Microbially mediated iron ore formation, Silicicum stratigraphic superunit, Rudabánya, Hungary

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Abstract

Mineralogical, petrological, geochemical and textural characterization of the Triassic Bódvaszilas Sandstone in the Rudabánya open pit and the Aggtelek Mts. were summarized. The pore-filling carbonate cement of the Lower Triassic Bódvaszilas Sandstone Formation of a proximal basin series (Rudabánya) was formed as the result of syngenetic and early diagenetic two step microbially mediated Fe mineralization (Fe-oxide formation by chemo-lithoautotrophic Fe-oxidizing microbes (FeOB) in suboxic neutrophylic environment, and Fe-carbonate by heterotrophic microbes in suboxic to anaerob environment based on mineralized microbially produced textural evidences). The carbonate in the higher parts of the formation (transition between Bódvaszilas Sandstone and the overlying formation, Szin Marl) was formed by the same metasomatic processes producing the former mined siderite ore in the Middle Triassic limestones and dolomites by the partial or complete Fe replacement of the syngenetic carbonate layers. Microbially mediated Fe enrichment also occured at distal basin position in Bódvaszilas Sandstone (Aggtelek Mts.). Later deep burial diagenesis effected the formation.

Keywords: Fe-oxidizing bacteria, iron ore, mineralized microbially produced texture, metasomatism

1. Introduction

After centuries of base metal and silver mining, the open pit and underground iron ore (limonite and siderite) mining of Rudabánya (Silicicum stratigraphic superunit, Lower-Middle Triassic, NE Hungary) went on from 1872 until 1985. Approximately 38 Mt of iron ore was excavated during this period, the recent geological resource exhibits 43 Mt of low grade iron ore (including limonite, siderite and ankerite with an average Fe content of 23.5 wt. %, and siliceous siderite) (Balla et al. 1987).

Similar iron ore deposits occur in the Alps-Carpathian region. In the Tethyan Realm the Triassic-Middle Jurassic was an important epoch of Fe mineralization (Hurai 2005). Fe deposits with variable reserves are distributed from Slovenia to Austria and Slovakia. The Silicicum unit was part of the European Continental Margin (continental margin of the Mesozoic Tethys) at that time. The siderite–sulphide veins and siderite replacement deposits of the Gemericum in Slovakia represent one of the largest accumulations of siderite in the world, with approximately 160 Mt of mineable $FeCO_3$ ore. Carbonate-replacement siderite deposits of the Gemericum hosted by a Silurian limestone belt are similar to stratabound siderite deposits of the Eastern Alps (e.g. Erzberg, Austria; Radvanec et al. 2004). The siderite–sulphide veins and siderite replacement deposits were classified as metamorphogenic, they were formed during several stages of regional crustal-scale fluid flow (multistage hydrothermal circulation via Variscan and Alpine mineralization phases) (Radvanec et al. 2004). The Ljubija siderite deposit in the Dinarides (Bosnia-Herzegovina) represent also hydrothermal–metasomatic Fe mineralization. Here the iron ore occurs as stratabound siderite and ankerite replacement-type bodies in limestones and as siderite-sulphide veins within shales. Superimposed Alpine retrograde metamorphic fluids were observed and might well be compared to the fluids linked to the formation of the Rudňany deposits in Gemericum. The potential resources of iron ore in the Ljubija district have been estimated to 500 Mt with 40 to 49 wt. % Fe (Palinkaš et al. 2008).

The renewed exploration of the Rudabánya ore deposit began in 2007 and it is resulted in the delimitation of newly recognized Fe, Pb, Zn, Ag and Cu enrichments and the determination of their formation. The additional aim of this work was to clarify the paleo-environmental conditions, trace the possible metal source and prepare an ore formation study of the Lower Triassic Bódvaszilas Sandstone Formation (BSF) which includes a previously un-mined sub-grade iron ore (local name is „siliceous sparry iron ore" or „creamspar").

During the investigation of this iron ore signs of microbial mediation were observed, which were formerly unknown in these rocks. This has initiated new investigations and as a result a new ore formation model was built up.

2. Geological setting

The Rudabánya iron and base metal deposits are hosted by Lower-Middle Triassic siliciclastic formations and carbonates which are located in the Aggtelek-Rudabánya Mts. in NE Hungary, in the Silicicum stratigraphic superunit of the Alps–Carpathians–Pannonian (ALCAPA) region (Fig. 1a). The Silicicum stratigraphic unit built up from Upper Permian – Lower Triassic evaporites (Perkupa Evaporite Formation), Lower Triassic siliciclastic formations and carbonates (Bódvaszilas Sandstone, Szin Marl, Szinpetri Limestone – tidal flat and shallow marine ramp facies) and Middle-Upper Triassic and Jurassic carbonates (Gutenstein Formation, Steinalm Formation, Dunnatető Limestone, Bódvalenke Limestone, Hallstatt Limestone – carbonate platform and basin facies) (Szentpétery & Less 2006) (Fig. 1b).

The later NNW-SSW striking main faults of the so-called Darnó Structural Zone divide the mineralized area into 100-1000 m wide slabs with differently structured paleozoic-mesozoic sequences (Fig. 1c). The Rudabánya ore deposit complex, is located in the most uplifted, 0.3-3 km wide central zone in the axis of the Darnó Zone. It consists of separate siderite blocks (> 1000

blocks) which are of carbonate and siliciclastic rocks in a tectonised clayey matrix (Pantó 1956; Hernyák 1967; Szentpétery & Less 2006; Földessy et al. 2010). The sizes of the lenticular-blocky siderite bodies are variable, their length varies between 60-600 m, their width between 10-100 m, their thickness are between 3-100 m (Kun 1989).

Previously several ore-forming models were bulit up about the iron mineralization of Rudabánya, some of them assumed magmatic origin (Nagy 1982; Balla et al. 1987). According to another scenario magmatism was not necessery to the iron ore formation, but the mixing between the pore waters of the Permian-Lower Triassic siliciclastic succession and the fissure waters of the Triassic carbonates were proposed (Csalagovits 1973; Fügedi et al. 2010).

