

Genesis of ferromanganese crusts in Jurassic pelagic limestones at Stankowa Skała, Pieniny Klippen Belt, Poland: sedimentological and petrological approach

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ABSTRACT: The ferromanganese crusts (FMC) and nodules at Stankowa Skała near Nowy Targ (Pieniny Klippen Belt, Poland) are developed in pelagic condensed limestones. The crusts appear on an uneven surface of limestones with thin-shelled *Bositra* bivalves dated to the (?)uppermost Bajocian -Callovian. The crusts are overlain by Oxfordian limestones rich in *Globuligerina*, containing Fe-Mn nodules and small fragments of calcite stromatolites rich in Mn, Fe, Ba oxyhydroxides. Petrological analyses of the FMC from Stankowa Skała indicate their hydrogenetic origin. Growth of the FMC was coeval with a period of a rapid oceanic floor spreading from the Bajocian to the Callovian, postulated for the Pieniny Klippen Belt in the Jurassic time on the basis of the palaeomagnetic studies.

INTRODUCTION

Ferromanganese crusts (FMC) and nodules are known from the Jurassic limestones of the Pieniny Klippen Belt (Western Carpathians) as well as of the Tatra Mts., Alps, Bethic Cordillera and Sicily (e.g. Jenkyns 1970; Corbin *et al.* 2000; Rojković *et al.* 2003; Gradziński *et al.* 2004; Mišik and Aubrecht 2004).

The FMC and nodules at Stankowa Skała near Nowy Targ, first described by Zydorowicz and Wierzbowski (1986), are developed in pelagic condensed limestones that belong to the Czorsztyn Limestone Formation (Birkenmajer 1977). The crusts appear on an uneven surface of limestones containing thin-shelled *Bositra* bivalves. The age of the rocks studied is estimated to be (?)uppermost Bajocian to Callovian (Jaworska 2000; Sidorczyk 2005). The FMC are overlain by the Oxfordian

limestones with *Globuligerina*, containing Fe-Mn nodules and small fragments of FMC rich in Mn, Fe, and Ba oxyhydroxides.

Manganese deposits are known from the oceanic floor, and were described for the first time due to the HMS Challenger cruise (1873-76). Since then manganese deposits have been the subject of numerous investigations. Information on the distribution and petrologic features of FMC has been reported by numerous authors (e.g. Bolton *et al.* 1988; Usui and Glasby 1998; Hein *et al.* 2000). Present-day ferromanganese crusts are known to be distributed widely across the world ocean bottom, usually on seamounts and plateaus, where the deposition rate is very low. The thickness of the present-day FMC varies from a few millimeters to 25 cm, and occurrences have been reported from depths of 400-4000 m. The textures of recent FMC are usually botryoidal, but other textural varieties

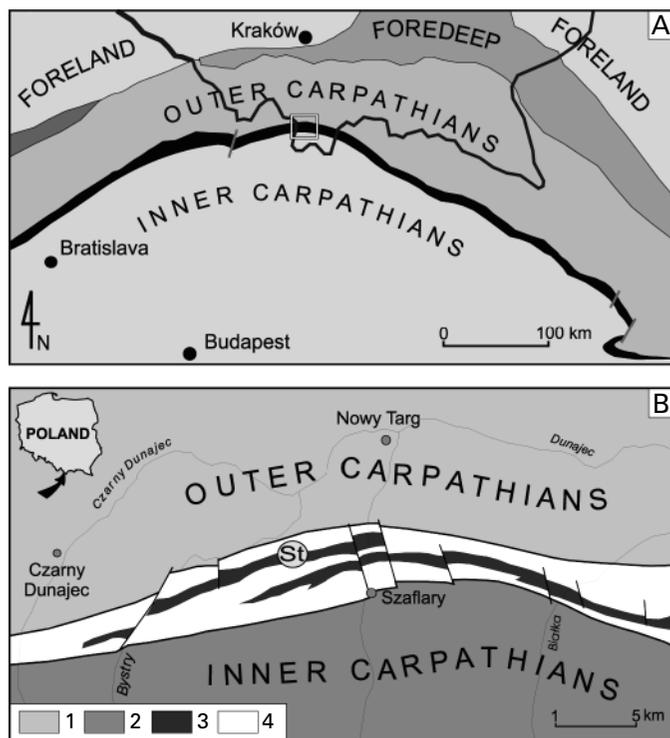


Fig. 1. A – Position of the Pieniny Klippen Belt (black strip) within the Carpathians; B – location of the Stankowa Skala (St) in the Pieniny Klippen Belt (base map after Birkenmajer 1963, 1977, simplified). 1 – Magura Paleogene flysch (Magura Nappe); 2 – Podhale Paleogene flysch (autochthonous); Pieniny Klippen Belt successions: 3 – Czorsztyn Succession; 4 – others successions.

including massive, layered, and columnar (=stromatolitic) have also been described. The mineralogy of FMC is dominated by extremely fine-grained hydroxides or oxyhydroxides (e.g. vernadite, birnessite, todorokite), and such a mineralogical composition caused intensive scavenging of trace elements (Co, Cu, Zn, Pb, Ta, Sr, P, REE, and PGE) from seawater. Sometimes these processes may even concentrate such high amounts of these elements so that their concentrations are of economic interest.

The genesis of recent FMC crusts has been discussed within hydrothermal, hydrogenetic, and diagenetic models (e.g. Bolton *et al.* 1988; Hein *et al.* 1994; Jung and Lee 1999; Hein *et al.* 2000). According to these models, the growth of FMC is a consequence of the high supply of manganese into seawater. The manganese source may be either the eroded continental crust or hydrothermal processes, related to submarine volcanic activity at mid-ocean spreading zones. The origin of the hydrothermal FMC is related to hydrothermal venting on the sea floor. The hydrogenetic model relies on slowly precipitating the metallic

component from seawater that forms the concentrations of manganese and iron, as well as Ni, Cu, and Co. The diagenetic processes are controlled by the dissolution of manganese minerals at the seawater-deposit interface in the oxygen minimum zone (OMZ), followed by diffusion of the manganese from these deposit into a more oxygenated environment (Jenkyns *et al.* 1991; Hein *et al.* 2000). Nevertheless, there are occurrences of Mn deposits which originated from a simultaneous action of the aforementioned processes (Dymond *et al.* 1984; Hein *et al.* 2000; Rojković *et al.* 2003; Jach and Dudek 2005).

