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How to cite

TODOROV, Ivaylo, SCHEGG, Roland Albert, CHOCHOV, Spartak. Maturity studies in the Carboniferous Dobroudja coal basin (northeastern Bulgaria): coalification, clay diagenesis and thermal modelling. In: International Journal of Coal Geology, 1992, vol. 21, n° 3, p. 161–185. doi: 10.1016/0166-5162(92)90022-O

This publication URL: https://archive-ouverte.unige.ch/unige:153989
Publication DOI: 10.1016/0166-5162(92)90022-O

International Journal of Coal Geology, 21 (1992) 161–185
Elsevier Science Publishers B.V., Amsterdam

Maturity studies in the Carboniferous Dobroudja coal basin (northeastern Bulgaria)—coalification, clay diagenesis and thermal modelling

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(Received December 9, 1991; revised version accepted March 26, 1992)

ABSTRACT

Todorov, I., Schegg, R. and Chochov, S., 1992. Maturity studies in the Carboniferous Dobroudja coal basin (northeastern Bulgaria)—coalification, clay diagenesis and thermal modelling. *Int. J. Coal Geol.*, 21: 161–185.

In northeastern Bulgaria Upper Paleozoic coals are only found in the Dobroudja Basin. This coal basin belongs to a Variscan foredeep which is at present covered by a thick (1300–1500 m) Mesozoic–Cenozoic complex (Moesian platform). The coal seams are associated with alternating sandstones, siltstones and shales deposited under fluvio-deltaic environmental conditions. Previous coalification studies on the basin have recorded high volatile to low volatile bituminous ranks. The construction of coalification profiles (increase of vitrinite reflectance with depth) in ten wells from the Dobroudja coal basin has enabled us to interpret the paleotemperature regime. The simulation of the burial and thermal history of the Upper Carboniferous formations in the Dobroudja coal basin yielded paleogeothermal gradients between 45 and 71°C/km. The results show an increase of the paleogeothermal regime from the northwest towards the southeast. The existence of a high paleoheatflow is in accordance with data from other Carboniferous basins in Europe. Due to high vertical paleogeothermal gradients and deep burial, the maturation of the formations was completed during the Late Carboniferous. The relatively large maturation range of the Upper Carboniferous sediments enables comparison among different thermal indicators (vitrinite reflectance, spectral fluorescence maximum, pyrolysis indices, illite crystallinity and bulk clay mineralogy) and their behavior in the course of diagenesis.

INTRODUCTION

The Carboniferous Dobroudja coal basin is part of the huge Variscan foredeep which extends for over 4000 km from southern Portugal to southern Poland and into the Black Sea (Ziegler, 1988). More than 60 coal seams are present in the Upper Carboniferous section of the Dobroudja coal basin. Pre-

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0166-5162/92/$05.00

vious studies indicate that the rocks are thermally mature (Nikolov, 1974; Siskov et al., 1985). The present geothermal gradient in the basin is about 22°C/km (Petrov et al., 1983). There is, however, evidence for a higher paleogeothermal regime during the Late Carboniferous. This may be explained by the widespread occurrence of andesite–basalt sills of Stephanian to Permian age. A high geothermal regime was also proposed for other Carboniferous basins and formations in Europe (Buntebarth et al., 1982; Kempter, 1987).

The aim of this paper is to gain a better understanding of the relationship between the maturation of the Dobroudja Basin rocks and its thermal history as no data on this subject have been published. Twelve of the wells in the Dobroudja coal basin were investigated and more than 200 core samples were taken. Vitrinite reflectance, spectral fluorescence photometry, Rock-Eval pyrolysis, illite crystallinity and bulk clay mineralogy were used for this study.

GEOLOGICAL SETTING

The Doubrodja coal basin was discovered in 1963 during oil exploration in northeastern Bulgaria and covers an area of probably more than 1000 km^2. It is located near the Black Sea coast, a few kilometers north of the city of Balchik (Fig. 1).

The subsurface Upper Carboniferous formations of the basin are covered by a thick (1300–1500 m) Mesozoic–Cenozoic sedimentary complex (Moesian Platform). The complex lies discordantly on the strongly eroded Carboniferous sediments. The huge Moesian Platform is limited by the Carpatic belt in the north and by the Balkans in the south.

Some 1300 m of Carboniferous clastic sediments are present in the study area (Fig. 2). Sediments comprise alternating sandstones, siltstones, shales and coal seams, which were formed in fluvial/deltaic environmental conditions (Minev, 1990). Some intercalated pyroclastic rocks are related to volcanic activity during the Late Carboniferous (Popova, 1988). The unconformities at the top of the Mogilistenska (L), Macedonska (M), Velkovska and Krupenska (N) formations indicate several erosional events during the Late Carboniferous (Tenchov and Janev, 1979). The most prominent erosional phase (due to an important tectonic inversion: Asturian phase) occured during the Stephanian and early Permian. Probably c. 2000–3000 m of Upper Carboniferous strata (including some sediments of the Westphalian D and the Stephanian) were removed (Nikolov, 1988).

The sparse and irregular sedimentary record of the Permian, Triassic and Early Jurassic indicates a calm and unsteady subsidence pattern following the Carboniferous episode of deep burial and subsequent uplift. A phase of prolonged subsidence, beginning in the Middle Jurassic and ending in the Late Miocene, led to the formation of the Moesian Platform.

