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PALAEOENVIRONMENTAL RECONSTRUCTION AND CLIMATE CHANGE IN SOUTH EASTERN EUROPE (NEOGENE KARLOVO LIGNITES, CENTRAL BULGARIA)

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Abstract: Neogene Karlovo Basin, Central Bulgaria was comparatively studied with other Bulgarian lignites for palaeoenvironment assessment. Petrographic and chemical methods were used. The data allowed floral reconstruction at the region and assumption for the climate during the corresponding geological time. The data of geochemical and petrographic studies gave proves for the long-term evolution of the Late Neogene on the South Eastern Europe connected with the decrease in palaeotropical elements and increase in arctotertiary taxa. Conifers remained main coal-forming vegetation predominantly represented by *Pinaceae*. Biomarker assemblage assumed insignificant *Cupressaceae*/*Taxodiaceae* contribution. Monoaromatic angiosperm-derived triterpenoids with ursane/oleanane skeleton proved the presence of dicotyledonous angiosperm-derived organic matter in the palaeoplant taxa as well. Palaeoenvironmental conditions within the forest swamp should be determined as limnic, with varying water table and seasonal drying.

Key words: Neogene, Bulgaria, lignite, palaeoenvironment, petrography, biomarkers

1. Introduction

Palaeoclimate reconstruction is based on the pollen analysis and plant macrofossil record. It is advisable for climate changes restoration, i.e. temperature, humidity and their oscillation within the time, to be familiar with the vegetation during the corresponding geological period. Molecular organic geochemistry has the same target – to find relationship between registered organic compounds and specific taxa. Currently limited studies correlate biomarkers to modern taxa and try to draw systematic and phylogenetic relationships (Otto and Wilde, 2001; Hautevelle et al. 2006). Once sufficient and unequivocal information is available for source specific markers, palaeoclimatic reconstructions will be possible and floral diversities during certain geological ages can be proposed. Such data also will enhance the knowledge on coal precursors and their diagenetic transformations during coalification.

2. Study area

Karlovo Basin is the eastern-most basin in the Sofia coal province (Fig.1). It represents a tectonic graben bounded by the Middle Stara Planina Mountain to the north and the Sredna Gora Mountain to the south. The basin is filled with up to 350 m of Neogene sediments which overlie basement rocks composed of Precambrian and Paleozoic gneisses and granitoides. According to Angelova et al. (1991) the sedimentation was controlled by the formation and development of asymmetric basement blocks having different subsidence rates. The most significant tectonic movements occurred in the northwestern part of the graben, where the thickest Neogene sediments were deposited.

Sedimentation commenced in a fluvio-lacustrine environment with deposition of up to 15m of sandy gravels (Chounev et al., 1966; Fig. 2). Subsequently, the interfingering of sediments from different fluvial sources resulted in deposition of horizontally and vertically alternating layers of greenish to grey-blue silty to sandy clays and layers of unsorted sands and gravels (Fig. 2).

Later, block displacements established lacustrine environments in the center of the northwestern block of the Karlovo Graben and resulted in the formation of up to 50m thick sediments, represented by several coal seams, diatomaceous clays and diatomites. Along the basin margin these interfingers with sandy sediments (Angelova et al., 1991). Temniskova et al. (1996) established multiple changes of benthic-epiphytic deep-water diatom species with planktonic ones which indicate frequent changes in water depth during the early stages of the deposition of the coal-bearing strata. Eleven coaly layers (Chounev et al., 1966) were formed, but only the topmost seam is up to 11m thick (Šiškov, 1985). Acidophilic diatom species suggested that coal formation occurred under acidic conditions.

3. Materials and methods

The present study is based on 24 samples from the main coal layer in Karlovo Graben. The samples originate from different drillings in the south-eastern part of the basin. Previously the samples were part of the studies of Kortenski and Dimitrov (1989), and Kortenski (1991) concerning the mineralogical and inorganic geochemical characteristic of the coal.

