Early coalification features as approached by solid state ^{13}C CP/MAS NMR spectroscopy

S. Kalaitzidis [a], A. Georgakopoulos [b], K. Christanis [a,*], A. Iordanidis [c]

[a] *Department of Geology, University of Patras, GR-26500 Rio-Patras, Greece*
[b] *Department of Mineralogy-Petrology-Economic Geology, School of Geology, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece*
[c] *Department of Geotechnology and Environmental Engineering, Technological Educational Institute of West Macedonia, Kila, GR-50100 Kozani, Greece*

Abstract

Solid state ^{13}C CP/MAS NMR spectroscopy and ultimate analysis have been applied to a study of samples from the Pleistocene Drama lignite and its successive modern analogue, the Philippi peat, in northeastern Greece. The succession from peat to lignite resulted in a C enrichment averaging 10.7% and depletion in H and O averaging 6.5 and 18.5%, respectively. Early coalification resulted in the degradation of methoxyl groups, carbohydrates and carboxylic groups, whereas the aliphatic carbons were less affected. However, organic geochemical alteration seems to depend strongly on the initial peatification conditions. The "aromaticity" decreases from the stage of peat to lignite, as a result of the significant degradation of lignin precursors.
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1. Introduction

One major question in coal geology refers to the geochemical features and transformation of organic molecules that take place during biochemical and early geochemical coalification. To understand coalification pathways, it is necessary to compare the features of coal and peat. However, this task is susceptible to limitations regarding mainly the geological conditions that control the depositional history of organic-matter-rich sediments. Solid state ^{13}C cross-polarization/magic angle spinning-nuclear magnetic resonance (^{13}C CP/MAS NMR) is an effective, non-destructive analytical technique for characterizing organic chemical structures in fossil fuels (Wilson, 1987; Snape et al., 1989). Suggate and Dickinson (2004) compared the ^{13}C NMR data from various coals of different rank and concluded that misleading results concerning coalification pathways can arise from comparing data from different coal types. Therefore, it is important to minimize the effect of any external factor that appears at the initial peatifica-

tion stage and could influence a comparative study of coals of different rank. The most important external factors are geologic setting, variations in the types of peat-forming plants, palaeoclimate, and the hydrogeological regime in the palaeomire (Göttlich, 1990). In order to diminish the effect of geological conditions, several important studies of laboratory simulations of humification/coalification pathways have been carried out using ^{13}C NMR in artificially "coalified" peat, wood, and humic substances (e.g., Behar and Hatcher, 1995; Orem et al., 1996; Freitas et al., 1999, 2002; Lu et al., 2001; Kelemen et al., 2002; Almendros et al., 2003). However, particularly at the stage of early coalification, nature behaves in a complex way, that cannot be completely described by artificial coalification pathways.

In the present paper, we discuss results from the ^{13}C CP/MAS NMR study of samples from the Philippi peat and the Drama lignite, focussing on the alteration of organic geochemical features in the peat to lignite stage. The study encompasses a first approach to a large-scale sampling scheme.

The Philippi peat is a modern analogue, representing the precursor stage, of the Drama lignite (Fig. 1). Peat

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* Corresponding author. Fax: +30 2610 997560.
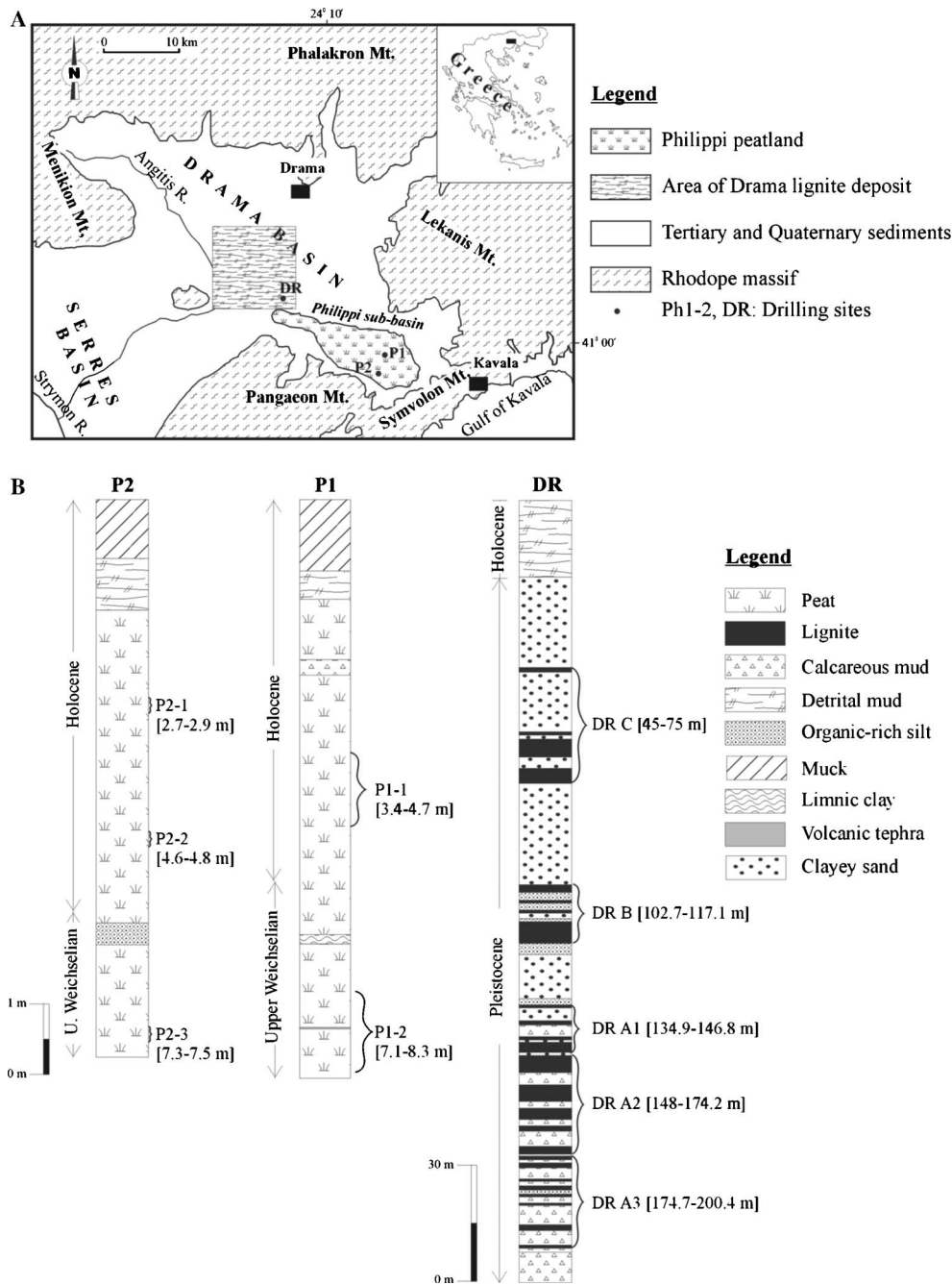*E-mail address:* christan@upatras.gr (K. Christanis).

