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Geochemical Aspect of Chemolithoautotrophic Bacterial Activity in the Role of Black Shale Hosted Mn Mineralization, Jurassic Age, Hungary, Europe

MÁRTA POLGÁRI ^{a,*}, KAZUE TAZAKI ^b, HIROAKI WATANABE ^b, TAMÁS VIGH ^c and ARNOLD GUCSIK ^d

^a Institute for Geochemical Research, Hungarian Academy of Sciences, H-1112, Budapest, Budaörsi str. 45.

^b Department of Earth Sciences, Faculty of Science, Kanazawa University, Kakuma, Kanazawa, Ishikawa 920-1192 Japan

^c Mangán Ltd. ÚRKÚT, H-8409, Hungary

^d Department of Soil Sciences, University of West Hungary, Sopron, Bajcsy-Zsilinszky 4, H-9400 Hungary

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ABSTRACT

The black shale-hosted ÚRKÚT Mn-mineralization is among the 10 largest deposits in the World. In this study optical and electron microscopy demonstrated the biological formation of Mn-Fe minerals in Mn-carbonate ores. The ED-XRF elemental content maps and SEM-EDX observation of the ores showed distribution of Mn, Fe, and Si banded layer structure whereas the Mg, Al, and K are randomly distributed, as well as to explain the role of microorganisms associated with Ca and P. In both samples abundant microorganisms were found in the dark brown and white layers. Optical micrographs of thin sections clearly showed various shapes of cellular materials, such as spherule, oval, and filamentous morphologies. SEM-EDX observation revealed Fe-rich and P-Ca components around microorganisms showing spherule, tubular, and filamentous cells. The present investigation strongly suggests that the Mn-Fe and Si minerals were associated with microorganisms as a biological organic product. The identity of the bacteria responsible for Mn mineral formation is unknown, but is tentatively assigned to Mn and Fe bacteria on the basis of morphology. The genesis of rocks and minerals have played a pivotal role in Toarcian age, and they may even have acted as life genetic system.

Key words: Microbial formation, Mn-Fe minerals, Clays, Black shale, ED-XRF elementary content maps, Electron microscopy

INTRODUCTION

The black shale-hosted Mn-mineralization of Jurassic age at ÚRKÚT is among the 10 largest deposits in the world. The ore reservoir of Mn-carbonate is 80 million tons. Mn contents are about 18 wt% whereas Fe contents are 10 wt%. The Mn-mineralization has been investigated by geological, mineralogical, and geochemical methods¹. On the basis of physical and geochemical studies on characterization of the deposit and contradictions were revealed by negative stable Carbon isotope data which confirmed the bacterially mediated Mn (IV) reduction via organic matter oxidation - Mn oxide proto ore - contra black shale were proceeded. A new interpretation of the ore formation due to microbial activity was suggested². Physical properties like very fine grain size (~1µm), the giant enrichment of metals in the formation through geologically very short period, and enrichments of peculiar elements, (such as Mn, Fe, Si, Mg, S, P, As, Co, Sr) had supported the new theory of biomineralization together with morphological characteristics. The biomineralization was risen up not only in the case of Mn minerals but also in the clay mineralization³. According

to geochemical elemental ratio characteristics, the source of mineralization was considered local hydrothermal vent system, and the effect of elemental enrichment was supposed microbial origin. Nano-scale mineralogical studies of celadonite supported the local hydrothermal origin⁴. Detailed studies made from powder preparations, cannot give information of the signs of formation processes based on textural studies, therefore we needed further micro- and nano-scale investigations of the ore samples.

Life arose on the young Earth as a natural chemical process. More than half a century of experimental research has underscored the dynamic interactions of atmosphere, oceans, and rocks that fostered this ancient transition from geochemistry to biochemistry^{5,6}. Cairns-Smith suggests that clay minerals carry a kind of genetic information in their complex sequences of point defects, layer orientations, and metal cation substitutions. Examples of clay-biochemical interactions of the clay montmorillonite catalyzes the polymerization of RNA from activated ribosome nucleotide and that montmorillonite accelerates the spontaneous conversion of fatty acid micelles into vesicles⁷. The physical and chemical interaction between microorganisms and soils in the ecosystems were discussed⁸. Biomineralization of

kaolinite, nontronite, and bentonite on living cells of microorganism in natural and cultivated systems has been reported^{9,10,11,12}. Bacterial cells can act as a nucleation site for minerals^{13,14}. Similarly, Tashiro and Tazaki¹⁵ showed that the layer of extracellular polymeric substances surrounding microbial cells act as a template in the formation of iron hydroxides. Theng and Orchard⁸ also suggested that multivalent cations might have served as cation bridges in the interaction between clays and microbial extra cellular polymeric substances.

In this study, natural occurrences of Mn-carbonate ores (samples 752 and 755) of Jurassic age, Hungary, Europe were investigated. The samples were observed at micro-meter scales using electron microscopy to confirm the basic role of microbial activity in ore mineralization processes in the natural texture of the samples. Two types of Mn-carbonate ores of samples 752 and 755 were focused to observe cellular-materials because of a large quantity of microorganisms still remained in the banded structure. We also discuss the mechanism of banded Mn-Fe mineral formations and clays around microorganisms. Study of these small-scale "biomineralization" can also contribute to a better understanding of the proposed environments not only in Jurassic age but also in the case of other black shale hosted Mn carbonate mineralizations.