According to the latest studies the Rudabánya ore deposit complex was formed in several periods. Three main deformation phases divided temporally the periods of ore formation (Földessy et al. 2010; Németh et al. 2013). A synsediment, stratiform, sedimentary-exhalative Pb-Zn-barite accumulation was formed in the pelitic and carbonatic, reductive Szin Marl as the earliest ore forming phase. A later metasomatism (probably of Cretaceous age) has introduced the siderite ores (local name is „sparry iron ore") hosted by the Lower-Middle Triassic Szinpetri Limestone, Gutenstein Dolomite and the un-mined sub-grade iron ore of Bódvaszilas Sandstone. In the third ore forming phase (related to Darnó Zone formation, probably of Paleogene age) mainly pyrite-bearing massive sulphide filled veins, and later Pb-, Zn-, Ag- and Cu-enrichments with barite were generated. The faults of the Darnó Zone promoted the latest, a probably low temperature sulphidic ore formation (As-, Sb-, Hg- and Ag-enrichments). In this last stage of the ore formation the siderite-bease metal ore formations were exhumed and oxidized near the surface, and a limonitic zone and secondary enrichments (native copper, malachite, cerussite, anglesite, smithsonite) were formed by subsurface solutions (Földessy et al. 2010). At the basis of the Miocene beds spherosideritic iron ore was also formed (Szakáll 2001).

3. Samples and methods

Representative samples of Bódvaszilas Sandstone (87) and siliceous sparry iron ore (creamspar, 20) were investigated from the Rudabánya open pit and from a surface outcrop in Rudabánya, and samples from Bódvaszilas Sandstone from the non-mineralized area (Aggtelek Mts.) were also collected (Fig. 1b).

The Bódvaszilas Sandstone samples are blueish-greyish green, locally red colored rocks. These are mainly grain-supported, well sorted, very fine- and rarely fine-grained quartzarenites and matrix-supported, well sorted, oligomict siltstones and claystones. The pale yellow „siliceous sparry iron ore" occurs as pore- and vein-fillings in the Bódvaszilas Sandstone and as massive ore in the transitional layers of the Bódvaszilas Sandstone and the overlying Szin Marl Formation.

Detailed macroscopic and microscopic petrographic investigations were done first to acquire information before other analyses (NIKON ECLIPSE 600 rock microscope, Institute for Geological and Geochemical Research, Budapest, Hungary). X-ray powder diffraction (XRD) of bulk rock samples for mineralogy was performed on a Bruker D8 Advance diffractometer (CuKα source, 40 kV, 40 mA, secondary graphite crystal monocromator, scintillation detector) at the Institute of Mineralogy and Geology, University of Miskolc, Hungary.

Electron microprobe analyses were done by the means back-scattered electron imaging (BSE) and energy dispersive spectrometry (EDS) for main and trace element distribution on a JEOL JXA-8600 Superprobe (15 kV, 20 mA, carbon coating, 60 s acquisition time) at the same institute.

The $^{13}C_{carb}$ and $^{18}O_{carb}$ stable isotopic analyses on siliceous sparry iron ore and total organic carbon analysis on siliceous sparry iron ore and the host siliciclastic succession were carried out bulk samples at the Institute for Geological and Geochemical Research and in the Geographical Institute, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budapest, Hungary.

Chemical analyses (major, trace and rare earth element) were made on Bódvaszilas Sandstone samples by ICP-MS and ICP-AES (ALS Chemex laboratories, Vancouver).

4. Results

4.1. Petrological and microtextural characteristics of Bódvaszilas Sandstone Formation

The Bódvaszilas Sandstone is a mature sediment based on the quantity and quality of the grains. The absence of unstable grains like polycrystalline quartz and lithic fragments, and the low quantity of feldspars are typical. The most frequent clastic constitiuent is monocrystalline quartz (approx. 85 %) and muscovite (10 %) by visual estimation. In low quantity other types of mica (altered phlogopite, biotite) may be present. The accessory minerals are zircone, apatite, rutile and monacite, rarely xenotime, schorl and ilmenite. As opaque mineral only disseminated, euhedral, rarely framboidal pyrite occurs commonly along the fractures and laminae. In the matrix of the formation chlorite (clinochlore), illite, and very rarely kaolinite and fine, dispersed hematite flakes occur.

The cement between the grains is built up from quartz and a large amount of carbonate (creamspar). The three types of the pale yellow carbonate are the following:

1. Small nests (diameter 1-5 mm) between the grains as the cement of the siliciclastic formation. The pore-filling nests or patches are present in the coarser grained sections (fine-grained sandstone). Where the rock is more compact, the abundance of this carbonate is less. In the pore-filling cement of the Bódvaszilas Sandstone and at the contact of the grains and the cement, both in Rudabánya and in the Aggtelek Mts. fine filamentous, pearl necklace-like microbial microtexture (mineralized microbially produced texture – MMPT) is widely prevalent (Fig. 2a,c,f). These textures often form colonies. Between the grains the clay minerals are very common.

2. Pore-filling creamspar in 1-2 cm wide veins crosscutting layering. At the margin of the sandstone and the vein coarse-grained, euhedral quartz is present.

3. In the upper part of the Bódvaszilas Sandstone, in the transition layers to the Szin Marl, several centimeters thick, contiguos sections. These are massive synsedimentary intercalations. Euhedral-subhedral quartz with sparse hematite flakes may be connected to the coarse grained (even 1 mm) sparite carbonate crystals. In the massive carbonate sections coarse-grained (even 0,5-1 mm) euhedral quartz crystals are also present (megacrystals, Scholle & Ulmer-Scholle 2003), occasionally a thin border line suggests the original quartz grain. In the massive carbonate sections and in the vein-filling carbonate along the cleavage faces of the sparite crystals, in negligible quantity, filamentous MMPT textures can also be observed (Fig. 2b). In the carbonate very rarely red colored clasts with pyrite, quartz and hematite are present.

