

Zn-Pb MINERALIZATION TYPES IN THE RUDABÁNYA ORE BEARING COMPLEX

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Abstract: The Rudabánya Ore Bearing Complex (NE Hungary) is composed of siderite and base metal sulfide mineralizations, hosted by Lower Triassic carbonate and siliciclastic succession of the Silicikum stratigraphic superunit in the Western Carpathians. The deposit lies inside a Neogene sinistral strike-slip fault zone (Darnó Zone), bordered by master faults. The ore bodies are dissected blocks in a stack of horses structure. Iron, copper and lead ore resources were previously explored and mined in the area. During a recent exploration program additional zones of zinc and lead ores have been discovered representing two genetic types. The first one is stratiform, bound to reductive facies pelitic siliciclastic rocks. The second one is a hydrothermal mineralization, controlled by faults and siderite block boundaries. Both types have similar mineral paragenesis: sphalerite, galena, pyrite, and barite. The two parageneses are distinguishable through their textural and geochemical fingerprints. Hydrothermal sphalerites show consistently higher Fe and Cd content than that of the stratiform ores, while in the hydrothermal galena higher Ag content was recognized. Both phases are affected by supergene alteration and late stage hydrothermal overprint, by which these distinguishing features were largely obstructed in the secondary products. The recognition of the different genetic types of Zn-Pb mineralization has economic consequences regarding both the continuity of ore mineralization and the ore potential of the broader surroundings.

Keywords: stratiform, hydrothermal, Zn-Pb ore, Triassic, Darnó Zone

1. INTRODUCTION

The area of the Rudabánya polymetallic ore occurrence is a traditional mine site in NE Hungary. The main products were limonite and siderite in the 19-20th centuries. Silver and copper were exploited before in the Medieval Age. Lead ore and barite resources have also been discovered in the mining area. The production was initially open-cast, also underground from the 1950s, with peak rates of mined iron ore of cca. 500,000 tons per year. In the last few years copper ore was also exploited in small-scale. The mine was closed in 1985, but a part of the resources is still intact. The 20th century mining produced in the original range of hills a series of open pits, partly merged. The partially un-reclaimed series of open pits and the accessible drifts provide abundant outcrops of the ore bearing rock complex. Beyond this, the documentation of more than 2000 boreholes is at hand.

The records of previous mining exploration and drilling logs contained frequent observations of galena, pyrite or chalcopyrite. Sphalerite was known as an accessory mineral before. Corresponding to this, historic assays were restricted to Fe, Ba, Pb and Cu content.

In an early rock chip geochemical sampling enrichments of silver, copper, manganese, lead and zinc have been detected both in carbonates and in siliciclastic rocks, with peak values in the barite-containing edge zones of the siderite ore bodies (Csalagovits 1973). In an orientative surface sampling program (Korpás et al., 1999) remarkable anomalies of silver and zinc were discovered. Stable isotope studies of the sulfide mineral species of the siderite ore deposit indicated MVT similarity (Hofstra et al., 1999).

The recent exploration results have shown that sphalerite is far more abundant than galena, although it is hard to recognize due to its fine grained character and pale color. Moreover, it is hosted mostly by such

siliciclastic rocks, which were not regarded previously as potential ores unlike carbonates.

The new base metal ore exploration program were initiated on the basis of these data, devoted to recognize the forms and characteristics of a potentially economic base metal mineralization. The program included mapping, sampling and assaying of surface outcrops, exploration trenches and boreholes. In this article we want to introduce the genetic types of the zinc and lead mineralizations, defined on the basis of assays and mineralogical analysis of ore samples. The prospecting of a new deposit type would significantly increase the mining potential of the occurrence.

2. GEOLOGICAL BACKGROUND

2.1. Stratigraphy, lithology and structure

The rocks of the Rudabánya Ore Bearing Complex belong to the Silicikum stratigraphic superunit (Szentpétery & Less 2006; Kovács et

al., 1989), which is widely distributed N from Rudabánya in the Silica Nappe (Fig. 1). The succession of the Silicikum (Table 1) starts with Permian evaporite (anhydrite and black shale, Perkupa Evaporite F), acting as decollement horizon during the nappe emplacement. The Lower Triassic comprises a transgressive succession of littoral sandstone and aleuolite (Bódvaszilás Sandstone F), shallow water marl (Szin Marl F.) and laminar or nodular limestone (Szinpetri Limestone F). The Anisian rocks are dark, euxin facies, thick-bedded or massive limestone and dolomite (Gutenstein F) followed by gray, platform facies limestone and dolomite (Steinalm F). In the further Middle and Upper Triassic part of the succession carbonate platforms and reefs alternating with basin facies rocks were developed. In the vicinity of Rudabánya basin facies formations occur up to the Middle Jurassic.

The Rudabánya deposit is situated in a regional strike-slip fault zone (Darnó Zone), active at least from the Late Oligocene up to the Pannonian (Late Miocene) (Zelenka et al., 1983; Szentpétery 1997; Földessy et al., 2010).

Table 1. Stratigraphic units of the Rudabánya Mts. in the vicinity of the ore bearing complex

Age	Formation name	Lithology
<i>Tertiary cover</i>		
Miocene – Pliocene, Pannonian	Edelény	Variegated clay, lignite, travertine, cross-bedded sand and pebbles (limnic and fluvial facies)
Upper Oligocene – Lower Miocene, Eggenburgian	Szuhogy Conglomerate	Variegated clay, sandstone, conglomerate (alluvial fan facies)
	Szécsény Schlier	Silt with micas, sand and pebbles
	Bretka Limestone	Biogenic, clastic limestone, conglomerate (abrasive facies)
<i>Basement rocks of the Silica and Turna Units</i>		
Lower – Middle Jurassic	Telekesvölgy	Olistostrome (red and green clay marl with limestone), crinoideal limestone, black shale (reductive, deep-water basin facies)
Lower – Middle Jurassic	Telekesoldal	Dark, cherty marl, olistostrome (shale with metarhyolite, sandstone, conglomerate) (reductive, deep-water basin facies)
Upper Triassic, Norian – Rhaetian	Hallstatt Limestone	Variegated (from light-grey to red) micritic limestone (pelagic, oxidative basin facies)
Middle-Upper Triassic, Anisian – Ladinian – Carnian	Bódvalenke Limestone	Reddish, cherty, aphanitic limestone, light grey coquina limestone, shale (oxidative starving basin facies)
	Dunnatető Limestone	Light-grey micritic limestone (eupelagic basin facies)
Middle Triassic, Anisian	Steinalm	Thick bedded light-grey limestone or dolomite (lagoon facies)
	Gutenstein	Thick bedded dark-grey dolomite or limestone (euxin lagoon facies)
Lower Triassic	Szinpetri Limestone	Grey, laminar or vermicular limestone, marl (subtidal facies)
	Szin Marl	Marl, siltstone, sandstone (subtidal facies)
	Bódvaszilás Sandstone	Red and greenish-grey sandstone, siltstone, shale (intertidal facies)
Upper Permian	Perkupa Evaporite	Variegated shale, dark-grey anhydrite and gypsum (hypersaline lagoon, sabkha facies)
<i>Basement rocks of the Uppony and Szendrő Units</i>		
Carboniferous	Szendrő Phyllite	Dark grey – black phyllite, graded metasandstone (turbidite, flysch)
Silurian–Carboniferous	Tapolcsány	Grey – dark grey siliceous shale, sandstone (euxin deep water facies)

