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Geologica 5

Západočeské muzeum Plzeň

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Fol. mus. rer. natur. Bohemiae occidentalis, Plzeň, Geologica

Recensent: Dr. Emil Jelínek, CSc.

Abstract. The boron contents of the Westphalian C to Upper Stephanian claystones, siltstones and tuffaceous rocks of the Carboniferous Basins of Central Bohemia were studied. The conclusion can be drawn that the environment of these sediments origin was of a freshwater character. This is consistent with most geological investigations so far carried out in this area. The higher boron contents have been established in red-coloured sediments (the Týnec and Líně formations). The drier rather arid climate was responsible for a more intensive desiccation of the basins, and, accordingly, the increased concentration of salts in the water of these basins; this was also reflected in the boron contents of the clay minerals.

INTRODUCTION

From the hitherto published geological, lithological, paleontological and petrographical papers it follows that the Carboniferous sediments of the Basins of Central Bohemia were mostly deposited in a fluvio-lacustrine environment. From earlier experience we know that boron, as an indicator of the salinity of the environment, manifests itself somewhat differently in separate regions and various time spans; it is difficult to state generally that some accurately limited values could exist for a freshwater, brackish or marine environments in all parts of the world. The results obtained from the study of the boron contents of marine and freshwater horizons of the Ostrava-Karviná coalfield (BOUŠKA, 1972) showed that boron can be used as a salinity indicator of the environment, but that in this coalfield area the sedimentation of typical marine horizons (according to fossils) occurred in a not very saline environment, as can be concluded from the low boron values. The limit values of boron for a marine environment measured in the rocks of the Ostrava-Karviná coalfield are so low that they equal those, regarded in other basins as typical of a freshwater environment. In the Ostrava-Karviná coalfield the following values have been established: an average 52 ppm B in marine horizon claystones, and an average amount of 25 ppm B for freshwater claystones, the lowest value 0.9 ppm B having been found in a sample of the grey laminated claystone from the freshwater Hugo Horizon (boring NP 268, depth 556.7—566.8 m) of the Jaklovec Member.

We were interested in the boron values of the sediments of the Basins of Central Bohemia, i. e. an environment considered to be a typically freshwater one. We wished to verify this opinion by geochemical investigations, particularly regarding the results presented by CÍLEK (1973), since the latter, obtained from the study of a single bore, do not fully support the generally accepted ideas.

GEOLOGY

The sediments of the Central Bohemian Carboniferous Basins extend over an area of about 3000 km^2. They divide into those of the Plzeň, Manětín, Žihle, Kladno—Rakovník, Roudnice and Mšeno Basins (Fig. 1). Originally, one extensive sedimentation basin existed there. HAVLENA (1971) attributes it the character of a pre-platform intramontane depression. The filling of this basin is continental. Any communication with the foredeep sea in the north can be unequivocally excluded.

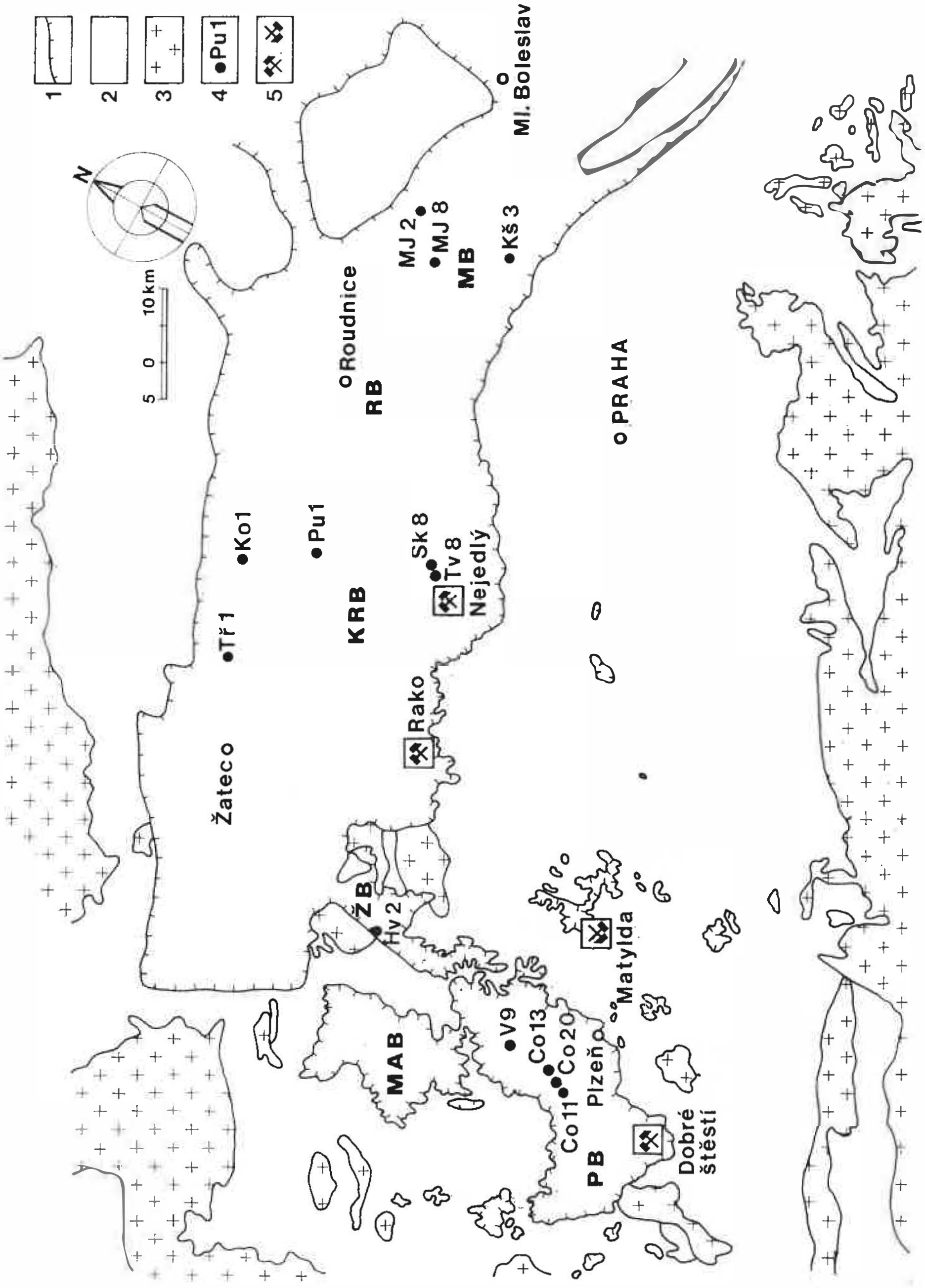

Fig. 1. Sketch map of the Central Bohemian Carboniferous Basins. 1 — Boundary of Carboniferous sediments, 2 — non-metamorphic or weakly metamorphic Proterozoic and Early Paleozoic rocks, 3 — igneous rocks of various ages, 4 — boreholes mentioned in the present paper, 5 — working and abandoned mines mentioned in the present paper.
PB — Plzeň Basin, MAB — Manětín Basin, ŽB — Žihle Basin, KRB — Kladno—Rakovník Basin, RB — Roudnice Basin, MB — Mšeno Basin.

