GEOLOGICKÝ ZBORNÍK — GEOLOGICA CARPATHICA, 36, 1, BRATISLAVA, FEBRUARY 1985,
Pp. 29—36

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BORON IN BLACK SHALES OF THE MALÉ KARPATY MTS. CRYSTALLINE COMPLEXES

(Figs. 2, Tabs. 2)

A b s t r a c t: The author discusses in this paper the low contents of boron in black shales of the Malé Karpaty Mts. crystalline complexes. It is assumed that this low contents are caused by low primary contents of B in the country and by metamorphism. It appears that such boron contents are a characteristic trait of the Malé Karpaty Mts. region, as it followed from the comparison with similar rocks of the Spišsko-gemerské rudohorie Mts. and some world localities. A genetic interpretation of the boron contents in the black shales suggests that they are littoral sediments.

Р е з ю м е: Автор в статье занимается низкими содержаниями бора в черных сланцах кристаллиникума Малых Карпат. Объяснение этих низких содержаний предполагается в низкой первичной концентрации бора в местности и в метаморфизме. Кажется, что такие содержания бора являются характерной чертой района Малых Карпат, как это видно из сравнения с похожими породами Спишско-гемерского рудогорья и некоторых мировых местонахождений. Генетическая интерпретация содержаний бора в черных сланцах намечает, что подразумеваются приближные осадки.

In geochemical interpretations of trace elements contents in black shales of the Malé Karpaty Mts. crystalline complexes (C a m b e l — K h u n, 1983) were conspicious low contents of boron (in most cases less than 50 $g.t^{-1}$) compared with the data for similar rocks from literature. There was not enough attention paid to the boron contents in the discussed rocks in the above quoted paper, and so we consider it necessary to return to this problem. All primary data (190 determinations of B contents by optical emission spectroscopy method, carried out in the Geological Institute of the Comenius University in Bratislava) as well as the geological condition in the area and criteria for subdivision of the set of samples into individual subsets are included in the above quoted paper.

A lot of data has been collected on the contents of boron in marine or freshwater sediments. Direct correlation of salinity with the boron contents was described by L a n d e r g r e n (1945), who studied the swedish Alum shale in two profiles; in one of them the boron content was 140 $g.t^{-1}$ and in the other one 90 $g.t^{-1}$ This lower boron content in the second profile was explained by a decrease caused by the contact influence of diabase dykes, which represented as much as a 35 per cent reduction of the boron content. To confirm this supposition the quoted author carried out a laboratory test — he heated the pulverised Alum shale to 800 °C for 4 hours; the decrease in

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B content was about 25 per cent. He also describes a decrease of B contents gradualy from Cambrian to Silurian; the increasing rate of sedimentation from Cambrian to Silurian could cause the decrease of boron contents in marine sediments. An increase in the rate of sedimentation brings about that the sediment is chemically less differentiated and B content in such material is lower. Similar correlation of boron content and paleosalinity was also described by other authors, e.g. Fredericson — Reynolds (1960); Curtis (1964); Porrenga (1969); Kraus (1975); Catto et al. (1981) and others. Some exactly opposite opinions, or such that admit only a small possibility of using the boron contents as a paleosalinity indicator (Janda — Schroll, 1959; Podelko, 1965; Spears, 1965; Levinson — Ludwick, 1966; Walker, 1968) have also been stated. Harder (1970) admits that boron could probably be one of those trace elements which shall be critical for differentiating marine and freshwater environment. Similar opinion is advocated by Nicholls (1963). Lerman (1966), who studied marine clays from Ripley and Peedee Formation in South Carolina (USA) informs about the unsuitability of boron as a paleosalinity indicator. The boron contents varied between 45 and 140 $g.t^{-1}$. The sample with the lowest B content was taken from undoubtedly marine strata containing belemnites and sea pelecypoda. However, such contents of boron are usualy given for freshwater environment (Tourtelot, 1964; Harder, 1961, 1970; Guljajeva — Lygalova, 1965).

