



Petrographic, palynofacies and geochemical characteristics of organic matter in the Saouef Formation (NE Tunisia): Origin, paleoenvironment, and economic significance

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ABSTRACT

Saouef lignite layers and carbonaceous shales are studied in order to reconstruct the origin and depositional environment of organic matter (OM), as well as to evaluate their economic potential. The study is based on organic compositions, bulk geochemical parameters, biomarker data, and carbon isotope composition of OM ($\delta^{13}\text{C}$). Lignite samples, collected next to the Saouef village, were macroscopically identified as stratified matrix coal or as humic coal. Rock Eval pyrolysis and the palynofacies analysis indicate the predominance of Type-III-IV kerogen (OM). The depositional environment fluctuated between terrestrial environments with a low water table to the limnic environment. The OM is derived from higher land plant remains (e.g. wood, root, bark) from a mixed vegetation including conifers and angiosperms, and emerged macrophytes. The dominance of huminite over liptinite and intertinite maceral groups, along with the phytoclasts, confirms the woody origin of the OM. A high bacterial activity is evidenced by the abundance of hopanoids in the extractable OM as well as by the amorphous OM content. The high measured TOC values exceeding 20 wt% in some samples may give an economic value of the organic layers of Saouef Formation. However, a $T_{\text{max}} < 435^\circ\text{C}$ and $R_r < 0.5\%$ induce the immaturity of the samples despite the presence of expelled bitumen in one sample.

1. Introduction

Lignite deposits in Tunisia occur in Cretaceous, Oligocene, and Miocene strata. However, only the Miocene lignites belonging to the Saouef Formation (Fm) are of greater geographical extension (Abbes, 1981, 1983). Saouef lignite layers were the object of several studies since 1922 in order to assess their economic utility as fossil fuels. Studies were resumed later by the SOREMIT (Société Mixte founded to establish a detailed study about lignite and coal resources) in 1939, and then by the National Mines Office in 1981. The studies revealed that the lignites of the Saouef Fm show a generally high ash yield (16%–70%; Freiberg, 1984) which restrict their utility as a combustible fossil fuel to the crises period.

The previous studies essentially were based on proximate analysis (moisture contents, ash and volatile matter yields, fixed carbon contents) and calorific values. Maceral composition, palynofacies and biomarker analyses are increasingly used for lignite/coal assessment and paleogeothermal reconstruction, as well as for the characterization of the peat-forming environment (Tyson, 1995; Batten, 1996; Taylor

et al., 1998; Kalaitzidis et al., 2004; Bechtel et al., 2005; Mendonça Filho et al., 2012; Suárez-Ruiz et al., 2012; Singh et al., 2017a,b,c; and many more). In the present study, the paleoecological (i.e. vegetation, climate) and paleoenvironmental conditions during deposition of the Saouef lignite layers in Tunisia, as well as their hydrocarbon potential, are evaluated first time by the combined petrographic, palynofacies and organic geochemical methods.

2. Geological setting

The Oligo-Miocene is characterized by a general extension expressed by a synsedimentary normal NW-SE faulting system (Philip et al., 1986) generating extensional basins (Rouvier, 1977). Thick continental to shallow marine silicoclastic sediments deposited during subsidence of the basins (Blondel, 1991; Bedir, 1995). The upper Miocene is marked by the rise of the Atlas orogeny in the Maghreb region due to the Africa-Europe collision causing the reversion of the extensional basins (Rouvier, 1977; Turki, 1985; Ben Ayed, 1986; Bedir, 1995). Tunisia was exposed to a NW-SE oriented compression during