In the Central Bohemian Basins the deposition of sediments probably took place under the conditions of an intense volcanic activity. HAVLENA and PEŠEK (1975) distinguish three volcanogenic stages yielding products of predominantly acid volcanism. In the lower parts of the oldest and the youngest stages, dyke-and effusive rocks also occur exceptionally. Otherwise tuffs and tuffites of mostly acid rocks prevail. Their quantitative representation in the individual formations is shown in Fig. 2.

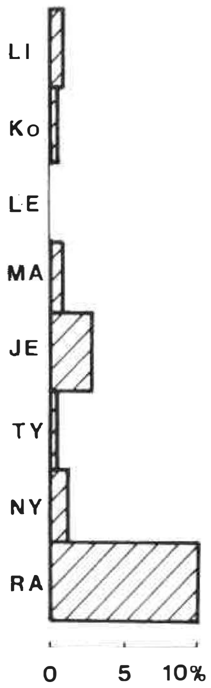

Fig. 2. Schematic illustration of the representation of volcanogenic rocks in the main and the partial lithostratigraphic units of the basins of Central Bohemia. RA — Radnice Member, NY — Nýřany Member, TY — Týnec Formation, JE — Jelenice Member, MA — Malesice Member, LE — Ledce Member, KO — Kounov Member, LI — Líně Formation.

Sedimentation in these basins took place from the Westphalian C (in many places it began in the Westphalian D or even in the Lower Stephanian) to the Upper Stephanian under conditions of probably intensive volcanic activity. The sediments settled on the Proterozoic (weakly metamorphosed shales), granitoid massifs and the earlier Paleozoic of the Barrandian. In the filling of the basins four formations have been distinguished. The two earlier consist mostly of fluvial sediments, the two later of sediments predominantly lacustrine.

The Kladno Formation divides into the Radnice and the Nýřany Members. The Radnice Member (Westphalian C) was deposited in isolated depressions, usually trending NE-SW. These sediments cover about 1/3 of the area of all the basins; they are very irregularly distributed, in some basins they are lacking throughout (Manětín and Mšeno Basins). The Nýřany Member (Westphalian D — Cantabrian) was deposited after a marked gap. They overlie discordantly the Radnice Member, often overlapping it markedly and heterochronously. In the whole formation mostly grey sediments prevail. Represented are: conglomerates, breccias, various types of psammites, siltstones, claystones, coal seams, tuffs and tuffites, rarely also acid eruptive rocks. The sediments were deposited mostly during incomplete sedimentation cycles. In the places where organic substances were produced, coal seams are encountered in the upper part of the sedimentation cycles.

Boron contents in the samples from bore Co 11 at Malesice (Plzeň Basin)

Table 1

Age	Formation	Member	Depth in metres	Boron content in ppm	Rock	Note
Stephanian	Líně		28.8	53	violetish-red micaceous siltstone	At the base of the formation
	Slaný	Kounov	82.47 93.93	47 46	grey-green claystone bituminous claystone so-called „švartna“	Mšec Horizon at the base of the unit
		Malesice	134.50 173.35	35 46*)	grey, finely micaceous siltstone grey laminated claystone	
	Týnec		219.80	56	green with red spots finely micaceous siltstone	
	Kladno	Nýřany	453.05	56	grey claystone	Approx. in the centre of the unit
Westphalian D			601.50	40	grey claystone	At the base of the unit (Komberk Horizon)
			602.40	40	coaly claystone	
			612.2	35	grey-reddish claystone	
			613.2	24	grey-greenish claystone with red spots	

*) For the boron content in this sample after disaggregation see Table 4.

The T ý n e c F o r m a t i o n (Cantabrian — Stephanian B) is almost devoid of coal, containing isolated volcanogenic layers. Except for breccias, it consists of rocks analogous to those in the underlying formation, but the aleuropelites are mostly variegated. The quantitative representation of the rocks and the structure of the sedimentation cycles also differ from those of the underlying unit (PEŠEK 1968). Compared with the Kladno and the subsequent Slaný Formations, the sediments of the Týnec Formation were deposited in an environment of somewhat arid climate.

The S l a n ý F o r m a t i o n (Stephanian B) has been divided into several partial units — members. At the beginning, psammites and psephites, analogous to those of the Týnec Formation, were deposited, but the colours of the aleuropelites changed to grey. The sedimentation of the Jelenice Member may have been terminated by a hiatus. The outset of the sedimentation of the Malesice Member can therefore be considered to have begun to settle isochronously over approximately the whole area of the basins. These sediments were deposited after a marked change of environment by the filling of the existing basins with sediments or by the damming of river beds (?). In a very quiet environment, in addition to supplied clastic material, claystones of the varvitic type (the Mšec Horizon reported by HAVLENA and PEŠEK 1975) were deposited. In the places where a slight influence of the transported fine detritic material had manifested itself, sandy siltstones and fine-grained sandstones settled. At the mouths of watercourses flowing into the basin, coarse clasts accumulated (Ledce Member). At the end of the deposition of the Slaný Formation the environment became shallower; the basins were gradually overgrown by peat-forming vegetation, of which coal seams formed.

The last unit — L í n ě F o r m a t i o n — consists mostly of sediments of lakes, probably ephemeral. Deep-red aleuropelites with reduction spots prevail over psammites and psephites. Abundant carbonate concretions, layers of silicites etc. furnish evidence of the fact that during the deposition of sediments of this unit the aridization of the climate had already begun, which, however, in the Bohemian Massif, culminated in the Permian.

