-ankerite is the essential mineral component, and in sample 10, albite. In the 0.5-1 cm broad bands of the samples 10 and 11, hyalophane is abundantly present. Sample 16 represents almost pure manganian ankerite.

THE MAIN CHARACTERISTICS OF THE MINERALS (Table 1)

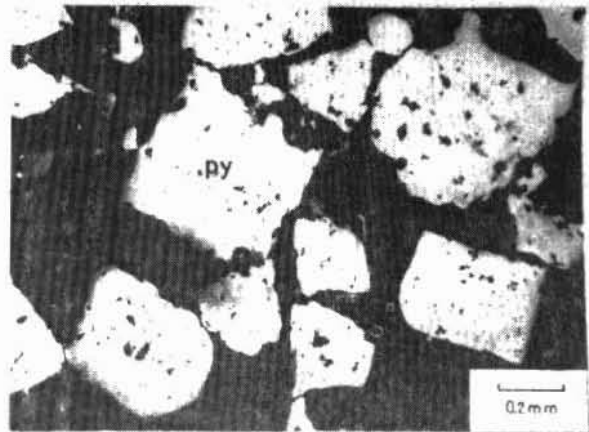
Siderite occurs predominantly in fine aggregates of anhedral (rarely euhedral) crystals from 0.05 to 0.3 mm in diameter. Siderite forms bands with allotriomorphic structure or it fills the interstices of other minerals, especially those of feldspars. The parameters of the unit cell of the siderite are: $a=4.680(2)$ Å and $c=15.314(5)$ Å. A part of the iron is replaced by Mg and Mn. **Quartz** is grained, the grains measure from 0.03 to 0.3 mm and are colorless in thin sections. The majority of crystals are pure, without inclusions, and irregular or wavy extinction due to strain is very rare. Quartz occurs as thin layers or elongated lenses of anhedral grains or dispersed in the layers built up of siderite or albite. **Albite** is the main feldspar mineral, excepting in the samples 10 and 11 where hyalophane is equal or the more dominant mineral. It occurs in plates, or lath-shaped sections, but also as porphyroblasts, measuring from 0.1 to 1 mm. Albite crystals, especially porphyroblasts contain numerous inclusions of other minerals. Twinning is polysynthetic according to Albite law and also according to Carlsbad twin law either alone or combined with albite twinning. In the conoscope light, the interference figure is biaxial positive with a large axial angle: dispersion is weak, red lesser than violet.

Magnetite is the main ore mineral. The magnetite porphyroblasts without chromian-spinel cores from the upper part of the profile (sample 2) was cleaned under a magnifying glass and submitted to the analyses with ICP and AAS methods. From five analyses we obtained the following results in %: 3.2-9.5 Si; 0.28-0.50 Mg; 0.37-0.62 Al; 0.08-0.24 Ca; 0.12-0.32 Mn, and in ppm 231-261 Sr; 394-599 Ba; 447- 693 Ti; 326- 735 Ni; 21-38 Co, 213-578 Cr; 57-118 Cu; 204-354 V, and 118-125 Zn. Partial quantitative analysis of the magnetite sample, rich in chromian-spinel cores taken from the numerous extremely narrow layers of dominantly fine-grained magnetite associated more or less with coarse-grained pyrite and numerous small masses of chalcopyrite occurring in the middle and lower part of the profile gave the following results: 1.42 % Cr_2O_3 ; 0.157 % Mg; 206 ppm Mn; 621 and 761 ppm Ni; 283 ppm Zn; and 62 ppm Co. The average magnetite sample from the whole profile, analysed by Jurković (BARIĆ, 1957) gave 0.2 and 0.3 % Cr_2O_3 . **Pyrite** is, next to magnetite, the second ore mineral in the deposit, much more present than the chalcopyrite. It occurs mainly as individual hexadrons from tenth micrometers to 3 mm in diameter or in small aggregates arranged in thinner or thicker layers. The bigger crystals are cataclased and many contain numerous various inclusions. The isotopic composition of the sulfur in pyrite, show the following values: sample A from the middle part of the profile $\delta^{34}S = +0.29$ ‰, and sample B from the lower part of the profile $\delta^{34}S = +0.43$ ‰. Analyses made by AAS method gave: sample A 468 ppm Co and 1357 ppm Ni; sample B 456 ppm Co, 1687 ppm Ni, and 882 ppm Cu.