The aim of this paper is to present conclusions on the origin of the FMC occurring at Stankowa Skala on the basis of sedimentological and petrological analyses.

GEOLOGICAL SETTING

The Pieniny Klippen Belt separates the Carpathians into the Outer and Inner domains (Fig. 1). Stretching for a distance of ca. 600 km from Vienna in the west to Romania in the east, it is built of mainly pelagic carbonates dating from the Jurassic and Cretaceous. Most of these deposits were formed on the submarine Czorsztyn Ridge and its southern slope (Birkenmajer 1986) and are developed as ammonitico rosso-type limestones.

Stankowa Skala is located near Zaskale village. The section studied is situated near the top and in the south-westernmost part of Stankowa Skala (49°26'4.1", 19°59'23.6"). Manganese crusts occur on the upper surface of the lower part (Fig. 3) of the Czorsztyn Limestone Formation (CLF; Birkenmajer 1977), which is developed in the form of red-grey and red-brown, hard, non-nodular limestones, represented by five distinct beds (beds: 1a, 1b, 2a, 2b, 2c, 0.9 m in thickness – see Fig. 2), attaining the thickness of a few up to a dozen or so, centimetres.

Two beds with the lowermost and the middle occurrences of the CLF (beds 1a and 2b) are developed as limestones with thin-shelled *Bositra* bivalves (so-called filaments), peloids and thin subordinate micritic laminae (for more details see Sidoreczuk 2005). Bed 2b contains small Fe-Mn nodules (for descriptions of the central and northern sections of Stankowa Skala – see Zydorowicz and Wierzbowski 1986). The limestones of this part of the section represent two types

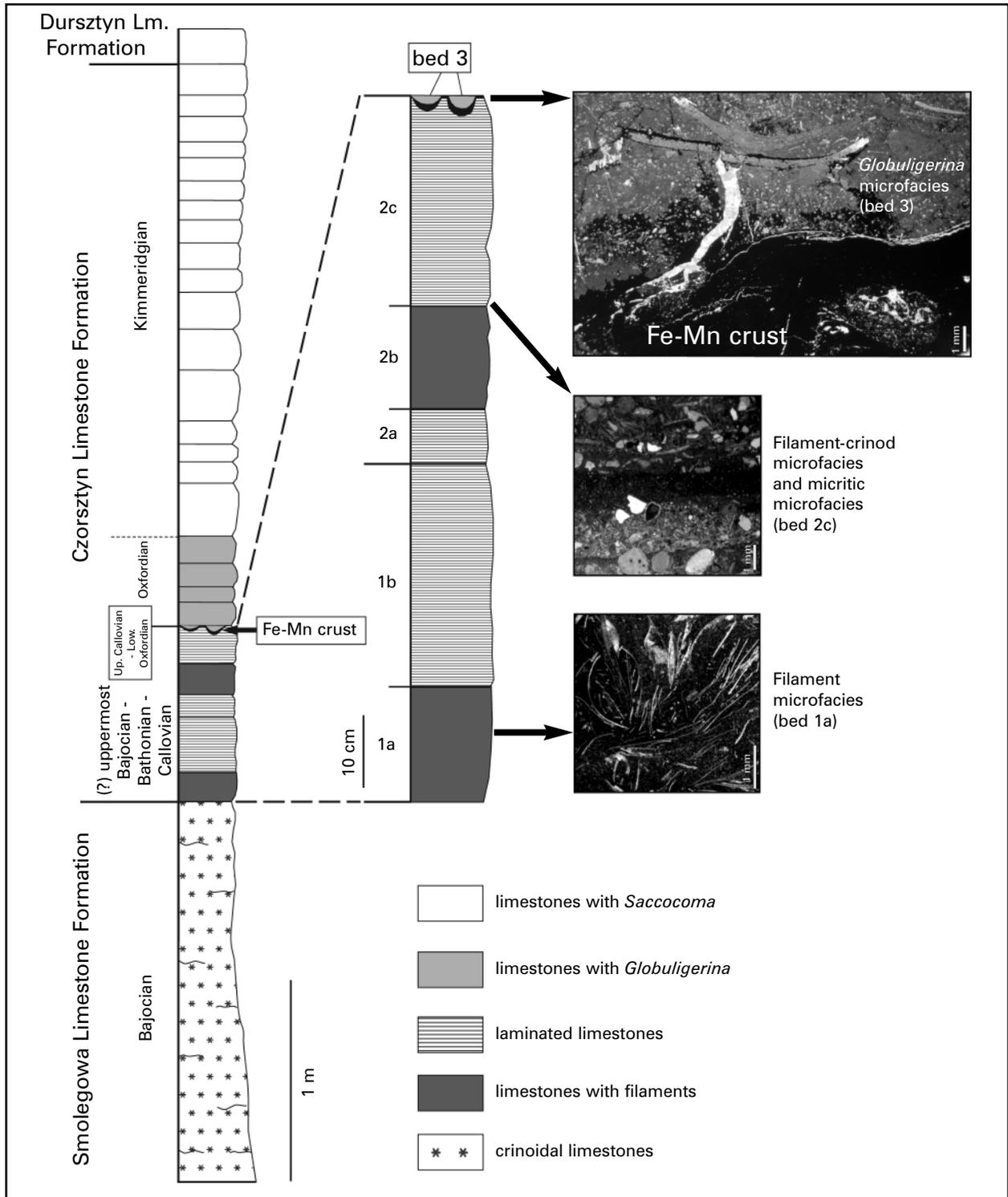


Fig. 2. Stankowa Skala section (after Kutek, Wierzbowski 1986; Jaworska 2000; Sidorczuk 2005).

