

Phosphogenesis in Jurassic black shale-hosted Mn-carbonate deposits, Úrkút and Eplény, Hungary: Investigations on archive sample drillcore Úrkút–136

Foszforitképződés a jura, feketepala környezetű Mn-karbonát telepeken (Úrkút, Eplény, Magyarország): az Úrkút–136 mélyfúrás archív mintájának vizsgálata

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(2 ábra, 4 táblázat)

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Tárgyszavak: Úrkút, foszforit, Mn-karbonát, feketepala, jura

Abstract

The present paper reports on an X-ray powder diffraction, EPMA and major/minor element determination-based mineralogical and geochemical characterisation of a phosphorous-rich (apatite > 50%) archive sample from the Jurassic black-shale hosted Mn-carbonate and Mn-oxide mineralization Úrkút, Transdanubian Range, Hungary. Besides the predominant carbonate fluorapatite (CFA) pyrite and quartz are present in the sample in larger amounts (~ 10%). The CFA has an XRD pattern typical of modern marine CFA deposits.

In the ore sequence phosphorite is present in thin layers and lenses at some stratigraphic levels. The sample analysed here has a U/Th ratio of less than 2 (0.92). The U/P₂O₅ ratio is 0.57×10⁻⁵. The ΣREE content is 519 ppm and the Ce/La ratio is 2.52.

The source of phosphorous was organic matter produced by high productivity in a zone of upwelling, which also produced the black shale. Based on the lithologic associations with Mn-carbonates and Mn-oxides, the Úrkút and Eplény phosphorites do not have analogues in the modern ocean basins. The geochemical similarity with the giant Jiantaishan, China deposit and the local geological features suggest that these Hungarian Jurassic phosphorites were formed below a zone of coastal upwelling, but in an anoxic to suboxic basin where black shales and Mn-carbonates also accumulated. Sea-level changes and redox fluctuations permitted the formation of thin diagenetic phosphorite layers in the sedimentary sequence. Both phosphorites and Mn-carbonates were formed by bacterially mediated early diagenetic processes.

Összefoglalás

Az úrkúti jura, feketepala környezetű, karbonátos és oxidos Mn-ércesedés egy foszfordús (apatit > 50%) archív mintájának ásványtani és geokémiai jellemzését végeztük el röntgen-pordiffrakciós, mikroszondás és fő-, valamint nyomelem vizsgálatok alapján.

Az uralkodóan karbonát-fluorapatitból (CFA) álló mintában jelentősebb mennyiségben pirit és kvarc mutatható ki (~10%). A karbonát-fluorapatit röntgen-diffrakciós jellemzői a modern tipikus tengeri előfordulásokhoz hasonlóak.

A vizsgált minta U/Th aránya kisebb, mint 2 (0.92). Az U/P₂O₅ arány 0.57×10⁻⁵. A össz ritkaföldfém tartalom 519 ppm, a Ce/La arány 2.52.

Az érctelepben a foszforit vékony rétegek, lencsék formájában jelenik meg néhány rétegtani szintben. A foszfor forrása a feláramlási övezetben jellemző nagy biogén produktivitásból eredő szervesanyag-tartalom lehetett, amely a feketepala képződésért is felelős.

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A Mn-karbonátok és Mn-oxidok litológiai kapcsolatai alapján az úrkúti és eplényi foszforitoknak a modern óceáni medencékben jellemző hasonló képződménye nem ismert.

A hatalmas kínai Tiantaishan Mn-ércesedés geokémiai sajátosságaihoz való hasonlóság, és helyi geológiai jellegzetességek alapján a magyar, jura időszerű foszforitok parti feláramlási övezet alatti zónában, anoxikustól szuboxidatív medencében keletkezettek, ahol a feketepala és Mn-karbonát képződés folyt. Tengerszint- és redox-változások az üledéksorozatban lehetővé tették vékony diagenetikus foszforit rétegek képződését. Mind a foszforit, mind a Mn-karbonát bakteriálisan befolyásolt korai diagenetikus folyamatok során képződött.

