Geol. vjesnik	Vol. 41	str. 317—339	Zagreb 1988.

UDC 553.445:550.42 *Izvorni znanstveni rad*

Lead Deposits in the Zrin District of Trgovska Gora in Croatia

Ivan JURKOVIĆ and Goran DURN

Rudarsko-geološko-naftni fakultet Sveučilišta u Zagrebu, Pierottijeva 6, YU — 41000 Zagreb

The paper gives a historical survey of mining operations in the Paleozoic of Trgovska Gora in Croatia, and a more detailed account of the Zrin district, with its former Zrin and Franz mines, where mining was conducted for silver-bearing galena in Illyrian and Roman times as well as in the Middle Ages. A survey of the paragenetic types of the Trgovska Gora ore occurrences is also given: (a) ankerites and ankeritised limestones; (b) siderites ± quartz ± very small amounts of sulfides; (c) cms or tens of cms of scale layered siderite-quartz deposits ± sulfides; (d) siderite deposits with chalcopyrite; (e) siderite deposits with Cu, Zn, Pb, Ni (Co) sulfides and sulfosalts; (f) siderite deposits with silverbearing galena.

The results of field and laboratory researches into microelements (Zn, Pb and Cu) are shown in all types of rocks and soils on 100 kms² surface area of the paleozoic zone. It was established that there is 3 times as much Zn and Cu and twice as much Pb in the silts and shales as in the sandstones. The general ratio of the metals is Zn > Pb > Cu. In the soils there are uniform amounts of microelements above all types of rocks, the ratio is Zn > Cu > Pb. Rocks in the vicinity of ore occurrences show no anomalies, but soils next to ore-bearing areas give anomalous values.

A more detailed account is given of the microphysiography and the sequence of hypogenic minerals in the Zrin district ore occurrences: pyrite I, quartz I, siderite I, pyrite II, quartz II, sphalerite with exsolutions of chalcopyrite I, chalcopyrite II, tetrahedrite I, tetrahedrite II (as exsolution in galena), mineral »T« with exsolutions of chalcopyrite III. and gersdorffite. In the hypergenic paragenesis relatively small amounts of the following were found: goethite, lepidocrocite, covellite, chalcocite, anglesite, malachite and azurite.

U radu je dat historijski prikaz rudarske djelatnosti u paleozoiku Trgovske gore u Hrvatskoj, a detaljnije za područje Zrin sa nekadanjim rudnicima Zrin i Franz gdje se u ilirsko, rimsko doba i srednjem vijeku rudarilo na srebronosne galenite. Dat je i pregled paragenetskih tipova rudnih pojava Trgovske gore: (a) ankeriti i ankeritizirani vapnenci; (b) siderit ± kvarc ± vrlo malo sulfida; (c) cms »or tens of cms of scale-layered siderite-quartz deposits« ± sulfide; (d) sideritska ležišta sa halkopiritom; (e) sideritska ležišta sa Cu, Zn, Pb, Ni (Co) sulfidima i sulfosolima; (f) sideritska ležišta sa srebronosnim galenitom.

Prikazani su rezultati terenskih i laboratorijskih istraživanja na mikroelemente (Zn, Pb i Cu) u svim tipovima stijena i tala na površini od 100 km² paleozoika. Utvrđeno je da u siltitima i šejlovima ima 3 puta više Zn i Cu i 2 puta više Pb nego u pješčenjacima. Opći odnos metala je Zn > Pb > Cu. U tlima je podjednako količina mikroelemenata nad svim tipovima stijena, odnos je Zn > Cu > Pb. Stijene u blizini rudnih pojava ne pokazuju anomalije, ali tla u susjedstvu orudnjenja daju anomalne vrijednosti.

Detaljno je prikazana mikrofiziografija i sukcesija hipogenih minerala u rudnim pojavama Zrin revira: pirit I, kvarc I, siderit I, pirit II, kvarc II,

sfalerit s izdvajanjima halkopirita I, halkopirit II, tetraedrit I, tetraedrit II (kao izdvajanja u galenitu), mineral »T« s izdvajanjima halkopirita III te gersdorfita. U hipergenoj paragenezi nađene su manje količine getita, lepidokrokita, kovelina, halkozina, anglezita, malahita i azurita.

Geographical location of the Trgovska gora

The Trgovska gora (Bešlinac) ore field is situated SSE of Zagreb at a distance of about 80 kms as the crow flies *(Fig. 1)*. Its SE and SW limits are formed by the frontier of Bosnia and Herzegovina, its NE limit by the main road Bosanski Novi — Dvor na Uni — Rujevac— Gvozdansko — Glina (along the river Žirovac), and its NW limit by the upper reaches of the Žirovac. The area lies in the catchment area of the river Una with the river Žirovac as its main tributary. Many of the streams running into this brook have a NW direction. The region has the features of low mountains. The highest summit is Ljubina (+577 m).

History of mining and geological operations (according to I. Jurković, 1962a)

In the Trgovska gora area numerous craters and slag heaps bear witness to intensive mining activity in search of iron and silver-bearing lead ores in Illyrian and Roman times. After the fall of the Roman Empire mining operations died out. Mining began again with the coming of the Saxons at the end of the 10th and the beginning of the 11th century. In 1453 King Matthias Corvin granted Count Peter Zrinski mining concessions for lead, silver, gold and other ores in the Trgovska Gora area.

The first mines were opened in the valley of the Majdan stream, and the fortress of Gvozdansko was built in order to protect them. Development reached its peak during the first half of the 16th century. In 1529 600 tons of lead ore was produced, with 8% Pb and 33 grammes per ton of Ag, or 50 tons of Pb, and 19.65 kgs Ag to a value of 30,000 ducats. From 1529 a forge for silver pfennigs operated in Gvozdansko on a concession from King Ferdinand. Turkish incursions (1561, 1574, 1576 and 1577) disrupted the operation of the mines. In January 1578 the Turks captured the fortress of Gvozdansko, demolished it, and flooded the mine workings. During the Middle Ages mining was carried out only for silver-bearing lead ore in the Majdan valley, Tomašica and Srebrenjak, and on our estimates 2 — 3,000 tons of lead and 800 — 1400 kgs of silver were extracted. There was also mining for hard limonite and iron ore for iron production.

In the 17th century mining activity lapsed, but at the beginning of the 18th century the Austrian court financed some prospecting, and from 1771, at the instigation of the Empress Maria Theresia, prospecting was pursued at a number of sites in the valley of the Majdan potok, Gradski potok, Srebrenjak and Tomašica (Wojtanek, 1772; B. Hacquet, 1789).

In 1797 the Trieste mining company founded the »Trgovi Ironworks« and opened iron mines at Kosna and Gvozdansko; in 1804 they built blast-furnaces at Kosna and near Trgovi. Because of financial problems the mines and the smelting plant were sold in 1832 to two businessmen, Planker and Jagern, who developed mining for copper ore at Gradski potok and abandoned mining for iron ore.

In 1840 the Viennese Ministry of Agriculture and Mines once more opened mines and, in 1842, a copper smelting plant. V. M. Lipold (1855) surveyed the Trgovska gora region giving a favourable assessment, and a businessman, Desiré Gilain bought the rights and established a limited company, »Trgovi Mines and Smelting Works Co. Ltd.«, Beślinac. From 1857 to 1874, 1845 tons of Cu ore and 83.5 tons of Pb ore were extracted. Prior to 1870 the firm was bought up by an entrepreneur called Frohm, who was succeeded by Mulay. Frohm converted the copper and lead smelting plant at Bešlinac into a blast furnace for the production of iron, because the price of copper and lead in the world market had sharply declined. For that reason work at the Gradski potok copper mine was discontinued.

After Frohm's death in 1894, T. Zloch (1897) assessed the ore reserves of all the mines and the geological conditions of Trgovska Gora, and both smelting works ceased to operate until 1900. In 1901 all the mining rights were bought by the »Société anonyme des hauts fourneaux, mines et forêts en Croatie, Trgovo—Bešlinac (Bruxelles)«. Copper mines were reopened at Gradski brook but all work was stopped in 1913 on account of deep wedge faults which limited the ore-bearing zone and because of the poverty of the ore beds. Subsequently all rights passed into the possession of the Anglo-German Bank, and, after 1918, into the possession of the »Vereinigte Berg- u. Hüttenwerke, A. G., Zagreb«. In 1941, the rights were bought by »Bata Ltd.«.

Prospecting was resumed in 1948, carried out by »Kordun Metal and Non-metal Mines«, and, in 1949, by the Ljubija iron ore mine, near Prijedor. Work was discontinued in 1950. From 1952 prospecting operations were taken over by »Sisak Ironworks«, mainly in connection with iron ore, but also partly in relation to copper deposits in the Gradski potok field, and lead ore at Srebrenjak, but these operations were also discontinued later.

