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OCCURRENCES OF Fe-Ti MINERALIZATION IN THE VICINITY OF THE VILLAGE OF MITRAŠINCI

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Abstract: This paper gives the results of the recent investigations of the ore occurrences in the vicinity of the village of Mitrašinci, first of all those carried out by electronic microprobe. The examinations were carried out on the main ore minerals from the ore parageneses and make an important contribution to the explanation of the mineral associations and to the determination of the genetic features of Fe-Ti occurrences in the area.

Key words: metallogeny; titanomagnetite ore occurrence; ore minerals

INTRODUCTION

In the region of the village of Mitrašinci near Berovo, eastern Macedonia, a horizon of amphibolitic rocks with occurrences of ferroan-titanic mineralization mainly represented by ilmenite, titanomagnetite, magnetite etc. has developed in a complex of precambrian metamorphic rocks.

The first data about the geologic structure in the area were given by Cvijić J. (1906), and later by Bončev G. (1920). Intensive geologic investigations of the occurrences of Fe-Ti mineralization which were

known as early as the First World War started in 1950. Studies were also carried out by The Iron Works Company, Skopje, in 1956, and Simić M. and Simić V. (1963) completed the first mineralogic-petrographic geophysical investigations. Dumurdžanov N. (1977, 1978) gives detailed data about the geologic structure and mineralization in the area. Spasovski O. (1992) studied the ore occurrences from metallogenetic aspect.

GEOLOGIC FEATURES

The ferroan-titanic ore occurrences within the zone (Kobilski Rid – Gromadna – Leskov Čukar – Dolga Poljana – Kasaplija) and the broader vicinity of the village of Mitrašinci are related to amphibolitic rocks which comprise part of the Precambrian metamorphic complex of the Serbo-Macedonian massif. Precambrian and Riphean Cambrian rocks, Paleozoic Tertiary and Quaternary sediments (Fig.1) are distinguished in the area.

Amphibolitic rocks occur in two horizons: a horizon of orebearing amphibolites and amphibolitic schists and a horizon of amphibolites, amphibolitic schists, megagabbros and metadiabases without ferroan-titanic minerals.

Orebearing amphibolites and amphibolitic schists occur as a horizon of a deeper stratigraphic level. The rocks from this horizon are discovered on the surface as a zone which is 12 km long. Ferroan-titanic minerals can be found along the whole zone, but they occur as small mineralized masses.

Amphibolites, amphibolitic schists, megagabbros and metadiabases without ferroan-titanic minerals represent a horizon which occupies a higher stratigraphic level in relation to the orebearing amphibolitic rocks. They are separated by a mass of gneisses and micaschists.

ORE OCCURRENCES

Ferroan-titanic ore occurrences, as stated before, are related to amphibolites and amphibolitic

schists of Precambrian age and occur as one horizon which begins from Kobilski Rid in the north, and

continues to the south via Gromadna towards Bliznakov Čukar and Kasaplija (Fig.1). On the basis of the available data and recent field investigations

the following ore occurrences can be distinguished: Kobilski Rid, Gromadna, Leskovica, Dolga Poljana and Bliznakov Čukar.