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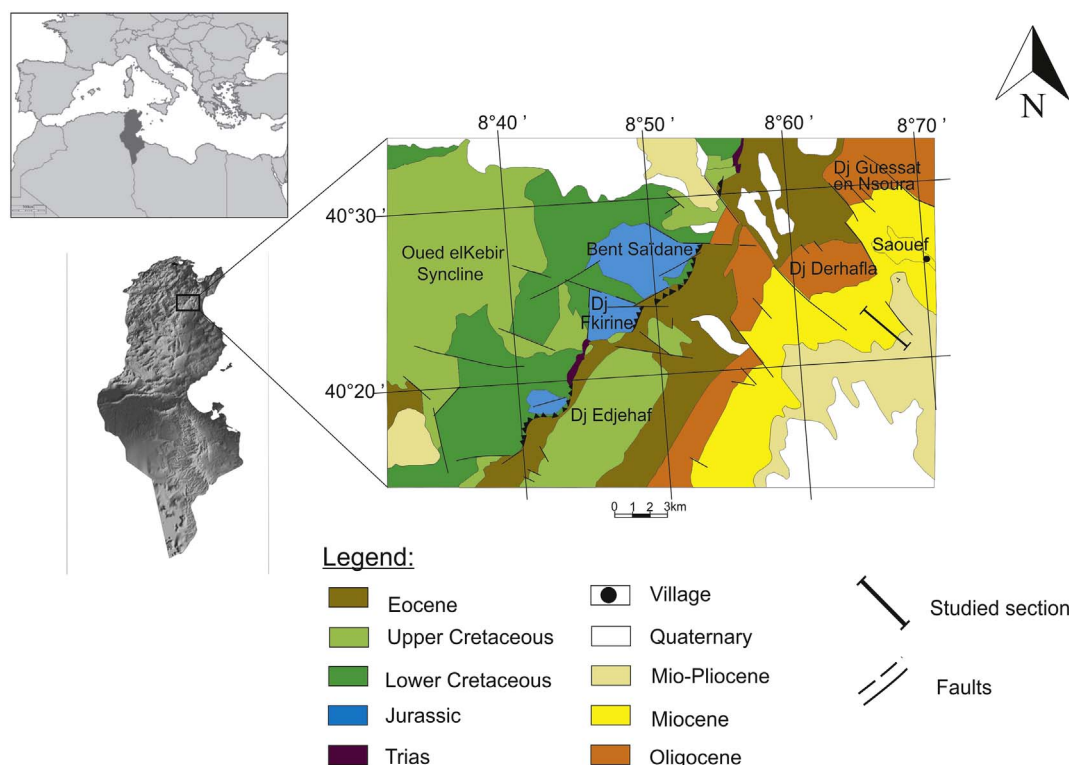


Fig. 1. Geographic location of the Saouef Syncline and the studied section (Freiberg, 1984, modified).

the Tortonian.

The Saouef Formation in the Saouef Syncline (Fig. 1) represents a regressive megasequence (Biely et al., 1972) resting directly on a transgressive shaly sequence known as Mahmoud Formation. The Saouef Fm contains alternating successions of fine sandstone and dark grey to brown clay with the presence of oysters and lignite layers, deposited in paralic basin. It was attributed by Hooyberghs (1977) to the Tortonian due to the presence of *Globorotalia acostaensis*. However, Bismuth (1984), Tayech (1984), and Mannai-Tayech et al. (1992, 1995) proposed a Serravallian-early Tortonian age. The important geographical extension and thickness of the Saouef Fm, reaching 2000 m thickness in Sahel areas, reflect the important subsidence during its deposition, during Oligo-Miocene (Blondel, 1991; Bedir, 1995). Based on the sequence analyses, the Saouef Fm is subdivided into units deposited during progradation and retrogradation, respectively. The subdivision was sometime a subject of controversy between authors, but it was an agreement that the lignite and carbonaceous deposit should be included in one unit (Abbes, 1983; Abbes, 1981; Mannai-Tayech, 2006, 2009; El Euch El Kondi, 2007; Ayadi, 2013; Moktar and Mannai-Tayech, 2014).

During this work, we are adapting the subdivision of Mannai-Tayech (2009) who divided the Saouef Fm into 4 units (Fig. 2): Unit I—first sandy deposits overlying on Mahmoud Clay, attributed also to the Beglia Fm by Abbes, 1981; Abbes, 1983. Unit II— is characterized by alternation between sandy bars with shale intervals. Unit III— the main subject of this work and characterized by the lignite and carbonaceous deposits within the alternation of sands and shales. This unit is further divided into 2 subunits: a and b, where in the Unit IIIa shales are dominating sands, and in the Unit IIIb sands are dominating shales. Unit IV— the last unit and is known as the shaly roof of the Saouef Fm, where this regressive Fm is sealed by a shaly interval.

The studied section (Fig. 3) has been taken from the Saouef Syncline (Fig. 1) where the Formation was defined for the first time. The syncline is located in the central north of Tunisia and oriented NE-SW. The Plio-Quaternary occupy the core of the syncline, which is inserted within the meridional termination of the Tunisian Dorsal to the west (presented in

this area by Bent Saidanen, Fkirine and Edjahaf mountains) and to the east by the Draa Souatir anticline, shown as Cretaceous domes in the geological map.

