# EVIDENCE OF BACTERIOGENIC IRON AND MANGANESE OXYHYDROXIDES IN ALBIAN-CENOMANIAN MARINE SEDIMENTS OF THE CARPATHIAN REALM (POLAND)

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Abstract: The Albian and Cenomanian marine sediments of the Silesian and Tatric basins in the Carpathian realm of the Western Tethys contain ferric and ferromanganese oxyhydroxides, visible macroscopically as brown stainings. They coat calcareous bioclasts and mineral clasts, fill pore spaces, or locally form continuous, parallel microlayers, tens of micrometers thick. Light-microscope (LM) and scanning-electron-microscope (SEM) observations show that the coatings contain elongated capsules, approximately 3–5 µm across and enriched in iron and manganese, which may be remnants of the original sheaths of iron-related bacteria (IRB). Moreover, the ferric and ferromanganese staining observed under LM is similar to bacterial structures, resembling the sheaths, filaments and rods formed by present-day bacteria of the *Sphaerotilus–Leptothrix* group. All of the possible bacteria-like structures are well preserved owing to processes of early diagenetic cementation. If the observed structures are fossil IRB, these organisms could have played an important role in iron and manganese accumulation on the sea floor during Albian–Cenomanian time. The most plausible source of metals for bacterial concentration in the Silesian Basin might have been submarine low-temperature hydrothermal vents, as previously was hypothesized for Cenomanian–Turonian deposits on the basis of geochemical indices.

Key words: iron, manganese, iron-related bacteria, Albian-Cenomanian, Silesian Nappe, Tatra Mts., Carpathians.

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## INTRODUCTION

Iron and manganese occur widely in various geological environments. Iron- and manganese-bearing minerals can be formed by inorganic precipitation or as a result of bacterial processes (e.g., Ferris *et al.*, 1988; Ghiorse and Ehrlich, 1992; Konhauser, 1998; Brown *et al.*, 2000; Kendall *et al.*, 2012). Iron oxidation by bacteria may be as much as 60 times faster than in abiotic reactions (Soggard *et al.*, 2000). Ferric oxyhydroxides formed by biological mediation are highly insoluble, with strong potential for preservation in the geological record (Haese, 2000; Croal *et al.*, 2004; Konhauser and Riding, 2012).

Bacteria that can catalyze the oxidation of Fe (II) and Mn (II) in modern environments are called iron-related bacteria (IRB; Noike *et al.*, 1983; Schrenk *et al.*, 1998; Francis and Tebo, 1999; Kirby *et al.*, 1999). These bacteria are able to accumulate the metal ions, either outside their cells or in the surrounding extracellular polymeric matrices. On the

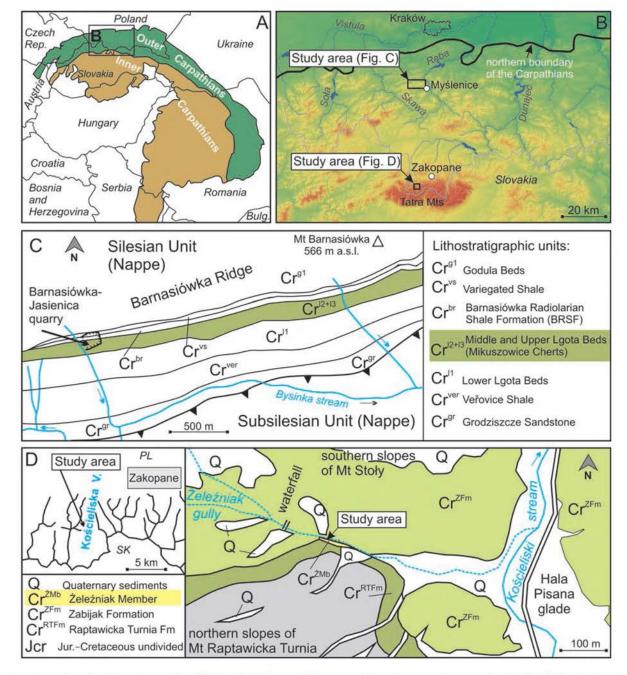
basis of this ability, the IRB can be broadly subdivided into groups, depending on the nature and site of the accumulated iron and manganese (e.g., Konhauser and Riding, 2012).

The fossilization of bacteria is most likely to occur, if they precipitated extracellular inorganic coatings. More resistant to later re-mobilization are metallic bacterial coatings, such as those created by modern IRB. Such encrustations are usually left as the only remnants after the decomposition of bacterial organic matter, providing valuable information on microbial activity in ancient environments.

Studies of IRB began in 19<sup>th</sup> century (summary in Cullimore and McCann, 1978). They were first reported by Ehrenberg (1836), who described *Gallionella ferruginea* from this group of organisms. So far, the earliest fossils, morphologically comparable with modern iron bacteria, are those recognized in the Precambrian cherts of the Gunflint Iron Formation (Schopf *et al.*, 1965; Schelble *et al.*, 2004).

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**Fig. 1.** Location of study areas. **A.** Simplified geological map of the Carpathians (brown and green colors) and their foreland. **B.** Location of study areas in the Western Carpathians on contour map (map after Bryndal, 2014). **C.** Geological map of study area on Barnasiówka Ridge (Wieliczka Foothills, Outer Carpathians; map after Burtan, 1964; Burtan and Szymakowska, 1964, Bąk *et al.*, 2001). **D.** Geological map of study area in Żeleźniak gully (Dolina Kościeliska valley, Tatra Mts., Inner Carpathians; map after Guzik, 1959).

