

**STABLE ISOTOPE EVIDENCE FOR THE ORIGIN OF THE JURASSIC MN-
CARBONATE ORE OF EPLÉNY,
TRANSDANUBIAN CENTRAL RANGE, HUNGARY**

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Abstract: A manganese carbonate ore sample from Eplény, Transdanubian Central Range, Hungary, consists of Mn calcite and Ca rhodochrosite, with moderate quartz. The Mn and Fe contents of the ore are 7.51% and 0.86%, respectively, giving an Mn/Fe ratio of 8.73. The $\delta^{13}\text{C}_{\text{PDB}}$ of that sample is -2.20‰, which indicates that the carbon was derived from seawater or from the dissolution of carbonate precipitated from seawater. The $\delta^{18}\text{O}_{\text{PDB}}$ is -0.25‰, indicating a low-temperature origin. The Eplény ore differs from the Úrkút Mn-carbonate ore in mineral, chemical, and C isotopic contents. While Úrkút Mn-carbonate mineralization occurred as the result of bacterial oxidation of organic matter coupled with Mn-oxide reduction in the early diagenetic zone of sulfate reduction, the Eplény ore was likely syndepositional or very early diagenetic precipitation from seawater, perhaps mediated of microbial activity.

Key words: Jurassic, Mn-carbonate, black shale, C-isotope, microbial, Hungary,

Introduction

Among the Jurassic Hungarian Mn-ore deposits, the Úrkút and Eplény deposits are worthy of mention from an economic point of view. The two Mn occurrences are about 40 km apart in the Transdanubian Central Range in the Bakony Mountains. Both deposits are associated with NW-SE fault systems. The Úrkút deposit is much larger, covering approximately 10 km², and has been exploited since 1917. The Eplény Mn-ore deposit is smaller and similar to the so called Csárdahegy-type Mn-ore of the Úrkút deposit (Cseh Németh and Grasselly 1966; Cseh Németh et al. 1980; Grasselly and Cseh Németh 1961; Szabó-Drubina 1959). The Eplény Mn-oxide ore was exploited both from open pits and underground mining between 1935-1975, when the mine was closed.

Analytical studies were made on the economically important oxide ore when the mine was operating, but there are few data concerning the Mn-carbonate ore, which is important from genetic point of view. After the mine was closed, there was no opportunity to collect new samples for modern investigations, and that is why it is very important to publish new data on a previously collected sample.

The aim of this paper is to contribute new mineralogical, chemical, trace element, and C and O stable isotope data of a Mn-carbonate-type ore sample of the Jurassic, Eplény deposit. The sample belongs to a collection which was collected in the 1960s by professor Gyula Grasselly, and was kindly offered for further study by the Petrological and Geochemical Department of Szeged University.

Geological Setting

The Eplény Mn-ore mineralization occurs in a fault-controlled area surrounded by Triassic carbonate rocks. The area shows strongly fractured zones and vertical and horizontal offsets along the faults. The Jurassic sequence at Eplény is discontinuous and rests on Triassic basement composed of white, pale-grey, microcrystalline, Dachstein-type limestone. The same type of carbonate sedimentation characterizes the lower Liassic limestone, which is oolitic and contains foraminifera and brachiopods. The upper part of the lower Liassic is red, pink, brachiopod-bearing limestone, red cherty limestone, and Hierlatz-type limestone (Hierlatz-, Tűzkövesárok- and Isztimér Limestone Formations). The middle Liassic consists of red nodular, or massive crinoidal, limestone and red- green spotted cherty limestone. In the crinoidal limestone near the ore bed, small Mn-oxide grains occur and in places, lenticular Mn-oxide ore occurs. In the NE part of the district, the ore overlies a disconformity marked by an irregular dissolved surface of the lower Jurassic Dachstein-type limestone. Its relief can reach 20-40 m, the average being 2-5 m (Szabó-Drubina 1959). Mn-oxide coatings on grain surfaces or along fractures in the limestone are common. In addition, the Mn-oxide rarely forms pseudomorphs after calcite. Most commonly, the Mn-oxide fills the dissolution holes and vugs in the Hierlatz-type limestone. Sedimentary dykes filled with lower or middle Liassic lime-mud are characteristically connected with the mineralization. Mn-replaced limestone is typical of this NE part of the mineralization, which is upper Jurassic in age.