Fig. 1. (A) Simplified geological map of Drama Basin showing the coring sites; (B) Philippi (P1, P2) and Drama (DR) lithological columns, as well as sampling schedule (the depth intervals in parentheses).

formation took place continuously from early Pleistocene until the drainage of the area in the 1940s (Melidonis, 1981; Wijmstra and Groenhart, 1983; Broussoulis and Yiakkoupis, 1994). However, the actual stratigraphical correlation between the two deposits is still under question. Net calorific values for both the peat sequence and the lignite seams range from 20 to 24 MJ/kg and random reflectance of the lignite measured on eu-ulminite A ranges between 0.12 and 0.20 (Melidonis, 1981; Georgakopoulos, 2000). The data obtained from the study of the Philippi peat and the Drama lignite have the advantage of being

comparable, since the peat-forming factors such as the type of helophytes and the hydrologic regime, were almost identical. Therefore, differences in the organic geochemical features can be assigned to coalification pathways. Of course, the conditions prevailing in the basin were certainly not stable through time. However, because each lignite sample represents a wide time span of deposition, the effect of short-term changes is compensated. Moreover, the peat samples correspond to two different periods of accumulation, namely Upper Weichselian and Holocene, which resulted in markedly different peat formations and hence

different peat features (Christanis, 1983; Kalaitzidis and Christanis, 2000, 2003).

The type of helophytes and the hydrologic regime were almost identical in the Philippi and the Drama palaeopeat-lands. Available coal-petrographic data show that in both cases macerals of the huminite group prevail with values up to 90 vol %. (on a total organic basis), whereas in most cases the macerals of the inertinite and liptinite groups reveal percentages lower than 15 vol % (Kaouras et al., 1991; Kalaitzidis and Christanis, 2000). There is a significant difference among the peat and the lignite samples in the contribution of telohuminite. The amount of telohuminite in the Philippi peat reaches in some cases up to 70 vol %, whereas telohuminite in the Drama lignite does not exceed 25 vol %. Nevertheless, attrinite is the prevailing maceral, indicating the herbaceous origin and the severe destruction of the organic tissues.

Additionally, the inorganic matter of the Philippi peat and the Drama lignite consists of similar minerals; the major mineral phases include calcite, quartz, K-feldspars, plagioclases, and clay minerals (Filippidis et al., 1996; Kalaitzidis and Christanis, 2000).

2. Materials and methods

Five peat samples were obtained from two shallow cores representing the Upper Weichselian and Holocene period of peat formation (Fig. 1; Table 1). The ash values ranged from 13.6 to 36.6 wt % on a dry basis, indicating high inorganic influx from the margins towards the mire during peat accumulation. The humification degree, according to the von-Post field method (Göttlich, 1990), ranges between 5 and 7. The peat-forming helophytes were mainly Cyperaceae such as *Cladium mariscus* and *Carex* spp., the overall features of the samples verify the rheotrophic character of the peatland (Christanis, 1983; Kalaitzidis and Christanis, 2002, 2003).

Five lignite samples representing three different lignite seams (Filippidis et al., 1996) were obtained from a borehole at the southern edge of the Drama lignite deposit (Fig. 1). The ash values determined at 750 °C range from 26.8 to 42.9 wt % on a dry basis (Table 1), also revealing a severe inorganic influence. The peat-forming plant species were similar to those forming the Philippi peat: Cyperaceae (*Cladium mariscus*, *Carex* spp.), Nymphaeaceae and *Typha* spp. (Antoniadis and Rieber, 1992).

Ultimate analysis (C, H, N and S) was performed at the Instrumental Analysis Laboratory of the University of Patras, using a Carlo Erba EA1108 C–H–N–S analyzer. Thermogravimetric analysis was applied to the peat samples, in order to determine the inorganic carbon content (C_{in}) of the carbonates. Briefly, the method encompasses the sequential oxidation of samples in the temperature ranges of 105–550 °C and 550–900 °C. The weight loss during the second ramp represents the CO_2 volatilization due to breakdown of carbonates. From this, C_{in} is calculated. The analyses were conducted using a Leica TGA 601 Thermogravimetric Analyser, at the Integrated Laboratories of the Netherlands Institute of Applied Geosciences (TNO-NITG) and the Department of Earth Sciences, University of Utrecht, The Netherlands.

NMR analyses were performed at the Large-Scale Facility Wageningen NMR Centre, 6700 ET Wageningen, The Netherlands. The samples were ground to pass through the 60-mesh sieve and were packed into a 7-mm diameter cylindrical zirconia rotor with Kel-F end-caps. A Bruker AMX300 spectrometer operating at 75.48 MHz on the ^{13}C and ^{1}H resonance frequency of 300.136 MHz was used for CP/MAS ^{13}C NMR experiments. Cross-polarisation with magic angle spinning (CP/MAS) was applied at 5 kHz. A contact time of 1 ms was used, while a pulse delay of 1 s was chosen. Chemical shifts, given in parts per million (ppm) are referred to the resonance signal of tetramethylsilane (TMS). More than 6000 scans were needed

Table 1
Results of proximate and ultimate analyses (C_{in}: inorganic carbon, db: dry basis, daf: dry, ash-free basis)

Sample	(% db)						(% daf)					Atomic ratios		
	Ash	C_{in}	C	H	N	S	C^a	H	N	O^b	S	H/C	O/C	C/N
P1-1	13.6	1.3	42.8	4.5	2.0	0.9	48.0	4.7	2.4	43.9	1.0	1.18	0.68	23.9
P1-2	33.9	0.7	36.5	4.2	1.7	1.7	54.2	4.4	2.6	36.2	2.6	0.97	0.50	24.1
P2-1	36.6	4.3	36.4	3.5	1.4	<0.1	50.5	3.6	2.2	43.7	—	0.85	0.65	27.4
P2-2	17.0	1.7	43.7	4.8	1.7	2.0	50.6	5.1	2.9	40.9	0.5	1.20	0.61	20.2
P2-3	27.3	0.3	38.7	4.3	1.7	2.0	52.8	4.5	2.4	37.6	2.7	1.02	0.53	25.7
Peat average							51.2	4.4	2.5	40.5	1.4	1.04	0.59	24.3
DRC	36.6	<0.1	34.3	3.8	1.4	1.6	54.1	4.0	2.2	37.2	2.5	0.89	0.52	28.9
DRB	26.8	<0.1	41.1	4.5	1.8	2.6	56.2	4.7	2.5	33.0	3.6	1.01	0.44	26.6
DRA1	37.9	<0.1	36.1	3.9	1.6	2.7	58.1	4.1	2.5	31.0	4.3	0.84	0.40	26.8
DRA2	39.4	<0.1	35.5	3.7	1.5	2.7	58.5	3.8	2.5	30.7	4.4	0.78	0.39	27.2
DRA3	42.9	<0.1	32.3	3.3	1.3	2.5	56.5	3.4	2.4	33.4	4.3	0.72	0.44	28.0
Lignite average							56.7	4.2	2.4	33.0	3.7	0.88	0.44	27.4

[a] Corrected for C_{in}.
[b] Calculated by difference.

to obtain acceptable S/N (signal/noise) ratio for our samples. The spectrometer was calibrated with glycine (H_2NCH_2COOH, MERCK standard). A line broadening (LB) of 100 Hz was applied before Fourier transformation.