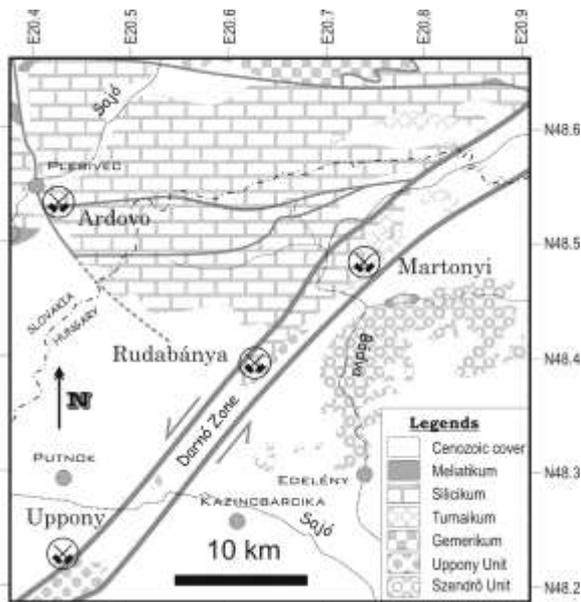


Figure 1. Geological scheme of the surroundings of Rudabánya

It forms a 1-5 km wide elevated, NNE-SSW striking ridge of Paleozoic and Mesozoic rocks, girdled with peripheral troughs filled by some 100 m thick Tertiary sediments. Uplifted remnants of Pannonian sediments on the top of the ridge indicate the long-lasting activity of the fault zone.

The Darnó Zone is the SE border of the Silica Nappe. This nappe itself has an imbricated structure, which is further complicated by the displacements of the Darnó Zone, emplacing fault blocks with variable stratigraphy next to each other.

In spite of this tectonized character, the stratigraphic succession can be broadly recognized also in the mining area (Figs 2, 3). The Permian evaporite and black shale can be observed in a gypsum-anhydrite dome at the Alsótelekes open pit (Zelenka et al., 2005) and in some drillholes reaching the formation. The rock lying over is greenish sandstone and siltstone, which can be identified with the Bódvaszilás Sandstone F.

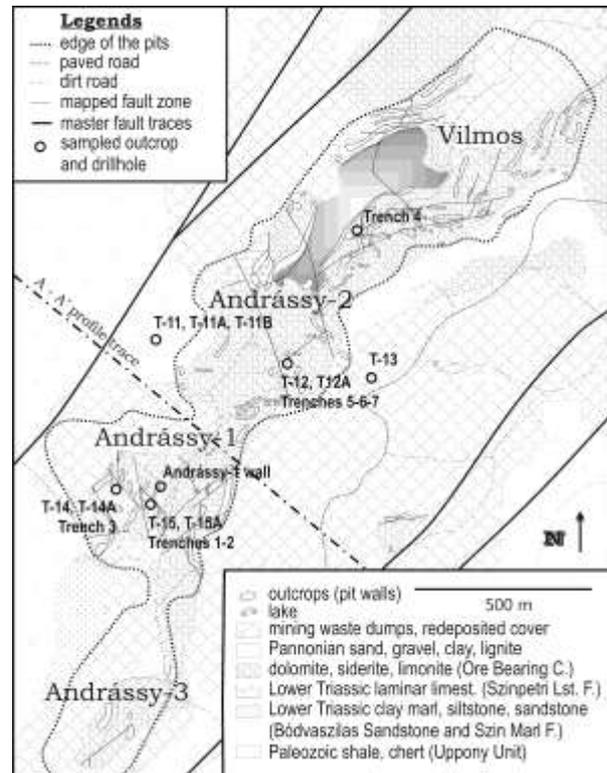


Figure 2. Geological map of the Rudabánya iron ore open pits

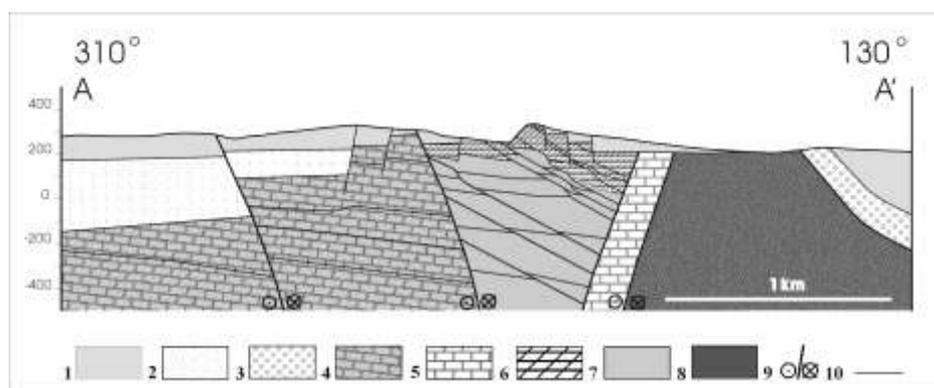


Figure 3. Geological profile across the Rudabánya iron ore open pits after Földessy et al. (2010). Legends: 1. Pannonian sediments (sand, silt, clay, pebbles, lignite), 2. Szécsény Schlier F. (sand, silt), 3. Szuhogy Conglomerate F. (pebbles, silt), 4. Upper Triassic sequence (cherty limestone, marl), 5. Middle Triassic sequence (platform limestone, cherty limestone, marl), 6. Lower Triassic ore bearing complex (dolomite, siderite, limestone, marl), 7. Permian – Lower Triassic sequence, basement of the ore bearing complex (sandstone, siltstone, shale, evaporite), 8. Uppony Unit (shale, siliceous shale, tuffaceous limestone), 9. Master faults of the Darnó Zone (sinistral strike slip), 10. Faults

The Rudabánya Ore Bearing Complex (Szentpétery & Less, 2006) can be derived from the material of the Szin Marl, Szinpetri Limestone and Gutenstein Formations. The siderite, barite and base metal deposits are hosted by dark grey carbonate (limestone, dolomite) and pelitic siliciclastic rocks (sandstone, siltstone, marl). The complex deformation history, repeated shortening (folding and thrusting) events produced an imbricate structure with 10-100 m scale carbonate blocks in pelitic siliciclastic matrix, as described by Pantó (1956). The rocks are intensely fractured, brecciated structure and flexural-slip folding of the laminated rock types are common features.

Some Middle and Upper Triassic formations of the Silicikum also occur in the vicinity of the mining area as well as Paleozoic low-grade metamorphic rocks from the Uppony and Szendrő stratigraphic units.

Tertiary sediments overlie these basement rocks unconformably. Oligocene-Miocene sediments are restricted to the edges of the mining area, although present with some 100 m thickness in the peripheral troughs. The direct cover of the ore bearing complex comprises unconsolidated fluvial and limnic sediments of Pannonian age, cross-bedded sand and clay with lignite seams. The unconformity implies that a considerable part of the ore bearing complex was exposed on the surface for long periods during the Tertiary, and, in consequence, an oxidized cap was formed before the Pannonian.

