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GEOCHEMICAL DIFFERENTIATION OF BLACK SHALES OF THE HARMÓNIA GROUP FROM THE CRYSTALLINE BASEMENT IN THE MALÉ KARPATY MTS.

(Figs. 6, Tabs. 4)

Abstract: In this paper the author points out the different geochemical characteristics of the Harmónia Group black shales and the crystalline basement in the Malé Karpaty Mts. on the basis of trace elements contents and sulphur distribution. The author puts forward a simple graphical method of discrimination of the black shales from both areas. An outline of a sedimentological interpretation of the black shales of the Malé Karpaty Mts. crystalline complexes, based on different geochemical symptoms, is also presented.

Резюме: В статье отмечается разная геохимическая характеристика черных сланцев гармонской серии и подстилающего кристаллиникума Малых Карпат на основе содержаний следов и распределения серы. Автор предлагает простой графический метод дискриминации обоих регионов. Также приведен очерк седиментологической интерпретации черных сланцев кристаллиникума Малых Карпат на основе разных геохимических признаков.

During the survey of the Sb-deposit Pezinok it was discovered by boring that in the mining district of this deposit the whole crystalline complex of the first productive zone in the Kolársky Hill area, which belongs to the older (basal) strata of the Pezinok-Pernek crystalline complex, is tectonicaly thrusted on the younger strata of the Harmónia Group, i. e. it is overlying the Harmónia Group.

The different geochemical characteristic of the black shales of the Harmónia Group compared with the black shales of the basal crystalline complex makes it possible to differentiate this two groups on the basis of trace elements contents. A similar differentiation of productive zones and other black shales in the crystalline complexes of the Malé Karpaty Mts. has already been carried out by discrimination analysis (Khun, 1977; 1980). The group of samples from outside of the productive zones was represented by undifferentiated samples from the Bratislava region, Harmónia Group and other localities in the Pezinok-Pernek crystalline complex, so that it was not possible to discriminate the Harmónia Group and the productive zones (for geological conditions see e. g. Cambel, 1958; Cambel — Khun, 1983). The discrimination analysis is a relatively difficult mathematical operation, necessitating at least a small computer. Because of this, in this paper we put forward and use a simple graphical method for differentiating the two sets using average contents and variation coefficient.

A wealth of information, which permits to consider the variation coefficient an important characteristic of geological objects, has already been accumulated

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in geochemistry and ore geology. Variability depends on the amount of substance on the rock, its chemical characteristics and on the geological process or processes which have formed the rock and the given substance, in our case the chemical element. Trace elements have variation coefficients up to 200—250 per cent, the main ore elements only about 20 per cent. Franckij (1970) proposes even to use the variation coefficient as the main geochemical parameter.

The graphical method, using average contents and variation coefficients is very simple. On the x-axis we put the average contents of the element and on the y-axis the corresponding values of the variation coefficient, separately for each element of the two sets. We connect then the points of corresponding elements. It is possible then to make an order of elements, according to the length of abscisses, showing the difference of average values and variation coefficients in both sets. For the basal crystalline complex and Harmónia Group the lengths of abscisses and so also the order in which the studied elements differ in variation coefficients and average contents are following (Fig. 1): V, B, Ni, Sr, Cr, Zr, Co. As we can see, when comparing this with Tab. 1,

