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BIOGENIC ORIGIN OF MANGANESE FLOWSTONES FROM JASKINIA CZARNA CAVE, TATRA MTS., WESTERN CARPATHIANS

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Abstract: Flowstones composed mostly of amorphic manganese oxides occur in Jaskinia Czarna Cave in the contact zone between Middle Triassic carbonates and Upper Jurassic-Lower Cretaceous limestones on a substrate diagenetically enriched in Mn and Fe minerals. In the SEM micrographs, the flowstones display a dome-like structure, which is characterized by non-porous microfabric in the dome centres and porous microfabric in the outer parts of the domes, and in the inter-dome spaces. The filament elements of porous microfabric and co-occurring globular bodies are recognised as mineralized biogenic structures, probably bacterial or fungal in origin. The Mn/Fe ratio in the flowstones is 72.1:1, while in the substrate it is about 1.32:1. High concentration of Mn is caused by preferencial microbial precipitation. A very high rate of manganese oxide growth also suggests their microbially mediated precipitation.

Abstrakt: Naciekowe polewy zbudowane głównie z amorficznych tlenków manganu występują w Jaskini Czarnej w pobliżu kontaktu utworów środkowego triasu i malmo-neokomu, na podłożu, które cechuje diagenetyczne wzbogacenie w mangan i żelazo. Polewy o miąższości 2 do 20 mm są zbudowane z amorficznych tlenków manganu. Obserwacje w SEM wykazały, że polewy składają się z kopulastych form mających w partiach centralnych zwięzłą, a w peryferycznych porowatą więźbę. Komponenty budujące porowatą więźbę - kłaczki i ciała globularne - zostały zidentfikowane jako struktury mikrobialne, prawdopodobnie bakteryjne lub grzybowe. Stwierdzone analizą chemiczną proporcje Mn/Fe w polewach wynoszą 72,1:1, natomiast w ich podłożu 1,32:1. Tak wysoka koncentracja manganu spowodowana jest jego preferencyjnym wytrącaniem przez mikroorganizmy. Wysokie tempo wzrostu badanych polew wskazuje również na mikrobialne wytrącanie tlenków manganu.

Key words: biomineralization, manganese oxides, karst, Tatra Mts.

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INTRODUCTION

Variable manganese deposits originate in various environments. They occur in marine basins (e.g., nodules, mineralized stromatolites, crusts), as well as in lacustrine, fluvial, and subaerial environments (e.g., nodules, crusts, desert varnish) (Dixon & Skinner, 1992). The problem of their origin has been extensively discussed in literature (e.g. Schweisfurth, 1971; Marshall, 1979; Nealson, 1983; Dixon & Skinner, 1992). Recently, several authors have promoted the biogenic model of the origin of some manganese deposits. This conception was confirmed by the experiments and discoveries of various microorganisms, mainly bacteria, fungi, blue-green algae and algae in modern manganese sediments (e.g. Krumbein, 1971; Dubynina, 1980; Nealson & Ford, 1980; Emerson *et al.*, 1982; Richardson *et al.*, 1988).

Manganese deposits also occur in the karst environments and have been observed in several caves. They form soft deposits, the so-called wad, or consolidated crusts (e.g., Moore, 1981; Hill, 1982; Peck, 1986; Jones, 1992a). The wad occurs in the cave clastic deposits (Cílek & Fábry, 1989) or forms a film which coats the walls of the cave passages (Moore & Sullivan, 1978; Gascoine, 1982; Hill, 1982; Kashima, 1983). The crusts occur on the walls of cave passages as well as within and on the surface of calcite speleothems (Moore, 1981; Rogers & Williams, 1982; Peck, 1986). The orgin of manganese cave deposits has been frequently related to the activity of microorganisms (Broughton, 1971; White, 1976; Hill, 1982; Cílek & Fábry, 1989). This problem was studied in detail by Moore & Sullivan (1978), Peck (1986), and Jones (1992a).

Manganese cave deposits have never been recognised in

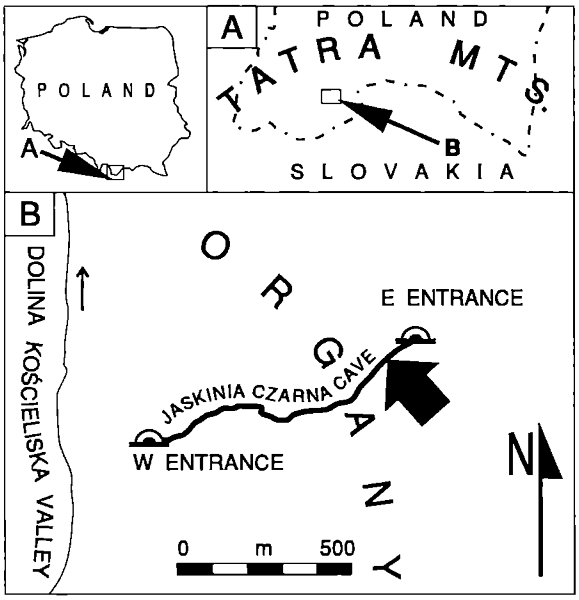

Fig. 1. Location of Jaskinia Czarna Cave in Western Tatra Mts., map B shows main passage of Jaskinia Czarna Cave; arrow indicates sampling place