Although by applying the CP/MAS method a relatively rapid acquisition of spectra with high signal-to-noise ratio is achieved, the quantification of carbon moieties is not always feasible due to effects from paramagnetic species and from free organic radicals, which cause the occurrence of spinning side bands (ssb) (Snape et al., 1989; Kawashima and Yamada, 1999). It has been observed that the ssb intensity increases as the content of para- and/or ferromagnetic impurities, free organic radicals and aromatic moieties increases (van Krevelen, 1993; Smernik and Oades, 1999). The intensity of the ssb is also proportional to the applied magnetic field and hence, in "high-field measurements" (e.g., 75.48 MHz for ^{13}C) the impact of ssb on the quantification of C-groups can be significant (e.g., Sfihi and Legrand, 1990). By applying high spinning rates (>10 kHz) the effect of ssb could be decreased (e.g., Gardinier et al., 2000); however, this has the disadvantage of also reducing the resolution of the spectra. It has also been reported (Franz et al., 1992; Pan and Maciel, 1993) that the CP method can underestimate the proportion of carbon functional groups by up to 50% and the aromaticity by up to 10%.

The measuring parameters in this study (high magnetic field at 75.84 MHz for ^{13}C and a low spinning rate at 5 kHz) proved efficient to provide a high resolution spectra, which was the main intention at this stage, but resulted also in the occurrence of ssb. Nevertheless, the ssb have a minor effect on the signal-to-noise ratio (see also section 3.2.) and thus do not affect the qualitative evaluation. On the other hand, the quantitative evaluation is probably affected, besides the fact that contact times of 1 ms were applied, which in most of the cases provide optimum quantification (Hatcher, 1988). Thus, in this study the integrated resonance intervals of each compound, corresponding to concentration percentage (relative quantition; see Smernik and Oades, 2000) should be regarded as a semi-quantitative approach.

3. Results and discussion

3.1. Elemental data as rank parameters

It is well known that during biochemical and further during geochemical coalification the C content increases, whereas the H and O contents decrease; hence, C–H–O composition is used as a rank parameter (van Krevelen, 1993). The average C (51.2 wt %), H (4.4 wt %) and O (40.5 wt %) contents (on a dry, ash-free basis, Table 1) of the Philippi samples are typical for peat. The relevant average values of the lignite samples (C = 56.7 wt %, H = 4.2 wt % and O = 33 wt %, Table 1) represent almost the initial coalification stage of lignite (Stach et al., 1982), as revealed also from the H/C vs. O/C van Krevelen dia-
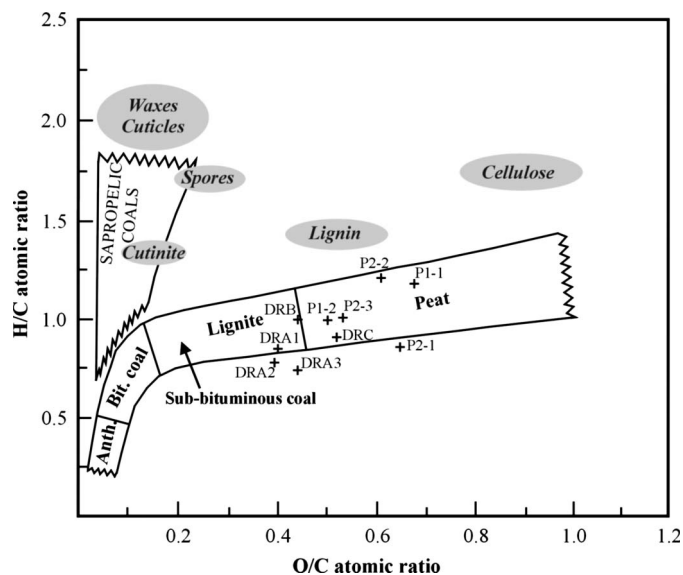

Fig. 2. Plot of Philippi peat and Drama lignite H/C versus O/C atomic ratio diagram (after van Krevelen, 1993); data for pure organic moieties from Tissot and Welte (1984).

gram (Fig. 2). The sulphur content of the lignite samples ($S_{av} = 3.7$ wt %) is significantly higher than for the peat samples ($S_{av} = 1.4$ wt.%); sulphur content reflects the availability of S, i.e., external sources and input of S, as well as the redox potential in the palaeomire. In both deposits, the inorganic influx originated from the same bedrock formations, hence it is inferred that during the formation of the Drama lignite the conditions in the palaeomire were more reducing than those in the Philippi mire. Nitrogen contents are almost similar for both sample groups, indicating no significant loss during the initial stage for the Drama lignite. The C/N atomic ratio is considered as an indicator of the source of humic substances in natural systems; non-vascular aquatic plants have a C/N in the order of 2–10, whereas vascular plants (helophytes) have a C/N >20 (Lu et al., 2000). Moreover, C/N ratio is reversely correlated to the degree of microbiological attack on the organic tissue during humification (Lu et al., 2000); hence it can be inferred that sample P2-2 that reveals the lowest C/N value was influenced by rather more intense humification. Additionally, the fact that the C/N atomic ratio of lignite ($C/N_{av} = 27.4$) is slightly higher than that of peat ($C/N_{av} = 24.3$), clearly demonstrates the release of NO_x during the humification process and subsequently the C-enrichment. The loss of nitrogen during the maturation of sediments deposited in aquatic environments has been well documented in marine and terrestrial environments (e.g., Krooss et al., 1995; Knicker, 2004).

The succession of peat to lignite corresponds to a C-enrichment averaging 10.7% and depletion in H and O averaging 6.5% and 18.5%, respectively (Fig. 3). An interesting aspect rising from the elementary data concerns the mass loss as a function of volatilization of
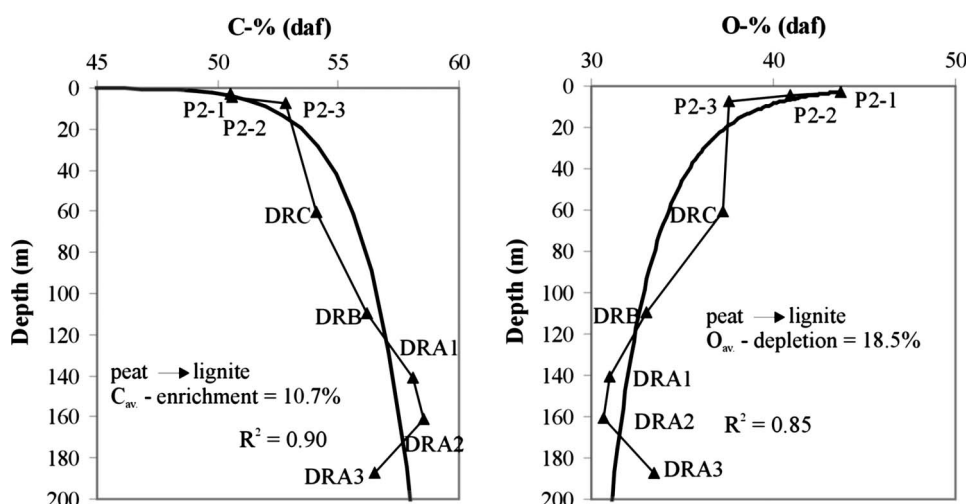
Fig. 3. Distribution of carbon and oxygen contents in Philippi peat and Drama lignite versus depth (the solid line represents numerical-fit; average C- and O-variations are calculated as lignite C- and O-differences from average peat values).

certain gaseous phases (e.g., CO_2, CH_4 and NO_x) during early coalification. The mass balance of C, H, N and O, calculated from the differences in average enrichment and depletion percentages between peat and lignite, reveals a deficiency of approximately 17%. This implies that the organic matter lost around 1/5 of its mass during the transformation of peat to lignite. The value of 17% is close to the lower limit of values (20–50%) reported for mass-balances during early diagenesis of organic matter in marine systems (Littke et al., 1997), indicating stronger degradation under marine in comparison to telmatic conditions.

