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Molecular-structural study of oxygen in coals
1. Geochemical bonds of oxygen in Paleogene coals

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К. Маркова, С. Вылчева, Ст. Лефтерова, В. Вычев - Молекулярно-структурные исследования кислорода в углях. 1. Геохимические связи кислорода в Палеогеновых углях. Распределение общего кислорода, его форм связи и геохимические связи изучались на болгарских палеогеновых углях. Применялись разнообразные петрографические и химические анализы. Аналитическая информация подвергалась статистическому, регрессионному и кластерному анализу. Количественное распределение форм кислорода в угольной макромолекуле позволило выявить развитие процесса углефикации. Хорошая корреляция между кислород-содержащими функциональными группами и разными мацералями дает онование предполагать, что карбоксильные группы могуть быть использованы для генетических индикаций. Установленные зависимости между содержанием углерода, отражательной способностью и содержанием >CO и -COOH дает основание использовать последние группы в качестве индикаторов углефикации.

Abstract. The distribution of total oxygen, its forms of binding and geochemical bonds have been studied in Bulgarian Paleogene coals. Various petrographical and chemical analyses have been carried out. The analytical data are quantitatively evaluated by means of statistical, regressional and cluster analyses. The quantitative distribution of the oxygen forms in the coal macromolecule enables the estimation of the coalification processes development. The good correlation between oxygen-containing functional groups and the different macerals suggests that the hydroxyl (phenol), carbonyl and carboxyl groups can be used as genetic indicators. The dependences established between the carbon content, respectively, the reflectance and >CO and -COOH content points that these groups are coalification indicators.

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Key words: oxygen in coals; Paleogene coals; Bulgaria; molecular structures; statistics

Introduction

Oxygen is involved in the structure of the coal macromolecule both as an element of the functional groups and in non-active forms. The behaviour of these structures is indicative of the various stages in the development of geochemically important processes. Thus coalification and weathering processes are connected with quantitative and qualitative changes in the total oxygen content and of its forms of binding (Abdel-Baset et al., 1978).

Very few are the papers related to these problems for Bulgarian coals (Angelova, 1961, 1962; Markova & Mincev, 1983; Markova, 1984; Markova et al., 1984). The aim of the present work is to study the oxygen distribution, its forms of binding and the geochemical bonds in Bulgarian Paleogene coals.

Materials and Methods

Eleven representative samples of Paleogene coals from various Bulgarian coal basins and

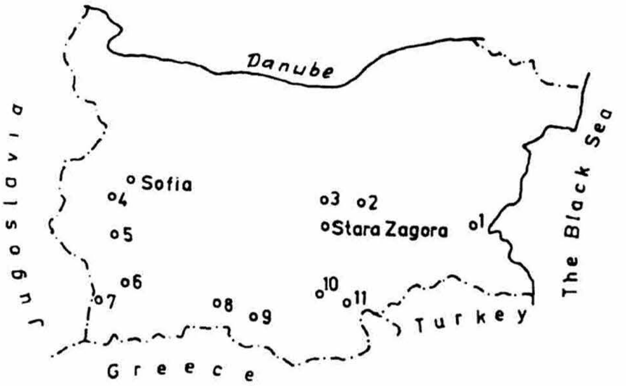

Fig. 1. Scheme of the Paleogene coal basins and deposits according to Siskov (1981)
1 - Bourgas; 2 - Borov Dol; 3 - Nikolaevo; 4 - Pernik; 5 - Bobov Dol; 6 - Pirin; 7 - Suchostrel; 8 - Mugla; 9 - Smolyan; 10 - Pchelarovo; 11 - Vulche pole

deposits were studied (Fig. 1) (Siskov et al., 1982). They have been sampled according to Bulgarian State Standard BDS 15550-82. Various petrographic and chemical analyses were applied. The proximate analysis includes the determination of moisture (W^a), ash (A^d) and volatile matter (V^{daf}). The ultimate analysis was carried out in "LECO" apparatus and the oxygen content was determined by difference.

The quantitative maceral analysis was performed according to Siskov et al. (1982). The reflectance studies were carried out on microscope-photometer PMT Standard Universal "Opton" with objective Antiflex-Epi 40^xoil and eye-piece 10^x at a monochromatic light (546 nm) and reference TF-5 with reflectance $R_o = 0.58$ %.

The oxygen-containing functional groups were determined by conventional methods: the hydroxyl (phenol) by barium hydroxide, the carbonyl ones with hydroxylaminohydrochloride and the carboxyl -COOH with calcium acetate. The content of each separate group is calculated with respect to the total oxygen content. The amount of the functional (OF) and non-functional oxygen (O_{NF}), which stands for the presence of heterocyclic structures with respect to the total oxygen content, has been determined.