the Western Carpathians. In this paper, however, we would like to describe and interpret the manganese flowstones which were found in the eastern part of Jaskinia Czarna Cave in the Tatra Mountains during the exploration in 1992. The main results were obtained by means of petrographic/mineralogical analyses. Preliminary results concerning the above problem have been already reported in the materials of local symposium (Gradziński *et al.*, 1995).

GEOLOGICAL SETTING

Jaskinia Czarna Cave is located on the eastern slopes of the Dolina Kościeliska Valley in the Tatra Mts. at an altitude of about 1200 to 1500 m a.s.l. (Fig. 1). It is more than 6 km long (Gradziński *et al.*, 1985). The cave is located in the tectonic allochtonous Organy Unit that is a part of the allochtonous Czerwone Wierchy Unit. Most of the cave passages originated in Middle Triassic dolomites and limestones, and only the eastern parts of the cave originated in Upper Jurassic-Lower Cretaceous limestones of the High-Tatric Succesion (Rudnicki, 1967; Grodzicki, 1978). Jaskinia Czarna Cave is probably Late Tertiary in age (Rudnicki, 1967; Głazek *et al.*, 1979).

The contact between Middle Triassic carbonates and Upper Jurassic-Lower Cretaceous limestones is well visible in the eastern part of Jaskinia Czarna Cave. The beds are overturned, dipping 45° to 55° SEE in this part of the cave. The contact is concordant with bedding in the scale of the cave. Commonly, neptunian dykes filled with ?Bajocian pink crinoidal limestones penetrate Middle Triassic carbonates below the contact zone. Similar neptunian dykes of variable size and orientation occur in an analogous geological situation in several outcrops of the High-Tatric Succession in the Tatra Mts., e.g. in Mała Świstówka (Szulczewski, 1963a) and Wyżnia Świstówka (Grochocka-Rećko, 1963).

Contrary to the view of Grodzicki (1978), the discussed contact between Middle Triassic carbonates and Upper Jurassic-Lower Cretaceous limestones is not tectonic. Only small-scale tectonic slides between beds, developed during folding, can be observed. It is a sedimentary contact, and a huge stratigraphic gap is caused by temporary lack of deposition and erosion. In the Czerwone Wierchy Unit, diverse Middle Jurassic deposits cover eroded Middle Triassic deposits (Lefeld, 1979). Jurassic deposits are represented by locally occurring Bajocian crinoidal limestones and red Bathonian limestones with rich nektonic fauna and a stromatolite (Krupianka Limestone Formation), and by partially nodular, pink and greyish Callovian limestones (a part of the Raptawicka Turnia Limestone Formation) (Grochocka-Rećko, 1963; Sieciarz, 1963; Szulczewski, 1963a; Bac & Grochocka, 1965). The formal lithostratigraphic units were distinguished by Lefeld (1985). Bathonian stromatolite is impregnated by iron oxides (Szulczewski, 1963b). The occurrence of haematite crusts in nodular Callovian limestones directly overlaing Triassic carbonates was observed in the western part of the Czerwone Wierchy unit (Bac & Grochocka, 1965).

Diagenetic impregnations of the iron and manganese oxides, visible exclusively in this cave, occur in Middle Triassic carbonates, as well as in Upper Jurassic-Lower Cretaceous limestones around the contact zone between these deposits. Iron and manganese minerals and calcite fill numerous small veins, which are up to 0.5 mm wide. One of the examined sections contains diagenetic deposits, which occur between Middle Triassic carbonates and Upper Jurassic limestones. They contain sigmoidal calcite cements (cf. Ramsay & Huber, 1989), iron-manganese structures of the opaque *Frutexites*-type (cf. Böhm & Brechert, 1993), and clasts of Triassic dolomites. These clasts display distinct features of pressure dissolution.

MATERIALS AND METHODS

The examined flowstones are developed on the walls of the cave exclusively on the substrate enriched in iron and manganese minerals close to the contact zone between Middle Triassic carbonates and Upper Jurassic-Lower Cretaceous limestones. Their most advanced development can be observed directly on the above mentioned diagenetic deposits. The flowstones form irregularly shaped crusts which occur locally in the isolated forms. The diameter of the crusts ranges from a few centimeters to a few decimeters. The external surface of the crusts is black in colour and displays an earthy luster. It is corroded as indicated by distinct, irregular corrosional pits. The isolated form of occurrence is probably due to the corrosion. The thickness of the crusts ranges from about 2 to more than 20 mm. Some parts of the flowstones are covered with a calcite speleothem which is up to 4 mm thick.