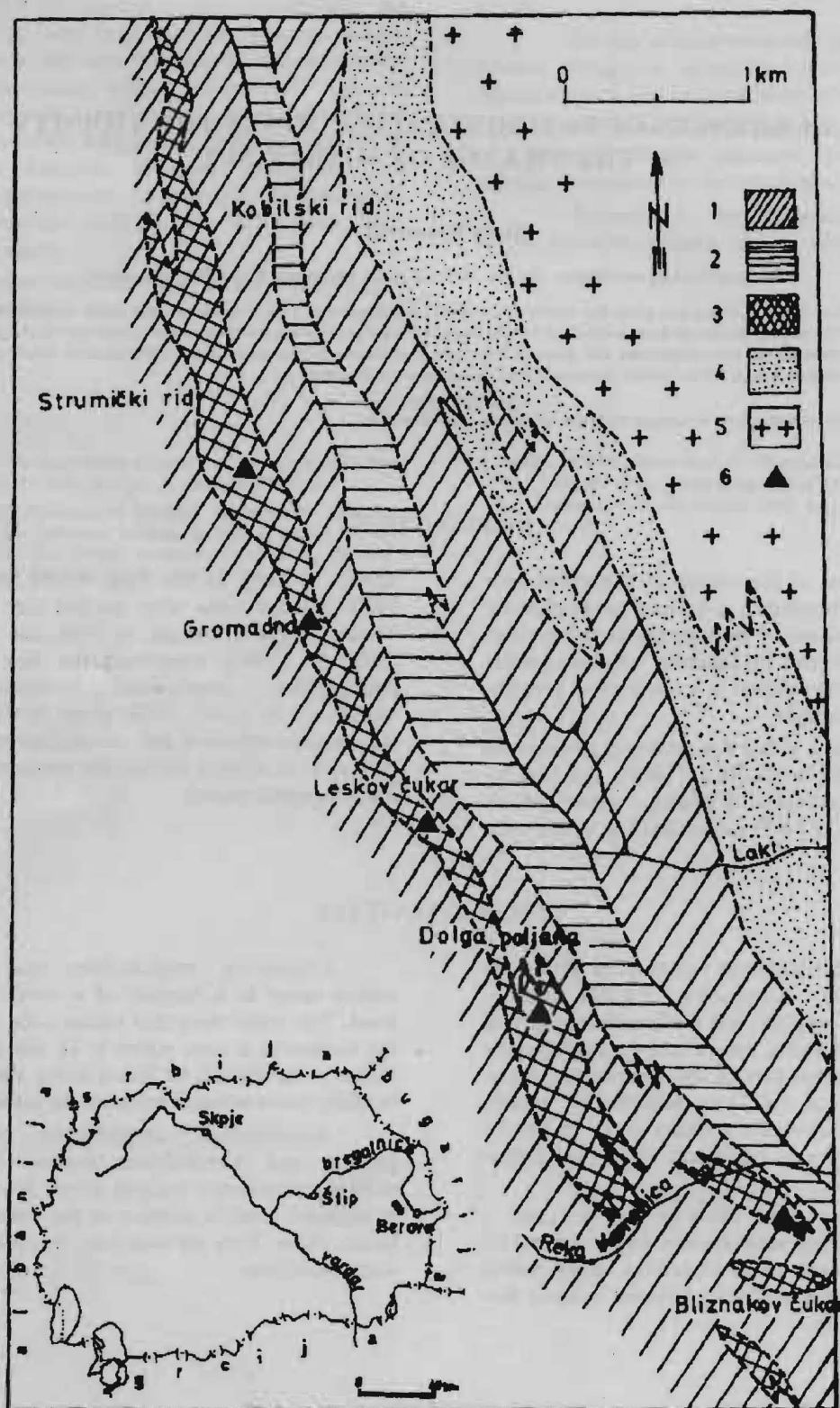


Fig 1. Geologic sketch map of the titanomagnetitic ore occurrences in the vicinity of the village of Mitrašinci. 1. gneisses; 2. micaschists; 3. ore mineralized amphibolites and amphibolitic schists; 4. non-ore mineralized amphibolites and amphibolitic schists; 5. gneisses; 6. ore occurrences

THE KOBILSKI RID ORE OCCURRENCE

This occurrence is situated in the northern part of the investigated zone, close to or at the very contact with the gneiss-micaschist series (Fig. 1).

The ore bodies and strips have a NW-SE strike with a NE dip. The ore mineralization in the distinguished amphibolitic masses contains the same mineralogical composition along its strike and depth. Nevertheless, the concentration of the ore minerals is not equally distributed. Generally, poor mineralization is developed and ore bodies with increased concentration are of small dimensions (Fig. 2).

The primary and unique mineralization bearers are magnetite, titanomagnetite and ilmenite and pirrotine, pyrite, chalkopyrite, chematite, martite and limonite occur as accessory minerals. Fig. 3 shows the manner of occurrence of the main ore minerals and Table I gives their chemical composition.

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Table I

Quantitative x-ray spectral microanalyses of the Kobilski Rid ore occurrence

Elements (%)	1	2	3	4	5
Fe	72.34	35.04	35.22	35.99	72.40
Ti	0.05	29.22	27.51	28.88	0.21
Mn	—	2.36	1.78	1.93	—
Al	0.57	0.37	0.23	0.32	0.40
Cr	—	0.14	—	—	—
V	0.22	—	—	—	—
Ni	0.41	0.34	0.29	0.18	0.39
O	26.40	32.54	34.90	32.67	26.58
Σ	99.99	100.00	99.93	99.97	99.98

1 and 5 are magnetite, 2, 3 and 4 are ilmenite
Analyst: H. Stančev (1992)

The table indicates that magnetite has a constant chemical composition which can be deduced from the Fe content of about 72%. As admixtures it contains small amounts of 0.05–0.21% Ti, 0.41–0.18% Ni and 0.22% V. Small amounts of 0.41–0.18% Ni, 2.26–1.78% Mn, 0.14% Cr and 0.57–0.23% Al were determined as admixtures in ilmenite.

