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ORIGIN, DEPOSITIONAL ENVIRONMENT AND MATURITY OF ORGANIC MATTER IN EOCENE COALS FROM TUNISIA

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ABSTRACT – The aim of this study was to determine the origin and geological history of coals from Tunisia, using organic geochemical approach. Five coal samples were examined. After bitumen extraction and maltene fractionation, biomarkers in aliphatic fractions were analyzed using gas chromatography-mass spectrometry (GC-MS). The precursor organic matter (OM) was mostly represented by terrestrial vegetation with evident marine influence. Coals were formed under suboxic to oxidizing conditions. The maturity of OM corresponds to late diagenesis/early catagenesis, indicating subbituminous coal rank.

Keywords: Coal, Origin and maturity of organic matter, Biomarkers, Gas chromatography-mass spectrometry.

INTRODUCTION

Coal is a heterogeneous organic substance of complex structure formed by the transformation of mainly plant remnant over the long geological time. Different types of coal vary in their composition, properties, and applications. Its composition and properties depend on precursor biomass, depositional settings and thermal maturity. Determination of the composition of biomarkers in the extractable organic matter of coal (bitumen) is significant for investigation in coal geochemistry. Biomarkers are compounds that almost fully retained structural similarity to their biological precursors. Therefore, biomarkers can indicate the sources and depositional environment of OM, as well as the intensity of diagenetic changes [1]. On the other hand, since biomarkers underwent isomerizations into thermodynamically more stable isomers, cracking and aromatization they are used for determination of the degree of maturity [1, 2].

The aim of this study was to identify biomarkers in Tunisian coals using GC-MS analysis and to estimate their origin, depositional conditions, and maturity based on biomarker's distributions.

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EXPERIMENTAL

Five coal samples from Tunisia were pulverized and extracted using the Soxhlet method by a dichloromethane/methanol mixture (88:12, v:v). Bitumen was isolated and then separated into asphaltenes and maltenes by precipitation with *n*-heptane. Maltenes were separated into three fractions using column chromatography on silica as a sorbent. Aliphatic fraction was eluted with *n*-hexane, aromatic with the mixture of *n*-hexane/dichloromethane (7:3, v:v) and polar compounds (NSO fraction) with the mixture dichloromethane/methanol (1:1, v:v).

Aliphatic fractions were analyzed using an Agilent 7890A gas chromatograph coupled with an Agilent 5975C mass detector. An HP-5-MS capillary column (30 m × 0.25 mm) was used. Biomarkers were identified based on their mass spectra and retention times in total ion chromatograms (TIC) and characteristic ion fragmentograms (*m/z*): *n*-alkanes (*m/z* 71), steranes and diasteranes (*m/z* 217) and hopanes (*m/z* 191).

RESULTS AND DISCUSSION

Bulk Organic Geochemical Parameters

The results of bulk composition of studied coals are shown in Table 1. The obtained results indicate that the bitumen content in all samples is below 0.3 %, with a predominant share of asphaltenes and NSO compounds, indicating low-rank coal [3].

Table 1 Bulk composition of coals

	(%) in coal	(%) in bitumen		(%) in maltenes		
Sample	Bitumen	Asphaltenes	Maltenes	Aliphatic Fraction	Aromatic Fraction	Polar Fraction
MD_0	0.052	51.40	48.60	25.00	11.53	61.54
MD_1	0.057	68.64	31.36	27.00	13.51	62.16
MD_2	0.035	59.49	40.51	9.38	3.13	53.13
MD_6	0.299	85.40	24.60	31.82	19.32	36.36
MD_8	0.225	96.48	23.52	56.25	18.75	68.75

Biomarkers in aliphatic fractions

The following types of biomarkers were identified in aliphatic fractions: *n*-alkanes, alkenes, isoprenoid aliphatic alkanes (norpristane, pristane, and phytane), hopanes, steranes and diasteranes (Figure 1). It can be seen that *n*-alkanes are the most abundant biomarkers in the aliphatic fractions of all samples. Alkenes and isoprenoids are second in abundance, while polycyclic terpanes (hopanes) are present in smaller amounts. Steranes are present in the lowest concentrations and cannot be seen in the total ion chromatograms of aliphatic fractions. Parameters calculated from the abundances of *n*-alkanes and isoprenoids are shown in Table 2.