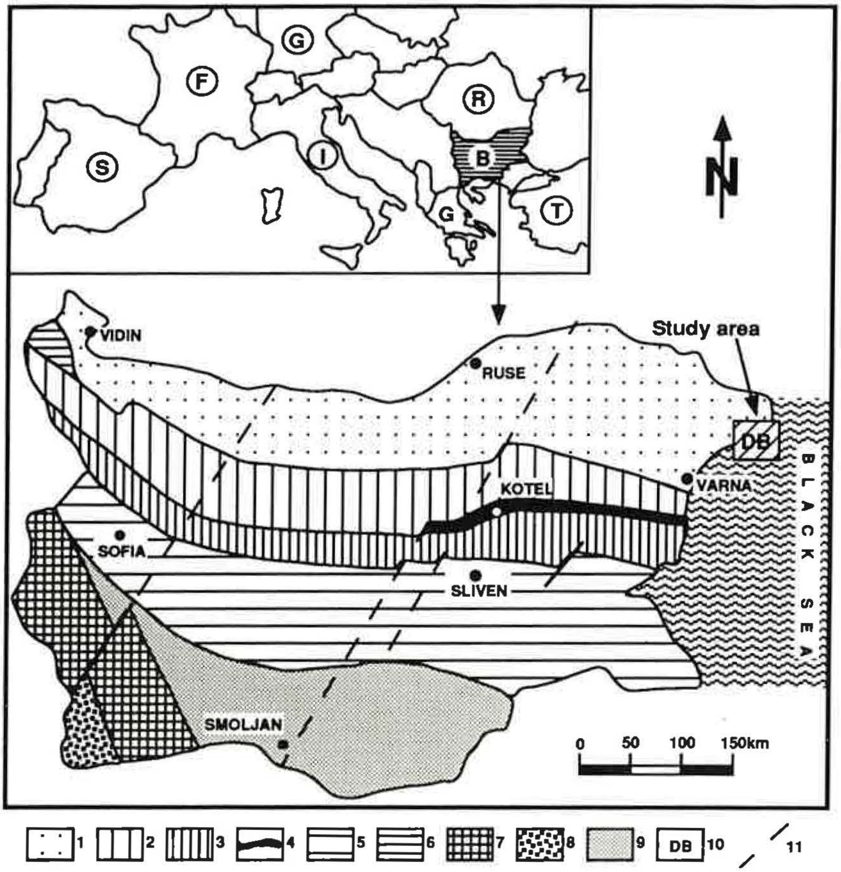

Fig. 1. Tectonic map of Bulgaria (insert map represents the location in Europe) (modified from Bonchev, 1980). *1* = Moesian platform; *2* = zone of the Prebalkan; *3* = zone of the Stara Planina; *4* = structural strip of the Kotel; *5* = zone of the Sredna Gora; *6* = zone of the southern Carpatic; *7* = zone of the Kraistides; *8* = massif of Dardanian; *9* = Rhodopian massif; *10* = Dobroudja coal basin; *11* = main transcurrent faults.

The main coal seams of the Carboniferous coal basin are humic, with 52% vitrinite, 12% liptinite and 20% inertinite, as well as 16% mineral matter (Sallabaseva and Siskov, 1983; Stefanova and Peeva, 1988). Detailed petrological investigations have shown the presence of sapropelic coals (cannels and bogheads), which were formed in typical lake–swamp environments (Sallabaseva and Mancheva, 1984). Some of the bogheads have an alginite content of up to 54% (Sallabaseva and Mancheva, 1982).

Previous coalification studies in the basin (Nikolov, 1974) documented high volatile to low volatile bituminous ranks (ASTM rank classes as published by Davis, 1978) or "flam" to lean bituminous ranks (Bulgarian State Standard 15193-80, as published by Siskov et al., 1985).

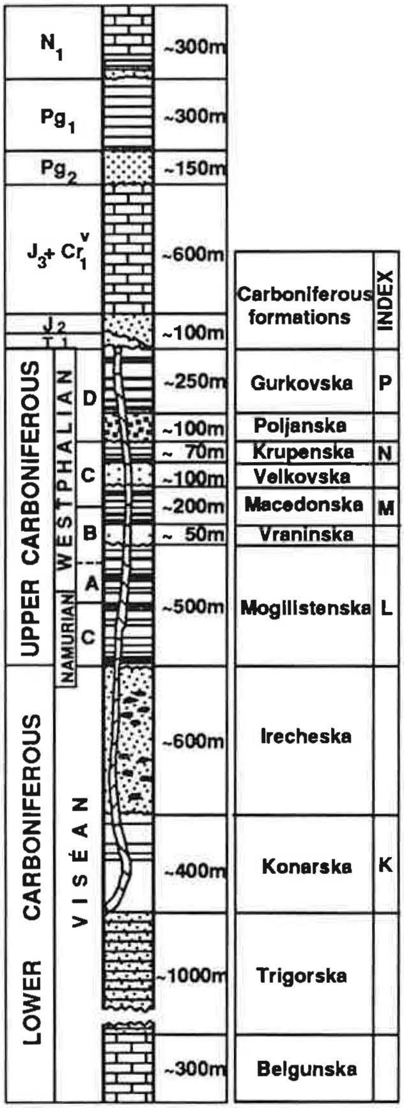

Fig. 2. Generalized stratigraphic section in the study area of the Dobroudja coal basin (modified from Konstantinova and Nikolov, 1974). N=Neogene; Pg=Paleogene; Cr=Cretaceous; J=Jurassic; T=Triassic.

In the basin contact thermal changes have occurred in coal seams due to igneous intrusions (olivine basalt sills) of Stephanian–Permian age (Tenchov, 1982). A zone of natural coke and semicoke occurs at the contacts with the sills (Nikolov, 1969).

MATERIAL AND METHODS

The cores from twelve wells were used for our investigations. Coal seams and phytoclasts were sampled for maturity studies. Some of these samples were collected for clay mineral analysis and organic geochemistry (Rock-Eval pyrolysis) in order to correlate the different thermal indicators. The samples were selected from various sites to attain a complete Upper Carboniferous stratigraphic sequence.

Vitrinite reflectance

Vitrinite reflectance measurements (more than 150 samples of coal seams and phytoclasts) were carried out on vitrinite using the procedure described by Stach et al. (1982). Mean random vitrinite reflectance was determined in normal white light at a wavelength of 546 nm and a measuring aperture size of 4 μm using a Standard Universal (Opton) microscope photometer. The average results are generally obtained from at least 40 (phytoclast samples) or 100 measurements (coal samples).

Fluorescence microscopy

Microscope fluorimetry measurements were carried out on polished coal sections with an excitation at 365 nm with a Leitz Orthoplan microscope photometer following the procedure described by Ottenjann et al. (1974). The measurements were performed on different sporinite populations (tenuispores) and on alginite (*Botrycoccus* type). The spectral fluorescence maximum (λ_{max}) was taken as a maturity parameter. The results were obtained from at least 15 measurements (30 curves) for each population in a sample.

Rock-Eval pyrolysis analysis

Pyrolysis analysis on 13 shale samples was carried out using a Rock-Eval II OSA.

Illite crystallinity and bulk clay mineralogy

The <2 μm fraction of the shale samples was used for X-ray analysis. Oriented specimens were prepared by pipetting suspensions of the <2 μm fraction onto glass slides. Slides were glycolated and run on an automatic powder D500 Siemens diffractometer from 2° to 60° 2θ, using CuKα radiation (40 kV, 30 mA) and a scanning rate of 2° 2θ/min. The crystallinity of the illite structure is characterized by the intensity and sharpness of the 10 Å illite peak (Robert, 1988; Weaver, 1989). The method of Kübler (1968) for determining the crystallinity index (CI) of illite was used for this study. Our CI data were compared to two standard samples (standards kindly provided by Dr. Arkai, Hungarian Mineralogical Institute) in order to define their position on Kübler's scale.

The method of Biscaye (1965) was used for establishing the semi-quantitative distribution of the clay minerals in the <2 µm fraction.

RESULTS AND INTERPRETATION

Vitrinite reflectance

For this study, ten coalification well profiles were constructed for the Upper Carboniferous formations in order to determine the paleotemperature regime in the basin. The thickness of the Upper Carboniferous formations in the studied well profiles varies between 158 m and 794 m (Table 1). Vitrinite reflectance values range between 0.59% and 1.45% R_o. The following average values were determined: Gurkovska formation (P) 0.68% R_o; Krupenska formation (N) 0.72% R_o; Macedonska formation (M) 0.79% R_o; Mogilistenska formation (L) 1.03% R_o. Our rank determinations correlate with previous coalification studies (Konstantinova and Nikolov, 1974; Nikolov, 1974) which have been carried out in other wells from the same sedimentary basin.

