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RARE EARTH ELEMENTS IN METAMORPHOSED BLACK SHALES OF THE MALÉ KARPATY MTS.

(*Figs.* 4, *Tabs.* 9)

Abstract: From the study of REE amounts in 80 samples of black slates in the crystalline complex of the Malé Karpaty and 10 samples of separated heavy fraction from these rocks, using the INAA method, the authors try to interpret the genesis of black shales. On the basis of arithmetic means, arithmetic standard deviations, coefficients of variation, geometric means and geometric standard deviations they compute the expected range of REE concentration within the 68 % and 95 % confidence intervals. The authors also discuss the causes of anomalous contents of La, Ce and Sm in some samples studied, and present the graphs showing REE contents standardized according to the values computed by Piper (1974).

Резюме: На основе исследования содержаний редкоземельных элементов в 80 пробах черных сланцев кристаллиникума Малых Карпат и 10 пробах сепарированных тяжелых фракций из этих пород, определенных при помощи метода INAA авторы проводят генетические интерпретации о происхождении черных сланцев. Они приводят значения средних арифметических, арифметических стандартных отклонений, вариационных коеффициентов, средних геометрических и геометрического стандартного отклонения. Эти данные они используют для вычисления ожидаемого диапазона концентраций редкоземельных элементов в исследованных породах в 68% и 95% интервалах достоверности. Они также приводят причины аномальности содержаний La, Ce, Sm в некоторых исследованных пробах и приводят графики, в которых содержания редкоземельных элементов нормализованы согласно значениям вычисленных Пипером (1974).

The geochemistry of REE in the slates of the Malé Karpaty crystalline complex was briefly discussed by the authors in the paper published in Geologický Zborník Geologica carpathica 3/1983.

As many analyses of black slates carried out using the neutron activation gave anomalous results, their rightness should be verified. Therefore, it is only in this study that the conclusive evaluation and interpretation are presented, when the essential rightness of anomalous REE contents in a part of black slates has been proved.

It was also expedient to publish in separate articles several supplementary interpretations and considerations which could not be included in Cambel—Khun's paper (1983) on account of the limited number of pages available. These supplements should mainly discuss the genesis of black slates and sulphidic ores they contain. The genetic conclusions and the question whether to assign the black slates to the productive zones of the underlying Pezinok--Pernek crystalline complex or to the Harmónia Formation, are nowadays of

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much importance for the study of the tectonics of the Malé Karpaty Mts. The supplements presented here chiefly issued from further investigations of Dr. Khun, who studied these questions within the scope of his dissertation work (Khun, 1983) and publishes the results in this number of the journal; his two contributions deal with boron and with the geochemistry of and differences between the rocks of productive zones and black slates of the Harmónia Formation.

Table 1

Compiled data on the REE contents in coal and black shales

Element	1	2	3	4	5	6
La	6.0	4.9	3.3	3.23	5	8
Ce	18.0	12.2	10.8	8.28	11	19
Sm	2.3	1.2	2.0	1.26	—	—
Eu	0.1	0.5	0.8	0.47	1	1.2
Tb	0.3	0.2	0.36	0.29	0.2	0.6
Yb	2.2	0.4	0.57	1.10	2	2.0
Lu	—	—	0.07	0.17	0.3	0.2

Explanations: Compiled data on the REE contents in coal and black shales: 1 — bituminous coal of the Kizelov basin (Jeršov, 1961); 2 — bituminous coal of West Pennsylvania; 3 — bituminous coal of South Illinois (both in Schonfield—Haskin, 1964); 4 — black sulphidic shale, Kambalda, Australian Bavinton — — Taylor, 1980); 5 — black graphitic phyllite, Chvaletice (Bouška et al., 1974); 6 — detto (Cháb et al., 1982). Contents given in $g.t^{-1}$; — not determined; only REE analysed in the Malé Karpaty black slates are listed.

The distinction of the black slates of the Harmónia Formation from slates of the productive zones of the Pezinok-Pernek crystalline complex is discussed by Andráš—Horváth in a contribution published here.