3. Materials and methods

The Miocene sedimentary OM was deposited mainly during the Serravallian-early Tortonian in the study area. The OM-bearing sediments include lignite layers and carbonaceous shales, are present mainly in the third unit of the Saouef Fm. The lithological section was next to the Saouef village (Fig. 1). The section covered the third unit of the sequence, and 17 samples were collected from the lignite and carbonaceous shale layers (Fig. 3). The samples were taken after digging of at least 20 cm to avoid the altered sediments and recent organic contaminations.

3.1. Carbon and sulphur analysis

Total carbon (TC) and sulphur (TS) contents of all the samples were determined on pulverized sample material (100–150 mg) using an Eltra Helios C/S Analyser. Samples were pretreated with 50% Hydrochloric acid to discard the inorganic carbon. 2 standards are loaded (coal standard for Sulphur content and calcite sample for carbon content) in order to calibrate the device. Then, Samples are loaded one by one into the combustion furnace. The programmed temperature starts from 1 °C a 1550 °C maximum. Samples are burnt in an oxygen atmosphere at 1550 °C. The combustion gasses (CO₂, H₂O, SO₂) coming from the furnace pass through a dust filter. The water vapor is chemically absorbed. CO₂ and SO₂ gas are detected in the additional infrared cells.

3.2. Rock Eval pyrolysis

Pyrolysis analysis (Espitalié et al., 1977) was performed on all samples using a Rock Eval 6 analyzer. Depending on the TOC content, 10 to 50 mg of each pulverized samples were heated gradually in an inert atmosphere.

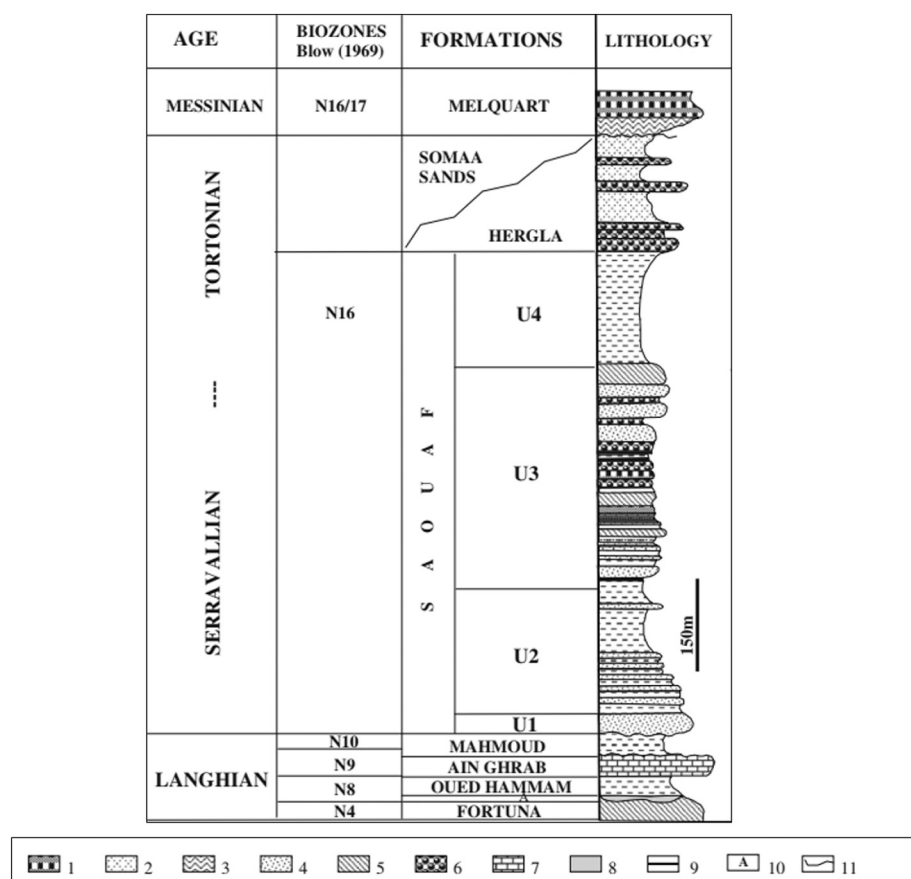


Fig. 2. Summary representation of the lithostratigraphy of the Miocene series, compared with the results concerning sedimentation and eustasy in the Cap Bon and Saouaf areas, and from well cuttings in the Gulf of Hammamet (Mannai-Tayech, 2009, modified).

