Composition of bituminous coal in dependence on environment and temperature of alteration

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A b s t r a c t . Bituminous coal from the proximity of red beds bodies of the Upper Silesian Coal Basin was altered by oxidation and thermally altered. This naturally altered coal was compared with laboratory-altered coal samples prepared at various temperatures and time, in oxidative and inert atmosphere, with weathered coal and with natural cokes. Comparison of samples was performed using coal petrographic and chemical analyses of individual coal samples.

A b s t r a k t . Černá uhlí pocházející z blízkého okolí pestrých vrstev hornoslezského černouhelného bazénu jsou tepelně a oxidačně alterovaná. Tato přírodně alterovaná uhlí byla porovnávána s laboratorně alterovanými vzorky uhlí připravenými při různých teplotách a čase, v oxidačním a inertním prostředí, se zvětralým uhlím na povrch vycházejících slojí a s přírodními koksy. Srovnání bylo prováděno zejména s využitím petrografických a chemických rozborů jednotlivých vzorků uhlí.

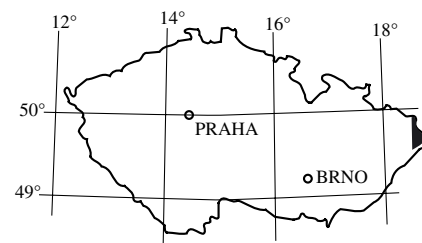K e y   w o r d s : oxidative alteration, thermal alteration, coal petrography.

Introduction

Bituminous coal is defined as coal with heat of combustion higher than 24 MJ.kg^{-1} (recalculated to moist ash-free basis) and mean reflectance of vitrinite $R_o > 0.6$ % (ECE-UN 1998). This coal originated by coalification of plant matter deposited in sequences dominated by clastic sediments under diagenetic conditions (thermal and pressure mode) of a given coal basin. Coalification proceeded under geologic time scale. In various coal basins (coal seams) coal matter differs in regard of different primary composition of plant matter and sedimentary environment. Composition of coal (e.g. elemental composition, volatile matter) and mean reflectance of vitrinite reflect final stage of coal metamorphism of a given sedimentary basin.

In post-sedimentary period, air oxygen and water may interact with coal thus giving way to low-temperature coal oxidation. In coal seams that, e.g., crop out on the surface or in mines in the proximity of the mining area or even on the piles with coal rests, the process of oxidation may lead to self-ignition of the coal. Heat formed during coal combustion or heat resulting from contact of the coal seam with emplaced magma may induce carbonisation of coal or even coke formation. Chemical and structural characteristics of coal matter are changed in a similar way during industrial processes (e.g. coking, carbonisation or coal combustion).

Interaction of coal with air results especially in an increase in oxygen content and also in changes of organic matter of coal (Králík 1980, Dobal and Sýkorová 1985, Jones et al. 1998, Klika 1998, Pánek and Taraba 1996).

A characteristic feature of oxidized coal is the higher solubility of some components in alkaline solutions. Constituents soluble in alkaline solutions (e.g. in alkaline hydroxide) are called humic acids. These compounds are characterized by their high concentration of oxygen (Butuzova et al. 1998, Ogunsola and Rao 1993, Steelink 1963). While humic substances are normally present in coal with lower degree of coalification (peat and lignite), in bituminous coal they are formed only by post-sedimentary oxidation.

Petrographic composition is an important factor that influences total change of coal matter. Another factor is the degree of coalification characterized by parameters: V^{daf}, R_o and elementary composition (Klika and Osovský 1999). Contraction cracks appear in coal which was thermally altered. Rims characterized by their increased light reflectance are present usually in vitrinite, which is the least resistant against thermal alteration. The rims originate more easily in coal with lower degree of coalification or under the temperature approaching the temperature of plastic state (Bend and Kosloski 1993, Dvořák and Kaloč 1973). Macerals of inertinite group are the most resistant to the formation of cracks, ability of liptinite to crack formation lies between those of vitrinite and inertinite (Tsai 1982). Weakly bleached rims originate at grain boundaries and around cracks, and gradually pass to non-bleached maceral. At higher temperatures of thermal alteration, rims are accentuated and their contrast is also much higher. Finally, bleaching involves the whole volume of the grains. Gas-coal shows the highest tendency towards the forma-

Table 1. List of coal samples.

Sample No.	Localities of coal samples (conditions and alteration types)	Photo No.
1	Non-altered coal from Lazy Mine, coal seam 512, type I	1
2	Alteration of sample No.1 by air at 100 °C, 30 days	
3	Alteration of sample No.1 by air at 150 °C, 14 days	
4	Alteration of sample No.1 by air at 200 °C, 7 days	2
5	Alteration of sample No.1 by air at 250 °C, 4 days	3
6	Alteration of sample No.1 by air at 300 °C, 4 days	4
7	Alteration of sample No.1 in inert atmosphere at 100 °C, 1 hour	
8	Alteration of sample No.1 in inert atmosphere at 200 °C, 1 hour	
9	Alteration of sample No.1 in inert atmosphere at 300 °C, 1 hour	
10	Alteration of sample No.1 in inert atmosphere at 400 °C, 1 hour	
11	Alteration of sample No.1 in inert atmosphere at 500 °C, 1 hour	
12	Alteration of sample No.1 in inert atmosphere at 600 °C, 1 hour	
13	Alteration of sample No.1 in inert atmosphere at 700 °C, 1 hour	
14	Alteration of sample No.1 in inert atmosphere at 800 °C, 1 hour	
15	Alteration of sample No.1 in inert atmosphere at 100 °C, 2 days	
16	Alteration of sample No.1 in inert atmosphere at 100 °C, 5 days	
17	Alteration of sample No.1 in inert atmosphere at 100 °C, 14 days	
18	Alteration of sample No.1 in inert atmosphere at 100 °C, 30 days	
19	Alteration of sample No.1 in inert atmosphere at 150 °C, 2 days	
20	Alteration of sample No.1 in inert atmosphere at 150 °C, 4 days	
21	Alteration of sample No.1 in inert atmosphere at 150 °C, 7 days	
22	Alteration of sample No.1 in inert atmosphere at 150 °C, 14 days	5
23	Alteration of sample No.1 in inert atmosphere at 200 °C, 1 day	
24	Alteration of sample No.1 in inert atmosphere at 200 °C, 2 days	
25	Alteration of sample No.1 in inert atmosphere at 200 °C, 4 days	
26	Alteration of sample No.1 in inert atmosphere at 200 °C, 7 days	6
27	Alteration of sample No.1 in inert atmosphere at 250 °C, 8 hours	
28	Alteration of sample No.1 in inert atmosphere at 250 °C, 1 day	
29	Alteration of sample No.1 in inert atmosphere at 250 °C, 2 days	
30	Alteration of sample No.1 in inert atmosphere at 250 °C, 4 days	7, 8
31	Alteration of sample No.1 in inert atmosphere at 300 °C, 8 hours	
32	Alteration of sample No.1 in inert atmosphere at 300 °C, 1 day	9
33	Alteration of sample No.1 in inert atmosphere at 300 °C, 2 days	
34	Alteration of sample No.1 in inert atmosphere at 300 °C, 4 days	10
35	Alteration of sample No.1 in inert atmosphere at 500 °C, 8 hours	11
36	Alteration of sample No.1 in inert atmosphere at 500 °C, 1 day	
37	Alteration of sample No.1 in inert atmosphere at 600 °C, 8 hours	12
38	Alteration of sample No.1 in inert atmosphere at 600 °C, 1 day	13
39	Naturally oxidative altered coal from Landek Hill, coal seam 103, type III/1	14
40	Naturally oxidative altered coal from 9. Květen Mine, coal seam 530, type III/1	15
41	Naturally oxidative altered coal from Lazy Mine, coal seam 512, type III/2	16
42	Naturally oxidative altered coal from Lazy Mine, coal seam 512, type III/2	17
43	Naturally oxidative altered coal from Lazy Mine, coal seam 512, type IV/2	
44	Naturally oxidative altered coal from Lazy Mine, coal seam 512, type IV/2	18
45	Thermally altered coal from Lazy Mine, coal seam 512, type II/1	19
46	Thermally altered coal from Lazy Mine, coal seam 512, type II/2	20
47	Natural coke, Čeladná, trial hole No-1, 1358.8–1358.9m, type V	
48	Natural coke, Čeladná, trial hole No-1, 1359.5–1359.6m, type V	
49	Natural coke, Čeladná, trial hole No-1, 1359.8–1359.9m, type V	21

Table 2. Characteristics of sample (No. 1) and laboratory oxidized samples (No. 2–6).