GEOLOGY

ÚRKÚT Mn-mineralization is located in the central Bakony Mountains (Transdanubia), in the North Pannonian unit of the Alps-Carpathians-Pannonian region (Fig. 1).

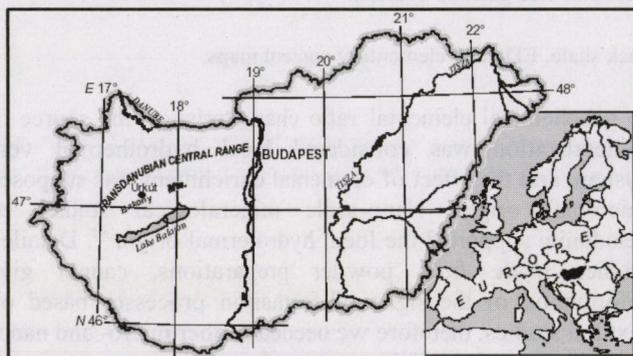


Fig. 1. Locality map of Jurassic Mn deposit in the Transdanubian Range

The deposit is Early Jurassic (Late Lias) and is within marine sedimentary rocks composed mainly of bioclastic limestone, radiolarian clay marlstone and dark-grey to black shale (Fig. 2)¹⁶. The black shale-hosted Mn mineralization occurred in a clayey marlstone (black shale) of Toarcian age in falciferum ammonite zone^{17,18}. The manganese deposits form a NE-SW trending unit of approximately 12 km length and 4-6 km width. Recently, the ore deposit of economic importance covers an area of 8 km².

Manganese mineralization is restricted to two intervals within the 40 m thick marlstone. The lower main bed is about 8-12 m thick and is underlain by 0.5 to 1 m thick clayey-

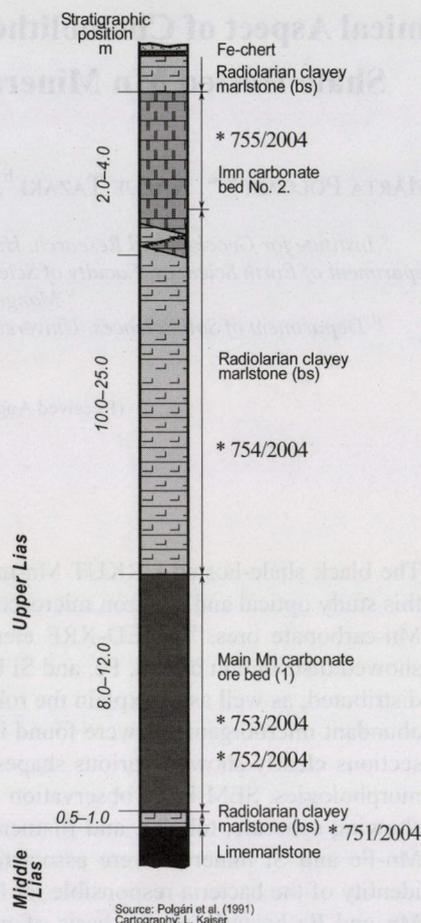


Fig. 2. General profile of the Mn carbonate ore with sample locations (Shaft No. III, +180m).

marlstone; the upper mineral zone, Bed No. 2 or second bed, is 2 to 4 m in thickness and is separated from the main ore bed by 10 to 25 m thick clayey-marlstone (black shale). At the base, the ore sections begin with a thin, greenish, organic-rich, pyritiferous clayey-marlstone containing enrichments of trace elements, namely Co, Ni and Cu in sulphide form, and Sr-bearing barite¹⁶. Concretions of thin layers with phosphate and chert were commonly found at the boundary of the marlstone and the underlying limestone. The rhodochrosite ore was composed of alternating grey, green, brown and black sections with finely laminated structure, very fine-grained clay minerals and the mixtures of carbonate¹⁹. Fine-grained (1-2 μm) rhodochrosite rock lacks coarse detrital clastics^{20,21}.

The mineralogical composition of the Mn-carbonate ore beds are composed of various minerals of rhodochrosite, siderite, 10Å- phyllosilicate (celadonite), smectite (nontronite), goethite, quartz, phos-phorite, pyrite, chlorite (tr), zeolite, feldspar (tr), while the black-shale consists of quartz, calcite, pyrite, smectite, 10Å-phyllosilicate (illite, celadonite), goethite, chlorite, zeolite (tr), and rutile. The main and trace elemental contents were characterized by the enrichment of variable valence and other biological elements such as Mn, Fe, S, P, Si, As, Co, Sr, Ba, Mg, Cu, Zn and REE (Ce). The average of main and trace elements in the ore were summarized in Table 1.