Legend — (1) Bioclast and oolite-bearing limestones, (2) Sands and red silts, (3) Messinian Gypsum, (4) Sands and sandstones, (5) Sandy clays, (6) Conglomerates, (7) Glauconite-bearing limestones, (8) Clays (Horizon A), (9) Lignite, (10) Horizon A, and (11) Unconformity.

3.3. Petrographic analysis

The maceral composition (vol%) and huminite (ulminite) random reflectance (% R_r) were estimated exclusively on lignite samples. Polished particulate pellets were prepared from crushed sample fragments of 1 mm size according to the ISO 7404-2 (2009), ISO 7404-3 (2009), ISO 7404-5 (2009) norms, and the ICCP nomenclatures (ICCP, 2001; Šýkorová et al., 2005; Pickel et al., 2017). The Leica DM4500P microscope was used for maceral analysis and reflectance measurements using the Petroglite 2.35 and MSP 200 software, respectively. The macerals were counted under white reflected light and blue-light excitation using the single-scan method.

3.4. Palynofacies analysis

The palynofacies analysis including the qualitative and quantitative assessment of the OM (kerogen) was performed using the microscopic observations under transmitted white light. The samples were treated by hydrochloric acid (HCl) and hydrofluoric acid (HF) to dissolve the mineral matter (carbonate and silica contents). The organic residue was used to mount slides for observation according to Batten (1996) and Batten and Stead (2005). At least 300 counts of particulate OM were carried out on each slide for the quantitative analysis. The classification of OM groups and subgroups follows the scheme proposed by Tyson (1995) and Mendonça Filho et al. (2010, 2011).

3.5. Organic geochemical analysis

The bituminous fraction was extracted from powdered samples via Dionex ASE 200 accelerated solvent extractor using dichloromethane (DCM) as an organic solvent for 1 h at 75 °C and 75 bar. For the elimination of the elemental sulphur, copper was added before the

extraction process. After evaporation of the solvent to 0.5 ml total solution in a Zymark TurboVap 500 closed cell concentrator, asphaltene were precipitated from a hexane-DCM solution (80:1) and separated by centrifugation. The hexane-soluble organic matter was separated into NSO compounds (polar fraction, which contains nitrogen, sulphur, and oxygen compounds), saturated hydrocarbons and aromatic hydrocarbons using medium pressure liquid chromatography (MPLC) with a Köhnen-Willisch MPLC instrument (Radke et al., 1980).

The saturated and aromatic hydrocarbon fractions were analyzed by a gas chromatograph (Trace-GC; ThermoScientific) equipped with a 30 m DB-1 fused silica capillary column (i.d. 0.25 mm; 0.25 µm film thickness) and coupled to a ThermoScientific ISQ quadrupole mass spectrometer. The oven temperature was programmed from 70° to 300 °C at a rate of 4 °C min⁻¹ followed by an isothermal period of 15 min. Helium was used as carrier gas. Samples were injected splitless while the injector temperature was 275 °C. The mass spectrometer was operated in the EI (electron ionisation) mode over a mass range from m/z 50 to m/z 650 (0.5 s total scan time). Data were processed with a Xcalibur data system. Identification of Individual compounds were identified based on retention times in the total ion current (TIC) chromatogram and comparison of the mass spectra with published data. Relative percentages and absolute concentrations of different compounds were calculated using peak areas in the TIC chromatograms in relation to those of internal standards (deuterated *n*-tetracosane and 1,1'-binaphthyl, respectively), or by integration of peak areas in appropriate mass chromatograms using response factors to correct for the intensities of the fragment ion used for quantification of the total ion abundance. The concentrations were normalized to the TOC content.