METHODS

Samples were crushed and pulverized and used for analyses. Five samples, whose fine clay fraction was used for the identification of boron in illite, were very finely ground and disaggregated in an aqueous environment. The powder of the sample was thoroughly stirred in water and the vessel with water was left standing for 24 hours. The second day the procedure was repeated. Only the third day the water was removed with the buoyant particles of especially clay minerals and quartz grains, and separated from the residual deposits. The fine-fraction particles were then separated by filtration. This fine fraction was dried at room temperature and then analyzed.

Boron was investigated using the spectro-photometric method. The determination was based on the formation of an ionic association between BF_4^{1-} and methylene blue, which can be readily extracted with 1,2 dichloroethane. In this way boron is transferred from an aqueous solution into a dichloroethane phase which, depending on the boron content, can be diluted by a suitable quantity of an organic solvent (1,2 — dichloroethane). The resulting solution was subjected to a spectro-photometric analysis. For details see KLÍKA (1971). The results are given in Tables 1—4. Each sample was analyzed two or three times, and in the Tables the averages are given.

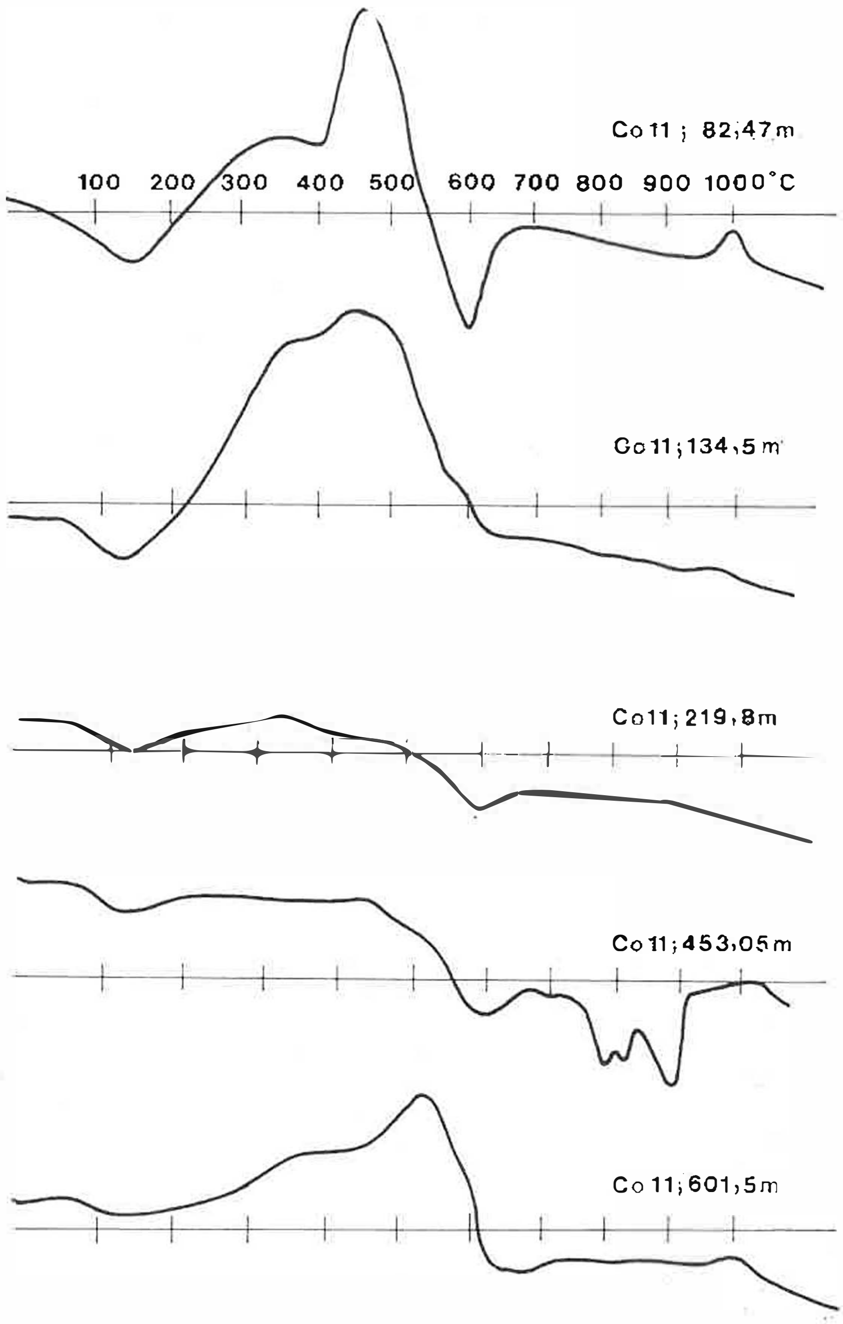

Fig. 3. DTA curves of the samples from bore Co 11.

Boron contents in the samples from bore MJ 8 at Jenichov (Mšeno Basin) Table 2

Age	Formation	Member	Depth in metres	Boron content in ppm	Rock	Note
Stephanian	Líně		186.50	62*)	deep-ruddy silty claystone	
			248.50	53*)	light-green claystone	Zdětín Horizon at the base of the formation
			360.80	68*)	ruddy micaceous silty claystone	base of the formation
	Slaný	Kounov	418.20	50	grey silty claystone	
		Malesice	547.0	39	grey laminated claystone	Mšec Horizon at the base of the unit
			555.50	40*)	grey laminated claystone	
		Jelenice	574.00	35	grey silty claystone	
	Týnec		634.3	58	variegated micaceous siltstone	
Westphalian D	Kladno	Nýřany	726.0	63	variegated claystone	

*) For the boron content in this sample after disaggregation see Table 4

Potassium oxide has been determined using flame emission photometry. The determination of K_2O in the fine fraction of five disaggregated samples was kindly carried out by RNDr. P. Povondra, CSc., of the Geological Institute of the Academy of Sciences, Praha. The results of these analyses are given in Table 8.