3.2. ^{13}C CP/MAS NMR

NMR spectra interpretation (Tables 2 and 3), as well as the interval of selected integrated areas, was based on previous data from peat, humic acids, lignite and higher rank coal samples (e.g., Wilson et al., 1984; Hammond et al., 1985; Hatcher, 1988; Solumn et al., 1989; Behar and Hatcher, 1995; Kidena et al., 1996; Miknis et al., 1996; Orem et al., 1996, 1999; Rumpel et al., 1998, 2000a,b; Freitas et al., 1999; Chefetz et al., 2000; Lorenz et al., 2000; Lu et al., 2000, 2001; Maryganova, 2000; Kelemen et al., 2002; Rumpel and Kögel-Knabner, 2002; Almendros

Table 2
Chemical shifts and assignment of resonances in ^{13}C CP/MAS NMR spectra of peats[a]

Chemical shift (ppm)	200	175	150	145	128	116	104	82	73	64	55	30	22	15
Molecular														
Ketone plus aldehyde	X													
Carboxylic acids		X												
Mono-phenols and derivatives			X											
Di-phenols and derivatives				X										
Non-protonated aryl					X									
Protonated aryl						X								
Anomeric carbons							X							
Aliphatic C–O (carbohydrates)								X	X	X				
Methoxyl C plus *N*-alkyl											X			
Aliphatic carbon														
Methylene												X		
Acetate methyl													X	
Methyl or alkyl chain														X
Macroscopic														
Waxes		X										X		X
Resins	X											X		X
Cellulose							X	X	X	X				
Hemicellulose		X					X		X	X			X	
Lignin			X	X	X	X				X				
Tannin			X	X			X			X				
Humic acids	X	X	X	X	X	X			X		X	X		X

[a] Hammond et al. (1985); Wilson (1987); Freitas et al. (1999); Lorenz et al. (2000).

Table 3
Functional groups and chemical shifts of main resonances in ^{13}C CP/MAS NMR spectra of Philippi peat and Drama lignite

Functional group	Chemical shift (ppm from TMS)						
	Holocene Peat P1-1, P2-1, P2-2	Upper-Weichselian Peat P1-2, P2-3	Drama lignite				
			DRC	DRB	DRA1	DRA2	DRA3
Aliphatic carbons							
Methyl (–CH$_3$)	∼14[a], 25		∼14	∼14	∼14		
Methylene (–CH$_2$)	32	32	32	32	32	32	32
Complex aliphatic carbons	∼43						
Methoxyl (–OCH$_3$) plus N-alkyl (NR$_3$)	56	56	56	56	56	56	56
Ether (ROR), Carbohydrates (C$_{al}$–O)	62, 73	62, 73	∼62, 73	∼62, 73	∼62, 73	73	∼62, 73
Anomeric carbons (C$_{an}$)	105	105	∼105	∼105	∼105		
Aromatic carbons (C$_{ar}$–H, C$_{ar}$–C)	116, 129	116, 129	129	∼116, 129	117, 130	128	129
Phenolic carbons (C$_{ar}$–OH)	148, 152	147, 153	147	∼147	147	147	147, 152
Carboxyl (–COOH, –COOR)	174	174	175	174	175	177	176
Ketonic ($>$C=O) and aldehydic (HC=O) carbonyls	196–200	196–200	196	197	198	196	194

[a] ∼: minor resonance peaks.

et al., 2003; Georgakopoulos, 2003; González et al., 2003), as well as from sapropelic sediments (Brown et al., 2000; Dick et al., 2002). Quantitation of NMR spectra was applied, using Lorentzian-curve model, in order to elucidate the relative concentration of each functional group in the samples and to obtain more numerical and comparable approaches for the transformations of organic compounds. Apart from problems arising from the reliability of ^{13}C CP/ MAS NMR spectra due to the presence of paramagnetic ions (ssb caused from clay minerals), restrictions in the applicability of quantitation can arise from overlapping resonance peaks from different organic compounds; thus, the values obtained are only indicative. The values for integrated peak areas were transformed to concentration per-

centages (Table 4), representing semi-quantitative results; moreover, it should be mentioned that the ssb were not taken into account to the quantitation. Due to the fact that the inorganic matter is almost similar for the lignite and the peat samples (Filippidis et al., 1996; Kalaitzidis and Christanis, 2002), with calcite being the prevalent mineral, the effect of ssb caused from Fe-impurities (e.g., clay minerals) is regarded as proportional, without affecting seriously the quantitation.

Peat and lignite ^{13}C NMR spectra, having an acceptable signal/noise ratio, are shown in Figs. 4A and B. The resonance curves have been resolved for different integrated areas for peat and lignite samples due to slight shifting of peak boundaries (Tables 3 and 4). The aliphatic carbons

Table 4
Solid-state ^{13}C CPMAS NMR relative quantitation[a]

Sample	% integrated areas							
(ppm):	0–48	48–62	62–95	95–110	110–144	144–165	165–190	190–220
	al	OCH$_3$	C$_{al}$–O	C$_{an}$	C$_{ar}$	C$_{ar}$–OH	COOH	$>$C=O
P1-1	20.9 ± 0.7	9.4 ± 0.6	21.4 ± 1.0	6.4 ± 0.6	19.4 ± 1.0	7.6 ± 0.6	8.9 ± 0.7	6.0 ± 0.5
P1-2	21.9 ± 0.8	11.2 ± 0.7	20.8 ± 1.0	6.7 ± 0.6	19.0 ± 1.0	8.0 ± 0.6	7.9 ± 0.8	4.5 ± 0.4
P2-1	20.1 ± 0.7	9.4 ± 0.6	22.8 ± 1.0	6.9 ± 0.7	18.5 ± 0.8	8.2 ± 0.6	8.8 ± 0.8	5.3 ± 0.5
P2-2	22.6 ± 0.8	9.7 ± 0.6	22.9 ± 1.1	6.1 ± 0.6	17.6 ± 0.8	7.4 ± 0.6	8.9 ± 0.8	4.9 ± 0.4
P2-3	21.6 ± 0.8	10.9 ± 0.6	21.1 ± 1.0	6.5 ± 0.6	19.4 ± 1.0	8.2 ± 0.6	7.4 ± 0.7	4.9 ± 0.4
Peat$_{average}$ (Cn$_{av}$)	21	10	22	6.5	19	8	8.4	5.1