Introduction

The Transdanubian Range of Hungary is an important region of Jurassic black shale-hosted Mn mineralization. The fine-grained (2–5 μm grain size) phosphorous-rich layers within the Mn-carbonate–Mn-oxide transitional zone at Úrkút and Eplény have been of interest since the study of these deposits began. In the early 1950s, SZABÓ-DRUBINA determined that at the Eplény Mine the hard, pale yellowish-grey carbonate- and altered chert-like layers and lenses consist of fluorapatite (SZABÓ-DRUBINA 1959), GRASSELLY & CSEH NÉMETH (1961) determined the distribution of Mn, Fe, P, and Si at the dip-slope shaft area of Úrkút. They found a positive correlation between P and SiO_2 and P and Fe contents (230 samples), and explained the latter by the chemisorption of PO_4 anions on the colloidal $\text{Fe}(\text{OH})_3$. The correlation of P and Fe contents on the shaft No. II samples could not be established (115 samples). CSEH NÉMETH (1963, referred to in POLGÁRI et al. 2000) found a Pycnodontida fish fossil in a large (20 cm) phosphate nodule in the Úrkút Mine. After his work, similar nodules were subsequently found. GRASSELLY (1968) determined the phosphorous-rich phase to be Fe-bearing carbonate-hydroxyl apatite, dahllite. It was initially thought that the distribution of phosphorous was uniform throughout the deposits. However, because the industrial utility of manganese ores is effected by the phosphorous content, which is higher than 0.2 wt.% in the Úrkút ore, a detailed study was made to determine the distribution of phosphorous. In the 1970s, it became clear that the rare-earth element (REE) contents and the phosphorous contents correlate positively (for details see POLGÁRI 2000 p. 569), and this initiated a push to look for a potential REE ore. It was finally concluded that REEs have no economic importance, but that search did increase our knowledge about the distribution of phosphorous. Because the appearance of the phosphorous-rich layers is very similar to the pale-carbonate layers and lenses and often occurs in claystones as very thin (millimetres) layers, the sampling many times mixed the layers, thereby masking the main characteristics of the phosphorite.

Only three samples from Úrkút and Eplény, each referred to as a “phosphorite type” have been investigated by modern methods in the previous decades, but none of these data were published (for details see POLGÁRI 2000, p. 119 sample #173; p. 122 samples #208–209). Only one of these samples (#173) actually shows some P enrichment (1.01 wt. %); therefore none of them is actually a phosphorite. This is why it is of special importance to give mineralogical details on the phosphorous-rich samples from that locality. In this paper we describe and analyse a well-documented sample from a real phosphorite bed using modern techniques.

Phosphogenesis has been described to occur in many sedimentary sequences and the origin of the phosphorites has been determined based on stratigraphy, textures, mineralogy, and chemical composition. As at Úrkút and Eplény, phosphorite that occurs in association with manganese mineralization can provide further information concerning the synsedimentary and diagenetic processes that produced both the Mn ore and phosphorite. The occurrence of P together with Mn, Fe, and Si is well known, and U, Th, and REEs can be enriched in the phosphates (STRACHOV et al. 1968; HEIN et al. 1999).

The aim of this study is to review the main characteristics of the Jurassic phosphorite from the Bakony Mountains, describe the relationship between the phosphorous and manganese mineralization, and compare the Úrkút and Eplény occurrences. In the framework of this study, we provide new data for an archived phosphorite sample from a drill core from the Úrkút area. It must be emphasized that the importance of preserving samples for future study is fundamentally important. Changing methods of investigation and lack of access to closed mines makes archived samples of particular value.

Geological setting and phosphorous distribution

As both the Úrkút and Eplény Mn deposits are the subjects of many papers in which many aspects of the geology of the deposits are considered (for a detailed list see POLGÁRI et al. 2000), this paper presents information concerning only the phosphorous-rich occurrences. The locations of Úrkút and Eplény are illustrated in Figure 1. in POLGÁRI et al. 2003.

Úrkút: The distribution of phosphorous was investigated for two reasons. First, to consider the high phosphorous content given that it is, detrimental to the quality of the Mn ore, and second to look for concentrations of REEs. It is difficult to recognize phosphorous-rich layers in the field because of their similar appearance to the varicoloured Mn-carbonate ore and claystone layers. The average phosphorous contents of the different Mn-ore types at Úrkút are summarized in Table 1.