3.6. Carbon isotope analysis

For carbon isotope analyses, powdered samples were treated with

Saouef Section

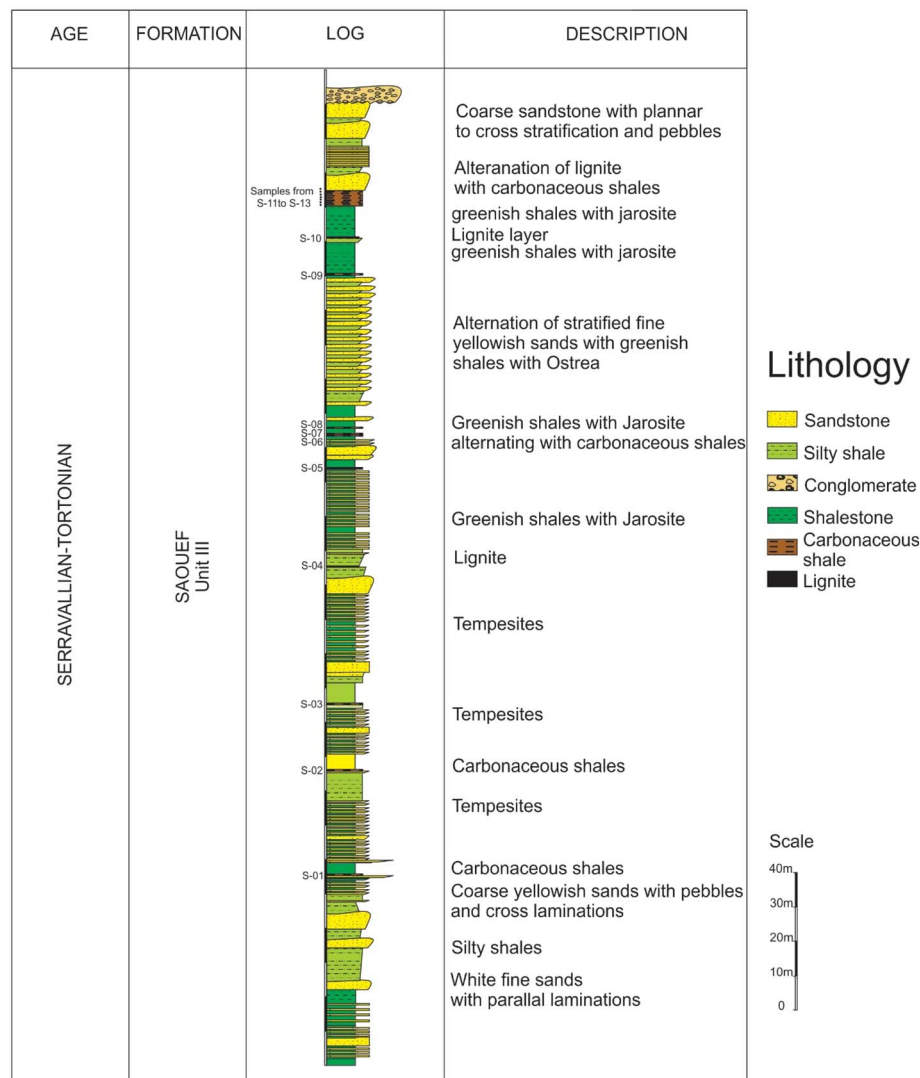


Fig. 3. Lithostratigraphic column of the Unit III of the studied Saouef section.

HCl acid to remove inorganic carbon. De-carbonated samples were placed into tin foil boats and combusted using an elemental analyser (Flash EA 1112) at 1020 °C in an excess of oxygen. The resulting CO₂, separated by column chromatography, was analyzed online by a ThermoFisher DELTA-V isotope ratio mass spectrometer. The ¹³C/¹²C isotope ratios of the CO₂ were compared with the corresponding ratio in a monitoring gas, calibrated against the Vienna-Pee Dee Belemnite (V-PDB) standard by the NBS-19 reference material. Stable isotope ratios are reported in delta notation (δ¹³C, Coplen, 2011) relative to the V-PDB standard. The reproducibility of the total analytical procedure is in the range of 0.1–0.2‰.

4. Results

4.1. Bulk geochemical data

The total organic carbon (TOC) contents range between 1.06 wt% and 21.45 wt% (Table 1). Samples S-04, S-08, S-10, S-14 and S-16 show high and eloquent TOC values. Total sulphur (TS) contents vary in the wide range between 0.09 wt% and 3.66 wt%. The TOC normalized yields of extractable organic matter (EOM) vary between 7.86 mg/g TOC and 39.86 mg/g TOC, as typically obtained from immature sediments. The extracts of all samples are dominated by NSO compounds

(22–65% of EOM) and asphaltenes (8–75% of EOM). The proportion of hydrocarbons is low. Saturated hydrocarbons are predominant over aromatic hydrocarbons in most samples, and the relative percentages of both together vary between 2 and 20% of the EOM (Table 1), as typical for sediments and coals of low maturity (Tissot and Welte, 1984).

Rock Eval pyrolysis revealed low contents of free hydrocarbons (S1: 0.04–0.77 mg HC/g of rock). The potential hydrocarbon contents, represented by the S2, show higher values and vary between 0.22 and 21.16 mg HC/g rock. Hydrogen index (HI) values below 100 mg HC/g TOC are obtained (Fig. 4). T_{max} values rarely exceed 435 °C, supporting the presence of immature OM (Table 1).

