

Microbially mediated iron ore formation, Silicic Superunit, Rudabánya, Hungary



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ABSTRACT

The mineralogical, petrological, geochemical and textural characterization of the Triassic Bódvaszilas Sandstone in the Rudabánya open pit and Aggtelek Mts. is summarized based on our investigations. The pore-filling carbonate cement in 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 a suboxic neutrophilic environment, and Fe-carbonate by heterotrophic microbes in a suboxic to anaerobic environment based on mineralized microbially produced textural evidences). The carbonate in the higher parts of the formation (transition between the Bódvaszilas Sandstone and the overlying formation, Szin Marl) was formed by the same metasomatic processes that produced the siderite ore in the Middle Triassic limestones and dolomites. These processes led to partial or complete Fe replacement of the syngenetic carbonate layers. Microbially mediated Fe enrichment also occurred at distal basin position in the Bódvaszilas Sandstone (Aggtelek Mts.). The formation later underwent deep burial diagenesis.

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1. Introduction

After centuries of base metal and silver mining, the open pit and underground iron ore (limonite and siderite) mining of Rudabánya (Silicic Superunit, Lower–Middle Triassic, NE Hungary) took place from 1872 until 1985. Approximately 38 Mt of iron ore were excavated during this period; the remaining reserves are estimated at 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–Carpathians 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 Silicic Superunit includes the highest, unmetamorphosed nappes of the Slovako-Carpathian tectonic system and the Silicic units contain sedimentary complexes of Late Permian to Late Jurassic age, also referred as Silicic Nappe System (Froitzheim et al., 2008) which were part of the

European Continental Margin (continental margin of the Mesozoic Tethys) at that time. The siderite–sulfide 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 FeCO₃ ore. Carbonate-replacement siderite deposits of the Gemericum hosted by a Silurian limestone belt are similar to the stratabound siderite deposits of the Eastern Alps (e.g. Erzberg, Austria; Radvanec et al., 2004). The siderite–sulfide veins and siderite replacement deposits were classified as metamorphogenic, and 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) also represents hydrothermal-metasomatic Fe mineralization. Here the iron ore occurs as stratabound siderite and ankerite replacement-type bodies in limestones and as siderite–sulfide veins within shales. Superimposed Alpine retrograde metamorphic fluids were observed and might well be compared to the fluids linked to the formation of the Rudabánya deposits in Gemericum. The potential resources of iron ore in the Ljubija district have been estimated at 500 Mt with 40 to 49 wt.% Fe (Palinkaš et al., 2008).

The renewed exploration of the Rudabánya ore deposit began in 2007 and has resulted in the delimitation of Fe, Cu and Pb ore resources which were previously explored and mined in the area, as well as newly recognized, additional Pb and Zn enrichments (Földessy et al., 2010;

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Németh et al., 2013) 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 (its local name is “siliceous sparry iron ore” or “creamspar”).

During the investigation of this iron ore signs of microbial mediation were observed, which was formerly unknown in these rocks. This initiated new investigations and led to the proposal of a new ore formation model. Similar models were not reported from the Alps-Carpathians region.

2. Geological setting and mineralization at Rudabánya

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 (Fig. 1a), in the Silicic Superunit of the Alps–Carpathians–Pannonian (ALCAPA) region (Fig. 1b). The Silicic Superunit is made up of 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 and Less, 2006) (Fig. 1c).

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. 1d). 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 composed of carbonate (limestone, dolomite) and siliciclastic rocks (sandstone, siltstone, marl) in a tectonized clayey matrix (Pantó, 1956; Hernyák, 1967; Szentpétery and 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, and their thickness between 3–100 m (Balla et al., 1987).

Previously several genetic models were suggested for the iron mineralization of Rudabánya, some of them assuming a magmatic origin (Nagy, 1982; Balla et al., 1987). According to another scenario, magmatism was not necessary for the genesis of the iron ore, rather mixing between the pore waters of the Permian–Lower Triassic siliciclastic succession and the fissure waters of the Triassic carbonates was proposed (Csalagovits, 1973; Fügedi et al., 2010).

According to the latest studies the Rudabánya ore deposit complex was formed in several superposed periods. Three main deformation phases divided temporally the periods of ore formation (Földessy et al., 2010; Németh et al., 2013). The earliest ore-forming phase was a synsedimentary, stratiform, sedimentary-exhalative Pb–Zn (galena, sphalerite) accumulation associated with barite and pyrite was formed in the pelitic and carbonatic, reductive Szin Marl. The stratiform type sphalerite-galena mineralization is lithology controlled, as it was found in calcareous siltstone only. This fine-grained ore is strongly affected by later deformation events, dissected into lenses or boudins in the low strength siltstone matrix (Németh et al., 2013). A later metasomatism (probably of Cretaceous age) introduced the siderite ores (the 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 the Bódvaszilas Sandstone.