Table 1

Chemical composition of manganese flowstones and of host diagenetic deposit; mean data for 5 samples, * mean data for 3 samples

	Mn (%)	Fe (%)	Ca (%)	Mg (%)	Ni (ppm)	Co (ppm)	Mn/Fe
Flowstones	48.3	0.67	6.14	1.86	443*	822*	72.1
Substrate	2.98	2.25	27.95	1.75	490*	406*	1.32

The samples were collected from manganese flowstones and from diagenetic deposits occurring in their substrate. These samples were examined in the laboratory using microsopic observation, chemical, and X-ray diffraction analyses.

Microscopy: The samples examined were collected from manganese flowstones, together with their substrate. Eight thin-sections were prepared. They have been analysed by means of petrographic microscope. Scanning electron microscope (SEM) images were obtained from natural parting surfaces and polished surfaces etched in 2.5% HNO_3 for 2.5 and 5 sec, respectively. A JEOL JSM-840 SEM coupled with a microprobe Link Analytical AN 10/85S were used.

Chemical analyses: The washed samples were crushed and powdered in a ball mill. They were dissolved in warm 18.5% HCl, or melted with Na_2CO_3 and dissolved in cold HCl. Ca content was determinated using complexometric titration. Atomic absorption analyses (AAS) was applied to estimate Mn, Fe, Mg, Ni, and Co contents using the ASA Perkin-400 atomic absorption spectrometer (Elmer product) with air-acethylen flame.

X-ray diffraction (XRD) analysis: XRD patterns were recorded by step scanning, with a Philips diffractometer and CuKα radiation, 0.05°step-size, 1 sec. counting time per size, and with a 5-50° 2Θ range of the take-off angle.

RESULTS

The chemical composition of the manganese flowstones was determinated using chemical analysis. Manganese is the dominant element of the examined flowstones. Iron content is insignificant (Tab. 1). The samples also contain Ca and Mg, as well as small amounts of Co and Ni. Si, Al, Ba, and K were detected only by microprobe analyses. The differences between the Mn/Fe ratio in the flowstone and in their substrate are very distinct (Tab. 1).

Lack of distinct peaks in the diffractograms indicates an almost total absence of crystalline phases and presence of amorphic substances in the flowstones (Fig. 2). Only in two samples, the possibility of occurrence of todorokite cannot be excluded on the basis of most intensive reflexes. However, the presence of these minerals has not been proven. Also only sporadic occurrences of crystalline phases were observed in the SEM images.

According to the above presented data, it can be concluded that the examined flowstones are mainly composed of amorphic manganese substances, which, moreover, contain some amount of Ca and Mg. Their chemical content can be related to birnessite or varieties there of, namely buserite, in which Ca, Mg, Mn, K, and H_2O occur between the Mn octahedral sheets (Post, 1992; Usui & Mita, 1995).

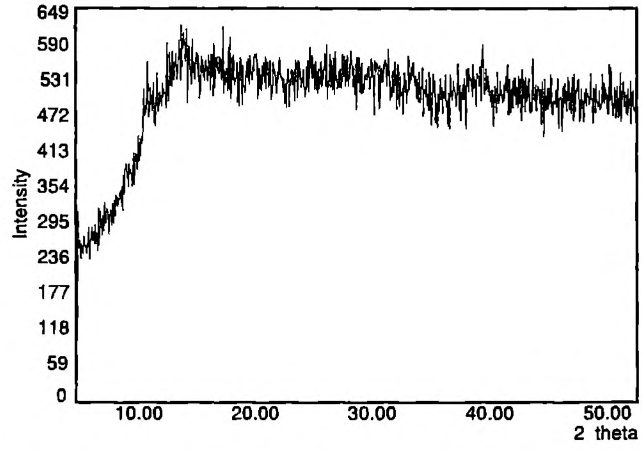

Fig. 2. Characteristic shape of diffractograms indicating presence of amorphic material, sample from manganese flowstone

It has been proven that the flowstones examined under the microscope in transmitted light are opaque. They are composed of dome-like structures about 100-150 μm in diameter, which are clearly visible in the SEM micrographs (Fig. 3). The central parts of the domes are characterized by a dense non-porous microfabric (Fig. 4). The outer parts of the domes and the inter-dome spaces show porous microfabric. This porous microfabric is composed of densely packed, irregularly twisted filaments which are more than 10 μm long (Fig. 5) but only 1 to 2 μm in diameter. Some of the adjacent filament agglomerates and the borders between them are difficult to distinguish.