MATERIAL AND METHODS

Rock samples were collected from black shale-hosted Mn deposits at ÚRKÚT Mine formed in Toarcian age. The sample locations are shown in Fig. 2. 752/2004, Main bed (1) Mn carbonate ore (black type, finely laminated, fine grained pink/brown or lor black layered and 755/2004, Second (upper) bed (Bed No. II) Mn carbonate ore (gray type, fine layered, fine grained) samples were studied by XRF Mapping, Optical microscopy, SEM-EDX, TEM and XRD.

Table 1. Some of the average main and trace element contents of the recently analysed ore types (number of samples are in brackets)

Rock types → Elements (w%) ↓	Mn carbonate ore (main bed) Black type	Mn carbonate ore (main bed) Green type	Bed No. II. Grey type	Black shale
Si	8,66 (15)	9,79 (14)	8,21 (10)	21,20 (14)
Al	1,93 (15)	1,24 (14)	1,55 (10)	4,14 (14)
Fe	8,88 (15)	7,94 (14)	13,75 (10)	5,96 (14)
Mn	22,90 (15)	19,38 (14)	12,75 (10)	3,12 (14)
Ca	2,70 (15)	1,71 (14)	7,91 (10)	5,25 (14)
Mg	2,73 (15)	1,25 (14)	1,76 (10)	1,34 (14)
K	1,05 (15)	1,77 (14)	0,73 (10)	1,26 (14)
Na	0,21 (15)	0,17 (14)	0,23 (10)	0,44 (14)
P	0,25 (15)	0,20 (14)	1,18 (10)	0,18 (14)
CO ₂	17,48 (12)	15,80 (14)	22,24 (4)	6,87 (13)
Ba ↓ (ppm)	473 (15)	170 (14)	263 (10)	335 (16)
Sr	131 (15)	93 (14)	608 (10)	265 (16)
Co	269 (15)	217 (14)	141 (10)	131 (16)
Ni	44 (15)	24 (8)	28 (10)	58 (16)
Zn	52 (15)	65 (14)	36 (10)	88 (16)
As	48 (13)	11 (11)	63 (10)	53 (14)
La	46 (14)	47 (13)	46 (10)	39 (14)
Ce	153 (14)	143 (13)	119 (10)	145 (14)
C _{org} (w%)	0	-	0	2,94 (6)

(ICP, AAS, INAA and wet chemical methods were used, for more details see 1,3)

751/2004* black shale under main bed and 753/2004* Main bed (2) Mn carbonate ore (green type, finely laminated, fine grained whitish/green layered) were investigated by XRF Mapping, Optical microscopy and SEM-EDX (*results of the samples were used but not discussed in detail).

A low-vacuum scanning electron microscope (LV-SEM, JEOL JSM-5200LV) equipped with an energy dispersive X-ray (EDX) spectrometer (Philips EDAX PV9800EX) was used to observe the micro morphology and its chemical composition.

Mineralogical investigations of clays and ore were performed by X-ray powder diffraction (XRD). A Rigaku Rinto 1200 X-ray diffractometer (CuK α radiation) operating at 40 kV and 30 mA, and a scanning speed of 1 - 20 sec./0.02 degree, was used. Chemical investigations of the samples were carried out by X-ray fluorescence using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray fluorescence detector (ED-XRF, JEOL JSX-3201; Rh-K α -ray).

The rock samples were cut in half and polished surface for optical microscopy and elemental content mapping. The analyses were carried out by an ED-XRF with equipment for X-ray probe scanning system (JEOL JSX-3600), using Rh K α , which operated at an accelerating voltage of 30 kV under the vacuum condition.

RESULTS

Sample 752 (Mn carbonate ore, dark brown: main ore bed)
The Mn carbonate ore was collected from main ore bed which banded layer structure is dark brown in color (Fig. 3). The ED-XRF elemental content maps of the sample 752 showed Mn and Fe elements were concentrated in dark brown layers whereas Si and Al elements were randomly distributed. The traces of Ca and P elements were also located in light brown layers suggesting microorganisms present. The Mn contents correlated closely with the concentration of Fe, Ca, and P elements.

The optical microscopic observation of the sample 752 showed abundant microorganisms presented in brownish and white brown layered structures (Fig.4). The micromorphology of the microbes showed spherical, elliptical, and filamentous shapes in white lens and layers.

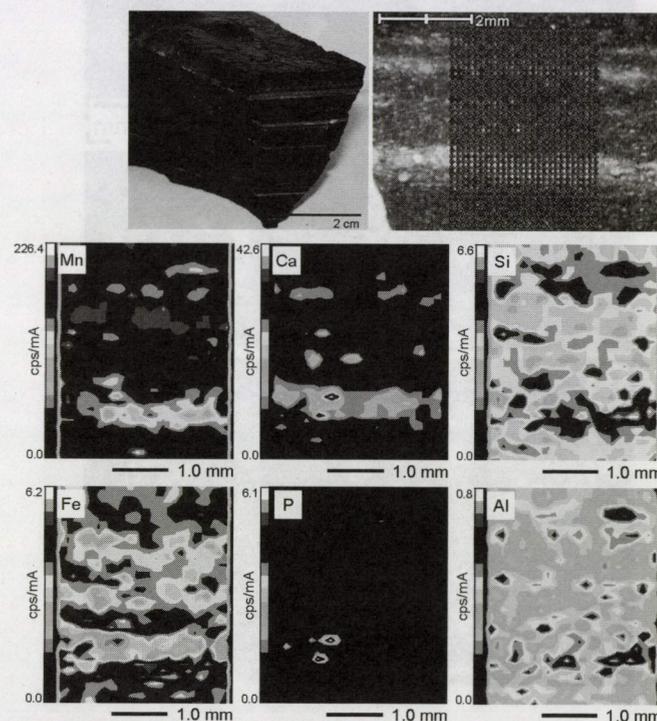


Fig. 3. ED-XRF elemental mapping of Mn-carbonate ores of sample 752 showing Mn and Fe banded layer structures whereas Si and Al elements are randomly distributed.