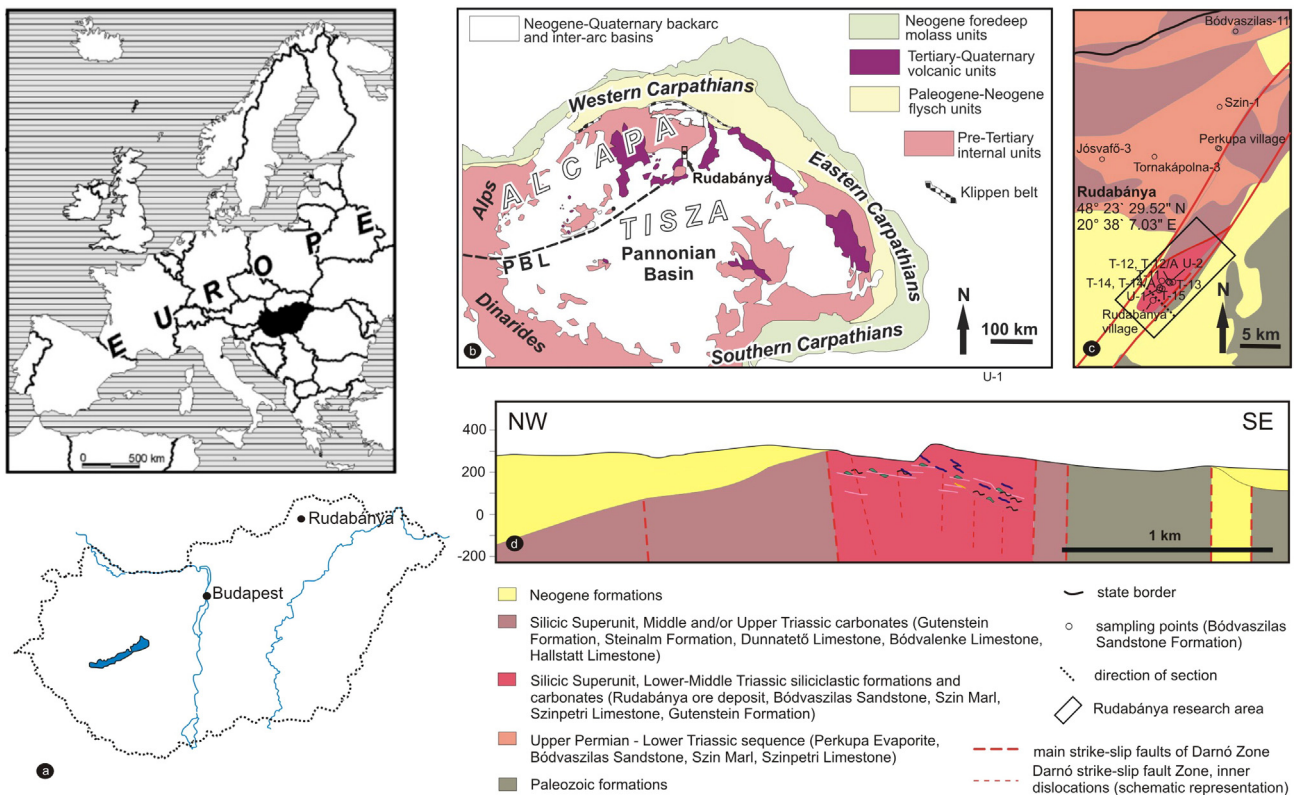


Fig. 1. (a) Location of the Rudabánya iron and base metal deposits in Europe and in Hungary. (b) Location of the Rudabánya iron and base metal deposit in the Alps-Carpathians region (after Fodor et al., 1999). (c) The Rudabánya research area and the sampling points of the Bódvaszilas Sandstone Formation. The entire area of the Rudabánya Mts., which is part of the Aggtelek–Rudabánya Mts. and includes the Rudabánya ore deposit, is located in the Darnó strike-slip fault Zone. The Mesozoic formations located west and east from the Zone cannot be correlated, as their original facies areas and tectonic locations are different, but the age of the formations is partly the same. (d) Geological section of the Rudabánya ore deposit (after Less et al., 1988).

In the third ore forming phase (related to the Darnó Zone formation, probably of Paleogene age, Földessy et al., 2010) mainly pyrite-bearing massive sulfide filled veins, and later Pb-, Zn-, Ag- and Cu-enrichments with barite were generated (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. Remobilization of primary stratiform ores during later hydrothermal processes is a possible explanation of their genesis (Németh et al., 2013). The faults of the Darnó Zone promoted the latest, sulphidic ore formation (As-, Sb-, Hg- and Ag-enrichments) probably of low temperature. In this last stage of the ore formation the siderite-base 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). Spherosideritic iron ore was also formed at the basis of the Miocene beds (Szakáll, 2001).

3. Samples and methods

Representative samples of the Bódvaszilas Sandstone (number of samples: 82) and siliceous sparry iron ore (hereinafter referred to as creamspars, number of samples: 18) from the Rudabánya open pit and from a surface outcrop in Rudabánya were investigated, and samples from Bódvaszilas Sandstone from the non-mineralized area (Aggtelek Mts.) were also collected (Table 1, Fig. 1c). All Bódvaszilas Sandstone samples from Rudabánya contain various amounts of creamspars.

The Bódvaszilas Sandstone samples are bluish-grayish 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 petrographic investigations were done first to acquire information before other analyses (Leitz Metalloplan microscope, University of Miskolc, Miskolc, Hungary, NIKON ECLIPSE 600 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 (CuK α source, 40 kV, 40 mA, secondary graphite crystal monochromator, scintillation detector) at the Institute of Mineralogy and Geology, University of Miskolc, Hungary.

Electron microprobe analyses were done by back-scattered electron imaging (BSE) and energy dispersive spectrometry (EDS) for main and trace element distribution on a JEOL JXA-8600 Superprobe (acceleration voltage: 15 kV, probe current 20 mA, acquisition time 60 s), with evaluation by ZAF correction software (using a self-developed database) at the same institute.

The $^{13}\text{C}_{\text{carb}}$ and $^{18}\text{O}_{\text{carb}}$ stable isotopic analyses on siliceous sparry iron ore and sparry iron ore were carried out on a Finnigan Delta Plus XP mass spectrometer with routinely used processing of samples at the Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budapest, Hungary.

The Total Organic Carbon analysis on siliceous sparry iron ore and the host siliciclastic succession was done on bulk samples on a Tekmar-Dohrmann Apollo 9000N TOC analyzer at 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 the Bódvaszilas Sandstone samples by ICP-MS (using lithium metaborate fusion: Ba, Ce, Cr, Cs, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Lu, Nb, Nd, Pr, Rb, Sm, Sn, Sr, Ta, Tb, Th, Tl, Tm, U, V, W, Y, Yb, Zr; and nitric aqua regia digestion: As, Bi, Hg, Sb, Se, Te) and ICP-AES (using lithium metaborate/lithium tetraborate fusion: SiO $_2$, Al $_2$ O $_3$, Fe $_2$ O $_3$, CaO, MgO, Na $_2$ O, K $_2$ O, TiO $_2$, MnO, P $_2$ O $_5$; using HF-HNO $_3$ -HClO $_4$ acid digestion, HCl

leach: Ag, Cd, Co, Cu, Mo, Ni, Pb, Zn; and with fire assay fusion: Au) (ALS Chemex laboratories, Vancouver) (Table 2).