Metamorphic processes, genesis and character of minerals in the slates of the Harmónia Formation and the Pezinok-Pernek crystalline are dealt with in the work ok Korikovskij et al. (1984); metamorphic minerals originating in the contact zone of the Modra granodiorite with the Harmónia Formation are described in this number of Geologický Zborník.

The study of REE contents in the black slates of the Malé Karpaty crystalline complex was based on 80 analyses of rocks and 10 analyses of heavy fractions separated from these rocks by the INAA method (ÚL ČSUP, Stráž pod Ralskem — Ing. P. Kotas, CSc.). All results of these studies are given in the paper of Cambel—Khun (1983). The present paper submits the subsequently computed arithmetic standard deviations, coefficient of variation, geometric mean and geometric standard deviation, which were not given in the former paper. These statistical characteristics are needed for the computation of the expected range of REE concentrations in the rocks studied as concerns the individual crystalline area individual rock types (Tables 2—9).

Table 2

Mean REE contents, other statistic characteristics, and computation of the expected range of REE contents in all analysed samples of the set of Malé Karpaty black states

Element	AM	AS	CV	GM	GS	Distribution type	Detection ratio	$\bar{x}$ g . t^{-1}	S	Expected range in g . t^{-1}	
										in 68 %	in 95 %
La	20.9	10.5	50.2	16.7	1.5	L	80 : 80	16.7	1.5	11.1 —25.0	7.4 —37.6
Ce	41.5	22.9	55.2	36.2	1.5	L	80 : 80	36.2	1.5	24.1 —54.3	16.1 —81.4
Sm	4.3	2.9	67.4	3.5	1.6	L	80 : 80	3.5	1.6	2.2 — 5.6	1.4 — 8.9
Eu	1.1	0.4	36.4	1.1	1.4	L	80 : 80	1.1	1.4	0.8 — 1.5	0.6 — 2.1
Tb	0.6	0.3	50.0	0.5	1.6	L	80 : 80	0.5	1.6	0.3 — 0.8	0.2 — 1.3
Yb	2.5	1.9	76.0	2.2	1.5	L	80 : 80	2.2	1.5	1.5 — 3.3	1.0 — 4.9
Lu	0.4	0.3	75.0	0.4	1.8	L	80 : 80	0.4	1.8	0.2 — 0.7	0.1 — 1.3
Σ REE	71.3			60.6							

n = 80

Explanations: Mean REE contents, other statistic characteristics and computed range of REE expected in all analysed samples of the set of Malé Karpaty black slates. Contents given in g . t^{-1}; AM — arithmetic mean; AS — arithmetic standard deviation; CV — coefficient of variation in %; GM — geometric mean; GS — geometric standard deviation; n — number of samples; L — lognormal type of distribution; detection ratio — first numeral — number of samples with REE content above the limit of provableness, second numeral — total numeral of samples analysed; $\bar{x}$ — mean content in distribution L, geometric mean; S — standard deviation, geometric in distribution L. In the last column — expected range.

From the REE contents in the analysed samples of crystalline schists it was evident that the analyses of heavy fractions separated from the rock and ore samples cannot be included in the total set of rocks in computing the means, especially because of low contents of low REE (La and Ce), in particular.

Table 3

Mean REE contents and expected concentration range in slate samples of all types (A, B, C) in productive zones

Element	AM	AS	CV	GM	GS	Expected range g . t^{-1}	
						v 68 %	v 95 %
La	16.8	10.8	64.3	12.3	2.6	4.7 —32.0	2.3 —83.1
Ce	28.0	19.3	68.9	20.9	1.8	11.6 —37.6	6.4 —67.7
Sm	4.6	3.2	69.5	3.6	1.5	2.4 — 5.4	1.6 — 8.1
Eu	1.3	0.5	38.5	1.1	1.4	0.8 — 1.5	0.6 — 2.1
Tb	0.6	0.3	50.0	0.5	2.0	0.2 — 1.0	0.1 — 2.0
Yb	3.0	1.7	56.6	2.5	2.0	1.2 — 5.0	0.6 —10.0
Lu	0.5	0.3	60.0	0.4	1.8	0.2 — 0.7	0.1 — 1.3
Σ REE	54.8			41.3			

n = 46

Explanations: Mean REE contents and expected range of concentration in slate samples of all types (A, B, C). Explanation as in Fig. 2. Lognormal type of distribution, detection ratio 46 : 46.