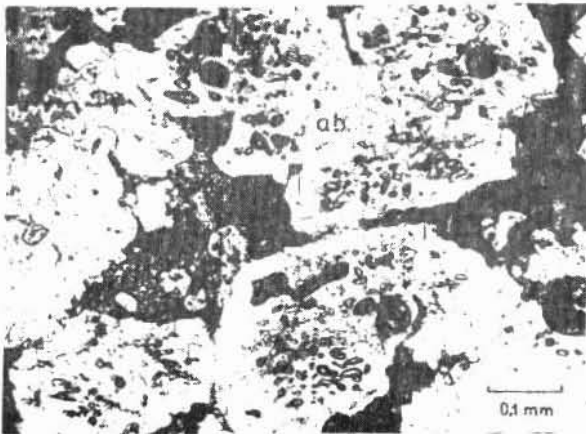
Manganian ankerite is coarser grained, between 0.3 and 1 mm, usual subhedral, having a tendency to euhedral crystals. Transparent, colorless or



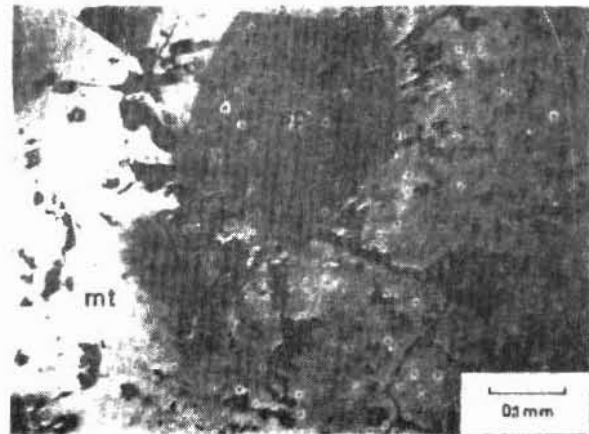
Phot. 1. Thin section. Magnetite (black), albite (ab), and siderite (si)



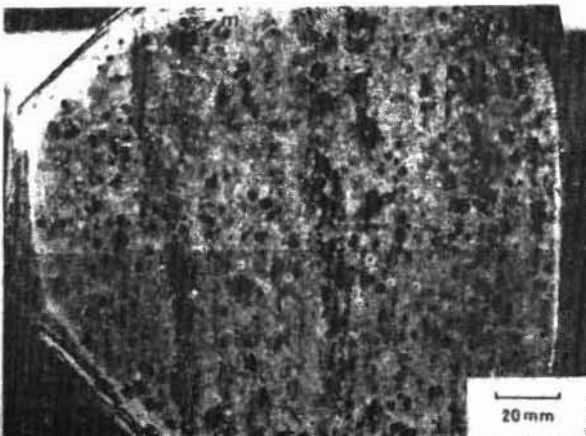
Phot. 2. Polished section. Porphyroblasts of pyrite (py) with inclusions of gangue minerals



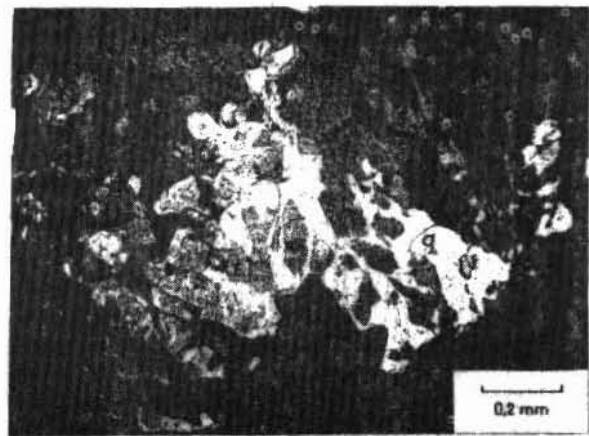
Phot. 3. Thin section. Porphyroblasts of albite (ab) with numerous inclusions