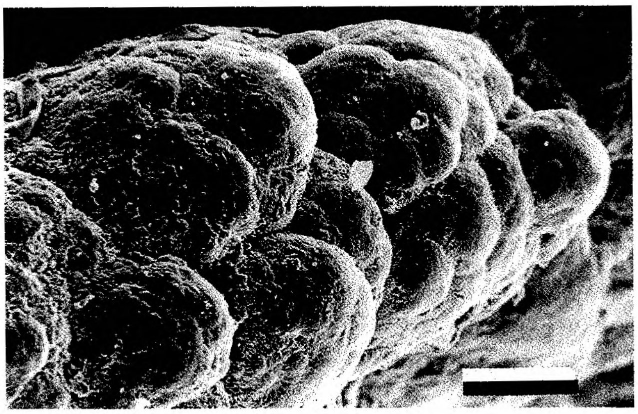

Fig. 3. General view of dome-like structure composing manganese flowstone; SEM photomicrograph, scale bar 100 μm

Globular bodies, oval or circular in shape, occur in the porous microfabric (Fig. 6, 7). They are from 0.5 to 3 μm in diameter. The globular bodies display either a smooth or sharply irregular surface with sharp irregularities. Some of

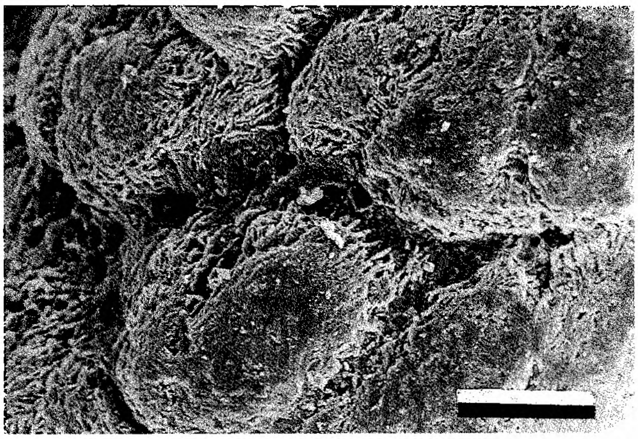

Fig. 4. Detailed view of dome-like structure, non-porous microfabric in central parts of domes and porous microfabric in their outer parts and inter-dome spaces. Domes are developed due to the faster growth of colony caused by quickest reproduction of microorganisms (probably bacteria); SEM photomicrograph, scale bar 50 μm

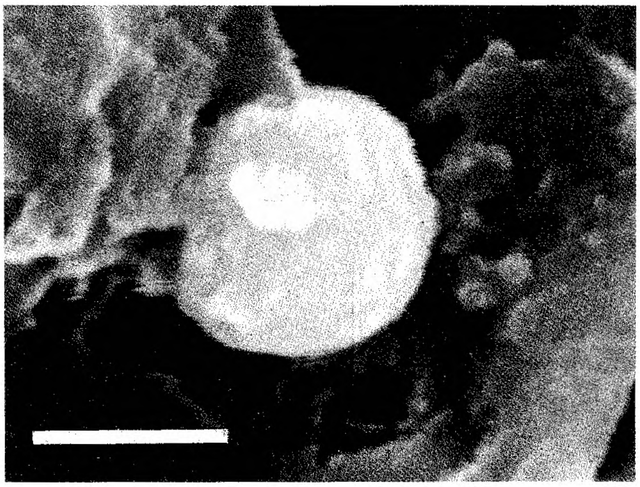

Fig. 6. Globular body of microbial (bacterial or fungal) origin occuring within porous microfabric; SEM photomicrograph, scale bar 1 μm

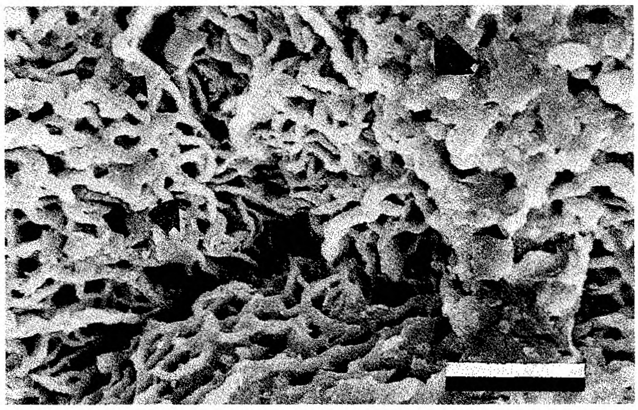

Fig. 5. Detailed view of porous microfabric composed of filaments and globular bodies (large arrow), agglomeration of adjacent filaments is visible (small arrow); SEM photomicrograph, scale bar 10 μm