4. Results

4.1. Petrological and microtextural characteristics of the Bódvaszilas Sandstone Formation

The Bódvaszilas Sandstone is a mature sediment based on the quantity and quality of the grains. The absence of unstable grains such as polycrystalline quartz and lithic fragments, and the low quantity of feldspars are typical. The most frequent clastic constituent is monocrystalline quartz (approx. 85%) and muscovite (10%) by visual estimation. Other types of mica (altered phlogopite, biotite) may be present in low quantity. The accessory minerals are zircon, apatite, rutile and monazite, 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 consists of quartz and a large amount of carbonate (creamspars in Rudabánya and similar in the Aggtelek Mts.).

The three types of the pale yellow carbonate (creamspars) 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. Fine filamentous, pearl necklace-like textures of assumed microbial origin (MMPT – mineralized microbially produced texture) are widely prevalent in the pore-filling cement of the Bódvaszilas Sandstone and at the margin of the grains, and at the contact of the carbonate cement and the grains also, both in Rudabánya and in the Aggtelek Mts. (Fig. 2B, c, f). These textures often form microbial-like colonies in which 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). MMPT is present in much lower quantity in the non-ore bearing distal basin area in the same formation (Aggtelek Mts., Bódvaszilas Sandstone Formation).
2. Vein-filling creamspars in 1–2 cm wide veins in crosscutting layering. At the margin of the sandstone and the vein coarse-grained euhedral quartz is present.
3. Massive syndimentary intercalations in the upper part of the Bódvaszilas Sandstone (transitional layers to the covering Szin Marl Formation). Euhedral–subhedral quartz with sparse hematite flakes may be connected to the coarse grained (up to 1 mm) sparite carbonate crystals. In the massive carbonate sections coarse-grained (up to 0.5–1 mm) euhedral quartz crystals are also present (megacrystals, Scholle and 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, filamentous MMPT textures can also be observed in negligible quantity (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 carbonate cement can be found in the quartz cement as inclusions.

Table 1
Location, lithology of the samples and the used methods.

Sample	Location	Lithology	Used methods*
T11/1	Rudabánya open pit, borehole T-11	Siltstone	1, 2, 3, 4
T11/2		Siltstone, creamspar	1, 2, 4
T11/3		Claystone–siltstone	1, 2, 3, 4, 6
T11/4		Siltstone, very fine-grained sandstone intercalations	1, 2, 6
T11/5		Very fine-grained sandstone, siltstone	1, 2
T11/6		Very fine–fine-grained sandstone	1, 2, 6
T11/7		Very fine-grained sandstone, siltstone	1, 2, 4
T12/1	Rudabánya open pit, borehole T-12	Very fine-grained sandstone	1, 2
T12/2		Very fine–fine-grained sandstone, creamspar	1, 2, 5
T12A/1	Rudabánya open pit, borehole T-12/A	Very fine-grained sandstone, siltstone	1, 2
T12A/2		Very fine-grained sandstone, creamspar	1, 2
T12A/3		Very fine-grained sandstone, creamspar	1, 2
T12A/4		Creamspar	1, 2, 5, 7, 8
T12A/5		Creamspar	1, 2, 3, 5, 6, 7
T12A/6		Creamspar	1, 2, 3, 5
T12A/7		Creamspar	1, 7
T13/2	Rudabánya open pit, borehole T-13	Very fine-grained sandstone	1, 2
T14/1	Rudabánya open pit, borehole T-14	Very fine-grained sandstone	1, 2
T14/2		Very fine-grained sandstone	1, 2
T14/4		Very fine–fine-grained sandstone	1, 2
T14/5		Very fine-grained sandstone, creamspar	1, 2
T14/6		Fine–medium grained sandstone, creamspar	1, 2
T14/7		Very fine-grained sandstone, siltstone, creamspar	1, 2
T14A/1	Rudabánya open pit, borehole T-14/A	Very fine–fine-grained sandstone	1, 2
T14A/2		Siltstone	1, 2
T14A/3		Very fine–fine-grained sandstone	1, 2
T14A/4		Siltstone, very fine–fine-grained sandstone	1, 2, 4, 6
T14A/5		Siltstone	1, 2, 6
T14A/6		Very fine–fine-grained sandstone	1, 2
T14A/7		Siltstone	1, 2
T14A/8		Very fine-grained sandstone, creamspar	1, 2, 3, 5, 7, 8
T14A/9		Very fine-grained sandstone	1, 2, 3, 5
T14A/10		Very fine-grained sandstone, creamspar	1, 2
T14A/11		Creamspar	1, 7
T15/KP1	Rudabánya open pit, borehole T-15	Creamspar	1, 2, 3, 5
T15/KP2		Creamspar	1, 3, 7
T15/1		Very fine–fine-grained sandstone breccia	1, 2, 5
T15/2		Very fine–fine-grained sandstone	1, 2, 3, 4
T15/3		Very fine-grained sandstone - siltstone breccia	1, 2, 3, 4
T15/4		Very fine–fine-grained sandstone	1, 2
T15/8		creamspar	1, 7
U1/1	Rudabánya open pit, borehole U-1	Very fine-grained sandstone, siltstone	1, 2
U1/2		Siltstone	1, 2, 3, 5, 8
U1/3		Siltstone, very fine-grained sandstone	1, 2, 5
U1/4		Very fine-grained sandstone, siltstone	1, 2
U1/5		Siltstone, very fine-grained sandstone	1, 2, 4, 5
U1/6		Siltstone, very fine-grained sandstone	1, 2, 5
U1/7		Very fine-grained sandstone, siltstone	1, 2
U1/8		Very fine-grained sandstone, siltstone	1, 2, 4, 5
U1/9		Claystone, siltstone	1, 2
U1/10		Very fine-grained sandstone, siltstone	1, 2, 3, 5
U1/11		Claystone, siltstone	1, 2, 4
U2/1	Rudabánya open pit, borehole U-2	Very fine-grained sandstone	1, 2
U2/2		Very fine-grained sandstone, siltstone, Claystone	1, 2
U2/3		Siltstone, claystone, creamspar	1, 2
BH/Rb-Gv/1	Rudabánya village	Very fine-grained sandstone, siltstone	1, 2
Sz1/1	Aggtelek Mts., borehole Szin-1	Very fine-grained sandstone, siltstone	1, 2, 4
Sz1/2		Siltstone, claystone	1, 2, 4
Sz1/3		Very fine-grained sandstone, siltstone	1, 2, 5
Sz1/4		Siltstone, very fine-grained sandstone	1, 2
Sz1/5		Siltstone, very fine-grained sandstone	1, 2, 5
Sz1/6		Very fine-grained sandstone	1, 2, 3, 5
Sz1/7		Very fine-grained sandstone	1, 2, 3
Sz1/8		Siltstone	1, 2
Sz1/9		Siltstone	1, 2
Sz1/10		Siltstone	1, 2
Sz1/11		Very fine-grained sandstone, siltstone	1, 2
Sz1/12		Very fine-grained sandstone	1, 2
Sz1/13		Very fine-grained sandstone, siltstone	1, 2
Sz1/14		Very fine-grained sandstone	1, 2
Sz1/16		Siltstone	1, 2
Sz1/17		Very fine-grained sandstone, siltstone	1, 2
Sz1/18		Siltstone, very fine-grained sandstone	1, 2, 5
Bsz11/1	Aggtelek Mts., borehole Bódvaszilás-11	Siltstone	1, 2, 3, 4
J3/1	Aggtelek Mts., borehole Jósvafő-3	Siltstone	1, 2, 3, 4