For the purpose of the present study, the samples from the neighboring drilling were combined into 3 bulk samples for the investigation of the organic geochemical composition of the coal. The position

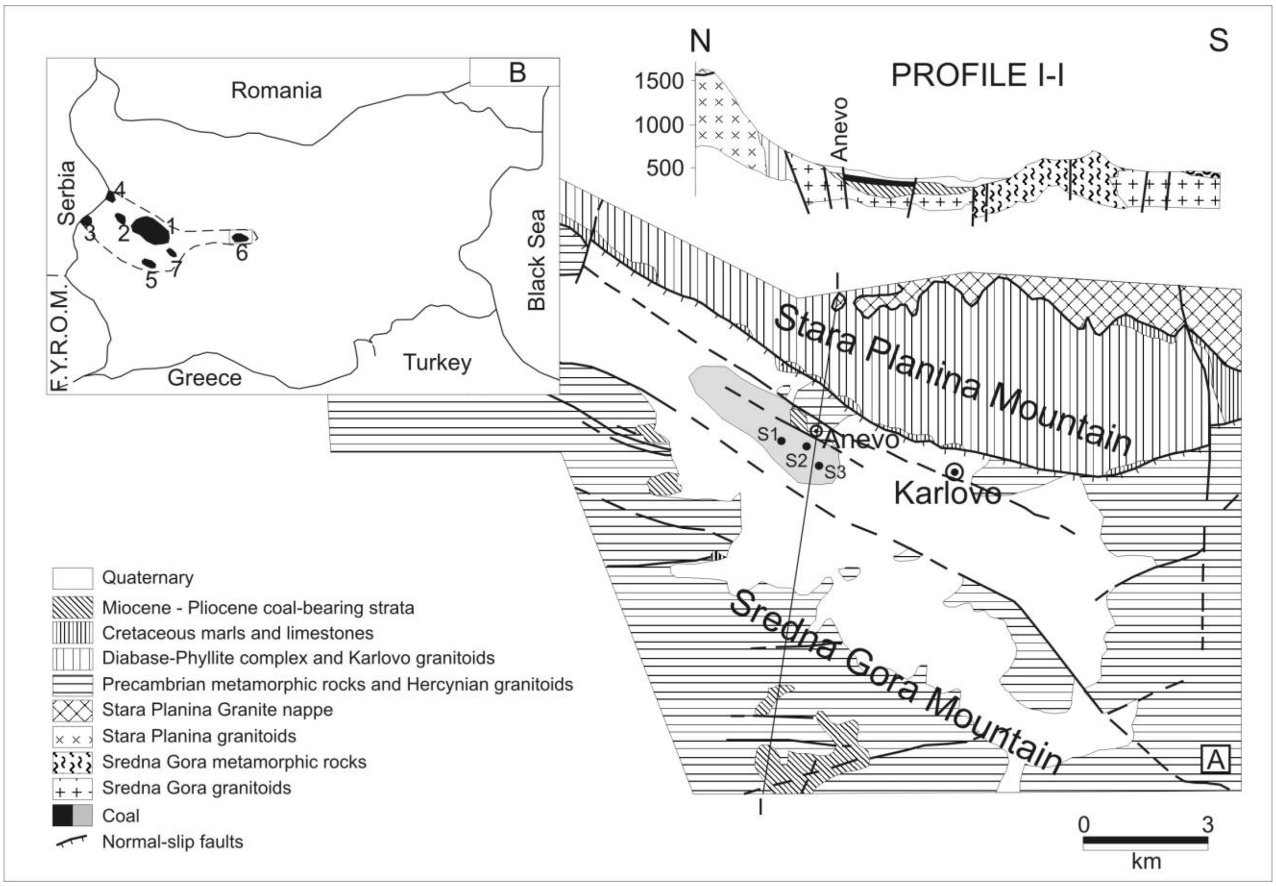

Fig. 1. Geological map (A) of the Karlovo graben (modified after Chounev et al., 1966; Angelova et al., 1991) and position of the basin within the Sofia coal province (C). S1, S2, S3 - the places of sampled; 1-Sofia basin; 2-Aldomirovtsi basin; 3-Belibreg basin; 4-Staniantsi basin; 5-Samokov basin; 6-Karlovo basin; 7-Chukurovo basin.

During the Late Pliocene, the lacustrine/palustrine depositional environment was replaced by a fluvial one. The latter resulted in the formation of alternations of sand, gravel, clay, and silt layers. These overlie the older washed-out lacustrine sediments with a sharp lithological boundary (Fig. 2; Angelova et al., 1991). The youngest deposits in Karlovo Basin are coarse-grained alluvial, proluvial, and talus sediments of Quaternary age.

of the samples within the coal basin is shown in Fig. 1.

For microscopic investigations, the samples were crushed to a maximum size of 1 mm, mounted in epoxy resin, ground and polished. Maceral analysis was performed by a single-scan method with Leica DM 2500 microscope using reflected white and fluorescent light. At least 350 points for each sample were counted.