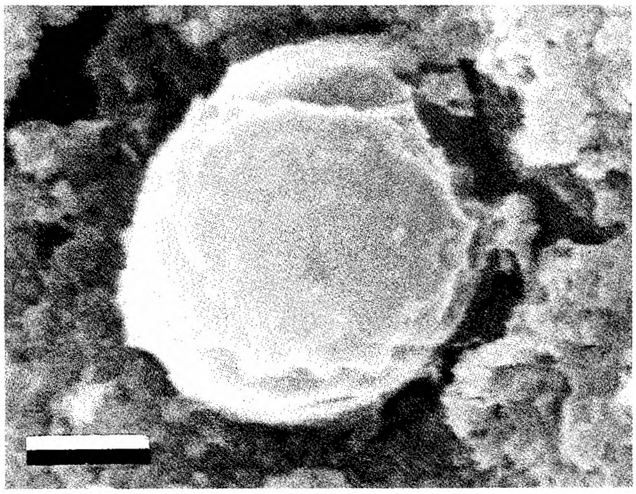

Fig. 7. Globular body of microbial (bacterial or fungal) origin: visible sharp outline is due to mineralization processes; sample etched in HNO_3 for 2.5 sec.; SEM photomicrograph, scale bar 1 μm

them form clumps, which are more than 5 μm in diameter (Fig. 8), others are distinctly fixed to the filaments. In the latter case, the borders between them and the filaments are obliterated and, similarly as between adjacent filaments, difficult to determine (Fig. 5).

DISCUSSION

The origin of variable manganese deposits is extensively discussed in literature, especially their biogenic versus non-biogenic origin (Marshall, 1979; Nealson, 1983; Ghiorse & Ehrlich, 1992). Some authors opt for the influence of microorganisms on the origin of manganese deposits, for instance deep-sea (Greenslate, 1974), fresh-water (Dubynina, 1980; Chapnick *et al.*, 1982), and soil nodules (Robbins, *et al.*, 1992), as well as desert varnish (Palmer *et al.*, 1986) and spring deposits (Hariya & Kikuchi, 1964; Mustoe, 1981). Moreover, precipitation of manganese oxides by microorganisms was shown in several experiments (e.g. Nealson & Ford, 1980; Nealson & Tebo, 1980; Mustoe, 1981; Emerson et al., 1982; Diem & Stumm, 1984; Greene & Madgwick, 1988). Biologically-induced and biologically-controlled processes of manganese-oxide precipitation have been distinguished (Skinner & Fitzpatrick, 1992). In the former of of these processes, manganese oxides are precipitated externally onto microbial cells as a result of the influence of microorganisms on the enviroment, especially through changes in pH and Eh. The latter process is connected with precipitation of manganese oxides within the cells or organs of microorganisms, probably by means of enzymes. However, a lot of controversies concerning the biological precipitation of manganese oxides still exists (Ghiorse & Ehrlich, 1992).

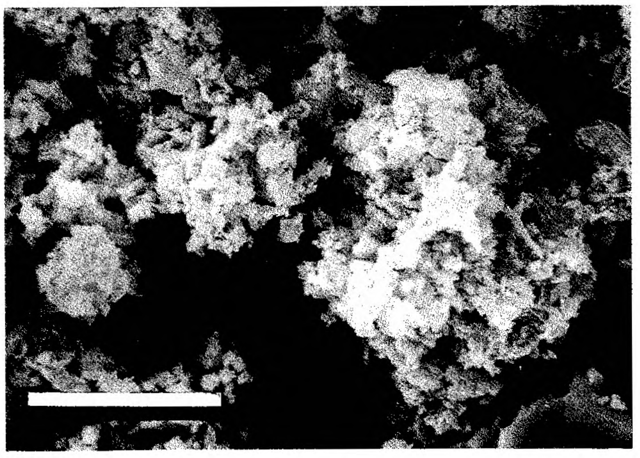

Fig. 8. Irregular three-dimensional clumps composed of globular bodies of microbial origin; sample etched in HNO_3 for 2.5 sec.; SEM photomicrograph, scale bar 10 μm

ORIGIN OF INTERNAL STRUCTURES

The size and shape of filaments, co-occurring globular bodies and the dome-like structures they form suggest their microbial origin. Correct determination of the origin of these structures is difficult because of their state of preservation. However, it is possible to compare the examined structure to the mineralized ones described so far.

Distinct dome-like structures in the examined flowstones (Figs 3, 4) can be caused by biogenic processes. Such a shape is typical of recent bacterial colonies (Carlile, 1979). The centers of the bacterial colonies are pushed up, this due to the fact that these centers are the area of quickest reproduction. Consequently, the domes are formed. Analogous structures of similar size occur in modern manganese spring deposits in the Hokkaido Island (Usui & Mita, 1995, fig. 6a). A similar, although smaller by one order of magnitude structure was documented in the Turonian microbial phosphatic stromatolites described by Krajewski *et al.* (1994, fig. 19).