Bacterial iron encrustations have been described in many Phanerozoic successions, especially occurring in conjunction with red sedimentary strata (e.g., Harder, 1919; Schopf and Fairchild, 1973; Karkhanis, 1976; Awramik *et al.*, 1983; Mamet *et al.*, 1997; Préat *et al.*, 1999, 2000, 2006; Boulvain *et al.*, 2001; Yongding *et al.*, 2004; Fortin and Langley, 2005; Mameth and Préat, 2006; Mason, 2008; Barale *et al.*, 2013).

In the present study, the authors report morphological and chemical data showing the presence of microbes, which may be remnants of the iron-related bacteria group in the mid-Cretaceous (Albian-Cenomanian) marine sediments of the Carpathians. They have been recognized in turbiditic beds of the Silesian Nappe (Outer Carpathians) and in a condensed phosphatic limestone of the High-Tatric Unit (Inner Carpathians). The primary goal of this paper is to determine whether the black-brown-orange staining with Fe-Mn oxyhydroxides, which form microscopically visible coatings on microfossils, may be traces of bacterial communities from the time of sediment deposition.

# **GEOLOGICAL SETTING**

# Outer Carpathians - Silesian Nappe

The Silesian Nappe is one of the largest tectono-facies units of the Outer Carpathians (Fig. 1A, B), composed of Upper Jurassic through Miocene deposits, mainly siliciclastic turbidites. These sediments were uprooted from their basement and thrust from the south during the Miocene (Oszczypko, 2004 and references therein). During Cretaceous-Palaeogene time, the sediments of the Silesian Nappe were deposited in an independent sedimentary realm, the Silesian Basin, which was a part of the Western Tethys domain, located near the southern margin of the European Platform (e.g., Książkiewicz, 1956, 1962, 1977; Golonka et al., 2002). Since the Berriasian through the Eocene, deposition in the Silesian Basin took place below the calcium compensation depth (CCD; Książkiewicz, 1975; Słomka et. al., 2006).

The sedimentary sequence studied here represents deep-water facies, composed of mm- to cm-thick siliciclastic to calcareous, partly silicified, fine-grained turbidites, which represent predominantly the T<sub>bde</sub> intervals of the Bouma sequence, intercalated with hemipelagic, non-calcareous claystones (Bak K. et al., 2001; Bak M. et al., 2005, 2011). The turbidites include quartz grains with variable amounts of carbonates, but the most distinguishing feature of these deposits is the high content of biogenic particles, including the spicules of siliceous sponges. Other numerous biogenic components are planktonic and calcareous benthic foraminifers, radiolarians, fragmented echinoid ossicles,

and inoceramid prisms (Bąk M. et al., 2011). The source for the redeposited mineral and biogenic material was the shelves rimming the northern edge of the Silesian Basin, corresponding to the margin of the Western Tethys. Non-calcareous claystones, which are interbedded with turbidites, represent deep-water sediments, deposited below the CCD (Bąk M. et al., 2005, 2011).

The turbidites are classified into three lithostratigraphic units (Fig. 2): the Middle Lgota Beds (Aptian – Middle Cenomanian), the Upper Lgota Beds (Mikuszowice Cherts; Middle–Upper Cenomanian) and the Barnasiówka Radiolarian Shale Formation (Upper Cenomanian – Lower Turonian). Their stratigraphy is based on microfossils (foraminifers, radiolarians), with the biostratigraphic subdivision correlated in part with the carbon isotopic curve (Bak K. et al., 2001; Bak M. et al., 2005; Bak K., 2007a, c; Bak M., 2011).

#### Inner Carpathians - High-Tatric Units

The High-Tatric units occurring in the Tatra Mts., belong to the Tatricum, a part of the Inner Carpathians (Central Western Carpathians; Plašienka, 2003). They consist of a para-autochthonous unit, which is a slightly displaced sedimentary cover of the crystalline core, and the allochthonous units, involved in several recumbent faults (e.g., Rabowski, 1959; Kotański, 1961; Książkiewicz, 1977; Jurewicz, 2005, 2012). These units comprise the sedimentary succession (mainly calcareous deposits) of the Lower Triassic through mid-Cretaceous (e.g., Lefeld, 1968).

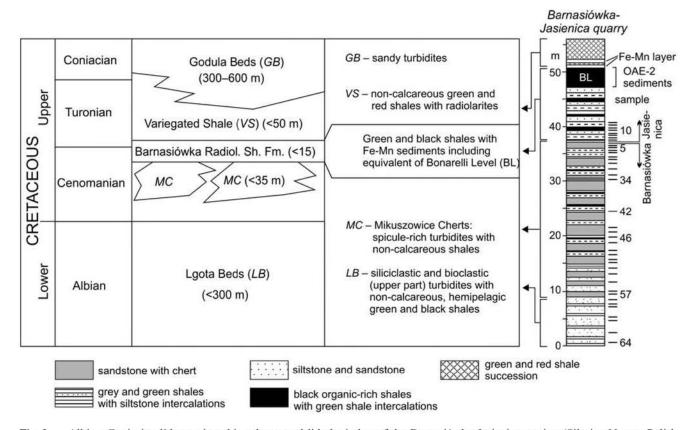


Fig. 2. Albian–Coniacian lithostratigraphic scheme and lithologic log of the Barnasiówka-Jasienica section (Silesian Nappe, Polish Outer Carpathians; Koszarski and Ślączka, 1973; supplemented by Bąk *et al.*, 2001).