The thickness of the Mn deposit is 6-8 m. The Mn-ore horizon consists of the following parts from the bottom to the top.

-Lower part: primary Mn-oxide ore in yellow, brown, phosphorus-rich clay;

-Upper part: dark-grey, pyritiferous claystone, marlstone with hard, nodular, lenticular, blocky, concretions, or poorly consolidated Mn-oxide ore bed

-Radiolarian claystone, marlstone (black shale) with blocky, lenticular, laminated Mn-carbonate-bearing claystone, marlstone.

The ore bed is divided into two parts by a fault. To the NE from this fault the hard, nodular, concretion-bearing Mn-oxide ore occurs, while on the uplifted SW side mainly poorly consolidated, layered, bedded-lenticular ore type can be found. To the NW, the amount of overburden (spoil) increases. The dark-gray finely laminated pyritiferous radiolarian claystone and marlstone is yellow, brown, or red in places, colors which are inferred to be depositional. Smectite is the dominant clay mineral type. Mn carbonate and phosphorite layers and nodules also occur within the Mn-oxide horizon.

The main occurrence of the Mn-carbonate-bearing marlstone (bed No II) is in a rifted fault-bounded graben. Heteropic facies characterizes the Mn-carbonate ore, which is black, or variagated claystone. Often in the black manganiferous claystone, the CaCO_3 content increases gradually grading into pale Mn carbonate layers. The hanging wall is claystone, similar to the heteropic facies described above.

Based on the work of Szabó-Drubina (1959), the Mn-carbonate layers are vary from soft to hard, depending on whether the relative amounts of rhodochrosite and other carbonate. The ore is very fine-grained and the porosity is 15-20%. The carbonate content is 35-50%, Mn is 15-18%, while SiO_2 is 20-28%. Small amounts of Fe and Al are also present. The amounts of calcite and rhodochrosite are contraversial, but equal amounts can occur. The P_2O_5 content is higher than 1% and the S content is 0.8-4.0%, which is in the form of pyrite.

The mineral content shows rhodochrosite- and calcite-rich thin layers alternation with and clay-rich (montmorillonite, pyrite) thin layers. Lesser amounts of detrital quartz and secondary limonite and glauconite occur as well.

Sample and Methods

One Mn-carbonate ore sample was found during a review of the collection of Professor Gyula Grasselly (Szeged) in 2001. The sample was collected in the 1960s from the underground mine +260 level, and had not been previously studied. This sample is typical of the Eplény ore and we characterized it using X-ray diffraction (USGS, Menlo Park); major and trace elements (except Si) were determined by ICP after multiacid digestion; and Si by Li-metaborate fusion, digestion, and ICP (XRAL Laboratories). Stable C and O isotopes were

determined by the USGS. The sample is pale grey, porous, homogenous, with faint layering. The outer surface is dark brown-grey because of oxidation of the Mn(II).

Data

Mineralogy

The main mineral components of the sample are Mn-calcite with much less Ca-rhodochrosite and moderate quartz.

Chemistry

The main and trace element data are summarized in Table 1. The Mn content of the ore is low the Mn/Fe is 8.73. Calcium is the main cation in the dominant carbonate phase. Silica is relatively high and occurs dominantly as quartz according to X-ray mineralogy. Minor clay minerals occur as shown by the low amounts of Al, K, Mg. The trace element and rare-earth element contents of the sample are very low.