Geological characteristics of the Trgovska Gora

Trgovska Gora is a paleozoic massif bordered by two large faults. In the NW, W and NE sector, an exceptionally pronounced fault forms an anomalous contact between the Upper Paleozoic sediments and various members of the Triassic and serpentine, while the other part to the SW leads to an anomalous contact of the Paleozoic wih the Werfenian of the Lower Triassic and with the Middle Triassic rocks.

The mountain is built of paleozoic sediments running generally in a NW—SE direction, and in the NE sector dipping to SW (at 50° to 90°). Within the sediments two series can be distinguished, an older series of clayey schists with alternations of thinner or thicker intercalations of silt sandstones, subgreywacke and greywacke (cšp), and a younger sandstone series with a decreasing number of intrusions of clayey schists in the hanging wall parts (cpš) (V. Majer, 1964; D. Devidé-Neděla, 1953).

On the basis of interim classifications of flora and fauna by D. Stur, (1868), V. Kostić (1956), Ž. Đurđanović (1968, 1973), the lower series is of the Devonian-Carboniferous age, while it is assumed (E. Tietze, 1872; D. Nevidé-Neděla, 1953) that the upper series is of the Lower Permian age.

In the salian phase of variscan orogeny an elevation and folding of paleozoic sediments came about, and the continental phase lasted until the uppermost Permian, when renewed transgression led to the sedimentation of a series of sandstones and the continued sedimentation of Werfenian strata of the Lower Triassic.

The ore occurrrences are linked to the older, lower series of sediments. They are affected by all the tectonic processes, like the rocks in which they are located, and are concordantly embodied in them. They belong, for this reason, to the variscan metallogenic epoch (I. Jurković, 1960, 1962a, b).

Paragenetic types of ore occurrences in the Paleozoic of Trgovska Gora

On the basis of earlier results of researches carried out by one of the authors of this paper (I. Jurković, 1952, 1953, 1960, 1962a and 1962b), and their revision in the light of a comparative analysis involving other paleozoic ore deposits in Croatia and Bosnia, it is possible to identify seven main paragenetic types in paleozoic sedimentary area of Trgovska Gora.

First type: *monomineral ankerites and ankeritised limestones and dolomites* with low iron content of 4—25 %, more rarely of up to 35 % Fe. They are found in a zone of clayey schists with intercalations and lenses of limestones and dolomitic limestones. Apart from ankerite, they contain a little quartz and very small quantities of pyrite and galena. The superficial areas are oxidized into high-grade limonite. Of 11 recorded occurrences the most important are Turski potok, Likarevac, Vidorija, Gubavac, Šestina Kosa, Barbara, and they are also found in a belt on the right bank of the Žirovac potok (brook), from the village of Gvozdansko in the north-west, then alongside the villages of Bešlinac, Trgovi and Grmušani, in the catchment area of the lower reaches of the water-courses Majdan, Velebit, Ljubina and Sočanica. From the economic point of view they are of little account, the exploitation of limonite was on a modest scale.

Second type: *siderite and siderite-quartz* occurrences are mostly 10—20 % quartz and 1—2 % sulfide, predominantly pyrite and chalcopyrite. They appear in the same zone as the ankerite occurrences. Of 14 recorded occurrences the most important are Kosna, Primorski Jarak, Gradina, Mautner, Breda, Šišmanovac, Resanović and Burazovac. The siderite is coarse-grained, and in the oxidization zone it takes the form of high-grade limonite. The occurrences are mainly on a very small scale. The siderite occurrences are in the form of layered lenses, irregularly edged layers, discontinuous series of lenses and nests concordantly lodged in schists.

Third type: *stratified or bedded siderite monomineral deposits.* In the area of Komorska Glavica, Gvozdansko, Dupalo and Janja Bara on the left bank of the Žirovac potok there are five registered occurrences in a zone of quartz and clay schists. The schists are slabs or tablets, and siderite occurs between them as intercalations in the form of layers or lenses from several mms to several cms, more rarely some ten cms thick. Packets of these rocks are formed with alternating layers of siderite and quartz-clay schists. Such composite strata attain a thickness of 10 m. The iron content is low, varying from 15—25 % Fe. The mineralisation has an outer appearance similar to itabirite.

Fourth type: *copper-bearing siderite deposits,* Gradski potok (brook) type. The bulk of these deposits is situated in the area between Hasanov Grob (+385 m.) and the upper reaches of the streams Gradski potok, Svinjica and Sredorak. The largest ore-bearing field is Gradski potok; apart from that there are smaller occurrences in Katarina, Julius, Karola, Franz and Svinjica. These are siderite occurrences with significant amounts of quartz, in places equal with the amounts of siderite, and chalcopyrite as the main sulfide mineral. There is also a little pyrite and silver-bearing galena, tetrahedrite ,marmatite, bornite, and microscopic quantities of gersdorffite (korynite). These ore fields were in part exploited in ancient times and in the Middle Ages for silverbearing galena and in the 18th and 19th century very intensively for copper ores. Copper ore occurrences are concordantly deposited in a series of clayey schists in the form of stratified veins and stratified series of lense-like bodies.

Fifth type: *siderite with silver-bearing galena* as the main sulfide mineral. Chalcopyrite, tetrahedrite, marmatite, and pyrite are subsidiary constituents, with gersdorffite (korynite) in microscopic quantities. Quartz is a significant gangue mineral.

These deposits occur west of the copper deposits in Gradski potok in the catchment area of the tributaries running into the Mali Majdan stream (Zrin and Franz workings), as well as in the catchment area of tributaries to the Velebit potok (Čatrnja and Jamsko workings). These occurrences also take the form of concordantly intruded beds (Lagergänge).

Sixth type: *siderites with polymetallic sulfide paragenesis.* This type of deposit is found in the catchment area of the Srebrenjak potok, a left-bank tributary of the river Una south-west of the town of Bosanski Novi (sites Adam, Eva, Srebrenjak, Marijana, Strgar), and in the Tomašica area, 4 kms SSW of Bosanski Novi, on the left bank of the Una, in Croatia. Siderite is the main mineral, there are perceptible amounts of quartz, very little barite (Tomašica), while galena, chalcopyrite, pyrite, tenantite, and sphalerite are involved in the paragenesis to the extent of several percent. A certain amount of Ni(Co) and Pb—Sb sulfosalts were identified microscopically (I. Jurković, 1960). The ore occurrences are concordantly intruded into paleozoic rocks.

Seventh type: *monomineral occurrences of barite* were discovered in the Tomašica area SSW of Bosanski Novi, not far from the polymetallic siderite occurrences there. Very small amounts of galena, pyrite and tetrahedrite are included in small scale occurrences of barite that are concordantly intruded into upper paleozoic sediments.

Pebbles of barite are found in the alluvium of the left bank tributaries of the river Una.

In the vicinity of the village of Gvozdansko in the NW part of Trgovska gora, near the junction with the Middle Triassic sediments in a tectonically highly dislocated zone, lense-shaped veins of barite with outcrops several meters long are found in right-hand wall of the narrow valley of the Gvozdansko potok. The maximum thickness of the barite measured 40 cms. Barite is the main mineral, it contains oxidised grains of pyrite, or even more small cavities formerly filled with small limonitised crystals of pyrite. Grains of galena may be seen here and there. In the gorge downstream there is a fair quantity of barite pebbles at a number of points.

The Ore-bearing district of Zrin

It is situated in the catchment area of the water-courses Ograda, Rudarski (Zrin) potok, Simonov potok and Dragušnica, which flow in narrow valleys between Mt. Pavlovo (+383 m.) to the west, and Hasanov Grob (+385 m.) to the east, and constitute the Mali Majdanski stream, which runs into the Majdan potok north of he village of Majdan; the Majdan is itself a right-bank tributary of the river Žirovac, entering it by the village of Gvozdansko (Fig. 2).

During the Middle Ages there was unusually intensive mining activity in the Zrin district and further south in the Čatrnja district with prospecting for silver-bearing lead ore which was extracted and smelted in a smelting works near Gvozdansko. Silver was extracted from the lead and silver coinage manufactured. The mines of this area were the basis of the economic power of the Counts Zrinski in the period from 1463 to 1578, in which year the Turks captured Gvozdansko and destroyed fortress, the smelting works, the forge and all the mining plant.

In the Zrin district two major mines, Zrin and Franz, operated, with three smaller works north of Zrin — Ilinička (Fe), Košujevac (Cu) and Ograda (Fe). At the end of the 18th and the beginning of the 19th century prospecting was resumed, first on the Zrin site, and then at all the other workings. That continued until 1870, when operations ceased except for the Franz mine, which produced copper ore during the period 1901—1914.