2.2. Iron and copper ore mineralization

The Rudabánya Ore Bearing Complex hosts iron and copper ore deposits with barite and lead mineralizations.

The siderite ore forms separate dissected blocks of various size from ten to a few hundreds of meters in diameter in a pelitic matrix. Pantó (1956) attributed this to a metasomatic alteration of tectonically preformed, brecciated and insulated Gutenstein dolomite blocks, with less impact on other sedimentary rocks. The sideritization was strong in the core of the uplifted ridge, weakening toward the edges.

The underlying Bódvaszilas Sandstone also contains sideritic veins and nests with quartz, and a small hematite ore body at Alsótelekes; hematite occurs as cement of the sandstone.

Copper sulfide (mainly chalcopyrite, bornite, tetrahedrite and tennantite) mineralizations occur as fine dissemination or patches bound to the siderite with 0.15% Cu content on average (Pantó, 1956).

Weathering and oxidation produced limonite, which also contains base metal enrichments in the form of carbonates, sulfates, oxides and native copper replacing primary sulfides, forming a rich supergene paragenesis with spectacular mineral specimens (Koch, 1985).

3. RECENT RESULTS

3.1 Exploration methods

The exploration started with outcrop mapping, identifying the structures (Földessy et al., 2010) and the mineralized rock bodies. After the first assay results it has become obvious that zinc plays important role in the assemblage. The Zn-bearing minerals are hard to discern in the host rock, even at high Zn grades. To overcome this problem, colorimetry was applied for the field detection of Zn-bearing minerals using zinc-zap (Hitzman et al., 2003). It reacts with secondary Zn minerals, forming bright red (also with Fe minerals, forming dark blue) stains, but with sphalerite the reaction is weak, so the dispersion zones were found rather than the highly concentrated primary ores.

The rock chip sampling covered all rock types of the ore bearing complex, but it was concentrated on rocks with visible sulfide content. More than 1000 rock chip samples from outcrops and trenches were assayed, maximum 2 m long channel samples were taken. The subsequent drilling program of 11 diamond drillholes supplied 416 samples from 1 m long intervals on average; deviations are due to lithological boundaries or poor core recovery. The crushed, homogenized and reduced material was assayed at the ALS Chemex laboratories using aqua regia digestion and ICP-AES for 35 elements, FA-AAS for gold.

A parallel soil geochemical sampling covered the NNE part and vicinity of the mining area. 440 soil samples were taken in a 200x50 m grid from the B horizon; waste dumps and inhabited areas were excluded. Samples were assayed by the same methods.

Opaque microscopy was used in a series of samples taken from critical points and outcrops. Polished sections were studied with binocular microscopes (Leica LMP, Zeiss Jenapol) in reflected light. To enhance the textural features, surfaces have been etched with small drops of Fackert-reagent (nitric acid and ethyl alcohol 1:3) for galena and with HNO₃ for the less reactive sphalerite, for an etching time of 2–10 seconds. After etching, samples were gently repolished.

X-ray diffraction (XRD) measurements were performed on BRUKER D8 ADVANCE diffractometer (radiation: CuK α ; measurement range: 5-65°; evaluation using BRUKER EVA software with

full-profile FPM evaluation by PDF2 database). Electron-optical and microprobe analysis was carried out on JEOL 8600 Superprobe (acceleration voltage: 15 kV, probe current 20 mA, acquisition time 60 s, with evaluation by self-developed ZAF correction software, using self-developed database).

3.2. Zn-Pb bearing parageneses

Our investigations have found Zn and Pb minerals in two different parageneses, with characteristics described in the following part.

Evidences of a new genetic type, sedimentary exhalative, stratiform Zn- and Pb-sulfide, barite and pyrite mineralization were found bound to calcareous siltstone lithology. The rock forming minerals are quartz (fragments of

10-100 μm diameter), phyllosilicate (illite and muscovite, lamellae of 10 μm) and dolomite. The sulfide mineralization is dominated by pyrite, sphalerite and galena. Sulfide-rich beds show compositional layering (Fig. 4A). The sequence of sulfides starts with the precipitation of pyrite I, then sphalerite and finally galena, but pyrite II was formed also later. Pyrite grains often show framboidal and collomorph texture (Fig. 4B). Galena is unoriented, fine-grained (10 μm scale), idiomorphic and often zoned. Etching has shown the mosaic texture formed due to dynamic recrystallization (Fig. 4C). Sphalerite (similar in size) is not recrystallized, but it can be zoned or twinned. The presence of fine-grained barite is also typical. Fibrous Pb-Sb sulfosalts, mainly of the jamesonite-boulangerite series, are also present as inclusions in the galena, often fractured in the deformed grains.