Table 1 (continued)

Sample	Location	Lithology	Used methods*
Tk3/2	Aggtelek Mts., borehole Tornakápolna-3	Very fine-grained sandstone, siltstone	1, 2, 3, 4
Tk3/3		Very fine-grained sandstone	1, 3
BH/1	Aggtelek Mts., BSF type locality (Perkupa village)	Very fine-grained sandstone	1, 2, 5, 6
BH/2		Siltstone	1, 2, 3, 8
BH/3		Very fine-grained sandstone, siltstone	1, 2
BH/4		Claystone, siltstone	1, 2
BH/5		Claystone, siltstone	1, 2
BH/310		Claystone, siltstone	1, 2, 3
BH/311		Very fine-grained sandstone	1, 2, 3, 5
BH/313		Very fine-grained sandstone	1, 2, 3
BH/6	Aggtelek Mts., Perkupa village	Siltstone, claystone	1, 2
BH/7		Siltstone	1, 2
BH/8		Very fine-grained sandstone, siltstone	1, 2
PV/I/1	Rudabánya open pit	Sparry iron ore	1, 3, 7
PV/I/2		Sparry iron ore	1, 3, 7
PV/II/1		Dolomite	1, 3, 7
PV/II/2		Sparry iron ore	1, 3

*Legend: 1. macroscopic investigation, 2. microscopic investigation (thin section, optical microscopy), 3. XRD on bulk samples, 4. XRD <2 μm (illite and chlorite crystallinity), 5. SEM, EPMA, 6. ICP-MS, ICP-AES, 7. Stable isotope analysis, 8. TOC analysis. For details see Fig. 1.

4.2. Mineralogy (XRD) of siliceous sparry iron ore (creamspar)

By XRD peaks of the R-3c space-group were observed, with $d(\text{Å})$ values 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 a 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 texture of the creamspar and its composition is very similar in the three types (pore-filling cement, vein fillings, massive carbonate sections). It often shows chemical zonation patterns, on the rhombohedron faces (Fig. 2e). The creamspar is always inhomogeneous in elemental composition, but it is always a Fe- and Mg-rich carbonate with low Mn content (never pure siderite or pure magnesite, always with excess substitution of Mg and Fe). The Fe and Mg ratio changes within several micrometer levels, and is independent of textural characteristics. In the analyzed samples the Fe content varies between 0.11 and 0.84 and the Mg content between 0.25 and 0.65 at.% in the RCO_3 theoretical formula (R: Fe, Mg, Mn, Ca) (Table 3, Fig. 3).

4.4. C and O isotopic values of the carbonate

The samples of the massive creamspar sections show negative C and O isotopic values: $\delta^{13}\text{C}_{\text{PDB}}$: −6.18‰ to −3.91‰; $\delta^{18}\text{O}_{\text{PDB}}$: −14.66 to −12.21 (‰) (Table 2, Fig. 4).

4.5. TOC values of the carbonate and the host rock

The Total Organic Carbon (TOC) content of the creamspar from the massive carbonate sections is between 0.38 and 2.63 wt.%, and the host rock (Bódvaszilas Sandstone) is 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 based on the accessory minerals and the La/Th and La/Co ratios (Bhatia and Crook, 1986, Table 2). Our observations reinforce the

opinion of Kovács et al. (2004) that the source area was the Permian molasse in the basement of the Gemericum (Bodor, 2014).

According to the geochemical environmental indicators (Wignall and Myers, 1988; Auluz et al., 2000; Rimmer, 2004; Yang et al., 2011) during the sedimentation and the early diagenesis oxic conditions existed (Table 2). Only the Th/U and V/Cr ratios of sample T14A/4 shows dysoxic conditions. According to the study of Bíró et al. (2015) paleoredox indicator element ratios must be used with caution, great care has to be taken in the complex interpretation of the data in microbially mediated systems, and the complex interpretation using mineralogy and microtexture can be recommended (microbially mediated selective element enrichments). Comparison of indicator patterns reflect different paleoredox conditions for the same samples (Bíró et al., 2015).