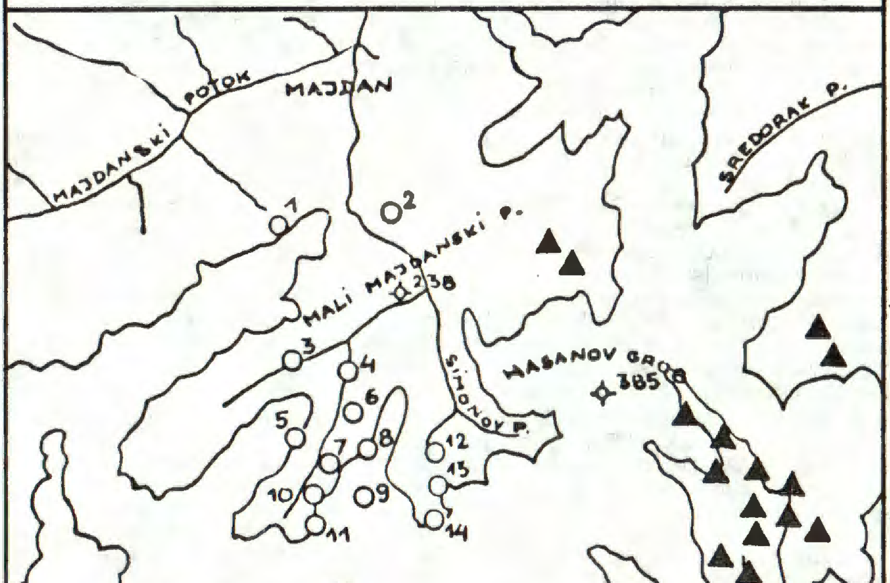
At the Zrin workings, which were opened with the adits Zrin and Leopold, the inclines Alexander and Francisca and the mine-shafts Leopold and Juliana revealed three parallel ore-bearing zones running in a general N—S or else NNW—SSE direction and dipping towards the E. The central zone was the richest and the most stable and was explored to a length of more than 250 m. To the north of it at a distance of some 15 m. is a second ore-bearing zone which is less rich and very unstable, while to the south at a distance of some 50—60 m. from the central zone, a third zone, relatively rich and with significant enrichment here and there, was opened up by the Alexander and Francisca inclines. During the

Fig. 2

Pb-Cu ORE DEPOSITS IN TRGOVSKA GORA

ORE DEPOSITS: O Pb (ZRIN) ● Pb (ČATRNJA)

▲ Cu (GRADSKI POTOK)



1. ILINIČKA ADIT 2. KOŠUJEVAC 3. OGRADA 4. KÜBECK 5. KOLAREC 6. ZRIN ADIT 7. JULIJANA SHAFT 8. LEOPOLD ADIT 9. LEOPOLD SHAFT 10. ALEKSANDAR INCLINE 11. FRANCISKA INCLINE 12. DONJI FRANZ ADIT 13. SREDNJI FRANZ ADIT 14. GORNJI FRANZ ADIT

period of prospecting in the 18th and 19th century there was partial exploitation of the third zone by incline workings and of the first zone in Zrin by means of an adit.

In the Franz working about 350 m. east of the Zrin mine, in the Simonov potok valley, a concordantly situated ore-bearing zone was opened in a shallow paleozoic synclinal structure with three adits at vertical intervals of 50 m. Prospecting and ore extraction was carried out in the west wing of the syncline with dip towards the E., and to a much lesser extent on the east wing with dip towards the W. According to various estimates by eye-witnesses the mineral deposits extended between 260 and 400 m., with a height of 80 m. (45° towards the E, alternatively NNE). In the Middle Ages silver-bearing galena was extracted from these working, while in the 18th and 19th century and the early 20th century it was mostly copper ore, with rather less lead ore.

The main mineral in both these former mine workings is coarse-grained siderite. According to F. Tućan (1907) siderite from the Zrin adit showed the following composition on quantitative chemical analysis: insoluble in HCl 0.89%, Al_2O_3 0.09%, FeO 56.65%, MnO 1.28%, CaO 0.23%, MgO 2.54%, traces of S, and CO_2 38.17%, overall 99.85%, or recalculated 91.22% $FeCO_3$, 2.07% $MnCO_3$, 0.41% $CaCO_3$, 5.33% $MgCO_3$, 0.09% Al_2O_3 and 0.89% insoluble residue. Along with siderite there are perceptible amounts of quartz.

Prospecting operations were carried out in the 18th and 19th century in an attempt to link the Zrin mine to the Čatrnja mine, but when this work was discontinued it was still 200—250 m. short of the proposed junction, which would have given a extension ore of 800 m. extending along the dip some 80—100 m. below the deepest medieval workings.

The following authors provide information on the ore deposits of the Zrin district: Wojtanek (1772) states that there was prospecting for lead ore; B. Hacquet (1789, IV) that on the dump at the Leopold adit he found galena in white quartz, clayey schists and coarsely crystallised brownish-red siderite with dispersed chalcopyrite in places. V. R. Zepharovich (1859) writes of dense masses of galena or of galena crystals on siderite, or of galena dispersed in siderite at Zrin. From the Franz mine he reports tetrahedrite, either dense or dispersed in siderite. F. v. Adrian (1868) states that the Zrin deposits had been opened to a length of 190 m. K. Ritter v. Hauer (1870) writes that there were deposits of lead and copper ores in the southern ore-bearing belt of Trgovska gora. He considers that the lead ore had largely been extracted during the Middle Ages. Along with chalcopyrite, the Zrin ore field contains silver-bearing galena and Zrin was reopened in 1869 by means of an adit which cut through four rich galena strata (»Bleierzblätter«). According to this author, the dumps in Majdan contain specimens with 20—30 lbs Pb and 1—2 ozs of silver, along with a fair amount of slag. M. Kišpatić (1901), listing minerals from Trgovska gora mentions silver-bearing galena from the Zrin site in paragenesis with siderite, quartz, chalcopyrite, and sphalerite. In the Franz adit he mentions tetrahedrite dispersed in siderite. F. Tućan (1908) worked out a quantitative chemical analysis of siderite from the Zrin adit. K. Reuter (1910) mentions the Franz adit in which the same type of minerals had been exposed as in the Gradina shaft of the Gradski potok district, the deposits extending to 400 m. at a depth of 83 m., but he states that no connection between Franz and Gradina could be established, because marked tectonic dislocations had blocked the way in the course of mining operations. Copper ores in both these working appear as compact stratified structures bound to siderite and quartz, or else change into individual lenses, ribbons, impregnations and incrustations. About 400 metres further on, in a hanging wall of gaithalian schists, according to Reuter, there is a hanging wall ore zone with silver-bearing galena and tetrahedrite, with chalcopyrite in places. It was opened in the Zrin district by the Leopold and Zrin adits, and Kolarec, as well as by numerous craters to a distance of 1.4 kms, and runs in the same NNW—SSE direction as those in Franz, but with the opposite inclination, i. e. ENE. He explains this by the displacement and slipping of strata. According to him, the Devonian sediments in the shape of thin plates of black schists have intercalations of coarse-grained sandstones in Zrin. In the context of a detailed account of ore occurrences of Trgovska Gora, K. v. Papp (1919) writes that the copper and lead ore deposits are sited in the western part of the Paleozoic, in Carboniferous schists (and not in the Devonian as claimed by Papp's reference), and that they take the form of symmetrical lenses, i. e. beds (»Lager«). It runs NNW—SSE, dipping towards WSW (50° to 60°) in its western parts (lead-bearing), and towards ENE in its eastern part (copper-bearing), forming a strongly vaulted anticline. Aleksijević (1922) also quotes the Franz mine as a copper ore deposit in his report. I. Turina (1933) mentions the existence of the Juliana mine in the Zrin district. F. Tućan (1941) writes of the abandoned Zrin adit as having siderite, with dispersed galena, chalcopyrite, pyrite and a little sphalerite. We find a more detailed account of the Zrin district in papers by I. Jurković (1953, 1962a, 1962b).

Paragenesis of the ore occurrences in Zrin district (fig. 3)

Hypogenic minerals: pyrite I, quartz I, siderite I, pyrite II, quartz II, sphalerite (marmatite), chalcopyrite I, chalcopyrite II, tetrahedrite I, tetrahedrite II (freibergite), mineral »T«, chalcopyrite III with exsolutions, galena, gersdorffite (korynite).

Metamorphic minerals: siderite II, hematite.