Oxidation of the Mn-carbonate ore had decreased the phosphorous content in the associated altered black shale. In the transition zone between the Mn-carbonate and Mn-oxide, the phosphorous content is higher compared to that in

Table 1. Range and mean phosphorous content of different ore types at Úrkút (POLGÁRI et al. 2000)

1. táblázat Különböző úrkúti Mn-ércfűpusok foszfor-tartalma és középértékei (POLGÁRI et al. 2000)

Rock type		Range (wt. %)	Mean (wt. %)
Mn-carbonate ore	Main bed (No. I)	0.1–0.8	0.4
	Bed No. II	0.1–1.6	0.8
Primary Mn-oxide ore	-	0–0.89	0.15
Secondary Mn-oxide ore	-	0–1.3	0.6
Black shale	Radiolarian clay marlstone	0.11–0.3	0.2
Altered clay marlstone	-	-	<0.1

Table 2. Major element contents (wt. %) of Úrkút and Eplény Mn-carbonate ores
2. táblázat Az úrkúti és eplényi Mn-karbonátos ércek fő kémiai összetétele (s%)

	1.	2.	3.	4. *	5.*	6.*
SiO ₂	12.6	8.64	13.10	n.d.	8.19	1.30
TiO ₂	0.05	0.14	0.45	Tr	Tr	Tr
Al ₂ O ₃	1.21	15.40	6.84	9.64	10.5	11.9
Fe	9.24	4.68	2.16	0.16	1.49	0.26
Fe ₂ O ₃	n.d.	6.69	2.72	0.23	2.13	0.37
FeO	n.d.	n.d.	0.34	n.d.	n.d.	n.d.
Mn	1.71	2.09	0.17	1.35	2.36	1.08
MnO	n.d.	2.71	0.22	1.75	3.06	1.40
MnO ₂	n.d.	n.d.	0.19	n.d.	n.d.	n.d.
CaO	33.20	22.40	37.60	43.00	38.60	40.70
MgO	1.05	0.82	1.39	0.73	1.40	0.43
K ₂ O	0.28	n.d.	1.48	0.01	0.45	0.07
Na ₂ O	0.76	n.d.	1.74	0.64	0.62	0.75
-H ₂ O	n.d.	0.29	n.d.	n.d.	n.d.	n.d.
CO ₂	n.d.	n.d.	21.50	n.d.	2.83	3.83
P ₂ O ₅	19.40	22.00	2.31	32.1	25.80	30.90
F	1.43	n.d.	n.d.	n.d.	n.d.	n.d.
S	n.d.	2.56	n.d.	n.d.	n.d.	n.d.
CaO/P ₂ O ₅	1.71	1.02	16.3	1.34	1.49	1.31
F/ P ₂ O ₅	0.07	-	-	-	-	-

- 1: 4 cm thick greyish-yellow laminated pyritiferous phosphorite layer, drillcore No. Ú-136, 209.50–214.50 m, current study, XRAL Laboratories, Canada
- 2: 4 cm thick greyish-yellow laminated pyritiferous phosphorite layer, drillcore No. Ú-136, 209.50–214.50 m, (analyst: SIMÓ B. Hungarian Geol. Inst., 1954)
- 3: Phosphorite lens, Csárdahegy, Úrkút (POLGÁRI et al. 2000, page 333–335).
- 4: E/18: yellowish-brown chert-like layers in yellow clay (Eplény Mine, W, 5th blind shaft, VII. level, left, 15–16 m, (analyst: SIMÓ B. Hung. Geol. Inst., 1958)
- 5: E/20: carbonate-like layers in yellow clay (montmorillonite, limonite, calcite by DTA) Eplény Mine, W, 5th blind shaft, VII. level, left, 58 m, (analyst: SIMÓ B. Hung. Geol. Inst., 1958)
- 6: E/22: yellowish-brown chert-like lens in brown clay (amorphous yellowish chert-like matrix with a few carbonate-grains, and thin clay-like beds in thin section), Eplény Mine, W, 5th blind shaft, VII. level, left 75–76 m (analyst: SIMÓ B. Hung. Geol. Inst., 1956)

* For sample location see POLGÁRI et al. 2003, Fig. 3 (u) .

Tr: traces; n.d.: no data

the Mn-carbonate ore. The major and trace element contents of a phosphorous-rich lens from the primary Mn-oxide ore at Csárdahegy (eastern part of the Úrkút Mn-mineralization) are listed in Tables 2 and 3. Unfortunately, determination of the mineralogy using modern techniques has not been made for this sample.