Table 4

Mean REE contents in productive zones, samples of A type

Element	AM	AS	CV	GP	GS
La	15.2	9.4	61.8	11.4	2.5
Ce	28.7	19.8	68.9	22.6	2.0
Sm	4.4	2.7	61.4	3.5	2.4
Eu	1.4	0.5	35.7	1.1	1.4
Tb	0.6	0.3	50.0	0.5	1.9
Yb	3.1	1.6	51.6	2.6	2.1
Lu	0.5	0.3	60.0	0.4	1.8
Σ REE	53.9			42.1	

n = 31

Explanations: Mean REE contents in productive zones, samples of A type. For explanation see Table 2.

This anomaly is obviously caused by a high amount of sulphidic minerals present in heavy fraction. The anomalous ratios of La/Ce contents are also observable in some rock samples in the groups B and C (samples with apparent content of sulphides and sulphide ores with organic matter) from the productive zones.

Table 5

Mean REE contents in productive zones, samples of B and C types (samples with megascopic pyrite or from ores)

Element	AM	AS	CV	GP	GS
La	20.2	12.6	62.4	14.2	2.3
Ce	26.7	18.4	68.9	17.5	2.8
Sm	5.4	4.3	79.6	3.8	2.5
Eu	1.3	0.6	46.1	1.1	1.5
Tb	0.7	0.4	57.1	0.6	2.1
Yb	2.8	2.0	71.4	2.3	1.8
Lu	0.4	0.3	75.0	0.4	1.9
Σ REE	57.5			39.9	

n = 15

Explanations: Mean REE contents in productive zones, samples of B and C types (samples with megascopic pyrite or from ores). For explanation see Table 2.

Table 6

Mean REE contents in samples from localities outside productive zones

Element	AM	AS	CV	GM	GS
La	24.7	5.5	22.3	24.1	1.2
Ce	56.3	14.4	25.6	54.0	1.4
Sm	3.8	0.9	23.7	3.7	1.3
Eu	1.1	0.2	18.2	1.1	1.2
Tb	0.5	0.2	40.0	0.5	1.3
Yb	1.9	0.6	31.6	1.8	1.4
Lu	0.3	0.1	33.3	0.3	1.7
Σ REE	88.6			85.5	

n = 18

Explanations: Mean REE contents in samples from localities outside productive zones. For explanation see Table 2.

In samples of the A type (samples without macroscopically visible sulphides) from the productive zones, nine samples contained anomalously low La, Ce and Sm amounts (Cambel — Khun, 1983). Such low contents are also recorded in the literature concerning the black shales but, regrettably, without

Table 7

Mean REE contents and expected concentration range in the Harmónia Formation (overlying Devonian-Lower Carboniferous complex)

Element	AM	AS	CV	GM	GS	Expected range g . t^{-1}	
						in 68 %	in 95 %
La	28.2	8.6	30.5	26.8	1.4	19.1—37.5	13.7—52.5
Ce	63.8	21.3	33.4	60.2	1.2	50.2—72.2	41.8—86.7
Sm	4.0	1.8	45.0	3.3	1.6	2.1— 5.3	1.3— 8.4
Eu	1.1	0.3	27.2	1.1	1.4	0.8— 1.5	0.6— 2.1
Tb	0.6	0.3	50.0	0.5	1.7	0.3— 0.8	0.2— 1.4
Yb	2.0	0.7	35.0	1.9	1.4	1.3— 2.7	1.0— 3.7
Lu	0.4	0.2	50.0	0.4	1.6	0.2— 0.6	0.1— 1.1
Σ REE	100.1			94.2			

n = 16

Explanations: Mean REE contents and expected concentration range in the Harmónia Formation (the overlying Devonian-Lower Carboniferous complex). For explanation see Table 2. Lognormal type of distribution, detection ratio 16 : 16.