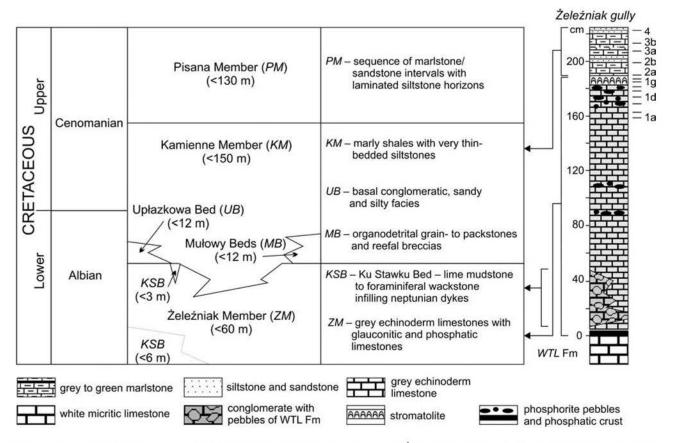


Fig. 3. Albian-Cenomanian lithostratigraphic scheme and lithologic log of the Żeleźniak section (Tatra Mts, Inner Carpathians; after Krajewski, 2003). WTL Fm – Wielka Turnia Limestone Formation

During Mesozoic times, the Tatra area was situated in the Western Tethys domain (e.g., Golonka *et al.*, 2000; Jurewicz, 2005), in proximity to the European plate (Grabowski, 1997). It was separated from the European Platform by the Pieniny (Vahic) Ocean, the Outer Carpathian basins and the shelf basins (Plašienka, 1999). An open marine depositional environment with pelagic and hemipelagic sedimentation characterized this area in the mid-Cretaceous.

The Albian-Cenomanian sediments have been classified as the Zabijak Formation in the Polish part of the Tatra Mts. (Krajewski, 2003). These deposits were disposed on the Valanginian-Albian platform carbonate rocks or contact tectonically with other sedimentary units (Passendorfer, 1930; Kotański, 1959; Lefeld, 1968; Masse and Uchman, 1997). The formation is clearly tripartite. Its base is represented by glauconitic limestone (Wielka Równień Bed) with an abundant invertebrate fauna and phosphate concretions (Passendorfer, 1930), locally with exotic crystalline pebbles (Passendorfer, 1930; Marcinowski and Wiedman, 1985, 1990) and lenses of gravelstone (Rabowski, 1959). They are overlain at places by a condensed phosphatic limestone embracing numerous hardgrounds, stromatolites, oncoids and pisolitic structures (Niegodzisz, 1965; Krajewski, 1981a-c). In the synsedimentary tectonic depression at Kominiarski Wierch, the limestone succession (Żeleźniak Member, Ku Stawku Beds; Krajewski, 2003) attains 60 m in thickness. The middle part of the Zabijak Formation is represented by pelagic marls, intercalated with hemipelagites (marly shales) and very thin-bedded turbiditic siltstones (up to 130 m thick; Kamienne Member; Krajewski, 2003). This succession passes upward into a succession (Pisana Member; Krajewski, 2003) consisting of thin, hemipelagic, marly shales and numerous thin- to medium-bedded turbidites, composed of the silty and sandy fractions (up to 120 m thick; Passendorfer, 1930; Rabowski, 1959; Kotański, 1961; Bac-Moszaszwili *et al.*, 1979; Uchman, 1997). These sediments (Kamienne and Pisana members) represent the Upper Albian through the Upper Cenomanian (Bak K. and Bak M., 2013).

## MATERIAL AND METHODS

This paper is based on data from fifty-two samples collected from two sections. The first of these sections is located in the central part of the Silesian Nappe (Outer Carpathians), 30 km south of Kraków, near the town of Myślenice, where the Albian–Turonian sediments, 75 m thick, crop out in the Barnasiówka-Jasienica Quarry (N 49°49'56.8921" and E 19°52'2.319") in the Barnasiówka Ridge, Wieliczka Foothills (Fig. 1B, C). The section comprises the uppermost part of the Middle Lgota Beds (MLB; about 20 m thick), the Mikuszowice Cherts (MC; 32 m thick), the Barnasiówka Radiolarian Shale Formation (BRSF; 14 m thick), and the noncalcareous Variegated Shale (about 10 m thick; Fig. 2). Ferruginous and manganese coatings are frequent in the entire Cenomanian part of the section.

The second section is located in the Polish part of the Tatra Mts. (Inner Carpathians), where the Albian-Cenoma-

nian sediments crop out in the Żeleźniak gully, a left tributary of the Kościeliska Valley, about 100 m below 3-m-high waterfall (N 49°14'37.0915" and E 19°51'24.3577"; Fig. 1B, D). The section comprises the uppermost part of the Żeleźniak Member (about 1.7 m thick) and the lowermost part of the Kamienne Member (about 0.3 m thick). Ferruginous coatings are frequent in the Upper Albian part of the section, at the top of the Żeleźniak Member.

The Fe-Mn coatings were analysed in thin sections from 39 samples, collected in the Silesian Nappe of the Outer Carpathians, and from 13 samples collected in the Tatra Mts. (Fig. 3). Photomicrographs of microfacies were taken, using a HITACHI S-4700 scanning electron microscope (Sample Bar-5, Bar-42, Z-1g), and a stereoscopic microscope Nikon SMZ1500 with digital camera (all the samples investigated). Chemical analyses of the mineral constituents of the ferruginous and manganese coatings were carried out using a JEOL T-300 SEM, equipped with an 860-500 energy-dispersive spectrometer (EDS), under conditions of 20–25 kV accelerating voltage, 1 em spot size of a beam focused on carbon-coated thin section, and counts acquired for 150 s. The data were corrected using the ZAF/PB software.

#### RESULTS

In the sediments of the Silesian Unit, iron and manganese occur as ferric and ferromanganese oxyhydroxides. They are visible macroscopically as brown, ferruginous staining, parallel to lamination. The detailed structure of brown, ferruginous coloration is visible only in microscopic studies of thin sections. The brown staining is present in different forms: (1) as coatings of microfossils and detrital grains, (2) as fillings of the primary pore spaces between grains, and (3) as micro-laminae, which are several micrometres thick. Fe-Mn coatings are present in turbidite layers in the Mikuszowice Cherts and Middle Lgota Beds, in four types of microfacies as: sublitharenite with microfossils, sublitharenite with sponge spicules, spiculitic sublitharenite, and biomicrite with foraminifers, radiolarians and sponge spicules (for a detailed description of the microfacies - see M. Bak, 2011; M. Bak et al. 2005, 2011).