Phot. 4. Polished section. Porphyroblast of magnetite (mt) with core of chromian spinel (sp)



Phot. 5. Polished section. Individual grains and small aggregates of magnetite (black) in gangue (albite, quartz, siderite)



Phot. 6. Thin section. Poikiloblastic intergrowths of quartz (q) and siderite (si)

Ψηφιακή Βιβλιοθήκη Θεσσαλονίκης - Τμήμα Γεωλογίας, Α.Π.Θ.

white. It builds up lense-shaped regular or irregular nests in the middle and lower parts of the ore profile, the part where the siderite is the main gangue mineral. It occurs in the "pressure shadows" of the microfolds and microflexures, especially in the middle part of the profile. X-ray diffraction powder pattern of the Mn-ankerite is presented in Fig. 3. The parameters of the unit cell are: $a = 4.826(2) \text{ \AA}$ and $c = 16.116 \text{ \AA}$. The carefully cleaned material from sample 16 was submitted to chemical analysis giving the following results in mole %: 47.59 CaCO_3 ; 22.59 MgCO_3 ; 17.10 FeCO_3 , and 12.72 MnCO_3 . BaCO_3 was absent. The obtained results confirm the manganese ankerite. Structure is dolomitic.

Hyalophane has been proved by X-ray diffraction powder in the samples 4 and 7 as an accessory mineral, and as a significant constituent in the samples 10 and 11. The analysis of sample 10 gave: 2.78 % BaO ; 1.00 % K_2O and 2.21 % Na_2O . The results correspond to the mineral composition of the sample: albite as the main mineral, siderite and hyalophane as significant constituents, whereas pyrite and magnetite are subordinate components. The structure of hyalophane is porphyroblastic or xenoblastic, in places in poikiloblastic intergrowth with individual or twinned albite porphyroblasts. In the thin sections of the samples 10 and 11, clean and transparent bigger hyalophane crystals and sieve textured (caused by numerous inclusions) porphyroblasts of albite form a mutual interpenetrating growth showing uniform optical orientation over the whole areas. In one case, a Carlsbad twin of albite is overgrown by regularly oriented hyalophane crystal and their axis $[001]$ and faces $\{010\}$ are parallel. Both indices of refraction of the albite are lower than N_y of hyalophane. The higher index of refraction of the albite in the section perpendicular to the second pinacoid is lower than N_y of hyalophane. Using convergent light with the Bertrand lense inserted, hyalophane is optical negative (determination by prof. M. Vragović). Crystals of albite are older than hyalophane which outgrows and inserts it.

Chromian spinel rimmed in places by **ferritchromit** occurs in the cores of considerable numbers of the bigger crystals of the magnetite in the middle and lower parts of the ore profile. The boundaries between Cr-spinel and ferritchromit or directly with magnetite are sharp or irregular (corroded), the sections of the Cr-spinel are triangular, octahedral or in very different irregular forms. Ferritchromit is absent or it occurs in the form of one or two extremely narrow rims (tenth micrometers and less). The reflectivity of Cr-spinel is much lower than the outer magnetite zone, the difference is especially greater in cedar oil. The reflectivity is dependent on the degree of metamorphism, and therefore the values vary from one grain to another. Some Cr-spinel cores exhibit brownish or red-brownish internal reflections, particularly in oil. The reflectivity of the ferritchromit is lighter than Cr-spinel, but distinctly darker than magnetite. Between two ferritchromit zones, the inner zone is slightly darker than the outer one. It is a fact that the Cr-spinel has been subjected to different grades of metamorphism from one grain to another which resulted in the different chemical compositions and slightly different parameters of the unit cell of magnetite. Four X-ray diffraction powder analyses from the four different samples of magnetite (samples 2, 6, 7 and 15) gave the values of the parameters of the unit cell of the magnetite without or with Cr-spinel cores varying only from $a = 8.393(2) \text{ \AA}$ to $8.396(2) \text{ \AA}$.

