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MAGNETITE-HEMATITE IRON ORE OCCURRENCES IN THE TRIASSIC-PALEOZOIC METAMORPHIC COMPLEX OF MEDVEDNICA MOUNTAIN, CROATIA

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Ključne riječi: željezna rudna ležišta, SEDEX-tip, donji paleozoik, Medvednica planina, Hrvatska

Abstract

Iron ore occurrences are situated on the south-eastern slopes of the Medvednica Mountain. They occur as discontinous, decameters long and 2-3.5 m thick bedded, poorly mineralized (15-35 % Fe) lenses. A narrow, 6 km long, ore zone strikes NE-SW from Tisova Peć to Pustodol-Adolfovac. It is spatially and genetically bounded to the basic volcanogenic-sedimentary series (SEDEX-type), metamorphosed in greenschists during Cretaceous under P 3-3.5 kbar and T 350-400°C. The main minerals of the paragenesis are: quartz, chlorite, hematite, magnetite, stilpnomelane, martite. Similar types of Neo-Proterozoic and Early Paleozoic iron deposits were found in eastern Bosnia - western Serbia, western Macedonia and in the Serbo-Macedonian Mass. In the Triassic period of the Dinarides, magnetite-hematite deposits occur only as iron skarns or as short veins and small sized bodies of pneumatolytic-hydrothermal origin genetically bounded to gabbro-diorite or syenite stock and dykes. In the Triassic vulcanogenic-sedimentary complexes occur only bedded deposits of red hematite, siderite, as well as locally with Mn-oxide ores. The arguments pointing for the Paleozoic age of the Mt. Medvednica iron deposits are more convincing than those proposing theoretically possible Triassic age.

The structures, textures and parageneses of the Mt. Medvednica magnetite-hematite occurrences are very similar only to the iron ores situated in the Early Paleozoic metamorphic complexes.

Sažetak

Željezne rudne pojave nalaze se na jugoistočnim padinama Medvednice. Javljaju se kao isprekidane, desetine metara duge i 2-3.5 m debele slabo orudnjene uslojene leće (15-35 % Fe). Uska rudna zona, 6 km duga, pruža se SI-JZ od Tisove Peći do Pustodol-Adolfovca. Prostorno i genetski orudnjenje je vezano za bazični vulkanogeno-sedimentni kompleks (SEDEX-tip ležišta) koji je u kredi metamorfoziran do facijesa zelenih škriljaca pri t = 350-400°C i tlaku od 3-3.5 kbara. Glavni minerali u paragenezi rudnih pojava jesu: kvarc, klorit, hematit, magnetit stilpnomelan i martit. Slični tipovi željeznih pojava i ležišta neoproterozojske i donjopaleozojske starosti nađeni su u istočnoj Bosni, zapadnoj Srbiji, zapadnoj Makedoniji te u srpsko-makedonskom metamorfnom pojasu. U trijasu Dinarida magnetitsko-hematitska ležišta javljaju se samo kao skarnovi ili kratke pneumatolitsko hidrotermalne žile genetski vezane za gabro-dioritske ili sijenitske štokove i dajkove. U trijaskim vulkanogenim sedimentnim kompleksima Dinarida javljaju se samo uslojena ležišta crvenog hematita, siderita i lokalno s manganskim oksidima. Argumenti za palozojsku starost željeznih ležišta Medvednice su mnogo uvjerljiviji nego za teoretski moguću trijasku starost. Strukture, teksture i parageneze magnetitsko-hematitskih pojava Medvednice su vrlo slične željeznim ležištima donjopaleozojskih metamorfnih kompleksa.

Introduction

The south-eastern part of Mt. Medvednica (1033 m) is composed of metamorphic rocks, Paleozoic and Triassic in age. Paraschists dominate and are represented by greywackes, subgraywackes, metasiltstones, crystalline limestones and dolomites, slates, phyllites, quartzites, marbles, and cipolins (Šikić et al., 1979, Basch, 1983, 1995).

In the paraschists, especially in carbonate rocks, fossils were found and identified in Uppermost Ordovician to Lower Silurian, Lower, Middle, Upper Devonian, Lower and Upper Carboniferous, Upper Permian and Middle-Upper Triassic (Gorjanović-Kramberger, 1908; Đurđanović, 1967a,b, 1968a,b, 1969, 1973; Kochansky-Devidé, 1981; Sremac and Mihajlović-Pavlović, 1983; Devidé-Nedéla and Kochansky-Devidé, 1990; Belak et al., 1995c, Belak, 2005).

Orthometamorphic rocks (metabasalts and meta-diabases, greenschists rock *senso stricto*, and subordinate epidote-sericite schists, stilpnomelane schists and amphibole schists) have a basic character with pronounced olivine – tholeiitic affinity (Kišpatić, 1918; Marić, 1959; Šikić et al., 1979; Vragović and Majer, 1980a,b; Pamić and Injuk, 1985-1986).

Belak (2005) classifies orthogreenschists into two groups: the first group is situated in the central part of Mt. Medvednica (Veliko and Malo Sljeme), displaying polyphase (progressive and retrograde) metamorphism (T=350-550°C, P=3-5 kbar). Protolith are Ti-rich basalts and diabases (T-MORB). The second group is interlayered in the sediments of the units Vidovec, Tusti breg, Stara pila, Vila Rebar. It is characterized only by progressive metamorphism (350-400°C and 2-3 kbar).

Belak et al. (1995a) identified four informal lithostratigraphic units: Sljeme, Adolfovac, Medvešćak and Bliznec, arranged from the oldest Sljeme unit to the youngest Bliznec unit. Later Belak et al. (1995b) described five informal lithostratigraphic units in Mt. Medvednica: Vidovec, Stari potok, Sljeme, Medvešćak and Bliznec. The Vidovec unit is only one (having) Upper Paleozoic age (C_2-P_1). Authors supposed Lower Triassic to Middle Triassic age of the Stari Potok unit and Middle Triassic age of the Sljeme and Medvešćak units. Fossils were found only in the stratigraphic unit of Bliznec (subunit Risnjak) and range from Upper Ladinian to Lower Carnian.

Belak (2005) identified eight informal units: Vidovec (age from S_1 to C_2), Stari potok (supposed T_1), Risnjak (unknown, T_{2-3}-J_1 or Pz_1), Tusti breg (T_2-T_{2-3}), Adolfovac (supposed T_{2-3} or Pz_1), Stara Pila (supposed T_{2-3}), Vila Rebar (T_2-T_{2-3}), and Sljeme (unknown, supposed Triassic). In the amended geological map made earlier by Šikić et al. (1979) and Basch (1983, 1995), Belak (2005) marked all informal units and magnetite-hematite ore occurrences in the Stara Pila unit. This unit is characterized by orthogreenschists (protoliths are pillow-lavas and diabases), as well as by metaradiolarites and paraschists (metashales, metasilicified clastics, and metatuffites). Thin metacarbonates and marbleized limestone beds are interstratified. The whole unit is irregularly ferruginous, locally mineralized with magnetite and hematite. The Stara Pila unit represents a deep marine facies of supposed Triassic age, although Paleozoic age is not excluded. Fossils are not detectable.

The whole Paleozoic-Triassic complex was affected by regional metamorphism. Šikić et al. (1979) claim that this metamorphism took place during the Variscan orogeny and ended in the Lower Permian Saalitic orogenic phase. Vragović and Majer (1980a,b) favoured two-phase metamorphism. Belak et al. (1995a) claim that the metamorphic complex of Mt. Medvednica was affected by three metamorphic phases: the first phase (Variscan) was synmetamorphic (clevage, foliation), the second phase (Cretaceous) was microfolding (with crenulation cleavage) and the third phase (Tertiary) was posttectonic with penetrative cleavage. Judik et al., (2004) are convinced that the Paleozoic rocks were affected by Eoalpine (122-110 Ma) very low- to low-grade and medium pressure regional metamorphism (P = 3-3.5 kbar, T = 350-400°C). Pamić and Jurković (2005) are of the opinion that the metamorphism of the metamorphic complex of the Mt. Medvednica is of Variscan age, though pervasively predeformed in Lower Cretaceous. The other Paleozoic complexes in the Dinarides are characterized by the Upper Carboniferous or Lower Permian orogenetic phase (lifting), as well as by a hiatus of varying length within the Middle-Upper Carboniferous and Middle-Upper Permian range.