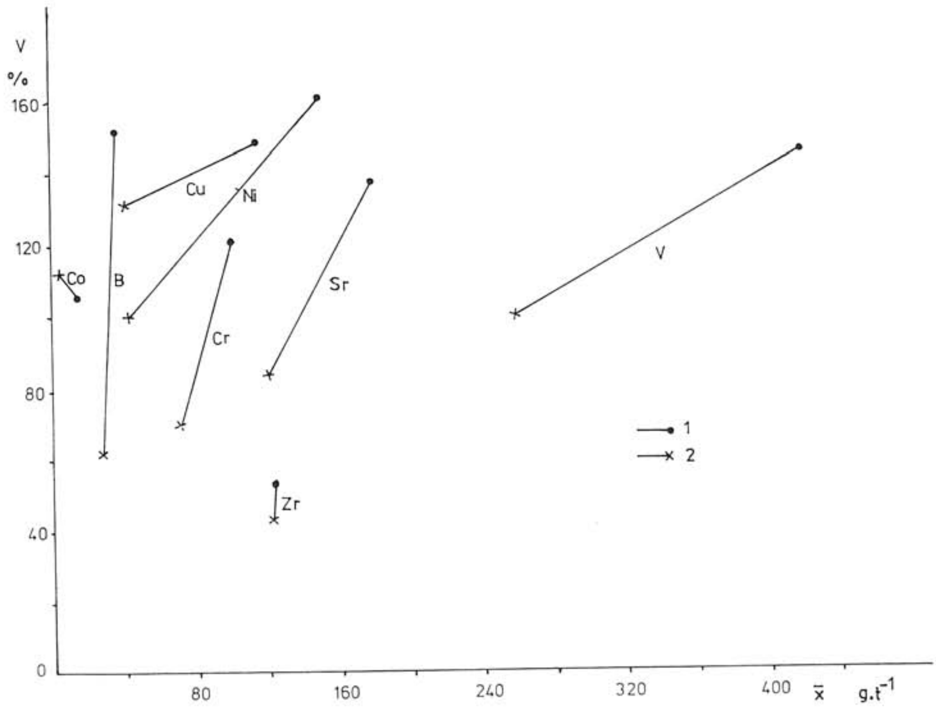

Fig. 1. Differentiation graph of black shales of the crystalline basement and of the Harmónia Group.

Explanations: V — variation coefficient in per cent; $\overline{x}$ — arithmetical mean of the contents of the element in g . t^{-1}; 1 — crystalline basement; 2 — Harmónia Group.

Table 1

Average contents of the discriminated trace elements in both studied areas

	Subjacent crystalline area as a whole				Harmónia Group			
	AM	AD	CV	GM	AM	AD	CV	GM
B	39	58	151	22	30	19	62	21
V	419	612	146	245	260	260	100	170
Cu	115	171	148	54	42	56	132	26
Ni	151	242	160	67	45	45	100	30
Co	15	16	106	7	7	8	111	3
Cr	102	123	121	77	73	51	70	57
Sr	178	245	137	102	121	83	68	92
Zr	121	53	44	108	125	66	53	98
n = 130					n = 47			

Explanations: Contents in g . t¹⁻. AM — arithmetical mean; AD — standard deviation; CV — variation coefficient; GM — geometrical mean; n — number of analysed samples. Primary results of analyses as well as names of analysts in Cambel — Khun (1983).

to the elements which differ most in average valus (V, Cu, Ni) is added boron with approximately the same contents in both sets (39 and 30 $g.t^{-1}$), but with substantialy higher variation coefficient on the basal crystalline complex, and strontium which with a high variation coefficient in the crystalline basement reflects the uneven distribution of carbonates in rocks of both complexes. We can verify the correctness of this order also by analyses of black shales from the bore hole KV-43 (Kolársky Hill, the results are in Tab. 2), on Fig. 2. As

Table 2

Results of analyses of bore cores from black shales, of the bore hole KV-43 in the Kollársky Hill area (Pezinok)

Metres	B	V	Cu	Ni	Co	Cr	Ba	Sr	Ti	Zr
310 m	<30	600	280	560	16	123	316	120	1780	159
315 m	<30	141	245	54	51	10	760	219	4100	209
368 m	<30	83	46	51	20	38	490	288	4600	302
398 — 402 m	<30	151	48	69	44	65	810	370	4700	182
406 — 409 m	<30	112	14	41	21	48	760	460	3900	251
423 m	<30	112	69	55	18	62	560	420	4300	186

Explanations: Contents in g . t¹⁻; analytist: M. Vančo, Geological institute of the Comenius University, analysis carried out by the optical emission spectroscopy method.

we can see on this figure, with increasing depth there is a decrease in the contents of V, Ni, Cu and Cr, and an increase in the contents of Sr. It was not possible to make a graph of boron contents, as they lied under the detection limit of the used optical emission spectroscopy method.

