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SEDIMENTARY LOW-MANGANESE HEMATITE DEPOSITS OF THE BUKOVICA AREA IN THE NORTHWESTERN MT. PETROVA GORA, CENTRAL CROATIA

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Middle-Permian Gröden deposits crop out on the surface of 0.8 km^2 in the Bukovica area and on the surface of 0.8 km^2 in the Mt. Loskunjska gora in the NW part of the Petrova gora Mountain. One half of the Bukovica Gröden deposits contains in its lowest parts 1 to 5 m (in average 2.5 m)thick hematite bed cutted in blocks by NE–SW stretching vertical, normal and reverse faults. The hematite bed is unconformably underlain by Lower Permian quartz-wackes (subgraywackes) intercalated with shales intercalations. Ore deposit is explored by 308 boreholes (10509 m) and by numerous adits, inclines and crosscuts on the underground surface of 0.4 km^2. From 1936 to 1941 and from 1953 to 1969 has been exploited 183000 t of ore with (in wt %): 34.0 SiO_2, 2.9 Al_2O_3; 59.0 Fe_2O_3; 0.15 MnO; 0.7 CaO; 0.4 MgO; 0.1 P, 0.37 S; 1.25 l.o. ign. Proven remaining ore reserves are 250.000 t. Paragenesis is investigated by microscopy of thin and polished sections, XRD, DTA, AAS analyses and by sedimentological analyses. Paragenesis major minerals are of hematite and quartz, with subordinate stable lithoclasts, muscovite (sericite) and scarce kaolinite, calcite, dolomite, and barite. Accessories are zircon, rutile, tourmaline, amphibole, garnet, apatite. Epigenetic veinlets and small nests are built up of quartz or calcite as the main neominerals associated with siderite, barite, kaolinite, pyrite, gypsum. Iron from the Bukovica hematite ore originated by land weathering during hot climate and transported by rivers and underground waters deposited in river beds, in flood plains and in shallow sea. Precipitation of the Bukovica iron ores took place after the Saalic orogenetic phase. At Hrastno (SE Slovenia) and at Rude nearby Samobor (Croatia), similar hematite deposits were found.

Ključne riječi: Srednjopermska niskomanganska hematitska ležišta; geotektonski položaj; XRD, AAS, DTA analize; Morfologija; Parageneza; Geneza; Bukovica; Hrvatska

Srednjopermski Gröden sedimenti pokrivaju površinu od 0.8 km^2 u području Bukovice i 0.8 km^2 u planini Loskunja u SZ dijelu Petrove gore. Oko polovine Gröden naslaga u Bukovici sadrži u svojim najdonjim dijelovima 1–5 m (u prosjeku 2,5 m) debeo sloj hematita rasjedan u blokove vertikalnim, normalnim i reversnim rasjedima pružanja NE–SW. Sloj hematita leži nesukladno na donjopermskim kvarcnim grejvakama (subgrejvakama) s interkalacijama šejlova. Rudno je ležište istraženo sa 308 bušotina (10509 m) i brojnim potkopima, galerijama, prečnicima i niskopima na podzemnoj površini od 0,4 km^2. Od 1936. do 1941. te od 1953. do 1969. izvađeno je 183000 t rude sa (u mas %) 34,0 SiO_2; 2,9 Al_2O_3; 59,0 Fe_2O_3; 0,15 MnO; 0,7 CaO; 0,4 MgO; 0,1 P; 0,37 S i 1,25 g.ž. Dokazane preostale rezerve iznose 250 000 t. Parageneza je istražena mikroskopski u providnim i rudnim preparatima, s XRD, DTA, AAS analizama te sedimentološkim analizama. Glavni minerali su kvarc i hematit s podređenim stabilnim litoklastima, muskovitom (sericitom), oskudnim kaolinitom, kalcitom, dolomitom i baritom. Akcesorije su cirkon, rutil, turmalin, amfibol, granat, apatit. Epigenetske žilice i mala gnjezdašca izgrađena su od kvarca ili kalcita kao glavnih neominerala asociranih sa sideritom, baritom, kaolinitom, piritom i gipsom. Željezo hematitnog ležišta Bukovica potječe iz kore trošenja na kopnu za vrijeme vruće klime i transportirano je rijekama i podzemnim vodama te taloženo u koritima rijeka, naplavnim ravnicama i u plitkim unutarnjim morima. Taloženje željezne rude u području Bukovice nastalo je nakon salske orogene faze. Kod Hrastnog (JI Slovenija) i kod Ruda blizu Samobora (Hrvatska) nađena su slična hematitska ležišta.

Introduction

In Mt. Petrova Gora (MPG) in central Croatia, sedimentary low-manganese hematite deposits occur only in the Permian Gröden beds. In the northwestern parts of MPG, unique outcrops of the Gröden beds are found **(Fig. 1)**. In Mt. Loskunjska gora, southwest of the River Radonja Gröden beds occur on the surface of 0.8 km^2, but unfortunatelly without any hematite occurrences. Further northeastward, in the upper courses of the brooks Bukovica and Živkovići, the Gröden beds occur with the surface area of about 0.8 km^2. Here, the Gröden beds are orebearing and in the area between the Bukovica brook and its tributary Svinjarski brook was active a mine during 1936–1941 with temporary breaks, and from 1953 to 1969.

The ore-bearing area is situated between the small town Vojnić in the south and Utinja railway station on the railway line Karlovac–Sisak in the north **(Fig.2)**.

Literature data on the geology and ore deposits of MPG

Geology. Hacquet (1789) published first data on Palaeozoic schists of the MPG area. On the first geological maps published in 1832 and revised in 1847 were separated Carboniferous formations in the central part of MPG, Mesozoic formations in its western part, Cenozoic formations in its northern part and diorites in the area nearby Topusko. Stoliczka (1861/1862) and Stur (1861/1862; 1863) described Gaithalian schists represented by schists, sandstones and quartz conglomerates which are surrounded by the Werfenian beds, Middle Triassic dolomites, melaphyres, greenstones and Cenozoic formations. Hauer (1867/1871), Tietze (1872), Pilar (1873) and Koch (1934) presented additional geological data on MPG.

Jurković (1958) with B. Šinkovec, D. Bošković and M. Gazarek mapped (scale 1:20000) and studied the southern barite-bearing area of MPG. They separated Late Carboniferous–Early Permian formations which are represented by shales deposited under unstable shallow-water conditions which grade upwards into microbrecciated subgraywackes interlayered with shales or quartz conglomerates. Subsequent tectonic movements gave rise to shallowing of the sea in which under presumed semiaridic climate quartz sandstones, quartz con-

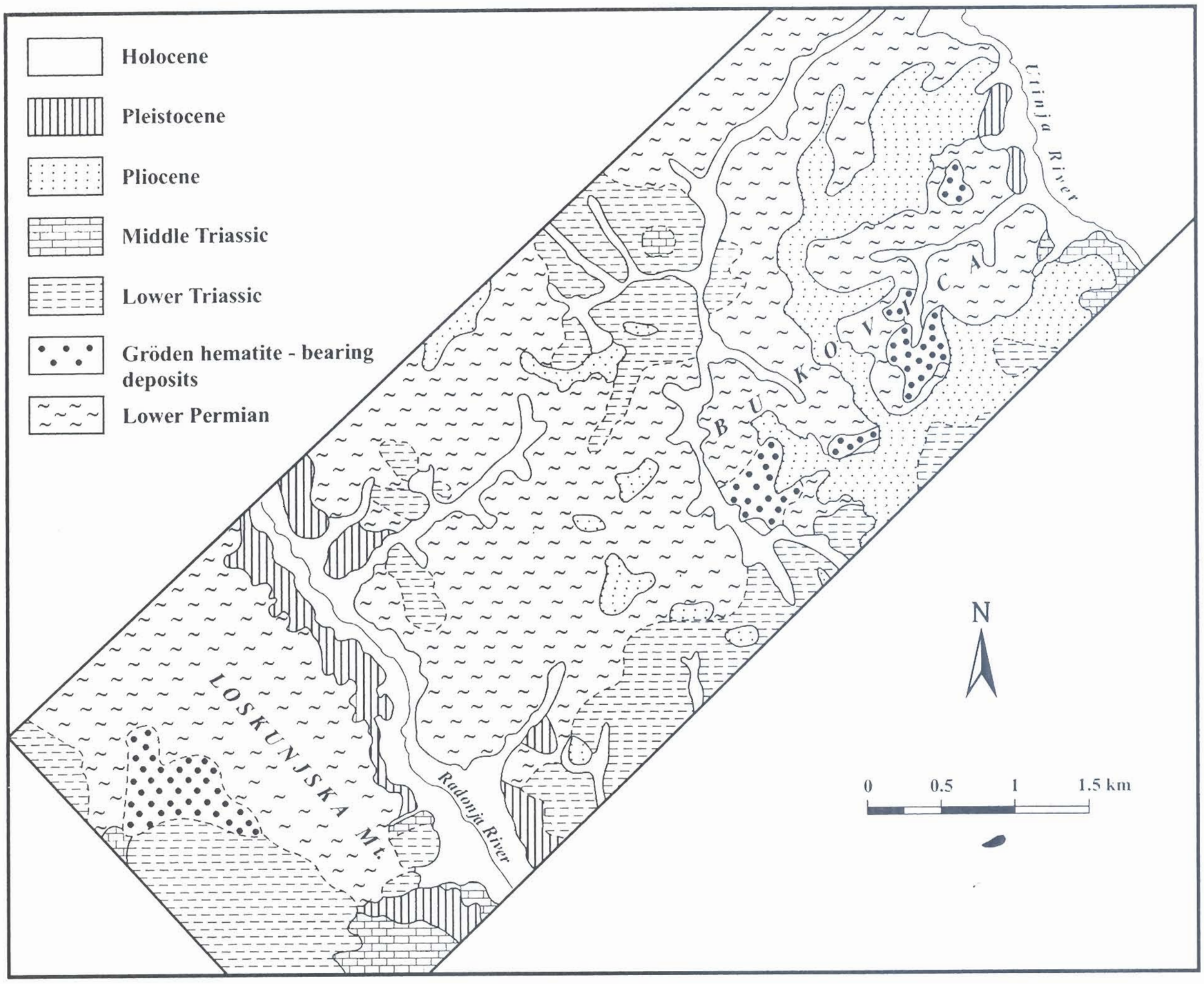


Fig. 1. Geological map of the area between Radonja and Utinja rivers in the NW - Petrova Mountain (mapped by D. Devidé - Nedĕla, L. Nikler and B. Sokač, 1960)

glomerates and, in some places, polymict »brecciated« coarse-grained conglomerates with fragments of older shales and subgraywackes were deposited. These rocks, some of which contain hematite enriched cement, are host rocks of significant barite deposits of the southern part of MPG and of siderite occurrences with abundant quartz and minor Fe, Cu and Zn sulphides in its northern part. Gröden beds rich in hematite cement were mapped in the southwestern part of MPG. The beds, which host hematite deposits in the area of Bukovica, are overlain by Scythian sediments.

Devidé-Neděla et al. (1960) mapped (scale 1:25.000) the broader area of MPG including the Bukovica hematite-bearing area. They separated older Upper Palaeozoic widespread shales and sandstones interlayered with quartz conglomerates and breccias, and unconformably overlying Permian Gröden beds (sandstones and shales, locally with hematite deposits) which occur as a narrow zone only in the area of Mt. Loskunjska gora and Utinja.

On the basic geological map, sheet Slunj (scale 1:100000), Korolija et. al. (1981) separated, as the oldest rocks, Lower Permian turbidites represented by rhytmic alternation of shales, siltites, sandstones with subordinate fine-grained conglomerates. Most common rock is unmature graywacke sandstone. The synorogenic flysch sequence is, after the Saalic orogeny, unconformably covered by Middle Permian coarse-grained quartz sandstones and conglomerates (protoquarzites) in which barite deposits occur. Overlying Permo–Triassic is represented by shales and varieties of graywackes and uppermost Permian Gypsum evaporite formation with some dolomites covered by Scythian clastic sediments.

Ore occurrences of MPG (Hauer, 1859; Stur, 1861/1862;1863; Pilar, 1873; Kišpatić, 1878, 1907; Marić, 1937; Tućan, 1947; Jurković, 1958, 1962).

a) Lower Permian zone of the eastern part of MPG, streching in the north-south direction, (Slavsko Polje–Kladuša), is 13 km long with a maximal width of about 4 km. It is built up of quartz sandstones, quartz conglomerates and, in some places, brecciated conglomerates which represent host rocks for significant monomineralic barite deposits in the southern part of the zone and minor quartz-siderite ± sulphides in its northern part.

b) In the Bukovica area, Gröden beds are host rocks of low-manganese hematite deposits. At Cetingrad and Mracelj, small gypsum-anhydrite deposits are found.

c) At Gornji Budački, Kuplensko and Cetingrad, sedimentary manganese oxide ores are found in Middle Triassic sedimentary rocks.

d) In the northern and northeastern part of MPG many occurrences of limonite, kaoline and manganese oxides in Pliocene sediments occur.

Hematite deposits of the Bukovica and Mt. Loskunjska gora areas

The Bukovica and of the Mt. Loskunjska gora areas are composed of Upper Palaeozoic and Scythian clastic sedimentary rocks covered by partially eroded Pliocene sediments (Devidé-Neděla, 1950, 1962; Jurković, 1958; Lukšić et al., 1981; B. Šćavničar, 1981).

Hematite deposits, which occur only in the Bukovica area, are spatially and genetically related to Late Palaeozoic Gröden beds (Tiringer, 1953; Ferenčić, 1956; Jurković, 1958, 1962; Šinkovec, 1961; Čop, 1962; Šimunić, 1972).

Geology of the Bukovica area (fig. 2)

Lower Permian Permo-Carboniferous

These rocks built up most of the area presented geological map on the **fig. 2.** Along the valleys of Bukovica, Svinjarski and Živkovići brooks, and Utinja river good outcrops of these rocks can be found. In the area of Matići, Grudići and along Popovac brooks, isolated and small outcrops occur. Rocks are in tectonic contact with all younger units.