	% integrated areas							
(ppm):	0–50	50–60	60–95	95–110	110–144	144–165	165–190	190–220
DRC	31.8 ± 1.0	5.9 ± 0.4	17.0 ± 0.6	5.1 ± 0.4	19.3 ± 0.7	7.8 ± 0.4	7.2 ± 0.5	6.5 ± 0.5
DRB	29.6 ± 0.8	6.9 ± 0.5	17.7 ± 0.6	5.7 ± 0.4	18.4 ± 0.6	9.0 ± 0.5	7.2 ± 0.5	5.6 ± 0.4
DRA1	32.1 ± 1.0	7.4 ± 0.6	16.4 ± 0.6	5.1 ± 0.4	19.2 ± 0.7	7.4 ± 0.4	6.5 ± 0.5	6.0 ± 0.5
DRA2	33.7 ± 1.0	6.8 ± 0.5	18.1 ± 0.8	4.9 ± 0.4	18.5 ± 0.6	6.9 ± 0.5	6.6 ± 0.5	4.7 ± 0.4
DRA3	31.3 ± 1.0	6.6 ± 0.5	19.1 ± 0.8	4.5 ± 0.4	19.0 ± 0.7	7.8 ± 0.5	7.4 ± 0.5	4.4 ± 0.4
Lignite$_{average}$ (Cn$_{av}$)	32	6.7	17	5.1	19	7.8	7.0	5.4
D_{p-L}[b]	+48	−34	−19	−22	+0.5	−1.4	−17	+6.5

[a] al, aliphatic C; OCH$_3$, methoxyl; C$_{al}$–O, polysaccharide; C$_{an}$, anomeric C; C$_{ar}$, aromatic C; C$_{ar}$–OH, phenolic C; COOH, carboxyl; $>$C=O, ketonic C.
[b] D_{P-L} represents average % difference in the relative amount of each functional group in lignite in relation to peat.

likely represent refractory cuticular waxes from vascular plants, microbial lipids, long chain hydrocarbons and fatty acids, and other compounds. The N-alkyl signal represents proteins. The polysaccharide units (i.e., carbohydrates) represent cellulose compounds, whereas aromatic along with methoxyl carbons represent lignin compounds (Table 2). In terms of maceral affinity, it can be roughly stated that the aliphatic carbons correspond to liptinite; polysaccharides and part of the aromatic carbons represent huminite, and part of the aromatic carbons are assigned to inertinite (Maroto-Valer et al., 1998).

3.2.1. Peat ^{13}C CP/MAS NMR

The samples reveal almost identical ^{13}C CP/MAS NMR spectra (Fig. 4A) with only minor differences between the Holocene and the Upper Weichselian peat (Table 3). The observed organic substances in the peat spectrum include: aliphatic moieties from cuticular waxes, resins and other lipid sources as mentioned above, methoxyl groups, carbohydrates, aromatic structures, carboxylic carbons, ketonic and aldehydic carbonyls. The aromatic region can be divided into three intervals: (1) the 144–165 ppm interval [O-substituted aromatic (phenolic) moieties indicating lignin], with the split peak at 148 and 152 ppm being characteristic for guaiacyl lignin (Stevenson, 1994); (2) the 120–144 ppm range attributed to non-protonated aromatic carbons, to which only one-carbon atom is ascribed; and (3) the 110–120 ppm region attributed to protonated aromatic carbons.

Quantitation reveals that in the peat samples, the prevalent organic moieties are carbohydrates, aromatic and aliphatic carbons (Table 4). These moieties indicate the predominance of remnants of cellulose and hemicellulose, lignin and more or less of tannins, which have not been yet biodegraded, i.e., lost during peatification. The features of the organic composition are comparable to those of previous studies on peat (e.g., Hammond et al., 1985; Freitas et al., 1999; Maryganova, 2000; Kelemen et al., 2002; Almendros et al., 2003), although differences in peak intensities among the samples are explained by differences in peat-forming plants or degree of humification. The relative amounts show that the cellulose content exceeds that of lignin, as well as that the combined occurrence of cellulose plus lignin predominates over organic lipids, waxes and resins. These aspects are indicative of the fact that the peat-forming elements were mostly herbaceous vascular plants and that the input of lipid-rich algal material was restricted, providing an indication of a low groundwater table in the palaeomire. However, H-rich plant litter (i.e., liptinite) such as leaves and barks that include significant amounts of cutin, roots-containing suberin, and spores, contributed to peat formation and hence, supplied the aliphatic carbon amounts.

Comparing the relative values obtained from Holocene versus Upper Weichselian samples (Table 4), it is apparent that the latter samples are richer in methoxyl groups than the Holocene samples, whereas a vice versa trend is apparent for aldehyde and ketone carbons. This variation in
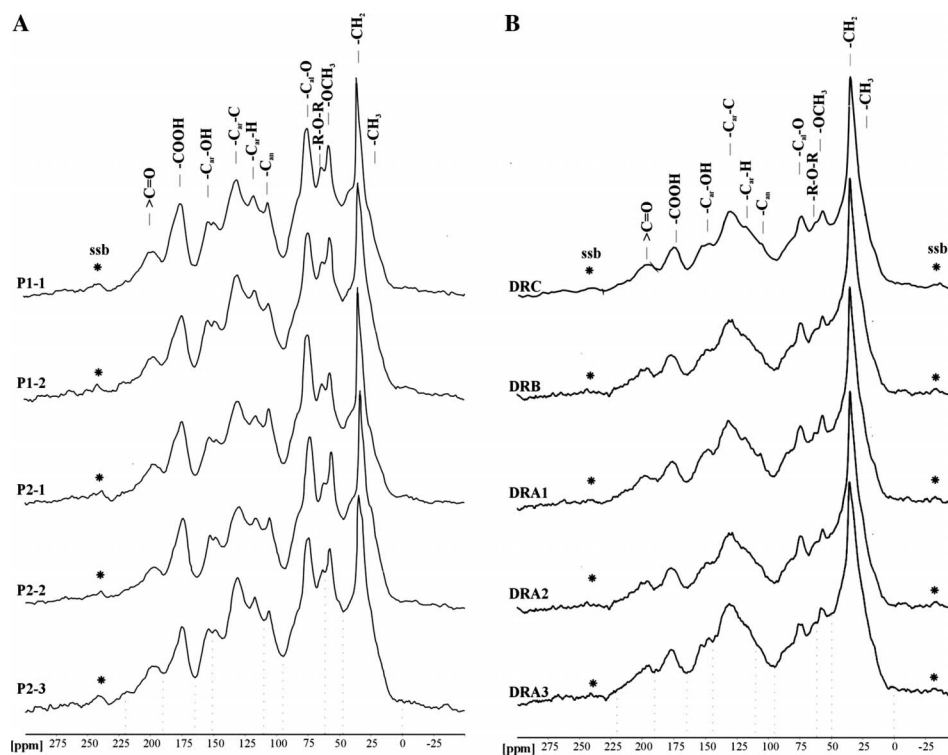