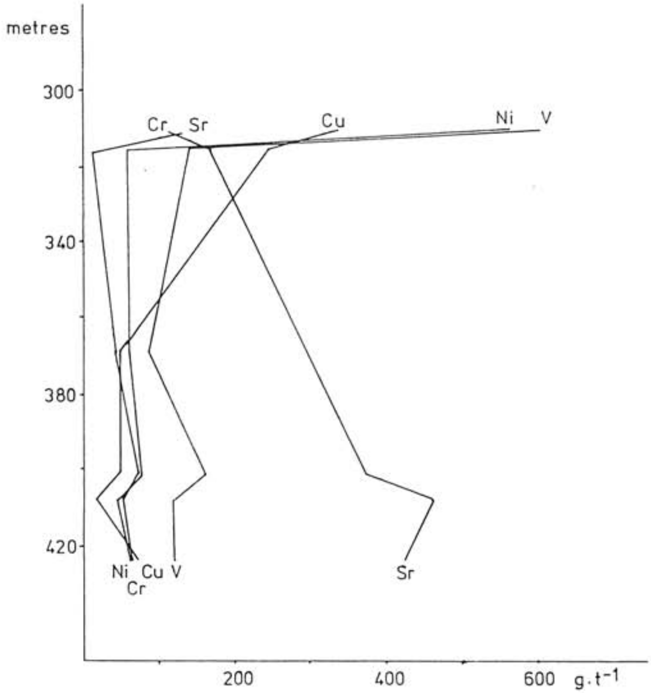

Fig. 2. Dependence of the contents of some trace elements in the black shales on depth in the bore hole KV-43 Kolársky Hill.

The above-mentioned trend, i.e. a decrease of V, Ni, Cu, Cr contents and an increase of Sr contents with increasing depth, is confirmed also by the analysis of black shales from different bore holes in the Kolársky Hill region, although without correction to different heights above sea level of the bore holes (Tab. 3). From the above stated facts it follows that on the basis of trace elements contents it appears very probable that the basal Pezinok-Pernek crystalline complex is in the area of the Pezinok ore deposit overlying the younger rocks of the Harmónia Group. A rapid increase of contents of some elements in the depth of about 320 m confirms the assumption that there is a tectonic contact between the two complexes which are in reversed position.

Black shales of the Harmónia Group can be distinguished from other black shales of the crystalline basement, especialy from the black shales of the productive zones, also on the basis of different slopes of the regresion graph of total sulphur contents vs. organic carbon contents. There were available 60 determinations of total sulphur contents by L u n g e's method (Tab. 4, C_{org}

Table 3

Results of analyses of bore cores from black shales from the Kolársky Hill area (Pezinok)

Sample number	85 A	67 A	176 A	178 A	177 A
Borehole	KV-18	KV-3	KV-11	KV-11	KV-24
Metres	83—91	130—131	479	479—489	482
V	340	380	224	141	129
Cu	320	234	51	30	10
Ni	219	410	41	20	20
Cr	120	104	101	123	85
Sr	89	191	275	159	370

Explanations: Contents in g . t^{1-}. Only the discriminating elements are included. Localisation of samples as well as names of analysts in Cambel — Khun (1983). The samples were analysed by the optical emission spectrocopy method.

in Cambel — Khun, 1983), the analysis was carried our in Central Laboratories of the Czechoslovak Uranium Industry in Stráž pod Ralskem. The specific distribution of sulphur in the productive zones and its substantialy higher contents in this zones than in other in other regions (bimodal distribution) is apparent in Fig. 3. Similar conclusion results from the comparison with Cu and Ni contents (Fig. 4 and 5), there was found no correlation of S and Cr. Leventhal (1979; 1983) states that when we put organic carbon contents on x-axis and sulphur contents on y-axis, the result is a linear correlation between S and C_{org} in sediments from euxinic marine environment; the regression line constructed by the least square method intersects the y-axis between the values 0.7 and 2 per cent. On the other hand, in sediments from an environment richer in oxygen the correlation between S and C_{org} is linear too, but the regression line intersects approximately the foot of the coordinates. Euxinic environment at the origin of black shales of the productive zones is clearly proved by Fig. 6, where the regression line intersects the y-coordinate at the value 1.22 per cent S. The distribution in other regions, where the sulphur contents are much lower, is different. The regression lines were not very reliable because of a very low correlation and so the graph is not included in this paper. But when experimentaly constructing the graph of the abovementioned correlation for this regions, the intersections of the regression lines were closer to the foot of the coordinates; this could point to an environment with a higher oxygen content than the productive zones, i.e. to the parts of the littoral facies closer to the shore. This assumption could be supported by the distribution of other two geochemicaly interesting elements, vanadium and chromium. The correlation V vs. Cr is used by Ernst (1970) to differentiate the oxydation-