The formation is compacted and the slightly lineated texture and the concavo-convex and rarely sutured grain contacts can be observed with dissolution at the margin of the grains, and the synthaxial quartz overgrowths on monocrystalline quartz grains. The authigenic quartz engulfs and replaces the pore-filling carbonate cement. Occasionally the remnants of the carbonate cement as inclusions can be found in the quartz cement.

4.2. Mineralogy (XRD) of siliceous sparry iron ore

By XRD peaks of the R-3c space-group were observed, with d(Å) values as intermediary between siderite and magnesite structure. The d(104) varies between 2.76 Å and 2.78 Å, indicating a larger range of substitutions. Intensities were affected by strong preferred-orientation, but applying the March-Dollase correction, we obtained relative intensities characteristic for the siderite lattice. The creamspar is usually accompanied by dolomite and quartz.

4.3. Chemistry of carbonate by EPMA

The chemical composition and crystal structure related properties of the creamspar from Bódvaszilas Sandstone is described for the first time. The texture of the creamspar and its composition is very similar in the three types (pore-filling cement, vein-fillings, massive carbonate sections). According to our observations it often shows chemical zonation patterns, on the rhombohedron faces (Fig. 2e). The creamspar is always inhomogeneous in elemental composition, but it is always Fe- and Mg-rich carbonate with low Mn content (never pure siderite or pure magnesite, it is always with excess substitution of Mg and Fe). The Fe and Mg ratio changes in several micrometers level, it is independent of textural characteristics. In the analysed samples the Fe content varies between 0.11 and 0.84, and the Mg content between 0.25 and 0.65 atoms in the RCO_3 theoretical formula (R: Fe, Mg, Mn, Ca) (Fig. 3).

4.4. C and O isotopic values of the carbonate

The samples of the vein-filling and massive creamspar sections show negative C and O isotopic values: $\delta^{13}C_{PDB}$: -6.18 ‰ - -3.91, the $\delta^{18}O_{PDB}$: -14.66 - -12.21 (‰).

4.5. **TOC values of the carbonate and the host rock**

The Total Organic Carbon content of the creamspar from the massive carbonate sections is between 0.38-2.63 wt. %, and the host rock is between: 0.05-0.06 wt. %.

5. Discussion

Some representative samples were selected for paleoenvironmental study. The host rock of the iron ore (BSF) was a mature, recycled sediment based on monomict mineral composition, derived from an acidic source area according to the accessory minerals and the La/Th and La/Co ratios (Bhatia & Crook 1986). Our observations reinforce the opinion of Kovács et al. (2004), that the source area was the Permian molasse in the basement of the Gemericum.

According to the geochemical environmental indicators (Wignall & Meyers 1988; Rimmer 2004; Yang et al. 2011) during the sedimentation and the early diagenesis oxic conditions were existed (Table 1).

Between the grains of the BSF (host succession), in the pore-filling cement, at the margin of the grains, and at the contact of the carbonate cement and the grains filamentous textures of assumed microbial origin (MMPT) are present that often form microbial-like colonies. The microbial fossils altered to goethite. Between the grains clay minerals are frequent (the gel-like layer around the colonies of bacteria altered to smectite, Fig. 2d). The characteristic microbial filaments along the cleavage faces of creamspar layers of the samples from Rudabánya were also observed nevertheless in smaller quantity. MMPT are present in much less quantity in the non-ore bearing distal basin area in the same formation (Aggtelek Mts., Bódvaszilas Sandstone Formation).

Several Fe (II) oxidizing microbes (FeOB) are known in shallow and deep marine environment, some bacteria carry out autotrophic metabolism, i.e. they synthesize their cell constituents from the inorganic materials of the environment. Four kinds of recent microbial Fe(II) oxidizing metabolism are reported (Ehrlich 1990; Fortin 1997; Konhauser 1998). The microbial Fe oxidizing processes are very effective (Ehrlich 1990). According to the mineralogy and the morphological features the presence of suboxic, neutrophylic microbial forms are the most probable. In suboxic, neutrophylic environment the Fe(II) oxidizing bacteria synthesize ferrihydrite (hydrous ferric oxyhydroxide), which transform to more stable mineral forms like goethite or hematite within a few months while quartz is segregating (Schwertmann & Cornell 2007). The iron-

oxide and the segregated quartz may form clay minerals (green clays, e.g. celadonite and/or smectite). Similar clay formation occurred in our samples and was also mentioned by Hernyák (1967).

The bacterial filaments are embedded in the pore-filling carbonate cement of Bódvaszilas Sandstone and at the margin of the grains. This observation suggest a that prior to the formation of creamspar there was not any intergranular cement (there are no residual cement), and the newly formed cement did not compact significantly. An external Fe-bearing solution reached and influenced this succession. It is possible that the microbes were present previously in the fluid-saturated siliciclastic succession nevertheless the Fe-bearing solution may have also transported them to the sediment. The microbes carried out autotrophic metabolism in order to gain energy. This produced ferrihydrite with the oxidation of Fe(II) from the Fe-bearing solution (first microbial cycle syn- to early diagenetic in suboxic neutrophylic environment). The ferrihydrite with the practically inert quartz grains, and the pore-fluids and the organic matter of the died microbes had formed an unstable system. As the organic matter is reactive, it reacted with the ferrihydrite which led to siderite and ankerite formation with the contribution of microbes via heterotrophic metabolism in suboxic to anaerob environment (Konhauser 1998). Additional ions in the Fe-bearing solution (Ca^{2+}, Mg^{2+}, HCO_3^-, etc.) and the organic C may form other mixed carbonates (second microbial cycle in suboxic/anoxic Eh, neutrophylic environment). The completeness of the process depends on the ratio of the available phases thus goethitic-hematitic parts may remain. The C isotope ratio of the forming carbonates is negative, which supports the mineralized organic C content. The negative C isotope ratio and the remnant organic matter (0.05-2.63 wt. %) of our samples also confirm the microbial contribution. The texture of the pore-filling creamspar is misleadingly similar to the creamspar formed in the carbonate layers nevertheless the high resolution optical microscopy explored textural features and differences, which highlight that the ore formation went on different ways in the siliciclastic and carbonate host succession.