In the Tatric sediments, only ferric oxyhydroxides are present. They are visible macroscopically as brown stainings in a phosphorite pebble lag with phosphatic stromatolites, which cover a composite hardground. The detailed microscopic examination of thin sections showed that ferruginous material with its characteristic coloration forms continuous, parallel microlayers, several micrometres thick, within stromatolites, infill rudimentary pore spaces in the sediment or replaces echinoderm plates.

## Fe-Mn coatings and infillings

Silesian Nappe sediments. Fe and Fe-Mn coatings have been observed on each type of calcareous and siliceous bioclasts. Foraminiferal tests at different stages in the development of replacement and/or coating structures (Figs 4A, B, G, H, 5A-C) are present in all microfacies types. The

Fe-Mn coatings also occur on calcified sponge spicules, the surfaces of which were covered by microlaminated brown encrustations (Fig. 4D, E). Similar encrustations were observed inside calcified spicules still possessing void remnants of the inner canal (Fig. 4B). Ferruginous coatings and infillings are present on radiolarian tests (Fig. 4G) and inside echinoderm ossicles, which were originally micro-porous (Fig. 4F). The brown pigment highlights their porous structure. It was also noted in the inter-granular pore space (Fig. 4B) that was filled by blocky or isopachous bladed calcite cement (Fig. 4B, G, H). The calcareous skeletons are partly or completely replaced by Fe and Fe-Mn oxyhydroxides (see Figs 4, 5). Coatings are accompanied by single microcrystals or aggregates of opaque minerals (Figs 4C, 5A-C). Some of the grains, especially calcified siliceous spicules of sponges are covered with thin coatings, sometimes with cracks (Fig. 7A, B).

The surfaces of clasts in very fine-grained, pelagic material are covered by Fe-Mn micro-laminated encrustations, tens of micrometres thick. They are associated with thin layers of organic matter (Fig. 4G, H). Such mats surround detrital grains and microfossils and fill skeletal grains (Fig. 4G, H).

Tatra Mts. sediments. Iron covers, coatings and fillings are present in sediments of the Żeleźniak Member, where fragmented echinoderm skeletons, including common holothurid plates (Fig. 6B) are covered with or replaced by Fe oxyhydroxides. Ferric coatings are accompanied isolated Fe-bearing microcrystals or aggregates of them (Fig. 6D). They usually form separate layers inside stromatolitic structures (Fig. 6A–D). These crystals are up to 5 μm in size. They are densely packed in aggregates that usually are less than 30 μm across (Fig. 6D).

#### Ultrastructure of brown staining

The examination of thin sections of microfacies from the Middle Lgota Beds at  $\times 1,000$  magnifications shows that the brown staining as grain coatings (Fig. 7A, B) consists of densely packed, elongated capsules, approximately 5  $\mu$ m across (Figs 7I, 8A, B). The walls of the individual capsules are 0.1  $\mu$ m thick. EDS analyses showed that the capsules are strongly enriched in iron and manganese (Fig. 8C, D). Other ultrastructures of brown staining, found in samples from the Middle Lgota Beds show a doughnut-like shape, 5–10  $\mu$ m in diameter. They form brown rims on the surfaces of biotite flakes (Fig. 7G).

Further Fe or Fe-Mn staining and coatings, observed in the Mikuszowice Cherts are fluffy, brown to black, disk-like stains of pigment, about 3–10 µm across (Figs 5A–C, 7C–E, H). In turn, the mentioned Tatric sediments contain rounded and dark Fe staining, arranged in the form of isolated clusters (Fig. 6C, D).

#### Grains with punctured surface

The surfaces of numerous calcareous grains, found in the Mikuszowice Cherts and the Tatric sediments bear traces of oval-shaped micro-depressions (Fig. 9A–D). These structures are wide and shallow, or small and deep, averag-