Table 4

Results of analyses of the total sulphur contents in individual studied regions

Pezinok—Pernek crystalline area Productive zones:						outside zones:	
Sample number	% S	Sample number	% S	Sample number	% S	Sample number	% S
5 A	1.10	35 A	3.80	58 A	0.96	26 A	0.07
7 B	1.57	36 A	5.70	70 B	1.76	31 A	0.07
8 B	1.30	41 A	1.56	116 B	0.73	111 A	0.05
10 B	2.61	44 A	1.35	118 A	2.96	112 A	0.01
12 B	3.84	49 A	4.38	119 A	0.61	120 A	0.01
13 B	0.95	51 A	1.67	137 B	0.71	123 A	0.15
14 B	1.70	53 B	7.01	142 A	1.26	139 A	0.01
15 B	3.51	54 A	5.35	148 A	2.72	141 A	0.07
33 C	2.10	56 A	3.30				
Harmónia Group						Bratislava area	
21 A	0.02	122 A	0.01	136 A	0.03	2 A	0.03
24 A	0.11	126 A	0.01	140 A	0.01	3 A	0.16
113 A	0.01	128 A	0.01	150 A	0.01	38 A	0.01
114 B	0.03	129 A	0.01	156 A	0.03	39 A	0.02
121 A	0.07	134 A	0.03	160 A	0.03	130 A	0.01
						133 A	0.01
						138 A	0.01
						149 A	0.01
						155 A	0.01
						157 B	0.01
						158 A	0.02

Explanations: Contents in per cent. The samples were analysed by Lunge's method in the Central Laboratories of the Czechoslovak Uranium Industry in Stráž pod Ralskem.

-reduction facies. According to the quoted author, in an environment without oxygen the V/Cr ratio varies between 2 and 10, in an environment with little oxygen it is close to 1. For different studied areas is the V/Cr ratio in the black shales following (calculated from average values in Cambel — Khun, 1983):

Pezinok-Pernek crystalline complex, productive zones	4.35
Pezinok-Pernek crystalline complex, outside zones	3.86
Harmónia Group	3.56
Bratislava region	2.71

We can see a gradual decrease of this ratio from the productive zones to the samples from the Bratislava region. Thus, the productive zones had the lowest

Eh in the time of sedimentation, i.e. they could represent deeper parts of sea compared with other areas. We can come to a similar conclusion by evaluating some other geochemical criteria, e.g. the low Th/U ratio in the shales of the productive zones (C a m b e l — K á t l o v s k ý — K h u n, 1981), the low boron

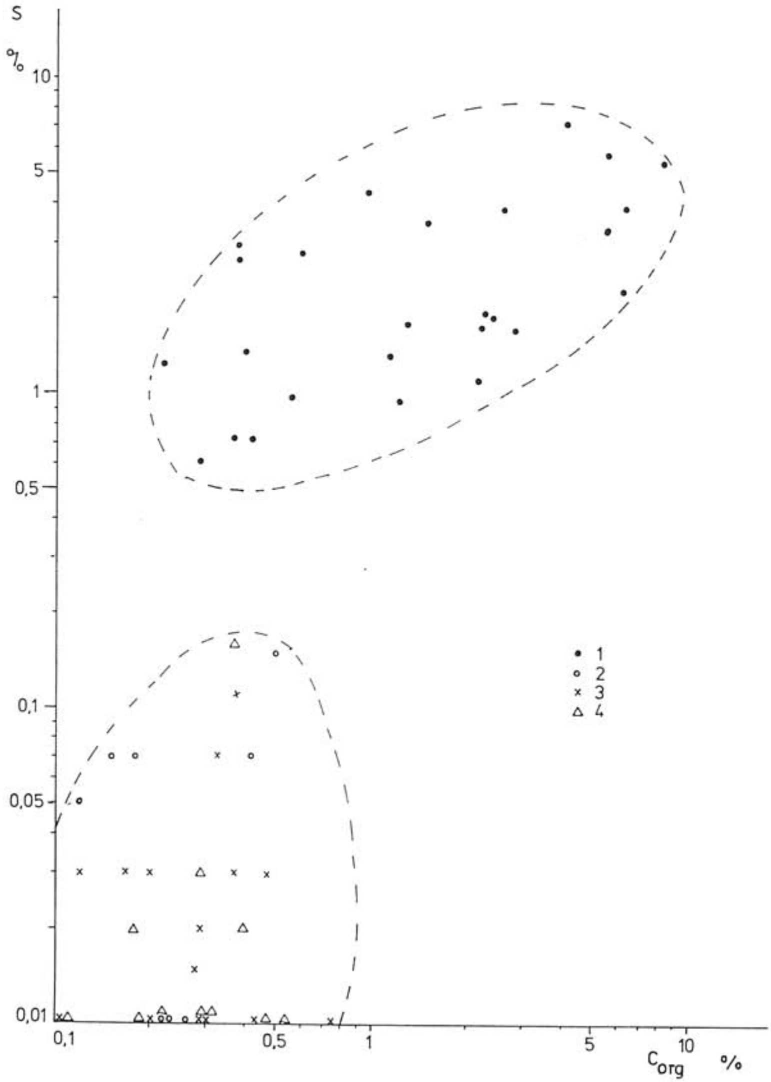

Fig. 3. Correlation graph of sulphur and organic carbon contents in the studied black shales.