The same patterns must be observed regarding the fact that it is part of the Dinarides in Mt. Medvednica, too (Herak, 1999). The occurrences of up to 11 m thick metaconglomerates (Šikić et al., 1979; Basch, 1983; Belak et al., 1995a) clearly indicate a powerful energetic event during the Paleozoic era. According to Neubauer et al. (1999), in the intra-Alpine Variscan belt, there is not a single Paleozoic complex that would have a continued stratigraphic range from Lower Silurian to Upper Triassic.

Ore deposits

Magnetite-hematite ore occurrences are situated on the south-eastern slopes of Mt. Medvednica. (Fig. 1b). The ore zone is 6 km long, although very narrow, striking from Pustodol-Adolfovac to Tisova Peć. The first 1.5 km of ore zone (Adolfovac-Bliznec Potok) contains the majority of ore outcrops. The ore zone consists of discontinuous decameters long, and 2 to 3.5 m thick bedded, poorly mineralized (20-35 % Fe) lenses. The ore bearing zone is characterized by quartz-chlorite schists, quartz-stilpnomelane-magnetite shists, quartz-stilpnomelane-chlorite-magnetite schists and iron-ore bearing schists.

The magnetite occurrence with veinlets of massive pyrite in the amphibole schists in the location south of Sv. Jakob was first described by Vukotinović (1860, 1871). He found a 7.2 metres thick limonite bed "concordantly inserted" in the same schists. These data were cited by Kišpatić (1901) and Tućan (1919). A significant amount of iron slag was found by Pilar (1883) in the source area of the Bliznec Potok brook. Kišpatić (1906) detected Mn-fayalite in this slag, verifying manganese-bearing siderite from the brook Slani Potok as smelted ore.

Geotectonic setting of Mt. Medvednica

Herak (1986) includes Mt. Medvednica in the Supradinaric geotectonic unit. Later, Herak et al. (1990) claim that this unit is part of the Inner Dinarides. Šikić (1995) called NW Croatia Mid-Transdanubian zone, and Pamić and Tomljenović (1998) Zagorje - Mid-Transdanubian zone. Herak (1999) describes the new geotectonic concept of the area between the Dinarides and the South Alps.

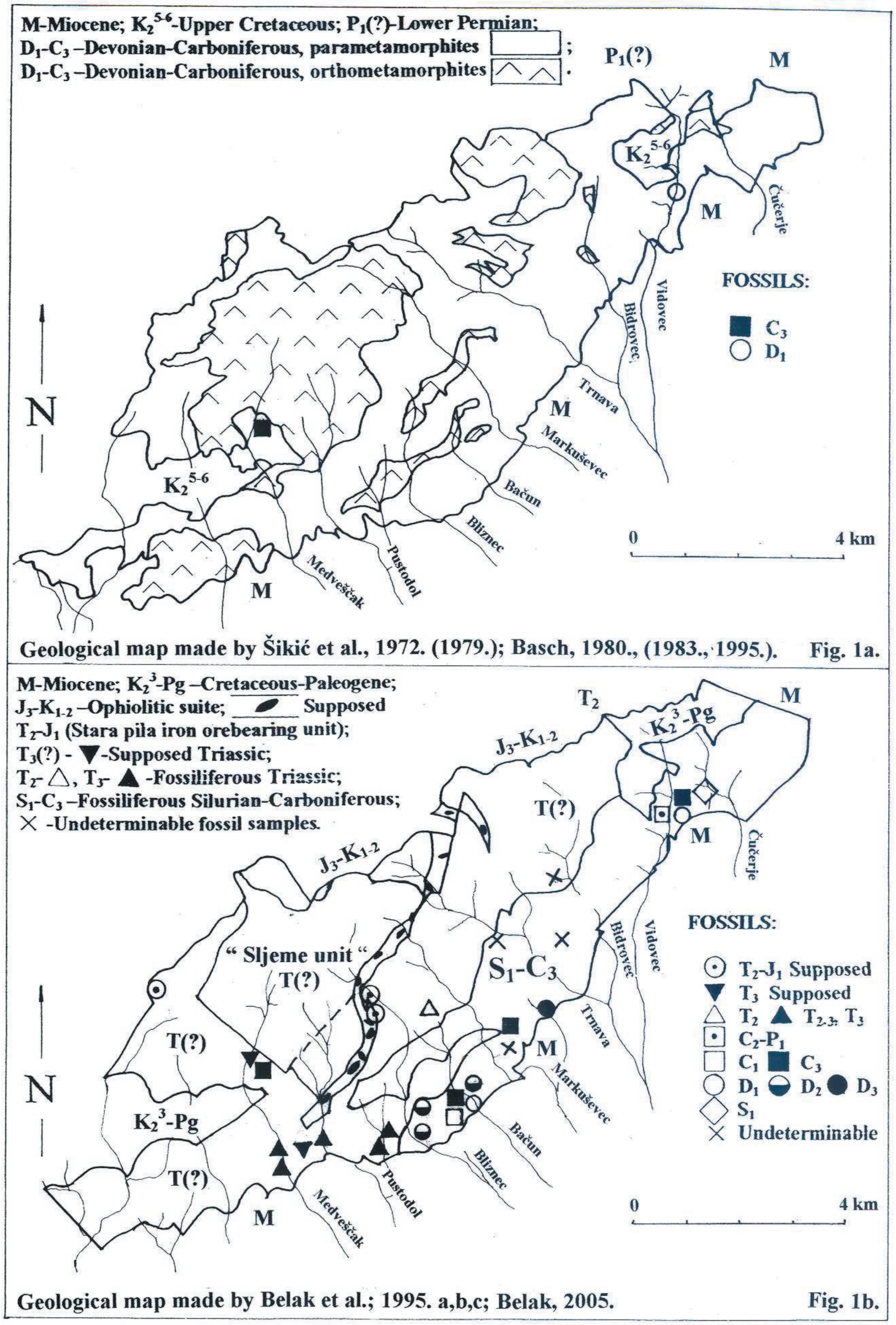

Figure 1a-b Geological map of the Medvednica Mountain Paleozoic-Triassic methamorphic complex, Croatia

Slika 1a-b. Geološka karta paleozojsko-trijaskog metamorfnog kompleksa Medvednice, Hrvatska

Investigations of the magnetite hematite ore occurrences

The first mining, geological, geophysical and optical investigations of these ores were carried out between 1954 and 1956 on the initiative of the ironworks "Željezara Sisak" (Šinkovec, 1954, 1957; Krulc, 1954, Jović and Mamužić, 1954, Jurković, 1955 and Crnković, 1955). Their unpublished reports are deposited in the Archive of the Institute for Geological Investigations (IGI), Zagreb. They merit to be represented in this paper.

Šinkovec (1954, 1957) described geological profiles of all trenches made in 1954 in the richest, 1.7 km long section, situated between the locations of Pustodol (+395) and the Bliznec Potok brook (+614). The lenticular ore bodies are 2.0-3.5 m thick and 10 to 100 m long. The entire mineralized zone streches NE-SW with a dip of 25-45° to the NW. The ore bodies consist of the alternations of very thin (0.03-0.8 mm to 5 cm) magnetite-hematite beds, separated by sharp boundaries of the thicker gangue-bearing beds. Hematite is cryptocrystalline or very fine grained (5-50 micrometers), oriented parallely to the schistosity of the host rocks. Magnetite, which is strongly martitized with average grain size of 0.1 to 3 mm, mostly occurs as individual idioblasts or as very small aggregates. Crude ore contained 16.2-25.4 % Fe^{3+}, 1.6 – 6.5 % Fe^{2+}, 0.37-2.4 % Mn, trace to 0.066 % S, 1.1 – 1.6 % P and 21.8-63.5 % SiO_2.