The origin of filaments (Fig. 5) may be related to cyanobacteria (blue-green algae), fungi, or bacteria. The total darkness deep in the cave, where the flowstones were sampled, suggests that fungi and bacteria are more likely to appear there. Such postulation can be taken into account in further discussion. According to Klappa (1979), fungal filaments are characterized by constant diameter and are not twisted. However, fungal hyphes obtained in the experiments carried out by Jones and Pemberton (1987) were distinctly twisted. Moreover, the examined porous microfabrics are very similar to those of manganese oxides obtained in the experiments of Golden *et al.* (1992, photo 1). In these experiments, the fungi were incubated and propagated on a substrate rich in manganese. The manganese oxides precipitated within the fungal mycelium. As the result of this experiment, a porous, so-called "open fabric", composed of buserite, was formed.

Although the porous microfabrics appear to be of fungal origin, their bacterial origin cannot be excluded. Jones and Motyka (1987, fig. 4C-D) illustrated a similar microfabric, called "the reticular patterns", which occurs in an opaque substance within calcitic stalactites. The substance is composed mainly of Mn and Ca, and subordinately of Al. The cited authors postulated bacterial origin of the substance. Moreover, some structures similar in size and shape to the examined filaments have been recognized in the Cretaceous pelagic phosphorous stromatolites in Spain (Martin-Algarra & Vera, 1994, fig. 17). They were interpreted as "string colonies of bacteria". However, contrary to the examined microfabric, the filaments in these colonies were more densely packed and consequently built a non-porous microfabric. The filaments in question are similar to the branches of the star-shaped colony of bacterium *Metalogenium* sp. (cf. Crear *et al.*, 1980). It is worth pointing out that this bacterium can precipitate manganese oxide (e.g. Marshall, 1979; Dubynina, 1980).

The examined globular bodies in the porous microfabric (Figs 6, 7) are probably mineralized bodies of bacteria or mineralized fungal spores, as suggested by their size and shape. The spherical and oval shape of these bodies corresponds with that of spores of fungi or the cocoid bacteria, despite the potential pleomorphism of the latter (cf. Nealson, 1983; Jones & Keddie, 1992). Similar, but calcified, bodies of bacterial origin are reported from carbonate deposits (Jones & MacDonald, 1989; Guo & Riding, 1992, 1994; Folk, 1993), and from manganese deposits, where they are composed mostly of manganese oxides (Nealson & Ford, 1980; Nealson, 1983). It is worth pointing out that the manganese replicas of baterial bodies were obtained in the laboratory experiments through biomineralization (Mustoe, 1981, fig. 2; Nealson & Ford, 1980, fig. 3C; Nealson & Tebo, 1980, fig. 3D; Emerson *et al.*, 1982, fig. 3E). For the experiments, the bacteria were extracted from the environments of manganese oxide formation. The shape and size of the examined globular bodies are similar to those obtained in the experiment described by the above cited authors.

The size of smaller globular bodies, which are 0.5-1.2 μm in diameter, is similar to the size of the spores of some fungi. Similar forms composed of calcite and covered with fine platelets of manganese oxides were found in caliche deposits in the Grand Cayman Island (Jones, 1992a, b). They are single or arranged in clusters. The size of globular bodies is unified in the clusters, contrary to those under discussion.

The smaller of the examined globular bodies form three-dimensional clumps (Fig. 8). The shape of the clumps corresponds to that of similar ones of calcified bacteria and nannobacteria described by Folk (1993). Similar forms occur in the living fresh-water stromatolites described by Szulc and Smyk (1994), interpreted as calcified clumps of bacterial cells. We are not able to decide if the examined smaller globular bodies are mineralized bacteria or spores due to their poor state of preservation and, mainly, because of the absence of external ornamentation. Nevertheless, their bacterial origin seems more plausible.

The biogenic microstructures above described are characterized by three-dimensional morphology and the lack of collapse. This can be seen as the evidence for biologically mediated mineralization processes. These processes occurred while the organisms were alive or during their death (cf. Johnes & Kahle, 1986; Jones & MacDonald, 1989). It can be concluded that the microorganisms, mainly bacteria and fungi, played an active role in the formation of the examined flowstones.

The amorphic state of the manganese oxide composing the flowstones strongly supports the concept of their microbial origin. The amorphic state of manganese oxides is much more common in deposits of biogenic origin and is regarded as one of the diagnostic criteria of such origin (Raymond *et al.*, 1992).

DIAGENETIC PROCESSES

The irregular shape and sharp outline of some globular bodies (Fig. 7) are probably connected with the process of mineralization, which causes the obliteration of the primary shape of biogenic structures. Early diagenetic processes of this type were clearly recognised in carbonate sediments (Guo & Riding, 1994; Szulc & Smyk, 1994; Verecchia & Verecchia, 1994). The mineralized microbial bodies become centres of calcite crystallization during further diagenesis. Similar phenomena were recorded during the precipitation of manganese oxides in several experiments (Nealson & Ford, 1980; Nealson & Tebo, 1980). Primarily well-defined bacterial bodies become centres of precipitation of manganese oxides in subsequently phases of the experiments. Some irregular lumps of manganese oxides were later formed around the centres. Similar early diagenetic processes probably caused the agglomeration of adjacent filaments as well as the obliteration of filament borders and their related globular bodies in the examined porous microfabric (Fig. 5).