The low quantity of microbial traces in the massive creamspar sections suggests that in the primarily carbonate host layers the creamspar probably generated not via microbial mediation but metasomatism, as the texture and the element distribution is rather similar to the younger, dolomite-hosted, metasomatic iron ores'. The zonation occurs occasionally by rhombohedron and completely similar to the observed zonation (Pantó 1956; Szakáll 2001) of the mined sparry iron ore formed in the Middle Triassic dolomites. The element exchange via metasomatism has moved forward paralell to the rhombohedron faces which has caused the characteristic zonation. The $\delta^{13}C$ and $\delta^{18}O$ isotope values of the creamspar from the Bódvaszilas-Szin transitional layers and the sparry iron ore samples from the Rudabánya open pit are similar to each other and the values are nearly the same as the siderite (sparry iron ore) samples of Hofstra et al. (1999). The similar texture observed by SEM-EDS and similar $\delta^{13}C$ and $\delta^{18}O$ values of the creamspar in the Bódvaszilas-Szin transitional layers and the sparry iron ore suggest, that the two type of iron ore presumably formed by the same process, i.e. metasomatism between the succession and a high Fe-bearing solution. It is possible that in these sections some microbial Fe oxidation also occured but its ratio to the metasomatism was negligible.

The examination of the carbonate cement of the samples from the Aggtelek Mts. (non-ore-bearing area) denotes that the Fe addition affected not only the Bódvaszilas Sandstone Formation of Rudabánya but the similar formation in the Aggtelek Mts. although by less intensity. In the pore-filling carbonate cement and at the margin of the grains the microbial filaments can be observed in the Bódvaszilas Sandstones samples of Aggtelek Mts. as well. Presumably the microbes participated in the Fe-oxidation in this area too, but the amount of Fe-bearing fluid flow could be low, and as a results did not form significant ore mineralization.

Concerning the source of Fe, the mafic rocks related to the Middle Triassic rifting represent the most probable scenario, which also fits well with other areas (Brusnytsin & Zhukov 2012; Maslennikov et al. 2012). The remnants of the mafic volcanism can be found in the Bódvavölgy

Ophiolite Formation (Fig. 4). This assumption fits well with the opinion of Szakáll (2001), that the metasomatism related to the metamorphic fluids of the Middle Triassic (early Alpine) rifting. The solution reacted with the sediments and sedimentary rocks in early diagenetic stage and according to the different host (sediment and rock) effective microbial Fe-oxidation (enrichment) or metasomatism and subordinate microbial Fe-oxidation occured. Based on the spatial distribution and the presence of the ore deposit in the succession, the ore formation went on during the early diagenesis. The presence of the microbial signs at the cleavage plains of the creamspar and the element distribution suggest that the sparite formation happened due to the metasomatism. Consequently, the creamspar of Rudabánya was formed in an early diagenetic sediment by microbial Fe-oxidation and metasomatism in proximal zone, while distal formation positions include only traces of the same processes.

Considering the euhedral quartz megacrystals in creamspar, the concavo-convex grain contacts and the syntaxial quartz overgrowths on monocrystalline quartz grains replacing the earlier creamspar, the low $\delta^{13}C$ and $\delta^{18}O$ values and the thickness (more than 2000 meters) of the Lower Triassic – Jurassic overlying formations, the succession was effected by deep burial diagenesis. According to the low illite and chlorite crystallization values, the BSF later might have suffered anchimetamorphism, nevertheless it needs further studies.

6. Conclusions

Mineralogical, petrographical and geochemical study of the Bódvaszilas Sandstone of the Rudabánya open pit and the Aggtelek Mts. were summarized as part of the current iron and base metal exploration in Rudabánya.

The composition and crystal structure of the historically identified „siliceous sparry iron ore/creamspar" of Bódvaszilas Sandstone were determined for the first time, which is an intermediate solid solution between siderite and magnesite.

In the lower section of the Triassic sequence, the pore-filling carbonate cement (creamspar) of the Bódvaszilas Sandstone Formation was formed in the early stage of diagenesis by two-cycled microbial Fe(II) mediation process. The creamspar in the higher parts of the formation (transition between Bódvaszilas Sandstone and Szin Marl) was formed by the same metasomatic processes producing the formerly exploited siderite in the Middle Triassic limestones and dolomites by the partial or complete Fe replacement of the earlier carbonate layers.

Minor Fe addition may have occured in Bódvaszilas Sandstone in the Aggtelek Mts, where the pore-filling cement is also microbialy mediated.

Considering the concavo-convex grain contacts and the syntaxial quartz overgrowths on monocrystalline quartz grains, the formation underwent deep burial diagenesis, however, according to the illite and chlorite crystallinity values the Bódvaszilas Sandstone might suffered not only (deep burial) diagenesis but at least anchimetamorphism both in the studied areas (Rudabánya, Aggtelek Mts.).