Sample No.	°C/days	[%]								
		A^d	V^{daf}	R_o	HA^{daf}	C^{at}	H^{at}	N^{at}	O^{at}	S^{at}
1	Nonalt.	4.86	31.6	0.88	–	55.67	38.57	0.73	4.96	0.07
2	100/30	4.40	31.3	0.91	0.10	–	–	–	–	–
3	150/14	4.31	35.3	0.98	4.46	57.22	28.96	0.79	12.89	0.14
4	200/7	4.10	39.2	1.06	39.78	57.62	28.16	0.82	13.25	0.15
5	250/4	4.94	42.6	1.29	50.21	60.84	20.94	1.08	16.98	0.16
6	300/4	6.91	47.3	1.32	14.38	60.18	18.58	1.50	19.53	0.21

radioactive radiation. The resolution of macerals decreases with increasing temperature and longer time intervals of heating, and other characteristics of coal are changed as well. The extent of post-sedimentary changes of coal matter depends on coal rank, temperature of alteration, rate and time of alteration, oxidative or inert environment, size of coal grains and pressure. According to Kozina et al. (1958) the most significant changes in coal matter occur at temperatures of 350–550 °C.

This paper describes, naturally altered coal from the neighbourhood of red beds bodies of the Upper Silesian Coal Basin, which was thermally and oxidatively altered. Naturally altered coal is compared from the petrographic and chemical point of view with samples of coal altered under various laboratory conditions (temperature, oxidative or inert atmosphere).

Samples, laboratory equipment and methods

The sample of non-altered coal from the Lazy Mine (sample No. 1) was used for laboratory oxidation and thermal alteration, which were performed at different time periods and at different temperatures. Sample No. 1 comes from the Lazy Mine (coal seam No. 512 of the Upper Silesian Coal Basin). The location and composition of sample No. 1 was specified in detail by Klika et al. (2000). Samples Nos. 2–6 were prepared using laboratory oxidation of non-altered coal while samples Nos. 7–38 were prepared by laboratory thermal alteration of coals in non-oxidative atmosphere. Samples Nos. 39 and 40 are naturally altered coals. Sample No. 39 comes from the outcrop of weathered coal of the Kateřina Seam at Landek Hill near Petřkovice; sample No. 40 comes from the vicinity of red beds bodies in the 9. Květen Mine. According to alteration types of coals, samples of naturally oxidized and

tion of the rims, being followed by fat coal and by coking-coal with the least common rim formation. The rims also appear during the transformation of coal matter to semi-coke or coke, i.e., under inert or reducing atmosphere. The rims were even observed after the interaction of coal with

thermally altered coals were chosen (Nos. 40–49). Sample No. 40 comes from the Seam No. 530 from the 9. Květen Mine, samples Nos. 41–46 from the Seam No. 512 (corridor No. 39706), which lies in the proximity of a body of red beds in the Lazy Mine. Samples Nos. 47–49 are natural cokes. The list of samples is given in Table 1.

According to the tentative classification of altered coal (Klika and Krausová 1993) the alteration types of coal samples were assigned to samples No.1 and Nos. 39–49 in Table 1. A tentative classification was suggested for different grades of thermal and oxidative alteration of coal. The following types were recognized:

Type I: Original coal – non-altered coal (sample No.1)
 II/1 – medium-high thermal alteration, no oxidation
 II/2 – very high thermal alteration, no oxidation
III/1 – medium oxidative and zero-low thermal alteration
IV/1 – high oxidative and zero-low thermal alteration
III/2 – medium oxidative and low-medium thermal alteration
IV/2 – high oxidative and low-medium thermal alteration
 V – natural cokes mineralized at contact with eruptive rock

Laboratory experiments were performed using a reactor with a saturating unit. The body of the reactor includes steel cover, which consists of individual segments connected by screws. A sample of input coal (No. 1) of grain size less than 1 mm was deposited in one segment between two copper nets. The temperature of the reactor was adjusted using a temperature control system. The reactor output is connected with the source of suction in order to ensure the flow of air (1.3 l/min). The volume of air was measured using a flowmeter. Samples of coal were heated in a reactor to reach temperature that remained constant throughout each experiment. Approximately 15 g of coal were used for each experiment (Klika et al. 2000).

The experiments in inert atmosphere were performed in tempered electric furnace. The sample of non-altered coal from the Lazy Mine (No. 1) was inserted into porcelain dish and closed with a cap. The dish was put into electric furnace, which was preheated to adequate temperature. For each experiment 10 g of coal were used. The airtight furnace was filled with nitrogen in order to obtain an inert atmosphere.

The samples of altered coal were characterized by chemical composition and by their petrographic character. The contents of carbon, hydrogen, nitrogen and sulphur were determined by classical elemental analyses, and oxygen was calculated from the difference to 100 %. Coal petrography was studied using Labophot NIKON microscope. Mean reflectance of vitrinite (R_o) was determined by reflex method. The calibration of mean reflectance of vitrinite R_o was performed with standard GGG (optical glass with reflection observed of 1.55 %). Parameters A^d (ash content), V^{daf} (volatile matter) and HA^{daf} (humic acids) were determined according to ČSN ISO 1171, ČSN ISO 441351 and ČSN ISO 562 (ČSN 441347 ČSN 441366) standards.

Experimental part

Non-altered coal

Laboratory alteration was studied using bituminous coal from the Lazy Mine (Seam No. 512) of the Upper Silesian Coal Basin (sample No. 1, Table 1). This coal has a mean reflectance of vitrinite of 0.88 % and has not reached the phase of critical metamorphism ($V^{daf} \sim 28$ %). It means that this coal has high scatter of some parameters, such as chemical composition, moisture and high variability of porosity and physical properties (Martinec et al. 1983).

Contraction cracks in vitrinite are not developed. Seams of the lower part of the Sedlové Member contain a high proportion of macerals of inertinite group: fusinite, semifusinite, micrinite less macrinite and inertodetrinite; among macerals of liptinite group, sporinite (Taylor et al. 1998) is present. The macerals are distinct and perfectly bounded in polished sections (photo 1) and deposited in parallel bands thus producing banded texture. The texture of fusinite tissue is mineralized by pyrite and siderite. The coal consists of 52 % vitrinite and 43 % inertinite. Macerals of liptinite group form the rest of the sample. Basic characteristics of sample No. 1 are given in Table 2.

Laboratory alteration of coal

Coal alteration under laboratory conditions was tested using non-altered coal (sample No.1) from the Lazy Mine. Experiments were performed at various temperatures in oxidative and inert atmosphere.

Oxidative and thermal alteration

The changes in composition of non-altered sample (sample No. 1) were evaluated in relation to temperature (from 100 to 300 °C) and time of heating (from 4 to 30 days) in oxidative atmosphere. The results of analytical analyses of sample No. 1 and oxidatively and thermally altered samples Nos. 2–6 are given in Table 2.

Mean reflectance of vitrinite increases with temperature of oxidation almost in a linear way from 0.88 % (sample No. 1) to 1.32 % (sample oxidized at 300 °C for 4 days – sample No. 6). The content of oxygen shows the same behaviour. The sample of altered coal at 300 °C has the highest content of oxygen (approximately by about 300 % higher than in non-altered coal). Increasing content of oxygen is not in a linear relation with the content of humic acids (HAs). They begin to decompose at temperatures above 250 °C (Table 2). The kinetics of laboratory oxidation and changes in chemical composition of the coal sample has been described before (Klika et al. 2000). In samples of HAs, which were prepared from oxidized coal in laboratory, the aromaticity index increases with increasing temperature from 78 % (HA prepared from coal oxidized at 150 °C) to 95 % (HA prepared from oxidized coal at 300 °C). These results were obtained using ^{13}C NMR solid state spectra of HAs. The oxygen content is relative-

Table 3. Thermal alteration of non-altered coal at various temperatures in atmosphere of nitrogen (1 hour).