The most widespread rocks are micaceous subgraywackes, subordinate are protoquartzites and coarse-grained quartz sandstones, more or less conglomeratic, and scarce are conglomerates. The sandstones are interlayered with shales and sandy shales grading, in some places, into slates and phyllites. In a few places fossil plant remnants (Calamites) and brachiopods' (Productus?) are found. Predominant sandstones show variations in sorting, angularity, proportions of matrix and muscovite, and granularity.

The oldest members occur in the Kartalije area and younger rocks, with decreased proportions of shales are found further southwestward. The whole unit has flysch features and originated in shallow, reductive environments under rapid erosion of the adjacent land.

Most of sandstones belong to feldspar-lithic graywackes. In immature detritus, quartz (60%) predominates over feldspars and lithoclasts and subordinate phyllosilicates and carbonates. Quartz is either irregular and rarely elongated and then heterogeneous or monocrystals, optically anormal and polycrystals, commonly sutured. Lithoclasts are stable, represented by quartzite, microquartzite, chert, granite, scarce volcanics and tuffs, and unstable, represented by pelitic schist, shale, phyllite, quartz-muscovite schist and sericite-chlorite schist. Feldspars (12–20%) are albite-oligoclase and scarce microperthite and orthoclase. Phyllosilicates are represented mainly by muscovite with subordinate biotite and chlorite which also make up pseudomatrix. Accessories are subangular green tourmaline, rounded zircon and subangular apatite. Subordinate matrix is of contact-type or pore-type, or pseudomatrix and is composed of illite, chlorite, quartz and scarce diagenetic carbonate.

In the rocks, small quartz veins (borehole U1), quartz veinlets with pyrite (V4 and M1), quartz-calcite veinlets (V5), pyrite impregnations (M3 and U2), pyrite nests and fragments of chlorite schist (P24) are frequently found.

Feldspar-lithic graywackes originated by strong erosion and rapid sedimentation nearby a high relief under cold and humid climate. They are characterized by moderate or weak sorting, dense packing and mainly irregular subangular grains.

Middle-Late Permian (Gröden sediments)

The end of the Lower Permian cycle is marked by a regional unconformity that represents a sedimentological gap. The Mid-Permian tectonic activity was responsible for this event. Very similar conditions were in the Southern Alps and in the adjacent Periadriatic regions (Broglio-Loriga & Cassinis, 1992).

Irregular thickening and thinning of the Gröden sediments over short distances suggests that sedimentation took place in a significantly differentiated topographic setting repeatedly affected by synsedimentary tectonics. Footwall rock surfaces are uneven, beds generally dip southward, but in some boreholes they are steep: 80° (borehole V_4), 45° (U_3) and very steep (U_1 and V_5), whereas Gröden deposits dip only under 5–10°. The Gröden Formation consists preponderantly of terrigenous clastics which were deposited in a semiarid setting. Fragments and pebbles of the clastic beds are derived from igneous, sedimentary and metamorphic rocks. Clastic facies represents former alluvial fans, braided stream deposits, flood plain deposits (overbank deposits), flood plain lobe, anastomosing stream, meander bar (point bar deposits), channel bar, detrital fan, inshore zones of lakes and shallow sea.

The lower part of the Gröden formation is composed of red, reddish, violet-brownish, grayreddish and pinkish sandstones, locally alternating with gray, greenish-gray and whitish sandstones. Size of irregular or elongated grains is commonly 0.03–0.2 mm, sphericity is low and sorting is moderate. In detritus quartz predominates over lithoclasts (quartzite, quartz-siltite), muscovite and very rare feldspar. Matrix is fine-grained quartz and sericite with subordinate hematite and, in some places, barite.

Hematite ore is included in the lowermost part of the Gröden formation composed of variegated quartz sandstones, conglomeratic sandstones, locally of breccia-like sandstones with abundant hematite matrix, strongly hematitized sandstones (15–30% Fe_2O_3) and hematite ore beds with 40–65% Fe_2O_3 or 35–45% Fe. Detritus of the sandstones is composed mainly of quartz with subordinate lithoclasts and rare muscovite. Matrix, composed mainly of hematite, fills pores and replaces frontally particles penetrating inside them in form of fine needles and minute plates. Matrix is composed of quartz and sericite. Hematite is frequently inserted along fissures and cracks (see microphotographs on the **Plate I** and **Plate II**).

Upper part is composed mainly of greenishgray, gray and whitish sandstones or conglomerates. Detritus is mature, sphericity of particles is high with comparatively good sorting. Quartz predominates over lithoclasts (quartzite, chert, igneous rocks) and scarce muscovite and feldspar. Subordinate matrix is composed mainly of chemogenic quartz and sericite. Accessories are green tourmaline and rounded zircon.

The Gröden sandstone series show evidence of diagenetic, epigenetic and retrograde alterations.

Lukšić et. al., (1981) identified in the Gröden formation six sedimentary phases (rhythms) which gave going upwards: first rhythm: hematitized sandstones (1–6 m); second rhythm: weakly hematitized sandstones with decreased size of grains, moderately sorted; third rhythm: »mud pebbles«, pebble conglomerates, breccia-conglomerates with fragments of schists and sandstones, characterized by irregular and cross-bedding, grading into conglomeratic sandstones and course-grained sandstones. The uppermost part includes moderately sorted middle-grained sandstones with scarce matrix (»grainflow«). This is a unique graduated unit; fourth and fifth rhythms: coarse-grained conglomeratic sandstones grading into medium- and finegrained sandstones in the uppermost parts; sixth rhythm: medium-grade sandstones and siltites with lamination due to colour differences and granularity, intercalated with fine-grained sandstones in the uppermost parts. Deposition took place in shallow marine environments under oxidizing conditions in the proximal zone. In older units predominate reddish and violet rocks and for the younger units are characteristic greenish and whitish colours.

The Permian Gröden (Val Gardena Sandstone) sequence is overlain by the shallow-marine Lower Triassic Werfenian Formation.

Early Triassic

Lower Triassic rocks are represented by fossiliferous variegated sandstones and shales. The Upper Permian Bellerophon formation is lacking in the Bukovica area, although it is known at Cetingrad and Mracelj bearing small gypsum-anhydrite deposits. In upper courses of the Bukovica brook and east of Međeđak grayishpinkish sandstones and violet siltites and shales occur. Detritus is represented with oval and spheric quartz, and mica. Here, these sediments are in tectonic contact with Early Permian and Gröden formations.

Middle and Late Triassic

On the left bank of the River Utinja, light gray and gray bedded fossiliferous dolomites occur (in the area out of the map).

Pliocene sediments unconformably overlie Permian and Triassic formations and frequently occur as erosional remnants 0–40 m thick. The Pliocene is represented by quartz sands, gravels, limonitized sandstones with mature detritus of quartz, quartzite, quartz schist and chert. The rocks are light gray or yellowishbrown in colour and horizontally bedded. In basal part, cement is commonly composed of limonite.

Pleistocene represented by sandy clays, loams, gravels and sands with rare limonite concretions is found only on the left bank of the Bukovica brook, opposite of the location Kasipovac.

Holocene is represented by clays and sands. They occur along the valleys of the brooks Bukovica, Svinjarski and Živkovići and their tributaries.

Tectonics

The Bukovica area is characterized by radial tectonics and all geological boundaries are faulted. The Gröden beds are strongly eroded and subsided along the faults. SW–NE-striking faults predominate over cross-cutting NW–SE and N–S directed faults. The faults are younger than the Late Triassic and older than the Pliocene. Lower Permian formations are strongly folded and faulted.

The highest altitude of Gröden sediments is on the Grudići-Pekići crest from where they come down from both sides towards the Bukovica brook in the south and towards the Svinjarski brook in the north. Some isolated Early Permian blocks included within the Gröden beds suggest inlluence of strong radial tectonics.

Data on sedimentological analyses

In **Table 1** are presented results of sedimentological analyses of rock and ore samples from the Bukovica area done by Obradović (1969). The sampling was organized by the first author. Analyzed samples were taken from hanging wall rocks (No. 274), hematite bed (No. 273) and footwall rock (No. 272).

The hangingwall rock is a very fine-grained sandstone, well sorted with low mode and skewness >1. The hematite-bearing rock is middle-grained sandstone, well sorted with skewness <1. The footwall rock is a medium-grained sandstone, well sorted, with high mode and skewness <1. Compositional differences of light and heavy fractions are as follows: **Light fraction:** lack of muscovite in hangingwall rock and hematite bed and its high content in footwall rock; higher content of orthoclase and weathered plagioclase in footwall rock. **Heavy fraction:** muscovite, tourmaline, garnet and amphibole occur in footwall rock but not in hanging wall rock; apatite and barite lack in footwall rock but not in the hanging wall rock; apatite and barite lack in footwall rock but are present in hanging wall rock. Zircon content is high in hanging wall and magnetite in footwall rock. Heavy fraction of the hematite is very similar as in footwall rock indicating that the first rock represented source material for unconformably overlying hematite bed.

Geology of the Mountain Loskunjska gora

On **Fig. 2a** is presented only the central segment of the geological map of the Mt. Loskunjska gora covered with Gröden sediments (Lukšić et al., 1981; B. Šćavničar, 1981). Stratigraphy, petrology and tectonics are almost identical as in the Bukovica area. Besides some small hematite ore fragments, so far, a single one autcrop of hematite ore bed has not been discovered.

Hematite deposits in the Bukovica area

History of the Bukovica mine

First mining explorations accompanied by modest production of hematite took place during the first world war in the Kasipovac and Bukovica brooks and was organized by »Ganz Company«, Budapest. Since 1920, the mining company »Željezni majdan i talionice, d.d. Ljubljana« intensified mining works and exploitation of low-manganese hematite ores, supplying the restored old ironworks in Topusko and the newely constructed ironwork in Jesenice (Slovenia). This company was the owner of the mining licence during the period 1919–1930.

In the period 1930–1947 the mining activity was organized by the company »Kranjska industrijska družba Jesenice (KID)« and by its enterprise »Željezni majdan i talionica d.d Ljubljana«. At the locations Kasipovac, Plandište, Popovac brook, Črna Jama, Pekići and Grudići, detailed mining explorations were carried out. Only prospecting trenches, shallow shafts and short adits were performed in the drainage basin of the Svinjarski and Živkovići brooks. The mining licence »Gizela I–VI«, covering 216 ha was alloted in 1936. Results of the mining activity of the Bukovica mine are presented in **Table 2** (Tiringer, 1953).

During the second world war (1941–1945) the Bukovica mine was not active. Since its nationalization in 1947, the owner of the mining licence was first »Rudnik

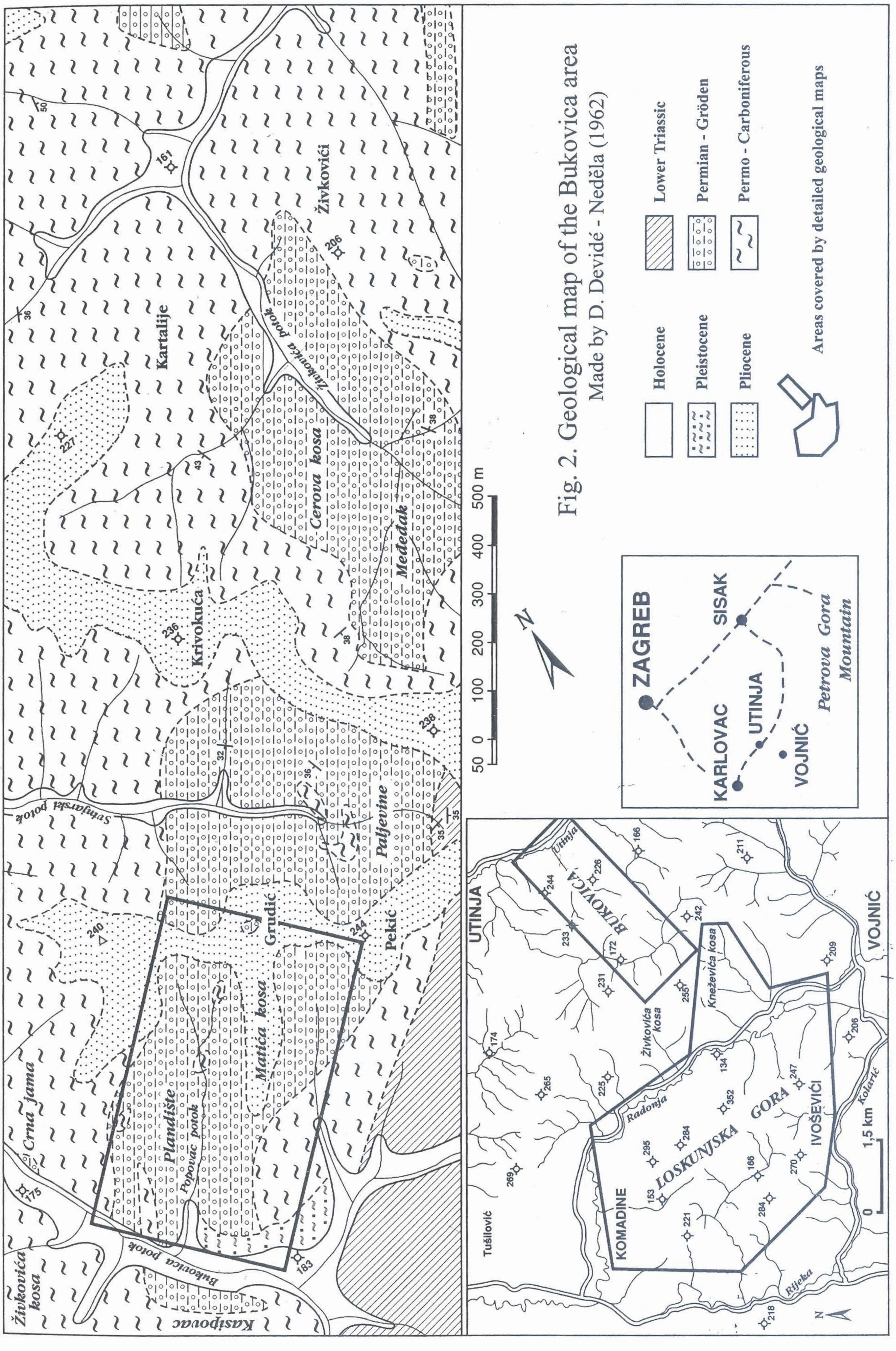


Fig. 2. Geological map of the Bukovica area
Made by D. Devidé - Nedĕla (1962)