Jović and Mamužić (1954) prepared the first detailed geological map (fig. 2) of an area that is 4 km long and 1 km wide, stretching from the Pustodol brook in the SW to the Trnava brook in the NE. In this area, ten iron ore outcrops have been found and investigated by trenches. They are situated in the orthogreenschists, very close to the contact with the parametamorphic schists. Krulc (1954) carried out certain geomagnetic measurements in the same area. The anomalies of 500-800 γ (locally 1000 γ) are very shallow, only 2-12 m. On the basis of these results, an underground adit was made in the location of Pustodol, in total 240 m long, cutting very poor mineralized beds. Crnković (1955) mapped an area of 40 km^2 (12 x 2.5-4.5 km) stretching from the brook Slani Potok in the NE to Medvedgrad in the SW. In the outermost NE part of this area he found the last iron ore outcrops Vučje Jame and Tisova Peć. Jurković (1955) conducted the first (unpublished) optical investigation of the ore samples from the Adolfovac location (see corresponding chapter in this paper). On the basis of the results of the above mentioned reports, Jurković (1959, 1962) and Jurković and Šinkovec (1978) published short reviews concerning the paragenesis, structures, textures and formation of the iron ores in the Pustodol – Tisova Peć zone.

Šikić et al. (1979), Basch (1983), Čepelak et al. (1986), Šinkovec et al. (1988), Jurković (1995), and Marković (1995, 2002) reported about the iron ores on the basis of the previous recorded data.

Author's investigations

Paragenesis, structure and texture of the iron ore occurrences; optical identification of ore and gangue minerals

Ore minerals are concentrated in certain thin beds (1-2 mm locally up to 5 cm). The strongly mineralized thin beds are significantly fewer than the weakly mineralized beds and bands. In places, strongly and weakly mineralized beds and bands alternate at very short intervals. Locally, one or more thin rich beds are followed by a thicker series of weakly mineralized beds that are sometimes almost sterile. Host rocks of the mineralized zone are: quartz-chlorite schist, magnetite-hematite-quartz chlorite schist, chlorite-quartz-hematite-magnetite-stilpnomelane schist.

Optical investigations of ore and gangue minerals

a) In transparent light

By microscopic investigations of the rock samples, in the profile vertically to the stretching of the beds, an entire transitive series of the rocks ranging from pure quartzites to actual chlorite-schists has been found. Between these end-members of the series there are several transitive members differing from each other only by higher quartz or higher chlorite content. Some members occur in thin beds of varying thickness. The beds were found that are barely 0.5 mm to 1 mm thick, as well as those reaching a thickness of several centimeters or even several decimeters. There are localities in which certain members, particularly quartzose schists occur in bands several meters powerful. In the locality of Adolfovac, there is a very frequent alternation of several members of the series. The alternation is random in as much as no pattern could be discerned.

The main petrogenic minerals are fine-grained ***quartz*** and ***chlorite***, white mica is subordinate or absent. Their respective quantities determine the petrographic character of a member in a "mineralized series." Among the more important minor mineral components, are: ***stilpnomelane, epidote, actinolite, garnet and tourmaline.***

A characteristic feature of this series of epimetamorphic rocks is the presence of garnet and tourmaline. In some samples garnet is very abundant and occurs as fine idiomorphic grains. Tourmaline has the form of strongly pleochroitic columnar crystals and is dispersed throughout the sample.

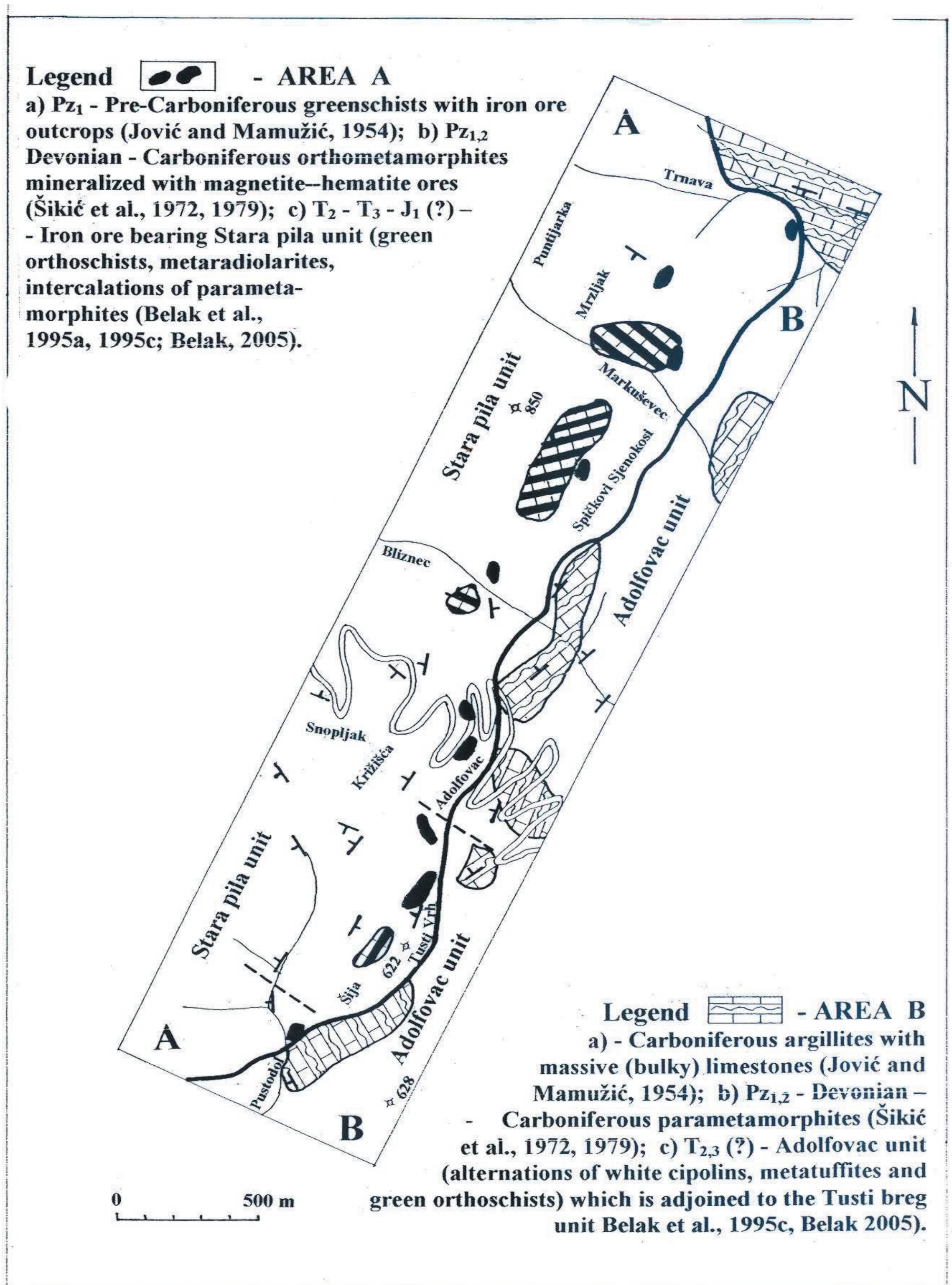

Figure 2 Iron-ore deposits between the Pustodol Creek and Trnava Creek, South-East Medvednica Mt., Croatia

Slika 2. Željezne rudne pojave između potoka Pustodola I potoka Trnava, JI Medvednica, Hrvatska *b) Investigations of polished sections in reflected light*

As far as ore minerals are concerned, ***magnetite, hematite, martite, pyrite, goethite lepidocrocite, psilomelane, calcite*** and common "***limonite***" were identified. Quantity-wise, the most abundant is hematite, then magnetite and martite, while other minerals are minor components.