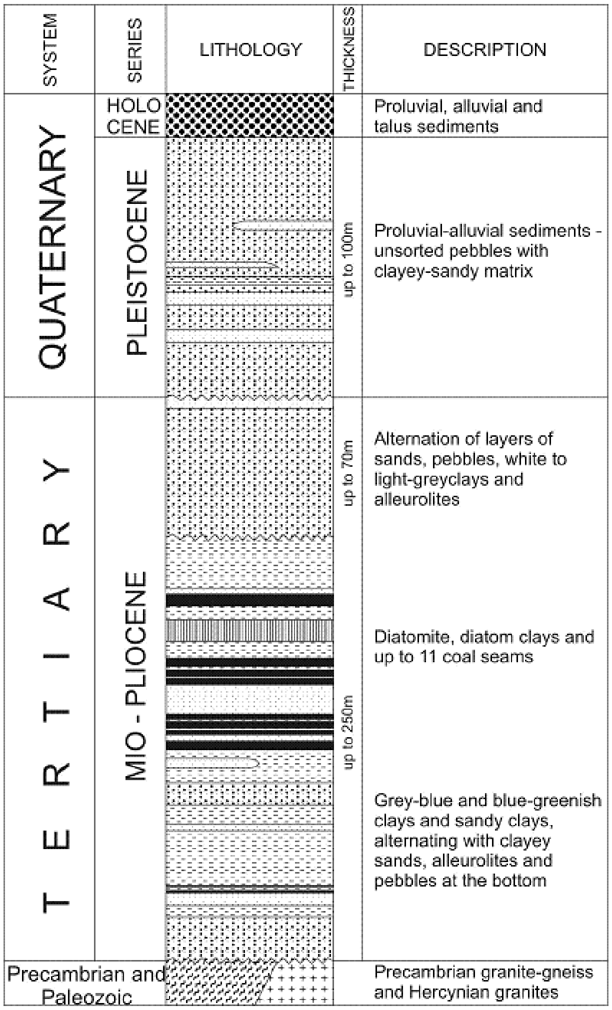

Fig. 2. Lithostratigraphic column of the Neogene in the Karlovo graben (modified after Chounev et al., 1966; Angelova et al., 1991).

The same protocol of bitumen preparation, separation and analysis as described in the previous paper for Chukurovo lignite is used (Stefanova et al., 2005). Individual compounds are identified by comparison of mass spectra with literature and library data. 2,4,6-Triethylbenzene is used as an inner standard for quantitative data interpretation. Contents of identified compounds are expressed in micrograms per gram “dry, ash free” coal sample (ug/g^{daf}).

4. Results and discussion

4.1. Maceral composition

The maceral composition of Karlovo lignite is dominated by the Huminite group macerals (Table 1). Their average contents in the bulk samples are around 80-80.8 %, but vary from 72.3 to 88.7 % in the individual samples. The organic matter is generally composed of groundmass, represented by both attrinite and densinite (Fig.3a) with contents reaching up to 82.5 % in the individual samples, but in the majority of the samples the amount of detrogelinite is mainly between 70 and 80%. Within the groundmass are scattered pieces of telohuminite macerals with different form and size. The subgroup is mainly represented by highly gelified eu-ulminite (Fig.3b, c) with contents varying significantly from 17.1 up to 50.5 %. Only small amount of it (about 4.6 to 6.7 %) is slightly less gelified and show transition to textinite (Fig. 3b). The latter is only a minor component of the organic matter in the studied lignite. Its average contents are between 4.6 and 6.7 %, but reach up to 10 % in some samples.

Unlike the other lignite basins in Sofia coal province, the studied lignite contains significant amount of liptinite macerals (from 16.7 to 18.2% - Table 1, and up to 24.9% in the individual samples). This is mainly due to the high contents of alginite (4.0 to 12.3%, Fig. 3a,e,f), and liptodetrinite (2.4 to 10.5 %, Fig. 3d). The rest of the macerals (microsporinite – Fig. 3f; cutinite – Fig. 3d; resenite, suberinite, fluorinite) from this group are usually an insignificant constituent of the organic matter with contents rarely exceeding 1 %.

Like most of the Tertiary coal basins around the world, Karlovo lignite contains only very small amounts of inertinite macerals – up to 2.5% (Table 1). The most abundant ones are funginite (Fig. 3a) with contents up to 2.7% in the individual samples, and inertodetrintie (up to 2.3% in the individual samples). The average contents of these macerals are however, much lower – around 1.0-1.5 % for the funginite and below 1.0% for the inertodetrinite (Table 1). In some of the samples can be observed also small lenses of fusinite and semifusinite, but usually their contents are less than 1%.