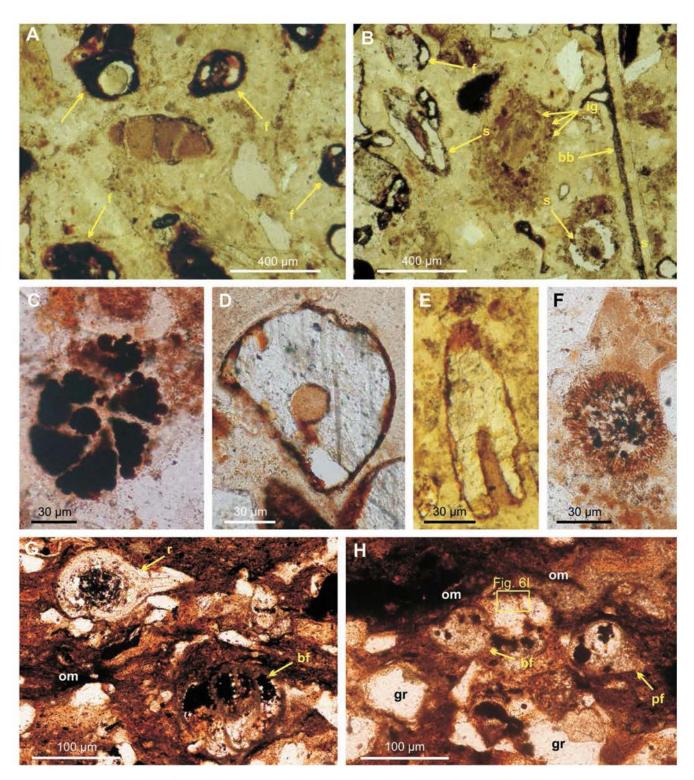


Fig. 4. Photomicrographs (plane polarized light) of ferric and ferromanganese oxyhydroxies staining, present in sublitharenite and biomicrites of Cenomanian turbidites from Silesian Nappe, Polish Outer Carpathians. A. Tests of benthic calcareous foraminifers (f), partly or completely replaced by ferruginous coatings within silicified biomicrite. B. Thin layer of bacterial biofilm-like structure (bb) inside and outside the canal of sponge spicules (s) and foraminiferal tests (f), and in inter-granular pore space (ig). C. Fe-Mn mineralization inside benthic foraminiferal test. Closely packed crystals tightly fill the interior of the chambers. D, E. Carbonate grain surface (calcified sponge spicule) showing Fe-Mn bacteria-like coatings. F. Cross-section of micro-porous echinoderm ossicles filled with ferruginous coatings. G, H. Parallel-laminated brown mat binds radiolarian skeletons (r), benthic (bf) and planktonic (pf) foraminiferal tests and detrital grains (gr) surrounded by some opaque flocks, most probably organic matter (om). A, B, D-F – sample Bar-42; C – sample Bar-57, G, H – sample Bar-64.

ing a few microns across. They usually include brown thin coatings inside the cavities.

## DISCUSSION

#### Bacterial nature of the Fe-Mn coatings

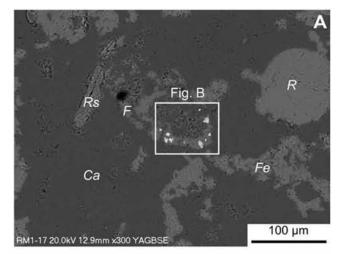
In general, the morphology itself is not considered as a conclusive indicator of the bacterial origin of ultrastructures. However, some unique shapes, e.g. the sheath-like ultrastructures and filaments, are usually considered to be of microbial origin, and in rare cases could be ascribed to particular groups of microorganisms (e.g., Van Veen *et al.*, 1978; Mulder and Deinema, 1992).

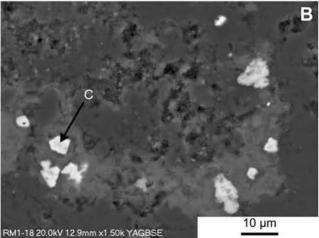
Densely packed, elongated capsules, approximately five micrometres in cross-section (Fig. 7I), are here interpreted as fossilized iron-related bacteria (IRB). SEM observations revealed bacteria-size capsules with hollow cores and oval outer shapes (Fig. 8). Very thin walls (0.1 µm thick) of the individual capsules (Fig. 8A, B) may be remnants of the metal bacterial sheath, occurring outside the cell membrane. The EDS analyses showed that the capsules are strongly enriched in iron and manganese (Fig. 8). This is why they resemble most probably fossilized bacteria of the *Leptothrix* group, because unlike other sheathed bacteria, they are able to oxidize both iron and manganese (Nelson *et al.*, 1999).

Another sign of a possible bacterial origin are doughnut-shaped forms, 5–10 µm across. They occur as brown, doughnut-like rims on the surfaces of biotite flakes (Fig. 7E, F). These structures resemble colonies of IRB from the *Siderocapsa* group, on the basis of the similarities in shape and dimensions with respect to modern *Siderocapsa* colonies, which form collar slime, impregnated with iron oxyhydroxies (e.g., Hardman and Henrici, 1939, fig. 1; Dubinina and Zhdanow, 1975, figs 8–11; Hanert, 2006).

Fe or Fe-Mn fluffy, brown to black, disk-like stains of pigment, about 3-10 µm across (see enlargements on Fig. 7C, E), are also possible evidence of bacterial origin. These structures in shape resemble assembled holdfasts of the Sphaerotilus-Leptothrix group, recovered from modern environments (Spring, 2006). The similarities are based on chemical composition, because these black to brown flecks contain Fe (Fig. 8). Moreover, there is a similarity to the morphological features of flecks and fluffy structures by comparison with laboratory isolated pure IRB from Sphaerotilus-Leptothrix cultures (Van Veen et al., 1978, figs 14, 18). The shape, dimensions and organization of these structures (Fig. 7C-E, H) resemble those in colonies of presentday species, such as Leptothrix lopholea, L. cholodnii and Sphaerotilus natans (figs 6a, 7b, c in Spring, 2006, after Rouf and Stokes, 1964, and Mulder and Deinema, 1992). In these bacterial colonies, holdfasts are rounded, impregnated with Fe and Fe-Mn oxides, and surrounded by thin, filamentous branching.

Another sign of possible bacterial activity in the sediments studied are oval-shaped micro-depressions of bacterial size, which puncture the surfaces of calcareous grains and bioclasts. Such structures can be interpreted as the pitting corrosion, left after bacterial activity. Bacterial punc-





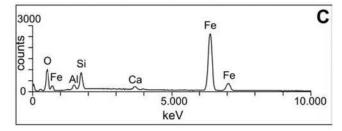
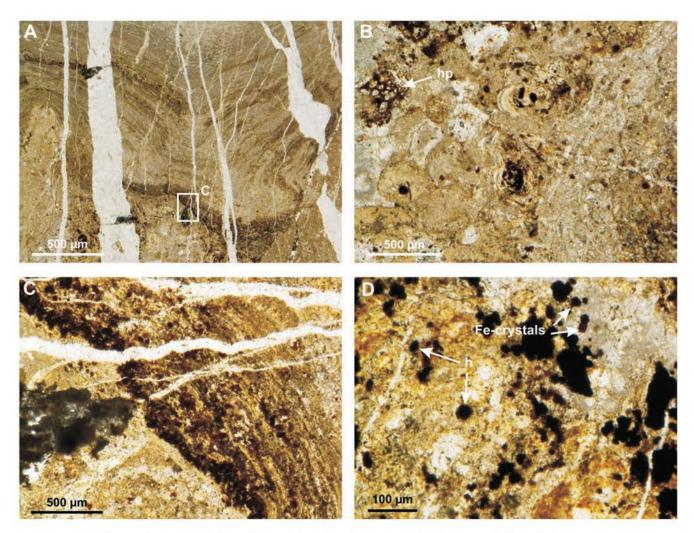