In the Tab. 1 are given the average contents of boron together with other statistical characteristics for the complete set of samples as well as for individual subsets. This boron contents in the black shales of the Malé Karpaty Mts. crystalline complexes, which are assumed to be of marine origin (Cambel — Khun, 1983), are very low in comparison with data from literature. This data have been several times analytically tested, so that we cannot presume an analytical error to be responsible for the difference.

There are several possibilities to explain the low boron contents in the black shales of the Malé Karpaty Mts. Porrenga (1967) summarised the factors which influence the boron contents in sediments. As one of the first factors he gives the concentration of boron in the country and the amount of boron "inherited" from the previous sedimentation, including the influence of chemical weathering. The gneisses and slates of the Malé Karpaty Mts. have relatively low contents of boron (Cambel — Khun, 1983), which practically correspond with boron contents in the studied black shales. The surrounding hornblende-bearing rocks could not as well influence the boron contents at the time of sedimentation of the black shales, because the concentration of boron in this rocks varies from 5.2 to 28.8 $g.t^{-1}$, the average is 14.7 $g.t^{-1}$ (Cambel — Kupčo, 1965; Cambel — Kamenický, 1982). It can be thus stated that the factor of primary concentration of boron in the country can have a strong influence on the boron contents in the studied black shales. It appears, as it follows from Tab. 2 when comparing boron contents in this rocks with similar rocks of the Spišsko-gemerské rudohorie Mts. and some world localities, that such boron contents are a characteristic trait of the Malé Karpaty Mts. region (the lowest enrichment coefficients of the Malé Karpaty shales by standardisation to average black shale, according to Vine — Tourtelot, 1970; colmn 8).

Table 1
Average boron contents in the complete set of samples and individual categories, divided according to criteria staded in Cambel — Khun, (1983)

	AM	AD	CV	GM	n
Set of all samples	36	49	138	25	190
Content of organic carbon					
C_{org} <0.5 %	28	28	100	19	71
C_{org} 0.5—3 %	37	52	140	24	41
C_{org} >3 %	51	73	143	32	32
Granularity					
Fine-grained	46	66	143	28	39
Medium-grained	35	45	130	21	144
Metamorphism rank					
Epi-	42	58	138	25	104
Mezo-, Kata-	30	37	122	19	79
Sulphide content					
Type A	37	56	150	17	110
Type B	40	48	120	19	41
Type C	41	48	118	20	9
Pezinok-Pernek crystalline area					
Productive zones as a whole	48	58	120	26	74
Productive zones — type A	46	62	135	22	40
Productive zones — type B +C	48	53	110	25	34
Subjacent crystalline area					
Pezinok-Pernek crystalline area outside productive zones	19	17	89	10	26
Bratislava area	27	27	100	15	24
Modra-Orešany area	73	165	224	54	6
Stratigraphy					
Subjacent crystalline area as a whole	39	58	151	22	130
Harmónia Group	30	19	62	21	47
Younger formations (Triassic)	38	47	122	24	8
Silica visually					
more	38	49	129	25	107
less	36	55	151	22	68
Biotite, garnet, feldspar	21	23	113	16	64
Amphibole	39	43	124	24	40
Hydrothermal alterations	52	69	134	30	24
Mylonitization, weathering	57	87	153	33	21
Higher portion of carbonates	51	65	128	28	33

Explanations: Boron contents are in $g . t^{-1}$; AM — arithmetical mean; AD — standard deviation; CV — variation coefficient in per cent; GM — geometrical mean; n — number of samples.

Table 2

Comparison table of average boron contents in the studied black shales of the Malé Karpaty Mts. crystalline complexes with similar of the Spišsko-gemerské rudohorie Mts. and some world localities

	Average content	Coefficient of enrichment	n
1	36	0.72	190
2	48	0.96	74
3	19	0.38	26
4	30	0.60	47
5	27	0.54	24
6	230	4.60	18
7	125	2.50	755
8	50	1.00	779
9	112	2.24	32
10	133	2.66	53
11	154	3.08	4
12	84	1.68	38

