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Terrestrial radioisotopes as paleoenvironmental proxies in sedimentary formations

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Abstract The presence of anomalous terrestrial radioisotopes must be suspected in black shale-hosted manganese ore deposits, based on high organic matter content, which is useful tool in genetic, among them paleoenvironmental investigations. Our work aims at the characterization of the paleoredox conditions of the Úrkút Manganese Formation based on comparison of terrestrial radioisotopes and selected element ratios. Paleoredox indicators were estimated on U/Th, δU, Ni/Co, V/Cr, V/(V + Ni) and Ce*. The results of paleoredox indicator element ratios show, that these methods must be used with caution (microbial selective element enrichments, mobilizations), and the complex interpretation using mineralogy and microtexture can be recommended.

Keywords Úrkút · Manganese ore · Paleoredox proxy · Enrichment factor · Microbial mediation

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Introduction

The Jurassic (Upper Lias) black shale-hosted Úrkút Mn-carbonate deposit (Úrkút Manganese Formation—ÚMF) is a huge deposit with more than 100 Mt of ore reservoirs. Characteristics of the deposit and ore types are summarized by Polgári [1] and Vigh [2]. The two step microbially mediated formation of the ÚMF was also proposed based on complex mineralogical, geochemical and textural interpretations by Polgári [1]. According to the model two cycles of bacterial activity triggered ore formation. Cycle 1 was a near-seabed aerobic chemolithoautotrophic cycle (synsedimentary phase) that was essential in sequestering metal ions (Mn^{2+}, Fe^{2+}) from solution via enzymatic Mn(II) oxidation. Mn-oxide proto-ore was deposited in the sediment pile, serving as a paleoenvironmental indicator of oxic conditions. Cycle 2 was an anaerobic/suboxic heterotrophic bacterial cycle (diagenetic phase) where early diagenetic bacterially mediated Mn(IV) and Mn(III) reduction processes took place via organic matter oxidation and Mn-carbonate mineralization. The ore sequence is laminated at the millimeter scale reflecting a series of Fe-rich biomats by Polgári [3].

The present work is a good example for geochemical results that can be partially attributed to the contribution of biological (microbial) factors. The bio-geochemical relationship between manganese and uranium is for instance versatile, and often difficult to interpret.

Paleoenvironmental characterization on the basis of major- and trace elements, as a further step, is important to get information on ore formation processes, as well as tracing element enrichment and mobilization. Syngenetic paleoenvironmental conditions of the black shale-hosted ÚMF were oxidative, supported by microbial Mn(II) oxidation as main process of sequestration of metal from ore

Table 1 Selected major and trace element composition of the Úrkút Manganese Formation