It can be seen that the maximum of *n*-alkanes is mainly at lower *n*-alkane homologues (C_{18}-C_{20}). The values of the CPI (Carbon Preference Index) [4] range from 0.71 to 1.10, indicating that the distributions of odd and even homologues are equal, or that in some samples even homologues predominate.

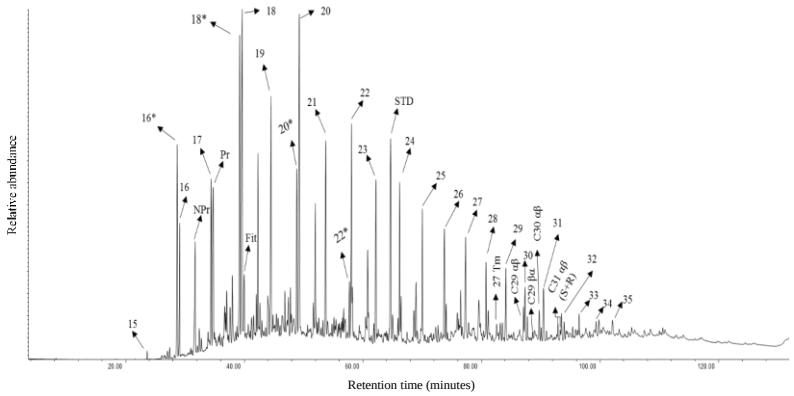

Figure 1 Total Ion Chromatogram (TIC) of the aliphatic fraction (sample MD0)

*The numbers correspond to the number of carbon atoms in *n*-alkane; * – alkene with the same number of carbon atoms as the nearest *n*-alkane; NPr – norpristane, Pr – pristane, Fit – phytane, STD – standard (deuterated tetracosane $C_{24}D_{50}$); C_{27} Tm – C_{27} 17α(H),22,29,30-trisnorhopane; αβ and βα indicate the configuration of hydrogen atoms at C-17 and C-21 in the C_{29}–C_{31} hopanes; R and S indicate the absolute configuration at C-22 in the C_{31} αβ hopane.

Table 2 Parameters calculated from the abundances of *n*-alkanes and isoprenoids

Sample	*n*-Alkane Maximum	CPI (C_{16}-C_{34})	Pr/Ph	Pr/*n*-C_{17}	Ph/*n*-C_{18}
MD_0	*n*-C_{18}	0.80	2.67	1.43	0.24
MD_1	*n*-C_{18}	0.88	2.96	1.18	0.23
MD_2	*n*-C_{20}	0.71	0.78	0.83	0.13
MD_6	*n*-C_{18}	1.06	2.49	2.69	0.83
MD_8	*n*-C_{31}	1.10	0.89	0.70	0.38

* *n*-Alkane Maximum – the most abundant *n*-alkane; $CPI_{17\text{-}33}$ – Carbon Preference Index calculated within the range of *n*-alkanes C_{16}-C_{34}, $CPI_{16\text{-}34} = 1/2 \times [\Sigma odd(n\text{-}C_{17} – n\text{-}C_{33})/\Sigma even(n\text{-}C_{16} – n\text{-}C_{32}) + \Sigma odd(n\text{-}C_{17} – n\text{-}C_{33})/\Sigma even(n\text{-}C_{18} – n\text{-}C_{34})]$ [7]; Pr/Ph = Pristane/Phytane.

Aliphatic isoprenoid alkanes pristane (Pr) and phytane (Ph) were identified in all samples. The Pr/Ph ranges from 0.78 to 2.96. The Pr/Ph for samples MD0, MD1, and MD6, is higher than 1 indicating oxidizing conditions in the sedimentation environment [5].

Parameters Pr/*n*-C_{17} and Ph/*n*-C_{18} are used to determine sample maturity. Also, the Pr/*n*-C_{17} ratio > 0.6 indicates terrestrial organic matter. In all samples, the ratio is higher than 0.6, suggesting prevalent terrestrial origin [6].

Polycyclic Alkanes of Sterane Type

In the aliphatic fraction of all samples, sterane biomarkers are present in the smallest amount compared to other types of compounds. In the ion fragmentograms (*m/z* = 217;

Figure 2) of all coal samples, the distributions and abundances of sterane biomarkers are similar.