Fig. 4. (A) ^{13}C CPMAS NMR spectra for Philippi peat samples and (B) Drama lignite samples (for functional group abbreviations see Table 3; ssb, spinning side bands).

methoxyl is peculiar, since it would be more reasonable if it followed the opposite trend, by decreasing during peatification, as the peat is subsiding through time. However, in conjunction with the fact that the humification degree (after von Post) is higher for the Holocene (7–9) and lower for the Upper Weichselian peat (6–7), it is suggested that the initial humification stages (i.e., aerobic microbiological activities) in the acrotelma played the most significant role in the variation in methoxyl content. During the Holocene, the wet and warm climatic conditions resulted in enhanced humification, contributing to the breakdown of methoxyl structures and the release of volatile compounds (CH_4, CO_2). Additionally, the relatively enriched mode of aldehydes and ketones in the Holocene samples corresponds to rather intense humification and the resulting enhanced formation of humic acids. However, the NMR spectra reveal a noisy curve in the region of the ketonic carbons, caused from ssb of the aromatics, and thus the numerical values are questionable.

3.2.2. Lignite ^{13}C CP/MAS NMR

The spectra for the Drama lignite are almost similar to each other (Fig. 4B) and to the spectra obtained from previous studies of similar rank coals (Orem et al., 1999; Iordanidis, 2002; Georgakopoulos, 2003). The main features (Table 3) include a sharp peak at 32 ppm (methylene), and more or less small and broad peaks at 56 ppm (methoxyl), 62, 73 and 105 ppm (carbohydrates), 128–130 ppm (aromatic C), 147 ppm (phenolic C), 174–176 ppm (carboxyl/amide C) 194–198 ppm (ketone and aldehyde C). The resonances reflect the occurrence of aliphatic compounds, as well as of cellulose, hemicellulose and lignin remnants that reveal the relatively low degree of coalification of the Drama lignite. Moreover the DRA3 spectrum reveals two peaks at 142 and 152 ppm, which probably reflect the occurrence of condensed tannins (Lorenz et al., 2000).

Quantitation of the lignite NMR spectra (Table 4) shows that the prevalent organic moieties are aliphatic carbons, followed by carbohydrates and aromatic carbons. Moderate values are counted for phenolic carbons, carboxyl/amide carbons and methoxyl groups, and lower values for aldehyde/ketone and anomeric carbons. The high concentration of aliphatic C implies that organic lipids, waxes and resins built a significant portion of the Drama lignite. However, maceral analyses conducted by Goodarzi et al. (1990) and Kaouras et al. (1991) revealed that the liptinite content is less than 15 vol %, indicating a low to moderate concentration, whereas huminite is the predominant maceral group. Therefore, it seems that the decrease in the carbohydrates and aromatic C peak-intensities due to the coalification impact caused the relative increase of aliphatic C values. In terms of a herbaceous or woody origin of the Drama lignite, the quantitation data are not sufficient to provide a clear answer, despite the fact that the lignin content is higher than cellulose, as elucidated from the aromatic plus phenolic C amounts in relation to carbohy-

drates and anomeric C. This is due to the fact that cellulose is more susceptible to degradation than lignin and even at the initial peatification stage, the structures that contain significant portions of cellulose are preferentially decomposed, leading to a relative increase in lignin content (Diessel, 1992). Nevertheless, as the herbaceous origin of the Drama lignite is known (Antoniadis and Rieber, 1992), the semi-quantitative data presented in Table 4 represent a first approach to evaluating the NMR results for known environments.

3.3. ^{13}C CP/MAS NMR and early coalification features

3.3.1. Organic geochemical alterations during early coalification

Generally, the activity of microorganisms (both aerobic and anaerobic) is the most important factor that affects the early coalification features (biochemical stage), resulting initially in the loss of methoxyl and the degradation of cellulose, and later on the loss of phenolic functional groups from lignin. At latter stages (geochemical stage of coalification), where pressure and thermal effects are significant, condensation of the aromatic structures has taken place resulting to the formation of more polycyclic structures (Hatcher, 1988; Diessel, 1992; Behar and Hatcher, 1995; Orem et al., 1999). Therefore, the organic geochemical transformations during peatification (peat) and early coalification (lignite) stages are different from those that occur in the later stages (sub-bituminous coal and higher rank coals) of geochemical coalification (Tissot and Welte, 1984; Diessel, 1992).

As a result of the young age of the samples and the shallow burial depth, the alterations of organic moieties from plant litter over peat to lignite are only affected by low to moderate lithostatic pressure (including the time effect) without any significant thermal effect. It is therefore evident that mainly biogeochemical activities, and specifically the activity of microbes, are responsible for the alterations of the organic matter. The most predominant alteration is the decrease in peak intensity for all the functional groups in the lignite samples except for that of aliphatic carbons (Figs. 4A and B). In particular, the resonance peaks for protonated aryl carbons [~116 ppm] and anomeric carbons [~105 ppm] almost disappear. On average the Drama lignite is about 48% relatively enriched in aliphatic carbons in relation to Philippi peat (Table 4, Fig. 5A). In addition, the lignite contains 34% less methoxyl carbon, 19% less polysaccharide-units, 22% less anomeric carbon, and 17% less carboxyl units than the peat (Table 4, Figs. 5B–E), implying the breakdown of these functional groups during early coalification. The calculated average decrease for polysaccharides and anomeric carbons indicates significant degradation of cellulose (almost 1/5 of the cellulose content of peat), during early coalification, which is mainly the result of processes by extracellular enzymes secreted by microorganisms (Hatcher and Clifford, 1997).
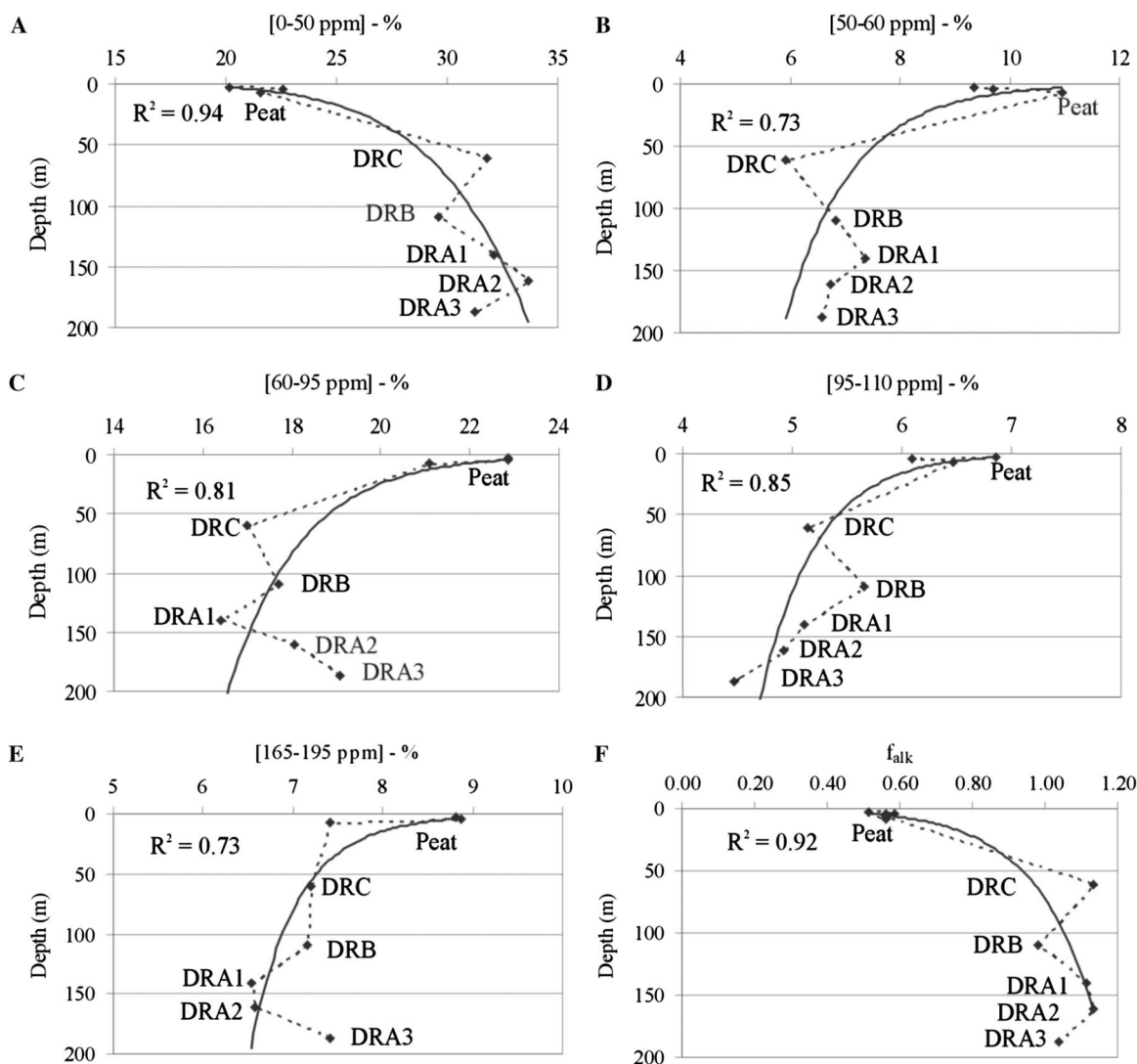
Fig. 5. Vertical distribution of ^{13}C CPMAS NMR parameters and f_{alk} index for Philippi peat and Drama lignite.