of microfacies: filament microfacies and filament-peloid with echinoderm microfacies. The remaining part of the CLF (beds 1b, 2a and 2c) is formed by distinctly laminated limestones. The laminae are

usually composed of micrite, bioclasts, peloids and detrital quartz grains. The laminated limestones of this part of the CLF represent the following microfacies types: echinoderm microfacies, peloid

microfacies, peloid-echinoderm microfacies, filament-crinoid microfacies, and micritic microfacies (Fig. 2). The limestones representing the lowermost part of the Czorsztyn Limestone Formation in the Stankowa Skala section have been assigned to the stratigraphic interval from the (?) uppermost Bajocian to the Callovian (Jaworska 2000; Sidoreczuk 2005).

The lower part of the CLF at Stankowa Skala is overlain by hard, non-nodular, micritic detrital limestones, which infill the surface depressions (bed 3; Figs 2; 3). At the bottom of bed 3, uneven, thick ferromanganese crust (FMC) occurs (Sidoreczuk and Nejbert 2006). The contact between the FMC and the underlying limestones is sharp, but the upper boundary is transitional and diffused. The thickness of FMC varies from 0.5 cm to 4 cm. Within bed 3, where abundant organogenic remains appear, sparse, small-scale (up to 2 cm in diameter) Fe-Mn nodules were also recognised. These limestones represent already the *Globuli-*

gerina (“*Protoglobigerina*”) microfacies of Oxfordian age (Jaworska 2000; Sidoreczuk 2005).

ANALYTICAL METHODS

The material for this study comprises 15 samples, which were collected at Stankowa Skala during field work in 2004-2006. Two, up to 2 cm thick crusts, and additionally one sample from the overlying limestones rich in small Fe-Mn stromatolite fragments were selected for detailed mineralogical and petrographical investigations. Petrographical study, employing both transmitted and reflected light microscopy, was done on the ECLIPSE E600W POL microscope at the Inter-Institute Laboratory for Study of Geomaterials in Warsaw. EPMA analyses of the crusts were performed by means of CAMECA SX100 at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances in Warsaw. These analyses were performed under the following instrumental conditions: accelerating voltage 15 keV, beam current 20 nA, and beam diameter up to 40 μm . Single mineral grains, well seen on BSE images, were analysed using a focused electron beam (1-2 μm). To avoid an overlapping of the Ce with the Ba analytical lines, the Ce L_{α} and the Ba L_{β} were used during EPMA investigation. Natural and synthetic materials distributed by SPI Supplies were used as calibrating standards. X-ray diffraction analyses were conducted using a DRON-1 diffractometer installed at the XRD Laboratory of IGMiP. Powdered samples of crusts were placed on the glassy plate and irradiated by CoK_{α} radiation. Data were collected over the range 5° to $70^{\circ} 2\theta$, in the step-scan mode employing $0.04^{\circ} 2\theta$ step-size, and counting time 8 s per step.

PETROGRAPHY AND MINERALOGY OF THE FERROMANGANESE CRUSTS AT STANKOWA SKAŁA

The FMC crusts from Stankowa Skala are grouped into two types depending on their manner of occurrence: (I) massive FMC up to 2 cm

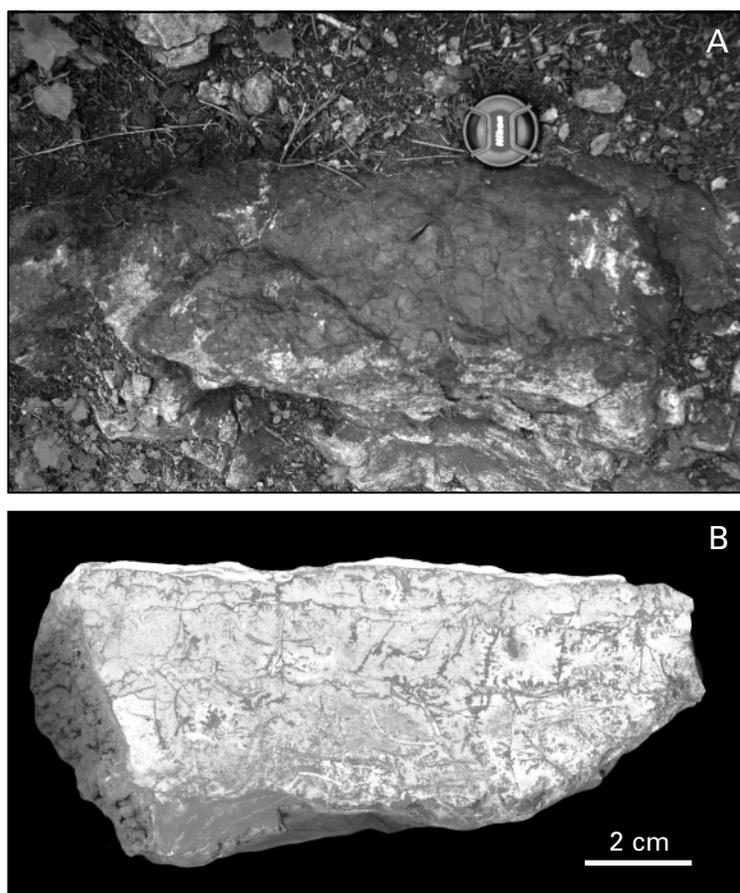


Fig. 3. Ferromanganese crust at Stankowa Skala: A – view of upper part of the ferromanganese crusts (FMC); B – cross-section of manganese crust with overlying bed 3.

