Theoretical model for Jurassic manganese mineralization in Central Europe, Úrkút, Hungary

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Abstract. The Transdanubian Range hosts a series of Mn carbonate, and cherty Fe- and Sr-rich Mn oxide mineralizations associated with varicoloured metalliferous clays near fracture zones of a N-NW–S-SE direction along the NE-SW trending mountain range. The Mn oxide deposits occur along the margins of black shale-hosted Mn carbonate mineralizations formed by bacterially mediated diagenetic processes.

Here we show a provisional model of the ore formation of the shale-hosted Mn carbonate deposits. According to this model, the role of prokaryotic bacteria in obtaining elements from solutions is of particular importance. Some, if not all, shale-hosted Mn carbonate deposits are of a biogenic sedimentary origin, such as the "Mn ore stromatolites" for which a hydrothermal/exhalative source for the metals has been demonstrated. Though the function of bacteria is not visible in these masked systems, it nonetheless completely changes the primary characteristics of the inorganic system. The deposits considered in this study can be explained as the remnants of a protorift or failed rift system that formed within submerged continental crust.

Key words: bacterial, hydrothermal, manganese, black shale, Jurassic, Europe

Introduction

The investigation of sediment-hosted manganese mineralizations has been carried out within the framework of six international research projects during the past two decades (Table 1).

The Jurassic Úrkút manganese deposit has been the subject of extensive mineralogical, geochemical, stable isotope, and organic geochemical studies, as summarized in Polgári et al. (eds) 2000.

Several attempts have been made to explain the complex formation of the Jurassic black shale-hosted Mn ore mineralization at Úrkút (Fig. 1) since 1917, when the mining of this deposit began (Cseh Németh and Grasselly 1966, Cseh Németh et al. 1971, 1980, Konda 1970, Szabó and Grasselly 1980, Szabó et al. 1981, Varentsov et al. 1988, Polgári et al. 1991, Polgári 1993, 2001, Polgári et al. 2000).

Past research has shown the relation of the ore deposit to the Toarcian anoxic oceanic event, as well as the role of upwelling marine currents, the remarkable amount of organic matter that accumulated due to algal booms on the shelf areas, and the concentration of Mn in the basin (for a summary see Polgári et al. 2000). A stable isotope study has shown that the reduction of Mn^{4+} during diagenesis resulted in the decomposition of organic matter (Polgári et al. 1991). Such processes have markedly altered the original features of the formation.

The formative conditions of the Mn carbonate ore have been recently explained as the derivation of Mn from distant hydrothermal centers. The Mn was subsequently transported by oxygen-poor water in the course of the oceanic anoxic event, and by precipitation and accumulation at redox interfaces (Polgári et al. 1991, Polgári 1993). The derivation of the clay material has proven to be problematic, as a terrestrial source could not be conclusively argued for on the basis of the clay's mineralogy and chemical composition (Al depletion and shortage of kaolinite). The Liassic clays of Úrkút are partly comprised of greenclays, celadonite, and nontronite of authigenic origin (Kaeding et al. 1983, Varentsov et al. 1988). The recent studies of Weiszburg and co-authors have shown the syngenetic mineralization of celadonite from solutions (see Mizák et al. 2000, Tóth et al. 2001).

The purpose of this paper is to give a tentative model for the interpretation of the Mn mineralization of the Jurassic Úrkút deposit.

Geological setting

The Transdanubian Range of Hungary is an important region of Jurassic black shale-hosted Mn mineralization. Úrkút is located in the central part of the Bakony Mountains,

Table 1. IGCP projects on sedimentary manganese mineralizations

Project No.	Duration	Title
111	1980–1985	Genesis of Manganese Ore Deposits
226	1986–1991	Correlation of Manganese Sedimentation to Paleoenvironments
254	l987–1992	Metalliferous Black Shales
318	1992–1996	Genesis and Correlation of Marine Polymetallic Oxides
357	1993–1997	Organics and Mineral Deposits
429	1998–2002	Organics in Major Environmental Issues

which belong to the North Pannonian unit of the Alpine-Carpathian-Pannonian region (see Fig. 1).

The largest Mn mineralizations occur in the Úrkút basin and at Eplény, which were formed by the NW-SE trending block faulting that characterized the Late Triassic and Jurassic tectonics of this region (Fig.1). The deposits are Early Jurassic (Late Liassic) in age, and occur within marine sedimentary rocks composed mainly of bioclastic limestone, radiolarian clay marlstone, and dark grey to black shale (Polgári 1993). Similar mineralizations of a smaller scale occur parallel to the largest ones along the fault zones. The Mn mineralization appears in two units.

The primary, cherty, Fe-rich and Sr-bearing Mn oxide mineralization occurs in varicoloured metalliferous clays on strongly dissolved limestone footwalls, in the form of blocks, nodules, and wad beds. It is in close proximity to fracture zones of a N-NW–S-SE direction along the NE-SW mountain trend (Úrkút-Csárdahegy and Eplény).

The thickness of this ore deposit is 6–8 m. Sedimentary dikes filled with red lime mud, varicoloured (red, green, brown) clays, carbonate debris, or Mn oxide are commonly associated with these ores.

These Sr-rich Mn deposits comprise the marginal parts of the black shale-hosted Mn carbonate mineralization, which was formed by bacterially mediated diagenetic processes (Polgári et al. 1991, Polgári 1993).