Several Fe (II) oxidizing microbes (FeOB) are known in shallow and deep marine environments, where some bacteria carry out autotrophic metabolism, i.e. they synthesize their cell constituents from the inorganic materials of the environment. Four kinds of microbial Fe(II) oxidizing metabolism are reported (Ehrlich, 1990; Fortin et al., 1997; Konhauser, 1998). Microbial Fe oxidizing processes are very effective (Ehrlich, 1990). According to the mineralogy and the morphological features the presence of suboxic, neutrophylic microbial forms is the most probable. In a suboxic, neutrophylic environment the Fe(II) oxidizing bacteria synthesize ferrihydrite (hydrated ferric oxyhydroxide), which transforms to more stable mineral forms like goethite or hematite within a few months while quartz is segregating (Schwertmann and Cornell, 2007). The iron-oxide and the segregated quartz may form clay minerals (green clays, e.g. celadonite and/or smectite). A 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 the BSF and at the margin of the grains. This observation suggests that prior to the formation of creamspar there was no intergranular cement (there is 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, or the Fe-bearing solution may have 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 dead microbes would have formed an unstable system. As the organic matter is reactive, it reacted with the ferrihydrite, which led to siderite and

W	ppm	18.0	54.0	104.0	1.0	34.0	3.0	W	ppm	3.30										
Mo	ppm	0.0	0.0	0.0	0.0	0.0	0.0	Mo	ppm	0.51										
As	ppm	1.2	1.2	1.3	0.5	0.9	1.6	As	ppm	0.80										
Cd	ppm	0.0	0.0	0.0	0.0	0.0	0.0	Cd	ppm	<0.02										
Sb	ppm	0.6	0.4	0.3	0.1	0.2	0.1	Sb	ppm	1.68										
Bi	ppm	0.0	0.2	0.1	0.0	0.0	0.1	Bi	ppm	0.11										
Ag	ppm	0.0	0.5	0.0	0.0	0.0	0.0	Ag	ppm	0.14										
Au	ppm	0.0	0.0	0.0	0.0	0.0	0.0	Au	ppm	0.74										
Hg	ppm	0.0	0.1	0.3	0.4	0.2	0.0	Hg	ppm											
Tl	ppm	0.0	0.0	0.0	0.0	0.0	0.0	Tl	ppm	<10										
Se	ppm	0.3	0.3	0.3	0.2	0.2	0.4	Se	ppm	1.00										
La	ppm	91.3	88.0	121.3	19.3	118.0	32.7	La	ppm	0.80										
Ce	ppm	71.6	69.4	92.3	16.9	89.3	30.1	Ce	ppm	2.96										
Pr	ppm	57.4	55.3	74.1	13.4	70.4	27.7	Pr	ppm	0.49										
Nd	ppm	42.5	41.4	54.7	10.3	51.5	24.2	Nd	ppm	3.20										
Sm	ppm	27.6	27.7	34.7	9.9	30.0	19.7	Sm	ppm	4.20										
Eu	ppm	13.3	13.0	11.3	13.4	14.8	9.8	Eu	ppm	3.82										
Gd	ppm	17.0	17.5	20.8	9.2	14.2	13.1	Gd	ppm	7.43										
Tb	ppm	13.6	14.3	16.0	7.9	9.0	10.3	Tb	ppm	1.35										
Dy	ppm	13.1	12.9	14.6	8.0	7.2	8.9	Dy	ppm	7.21										
Ho	ppm	11.6	11.5	12.6	6.6	5.9	7.8	Ho	ppm	1.30										
Er	ppm	11.4	11.8	12.4	6.5	5.9	7.3	Er	ppm	3.34										
Tm	ppm	11.8	12.4	13.5	6.7	6.5	7.3	Tm	ppm	0.55										
Yb	ppm	10.4	11.0	12.4	6.0	6.5	6.6	Yb	ppm	3.99										
Lu	ppm	11.0	11.8	13.6	6.0	7.6	7.1	Lu	ppm	0.63										
								Sc	ppm	4										
TOC	wt%				0.38		2.63	0.06		0.05										
Th/U		4.8	4.8	5.4	3.3	5.2	5.4	$\delta^{13}\text{C} (\text{‰})_{\text{PDB}}$	‰	-4.77	-5.60	-3.91	-5.18	-6.18	-5.23	-5.09	-4.69	-3.67	-3.45	
U/Th		0.2	0.2	0.2	0.3	0.2	0.2	$\delta^{18}\text{O} (\text{‰})_{\text{PDB}}$	‰	-13.44	-13.55	-12.21	-14.39	-14.66	-12.96	-13.96	-13.88	-11.50	-11.77	
V/Cr		1.3	1.1	0.6	3.2	1.1	1.2													
Ni/Co		3.6	2.9	2.0	2.0	4.7	0.3													
La/Th		2.78	2.70	2.26	1.80	2.98	2.09													
La/Co		4.79	3.59	4.94	2.37	14.43	2.00													