The results point out that mainly the O-rich and not H-rich functional groups are affected by the alteration during early coalification in the Drama basin. This finding coincides with the generally accepted model of biochemical and geochemical coalification (Diessel, 1992; Hatcher and Clifford, 1997), according to which the early physico-chemical alteration includes dehydration and decarboxylation with the release of H_2O and CO_2 as end products, followed (at the next stage) by demethylation with the release of CH_4 and H-bearing fluids. Nevertheless, CH_4 is also released during peatification (Clymo, 1983) but at a rate lower than that of CO_2, primarily depending on the availability of O_2 for micro-organisms to decompose plant litter. The degradation mode of the organic matter can be assessed also by using the ratio (f_{alk}) of alkyl-C [aliphatic C: 0–50 ppm] versus O–alkyl-C [50–110 ppm], which is proportional to the extent of humification (Lorenz et al., 2000; Rumpel et al., 2002). The average lignite f_{alk} (1.08) is significantly higher than the average peat f_{alk} (0.56), revealing the intense decomposition of O–alkyl-C

moieties like cellulose during early coalification (Table 5, Fig. 5F).

There is no clear trend for the distribution of aldehyde and ketone carbons in relation to the progress of coalification, since the values are highly scattered among the samples (Table 4), and this may be due to ssb masking changes in the signal.

A quite non-conventional aspect emerged by comparing the total integrated resonance-area (I-a = area of [225–0 ppm]) of lignite samples with that of peat samples (comparison among simulated spectra of average peat and lignite resonance-areas). The resonance curves of the lignite spectra cover approximately $D_{(I-a)} = 21 \pm 3\%$ less area (on average) than that of the peat spectra (Fig. 6). This decrease could be an index of mass reduction, and it is very close also to the C–H–N mass-balance value (17%) obtained from the elemental analyses. This means that almost 1/5 of the peat mass has been lost during coalification till the stage of immature lignites, due to the loss of volatile elements and immigration of liquid phases and

Table 5
^{13}C NMR quantitation indices

Sample	fa′ [a]	fa$_c$′ [b]	f_{alk} [c]
P1-1	0.33	0.39	0.56
P1-2	0.34	0.39	0.56
P2-1	0.34	0.39	0.52
P2-2	0.31	0.36	0.58
P2-3	0.34	0.39	0.56
Peat$_{average}$	0.33	0.38	0.56
DRC	0.32	0.37	1.13
DRB	0.33	0.38	0.98
DRA1	0.32	0.36	1.11
DRA2	0.30	0.34	1.13
DRA3	0.31	0.35	1.04
Lignite$_{average}$	0.32	0.36	1.08

[a] fa′ = [95–165 ppm]/[total peak area] (Stevenson, 1994).

[b] fa$_c$′ = [95 − 165 ppm]/[total peak area − (165 − 220 ppm)] (Stevenson, 1994).

[c] f_{alk} = [0–50 ppm]/[50–110 ppm] (Lorenz et al., 2000; Rumpel et al., 2002).
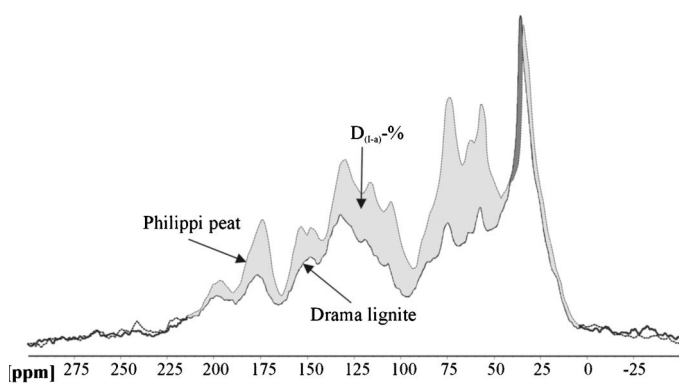
Fig. 6. Comparative view of Philippi peat and Drama lignite ^{13}C CP/MAS NMR spectra ($D_{(I-a)}$-%: integrated-area difference).

the subsequent chemical rearrangements of organic molecules that also conduce to the volume compaction of organic sediments. However, further research is required in order to check this assumption.

3.3.2. Aromaticity during early coalification

One of the most important issues in coal geology concerns the transformation of organic moieties to aromatic structures through coalification. NMR studies effectively proved this trend by introducing the aromaticity concept (e.g., Hatcher, 1988; Solumn et al., 1989; Orem et al., 1996; Suggate and Dickinson, 2004), although there are many different approaches to how aromaticity index (i.e., the percentage of carbon that is aromatic) is measured, due to the impact of overlapping resonance peaks, particularly in cases of the presence of significant cellulose and lignin remains. The most common assessments of aromaticity from the ^{13}C NMR spectra rely on the determination of the ratio of aromatic region per either total resonance-curve

area or the total area excluding carboxyl and carbonyl regions (Stevenson, 1994).