Hypergenic minerals: anglesite, chalcocite, covellite, goethite, lepidocrocite, malachite, azurite.

Siderite is the main mineral of the ore occurrences in the ore-bearing district of Zrin. Quartz comes next in quantity after siderite. With the naked eye we were able to identify galena, chalcopyrite, pyrite, tetrahedrite and, very rarely, sphalerite. Galena is the main sulfide mineral.

Microphysiography of the minerals

Hypogenic minerals:

Pyrite I appears in the majority of specimens prepared for microscopic analysis (60 % of specimens) as individual rounded corroded grains in siderite I. Apart from the individual grains, we may also note accumulations of rounded grains of pyrite I. In one specimen we also observed a few idiomorphically developed crystals of pyrite I. The initial phase of oxidization of pyrite I into goethite and lepidococrite was perceptible only here and there.

Quartz I is a subsidiary component in the paragenesis. It features in individual ore specimens as rounded, corroded individual or aggregated grains in siderite I. Together with pyrite I it represents the oldest (first) generation of mineralisation, or relics of detrital quartz particles.

Siderite I is the main mineral in all the microscopically prepared specimens. It is in the form of large crystals or idiomorphically developed, with very clear to perfect cleavage, very pronounced reflective pleochroism and very strong anisotropic effects. It embodies corroded or strongly resorbed grains of pyrite I and quarz I from the first generation of mineralisation. The younger generation of quartz II, sulfides and sulfosalts replaces siderite I. In the case of the majority of younger minerals there is a clear succession in the crystallisation: pyrite II → quartz II → sphalerite (marmatite) → chalcopyrite II → tetrahedrite I → galena. It is only the position of the Ni-minerals that is not entirely clear. Of the minerals of this third generation of mineralisation, the

Hypogenic an hypergenic minerals Fig.3

Succession, intensity and extensiveness

(Redoslijed izlučivanja, intenzitet i ekstenzitet)

Phases of succession	MINERALS -(Minerali)		Intensity	Extensiveness
	Hypogenic (primarni)			
I	PYRITE I	PIRIT I		
I	QUARTZ I	KVARC I		
II	SIDERITE I	SIDERIT I		
III a	PYRITE II	PIRIT II		
III a	QUARTZ II	KVARC II		
III a	GERSDORFFITE	GERSDORFIT		
III b	SPHALERITE	SFALERIT		
III b	×CHALCOPYRITE I	HALKOPIRIT I		
III b	CHALCOPYRITE II	HALKOPIRIT II		
III b	TETRAHEDRITE I	TETRAEDRIT I		
III b	MINERAL "T"	MINERAL "T"		
III b	×CHALCOPYRITE III	HALKOPIRIT III		
III c	GALENA	GALENIT		
III c	×FREIBERGITE	FRAJBERGIT		
MINERALS FORMED BY METAMORPHOSIS				
Hypogene phase	SIDERITE II	SIDERIT II		
Hypogene phase	HEMATITE	HEMATIT		
HYPERGENIC (sekundarni)				
Secondary minerals	ANGLESITE	ANGLEZIT		
Secondary minerals	GOETHITE	GETIT		
Secondary minerals	LEPIDOCROCITE	LEPIDOKROKIT		
Secondary minerals	CHALCOCITE	HALKOZIN		
Secondary minerals	COVELLITE	KOVELIN		
Secondary minerals	MALACHITE AZURITE	MALAHIT AZURIT		

× .. exsolutions (izdvajanja)

most abundant are quarz II and galena, followed by chalcopyrite, then tetrahedrite, with sphalerite and the Ni-minerals least represented. The minerals of the youngest generation replace siderite I along the rhombohedral plane of cleavage, at micro-fissures, on the edge of siderite grains. This mode of replacement leads to the formation of irregular systems of micro- and macro-veins, especially of quartz II and galena but also irregular nests and small masses which here and there incorporate the remains of corroded siderite (sieve-like, insular structures), especially in galena. In individual drusy spaces bordered by siderite I and quartz II there are »plages« of tetrahedrite I and tetrahedrite I with accrued small masses of chalcopyrite II. The largest masses of tetrahedrite I form »plages« with galena. In some specimens siderite I displays in crossed nicols red or brown internal reflexes and assumes the appearance of so-called »Braunspat« with the initial phase of hematitisation. In some specimens oxidization of siderite I into goethite is in the initial stages along the plane of cleavage. Cataclased and tectonically stressed parts of siderite I are more strongly limonitised. In one ore sample we noted how siderite I cements fragments of black argillaceous slate. In more strongly cataclased parts of siderite I recrystallites of fine grained siderite II can be seen.

Pyrite II is clearly observed only in one microscopically prepared specimen. In this specimen siderite I had been replaced to a considerable degree by a younger generation of sulfides, sulfo-salts and quartz II, and it was possible to determine the sequence of formation of these minerals.

Quartz II is, after siderite and allong with galena, the most plentiful mineral in the ore paragenesis and it is present in the majority of ore samples. Quartz II, together with sulfides and sulfo-salts, replaces siderite I at cleavage planes, fissures and the edges of siderite I grains, creating micro-grain systems and scattered small masse and »plages« of younger minerals. Considering that there is a chronological sequence in the crystallisation of these most recent minerals, quartz II, which, along with pyrite II, is the oldest in the series, is also subject to partial replacement by later crystallised sulfides and sulfo-salts. In the drusy spaces formed by replacement between siderite I and quartz II, larger or smaller masses of individual sulfides and sulfo-salts, or sometimes several of them together, have crystallised, most often tetrahedrite I and galena or tetrahedrite I and chalcopyrite II. In one of the rather larger quartz II masses which has replaced siderite I there are microscopically small masses of gersdorffite (korynite), tetrahedrite I and chalcopyrite II.

Sphalerite (marmatite) is found in a third of the ore specimens in very small quantities, the smallest of all other sulfides and sulfo-salts of the third generation, except gersdorffite and mineral »T«. The sphalerite is of marmatite type, contains quantities of iron in its crystallographic lattice, and manifests dark brownish-black internal reflexes. Looked at with the naked eye, it is black in colour. In some ore specimens we can observe within the sphalerite an exsolution of chalcopyrite I in the form of microscopically small droplets and lamellae, which also indicates the relatively high temperature of crystallisation (above 200 °C). The sphalerite is in part somewhat older than the chalcopyrite II, because the latter replaces it, but also in part coeval with it, because we can observe accreted masses of the two minerals. We also observed accreted masses of sphalerite and tetrahedrite I, all of which indicates relatively brief time differences in the crystallisation: sphalerite → chalcopyrite II → tetrahedrite I. In some »plages« of sphalerite there are small masses of tetrahedrite I and chalcopyrite II with no visible evidence of mutual replacement.

Chalcopyrite I was noted in a fifth of the specimens, in a majority of those containing sphalerite. It takes the form of droplets and lamellae exsoluted on the crystallographic plates of sphalerite. In consequence of additional pressure a proportion of these exsolutions lose their original shapes and aggregrate to form larger, irregular shapes.

Chalcopyrite II is present in the majority of the ore specimens, and, after galena, is the most plentiful sulfide; it belongs to the most recent generation of mineralisation. It occurs most frequently in association with tetrahedrite I, galena, and very rarely with sphalerite. It replaces siderite I, quartz II, and sometimes also sphalerite. It forms small accreted masses with tetrahedrite I ,sometimes also with sphalerite, which indicates that these minerals were to some extent crystallised simultaneously. In places we observed that tetrahedrite II and galena replace chalcopyrite, which remains in them as small irregular residues. Chalcopyrite II is older than galena and in part also older than tetrahedrite I. In »plages« of sphalerite we observe it together with tetrahedrite I. In one rather larger mass of quartz II which replaces siderite I, microscopically small masses of tetrahedrite I and chalcopyrite II can be seen in association with gersdorffite. Significant for the determination of the mineralisation sequence is the presence of idiomorphically developed small crystals and skeletal forms of gersdorffite (korynite) and chalcopyrite II. Considering that the ore specimens for microscopic examination were taken from the lower parts of the Zrin deposits, these are very rare signs of incipient oxidisation of chalcopyrite II and its weathering into the descendent minerals chalcocite along systems of micro-fissures.