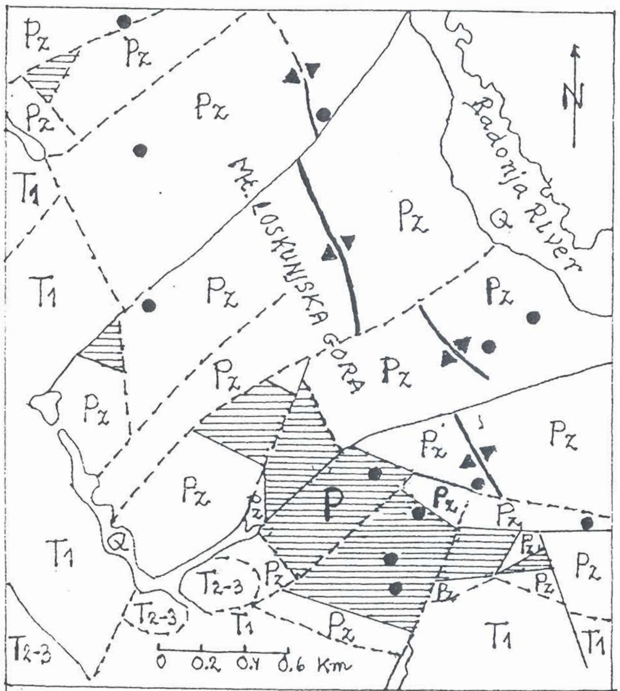


Fig. 2a. Geological map of the central part of the Loskunjska gora Mountain made by Lukšić et al. (1981).
Q - Quaternaire T_{2-3} - Middle/Upper Triassic T_1 Lower Triassic
P - Permian Pz - Upper Palaeozoic; ● rock samples analyzed by B. Šćavničar (1981); anticlinal axis

željezne rude Ljubija« and afterwards, from 1951 »Željezara Sisak« which resumed in the period 1953–1956 underground mining works, deep drilling, geological and geophysical prospections and surficial mining explorations (Devidé-Neděla, 1950; Ferenčić, 1956; Jurković, 1958). The exploration was financially supported by the Federal Geological Institute, Beograd. Based on good exploration results, starting with 1953, intensive production of hematite ores obtained by adits nos. 5, 8 and 9 and from 1960 by the incline no 11 (Šinkovec, 1961) was maintained.

In the Bukovica mine and in the surrounding area of Mededak Forest, Živkovići brook, the new intensive exploration and mining activity was organized during the period 1960–1968. It was financed by the Federal Geological Institute and Union of Yug. Ironworks, Beograd and by Ironworks, Sisak (Šinkovec, 1961; Čop, 1962; Jurković, 1962; Devidé-Nedela, 1962; Šimunić, 1972). The break of the activity of the Topusko ironwork caused the closure of the Bukovica mine.

Table 3 presents the total production of hematite ores (in tonnes) for each year during the period 1936–,1969. The Bukovica mine gave 182403 of low-manganese hematite averaging (in wt%): 42 Fe, 0.20 Mn, 33 SiO_2, 1–4 Al_2O_3, 0.05–0.09 P, 0.1–0.2 S and 3.5 H_2O.

Data on investigation of hematite ore deposits

In the Bukovica area, Permian hematite-bearing Gröden sedimentary rocks cover a total surface area of 793750 m^2 (0.8 km^2) – see **Table 4.**

In the area of Matića Kosa–Grudići–Pekići, between Plandište and Paljevine, hematite-bearing Gröden deposits occur at the surface below a thin Pliocene cover.

Field data

On the geological map of the Bukovica area (**Fig. 2**) is marked the surface of 690 x 410 = 282900 m^2 which was comprised by the most intensive mining exploration. This surface is presented on the geological sketch (**Fig 3**) on which are plotted small open casts, and positions of the underground mining works. The adits 5, 8 and 9, and the inclines No 11 and No 12 gave the major part of the exploited ores. Outside this area explorations by trenches, short adits, shafts and some boreholes were carried out.

Geophysical investigation

Geophysical prospecting, carried out by Krulc (1954) and Zagorac & Škarica (1955), included measurements of vertical intensity of the earth magnetic field using the stepmethod with two field variometers and with third magnetic balance which measured daily changes of the magnetic field. On hematite samples on the outcrops of hematite bed, magnetic susceptibility of ores was measured, but the obtained results had been negative. The intepretation of these both geophysical measurements had been uncertain. Some boreholes which checked weak geophysical anomalies (15–25 γ) were positive only in the case where a thick hematite bed lied shallow below the surface (as for example, borehole P_{35} with 4 m thick hematite at depths of 10–15 m).

Mining explorations

First geological and mining exploration with an initial production of the Bukovica area took place between 1914 and 1940 with two particularly intensive periods: 1914–1918 and 1936–1940. The Bukovica mine produced during the period between 1936–1941 26.600 t of low- manganese hematite ores averaging 36.8% Fe, 0.18% Mn and 39.3% SiO_2.

The second and main phase of the mining activity lasted from 1953 to 1969 but afterwards the Bukovica mine was closed and abandoned.

Drilling. Based on data of the first geological map (Devidé-Neděla, 1950), first drilling was organized in 1953.

The best results were obtained on the series P 1–16 with 8 positive boreholes. Based on these data, two new main inclines (No 11 and No 12) were opened. At Kasipovac and Matići Kosa–Grudići, very strongly tectonized zones were identified by drilling carried out in 1953–1955.

Intensive underground mining exploration and exploitation of hematite ores lasted in the period 1955–1960.

The drilling intensified in 1961–1962 and continued in 1963–1968 but with reduced intenseness. New series BK 1–3 and BK 7–10 were drilled in 1979 in the Međedak area; two boreholes gave positive results.

In total 308 boreholes drilled 10509 m during the periods 1939–1940, 1953–1955, 1960– 1968 and in 1979 (**Table 5**).

Underground mining works

Investigated hematite bed, with exploited and unexploited parts is presented on the **fig. 3a.** The hematite bed is dismembered in numerous uplifted or lowered down separate parts. Exploitation of hematite ores was carried out on the surface of 33000 m^2. Unexploited ore reserves remained on the surface of 44300 m^2, sterile blocks within the exploited zone have the surface of 16000 m^2 and sterile blocks outside the ore block have the surface of 16400 m^2.

Table 1. Data of sedimentological analyses (Obradović, 1969)

Light fraction in wt%	Quartz Q	Feldspar fd	Muscovite mu	Calcite cc	Weathered grains g
274 273 272 98.1 99.0 97.8	274 273 272 54 60 55	274 273 272 4 6 7	274 273 272 - - 10	274 273 272 0.8 0.4 1.7	274 273 272 39 32 25
Heavy fraction in wt% 1.9 1.0 2.2	zircon Zr 30 9 8	magnetite Mt 10 10 59	rutile Ru 8 7 6.5	apatite Ap 2 - -	siderite Sd 3 - 2
Weath. grains 39 56 10	barite ba 2.2 5 -	amphibole am - 2 1.5	garnet gr - 5 3	tourmaline tu - 6 5	muscovite mu - - 15
Smaller quartile Q3 0.09 0.33 0.42	median mode Md 0.06 0.26 0.32	larger quartile Q1 0.04 0.16 0.24	sorting coefficient So 1.45 1.45 1.31	Skewness sk 1.07 0.87 0.98	

Table 2. Production, export (expedit) and manufacture of hematite ores from the Bukovica mine during the period 1936-1942 (Tiringer, 1953)

Year	Production cca in t	Export to ironworks in tonnes					Manufacture in tonnes			
		Jesenice	Sulzan Werfen	Topusko	Caprag	Total	Jesenice	Sulzau Werfen	Topusko	Caprag
1936	4500									
1937	4500	660	5431	1422		7513				
1938	4500	610	2605.6	4117.3		7332.9	1281			
1939	4500	4303				4303	2833		3000	1000
1940	>7500	4253		107	2085	6445	2903			
1941		?					1248			
1942		?					2461			
1936 1942	26600	9826	8036,6	5646,3	2085	25593,9	10726	8000	3000	1000

Table 3. Bukovica mine. Production of hematite ore (t) (by M. Čop, 1991)

Year	Production	Year	Production	Year	Production
1936					
1941	26.600t	1958	12.724	1964	12.228
1953	5.539	1959	12.334	1965	12.144
1954	6.870	1960	12.094	1966	10.903
1955	9.672	1961	12.447	1967	-
1956	11.430	1962	11.079	1968	3.042
1957	10.802	1963	12.160	1969	335

In total: 1936-1941 + 1953-1969 = 182.403 t

Table 4. Surface of Gröden deposits in the Bukovica area (by M. Čop, 1991)

Location	m	m^2
Kasipovac	225 x 50	11250
Plandište	575 x 325	187500
Paljevine	500 x 400	200000
Međeđak	650 x 425	275000
NW Živkovići	475 x 60	27500
SE Živkovići	800 x 115	92500
Total:		793750

Outside this main mineralized zone, there is a mineralized area with 72000 m^2 and 20000 m^2 out of it lies at the depth with the altitude of +120 to 125 m (due to reverse fault) – see **Fig. 3a.**

The Kasipovac location, exploited in the first phase (1914–1918) was abandoned due to very strong tectonic dislocations and also the location Črna Jama with 21000 t of hematite ores due to high manganese content.

Forms of ore deposits

Earlier investigators (Devidé-Neděla, 1950,1962; Tiringer, 1953; Ferenčić, 1956; Jurković, 1958, 1962; Šinkovec, 1961) considered that hematite ores form shorter or longer, thinner or thicker lenses and lensoid discontinuous beds as a persistent unit at the base of the Gröden beds. Čop (1962) first has foreseen the bedded character of the hematite ore. He found out that hematite ores of the Bukovica (Kasipovac) and Svinjarski (Plandište, Matići, Grudići, Pekići) brooks with surface area of 200000 m^2 represent in fact a spacious but single hematite bed. This thick ore bed is desintegrated and dismembered in many smaller or bigger blocks by NNE–SSW–trending mainly vertical faults, but also normal

Table 5. Drilling data from the Bukovica mine area (by M. Čop, 1991)

Year	Bore holes in m					Posi-tive	Minera-lized length	Aver. thickness	Mapped by	Investors
	Series	Num-ber	Total length	Average	Per Year					
1939 1940	BM 1-30	30	700.0	23.3	700.0					KID 6.67 %
1953	H 1-13	13	809.9	62.3	809.9					
1954	K 1-14	14	264.3	18.9						Federal Geological Institute Belgrade 164 bore-holes with 5982.7m = 56.93%
	P 1-16	16	616.2	38.5	880.5	7	22.6	3.22	ŠI	
1955	A 1-10	10	120.6	12.1						
	Ž 1-3	3	83.0	27.7						
	C 1-3	3	45.5	15.2						
	G 1-29	29	554.9	19.1	804.0					
1960	P 17-31	15	667.7	44.5	667.7	6	20.6	3.43	ČO-ŠI-PO	
1961	P 32-37	6	209.9	35.0		3	5.2	1.73	ŠI-PO	
	U 1-5	5	311.8	62.4		3	4.0	1.33	ČO	
	M 1-17	17	896.6	52.7		8	18.8	2.35	ČO-PO	
	V 1-5	5	238.5	47.7	1656.8					
1962	P 38-46	9	299.7	33.3		7	21.3	3.04	ČO	Union of Yugoslav Ironworks (UYI) and Ironworks Sisak (IS) 107 boreholes 3293.8m = 31.34%
	U 6-22	17	820.1	48.2		9	31.6	3.51	ČO-PO	
	M 18-19	2	44.0	22.0	1163.8	1	3.0	3.00	ČO	
1963	P 47-67	20	693.3	33.0	693.3	18	48.6	2.70	ČO-PO	
1964	P 68-99	32	761.1	23.8	761.1	13	32.0	2.46	ČO	
1966	P 100-126	28	833.4	29.8		13	23.6	1.82	RA	
	M 20-23	4	200.0	50.0	1033.4	3	7.8	2.60	RA	
1967	P 127	1	22.0	22.0		1	6.1	6.10	RA	
	M 24-33	10	335.0	33.5		7	16.6	2.37	RA	
	U 23-24	2	75.0	37.5	432.0	2	3.5	1.75	RA	
1968	U 25-34	10	374.0	37.4	374.0	8	19.3	2.41	RA	
1979	BK 1-3	3	200.5	66.6		2	11.8	5.90	VI-LE	SIZ III + UYI + IS 5.07 %
	BK 7-10	4	332.0	83.0	532.5					
Total		308	10509.0	34.1	10509.0	111	296.4	2.67		

Authors: ŠI - Šinkovec ČO - Čop PO - Polak RA - Rajković LE - Leskur VI - Vitaljić
Bore hole series: BM - Bukovica mine; H - Matića Kosa-Grudići; K - Kasipovac; P - Plandište; A - Bukovica brook valley; Ž - Živkovića Kosa; C - Crna Jama; G - Paljevine; U - Mine buildings; M - Matića Kosa; V - Pekići; BK - Međeđak.

and reverse faults. Younger E–W or WNW–ESE–trending faults rarely occur.

This compact mineralized area is limited on the northwestern boundary of the mine by normal NNE–SSW–trending fault with very steep dip.

Figure 3 shows the altitudes and depths of separate smaller blocks with the surfaces from 100 to 750 m^2 and bigger blocks with surfaces from 1230 to 4670 m^2. They lie on +160 to 210 m but mainly between +170 and 200 m. High altitude differences are 15–25 m between bigger blocks and only 5–10 m between the smaller blocks included in the bigger one. Only two exceptions are two smaller ore blocks found by boreholes M–15 and M–16 on the altitudes of +120 m and +125 m brought about by reverse faulting and thrusting of Early Permian sediments onto the Gröden Formation.

The hematite bed dips very gently towards the SW; the differences in altitudes between the northeastern part (+190 to +210 m) and the southwestern part (+110 to +180 m) is only 20–40 m. In some boreholes the hematite bed occur twice due to reverse faults or in the case when borehole penetrates vertical fault. **Figure 4** shows the most characteristic cross-sections and the position of boreholes.