Table 8

Mean REE contents and expected concentration range in samples from the Bratislava area

Element	AM	AS	CV	GM	GS	Expected range g.t^{-1}	
						in 68 %	in 95 %
La	22.1	3.6	16.3	21.8	1.2	18.2—26.2	15.1—31.4
Ce	48.8	14.5	29.7	45.9	1.3	35.3—59.7	27.1—77.6
Sm	3.5	0.9	25.7	3.5	1.2	2.9— 4.2	2.4— 5.0
Eu	1.1	0.3	27.3	1.0	1.3	0.8— 1.3	0.6— 1.7
Tb	0.6	0.2	33.3	0.5	1.5	0.3— 0.7	0.2— 1.2
Yb	1.9	0.6	31.6	1.8	1.5	1.2— 2.7	0.8— 4.0
Lu	0.3	0.1	33.3	0.3	1.4	0.2— 0.4	0.1— 0.6
Σ REE	78.3			74.8			

n = 8

Explanations: Mean REE contents and expected concentration range in samples from the Bratislava area. For explanation see Table 2. Lognormal type of distribution, detection ratio 8 : 8.

any attempt at the explanation of this finding. Very low REE amounts are also in coal. Table 1 lists analyses, refered to in the literature, of samples with low REE contents in coal and black shales. The distribution of REE in the rocks examined is shown in Fig. 1, and the mean values together with

Table 9

Mean REE contents and expected concentration range in the crystalline basement involved

Element	AM	AS	CV	GM	GS	Expected range $g.t^{-1}$	
						in 68 %	in 95 %
La	19.0	7.6	40.0	15.6	1.4	11.1—21.8	7.9—30.6
Ce	35.9	18.8	52.4	30.2	1.7	17.8—51.3	10.4—87.2
Sm	4.4	2.2	50.0	3.6	1.5	2.4— 5.4	1.6— 8.1
Eu	1.2	0.4	33.3	1.1	1.3	0.8— 1.4	0.6— 1.8
Tb	0.6	0.3	50.0	0.5	1.6	0.3— 0.8	0.2— 1.3
Yb	2.7	1.1	40.7	2.3	1.4	1.6— 3.2	1.1— 4.5
Lu	0.4	0.2	50.0	0.4	1.7	0.2— 0.7	0.1— 1.1
Σ REE	64.2			53.7			

n = 64

Explanations: Mean REE contents and expected concentration range in the crystalline basement involved. For explanation see Table 2. Lognormal type of distribution, detection ratio 64 : 64.

other statistical characteristics for individual areas and rock types are given in Tables 2—9. The very low content of humic carbon C_{hum} established in all samples (as far as complete analyses of organic matter were available) indicates that the low REE contents in nine samples from the productive zones could only partly be influenced by humified coal material brought from the continent into the littoral zone of the sea. It is more probable that the organic matter combined with the minerals of the amphibole group (mainly actinolite) and the presence of amphibolites in the productive zones were responsible for these low contents. The low REE contents in the amphibolites of the Malé Karpaty also point to this hypothesis (Cambel—Spišiak, 1979; Cambel—Kamenický, 1982), similarly as the finely dispersed pyrite present in all black slates. Low contents of the La, Ce and Sm can neither be explained by metamorphic effects.

For the black slates of the Malé Karpaty the generally accepted fact that the REE contents in rocks are little affected by metamorphism can be confirmed (Haskin et al., 1968; Cullers et al., 1974; McLennan et al., 1979). The samples from the Malé Karpaty have been divided into epimetamorphosed and meso- to katametamorphosed according to the metamorphic grade (for division criteria see Cambel—Khun, 1983).

In order to avoid distortion of the data, nine samples with anomalously low contents of La, Ce and Sm from the productive A-type zones, all samples of B and C types from the group of productive zones and heavy fractions have not been included in computation.