In general, the petrographic composition of the studied samples is similar to that established previously by Zdravkov et al. (2006). Based on the calculation of the maceral indices the palaeoenvironmental conditions within the forest swamp should be determined as limnic, with varying water table and seasonal drying.

4.2. Bulk characteristics

The data for extracts separated into aliphatic, aromatic and polar fractions on Silicagel column are summarized in Table 2. Different homologue series will be discussed separately.

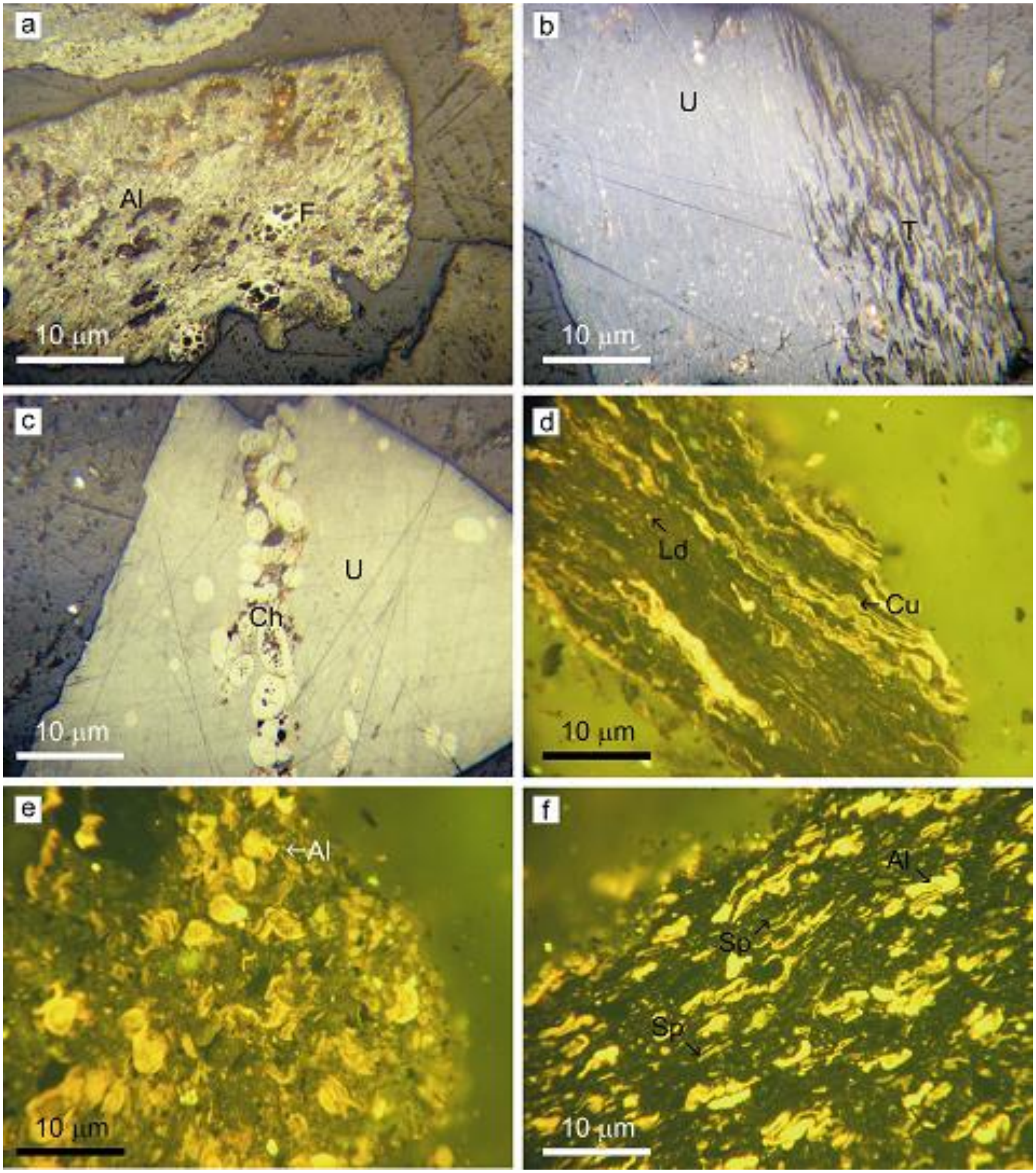

Fig. 3. Microphotographs of Karlovo lignite: a) Alginite (Al) and Funginite (F) in attrinite-densinitic groundmass, reflected white light, oil immersion; b) Highly gelified ulminite (U) in association with textinite (T), reflected white light, oil immersion; c) Highly gelified ulminite (U) with corpohuminite (Ch) bodies in former cell walls, reflected white light, oil immersion; d) Cutinite (Cu), associating with liptodetrinite (Ld) fragments, blue excitation light, oil immersion; e) Multiple alginite (A) bodies and fragments, blue excitation light, oil immersion; f) Alginite (A) and single microsporinite bodies (Sp), blue excitation light, oil immersion.

4.3. Aliphatic lipids

4.3.1. n-Alkane distribution

GC-MS reveals the presence of *n*-alkanes and terpenoids (Table 3, Fig.4) in the neutral fractions. *n*-Alkanes distribution is bimodal with two distinct maxima at *n*-C_{16} and *n*-C_{29}. The calculated values for CPI are S1= 3.5, S2 = 4.0 and S3= 2.0. The CPI magnitudes may be explained by the contribution of epicuticular wax from higher plants. There are at least two sources of *n*-alkanes: (a) shorter chains might be from algal or bacterial contributions to the palaeomire, and (b) the longer chains from terrestrial sources. The lower value calculated for sample S3, CPI = 2, comparing to the other ones, is an indication for the algal prevalence.

4.4.2. Diterpenoids

Diterpenoids are distributed mainly in gymnosperms and in only a few angiosperms among con-