Explanations: 1 — productive zones; 2 — samples from localities outside productive zones in the Pezinok-Pernek crystalline complex; 3 — Harmónia Group; 4 — Bratislava region.

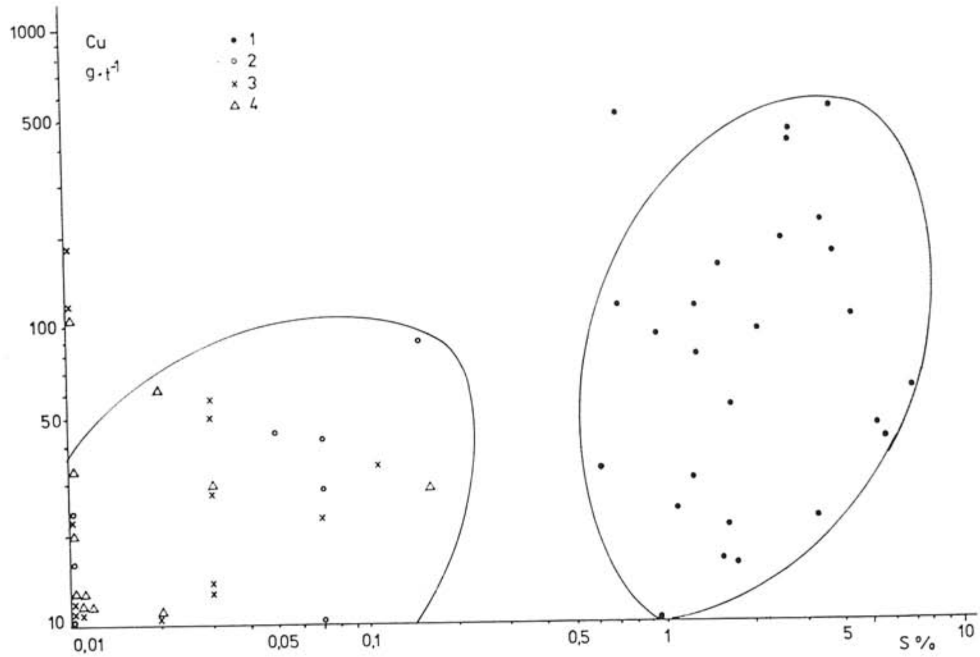

Fig. 4. Graph of the dependence of sulphur contents on copper contents in the studied samples.

Explanations as Fig. 3.

and rare earths elements contents (published in this rewiew), the distribution of organic matter in the studied rocks (Cambel — Šimánek — Khun, in this rewiew).

On the basis of the abovediscussed geochemical symptoms, we can try to outline a sedimentologic interpretation of the genesis of black shales of the Malé Karpaty Mts. Though, this is more hypothetical than real for the time being, in spite of a lot of new information gained from geological survey in the last years; this has nevertheless left some basic questions unanswered. It is possible then to classify the studied black shales as sediments of the littoral facies of the continental shelf. It is difficult to use in this case the traditional and most frequently used model of an isolated basin, based mainly on the analogy with the Black Sea, because especially in the Pezinok-Pernek crystalline complex the shape of the black shale horizons is elongated (the zone I a, b is found practically in the whole crystalline complex — Cambel, 1959; Cambel — Jarkovský, 1967). The most suitable, as it appears, is the model of continental shelf s.l. (Didyk et al., 1978). It is necessary to use two different models of sedimentation in a shallow epicontinental sea, based on the conception of the model of continental shelf (Hallam, 1981), for the productive zones. For the Harmónia Group, it could be the model of stagnation in an epicontinental sea caused by an increased production of organic matter, constant climate and slight sloping of the sea bottom towards