The scanning electron microscopy of sample 752 revealed small microbes in the flaky materials which were difficultly found, because of covering materials (Fig. 5 arrows). The EDX analyses of covering materials on the microorganisms indicated that the flaky materials are the mostly Mn-rich components with Si, Ca and little amount of Fe contents (Fig.

5, A-1). The spherical forms are much more Ca rich with lower Mn, Fe, and Si contents (Fig. 5, A-2). The tubular microorganisms are Si and Mn rich associated with Ca and smaller amounts of Mg, Al and P (Fig. 5, B-2, C-1). The angular materials composed of mainly Mn suggesting Mn-minerals of rhodochrosite and manganite which were identified by XRD method (Fig. 5, C-2).

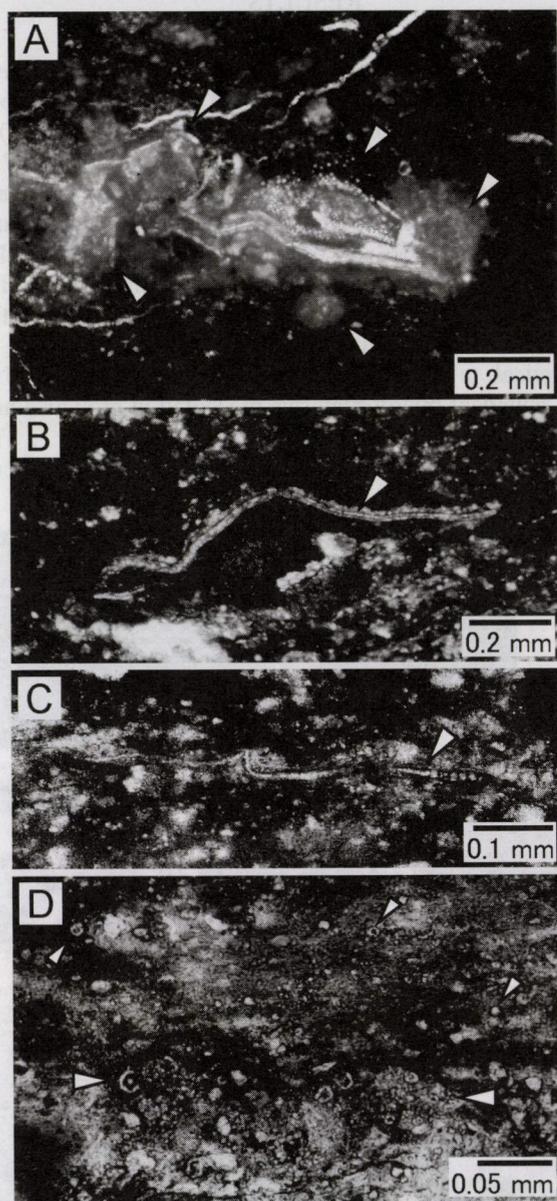


Fig. 4. OM observation of Mn-carbonate ores of sample 752 showing abundant microorganisms (arrows).

TEM micrographs showed abundant bacterial cells changed to graphite crystalline materials (0.31-1 nm, Fig. 6).

In brown layers, smectite, rhodochrosite MnCO_3 , manganite MnO(OH) , goethite, and calcite were identified by XRD analyses. The peak at 15.3 Å has shifted to 17.1 Å which conform to smectite minerals showing expandable sample 752 by using EG treatment. In white layer smectite,

rhodochrosite, and calcite were determined. The most of XRD mineralogical data were agreed with TEM micro