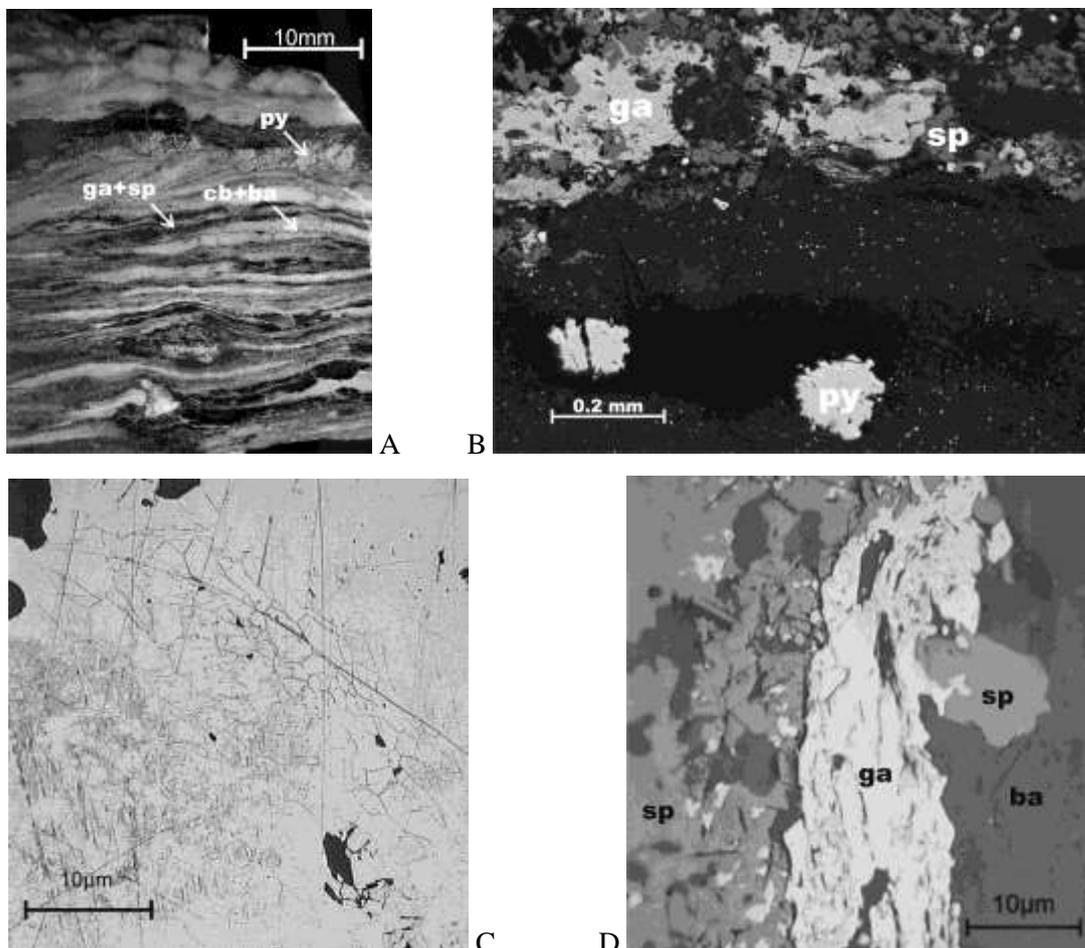


Figure 4. Texture of the stratiform Zn-Pb mineralization

A. Macroscopic texture on a polished surface of a sample from the stratiform sulfide mineralization. Sphalerite-galena enriched layers deformed in a ductile manner (dark) alternating with fractured layers of barite, carbonates and pyrite (light) in microsequences. Rudabánya, Vilmos mine district. **B.** Boundary of a sphalerite (sp)-galena (ga) enriched layer and siltstone matrix with collomorph and disseminated pyrite (py) on polished surface. Rudabánya, Andrásy II. mine district. **C.** Dynamically recrystallized galena from the stratiform sulfide mineralization. Mosaic texture on etched polished surface. Rudabánya, Andrásy I. mine district. **D.** Phyllosilicate lamellae (dark lines) unoriented in sphalerite (sp, left) and oriented in galena (ga, middle zone). Rudabánya, Andrásy I. mine district.

Stratiform character is generally hard to recognize on outcrop scale, because the hosting siltstone was subjected to strong shear between the relatively rigid carbonate blocks during the later tectonic movements. The sulfide-rich beds or lenses were dissected into boudins in the folded siltstone matrix. The incompetent layers without sulfides or those dominated by the galena show a well-observable fabric determined by the tectonic reorientation of phyllosilicate lamellae (observed frequently as inclusions in plastically deformed galena), while in the competent mineral grains like pyrite- and sphalerite the phyllosilicate lamellae rest as not oriented primary inclusions (Fig. 4D).

The epigenetic barite and sulfide mineralization bound to the rim zones of the siderite blocks is known from previous studies (Pantó, 1956; Nagy, 1982; Koch, 1985; Hofstra et al., 1999; Szakáll, 2001). Sulfides (pyrite, galena, sphalerite) and barite form alternating, cm scale, dark and light bands or fill the voids in the carbonate matrix. Sphalerite is more abundant than galena. The grain size of the sulfides is variable, the galena grains are mostly elongated and bent. Szakáll (2001) described corroded, light brown, low-iron sphalerite aggregates partly substituted by galena; our observations support this description. The carbonate crystals are usually zoned with changing composition (siderite, ankerite, ferroan dolomite, magnesite, Fig. 5). Barite, galena and carbonates frequently contain fibrous sulfosalt inclusions; Szakáll (2001), Szakáll & Kovács (1995) described silver-

containing sulfides and sulfosalts like pyrargyrite, proustite, xanthokon, pyrostilpnite and stephanite. He also observed acanthite and native silver in the galena. The copper sulfides like chalcopyrite, tetrahedrite, tennantite and bornite appear as accessories in the Zn-Pb-enriched edge zone, being present commonly as disseminations inside the siderite blocks.

The sulfide mineralization bound to the matrix of fault breccia zones in siltstone and dolomite has similar composition as the one in the carbonate rim zone. Sulfide grain size can be coarse. Barite can be present, but sparry calcite is the most abundant matrix-forming mineral. Copper sulfides are lacking.

Two subsequent alterations transformed the original parageneses, mainly the epigenetic mineralization hosted by carbonate rocks. The first was a supergene alteration after the assemblage has emerged into near-surface position. This produced limonite from the siderite. Galena becomes transformed mainly into cerussite and bindheimite, sphalerite into smithsonite and hemimorphite (Kristály et al., 2010). Partial transformation is generally observable on all samples collected from the surface, including the ones from the stratiform mineralization, which may be the result of recent weathering. Limonite formation is, however, not only a recent process, as some siderite blocks are thrust over limonite. The second alteration, late stage silicification affected the already developed paleo-gossan. This alteration produced vuggy texture in the carbonates hosting a low-temperature paragenesis with variable sulfate and sulfide minerals like pyrite, marcasite, cinnabar and gypsum.

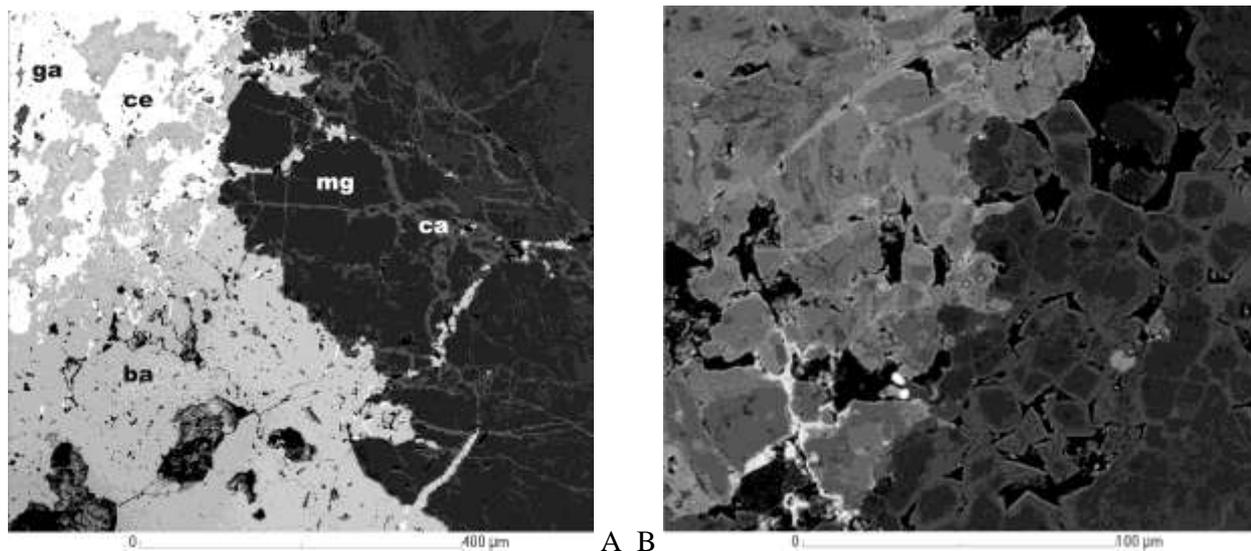


Figure 5. BSE image of a sample collected from epigenetic ore, Trench 4.