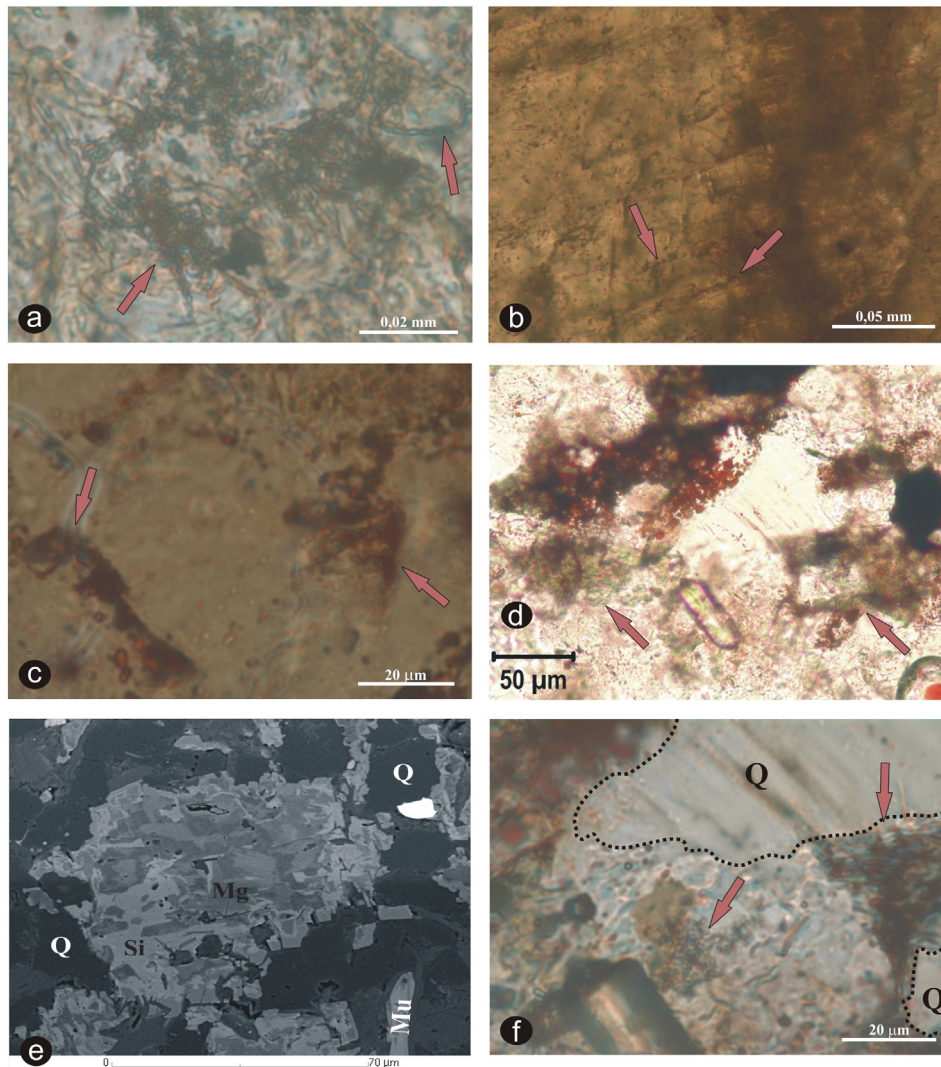


Fig. 2. (a) Filamentous, pearl necklace-like mineralized microbially produced texture (MMPT) in pore-filling carbonate cement (Rudabánya) (Sample U1/3). (b) Filamentous textures (MMPT) along the cleavage faces of the sparite crystals in the massive carbonate sections (Rudabánya) (Sample T12A/6). (c) Filamentous, pearl necklace-like MMPT in pore-filling carbonate cement (Aggtelek Mts.) (Sample BH/311). (d) Green clay minerals between the grains of the Bódvaszilas Sandstone (Sample U1/10). (e) Texture of pore-filling creamspars by EPMA (Q – quartz grains, Si – siderite, Mg – magnesite, Mu – muscovite) (Sample U1/2). (f) Texture of pore-filling creamspars by optical microscopy (Q – quartz grains, arrows: MMPT) (Sample U1/10). (All photos were taken by S. Bodor.).

ankerite formation with the contribution of microbes via heterotrophic metabolism in a suboxic to anaerobic environment (Konhauser, 1998). Additional ions in the Fe-bearing solution (Ca^{2+} , Mg^{2+} , HCO_3^- , etc.) and the TOC 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 $\delta^{13}\text{C}$ values of the forming carbonates are negative, which supports the mineralized organic C content. The negative $\delta^{13}\text{C}$ values and the remaining organic matter (0.05–2.63 wt.%) in our samples also confirm the microbial contribution. The texture of the pore-filling creamspars is misleadingly similar to the creamspars formed in the carbonate layers; nevertheless, high resolution optical microscopy revealed textural features and differences (distribution and quantity of MMPT), which highlight that the ore formation occurred in different ways in the siliciclastic and carbonate host succession.

The low quantity of microbial traces in the massive creamspars sections suggests that in the primarily carbonate host layers the creamspars was probably generated not via microbial mediation but by metasomatism, as the texture and the element distribution is rather similar to the younger, dolomite-hosted, metasomatic iron ores.

Zonation occurs occasionally by rhombohedron and is completely identical 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 moved forward parallel to the rhombohedron faces, which caused the characteristic zonation. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope values of the creamspars from the Bódvaszilas-Szin transitional layers and the sparry iron ore samples from the Rudabánya open pit are similar to each other (Table 2, Fig. 4) and nearly the same as those of the comparative siderite (sparry iron ore) and its host rock (brecciated dolomite) samples of Hofstra et al. (1999) from Rudabánya (Fig. 4). The samples from Rudabánya were compared to the siderite-sulfide veins of the Gemicum and the stratabound siderite replacement iron ore deposits of the Gemicum (Radvanec et al., 2004) also (Fig. 4). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the studied creamspars and sparry iron ore samples from Rudabánya are in the range of the iron ore mineralizations of the Gemicum, and concentrate mainly in the field of stratabound iron ore deposits of the Gemicum (Fig. 4). The similar texture observed by SEM-EDS and similar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the creamspars in the Bódvaszilas-Szin transitional layers and the sparry iron ore suggest that the two types of iron ore were presumably formed by the same process, i.e. metasomatism by a high Fe-bearing solution. It

Table 3
Chemical composition of massive symsedimentary intercalations in the transitional layers (creamspar) determined by EPMA.