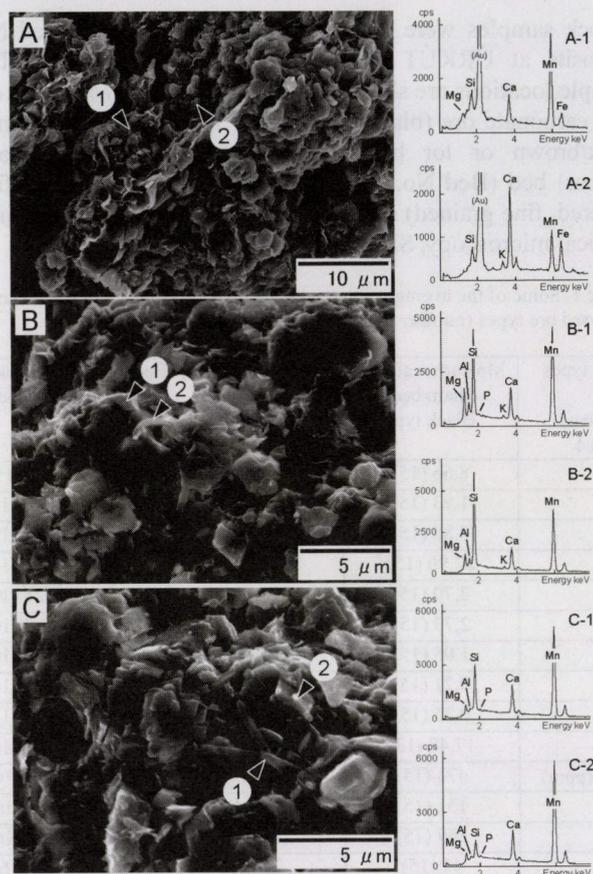


Fig. 5. SE micrographs of Mn-carbonate ores of sample 752 showing small sized microorganisms (arrows). The energy dispersive electron micrographs of flaky materials are rich in Mn.

morphology. But, flaky graphite could not be detected by XRD, because its amount was under detected limit.

Sample 755 (Mn carbonate ore, brownish gray: 2nd ore bed)

The ED-XRF elemental content mapping showed high Fe distribution in almost all layered structures (Fig. 7). The Mn element distributed in darker brownish gray layers whereas high Si contents located in lighter parts. The small amounts of Al, P, and Ti elements were found in darker layers.

The optical micrographs of sample 755 showed spherical microorganisms were lining-up in the banded structures (Fig. 8). Framboidal pyrite crystals were found under refraction image. The filamentous materials were placed parallel to the banded layers.

The scanning electron micrographs of sample 755 revealed presence of various smaller microorganisms, such as filamentous, spherical, tubular, and ribbon typed bacteria (Fig. 9 arrows). The EDX analyses of fragments are rich in Ca and Mn elements with high background of organics (Fig. 9, A-1) whereas needle-like materials are P and Ca rich with low background of inorganics (Fig. 9, A-2). Thin filmy materials covering on the surface contained mainly Si element with low background of organics (Fig. 9, B-1 and B-2).

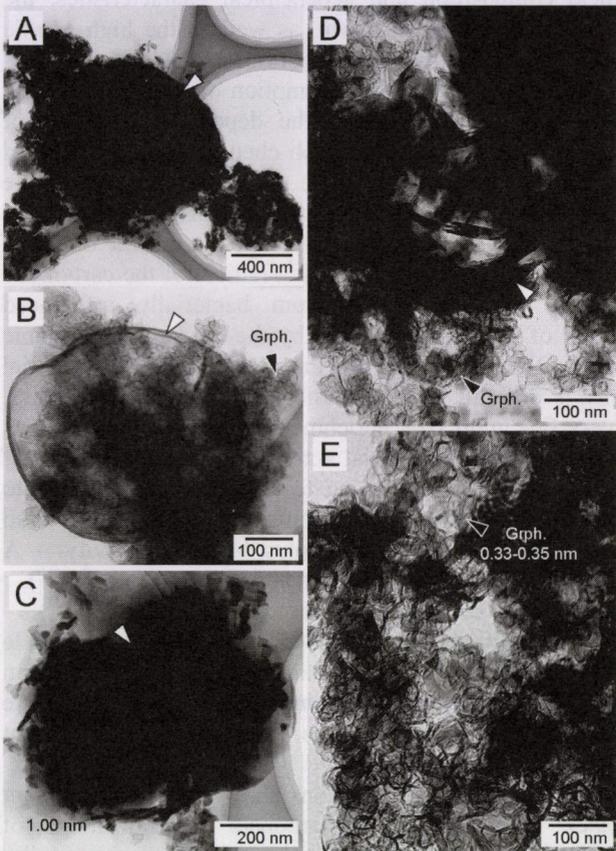


Fig. 6. TEM micrographs of sample 752 show abundance of nm- sized bacteria. Most bacterial materials were replaced by graphite (black arrowheads labeled "Grph" are Graphite) and other minerals (white arrowheads: bacteria, bacteria encrusted with minerals). E shows graphite.(0.33-0.35 nm lattice dimension). 1.00-1.10 nm lattice dimension shows clay minerals.

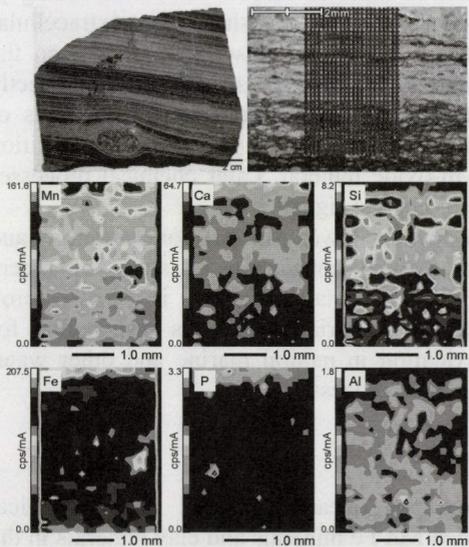


Fig. 7. ED XRF elemental mapping of Mn-carbonate ores of sample 755 showing high Fe distributed in all banded layer structures whereas Mn and Si elements are located in darker gray layers