A. Barite (ba) and galena (g), partly altered to cerussite (ce) grow over and fill the voids of a Mg-carbonate (mg) breccia cemented by calcite (ca). **B.** Zoned carbonate grains; left side: dolomite cores changing to calcite rims; right side: grains with variable Fe-content, changing from ferroan magnesite cores to Mg-siderite rims

Table 2. Calculated linear correlation coefficients for concentration data from 314 core samples assayed with the same method. Bold figures indicate values over 0.5 or below -0.5, bold and underlined figures indicate values over 0.7, correlations accepted as existing. Shaded columns indicate elements, for which the concentration did not reach the detection limit in more than half of the samples

	Ag	Al	As	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	La	Mg	Mn	Mo	Na	Ni	P	Pb	S	Sb	Sc	Sr	V	Zn	Au	
Ag	1.00																												
Al	-0.14	1.00																											
As	0.45	-0.22	1.00																										
Be	-0.05	0.26	0.03	1.00																									
Bi	0.13	-0.21	0.37	-0.13	1.00																								
Ca	-0.06	-0.53	0.14	-0.18	0.16	1.00																							
Cd	0.82	-0.08	0.27	-0.07	-0.06	-0.15	1.00																						
Co	-0.08	0.13	-0.08	0.27	-0.14	-0.10	-0.04	1.00																					
Cr	-0.15	0.87	-0.24	0.23	-0.21	-0.51	-0.09	0.11	1.00																				
Cu	0.21	-0.25	0.51	-0.14	0.68	0.25	-0.01	-0.17	-0.22	1.00																			
Fe	0.03	-0.17	0.08	-0.31	0.35	-0.38	-0.07	-0.18	-0.19	0.26	1.00																		
Hg	0.25	-0.02	0.19	0.18	-0.02	-0.08	0.38	0.06	-0.03	-0.02	-0.08	1.00																	
K	-0.12	0.32	-0.08	0.80	-0.32	-0.31	-0.06	0.30	0.31	-0.33	-0.43	0.14	1.00																
La	-0.19	0.62	-0.22	0.43	-0.29	-0.40	-0.11	0.17	0.64	-0.33	-0.37	-0.01	0.57	1.00															
Mg	-0.11	-0.44	0.18	-0.54	0.29	0.53	-0.18	-0.16	-0.44	0.33	0.12	-0.10	-0.53	-0.48	1.00														
Mn	-0.12	-0.30	-0.11	-0.19	0.05	-0.23	-0.14	-0.12	-0.28	-0.02	0.81	-0.10	-0.30	-0.36	0.00	1.00													
Mo	0.07	0.00	0.21	0.60	-0.02	-0.08	0.00	0.18	-0.02	0.00	-0.21	0.14	0.57	0.19	-0.10	-0.22	1.00												
Na	-0.11	-0.14	0.09	-0.05	0.11	0.32	-0.14	-0.09	-0.05	0.16	-0.09	-0.09	-0.07	-0.08	0.20	-0.03	-0.02	1.00											
Ni	-0.11	0.42	-0.09	0.81	-0.29	-0.33	-0.04	0.35	0.43	-0.34	-0.45	0.18	0.87	0.62	-0.56	-0.33	0.57	-0.10	1.00										
P	-0.18	0.67	-0.24	0.65	-0.34	-0.51	-0.10	0.28	0.65	-0.37	-0.44	0.08	0.78	0.76	-0.68	-0.42	0.37	-0.16	0.83	1.00									
Pb	0.85	-0.05	0.28	-0.03	-0.06	-0.15	0.86	-0.03	-0.07	-0.04	-0.06	0.43	-0.03	-0.10	-0.18	-0.11	0.01	-0.15	-0.02	-0.07	1.00								
S	0.70	-0.16	0.52	0.01	0.18	-0.08	0.61	0.02	-0.18	0.15	0.02	0.34	0.03	-0.14	0.03	-0.14	0.25	-0.10	0.07	-0.12	0.59	1.00							
Sb	0.34	-0.25	0.65	-0.19	0.42	0.28	0.18	-0.15	-0.23	0.71	0.11	0.10	-0.29	-0.29	0.33	-0.08	-0.01	0.13	-0.29	-0.36	0.14	0.34	1.00						
Sc	-0.21	0.59	-0.25	0.63	-0.38	-0.50	-0.13	0.31	0.51	-0.42	-0.22	0.08	0.74	0.56	-0.58	-0.11	0.37	-0.11	0.80	0.78	-0.08	-0.08	-0.38	1.00					
Sr	-0.01	-0.27	-0.06	-0.06	0.01	0.08	-0.02	-0.07	-0.24	0.01	0.17	-0.07	-0.16	-0.25	-0.10	0.33	-0.11	0.01	-0.19	-0.29	-0.01	-0.10	-0.03	-0.21	1.00				
V	-0.18	0.93	-0.22	0.21	-0.11	-0.56	-0.15	0.15	0.87	-0.18	-0.02	-0.03	0.27	0.57	-0.36	-0.18	0.02	-0.09	0.38	0.60	-0.10	-0.16	-0.23	0.60	-0.32	1.00			
Zn	0.81	-0.08	0.27	-0.04	-0.06	-0.16	0.97	-0.03	-0.09	-0.03	-0.08	0.51	-0.03	-0.10	-0.19	-0.15	0.03	-0.15	-0.01	-0.08	0.88	0.61	0.15	-0.10	-0.02	-0.14	1.00		
Au	-0.02	-0.02	-0.03	-0.06	0.01	-0.11	-0.02	-0.03	-0.06	0.02	0.24	-0.02	-0.06	-0.07	0.03	0.22	-0.04	-0.01	-0.05	-0.07	-0.03	-0.04	-0.01	0.09	-0.06	0.03	-0.03	1.00	

Table 3. Silver, lead and zinc content and ratios of selected assayed ore samples with Pb contents exceeding 0.5%