Sample		Mn (wt%)	Fe (wt%)	V (ppm)	Co (ppm)	Ni (ppm)	Cr (ppm)	Th (ppm)	U (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)
Formation	Rock type											
Eplény Limestone Formation	Cherty limestone				15.30	71.38		6.00	1.32	25.04	40.81	23.72
					18.27			6.06	0.99	25.82	42.13	24.62
Kisgerecse Marl Formation	Marlstone (Ammonitico rosso)				4.32	45.56		1.28	0.37	13.59	26.48	13.74
					8.27	111.68		2.17	0.46	17.23	37.18	17.47
ÚMF Cservár Chert Bed	Chert				22.04	165.53		2.08	0.95	16.46	76.75	20.47
					22.60	56.25		0.99	0.81	15.20	74.57	20.24
Úrkút Manganese Formation	Grey layered Mn-carbonate	6.76	7.20	40.00	62.50	32.00	34.21	2.40	3.30	157.6	730.4	156.6
	Black shale	9.79	8.69	58.00	65.60	26.00	47.89	4.20	0.60	24.6	112.3	26.3
	Brown-grey layered Mn-carbonate	14.41	16.02	45.00	223.40	34.00	20.53	2.30	0.30	25.8	108.2	31.9
	Brown-grey layered Mn-carbonate	0.80	8.45	113.00	25.30	50.00	61.58	4.50	0.90	18.2	62.6	24.3
	Brown-grey layered Mn-carbonate	1.04	6.66	102.00	41.30	41.00	61.58	5.90	1.50	21.7	87.5	24.5
	Beige layered Mn-carbonate	1.59	7.57	98.00	38.00	42.00	61.58	4.50	1.20	29.3	104.1	33.6
	Beige layered Mn-carbonate	0.46	5.53	146.00	19.50	49.00	75.26	6.20	1.20	19.5	51.6	21.1
	Black shale	2.35	3.66	156.00	21.20	51.00	47.89	6.30	1.80	28.9	93.1	30.7
	Black shale	0.98	5.55	154.00	73.90	88.00	68.42	10.30	3.30	30.9	101.4	29.9
	Black shale	1.11	7.04	179.00	90.00	82.00	88.95	9.10	2.90	51.6	236.6	54.1
	Grey layered Mn-carbonate	17.25	8.34	54.00	230.90	50.00	13.68	2.10	0.90	42.2	148.2	45.3
	Grey layered Mn-carbonate	29.62	3.12	54.00	278.90	42.00		1.40	0.80	33.9	120.1	30.9
	Grey layered Mn-carbonate	25.12	5.25	55.00	563.00	58.00		1.90	0.90	48.8	162.1	46.7
	Grey layered Mn-carbonate	23.63	6.67	71.00	261.90	29.00		1.30	0.70	50.0	158.7	39.3
	Grey layered Mn-carbonate	24.27	6.88	49.00	116.00			1.40	0.30	50.3	165.5	40.6
	Green layered Mn-carbonate	18.21	10.39	65.00	65.40			1.20	0.40	47.9	154.0	39.8
	Brown-grey layered Mn-carbonate	23.13	6.55	62.00	260.70	41.00	13.68	2.10	0.60	65.8	252.4	62.2
	Grey layered Mn-carbonate	11.53	4.76	101.00	351.50	62.00	34.21	4.50	5.00	32.0	111.0	30.7
	Brown layered Mn-carbonate	28.35	1.36	20.00	453.60	75.00	0.00	2.40	0.60	34.4	133.2	28.6
	Brown-black layered Mn-carbonate	11.78	17.28	84.00	181.60	54.00	20.53	3.10	0.50	36.2	147.9	29.6
	Brown-black layered Mn-carbonate	26.90	5.52	34.00	181.20	44.00	0.00	2.00	0.30	64.4	251.0	51.9
	Brown-black layered Mn-carbonate	22.38	17.77	79.00	457.70	92.00	27.37	4.40	1.90	29.6	108.7	23.5
	Brown-black layered Mn-carbonate	37.13	9.69	49.00	382.70	64.00	13.68	2.60	3.40	32.4	139.5	27.6
	Green layered Mn-carbonate	13.29	4.57	37.00	243.80	20.00		1.70	0.80	26.3	90.8	21.9
	Black shale				1850.03	239.28		5.06	1.93	85.69	273.86	84.48
	Black shale				398.05	138.73		8.47	3.94	53.26	163.89	50.41
	Black shale	0.06	4.33	206.00	398.10	109.00	88.95	11.20	4.90	93.2	358.6	93.0
ILF Bocskorhegy Member	Greenish grey calcareous marl	0.35	3.39	77.00	80.50	35.00	54.74	11.10	2.00	36.5	90.1	34.5
Isztimér Limestone Formation	Limestone				13.24	129.94		4.66	0.46	20.08	29.23	19.77
					44.27	145.52		9.49	0.93	34.65	56.33	36.57
					8.84	30.37		1.64	0.23	11.93	14.70	9.92
		0.29	1.48	39.00	6.10		20.53	4.70	0.80	18.0	32.3	17.7

forming fluids, and the organic matter-rich character of the ores is the result of a high productivity and high accumulation rate. This oxidative paleoenvironment is not favourable for primary uranium accumulation, because uranium accumulates in U(IV) form in reducing environments, it can further be oxidized to U(VI). In a sedimentary environment, Eh–pH relations and other factors, such as abundant organic matter, strongly control the possibilities of uranium, and thorium enrichment [1].

Our work investigates the paleoredox conditions of the ÚMF—including the footwall (Isztimér Limestone Formation Bocskorhegy Member) and the hanging wall (Kisgerecse Marl and Eplény Limestone Formations)—via the comparative examination of U/Th, δU, rare earth element (REE) patterns, and other trace elements. This offers a case study in comparison with a sedimentary ore formation investigated and interpreted in detail by complex measurements.