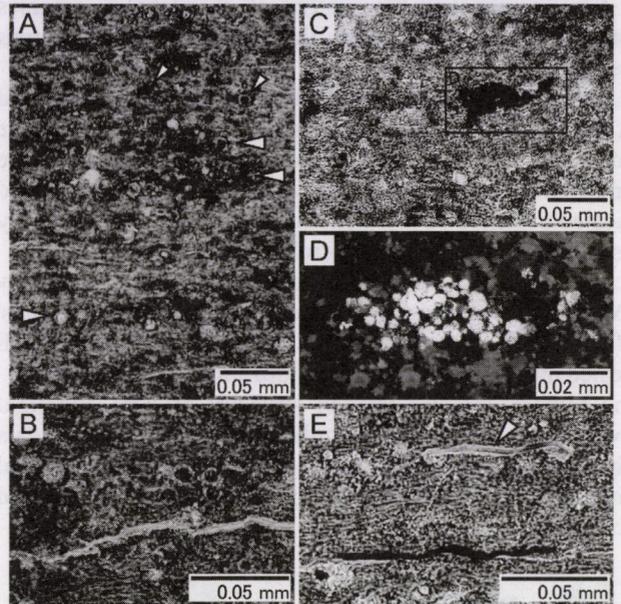


Fig. 8. OM microscopic observation of Mn-carbonate ores of sample 755 showing abundant microorganisms. Framboidal pyrite is located in certain layers under refraction image.

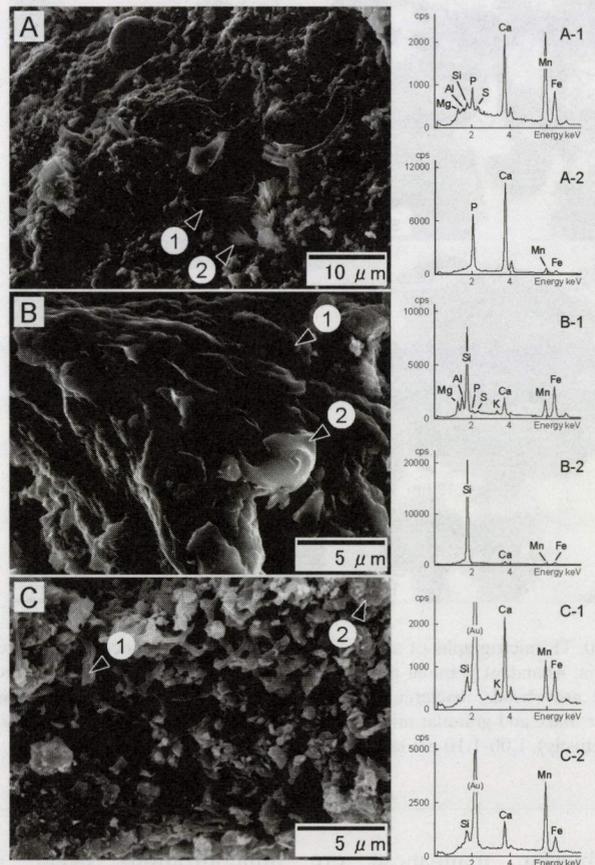


Fig. 9. SE micrographs of sample 755 showing some bacterial cell walls, thin films, and filamentous bacteria (arrows). Energy dispersive X-ray analyses of microorganisms indicated Mn-, Ca- and Fe-rich composition.

Filamentous materials composed of large amount of Ca with Mn-Fe elements and high background of organics (Fig. 9, C-1). For comparison, the matrix of the tubular organics contained higher Mn content than that of the filamentous ones (Fig. 9, C-2).

In general the EDX spectra of microorganisms indicated that the most abundant elements were Si, Ca, Mn, and Fe associated with high background suggesting the biomineralization around cells, whereas the low background indicated presence of inorganic minerals. SEM revealed only presence of 1-10 μm - sized microbes in Figs. 5 and 9.

Bacteria were very small sized and very hard to observe by SEM, because of Mn-Fe, Si, and Ca minerals on the cells' surfaces. Therefore we needed TEM observation which revealed nm- sized bacterial mineralization (Figs. 6 and 10).

The sample 755 has layered structure of dark and light brownish gray in color. According to XRD analytical data both of the layers showed almost the same mineralogical composition, such as rhodochrosite, chlorite, apatite, and calcite.