Tetrahedrite I is a mineral of the third generation of mineralisation, the quarz II, sulfide and sulfo-salts phase. In polarised reflected light it is grey in colour, probably Sb(As) tetrahedrite. It visibly replaces siderite I, quartz II and sphalerite, also in part chalcopyrite II. It accretes to chalcopyrite II, but also contains the latter in the form of residues arising from replacement. Tetrahedrite is older than galena and somewhat more recent than chalcopyrite II; in quantity it is less than both these minerals, in particular a great deal less than galena. Tetrahedrite I is mostly in »plages« between siderite I and quartz II, in association with galena. The largest such mass of tetrahedrite I measured 0.7 × 0.2 mms. Tetrahedrite I together with chalcopyrite II was observed in the »plages« of sphalerite. In siderite I it was noted in association with skeletal gersdorffite, and in quartz II with gersdorffite and chalcopyrite II. Tetrahedrite I was observed in half of the ore specimens analysed.

Tetrahedrite II is silver-bearing tetrahedrite or freibergite. This mineral is the main bearer of Ag in the ore deposits on the Zrin site. In refracted polarised light, it is olive in colour with yellow tints. It appears as exsolutions in galena. Relatively little is left of the original forms of tetrahedrite II exsolutions (droplets, oval shapes, lamellae), subsequent amalgamations have formed rounded masses or irregularly shaped masses alone, or in association with chalcopyrite II. The dimensions of these shapes vary between 5 to 100 μm, one of the largest measured 150 $\times$ 100 μm. The larger tetrahedrite II masses were accreted to chalcopyrite II, less often to sphalerite. It is very difficult to distinguish which part of the tetrahedrite pertains to the exsolutions, and which part is a residue of the replacement of larger masses of tetrahedrite I by more recent galena which bore silver and exsoluted it on cooling as tetrahedrite II.

Galena is the main sulfide mineral of the ore deposits on the Zrin site. It is coarse-grained, often with very clearly pronounced hexahedral cleavage (100). It belongs to the most recent phase of mineralisation, the phase in which considerable replacement of siderite I took place. In the more younger veins, nests and small masses of quartz II, sulfides and sulfo-salts, galena is, after quartz II, the most abundant mineral. As the youngest mineral, galena replaces and embodies the residues of all the other, older minerals, especially quartz II. In places galena manifests the »sieve-like structure« of residues of replaced siderite I. Galena contains exsolutions of tetrahedrite II (freibergite), less commonly in the form of droplets and ovals, more often as subsequently aggregated into fairly large irregular masses. In the prestructuring phase such masses accrete to chalcopyrite II, sphalerite left from replacement by galena. Galena is frequent in the »plages« between siderite I and quartz II, either alone or in association with tetrahedrite II, chalcopyrite II, occasionally also with sphalerite. In a few prepared specimens we observed incipient oxidisation of galena into anglesite.

Gersdorffite (korynite) — NiAs(Sb)S was identified only in some of the ore specimens. It is developed either idiomorphically or in skeletal forms. Small idiomorphically developed crystals are of octohedral habit with well developed (100), (110) and (111) plates. Gersdorffite of this kind we found most often in chalcopyrite II. It appears in skeletal form in chalcopyrite II and siderite I. In the form of microscopically small masses in association with tetrahedrite I and chalcopyrite II we find it in quartz which has replaced siderite I. Gersdorffite has a high lustre in refracted light, almost equal to the lustre of pyrite. It is white in colour when looked at in air with one nicol, but in cedar oil it shows a very faint pink tinge. It polishes extremely well. Etching with conc. HNO_3 gave a positive result. Its relief is distinctly lower than that of pyrite, but higher than the relief of chalcopyrite II. It is composed of two components, α and β which differ in hardness, as well as in relief in polished specimens. Its cleavage is visible at (100).

Mineral »T« was found in one ore specimen which contained all the minerals identified, with siderite I forming the predominant part of the ore. In part of the siderite I which had been most intensively replaced by more recent quartz II, pyrite II, sphalerite, chalcopyrite II, tetrahedrite I and galena we observed a fairly large mass of mineral »T«, similar to tetrahedrite in its optical properties. It is characterised by numerous exsolutions of chalcopyrite III which contains lamellae of a pink coloured mineral (pyrhotite or cubanite?) and lamellae of an unidentified mineral which is white in refracted light.

Chalcopyrite III is found only as exsolutions in mineral »T«. It contains lamellae of a pink mineral (pyrhotite or cubanite?) and of a white unidentified mineral.

Minerals formed by postgenetic metamorphosis

Hematite features in the brown coloured siderite which miners call »Braunspat«. This type of siderite has red or brownish red interior reflexes from microscopic or submicroscopic hematite dust. This »hematitisation« of siderite arose either in the rejuvenation phase of the deposits, when high temperature hot springs bearing Ni and Co ions caused heating of the siderite and the initial phase of its oxidisation into hematite (pyrometamorphic process according to H. Schneiderhöhn, 1941), or else partial hematitisation came about during later tectonic movements, in the post-mineralisation phase in a period of more recent orogenesis, a view to which we are more inclined.

Siderite II is apparent in those parts of the deposits which have been more strongly affected by tectonic movement, and where tectonic stresses, cataclasis and milonitisation are more marked. Under the influence of these processes coarse grains and crystals of siderite are affected by fissures, cataclases, pulverisation, while local pressures were so strong that they brought about recrystallisation into fine-grained aggregates of siderite II. Some of these recrystallised aggregates are spatially and optically aligned, orientated, and the grains may assume spindly shapes. Because of its fine grain siderite II is more subject to oxidation into goethite.

Hypergenic minerals

Anglesite is a product of the oxidisation of galena. In the initial phases oxidisation takes place along the hexahedral cleavage plane of galena or at fissures.

Covellite and *chalcocite* are products of the weathering principally of chalcopyrite II, and to a lesser extent of tetrahedrite I on the lower levels of the deposits. Replacement by these minerals takes place on a microscopically fine network of cracks of Cu-sulfides and sulfo-salts.

Lepidocrocite is a product of the oxidisation of pyrite, and to a lesser degree of chalcopyrite II and tetrahedrite I.

Goethite is the most plentiful hypergenic mineral in the ore specimens analysed. It is primarily a product of oxidisation of siderite I, then of siderite II, but also to some extent of iron and copper minerals in the deposit. In the case of siderite I, oxidisation into goethite takes place along the rhombohedral plane of cleavage, and in the case of other minerals along systems of fissures.

Malachite and *azurite* were observed only here and there as products of the weathering of primary Cu-minerals or on descendent Cu-minerals.

All the specimens submitted to microscopic analysis in refracted polarised light were taken from the adits and shafts of the lower levels of the Zrin district which have only been affected here and there by the initial phase of oxidisation. The surface levels of the ore deposits which have been exploited to a considerable degree at various periods were not examined; at these levels oxidisation has advanced to a significant degree.

Sequence of mineralisation

Mineralisation began with the deposition of small quantities of the first and oldest generation of minerals, involving *quartz I* and *pyrite I*. We find them in the form of relict grains, mainly of microscopic dimensions, remaining from replacement and resorption processes of the younger mineralisation phases. Most of these relics are in siderite I and quartz II. Partly quartz I is of detrital origin.

The succeeding second generation is the main mineralisation phase, in which the deposition of *siderite I* took place. This mineral is predominant in the ore occurrences of the Zrin and Franz mines, but also in almost all the other sulfide deposits of Trgovska Gora. It is often of reddish brown colour (Braunspat) from microscopically fine dispersed *hematite.*

The third generation is the phase in which *quartz II,* sulfides and sulfosalts, copper, lead, zinc and nickel were separated out. We may divide it into three sub-phases.

In the first sub-phase there is considerable silicification of siderite I and the formation of veinlets, nests and larger or smaller masses of *quartz II,* with a little *pyrite II* and *gersdorffite (korynite).* The amounts of gersdorffite are very small, but its extent is considerable. After siderite I, quartz II is the most plentiful mineral. Usually there is 10—20 % in the ore mass, locally (the Franz deposit) it may be equal to siderite.

In the second sub-phase, which is characterised by the occurrence of Zn — Cu minerals, the oldest mineral is ironrich *sphalerite (marmatite)* with exsolutions of exceptionally fine, sometimes almost sub-microscopic droplets of *chalcopyrite I.* Sphalerite is quantitatively an entirely subsidiary mineral. The sequence continues with *chalcopyrite II,* which is considerably more plentiful, in the Franz mine more plentiful even than galena. In this sub-phase we also observe *tetrahedrite I,* of which there is relatively little, except in the Franz deposits, where there is significantly more. It is of the same age as chalcopyrite II (mutual boundaries) or rather younger than it. To the same group of minerals probably also belongs *mineral »T«,* similar to tetrahedrite, with abundant exsolutions of *chalcopyrite III,* which itself contains lamellae of two other minerals which we were unable to identify because its dimensions were too small.

In the third sub-phase the most recent sulfide mineral crystallises: silver-bearing galena which is quantitatively the principal sulfide mineral in the Zrin mine except for the Franz deposits, where there is rather more chalcopyrite II. The galena contains numerous exsolutions of *freibergite,* or Ag-tetrahedrite in the form of rounded, oval and irregular microscopically small masses.