Chalcopyrite is rather often present in the deposit, but in relatively small quantities. The dimensions of the very fine-grained aggregates of the chalcopyrite vary between 30 and 70 micrometers, rarely more. It occurs either in irregular aggregates within gangue minerals or more often in oval and rounded inclusions in the porphyroblasts of magnetite and pyrite. Tiny aggregates of some **enargite** grains are grown together with chalcopyrite or occur alone. Very rarely there are some **bornite** aggregates with fine spindles of chalcopyrite and lamellar **idaite** (?). Certain porphyroblasts of the pyrite contain **siegenite** which is partially decomposed in lamellar **millerite**. Only a few isolated grains of **silver** or of **gold** in the ore indicate the presence of

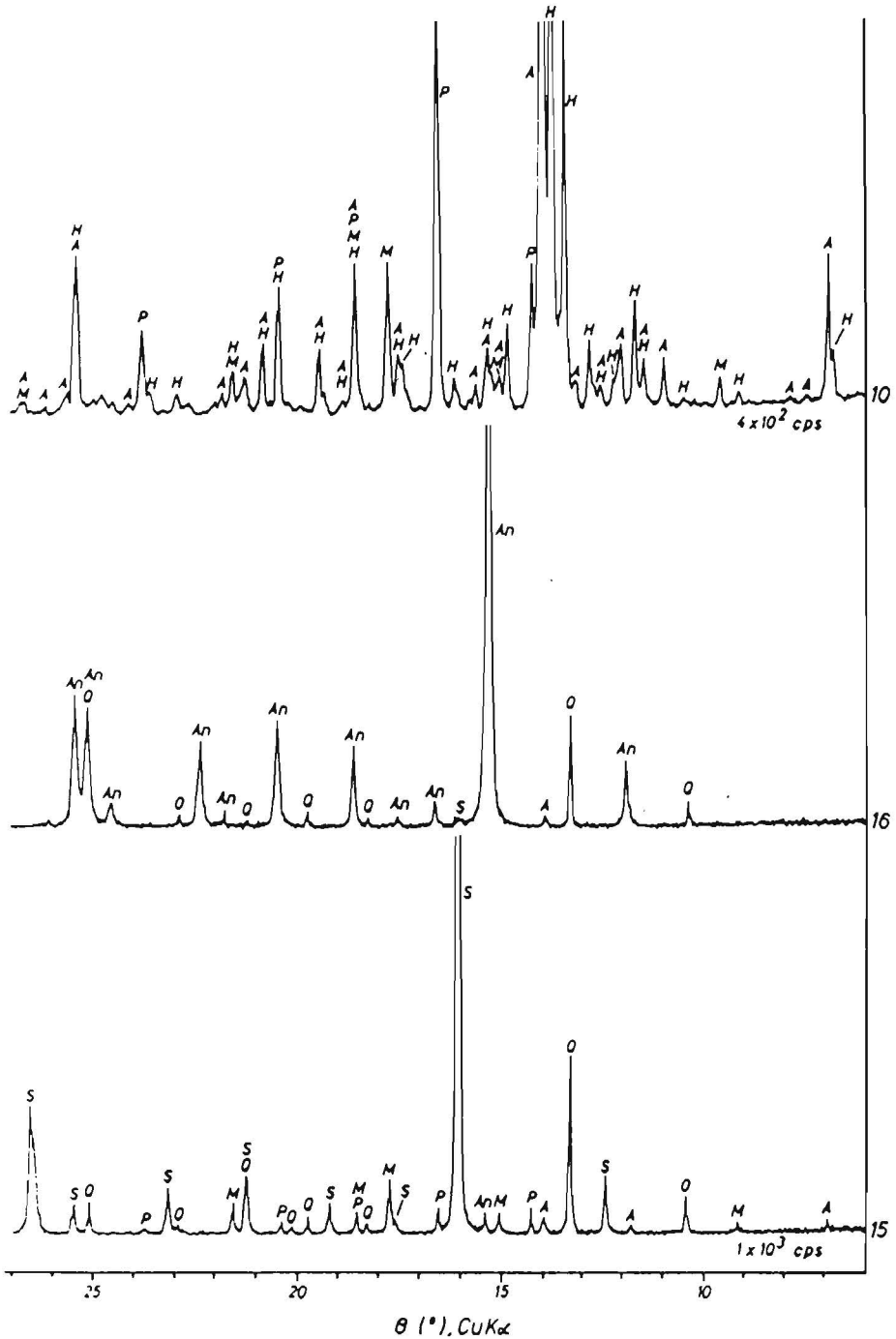


Fig. 3. X-ray powder diffraction patterns of samples from the ore deposit Busovača. 10, 16 and 15 are the numbers of samples. H-hyalophane, A-albite, M-magnetite, P-pyrite, Q-quartz, S-siderite, An-ankerite.

these two elements in the lattice of the pyrite or chalcopyrite. **Martite** replaces only rare grains of the magnetite along the cleavage traces and locally along microcracks.