Table 1. Maceral composition of coal from Karlovo basin, % daf.

Sample	T	U	Ph	G	At	D	Hum	Sp	Cu	R	Sb	Al	Fl	Ld	Lipt	Fs	Id	F	Inert	MM
S1	5.1	33.3	2.6	0.8	31.0	*7.9*	80.7	0.7	0.7	1.0	0.3	8.3	0.6	5.5	17.1	0.1	0.6	1.5	2.2	23.5
S2	6.7	37.6	2.6	0.0	16.4	*17.5*	80.8	0.3	0.9	1.7	1.2	6.0	0.3	6.3	16.7	0.4	0.9	1.2	2.5	9.7
S3	4.6	32.3	3.4	0.2	27.5	*12.0*	80.1	0.4	1.0	0.6	1.0	8.0	0.0	7.2	18.2	0.1	0.6	1.0	1.7	19.3

T = Textinite; U = ulminite; Ph = Phlobaphinite; G = Gelinite; At = Attrinite; D = Densinite; Hum – Huminite group; Sp = Sporinite; Cu = Cutinite; R = Resinite; Sb = suberinite; Al = alginite; Fl = Fluorinite; Ld = Liptodetrinite; Lipt – Liptinite group; Fs = Fusinite; Id = Inertodetrinite; F = Funginite; Inert – Inerinite group; MM – mineral matter.

Pristane (Pr) is less abundant compared to phytane (Ph). This proportion is not typical for non-marine shales and coals because Pr is normally dominant in coal extracts. In our case the Pr/Ph ratio is < 1, which could be interpreted as an indication of a reducing environment during deposition.

Table 2. Bulk characteristics of samples and their bitumen extracts, in %.

Sample	Moisture	Ash	Bitumen				
			Yield	Fractions			Asph.
				Neutral	Arom.	Polar	
S1	6,9	30,2	2,2	10,3	15	65,3	1,6
S2	7,8	24,1	2,6	8,8	11,1	64,4	1,8
S3	7,7	23,7	2	18,2	11,5	64,5	1,3

4.3.2. n-Alkan-2-one distribution

A homologous series of long-chain acyclic *n*-alkan-2-ones with "odd" numbered homologues prevalence are determined in the extracts. The distributions of the long-chain *n*-alkanes and *n*-alkan-2-ones, i.e., *n*-C_{24} to *n*-C_{33}, are similar. All samples maximize at *n*-C_{31} and the "odd" homologues dominate. The similarity in distribution patterns suggests a product-precursor relationship. High quantities of isoprenoid C_{18} ketone (6,10,14-trimethyl-pentadecan-2-one) are registered as well. This ketone is supposed to be derived from microbial degradation of phytol and is often present in products of extraction or pyrolysis of fossil materials.