Sample No.	°C	[%]							
		A^d	V^{daf}	R_o	C^{at}	H^{at}	N^{at}	O^{at}	S^{at}
7	100	3.95	29.37	0.90	56.88	37.61	0.74	4.64	0.12
8	200	4.84	28.28	0.91	57.57	36.82	0.67	4.80	0.14
9	300	4.11	28.06	0.94	57.54	36.42	0.86	5.05	0.13
10	400	5.47	22.87	1.16	58.86	35.74	0.71	4.54	0.15
11	500	5.88	11.44	1.98	63.96	30.33	0.90	4.69	0.13
12	600	6.40	5.45	3.31	71.38	24.40	0.97	3.09	0.17
13	700	5.78	2.74	5.17	78.06	18.26	1.01	2.52	0.16
14	800	5.79	0.99	5.48	83.98	11.76	0.83	3.21	0.22

Table 4. Thermal alteration of non-altered coal (No.1) at various temperatures and time in atmosphere of nitrogen.

Sample No.	°C/days	[%]		
		A^d	V^{daf}	R_o
15	100/2	4.22	30.09	0.90
16	100/5	3.89	30.12	0.93
17	100/14	4.23	29.47	0.95
18	100/30	4.05	31.39	0.98
19	150/2	4.39	30.02	0.98
20	150/4	3.72	31.65	1.01
21	150/7	3.95	32.70	1.05
22	150/14	3.99	35.29	1.08
23	200/1	4.00	31.59	0.86
24	200/2	3.95	34.14	0.88
25	200/4	3.87	36.85	0.86
26	200/7	4.20	39.19	0.94
27	250/0.33	4.19	30.04	0.83
28	250/1	4.15	32.44	0.90
29	250/2	4.22	35.02	0.92
30	250/4	4.27	42.31	0.92
31	300/0.33	4.56	29.48	0.83
32	300/1	4.52	31.83	0.89
33	300/2	5.25	37.85	0.91
34	300/4	5.75	42.37	0.92
35	500/0.33	6.24	9.92	2.76
36	500/1	5.72	8.39	3.05
37	600/0.33	6.43	4.39	4.20
38	600/1	4.70	3.77	4.72

ly highest in carboxyl groups, lower in hydroxyl groups and the least in carbonyl groups.

No optical changes of coal matter were found during thermal alteration of coal in air atmosphere during 30-days heating at 100 °C (sample No. 2) and during 14-days heating at 150 °C (sample No. 3). The first optical changes are seen in coal sample No. 4, prepared at 200 °C (7 days). These changes can be linked with rapid increase in HAs content. Vitrinite macerals are oxidized to HAs forms most easily. Lackluster to diffusive bleaching of grain rims can be seen in Photo 2. With further increase in temperature (to 250 °C) bleaching propagates towards the centre of the grains with only small areas of original sample being preserved (Photo 3, sample No. 5). With increasing temperature, liptinite undergoes sectional fusinitation (Taylor et al. 1998), and its structural resolution and mean reflectance reaches values of vitrinite reflectance. At temperatures of 250 °C (4 days) to 300 °C (4 days) (sample No. 6) a network of cracks develops. The cracks are mostly curved. Systems of micropores are formed due to degasification of the coal matter. The resolution of macerals continuously disappears, liptinite is altered, and after 4-days oxidation

only vitrinite and resistant fusinite and macrinite positions can be observed (Photo 4). The mean reflectance of vitrinite increased to 1.32 % with maximum R_o value of 1.55 %.

Thermal alteration in inert atmosphere

The process of thermal alteration of sample No. 1 was performed using two series of experiments. The first one (samples Nos. 7–14) was prepared at temperatures of 100–800 °C in inert atmosphere of nitrogen with short time of heating (1 hour, Table 3). The second one (samples Nos. 15–38) was prepared at temperatures of 100–600 °C in inert atmosphere of nitrogen with time of alteration longer than 1 hour (see Table 4).

Heating-induced changes in maceral composition and in microtexture of coal are observed. At the temperature of 150 °C (14 days) (sample No. 22, Photo 5), primary microtexture of original coal is still present, but very weak edge appears on the surfaces of individual grains. Macerals can be well identified and their shapes are well contoured. At the temperature of 200 °C (14 days) (sample No. 26, Photo 6), formation of distinct alteration rims can be observed in grains rich in vitrinite; inertodetrinite is still present. At the temperature of 250 °C (4 days) (sample No. 30, Photo 7), changes in vitrinite and especially in microtexture are observed. The first contraction cracks appear and the cavities of macropores start to open. Zonal transformation of megaspore of the same sample is documented in Photo 8.

At 300 °C (1 day, sample No. 32, Photo 9), zonal alterations of grains rich in both vitrinite and vitrinite with inertodetrinite appear in various intensities. The destruction of inertodetrinite begins together with slow loss of maceral contours. Contraction cracks remain preserved in sample No. 34 (Photo 10) even after 4-day heating and increased sizes of macropores are observed in altered vitrinite. Radical changes appear at 500 °C (8 hours, sample No. 35, Photo 11). Macropores are formed in grains originally rich in vitrinite due to swelling, and only residual fusinite grains still remain. At the temperature of 600 °C, alterations of sample No. 37 (8 hours, Photo 12) and sample No. 38 (1 day, Photo 13) is very advanced and the texture of semi-cokes begins to appear. Vitrinite is altered and shows higher mean reflectance. The development of macropores is at maximum. Metavitrinite creates walls of big bubble pores of different size in dependence on primary maceral composition. Contours of macerals disappear.

The relation between mean reflectance of vitrinite R_o and temperature (samples Nos. 7–14) is given in Fig. 1. R_o value did not practically change up to 350 °C. An increase in R_o is evident from 350 °C to 700 °C; this value seems to be stable at the temperature of 800 °C. This trend has been documented in many papers (Taylor et al. 1998, Chudý 1992, Honěk and Martinec 1999). Bílková (2001) found similar relation for bituminous coal from the Dukla Mine that is similar to sample No. 1 (Table 1) in its composition. The data for samples of natural cokes (samples Nos. 47–49) are also plotted in Fig. 1.

Simultaneously with the increase in R_o values, the content of C^{at} also increases. The content of C^{at} increases very slowly up to 400 °C in samples altered for 1 hour (Table 3, samples Nos. 7–10) and then rapidly increases at higher temperatures (samples Nos. 11–13). At 800 °C, the content of carbon reaches its maximum of 83.98 % (sample No. 14). A similar relation holds for R_o and temperature (see Table 3). The correlation coefficient (r) of the relation between R_o and C^{at} calculated from data presented in Table 3 is 0.9930. The regression equation between the two values (Fig. 2) can be expressed as follows:

$$R_o = 0.1823C^{at} - 9.5578 \qquad (1)$$

The same data (Table 3) show that the relation between R_o and the content of H^{at} has an opposite trend (Fig. 2). Correlation coefficient (r) between values R_o and H^{at} is 0.9891, and the regression equation has the form:

$$R_o = -0.1956H^{at} + 8.1379 \qquad (2)$$

Both relations (eqs.1 and 2) including the samples Nos. 45–49 are plotted in Fig. 2. Contents of oxygen O^{at}, nitrogen N^{at} and sulphur S^{at} differ only a little during thermal alteration.

The relation between volatile matter V^{daf} and temperature for samples Nos. 7–14 is plotted in Fig. 3. This relation is opposite to the relation between R_o and temperature plotted in Fig. 1. The content of volatile matter decreases only a little up to 350 °C and then decreases rapidly at higher temperatures. Similarly as it was observed before (for R_o changes) the maximum change of V^{daf} appears in temperature interval of 350 °C to 600 °C. Then, at higher temperatures, the content of volatile matter slowly decreases. A functional relation was also found between volatile matter and the content of C^{at} and the content of H^{at} (Fig. 4). The correlation coefficient (r) of the relation between V^{daf} and C^{at} is 0.9952, and the related regression equation has the following form:

$$V^{daf} = 9.976 \times 10^{15} \times (C^{at})^{-8.27} \qquad (3)$$

The V^{daf} and H^{at} data from the same Table 3 were used as well and the best shape of regression equation was evaluated. This equation can be written as follows:

$$V^{daf} = 5.10^{-4} \times (H^{at})^{3.00} \qquad (4)$$

The correlation coefficient of the equation (4) is 0.9903.