Sample	Measured area	Fe (at.%)	Mg (at.%)	Mn (at.%)
T14A/8	I-1	58.01	39.30	2.68
T14A/8	I-2	52.01	45.86	2.12
T14A/8	I-3	56.13	41.16	2.71
T14A/8	I-4	52.66	45.51	1.82
T14A/8	I-5	48.04	49.71	2.25
T14A/8	I-6	64.78	31.83	3.39
T14A/8	I-7	62.75	33.61	3.65
T14A/8	I-8	60.33	37.17	2.50
T14A/8	I-9	54.18	43.80	2.02
T14A/8	I-10	63.04	32.71	4.25
T14A/8	I-11	51.23	47.02	1.74
T14A/8	I-12	54.07	44.17	1.76
T14A/8	I-13	61.81	34.73	3.46
T14A/8	I-14	64.71	32.06	3.22
T14A/8	I-15	62.48	33.89	3.63
T14A/8	I-16	44.52	53.56	1.93
T14A/8	I-17	61.13	35.04	3.83
T14A/8	I-18	62.57	34.24	3.19
T14A/8	I-19	46.53	51.64	1.82
T14A/8	I-20	49.34	48.84	1.82
T14A/8	I-21	45.28	53.62	1.10
T14A/8	I-22	61.61	35.60	2.79
T14A/8	III-1	69.98	24.98	5.04
T14A/8	III-2	49.88	47.34	2.78
T14A/8	III-3	47.31	50.22	2.47
T14A/8	III-4	60.21	35.92	3.87
T14A/8	III-5	55.38	42.42	2.21
T14A/9	I-1	42.43	55.10	2.47
T14A/9	I-2	35.96	62.85	1.19
T14A/9	I-3	69.67	25.34	4.99
T14A/9	I-4	46.87	50.46	2.67
T14A/9	I-5	69.53	26.37	4.10
T14A/9	I-6	40.33	57.64	2.03
T14A/9	I-7	33.31	65.32	1.37
T14A/9	I-8	55.72	40.68	3.60
T14A/9	I-9	60.22	36.45	3.33
T14A/9	I-10	67.36	27.41	5.23
T14A/9	I-11	37.98	61.56	0.46
T14A/9	I-12	39.36	59.61	1.02
T14A/9	I-13	62.15	33.48	4.37
T14A/9	I-14	46.27	51.78	1.95
T14A/9	I-15	47.43	50.22	2.35
T14A/9	I-16	45.69	52.46	1.85
T14A/9	III-1	21.96	76.00	2.04
T14A/9	III-2	48.28	49.71	2.01
T14A/9	III-3	60.98	35.19	3.83
T14A/9	III-4	50.02	47.62	2.36
T14A/9	III-5	47.81	50.34	1.85
T14A/9	III-6	48.96	48.92	2.13
T14A/9	III-7	59.34	36.89	3.78
T14A/9	III-8	40.98	57.75	1.27
T15/KP1	I-1	20.97	78.05	0.98
T15/KP1	I-2	22.02	76.32	1.65
T15/KP1	I-3	51.12	47.21	1.67
T15/KP1	I-4	38.13	59.87	2.00
T15/KP1	I-5	38.49	59.48	2.04
T15/KP1	I-6	21.92	76.86	1.22
T15/KP1	I-7	52.30	45.80	1.90
T15/KP1	I-8	53.59	44.38	2.04
T15/KP1	I-9	52.41	45.76	1.82
T15/KP1	I-10	38.87	59.42	1.71
T15/KP1	I-11	38.27	59.65	2.08
T15/KP1	I-12	52.72	45.53	1.74

is possible that in these sections some microbial Fe oxidation also occurred, but its extent was negligible.

The examination of the carbonate cement of the samples from the Aggtelek Mts. (non-ore-bearing area) indicates that the Fe addition affected not only the Bódvaszilas Sandstone Formation of Rudabánya but similar formations in the Aggtelek Mts. although with less intensity (the composition of the cement is mainly Fe-bearing dolomite, ankerite

or siderite). Microbial filaments can be observed in the pore-filling carbonate cement and at the margin of the grains in the Bódvaszilas Sandstone samples of the Aggtelek Mts. as well (Fig. 2b). Presumably the microbes were involved in the Fe-oxidation in this area too, but the amount of Fe-bearing fluid flow may have been low, and as a result significant ore mineralization did not form.

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 (Brunsitsyn and Zhukov, 2012; Maslennikov et al., 2012). The remnants of mafic volcanism can be found in the Bódvavölgy Ophiolite Formation (Szentpétery and Less, 2006) (Fig. 5). This assumption fits well with the opinion of Szakáll (2001) that metasomatism is related to the metamorphic fluids of the Middle Triassic (early Alpine) rifting. The solution reacted with the sediments and sedimentary rocks in the early diagenetic stage and depending on the different hosts (sediment and rock) effective microbial Fe-oxidation (enrichment) or metasomatism and subordinate microbial Fe-oxidation occurred. Based on the spatial distribution and the presence of the ore deposit in the succession, ore formation went on during the early diagenesis. The presence of microbial signs at the cleavage plains of the creamspar and the element distribution suggest that the sparite formation occurred due to metasomatism. Consequently, the creamspar of Rudabánya was formed in an early diagenetic sediment by microbial Fe-oxidation and metasomatism in the 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and the thickness (more than 2000 m) of the Lower Triassic–Jurassic overlying formations, the succession was affected by deep burial diagenesis (Bodor, 2014). According to the low illite and chlorite crystallization values, the Bódvaszilas Sandstone Formation might later have suffered anchimetamorphism (Bodor, 2014); this requires further study.

6. Conclusions

A mineralogical, petrographical and geochemical study of the Bódvaszilas Sandstone of the Rudabánya open pit and the Aggtelek Mts. was carried out 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 the Bódvaszilas Sandstone were determined for the first time, and it was found to be an intermediate solid solution between siderite and magnesite (Bodor et al., 2013; Bodor, 2014).

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 a two-cycled microbial Fe(II) mediation process. The creamspar in the higher parts of the formation (transition between the Bódvaszilas Sandstone and Szin Marl) was formed by the same metasomatic processes – the partial or complete Fe replacement of the earlier carbonate layers – that produced the formerly exploited siderite in the Middle Triassic limestones and dolomites.