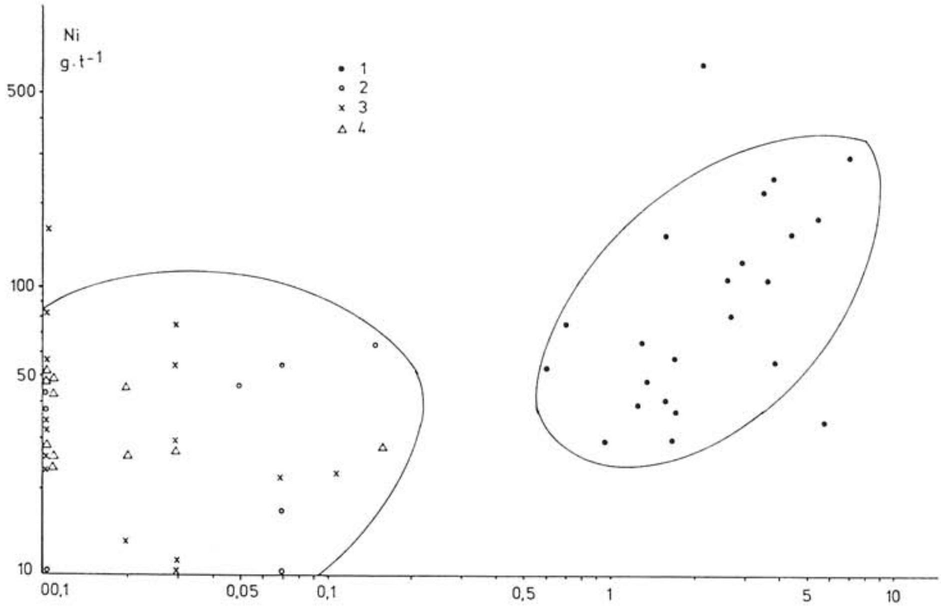

Fig. 5. Graph of dependence of the contents of S on the contents of Ni in the studied samples.
Explanations as Fig. 3.

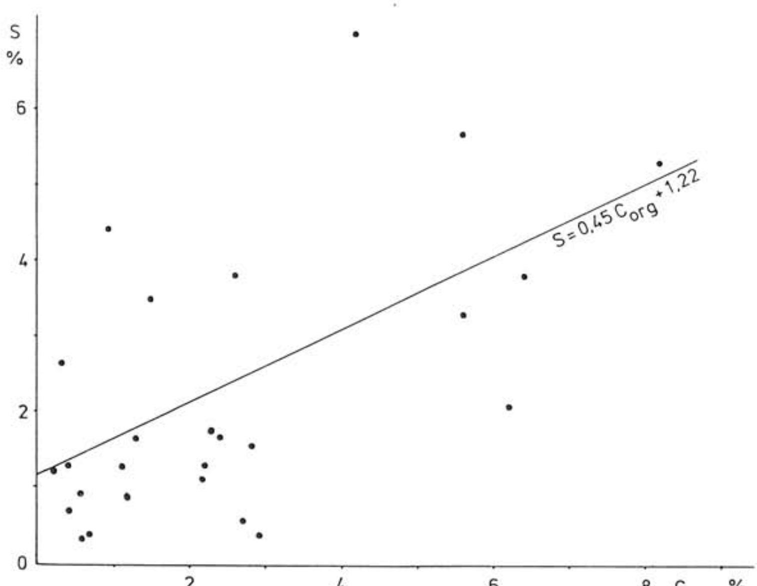

Fig. 6. Regression line S vs. C_{org} of the samples from the productive zones.

open sea, which limited water circulation and supressed wawe motion caused by tides and wind.

In the productive zones area, it could be the case of a local deepening of the sea in the form of elongated belts, caused by flexures; this could, in a period of tectonic lull, lead to the origination of isolated basins of stagnating water, i.e. deeper and from the shore more distant parts of the epicontinental sea (Drake et al., 1982). This is confirmed by different geochemical symptoms. In both cases, i.e. in the productive zones as well as in the Harmónia Group, the sedimentation took place evidently under the active wave zone (low energy level, Selley, 1976) The sedimentation in the productive zones was connected with basic volcanism, which was the source of the increased contents of some elements; it could be also responsible for the increased contents of organic matter in this area, caused by an increased expansion as well as perishing of organisms. The development of the volcanism was pulsating and periodical; it took place probably in two main and several partial periods (Cambel, 1959; 1962). The source of the volcanism could lay in the fault zone. Each period had an interval of more massive extrusions of basic magma, after which came an interval of smaller extrusions connected with intensive exhalation activity and ejection of pyroclastics of basic volcanism. The sediments of this period are represented by productive ore-bearing zones with deposits of pyrite and with increased contents of polymetalic elements. In the Harmónia Group the conditions of sedimentation were evidently more peaceful; the interchange of pelitic and more detritic sediments could have been caused by transgressions and regressions of the sea.

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