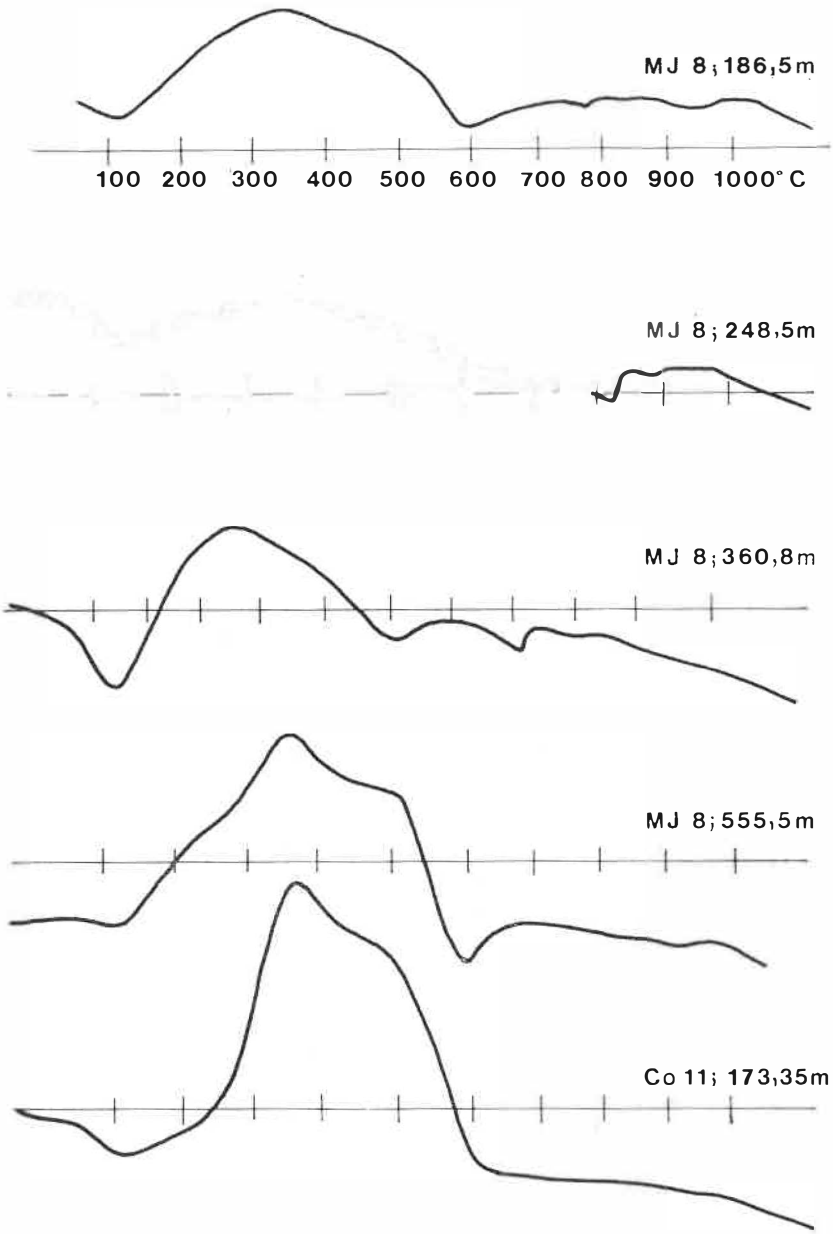

Fig. 4. DTA curves of the fine fraction of the disaggregated samples.

The selected samples from bore Co 11 and the fine fraction of the disaggregated samples were studied by means of DTA, DTG and TG, using the Derivatograph automatic apparatus in the thermographic laboratory of the Institute of Geological Sciences of Charles University, Praha, under the following conditions: 600 g weighed portion, temperature up to 1200 °C, sensitivity limit of TG (GTA) = 200mg, DTG (d GTA) 1/10, DTA 1/10, heating at 10 °C/1 min. The DTA curves are drawn in Figs. 3 and 4. Weight losses are given in Tables 5 and 6.

The fine fraction of the disaggregated samples was also subjected to X-ray analysis. This was carried out on MIKROMETA 2 X-ray diffractograph under the following conditions: CuK$\alpha_{1,2}$ radiation (λ = 1.5418 Å), 18 mA, 35 KV. The diffraction data are given in Table 7.

BORON AS AN INDICATOR OF THE ENVIRONMENT

In compounds, boron is trivalent, having a small ionic radius (0.22 Å). Its properties and behaviour are similar to those of carbon or silicon. Boron can be classified as a typical lithophile element.

GOLDSCHMIDT and PETERS (1932) called attention to the fact that boron plays a role especially in the process of marine sedimentation. Sea water contains on the average 4.6 ppm B, mostly in the form of non-dissociated boric acid, whilst it is almost entirely lacking in most fresh waters (0,01 mg/l). During sedimentation, boron is extracted from sea water. Small amounts of boron may play part in the origin of syngenetic or authigenic tourmaline, but the most important process is the fixation of boron to clay minerals, especially the K-clay minerals illite and glauconite. Thus it can be concluded that clays sorb boron in an amount proportional to the boron content in the solution. But the experiments have revealed that it does not depend on concentration only, but also on the reaction time interval and temperature of the aqueous solution. The sorption capacity of illite, montmorillonite, halloysite and glauconite are similar, but other clay minerals, e. g. kaolinite, show a much lower degree of this capacity. Evidently Al-B diadochy is involved in outer tetrahedral positions of clay minerals, although the boron-silicon diadochy has been confirmed by STUBICAN and ROY (1962) who studied the X-ray diffraction patterns and infrared absorption spectra of synthetic boron clays. Boron is fairly firmly fixed in clay minerals, especially illite. It cannot be removed from clays even by leaching with a hot mineral acid. It seems that the contribution of the boron absorption on the surface of clay minerals is small. Otherwise it would be possible to wash it out as in the case of boron readily washed from soil with boiling water. Boron cannot be washed out from clay minerals without breaking their structure. FREDERICKSON and REYNOLDS (1960) as well as WALKER (1968) argue that boron entered the tetrahedral positions during the illite authigenesis.

The distinction between freshwater and marine sediments, generally of pelitic nature, was studied geochemically by DEGENS (1965), KELLER (1970), KEITH and DEGENS (1959), POTTER et al. (1963), ERNST et al. (1958), REYNOLDS (1965), REYNOLDS (1972), WALKER (1972) and, in Czechoslovakia, by MICHALÍČEK (1967), BOUŠKA (1972) nad others. Their observations indicated that boron is especially sensitive to salinity. Therefore, it is a suitable agent for distinguishing the character of the primary environment. According to literary data (e. g. DEGENS 1965, REYNOLDS 1972), marine claystones and shales usually contain about 100—200 ppm B as against 10 to 50 ppm only for freshwater deposits. However, these values cannot