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

Considering the concavo-convex grain contacts and the syntaxial quartz overgrowths on monocrystalline quartz grains, the formation underwent deep burial diagenesis (Bodor et al., 2013; Bodor, 2014); however, according to the illite and chlorite crystallinity values the Bódvaszilas Sandstone might have undergone not only (deep burial) diagenesis but also anchimetamorphism in both of the areas investigated (Rudabánya and the Aggtelek Mts.) (Bodor, 2014).

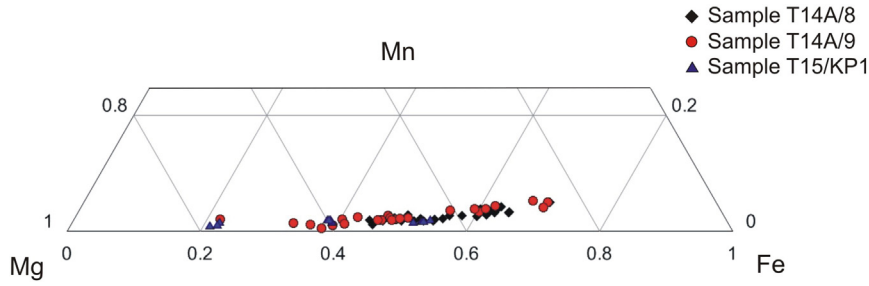


Fig. 3. Composition of creamspars samples on the Fe–Mg–Mn diagram.

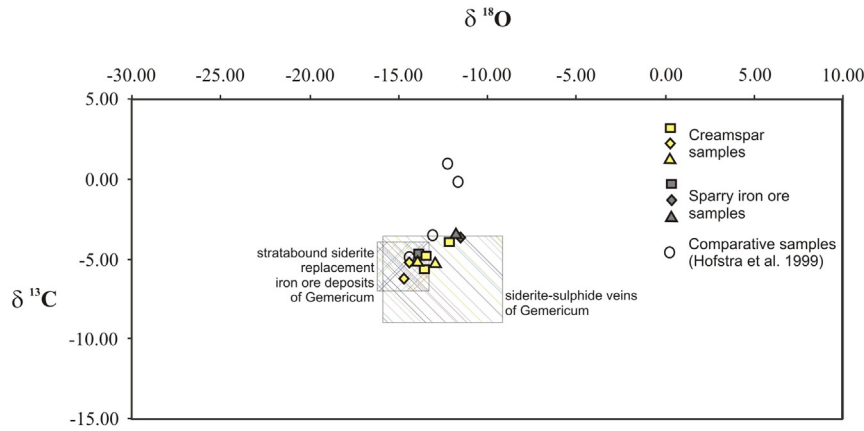


Fig. 4. C and O isotope values of the creamspars and sparry iron ore samples with the comparative sparry iron ore and brecciated dolomite samples of Hofstra et al. (1999) on the $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ diagram.

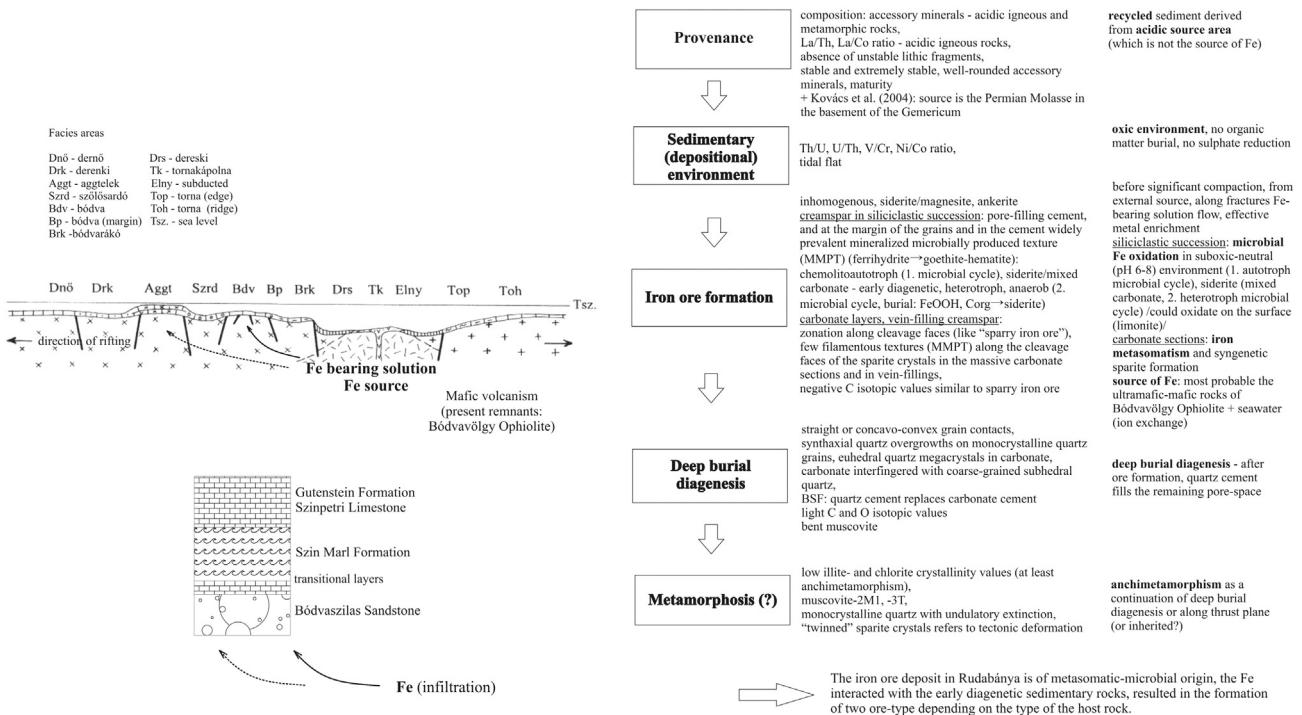


Fig. 5. The evolution of the Lower Triassic Bódvaszilás Sandstone according to Bodor et al. (2013), Bodor (2014) and this study. Geological section after Szentpétery and Less (2006).

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