Fig. 5. A–C. SEM BSE images and EDS analysis of biomicrite in Cenomanian turbidites from Silesian Nappe, Polish Outer Carpathians. A. Foraminiferal (F) test wall replaced by iron. Destruction of the wall started both from outside and inside of the test. (Ca) indicates the area of high content of calcium carbonate. (Fe) indicates the area of elevated iron content in places where brown pigment occurs. (R) – Radiolaria, (Rs) – radiolarian spicule. B. Close-up of benthic calcareous foraminiferal test, partly replaced by remnants after bacteria-like filaments and holdfasts. Iron oxide crystals could arise as a result of recrystallization of bacterially precipitated iron oxyhydroxides. C. EDS spectrum of the iron oxide crystal (C) analysis in the spot marked on Figure B. A–D – sample Bar-5.

turing is commonly known from different, modern, aquatic environments (e.g., Thorseth, et al., 1995, figs 1–7, 11; Ullman et al., 1996, fig. 1; Lüttge and Conrad, 2004, figs 3–6; Brehm et al., 2005, figs 1–3; Davis et al., 2007, figs 1–14).

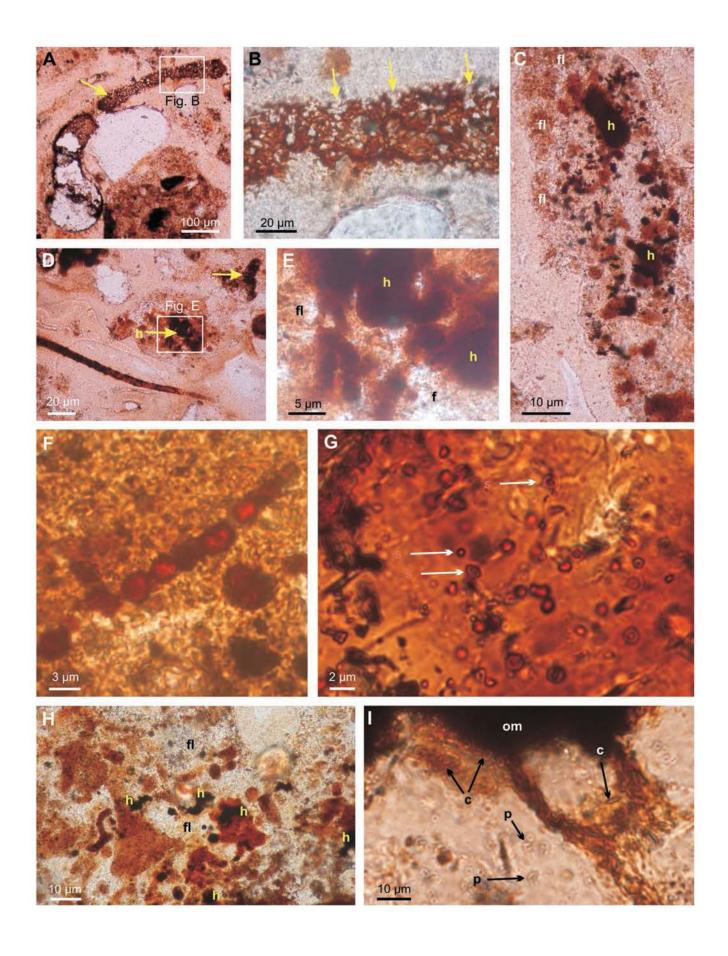


**Fig. 6.** Photomicrographs (plane polarized light) of Fe-bearing micro-laminas forming seams in Late Albian stromatolite structures from Tatra Mountains. **A.** Parallel-laminated stromatolite developed on a rugged substrate. **B.** Photomicrograph of stromatolite and the surrounding marl with bioclasts. One of them is holothurid plate (hp), replaced by Fe oxyhydroxides. **C.** Close-up of Figure A showing details of lamination in stromatolite. Dark layer consists of densely packed Fe-bearing crystals. **D.** Close-up of dark seam with Fe-bearing crystals (Fe-crystals). They grew in brown pigment, resembling remnants after bacterial holdfasts (h). A–D – sample Z-1g.

Fe and Fe-Mn oxyhydroxides, visible as coatings on benthic foraminiferal tests, are present at various stages of advancement of this process. An initial stage is represented by microboring fronts that show irregular Fe-Mn infilling zones, extending from the external surfaces of the test walls inward (Fig. 4A–B). An advanced stage is represented by tests completely replaced and fringed by dense layers of brown to black coatings, which make the remnants of the walls much thicker than the originals (Fig. 4A).

Some clasts and bioclasts in very fine-grained pelagic material, associated with thin layers of organic matter, are covered by Fe and Fe-Mn micro-laminated encrustations.