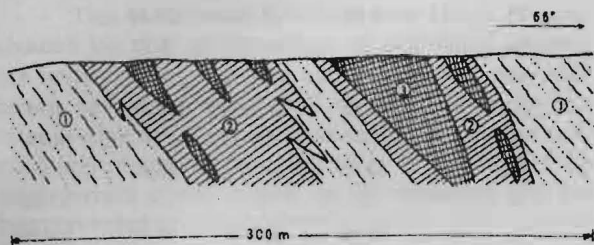


Fig. 2. Cross-section through the Kobilski Rid ore occurrence
1. strip micaceous gneisses; 2. poorly ore mineralised amphibolites and amphibolitic schists (Fe < 10%); 3. ore bodies with increased concentration of Fe-Ti minerals (Fe > 10%).

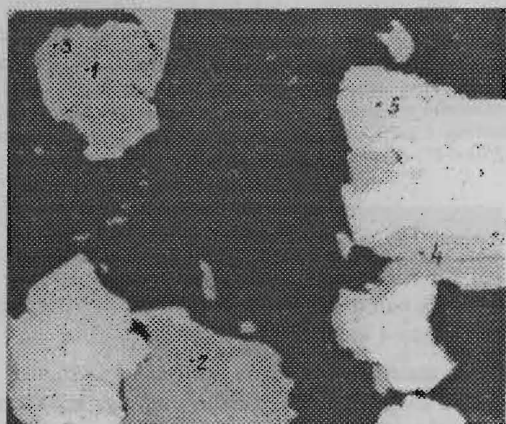


Fig. 3. Microphotograph of ilmenite-magnetite aggregate in COMPO regime from the Kobilski Rid ore occurrence.
Magn. 100 ×

THE GROMADNA ORE OCCURRENCE

This ore occurrence is a continuation of the Kobilski Rid – Kasaplija ore occurrence. Small ore bodies separate within the occurrence which, after short distances, wedge out along their length and depth but lie concordantly within the amphibolites and the amphibolitic schists (Figs. 1 and 4). The ore bodies commonly occur as lenses which are 0.3 to 0.5 m thick which can be traced up to 100 m along their strike. These lens shaped ore bodies are arranged in sequences like rosaries.

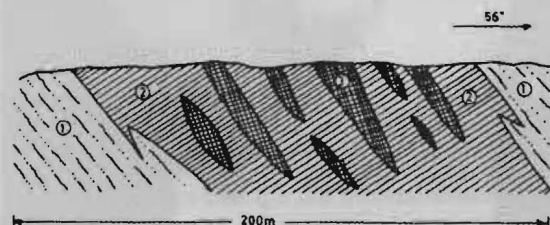


Fig. 4. Cross-section through the Gromadna ore occurrence
1. strip micaceous gneisses; 2. poorly ore mineralized amphibolites and amphibolitic schists (Fe < 10%); 3. ore bodies with increased concentration of Fe-Ti minerals (Fe > 10%).

The unique bearers of the ore mineralization are titanomagnetite, ilmenite and magnetite, whereas pirrhotine, pyrite, chalkopyrite, pentlandite, chematite, rutile, limonite and lepidocrocite occur as accessory minerals. Fig. 5 shows the morphological shape and the manner of occurrence of the main ore minerals.

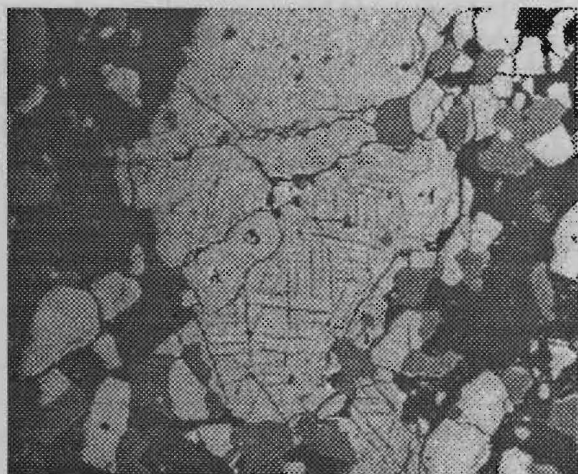


Fig 5. Microphotograph of the mineral paragenesis in COMPO regime from the Gromadna ore occurrence. Magn. 100 \times .
1. magnetite; 2. lamellar separations of ilmenite;
3. alotriomorphic grain of ilmenite; 4. pirrhotine