Explanations: Boron contents in $g . t^{1-}$; n — number of samples. Enrichment coefficient was calculated by standardisation to average black shale, column 8. 1 — black shales of the Malé Karpaty Mts. crystalline complexes, coplete set; 2 — the same, productive zones; 3 — the same, outside the zones; 4 — the same, Harmónia Group; 5 — the same, Bratislava region; 6 — black shales from different localities of the Spišsko-gemerské rudohorie Mts. (Slovinky, Rudňany, Breznička — Khun, 1983); 7 — graphitic phyllites of the ore deposit area of Rudňany (Matula — Rényi, in press); 8 — average black shale (Vine — Tourtelot, 1970); 9 — near shore black shales (Tourtelot, 1964); 10 — black shales which sedimentated at a greater distance from shore (Tourtelot, 1964); 11 — pyritic black shales (Hirst — Kaye, 1971); 12 — black shales from the Atlantic ocean bottom Brumsack, 1980).

Another important factor is the presence and kind of organic matter. Curtis (1964) brought attention to Bader's hypothesis (Bader in Curtis, 1964), that some clay minerals including illite can quickly and strongly adsorbe organic matter from solution in quantities of as much as 350 per cent of their own weight. It is assumed that such mechanism can prevent boron sorption in natural environment. But it was also stated that organic matter does not have any influence on boron contents in sediments (Tourtelot, 1964; Eagar — Spears, 1966). There was not ascertained any correlation of boron and organic carbon in black shales of the Malé Karpaty Mts. (Khun, 1977; 1983), so that we cannot assume the above described process, where boron sorption can be prevented by soluble organic molecules, i.e. a negative correlation of boron and organic carbon, to take place. The dependence of boron contents on the grain size of the rock, as stated by Harder (1961), was confirmed in the studied rocks. The finer-grained varieties have higher boron contents than the medium-grained ones, (Tab. 1). Dependence of decreasing boron contents on increasing grade of metamorphism, which was stated by several authors (Harder, 1961, 1970; Porrenga, 1967; Aleksandrov et al., 1968), was also confirmed. It appears that this process of decreasing of the boron contents is common in the Malé Karpaty Mts. A convincing example of the decrease in boron contents with increasing grade of metamorphism in metapelites of the Malé Karpaty Mts. from the profile Záhorská Bystrica—Holý Vrch is given by Janák (1980). Average boron contents in different metamorphic zones are following:

	B $(g.t^{-1})$	Number of samples
Chlorite zone	71	5
Biotite-garnet zone	32	8
Staurolite zone	26	14
Sillimanite zone	11.6	10

From the facts stated up to now we can assume that primary concentration of boron in the country together with metamorphism could be most probably responsible for the low boron contents in the studied black shales of the Malé Karpaty Mts. It follows that in this case we cannot use solely boron contents as an indicator for marine sedimentation environment of this rocks. Most probably a part of boron is fixed in illite, which is the most advantageous host for boron and potassium; a smaller portion is sorbed. Certain correlation between boron and potassium can be observed on Fig. 1. According to Harder (1970), the adsorbed boron is not suitable for solving geological problems, as this bonds are weak in comparison with the bonds in the structure of illite.

A very interresting fact was published by Dewis et al. (1972). They state that boron contents in sediments increase with increasing distances from the shore or estuaries; its suitability as a paleosalinity indicator they also consider