Fig. 7. Photomicrographs (plane polarized light) of ferric and ferromanganese oxyhydroxies staining resembling bacteria-like ultra-structures in Cenomanian turbidites from Silesian Nappe, Polish Outer Carpathians. A. Inner canal of sponge spicule (arrow) filled by biofilm-like structure. B. Close-up of Fig. A showing cracks in biofilm-like structure (arrows). C. Brown amorphous iron oxide/oxyhydroxide forming fluffy, disk-like stains of pigment, 3–10 μm across, resembling bacterial holdfasts (h). They are surrounded by or attached to area resembling bacteria-like filaments (fl). D. Disk-like stains of pigment, resembling bacterial holdfasts (h). Mutual arrangements of grains and cement in relation to stains of pigment. E. Details of disk-like stains of pigment resembling bacteria-like holdfasts (h) surrounded by flocculent area (fl) resembling conglomeration of bacterial filament (f). F. Fe-Mn-bearing minerals arranged in chain as long and wide as bacteria-like filament. G. Brown circular staining on biotite surface are of doughnut-like shapes (s), resembling bacterial colony from *Siderocapsa* group. H. Disk-like stains of pigment, resembling bacteria-like holdfasts (h) and bacteria-like filaments (fl). These structures are spread in the intergranular pore space, filled by subsequent blocky calcite cement. I. Coating surrounding foraminiferal test with numerous elliptical forms, resembling bacteria-size capsules (c). Pitting (p) on the calcite crystals developed in empty space inside chamber of a foraminiferal test. Organic matter (om). A–E – sample Bar-57, F – sample Bar-57, G, I – sample Bar-64, H – sample Bar-42.



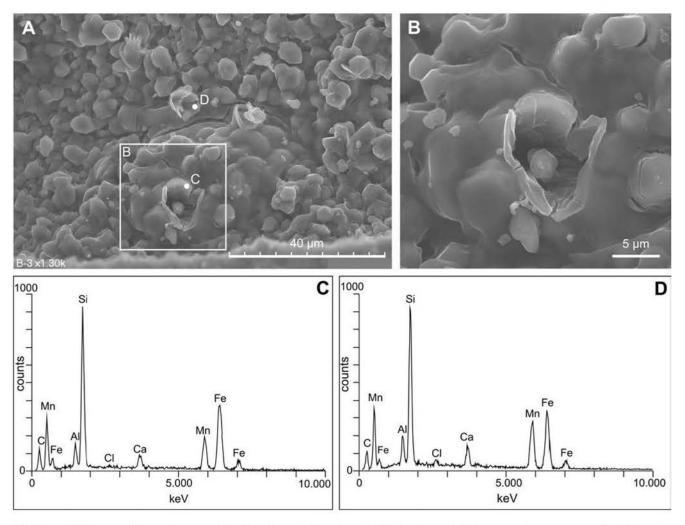


Fig. 8. SEM images of forms interpreted herein as bacterial capsules. A, B. Capsules stuck in intergranular pore space of sublitharenite layer in sample Bar-42 in Cenomanian turbidites from Silesian Nappe, Polish Outer Carpathians. C, D. Results of the EDS analyses of the capsule walls.

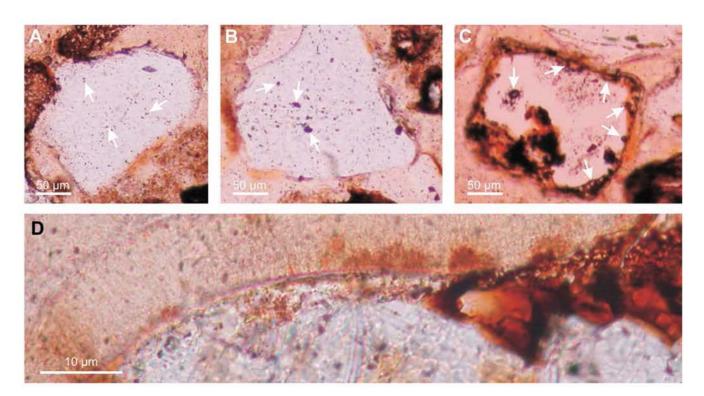
Such encrustations are tens of micrometres thick, forming a padding inside the chambers of microfossil tests and also the inner canals of sponge spicules (Fig. 4C). Such a cover might represent fossilized biofilms, left after bacterial activity and metal precipitates (Fig. 5A–C). Locally, such biofilm-like structure possesses a network of cracks (Fig. 7A, B).

## Conditions of growth of iron-related bacteria

#### Living conditions of modern iron-related bacteria

Modern species of IRB can live and precipitate iron and/or manganese oxyhydroxides under specific conditions. On the basis of the constraints on the growth of modern IRB, it is possible to interpret the conditions that dominated in the bottom environments of the Silesian Basin and the Tatric Basin during sedimentation of the sediments studied. Modern *Leptothrix* species are widely distributed in aquatic environments, characterized by a pH range of 6.5–7.5, a low oxygen gradient, temperatures between 10–35°C, and a supply of iron and manganese ions (Alt, 1988; Emerson and Moyer, 2002; Spring, 2002). Such habitats may occur

worldwide today, both on land and in marine environments. The most typical are natural iron seeps in freshwater wetland areas, forest ponds and iron springs (Ghiorse and Ehrlich, 1992). In freshwater and brackish environments, there is evidence of a relationship between IRB and the formation of ferromanganese nodules (Huckriede and Meischner, 1996; Trokowicz, 1998; Stein et al., 2001). However, the most probable analogue for IRB occurrences in the Silesian and Tatric basins can be found in oceanic settings. In such environments, the IRB are known to be associated with volcanic springs (Hanert, 2002) or hydrothermal venting areas (Dymond et al., 1989; Sibuet and Olu, 1998; Sun et al., 2011), where they form abundant communities composed of numerous taxa (e.g., Van Dover, 2002). Biological data published so far present approximately 55 deep-water and 62 shallow-water hydrothermal vent ecosystems in modern oceans (Tarasov et al., 2005; Dando, 2010). Discoveries of Leptothrix ochracea have been reported from the Loihi shield volcano, located on the Hawaiian archipelago (Emerson and Moyer, 2002), and also in the vicinity of thermal vents on the Juan de Fuca Ridge in the NE Pacific



**Fig. 9.** Photomicrographs (plane polarized light) of ferric and ferromanganese oxyhydroxies staining resembling bacteria-pitted corrosion on carbonate grains in Cenomanian turbidites from Silesian Nappe, Polish Outer Carpathians. **A–C.** Examples of corrosion pits (arrows) on grain surface. Traces of corrosion visible as micrometer-size pit cavities (arrows). Pits are covered with membrane of ferrous coatings. **D.** Close-up view of surface of calcified sponge spicule with pitted corrosion. A–D – sample Bar-5.