THE LESKOVICA ORE OCCURRENCE

This occurrence is situated 500 m south of the Leskov Čukar peak and is a south east continuation of the Kobilski Rid ore zone. The ore mineralization appears as impregnations, amphibolites and amphibolitic schists. The investigations carried out near

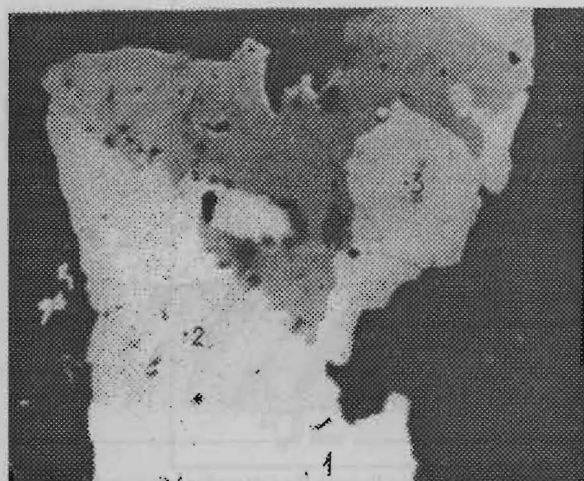


Fig 6. Microphotograph of the mineral paragenesis in COMPO regime from the Leskovica ore occurrence. Magn. 100 \times

The chemical composition of the main ore minerals from the Gromadna ore occurrence is shown in Table II.

Table II

Quantitative x-ray spectral microanalyses of the oxide-sulphide minerals from the Gromadna ore occurrence

Elements (%)	1	2	3	4
Fe	76.68	38.35	33.97	61.98
Ti	0.68	25.50	29.68	—
Mn	—	1.25	2.22	0.10
Al	0.28	—	—	—
Ni	0.52	0.40	0.29	1.14
Cu	—	—	—	0.30
O	21.83	34.50	33.83	—
S	—	—	—	37.48
Σ	99.99	100.00	99.99	100.00

1 is magnetite, 2 and 3 are ilmenite, 4 is pirrhotine
Analyst: Stančev H. (1992)

It can be concluded that magnetite is rather pure and as admixtures it contains small amounts of 0.68% Ti, 0.28% Al, and 0.52% Ni. The Table also indicates that ilmenite contains small admixtures of 1.25–2.22% Mn and 0.29–0.40% Ni, whereas as admixtures pirrhotine contains 0.10% Mn, 0.14% Ni and 0.30% Cu.

Leskovica revealed an ore body which is 70 m long and from 0.2 to 4 m thick.

The main ore minerals are titanomagnetite, ilmenite and magnetite and pirrhotine, pyrite, arsenopyrite, chalkopyrite, martite, chematite, pentlandite, anatase, rutile and leucosene are accessory minerals. The manner of occurrence and the relations between the main ore minerals are given in Fig. 6.

The chemical composition of the main minerals is given in Table III.

Table III

Quantitative x-ray spectral microanalyses of magnetite, ilmenite and limonite

Elements (%)	1	2	3	4
Fe	72.36	36.71	35.38	53.65
Ti	0.14	29.67	28.68	3.62
Mn	0.08	2.05	2.07	—
Mg	—	0.29	—	—
Al	0.34	0.38	0.36	—
Ni	0.36	0.29	0.34	0.41
Cr	0.03	—	0.11	—
O	26.67	30.62	33.07	42.35
Σ	99.98	100.01	100.01	100.03

1 is magnetite, 2 and 3 are ilmenite, 4 is limonite

Analyst: Stančev H. (1992)

From the table we can see the chemical compositions of the oxide minerals, first of all magnetite, ilmenite and limonite. The chemical composition of magnetite and ilmenite does not differ from the

chemical composition of the same minerals in the previously mentioned ore occurrences. Limonite is very pure and contains very small amounts of Ti (3.62%) and Ni (0.41%).

THE DOLGA POLJANA ORE OCCURRENCE

This occurrence is located near Dolga Poljana, about 8 km SW of the village of Mitrašinci. Several ore bodies of impregnated and massive ore mineralization have been discovered so far. The ore bodies often wedge out along their strike and dip but lie concordantly in amphibolitic rocks (Fig. 7). Because of the thick terrain cover, a NW or SE extension has not been revealed so far.