The black shale-hosted Mn mineralization occurs in a clayey marlstone (black shale) of Toarcian age (Falciferum ammonite zone, Géczy 1972). The marlstone rests conformably on Middle Liassic carbonate rocks that formed at the center of the depositional basin (Fig. 2). The marlstone is about 40 m thick in the middle, but thins out towards the basin margins (Szabó et al. 1981). The Mn deposits form a NE-SW trending unit, approximately 12 km in length and 4–6 km wide. The ore deposit of economic importance covers an area of 8 km^2.

The Mn mineralization is restricted to two intervals within the marlstone (Fig. 3). The lower main bed is about 8–12 m thick and is underlain by 0.5 to 1 m thick clayey marlstone. The upper mineralized zone, Bed No. 2, is 2 to 4 m in thickness and is separated from the main ore bed by a 10 to 25 m thick clayey marlstone. At the base the ore sections begin with a thin, greenish, organic-rich, pyritiferous clayey marlstone, containing enrichments in trace elements such as Co, Ni, and Cu in sulfide form, and Sr-bearing barite (Polgári 1993). Concretions and thin layers of phosphate and chert are common at the boundary of the marlstone and the underlying limestone. A rhodochrosite ore section is composed of alternating grey, green, brown, and black sections of finely laminated, very fine-grained clay mineral and carbonate mixtures (Cseh Németh and Grasselly 1966). The fine-grained (1–2 μm) rhodochrosite rock lacks coarse detrital clastics (Szabó-Drubina 1959). The formation is micro laminated lenticular, microlenticular, or microstratified detrital. Microlaminae are $1.5 \cdot 10^{-5}$ m thick. Fossils occur only rarely as fish remnants and as silicified, manganized, or carbonized plant fragments.

Results

Mineralogy

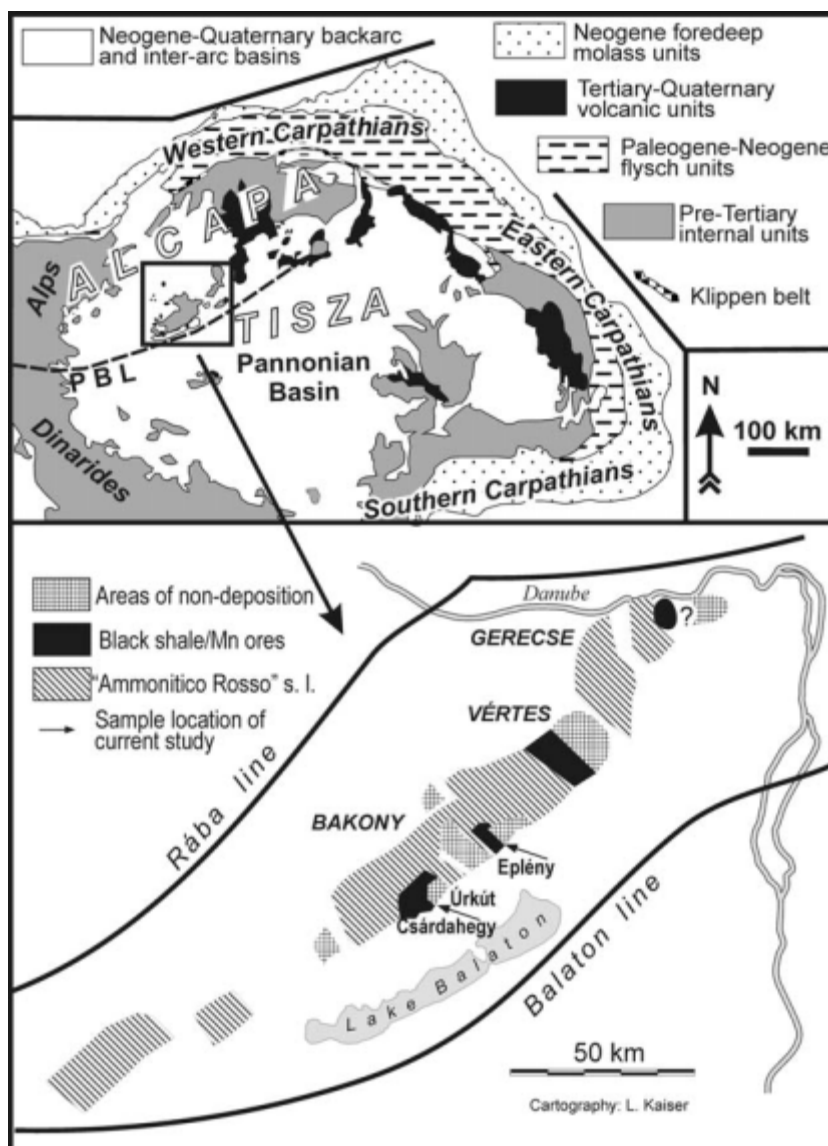The Mn oxide ore consists of hollandite, pyrolusite, cryptomelane, todorokite, and manganite.