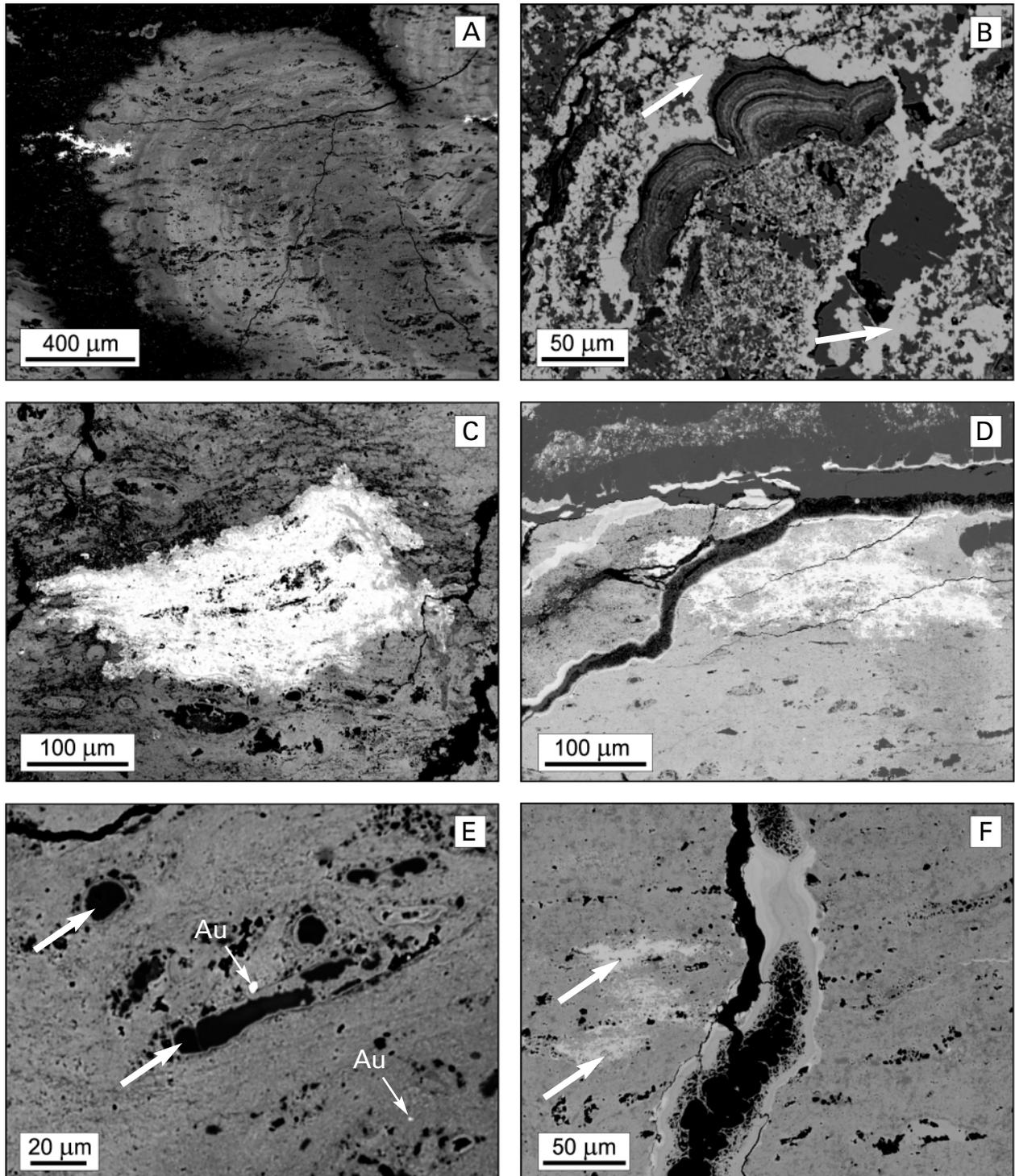
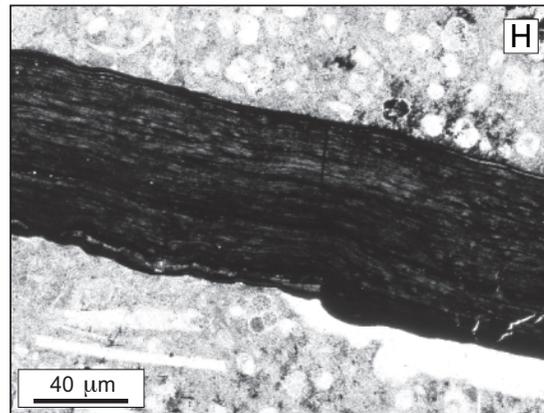
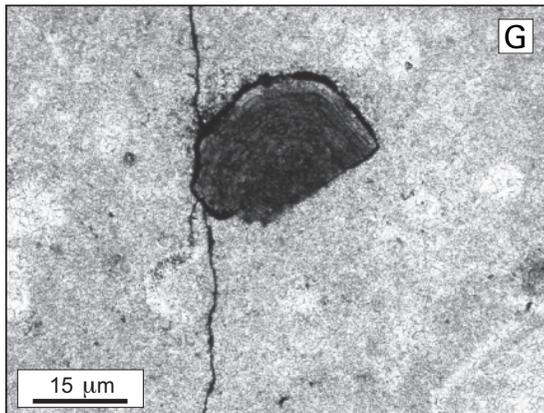
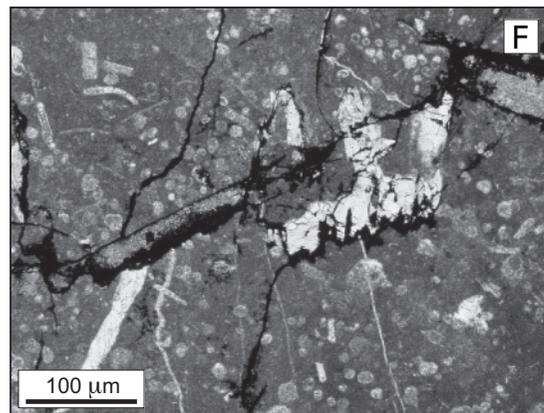
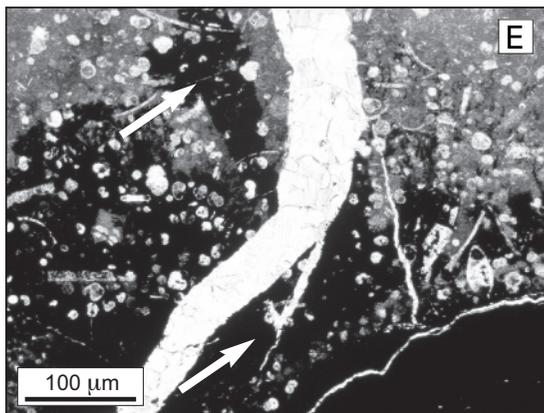
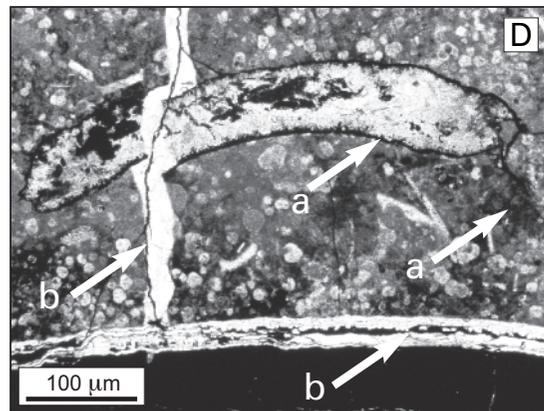
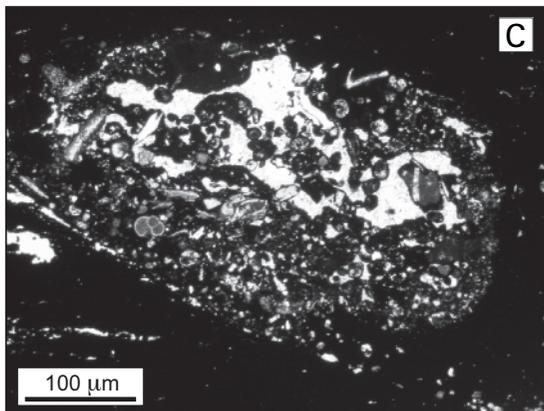
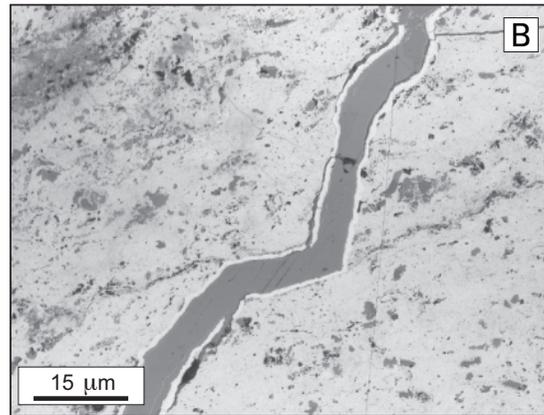
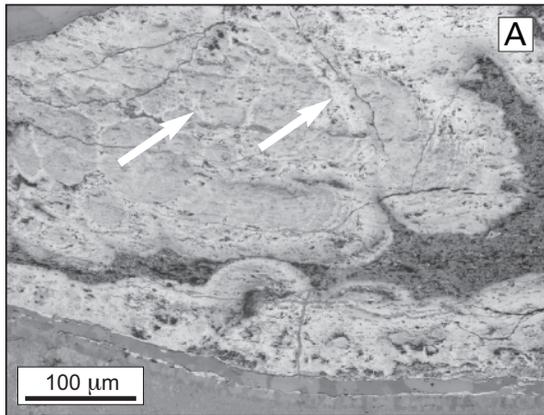