Borehole or outcrop	Interval or sample id.	Ag (ppm)	Pb (ppm)	Zn (ppm)	Ag/Pb ratio	Zn/Pb ratio
<i>Epigenetic type Pb-Zn ores</i>						
T-12/A	11.2 – 12.2	5.20	540	4470	0.0096	8.278
T-12	52.3 – 54	12.60	594	3380	0.0212	5.690
T-12	47.6 – 49.1	8.40	837	4820	0.0100	5.759
T-11/B	50.1 – 51	3.00	923	925	0.0033	1.002
T-15	1 – 2	48.30	942	2340	0.0513	2.484
T-12	87.1 – 88.6	1.50	1010	1140	0.0015	1.129
T-15/A	0 – 1	8.80	1060	2800	0.0083	2.642
T-15	2 – 3	27.60	1280	1455	0.0216	1.137
T-11/B	51.0 – 51.7	9.10	1350	451	0.0067	0.334
T-15	0 – 1	15.90	1560	3610	0.0102	2.314
T-14/A	18 – 19	38.80	1965	13200	0.0197	6.718
T-14/A	19 – 20	52.30	2470	6390	0.0212	2.587
T-15	5.6 – 6.4	84.20	6040	38700	0.0139	6.407
T-14	12 – 13	45.40	6260	81200	0.0073	12.971
T-12/A	25.3 – 26.9	59.20	6400	34400	0.0093	5.375
T-15/A	7 – 8	39.70	7420	297	0.0054	0.040
T-14	11 – 12	44.60	8530	56300	0.0052	6.600
T-12	50.9 – 52.3	60.70	10250	54600	0.0059	5.327
T-12/A	22.7 – 23.7	107.00	19400	149000	0.0055	7.680
T-12/A	31.6 – 32.4	85.90	19900	79400	0.0043	3.990
T-12/A	23.7 – 25.3	93.00	21400	111500	0.0043	5.210
Mean value		40.53	5721	30970	0.0117	4.461
<i>Stratiform type Pb/Zn ores</i>						
T-11	65.7 – 67.2	7.10	631	5440	0.0113	8.621
T-14/A	1 – 2	2.00	1395	6530	0.0014	4.681
T-14	2 – 3	2.80	1970	24800	0.0014	12.589
Trench 7	27.0 – 29.0	22.30	2840	13200	0.0079	4.648
T-14	0 – 1	4.90	3630	31800	0.0014	8.760
T-14	1 – 2	3.30	5790	36600	0.0006	6.321
Trench 3	80811103	7.00	6100	36400	0.0011	5.967
Trench 3	80811104	11.00	6500	51400	0.0017	7.908
T-11/B	61.0 – 62.4	23.90	7950	225	0.0030	0.028
Trench 3	90519008	17.70	8200	32200	0.0022	3.927
Andrássy I. wall	80825003	8.00	8800	12100	0.0009	1.375
Andrássy I. wall	80825002	8.00	9400	16900	0.0009	1.798
T-14/A	0 – 1	18.00	11650	51100	0.0015	4.386
Trench 3	80811105	34.00	21800	118000	0.0016	5.413
T-14/A	17 – 18	97.40	26200	63500	0.0037	2.424
Trench 3	90519006	74.20	37400	178000	0.0020	4.759
Trench 3	90519007	89.00	59400	157000	0.0015	2.643
Andrássy I. wall	80825004	53.00	216000	91600	0.0002	0.424
Mean value		26.87	24203	51488	0.0025	4.815

3.3. Chemical composition of the Zn-Pb ore and its country rocks

To detect the geochemical affinities of the major and accessory elements in the mineralized rock body, variable parameters (e. g. concentration ratios and distribution parameters) were calculated from the comparable assay results of rock chip and core samples; linear correlation coefficients were calculated from the 35 element

assay of 314 core intervals. Although the distribution is not normal for any of the elements, linear correlation coefficients were accepted as indicating a possible correlation over 0.5 and existing correlation over 0.7 values.

The rocks of the ore bearing complex are enriched dominantly in Fe, Ba, Cu, Zn and Pb. These elements, however, are not correlated with each other (except Zn and Pb) (Table 2). Despite of the important role of barite in the paragenesis we did not evaluate

barium due to serious inconsistencies experienced in the results of different methods (wet assay, XRD, ICP MS). A possible correlation of Zn and Pb (and, additionally, Ag, As and Cd) with sulfur indicates the occurrence of these elements mainly in sulfides and sulfates, while Fe and Cu are abundant in carbonates and oxides. The amount of Zn generally exceeds Pb by a 4.5 – 5 factor on average (Table 3). In the supergene zone this ratio decreases due to the more intense leaching and mobilization of the Zn and low mobility of Pb, but Zn enrichments form a some m wide halo around the originally mineralized rock body.

The Cd is very strongly correlated with the Zn, showing its occurrence in sphalerite; the calculated linear correlation coefficient is 0.97. In samples from supergene Zn enrichment zones Cd is lacking. The Cd/Zn ratio is markedly low (typically <0.002) in stratiform ores compared to the epigenetic type ore (typically between 0.002 and 0.0035) (Fig. 6). Similarly, the Ag/Pb ratio is low in the stratiform and higher in the epigenetic ore type (Table 3). The Ag is well correlated with Pb, Zn and Cd, but not with Cu, although it also occurs with Cu enrichments (possibly in fahlore).

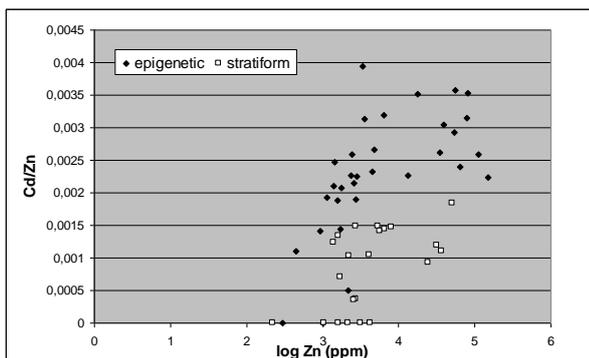


Figure 6. Diagram showing Cd/Zn ratios from the assayed core samples with Zn or Pb content exceeding 0.5% as a function of the Zn content (0 values indicate Cd content below detection limit).

10-10 sphalerite grains in each identified samples of different genetic types were measured by electron microprobe. Apart from some zoned crystals and aggregates showing overgrown younger phases, the measured values were uniform within the individual grain boundaries. It was consistently lower than 0.5% in samples from the stratiform ore type, while it varied between 2–5% in the samples from the epigenetic ore. There are iron-free sphalerite grains also in these samples attached to collomorph pyrite assemblages as relic fragments from the stratiform ore (Fig. 7).

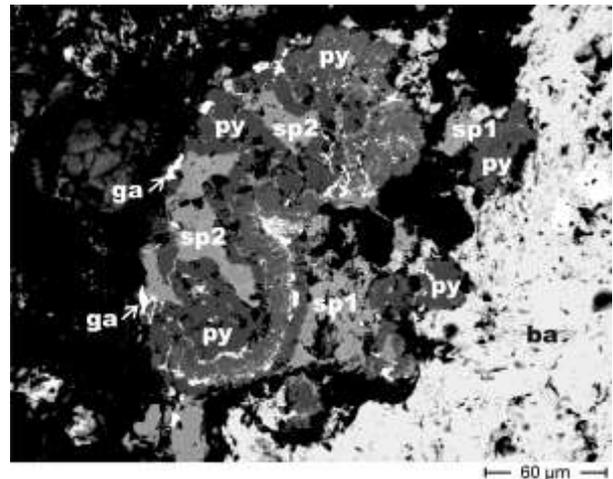


Figure 7. BSE image of a sample collected from epigenetic ore. Collomorph, truncated pyrite grains (py) and iron-free sphalerite (sp1) grown over pyrite on the rim of a barite mass (ba) form a fragment preserving the texture of the stratiform ore. The fractures of this fragment are filled with galena (ga) and sphalerite containing 1.5–2.5% iron (sp2) of the barite and sulfide mineralization.