Instead of being evenly distributed across the "mineralized belt," ore minerals are more concentrated in certain thin beds. The strongly mineralized thin beds are significantly fewer than the weakly mineralized beds and bands. In places strongly and weakly mineralized thin beds alternate at very short intervals. Locally one or more thin, rich beds are followed by a thicker series of weakly mineralized beds that are sometimes almost sterile.

Magnetite is developed idiomorphically. It is characterized by simple crystallographic forms: (111), (110) and (110) or their combinations. Individuals of magnetite are of considerable size, appearing like porphyroblasts (idioblasts) in a fine-grained mass of other ore and gangue minerals. Size varies on average between 0.2 and 0.5 mm. There are also some individuals measuring 1-2 mm, very rarely 3 mm, as well as those measuring less than 0.2 mm.

The individuals of magnetite occur mainly as single crystals, less frequently as aggregates of two, three or more crystals. The re ectivity of the magnetite is moderate, while its color is grey with marked brownish tints. Relief is high, although visibly lower than that of martite. It is isotropic. Magnetite is characterized by low content of manganese in its crystal structure.

Magnetite is concentrated in certain beds of varying thickness. Its distribution in these beds is of uneven density. While some thin beds contain magnetite in over half of their volume, others contain only isolated, rarely dispersed grains. Some of the hematite-rich beds do not contain any magnetite. ***(Plate I, photo 3)***

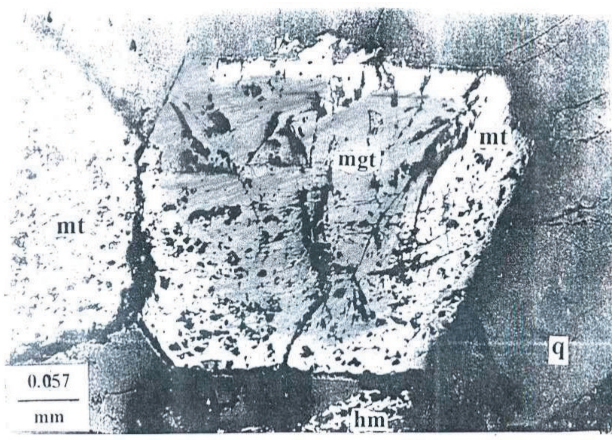

Plate I, photo 1 Porphyroblast of magnetite (mgt) affected by martitization (mt), hematite (hm), quartz (q)
Poča I, slika 1. Porfiroblast magnetita (mgt) martitiziran (mt) hematit (hm), i kvarc (q) *B. Šinkovec (1957)*

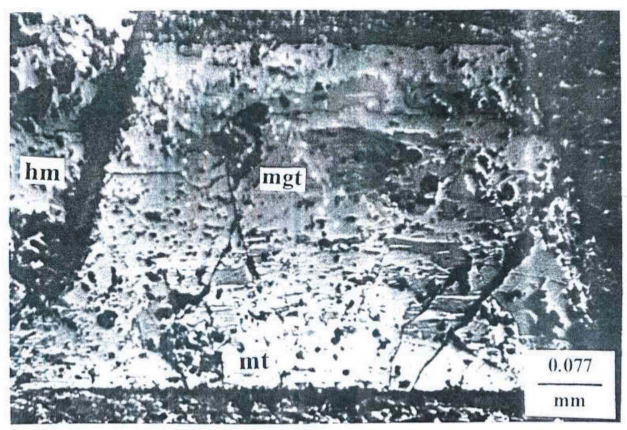

Plate I, photo 2 Magnetite porphyroblast (mgt) chie y martitized (mt) along (111) or frontaly; fine hematite leaves (hm) around hematite
Poča I, slika 2. Magnetitni porfiroblast(mgt), uglavnom martitiziran (mt) duž plohe (111) ili frontalno; sitni listići hematita (hm) oko hematita *I. Jurković (1955)*

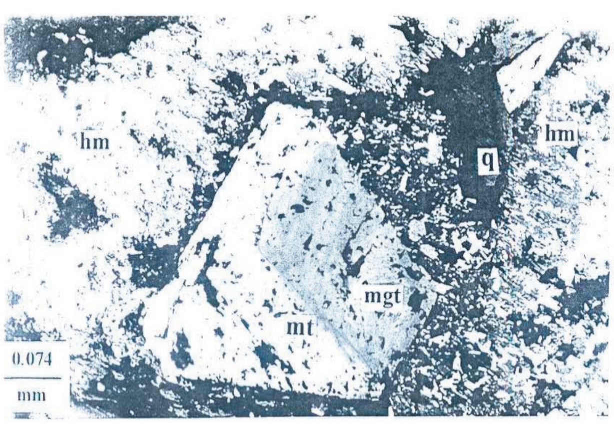

Plate I, photo 3 Porphyroblast of magnetite (mgt) strongly martitized (mt); dense mass of fine hematite leaves (hm)
Ploča I, slika 3. Porfiroblast magnetita (mgt), jako martitiziran (mt); gusta masa sitnih hematitnih listića (hm) *B. Šinkovec (1957)*

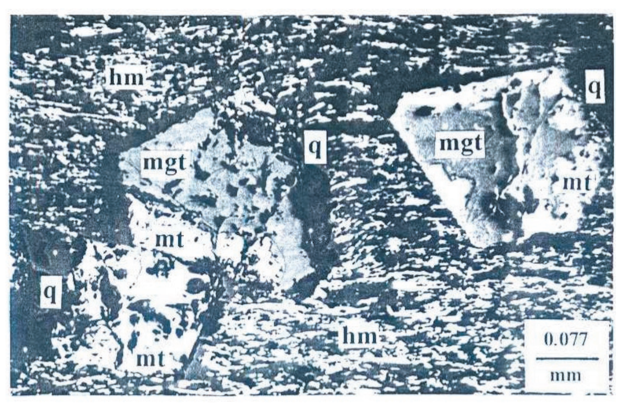

Plate I, photo 4 Cataclased magnetite porphyroblasts (mgt), partially or completely martitized (mt); dense strings of fine hematite leaves (hm); quartz (q)
Poča I, slika 4. Kataklazirani porfiroblasti magnetita (mgt), djelomično ili potpuno martitizirani (mt); guste trake sitnioh hematitnih listića (hm); kvarc (q) *I. Jurković (1955)*

Magnetite is visibly cataclased. Cataclasis has not equally strongly affected all the ore beds. The cataclases are of irregular form, very rarely along the crystallographic planes (111). Typically, the cataclasis is the result of the postore tectonic activity. This conclusion is based on the fact that the cataclases were not a conduit for progression of the process of martitization. Instead, it was already martitized individuals of magnetite that were affected by cataclases. The cataclased crystals of magnetite are in many areas cemented by a younger generation of quartz, which normally occurs in the rock in the form of the thinner or thicker veinlets cutting diagonally across the beds. This generation of quartz belongs to the posttectonic phase.

Magnetite is affected by the process of martitization in various stages of advancement; from the initial stage, where the grains of magnetite are transformed into martite only in certain marginal areas, to the fully martitized individuals ***(Plate I, photos 1 and 2).***

Martitization begins at the margins of crystals and advances either frontally or along the octahedral structural planes, or both. Thin lamellas created along (111) the magnetite spread into plates. The plates merge into increasingly large surfaces, until all of the crystal is transformed into martite. Interestingly, in certain thin beds magnetite is predominantly transformed into martite in the form of an extraordinarily fine net crystallographically oriented, while in other thin beds it is transformed by the so-called marginal martitization.

Martitization took place at relatively higher temperatures and under higher partial pressure of the oxygen. The most preferential direction was parallel to the schistosity of the rock, which is indicative of tectonic activity (pressures) during the process. In terms of chronology, the martitization of magnetite occurred after the formation of the porphyroblastic magnetite, and before the tectonic stage, during which magnetite was cataclased.