The development of non-porous microfabric in the dome centres can be attributed to the above processes. However, the possibility of late-diagenetic origin of microfabric cannot be excluded. An alternate dissolution and recrystallization can lead to the formation of such a microfabric and can be caused by alternating drying and wetting or weathering of manganese oxides (Dixon & Skinner, 1992). The latter processes caused the corrossion of the flowstone surfaces. The insignificant occurrence of todorockite, which can result from transformation of other manganese oxides (Giovanoli, 1980; Golden *et al.*, 1987, 1992), might have resulted from diagenetic processes as well.

Mn/Fe RATIO

The Mn/Fe ratio distinctly differs in the examinated flowstones and their substrate (Tab. 1). The Mn/Fe ratio in the examined flowstones is higher by a few orders of magnitude than its average value in sedimentary rocks, which ranges from 1:40 to 1:60 (Stanton, 1972). It is worth emphasizing that mangenese oxides are less stable then iron oxides (cf. Marshall, 1979; Skinner & Fitzpatrick, 1992). Consequently, the precipitation of manganese oxides from the solution containing Fe and Mn should be accompanied by a precipitation of iron oxides (Krauskopf, 1957; Stanton, 1972; Ostwald, 1992).

So high Mn/Fe ratio in the examined samples has not been recorded even in deep-sea manganese nodules and crusts, where its average value is about 1:1 (Cronan,1977, tab 2-II; Bolton *et al.*, 1988, tab. 5). A similarly high Mn/Fe ratio has been recorded in the submarine hydrotermal manganese crusts (Bolton *et al.*, 1988, tab. 6) and the manganese sinter aprons of continental hot-springs (Stanton, 1972, tab. 461). Bolton *et al.* (1988 p. 81) connected such a high Mn/Fe ratio in the submarine hydrothermal deposits with "an early precipitation of Fe in the form of silicate, oxide, oxyhydroxide or sulphide before hydrothermal fluids debouched onto the seafloor". This mechanism could not have been applied to the examined flowstones.

The possibility of a potential, selective supply of Mn in the solution caused by selective dissolution is also excluded. This can be proven by the lack of characteristics of selective dissolution of manganese oxide in the substrate. Selective dissolution would be inconsistent with the experiment results which prove that the Mn/Fe of dissolved rocks is similar to that of the obtained solution (Krauskopf, 1957).

The high Mn/Fe ratio in the examined flowstones can be explained by biologically mediated precipitation. The absence of calcite in the examined flowstones suggests an acid enviroment during their formation, the presumed pH level below 7.8. The possibility of selective precipitation of manganese by microorganisms was suggested by Krauskopf (1957), Stanton (1972), Jones and Kahle, (1985) and Ostwald (1992). Moreover, a high Mn/Fe ratio, about 50:1, was recorded in the manganese laminae that occur in the carbonate sediments of Red Sea (Garber *et al.*, 1981). Ehrlich and Zapkin (1985) postulated that manganese oxides from the laminae are of biogenic origin.

DEPOSITIONAL RATE

Hem (1981) calculated the precipitation rate of inorganic manganese oxides to be approximately a few-tenths of a millimeter per million years. The negligible significance of inorganic precipitation of manganese oxides from solution is confirmed by experiment data (Diem & Stumm, 1984). Taking into account the evolution of the Tatra Mts., the examined flowstones are most probably not older than Late Miocene in age. The time of their formation was probably strongly limited by Late Pliocene climatic cooling and Pleistocene glaciations. It can be calculated that the period of potential availability of a manganese bearing solution was not long enough to allow the formation of several-mm-thick flowstone. The precipitation processes of the examined flowstones were most likely much more efficient that known inorganic processes. This strongly suggests biologically mediated precipitation (cf. Ghiorse & Ehrlich, 1992), since these processes are faster by several order of magnitude. Several examples of very fast microbially mediated oxidation of manganese in natural conditions were described. For instance, Marshall (1979) provided several examples of such processes. Their occurrence in hydroelectric pipelines resulted in precipitation of 10-mm-thick layer of manganese oxides which only lasted half a year. Similar annual rate of precipitation of manganese oxides was noted in hot-spring deposits of the Yuno-Taki Springs in Japan, where the precipation processes are accelerated by microbial mediation (Usui & Mita, 1995). Chapnick *et al.* (1982) suggested the influence of microorganisms on precipitation of manganese oxides in Oneida Lake, where the precipitation rate is about 1 mm/y (Dean *et al.*, 1981). Moreover very high rate of microbially mediated precipitation of manganese was, moreover, revealed in several experiments (cf. Nealson & Ford, 1980; Nealson & Tebo, 1980; Mustoe, 1981).