Muscovite in the form of very fine plates and foliae, greenish in color, similar to the phengite, exhibits very weak pleochroism, parallel extinction and cleavage. Together with **biotite** and **chromian chlorite** (identified by spectrographic analysis by SIMIĆ, 1956) muscovite is concentrated along the layers and lense-shaped aggregate of the magnetite, in places wrapping around magnetite. The plates of the foliated minerals are often bent or entangled.

Ilmenite, **rutile**, **leucoxene** occur as inclusions in the magnetite porphyroblasts. Fine crystals of **tourmaline** are visible within biotite plates, and together with minute crystals of **zircon** and **apatite** in the interior of the porphyroblasts of albite.

QUARTZ-HYALOPHANE ALPINE-TYPE VEINS

Over 75 subparallel fractures, mainly extremely narrow from some micrometers to 5 cm, only five from 10 to 25 cm cut almost vertically the metamorphic ore deposit and the surrounding schists stretching N-S, and dipping with 80° to the west. The fractures are filled partly or completely in the lense-shaped or columnar forms with relatively big crystals (3-5 to 10-15 cm) of **quartz** and **hyalophane**. The mutual ratios of quartz to hyalophane varie from 7:2 to 1:3. **Siderite I**, **siderite II**, **apatite**, **muscovite**, **anhydrite**, **hematite**, **rutile**, **albite**, **anatase I**, **anatase II**, **pyrite**, **quartz II**, and **aragonite** are only accessories.

The first generation of the vein minerals consists of strongly limonitized minute crystals of **siderite I**, then of the rare pale greenish, thin flattened **muscovite** and mostly isometric, 1-3 mm in diameter colorless prismatic and pinacoidal, rarely platy crystals of fluor-rich **apatite**, partly grown in siderite I. This mineral assemblage covers partly the walls of cracks and fissures, and it represents the basis for the following crystallization. The second generation of the veins consists of **quartz I** with inclusions of colorless, maximum 0.2 mm long crystals of **anhydrite**, partly or completely included black flattened crystals, 0.5 to 5 mm long, of **hematite**, and with brownish-yellow, acicular crystals of **rutile** up to 1 mm long and below 0.1 mm wide. The quartz I crystals, colorless, or rarely smoky colored, rich on crystallographic faces are flattened along a pair of prismatic planes and elongated along a horizontal crystallographic axis. The crystals measure some cm to 15 cm: rarely they are individual crystals, mostly twinned according to Dauphine twin law, and more rare by to Brazil twin law.

Crystallization follows of **hyalophane I** crystals represented with Carlsbad and rarely Cunnersdorf twins which overgrow the fracture walls or crystals of quartz I. Slightly older is thin tabular, rarely thicker tabular on (010), 1-10 mm long crystals of **albite**. Its composition in mole % is: 81 **Ab**: 7.6 **An**: 10.4 **Or**, and 1.0 **Cn**. Albite is rarely individualized, more often is twinned according to Albite twin law, more rarely to Carlsbad twin law. Being younger, hyalophane crystals outgrew and inserted albite crystals. Sometimes albite is overgrown with regularly oriented crystals of hyalophane.