Vitrinite reflectance data in the study wells show a regular increase with depth. Linear (first order) regression lines generally fit the profiles best (Fig. 3). The R_o profiles are restricted to the Upper Carboniferous because no core sections from the Mesozoic were available. The shape of the reflectance profile may be affected by high temperature, short-term events (olivine basalt sills). Therefore, anomalous high R_o values near sills have not been taken into account when computing the regression equations. Regression equations yield reflectance gradients between 0.026% R_o/100 m and 0.069% R_o/100 m (Table 1). The reflectance gradients are noticeably higher in those wells where sediments of Namurian C and Westphalian A age are present (Fig. 3).

Implications for thermal history

A variety of methods can be used for the interpretation of coalification results. The determination of vitrinite reflectance profiles is particularly useful for estimating zones of potential hydrocarbon generation in sedimentary basins. It can be also used for a number of other geological applications such as the determination of paleogeothermal gradients (Buntebarth and Middleton, 1986; Kalkreuth and McMechan, 1988), the recognition of normal faults, thrust faults or inverted strata in drill wells (M. Teichmüller et al., 1979) or the estimation of the amount of erosion (Dow, 1977; Haquebard, 1977). Another approach for the interpretation of coalification results is thermal mo-

TABLE 1

Vitrinite reflectance data and paleogeothermal gradients

Well	Profile (m)	Age	Paleodepth (m)	Erosion (m)	R_o range (%)	No. R_o values	$\%R_o/100$ m	PGG (°C/km)	T_{max} (°C)
90	794	wC, wB, wA	2804	2050	0.74–1.08	10	0.037	47	152
110	650	wB, wA	2571	1950	1.06–1.45	12	0.060	62	179
141	569	wC	2121	1850	0.68–0.91	10	0.028	54	135
200	465	wD, wC	1959	1500	0.63–0.82	24	0.040	55	128
201	426	wC, wB	2492	2090	0.59–0.87	21	0.026	45	132
204	158	wC	2050	1900	0.78–0.85	6	0.033	57	137
205	426	wC, wB	2065	1650	0.64–1.05	23	0.036	54	135
206	339	wB	2126	1800	0.73–0.94	12	0.034	56	138
208	410	wC, wB	1972	1570	0.67–0.88	15	0.032	55	130
219	549	wB, wA, nC	2233	1700	1.06–1.43	9	0.069	71	180

wA, wb, wC, wD = Westphalian A–D; nC = Namurian C; PGG = paleogeothermal gradient calculated with the EASY%Ro model of Sweeney and Burnham (1990), mean annual surface temperature 20°C; T_{max} = maximum paleotemperature.

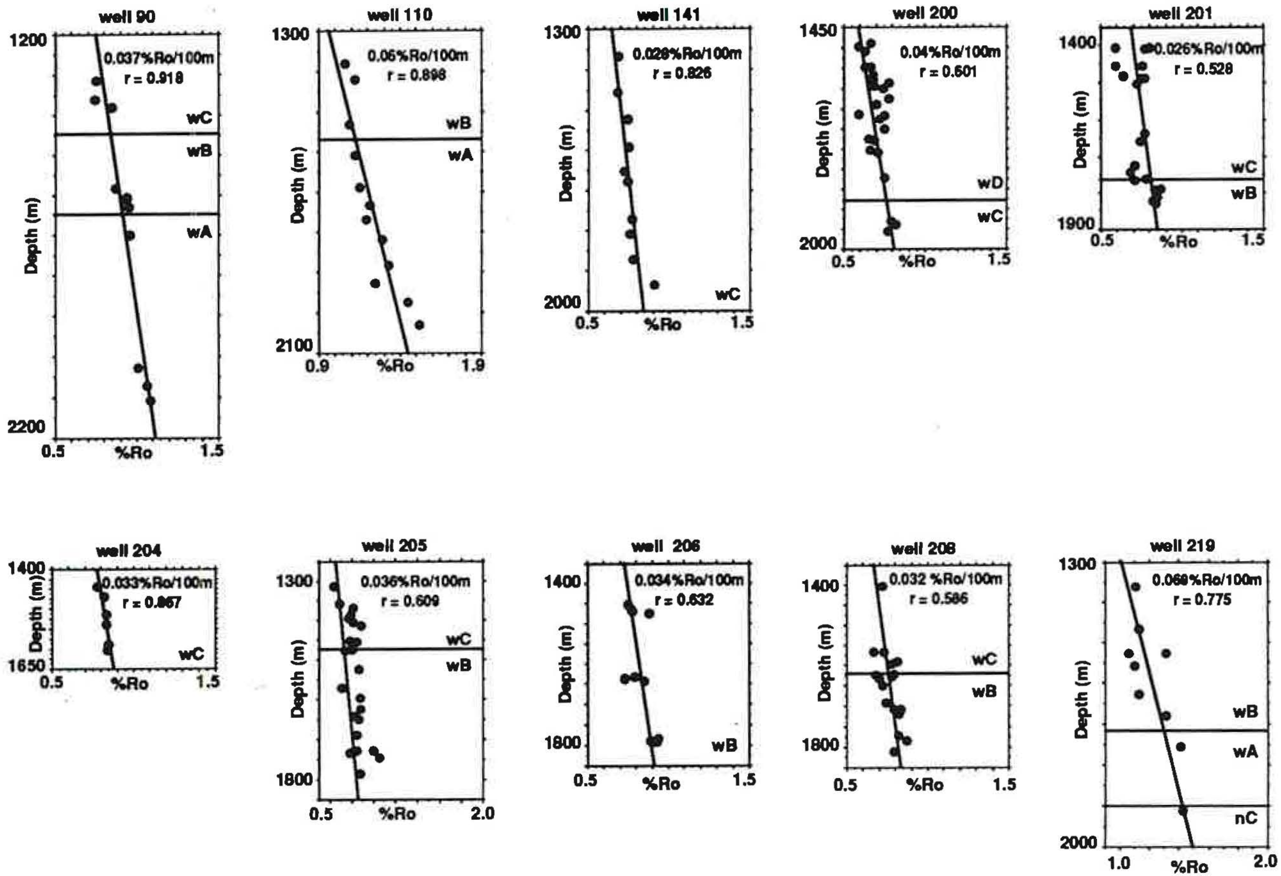

Fig. 3. Coalification profiles of ten wells in the Dobroudja coal basin with first-order regression lines. *nC*=Namurian C; *wA*=Westphalian A; *wB*=Westphalian B; *wC*=Westphalian C; *wD*=Westphalian D.

delling using burial history curves (Hood et al., 1975; Lopatin, 1976; Waples, 1980; Lerche et al., 1984). One of the recent models—EASY%Ro—uses an Arrhenius first order parallel reaction approach with a distribution of activation energies (Sweeney and Burnham, 1990).

Our approach for evaluating the paleogeothermal conditions of the Dobroudja coal basin was as follows:

(1) Construction of burial history curves for each well using the BACKSTRIP 89 program (Loup, 1992). This basin analysis program, developed at the Department of Geology in Geneva, takes into account, among other parameters, decompaction and erosion. The amount of erosion was approximated by using the measured R_o profiles. The intercept of the logarithmic reflectance gradient with zero coalification is commonly inferred to represent an estimate of the thickness of eroded sediments (Dow, 1977).

(2) The time–temperature history for each formation in a well may be determined using burial history curves, an initial set of "realistic" paleogeothermal gradients and mean annual paleosurface temperatures.