On the basis of numerous longitudinal and transversal geological profiles based on 197 boreholes (111 positive) it was constructed block-diagram of the main part of the hematite deposit **(Fig. 5)**. The block-diagram demonstrates the spatial position of the hematite bed, its dismembering into blocks by vertical faulting, amounts of jumps, exploited parts of the ore bed, remained unexploited parts, two blocks below reverse faults barren zones and others. The block-diagram also verified the bedded character of the hematite deposit.

Thickness of the hematite bed

In **Figure 6** and **Table 6** are included data on the thickness of the hematite bed obtained in 111 positive boreholes from a total of 201 boreholes.

Average apparent thickness is 2.68 m. On the basis of average thickness on 21 ore blocks, utilized for the calculation of ore reserves (Čop, 1991), an average

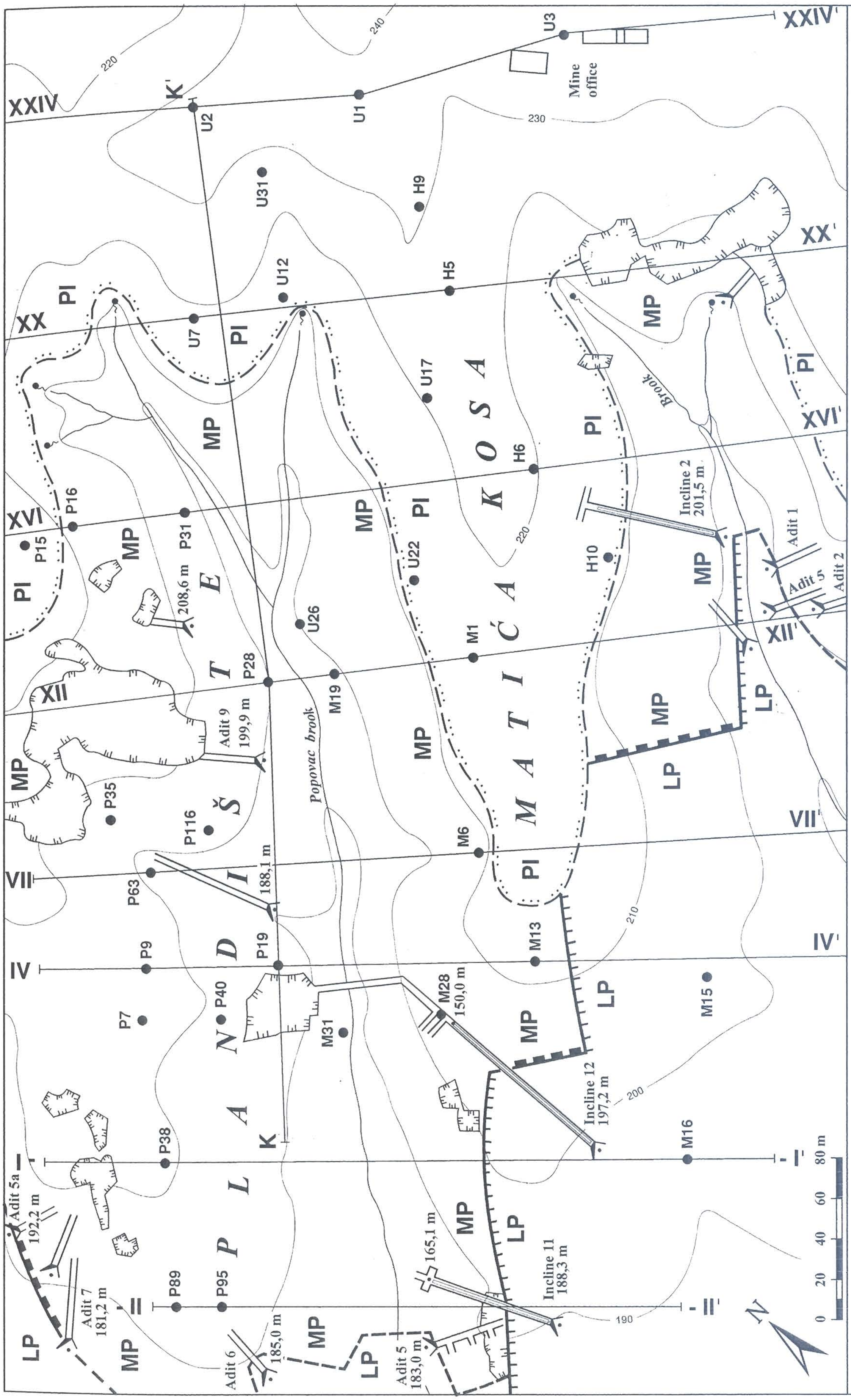


Fig. 3. Geological sketch with Bukovica mine (by M. Čop). ⟩═ adits and inclines; M32 bore - holes; LP Lower Permian; MP Middle Permian; Pl Pliocene. Geological boundaries limited by reverse fault (▬▬); normal fault (┬┬┬); erosional-transsgresive discordance (-·-·-); —190— isohypse.

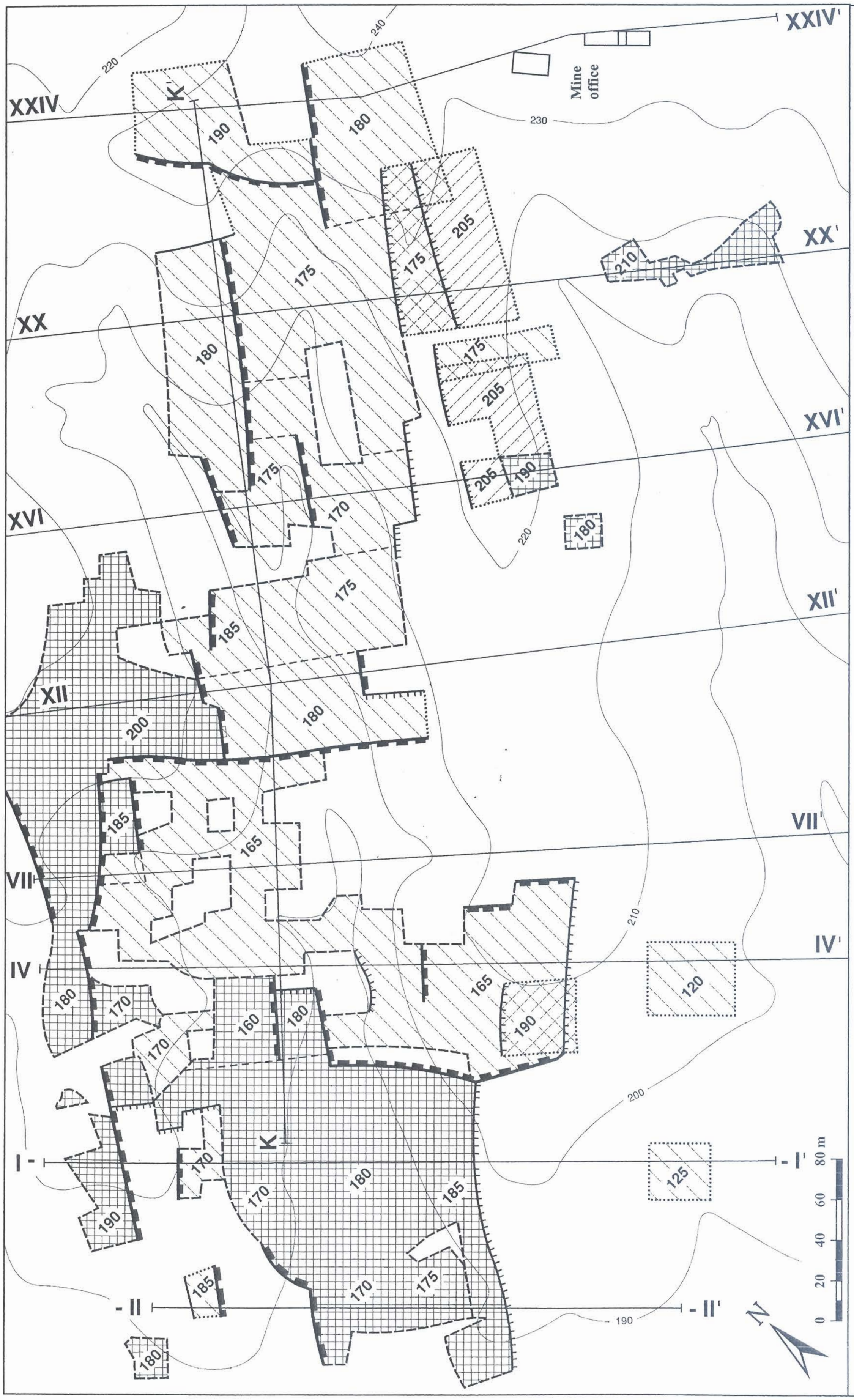


Fig. 3. a Underground mining works (made by M. Čop). ▦ exploited parts of hematite bed; ▧ ▨ investigated, non exploited parts of hematite bed; 170, 205 etc. are altitudes of hematite bed; —190— isohypse.

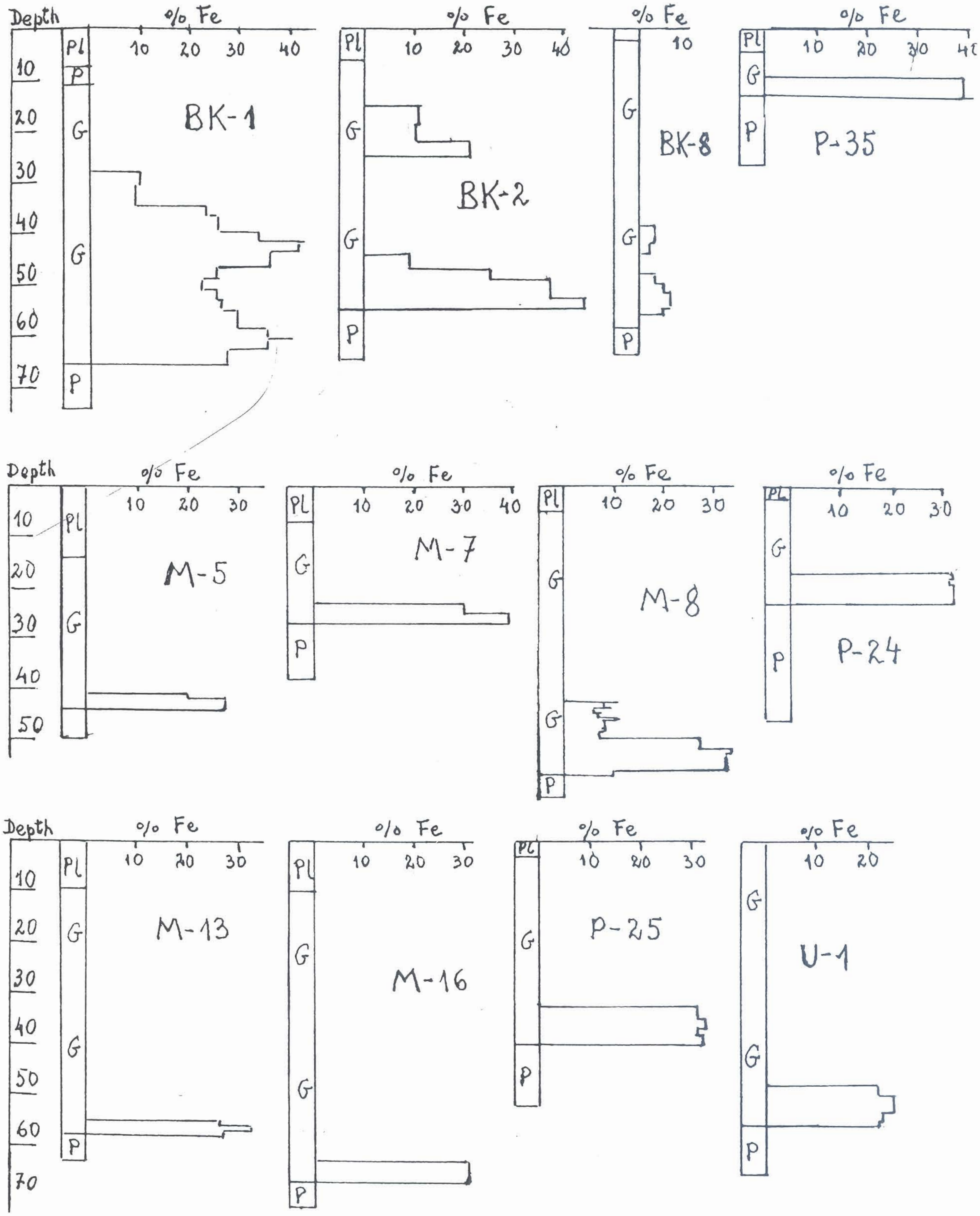


Fig. 4. Characteristic cross-sections of bore-holes in the Bukovica area

Mapped by: M. Čop, 1960 (P-24, P-25); M. Čop, 1961 (M-8, M-13, M-16, U-1); D. Polak, 1961 (P-35, M-5, M-7); Vitaljić-Leskur, 1979 (BK-1, BK-2, BK-8).