REEs in phosphorous-rich phases: The purpose of previous electron-microprobe studies was to show the different types of phosphorous-rich phases that contain REE – those data are listed in Table 4. The study started in 1965 when J. KONDA (pers. com.) determined that 100 ppm Eu occurred in one sample. A systematic investigation started in 1968, in which 93 samples were analysed for Y, REEs, Mn, Fe, SiO₂ and P from an industrial point of view. This set of samples included all Mn-ore types. The correlation coefficient between phosphorous and total REEs was +0.77 (KOVÁCS 1970). We note that phosphorous-rich samples

Table 3. Trace element (ppm) contents and element ratios of the Úrkút and Eplény Mn-carbonate ores

3. táblázat Az úrkúti és eplényi Mn-karbonátos ércek nyomelemtartalma (ppm) és néhány elem kapcsolata

	1.	3.	7.	8.		1.	3.	7.	8.
Au	bdl (<8)	-	-	-	U	1.1	181	31	6.4
Li	9.0	-	-	-	Rb	-	50	25	25
Be	1.0	-	-	-	Y	90	-	-	-
Ga	bdl (<4)	-	-	-	Nb	bdl (<4)	-	-	-
Cd	bdl (<2)	-	-	-	La	99	428	440	340
Sn	bdl (<5)	-	-	-	Ce	249	1104	820	1500
Bi	bdl (<10)	-	-	-	Nd	73	273	230	300
Ag	bdl (<2)	-	-	-	Sm	13.2	180	51.7	96
Ba	262	720	1200	6200	Eu	3.0	22.2	11.8	19.6
Sr	bdl (<2)	980	3800	3400	Dy	16.9	-	-	-
Co	117	128	5	360	Gd	17.6	-	-	-
Cr	-	-	-	-	Tb	2.9	124	12	15
Cu	15	32	0	0	Yb	5.4	159	68.8	26.5
Ga	bdl (<4)	-	-	-	Lu	0.79	29.1	9.9	3.37
Mo	2	-	-	-	Ho	2.72	-	-	-
Ni	34	48	4	100	Er	8.50	-	-	-
Pb	12	14	0	200	Tm	1.00	60	17	8
V	13	-	-	-	Ta	bdl (<40)	-	-	-
Zn	26	62	41	130	Pr	19.1	-	-	-
Sc	bdl (<2)	13	11	7.9	U/P ₂ O ₅ *	0.056	78	-	-
Cr	12	69	15	20	U/Th	0.92	38	155	2.67
As	79	15	8	55	ΣREE	519	2322	1661	2308
Hf	-	1.6	0.2	0.2	Ce/La	2.52	2.58	1.86	4.4
Th	1.2	4.8	0.2	2.4	-	-	-	-	-

1 and 3 as in Table 2

7: Phosphorite from Mn-oxide ore, Eplény Mine (POLGÁRI et al. 2000, page 349–351.)

8: Mn-oxide ore adjacent to phosphorite, Eplény Mine (POLGÁRI et al. 2000, page 349–351.)

* times 10⁴

bdl: below detection limit

Table 4. Phosphorous-rich grains in Úrkút Mn-carbonate ore analyzed by EPMA*

4. táblázat Foszforsódús szemcsék az úrkúti karbonátos Mn-érceben (elektron-mikroszondás megfigyelések)

Elements	Probable mineral phase	Grain size (µm)	Number of samples	Number of mineral grains
Ca, P	Apatite	10–60	10	10
Ca, P	Apatite	20–60	4	9 (locally many)
Ca, Ce, P	Ce-bearing apatite	2–5	3	6
Ce, Ti, K, Ca, P	Ce-Ti-K-bearing apatite	2–10	3	5
La, Ce, Ca, Ca, P	REE-bearing apatite	5	1	1
Ce, P	Monacite	1–30	6	6
Ni, P	?	30	1	1

* 80 samples from the Mn-carbonate and black shale of Úrkút were investigated by EPMA, from which 28 contained P-rich phases (POLGÁRI 1993)

without enrichments of REEs occur in both the Mn-oxide/Mn-carbonate transition zone and in ore-bed No. II. In the main ore bed and in ore bed No. II, high phosphorous-contents without REE enrichments are typical, whereas at Csárdahegy phosphate contains REE enrichments. Higher REE contents occur in the lower part of the main ore bed, closer to the underlying rocks than the other parts of the ore bed. The highest concentrations can be found at Csárdahegy, (Úrkút) and in Eplény close to old fractures, where phosphorous and REE contents are strongly correlated.