Figure 1. Location of the Jurassic Mn mineralizations of Hungary (Early Toarcian paleogeographical sketch map is after Vörös and Galácz 1998, slighly modified).
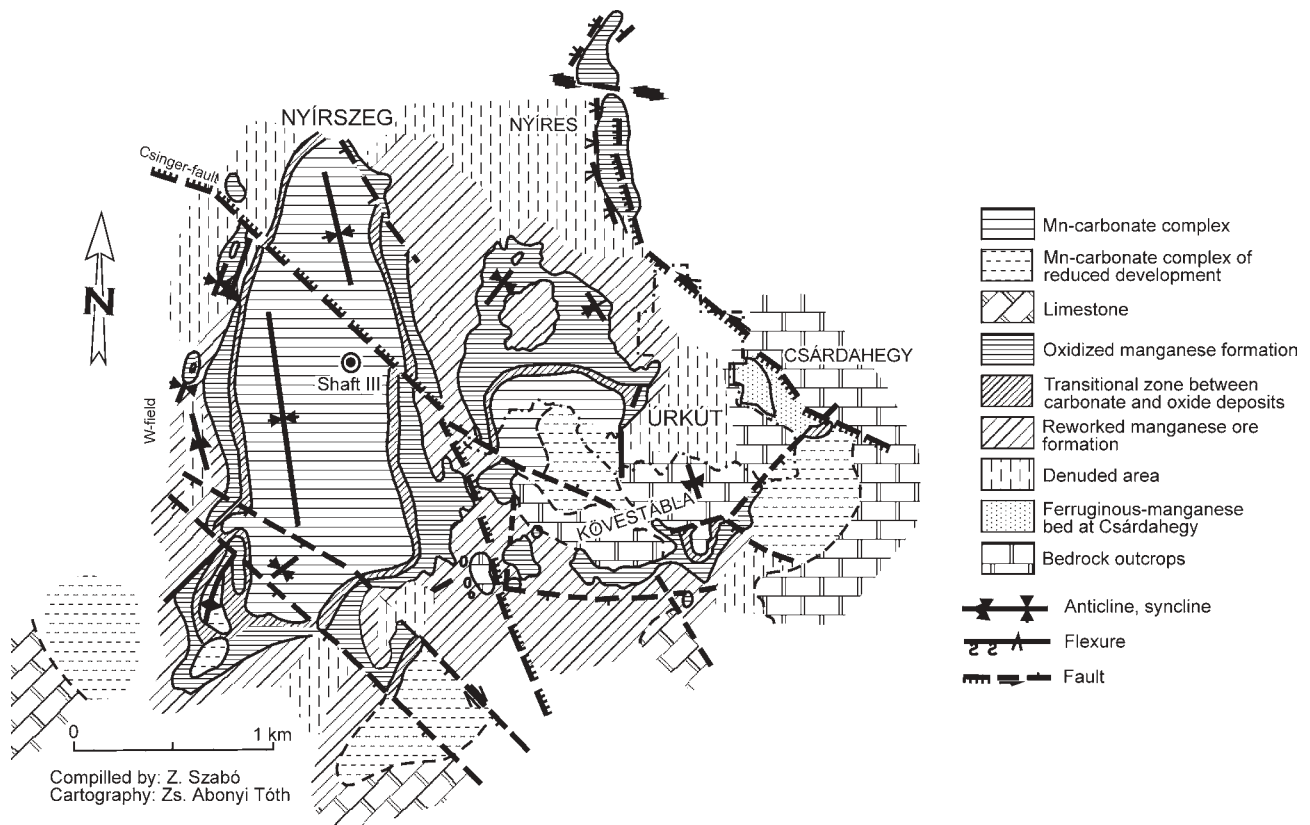
Figure 2. Geological sketch map of the Úrkút manganese mineralization.

The Mn carbonate ore beds are composed of the minerals rhodochrosite, siderite, 10Å-phyllosilicate (celadonite), smectite (nontronite), goethite, quartz, phosphorite, pyrite, chlorite (traces), zeolite, and feldspar (tr), while the black shale consists of quartz, calcite, pyrite, smectite, 10Å-phyllosilicate (illite, celadonite), goethite, chlorite, zeolite (tr), and rutile.

Chemistry

The Mn oxide ore may be chemically characterized as an inhomogeneous, ferruginous, and siliceous. The samples are amorphous to very fine-grained, and are thus not able to be separated by physical methods. The SiO_2, Fe, and Mn contents are determined by the dominant phase of a given sample. The Fe content varies on a broad scale (3.87–20.60 wt.%), as does the SiO_2 (1.69–46.30 wt.%). Smaller amounts of CaO indicate the carbonate content of the samples. The K_2O content appears in cryptomelane, and some phillosilicate (Al_2O_3) also occurs. Compositional data plotted on a Bonatti et al. (1972) ternary diagram (Fe-Mn-/Co+Ni+Cu/*10) shows that all the samples fall within the hydrothermal field. Toth (1980) suggested hydrothermal/diagenetic fields, and on the basis of our interpretation we suggest the hydrothermal/diagenetic/biogenic field nominations. The trace element ratios also suggest a hydrothermal origin for this formation (Polgári et al. 2003).

The Sr content goes up to 1.36 wt%, and that of Ba up to 0.9 wt%. Mn and Sr correlate positively, mainly in the high Mn-bearing samples (r: 0.67) characterized by hollandite-type mineralogy. Low amounts of terrigenous constituents (Al_2O_3/TiO_2) also correlate positively (r: 0.84). Neither Fe and Sr, nor Al_2O_3 and MnO_2, vary systematically. The levels of Co found in the current study are within the range typical of hydrothermal deposits (i.e. < 300 ppm). Some samples are Fe-rich, while others are Mn-rich, the fractionation of the two elements being strong (0.47–13.11).

The geochemical features of the Mn carbonate ore are characterized in detail in Polgári (1993), and in Polgári et al. (2000).

The main and trace element content is characterized by the enrichment of variable valence and other biophile elements, such as Mn, Fe, S, P, Si, As, Co, Sr, Ba, Mg, Cu, Zn, and REE (Ce).

Interpretation and discussion

In summarizing our knowledge concerning the source of the Mn, it can be stated that the source cannot be assigned to terrestrial weathering and fluvial transport, as neither the Jurassic limestone nor the crystalline basement has provided the material of the ore deposits.