The analytical data was subjected to conventional descriptive statistical evaluation including multivariate classification procedures (Davis, 1973; Vuchev, 1983).

Results and analysis

The total oxygen content in the coals from the Fore-Balkan province decreases in the following order: Bourgas-Nikolaevo-Borov Dol; from the Pernik province: Pernik-Bobov Dol-Pirin-Suchostrel and in the coals from the Rhodope's province: Pchelarovo-Mugla-Vulche pole-Smolyan (Table 1, Fig. 2-1^A). At the same time the amount of hydroxyl groups is higher and that of carbonyl and carboxyl-containing groups is lower. The content of -OH in the samples from the Fore-Balkan province drops from Bourgas to Nikolaevo and Borov Dol. For the Pernik province it decreases from Pernik to Bobov Dol-Suchostrel-Pirin and for the Rhodope province the order of decrease is from Smolyan to Pchelarovo-Mugla-Vulche pole (Fig. 2-1^B).

Table 1
Chacteristics of the initial coal samples

Coal provinces	Coal basins and deposits	Proximate analysis (%)			Ultimate analysis (%)							Maceral composition (%)*			Reflectance R_o (%)
		W^a	H^d	V^{daf}	C**	H**	N**	S**	O**	H/C	O/C	Huminite-Vitrinite (H-V)	Liptenite-Exinite (L-E)	Inertinite (I)	
Fore Balkan	Bourgas	14.5	21.0	47.6	70.4	7.0	2.1	1.3	19.2	0.84	0.20	84	15	1	0.38
	Borov Dol	7.3	7.3	44.0	75.7	5.4	2.2	1.0	15.7	0.86	0.16	85	4	1	0.56
	Nikolaevo	6.3	23.8	42.6	74.8	5.1	2.0	1.2	16.9	0.82	0.16	85	14	1	0.47
Pernik	Pernik	5.8	9.1	41.8	74.2	4.8	1.7	1.2	18.1	0.78	0.18	90	7	3	0.48
	Bobov Dol	6.9	22.0	45.0	74.6	5.4	1.5	1.4	17.1	0.88	0.17	90	8	2	0.43
	Pirin	6.5	3.9	44.0	75.1	5.4	2.3	1.3	15.9	0.86	0.16	86	13	1	0.53
	Suchostrel	2.5	6.3	29.1	85.1	5.1	1.2	1.2	7.4	0.71	0.07	89	2	9	0.95
Rhodope	Mugla	10.0	8.2	42.4	73.7	5.3	1.2	1.2	18.6	0.88	0.19	80	15	5	0.47
	Smolyan	9.8	13.1	40.3	78.1	5.4	1.3	1.2	14.0	0.84	0.14	91	8	1	0.83
	Pchelarovo	7.0	34.5	46.5	74.0	4.2	1.4	1.1	19.3	0.68	0.19	93	6	1	0.48
	Vulche pole	6.1	54.3	-	74.8	5.3	1.0	0.9	18.0	0.86	0.18	87	12	1	0.43

*organic matter basis
** daf

The amount of carbonyl groups for the same coals is considerably smaller compared to that of the hydroxyl ones (Fig. 2-2^B). While in the Fore-Balkan province it follows the sequence found for the hydroxyl groups, for the Pernik basin these groups change from north to south, i.e. from Pernik to Bobov Dol-Pirin-Suchostrel. For the Rhodope province the content of >CO decreases in the following order: Pchelarovo-Vulche pole-Mugla-Smolyan.

The content of carboxyl groups in the coals from the Fore-Balkan province follows the same patter as that of the hydroxyl and carbonyl groups. It has been found that the change in the -COOH content for the Pernik region is the same as that of >CO (Fig. 2-3^B).

The total sum of oxygen-containing functional groups in the coals from the Fore-Balkan province decreases gradually from Bourgas basin to Nikolaevo and Borov Dol; for the Pernik province it follows the order Pernik-Bobov Dol-Pirin-Suchostrel, whereby the coals from the first two basins are characterized by equal content of there groups. The content of oxygen-containing functional groups in the coals from the Rhodope province changes as follows: Pchelarovo-Mugla-Vulche pole (Fig. 2-III).

These observations show that the polymerisation and polycondensation,i.e. the coalification processes are accelerated following the same pattern for each one of the provinces separately.