Materials and methods

Total of 39 samples from the whole profile of the black shale-hosted manganese ore were investigated for their major, and trace element composition (Table 1). The manganese ore samples (0.1 g) were decomposed in a microwave digestion system (MLS 1200 Mega, Milestone, Italy) using an acid mixture of HNO_3, $HClO_4$, and HF (Tama Chemicals Co., Ltd. Japan) and high purity water produced by Milli-Q water purification system (EMD Millipore, Germany).

The main- and trace elements were analyzed using an inductively coupled plasma mass spectrometer instrument, Agilent 7500 (Agilent Technologies, Japan). Before the measurements, standard solutions were prepared from XSTC-1 and XSTC-331 multi-element standard solutions (Spex CertiPrep, USA) at 0, 100, 500, 2500, 5000 ppt to gain calibration curves. Rh standard (1 ppb) was used as an internal standard. To validate the analytical procedure, JLK-1 (Japan) and GBW-07312 (China) certified reference materials were used.

To clarify the paleoredox conditions, indicator patterns were calculated from the original dataset given in Table 1 [4–8]. The amount of authigenic uranium ($U_a = \delta U$) was calculated after Wignall and Myers [4] according to the following formula, which assumes that the Th has detrital origin in the sedimentary system (accumulating as debris material), and it's average rate related to U is:

$$U_{det} = Th/3,$$

So, the authigenic uranium is:

$$U_a = U_{total} - Th/3.$$

Ce* was calculated according to the following formula evaluated by Jeans [7]:

$$Ce*_{(PAAS)} = \log[3\ Ce_{PAAS} / (2\ La_{PAAS} + Nd_{PAAS})]$$

Mn* was calculated according to the following formula by Macchour [8]:

$$Mn* = \log[(Mn / Mn_{PAAS}) / (Fe / Fe_{PAAS})];$$
$$\text{PAAS: Post Archean Average Shale}$$

Enrichment factors (EF) are routinely used in sedimentary geochemical studies for comparison of major and trace elements (also REE) of the samples to an average composition, in the recent case the Average Shale. Relative enrichment is characterized by $EF > 1$, while relative decrease is characterized by $EF < 1$.

The concentration of an element in sedimentary environments is determined by allochthonous and autochthonous processes. Based on this scenario the so called "not detrital" concentration can also be calculated, which represents the excess concentration in ppm. This excess concentration is the result of a process acted in the sedimentary basin during sediment accumulation or diagenesis after burial. Positive values mean excess of the element, while negative values mean decrease.

Enrichment factor and excess were calculated according to the following formulas:

$$\text{Enrichment factor (EF)} = (\text{element} / \text{Al})_{\text{sample}} / (\text{element} / \text{Al})_{\text{AS}}$$

$$\text{Excess (EX)} = \text{element} - \text{Al}_{\text{sample}} (\text{element} / \text{Al})_{\text{AS}};$$

AS: Average Shale [9].

Results and discussion

The enrichment factor and excess data of the studied elements show that only for the U and Th it is around zero,