The mean contents are as follows ($g \cdot t^{-1}$):

Metamorphism: epi-, 37 samples		meso-, kata-, 19 samples
La	23.7	23.9
Ce	48.3	50.1
Sm	4.1	4.6
Eu	1.1	1.2
Tb	0.6	0.5
Yb	2.7	2.3
Lu	0.5	0.5
REE	81.0	83.1

The samples from areas outside the productive zones and from the Harmónia Formation provide a different picture of the La and Ce distribution. All these samples have a lower content of organic matter. From the steady La/Ce ratio we may infer that during their deposition the sedimentary conditions were more uniform, quieter, and the lithology was more normal without the accompaniment of basic volcanism, which predominated and influenced the sedimentation of rocks of the ore-bearing zones. This is well demonstrated in Fig. 2, which clearly shows a lower variation of REE elements in the black slates of the Harmónia Formation relative to the slates of the productive zones. It is noteworthy that the samples from the area of the Harmónia Formation have the highest mean contents of REE among the studied samples of black slates in the Malé Karpaty crystalline complex (Tab. 7). This fact may provide evidence of their younger age, which is also shown by palynological finds. The enrichment of younger sediments in REE relative to the old ones is reported by Wildeman — Haskin (1973), Balašov — Tugarinov (1976), Nance — Taylor (1976). Higher REE contents in black shales from Kambala (Australia) are correlated with age by Bavinton — Taylor (1980), who assessed a pronounced trend towards the increase of the total REE content in younger sediments. On the basis of the $\Sigma Ce/\Sigma Y$ ratio Ronov et al. (1972) assumes a relative enrichment in lighter REE to be characteristic of the younger sediments. In the black slates of the Malé Karpaty the values of this ratio are the following (without the Y content, which was not determined):

Crystalline basement	$\Sigma Ce/\Sigma Y$	16.3
Harmónia Formation	$\Sigma Ce/\Sigma Y$	32.4

Linear dependence of the enrichment of the Harmónia Formation in lighter REE assessed from the La/Yb ratio is shown in Fig. 3.

From the viewpoint of facies analysis, the increase in the total content of REE towards the continent and synchronous enrichment in light REE are described by Balašov et al. (1964); Ronov et al. (1967); Cullers et al.

(1975) and Cullers et al. (1979). The samples from the productive zones would then represent in the littoral facies of the Malé Karpaty black slates the most distant part from the shore. The assumption of the offshore origin of black slates of the productive zones, based on the REE contents is also supported by the marked deficit of Ce (Fig. 4).

The Ce deficit in ore-bearing sediments deposited at a greater distance from the shore was assessed by Bender et al. (1971) and Piper—Graef (1974). The sorption of all REE in sediments increases from the marginal to offshore parts of the sea, as well as the difference between Ce and other REE; this implies that Ce must be preferentially sorbed in the supplied terrigenous silicate material nearer to the shore (in fact the highest Ce contents are in the Harmónia Formation). The difference in sorption capacity of Ce and the remaining REE is connected with its oxidation to Ce^{4+}.