Both the regression relations are demonstrated in Fig. 4, where the data for natural cokes (samples Nos. 47–49) are also shown. Contrary to the time factor, these natural coke samples are not far from regression curves calculated from the data obtained from 1-hour laboratory heating experiments.

Because R_o and V^{daf} have high correlation coefficients with both C^{at} and H^{at}, there is a good probability of their good mutual correlation. The samples Nos. 7–14 (Table 3) were evaluated and the best regression equation was determined. Its form for one-hour heating experiments is as follows:
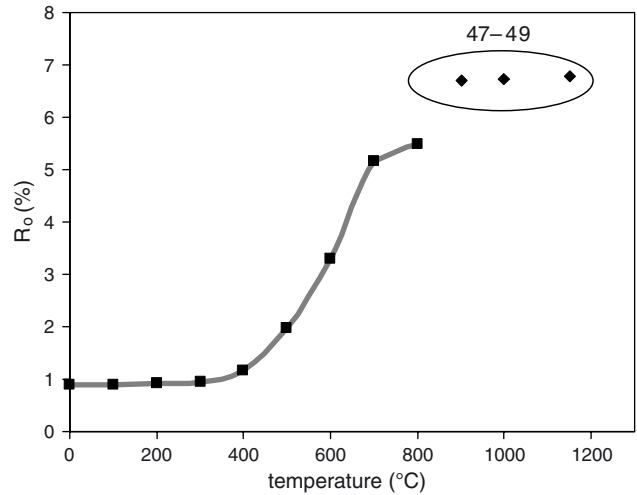

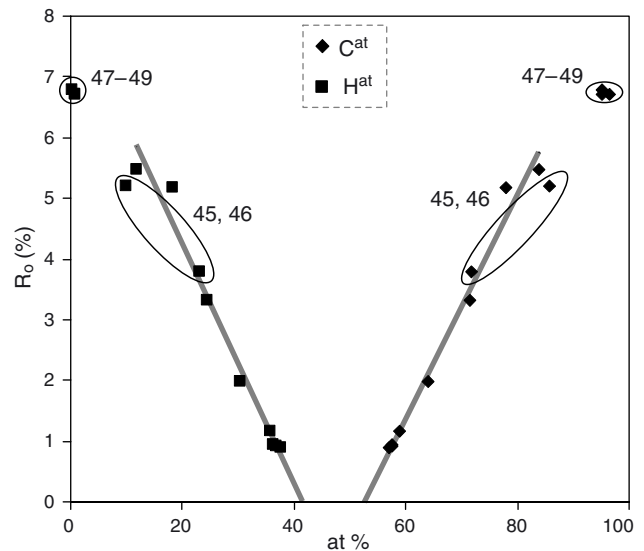Fig. 1. Relation between mean reflectance of vitrinite R_o and temperature.

Fig. 2. Relation between mean reflectance of vitrinite R_o and atomic percentages of C^{at} and R_o and atomic percentages of H^{at}.
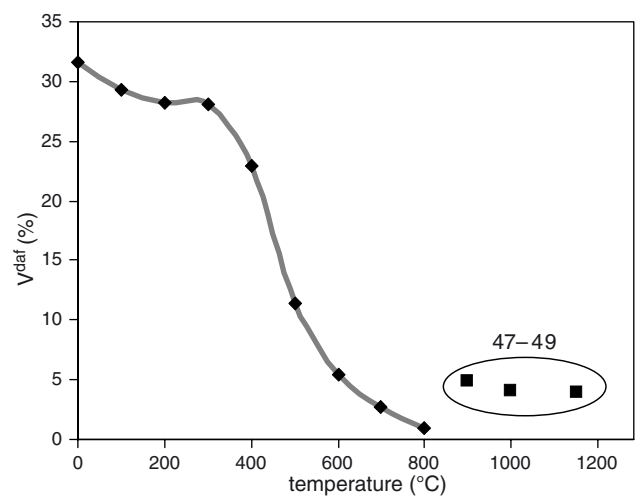

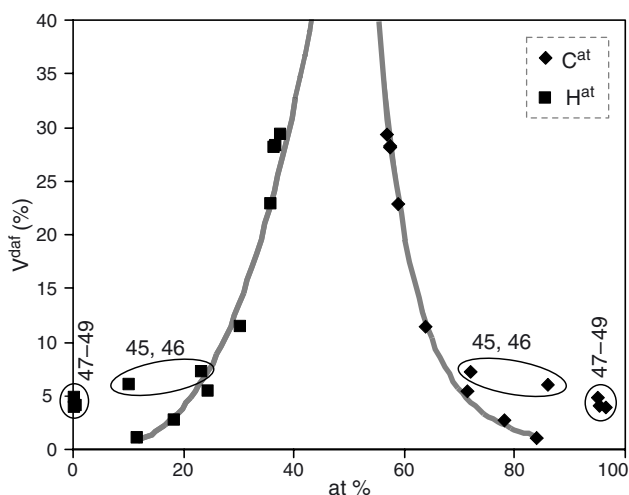Fig. 3. Relation between volatile matter V^{daf} and temperature.

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Fig. 4. Relation between volatile matter V^{daf} and atomic percentages of C^{at} and V^{daf} and atomic percentages of H^{at}.
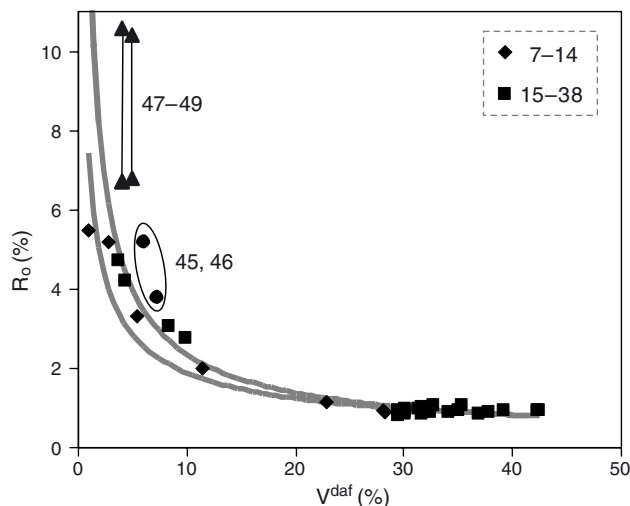

Fig. 5. Relation between mean reflectance of vitrinite R_o and volatile matter V^{daf}.

$$R_o = -7.3963 \times (V^{daf})^{-0.5949} \tag{5}$$

The correlation coefficient (r) between values R_o and V^{daf} is 0.9718.

The samples Nos. 15–38 (Table 4), which were thermally altered in inert atmosphere for up to 30 days, were also independently evaluated and the best regression equation was determined. Its form is:

$$R_o = 13.445 \times (V^{daf})^{-0.7593} \tag{6}$$

The correlation coefficient (r) between R_o and V^{daf} is 0.9759.

Both the relations (eq. 5 and 6) are plotted in Fig. 5 and show that R_o values are a little bit higher for given V^{daf} with longer time and at lower temperatures of heating (samples Nos.15–38). Samples of thermally altered coals from the vicinity of red beds bodies (samples No. 45–46) and samples of natural cokes (samples Nos. 47–49) are also plotted in Fig. 5. The parameters of these samples relate to much longer time of alteration that ran at probably lower temperature than in both laboratory experiments.

Naturally altered coal

The basic forms of secondary alteration of coal seams in the Czech part of the Upper Silesian Coal Basin are (Klika and Kraussová 1993, Dopita 1997):

(1) Surface low-temperature oxidation of coal seams on the surface of Carboniferous paleohighs. For example, outcrops of coal seams to Carboniferous paleorelief at Landek Hill near Petřkovice (sample No. 39, alteration type III/1).