Hematite is concentrated in thin beds of varying thickness and with varying density of distribution ***(Plate II, photo 7).***

Individuals of hematite are either plated or short columnar. Dimensions are microscopically tiny, on average less than 50 microns long and less than 10 microns wide. Crystals of somewhat greater length are rare, while the small ones, measuring less than 10 microns in length, occur in significant numbers. Hematite is more abundant than magnetite. While magnetite beds regularly contain some quantity of hematite, sometimes even in very dense agglomerates, at the same time there are quite a few beds of hematite containing no magnetite at all. In many hematite beds, the hematite is spatially oriented. The crystals are arranged so that their longer edges are parallel to the schistosity (see ***Plate II, photos 1, 2, 3).***

This is particularly emphasized in those sections of the ore zone profile, in which the thin beds of quartz and chlorite alternate at microscopically short intervals. In such sections of the zone, a directed pressure was the most prominent. In thicker beds of quartzite, the hematite crystals are more irregularly arranged and, interestingly, they are thicker and have shorter columnar form. ***(Plate II, photo 5)***

In certain beds containing mainly chlorite, which show obvious signs of disturbance, the hematite plates are bent, folded and often in bundles. Very thin ***hematite*** needles of the second generation irregularly scattered and sparsely dispersed can be observed in the ***secondary quartz.***

In those beds where hematite has very densely crystallized, initial signs of hematite recrystallization were also detected.

The mode of hematite occurrence in the form of thin and extremely tiny plates and leafs, as well as its truly striking spatial orientation and connection with epimetamorphic schists, point to a metamorphic character of the ore deposit.

Hematite shows clear bire exion, particularly martite. Anisotropic effects are strong. Deep red internal re ections are occasionally visible in the air. In cedar oil they are abundant and more pronounced.

Stilpnomelane is particularly iron bearing mineral. It shows strong pleochroism in yellow-reddish-brown colours. Stilpnomelane occurs in the form of thin leaves or rays.

Lepidocrocite (Rubinglimmer) is vastly less abundant than magnetite or martite. It occurs perhaps to a minor extent in the last stage of martitization, and to a greater extent as a product of descending solutions circulating along the cataclases of magnetite. Very rarely lepidocrocite was found in gangue, in the parties that are more strongly disturbed, appearing in the forms of needles and spatially oriented series. It is silver-white, darker than hematite and has a lower relief.

Common limonite was identified in polished sections affected by the process of oxidation. Since magnetite and hematite are very resistant, the aformentioned process is very poorly developed. Limonite is easily recognized by colloidal forms and yellow-brownish internal re ections.

Secondary quartz occurs in younger fissures, acting as cement. Very often it cements also the cataclased crystals of magnetite.

Other minerals found in the orthogreenschists

The single minerals that were found and studied in the greenschists were described by different authors: meerschaum (sepiolite) by Tućan (1915); amphibole asbestos by Tućan (1922); epidote by Barić and Tućan (1925); actinolite-asbestos (amianthus) by Barić (1975); garnet and tourmaline by Marić (1959); chloritoid by Vragović and Majer (1980a, 1980b), then Majer et al. (1992/1993); amphibole, epidote, chlorite, albite, microcline and pyrite veinlets in the position of Zahurte,

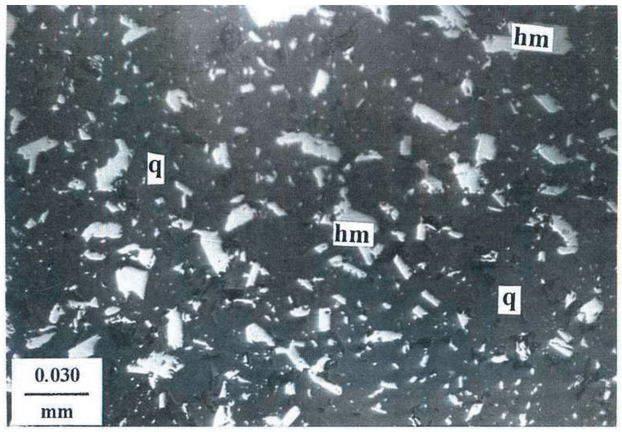

Plate II, photo 5 Irregularly arranged short columnar hematite crystals (hm) inside thicker quartzite bed (q)

Ploča II, slika 5. nepravilno poredani deblji, kratko stubasti kristalići hematite (bijelo) unutar debljeg proslojka kvarcita

I. Jurković, (1955)

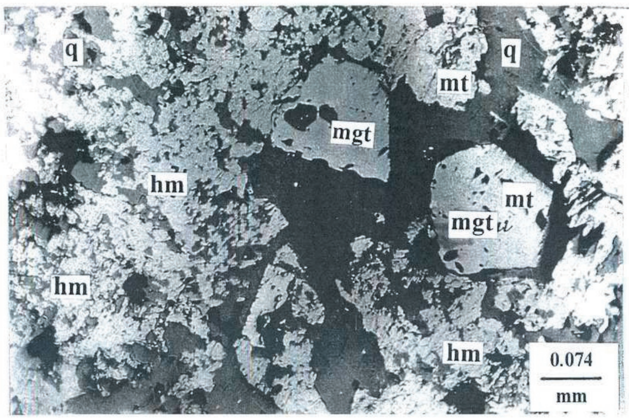

Plate II, photo 6 Irregular agglomeration of hematite crystals (hm) in fine grained quartz (q-black); two magnetite porphyroblasts (mgt) in initial phase of martitization (mt)

Ploča II, slika 6. Nepravilne nakupine hematite (hm) u masi kvarca (z, tamnosivo). Dva porfiroblasta magnetite (mgt) u početnoj fazi martitizacije (mt) *B. Šinkovec, (1957)*

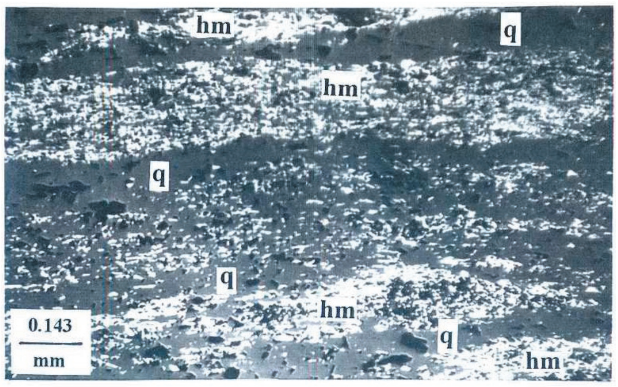

Plate II, photo 7 Alternation of hematite (hm) rich thin beds with thicker richer quartz beds (q)

Ploča 2, slika 7. Proslojci hematite (hm, bijelo) odijeljeni kvarcom (q, tamnosivo). Proslojci se razlikuju širinom i gustoćom

I. Jurković, (1955)

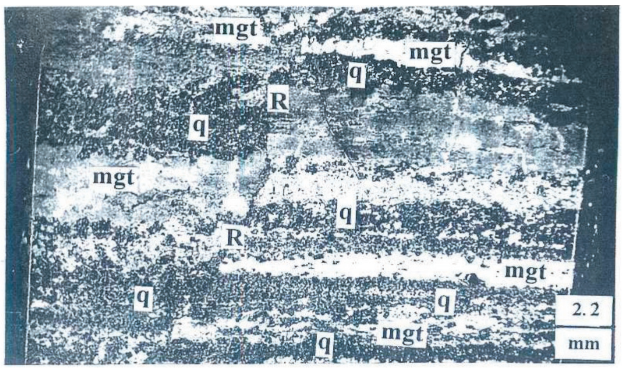

Plate II, photo 8 Magnetite thin beds (mgt) alternate with thicker quartz beds (q). R – microfault (sleap 5 mm)

Ploča II, slika 8. Proslojci magnetite (mgt, bijelo) u izmjeni s proslojcima kvarca (q, crnosivo). R - mikrorasjed sa skokom 5 mm.