(3) This time–temperature history is then used in the EASY%Ro model of Sweeney and Burnham (1990) to simulate the vitrinite reflectance history for each formation.

(4) Comparison between the modelled and measured vitrinite reflectance enables optimization of the paleogeothermal model: the thermal constraints are changed until there is a fit between the modelled and the observed values.

The authors are aware that this approach will not result in a unique solution. Several thermal histories may lead to the same maturation profile. Therefore, it is important to begin with an appreciation of the tectonic history on the basin. The most crucial point of the approach is the estimate of the thickness of Upper Carboniferous deposits which have been eroded. As stated by Majorowicz et al. (1990), well profile coalification gradients have significant uncertainties which are propagated in erosion and paleogeothermal gradient calculations. In addition, the choice of the zero coalification R_o value can lead to differences in the estimate of erosion of several hundred meters. Consequently it is evident that our calculations cannot be more than a first approximation. The results produce the order of magnitude of the paleogeothermal gradients and, at best, a first order variation rather than an exact picture of the paleogeothermal conditions of the Carboniferous Dobroudja Basin.

In this study the subsidence histories of ten wells have been reconstructed. The amount of the Carboniferous section eroded ranges from 1500 to 2100 m (Table 1). The order of magnitude of these values is in accordance with estimates in other Carboniferous basins (R. Teichmüller and M. Teichmüller, 1986; Kempter, 1987). Such overburden can only be assumed if thick Westphalian D and (or) Stephanian sequences were deposited in the study area.

Reconstructed maximum paleodepths during the Late Carboniferous range from 1700 m to 2800 m (Table 1).

The present temperature profile in the basin is strongly disturbed and affected by circulating water in the Upper Jurassic and Lower Cretaceous car-

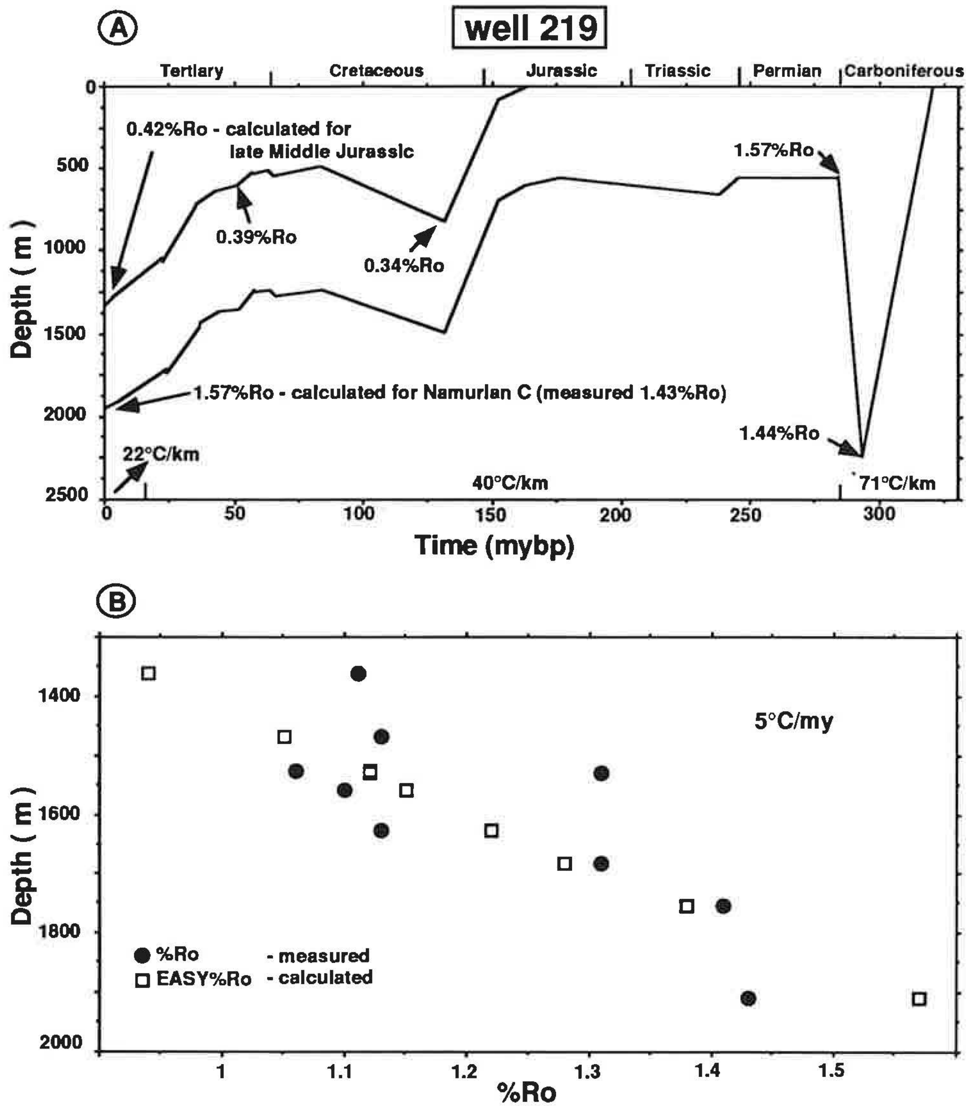

Fig. 4. Thermal modelling. (A) Burial history for Namurian C and the late Middle Jurassic in well 219 with evolution of calculated vitrinite reflectance values through time using the EASY%Ro model. (B) Comparison of measured and calculated (using the EASY%Ro model for the thermal history shown in A) Late Carboniferous R_o values in well 219. A constant heating rate of 5°C/Ma and a mean annual surface temperature of 20°C were assumed during the Late Carboniferous.

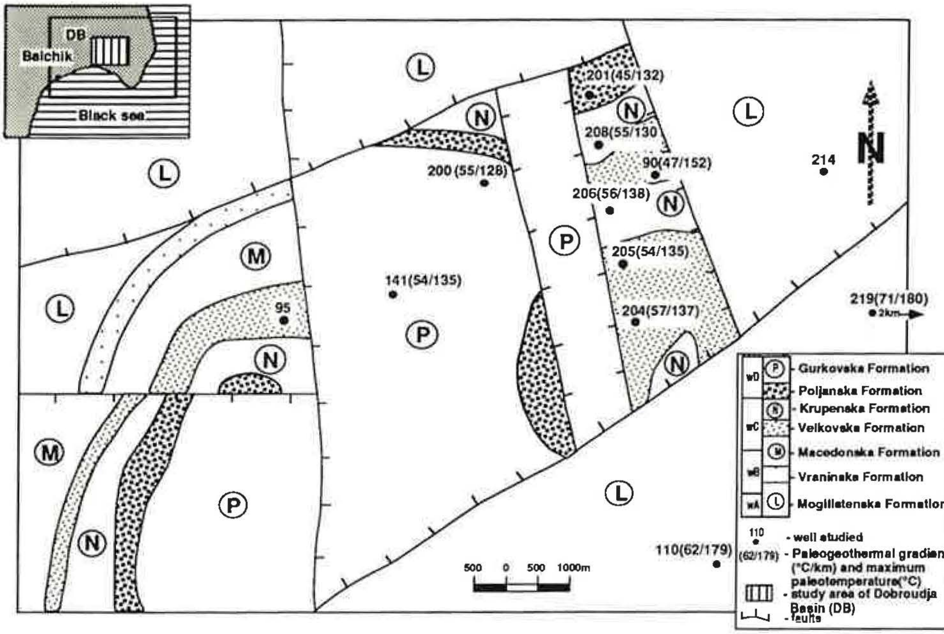

Fig. 5. Lateral distribution (sketch subsurface map modified from Nikolov, 1988) of the paleogeothermal gradients and maximum burial temperatures during the Late Carboniferous (Wesphalian A–D) in the study area. The gradients were calculated with the EASY%Ro model on the basis of 142 reflectance data from ten wells.

bonate rocks. The average present geothermal gradient in the basin down to 1500 m is 15°C/km and at greater depths 22°C/km (Petrov et al., 1983).