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References

329 Balla, L., Blitzer, Gy., Doszpoly, J., Harnos, J., Sóvágó, Gy., Szuromi, B., Varga, L. 1987. Iron ore
330 mining of Rudabánya, documentation of the closure of the mine, University of Miskolc,
331 Miskolc, 441 pp.
332 Bhatia, M.R. & Crook, K.A.W. 1986. Trace element characteristics of graywackes and tectonic
333 setting discrimination of sedimentary basins. Contributions to Mineralogy and Petrology 92,
334 181-193.
335 Brusnitsyn, A.I., Zhukov, I.G. 2012. Manganese deposits of the Devonian Magnitogorsk
336 palaeovolcanic belt (Southern Urals, Russia). Ore Geology Reviews 47, 42–58.
337 Csalagovits, I. 1973. Results of the geochemical and ore forming studies of the Triassic succession
338 in the Rudabánya area. Annual report of the Hungarian Geological Society from 1971, 61-
339 90.
340 Ehrlich, H.L., 1990. Geomicrobiology, 2nd ed. M. Dekker, New York (N.Y.). 719 pp.
341 Fodor, L., Csontos, L., Bada, G., Győrfi, I., Benkovics, L. 1999. Tertiary tectonic evolution of the
342 Pannonian Basin system and neighbouring orogens: a new synthesis of paleostress data. In:
343 Durand, B., Joliver, L., Horváth, F., Séranne, M. (Eds.): The Mediterranean Basins: Tertiary
344 extension within the Alpine Orogen. Geological Society. Special Publications, London, 156,
345 298–334.
346 Fortin, D., Ferris, F.G., Beveridge, T.J., 1997, Surface-mediated mineral development by bacteria,
347 *in* Banfi eld, J., and Nealson, K.H., eds., Geomicrobiology: Interactions between microbes
348 and minerals: Mineralogical Society of America Reviews in Mineralogy Volume 35, p. 162–
349 180.
350 Földessy, J., Németh, N., Gerges, A. 2010. Preliminary results of the re-exploration of the
351 Rudabánya base metal ore deposit. Bulletin of the Hungarian Geological Society, 140, 3,
352 281–292. (in Hungarian)
353 Fügedi, U., Szentpétery, I., Chikán, G., Vatai, J. 2010: The Rudabánya-Martonyi mineralisation:
354 possible geochemical reconstruction. Carpathian Journal of Earth and Environmental
355 Sciences 5/2, 81–88.
356 Hernyák, G., 1967. Siliceous siderite and hematite in the Lower Triassic (Seis) of Rudabánya (NE-
357 Hungary). Földtani kutatás. 10, 1, 1-6. (in Hungarian)
358 Hofstra, A.H., Korpás, L., Csalagovits, I., Johnson, C.A. & Christiansen, W.D. 1999. Stable
359 isotopic study of the Rudabánya iron mine, a carbonate-hosted siderite, barite, base-metal
360 sulfide replacement deposit. Geologica Hungarica, Series Geologica 24, 295–302. (in
361 Hungarian)

362 Hurai, V. 2005. ‘‘Siderite mineralization of the Gemericum superunit (Western Carpathians,
363 Slovakia): review and a revised genetic model’’ [Ore Geology Reviews 24, 267–298]—a
364 discussion. – Ore Geology Reviews 26, 167–172.
365 Konhauser, K. O. 1998: Diversity of bacterial iron mineralization. – Earth-Science Reviews 43, 91–
366 121.
367 Kovács, S., Less, Gy., Hips, K., Piros, O., Józsa, S. 2004: Aggtelek-Rudabánya units, in: Haas, J.
368 (ed.): Geology of Hungary. Triassic, ELTE Eötvös Kiadó, Budapest, 197-216. (in
369 Hungarian)
370 Less, Gy., Grill, J., Gyuricza, Gy., Róth, L., Szentpétery, I. 1988: 1:25000 scale geological map of
371 the Aggtelek-Rudabánya Mts., Hungarian Geological Institute, Budapest (in Hungarian)
372 Maslennikov, V.V., Ayupova, N.R., Herrington, R.J., Danyushevskiy, L.V., Large, R.R. 2012:
373 Ferruginous and manganiferous haloes around massive sulphide deposits of the Urals. – Ore
374 Geology Reviews 47, 5–41.
375 Nagy, B. 1982. The comparative ore forming study of the Rudabánya ore deposit. Annual report of
376 the Hungarian Geological Society from 1980, p. 45–58.
377 Németh, N., Földessy, J., Kupi, L. & Iglesias, J.G. 2013. Zn-Pb mineralization types in the
378 Rudabánya ore bearing complex. Carpathian Journal of Earth and Environmental Sciences,
379 8, 1, 47–58.
380 Palinkaš, L. A., Šoštarić, S. B., Palinkaš, S. S. 2008: Metallogeny of the Northwestern and Central
381 Dinarides and Southern Tisia. Ore Geology Reviews 34, 501–520.
382 Pantó, G. 1956. Geology of the Rudabánya iron ore ridge. Yearbook of the Hungarian Geological
383 Institute, 44, 2, 329–637. (in Hungarian)
384 Rimmer, S. 2004. Geochemical paleoredox indicators in Devonian–Mississippian black shales,
385 Central Appalachian Basin (USA). Chemical Geology 206, 373–391.
386 Scholle, P. A. & Ulmer-Scholle, D. S. 2003. A color guide to the petrography of carbonate rocks:
387 grains, textures, porosity, diagenesis, AAPG Memoir 77, Tulsa (Oklahoma, U.S.A.), p. 459.
388 Schwertmann, U., Cornell, R.M., 2007. Iron Oxides in the Laboratory: Preparation and
389 Characterization, Wiley-VCH, p. 188.
390 Szakáll, S. 2001. The Minerals of Rudabánya. Kőország Kiadó, Budapest, p. 176. (in Hungarian)
391 Szentpétery I. & Less Gy. (Eds.) 2006. Geology of the Aggtelek-Rudabánya Mts. Explanations to
392 the 1:25000 scale geological map of the Aggtelek-Rudabánya Mts. published in 1986.
393 Hungarian Geological Institute, Budapest, p. 92. (in Hungarian)

394 Yang, B., Hu, B., Bao, Z., Zhang, Z. 2011. RFF geochemical characteristics and depositional
395 environment of the black shale-hosted Baiguoyuan Ag-V deposit in Xingshan, Hubei
396 Province, China. Journal of Rare Earths 29/5, 499–506.
397 Wignall, P.B., Myers, K.J. 1988. Interpreting the benthic oxygen levels in mudrocks: a new
398 approach. Geology 16, 452–455.
399

Figure captions

Fig. 1.