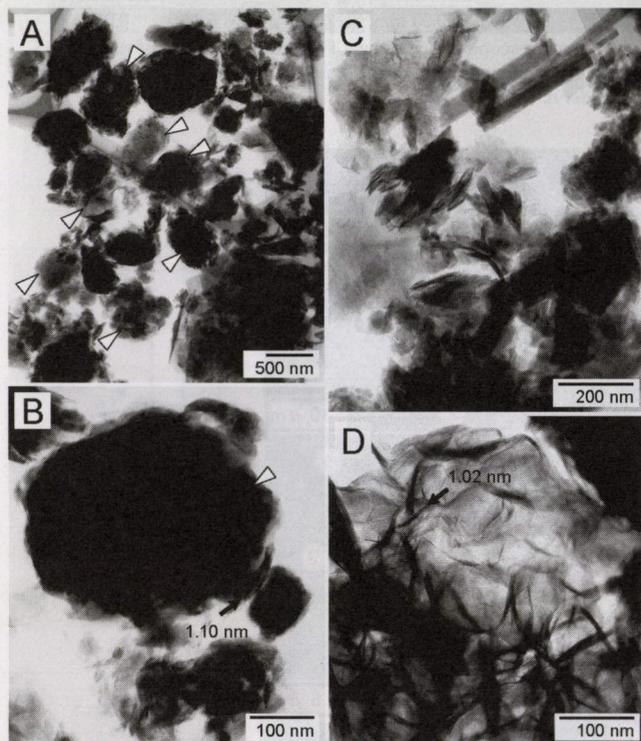


Fig. 10. TE micrographs of sample 755 show abundance of nm- sized bacteria. Abundant granular minerals were observed with bacterial materials (white arrowheads: bacteria, bacteria encrusted with minerals). C shows tubular, flake and granular minerals (apatite, clay minerals and rhodochrosite, respectively). 1.00-1.10 nm lattice dimension shows clay minerals.

DISCUSSION

Carbonatic manganese ore mineralizations occur in environments rich in organics (black shale, biogenic pyrite, etc) and are of laminitic texture. It has established that their chemical composition is characterized by the enrichment of biophilic elements (Mn, Fe, Mg, Sr, S, and P, As, Co, Ni, and

Ce, U) and very small grain size ($\sim 1 \mu\text{m}$). Evidences of the chemical composition and geochemical characteristics, the joint occurrence of Fe and Mn, as well as the high Mn/Fe ratio, the local selective enrichment of P, Sr, Mg, As, Si, and Ce are in harmony with the assumption of bacterial activity. According to the features of the deposit, two cycles of bacterial activity- a primary aerob chemolithoautotrophic and an anaerob bacterial cycle - are supposed to influence the mineralization. The anaerobe system overprinted the primary one, in the frame of which is proved by the organic origin of the carbon contained in the (CO_3^{2-}) radical of the carbonatic manganese ore, originating from bacterially influenced reduction of Mn^{4+} accompanied by the oxidation of organic matter²²). The separation of the two cycles of bacterial activity is difficult, or not possible as some characteristics, like very fine grain size, enrichment of bioessential elements are characteristic of bacterial activity in general. In spite of these difficulties the following features can be attributed to the primary aerobe Mn^{2+} oxidation and sinking the metals to sediments by chemolithoautotrophic bacterial activity: - A huge mass of material was formed at a high rate ($\times 10^5$ - 10^6).

High N/C ratio (Sajgó personal communication, 2003,²³).

- Geochemically the high Mg content of the black shale hosted Mn-carbonate mineralizations can be suggested as an evidence of primary aerobe chemolithoautotrophic signature in formation of giant deposits, on the basis of recent analogies^{3,24}.

Previous chemical investigations showed high Mg content of black shale hosted Mn-carbonate mineralizations of ÚRKÚT (2,5-8 w% MgO ,^{25,26,27}) as well as for similar deposits, for Molango²⁷, and Chinese deposits²⁸.

Mn-oxides and manganates are formed by both chemical and bacterial oxidation from Mn(II) in variegated water systems but recent analogies support that bacterial activity is the most important in most of cases^{29,30,31,32}). According to detailed experimental studies it was shown that extracellular polymers of bacteria catalyze the adsorption of Mg on the surface of the cells. So the bacterial spores not only directly oxidize Mn(II) to Mn(IV) but in the very early stages of oxidation bacterial activity influence the cation composition of the forming Mn-oxide mineral. Later chemical processes start to erase the biological signal³⁴

Bacterial activity favours lower Mn (II) concentrations and temperatures. As a final conclusion of study of recent analogies and experimental studies is that aerob chemolithoautotrophic bacterial activity is responsible for direct Mn (II) oxidation in natural marine and other water environments as a main process.

CONCLUSION

Electron micrographs clearly showed the biological formation of banded Mn-Fe minerals and clay minerals in the Mn-carbonate ore in Jurassic age, Hungary, Europe. The chemical analysis of the Mn-carbonate ore showed Mn, Fe, and Si, Al as the major elemental composition. X-ray diffraction, ED-XRF, and SEM-EDX analytical methods used in this study suggested new ordered Mn-, Fe-, and clay

mineralization. This shows that microbial activity may play a significant role in the Mn-Fe carbonate ore, and that this may be a common occurrence in Jurassic. It is likely that the Mn-Fe banded minerals and clay minerals associated with microorganisms are the bioorganic product of microbial activity. The banded Mn-Fe minerals formation in the ore beds may be substantially enhanced by the presence of microorganisms.