Table 1: Main and trace element data of the Mn-carbonate ore of Eplény

Main elements (%wt)		Trace elements (ppm)		Trace elements (ppm)		Trace elements (ppm)	
SiO ₂	21.6	Au	<8	Cr	9	Y	31
TiO ₂	0.08	Li	13	Cu	9	Nb	5
Al ₂ O ₃	1.62	Be	<1	Mo	<2	La	30
Fe	0.86	Ga	<4	Ni	15	Ce	153
Mn	7.51	Cd	<2	Pb	13	Nd	31
CaO	32.5	Sn	<5	V	19	Eu	<2
MgO	1.12	Bi	<10	Zn	17	Yb	2
K ₂ O	0.43	Ag	<2	Sc	4	Ho	<4
Na ₂ O	0.05	Ba	32	As	<10	Ta	<40
P ₂ O ₅	0.25	Sr	137	Th	7		
Mn/Fe	8.73	Co	13	U	<100		

Stable isotopes

The $\delta^{13}\text{C}_{\text{PDB}}$ is -2.20‰, which indicates that the carbon was derived from seawater bicarbonate, or from the dissolution of carbonate precipitated from seawater. The $\delta^{18}\text{O}_{\text{PDB}}$ is -0.25‰, which indicates a low-temperature origin.

Discussion

Many papers on the origin of Mn-carbonate deposits and on C isotopes have been published (e.g., Froelich et al. 1979; Coleman 1985; Okita et al. 1988). Many papers have established a genetic model for Mn-carbonate deposits in which Mn-oxyhydroxide formed first and then

during early diagenesis under reducing conditions, Mn^{4+} is reduced to Mn^{2+} coupled with bacterial oxidation of organic matter. The $\delta^{13}\text{C}_{\text{PDB}}$ for these Mn carbonates varies from about -10 to -30‰, depending on the amount of mixing of seawater bicarbonate (0‰) and CO_2 released during bacterial oxidation (about -22 to -32‰) of organic matter. Mn carbonate precipitated from seawater will have a $\delta^{13}\text{C}_{\text{PDB}}$ value of around 0‰.

Based on analyses of black shale-hosted Mn-carbonate ore deposits, giant deposits such as Moanda, Gabon, Taojiang, China, and Úrkút, Hungary belong to this type of deposit (Hein et al. 1989; Polgári et al. 1991). It has been shown recently that some black shale-hosted Mn-carbonate deposits have $\delta^{13}\text{C}_{\text{PDB}}$ values around 0‰ (Fan et al. 1996). Fan et al. (1996) compared seven Chinese deposits and concluded that the Gaoyang-type Mn carbonate was syngenetic. They described a sequence that evolved from anoxic (black shale) deposition to sedimentation under slightly oxidizing condition when the Mn carbonate ores were deposited.

Under anoxic conditions, Mn^{2+} is not precipitated, but remains in dissolved form in basin waters. When the environment changes to slightly oxidizing and alkaline, large amount of the Mn can be precipitated directly to form Mn carbonate. Study of black shale-hosted Mn deposits shows that microbes were involved in the ore-forming processes in several ways. The catalytic effect of microbes is fundamentally important in the cycling of manganese on local and global scales. During sedimentation, the effect of the microbes can be direct or indirect. Respiration of microbes produce HCO_3^- and CO_2 , which are assimilated by algae, therefore the pH of the seawater increases and under these conditions rhodochrosite can precipitate directly from the seawater. In the diagenetic zone of sulfate reduction, microbially formed HS^- can reduce Mn oxide and the Mn^{2+} produced can combine with seawater bicarbonate or CO_2 produced during the same diagenetic stage and precipitate directly as rhodochrosite; at the same time, the HS^- is oxidized to SO_4^{2-} to support the further activity of sulfate reducing bacteria.

Conclusions

The Mn-carbonate ore of the Eplény Mn deposit is a Mn calcite and Ca rhodochrosite from mineralogical point of view. The Mn content of the ore is 7.51%. The trace element content of the ore is low. The C isotope data indicates that C was derived from seawater, possibly by direct precipitation from seawater. The precipitation was probably mediated by microbial interaction in the sedimentary basin.

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