Following their formation the ore occurrences underwent considerable diagenetic and anhymetamorphic processes. Through the effects of regional metamorphosis in the folding phase (salian phase of variscan orogeny according to D. Devidé-Neděla 1953), an increase of pressure and temperatures brought about primarily a precrystallisation of the original mineral masses, hematitisation of siderite (pyrometamorphosis according to H. Schniederhöhn (1923), in relation to the siderite veins of the Siegerland), strains in the minerals, optical anomalies, cataclasation, milonitisation, the creation of recrystallates of siderite II, aggregation into irregular small masses of lamellae and droplets of freibergite in galena in places aligned recrystallates of siderite II with spindle-shaped small crystals, etc.

Even after variscan folding younger orogenetic processes and slips also continued to affect the rocks and ore deposits.

Hypergene processes arose even in the Tertiary, so that ore occurrences exposed on the surface through erosion were also subject to processes of oxidation and cementation.

An account of the genesis of the ore deposits in the Zrin district and of other ore fields of Trgovska Gora is given in a separate paper: I. Jurković (1988): Hercinska metalogeneza rudnih ležišta Trgovske gore u Hrvatskoj (Hercynian metallogeny of the ore deposits in Trgovska gora in Croatia).

Geochemical researches

During 1984/85 estimates were made in the Trgovska gora area of the content of the microelements Zn, Pb and Cu in the paleozoic rocks and the soils which cover them over a surface area of 100 kms^2 (G. Durn, 1985). 38 specimens were collected (one per 2.5 kms^2); sandstones, sub-greywacke, and greywacke were collected separately from silts and shales. Soil samples were taken from the second or B soil horizon, which is 5—15 cms thick in Trgovska gora. It is brown in colour and consist of sand and clay, with fragments of the native rocks. Above the B horizon is the first or A horizon, blackish grey in colour, the surface horizon which is 10 to 20 cms thick, rich in organic substance, and mixed on its lower levels with clay and sand. The separation of samples of the sandstone group of rocks from samples of silts and shales was undertaken, because the silts and shales are richer in clay components and hence more adapted to the absorption of microelements. The samples were taken at such intervals that they cover the test area as uniformly as possible, whether the ground contains minerals or whether it lacks known ore deposits. To the north, east and south the limit of the research area coincided with the borders of the paleozoic rocks, and to the west with the line Komora — Debelo Brdo.

The geochemical research was conducted in the context of a metallogenetic survey map of Croatia. Goran Durn, Boris Šinkovec and Ladislav Palinkaš took part in the field-work. The laboratory analyses, the determination of statistic parameters and the geochemical interpretation were carried out by G. Durn, with the advice of L. Palinkaš.

Analyses of Zn, Pb and Cu were carried out by the AAS method (atomic absorption spectrophotometry) on an SP9 — Philips apparatus in the Institute for Mineralogy, Petrology and Economic Geology of the Mining, Geology and Oil Engineering Faculty of Zagreb University. All the samples of rocks and soils collected from the Trgovska gora area were dissolved in a mixture of HCl and HNO_3 in the proportion of 3 : 1.

The results obtained were subjected to statistical analysis and diagrams of frequency, mean value $\bar{x}$ and standard deviation σ (s) were worked out. This treatment made it possible to distinguish between background and abnormal values for the content of microelements. G. Durn (l. c.) utilised a histogram of normal and log-normal distribution. The frequency distribution is shown in diagrams of cumulative frequency according to Tennant and White, who give two partial distributions: background and mineralisational.

In dealing with the geochemical analytical data for the Trgovska gora rocks all the analyses were taken into account, since there were no markedly anomalous values. As the threshold of anomaly or the upper limit of fluctuation of the mean background we may conditionally take the mean value $\bar{x}$ plus twice the value for the magnitude of the standard deviation $\bar{x} + 2s$. The threshold of anomaly, or $\bar{x} + 2s$ includes 95 % of all values for the background distribution, and the 2.5 % of values which exceed the defined magnitude are considered anomalous. This value represents the upper limit of anomaly, and the so-called »break point« and its value was used as the lower limit of anomaly.

In analysing the data obtained from the Trgovska gora soil samples, a relatively small number of samples which had values greater than $\bar{x} + 3s$ were eliminated. Following their elimination, the mathematical calculations were repeated and $\bar{x}$ (mean value) and s (σ) (standard deviation) were calculated.

Results of the analysis of rocks for microelements

The mean value $\bar{x}$ and the standard deviation s were calculated for each of the microelements Zn, Pb and Cu, and the value $\bar{x} + 2s$ was taken as the threshold of anomaly *(Table 1)*.

Table — Tablica 1

	Sandstones (pješčenjaci)			Silts and Shales (siltiti i šejlovi)		
in ppm	Zn	Pb	Cu	Zn	Pb	Cu
$\bar{x}$	38,1	16,5	9,7	116,6	31,4	25,6
s	28,3	7,3	6,2	27,7	15,6	8,9
$\bar{x} + 2s$	94,7	31,1	22,1	172,0	62,6	43,4

Table 1 shows that the Zn and Cu content in the silts and shales of Trgovska gora is 3 times greater than the content of these elements in sandstones and greywackes, while the Pb content is twice as great. Silts and shales contain significantly more clay components and hence have a greater capacity for the absorption of microelements.

According to H. E. Hawkes — I. S. Webb (1968) sandstones contain on average from 5 to 20 ppm Zn, from 10 to 40 ppm Pb, and from 10 to 40 ppm Cu, while shales have from 50 to 300 ppm Zn, about 20 ppm Pb, and from 30 to 150 ppm Cu. If we compare these values with those in Table 1, we see that the Zn, Pb and Cu content of the Trgovska gora rocks is within these average values. The reciprocal quantitative relationship of microelements in the Trgovska gora rocks can thus be expressed as Zn > Pb > Cu.

Correlation coefficients for Zn, Pb and Cu in the type of rocks examined on Trgovska gora were separately calculated *(Table 2)*. From Table 2 it is clear that there is a relatively high correlation between Zn and Cu in the sandstones (on account of the similarity in their geochemical properties), while the correlation between Zn and Pb and between Cu and Pb is low. In shales and silts there are very low correlations between all three elements.

Table — Tablica 2

Correlation coefficient (koeficijent korelacije)

Rocks	Sandstones (pješčenjaci)			Silts and shales (siltiti i šejlovi)		
	Zn	Pb	Cu	Zn	Pb	Cu
Zn		0.20	0.73		0.48	—0.03
Pb	0.20		0.21	0.48		0.22
Cu	0.73	0.21		—0.03	0.22	

Results of soil analysis for microelements

Table 3 shows the values for $\bar{x}$, s and $\bar{x} + 2s$ in the case of the analysis of soils from Trgovska gora, with normal distribution and log-normal distribution shown separately.

Table — Tablica 3

Values (vrijednosti) for $\bar{x}$, s and $\bar{x} + 2s$ in soils (tlima)

in ppm	Samples of soils (uzorci tla)					
	normal distribution (normalna razdioba)			log-normal distribution (lognormalna razdioba)		
	Zn	Pb	Cu	Zn	Pb	Cu
$\bar{x}$	76.5	31.6	45.0	4.25	3.4	3.7
s	33.2	14.3	22.0	0.37	0.43	0.46
$\bar{x} + 2s$	142.9	60.2	89.0			
Break point	120	43	—			

The following *Table 4* shows the correlation coefficients between the Zn, Pb and Cu content of the Trgovska gora rocks in relation to the content of these elements in the soils.