Fig 7. Cross-section through the Dolga Poljana ore occurrence
1. strip shaped micaceous gneisses, 2. poorly ore mineralized amphibolites and amphibolitic schists ($Fe < 10\%$); 3. ore bodies with increased concentration of Fe-Ti minerals ($Fe > 10\%$)

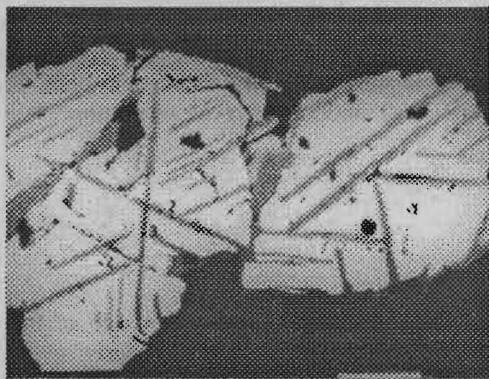


Fig 8. Microphotograph of a large grained magnetite aggregate with ilmenite lamellae in COMPO regime

The main ore mineralization bearers are magnetite, and titanomagnetite, but ilmenite and pirrhotine, pyrite, chematite, martite, rutile etc. appear as accessory minerals. The chemical composition of magnetite, ilmenite and pirrhotine are given in Table IV.

Table IV

Quantitative x-ray spectral microanalyses of magnetite, ilmenite and pirrhotine from the Dolga Poljana ore occurrence

Elements (%)	1	2	3	4
Fe	71.39	41.96	35.08	61.02
Ti	0.34	23.31	29.44	—
Mn	0.09	1.44	1.97	—
Mg	0.25	—	—	—
Ni	0.49	0.29	0.41	0.15
Al	0.53	0.22	0.23	—
Cr	—	0.08	0.05	—
O	26.89	32.70	32.50	—
S	—	—	—	38.82
Σ	100.00	100.00	99.99	100.00

1 is magnetite; 2 and 3 are ilmenite; 4 is pirrhotine

Analyst: Stančev H. (1992)

Table IV shows that the chemical compositions of magnetite and ilmenite are identical to those in the previously described ore occurrences. The pirrhotine from this occurrence is very pure and as admixture it contains very small amounts of 0.15% Ni.

THE BLIZNAKOV ČUKAR ORE OCCURRENCE

Two ore bodies which are about 2.5 m thick have been discovered in this occurrence. They can be traced about 250 m along their strike. Their ferroan-titanic mineralization is related to amphibolitic rocks and to their contacts with gneisses and concordantly lies within the amphibolitic masses. Petrologic exami-

nations have shown that the ore mineralization occurs only in the granate amphibolites, whereas in amphibolitic rocks without granates it is absent. Poor mineralization is developed in most of the deposit and the ore bodies with large concentrations are of small dimensions.

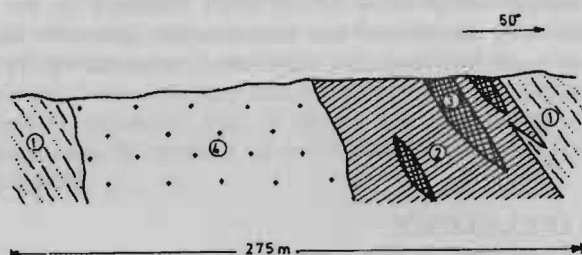


Fig 9. Cross-section through the Bliznakov Čukar ore occurrence
1. strip shaped micaceous gneisses; 2. poorly ore mineralized amphibolites and amphibolitic schists ($\text{Fe} < 10\%$), 3. ore bodies with increased concentrations of Fe-Ti minerals ($\text{Fe} > 10\%$), 4. massive biotite granites.

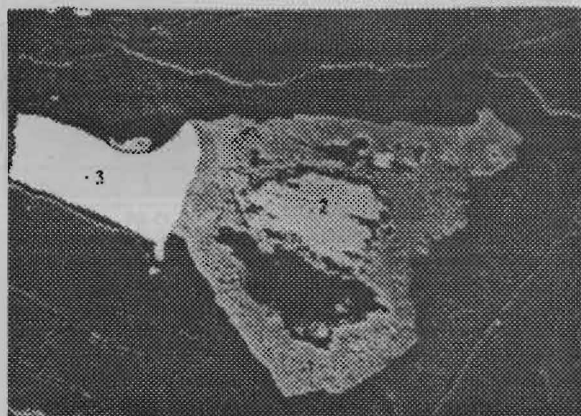


Fig 10. Microphotograph of large grained limonite aggregate in association with pyrite and chalkopyrite in CAMPO regime.
Magn 100 ×

The main mineralization bearers are ilmenite, titanomagnetite and magnetite. Pirrhotine, arsenopyrite, chalkopyrite, rutile, titanochematite, chematite, limonite, anatase and leucosen are also determined in the mineral association.