B. Šinkovec, (1957)

barite with intercalation of bedded magnetite and chlorite in Bijelo Bukovlje, south of Brestovsko, by Čepelak et al. (1986), while Šinkovec et al. (1988) published the first paragenesis of the metamorphosed bedded barite occurrences south of Brestovac. They consist of barite as the main mineral, with thin beds of magnetite and chlorite. Subordinate minerals are stilpnomelane, quartz, muscovite, albite, pyrrhotite, chalcopyrite, apatite, martite. Barite grain is characterized by (L + V) inclusions, rich with CO_2. The $\delta^{34}S$ = 26,6 ‰ of the sulphate sulphur was defined by D. Šiftar. Belak and Tibljaš (1998) described garnet, omphacite, glaucophane, crossite and white mica from blue-schists in the source area of the Žitomirica brook, west of the village of Gornje Orešje. In his dissertation, Belak (2005) presented all results obtained by optical, chemical, and geothermobarometric investigations of the minerals from greenschists and blueschists in Mt. Medvednica.

Copper, lead, zinc and barite occurrences

Copper ore occurrences (Fig. 3)

In the Paleozoic-Triassic metamorphic complex of Mt. Medvednica some very small, only of mineralogical interest, copper ore occurrences were found. The most significant are: 1) one siderite vein with **chalcopyrite, pyrite, goethite, chalcocite and malachite** in the greenschists of the Mikulić brook was investigated by adit in 1860 (Čepelak et al., 1986; Marković, 1995). The selected samples of the crude ore gave 5.2, 14.2 and 17.1 % Cu; 2), **quartz** ore occurrence with **chalcopyrite, pyrite, sphalerite** and **malachite** in the metapelites south of the St. Jakob. 3) copper ore occurrence, north of the village Bačun.

Lead and zinc deposits (Fig. 3)

The small-sized lead-zinc deposit Sv. Jakob is situated on the southeastern slopes of the Mt. Medvednica. The host rocks are dolomites of unknown age, Upper-Paleozoic (Šikić et al., 1979) or supposed Triassic (Belak et al., 1995b,c; Belak 2005). The ore deposit occurs in the form of veins, veinlets, lenses and impregnations. The first detailed unpublished paragenesis gave Šinkovec et al. (1988). It consists of galena as the main ore mineral, subordinate are **sphalerite, pyrite, anglesite, cerussite, calcite, dolomite** and **quartz.** Radanović-Gužvica and Zebec (1995) identified small-crystals of wulfenite. Ore contains 485 g/t Ag (Pilar 1883).

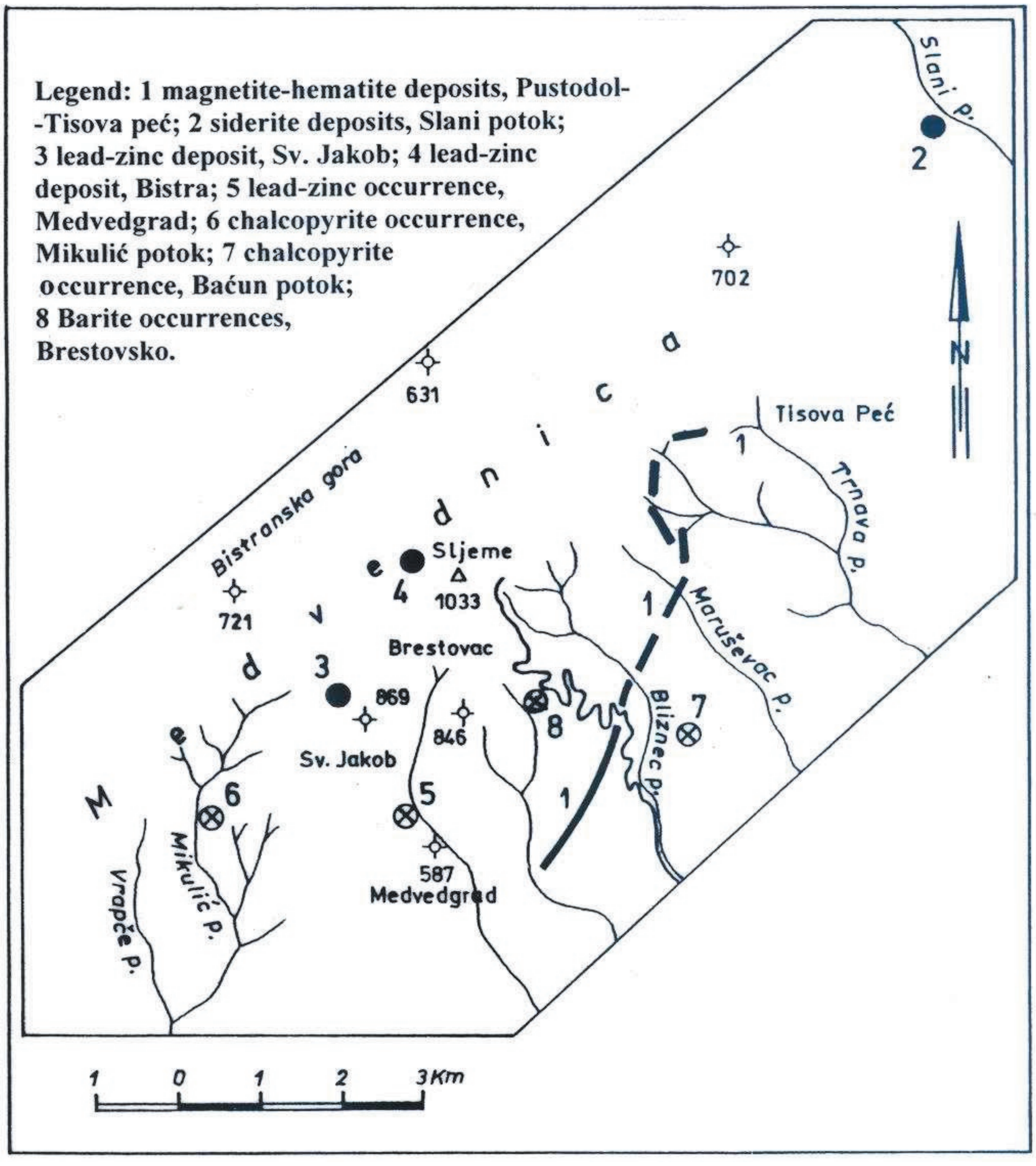

Figure 3 Iron, copper, lead-zinc, and barite old mines (•) and occurrences (◦) in the Paleozoic-Triassic methamorphic complex of Mt. Medvednica

Slika 3. Željezne, bakrene, olovno-cinkane i baritne rude bivših rudnika (•) te njihove pojave (◦) u paleozojsko-trijaskom metamorfnom kompleksu planine Medvednica

The data of the mining activity are preserved in the Archive of the Croatian geological survey, Zagreb. Some data concerning the ore deposit Sv. Jakob can be found in the papers published by Vrbanić (1883); Pilar (1883), Kišpatić (1901), Jurković (1962), Šikić et al. (1979; Čepelak et al. (1986), Marković (1995).

The ore deposits are mined by 5-6 adits and by numerous short crosscuts. The last cleaning of the underground works was executed between 1954 and 1956, later this mine was abandoned.

Borojević-Šoštarić et al.(2004), and Borojević-Šoštarić (2004) studied uid inclusions of calcite and quartz wafers. They determined homogenization temperature Th is (80°-230°C); composition (H_2O-NaCl-$CaCl_2$); and (7-19 equ. wt % NaCl) in uid inclusions. The stable isotope investigations were done on galena ($\delta^{34}S$ Pbs = 6.8 – 8.4 ‰, $\delta^{34}S$ ZnS = 8.4 – 10.1 ‰). Authors are convinced of MVT (Mississippi Valley type) ore mineralization formed under in uence of warm basinal brines mixed with less saline, colder meteoric uid.