Based on the available mineralogical and geochemical data from studies utilizing stable C and O isotopes, SEM, EPMA, and the examination of thin sections, two Mn-sources must be considered for the Upper Liassic manganese reservoir of the Bakony Mountains:

55

Stratigraphic
position
m

Radiolarian clayey
marlstone (bs)

2.0–4.0

Mn carbonate
bed No. 2

Upper Liassic

10.0–25.0

Radiolarian
clayey marlstone
(black shale)

8.0–12.0

Main Mn
carbonate
ore bed No. 1

0.5–1.0

Radiolarian clayey
marlstone (bs)
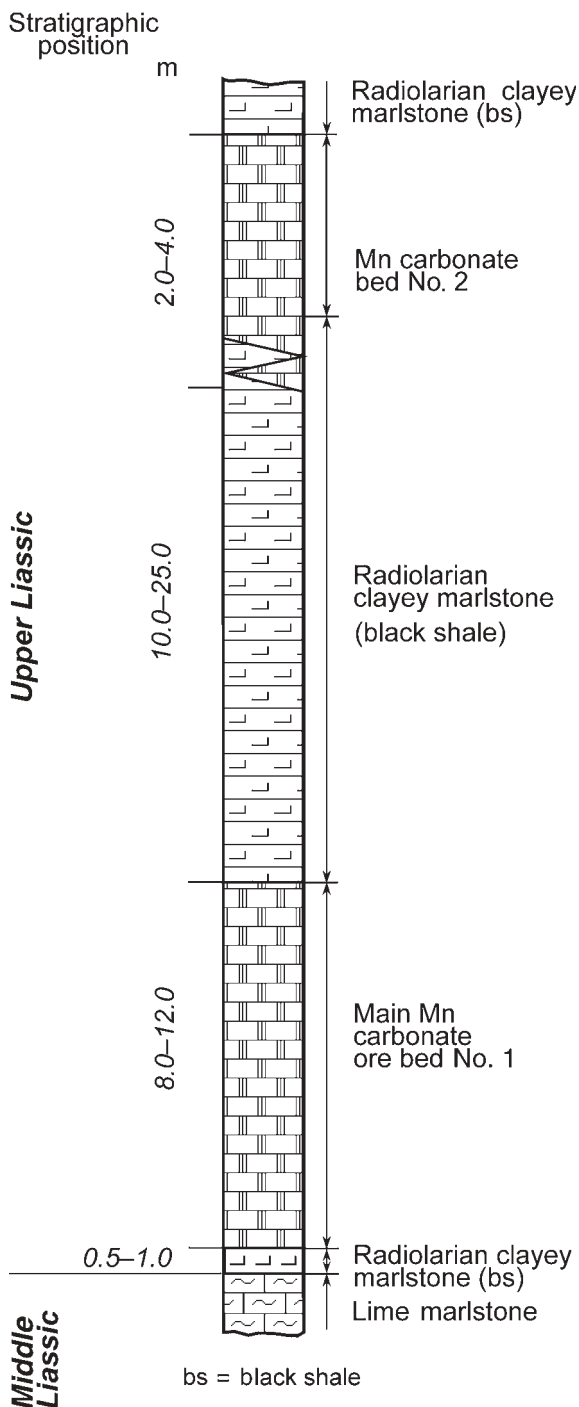
Lime marlstone

*Middle
Liassic*

bs = black shale

Figure 3. Idealized section of Mn carbonate ore mineralization.

1. The local, deep fault system that can be bound to Liassic rifting in the central axis of the Transdanubian Range.

2. Outlying Toarcian volcanism.

The brown, ferrous, authigenic precipitations are essentially characteristic of volcanic and hydrothermal (exhalation) sediments. In the vicinity of the Mn mineralization, the signs of its endogenous origins are apparent; these include the strong dissolution of the footwall limestone, and the presence of sedimentary dikes and fissure zones. The mineralization was guided by structural features.

The close connection of the mineralized localities, with the footwall characterized by strong alteration, suggest local endogenous sources for the mineralization instead of distant hydrothermal process with material transported by a megaplume.

Some contribution of volcanic material (tuff) to the clay content of the ore horizon can be assumed to have been partly weathered in the seawater and then completely altered during diagenesis (Polgári 2001). The considerable smectite and smaller zeolite contents of the clays could have originated from this volcanic material.

The analytical results from investigations of the Mn-rich formations allow us to explain the diagenetic processes quite well. However, the interpretation of the genetic processes of the sediment-hosted Mn mineralizations has remained unclear, as attempts to harmonize the structural, textural, mineralogical, chemical, and isotopic characteristics have not led to unequivocal results.

On the other hand, the current development of research methods in the field of microbial geochemistry has allowed the investigation of recently active biogeochemical systems, which have produced relevant results (Jannash and Wirsen 1981, Cowen et al. 1986, Mandernack and Tebo 1993, Mandernack et al. 1995, Moffett and Ho 1996). Biomineralization studies of the so-called bioindicator minerals (Fe oxide, Mn oxide, pyrite, phosphorite, etc.; Skinner 1993) have clarified the biologic relationships of many elements that occur in mineralized environments. Furthermore, recent laboratory experiments have given significant results concerning the interaction between microbal metabolism and these elements.