Eplény: In Eplény, the phosphorous-rich layers occur in the lower part of the mineralized sequence in yellow-brown claystone, and in the upper part of the deposit in dark-grey pyritiferous claystone. The phosphorous-rich phase was first thought to be Mn- and/or Ca-carbonate. REE investigations began in 1967 and discovered high concentrations of Ce (2000 ppm), Nb (24 ppm), and Y (1300 ppm) (J. KONDA pers. com.). Some major and trace element analyses from the 1950s, 1960s, and 1980s are presented in *Tables 2 and 3*.

Sample and methods

During a review of archive samples, a very phosphorous-rich specimen was found from drillcore Ú-136 (sample #DMUI36, deposited at the Laboratory for Geochemical Research, HAS, Budapest).

The sample was analyzed by X-ray diffraction for the major mineral phases (USGS, Menlo Park; for the details of the technique applied see POLGÁRI et al. 2003).

For the spacial distribution of the mineral phases the sample was studied by routine EPMA methods in the Laboratory for Geochemical Research HAS (Jeol Superprobe 733; analyst: G. NAGY).

The chemical composition was determined in the XRAL Laboratories, Canada. The sample was analyzed for 40 major, minor, and trace elements using acid digestion in conjunction with inductively coupled plasma-atomic emission spectrometry (ICP-AES). For the 40-element analysis (referred to as ICP-40), a split was dissolved using a low-temperature (<150 °C) digestion with concentrated hydrochloric, hydrofluoric, nitric, and perchloric acids. The acidic sample solutions were taken to dryness and the residue was dissolved with 1 ml of aqua regia and then diluted to 10.0 g with 1% (volume/volume) nitric acid. Strontium and Ba concentrations were determined by both ICP-40 and ICP-16 (see below) techniques, which produced comparable datasets. Manganese concentrations were also provided by both ICP techniques which have comparable accuracy and precision. However, the ICP-40 data set is the only one reported because it has a much lower detection limit: 4 parts per million (ppm) compared to 100 ppm for ICP-16.

Another split for each sample was fused with lithium metaborate then analyzed by ICP-AES after acid dissolution of the fusion mixture. This technique, referred to as ICP-16, provides analysis of all major elements, including Si, and a few minor and trace elements. Cherts are very high silica rocks yet the accuracy of Si determinations are quite good, probably about 2–4% based on the total-

oxide sums. Si measurement is not possible using the 4-acid digestion ICP-40 technique because it is lost as a volatile fluoride compound during digestion. Analysis of major elements using the fusion technique also provides a compositional check on the concentrations of these same elements as measured by acid digestion. Titanium and Cr were analyzed using both ICP techniques, but only data from the ICP 16 technique are used because the fusion technique more completely digests resistant minerals that might contain those elements.

Selenium concentrations were determined using hydride generation followed by atomic absorption (AA) spectrometry. Selenium was not reported using either of the ICP techniques, as it is generally volatilized during sample preparation. The hydride generation combined with the AA technique was also used to determine concentrations of As, Sb, and Tl. The hydride analytical technique is considered to be more sensitive than the acid digestion ICP-AES analytical technique for As, as are the data reported here. Mercury was determined by cold vapour atomic absorption spectrometry.

Results of analyses of the archive sample

Macroscopically the sample is yellowish-grey and hard, and dark-brown pyrite grains and porosity differences define the layering (1 mm scale).

Based on the X-ray diffraction, carbonate-fluorapatite (CFA) is a major component, pyrite and quartz are moderate components, while gypsum, a product of secondary oxidation, is a minor-trace component of the sample. The CFA has an XRD pattern typical of CFA from modern marine phosphorite deposits.

The EPMA studies demonstrate a very fine-grained matrix where phosphorous shows both a wavy layer-like and nodular distribution (Figs 1, 2). The phosphorous-poor parts of the matrix (brighter areas of Fig. 1 and 2) are enriched with Mn and Fe. Calcium is also present in the phosphorous-poor regions. These regions may represent a mixture of apatite and (mixed?) carbonates. Pyrite and, rarely, quartz grains of around 5 μm occur in the matrix. Besides the elements belonging to the above outline, mineral phase traces of Na and Mg were also detected by EPMA in some regions of the sample.

The chemical composition of the sample (major and minor elements) is given in Tables 2 and 3 (anal. #1).