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REFERENCES

- 1) Polgári, M., Szabó, Z. and Szederkényi, T. (Eds.), (2000). Manganese Ores in Hungary, Szeged, Juhász Publish House, Szeged, Hungary, pp. 675.
- 2) Polgári, M., Szabó-Drubina, M., Szabó, Z. (2004) *Bull. of Geosciences*, Czech Geological Survey. **79/1**, 53-61.
- 3) Polgári M., Szabó-Drubina M., Szabó Z., Abonyi Tóth Zs., Vigh T. (2005) submitted to *Mineralium Deposita*
- 4) Weiszburg T.G., Tóth E., Beran A. (2004) *Acta Miner. Petr. Szeged*, **45/1**, 65-80.
- 5) Hazen, R.M. (2005) *Elements*, **1**, 135-137.
- 6) Nisbet, E. G., Fowler, C. M. R. (1996) MacLeod, C. J., Tyler, P. A., Walker, C. J. (eds) *Geol. Soc. Spec. Publ.* **118**, 239-251.
- 7) Hanczyc, M.M., Fujikawa, S.M., and Szostak, J.W. (2003) *Science*, October 24, **302**, 618-622.
- 8) Theng, B.K.G and Orchard, V.A. (1995) Environmental impact of soil component interactions, P.M. Huang, J. Berthelin, J.M. Bollag, W.B. McGill and A.L. Page (eds.), CRC press, Florida, **3**, 123-139.
- 9) Tazaki, K. (1997) *Clays and Clay Minerals*, **45**, 203-212.
- 10) Ueshima, U., Mogi, K. and Tazaki, K. (2000) *Clay Science Japan*, **39**, 171-183.
- 11) Asada, R. and Tazaki, K. (2000) *Clay Science Japan*, **40**, 24-37.
- 12) Tazaki, K. (2000) *Clays and Clay Minerals*, **48**, 511-520.
- 13) Ferris, F.G., Beveridge, T.G and Fyfe, W.S. (1986) *Nature*, **320**, 609-611.
- 14) Sara, M. and Sleytr, U.B. (2000) *J. of Bacteriology*, **182**, 859-868.
- 15) Tashiro, Y. and Tazaki, K. (1999) *Earth Science*, **53**, 27-35.
- 16) Polgári, M. (1993) Manganese geochemistry reflected by black shale formation and diagenetic processes - Model of formation of the carbonatic manganese ore of ÚRKÚT, Special series of Hungarian Geological Institute, 211 (Karpati Publish House, Ushgorod, pp. 211.
- 17) Géczy B. (1972) *Ann. Univ. Sci. R. Eötvös (Budapest). Sect. Geol.*, **16**, 99-114.
- 18) Szabó, Z., Grasselly, Gy., Cseh Németh, J. (1981) *Chem. Geol.* **34**, 19-29.
- 19) Cseh Németh J. and Grasselly Gy. (1966) *Acta Miner. Petr. Univ. Szegediensis*, **17**, 2, 89-114.
- 20) Szabóné Drubina, M. (1959) *Econ. Geol.*, **54**, 1078-1093.
- 21) Polgári, M., Philippe, M., Szabó-Drubina, M., Tóth M. (2005) *N. Jb. Geol. Paläont. Mh.*, **3**, 175-192.
- 22) Polgári, M., Okita, P. M., Hein, J. R. (1991): Stable Isotope Evidence for the Origin of the ÚRKÚT Manganese Ore Deposit, Hungary. *Journal of Sedimentary Petrology*, **61/3**, 384-393.
- 23) Meyers P, Stefano B. (2004) 32th International Geological Congress, Florence, Italy, 20-28 August, 2004, Abstracts I., 753.
- 24) Mandernack, K. W., Post, J., Tebo, B. M. (1995) *Geochim. et Cosmochim. Acta.* **59**, 4393-4408.
- 25) Szabó, Z. and Grasselly, Gy., (1980). In: Varentsov, I.M. and Grasselly, Gy. (eds): *Geology and Geochemistry of Manganese*, **2**, Akadémiai Kiadó, Budapest, 223-236.
- 26) Vető, I. (1998) Abstract, 15th International Sedimentological Congress, Alicante, 1998, 796-797.
- 27) Lantos, Z., Vető, I., Földvári, M., Kovács-Pálffy, P. (2003) *Acta Geologica Hungarica.* **46/4**. 321-340.
- 28) Hein, J. R., Fan, D. L. (1999) *Ore Geology Reviews.* **15/1-3**.
- 29) Emerson, S, Kalthorn, S, Jacobs, L, Tebo, B. M, Nealson, K. H, Rosson, R. A. (1982) *Geochimica et Cosmochimica Acta.* **46/6**, 1073-1079.
- 30) Tebo, B. M, Nealson, K. H, Emerson, S, Jacobs, L. (1984) *Limnology and Oceanography.* **29/6**, 1247-1258.
- 31) Nealson, K. H., Tebo, B. M., Rosson, R. A. (1988) *Advances in Applied Microbiology.* **33**, 279-318.
- 32) Tebo, B. M. (1991) *Oceanographic Research Papers*, **38**: S883-S905 Suppl. 2.
- 33) Tebo, B. M, Nealson, K. H, Rosson, R. A. (1988) *Advances in Applied Microbiology.* **33**, 279-318.