(2) Thermal alteration of coal without oxidation.
   a) Coal seams in the proximity of red beds bodies. Coal from the proximity of these bodies was thermally altered to a different extent (samples Nos. 45 and 46, alteration type II/1 and II/2). This alteration is not associated with coal oxidation.

b) Thermal alteration associated with the formation of natural coke (samples Nos. 47–49, alteration type V) at contact of coal seams with intrusive bodies of Permian – Carboniferous eruptive rocks (Kožušníková and Pěgřimočová 2001) or at contact with neoidic basalts (Dvořák and Dopita 1968).

(3) Thermal alteration of coal seams connected with oxidation and burning of coal matter. This alteration occurs in coal seams and also in the surrounding rocks in the proximity of red beds bodies. Coal from the vicinity of red beds bodies shows a different extent of thermal and oxidative alteration (sample No. 40, alteration type III/1; samples No. 41 and No. 42, alteration type III/2; samples No. 43 and No. 44, alteration type IV/2).

Except IV/1, all alteration types of coal are presented in Table 5.

Oxidative and thermal alteration

Samples Nos. 39–44 are of different grade of oxidation and thermal alteration with a wide range of mean reflectance of vitrinite: 0.80 % (sample No. 40) to 2.35 % (sample No. 43). The ultimate and proximate analyses of samples of weathered coal from Landek Hill (sample No. 39) and samples from the vicinity of red beds bodies (samples Nos. 40–44) are given in Table 5. Samples with high and medium thermal alteration unaffected by oxidation (samples Nos. 45–49) are given in the same table.

As shown by the analyses of functional groups of sample No. 39 (sample of weathered coal), oxygen was bound especially in carboxyl and carbonyl groups, while hydroxyl groups were not present. Quite different content of functional groups was observed in sample No. 40. The highest amount of oxygen was present in hydroxyl, less in carboxyl and carbonyl groups. Alteration type III/1 has, in contrast to types III/2 and IV/2, a high content of humic acids (HAs) (HAs in alteration types III/2 and IV/2 are

thermally decomposed, Klika et al. 2000). Alteration type III/1 has lower total oxygen and carbon contents and higher hydrogen content. Alteration type IV/2 was the most oxidatively and thermally altered and has low HAs and hydrogen contents and the highest carbon and oxygen contents. Mean reflectance of vitrinite is also higher than in alteration types III/1 and III/2.

Naturally oxidatively altered samples in polished section are shown in photos 14–18. Sample No. 39 is weathered coal with a high degree of coalification prior to alteration (R_o = 1.6 % and V^{daf} = 18 %; Klika 1998). As a result of weathering, the volatile matter (V^{daf}) content increased up to the value of 27.33 % while vitrinite reflectance (R_o) did not change. The composition of coal is given in Table 5 and polished section of the sample is shown in Photo 14.

Sample No. 40 is the same alteration type as the previous sample, but its rank and petrographic character is somewhat different (Photo 15). In samples No. 41 and 42 (alteration type III/2) a very dense network of contraction cracks (Photo 16) and pores (Photo 17) is developed.

The porous structure of samples Nos. 43 and 44 originated probably as a result of degasification of coal matter at higher temperatures at which the samples were altered (alteration types IV/2). Grains of these samples show irregular reflectance of vitrinite (Photo 18), which was not observed in laboratory samples. Liptinite is totally altered.

Thermal alteration in inert atmosphere

Samples Nos. 45 and 46 are products of natural thermal alteration of coal without presence of oxygen. The characteristics and localization of coal samples have already been described (Klika 1998). Data from Table 5 indicate that the composition of these coals differs from the previous group of oxidized coals. Thermally altered coal is characterized by low oxygen and hydrogen contents and a higher carbon content (72–86 %). The mean reflectance of vitrinite reaches 5.2 %, volatile matter is reduced to 6 %, and no humic acids are detectable. The sample No. 46 (alteration type II/2) is of a higher grade of thermal alteration than sample No. 45 (alteration type II/1). Thermally altered coals have the character of semi-coke with a high mean reflectance of vitrinite and high number of pores (Photos 19 and 20).

Samples Nos. 47–49 are naturally thermally altered cokes (Kožušníková and Pěgřimočová 2001). They originated on the outer contact of coal seam with eruptive rock (dioritic porphyrite). The melting and creeping temperature points of this rock lie in the range of 1300–1400 °C. Coke is secondarily mineralized by quartz, carbonate,

pyrite and zeolites. It is characterized by low V^{daf} values (3.95–4.88 %), high content of C^{at} (95.16–96.42 %) and low content of H^{at} (0.18–0.7 %). Natural cokes are characterized by their total transformation of macerals and texture. They relate to the highest thermal transformation of coal. The texture differs depending on coal reflectance. The fine mosaic phase consists of two components. The first one, denoted as R_{GG}, consists of grey groundmass and corresponds to a relict vitrinite structure; its reflectance is 6.71–6.79 % (metaanthracite). The second one, denoted as R_{WG}, consists of white-grey groundmass and corresponds to the carbonaceous phase; its reflectance is 10.40–10.66 %. The rests of fusinite and inertodetrinite are preserved as thermally affected fragments. The numerous pores are filled by secondary mineralization, especially near the outer border of coking zone (Photo 21).

Conclusion

The range and type of changes of coal matter during post-sedimentary alteration depend on the rank, temperature, rate of heating, pressure, environment and time. The aim of this work was to compare samples of oxidatively and thermally altered bituminous coal from the proximity of red beds bodies with weathered samples from outcrops of coal seams and with coal samples prepared by laboratory oxidation and thermal alteration.

The characteristics of coal altered under oxidative and low-temperature conditions can be summarized as follows:

Oxidative rims along the cracks and grain edges were revealed by microscopic study of coal samples. These rims are characterized by their higher light reflectance.

Contents of volatile matter V^{daf}, oxygen and hydrogen are lower, and mean reflectance of vitrinite (R_o) and carbon content are higher than in non-altered coal.

Humic acids are present in oxidatively altered coal samples. Their content depends on the temperature and time of alteration.

As suggested by the character and petrography of all altered coal samples, altered coal from the proximity of

Table 5. Characteristics of naturally altered coal samples.

Sample No.	Altered type	[%]									
		A^d	V^{daf}	R_o		HA^{daf}	C^{at}	H^{at}	N^{at}	O^{at}	S^{at}
39	III/1	9.05	27.33	1.60		20.16	59.28	30.64	1.01	8.97	0.10
40	III/1	9.18	31.21	0.80		37.78	58.74	29.95	1.02	9.80	0.49
41	III/2	9.06	25.88	1.54		0.93	64.10	25.07	1.35	9.45	0.03
42	III/2	6.32	24.66	1.28		0.60	66.40	24.56	1.27	7.60	0.17
43	IV/2	9.78	28.75	2.35		1.01	68.55	18.24	2.16	10.92	0.13
44	IV/2	12.90	33.00	2.10		1.08	63.26	21.03	3.03	12.49	0.19
45	II/1	10.48	7.21	3.80		0.00	71.89	23.25	0.93	3.83	0.10
46	II/2	5.59	6.01	5.20		0.00	85.88	10.08	0.79	3.23	0.02
47	V	14.29	4.04	6.72+	10.66*	0.00	95.25	0.70	0.51	3.24	0.30
48	V	17.14	4.88	6.79+	10.40*	0.00	95.16	0.18	0.43	3.93	0.30
49	V	8.16	3.95	6.71+	10.58*	0.00	96.42	0.35	0.49	2.54	0.20

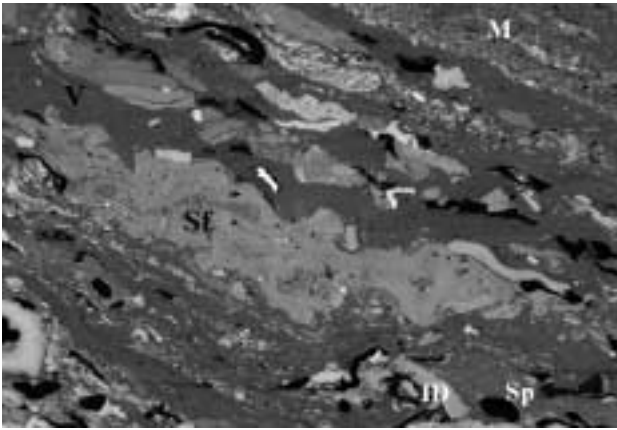+ R_{GG} reflectance of grey groundmass; * R_{WG} reflectance of white grey groundmass