The simulation of the maturity was based on the assumption that paleogeothermal gradients were constant within the each section during the Late Carboniferous. As we have little information on the variation of the paleogeothermal gradient during the Cenozoic, Mesozoic and Permian, some approximations have been made. Modelling of the vitrinite reflectance evolution for the Middle Jurassic (Fig. 4A) using a constant paleogeothermal gradient of 40°C/km during the Mesozoic and Early Cenozoic resulted in values corresponding to R_o data (0.41–0.49% R_o, Stefanova and Peeva, 1988, their fig. 22, p. 110) for the same formation measured in neighboring parts of the study area. We assume that the low present geothermal gradient prevailed only during the Late Cenozoic.

Figure 4 shows the simulation of the vitrinite reflectance data in well 219. In order to fit the measured values, a paleogeothermal gradient of 71°C/km during the Carboniferous was assumed (Fig. 4A). The fit is demonstrated by the comparison between the measured and calculated R_o values of the Upper Carboniferous formations (Namurian C to Westphalian B) in well 219 (Fig. 4B). The results for the ten study wells are summarized in Table 1. The paleo-

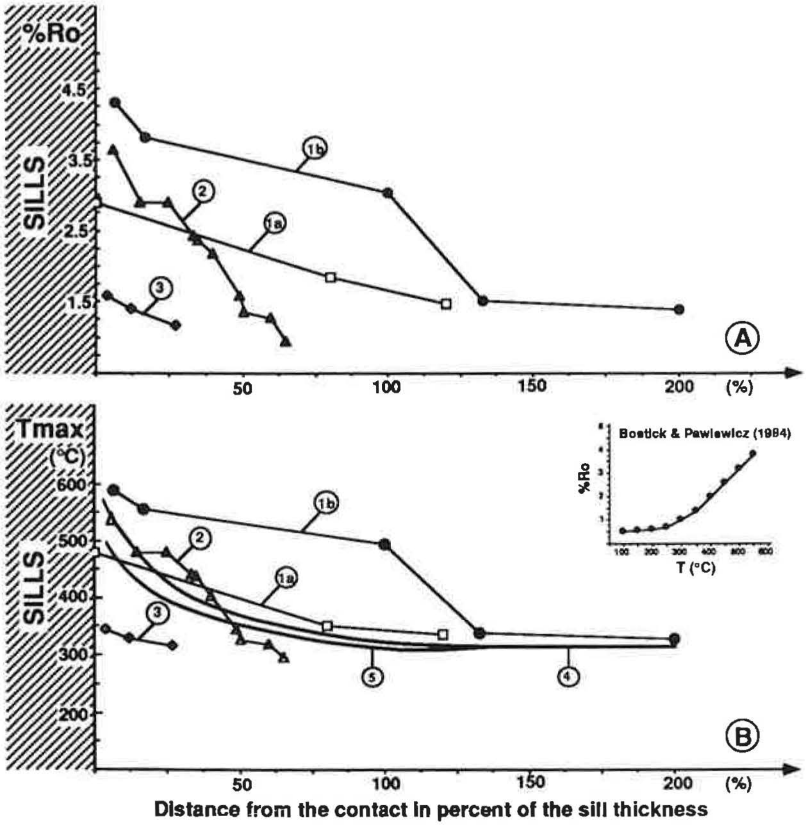

Fig. 6. (A) Vitrinite reflectance distance and (B) maximum palaeotemperature distance curves from the contacts of various sills in the Dobroudja coal basin (modified from Todorov et al., 1989). The temperatures were derived from measured vitrinite reflectance values (Nikolov, 1969) using a diagram published in Bostick and Pawlewicz (1984). *1*=well 51, *1a*=below the sill, *1b*=above the sill; *2*=well 52; *3*=well 56; *4*=modelled curve for the sill in well 51 (15 m thick and with an intrusion temperature of 1000°C); *5*=modelled curve for the sill in well 52 (2 m thick and with an intrusion temperature of 1000°C). Curves 4 and 5 are modelled according to the procedure described by Horvath et al. (1986).

geothermal gradients (PGG) range between 47°C/km and 71°C/km, and the maximum burial temperatures from 128 to 180°C. The PGG are higher in wells where sediments of Westphalian A and Westphalian B age are present than in those where sediments of Westphalian C and Westphalian D age occur (Table 1). The map in Fig. 5 shows that higher paleotemperature conditions prevailed in the southeastern part of the study area (Fig. 5, wells 110 and 219). This hypothesis coincides with other observations. According to Konstantinova and Nikolov (1974), coalification gradients and coal rank of Upper Carboniferous formations increase in the same direction, indicating a higher paleogeothermal regime in the southeast.

Our results indicate that, due to rapid deep burial and high paleotemperature gradients, the coalification of the Upper Carboniferous formations in the Dobroudja Basin was completed by the end of the Carboniferous (Fig. 4A). The rank of the coals does not increase during the Mesozoic and Cenozoic, even when modelling with paleogeothermal gradients which are much higher than those of the Upper Carboniferous. The characteristic contact metamorphism of the coal seams caused by the intrusion of the olivine basalt sills support this conclusion. Vitrinite reflectance increases rapidly to values of up to 4.33% R_o (Fig. 6A) near the sills (Nikolov, 1969). The vitrinite reflectance versus distance profiles from the sill contact zones enable the determination of maximum paleotemperatures (Bostick and Pawlewicz, 1984). The paleotemperatures inferred by this method range from 296 to 590°C (Fig. 6B). Modelling of these data using the approach of Horvath et al. (1986) confirms these estimates and indicates a short duration for these heating events (Todorov et al., 1989). The high temperatures led also to the formation of a zone of natural coke and semicoke (Nikolov, 1969). This is a typical process for bituminous coals after short-term heating. In contrast:

"brown coal undergoes extensive loss of moisture... and does not, in general, become plastic on heating"

as stated by Stach et al. (1982). In other words, during the emplacement of the sills, which are of Stephanian–Permian age, the organic matter has already achieved the bituminous rank stage.

Fluorescence

Eighteen coal seam samples with a relatively high content of liptinite macerals (up to 12%) were studied. The thermal maturity of these coals varied between 0.62% R_o and 1.23% R_o (Table 2). According to Sallabaseva and Mancheva (1982) vitrinite reflectance can be significantly suppressed in algae-rich layers. In order to avoid this problem R_o measurements were carried out on the vitrinites of vitrite layers only.