Contents of boron in the rocks of the Central Bohemian Basins

Table 3

Age	Formation	Member	Sample designation	Further data (depth)	Locality	Rock	B content in ppm	Note
Stephanian	Líně		bore HV 2	about 30 m	Žihle	ruddy-red, two-mica siltstone intercalated with light green claystone	74	about 150 m above the base of the formation
			bore Ko 1	309.9 m	Koštice	brick-red clayey siltstone	60	at the base of the formation
	Slaný	Malesice	bore V 9	22.5 m	Žilov	grey claystone with weakly marked lamination	63	upper part of the unit
			bore TV 18	34.6 m	Třebichovice	grey micaceous siltstone	30	
			bore TV 18	65.3 m	Třebichovice	grey laminated claystone	39	Mšec Horizon
			bore Co 13	105 m	Chotíkov	grey laminated claystone	60	
			bore Sk 8	21.2 m	Skury	grey laminated claystone	41	
			bore Ko 1	408.4 m	Koštice	grey laminated claystone	61	
			bore Kš 3	205.3 m	Košátky	grey laminated claystone	43	
			bore MJ 2	972.0 m	Stránka	grey laminated claystone	45	

Contents of boron in the rocks of the Central Bohemian Basins

Table 3 (Continuation)

Age		Formation	Member	Sample designation	Further data (depth)	Locality	Rock	B content in ppm	Note
		Týnec		bore Co 13	126.8 m	Chotíkov	red silty claystone	67	uppermost part of the formation
				bore Tř 1	305.5 m	Třtěno	brick-red micaceous siltstone	24	base of the formation
Westphalian	D	Kladno	Nýřany	dump of the Dobré štěstí mine		Dobřany	grey clayey siltstone	36	lower half of the member
				bore Co 20	497.05 m	Malesice	brick-red siltstone	45	Komberk Horizon base of the member
	C		Radnice	dump of the RAKO mine		Rakovník	white-grey claystone probably with tuffaceous admixture	51	upper part of the member (the Lubná Coal)
				Nejedlý mine gallery No. 4004	coal-field Kačice	Libušín	grey claystone	77	parting in the Main Kladno Coal
				Matylda 1 mine cross cut at the pillar		Břasy	light-grey tuff to tuffite „whetstone"	32	Whetstone Horizon

be regarded as accurately drawn, as many factors are known to exert an influence, sometimes quite substantial.

The boron content in carbonates is low (about 20 ppm) being controlled by the content of the illite present. Sandstones usually contain about 35 ppm B. The proportion of boron may be higher in the presence of detrital tourmaline or authigenic tourmaline (overgrowths about detrital cores). For instance, MOORE (1963) has established concentrations of 65 ppm B in recent sands from Buzzards Bay (Massachusetts) and, locally, even 168 ppm B in beach sands. In this case, mechanical concentration of boron is involved. The boron content depends on the tidal energy and the coefficient of sorting. When tidal energy decreases, mostly light minerals only are transported, and the residual environment becomes enriched in tourmaline.

Boron contents in the fine fraction of the disaggregated samples from bores Co 11 (Plzeň Basin) and MJ 8 (Mšeno Basin) — Table 4

Age	Formation	Member	Designation of sample	Depth in metres	Boron content in ppm	Rock
Stephanian	Líně		MJ 8	186.50	73	deep-ruddy silty claystone
				248.50	73	grey laminated claystone
				360.80	74	ruddy micaceous silty claystone
	Slaný	Malesice		555.50	40	grey laminated claystone
			Co 11	173.35	55	grey laminated claystone

Evaporites display higher salt content and, in extreme cases, also contain hydrated borates of Ca, Na and Mg (colemanite, borax, kernite etc.). This contributes to the anomalous high B content in the rock.

The boron content may also be influenced by the presence of volcanic material. CODY (1970) recorded a higher B content even for certain terrestrial sediments than the amount occurring in marine sediments. The volcanogenic components probably play an important role there. The enrichment in boron may take place at tectonic lines or may be due to the influence of thermal springs or exhalation as, for instance, in New Zealand. The silt: sand proportion in a clay rock considerably diminishes the boron contents as do carbonates. Also kaolinitic clay rocks usually have a B content lower than that occurring in illitic rocks. Illitic clays and claystones commonly contain more boron than do non-illitic rocks. The environments in which illite originates and accumulates are evidently most suitable for the taking up and bonding of boron. A preferential enrichment in boron has often been mentioned for illite.

The dependence between the B content in illite and that in water was regarded by REYNOLDS (1965) as due to the salinity of the environment in which the illite had been deposited. The latter author studied the concentration of boron in Precambrian seas. The relative paleosalinity is usually determined by establishing the B content in illite of the sedimentary rocks. The sample is disaggregated by washing and the clay fraction is separated. Attention is devoted to preventing as far as possible the contamination of the detritic tourmaline, mica or feldspar. The sample is then analyzed for boron and potassium. The possible presence of the minerals

Loss in weight at TG of the samples from bore Co 11 (Plzeň Basin) Table 5

Depth in metres	Fired residue after DTA	Weight loss in %
82.47	light beige, crumbly	11.66
134.50	light rusty, crumbly	9.67
219.80	rusty brown, baked	10.33
453.05	brownish, crumbly	22.67
601.50	orange-beige, crumbly	10.50

considered is investigated by X rays. If no presence of such minerals is found, the analysis is based on the relation

$$\text{ppm B in illite} = \text{ppm B in sample} \cdot \frac{7.7}{\%\ K_2O \text{ in sample}}$$

The value 7.7 is used as the percentage of K_2O in a pure, hypothetic illite. Of course, corrections are necessary if, e. g. the presence of authigenic K-feldspar has been established, etc. The values of paleosalinity obtained in the above-mentioned way yield a reliable basis for judging the known paleo-geographic situation (REYNOLDS, 1965).

The sedimentary rocks taken from marine horizons with preserved fossils yielded values approaching about 450 ppm B in illite. Amounts around 2000 ppm B occur in the illites associated with evaporites; values as low as 125 ppm B have been measured in illites from brackish water deposits of Upper Cretaceous coal-clay sequences (REYNOLDS, 1972).

It should be noted that the B contents in coal ashes are usually distinctly higher than those in claystones in the vicinity of seams when both materials compared derive from the same geological unit and the same geographic area (SOMASEKAR, 1971). With increasing metamorphism the boron content of clayey rocks decreases. Even epizonal metamorphism may be responsible for the decrease of the boron content to a half in the rocks mentioned.