(a) Location of the Rudabánya iron and base metal deposit in the Alp-Carpathian region (after Fodor et al., 1999)

(b) The Rudabánya research area and the sampling points of Bódvaszilas Sandstone Formation

(c) Geological section of Rudabánya ore deposit (after Less et al. 1988)

Fig. 2.

(a) Filamentous, pearl necklace-like mineralized microbially produced texture (MMPT) in pore-filling carbonate cement (Rudabánya)

(b) Filamentous textures (MMPT) along the cleavage faces of the sparite crystals in the massive carbonate sections (Rudabánya)

(c) Filamentous, pearl necklace-like MMPT in pore-filling carbonate cement (Aggtelek Mts.)

(d) Green clay minerals between the grains of Bódvaszilas Sandstone

(e) Texture of pore-filling creamspar by EPMA (Q – quartz grains, Si – siderite, Mg – magnesite)

(f) Texture of pore-filling creamspar by optical microscopy (Q – quartz grains, arrows: MMPT)

Fig. 3. Composition of creamspar samples on the Fe-Mg-Mn diagram

Fig. 4. The evolution of the Lower Triassic Bódvaszilas Sandstone according to this study (Geological section after Szentpétery & Less Gy. 2006)

Table

Table 1. Geochemical environmental indicators of some representative samples of Bódvaszilas Sandstone

Sample	Th/U	U/Th	δU	V/Cr	Ni/Co
BH/1	5.41	0.18	-0.85	1.15	0.33
T11/3	4.78	0.21	-1.50	1.30	3.57
T11/4	4.76	0.21	-1.47	1.14	2.89
T11/6	5.44	0.18	-2.94	0.59	2.00
T14A/4	3.32	0.30	-0.13	3.20	2.00
T14A/5	5.16	0.19	-2.03	1.05	4.67

Figure

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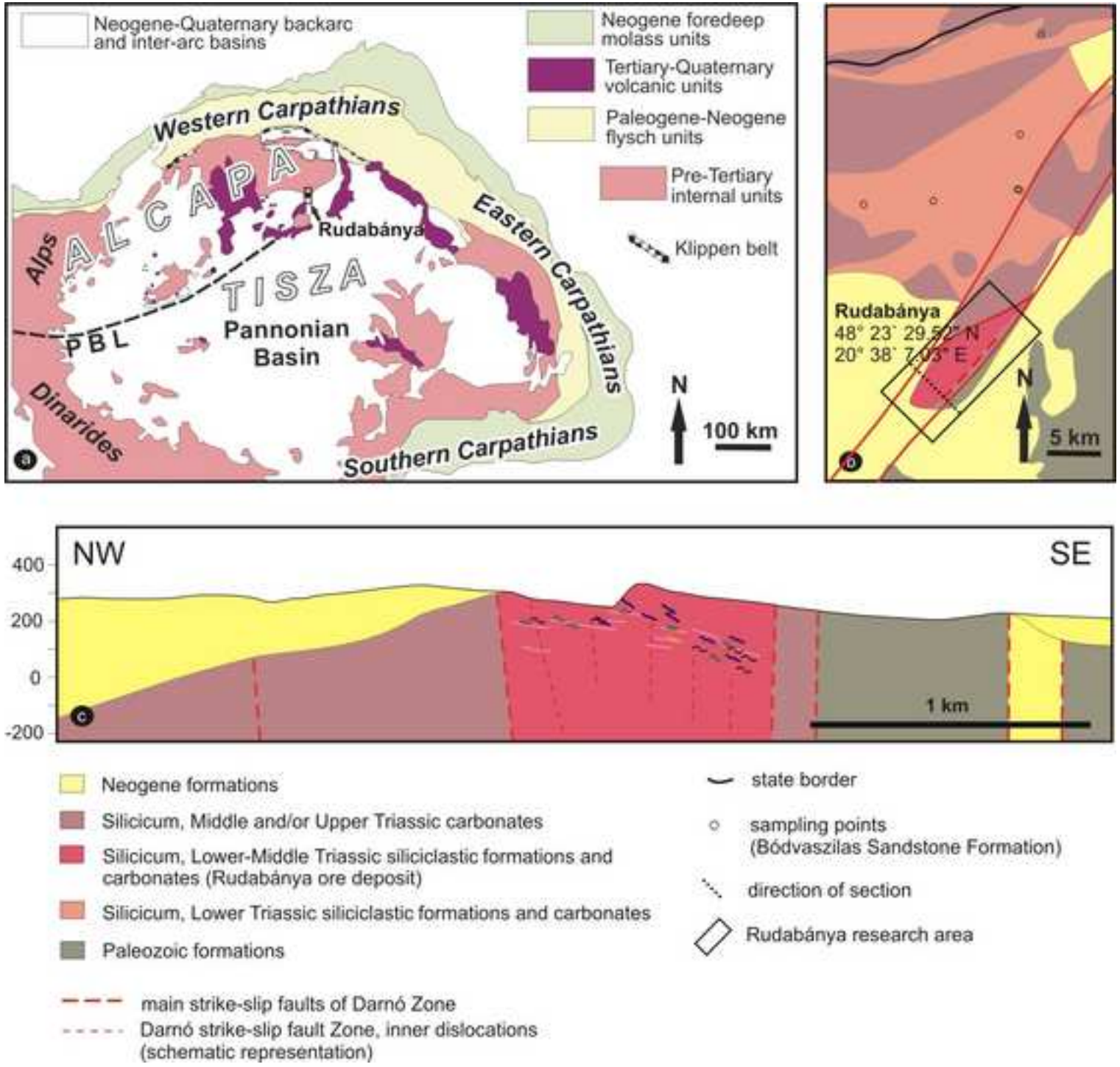