Abandoned lead-zinc deposit **Bistranska gora** (French mines) is situated on the northwestern slopes of the Mt. Medvednica in the upper course of the Bistra brook. A series of irregular quartz-calcite veins with abundant galena stretching NE-SW with dip of 40°-80° toward NW occur in the carbonate rocks of unknown age. The paragenesis contains numerous accessory minerals: **sphalerite, chalcopyrite, pyrite, dolomite, marcasite, orpiment, anglesite, cerussite, goethite, chalcocite, covellite, malachite, azurite.** Crude ore is relatively poor (Šikić et al., 1939; Čepelak et al., 1986; Šinkovec et al., 1988; Marković, 1995). French count Carion opened here lead-zinc mine at the end of the 18. century with underground mining works (5-6 adits). The attempt of its restoration (1954-1956) was not successful.

Palinkaš (1988) studied lead isotopes on the galena samples from the Bistra deposit. The obtained values were 341 Ma and 293 Ma, both indicating Carboniferous age of the mineralization. Later, some geologists (Belak et al., 1995c, Belak 2005; Borojević-Šoštarić, 2004) claimed Triassic age. In such case lead from the Bistra deposit should be of B-type, like lead in the Bleiberg-Mežice deposits.

Discussion

In the published scientific papers and professional reports, there are very different opinions concerning the age of the Mt. Medvednica metamorphic complex, as well as the age and genetic type of the magnetite-hematite occurrences.

Neo-Proterozoic age of the iron-bearing host rocks is supposed by Šinkovec (1957), Miholić (1958), and Popović (1986c); Early Paleozoic age by Crnković (1955, 1963), Jurković (1962, 1995), and Pamić and Jurković (2002); Devonian-Carboniferous by Šikić et al. (1979), Basch (1983, 1995), Čepelak et al. (1986), Šinkovec et al. (1988); Belak, et al. (1995a), Šikić (1995) and Marković (1995, 2002); Early Mezozoic by Marić (1959); Middle Triassic by Belak et al. (1995b, 1995c); Middle-Upper Triassic – Lower Jurassic, but not excluding Early Paleozoic age by Belak (2005). The majority of these scientists think that the magnetite-hematite occurrences are genetically related to the gabbro-diabase magma of the Triassic or Paleozoic volcano-sedimentary formations. Some of them argued for itabirite type, or iron-quartzite-type. Solely Marić (1959) argued for the pneumatolytic-hydrothermal origin related to the Triassic gabbro-diabase magma.

In the continuation of this paper, the tectonic setting, paragenesis, structure and texture of all magnetite-hematite deposits of Neo-Proterozoic, Early Paleozoic and Triassic age situated in the Dinarides, the Pelagonides and in the Serbo-Macedonian Mass, will be compared with the Mt. Medvednica magnetite-hematite occurrences.

The Neo-Proterozoic, also called the Lower metamorphic complex of the Serbo-Macedonian Mass, contains numerous small stratiform ore deposits composed mostly of magnetite, and locally of hematite in the amphibolites of Mts. Pasjača and Čar-Sedlar and in the gneisses of the Žitni Potok area. The protoliths of these host rocks and ore deposits were volcanogenic-sedimentary and sedimentary formations. In the Ripheam-Lower Cambrian, the Upper or Vlasina complex is characterized by small stratiform magnetite deposits within the greenschists, locally in amphibolites of the Crna Trava and Lake Vlasina. The protoliths are also volcanogenic-sedimentary formations (Janković, 1990; Janković et al., 1997).

In the Cambrian-Ordovician fossiliferous schists of Mts. Stogovo, Karaorman, Slavej and Babuna (western Macedonia) numerous small-sized stratiform chamosite and magnetite deposits (20-38 % Fe) have been found. These deposits are also related to the Early Paleozoic volcanogenic-sedimentary association, dominantly basic in character (Petkovski and Ivanovski, 1980).

In the Drina-Ivanjica metamorphic complex, occur various small sized bedded iron and manganese small ore deposits, Cambrian and Ordovician in age, and underlain by Neo-Proterozoic. Different ore parageneses occur in the upwardly sequential zones: 1) Fe-chlorite (thuringite) with up to 15% magnetite; 2) Fe-chlorite with hematite; 3) magnetite and Fe-bearing quartzites and 4) magnetite-bearing zone (Kubat, 1969, 1974; Popović, 1983, 1986a, b,c; Popović and Tomičević, 1990). Ore occurrences are 0.3 to 1 m thick with 11-35 % Fe.

In the northeastern part of the Mid-Bosnian Schist Mountains (Busovača area) of presumed Cambrian-Ordovician age, a few ferruginous quartzites, 0.3-0.5 m thick, consisting of quartz, magnetite, Fe-chlorite, and hematite are interlayered in the Early Paleozoic metamorphites (Jurković, 1956, 1957; Hrvatović, 1996). A very interesting, although uncommon Cr-Fe-Cu-Zn-Ba-bearing spinel deposit, bounded to the basic metamorphic magmatic rocks, situated in the Early Paleozoic metamorphic complex of Busovača area, was studied by Jurković and Jakšić (1994) and Jurković and Slovenec (1998).

All Neo-Proterozoic and Early Paleozoic iron deposits are stratabound or stratiform. The parageneses, structures and textures are mutually very similar throughout the Dinarides and the Serbo-Macedonian Mass.

Triassic magnetite-hematite deposits occur only as iron skarns bounded to exo- and endo contact-metamorphic zones of gabbro-diorite intrusives. The biggest skarn deposits are genetically bounded to the Jablanica gabbro stock (Marić, 1929; Cisarz, 1956), followed by the Mt. Radovan skarns which are genetically related to the largest gabbro-diorite Triassic plutonic body (40 km^2) in the Dinarides (Majer and Jurković, 1958; Šarac and Pamić, 1981; Jurković and Pamić, 1999). Smaller skarn and veiny magnetite-hematite deposits are bounded to the small gabbro dykes at Ustirama and to the smaller albite diabase dykes at the village of Crima, both south of the town of Prozor. In the Triassic volcanogenic-sedimentary formations of the Konjic, Jablanica, Prozor and Donji Vakuf areas, only bedded red hematite, siderite and manganese oxides ores formed. The big red hematite-siderite deposits, were formed in Central Bosnia, in the Vareš area (Čelebić, 1967).

In the Čajniče area (SE Bosnia), very small pneumatolythic-hydrothermal low manganese iron deposits consisting of fine-grained magnetite, and a significant amount of pyrrhotite, subordinate pyrite, have been found. Gangue minerals are calcite and quartz. Ore contains 40% Fe, 0.3 % Mn, 20 % SiO_2, 2.8 % S. Ore deposits are in the form of irregular bodies and short veins which are situated in the contact areas between granosyenites and diorites with Middle Triassic sedimentary rocks and tuffs (Kulenović, 1987; Šarac and Pamić, 1981).

From the above mentioned review of the magnetite-hematite deposits in the Dinarides and the Serbo-Macedonian Mass, it is obvious that two different genetic types of these deposits have been formed. The older iron type is Neo-Proterozoic and Early Paleozoic in age, relatively small, and stratiform, related to the volcanogenic-sedimentary formations, and basic in character. The paragenesis of this type consists of magnetite, hematite, quartz, chlorite ± stilpnomelane, ± chamosite, ± iron-chlorite (thuringite) + white mica, ± actionolite, ± epidote, ± white mica ± rare Fe-Cu sulphides.

The younger genetic type, Middle Triassic – Upper Triassic-Lower Jurassic (?) in age, is characterized by small and middle sized exo- and endometamorphic skarns, locally by very small pneumatolytic-hydrothermal irregular bodies and veins. In these deposits the main minerals are Si, Al, Fe, Ca and Mg gangue skarn minerals. Irregular bodies, beds, veins of magnetite, less hematite, then pyrrhotite and pyrite occur within skarn. In the pneumatolytic hydrotermal deposits the main ore minerals are magnetite and Fe-Cu sulphides, while hematite is subordinate. All these Triassic magnetite-hematite deposits are related either to the gabbro-dioritic stocks and dykes or to the small granosyenite and diorites bodies.

The magnetite-hematite deposits in the Medvednica Triassic-Paleozoic metamorphic complex are by their structure, texture, genetic type and paragenesis of the ore and gangue minerals, very similar or relevant to the iron deposits of the Early Paleozoic metamorphic complexes throughout the Dinarides and the Serbo-Macedonian Mass.