Photo 1. Sample No. 1. Non-altered dull-banded bituminous coal. Banded texture is created with oblong and oblate shape of semifusinite (Sf) and grey vitrinite matter (V), which dominate over micrinite (M), sporinite (Sp) (almost black formation) and inertodetrinite (ID). The contraction cracks, which originated in vitrinite during coalification, absent.
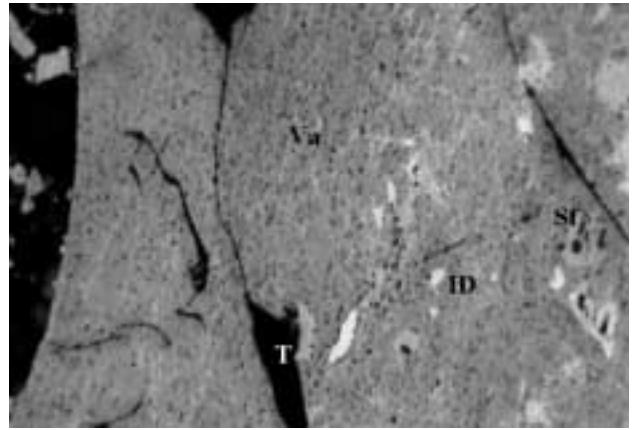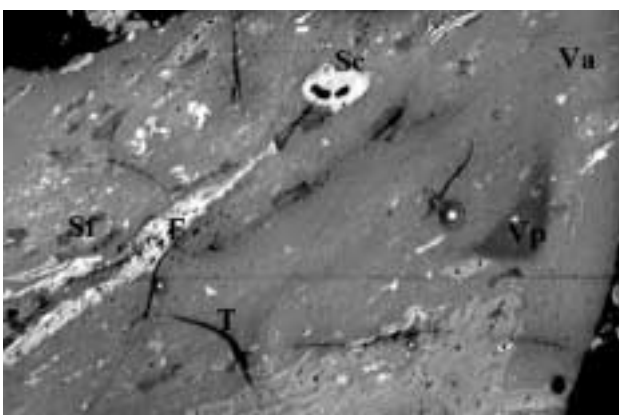

Photo 4. Sample No. 6. Laboratory oxidative alteration of sample 1 at 300°C/4 days. Grain of strongly blanched vitrinite (Va) with numerous micropores (dark points of grey vitrinite) with islet semifusinites (Sf) and inertodetrinites (ID). Thermally activated cracks (T) appear.
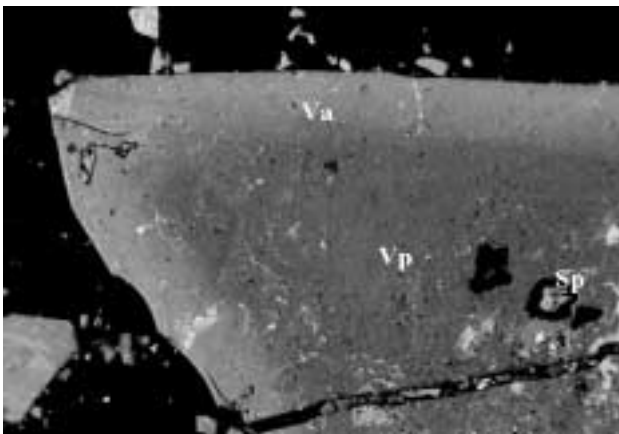
Photo 2. Sample No. 4. Laboratory oxidative alteration of sample 1 at 200 °C/7 days. The grain of vitrinite with weak blanching (Va) of grain edge. Inner part of grain of almost non-metamorphosed vitrinite (Vp), which close small spores (Sp), is preserved.
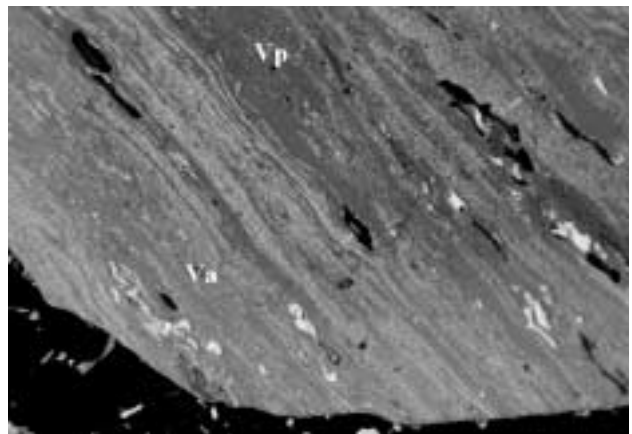
Photo 5. Sample No. 22. Laboratory alteration of sample 1 in inert atmosphere at 150 °C for 14 days. Zonally altered grain of coal with fine diffusive rim around the border of grain, which is created by light vitrinite (Va). The nucleus of grain is created by original vitrinite (Vp).

Photo 3. Sample No. 5. Laboratory oxidative alteration of sample 1 at 250°C/4 days. Grain of strongly blanched vitrinite (Va) with islet rests of original vitrinite (Vp) with blanching of grain edge. Inside the grain non-metamorphosed fusinite (F) and semifusinite (Sf) is retained. Thermally activated cracks (T) appear. Altered vitrinite close sclerotium (Sc).
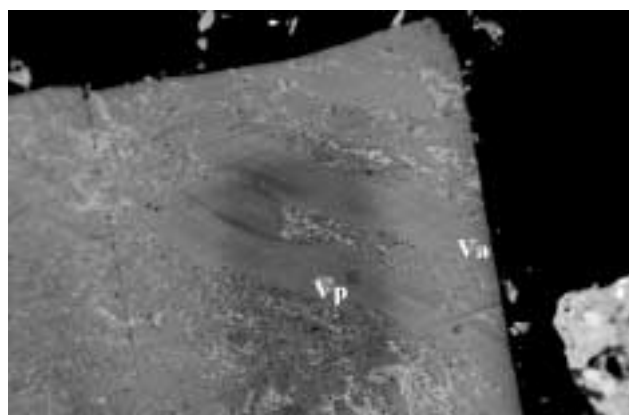
Photo 6. Sample No. 26. Laboratory alteration of sample 1 in inert atmosphere at 200 °C for 7 days. The grain with weak blanching edge is created by altered vitrinite (Va). Also nucleus of vitrinite (Vp) closing particles of inertodetrinite is seen.
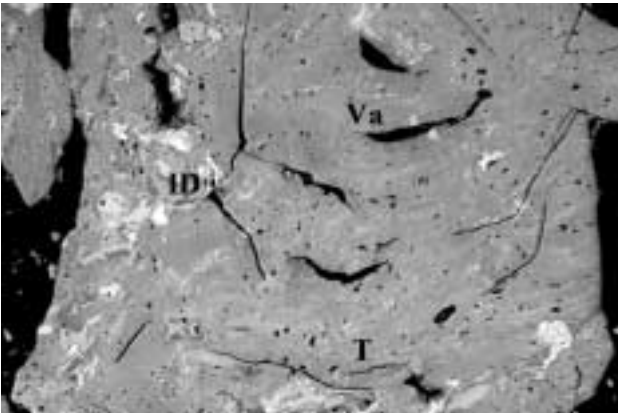
Photo 7. Sample No. 30. Laboratory alteration of sample 1 in inert atmosphere at 250 °C for 4 days. Altered grain of coal with many contraction cracks (T) and with fine pores in blanched vitrinite (Va). Also inclusions of inertodetrinite (ID) are seen.
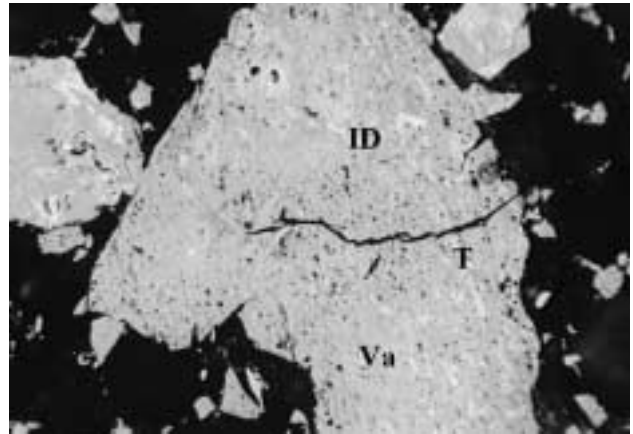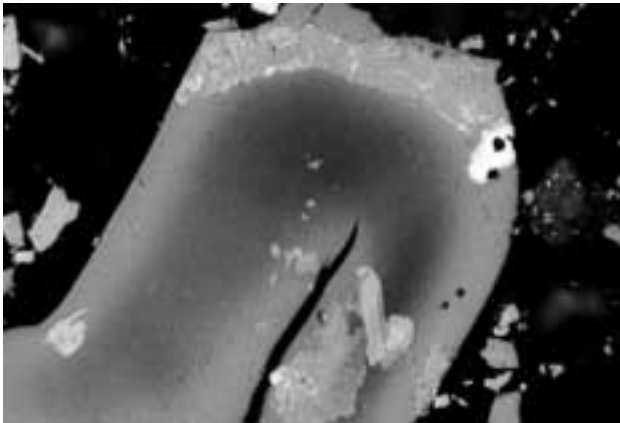