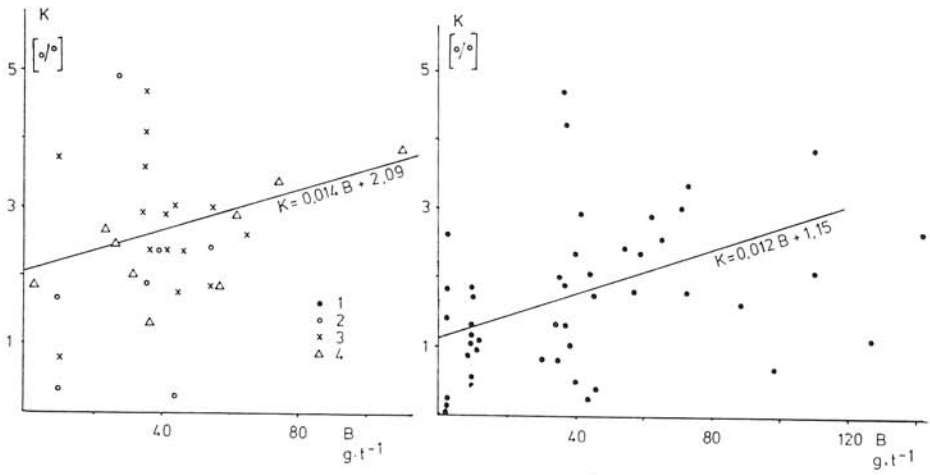

Fig. 1. Correlation graph of boron and potassium.
Explanations: 1 — Pezinok-Pernek crystalline complex; productive zones; 2 — the same outside productive zones; 3 — Harmónia Group; 4 — Bratislava region. Potassium contents were determined by the radiometry method in the Geological Institute of the Slovak Academy of Sciences in Bratislava, by Dr. Kátlovský, CSc.

questionable. A similar increase of boron contents with the distance from shore was described by Podelko — Lygalova (1970). The highest boron contents in different studied areas had shales of the productive zones — 48 g.t^{-1} (if we neglect non-representative data from the area Modra-Orešany because of small number of samples), and so they could represent the part of littoral facies most distant from the shore. Catto et al. (1981) ascertained by comparing the samples taken from the surface and in depth that exposure of the sediment to atmosphere and fresh water decreases the contents of boron and vanadium, i.e. the productive zones could represent the deeper part of sea.

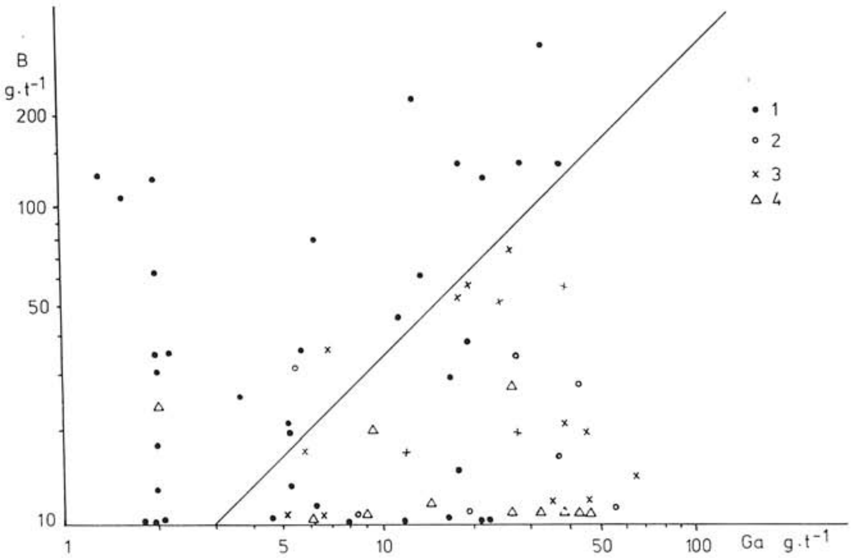

Fig. 2. Graph of the dependence of boron contents on galium contents (according to Keith — Degens, 1959).
Explanations as Fig. 1. Galium contents were determined by neutron activation analysis in the Central Laboratories of the Czechoslovak Uranium Industry in Stráž pod Ralskem, by Ing. Kotas, CSc. The field of the shales of marine origin lies above the line.

The more marine character of black shales of the productive zones proves also the graph showing the dependence of boron contents on galium contents (Fig. 2) presented by Keith — Degens (1959). The majority of the samples falls into the field of marine environment, the samples from other regions would then represent more or less brakic environment, or areas closer to the shore. This assumptions were confirmed also by the distribution of other trace elements (e.g. V, Cr, U, Th) as well as by the distribution of organic matter in the black shales of the studied regions (Khun, 1983).

Translated by K. Fellegiová

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Review by B. CAMBEL Manuscript received August 13, 1984