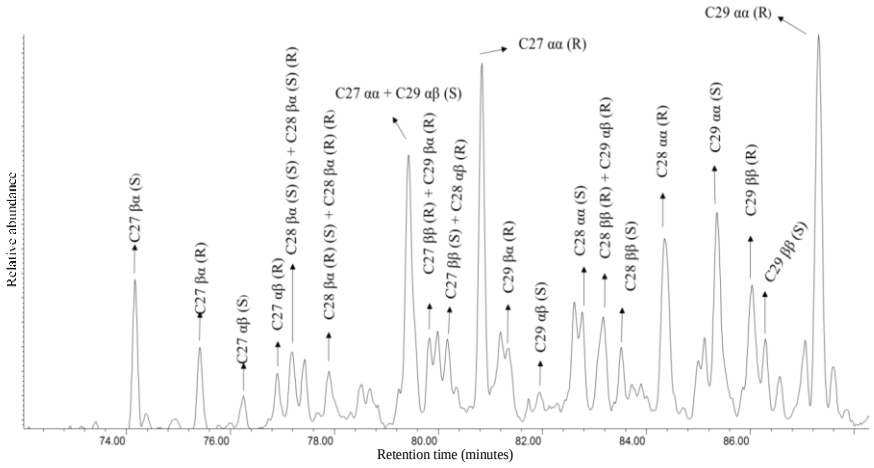

Figure 2 Distributions of steranes and diasteranes (*m/z* = 217) in coal samples (sample MD8)

*βα and αβ indicate configuration of hydrogen atoms at the C-13 and C-17 in diasteranes; S and R denote absolute configuration at the C-20 and C-24 in steranes and diasteranes; αα and ββ indicate configuration at C-14 and C-17 in 5α(H) steranes.

Data from Figure 2 indicate that content of regular (5α(H)14α(H)17α(H)20R) C_{28} sterane is the lowest in all samples (7.24-27.5 %). Biogenic precursors of C_{28} steranes originate from lacustrine environments. The percentages of regular C_{27} (32.40-47.64 %) and C_{29} (36.07-45.12 %) steranes are approximately equal. Precursors of C_{27} steranes are biogenic steroids most abundant in marine environments, while main precursors of C_{29} steranes are of terrestrial origin (higher plants). Evidence for a marine environment involves the presence of C_{30} steranes, which do not contain a methyl group on ring-A [7]. In the ion fragmentograms, *m/z* = 217 of all coal samples, the presence of C_{30} steranes does not appear or is present in such low quantities that it cannot be detected. Therefore, it can be assumed that the origin of the OM of coal samples is mostly terrestrial, with certain marine influence.

Polycyclic Alkanes of Terpane Type

The terpane distribution is characterized by the dominance of pentacyclic terpanes, i.e., hopanes C_{27}-C_{35}, except for the C_{28} homologue, which is absent. In the ion fragmentograms (*m/z* = 191; Figure 3) of all coal samples, the distributions and abundances of hopane biomarkers are similar.

A decreasing trend with the increase of number of carbon atoms followed by the $C_{35}(S)/C_{34}(S) \leq 0.70$ (Table 3) is indicative for suboxic-oxidizing depositional environment. This is in agreement with the Pr/Ph ratio which is > 1 in most samples (Table 2). The steranes/hopanes ratio (Ster/Hop; Table 3) is notably lower than 1, indicating terrestrial

or microbiologically reworked organic matter [3]. In the hopane distribution, C_{30} homologue predominates (Figure 3). Besides aerobic bacteria, precursors of C_{30} hopane are diploptene (C_{30} hop-22(29)-en) and diplopterol (C_{30} hopan-22-ol) which occur in lichens, ferns and mosses [8].