Plate 1

BSE images showing mineralogy and petrography of ferromanganese crusts at Stankowa Skala: A – massive ferromanganese crust with well preserved botryoidal texture and irregular aggregate of Ce-, Fe-rich minerals (white); B – fragment of thin ferromanganese crust (note well visible stromatolitic texture) inside limestone, and later generation (diagenetic?) of Mn, Ba-rich oxyhydroxides (arrowed); C – large aggregate of Ce-Fe-rich minerals (white) inside massive ferromanganese crust; D – two generation of calcite veins (I and II generation) cutting massive ferromanganese crust; large white patches inside ferromanganese crust consist of intergrowths of Ce-, Fe-rich minerals with fine, unidentified phosphates; E – fragment of massive manganese crust with preserved relics of fossils (arrowed) and fine intergrowths of native gold (Au); F – irregular patches of Ce-, Fe-rich minerals (arrowed) and thin calcite – Ba-Mn oxide (hollandite) vein in ferromanganese crust. BSE images were taken using Cameca Sx100; beam condition 15 keV, 20 nA.



thick occurring in the boundary zone between thin-shelled *Bositra* bivalves (uppermost Bajocian to Callovian) and limestone rich in *Globuligerina* (Oxfordian); and (II) small fragments of Fe-Mn stromatolite, enclosed in the Oxfordian limestone rich in *Globuligerina*.

The massive FMC of (I) type reveal well preserved botryoidal textures, typical of numerous present-day and ancient ferromanganese crusts. Micrographs of polished surfaces display fine layers of manganese minerals (Pls 1, 2), locally with thin Fe-Mn zones enriched in Pb and Ba oxyhydroxides (Pl. 2: A). Poorly preserved fossil remnants occurring within the FMC of (I) type were also recognised (Pls 1: E; 2: C). This type of FMC is composed of Fe, Mn, Ba oxyhydroxides (rich in Ca, as well as Cu, Ni, and Co), calcite and minor amount of quartz. XRD data indicate that the main mass of the FMC is composed of fine-grained intergrowths of poorly crystallized 10Å manganate (todorokite) and goethite. White patches visible on BSE images (Pl. 1: A, C, D, F) consist of intergrowths of unidentifiable Ce-, Fe-rich minerals (probably carbonates) with fine-grained phosphates. The average chemical composition of these intergrowths is: 31.04 wt. % Ce, 14.54 wt. % Fe, 2.14 wt. % Ca, 1.5 wt. % Mn, and 2.68 wt. % F. In massive FMC small, individual euhedral crystals of native gold (Pl. 1: E) were also determined. The crusts were cut by thin veins, filled by calcite or calcite-hollandite aggregates (Pls 1: D, F; 2: B, D, E).