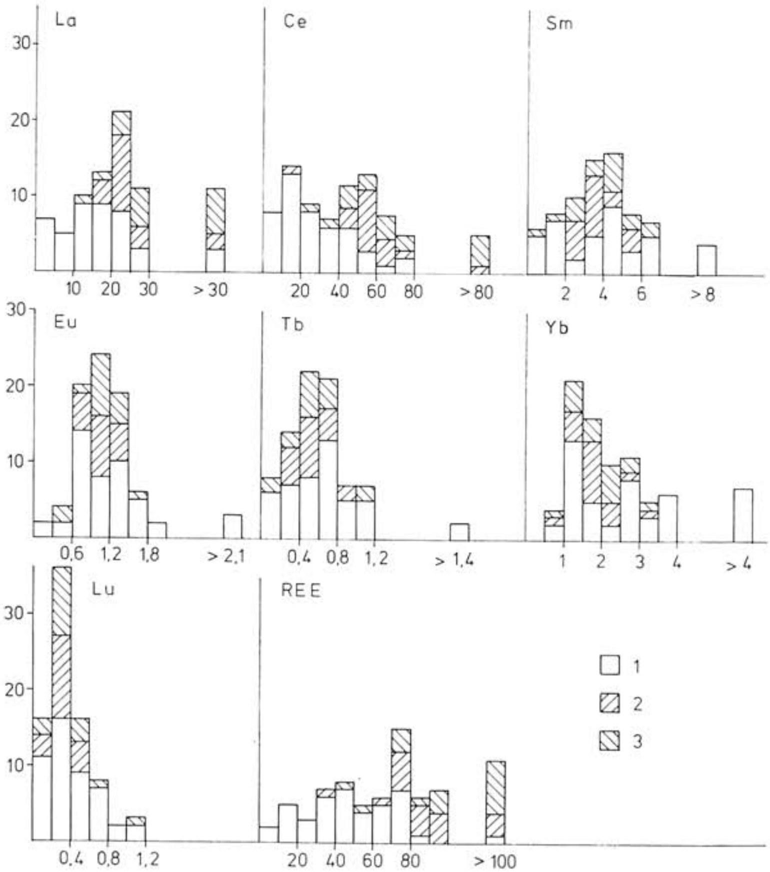
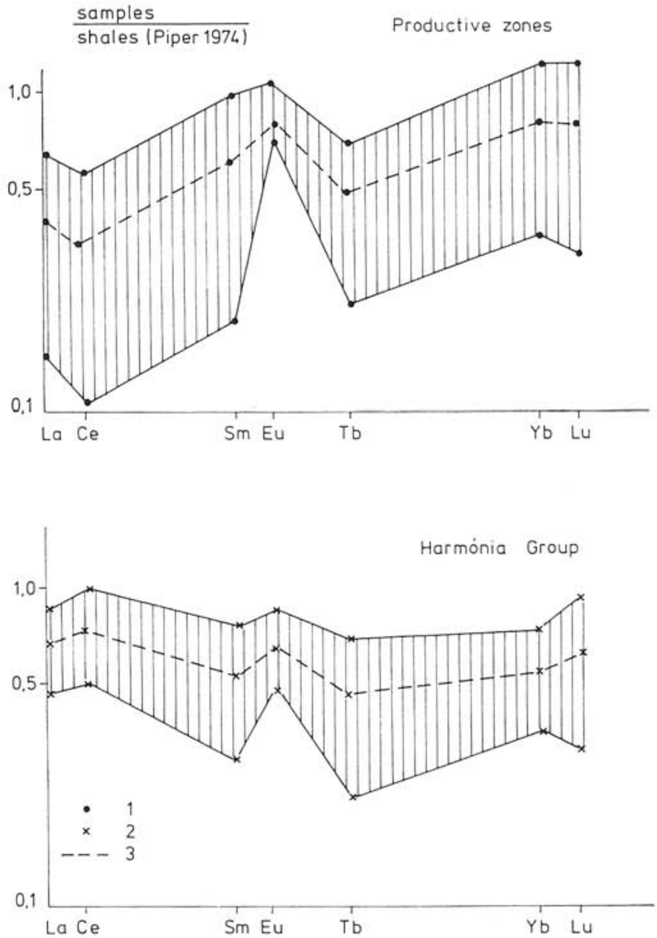


Fig. 1. Histograms of REE distribution in black slates studied.
Explanations: Contents in $g \cdot t^{-1}$. 1 — productive zones; 2 — areas outside the zones; 3 — Harmónia Formation.

Fig. 4 exhibits a striking Eu anomaly. A relatively inexpressive Eu anomaly in black slates of the Malé Karpaty was referred to by C a m b e l — K h u n (1983); in their study the mean REE contents in individual areas were standardized to 20 chondrites (S c h m i t t et al., 1963 in H a s k i n et al., 1968). As noticed by P i p e r (1974), this mode of standardization however rules out a comparison in individual marine facies, because the relative concentrations of REE in these evolution facies differ extremely from chondrites. Therefore, he computed from the mean REE contents in North American and European shales and of those of



Fg. 2. Distribution of REE in productive zones and in the Harmónia Formation standardized to shales, according to P i p e r (1972).
Explanations: Contents in g . t^{-1}. Shaded field represents the area obtained by computation of AM±S. 1 — productive zones; 2 — Harmónia Formation; 3 — arithmetic mean AM; S — arithmetic standard deviation.

the Russian platform the following values that he recommends as standards for the REE contents in marine shales (g . t^{-1}):

La	41	Tb	1.23
Ce	83	Dy	5.5
Pr	10.1	Ho	1.34
Nd	38	Er	3.75
Sm	7.5	Tm	0.63
Eu	1.61	Yb	3.53
Gd	6.35	Lu	0.61