Photo 8. Sample No. 30. Laboratory alteration of sample 1 in inert atmosphere at 250 °C for 4 days. Zonally altered megaspore with fine blanched diffusive edge around spore and around central spore cavity.
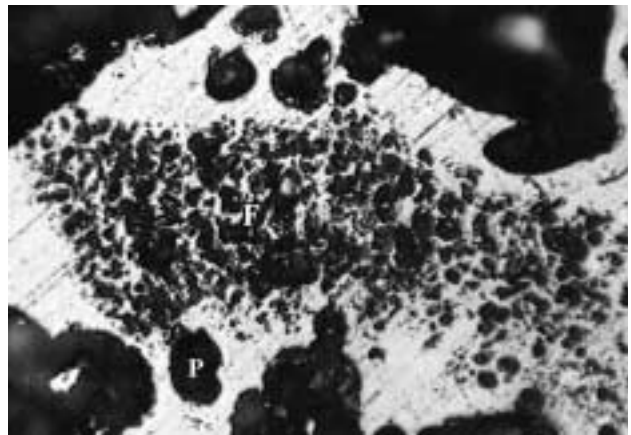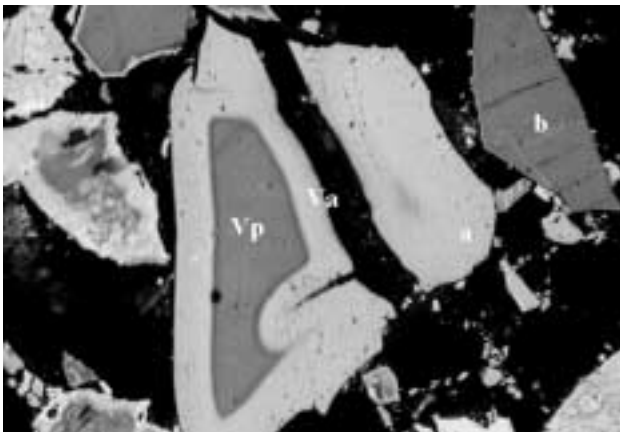

Photo 9. Sample No. 32. Laboratory alteration of sample 1 in inert atmosphere at 300 °C for 1 day. Zonally altered grain of coal is situated in the centre of photo. The nucleus that is created by vitrinite (Vp) is separated by edge around the border of grain, which is created by brighter vitrinite (Va). The other grains have edges about different thickness in dependence on macerals composition, size of the particles and orientation of polished section with regard to the surface of the grain. The grain (a) represents tangential cut in rim of a grain; the grain (b) does not show evidence of alteration.

Photo 10. Sample No. 34. Laboratory alteration of sample 1 in inert atmosphere at 350 °C for 4 days. Altered grain of blanched vitrinite (Va) with many particles of inertodetrinite (ID), contains contraction cracks (T) and nets of fine macropores (dark points).

Photo 11. Sample No. 35. Laboratory alteration of sample 1 in inert atmosphere at 500 °C for 8 hours. Markedly altered grains of coal with traces of swelling (big spherical pores P), in middle part the structure of fuzinite (F) is preserved.
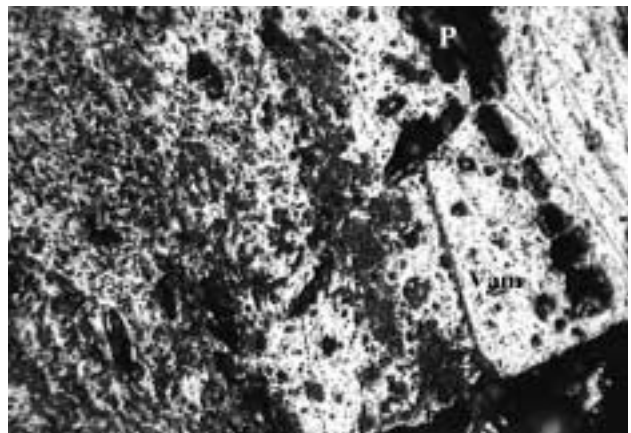

Photo 12. Sample No. 37. Laboratory alteration of sample 1 in inert atmosphere at 600 °C for 8 hours. Thermally quite metamorphosed coal with character of semi-coke with increased mean reflectance of metamorphosed vitrinite (Vam) and with many macropores (P).
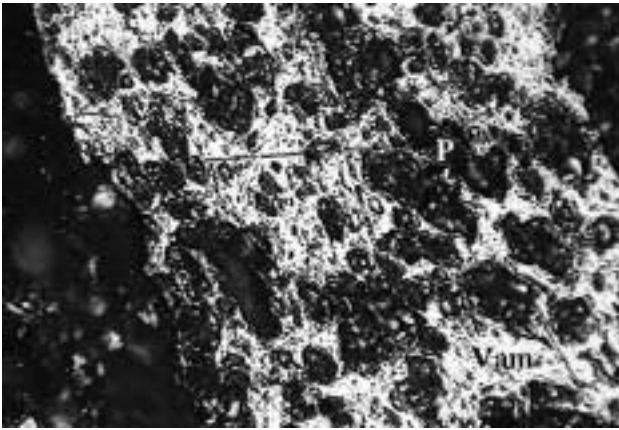
Photo 13. Sample No. 38. Laboratory alteration of sample 1 in inert atmosphere at 600 °C for 1 day. Thermally quite metamorphosed coal with character of semi-coke with increased mean reflectance of metamorphosed vitrinite (Vam) with many macropores (P).
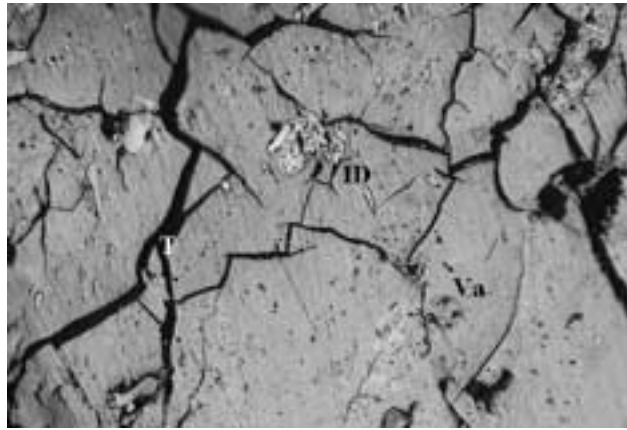