The experimental results reveal that the content of functional groups in the Paleogene coals from the various coal basins changes as follows: in the samples from the Fore-Balkan province from 43.7 to 26.4 %, for the Pernik province from 44.3 to 28.2 % and for the Rhodope's province from 49.8 to 29.0 % (Fig. 2-2^A). The amount of functional oxygen is smaller than that of the non-functional one for all Paleogene coals. The coals from the Smolyan coal basin show minimum difference (0.42) between these two forms regardless of their higher degree of coalification (R_o= 0.83 %). Relatively small is this difference for the samples from Pernik and Bobov Dol. This is probably due to the similar coalification degree and the identical coal-forming environments.

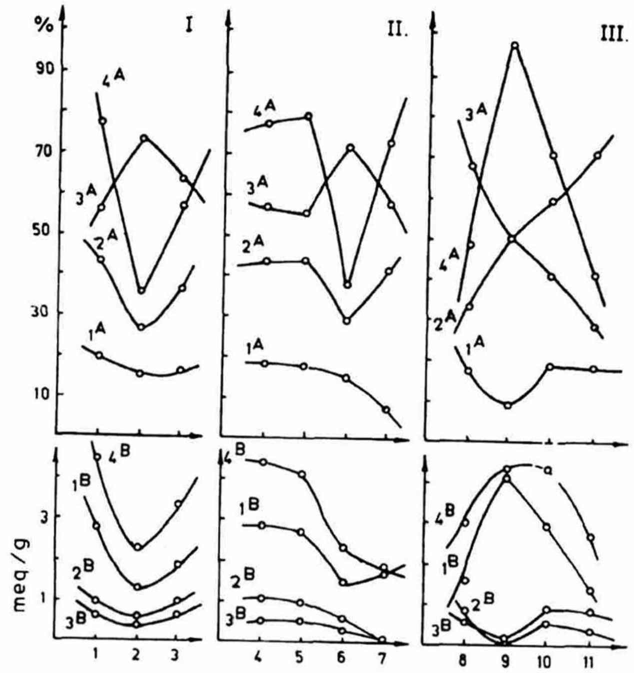

Fig. 2. Distribution of the oxygen forms
Coal provinces: I - Fore-Balkan; II - Pernik; III - Rhodope
Coal deposits: 1 - Bourgas; 2 - Borov Dol; 3 - Nikolaevo; 4 - Pernik; 5 - Bobov Dol; 6 - Pirin; 7 - Suchostrel; 8 - Mugla; 9 - Smolyan; 10 - Pchelarovo; 11 - Vulche pole
1^A - total oxygen (O_t); 2^A - functional oxygen (O_F); 3^A - nonfunctional oxygen (O_{NF}); 4^A - O_F/O_{NF}; 1^B - hydroxyl groups (-OH), meq/g, 2^B - carbonyl groups (>CO), meq/g; 3^B - carboxyl groups (-COOH), meq/g; 4^B - sum of (-OH + >CO + -COOH), meq/g