Publications that emphasizing the inorganic approach utilize results from both organic and inorganic interactions. Though they tend to summarize the resulting processes as being characteristic of inorganic processes, they frequently refer to the importance of biological activity. In most cases the authors consider the activies of marine plankton, such as radiolaria, foraminifera, coccoliths, and diatoms, and in the case of Ba they often refer to the role of organisms in its enrichment.

In organic geochemistry, publications have appeared during the past few years dealing with the very complex microbial interactions in active cold and hot hydrothermal vent systems (e.g., Mandernack and Tebo 1993). Examples of these types of environments are the bacterial mats of continental geyser fields (such as in Yellowstone National Park, USA, and on New Zealand). The authors of these papers frequently assign the basic role of microbial activity to numerous element cycles (e.g., Mn, Fe, S, P, Mg, V, Sr, Co, As, Si, Zn). Such papers refer to the complex, multi-faceted nature of the interaction between the biota and the inorganic world. The biota in question is assumed to have existed from an early period of earth history, and the effects of its activity could have been global (such as the increase of atmospheric oxygen, and the spread of stromatolite systems). Though the role of primary bacterial effects in black shale-hosted Mn mineralizations has recently been demonstrated (Fan et al. 1996), the above mentioned reasons make it apparent that the investigation of Mn mineraliza-

tion requires a multidisciplinary approach. Detailed characterizations of individual planetary processes have appeared from both the organic and inorganic fields of research, but without a synthesis of the two the reconstruction of the relevant processes cannot be accomplished in most cases.

It must be stated that the investigation of microbial activity in the origins of Mn-mineralized sedimentary environments (before metamorphism) is important. Furthermore, these formations correspond to environments in which prokaryotic bacteria may have flourished in the geologic past. Different groups of bacteria may have interacted with each other and with the inorganic environment, and a given formation will be the result of these complex interactions. For instance, evidence of bacterial activity has been found in the sediment-hosted Mn ores of China (Fan et al. 1996), in deep sea nodules (Ehrlich 1990), and in the pisolites of the Groote Eylandt ore deposit (Trudinger et al. 1980).

The activity of microorganisms has a potentially global and fundamental effect on the inorganic environment. Moreover, such activity might alter and even eliminate those characteristics which can be investigated by the traditional methods for inorganic systems.

It is probable that prokaryotic bacteria played a fundamental role in the metal enrichment of the Úrkút deposit. Mineral formations of this kind must therefore be viewed as the result of variable interactions between the biota and the inorganic environment. Modern analogs of these environments probably include hydrothermal vent systems, or other areas where conditions in which bacteria can flourish occur. Without the catalytic effect of these organisms, many such ore deposits would never have been created. Ore deposits such as the Mn ore stromatolite systems are examples of the close interaction of the living and inorganic worlds. Investigating and explaining the characteristics of these deposits is complicated, as the primary microbial system may transform and/or hide the characteristics of the original inorganic conditions. The microbes can interact directly or indirectly with many elements, especially those of variable valence, such as Mn, Fe, Co, and Ce. In this way the Mn/Fe, La/Ce, Co/Mn, and Zn/Mn ratios, and Ce anomalies, can change. Such alterations can cause difficulties in explanation. Other elements are fundamental for cell-building and various metabolic processes, which can entail selective enrichment. The specific elemental content of the sedimentary Mn deposits, the enrichment of P, Mg, As, Sr, Ba, S, Fe, and Mn, the unusual character of the ratios of elements and their anomalies (e.g., Ce-anomaly) can be explained by microbial processes. It is important to note that minerals formed directly or indirectly by microbes do not differ from those formed by inorganic processes, though in some cases the former can preserve some characteristic signs of biogenic processes (e.g., phosphorite algae mats).

In these deposits the processes of diagenesis can also cause considerable changes in isotopic geochemistry and composition. When a large quantity of bacteria dies in the sediment, it becomes a large mass of very reactive organic matter. Bacterial systems play a fundamental role in the

consuption of the organic matter during decomposition. These secondary bacterial cycles differ from the primary ones. Thus, during diagenesis the activity of microbial systems that consume organic matter can conceal the primary characteristics of the environment.

Mn ore deposits such as that at Úrkút occur in low temperature, marine, sedimentary environments. It is interesting that the various black shale-hosted Mn carbonate deposits have similar thicknesses, around 40–50 m, some individual beds of which are a few metres thick. The ore is very fine-grained, the average grain sizes being 1–5 μm, though the clustering of fine particles into 10–15 μm masses is very common. The deposits are well layered and bedded. Features that are characteristic of contemporary rifting commonly occur in the surroundings of these mineralizations [China (Hein and Fan 1999), Molango, Úrkút]. It seems that the period during which the bacteria flourish is limited, and that the system expires after a time. Such a short duration of activity may be due to the high oxygen demands of systems that quickly consume the available oxygen content (Huckriede and Meischner 1996). The well-bedded ore structure certainly demonstrates the absence of bioturbation by benthic organisms.

In summary, it can be stated that:
1. An understanding of the formation of black shale-hosted Mn carbonate deposits requires innovative reconsideration. The important and fundamental effects of bacteria in these mineralizations must not be neglected.
2. The investigation of the conditions under which the black shale-hosted Mn carbonate deposits formed must be interdisciplinary.
3. Some, if not all, of the black shale-hosted Mn carbonate deposits appear to be of a biogenic-sedimentary origin (a hydrothermal/exhalative element source can be assumed; Polgári et al. 2003).
4. These mineral deposits can be viewed as the remains of complex, energetic, living systems. Though the bacteria are not visible, the results of their activity completely changed the original characteristics of the inorganic system. The enrichment of variable valence and other biophile elements (such as P, S, Fe, Mn, Co, As, Cu, Mg, Sr, Ba, Ni, and Zn) is characteristic of such bacterial activity. The role of bacteria in precipitating elements from solution is fundamental to these processes.
5. The geochemical methods applied to investigating the genetic aspects of these deposits must be used with caution. This is because the effects of the biota and the diagenetic processes significantly alter the original character of the inorganic system. The above-mentioned considerations lead to a more unified explanation of the origins of the Jurassic black shale-hosted Mn carbonate mineralization at Úrkút.