RESULTS AND DISCUSSION

The results of our boron determination in 36 samples of the Carboniferous sediments of the Central Bohemian Basins may be judged in connection with the above data. Tables 1, 2, 3 show the B contents, the localities and the stratigraphic position of the samples under study, and give a brief petrographic description of the rocks. The samples studied derive from the bore Co 11 at Malesice in the Plzeň Basin and the bore MJ 8 at Jenichov in the Mšeno Basin in order to obtain a picture of the presence of boron in the stratigraphically succeeding units appearing in the geological sections through the sediments encountered by the above-mentioned borings. The samples given in Table 3 supplement the preceding geological sections especially in the horizontal direction. The boron contents found range from 24 ppm (bore Co 11, 613.2 m, bore Tř 1, 305.5 m) to 77 ppm (Nejedlý mine, gallery No. 4004), i. e. they are low, especially if a possible proportion of volcanic material in the sediments is taken into consideration. The average values of all samples examined is 48.4 ppm B. This, compared with the literary data, is a value quite characteristic of a freshwater environment. The volcanic activity here was intensive (PEŠEK, 1972), particularly during the sedimentation of the lower part of the Kladno Formation (Radnice Member) — where the tuffaceous material is concentrated in a few layers of major thicknesses — and in many places of the Líně Formation — where numerous rather thin layers occur, consisting of volcanogenic material, today already strongly affected by kaolinitic weathering. The volcanogenic material was very often supplied into the sediments of the Líně Formation, but the thickness of these volcanogenic layers is small as compared with that of the Radnice Member. A tuffaceous component is present, for example, in the sample from the Rako mine near Rakovník, containing 51 ppm B, or in the sample from Břasy (Matylda colliery) with 32 ppm B

Loss in weight at TG of the disaggregated samples — Table 6

Locality	Depth in metres	Fired residue after DTA	Weight loss in %
MJ 8	186.50	rusty, crumbly	8.17
MJ 8	248.50	light-orange, baked	12.17
MJ 8	360.80	red-brown, strongly baked	9.33
MJ 8	555.50	light-orange, crumbly	8.00
Co 11	173.35	rusty, baked	10.67

only (the influence of a silt component in the sample). In both these samples, the influences exerted by volcanic material cannot be clearly recognized, but at least no conspicuous boron content was found. It should be noted that both these tuffaceous samples are dominantly kaolinitic. Kaolinite represents an essential constituent in the claystones of the Kladno and Týnec formations, while in the Slaný Formation the proportions of illite and kaolinite are different. The samples studied from the Líně Formation show predominance of illite. From this survey of the essential rock-forming minerals in the above-mentioned formations, and from what was said in the preceding chapter, it follows that the illitic claystones of the Líně Formation should be richest in boron. This has also been fully confirmed by our investigation. The samples derived from the Líně Formation contained consistently higher amounts of boron. This is visible in Table 9, where the average B contents in the formations and layers of the Central Bohemian Basins are tabulated according to the results shown in Tables 1—3.

In order to verify the presence of clay minerals in some samples from drill cores of the bore Co 11, DTA, DTG and TG analyses were carried out. The respective curves are shown in Fig. 3, weight losses in Table 5. The sample taken from this bore from a depth of 82.47 m exhibits the course of its curve typical of kaolinite (endothermic effect at 600°, exothermic at 1000 °C). Burning of organic substances appears by an exothermic peak within the temperature range 300—520 °C. In evaluating the peaks of the burning of organic substances in the section of bore Co 11 studied, a shift of the exothermic effect to higher temperatures with increasing depth of the sampling site was observed. This is evidently connected with the higher

X-ray data of samples disaggregated by water

Table 7

Bore MJ 8								Bore Co 11		V. I. Micheev, 1957						Note
depth 186.5 m		248.5 m		360.8 m		555.5 m		173.35		Quarz (256)		Illite (840)		Kaolinite (805)		
I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	
				10	13.1 Å											chlorite 13.7 Å
80	9.9 Å	20	9.9 Å	70	9.8	40	9.8 Å	70	9.9 Å			8	9.9 Å			(Micheev 860)
60	7.1			50	6.9	60	7.1	70	7.1					10	7.14 Å	chlorite 6.94 Å
				30	4.95					6	4.9 Å			1	4.84	
50	4.42	30	4.45	30	4.45	20	4.45	50	4.47			10	4.46	3	4.48	
														4	4.36	
50	4.24	30	4.25	20	4.24	30	4.24	40	4.25	5	4.24	4	4.28			
														4	4.17	
												4	4.10	2	4.09	
		5	3.86									6	3.87	2	3.85	
														2	3.73	
60	3.56					20	3.56	40	3.54			5	3.64	10	3.57	
15	3.50			15	3.51	20	3.50									chlorite 3.50 Å
100	3.33	100	3.33	100	3.33	100	3.33	100	3.34	10	3.34	10	3.35	3	3.32	
5	3.10							10	3.11			5	3.09			calcite 3.029 Å
		20	3.028	10	3.02											(Micheev 424)
15	2.99	30	3.001					15	2.99							carbonate of ankerite
15	2.86			10	2.82			5	2.85			6	2.85			type
														4	2.77	
		20	2.560			10	2.56	10	2.56			10	2.56	4	2.559	
10	2.46	15	2.452					10	2.462	5	2.45	5	2.45	6	2.489	
		5	2.390					5	2.390			6	2.39	4	2.378	
														8	2.338	
5	2.26	10	2.279					10	2.284	5	2.28			6	2.291	
10	2.21									4	2.231	5	2.235	1	2.248	
		5	2.127					5	2.131	5	2.123	6	2.140	2	2.186	
5	1.994	10	2.076	10	1.995			10	1.990	6	1.988	4	1.975	6	1.993	chlorite 1.993 Å
												4	1.940	3	1.940	
														2	1.896	
5	1.817	10	1.817	20	1.813	10	1.812	10	1.812	9	1.813			5	1.786	
											etc.		etc.			

degree of coalification of the organic matter with increasing depth. In the sample from a depth of 82.47 m a minor percentage of illite may also be present, but its reaction is veiled by a strong effect of kaolinite. We draw this conclusion according to its endothermic effect at low temperatures.

The micaceous mineral (illite — sericite) has been identified from the course of the other DTA, TG and DTG curves. The clay mineral in these samples is mostly illite ranging in grain size from the finest to coarser fractions. Thus, in this micaceous mineral, gradual decomposition takes place, reflected in the course of the TG and DTG curves. In the sample from a depth of 453.05 m an additional mineral is present — a carbonate approaching ankerite and possibly also chlorite. The presence of a carbonate is evident even macroscopically and is accounted for by a higher weight loss during the TG analysis (see Tab. 5).