The bulk of hyalophane mass occur immediately after crystalization of albite and hyalophane I. **Hyalophane II** is in the form of Manebach twins, Manebach-Baveno furlings (the major part) and partly as individual crystals. The crystals are transparent, clean, rarely pale-yellowish: their length can reach 15 cm, crystals between 5-7 cm are not rare. The composition expressed in mole % (from 5 analyses) is: 35.00-40.78 **Cn**, 1.08-1.74 **An**, 38.25-49.39 **Or**, and 14.44-20.97 **Ab**. **Nz-Nx** = 0.004: **2V** = -70 to -81°: **a:b:c** = 0.6557:1:0.5516. This twinned group of hyalophane crystals contains as inclusions a major part of hematite crystals, rarely grown with rutile, locally covered with small dark-brown red colored, transparent crystals of **anatase I**, older, isometric, more rare, and **anatase II**, younger, more often with pointed pyramidal forms of crystals. Powder of small, limonitized **siderite II** covers locally hyalophane

II crystals.

The last phase of succession is represented with the major part of individual crystals of **hyalophane** III or partly oriented grown onto older hyalophane I and II crystals. Small crystals of **quartz** II and **aragonite** cover some crystals of older generations. **Pyrite** hexadrons, characteristically striated, maximally 0.5 mm in length, occur in the marginal parts of hyalophane crystals or fill the microcracks in quartz and hyalophane.

METALLOGENETIC CONSIDERATIONS AND EVOLUTION OF THE PRIMARY DEPOSIT

Geotectonic setting. The Zagrlski brook metamorphic deposit was initially formed in a subsiding through in which active turbiditic sedimentation during the upper part of the Lower Palaeozoic produced the pelito-psammitic protolith of the Busovača schist formation. Subvolcanic activity, spatially bounded with a zone of initial continental rifting or seafloor spreading produced (ultra) mafic protolith in the Zagrlski brook area interlayered with schists of the Busovača formation. The same geotectonic setting was attributed to the Brestovsko deposit, situated 15 kms SE from Busovača, interlayered within actinolite-epidote schists. The interlayered deposit contains, dominantly, coarse grained barite with thin bands, parallel to schistosity of the host rock, composed of columnar actinolite, plates of muscovite, columnar tourmaline, rutile, and quartz. Coarse grained magnetite is characterized by exsolution lamellae of ilmenite. Pyrite and chalcopyrite are the main sulfide minerals, subordinate are siegenite, bornite, tetrahedrite, chalcocite, millerite and as accessories molybdenite and gold (JURKOVIĆ, 1953). The Zagrlski brook deposit is comparable to Fe-Cu-Co-Zn-Ni deposit containing the detrital chromite, located in the Sykesville district, Maryland related to ultramafic rocks (CANDELA et al., 1989), then to the Matchless metamorphosed massive sulfide deposit in Namibia, related to the basic magmatic rocks (KLEMD et al., 1989) and to the Outokumpu copper sulfide deposit in Finland (PELTOLA, 1981). In these and in many similar deposits, around the world, mineralization occurs at the contact between the ultramafic rocks and the metapelites.

Formation of the primary deposit. The Zagrlski brook deposit exhibits the stratiform nature and many features characteristic of chemically precipitated sedimentary rocks on the sea-floor at/or below the sediment-seawater interface. Metal sulfides were precipitated from convecting hydrothermal fluids generated by the reaction of seawater with magmatic rock and permeable unconsolidated sediments. This process was contemporaneous with the deposition of pelito-psammitic sediment and premetamorphic hydrothermal alteration of the wall rocks by reaction with metal-bearing fluids. Rhythmic alteration of the very great number of the thin layers, some of those being extremely finely laminated built up of very different grain size in the separate layer and of very different chemical and mineral composition, without a sign of stronger homogenization renders it possible to recognize the vertical stratigraphical succession of the primary ore making process, and the pulsation of the metal influx with the pelito-psammitic detritus.

Hydrothermal alteration. The mineralization occurred in a relatively narrow zone, one meter thick, characterized by alternation on a scale of mms to cms of aluminium richer chlorite-albite bearing schists with, on aluminium impoverished, biotite-chlorite-ankerite-actinolite schists, both with subordinate amounts of ore minerals. This zone can be interpreted as a mixed unit, containing both a clastic and a chemical precipitate component, which was partly hydrothermally altered prior to metamorphism. Such a mixed zone is named black-wall zone according to KLEMD, et al., (1989) or marker-schist according to CANDELA et al., 1989. Albite-chlorite schist in this mixed zone in the Zagrlski brook area has increased content of SiO_2 , Na_2O , Al_2O_3 , Fe_2O_3 and decreased content of MgO , CaO , K_2O and CO_2 in relation with the biotite-chlorite-ankerite schist. This zone is a diffusion barrier for the MgO from the ultramafic rock and for the alkali and earth-alkali from the sediments. This mixed zone is attributed partly to hydrothermal alteration during the

process of mineralization, but also significantly to metasomatism during regional metamorphism. The hydrothermal alteration depleted magmatic rock and sediment in Ca, Na, Si, and enriched in Fe, Ba, Mn, Ni, Co, Cu, and S leading to silification, albitization, chloritization, sulfidization, and sideritization (ankeritization).