Conclusion

The development of the Úrkút deposit can be tentatively described by the following series of processes:

1. Rifting that occurred during Sinemurian-Pliensbachian tectonic activity created fractures and deep faults. The increase of endogenic thermal effects, such as degassing and the release of solutions, along with the mixing of syngenetic ash falls with the marine sediments caused the metasomatic infiltration of Fe into the carbonate rocks. The red, nodular carbonate rocks of reduced thickness are assumed to be the deteriorated footwalls of the mineralization. The nodular marly appereence, clay horizons, and some of the common chert layers can be interpreted as the results of ash fall mixing with the sediments. The fine grained volcanic material became completely altered in the marine environment (Fig. 4). At some localities weak signs of Pliensbachian (Domerian) hydrothermal metal enrichment can also be determined.

2. Hydrothermal emanations in the deep fault zones began in the Toarcian, which caused the dissolution of the carbonate basement (forming karst-like features) and the Mn-Fe replacement along the fault zones. The primary Mn oxide mineralization occurred in the form of brown, ferrous Mn oxide blocks connected to brown chert and varicoloured metalliferous clays (black, brown, yellow, red, grey and white) close to the supposed vent centres (Úrkút-Csárdahegy, Eplény). The formation of clay and celadonite (Fe-bearing mica) occurred from the locally enriched ion concetrations which infiltrated the sediment pile (Tóth et al. 2001). The vent system created an optimal environment for the flourishing of various prokaryotic bacteria (with abundant Mn, Fe, S, etc.), in which bacterial activity caused the precipitation of large amounts of metal ions in the form of very fine-grained oxyhydroxides. Meanwhile, the accumulation of dead bacteria created a mass of very reactive organic matter. These processes created the mass of the proto-ore of the Mn carbonate ore deposit. The period during which these processes occurred was characterized by an oxidative environment with high oxygen requirements. This can be considered as Phase I, the primary oxidizing bacterial system cycle. Such large Mn carbonate deposits would probably not have accumulated without the flourishing of bac-
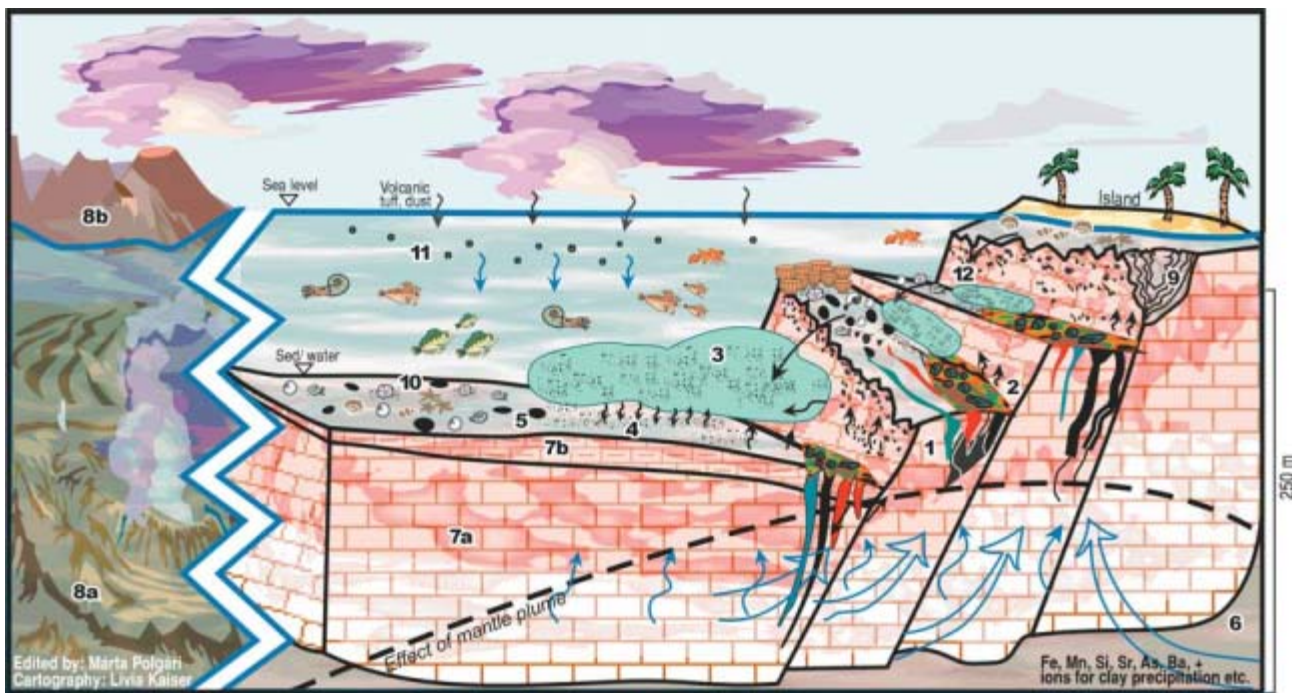