The highest boron content, 77 ppm, has been found in the sample from the Nejedlý mine at Libušín. A grey claystone is involved, forming a parting in the Main Kladno Coal. The coal at fissures in the vicinity of the parting is mineralized with SiO_2, and this process may have led to a partial enrichment in B. In addition, the seam itself is fairly rich in boron as has been reported by SOMASEKAR (1971). This could produce a higher boron content in the claystone parting of this coal seam.

Nevertheless, even this highest boron content still lies in the field not characterizing an original marine environment.

The second sample with a higher content of B (74 ppm) comes from the borehole HV 2 at Žihle. It belongs to the Líně Formation. The bore was located in the proximity of the marginal fault bounding the filling of the basin against the Tis granite massif, where a secondary increase of boron content could have taken place. But it appeared that all the samples studied, derived from the Líně Formation, are rich in boron, and therefore further connections were sought. The results are demonstrated by Table 9, showing the average contents of boron occurring in the main and partial lithostratigraphic units of the Central Bohemian Basins. The highest average B contents exist in the Líně Formation — 61.7 ppm, and the Týnec Formation — 49.0 ppm (irrespective of the average boron content in the Radnice Member, which is distorted by the high content of B in the parting of the Main Kladno Coal — the number of the samples studied from the Radnice Member being small and therefore insufficient for an accurate evaluation; without this maximum value the Radnice Member would display the average value computed from two samples — 41.5 ppm B — which would be nearer to reality). The Líně and Týnec Formations were earlier designated as the Upper and Lower Red formations because of the predominating variegated character, particularly of aleuropelites, in these units. The origin of their colour may be in connection with the aridization of the climate at the time of depo-

Boron content recomputed for illite of the disaggregated samples — Table 8

Locality	Depth in metres	K_2O (Analyst P. Povondra)	Boron content in illite
MJ 8	186.50	3.65 %	154.0 ppm
MJ 8	248.50	3.11 %	180.7 ppm
MJ 8	360.80	4.45 %	128.0 ppm
MJ 8	555.50	3.00 %	102.6 ppm
Co 11	173.35	3.61 %	117.3 ppm

sition of the sediments of these units, especially in the Líně Formation. The higher aridity of the climate was evidently responsible for the higher evaporation, desiccation of the basins, which led immediately to enhanced concentration of salts including boron in the waters of the sedimentation basins. The clay minerals of the sedimentary rocks originated under such conditions contain higher amounts of boron. In fact, from Table 9 it follows that two distinct cycles existed, dependent on variations in climate. From the low part of the lithostratigraphic section upward, enrichment in boron took place, mainly beginning from the Radnice Member (if for it an average value of 41.5 ppm B is considered as probable) toward the overlying beds where a maximum B content is present in the red claystones and siltstones of the Týnec Formation. This terminates the low geochemical cycle. The second cycle begins in the Jelenice Member and there too the B content increases in the direction toward the overlying beds. The boron enrichment culminates in the rocks of the Líně Formation. This fact is very important in our opinion, and fully corresponds to the geological conditions in the Carboniferous Basins of Central Bohemia. We prefer to designate such changes as geochemical cycles. The results of our investigations fully agree with those of Ernst (1966) who studied the Ruhr and Saar Basins where boron contents also rise markedly with the climate changing to hot or arid.

There is one case which does not completely fall within the above-described scheme — the Komberk Horizon at the base of the Nýřany Member, which is also characterized by its variegated, predominantly red, clay-silt sediments. The average B content of its sediments (36.8 ppm B — Tab. 9) is markedly lowered by the samples from the bore Co 11 (Table 1) from depths of 612.2 m and 613.2 m. These samples, however, came from the boundary between the Komberk Horizon and the underlying Radnice Member. If the B values in these samples are not designated as belonging to the Komberk Horizon and are already designated to the Radnice Member, then the average B content in the rocks of the Komberk Horizon is 45.2 ppm B (from 4 samples), the B content of the Nýřany Member (non-differentiated) 45.5 ppm (from 6 samples) and that of the Radnice Member 42.4 ppm B (from 5 samples).

From Tables 1, 2 and 3 an interresting fact also follows, which, however, has not yet been fully verified. Namely, the samples from both boreholes or from a single sampling site in the geographical sense, although stratigraphically different, may show analogous boron contents (the samples from borehole Co 11, MJ 8, Ko 1, Tv 18 and Co 13). This suggests that the horizontal difference or vertical persistence of boron contents in a locally limited area within the same basin may be due to local conditions. For instance, the position in the centre or margin of the basin, or local tectonic, thermal or exhalation influences may be decisive.

On the basis of REYNOLDS' (1965) paper we have determined the boron content in selected samples recomputed for illite (see Table 8). The samples were disaggregated by washing, and the fine fraction, after drying at room temperature, was subjected to DTA analysis and X-ray examination. The results are shown in Fig. 4 and Tables 6 and 7. From the DTA curves and the course of the DTG and TG in the five samples illite has been determined as the dominating mineral; in samples MJ 8 — 186.5 m, MJ 8 — 248.5 m and MJ 8 — 360.8 m the presence of minerals from the chlorite group may be assumed. In all five samples, burning of organic substances took place. The lowest amount of organic substance is present in sample MJ 8 — 248.5 m. X-ray examination confirmed the presence of the following minerals in the sample: illite, quartz or also kaolinite and a small amount of chlorite and carbonate respectively. These minerals do not influence the recomputation; thus, after the determination of boron in fine fractions of the disaggregated samples (Table 4) and

Average boron contents from Tables 1—3

Table 9

Age		Formation	Member	Horizon	Average boron content in ppm	Number of analyses
Stephanian		Líně			61.7	6
		Slaný	Kounov		47.7	3
			Malesice (upper part)		46.5	2
			Malesice (average)	Mšec	43.7	8
					45.5	10
			Jelenice		35.0	1
		(average)			45.2	14
		Týnec			49.0	3
Westphalian	D	Kladno	Nýřany (upper part)		46.0	2
			Nýřany (average)	Komberk	36.8	5
					40.8	7
	C		Radnice		53.3	3
		(average)			44.6	10

determination of K_2O (Table 8) the boron content was computed, which in selected samples is bound in illite. The results are given in Table 8. Two samples from the Malesice Member of the Slaný Formation and 3 samples from the Líně Formation were chosen for study. The samples from the Malesice Member display low boron contents in illite (102.6 ppm and 117.3 ppm), those from the Líně Formation contain 128.0 ppm, 154.0 ppm and 180.7 ppm B bound in illite. These higher values fully agree with our previous data and only confirm the fact that the Líně Formation was deposited during the commencement of aridization of the climate, when the boron content in water was increased. The B contents in the illite from the samples derived from the Líně Formation, although higher, by no means attain the values given in the literature for a marine environment (about 450 ppm B in illite). A brackish environment can hardly be assumed in this case (compare CÍLEK, 1972, and our discussion of this subject, BOUŠKA et al., in print) when the above-mentioned facts can be explained quite convincingly by the climatic changes and, particularly, when no geological or lithological prerequisites exist for it. All geological investigations account for a freshwater and fluviolacustrine environment of the sediments of the Central Bohemian Basins, and our investigations of boron contents in claystones or also siltstones confirm this opinion.