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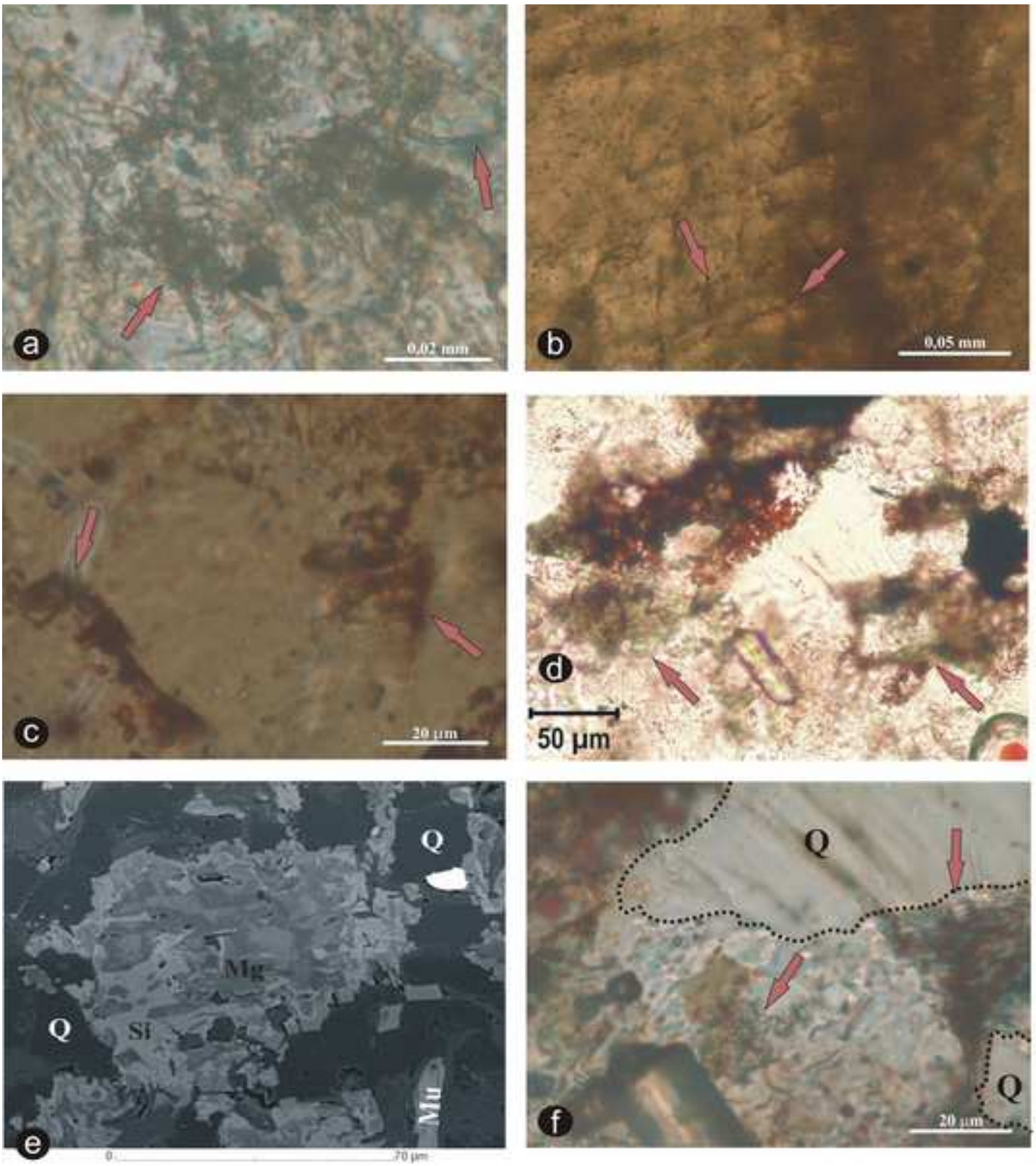

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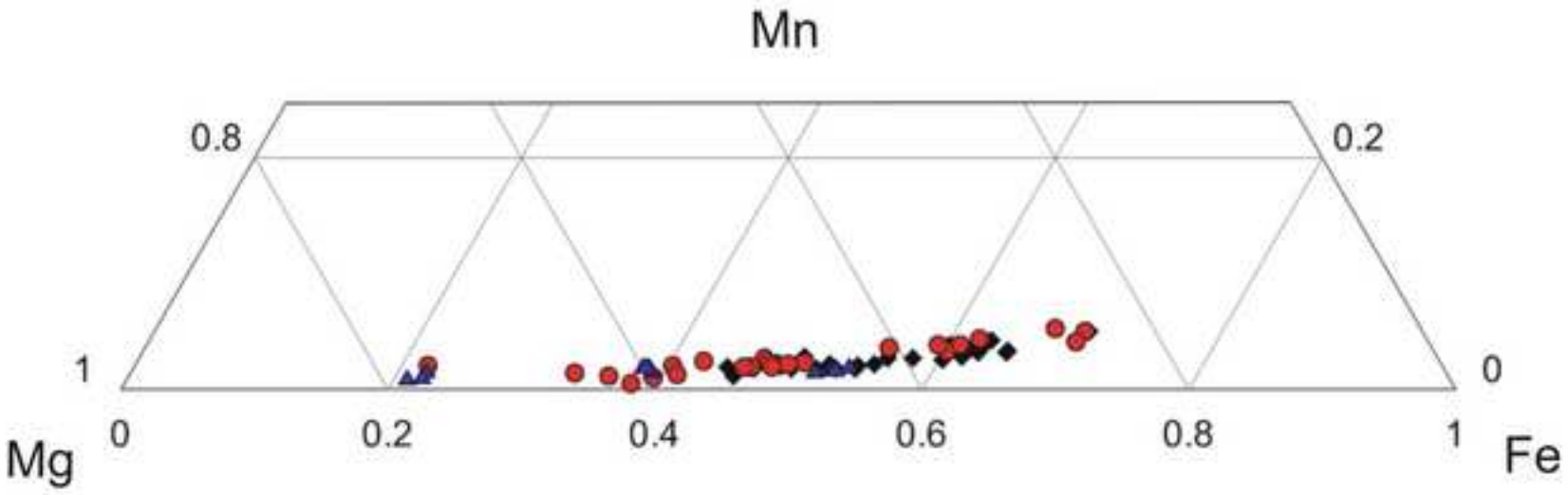