The spectral maximum (λ_{max}) of sporinites shifts with increasing rank (Fig. 7) from 640 nm (0.62% R_o) to 680 nm (1.12% R_o). Fluorescence spectra of high volatile bituminous samples show double-peak curves disappearing at higher ranks. The relationship (r=0.89) between the λ_{max} of sporinite and vitrinite reflectance (Fig. 8) shows a similar trend to the one obtained by Ottenjann (1980). The good correlation confirms the use of λ_{max} as valuable indicator of thermal maturity.

The presence of alginite in the coal seams allowed comparison of fluorescence spectra of alginites with those of sporinites. The samples were taken from thin sapropelic layers in the coal seams (cannels and boghead mainly). The R_o values for these samples ranged from 0.66% to 0.89% R_o. In some

TABLE 2

Vitrinte reflectance and spectral flouresence maixima of sporinite and alginite from coal seams in the Dobroudja coal basin

Sample	Formation	% R_o	λ_{max}	
			Sporinite	Alginite
Well 90				
6-90	M	0.74	656	
6-90	M	0.74	651	
21-90	M	0.85	657	
93-90	L	0.94	659	
168-90	L	1.06	676	
Well 95				
1-95	M	0.66	653	562
8-95	M	0.65	649	
Well 110				
17-110	L	1.12	680	
18-110	L	1.12	680	
32-110	L	1.23	n.m.	
Well 141				
1-141	N	0.72	650	580
2-141	N	0.74	647	
6-141	M	0.76	645	
10-141	M	0.78	648	
14-141	M	0.85	652	625
16-141	M	0.89	653	640
17-141	M	0.81	663	608
22-141	M	0.91	660	
Well 168				
13-168	P	0.62	640	

P = Gurkovska Formation; N = Krupenska Formation; M = Macedonska Formation; L = Mogilistenska Formation; n.m. = not measurable.

samples well preserved structures of *Botryococcus* colonial forms were observed.

As shown in Fig. 9, alginites display fluorescence spectra at shorter wave lengths (λ_{max} from 560 nm to 640 nm, Table 2) in comparison with those of sporinites from the same coal seam. Double-peak spectra are a common feature of alginites. With increasing rank, alginite spectra converge with those of sporinite. The structure of the alginite (*Botryococcus* type) becomes less distinctive and products (exsudatinites) which strongly fluoresce are formed and occupy cracks in the vitrinite mass.

Rock-Eval pyrolysis

Rock-Eval pyrolysis was performed on thirteen shale samples taken from different wells. The maximum pyrolysis temperature (T_{max}) varied from

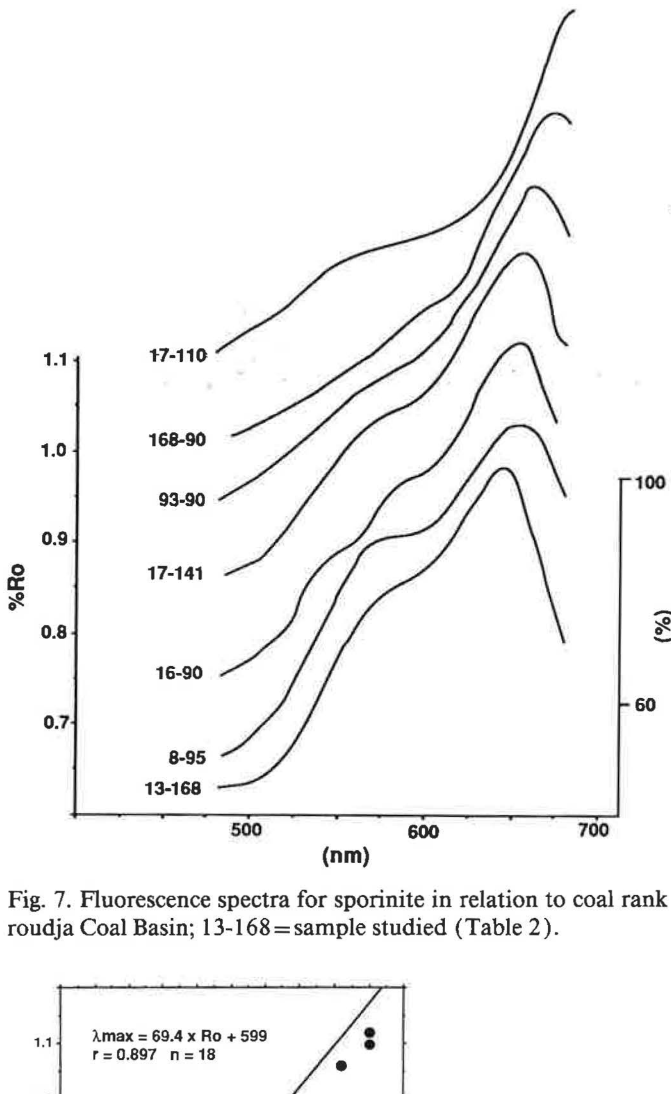

Fig. 7. Fluorescence spectra for sporinite in relation to coal rank for coal samples in the Dobroudja Coal Basin; 13-168 = sample studied (Table 2).

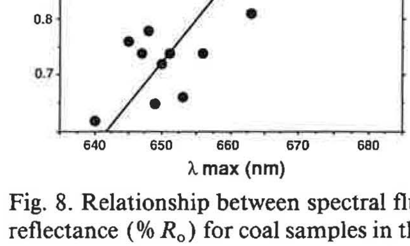

Fig. 8. Relationship between spectral fluorescence maximum (λ_{max}) of sporinite and vitrinite reflectance (% R_o) for coal samples in the Dobroudja coal basin.

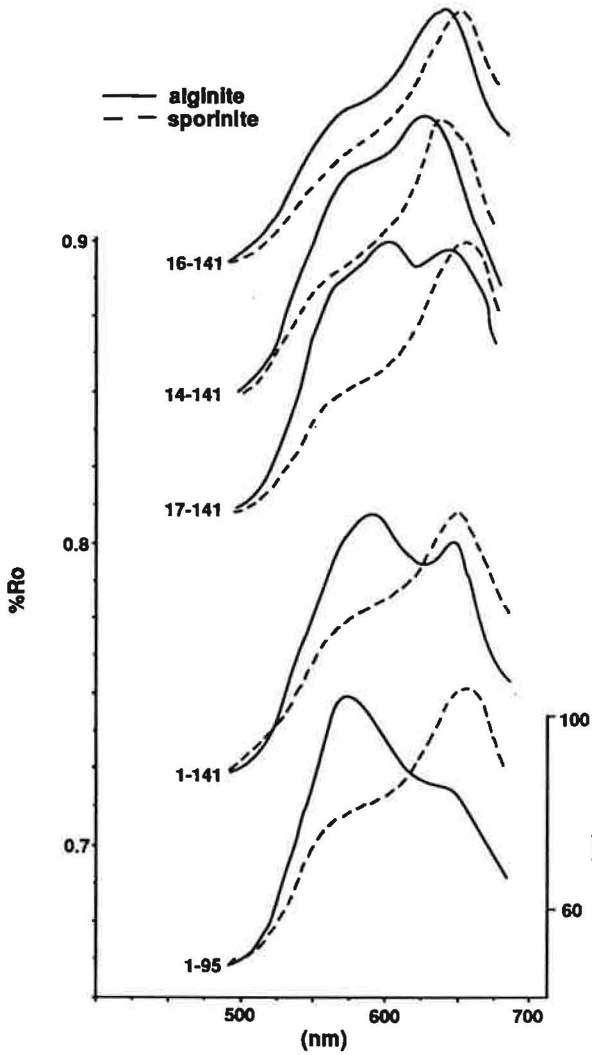

Fig. 9. Fluorescence spectra for alginite (*Botryococcus* type) and sporinite from the same coal seam in relation to coal rank in the Dobroudja coal basin; 1-95 = sample studied (Table 2).