Fig. 10 shows a limonite aggregate in association with pyrite and chalkopyrite.

The chemical compositions of limonite, pyrite and chalkopyrite from the Bliznakov Čukar ore occurrence are given in Table V.

Table V

Quantitative x-ray spectral microanalyses of oxide-sulphide minerals

Elements (%)	1	2	3
Fe	42.80	45.38	31.04
Ca	0.91	—	—
Mn	4.63	—	—
Al	0.58	—	—
Ni	0.34	0.09	0.07
Si	0.32	—	—
Cu	—	0.26	33.05
O	50.39	—	—
S	—	54.27	35.84
Σ	99.99	100.00	100.00

1 is limonite; 2 is pyrite; 3 is chalkopyrite

Analyst: Stančev H. (1992)

The table shows that limonite contains small amounts of Mn, Ca, Al, Si, Ni etc. as its admixtures. The table also indicates that chalkopyrite is fairly pure and its values are close to the theoretical ones. It contains very small amounts of Ni as admixture.

GENETIC FEATURES

The formation of Fe-Ti ore occurrences within the Kobilski Rid – Gromadna – Leskov Čukar – Dolga Poljana – Bliznakov Čukar – Kasaplija ore zone took place in complex geologic conditions and processes. The changability of the physical-chemical and geological conditions which controlled the concentration and the separation of the ore minerals had a great influence on the formation of these ore occurrences.

The main ore minerals (ilmenite, magnetite and titanomagnetite) are formed in an intermagmatic stage and crystallization differentiates. However, we must also bear in mind that this stage was preceded by a poorly expressed liquid magmatic sulphide segregation process represented by pyrite, pirrhotine, chalkopyrite and pentlandite, Ivanov (1976), Jašmakovski (1976). This is supported by the presence of the first old sulphide inclusions in the ferroan-titanic oxide crystals.

The mechanism in the occurrence of the titanomagnetites was as follows: As early as in the magma source, titanomagnetite crystals were formed at high temperature. They were the "phenocrysts" in which titanium was implaced as a homogenous hard solution because of the thermal expansion in the crystal lattice. During the magma intrusion to the surface, with the gradual decrease of temperature the crystal lattice reduced so that the relatively large titanium cations pressed out and concentrated as a separate phase forming ilmenite along parallel strikes with octahedral and hexahedral planes over the previously formed titanomagnetites.

Besides its presence in titanomagnetite, ilmenite also forms as an individual mineral. This is explained by the titanium surplus which could not completely join the hard titanomagnetitic solutions and formed an individual ilmenite phase.

In addition to this intramagmatic process there is data about a submarine exhalation phase which is related to the magnetites without titanium contamination (ilmenite). This is supported by the occurrence of this phase in various schists of volatile origin where, besides magnetite, there is fine acicular chematite (specularite) and sulphides (pyrite) related to the redox potential variation. The complex genesis of these ore occurrences is also proved by the existence

of intensive metasomatic changes of the basic and sedimentary rocks by additional feldsparization which is ascribed to the Hercinian granitoids of the precambrian complex in which this titanite-magnetite mineralization lies. All this resulted in multifold progressive and retrograde metamorphism which did not have a significant influence on the mineral paragenesis of the titanomagnetites from Mitrašinci.

CONCLUSION

On the basis of the metallogenetic analysis several horizons of basic magmatism in the Precambrian complex were determined of which only the Kobilski Rid – Gromadna – Leskov Čukar – Dolga Poljana – Bliznakov Čukar – Kasaplija horizon is ore bearing.

The studies of the mineral paragenesis indicate the magmatic origin of the titanomagnetites with a

poorly expressed liquid magmatic sulphide stage and a significant stage of crystallization differentiates with titanomagnetite and ilmenite. These stages are accompanied by deep-sea exhalations.

Studies carried out by electronic microprobe discovered certain moments related to the internal structure of the more significant ore minerals from the investigated ore zone.

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