Based on the major element data apatite represents more than the half of the sample. The $\text{CaO}/\text{P}_2\text{O}_5$ ratio is 1.71 which is higher than that for most of the cation and anion substituted francolite (1.621) end of the fluorapatite (1.318) range (MANHEIM & GULBRANDSEN 1979, MCCLELLAN & VAN KAUWENBERGH 1990). The $\text{F}/\text{P}_2\text{O}_5$ ratio (0.07) is closer to the fluorapatite end (0.089) than to most of the substituted francolite (0.148) end of the range (MCCLELLAN & VAN KAUWENBERGH 1990). These observations also support that part of the calcium which is not connected to the apatite phase.

Silicon is present predominantly as quartz (about 10%), the rest of it may be connected to minor, not yet identified aluminosilicate phase(s). This phase(s) may

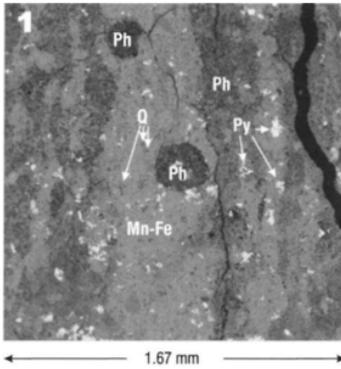


Fig. 1 Backscattered electron image of laminated phosphorite sample from drillcore Ú-136. (Laboratory for Geochemical Research, Budapest). Py: pyrite, Ph: phosphorite, Q: quartz, Mn-Fe: Mn-Fe-carbonate

1. ábra. Rétegzett foszforit visszaszórt elektronképe (Ú-136. fúrás, MTA, GKL, Budapest). Py: pirit, Ph: foszforit, Q: kvarc, Mn-Fe: Mn-Fe-karbonát

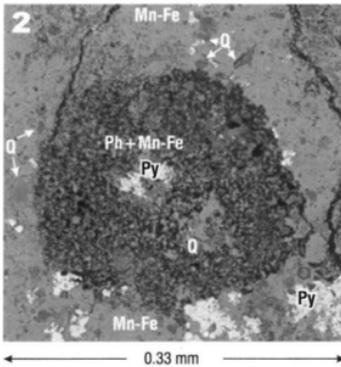


Fig. 2 Backscattered electron image of laminated phosphorite sample from drillcore Ú-136; close-up of Fig. 1 spheroidal fine-grained phosphorite and Mn-Fe-carbonate around pyrite. Py: pyrite, Ph: phosphorite, Q: quartz, Mn-Fe: Mn-Fe-carbonate (The EPMA photos were made by Dr. Géza NAGY, Laboratory for Geochemical Research, HAS, Budapest, 2002)

2. ábra. Az 1. ábra nagyított képe, finomszemcsés foszforit gumó és Mn-Fe-karbonát pirit körül. (Az elektronmikroszkóp felvételeket Dr. NAGY Géza készítette, MTA, GKL, Budapest, 2002)

also contain the Al, Mg and Na which are present. We note that Mg and Na may also be substituted for Ca in the CFA.

The sulphur content was not measured, but based on the presence of pyrite we assign most of the iron to pyrite (estimated amount 10–13%).

Comparison of the Úrkút and Eplény phosphorites

The Csárdahegy, (Úrkút) and Eplény phosphorous-rich beds are similar. Both are concentrated in the lower part of the Mn ore and in the vicinity of fault zones. Scientific and industrial research has determined that the highest REE, U, and Th concentrations occur in these phosphorous-rich layers (GRASSELLY & PANTÓ 1988). Secondary enrichment of phosphorous in the Mn-carbonate/Mn-oxide transition zone occurs at both Úrkút and Eplény, whereas the phosphorous content decreases in the secondary oxide ore. Úrkút bed No. II is enriched in phosphorous without REE enrichment. In general, REEs at Úrkút and Eplény are associated with carbonates (eg. bastnaesite) and phosphates.