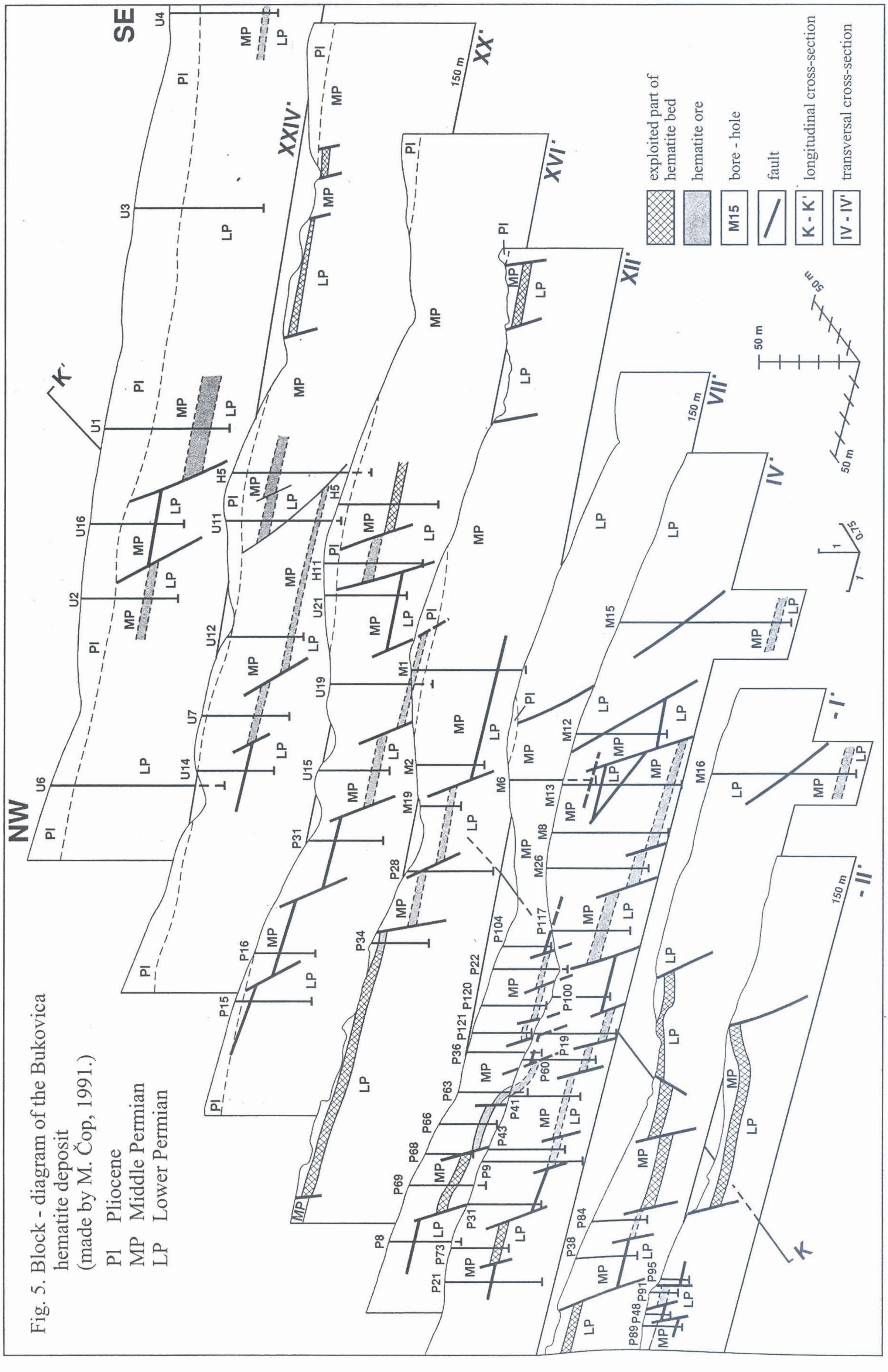


Fig. 5. Block - diagram of the Bukovica hematite deposit (made by M. Čop, 1991.)

Pl Pliocene
MP Middle Permian
LP Lower Permian

Table 6. Average thickness of the hematite bed (by M. Čop, 1991)

Bore-holes			Mineralized	Average thickness(m)
Location	Number	Positive		
P - Plandište	127	68	180,0	2,65
U - Office buldings	34	22	58,4	2,65
M - Matići	33	19	46,2	2,43
BK - Međeđak	7	2	13,4	6,70
Total:	201	111	298,0	2,68

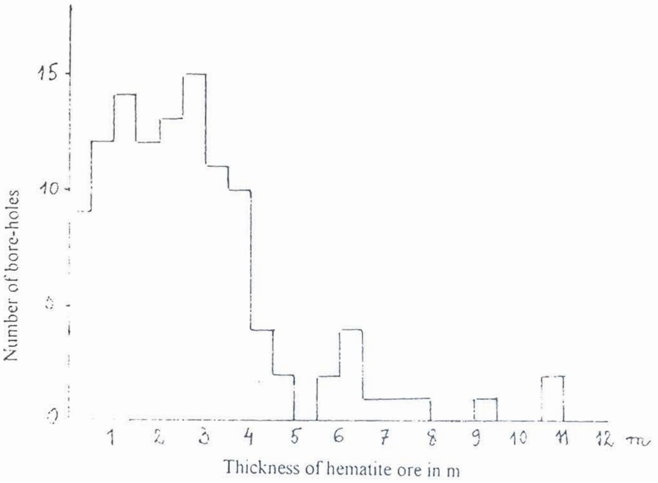


Fig. 6. Average thickness of the hematite ore in the Bukovica mine (made by M. Čop, 1991)

Table 7. Chemical composition of the exploited crude hematite ores during the periods 1937-1940 (by J. Tiringer, 1953), **1954-1955** (by A. Ferenčić, 1956) and **1960-1968** (by M. Čop, 1962, 1991)

Year	SiO_2	Al_2O_3	Fe_2O_3	Fe	MnO	CaO	MgO	P	S	L.o.i.	H_2O^-
Period from 1937 to 1940	37.24	4.57	53.22	37.29	0.15			0.05	0.25		
	36.44	5.60	54.04	37.79	0.15			0.06	0.10		
	44.05	5.50	46.15	32.27	0.15			0.06	0.06		
	36.35	4.50	57.14	39.96	0.16			0.08	0.12		
	42.00	2.20	51.48	36.80	0.30			0.075	0.06		
1937-1940	39.30	4.47	52.43	36.82	0.18			0.065	0.12		
1954-1955	29.00		61.48	43.00	0.07			0.01 to 0.56	0.012 to 0.310		
	43.00		51.47	36.00	0.65						
	36.60		58.62	41.00	0.20						
1960	32.60		62.08	43.42	0.17						3.31
1961	32.40	2.79	60.06	42.00	0.23	1.16	0.36	0.17	0.36	1.50	4.40
1962	32.21	4.07	59.48	41.60	0.21	0.75	0.32	0.096	0.32	1.70	5.20
1963	31.46	4.51	60.23	42.13	0.18	0.76	0.17	0.067	0.30	1.60	4.60
1964	35.09	3.73	57.19	40.00	0.16	0.82	0.40	0.068	0.36	1.49	4.90
1965	35.07	3.97	56.33	39.40	0.14	0.55	0.12	0.113	0.33	1.79	3.60
1966	35.00	3.66	56.73	39.68	0.15	0.63	0.21	0.210	0.47	1.67	4.34
1968	34.72	5.42	53.99	37.71	0.15	0.99	0.51	0.160	0.43	2.15	3.40
1969	35.08	4.33	56.92	39.46	0.18	0.93	0.23	0.160	0.34	1.79	3.30
1961/1969 average	33.44	3.85	58.17	40.68	0.18	0.79	0.27	0.12	0.36	1.65	4.45

Table 8. Chemical composition of the crude ore (channeled samples) taken by M. Čop (1991) from the incline No 12, Bukovica mine

No	SiO_2	Fe	Fe_2O_3	Mn	L.o.i.	No	SiO_2	Fe	Fe_2O_3	Mn	L.o.i.
1	29.49	44.79	64.04	0.065	0.83	15	34.93	41.32	59.08	0.098	1.55
2	30.71	44.57	63.56	0.080	1.09	16	38.94	37.98	54.30	0.098	0.43
3	31.20	44.79	64.04	0.065	0.60	17	39.84	37.87	54.14	0.065	0.55
4	31.14	43.78	62.59	0.065	0.63	18	33.53	42.89	61.32	0.065	0.65
5	28.80	44.90	64.19	0.065	0.66	19	30.84	44.12	63.08	0.065	1.00
6	33.37	42.45	60.69	0.098	0.43	20	32.52	43.00	61.48	0.065	0.78
7	35.09	41.33	59.09	0.130	1.01	21	31.76	44.79	64.04	0.120	0.96
8	47.82	31.16	44.55	0.160	0.58	22	29.47	44.79	64.04	0.090	0.93
9	44.66	34.18	48.87	0.070	0.37	23	37.62	34.96	49.98	0.130	0.98
10	30.26	43.45	62.12	0.070	1.25	24	31.92	40.43	57.80	0.130	1.47
11	39.14	38.30	54.76	0.030	0.81	25	35.02	40.88	58.45	0.130	1.03
12	30.09	45.02	64.37	0.120	0.98	26	36.94	40.43	57.80	0.066	0.49
13	37.29	42.44	60.68	0.080	0.75	27	30.77	44.23	63.24	0.049	0.72
14	30.90	41.88	59.88	0.065	0.54	28	40.99	37.19	53.17	0.006	0.96

	SiO_2	Fe	Fe_2O_3	Mn	L.o.i.	Al_2O_3	CaO	MgO	P	S	Na	K
1-5	30.60	45.08	64.45	0.07	0.77	0.94	0.98	0.70	0.065	0.49	0.073	0.221
6-14	37.00	40.32	57.65	0.09	0.80	1.54	0.66	0.70	0.055	0.295	0.089	0.379
15-28	34.65	41.55	59.40	0.09	0.94	2.48	0.42	0.30	0.089	0.422	0.080	0.560
1-28	34.68	41.79	59.75	0.09	0.86	1.88	0.60	0.51	0.073	0.393	0.082	0.437

thickness of 2.8 m for 278000 t of hematite ores was obtained.

Calculations of ore reserves

Based on first 30 boreholes, carried out by KID in 1939/1940, the ore reserves of 30000 t and 30000 t probable ore reserves averaging 36.82% Fe, 0.18% Mn, 39.30% SiO_2, 4.47% Al_2O_3, 0.06% P and 0.12% S were calculated. In 1941 KID gave 60000 t sure, 60000 t probable and total of 100000 t of presumed ore reserves. The Geological Institute, Zagreb estimated in 1954 the total reserves of 50000–80000 t. In 1956 the Sisak ironwork (Ferenčić, 1956) evaluated. 100000–110000 t sure and possible reserves plus 150000 t probable reserves.

First more precize evaluation of the ore reserves using the block method was made by Čop (1962) for the surface area of 33000 m^2 and 21 separated blocks. The calculation gave 150.270 t possible reserves and 40.880 t probable reserves (in total 191.150 t) with average chemical composition: 42% Fe, 0.20% Mn, 33% SiO_2, 1–4% Al_2O_3, 0.05–0.09% P_2O_5 and 0.1–0.2% S.

The Sisak ironwork in 1963 estimated 12400 t sure reserves, 104600 t possible reserves and 231000 t probable reserves.

The Croatian Republic commission for the evaluation of the ore reserves approved in 1964. as follows: 13000 t sure, 110000 t possible and 244000 t probable (in total 367000 t) ore reserves; exploitable reserves are 348500 t with 41.6% Fe, 0.1% Mn, 36.5% SiO_2, 0.09–0.05% P and 0.1–0.2 S. Besides that, not exploitable ore reserves of 21000 t on the dump at Črna Jama containing high contents of manganese were estimated.

Later evaluations were decreased for the exploited ore in each year.

Chemical composition of hematite ore

Table 7 presents chemical composition of crude hematite ores delivered each year to the consumers. Average chemical composition (in wt%) is as follows: SiO_2 33.44, Al_2O_3 3.85, Fe_2O_3 58.17 (Fe 40.68), Mn 0 0.18, CaO 0.79, MgO 0.27, P 0.12, S 0.36, H_2O^- 4.45 and ignition loss 1.65. According to our opinion these are the most exact results. Analyses carried out on cores of boreholes gave 88.5% of the standard value for Fe. This difference is due to the loss of fine- grained hematite during the drilling. Analyses of mud circulating in boreholes gave 78.7% Fe of the standard average analysis.

Čop (1991) attempted to verify average chemical composition of hematite ores along incline no 12. and its crosscuts. He took 28 samples with reciprocal distances

Table 9. Comparison of the chemical composition between exploited crude ores and of samples taken from the incline No 12 (by M. Čop, 1991)

Table 9.	SiO_2	Al_2O_3	Fe_2O_3	Fe	MnO	CaO	MgO	P	S	lost of ign.	Na	K
74358 t (1961/69)	33.44	3.85	58.17	40.68	0.18	0.79	0.27	0.12	0.36	1.65	n.d.	n.d.
channeled samples	34.68	1.88	59.75	41.79	0.12	0.60	0.51	0.07	0.39	0.86	0.08	0.44

Table 10. Bukovica mine. Contents of trace elements (in ppm). Analyst: S. Miko, Zagreb, 1993.

	Host rocks				Hematite ore from drill cores								Veins	
Element	Hanging wall		Footwall		B1/1	B1/2	B2	B3/1	B3/2	B4	B5	B6	Hematite	Siderite
Ba	64	53	233	166	65	68	230	258	390	64	187	627	106	1564
Co	<1	3	6	4	<1	<1	<1	<1	<1	<1	<1	<1	<1	46
Cr	29	339	98	62	63	71	163	7	6	83	8	2	107	6
Cu	8	8	27	29	16	22	20	21	15	22	16	14	25	30
Hg	0.18	0.24	0.54	0.35	1.7	1.7	3.5	0.3	0.3	0.2	2.2	0.2	0.3	0.4
Mn	1502	1229	362	832	763	383	72	208	150	62	542	166	1685	3382
Ni	48	210	63	49	100	95	134	52	51	94	52	61	110	91
Sr	133	144	36	40	123	77	440	96	180	78	134	411	71	140
V	109	95	164	n.d.	n.d.	25	36	24	40	48	45	n.d.	22	283
Zn	107	114	88	74	105	91	73	65	75	55	82	65	79	77
Zr	13	47	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
P	131	153	50	333	399	569	847	282	320	42	361	241	253	50

of 10 m using the channel sampling method in the incline perpendicularly to strike of the hematite bed **(Table 8)**.

In **Table 9** are compared two most approximative chemical compositions: A 74.358 t of crude hematite ores delivered 1961/1969 to the ironworks and B average chemical composition of 28 channelled samples taken along incline no 12 in the Bukovica mine.

Paragenesis of the hematite ore

Hematite, major ore mineral, is extraordinarly fine-grained (1–15 microns) and only in some places up to 15–50 microns. In micropores of dense hematites, detrital quartz grains can be found which include needle- to columnarlike intersections of automorphic hematite crystals. Hematite cements detrital quartz, chert, quartzite and muscovite whose size of grains is 0.6–1.5 mm. The hematite also fills pores and frontally replaces detritus penetrating inside grains in form of fine needles and minute plates. Where cataclasized, hematite fills or is squeezed into fine cracks and fissures. In some boreholes at the base of hematite bed, an extraordinarilly fine-grained siderite makes cement of detrital particles. Microphotographs **(Plates I and II)** display diversities of hematite structures and textures.