4.4. Terpenoids

4.4.1. Sesquiterpenoids

Hydrocarbons based on the cadinane skeleton are common constituents of resins, ambers, and petroleum with a terrigenous input component (Simoneit et al. 1986; Otto and Wilde, 2001). Subordinated quantities of sesquiterpenoid are determined. In all samples are registered cedrane and reduced cadalene derivatives.

temporary plants. The "regular" abietane skeletal type of diterpenoids is represented by fichtelite and abietane (Fig.5). These compounds are often found in pine wood submerged in peat. The "regular" abietanes occur in all conifer families except *Phyllocladaceae*. The "phenolic" abietanes, i.e. ferruginol, sugiol, etc., are expected in the aromatic/polar fractions as in other Bulgarian lignites, i.e. Maritza-East, Chukurovo, etc. (Stefanova et al. 2002; Stefanova and Simoneit, 2008). There are no polar diterpenoids in the analyzed samples. A high preponderance of fichtelite and negligible contents of 16α(H)-Phyllocladane are registered in all samples. Minor quantities of partially aromatized abietane structures are also found (Fig.5).

Diterpenoids in Karlovo lignite are the dominant biomarkers in bitumen extracts but several peculiarities should be emphasized, namely: (i) subordinating quantities of 16α(H)-Phyllocladane (Fig. 5); (ii) and, total absence of polar diterpenoids;

4.4.3 Triterpenoids

Triterpenoids in fossils are hypothetically divided into two groups, hopanoids and non-hopanoids (Bechtel et al. 2005). Hopanoids are indicators of microbial activity while non-hopanoids are source-related components. Hopanoids in some Bulgarian lignites have been already discussed (Stefanova et al., 1995; 2005; Bechtel et al., 2005).

Non-hopanoids with lupane, ursane and oleanane skeletons are markers for a palaeoswamp with angiosperm predominance. The most abundant in samples under consideration are oleanane-type triterpenoids like β–amyrone. It should be noted that the presence of C-3 functionalized triterpanes (alcohols, acids, ketones, esters, etc.) makes them more susceptible to microbial or photochemical degradation to des-A-ring products (Des-A-lupane). A peculiarity of samples under study is the appreciable quantity of Lupan-3-one, M^+ 426, m/z 205 (100%), m/z 383 (M^+- 43).

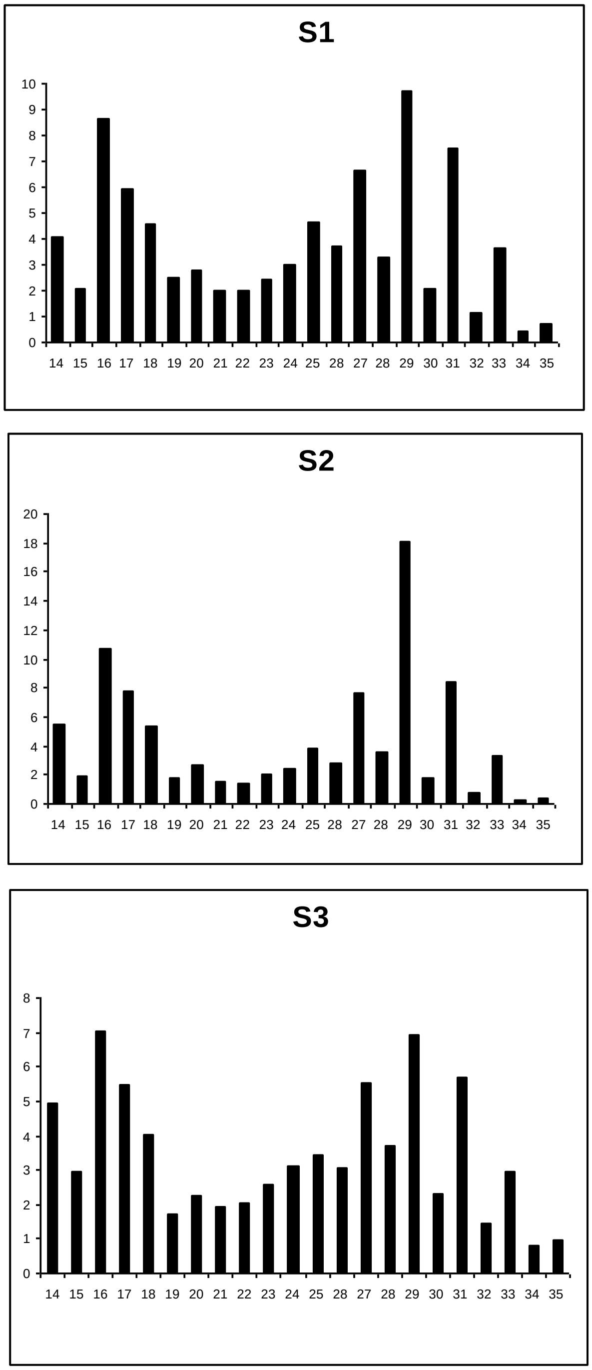

Fig. 4. Patterns of n-alkanes distributions in rel. % (numbers corresponds to the carbon numbers in alkanes).