The representative chemical composition of the massive FMC determined by means of EPMA is given in Fig. 4. The Mn and Fe contents range from 21.30 wt. % to 47.10 wt. % and 0.71 wt. % to 31.89 wt. %, respectively. The FMC is enriched in Ba, whose content is between 2.94 wt. % and 12.07 wt. %. Ce is always present and varies from 0.20 wt. % to 1.1 wt. %. The total amount of Co+Ni+Cu does not exceed 0.45 wt. %. Trace amounts of P, K, and Na were also measured. Two varieties within massive FMC were distinguished based on their petrography and chemical composition; massive ferromanganese crust with low Pb content (below 0.49 wt. %) and

well preserved botryoidal texture (B), and thin bright zones (C) occurring within massive ferromanganese crust that are enriched in Pb (up to 12.06 wt. %, see Fig. 4). Both varieties are characterized by high Mn/Fe and Mn/Ba ratios that reach up to 19.21 and 7.87, respectively.

The second type (II) of the FMC, recognised in the Stankowa Skala section, consists of crushed fragments of thin Fe-Mn crust featuring well developed stromatolitic texture. The thickness ranges from a few to 100 µm (Pl. 2: G, H). These were recognised within the *Globuligerina* limestone of the Czorsztyn Limestone Formation (Fig. 2). Contrary to the massive FMC, the oxide mineralogy of stromatolitic FMC is dominated by calcite and goethite. Manganese minerals are commonly submicroscopic in size and they are evenly distributed within each preserved fragment of the FMC. The fragments of the stromatolitic crust are characterized by high amounts of Fe (from 18.36 wt. % to 39.89 wt. %). The Mn/Fe ratio of these crusts does not exceed 1.62, in contrast to the massive FMC, where these ratios sometimes attain 40.84. These FMC are enriched in Co, Ni, and Cu; the concentration of these elements reaching up to 0.85 wt. %, 0.46 wt. %, and 1.33 wt. %, respectively. On the discrimination diagram of Hein *et al.* (1994) the chemical compositions of FMC are plotted within the field of hydrogenetic manganese deposits (Fig. 5). The chemical compositions of this FMC type, described as fragments of stromatolitic crust (A), are presented in Fig. 4. This type of FMC shows a high Mn/Ba ratio up to 20.53.

Manganese minerals, diagenetic and epigenetic in origin, are common within the pelagic limestone studied. They occur in different textural varieties, *e.g.* infillings of pore spaces, stylolites and thin veins (Pls 1B; 2: D-F). They were also recognized in massive FMC where thin Pb-Ba rich veins and/or zones in polygonal arrangement were observed (Pl. 2: A). A classic example of epigenetic manganese concentrations are hollandite within thick calcite veins that cut both the FMC and the host limestone (Pls 1: D, F; 2: B, D, E). Diagenetic and epigenetic

Plate 2

Petrography of manganese crust at Stankowa Skala. A – fragment of massive manganese crust showing characteristic botryoidal texture, arrows indicate veins and/or zones within massive crust enormously enriched in Pb; B – thin calcite-hollandite vein in massive manganese crust; C – fragment of pelagic limestone surrounded by massive manganese crust (black); D – contact of the massive manganese crust with Oxfordian limestone rich in *Globuligerina*. Note subordinate concentrations of Mn-minerals inside limestone (marked as “a”), probably of diagenetic origin, and late calcite veins (marked as “b”); E – diagenetic/epigenetic (?) concentrations of Mn-minerals (arrowed) replaced matrix of the Oxfordian limestone at contact zone with massive manganese crust (black); F – epigenetic Mn-minerals marked stylolites developed in Oxfordian limestone; G-H – well preserved fragments of the Co-enriched ferromanganese crust inside Oxfordian limestone. All photographs were taken using NICON ECLIPSE E600W POL microscope; A-B – reflected light, one nicol; C-H – transmitted light, one nicol.

masses of Mn aggregates are Mn (up to 50.49 wt. %) and Pb, Ba enriched, up to 3.14 wt. % and 10.39 wt. %, respectively. The chemical compositions are close to the diagenetic field on the diagram of Hein *et al.* (1994). More data about the chemical composition of these Mn concentrations are presented in Fig. 4, where they are described as diagenetic varieties of Mn oxyhydroxides (D). The Mn/Fe ratio of these diagenetic concentrations is very high and reaches up to 246.3.

DISSCUSSION

Manganese influx into the pelagic realm is commonly referred to hydrothermal activity at the ocean floor, related to ocean floor metamorphism that altered the upper part of the oceanic crust (Coleman 1979). These processes are especially intensive at mid-ocean ridges and along transform faults, where the numerous outflows of hot hydrothermal water come up to the surface of the ocean floor (Hein *et al.* 1997). During these processes a large amount of Mn, Fe, Ca, Co, Ni, and Cu is released into the seawater, especially in the periods of fast sea-floor spreading (Hein *et al.* 1997). Another source of manganese could be diagenetic processes taking place in the upper part

of deposits which had accumulated on the oceanic floor, particularly in the contact zone with poorly oxidized waters. Such a situation is observed in the oceanic water of the northern hemisphere as well as in some parts of the Pacific and Indian Oceans (Hein *et al.* 2000). Dissolution of the manganese-rich minerals within deposits in contact with oxygen minimum zone (OMZ) horizon, and diffusion of the manganese into the upper and/or lower OMZ, led to deposition of Mn-rich deposits beneath the OMZ (for details of this model see Graybeal and Heath 1984; Jenkyns 1988; Jenkyns *et al.* 1991).