435 °C to 501 °C (Table 3). There was a good correlation ($r=0.89$) between the reflectance values (% R_o) of paragenetic vitrinite phytoclasts and T_{max} (Fig. 10). Similar positive correlations have been established by Espitalié (1986). The HI–T_{max} diagram shows that the shales consist of type II and type III organic matter (Fig. 11), with small oil and gas generation potential. The oil and gas potentials increase with increasing organic content (Table 3).

TABLE 3

Rock-Eval pyrolysis indices of shales and vitrinite reflectance of phytoclasts

Sample	% R_o	S1 (mg HC/g rock)	S2 (mg HC/g rock)	T_{max} (°C)	TPI (S1/ S1+S2)	HI (mg HC/g TOC)	TOC (%)
Well 205							
3-205	0.65	0.02	0.39	435	0.05	63	0.60
24-205	0.84	0.05	0.81	446	0.05	94	0.85
25-205	0.88	0.03	0.68	444	0.04	79	0.85
17-205	0.89	0.01	0.45	454	0.03	120	0.38
Well 206							
45-206	0.83	0.15	4.66	437	0.04	154	3.04
29-206	0.94	0.05	0.47	444	0.10	87	0.51
Well 208							
36-208	0.88	0.33	1.54	435	0.03	189	0.81
Well 214							
8-214	1.03	0.08	0.94	446	0.08	150	0.62
Well 219							
8-219	1.08	0.05	0.62	474	0.08	80	0.80
9-219	1.13	0.05	1.49	478	0.03	133	1.12
2-219	1.15	0.03	0.17	498	0.14	61	0.28
6-219	1.18	0.01	0.21	499	0.04	81	0.27
19-219	1.34	0.01	0.18	501	0.14	55	0.32

TPI=Total production index; HI=hydrogen index; TOC=total organic carbon; T_{max}=maximum pyrolysis temperature. Two measurements were performed for every sample.

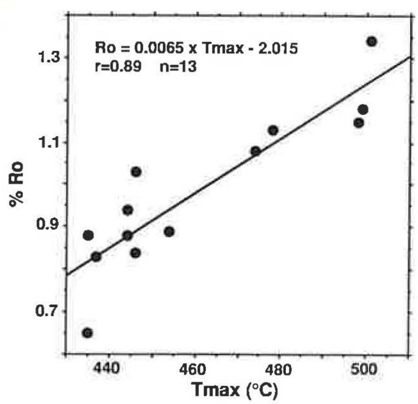

Fig. 10. Relationship between vitrinite reflectance (% R_o) and pyrolysis maximum temperature (T_{max}) for shale samples in the Dobroudja coal basin.

Illite crystallinity

The crystallinity index (CI) varies from 0.223° to 0.335° (2θ). This indicates that the samples studied are in the anchizone field. There is only a weak

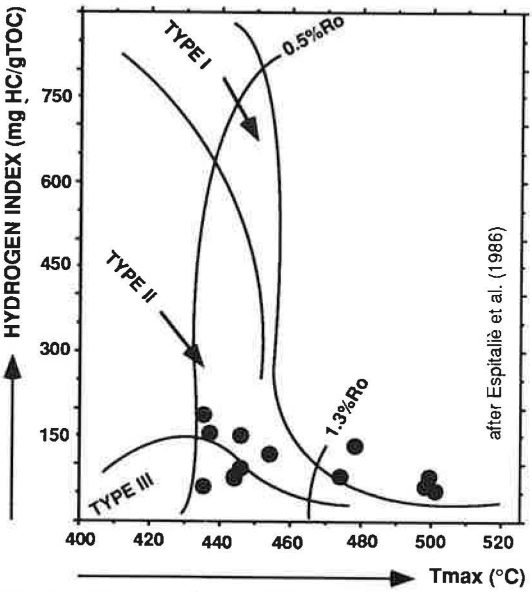

Fig. 11. Hydrogen index (HI) versus maximum pyrolysis temperature (T_{max}) diagram. Type of organic matter determined by the Rock-Eval pyrolysis of shales in the Dobroudja coal basin (after Espitalié et al., 1986).

positive relationship ($r = 0.37$) between the CI values and the vitrinite reflectance of the phytoclasts. This confirms previous considerations of several authors (Heroux et al., 1979; Kübler et al., 1979; Robert, 1988) which state that the CI of illite seem to be only indicative of diagenesis at the end of the oil generation phase.

Three samples which were taken near sill contacts (Table 4, well 219) show that there are no characteristic changes of the illite crystallinity, although paragenetic phytoclasts (1.49–2.31% R_o) indicate temperatures between 300° and 450°C (Fig. 6). Ward et al. (1989), in a similar investigation, noticed changes of the clay minerals at temperatures between 400° and 650°C. The duration of heating is another important parameter which has to be taken into account. The existence of the paleotemperature anomalies caused by the sills is probably not more than a few months (Todorov et al., 1989). Therefore, the short period of heating caused by these intrusions did not significantly affect the illite crystallinity within the host rock.

Bulk clay mineralogy

The analysis of 37 samples (Table 4) shows that the shales of the Upper Carboniferous Dobroudja basin are composed mainly of illite (22–70%), kaolinite (19–56%) and chlorite (11–86%). The occurrence of kaolinite is a

TABLE 4

Crytallinity index of illite, clay mineral content in the $<2\ \mu m$ fraction of shales and vitrinite reflectance of phytoclasts

Sample	Formation	% R_o	Cl ($\Delta 2\theta°$)	I (%)	K (%)	Ch (%)
Well 200						
2-200	P	0.78	0.305	52	28	20
Well 205						
3-205	M	0.65	0.255	35	21	44
13-205	M	0.77	0.260		n.d.	
15-205	M	0.88	0.272	26	–	74
17-205	M	0.89	0.291		n.d.	
24-205	M	0.84	0.265	52	48	–
34-205	L	0.87	0.272	26	31	43
33-205	L	0.85	0.275	54	28	18
46-205	L	0.95	0.241		n.d.	
51-205	L	0.94	0.260	32	33	35
Well 206						
47-206	M	0.68	0.300		n.d.	
44-206	M	0.64	0.272		n.d.	
31-206	M	0.88	0.312	62	38	–
29-206	M	0.94	0.260		n.d.	
17-206	L	0.86	0.326	55	45	–
12-206	L	0.89	0.252	14	–	86
Well 208						
12-208	L	0.67	0.272		n.d.	
19-208	L	0.78	0.262	54	19	27
31-208	L	0.82	0.286	32	29	39
35-208	L	0.79	0.335	40	40	20
Well 214						
1-214	L	1.04	0.235		n.d.	
3-214	L	1.10	0.223		n.d.	
5-214	L	1.08	0.241		n.d.	
7-214	L	0.99	0.288		n.d.	
8-214	L	1.03	0.275	30	22	48
Well 219						
1-219	L	1.06	0.291	60	40	–
2-219	L	1.15	0.308	70	19	11
6-219	L	1.18	0.245	55	27	18
8-219	L	1.08	0.275		n.d.	
9-219	L	1.13	0.300	44	56	–
11-219	L	1.20	0.225		n.d.	
12-219	L	1.61x	0.230		n.d.	
13-219	L	1.41	0.229		n.d.	
17-219	L	1.49x	0.225	30	26	44
18-219	L	–	0.235	22	34	44
19-219	L	1.35	0.265		n.d.	
23-219	L	2.31x	0.220		n.d.	