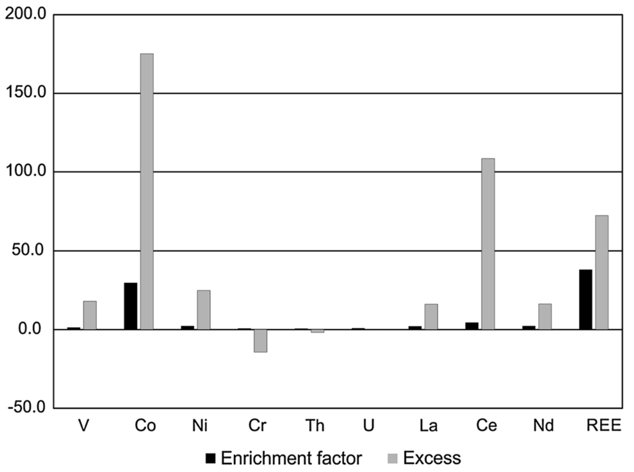


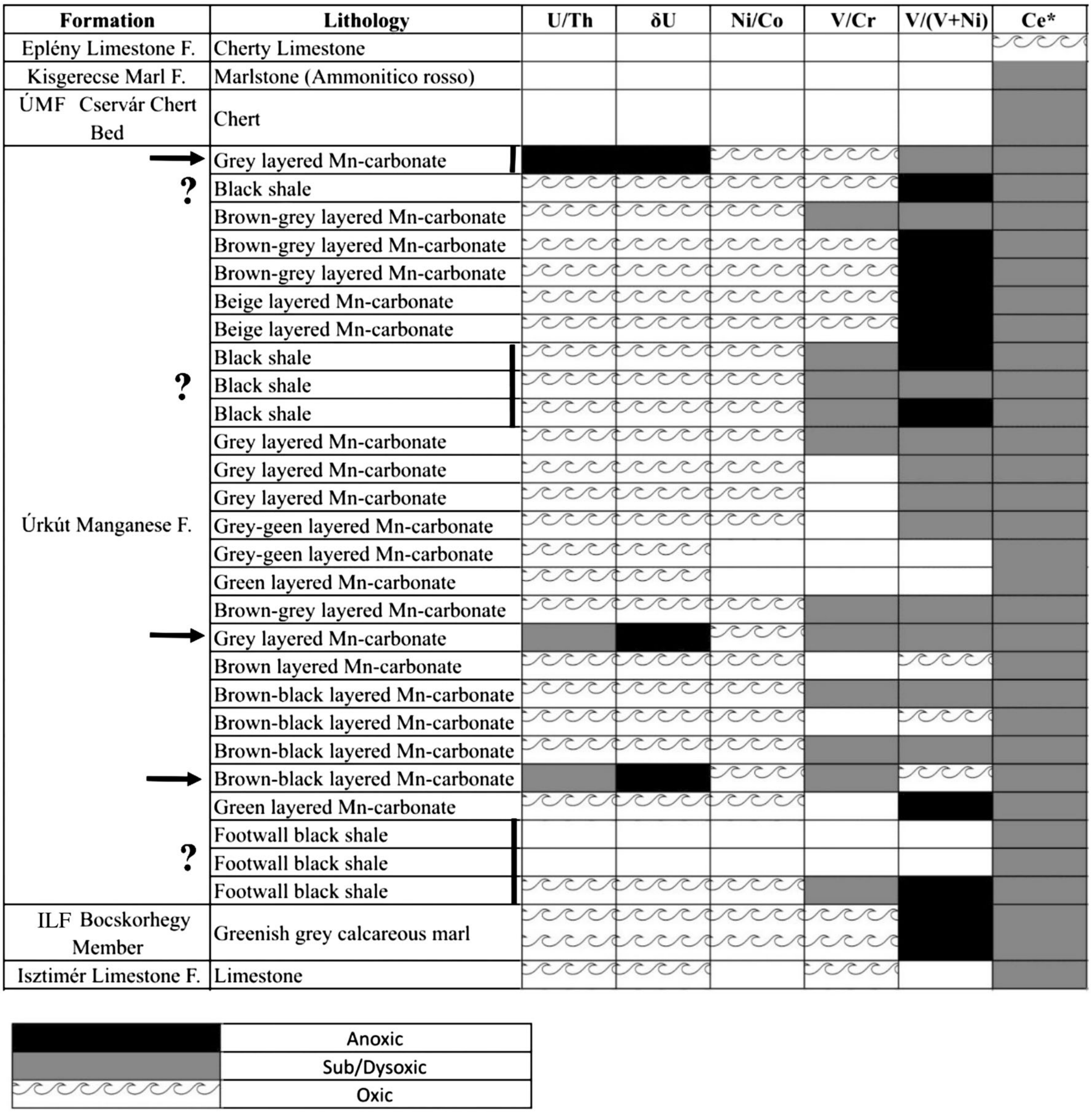
Fig. 1 Enrichment factor and excess (medians in ppm) of the elements

Table 2 The paleoredox indicators

Indicator	Oxic	Suboxic	Anoxic
Ni/Co [5]	<5.00	5.00–7.00	>7.00
V/Cr [5]	<2.00	2.00–4.25	>4.25
V/(V + Ni) [5]	<0.46	0.46–0.60	>0.54
U/Th [6]	<0.75	0.75–1.25	>1.25
δU [4]	<5.00	5.00–12.00	12.00
Ce* [7]	<1.00	>1.00	
Mn* [8]	>1.00	<1.00	

while the others exhibit selective enrichments (Fig. 1). The redox conditions calculated on these elements do not reflect the conditions during ore formation (Table 2). The most enriched elements are cobalt and REE, caused most probably by synsedimentary biogenic (microbial) effects. Cobalt and some REE are microbially active elements (e.g. cerium: Cofactors for e.g. the methanol dehydrogenase of the methanotropic bacterium *Methylacidiphilum fumariolicum*, manganese oxidizing microbes; cobalt: Active nutrient for bacteria and algae, manganese oxidizing microbes).