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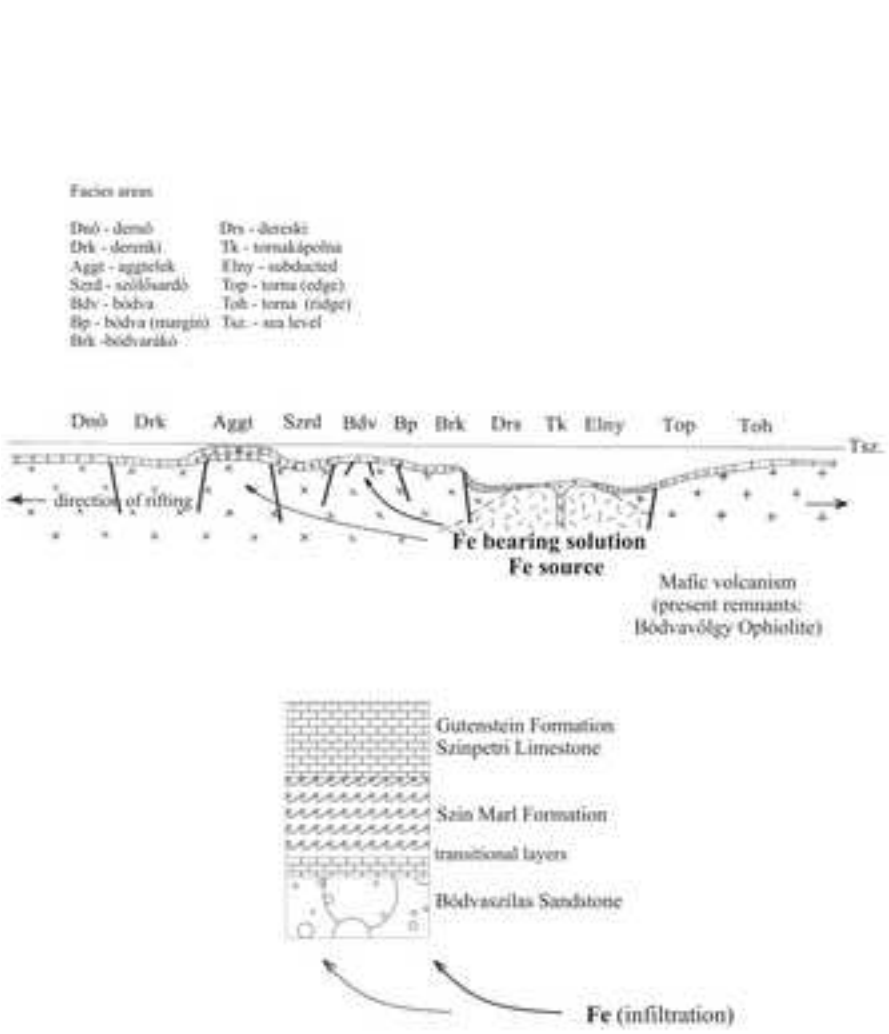

Provenance

composition: accessory minerals - acidic igneous and metamorphic rocks,
La/Th, La/Co ratio - acidic igneous rocks,
absence of unstable lithic fragments,
stable and extremely stable, well-rounded accessory minerals, maturity
+ Kovács et al. (2004): source is the Permian Molasse in the basement of the Gemericum

recycled sediment derived from **acidic source area** (which is not the source of Fe)

Sedimentary (depositional) environment

Th/U, U/Th, V/Cr, Ni/Co ratio,
tidal flat

oxic environment, no organic matter burial, no sulphate reduction

Iron ore formation

inhomogeneous, siderite/magnesite, ankerite
<u>creampar in siliciclastic succession</u>: pore-filling cement, and at the margin of the grains and in the cement widely prevalent mineralized microbially produced texture (MMPT) (ferrihydrite→*goethite-hematite): chemolitoautotroph (1. microbial cycle), siderite/mixed carbonate - early diagenetic, heterotroph, anaerob (2. microbial cycle, burial: FeOOH, Corg→*siderite)
<u>carbonate layers, vein-filling creampar</u>:
zonation along cleavage faces (like "sparry iron ore"),
few filamentous textures (MMPT) along the cleavage faces of the sparite crystals in the massive carbonate sections and in vein-fillings,
negative C isotopic values similar to sparry iron ore

before significant compaction, from external source, along fractures Fe-bearing solution flow, effective metal enrichment
<u>siliciclastic succession</u>: **microbial Fe oxidation** in suboxic-neutral (pH 6-8) environment (1. autotroph microbial cycle), siderite (mixed carbonate, 2. heterotroph microbial cycle) /could oxidate on the surface (limonite)/
<u>carbonate sections</u>: **iron metasomatism** and syngenetic sparite formation
source of Fe: most probable the ultramafic-mafic rocks of Bódvavölgy Ophiolite + seawater (ion exchange)

Deep burial diagenesis

straight or concavo-convex grain contacts,
synthaxial quartz overgrowths on monocrystalline quartz grains, eubedral quartz megacrystals in carbonate,
carbonate interfingered with coarse-grained subhedral quartz,
BSF: quartz cement replaces carbonate cement
light C és O isotopic values
bent muscovite

deep burial diagenesis - after ore formation, quartz cement fills the remainder pore-space

Metamorphosis (?)

low illite- és chlorite crystallinity values (at least anchimetamorphism),
muskovite-2M1, -1T,
monocrystalline quartz with undulatory extinction,
"twinned" sparite crystals refers to tectonic deformation

anchimetamorphism as a continuation of deep burial diagenesis or along thrust plane (or inherited?)

The iron ore deposit in Rudabánya is of metasomatic-microbial origin, the Fe interacted with the early diagenetic sedimentary rocks, resulted two ore-type depending on the type of the host rock.