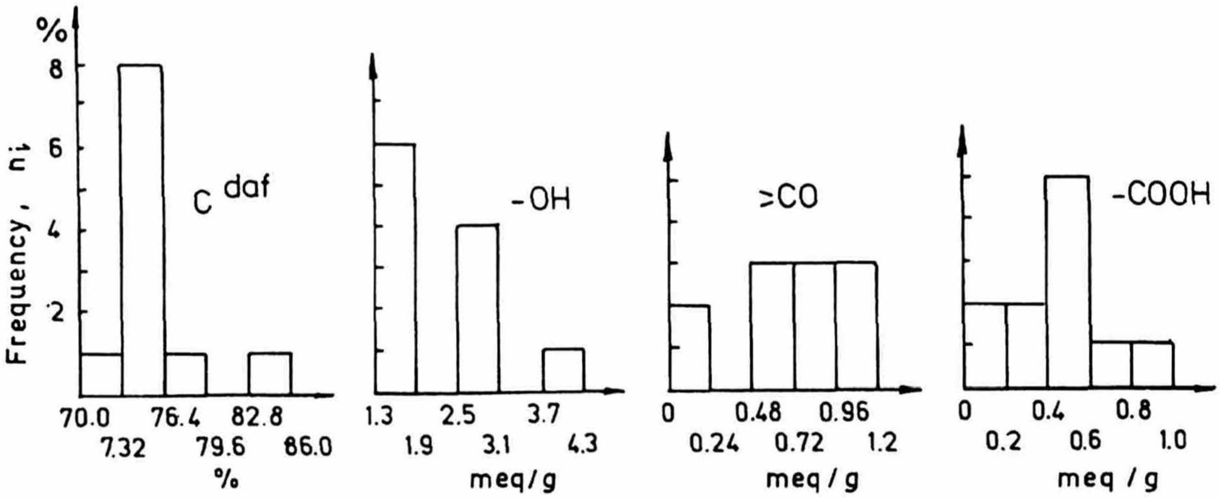

Fig. 3. Frequency Histograms of Distribution

Table 2
Generalized numerical characteristics of coal parameters

Parameter	Number (n)	Mean ($\bar{x}$)	Variance (σ^2)	Standard deviation (σ)	Skewness (S_k)	Kurtosis (E)
Carbon, C^{daf}	11	75.500	13.423	3.664	1.37	3.46
Hydroxyl groups, -OH	11	2.264	0.798	0.893	0.70	-0.71
Carbonyl groups, >CO	11	0.716	0.120	0.346	-0.66	-1.15
Carboxyl groups, -COOH	11	0.443	0.065	0.254	-0.36	-0.94
Huminite-Vitrinite, H-V	11	82.273	14.019	3.744	-0.28	-1.11
Liptenite-Exinite, L-E	11	9.455	20.873	4.569	-0.14	-1.61
Inertinite, I	11	2.364	6.455	2.541	1.62	1.39
Reflectance, R_o	11	0.546	0.032	0.179	1.27	0.06

Table 3
Results of the regression analysis

Number (n)	EQUATION	Correlation coefficients (r)	Standard error σ
11	$CO=5.82 - 0.07C$	-0.71	0.26
11	$COOH = 4.50 - 0.05C$	-0.81	0.15
11	$COOH=5.24-1.20+0.55CO$	0.74	0.18
11	$CO = 0.27 + 1.02\ COOH$	0.74	0.18
11	$R_o = -2.85 + 4.49 - 0.2C$	0.92	0.08
11	$C^o = 65.17 + 18.91\ R_o$	0.92	1.70

at $r_{0.05;\,11} = 0.60$

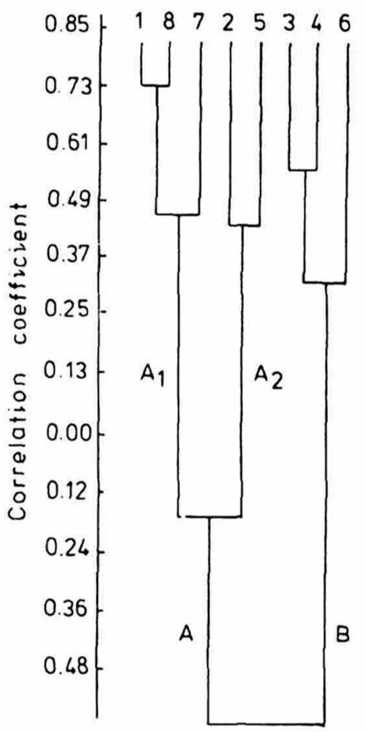

Fig. 4. Dendrogram of Cluster Analysis
1. Carbon, C^{daf}; 2. Hydroxyl groups (-OH); 3. Carbonyl groups (>CO); 4. Carboxyl groups (-COOH); 5. Huminite-vitrinite (HV); 6. Liptinite-exinite (L-E); 7. Inertinite (I); 8. Reflectance (R_o)

The ratio between the functional and non-functional oxygen (O_F/O_{NF}) is within the range from 0.36 to 0.78 for the Fore-Balkan coal province, form 0.39 to 0.80 for the Pernik province and from 0.41 to 0.71 for the Rhodope's province (Fig. 2-4[A]). The minimum and maximum values for the three coal provinces are quite close except the coals from Smolyan (0.99).

The chart for the distribution of the oxygen-containing functional groups shows a great variety (Fig. 3).

Generally, the coals are characterized by two types of distribution with relation to the carbon content. The latter has been calculated per a combustible coals mass. The first type includes samples with carbon content of 70.0-79.6 % and it is distinguished by a normal Gaussian distribution. The second type comprises a small part of the samples with carbon content of 82.8-86.0 %. The maximum of the first peak includes the samples from Nikolaevo, Borov Dol, Pernik, Vulche pole, Mugla and Pchelarovo (Fig. 3).

The same coals are related to three types of distribution with relative frequencies of 55, 36 and 9 % with respect to the hydroxyl groups content.

Two types of distribution are obtained in relation to the carbonyl groups amount. The first one is of relative frequency of 19 % and comprises the samples from Suchostrel. The second distribution shows a tendency of high and stable concentration of the groups from 0.48 to 1.2 % and includes the main part of the samples (Fig. 3).