All geological and petrological features of FMC at Stankowa Skala correspond to diagnostic features of hydrogenetic FMC deposits (*cf.* Jach and Dudek 2005). The chemistry of FMC also corresponds to hydrogenetic rather to diagenetic accumulation of the manganese minerals (Fig. 5). However, detailed petrographical investigations show that primary Fe, Mn, Ba associations were strongly modified by later diagenetic and epigenetic processes (Pls 1: B, D, F; 2: A, B, D-F). The presence of the patches rich in unidentified Ce-minerals (Pl. 1: A, C, D, F) and the high amount of Ce within Mn minerals (Fig. 4) can be attributed to an intensive scavenging of Ce from the seawater that took place in depositional environments character-

| | Fragment of the stromatolitic crust (A) | | | Massive ferromanganese crust, up to 2 cm in thickness, with well preserved botryoidal texture (B) | | | | | | Thin veins in massive FMC, Pb and Ba enriched (C) | | | Different diagenetic varieties of Mn oxyhydroxides (D) | | |
|----------|---|-------|-------|---|-------|-------|-------|-------|-------|---|-------|-------|--|--------|--------|
| | | | | | | | | | | | | | | | |
| Fe | 38.42 | 18.36 | 22.30 | 9.26 | 15.66 | 22.83 | 2.72 | 3.92 | 20.77 | 2.38 | 2.25 | 7.93 | 0.38 | 0.19 | 0.25 |
| Mn | 1.85 | 29.77 | 26.12 | 40.86 | 36.38 | 22.06 | 45.88 | 45.87 | 30.35 | 42.90 | 43.18 | 38.51 | 46.42 | 46.48 | 46.79 |
| Ba | 0.09 | 2.80 | 2.40 | 6.68 | 5.52 | 3.89 | 10.81 | 8.54 | 4.75 | 5.48 | 5.83 | 4.90 | 10.24 | 9.90 | 10.34 |
| Ce | 0.10 | 0.25 | 0.08 | 0.51 | 0.48 | 0.30 | 0.73 | 0.39 | 0.38 | 1.11 | 0.82 | 0.58 | 1.21 | 1.20 | 0.97 |
| Pb | 0.23 | 0.32 | 0.11 | 0.33 | 0.17 | 0.49 | 0.01 | 0.13 | 0.14 | 12.06 | 11.63 | 9.60 | 2.19 | 2.48 | 1.32 |
| P | 0.09 | 0.14 | 0.15 | 0.06 | 0.12 | 0.09 | 0.05 | 0.04 | 0.14 | 0.07 | 0.07 | 0.10 | 0.10 | 0.07 | 0.03 |
| K | 0.72 | 0.04 | 0.08 | 0.17 | 0.17 | 0.10 | 0.08 | 0.11 | 0.19 | 0.04 | 0.03 | 0.13 | 0.01 | 0.07 | 0.09 |
| Cl | 0.03 | 0.03 | 0.03 | 0.01 | 0.03 | 0.24 | 0.00 | 0.00 | 0.04 | 0.01 | 0.00 | 0.00 | 0.09 | 0.00 | 0.00 |
| Na | 0.04 | 0.08 | 0.06 | 0.10 | 0.08 | 0.02 | 0.13 | 0.11 | 0.08 | 0.06 | 0.03 | 0.06 | 0.08 | 0.10 | 0.12 |
| Mg | 3.08 | 0.30 | 0.35 | 0.42 | 0.47 | 0.33 | 0.17 | 0.29 | 0.57 | 0.08 | 0.09 | 0.24 | 0.11 | 0.13 | 0.16 |
| Ca | 0.48 | 2.05 | 1.92 | 1.70 | 1.43 | 0.81 | 1.35 | 1.69 | 1.25 | 1.11 | 1.08 | 1.03 | 1.49 | 1.46 | 1.48 |
| Al | 4.17 | 1.34 | 1.44 | 0.69 | 0.83 | 1.12 | 0.24 | 0.27 | 1.24 | 0.38 | 0.39 | 0.83 | 0.32 | 0.27 | 0.27 |
| Si | 7.76 | 0.40 | 0.71 | 0.70 | 0.50 | 0.88 | 0.14 | 0.18 | 1.28 | 0.24 | 0.28 | 0.98 | 0.09 | 0.08 | 0.06 |
| Ti | 0.78 | 0.74 | 0.90 | 0.18 | 0.23 | 0.36 | 0.07 | 0.12 | 0.35 | 0.04 | 0.07 | 0.13 | 0.03 | 0.01 | 0.00 |
| Ni | 0.40 | 0.00 | 0.23 | 0.03 | 0.10 | 0.09 | 0.02 | 0.02 | 0.11 | 0.00 | 0.04 | 0.08 | 0.02 | 0.00 | 0.00 |
| Cu | 0.00 | 1.33 | 1.30 | 0.07 | 0.18 | 0.07 | 0.03 | 0.03 | 0.11 | 0.04 | 0.24 | 0.00 | 0.15 | 0.00 | 0.11 |
| Co | 0.85 | 0.11 | 0.20 | 0.08 | 0.00 | 0.09 | 0.01 | 0.07 | 0.00 | 0.09 | 0.00 | 0.10 | 0.05 | 0.05 | 0.06 |
| Zn | 0.15 | 0.09 | 0.10 | 0.00 | 0.00 | 0.00 | 0.05 | 0.07 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.01 | 0.06 |
| TOTAL | 59.23 | 58.12 | 58.49 | 61.83 | 62.35 | 53.80 | 62.50 | 61.87 | 61.76 | 66.07 | 66.04 | 65.19 | 63.02 | 62.49 | 62.13 |
| Mn/Fe | 0.05 | 1.62 | 1.17 | 4.41 | 2.32 | 0.97 | 16.85 | 11.71 | 1.46 | 18.05 | 19.21 | 4.86 | 121.92 | 246.30 | 190.74 |
| Co+Ni+Cu | 1.26 | 1.44 | 1.73 | 0.17 | 0.28 | 0.26 | 0.07 | 0.12 | 0.22 | 0.13 | 0.29 | 0.17 | 0.22 | 0.05 | 0.17 |
| Ba/Fe | 0.00 | 0.15 | 0.11 | 0.72 | 0.35 | 0.17 | 3.97 | 2.18 | 0.23 | 2.31 | 2.59 | 0.62 | 26.89 | 52.49 | 42.17 |
| Mn/Ba | 20.53 | 10.63 | 10.88 | 6.12 | 6.60 | 5.66 | 4.24 | 5.37 | 6.39 | 7.82 | 7.40 | 7.87 | 4.53 | 4.69 | 4.52 |
| Ba/Ca | 0.19 | 1.37 | 1.25 | 3.93 | 3.87 | 4.80 | 7.98 | 5.05 | 3.80 | 4.96 | 5.39 | 4.76 | 6.88 | 6.80 | 6.97 |
| Pb/Mn | 0.13 | 0.01 | 0.00 | 0.01 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.28 | 0.27 | 0.25 | 0.05 | 0.05 | 0.03 |
| Pb/Ba | 2.60 | 0.11 | 0.05 | 0.05 | 0.03 | 0.13 | 0.00 | 0.02 | 0.03 | 2.20 | 1.99 | 1.96 | 0.21 | 0.25 | 0.13 |
| Pb/Ca | 0.49 | 0.16 | 0.06 | 0.19 | 0.12 | 0.61 | 0.01 | 0.08 | 0.11 | 10.92 | 10.76 | 9.34 | 1.47 | 1.70 | 0.89 |