CONCLUSIONS

1. The flowstones from Jaskinia Czarna Cave are made up of amorphic manganese oxides.

2. The flowstones are composed of dome-like structures which are characterized by non-porous microfabric in the dome centres and porous microfabric on the outer parts of the domes as well as in the inter-dome spaces. The porous microfabric is composed of filaments and co-occurring globular bodies.

3. The filaments and globular bodies are of biogenic origin. They are mineralized bodies of bacteria and/or fungi. Similar structures, obtained in some experiments and observed in fossil materials, are described in several publications.

4. Non-porous microfabric in the centre of domes and obliteration of the biogenic structures is caused by diagenetic processess.

5. A very high Mn/Fe ratio in the flowstones indicates a preferencial precipitation of manganese oxides by micoorganisms.

6. The accumulation rate of flowstones is much higher than that known during inorganic precipitation, which suggests a microbially mediated precipitation.

7. A zone of concat between Middle Triassic carbonates and Upper Jurassic - Lower Cretaceous, rich in Mn/Fe, is most probably the source of the Mn.

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Streszczenie

BIOGENICZNE POCHODZENIE POLEW MANGANOWYCH W JASKINI CZARNEJ W TATRACH, KARPATY ZACHODNIE

Michał Gradziński, Michał Banaś & Alfred Uchman

We wschodniej części Jaskini Czarnej stwierdzono występowanie polew zbudowanych ze związków manganu. Polewy mają miąższość od 2 do 20 mm i występują w postaci nieregularnych płatów na ścianach jaskini. Płaty mają rozmiary od kilkunastu centymetrów do kilku decymetrów. Polewy mają korozyjną zewnętrzną powierzchnią. Części polew manganowych są pokryte polewami kalcytowymi o miąższości do 4 mm. Celem badań było określenie genezy polew manganowych.

Występowanie polew manganowych jest związane z kontaktem utworów środkowego triasu i malmo-neokomu widocznym w wielu miejscach we wschodniej części Jaskini Czarnej (Fig. 1). Kontakt ten błędnie uważany za kontakt tektoniczny, ma w rzeczywistości charakter luki stratygraficznej związanej z usunięciem osadów i okresowym brakiem depozycji. Zarówno utwory triasu jak i malmo-neokomu w pobliżu kontaktu są diagenetycznie wzbogacone w tlenki żelaza i manganu. Ograniczone występowanie polew manganowych wskazuje na pochodzeniu budującego je manganu ze strefy kontaktu utworów triasu i malmo-neokomu.

Średnią zawartość głównych pierwiastków w polewach manganowych i ich podłożu przedstawia Tabela 1. Badane polewy są zbudowane głównie z amorficznych tlenków manganu (Fig. 2). Obserwacje w SEM wykazały, że polewy zbudowane są z form kopulowatych o średnicy ok. 100-150 μm (Fig. 3). Centralne części kopuł charakteryzują sie zwartą, a peryferyczne porowatą mikrowięźbą (Fig. 4). Elementami budującymi porowatą mikrowięźbę są nieregularnie zwinięte kłaczki o średnicy do 2 μm (Fig. 5), oraz ciała globularne o owalnych lub okrągłych kształtach i średnicy 0,5 - 3 μm (Fig. 6-8).

Formy analogiczne do opisanych ciał globularnych są w literaturze opisywane jako zmineralizowane ciała bakterii. Są one powszechne przede wszystkim w formie skalcyfikowanej w różnorodnych osadach węglanowych, ale opisano także podobne formy zbudowane z tlenków manganu. Analogiczne struktury otrzymane w wyniku eksperymentalnej mineralizacji ciał bakteryjnych są opisywane w literaturze. Również w wyniku eksperymentów, po inkubacji grzybów na podłożu bogatym w mangan, otrzymano formy o charakterystycznej mikrowięźbie podobnej do występującej w opisywanych polewach manganowych.

Obecność struktur biogenicznego pochodzenia (bakteryjnego i grzybowego) sugeruje czynny udział mikroorganizmów w wytrącaniu tlenków manganu budujących omawiane polewy. Wniosek powyższy potwierdza: (i) amorficzna forma tlenków manganu, która zdecydowanie częściej charakteryzuje utwory biogenicznego niż abiogenicznego pochodzenia, (ii) miąższość polew, która gdyby były one wytrącane wyłącznie na drodze fizykochemicznej świadczyłaby o długotrwałym (rzędu setek tysięcy lat) czasie powstania polew, co jest trudne do przyjęcia, oraz (iii) oraz separacja manganu od żelaza świadcząca o preferencyjnym wytrącaniu manganu (Tab. 1).