Source of metal. Copper, partly iron, cobalt, nickel, barium, manganese were most likely derived from underlying magmatic rock, alkali and earth-alkali metals from sediments. According to the its isotopic composition, sulfur was probably derived from (ultra) mafic volcanism. Most likely a predominant portion of the metal influx occurred during sea-floor hydrothermal activity. The chromite occurrence in the Zagrlski brook deposit is not entirely explained, although we are inclined to detrital influx of chromite grains taking into consideration the texture and structure of the deposit. The same opinion is emphasized by CANDELA et al., 1989 for the Sykesville deposit. The greater part of the magnetite grains and crystals of the layers located in the middle and lower part of the ore profile, having the chromian-spinel cores, must be attributed to the detrital chromite which is metamorphosed during regional metamorphism. The problem is open with regard to the magnetite layers in the upper part of the ore profile. This magnetite contains no chromian-spinel core. Two possibilities are probable: magnetite is derived from completely metamorphosed chromite or it represents metamorphosed ferruginous sediments related to the submarine exhalative activity. The very similar paragenesis of the microelements in this magnetite in relation to those with chromian-spinel cores enriched with chromium, zinc, cobalt, and impoverished in magnesium and iron indicates an origin derived from chromite.

Prograde regional metamorphism. During the Alpine (Dinaric) regional metamorphism some remobilization of Cu, Ni, Co, Fe, Ba, Mn, and S, and certain homogenization of the sulfide composition, took place. Formation of porphyroblasts (idioblasts and xenoblasts) of magnetite, pyrite, albite, hyalophane occurred during this time. The dominant number of porphyroblasts have "poikiloblastic" (Einschussieb) texture. The inclusion grains are smaller than those outside which had opportunity to grow. Myrmekitic (interpenetrating) intergrowths of albite and hyalophane porphyroblasts are often. Plastic and soft minerals as chalcopyrite, enargite, bornite, siderite, manganian ankerite are so intensively recrystallized, they occur as cementing minerals or fill interstices between porphyroblasts of feldspars (albite and hyalophane) and the hard ore minerals (magnetite and pyrite). The transformation of argillaceous sediments by the fixation of sodium and silica from the fluids due to sodium metasomatism gave rise the formation of neo-albite and/or neo-quartz layers. These neominerals are clean, optically normal. The later development of the albite under low-temperature conditions (350-450°C) is due to recrystallization, and the internal migration of alkalis and silica, and leads to the formation of both sodium and potassium-barium-rich hyalophane. Very characteristic for this phase is the association of the coarse grained manganian ankerite with the hyalophane (COATS et al., 1984). The microphysiographic features and chemical transformation of the chromite in the narrow zoned ferritchromit and in outer magnetite zone correspond to the description and to the consideration reported by PORTER and MCKAY (1981), CANDELA et al., 1989 and LAMBERG and PELTONEN, (1991). The different opinions are regarding the origin of ferritchromit: during the prograde metamorphism, or during the retrograde metamorphism. On the basis of the microscopical investigations we emphasize the latter.

Retrograde metamorphism. This phase in the evolution of the deposit in the Zagrlski brook area is characterized by: (a) decomposition of siegenite and formation of exsolution lamellae of millerite, (b) decomposition of bornite and formation of chalcopyrite and covellite blebs, and idaite (?) lamellae, (c) formation of ferritchromit rims around chromian-spinel cores, (d) martitization of magnetite, (e) delimitation of gold from the pyrite and/or chalcopyrite lattice etc.

Formation of quartz-hyalophane veins. According to G. H. Čedžemov,

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