Oxygenated pentacyclic triterpenoids, i.e., friedelin, α/β−amyrins/amyrones, are present in aromatic fractions. All abovementioned triterpenoids prevail in the surface waxes of the easily degraded leaves of angiosperms. The dominant triterpenoid in all aromatic fractions is friedelin which is a common component of epicuticular waxes (Logan *et al*., 1995). The same functionalized triterpenoid is already registered in the previous study dedicated to Chukurovo coal progenitor *Taxodium dubium* (Stefanova, 2004; Stefanova and Simoneit, 2008)

Monoaromatic angiosperm-derived triterpenoids with ursane/oleanane skeleton (SIM m/z 145) are with low abundance and distributed in neutral and aromatic fractions according to molecular mass, dinoroleana-1,3,5(10),13(18)-tetraene, (M^+ 376) and dinoroleana-1,3,5(10)-triene (M^+ 378). Higher homologue with M^+ 392 is tentative identified as well. Stout (1992) described these compounds as characteristic for Tertiary angiospermous lignite. It is presumed that all oleanane, ursane triterpenoids could be formed by a progressive amyrin aromatization. Triterpenoids and their monoaromatic analogues support the presence of appreciable dicotyledonous angiosperm-derived organic matter in the palaeoplant taxa of Karlovo lignite.

4.4.3.1. Hopanoids

The 22R-17α(H),21β(H)-homohopane ($H_{31\alpha\beta}$ M^+426) is the only prominent peak of the hopane distribution in SIM m/z 191 of neutrals. There are negligible quantities of $H_{27\beta}$, M^+ 370 and other H_{31} stereoisomers ($H_{31\beta\alpha}$ and $H_{31\beta\beta}$). The contribution of microorganism biomass during the diagenetic transformation of the parent organic matter can supply hopanoids.

In aromatic fractions SIM m/z 191 visualizes low quantities of hopanoid ketones, i.e. C_{27}, 17β(H)-trisnor-hopane-21-one (M^+ 384, maximal peak) and C_{29}, α-Adiantone (M^+ 412). One D-ring monoaromatic hopane with M^+ 364 is registered in neutral fractions.

4.5. Steroids

Stigmastan-3-one, M^+ 414 is present in all extracts. The C_{28} and C_{29} steroids are highly abundant in the

Table 3. Biomarkers contents, in microg/g daf coal

Sample	Alkanes	Terpenoids				Hopanes	Steranes	Friedelin
		Sesqui-	Di-	Ses-	Tri-			
S1	40,6	1,3	40,3	1,3	3,0	14,5	0,9	14,4
S2	17,2	0,0	47,6	0,8	1,1	10,9	0,7	14,4
S3	79,2	0,0	52,0	1,2	4,9	24,8	1,0	17,0

plant kingdom and reflect the input of detritus from higher plants (Oros and Simoneit, 1999). The steroids are nonspecific markers because sitosterol, the biological precursor, is ubiquitous in nature.

are abundant as in other Bulgarian lignites, i.e. Maritza-East, Chukurovo, Sofia coal-bearing deposits due to fichtelite and abietane. The total absence of polar diterpenoids is a hint for the lower