In cases of low rank coals like the Drama lignite and the Philippi peat, it is reasonable that the aromatic region [110–165 ppm] primarily corresponds to lignin remains and not to re-organized organic molecules. Quantitation revealed that the amounts of aromatic and phenolic C in lignite samples are similar or slightly lower than in peat samples (Table 4). However, from the NMR spectra (Figs. 4A and B) it is evident that the aromatic region [110–165 ppm] for the lignite samples has a shape totally different from the corresponding area in the peat samples. In order to elucidate possible variations in aromaticity, several indices are proposed in the literature. However, as already mentioned, due to the applied measuring conditions of the NMR equipment and the attendant occurrence of ssb, from both inorganic paramagnetic ions and the free organic radicals, the values in this study are only indicative. Hatcher (1988) and Kelemen et al. (2002) used the fa′ index (Table 5) to assess the aromatic fraction of coals of variable rank. The values obtained for peat are between 0.31 and 0.34, within the range (fa′ = 0.24–0.36) reported by Kelemen et al. (2002) for fresh peats, whereas values for lignite samples are similar or slightly lower (0.30–0.32). Lignite fa′ values are significantly lower than the respective values for Miocene lignites (fa′ = 0.48–0.57) reported by Hatcher (1988). This controversial trend, apart from reflecting the low degree of alteration of the Drama lignite from the peat stage, brings up for discussion the problematic approach of the concept of aromaticity in such early-coalified sediments. This variation is similar even if the carboxylic and carbonyl carbons are excluded (fa$_c$′); in this case, aromaticity values for peat range between fa$_c$′ = 0.36 − 0.39 and for lignite fa$_c$′ = 0.34 − 0.38 (Table 5), the latter being almost similar to the fa$_c$′ (0.26–0.39) values reported by Iordanidis (2002) for the Late-Pliocene Amyntaeon-Apophysis lignite in the Ptolemais Basin.

Hammond et al. (1985), in a thorough study of Canadian peats, suggested that aromaticity in peat may have a different meaning from that for higher rank coals, since in many cases aromaticity reflects the nature of plant residues rather than the humification stage. The relative resistance of lignin during humification (Diessel, 1992) causes a masking effect on the aromaticity level. Therefore, we infer that the fa′ values obtained for the peat samples primarily reflect the significant amounts of lignin-rich structures accumulated within the peat. Lignin-rich structures, originating from roots and stems of both woody and herbaceous plants, are regarded as precursors of telohuminite, the amount of which in the Philippi peat reaches up to 70 vol % (on a total organic basis; Kalaitzidis and Christanis, 2000). However, current micropetrographic work on the peat samples shows that during progressive humification, the most fragile telohuminite degrades and finally, the residues contribute to detrohuminite formation. In contrast, the telohuminite in Drama lignite does not exceed 25 vol % (on total organic basis; Kaouras et al., 1991),

which primarily reflects the herbaceous origin and more or less the low preservation degree of the initial plant tissues. This implies a moderate to high degree of humification that, apart from cellulose degradation, resulted in partial decomposition of lignin. However, this partial decomposition of lignin probably took place during the alteration stage from peat to lignite and not at the peatification stage. This aspect is inferred from the fact that the amount of telohuminites (lignin-rich tissues) seems to decrease from the stage of peat to lignite. The degree of lignin decomposition is reflected in the significant decline in methoxyl (demethoxylation) and protonated aryl peak intensities, as well as the moderate decrease in phenolic carbon. As figured out also by previous studies on the coalification characteristics that combined ^{13}C NMR and GC–MS data (e.g., Stout et al., 1988; Orem et al., 1996; Hatcher and Clifford, 1997) at this early coalification stage, catechol-like structures, i.e., the products of lignin degradation (Behar and Hatcher, 1995), are incorporated within the humic acid fraction due to humification, without a condensation effect to provide aromatic moieties. In this sense, since the fa′ values for lignite samples are similar or even lower than those for peat samples, it is evident that the Drama lignite seems to be at a degradation level (i.e., conversion of large biomolecules into smaller chemical species) started at the early peatification stage, rather than in a condensation level (formation of aromatic units), which has already occurred but will be more evident at higher rank stages. Therefore, it can be postulated that the fa′ values obtained for the Drama lignite correspond to the initial stages of variation in aromaticity level during humification/coalification. Hence, the reversed order of fa′ values among peat and lignite samples seems reasonable.

4. Conclusions

The study of the Pleistocene Drama lignite and the Upper-Weichselian/Holocene Philippi peat, by means of ultimate and ^{13}C CP/MAS NMR analyses provided interesting aspects concerning early coalification features, since peat-forming conditions in the Drama palaeomire were almost similar to these in the recent Philippi mire.

Elemental data revealed the immature nature of the Drama lignite, and according to mass-balance calculations the succession of peat to lignite resulted to the loss of approximately 17% of the organic matter, probably in the form of small molecules (e.g., CO_2, CH_4, NO_x).

The ^{13}C CP/MAS NMR spectra of the Philippi peat samples indicate a significant occurrence of carbohydrates and lignin compounds, along with tannins and aliphatic carbons. The semi-quantitative results coincide with the fact that sedges, mainly Cyperaceae, were the predominant helophytes. Minor differences related to different peatification conditions are evident: demethoxylation progressed more rapidly during the ameliorated climate of the Holocene, in accordance with the humification degree, than during the Upper Weichselian; demethylation shows a

reversed trend. The ^{13}C CP/MAS NMR spectra obtained for the Drama lignite are indicative of its low rank and reveal an intense peak for aliphatic carbons, which constitute the predominant organic moieties, as well as for aromatic carbons and polysaccharides.

The comparison of peat and lignite quantitation reveals a degradation of methoxyl groups, carbohydrates and carboxylic groups during early coalification, whereas the aliphatic carbons were less affected. However, organic geochemical alteration during coalification seems to strongly depend on the initial peatification conditions, meaning on the intensity of bacterial degradation. Variances in early demethoxylation, decarboxylation and cellulose-degradation degrees in the peatigenic layer affect the distribution of carboxyl, methoxyl groups and polysaccharides among the lignite samples. Our results are consistent with previous studies of early coalification. It is clear that during early coalification the major organic geochemical alteration process is degradation of cellulose, whereas degradation of lignin is less intensive. The preferential preservation of lignin structures in peat samples results in similar or even higher aromaticity compared to the lignite samples. This means that the aromaticity in peat has a totally different origin than in coals. Peat aromaticity refers to lignin remnants, whereas aromaticity in coals refers to condensed aromatic structures.

The overall comparative features suggest that the NMR results obtained reflect primarily traces of early peatification processes and secondarily, coalification pathways. Further study of the Philippi peat and the Drama lignite sequence, at a high-resolution sampling scale, will contribute to understanding the succession of peatification and early coalification processes.

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