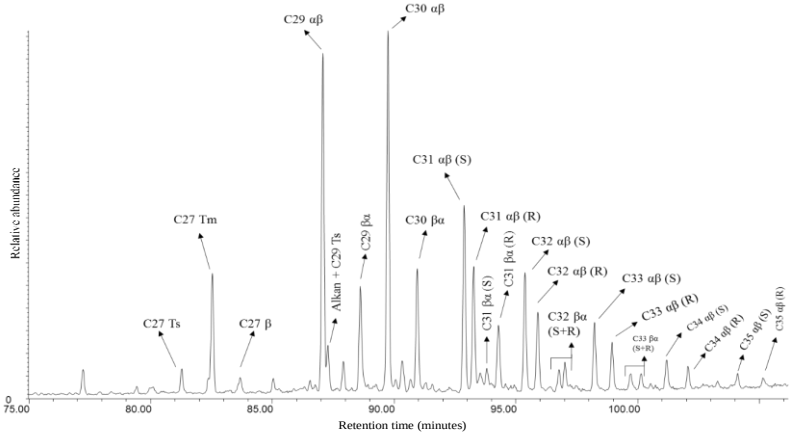

Figure 3 Distribution of hopanes (*m/z* = 191) in coal samples (sample MD0)

*α and β define the configuration at C-17 in C_{27} and hopanes; αβ and βα define the configuration at C-17 and C-21 in C_{29}–C_{35} hopanes and moretanes; R and S define the configuration at C-22 in C_{31}–C_{35} hopanes and moretanes; C_{27} Tm – C_{27} 22,29,30-trisnorhopane; C_{27} Ts – C_{27} 22,29,30-trisnorneohopane; C_{29} Ts – C_{29} 30-norneohopane.

Table 3 Source parameters calculated from the abundances of hopane biomarkers

Sample	% C_{31} αβ in ΣC_{31}-C_{35} αβ	% C_{32} αβ in ΣC_{31}-C_{35} αβ	% C_{33} αβ u ΣC_{31}-C_{35} αβ	% C_{34} αβ in ΣC_{31}-C_{35} αβ	% C_{35} αβ in ΣC_{31}-C_{35} αβ	C_{35}(S)/C_{34}(S)	Ster/Hop x 10^5
MD_0	42.69	28.59	16.24	8.27	4.19	0.50	1.29
MD_1	40.15	27.06	19.19	8.59	4.99	0.60	1.20
MD_2	36.89	28.44	14.25	12.57	7.83	0.62	5.67
MD_6	41.24	25.38	16.56	10.28	6.53	0.60	2.65
MD_8	38.96	25.73	16.95	10.39	7.97	0.70	2.17

*C_{35}(S)/C_{34}(S) – ratio of C_{35} 17α(H)21β(H)22(S) hopane and C_{34} 17α(H)21β(H)22(S) hopane;
Ster/Hop = [Σ(C_{27}–C_{29})5α(H)14α(H)17α(H)(20S+20R)-steranes]/[Σ(C_{29}–C_{33})17α(H)21β(H)-hopanes].

Table 4 Maturation parameters calculated from the abundances of hopanes

Sample	Hopane Maximum	C_{30}mor/C_{30}hop	C_{31}αβ 22S/(22S+22R)	Ts/(Ts+Tm)	C_{29}Ts/C_{29}hop
MD_0	C_{30} αβ	1.00	0.58	0.18	0.14
MD_1	C_{30} αβ	0.30	0.57	0.20	0.18
MD_2	C_{30} αβ	0.18	0.58	0.38	0.35
MD_6	C_{30} αβ	0.15	0.63	0.50	0.34
MD_8	C_{30} αβ	0.19	0.58	0.52	0.33

*C_{30}mor/C_{30}hop – ratio of C_{30} 17β(H)21α(H)-moretane and C_{30} 17α(H)21β(H)-hopane; C_{31}αβ 22S/(22S+22R) – ratio of C_{31} αβ 22S and 22R epimers.

The value of the C_{30}mor/C_{30}hop ratio is ≥ 0.15 (Table 4) indicating that OM does not reach maturity which corresponds to vitrinite reflectance (%Rr ~ 0.70-0.75). On the other hand, the ratio of thermodynamically more stable 22S and less stable 22R epimers of C_{31} (Table 4) reached the equilibrium value of 0.57-0.62 [3]. This result implies an initial stage of catagenesis (%Rr ~ 0.60).

CONCLUSION

Based on the organic-geochemical approach, the following conclusions can be drawn: 1) The examined coal samples are low-rank subbituminous coal; 2) Precursor organic matter was predominantly of terrestrial origin, with certain marine influence (fluvial-deltaic environment) and was deposited under suboxic-oxidizing conditions; 3) Maturity of OM corresponds to late diagenesis/early catagenesis.

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