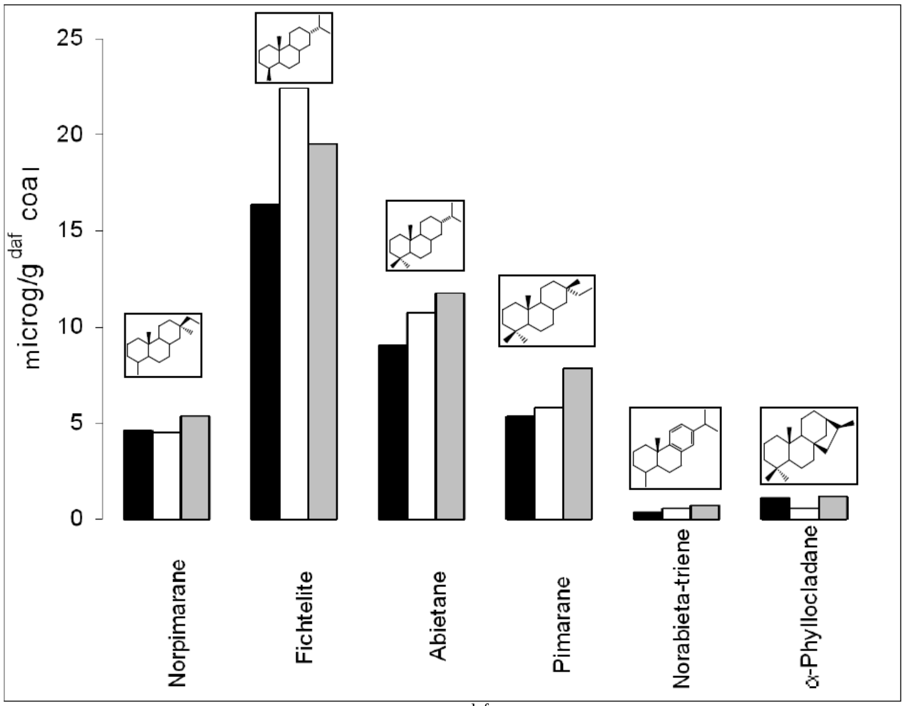

Fig. 5. Contents of diterpenoids in microg/g^{daf} coal. (■ – S1; □ – S2; ◘ - S3).

Coals contain lower quantities of steranes comparing to hopanes (by comparison of the intensities in the mass fragmentograms m/z 191 and m/z 217). Nevertheless, only in sample S3 m/z 217 visualizes the C_{27}, C_{28}, C_{29} whole range of steranes and diasteranes with strong dominance of 20R-$\alpha\alpha\alpha C_{27}$ homologue. The position in the triangular diagram for the relative contents C_{27} (40 %) C_{28} (28 %), C_{29} (32 %) indicates "estuarine or bay" formation of organic matter for S3 sample.

5. Implications for palaeovegetation

Karlovo lignites (Central Bulgaria) are well studied from geological, petrological and palaeobotanical point of view (Šiškov, 1985; Vălčheva and Trifonov, 1986; Stefanova and Valceva, 1994; Zdravkov et al. 2006). According to Ivanov and Slavomirova (2004) the age of the flora-bearing sediments covers the time span Pontian-Pliocene as is proven by geological data and diatom analysis. The biomarker assemblage of Karlovo lignite strongly differs from the other Neogene lignites in Bulgaria. The most striking peculiarity is the negligible content of tetracyclic diterpanes, i.e. 16α(H)-Phyllocladane). Diterpenoids contribution of *Cupressaceae*/*Taxodiaceae* to the palaeomire. This coal progenitor is highly abundant in coal forming swamp but its importance declines with the advance of geological time. Inasmuch Karlovo lignite palaeoflora is from Upper Miocene and Pliocene the role of arctotertiary species in plant communities increases and becomes dominant in mesophytic forest. Respectively, it is supposed that *Cupressaceae*/*Taxodiaceae* gradually decreases due to drying and *Pinaceae* increases as better adapted to the colder and arider climate during Pliocene in Central Bulgaria. There are proves for the existence of flooded areas as well. Steranes are distributed in one of the samples and determines organic matter formed in limnic ecosystems. Angiosperms should not be neglected as there are mass spectral indications for the presence of *Quercus, Ulmus and Betula* in the palaeocommunites. Especially high *Betula* abundance could be assumed due to the presence of its biomarkers Des-A-lupane and Lupan-3-one.

6. Conclusions

The results of organic geochemical and petrographic study of Karlovo lignite (Central Bulgaria) give us proves for the long-term evolution of the Late Neogene on the South Eastern Europe. The biomarker assemblages of samples under consideration are determined by the decrease in the palaeotropical elements and gradual increase in the arctotertiary taxa. Conifers remain main coal-forming vegetation predominantly represented by *Pinaceae*. Monoaromatic angiosperm-derived triterpenoids with ursane/oleanane skeleton prove the presence of dicotyledonous angiosperm-derived organic matter in the palaeoplant taxa. The palaeoenvirmental conditions within the forest swamp should be regarded as limnic with varying water table and seasonal drying.

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