4. DISCUSSION

4.1. Controls and stages of the Zn-Pb mineralization

Historically the Rudabánya deposit was a perpetual challenge to the geologists due to superposed mineralizations and tectonic disturbance. The paragenesis of the siderite bodies and the ore generating metasomatic alteration of original dolomite blocks was thoroughly described by Koch et al., (1950), defining interstitial mineral sequences. Pantó (1956) regarded the imbrication and brecciation as the main control of both the iron ore and the sulfide mineralization, on the course of a single long-lasting metasomatic event. He attributed the rim alteration ('baritic spar rim') to the impermeability of the enveloping clay marl, but also mentioned veins along fault zones. Later studies (Csalagovits, 1973; Hernyák, 1977), recognizing different mineralization phases, interpreted the deposit as polygenetic. A later base metal exploration program indicated that galena enrichments occur in other rocks than siderite (Hernyák et al., 1981). This exploration report suggested both the synsedimentary, sedimentary-exhalative or the epigenetic origin as possible.

The new results showed that the stratiform type sphalerite-galena mineralization is lithology-controlled, as it was found in calcareous siltstone only. It matches several characteristics of the typical sediment-hosted stratiform Pb-Zn ores in mineralogy (composition, grain size, texture) and lithological environment (fine-grained clastics and carbonates,

reductive facies and organic matter content) as well (Gustafson & Williams, 1981; Large et al., 2006). The role of underlying evaporite as sulfur source is also possible. The mineralization was not found in the directly underlying porous sandstone affected by later siderite metasomatism, suggesting rather a lateral synsedimentary exhalative than an ascendent metasomatic origin. As the deposit is detached in the Darnó Zone from its original environment, the geodynamic setting remains unknown, but it leaves open a question if other similar, still unknown ore bodies are present in the same stratigraphic horizon of the Silicikum superunit.

The epigenetic, baritic and breccia type Zn-Pb mineralization is bound to fault zones, in the matrix of fault breccias or veins (Hernyák, 1977). It occurs in the boundary zone of siderite blocks, also in calcareous siltstone, limestone and dolomite. Fault zones and related veins have at least three subsequent generations (Földessy et al., 2010). The Zn-Pb mineralization fills the breccia zones of faults active in the Darnó system, overprinting older structures, which also can host this mineralization type due to their retained fluid conductivity. Remobilization of primary stratiform ores during later hydrothermal processes is a possible explanation of their genesis. The earlier pyrite and copper sulfide mineralization, as well as late stage silicification, also controlled by fault zones, can locally coincide with this mineralization type.

The recognition of the Zn-Pb ore types of Rudabánya and the resolution of mineralization phases makes the depositional model easier to approach. The coinciding occurrence of Cu and Zn-Pb ores, which is rare in sediment-hosted deposits, was produced by separate mineralizing events.

4.2. Possible analogies and regional Pb-Zn ore occurrences

Significant sediment hosted polymetallic ore mineralizations are known in widely different metallogenic regions of Europe. Rammelsberg (Harz, Germany) of Devonian age and the Irish Pb-Zn district (Navan, Galmoy, Lysheen) of Lower Carboniferous age are known as stratiform sedimentary exhalative deposits, and show formational and paragenetic similarities to the older stratiform Pb-Zn ores of Rudabánya. The Lower Silesian Bytom, Olkusz and Tarnówskie Góry (Bytom, Olkusz, Trzebieńka) occurrences in Poland are of epigenetic character, similarly to

the late Pb-Zn mineralization of Rudabánya. However, their development was linked to karstified limestone and dolomite, in contrast to the Rudabánya mineralization, with definitely replacement metasomatic character (De Vos et al., 2005).

The Silicikum superunit is widely regarded analogous with the contemporaneous successions of the Calcareous Alps, which contain several carbonate-hosted Zn-Pb deposits, like Raibl, Bleiberg and Mezica (Czerny, 1989). The Alpine deposit type, bound to Mesozoic carbonates, shows certain similarities with the first stage mineralization. It is characterized by facies controlled ore distribution, sedimentary or diagenetic textures and lack of deleterious metals. These deposits are supposed to be genetically connected with the Periadriatic Lineament, like Rudabánya with the Darnó Zone. Pb isotope studies indicate remobilisation from Paleozoic deposits by brines circulating in the rupture zone (Köppel & Schroll, 1985).

Rudabánya, although unique in its complexity, is not the only Zn-Pb mineralization of the region. The Ore Bearing Complex ends abruptly along NNE-SSW striking master faults of the Darnó Zone on both sides. Probably the truncated extensions could be found in displaced position along the zone. One candidate for such an extension is the Martonyi deposit, 15 km NE from Rudabánya. Its position and distance corresponds to the Miocene sinistral sense strike-slip of the Darnó Zone. Rudabánya-type limonite blocks in Tertiary matrix are known also at Uppony, 25 km SW from Rudabánya (Pantó, 1954; Pantó, 1956).

Another minor Zn-Pb deposit in the Silicikum is at Ardovo, hosted by the same dark Anisian dolomite as the Rudabánya siderite ores. This mine, producing mainly secondary smithsonite ore, was exhausted in the first part of the 20th century (Papp, 1916; Balogh, 1940; Grecula & Kobulsky in Grecula et al., 1995). Other proximal occurrences of the Gemerikum are metamorphosed, Devonian volcanogenic stratiform or vein-type mineralizations (Grecula et al., 1995).

A major volcanogenic porphyry copper deposit and attached sphalerite-galena ore is known on the WNW side of the Darnó Zone at Reck (Baksa et al., 1980; Földessy & Szabó, 2008). The Oligocene age of this mineralization precedes the demonstrated large-scale sinistral displacements of the zone (Zelenka et al., 1983; Szentpétery, 1997), which means, this deposit and Rudabánya might have been more proximal in that time.

5. CONCLUSIONS

The Rudabánya Ore Bearing Complex contains two types of primary Zn-Pb ores. The main Zn and Pb

minerals are sphalerite and galena, although weathering processes have produced carbonates, sulfates and other secondary minerals.

The first generation of the sphalerite-galena mineralization associated with barite and pyrite is synsedimentary with evidences indicating sedimentary-exhalative origin, and bound to the pelitic siliciclastic rocks of the ore complex. These rocks belong to the Lower Triassic series of the Silicikum superunit. This mineralization certainly has preceded the metasomatic alteration of the carbonate rocks of this complex. This fine-grained, stratiform ore is strongly affected by later deformation events, dissected into lenses or boudins in the low strength siltstone matrix.

The second generation is bound to fault zones as vein filling or breccia matrix, often forming a rim facies of the siderite ore bodies, associated with barite, pyrite, other sulfide and Fe-Mg-containing carbonate minerals.

The two types show also geochemical differences: the late stage sphalerite has a higher Cd and Fe-content; the late stage galena contains significantly higher amount of silver than its early synsedimentary counterpart.

Giving evidences of a new synsedimentary zinc-lead mineralization model in this zone may give rise to new economic ore potential of the analogous Lower Triassic sedimentary complexes.