Figure 4. Idealized sketch profile of the Mn deposition (proximal and distal facies) during Jurassic time: the oxidative bacterial system cycle.
Proximal Mn facies and its environment:
1. Dissolved limestone footwall, sedimentary dikes, red-brown-green lime marl and clay infillings, manganized limestone zones (black).
2. Cherty Fe and Mn oxide blocks (with high Sr-content) in varicoloured metalliferous clay.
Distal Mn facies (close to source):
3. The flourishing of prokaryotic bacterial system, the bacteria-induced precipitation of Mn and Fe in the form of metallic oxides.
4. MnOOH, FeOOH proto ore, green-clay (celadonite) formation, phosphorite, organic matter (dead bacteria and other organisms) and pyrite accumulation.
Distal Mn facies (far from the source, dissemination-contamination of Mn on a large scale):
5. Mn nodules and encrustations, Mn or Mn-Fe hard grounds.
General key:
6. Triassic shallow-marine basement, platform.
7. Lower-Middle Liassic limestone (a), lime marl (b), shallow-marine pelagic sequence.
8. Submarine (a) and terrestrial (b) volcanism in the surrounding region (no direct connection with volcanic rocks known in the studied area).
9. Reef.
10. Bio detritus (ammonites, brachiopods, molluscs, sponges, crinoids, echinoids, ostracods, and fish remnants).
11. Planktonic organisms (radiolaria, foraminifera, and bositra).
12. Resedimentation.
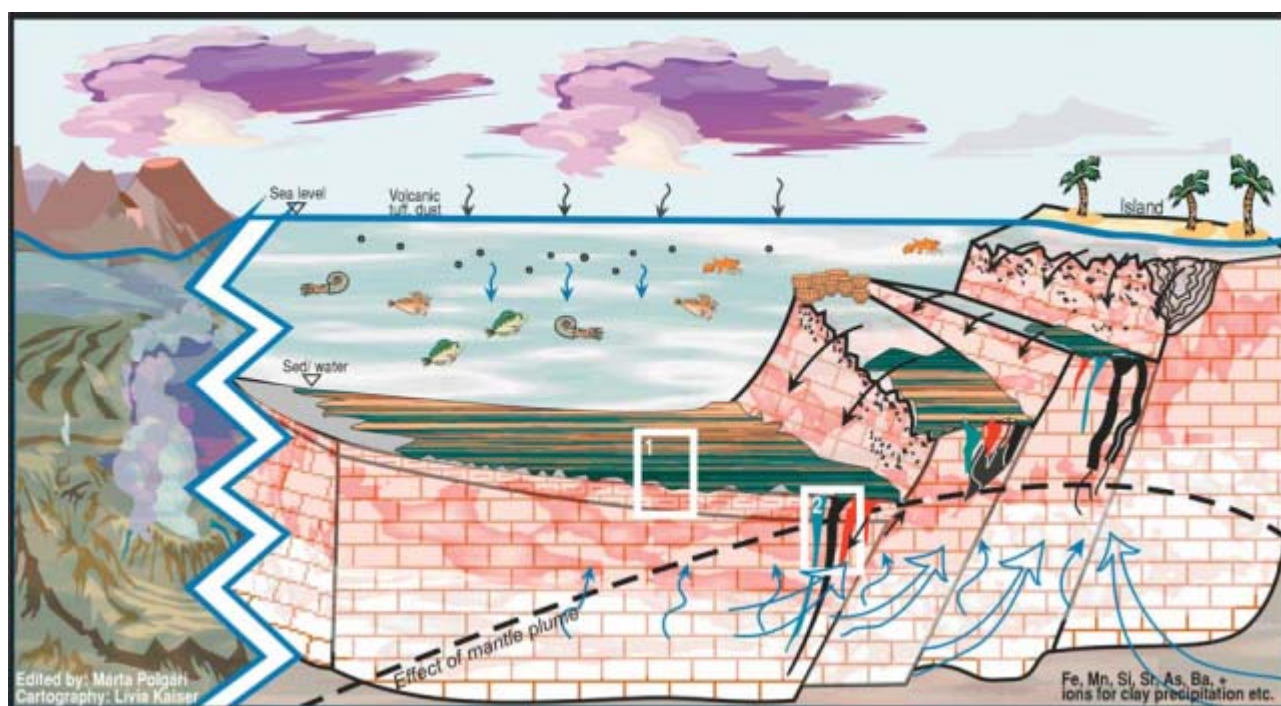Arrows show the direction of material flow.

Figure 5. Idealized profile of Mn deposition (proximal and distal facies) during the Jurassic. Suboxic-reductive bacterial system cycle. Diagenetic Mn carbonate ore formation. 1. Bacterially mediated consumption of organic matter (enzymatic and total processes) by Mn^{4+}, Fe^{3+}, SO_4^{2-}, e.g. diagenetic $MnCO_3$, Fe-nontronite-Fe-mica (celadonite), pyrite (bacterial and inorganic), phosphorite formation. Continuous clay formation with two levels of Mn carbonate mineralization. 2. Squares No. 1 and 2 show positions of Fig. 6 and 7.

teria. The complex bacterial activity masks and modifies the primary characteristics of the inorganic system (such as elemental ratios, trace element contents, isotope signals, etc). The evidence of bacterial activity in the form of bacteriopyrite, Fe-bacteria in chert, and magneto-tactite are common. Some Fe-bacteria show a strong affinity for Sr in hydrothermal systems, but in the solid state Sr is captured in Mn oxides, probably due to their mineralogical structure. The hydrothermal efflux shows a double maximum which caused the deposition of two ore beds.