Table — Tablica 4

Correlation coefficient rocks/soils

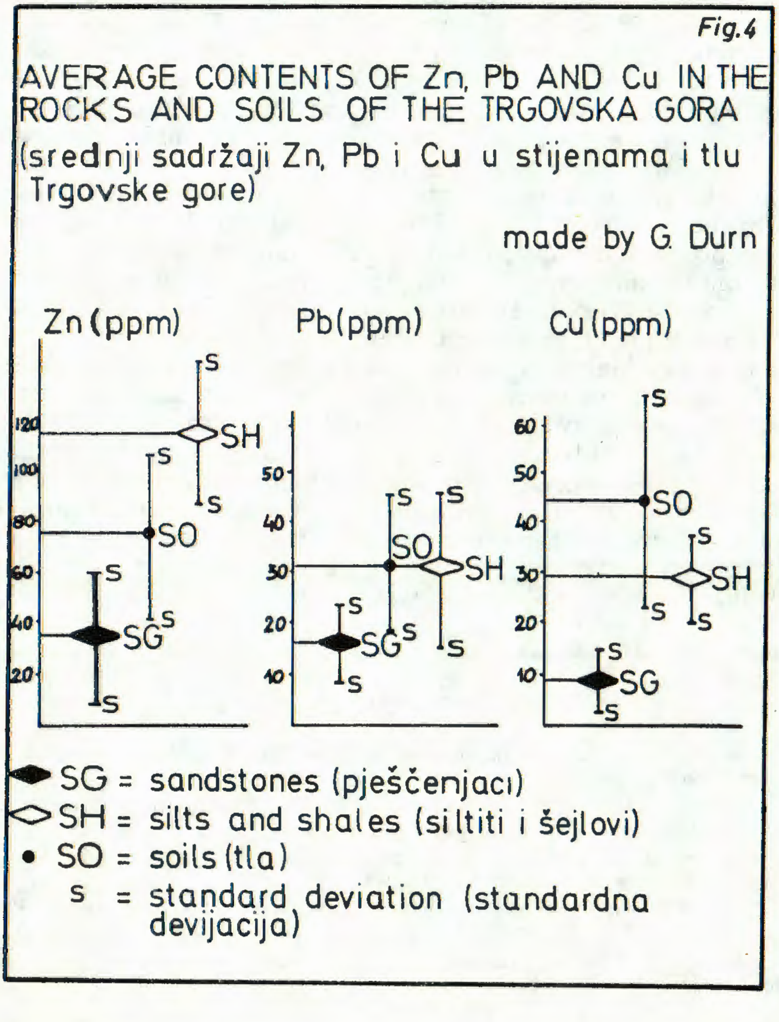
Koeficijent korelacije stijene/tla

Rocks/soils	Sandstones/soils (pješčenjaci/tlo)			Silts and shales/soils (siltovi i šejlovi/tla)		
	Zn	Pb	Cu	Zn	Pb	Cu
Zn	—0.10			—0.72		
Pb		0.86			0.86	
Cu			—0.42			—0.18

Table 4 indicates a high correlation coefficient for Pb in the rocks in relation to soil (the reason is the low mobility of Pb), while these coefficients are very low for Zn and Cu (these two microelements are mobile and leach out of surface materials).

Conclusions

Analysis of the microelements Zn, Pb and Cu in the rocks and soils of Trgovska gora have shown that the relationship Zn : Pb : Cu in rcks = Zn > Pb > Cu, while in soils the relationship in Zn > Cu > Pb. Moreover, in soils the relationship of the values for all three elements is more uniform than in rocks (*Table 5* and Fig. 4), which is the result of pedogenetic action. Although there are significant differences in the content of individuel microelements in various types of rocks, the



Tablica — Table 5

Average contents of microelements in the rocks and soils of Trgova gora (Srednji sadržaj mikroelemenata u stijenama i tlu Trgovske gore u ppm)		Zn	Pb	Cu
Rocks (Stijenc)	Sandstones (pješčenjaci)	38.1	16.5	9.7
	Silts, shales (siltovi, šejlovi)	116.6	31.4	25.6
Soils (tla)		76.5	31.6	45.0

weathering process compensates for the difference because of the rapid erosion of sandstones, and the soils above sandstones, shales and silts have equal amounts of microelements.

The distribution of Zn, Pb and Cu in rocks is within the limits of the background distribution. A certain number of anomalous results are not located in the vicinity of ore occurrences. The highest value for Zn, 162.5 ppm, is in sample 31; for Pb, 7.1. ppm, (sample 26, Stambolije); and for Cu, 97.5 ppm, (sample 35, Meterize). In sandstones there is a very high correlation between Zn and Cu, and a very low correlation between Pb and the other two elements. In shales and silts the correlation for all three elements is very low.

In soils the microelement content is more uniform, with increased content in the vicinity of ore occurrences, and near highways and settlements, on account of contamination. The largest anomalies in microelement content amounted to 206 ppm for Zn (sample 12, Puhovac), 2250 ppm for Pb (sample 11, Pb deposit near Hasanov Grob), and 300 ppm for Cu (sample 11, Hasanov Grob).

There is a very high correlation between Pb in rocks and Pb in soils, but for Zn and Cu this coefficient is very low. The reason for this is the considerable immobility of Pb in exogenic geochemical processes.

The sandstones (subgreywacke and greywacke) of Trgovska gora contain 2 to 3 times more Zn, Pb and Cu than the sandstones of Petrova gora (G. Durn, 1985), which is a consequence of the major differences in geochemical characterisaics of the metallogenesis of Petrova gora (I. Jurković, 1958) and Trgovska gora (I. Jurković, 1960).

Received: 6. 1. 1988.

REFERENCES

Aleksijević, N. (1922): Procjena rudnog područja Bešlinac iz god. 1922. 26 str. Arhiv Zavoda za geol. istr. Zagreb.

Andrian, v. F. (1868): Die Erzlagerstätten bei Tergove in der croat. Militärgrenze. — *Verhandl. geol. Reichsanstalt, Wien.*

Devidé-Neděla, D. (1953): Tumač geološke karte Trgovske gore, Zagreb 1953. Arhiv Zavoda za geol. istraživanja, Zagreb.

Durn, G. (1985): Geokemijska istraživanja stijena i tla paleozoika Petrove i Trgovske gore, 49 str., Zagreb, 1985, (manuskript).

Đurđanović, Ž. (1966): Coniconchia in Croatia. — *Bull. Scient., Conseil Acad. Youg. (A), 11/7—9,* 174, Zagreb.

Đurđanović, Ž. (1968): Konodonte donjeg devona i donjeg karbona zapadno od Dvora na Uni (Hrvatska, Jugoslavija). — *Geol. Vjesnik, 21,* 93—102, Zagreb.

Đurđanović, Ž. (1973): O paleozoiku i trijasu Medvednice (Zagrebačka gora) i područja Dvora na Uni na temelju konodonta. — *Geol. Vjesnik, 25,* 29—46, Zagreb.

Geinitz, H. B. (1868): Ueber die fossilen Pflanzenreste aus den Schiefergebirge von Tergove in Croatien. — *Verhandl. geol. R. A. Wien,* 155.

Hacquet, B. (1789): Oryctographia carniolica, oder physikalische Erdbeschreibung des Herzogthumes Krains, Istrien und zum Teil der benachbarten Länder. Theil IV, Leipzig.

Hauer, K. (1870): Izvještaj o rudnim pojavama Trgovske gore, prevod. Arhivski materijal.

Hawkes, H. E. & Webb, I. S. (1968): Geohemija i istraživanje mineralnih sirovina. Izdanje Zajednice jug. univerziteta, 351 str., Beograd.

Jurković, I. & Devidé-Nedela, D. (1952): Rudno područje Bešlinac. Dio I. Rudna ležišta i geološka karta s tumačom, Zagreb, Arhiv Zavoda za geol. istr.

Jurković, I. (1953): Rudno područje Bešlinac. — Arhiv Zavoda za geol. istr., Zagreb.

Jurković, I. (1958): Metalogenija Petrove gore u jugozapadnoj Hrvatskoj. — *Geol. Vjesnik, 11,* 143—228, Zagreb.

Jurković, I. (1960): Polymetal Parageneses of the ore occurrences in the catchment area of the Srebrenjak brook south of the town Dvor na Uni in Crotia. — *Geol. Vjesnik, 13,* 149—161, Zagreb.

Jurković, I. (1962a): Studija metalogene oblasti Trgovske gore. Dio II. Arhiv Zavoda za geol. istr., 79 str., Zagreb.

Jurković, I. (1962b): Rezultati naučnih istraživanja rudnih ležišta u NR Hrvatskoj, *Geol. Vjesnik, 15/1,* 249—294, Zagreb.

Jurković, I. (1988, in press): Hercinska metalogeneza rudnih ležišta Trgovske gore u Hrvatskoj. — *Geol. Vjesnik, 41,* 369—393, Zagreb.

Kišpatić, M. (1901): Rude u Hrvatskoj, *Rad JAZU, 147,* Zagreb.

Kostić, V. (1956): Gornjokarbonski korali iz Trgovske gore (Banija). — *Geol. Vjesnik, 8—9,* 115—122, Zagreb.

Lipold, M. V. (1855): Die Erzlagerstätten nächst Trgove im zweiten Banat-Regimente der Kroatischen Militärgrenze. — *Jahrb. geol. Reichsanst. 7,* 484—850, Wien.

Majer, V. (1962): Studija metalogene oblasti Trgovska gora, Dio I., Zagreb, Arhiv Zavoda za geol. istr.