Discussion of the trace element geochemistry

The trace elements V, Co, As, Y, and REEs show some enrichment over their crustal abundances. U and Th contents fall into two groups. The sample analyzed here has a U/Th ratio of less than 2 (0.92) and three samples analyzed earlier have ratios greater than 2 (2.67, 38, 155) (Table 3). The low ratio is 2.8 times smaller than the lower end of the ratios (2.6–918) for continental margin, plateau and insular phosphorites, whereas the other three fall within that range (KOLODNY & KAPLAN 1970; VEEH et al. 1974; BIRCH et al. 1983; ROE et al. 1983; THOMSON et al. 1984; VON RAD & RÖSCH 1984; PIPER et al. 1988, 1990). The U/P₂O₅ ratio of the sample analysed here is 0.57×10^{-5} . The Σ REEs vary widely (519–2322 ppm) with a mean of 1703 ppm (Table 3). These contents are much higher than those of Cenozoic phosphate-rich rocks in the Equatorial Pacific Seamount Deposits (mean 356 ppm) reported by HEIN et al. (1993). This can also be stated with respect to the Cambrian phosphorites of the Tiantaishan manganese-phosphorite deposit of China (mean 137 ppm, HEIN et al. 1999), as well as the Peru and Chile margin phosphorites (mean 179 ppm, PIPER et al. 1988). The Ce/La ratio of the Úrkút and Eplény samples vary between 1.86–4.4 (mean 2.84). These are much higher than central Pacific phosphorites (0.07–0.44, HEIN et al. 1993), except for a hydrothermal sample, which is 2.33. The Ce/La ratios of the Chinese deposits resemble seawater values below the oxygen minimum zone, 0.44 (DE BAAR et al. 1985).

The Úrkút and Eplény phosphorites were probably formed in an organic matter- and pyrite-rich environment, which is characteristic at continental margins and oceanic plateaus. In contrast, the central Pacific seamount deposits represent phosphogenesis in an organic matter-poor environment (HEIN et al. 1993).

Phosphorite formation environments

Present-day phosphorites generally occur in four geographic-tectonic settings in the ocean basins:

- On continental shelves and slopes beneath zones of coastal upwelling, phosphorites form during early diagenetic processes very near the seawater-sediment interface in an organic matter-rich environment (BURNETT 1977, FROELICH et al. 1988, GLENN & ARTHUR 1988). More rarely, shelf phosphorites form in an organic matter-poor environment.

- On submarine plateaus, ridges, and banks phosphorite forms from cementation and replacement of carbonates in an organic matter-rich environment.

- On islands, atolls, and atoll lagoons the phosphorite replaces and cements reef carbonates within the freshwater lens, or within the seawater-freshwater mixing zone (sea-level changes). The source of phosphorous is primarily guano, but may also include weathering of volcanic rocks and humic and sapropelic organic matter.

– Mid-plate seamount phosphorites are widely distributed but are the least studied of marine phosphorites. They result from the replacement of carbonates by CFA in a suboxic, but organic matter-poor environment (HEIN et al. 1993).

Phosphorites occur in a wide variety of forms. Element ratios indicate the existence of four types of phosphorites. Uranium and Th contents are low and total REE contents are generally high in marine phosphorites. REE ratios and shale-normalized REE patterns demonstrate that the REEs and host CFA were derived from seawater or slightly modified pore waters. For seamount phosphorites, the main episodes of phosphogenesis occurred at times of climate transition (HEIN et al. 1993).

Of these four deposit types, only seamount phosphorite deposits have significant manganese deposits that occur with them. However, those manganese deposits are oxide deposits and occur with subequal amounts of iron oxide. No primary manganese carbonate occurs. Thus, the Úrkút and Eplény phosphorites do not fit into any of these four categories.

There is one huge fossil manganese-carbonate – phosphorite deposit (Tiantaishan, China) that shows similar geochemical characteristics to the Hungarian Jurassic phosphorous-rich manganese ore deposits. (But the Hungarian deposits are very small in comparison). An exact modern analogue does not exist either for the Tiantaishan depositional and tectonic environment; that would require a recent geological breakup of a supercontinent and the formation of narrow seaways. However, elements of several modern depositional systems, like the Baltic Sea, Black Sea, and continental margin upwelling systems, such as the Peru-Chile margin, display some characteristics that may be applicable to the Chinese and Hungarian deposits (HEIN et al. 1999).

Conclusion

The first full analysis of a really phosphorous-rich sample from the Jurassic black-shale hosted Mn-carbonate and Mn-oxide mineralization of the Transdanubian Range (Úrkút, Eplény) suggests that these phosphorites formed below a zone of coastal upwelling. However, this took place in an anoxic to suboxic basin where black shales and Mn-carbonates also accumulated. Sea-level changes and redox fluctuations permitted the formation of thin diagenetic phosphorite layers within these black shale and Mn-carbonate sequences. Both the phosphorites and Mn-carbonates were formed by bacterially mediated early diagenetic processes.

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