Based on sedimentological analysis **(Table 1)**, hematitized quartz sandstone from the lowermost part of the Gröden beds contains 99% of light fraction and 1% of heavy fraction. Mineral composition of the light fraction is as follows: 60% quartz and lithoclasts, 6% feldspar, 0.4% calcite and 32% weathered grains. The heavy fraction contains: 9% zircon, 10% magnetite, 7% rutile, 5% barite, 2% amphibole, 5% garnet, 6% tourmaline and 56% weathered grains covered and masked by hematite films.

Trace elements

In **Table 10** are presented trace element data for hematite samples from direct hanging wall rocks and direct footwall rocks of the hematite bed. The analyses were carried out by Miko (1993) using the AAS method.

Hanging wall rock samples contain hightened values of Mn, Ni, Sr, Zn and Zr in comparison with footwall rock samples, but decreased values of Ba, Cu, Hg. Values of Cr, V, P are not comparable. Samples of hematite ores are characterized by increased, but very variable values of Ba, Cr, Mn, P, Sr and by very low Co and Zr values. Composition of trace elements of hematite ore is more similar to those of footwall rocks, except for Co and Sr. Trace elements in the epigenetic hematite vein do not differ from the hematite bed ore except for Mn. Epigenetic siderite-barite-pyrite vein differs by increased values of Ba, Co, Mn, V, and by decreased value of P.

Neominerals of the hematite bed

In numerous samples of hematite ores, numerous white veinlets, or oval irregular nests, breccia-like aggregates of different size can be megascopically or microscopically recognized.

Table 11. Neominerals in hematite bed (by D. Slovenec)

	Q	Mu	Kl	Sd	Cc	Ba
1 Fragments in ore breccia	++++	+++	++			
2 Fragments in ore breccia	+++					+++
3 White calcite vein	+			++	++++	++
4 White quartz vein	++++	++	+			
5 Differently sized fragments	++++	+				++
6 Different sized fragments	++++	++.				+++

Q - quartz Mu - muscovite Kl - kaolinite Or - orthoclase Sd - siderite Cc - calcite Ba - barite

Table 12. Results of DT analyses (made by V. Babić, 1992)

Sample	Range of temperature			°C
	20-450	450-600	>650	20-1000
HW 1	1.10	5.14	6.61	12.85
HW 2	0.55	7.20	3.43	11.18
He 1	0.32	3.95	2.63	6.90
He 2	0.29	2.62	0.87	3.78
He 5	0.32	2.27	2.60	5.19
FW 1	0.74	6.17	-	6.91
FW 2	1.06	4.76	-	5.82
Sd 1				11.80

Legend: see text

Data of XRD analyses of such veinlets and nests, carried out by Slovenec, are presented in **Table 11** which shows that quartz veins or nests with muscovite ± kaolinite ± barite predominate over calcite veins with barite, siderite and quartz.

At Plandište a siderite vein, a few centimetre thick cutting the hematite bed was found. It is of bysymmetric pattern: both external sides of the vein are built up of coarse-grained pyrite, the next internal zone is composed of coarse-grained brown siderite, whereas its internal part is filled by coarse-grained white barite. d^{34}S of this barite is +19.52‰ suggesting its Triassic age. At Kasipovac a thin vein with cataclased, partly milionitized pyrite which lies in the quartz-calcite matrix has been found.

Correlation of the Bukovica hematite bed with its hanging- and footwall rocks

DTG, DTA and TG analyses were carried out on samples from the hematite ore horizon. (He1, He2, H5), hanging wall rocks (HW 1, HW2), footwall rocks (FW 1, FW2), and a siderite vein (Sd) cutting the hematite bed. The analyses were carried out by Babić (1992) using the authomatic derivatograph »MOM«, Budapest under following laboratory conditions: heating 10 °C/min; duration 100 min., TG = 500 mg, termopair PT and Pd + 10% Rh; reference material A1203 heated at 1500C **(Figs. 7 and 8).**

Range from 20° to 450° C indicates dehydration of clay minerals; range 450° to 600 °C indicates dehydroxidation and desintegration of iron hydroxides, chlorite and clay minerals; range 650^0–1000 ^{0}C marks dissociation of C0$_2$ and desintegration of carbonate minerals (calcite, dolomite and siderite). In hanging wall rocks predominate clay minerals and carbonates, whereas in the footwall rocks predominate chlorite-group minerals. Samples from the hematite horizon are similar to the ones from hanging wall rocks **(Table 12).**

X-Ray powder diffraction analyses were carried out on eight samples in order to define mineral phase composition of the hematite bed (He) and its hanging wall (HW) and footwall (FW) rocks, and siderite veins (Sd) cutting the hematite bed. Combining data of DTA, TGA and DTG analyses (Babić, 1992) and XRD analyses from the samples, and potassium content determined by the XRF method, semiquantitative mineral composition was obtained **(Table 13).** The data obtained indicate clear differences in composition between footwall (FW) rocks and hanging wall (HW) rocks what fits with petrographic data (Jurković, 1958; Devidé-Neděla et al., 1962; Šćavničar, 1981). The footwall rocks contain predominant muscovite, abundant chlorite and feldspar (plaogioclase) and subordinate kaolinite and hematite; dolomite is absent. Hanging wall rocks contain more hematite, kaolinite and dolomite; chlorite and plagioclase are absent. Composition of the hematite bed is similar in composition to hanging wall rocks but with the difference that the significant part of quartz is replaced by hematite.

Genesis

A. General review

There are various opinions on different aspects of non-volcanogenic hematite genesis. a) **Geological settings.** Kimberley (1978) described such a type of iron deposits as sandy, clayey and oölitic shallow-inland-sea

Table 13. Semiquantitative mineral composition of hangingwall rocks (HW), footwall rocks (FW) and hematite bed (He) (in %) (by D. Slovenec)

	Q	Mu	Kl	Chl	Or	Pl	Hm	Py	Dol	Sd	Ba	An	Gy
HW1	40	20	++		+		++		10-15	++			
HW 2	45	20	++		+		++		5-10	++			
He 1	15	5	+				++++		5-10	++		+	
He 2	15	5	+				++++		<5	++			
He 5	<5	5	+				++++		5	+	+		
FW 1	35	30	+	+++		20	+			+			+
FW 2	35	30	++	+++		15	+			++			+
Sd	40							++		++++		+	

Legend: Q quartz Mu muscovite Kl kaolinite Chl chlorite Or orthoclase Pl plagioclase

Hm hematite Py pyrite Dol dolomite Sd siderite Ba barite An anhydrite Gy gypsum

++++ dominant mineral; +++ significant share ++ low share + very low share

He 1 and He 2 are very rich hematite ores; Sd is quartz-siderite vein

iron formation (SCO–IF). These formations are epicontinental sediments originated by chemical precipitation from river waters that entered saline lakes and geosynclines (Guilbert and Park, 1986). Chauvel and Dimroth (1974) suggested that hematite and silica-carbonate facies accumulate from peritidal to deep basinal zone environments, i.e. from the sea level to depths of 50–100 m. Because iron mineral facies is a function of Eh, it is commonly presumed that oxides originate in shallow water, whereas silicates, carbonates and sulphides originate in deeper water.

Oxidized (hematite) facies and weakly reduced (silicate) phases originate in areas of sand accumulation. Muds deposited in low organic productivity environments also will give rise to hematite or iron silicate formation. Krauskopf (1956) and Listova (1961) calculated separate precipitation of manganese and iron oxides in sea water and obtained differentiated results in basinal inshore zone due to various geochemical mobility of iron and manganese compounds. Smirnov (1976) is of the opinion that iron ores begin to accumulate first near the top of shelf and manganese ores in its lower parts. It is noticed transition from oxides to carbonates to silicates going from the shore towards the deepened parts of the basin.

b) **Source of iron, manganese and silica.** The source is continental crust of weathering, the desintegration products of which are washed off by surface and subsurface waters. Most of iron is mobilized by the decomposition of rocks enriched in iron or older iron deposits (Strakhov, 1962). These metals reach into solutions only from highly mature crust of weathering, with evacuation from it by various electrolytes that make their transport in colloidal solutions difficult.

c) **Transport of metals** takes place by fine suspensions, colloidal solutions and true solutions. In soluble compounds iron is transported mainly as $Fe(OH)_3^{3+}$ – sol protected by an organic colloid or silica sol. Smaller fractions migrate in form of organic ferric or ferrous compounds, whereas an even smaller amount is carried out in true solutions of ferrous carbonate, bicarbonate, sulphate, sulphide (Smirnov, 1976).

Garrels & MacKenzie (1971); Garrels et al., (1973) state that iron enter into sedimentary systems in colloidal form or as coarser detritus directly by weathering and,depending on local Eh, pH and ion conditions, can be involved in diagenetic reactions. Dimroth (1976) indicates that Phanerozoic iron was transported as (a) detrital ferric hydroxide sols and oxide film on clayey and silty detritus, and (b) ferrous ion in reduced unaerated waters. Guilbert and Park (1986) believe that ordinary river waters can dissolve and transport enough iron and manganese; this is, according to Strakhov (1962), 0.2 to 1.5 mg/l, iron, between 0.007 and 0.08 mg/l manganese and 13 ppm/l silica (Mason, 1966) to account for the amount in iron formations.

d) **Preciptitation of iron and manganese.** Gulbert and Park (1986) claim that iron and manganese can be transported as complex ions or hydrolisates such as $FeCl_2 \cdot nH_2O$ or $Fe(OH)_3 \cdot nH_2O$, as ferrous and ferric ions and precipitated as a flocculate by an agglomeration and settling, or as a direct chemical precipitate. First sedimentation product is probably limonite, either goethite or hematite, which diagenetically dehydrate and become compact. Strakhov (1962) states that iron compounds are deposited within inshore zones of lakes and seas by the influence of electrolytes dissolved in waters which give rise to coagulation of colloidal metal compounds. This process takes place especially in high coastal relief areas affected by long-lasting peneplanation and cut by many small rivers and groundwaters seeping along the shore.

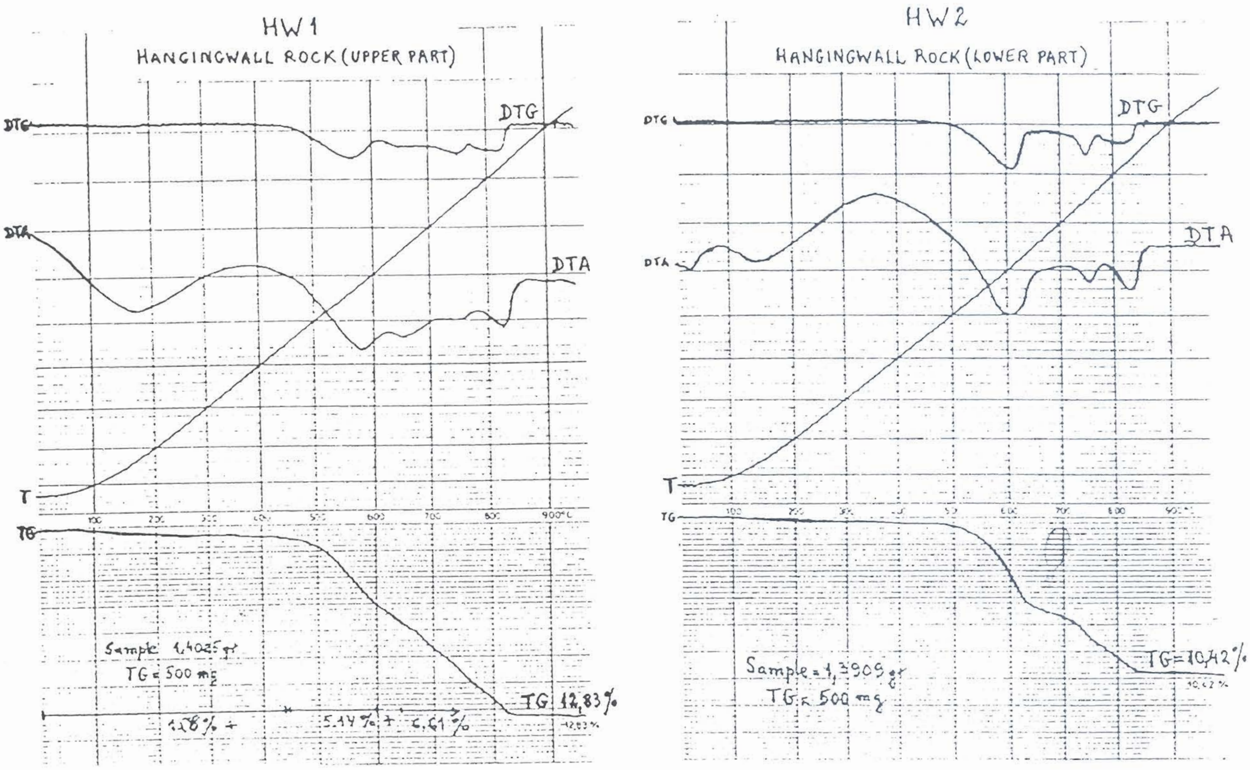
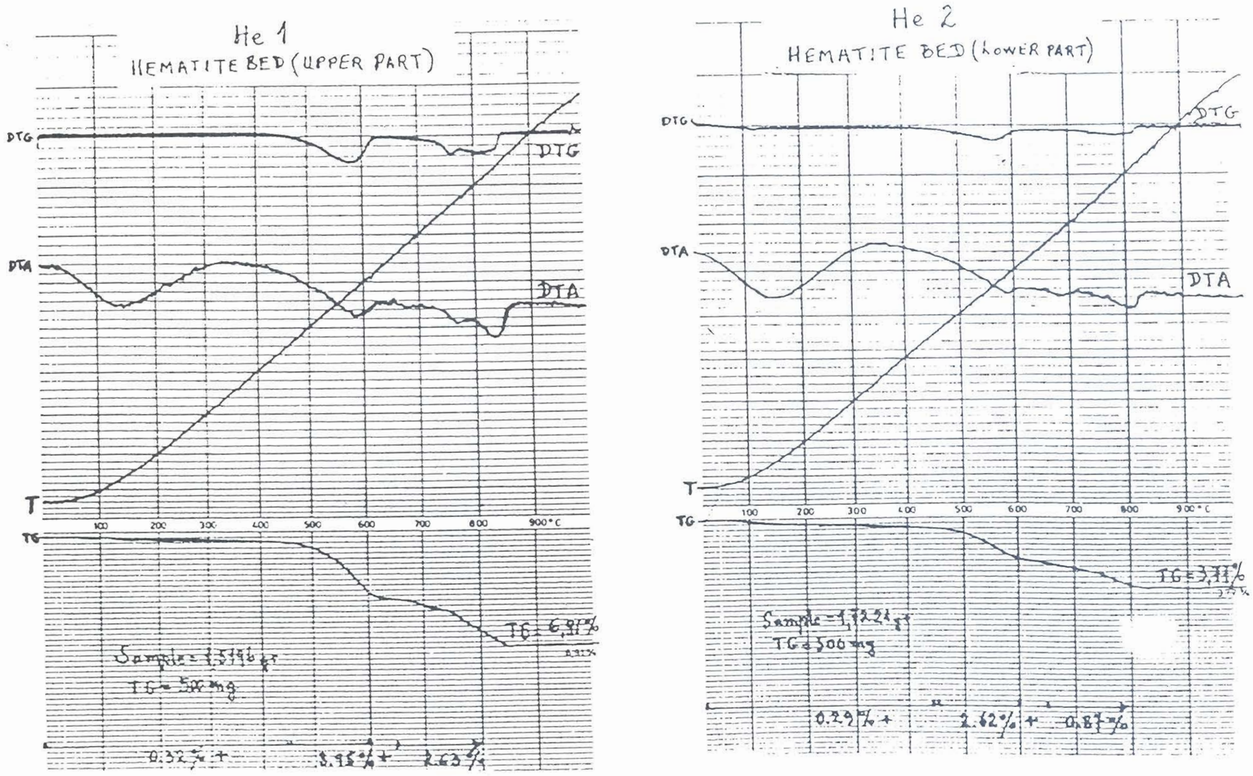