Fig. 4. Selected chemical analyses of FMC crust at Stankowa Skala. The bracketed letters A, B, C, D correspond to the textural varieties of manganese accumulations described in text and on the Figure 5. Sample Sta-3a, concentration of all elements in wt. %.

ized by a slow rate of deposition (Hein *et al.* 1997; Koschinsky and Hein 2003). Such enrichment probably resulted in a positive Ce anomaly that is a characteristic feature of the FMC originating during hydrogenetic processes (Glasby *et al.* 1997; Rojković *et al.* 2003; Jach and Dudek 2005).

Two types of the FMC which occur at the Stankowa Skala section confirm their early origin, coeval with the pelagic sedimentation. The field observation shows that some parts of the (I) type of FMC, growing up at local elevations, could be broken up and redeposited in the form of tiny fragments to form the (II) type FMC within *Globuligerina* limestone (Pl. 2: G-H). These fragments of FMC remained unchanged by later diagenetic and epigenetic processes, preserving the primary chemical composition (Fig. 5), probably due to protection by pelitic limestone with a poorly developed porosity. Thick FMC crusts of the (I) type, developed between the contrasting microfacial limestones (Fig. 3) were probably more susceptible to later diagenetic and epigenetic alteration (Fig. 2; Pls 1: D, F; 2: B, D-F). Such a hypothesis is supported by a shift of the plot position within the diagram of Hein *et al.* (1994) towards the diagenetic field (for details see Fig. 5).

The wide distribution of ferromanganese crusts within the deposits of the Tethys-Ligurian Sea (including pelagic deposits of PKB) during the Late Callovian corresponds to the tectonic events related to sea-floor spreading in the Tethys-Ligurian Sea (Corbin *et al.* 2000). The first oceanic crust in the Tethyan-Ligurian Sea is dated from Late Callovian to Early Oxfordian (Boillot *et al.* 1984). Recent palaeomagnetic data from the Pieniny Klippen Belt indicative of a significant palaeolatitudinal shift in the Middle Callovian – Early Oxfordian time span (c.a. 1000 km; Lewandowski *et al.* 2005; Lewandowski *et al.* 2006), are in line with this hypothesis. These observations, together with sedimentological evidence from the peri-Tethyan area situated to the North of the Pieniny Basin, point to a continental scale geotectonic event that took place in mid-late Jurassic time and changed the marine environment of sedimentation (“Metis Geotectonic Event” – see Matyja, Wierzbowski 2006).

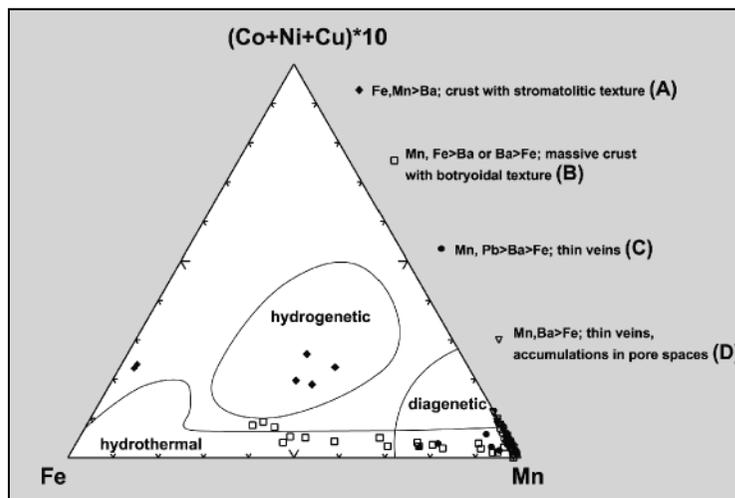


Fig. 5. Ternary diagram showing chemistry of the manganese crusts from Stankowa Skala (Pieniny Klippen Belt). Chemical composition from EPMA (defocused electron beam up to 40 μm). Discrimination fields after Bonatti *et al.* (1972) and Hein *et al.* (1994).

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