Cl=crystallinity index after Kübler (1968); x=influenced by contact metamorphism; I=illite; K=kaolinite; Ch=chlorite; P=Gurkovska Formation; N=Krupenska Formation; M=Macedonska Formation; L=Mogilistenska Formation; n.d.=not determined.

common feature of many Carboniferous coal basins (Weaver, 1989). The relatively high content of kaolinite in the samples studied (average of 29%) is probably due to weathering under tropical conditions and could also be related to the phases of intensive volcanic activity during the Late Carboniferous (Popova, 1988).

Detrital chlorite occurs in most shales and it is therefore difficult to determine whether diagenetic chlorite is present (Helling, 1988; Weaver, 1989).

A detrital origin for the illite is supported by the CI data (0.223°–0.335° 2θ) which indicate anchimetamorphic conditions. The CI data does not correspond to the vitrinite reflectance data. The clear discrepancy between coalification data, indicating low-temperature conditions, and CI data, indicating anchimetamorphic grade (see table 3 in Kübler et al., 1979), can be explained by a detrital origin for the illite.

The clay mineral assemblage seems to reflect the detrital input and weathering conditions of the sediments rather than post-depositional alteration processes.

There are, nevertheless, possibilities for assessing the paleogeothermal conditions. Kaolinite in shales exists in a wide temperature range (up to 375°C) but it appears that kaolinite commonly persists up to a temperature of 200°C (Weaver, 1979; 1989). This makes it possible to at least set an approximate upper temperature limit. Another indication is the absence of smectite and mixed-layer series in the shale samples studied. It may be possible that neither smectite nor mixed-layer minerals were present in the sedimentary environment, but this seems rather unlikely. Mixed-layer clay minerals are a common constituent of the clay mineral assemblages in shaly formations of European Carboniferous coal basins (Srodon, 1979; Weaver, 1989, pp. 619). Mixed-layer illite/smectite (with 30% expandable layers) have been identified in sediments of the Gurkovska Formation as well as in the tonsteins of the Mogilistenska Formation (Popova, 1988). The initiation of the illitization process begins at temperatures of about 50–60°C (Weaver, 1979; Barker et al., 1986; Pollastro and Barker, 1986). At temperatures of about 130°C the percentage of illite layers increases to 80–90% (Hower et al., 1976; Reynolds, 1985). Samples studied are mainly from the Macedonska and Mogilistenska Formations which were exposed to high maximum temperatures (128–180°C, Table 1). Therefore the transformation of smectite to illite was probably completed. We also suppose that these diagenetic illites occur only in small quantities and are masked volumetrically by the ubiquitous detrital ones, which make them unrecognizable.

DISCUSSION AND CONCLUSIONS

The results of our thermal history reconstruction indicate a regime of high paleogeothermal gradients 45–71°C prevailing in the Dobroudja Coal basin during the Late Carboniferous and probably Early Permian. A pronounced increase in the geothermal gradient in the Variscan crust from the early Paleozoic rifting stage to the final stage of the Variscan orogeny was postulated by Weber (1984). During the Late Carboniferous the paleogeothermal gradients reached 60–80°C/km even in the sub-Variscan foredeep of the Ruhr area (Buntebarth et al., 1982). Our results confirm these observations.

The widespread occurrence of andesite–basalt dykes, as well as of acid pyroclastic rocks in the Dobroudja Coal basin is an argument for a high heat flow. The dykes can be related to the final calc-alkaline bimodal volcanism of Stephanian–Permian age (Perekalina, 1981). Cutting the Namurian and Westphalian strata, they are concentrated mainly in the eastern part of the basin. Our results indicate that the paleogeothermal gradients increase in the same direction (Fig. 5).

A section of thick Carboniferous sediments (2300 m) of Upper Visean to Westphalian D age was recovered from a well in the Black Sea about 10 km offshore (Nikolov et al., 1990). These sediments have been correlated with Carboniferous formations onshore. The presence of acid volcanic and pyroclastic rocks in certain intervals, as well as the high maturity of these sediments (2–2.5% R_o, V. Gorshkov, personal communication, 1991) support the hypothesis of a southeastern increase of the paleogeothermal regime in the basin.

The information derived from the present investigations can be summarized as follows:

(1) *Vitrinite reflectance, thermal modelling and paleogeothermal gradients*: The simulation of the burial and thermal history of the Upper Carboniferous formations in the Dobroudja coal basin yielded paleogeothermal gradients between 45–71°C/km. This is in accordance with data from other Carboniferous basins in Europe as well as with the increase of the geothermal gradients in the course of the Variscan orogeny. Our results indicate that the geothermal regime increases towards the southeast. This hypothesis would explain the regional increase of coalification in the basin (Konstantinova and Nikolov, 1974) from the northwest to southeast. The high paleogeothermal gradients and the deep burial of the strata make it likely that the formations completed their entire maturation during the Late Carboniferous.

(2) *Fluorescence*: The spectral maximum (λ_{max}) of sporinites and alginites shifts with increasing rank. The alginite from the coal seams display a fluorescence spectra at shorter wavelengths in comparison with those of the sporinite in the same coal seam. With increasing maturation the alginite spectra converge with those of the sporinite, at a coalification level of 0.8–0.9% R_o. There is a good correlation (r=0.89) between λ_{max} of sporinite and vitrinite reflectance.

(3) *Rock-Eval pyrolysis*: The shales in the basin consist of type II and type III organic matter with poor source capacity. There is a significant positive

relationship between maximum pyrolysis temperature and vitrinite reflectance.

(4) *Illite crystallinity and bulk clay mineralogy*: The discrepancy between coalification data, indicating low-temperature conditions, and illite crystallinity data, indicating anchimetamorphic conditions, can be explained by a detrital origin for the illite. Smectite or mixed-layer clay minerals seem to have already disappeared.

ACKNOWLEDGMENTS

This research project was sponsored by the Bulgarian Committee of High Education (project 913) as well as by the Swiss National Science Foundation (project 2.107-0.86). We very much thank H. Nestler (Freiberg), J. Senftle (Plano), G. Siskov (Sofia), B. Ujetz (Geneva), N. Volkmann (Freiberg) and W. Wildi (Geneva) for reviewing the manuscript and for their numerous suggestions. A special thanks for the critical comments of P. Robert (St. Gaudens) and of an anonymous reviewer.

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