Fig. 7. DTG, DTA and TG analyses of the samples taken from the hangingwall rock and from hematite ore (analyzed by V. Babić, 1992)



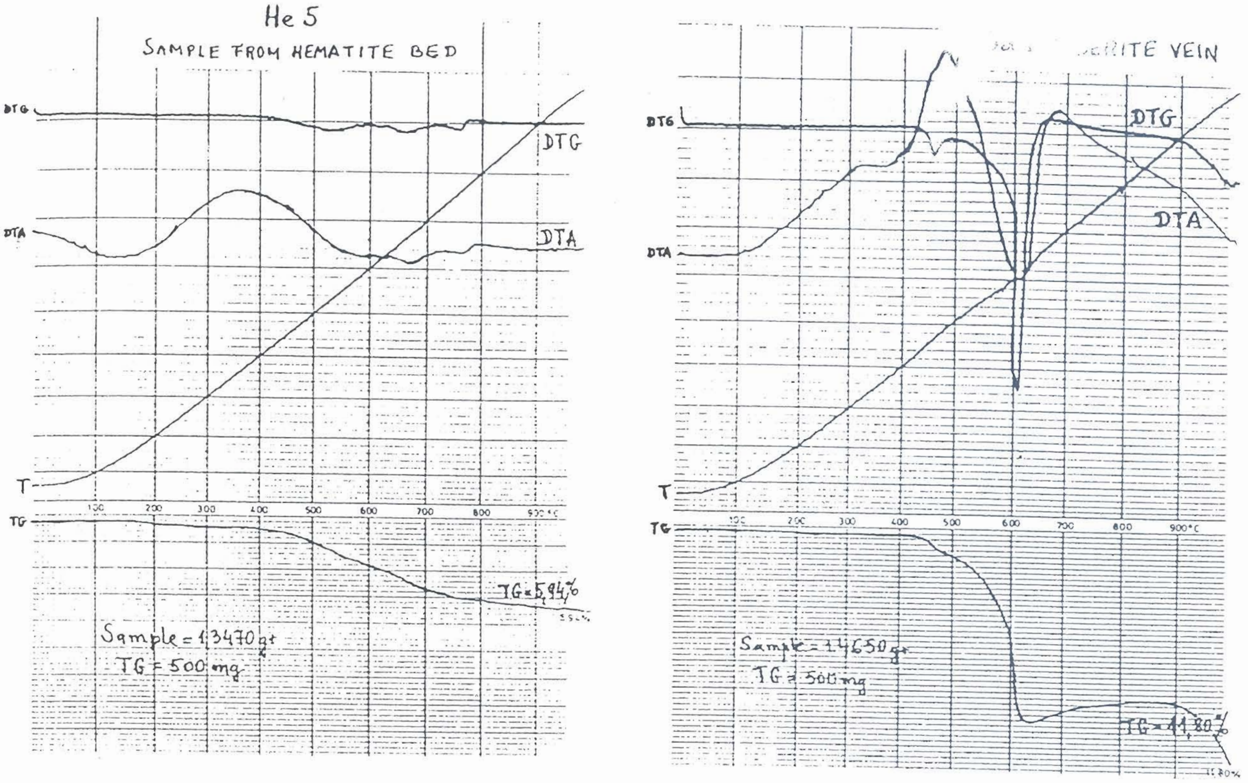
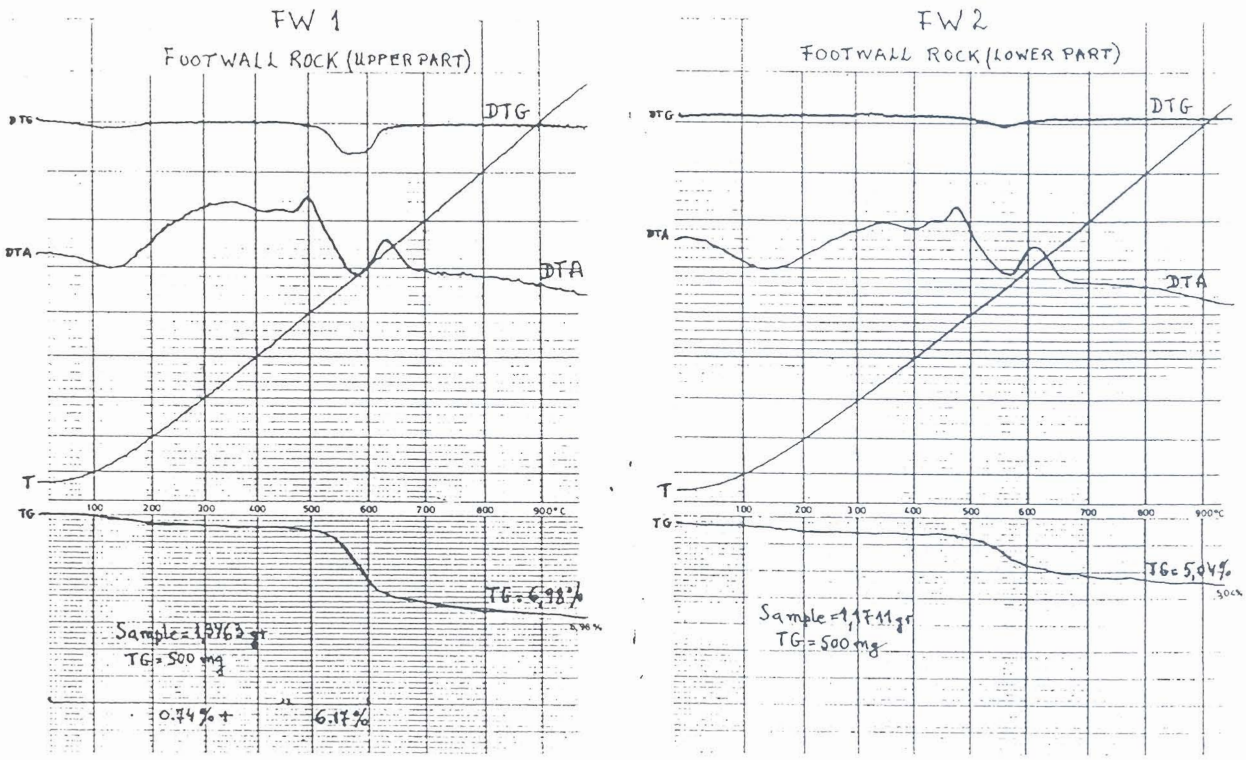


Fig. 8. DTG, DTA and TG analyses of the samples taken from the footwall rock and from one siderite veinlet (analyzed by V. Babić, 1992)



e) **Diagenesis.** Stability of iron ore minerals is a function of Eh, pH, pCO_2 and pS^{2-} of the pore solutions. Oxidizing diagenetic conditions can be maintained only in clean-water sands and in muds with extremely low concentrations of organic matter. For that reason, it can be expected that hematite can be generated mainly in cemented allochemical iron-formations and in matrix cherts deposited in very low organic productivity environments. Siderite precipitates at very low Eh and pS^{2-} and, therefore, it originates during the diagenesis of delta-swamp mud and in similar fresh-water deposits with high contents of organic matter.

B. Genesis of the Bukovica low-manganese iron ores

The area of Bukovica and Mt. Loskunjska gora emerged after the sedimentation of Lower Permian psammites and pelites and the emersion phase persisted up to the formatoin of Gröden deposits. In these outmost part of Mt. Petrova Gora, younger horizons of the Lower Permian are not developed which are commonly composed of quartz sandstones, quartz conglomerates and, in some places, of polymict brecciated very coarse-grained conglomerates. The polymict conglomerates contain fragments of shales and subgraywackes indicating that during their sedimentation this area represented, at least partly, a land. All barite and siderite depositis of the eastern part of Mt. Petrova Gora area spatially relate to these rocks (Jurković, 1958; Devidé-Neděla et al., »1960; Jurković & Palinkaš, 1996).

Gröden deposits originated during a new transgressive phase, after short-lasting Saalian orogenic phase, in the span between the Early and Middle Permian. Sedimentation of basal coarse-grained sandstones and fine-grained quartz conglomerates took place at the surface with unconformity and sharp mutual contact lines with underlying formations. The surrounding peneplained land gave rise to the abundant Fe influx, mainly in the form of $Fe(OH)_3{}^{3+}$– sol protected by organic or silica sol, in form of films on clay and silt particles, and smaller fractions in form of organic ferric and ferrous compounds or simple iron true solutions.

Precipitation took place in river beds, in flood plains, and in inshore zones of the shallow sea an lakes. On the land prevailed warm and arid climate of +21.3 °C during the Middle Permian, and arid and hot of 25.7 °C during the Late Permian (Polšak and Pezdić, 1978).

In the lowermost part of the hematite unit overlying directly older Lower Permian sediments, heavy fraction is abundant in same minerals (garnet, amphibole and tourmaline) but, as distinguished from the Gröden beds, it does not contain apatite.

During diagenesis along very contact between Lower Permian sandstones and hematite horizon, very thin layer of extremely fine-grained siderite and of fine-grained pyrite can be locally noticed (Jurković, 1958; Tiringer, 1953). The siderite and pyrite originated in places where changes in Eh occurred in direct contact with pore waters enriched in coaly matter from underlying sediments. Hematite originated by diagenesis (dehydratation and compaction) and this was accompanied by corosion of quartz and lithoclast grains, penetration of minute hematite needles and plates in these grains. The hematite even mechanically penetrated during later geological epochs in fissures of the detrital grains. Within hematite bed, numerous quartz or calcite veinlets, small nests and agglomerates, with or without barite, muscovite, kaolinite and siderite originated during late diagenesis or epigenesis.

Due to various geochemical mobility of iron and manganese compounds they behaved differently in the inshore zone. That is the reason why the Bukovica hematite deposits contain minimal content (0.1–0.2%) of manganese. Only in the outmost southwestern part of the Bukovica mine, at the location Črna Jama (Crna Jama on the **fig. 2**), outcrops of the hematite bed with increased content of manganese have been found and investigated (Tiringer, 1953).

C. Other similar hematite deposits

At the village **Hrastno** (locations Hrib, Vihr, Cirnik, Dule), 5 km north of the town Mokronog, in the south-eastern Slovenia, small-sized-low-manganese hematite ores occur (Berce, 1954, 1956). Mining investigation and modest exploitation of ores by short adits and shaft was carried out before 1857, reactivated in 1912, 1936 and 1952, but without positive results.

Ore beds are 0.8 to 3.0 m thick with very variable content of iron: 25–76% Fe_2O_3 and 18 to 70% SiO_2 but only 0.05 to 0.1% Mn. The hematite ore occurs within thick deposits of red, rarely violet red sandstones and shales. According to Berce (1954) hematite is of presumed Scythian or Permian age, or Scythian (Berce, 1956), or Middle Permian (Gröden facies) Pleničar and Premru (1977) and Drovenik et al., (1980). Ore-bearing horizon is in tectonic contact with underlying Upper Carboniferous black shales. Hanging wall rocks are micaceous shales in alteration with fine-grained sandstones of Scythian age.

Plate I

Bukovica hematite deposit. Microphotographs of polished sections of ore and host rocks (Gröden sandstones).

Phot. 1 Gröden, quartz sandstone good sorted. Angular and subangular particles of quartz, rare stable lithoclasts and scarce muscovite ar embedded in the matrix built up of hematite, sericite, micrograined quartz and locally of carbonates.

Phot. 2 Breccia-like conglomeratic Gröden sandstone. Composition is similar to that in the phot 1. Two bigger quartz particles (q) contain older pyrite (py, white). In the upper right corner bigger masses of hematite (he) and in the left lower corner hematite replaces (corrodes) detrital particles.

Phot. 3 Partially hematitized Gröden sandstone. Detrital particles are very porous. Hematite (white) fills intergranular space or corrodes detritus frontally.