Majer, V. (1964): Petrografija paleozojskih sedimenata sjeveroistočnog dijela Trgovske gore. — *Geol. Vjesnik, 17,* 79—92, Zagreb.

Miladinović, M. (1966): O nekim problemima geologije i tektonike severnog dela Bosanske Krajine. — *Geološki Glasnik, 11,* 313—345, Sarajevo.

Papp, v. K. (1919): Die Eisenerz- und Kohlenvorräte des ungarischen Reiches, 544—573, Budapest.

Reuter, K. (1910): Die Bešlinacer Bergbauverhältnisse, Bešlinac. In Papps: Die Eisenerz- und Kohlenvorrätte des ung. Reiches, Budapest, 1919.

Schneiderhöhn, H. (1923): Vorläufige Mitteilungen über pyrometamorphen Paragenesen in der Siegerländer Spateisensteingängen. — *Zeitschrift f. Krist., 58.*

Stur, D. (1863): Bericht über die geologische Uebersichts-Aufnahme im mittleren Theile Croatiens. *Jahrb geol. R. A. Bd 13, Heft 4,* Jahrgang 1863, 485—523, Wien.

Stur, D. (1868): Fossile Pflanzenreste aus den Schiefergebirge von Tergove in Croatien. *Jahrb., R. A., 18,* 131, Wien.

Suess, E. (1868): Ueber des Schifergebirge von Tergove und die geologischen Verhältnisse von Raibl., *Verh. geol. R. A., p. 169, Wien.*

Tietze, E. (1871): Die Umgebung von Žirovac in Croatien. — *Verhandl geol. Reichsanst.,* 1871, p. 221.

Tietze, E. (1872): Das Gebirgsland südlich Glina in Croatien, ein geologischer Bericht. — *Jahrb. geol. R. A. Bd. 27, Jhrg. 1872,* 253—278, Wien.

Tućan, F. (1907): Sideriti Samoborske, Petrove i Trgovske gore. *Nastavni Vjesnik, knjiga 17, sv. 1,* Zagreb.

Tućan, F. (1941): Mineraloško-petrografsko istraživanje Trgovske gore. — *Ljetopis JAZU, 53,* Zagreb.

Wojtanek, N. (1772): Karta rudarskih istraga kraj Trgova iz god. 1772. Arhiv Zavoda za geol. istr., Zagreb.
Zepharovich, v. V. R. (1873): Mineralogisches Lexicon II, Wien.
Zloch, T. (1897): Procjena rudokopa i talionica Bešlinac—Trgove, god. 1897., prevod sa njem. jezika, 16 str., Arhiv Zavoda za geol. istr., Zagreb.

Olovna ležišta u rudnom području Zrin u Trgovskoj Gori, Hrvatska

I. Jurković i G. Durn

U radu je dat historijski prikaz rudarske djelatnosti u paleozoiku Trgovske gore u Hrvatskoj, a detaljnije za područje Zrin gdje se rudarilo na srebronosne galenite u ilirsko, rimsko i srednjovjekovno doba (sl. 1 i 2).

Nakon kratkog pregleda stratigrafskih i tektonskih odnosa te oblasti u članku je iznesena karakteristika sedam paragenetskih tipova rudnih pojava u Trgovskoj gori. To su: (a) monomineralne ankeritske pojave s niskim sadržajem željeza od 4—25%, rjeđe do 35% Fe. Pojave su vezane za manje ili veće pojave vapnenjaka i ankeritiziranih vapnenjaka unutar određenih stratigrafskih horizonata starije serije glinovitih škriljavaca (cšp), (b) sideritske i kvarcno-sideritske pojave u vidu tanjih ili uslojenih ležišta ili lećastih tijela u istim stratigrafskim horizontima kao i ankeriti, (c) stratificirana ili uslojena monomineralna sideritska ležišta slabe kvalitete zbog brojnih interstraticiranih slojeva kavrcovitih glinenih škriljavaca, (d) bakronosna sideritska ležišta, tip Gradski potok. Osim krupnijekristalastog siderita (Tip Braunspat) koji je glavni mineral svih tih pojava ima značajnije kvarca, a od sulfidnih minerala najviše halkopirita te manje količine pirita, tetraedrita, galenita, bornita, sfalerita i NiCo minerala (gersdorfita), rudne pojave su se eksploatirale u 18. i 19. stoljeću; (e) sideritska ležišta sa srebronosnim galenitom u kojima je osim siderita kao glavnog minerala dosta kvarca. Galenit sa izdvajanjima frajbergita je glavni sulfidni mineral. Mjestimice ima halkopirita i više od galenita, ali pretežno je podređen. Od ostalih minerala ima tetraedrita, vrlo malo sfalerita marmatitskog tipa s izdvajanjima halkopirita. Karakteristično je i prisustvo gersdorfita (korinita); (f) sideritska ležišta polimetalnog karaktera, tip Srebrenjak u kojima je siderit glavni mineral, uz njega ima dosta kvarca, mjestimice malo barita, a od sulfida uz srebronosni galenit, javljaju se halkopirit, tetraedrit i Ni(Co) minerali gersdorfit, lineit i bravoit, te Pb—Sb sulfosoli; (g) monomineralne baritne pojave s malo sulfida, koje se javljaju kod Gvozdanskog i u pritocima lijeve obale Une.

U ležištima područja Zrin koje se nalazi u slivnom području sastavaka Malog Majdanskog potoka koji se kod sela Majdan ulijeva u Majdan potok (desni pritok Žirovca), na uzorcima rude uzetih sa iskopa u donjim neoksidiranim dijelovima rudišta Zrin i Franz izvršena je detaljna mikroskopska studija poliranih preparata rude. Utvrđena je ova parageneza: od hipogenih minerala pirit I, kvarc I, siderit I, pirit II, kvarc II, gersdorfit, sfalerit s izdvajanjima halkopirita I, halkopirit II, tetraedrit I, mineral »T« s izdvajanjima halkopirita III, frajbergit kao izdvajanja u galenitu i galenit. Od hipergenih minerala utvrđeni su u malim količinama anglezit, kovelin, halkozin, lepidokrokit, malahit, azurit i nešto više getita. U epigenetskoj hipogenoj fazi došlo je do formiranja praškastog hematita unutar siderita (Braunspat) te do stvaranja rekristalizata siderita II i brojnih kataklastičnih pojava i optičkih anomalija, naročito na kvarcu II. To su po našem mišljenju piromorfni i metamorfni procesi.

Dat je i prikaz sukcesije mineralizacije u tri faze s time da je treća, najmlađa faza razdvojena u tri podfaze. Redoslijed mineralizacije, intenzitet i ekstenzitet minerala prikazan je na slici 3.

Za sve minerale date su detaljno mikrofiziografske karakteristike.

Na kraju rada prikazani su rezultati geokemijskih istraživanja na mikroelemente Zn, Pb i Cu u svim stijenama i tlima na površini od 100 km^2 paleozojskog terena Trgovske gore.

Uzorkovani su pješčenjaci, grauvake i subgrauvake zasebno od siltita i glinovitih škriljavaca (šejlova). Analize su izvršene na AAS aparatu firme Philips SP9. Statističkom obradom analiza izrađeni su dijagrami frekvencije, srednja vrijednost $\bar{x}$ i standardna devijacija s. Analize su pokazale slijedeći odnos mikroelemenata u stijenama Trgovske gore Zn > Pb > Cu, a u tlima nad tim stijenama taj odnos je izmijenjen Zn > Cu > Pb. U tlima je u priličnoj mjeri izražen ojednak sastav sva tri mikroelementa dok je u stijenama dosta različit što lijepo ilustrira tabela 5. Izjednačavanje srednjeg sadržaja mikroelemenata u tlima je rezultat pedogeneze. Nema mnogo anomalija sadržaja u stijenama, ali i te koje postoje nisu u vezi s orudnjenjem. Obrnuto anomalije u tlima vezane su na blizinu rudnih pojava, naselja i prometnice. Postoji vrlo velika korelacija između Pb u stijenama i Pb u tlima, dok je koeficijent korelacije za Zn i Cu vrlo nizak. Razlog je u imobilnosti Pb. Iz tabele 5 se vidi da je sadržaj mikroelemenata u siltovima i šejlovima nekoliko puta veći od sadržaja tih mikroelemenata u pješčenjacima Trgovske gore. Razlog tome je sposobnost adsorpcije glinene komponente u siltovima i šejlovima u odnosu na krupnijezrnate i siromašnije na glinenoj komponenti pješčenjake. Analize su pokazale da pješčenjačka serija stijena Trgovske gore sadrži dva do tri puta više mikroelemenata (Zn, Pb i Cu) nego pješčenjaci Petrove gore.