Although the Medvednica type of magnetite-hematite ore deposit is not known in the Triassic formations of the Dinarides, in theory it may be possible to prove the Triassic age of these deposits. The solution of this problem requires juxtaposition of all the known arguments for the Early Paleozoic hypothesis and the Triassic hypothesis.

a) The age of the separate lithostratigraphic unit. The best known unit is the Vidovec unit (S_1 – C_3), but it is not an iron-bearing unit. This unit covers 1/3 of the Medvednica metamorphic complex. The Vidovec unit borders with the Miocene on the SE side (Šikić et al., 1979) and with the Tusti breg – Vila Rebar units on the NW side (Belak et al. 1995c; Belak, 2005). Đurđanović (1973), and Belak et al. (1995c) identified Middle – Upper Triassic fossils in the SW part of these units. Belak et al. (1995c) found Middle Triassic conodonts in the area between the Bliznec and Markuševac brooks. Đurđanović (1973) could not determine conodonts from the three locations in the upper course of the Trnava brook (Fig. 1b). In the last third of the Mt. Medvednica metamorphic complex (composed of the Stara Pila, Risnjak, Stari potok, Adolfovac and Sljeme units), detectable fossils have not been found. This fact resulted in varied or even con icting opinions concerning the age: Paleozoic age (Šikić et al., 1979, Belak et al. 1995a), and Triassic age (Belak et al., 1995b, 1995c; Belak, 2005). Belak (2005) stated his opinion that the formations of the Risnjak and Stara pila units were deep marine, favouring the Triassic, although not excluding the Early Paleozoic age.

b) Isotopic analyses.

1) Pb isotopes were investigated in the galenas from the old lead-zinc mines (St. Jakob and French mines) situated in the Stari Potok unit (Palinkaš, 1985; Šinkovec et al. 1988). The value obtained by the single-stage evolution model was 293 Ma (Gzelian, Upper Carboniferous), while 341 Ma (Visean, Lower Carboniferus) was obtained by two-stage evolution model. The measurements were made at the Florida State University, Talahassee. If the application of some other methods of measurement proves the Triassic age of limestones and dolomites in

which the Pb-Zn ore deposits of Mt. Medvednca are formed, it would be the B-type of lead, like the lead found in the Triassic Pb-Zn ore deposits at Bleiberg (440 Ma) and Mežice (420 Ma). This type of lead can be interpreted by remoblization of the older, Carboniferous Pb-Zn ore deposits.

2) The barite from the metamorphosed barite deposit of Brestovsko (Jurković, 1962; Šinkovec et al., 1988) gave $\delta^{34}S$ = +26.6 ‰ (made by D. Šiftar). This value ranging from +22 to +31 ‰ corresponds to the Upper Devonian sea water sulphate. In the Cambrian $\delta^{34}S$ values of sea water sulphate vary, this range is from +26 to +35 ‰, and in the Middle Triassic-Lower Jurassic from +15 to +17 ‰ (Claypool et al., 1980). According to these values, the Stari Potok unit and the Brestovsko area shoud be Paleozoic in age.

c) Metamorphism as arguments

Šikić et al., (1979) noticed the metamorphosed pelitic-psamitic intercalations of quartzose microbreccias and conglomerates in the parametamorphites. Pebbles, subangular or subrounded, have diameters ranging from 2 mm to 2 cm. In the lower course of the Bliznec Potok brook, Belak et al., (1995a) found grey and dark grey, 11 m thick metaconglomerate beds. Pebbles, ranging from a few mm to 7 cm in diameter, consist of sparitized micrites and pelmicrites, as well as of marble characterized by very different structures and textures. Their source material are carbonate rocks. Belak et al. (1995a) believe that formation of these thick conglomerate beds indicates powerfull energetic conditions during the sedimentation process.

Pamić and Jurković (2005) are of the opinion that, on the basis of the geological and isotopic age, the Mt. Medvednica metamorphic complex had two-phase dynamic evolution. The older deformation phase took place in Upper Carboniferous, when the Silurian-Carboniferous formation was affected by the main Variscan orogenetic phase. Later, in Lower Cretaceous, it was affected by the penetrative metamorphism (overprint) which effaced all primary Variscan structures. In the Dinarides, all Paleozoic complexes survived similar evolution. Neubauer et al. (1999) advocated the same opinion concerning the Pre-Alpine Paleozoic complexes inside the Inner Alpine belt.

The rocks of epidote-amphibole facies formed at 4-5 kbar and 400-500°C have been found on the WNW, SW and N slopes of the Puntijarka ridge, which is situated ENE of Veliko Sljeme. Kišpatić (1906) was the first to find garnet phyllite and disthen-quartz phyllite on the Puntijarka ridge. Marić (1959) described garnet-biotite schist (hornfels). Crnković (1963) found samples of chloritoid schist which were examined by Vragović and Majer (1980a,b). They determined a chloritoid schist with very high Fe/Mg ratio of 5-6: 1, supposing 4.5-5 kbar and t = 400-500°C. They were the first to indicate subduction processes during formation of these schists. In the same area, Šikić et al. (1979) found chloritoid schists (defined by P. Raffaelli, 1972). Belak (2005) investigated quartz-chlorite-muscovite chloritoid schists, characterized by chloritoid porphyroblasts (0.75-1.5 mm) with 87 %. Fe, 1.5 % Mg and 1.4 % Mn. They were affected by two-phase deformation.

d) Ore bearing units

Lead and zinc deposits occur only in the Stari Potok unit which is Paleozoic (S_1 - C_3) (Šikić et al., 1979) or Triassic in age (Belak, et al. 1995c, Radovanić-Gužvica and Zebec, 1995, Borojević-Šoštarić, 2004, Belak, 2005).

Iron ore (magnetite-hematite) deposits occur only in the very narrow, 6 km long Stara Pila unit, characterized by deep marine facies, supposed T_2-T_3-J_1 or less probably Early Paleozoic in age (Belak, 2005).

Conclusion

The Medvednica iron ore deposits display paragenesis, structure, and texture identical to all other Neo-Proterozoic and Early Paleozoic magnetite-hematite deposits in the Dinarides and in the Serbo-Macedonian Mass. Protoliths are sedimentary submarine limonite deposits related to the volcanogenic formations basic in character, metamorphosed later during regional metamorphism. Such type of magnetite-hematite deposits has not been discovered in the Dinaridic Triassic formations. There occur only contact-metamorphic skarns and rare pneumatolytic-hydrothermal bodies and veins.

According to Belak (2005) the iron-bearing zone in Mt. Medvednica (the Stara Pila unit) is characterized by deep marine facies, lack of detectable fossils and metamorphism in the lower greenschist facies (chlorite and stilpnomelane zone),

The Stara Pila unit is built up of the green orthoschists, metaradiolarites, paraschists and thin interlayered metamorphosed and marbleized carbonate rocks. The carbonate rocks comprise non-identifiable fossils, “filaments” and recrystallized carbonatized radiolarites, but no conodonts. These rocks are adjoning to the supposed Anisian rocks of the Tusti Breg unit and therefore, according to Belak (2005), this unit is Triassic in age.

However at present the arguments for the Early Paleozoic age of the Mt. Medvednica magnetite-hematite ore deposits are more convincing.

In the case that these deposits are Triassic age, which is theoretically possible, it would represent a discovery of an uncommon genetic type in the Triassic of the Dinarides, which would be very interesting for economic geologists.

It is possible that the magnetite-hematite bearing Stara Pila unit had reached the epidote-amphibole metamorphic facies during the Cretaceous metamorphism. Such metamorphic facies enables formation of magnetite porphyroblastic texture. Chloritoid porphyroblasts in the Puntijarka area were formed under similar PT conditions. Later, by retrograde metamorphism the mineral assemblages of epidote-amphibole metamorphic facies of these units were replaced by mineral assemblages of lower greenschist facies. Very strong martitization of magnetite porphyroblasts indicates a possible similar metamorphic process.

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