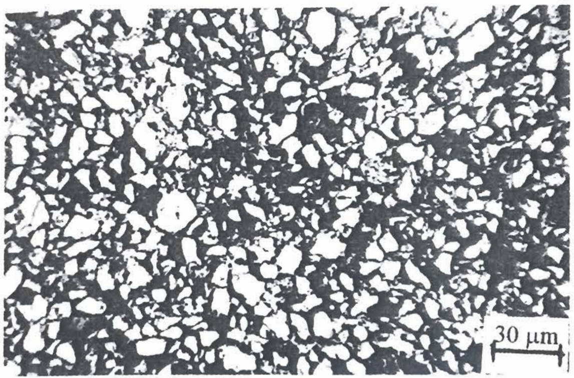
Phot. 4 Strongly hematitized Gröden conglomeratic sandstone. hematite (white) is micrograined or in different colloform structure.

Phot. 5 Compact very finegrained hematite ore with over 60% Fe_2O_3. Matrix is exceptionally scarce.

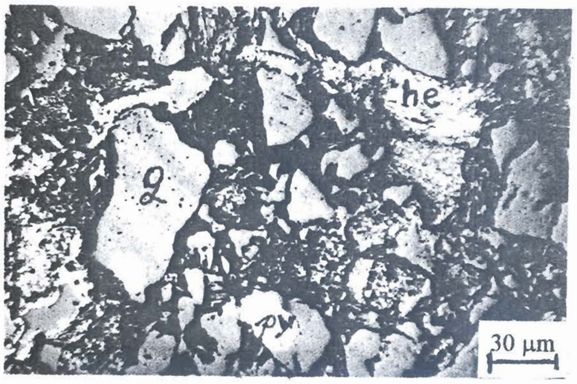
Phot. 6 Gröden conglomeratic sandstone, poorly hematitized (white). Horizontal thiny veintlet of neocalcite in the middle of the polished section.

Phot. 7 Conglomeratic Gröden sandstone. Differently sized detrital particles of quartz (q) and lithoclasts (l) partially or completely hematitized (white).

Phot. 8 Compact micrograined and finegrained hematite (he) cutted by younger diagenetic or epigenetic veinlet built up of hematite (white), carbonates (gray) and other gouge minerals.



Phot. 1



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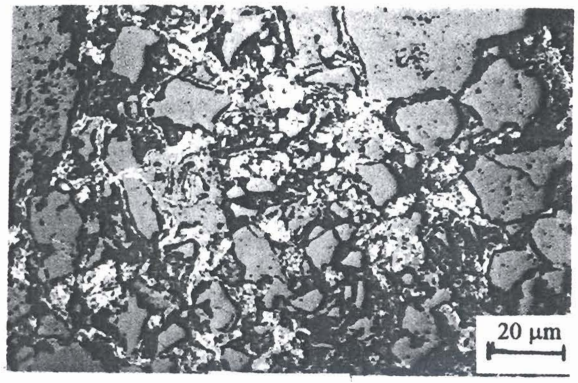

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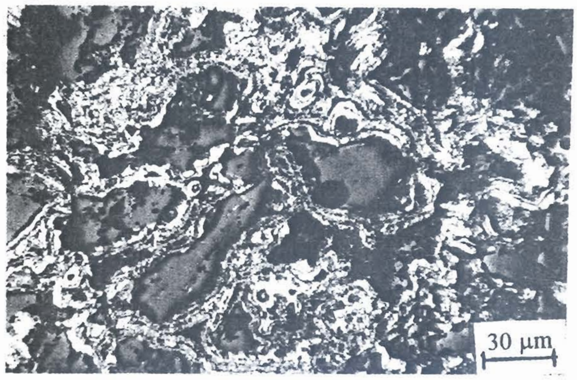

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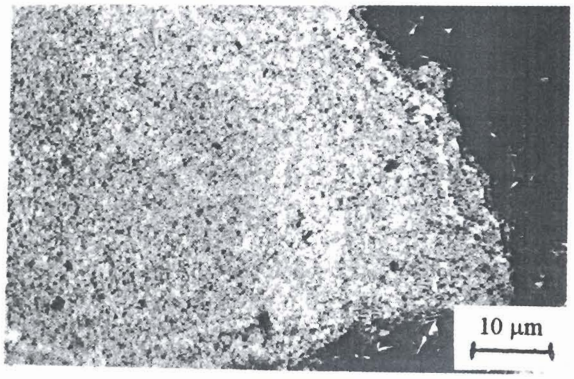

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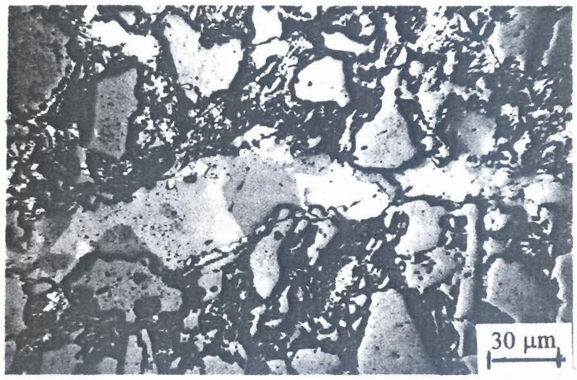

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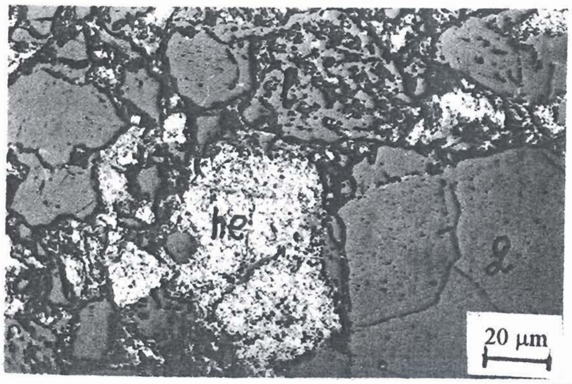

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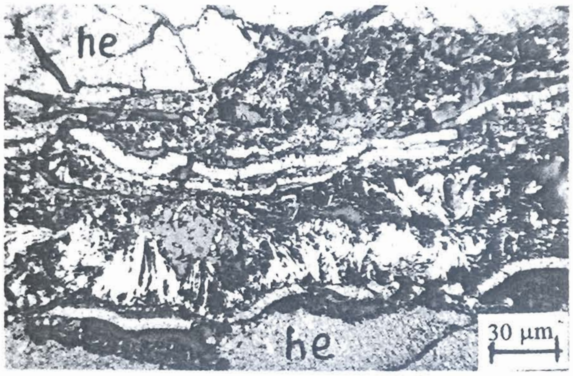

Phot. 8

Plate I

Hematite ore formed during arid climate, precipitated in shallow lagoons as iron hydroxide, and subsequently was transformed in hematite.

Similar deposits occur at **Rude,** nearby the town of Samobor, 25 km west of Zagreb (Jurković, 1962; Šinkovec, 1971). Hematite occurrences are related to the Upper Palaeozoic ferrugineous sandstones and fine-grained quartz conglomerates. The hematite-bearing area is 1.5 km long, stretching NE–SW along the Gradna brook. The hematite ore occurrences are small-sized with lengths of 5–30 m and 1–4 m thick. Laterally, the ore grades towards hanging wall rocks and fotwall into hematitized sanstones containing 8–30% Fe. Herak (1956) ascribed Permian age to the host rocks of the Rude hematite and siderite deposits.

Major hematite is very fine grained (1–10 micrometers) forming bigger or smaller aggregates, compact or porous. Quartz is detrial or chemogene, barite occurs as veintles and small lenses. Matrix is composed of hematite and quartz. The ore is often microbrecciated. Chemical composition of the average ore composite is as follows: 59.2% Fe_2O_3, 19.6% SiO_2, 1.4% Al_2O_3, 0.15% Mn, 17.9% $BaSO_4$, 0.016% P (Šinkovec, 1971). To this day is not explained the genetical and spatial relation between these hematite occurrences and the neighbouring copper-bearing siderite deposit. Jurković (1962) considers that the ore deposits of siderite, hematite, gypsum, anhydrite and dolomite formed as chemical precipitates in the shallow sea. The origin of iron ion is either juvenile or terrigenous. Šinkovec (1971) emphasizes exhalation sedimentary origin for siderite and hematite ore bodies. The hydrothermal activity was taking place in three phases, separated by two tectonic deformations. Jurković & Palinkaš (1996) attribute the Rude hematite deposit to the SCO–IF type.

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Plate II

Bukovica hematite deposit. Microphotographs of polished sections of ore and host rocks (Gröden sandstones).

Phot. 9 Poorly hematitized Gröden sandstone. In the centre a bigger lithoclast and angular pyrite (white) fragments.

Phot. 10 Strongly hematitized Gröden sandstone. Hematite (white) fills the intergranular space of quartz and lithoclast. In the centre angular pyrite fragments (white) lie in the carbonate gauge (black).

Phot. 11 Druse filled with specular hematite (white), finegrained and laminar (tabular, thin sheeted) growing from the walls of the druse towards the centre. Druse is encircled by microgranular colloform hematite (gray).

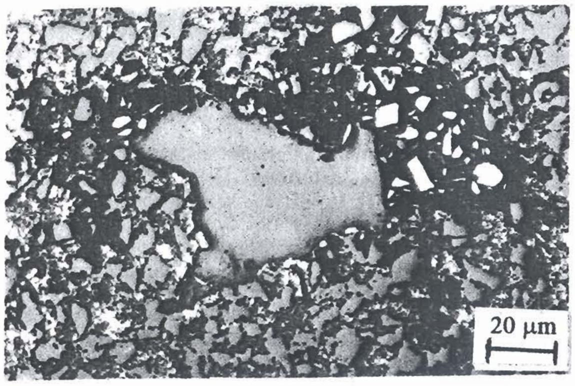
Phot. 12 Reniform aggreates of pure hematite with high reflectance (white) in the microgranular hematite intimately mixed with gauge minerals (gray).

Phot. 13 Reniform aggregates: typically rhythmic botryoidal colloform masses and rhythmic concentric forms of hematite (white, grayish-white) with quartz and carbonates (black, dark grey).

Phot. 14 Finely rhythmically precipitated hematite, mostly with lower reflectances. On the left and in the middle, in the rhythmical material, beginning of formation in well crystallized state (white).

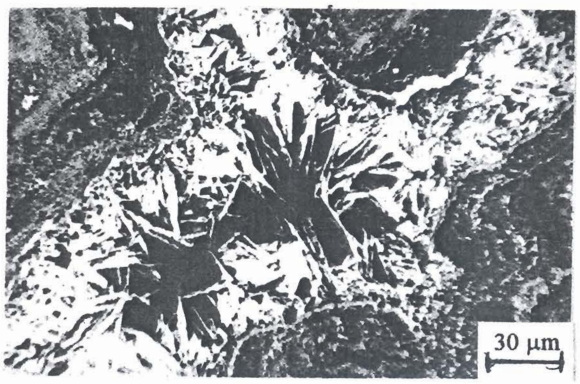
Phot 15. Pyrite (py) – siderite (sd) – barite (ba) veinlet, 3–4 cm thick cuts the Gröden sandstone (gs). The $\delta^{34}S$ of barite is +19.50‰

Phot 16 Detail from the phot. No 15. Coarsegrained, pentagonal dodecahedron fissured pyrite crystals (py) are the oldest minerals, followed by xenomorphic, coarsegrained pleochroitic siderite (sd) and by coarsegrained baryte (ba).



Phot. 9

Phot. 10



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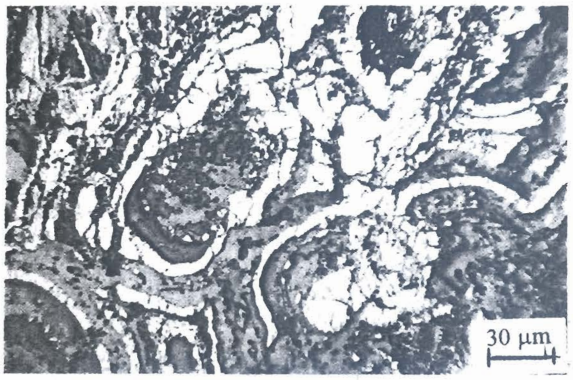

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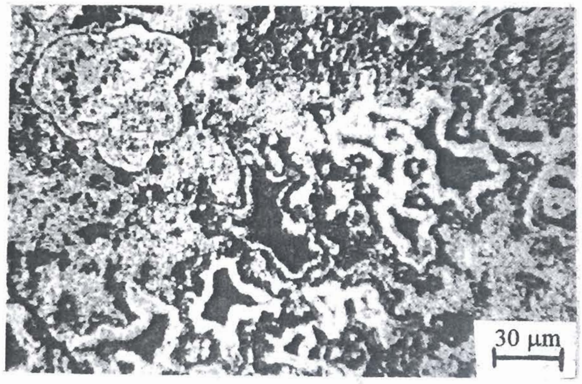

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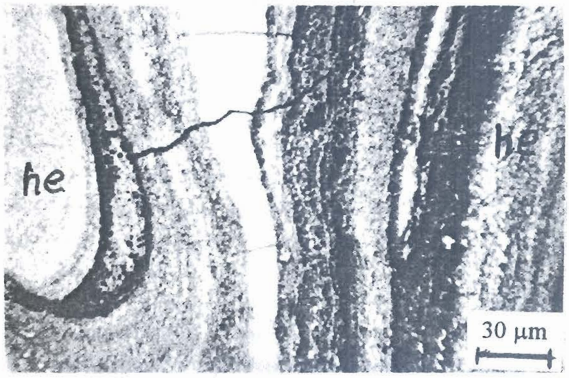

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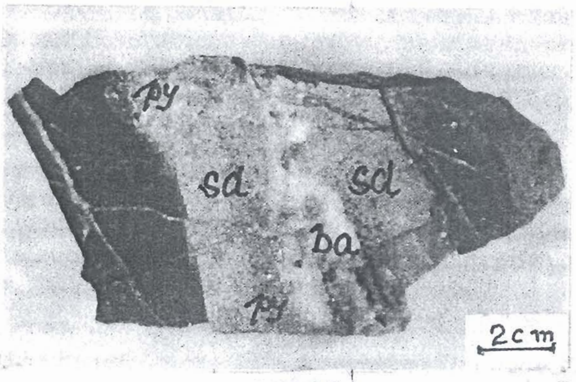

Phot. 15

Phot.16

Plate II

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