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REFERENCES

- Baksa, Cs., Cseh-Németh, J., Csillag, J., Földessy, J. & Zelenka, T.** 1980. *The Recsk Porphyry and Skarn Copper Deposit, Hungary*. In Janković, S. and Sillitoe, R.H. eds. *European Copper Deposits*. SGA Spec. Publ., 1, Belgrade, 73–76.
- Balogh, K.** 1940. *Data on geological features of Ardovo*. Tisia, 4, 151–200. (in Hungarian and German)
- Czerny, I.** 1989. *Carbonate hosted lead-zinc deposits of the Alpine and other Mesozoic successions. The importance of their geology, stratigraphy and facies dependence for prospecting and evaluation*. Archiv für Lagerstättenforschung der Geologischen Bundesanstalt, 11, 5–126. (in German)
- Csalagovits, I.** 1973. Results of geochemical and ore genetical investigations of a Triassic sequence in the vicinity of Rudabánya. Annual report of the Hungarian Geological Institute for 1971, 61–90. (in Hungarian).
- De Vos, W., Batista, M.J., Demetriades, A., Duris, M., Lexa, J., Lis, J., Marsina, K. & O'Connor, P.J.** 2005. *Metallogenic mineral provinces and world class ore deposits in Europe*. In Salminen, E. ed., *Geochemical Atlas of Europe* (<http://weppi.gtk.fi/publ/foregsatlas/article.php?id=8>).
- Földessy, J. & Szabó, G.** 2008. *The mineralizations of the Recsk Deeps and Lahóca – short geological overview*. Transactions of the University of Miskolc Series A, Mining 73, 85–98.
- Földessy, J., Németh, N. & Gerges, A.** 2010. *Preliminary results of the re-exploration of the Rudabánya base metal ore deposit*. Földtani Közlöny 140(3), 281–292. (in Hungarian).
- Grecula, P., Abonyi, A., Abonyiová, M., Antaš, J., Bartalský, B., Bartalský, J., Dianiška, I., Drnzik, E., Ďud'a, R., Gargulák, M., Gazdačko, L', Hudáček, J., Kobulský, J., Lőrincz L., Macko, J., Návesňák, D., Németh Z., Novotný, L., Radvanec, M., Rojkovič, L., Rozložník, O., Varček, C. & Zlocha, J.** 1995. *Mineral Deposits of the Slovak Ore Mountains 1, Mineralia Slovaca*, Monograph, v. 1. Geocomplex, Bratislava, 834. (in Slovakian with English summary)
- Gustafson, L.B. & Williams, N.** 1981. *Sediment-hosted stratiform deposits of copper, lead, and zinc. Seventy-Fifth Anniversary Volume*, Economic Geology, 139–178.
- Hernyák, G.**, 1977. *Structural analysis of the Rudabánya Mts. based on explorations of the last 20 years*. Földtani Közlöny 107, 368–374. (in Hungarian)
- Hernyák, G., Harnos, J., Gulyás, P.-né, Bics, I. & Balla, L.** 1981. *Rudabánya Mts. base metal exploration results between 1971–1980 and further exploration tasks*. OÉÁ Exploration Report, manuscript (in Hungarian)
- Hitzman, M.W., Reynolds, N.A., Sangster, D.F., Allen, C.R. & Carman, C.E.** 2003. *Classification, Genesis, and Exploration Guides for Nonsulfide Zinc Deposits*. Economic Geology 98(4), 685–714.
- Hofstra, A.H., Korpás L., Csalagovits I., Johnson, C.A. & Christiansen, W.D.** 1999. *Stable isotopic study of the Rudabánya iron mine, a carbonate-hosted siderite, barite, base-metal sulfide replacement deposit*. Geologica Hungarica, Series Geologica 24, 295–302. (in Hungarian)
- Koch S., Grasselly Gy. & Donáth É.** 1950. *The minerals of the Hungarian ore deposits*. Acta Mineralogica–Petrographica 4, 1–41. (in Hungarian with English summary)
- Koch, S.**, 1985. *Minerals of Hungary*. 2nd revised ed: Akadémiai Kiadó, Budapest, 562. (in Hungarian)

- Korpás, L., Hofstra, A.H., Ódor, L., Horváth, I., Haas, J. & Zelenka, T.** 1999. *Evaluation of the prospected areas and formations.* Geologica Hungarica, Series Geologica 24, 197–294. (in Hungarian)
- Kovács, S., Less, Gy., Piros, O., Réti, Zs. & Róth, L.** 1989. *Triassic formations of the Aggtelek-Rudabánya Mountains (NE Hungary).* Acta Geologica Hungarica 32(1-2), 31–63.
- Köppel, V. & Schroll, E.** 1985. *Origin of the Pb in Triassic Pb-Zn mineralizations in the Eastern and Southern Alps. Results of isotope geochemical studies.* Archiv für Lagerstättenforschung der Geologischen Bundesanstalt 6, 215–222. (in German).
- Kristály, F., Szakáll, S., Németh, N. & Zajzon, N.** 2010. *Texture types of the smithsonite in the Rudabánya carbonate ore deposit.* Transactions of the Miskolc University, Series A, Mining 79, 27–38. (in Hungarian)
- Large, R.R., Bull, S.W., McGoldrick, P.J., Walters, S., Derrick, G.M. & Carr, G.R.** 2006. *Stratiform and Strata-Bound Zn-Pb-Ag Deposits in Proterozoic Sedimentary Basins, Northern Australia. 100th Anniversary Volume, Economic Geology*, 931–963.
- Nagy, B.** 1982. *A comparative metallogenetic study of the Rudabánya mineralization (N Hungary).* Annual report of the Hungarian Geological Institute for 1980, 45–58. (in Hungarian)
- Pantó, G.** 1954. *Mining geological explorations in the Uppony Mts.* Annual Report of the Hungarian Geological Institute from 1952, 208 (in Hungarian)
- Pantó, G.** 1956. *Geology of the Rudabánya iron ore ridge.* Yearbook of the Hungarian Geological Institute, 44(2), 329–637. (in Hungarian)
- Papp, K.** 1916. *Iron ore and coal reserves of the Hungarian Empire.* Hungarian Geological Institute, Budapest, 964. (in Hungarian)
- Szakáll, S.** 2001. *The Minerals of Rudabánya.* Kőország Kiadó, Budapest, 176. (in Hungarian)
- Szakáll, S. & Kovács, Á.** 1995. *Silver minerals from Rudabánya.* Acta Mineralogica-Petrographica 36, 5–15.
- Szentpétery, I.** 1997. *Sinistral lateral displacement in the Aggtelek-Rudabánya Mts. (N Hungary) based on the facies distribution of Oligocene and Lower Miocene Formations.* Acta Geologica Hungarica 40(3), 265–272.
- Szentpétery, I. & Less, Gy. eds.** 2006. *Geology of the Aggtelek-Rudabánya Mts. Explanations to the 1:25000 scale geological map of the Aggtelek-Rudabánya Mts. published in 1986.* Hungarian Geological Institute, Budapest, 92. (in Hungarian).
- Zelenka T., Baksa, Cs., Balla, Z., Földessy, J. & Járányi-Földessy, K.** 1983. *Is the Darnó Lineament a Mesozoic paleogeographic border?.* Földtani Közlöny 113(1), 27–37. (in Hungarian)
- Zelenka, T., Kaló, J. & Németh, N.** 2005. *The structure of the gypsum-anhydrite dome at Alsótelekes.* Földtani Közlöny 135(4), 493–511. (in Hungarian)

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