In the graphic representation standardized in this way, the positive Eu anomaly is still more pronounced. The positive Eu anomaly in black shales was stabilished by several authors, as e. g. Cullers et al., 1975; Bavinton — Taylor, 1980 and Mitropoulos, 1982. They interpret it in terms of local accumulation of Eu in plagioclase detritus, or chemical interaction with sea

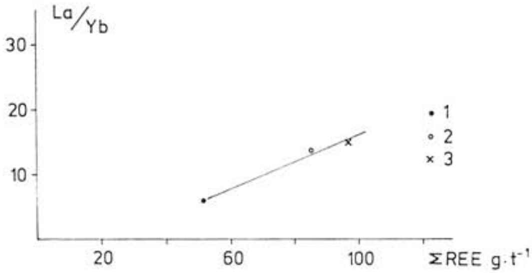


Fig. 3. Graph showing the La/Yb ratio to the total REE content.
Explanations: Contents of REE in g . t^{-1}. 1 — productive zones; 2 — localities outside the zones; 3 — Harmónia Formation.

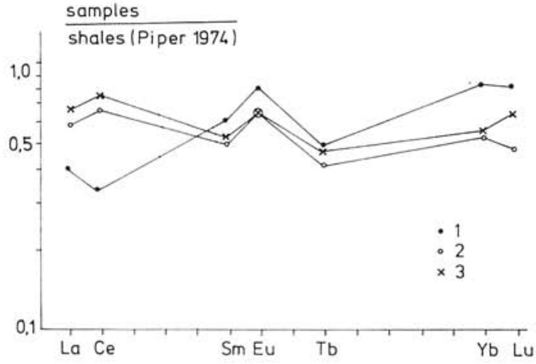


Fig. 4. Graph showing the distribution of REE in individual areas, standardized to shales according to Piper (1972).
For. explanation see Fig. 3.

water during prolonged submarine weathering, or precipitation from hydrothermal solutions. Mitropoulos (1982) describes the increase of positive Eu anomaly in black metapelites with increasing distance of their occurrence from a granite intrusion, as being caused by the change in O_2 regime. The positive Eu anomaly may also be inherited from the source rocks of the supply area. This hypothesis could be applied to the Malé Karpaty black slates, as all the neighbouring amphibolites show a positive Eu anomaly (Cambel — Spišiak, 1979) but it is difficult to explain the rather remarkable difference in its value in samples taken from the productive zones and other areas.

The expected range of the REE concentrations in black slates from the individual areas was computed using the procedure that was applied by Čadková (1981) for the Carboniferous and Permian sediments of the Bohemian Massif. Tables 2, 3, 7, 8, 9 show which concentrations of REE in particular areas can be expected in the 68 % and 95 % intervals of confidence. Table 2 presents a complete survey of computations for the whole set of black slates from the Malé Karpaty crystalline complex.

The distribution of REE in black slates of the Malé Karpaty Mts. standardized to the La content (La = 1.00) agrees surprisingly with similarly standardized analyses recorded by Haskin — Gehl (1962) and applied by Taylor (1965). From this conformity it can be inferred that the black shales do not exceed the framework of normal sedimentary processes.

	Haskin — Gehl (1962)	80 samples of M. Karpaty black shales
La	1.00	1.00
Ce	2.00	1.98
Sm	0.20	0.20
Eu	0.040	0.052
Tb	0.030	0.029
Yb	0.10	0.12
Lu	0.017	0.019

In conclusion, it should be stated that the data on the REE contents in the black slates of the Malé Karpaty crystalline complexes are results of 3 times repeated analyses, but that we cannot guarantee all analytical errors are excluded (see control analyses of Khun, 1983). From this it follows that in applying the results obtained by INNA method (instrumental neutron activation) we must proceed very considerately, and that a very close co-operation of analysts and geochemists is needed to avoid publishing low-quality or wrong analyses.

This cooperation is evolved between Slovak Academy of Sciences, the Faculty of Sciences, UK (Cambel — Khun) and the analysts of the Central Laboratory, Uranium Industry in Stráž pod Ralskem. The authors are obliged to Ing. P. Kotas CSc, who deserved well of this collaboration.

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