Photo 16. Sample No. 41. Naturally oxidative and thermally altered coal (alteration type III/2). The grain of strongly blanched vitrinite (Va) with many contraction cracks (T) with inclusions of inertodetrinite (ID).
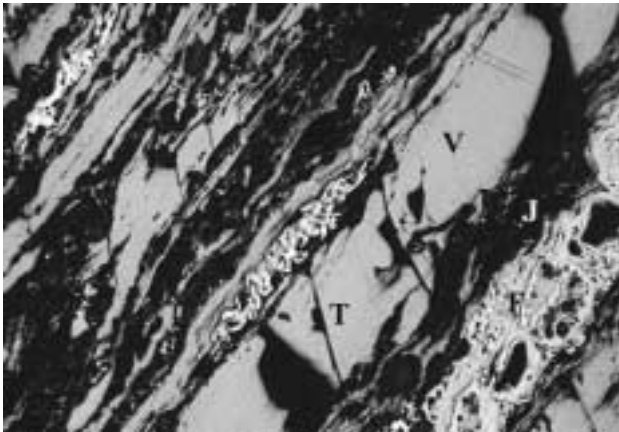

Photo 14. Sample No.39. Naturally oxidized black coal (alteration type III/1) from seam Kateřina, outcrop of seam in Landek Hill near Petřkovice. Coal is laminated by claystone (J), which together with vitrinite zones and fusinite netting (F) signify banded texture of coal. Vitrinite's coal is primary high coalificated deep under coalification step. In zones of vitrinite (V) are parallel cracks of coalificated contraction cracks (T).
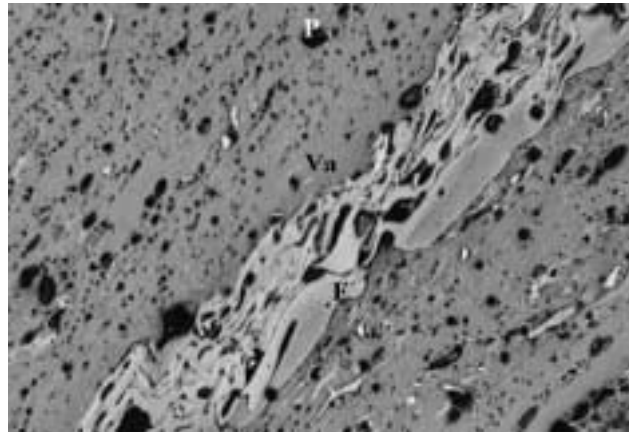

Photo 17. Sample No. 42. Naturally oxidative and thermally altered coal (alteration type III/2). Grain of strongly blanched vitrinite (Va) with many macropores (P) and strips of fusinite (F).
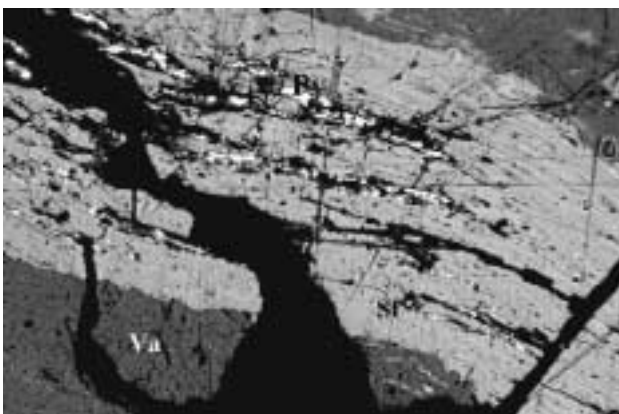

Photo 15. Sample No. 40. Naturally oxidized coal with alteration type III/1. Oxidative altered vitrinite (Va) together with zones of semifusinite (Sf) sandwiched with strips, which are created by small grains of pyrite (Py).

Photo 18. Sample No. 44. Naturally thermally and highly oxidative altered coal (alteration type IV/2). Grains of blanched vitrinite (Va) with contraction cracks (T).

red beds bodies is most similar to oxidized coal at temperatures below 150 °C in a laboratory.

Thermally altered bituminous coal in inert atmosphere from the proximity of red beds bodies was compared with samples from deeper parts of the Upper Silesian Coal Basin (natural cokes and semi-cokes) and with samples of coal thermally altered in a laboratory in inert atmosphere. The results of thermal alteration can be summarized in the following issues:

The most significant changes in coal matter were observed at temperatures of 350–550 °C.

Non-oxidative rims were also observed during the microscopic study of the polished sections of coal samples. The structure of naturally thermally altered samples is more homogenous compared to that of samples thermally altered in a laboratory.

Regression equations were calculated from the characteristics of these coals. These are:

volatile matter (V^{daf}) versus carbon content, V^{daf} versus hydrogen content, mean reflectance of vitrinite (R_o) versus carbon content, R_o versus hydrogen content and V^{daf} versus R_o. Correlation coefficients of all regression equations mentioned above are higher than 0.97. The characteristics of naturally thermally altered coal are close to the calculated data.

Sample No. 46 (naturally thermally altered sample, alteration type II/2) is similar to sample No. 14 (sample prepared by laboratory thermal alteration in inert atmosphere, heated at 800 °C for 1 hour). Sample No. 14 was more degasified during its alteration. Sample No. 45 (naturally thermally altered sample, alteration type II/1) is similar to sample No. 12 (sample prepared by laboratory alteration in inert atmosphere, 1 hour at 600 °C). Thermal alteration of natural samples is considered to run under temperature of 800 °C.

Natural cokes from the contacts with eruptive rocks represent an extreme example of thermally altered bituminous coal. They are characterized by total transformation of macerals and texture. The mosaic optical anisotropic texture consists of two components. One of them is a rest of vitrinite (metaantracite) and the second is new carbonaceous phase with the reflectance of 10.4–10.66 %.

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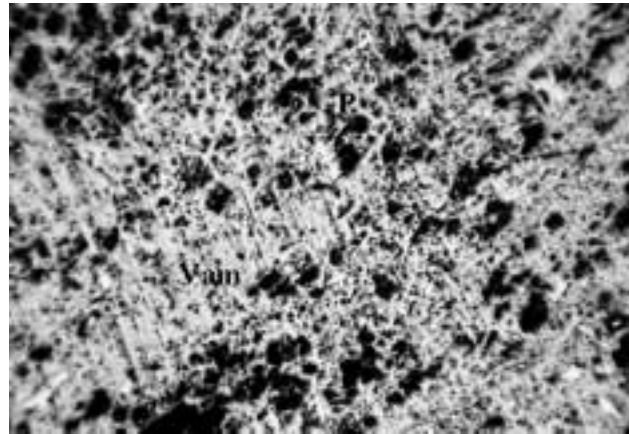Dobal V., Sýkorová I. (1985): Changes in coal matter during oxidation. Uhlí 33, 113–117. (in Czech)

Photo 19. Sample No. 45. Natural thermal (without oxidation) alteration of coal (alteration type II/1). Totally thermally metamorphosed coal with character of semi-coke with increasing mean reflectance of metamorphosed vitrinite (Vam) and many macropores (P).

Photo 20. Sample No. 46. Natural high thermal alteration of coal (II/2). Totally thermally metamorphosed coal with character of semi-coke with increasing mean reflectance of metamorphosed vitrinite (Vam) and many fine macropores (P). The texture of coal matter is very homogenous.
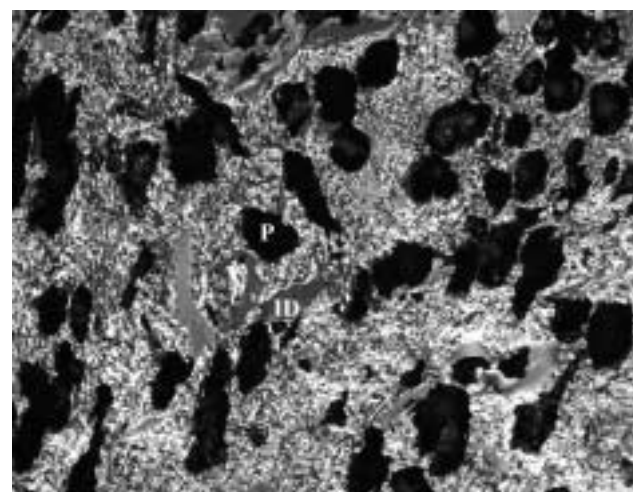

Photo 21. Sample No. 49. Natural high thermal alteration of black coal in contact of seam with eruptive rock leading to formation of mineralised coke (V) at temperatures ~ 1100–1300 °C. Primary matter of natural coke is grey and white, pores (P) are black and fragments of original inertinite macerals (ID) are dark grey. Zoom ×360.

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