CONCLUSIONS

The relatively low boron contents of all the samples studied, i. e. of claystones or siltstones, respectively, from the Carboniferous of Central Bohemian Basins, attest to freshwater environment of origin. The established boron contents range from 24 ppm to 77 ppm. The average value is 48.4 ppm B. This is consistent with most geological investigations so far carried out in this area. Higher boron contents have been found in red sediments (the Týnec and Líně formations) which were deposited at the outset of aridization of the climate. The desiccation of the basins associated with this was responsible for a higher concentration of the salts in the water of the basins and, immediately, was also reflected in the increased boron content of the clay minerals, especially illite, in the sedimentary rocks of the Carboniferous of Central Bohemia.

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VLADIMÍR BOUŠKA, ZDENĚK KLIKA a JIŘÍ PEŠEK

GEOCHEMICKÁ ÚLOHA BÓRU V SEDIMENTECH STŘEDOČESKÝCH KARBONSKÝCH PÁNVÍ

Při sedimentaci je bor extrahován z mořské vody a vázán převážně na jílové minerály typu illitu a glaukonitu. Pokusy ukázaly, že nezávisí jen na koncentraci boru v roztoku, ale také na reaktivním čase a teplotě vodního roztoku. Sorpční kapacity illitu, montmorillonitu, haloysitu a glaukonitu jsou podobné, ale jiné jílové minerály, např. kaolinit ji mají mnohem nižší. Jde zřejmě o Al — B diadochii ve vnějších tetraedrických pozicích jílových minerálů, i když diadochie B — Si je také zmiňována Stubicanem a Royem (in Walker 1968). Frederickson a Reynolds (1960) a Walker (1968) předpokládají, že bor vstoupil do tetraedrických pozic během illitové autogeneze. Rozdíl v obsahu boru mezi sladkovodními a mořskými sedimenty převážně pelitické povahy uvádí řada autorů, např. Degens (1965), Reynolds (1965), Walker (1968) aj. Jejich pozorování dokazují, že bor je velmi citlivý na určení původní salinity prostředí. Podle literárních údajů obsahují mořské jílovce a břidlice zpravidla kolem 100—200 ppm boru, proti 10—50 ppm boru u sladkovodních uloženin.

Závislost mezi obsahem boru v illitu a obsahem boru ve vodě byla vztažena na paleosalinitu prostředí prekambrických moří, ve kterých byl illit uložen (Reynolds 1965). Tato relativní paleosalinita se určuje zjištěním obsahu boru v illitu přepočtem z jeho reálného obsahu v sedimentární hornině. Vzorek je plavením rozložen a u jemné jílové frakce stanovíme jednak bor jednak K_2O. Dbáme na to, aby pokud možno nastala jen minimální kontaminace detritického turmalínu, slídy nebo živce. Eventuální přítomnost uvažovaných minerálů zjišťujeme rentgenograficky. V případě, že není žádný takový nerost přítomen, vypočteme obsah boru v illitu podle vztahu:

$$\text{B (ppm) v illitu} = \text{B (ppm) ve vzorku} \cdot \frac{7{,}7}{\%\ K_2O \text{ ve vzorku}}$$

Hodnota 7,7 je použita jako procentový obsah K_2O v čistém hypotetickém illitu. Sedimentární horniny odebrané z mořských horizontů se zachovanými fosiliemi (Reynolds 1965) poskytly hodnoty blízké 450 ppm B v illitu. Kolem 2000 ppm B mají illity sdružené s evapority a hodnoty kolem 125 ppm B byly zjištěny u illitů z brakického prostředí svrchnokřídových uhlonosných sedimentů (Reynolds 1972).

Vycházejíce z těchto zkušeností bylo odebráno 36 vzorků pelitů, prachovců a hornin s tufogenní příměsí ze středočeských karbonských pánví, které až dosud byly považovány za „limnické" pánve. Autoři chtěli tyto názory potvrdit geochemickými výzkumy. Uloženiny středočeských pánví jsou převážně fluvio-lakustrinního původu. Jejich stáří je westfal C — svrchní stefan. Rozdělují se do čtyř souvrství na: kladenské, týnecké, slánské a líňské souvrství, z nichž sedimenty týneckého a líňského souvrství (převážně pestře, resp. červeně zbarvené) se patrně ukládaly v aridnějším prostředí, než uloženiny zbývajících dvou (převážně šedých) jednotek. Geografické členění pánví je znázorněno na obr. 1. Nerovnoměrné zastoupení hornin s vulkanogenní příměsí je zřejmé z obr. 2. Tabulky 1—4 a tabulka 9 udávají obsahy B ve studovaných vzorcích. Poslední z nich je shrnutím všech dat.

Relativně nízké obsahy boru u všech studovaných vzorků středočeských karbonských pánví ukazují na sladkovodní prostředí vzniku sedimentů těchto pánví. Obsahy boru kolísají od 24 ppm do 77 ppm. Průměrná hodnota je 48,4 ppm B. Zjištěná data jsou v souladu s dosavadními geologickými výzkumy středočeského karbonu. Zvýšené obsahy boru byly zjištěny v červených sedimentech týneckého a líňského souvrství, které se ukládaly v době zvýšené aridizace klimatu. S tím související vysychání pánví vedlo bezprostředně ke zvýšení koncentrace ve vodách pánví a odrazilo se také ve zvýšeném obsahu boru v jílových minerálech (především illitu) sedimentárních hornin středočeského karbonu. Z rozdílného zastoupení boru v základních litostratigrafických jednotkách středočeských pánví lze v závislosti na klimatu uvažovat o stanovení dvou geochemických cyklů. Každý z nich zahrnuje dvě litostratigrafické jednotky (šedé a červené sedimenty); je charakterizován stoupajícím obsahem boru směrem do nadloží.

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