The carboxyl groups lead to a homogeneous distribution with a moderate symmetry whereby the curve is shifted slightly to the left (Fig. 3).

The results of the correlation and regression analysis show that a definite statistical dependence between the carbon content and that of the hydroxyl groups could not be established.

This fact has been proved earlier by Abdel-Baset (1978) for coals from the eastern, internal and western locations in USA with carbon content of 73.9 -90.4 %. However, a good correlation between the carbon content/carbonyl groups content, and the carboxyl groups content (Tables 2 and 3) has been obtained (Table 3).

Two groups A and B (Fig. 4) are obtained from the cluster analysis based on the correlation coefficient. Group A is divided into two subgroups A_I and A_2. The first one combines the following parameters: reflectance R_o %, carbon content - C^{daf} % and the inertinite content - I, %. The second subgroup A_2 includes: the huminite-vitrinite content — H-V, % and the hydroxyl groups content, meq/g. Group B comprises the content of carbonyl and carboxyl groups and that of liptenite-exinite L-E.

The results of the complex studies demonstrate a great variety in the distribution of oxygen. The difference between the oxygen content in the samples from the different coal basins is negligible and is about 5 %. The complex heterocyclic oxygen-containing groups are prevailing and the content of functional oxygen is lower. The concentration of hydroxyl groups is higher compared to that of carbonyl and carboxyl ones. Hence, it may be assumed that part of the hydrophilic groups have been released during coalification (Tissot & Welte, 1978). Obviously, the evolution of the hydroxyl group is impeded strongly, while the carboxyl groups are released more intensively. Probably, the positive relation found between the hydroxyl content and the per cent of macerals for the huminite-vitrinite group may be related to the peculiarities of the macromolecule structure. Vitrinite, being the final product of the microbiological dispersion of wood at lower values of the oxidation potential, appears to be a geopolymer. Its macromolecular structure has a high aromaticity degree and contains a great number of phenolic and carboxylic groups. These arguments suppose and explain the good correlation between huminite-vitrinite and hydroxyl groups and allows the latter to be used as genetic markers. Although the similar content (%) of huminite-vitrinite in some of the Paleogene samples studied the content of -OH in them is different. This determines the difference in the structure of huminite-vitrinite macerals and is closely connected with the various plant debris, the gelification degree and the biochemical and geochemical processes that have taken place in them.

The good correlation established between the liptinite macerals and carboxyl groups is probably due to the higher amount of resinous structures in them (Fig. 4). Consequently, the carbonyl and first of all the carboxyl groups can be used as genetic indicators.

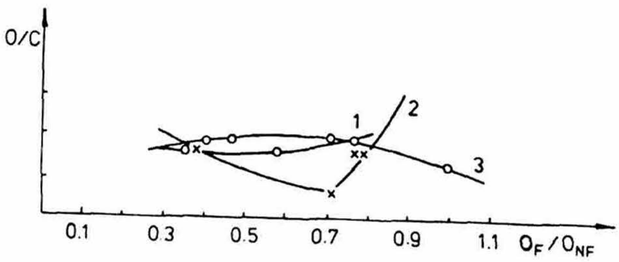

Fig. 5. Relationship between O/C and O_F/O_{NF} for the coal provinces
I - Fore-Balkan; II - Pernik; III - Rhodope

The difference found in the distribution of the oxygen forms in the Paleogene coals might be allocated both to the different compositions of the parent plant debris, its transformation and to the coalification processes occurring in them. This has been confirmed by the various coalification degree and by the ratio O/C, O_F/O_{NF} of the coals from the three provinces under study (Fig. 5). While the coalification degree of the coals from the Fore-Balkan province increases from east to west, in the Pernik province it rises from north to south. This observation has been earlier proved by the petrographic studies of Valceva (1989). The intensity of the coalification for the Rhodope's province is higher and according to Siskov et al. (1988) this is due to the increased thermal flux resulting from the intensive Paleogene vulcanisation.

Conclusions

The results obtained show that the character and the quantitative distribution of oxygen forms in the coal macromolecule allow the evaluation of the coalification which has occurred in the Paleogene coals. The intensity of these processes is similar for the Fore-Balkan and for the Pernik provinces and increases in the Rhodope' s province. The rise of the intensity for the Fore-Balkan is directed to west and for the Pernik province from north to south.

The strong correlation between the oxygen containing functional groups and the different macerals makes possible the application of hydroxyl, carbonyl and carboxyl groups as genetic or coalification markers.

Acknowledgement

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