It seems that the clay formation was continuous, and the higher amount of organic matter in the black shale was preserved in the absence of oxidizing agents such as Mn^{4+} and Fe^{3+}. The pyrite content is considerable in these horizons. The effects of the active hydrothermal vent systems were fundamental in the formation of the black shales. Contributions from volcanic ash falls could also have occurred during this period; this could explain some of the unusual local features, but the ash falls did not become a dominant source of sediment. Evidence of submarine earthquakes is visible in the form of mud slides and other disturbances of the soft sediments.

3. Following burial and the end of the hydrothermal activity, the supply of extra elements stopped. This was probably the result of stronger volcanic eruptions in the late Toarcian, material from which accumulated into a 20–30 cm thick layer in the sedimentary basin. The resulting hyaloclastic layer became completely altered into brown chert and green celadonitic clays; it is this horizon which covers the Mn-mineralization in the area. Following

cessation of the volcanic activity, the conditions reverted back to normal carbonate sedimentation. This formation of the Lower Dogger age contains a large amount of micro-fossils. In the Aalenian-Bajotian strong silicification of the Bositra-bearing limestones occurred, the green-gray colour of these rocks being caused by their finely disseminated celadonite content. This unusual type of formation occurs in the vicinity of Mn-mineralized zones. Diagenetic processes began within the buried sediment, starting with the activity of reducing bacterial systems. Thus Phase II of the geochemical history of this ore deposit began, which period can be described as the reductive bacterial system cycle (Figs. 5, 6, 7). Diagenetic Mn carbonate ore formation occurred during this phase, while the total consumption of organic matter took place. The formation of Fe-nontronite and green mica (celadonite) continued. These diagenetic processes altered the primary features of this deposit, with further changes in the ratios of elements, and the creation of the unusual stable isotope character of the Mn carbonates.

4. In the upper Dogger and Malm periods there was additional, though distant, volcanic activity which again contributed tuff material. This resulted in the deposition of clay layers within the radiolarite and limestone strata, and is evident from the chert layers and the nodular character of the sediments. Post-sedimentary tectonic activity at the Jurassic/Cretaceous boundary caused the folding and fracturing of the area, during which the elevated parts of the deposit were strongly eroded and the secondary Mn oxide formation took place. During these oxidizing processes the primary element distribution again changed, while the

Figure 6. The contact between the limestone footwall (red) and the thin-layered brown-green-gray Mn carbonate ore mineralization. Úrkút Manganese Mine, shaft No. III, 241 mBf (photo by Gyula Kertész).
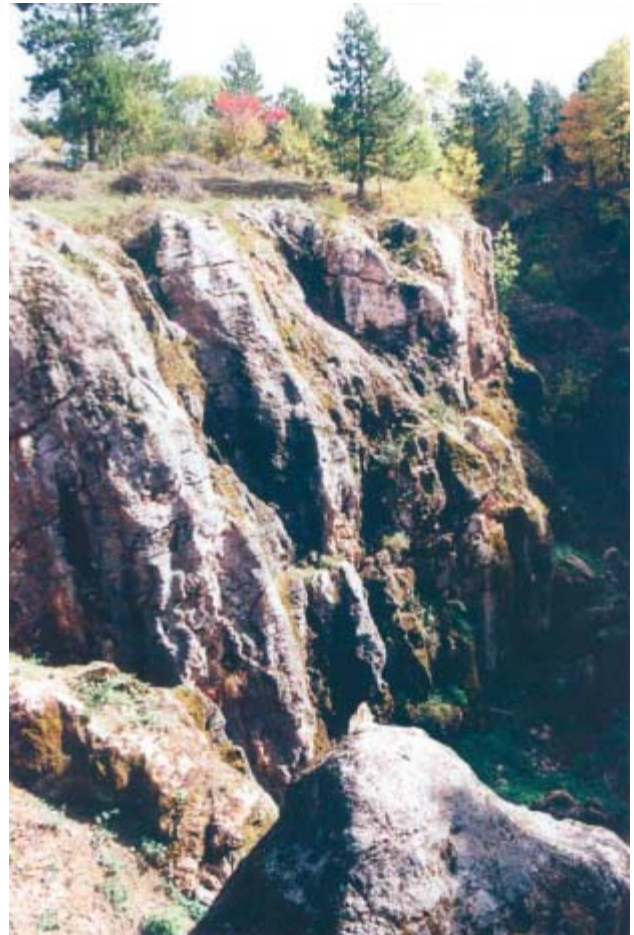

Figure 7. The dissolved limestone surface on land after the exhaustive mining of the cherty Fe, Mn oxide ore and the secondary oxidized Mn ore, Csárdahegy-Úrkút (photo by Gyula Kertész).

agressive solutions of pyritic alteration caused the strong dissolution of the basement.

The final conclusions are that the black shale-hosted Mn carbonate mineralization at Úrkút is biogene in origin, that it accumulated in a marine environment, that the source of the metals and clays were local hydrothermal vent systems along deep fault zones, and that the ore is a Mn-ore stromatolite with a volcanic tuff component. Later diagenetic processes created the Mn carbonate ore deposit. The modern analog of such an environment could be the flourishing prokaryotic bacteria colonies located in submarine vent systems. Collectively, these deposits can be explained as the remnants of proto-rifts or failed rift systems on continental crust in a submarine environment. Though a direct connection with volcanic rocks is not conclusively known with reference to these deposits, some of their characteristics are consistent with the interpretation that they represent hydrothermal vent systems of cooler temperatures.

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