Ocean (Kennedy et al., 2003). In each case, the *Leptothrix* species can live in the vicinity of low-temperature hydrothermal vents.

## Bacteria-like structures in relation to sea-floor conditions

The relationship of the possible bacteria-bearing coatings to mineral grains and cement in the microfacies studied indicates that the encrustations grew in soft, unconsolidated sediment. This can be demonstrated by the exclusive occurrence of the remnants of bacteria-like structures in the original pore spaces or on the surfaces of terrigenous and biogenic clasts. The subsequent carbonate and silica cementation enveloped the Fe-Mn staining of possible bacterial origin and filled up the pore spaces. All these delicate structures were preserved, owing to rapid cementation. Calcite cement occurs in the two areas studied, while silica is characteristic mainly for the Middle Lgota Beds and Mikuszowice Cherts of the Silesian Nappe.

Most modern IRB require slowly running waters for effective growth (Spring, 2002). The bottom environments of the Silesian and Tatric basins could have created such habitats for bacteria during the Albian and Cenomanian. The succession studied of the Silesian Nappe comprises sediments, deposited by low-density turbidity currents with long-lasting periods of non-deposition, evidenced by the low accumulation rate, not exceeding 7 mm/kyr and numerous hiatuses (Bąk K., 2007b; Bąk M., 2011). Consequently, these sediments could have included both the intact bacteria-like mats, growing under calm depositional conditions, and Fe-Mn layers encompassing chaotically redistributed

and disintegrated bioclasts, related to episodes with diluted turbidity flows.

In the Tatric Basin, layers containing small Fe-bearing crystals also grew under conditions of very low sedimentation rates (Krajewski, 1981b). These crystals, which were probably formed on IRB remnants, are present in phosphatic-siliceous-ferric or ferric-siliceous laminae inside stromatolites. The origin of these laminas previously was interpreted as an effect of early cementation and replacement processes, which took place in the primary calcareous material of stromatolites (Krajewski, 1981b). It is possible that the IRB used the iron precipitated in these processes for the construction of their sheaths.

## Source of ferrous and manganese ions for IRB activity

According to Bennet et al. (2008), modern submarine vents could provide even 12–22% of the global deep-ocean dissolved Fe. An example of organic interaction with hydrothermal Fe came from a study of the oxidation rates of dissolved Fe(II) in hydrothermal plumes over the Central Indian Ridge (Statham et al., 2005). The IRB are typical microorganisms which could live in areas of active hydrothermal venting provide solutions containing Fe ions. They include mainly the Sphaerotilus–Leptothrix group, encrusted with ferric hydroxide (Sphaerotilus) or ferromanganese oxides (Leptothrix) (Mulder and Van Veen, 1963; Spring, 2002). In such environments, the IRB build tubular sheaths, precipitated outside the singular cells, or/and arrange cells in long filaments shielded by metallic cover.

The specific bacteria-like ultrastructures, such as sheaths, filaments and rods from the sediments studied, which resemble the morphotypes of present-day *Leptothrix* living around low-temperature hydrothermal vents, may indicate the occurrence of such vents on the deep sea floor of the Silesian and Tatric basins during the Albian and Cenomanian. The occurrence of hydrothermal vents during Late Cenomanian–Early Turonian times, as the source for manganese, iron and other metals has been suggested for the Outer Carpathian basins. Previously assigned geochemical indices (Bąk K., 2006, 2007a–c) for an association of Fe, Mn and micro-elements in two ferromanganese layers indicate that they might have been derived from hydrothermal fluids.

The origin of ferric oxyhydroxides in Late Albian stromatolites of the Tatric Basin is not the subject of detailed interpretation because of the lack of geochemical data from these sediments.

## CONCLUSIONS

The Cenomanian marine sediments of the Outer and Inner Carpathians contain Fe- and Fe-Mn oxyhydroxides that are visible macroscopically as brown staining. The SEM observations show that most of them consist of densely packed, elongated capsules, approximately 5 µm across, interpreted as fossilized iron-related bacteria (IRB). The walls of the individual capsules, 0.1 µm thick, may be remnants of the original metallic bacterial sheath occurring outside the cell membrane. The capsules show elevated iron and manganese content; that is why they resemble most probably fossilized bacteria from the *Sphaerotilus–Leptothrix* group.

The Fe-Mn coatings, left after possible the IRB activity were formed on calcareous clasts and bioclasts. They also fill the pore spaces between mineral clasts and bioclasts and locally form continuous micro-laminations. All bacterialike structures were well preserved, owing to rapid cementation by calcite and silica.

The relationship between the bacteria-bearing coatings, the mineral grains, and the cement suggests that the possible IRB grew in a surficial layer of soft sediments.

The bacteria-like structures described here possess forms very similar to that of present-day bacterial sheaths, filaments and rods from the Sphaerotilus-Leptothrix group. This similarity leads the authors to further interpretation of the possible environmental conditions prevailing at the bottom, if bacteria from this group could exist there and formed the incrustations. Because present-day bacteria from the Leptothrix group can live around low-temperature hydrothermal vents, the authors suggest possible similar conditions on the deep-sea floor of the Silesian and Tatric basins. This may further indicate that bacteria could have played an important role in iron and manganese accumulation in the basins. The occurrence of hydrothermal vents during Cenomanian-Turonian times was suggested previously, using geochemical indices for the sediments in the Outer Carpathian basins.

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