Comparison of indicator patterns reflect different paleoredox conditions for the same ore beds. U/Th and δU proxies fit with results of Polgári [10] marked by arrows in Fig. 2, but in the case of black shale horizons the results contradict earlier interpretations, indicating oxic formation conditions. Black shale horizons contain high amounts of organic matter and pyrite originated from microbially mediated sulphate reduction in an anoxic environment, a condition reflected by the prevailing mineralogy. In the



Formation		Lithology	U/Th	δU	Ni/Co	V/Cr	V/(V+Ni)	Ce*
Eplény Limestone F.		Cherty Limestone						～
Kisgerecse Marl F.		Marlstone (Ammonitico rosso)						▨
ÚMF Cservár Chert Bed		Chert						▨
Úrkút Manganese F.	→	Grey layered Mn-carbonate	■	■	～	～	▨	▨
	?	Black shale	～	～	～	～	■	▨
		Brown-grey layered Mn-carbonate	～	～	～	▨	▨	▨
		Brown-grey layered Mn-carbonate	～	～	～	～	■	▨
		Brown-grey layered Mn-carbonate	～	～	～	～	■	▨
		Beige layered Mn-carbonate	～	～	～	～	■	▨
		Beige layered Mn-carbonate	～	～	～	～	■	▨
		Black shale	～	～	～	▨	■	▨
	?	Black shale	～	～	～	▨	▨	▨
		Black shale	～	～	～	▨	■	▨
		Grey layered Mn-carbonate	～	～	～	▨	▨	▨
		Grey layered Mn-carbonate	～	～	～		▨	▨
		Grey layered Mn-carbonate	～	～	～		▨	▨
		Grey-geen layered Mn-carbonate	～	～	～		▨	▨
		Grey-geen layered Mn-carbonate	～	～				▨
		Green layered Mn-carbonate	～	～				▨
		Brown-grey layered Mn-carbonate	～	～	～	▨	▨	▨
	→	Grey layered Mn-carbonate	▨	■	～	▨	▨	▨
		Brown layered Mn-carbonate	～	～	～		～	▨
		Brown-black layered Mn-carbonate	～	～	～	▨	▨	▨
		Brown-black layered Mn-carbonate	～	～	～		～	▨
		Brown-black layered Mn-carbonate	～	～	～	▨	▨	▨
	→	Brown-black layered Mn-carbonate	▨	■	～	▨	～	▨
		Green layered Mn-carbonate	～	～	～		■	▨
		Footwall black shale						▨
	?	Footwall black shale						▨
		Footwall black shale	～	～	～	▨	■	▨
ILF Bocskorhegy Member		Greenish grey calcareous marl	～	～	～	～	■	▨
Isztimér Limestone F.		Limestone	～	～		～		▨

■	Anoxic
▨	Sub/Dysoxic
～	Oxic

Fig. 2 Distribution of oxic, suboxic and anoxic conditions along the profile of ÚMF based on selected calculated indicator patterns

case of grey and brown-black manganese carbonate ore beds, the U/Th and δU proxies more or less support each other and the results of the other paleoredox proxies, concerning the suboxic–anoxic conditions. These interpretations are also supported by the clay mineralogy [10], which indicates the role of diagenesis in the organic matter-rich environment, and transport effects observed in the under- or overlying black shale horizons.

Conclusion

Our project presents results from paleoproductivity evaluation and the analyses of enrichment factors and detrital element quantity comparisons in a microbially mediated manganese ore deposit. Enrichment factors were compared with previous data regarding the utilization of trace elements in biological, microbially mediated sedimentary systems. According to paleoproductivity and enrichment factors, we can assume that biological (microbial) activity played a role in selective element enrichment during the formation of the manganese ore deposit. Uranium and thorium are suitable as paleoredox indicators, but great care has to be taken in the complex interpretation of the data in such microbially mediated systems.

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