4.2. Petrographic composition

The studied Saouef samples have been classified as stratified matrix coal (Taylor et al., 1998), or as a humic coal (Combaz, 1980). However, the main organic matter rich layers consist mainly of carbonaceous shales (mineral-rich coal; Taylor et al., 1998). The microscopic examination of such samples (Fig. 5; Table 2) shows that the carbonaceous samples S-8, S-15 and S-17 contain high amounts of mineral matter (55, 54, and 43 vol%, respectively) and low percentages of pyrite (< 4 vol%). However, lignite samples S-4, S-5 and S-10 show lower percentages of mineral matter (7.8, 25 and 8.5 vol%,

Table 1

Bulk organic geochemical data of the studied samples from the Saoeuf section.

Sample	TOC	Total S	S ₁	S ₂	HI	PI	T _{max}	EOM	Sat. HC	Aro. HC	NSO	Asphaltenes	Δ ¹³ C	TOC/S
	(wt%)	(wt%)	[mg HC/g]	[mg HC/g]	[mg HC/g TOC]		[°C]	(mg/g TOC)	(%. EOM)	(%. EOM)	(%. EOM)	(%. EOM)	(‰/‰, PDB)	
S-01	1.53	0.09	0.035	0.435	28.45	0.07	436	27.05	11.4	1.7	28	59	−25.16	16.86
S-02	1.88	0.17	0.06	0.29	15.39	0.17	443	30.25	3.2	0.3	38	59	−25.28	11.09
S-03	4.33	0.24	0.12	1.715	39.60	0.07	427	23.29	6.2	3.3	38	52	−25.18	18.26
S-04	16.71	1.47	0.29	7.985	47.79	0.04	417	16.40	3.0	4.3	41	52	−24.99	11.34
S-05	2.67	3.66	0.31	12.19	56.82	0.02	411	21.05	3.4	3.2	55	39	−25.1	5.86
S-06	1.06	0.22	0.05	0.255	24.12	0.16	428	39.76	8.2	0.2	48	44	−25.1	4.88
S-07	2.21	0.32						34.30	5.9	3.3	33	58	−24.78	6.86
S-08	13.04	0.80	0.77	9.725	74.57	0.07	425	36.23	3.3	1.5	44	52	−24.9	16.33
S-09	8.42	1.31	0.165	3.96	47.05	0.04	414	17.47	5.9	0.7	56	38	−25.97	6.45
S-10	20.57	1.81	0.68	21.155	102.83	0.03	413	21.03	2.1	0.5	22	75	−26.24	11.35
S-11	3.15	0.19	0.225	0.835	26.53	0.21	429	24.09	3.4	3.5	36	57	−26.29	16.14
S-12	1.16	0.52	0.095	0.215	18.49	0.31	420	35.69	6.2	8.4	57	28	−25.61	2.25
S-13	1.40	0.27	0.065	0.225	16.11	0.22	429	19.91	2.5	5.7	66	26	−25.52	5.21
S-14	2.19	0.28	0.065	0.425	19.39	0.31	420	10.77	5.2	8.4	36	51	−26.19	7.79
S-15	3.14	1.17	0.16	0.61	19.41	0.21	392	10.77	4.28	2.98	56.3	36.44	−26.45	2.69
S-16	2.61	2.20	0.055	0.275	10.55	0.17	397	7.85	1.9	7.1	83	8	−26.09	1.19
S-17	7.9	2.9	0.1	0.4	14.9	0.1	384	12.2	5.4	0.2	38.4	55.9	−25.6	2.76
Total average	6.63	1.03	0.19	3.60	34.14	0.13	420.85	23.90	4.60	3.29	46.52	45.58	−25.56	8.66

TOC = Total organic carbon, Total S = Total Sulphur, S₁ = Free hydrocarbon peak, S₂ = Potential hydrocarbon peak, HI = hydrogen Index, PI = Production index, EOM = Extracted organic matter, Sat.HC = Saturated hydrocarbons, Aro.HC = Aromatic hydrocarbons.

respectively). Framboidal pyrite accounts are important and constitute one of the major mineral component in the lignite samples S-4, S-5 and S-10 with 2.6, 2.10 and 5.2 vol%, respectively.

Maceral analysis reveals that lignite and carbonaceous samples are

composed mainly of macerals of the huminite group (Table 2). Only in sample S-8, inertinite group predominates. Amongst huminite, telohuminite (exclusively ulminite) dominates over detrohuminite in the lignite. Average percentages of telohuminite are 69 vol% in lignite

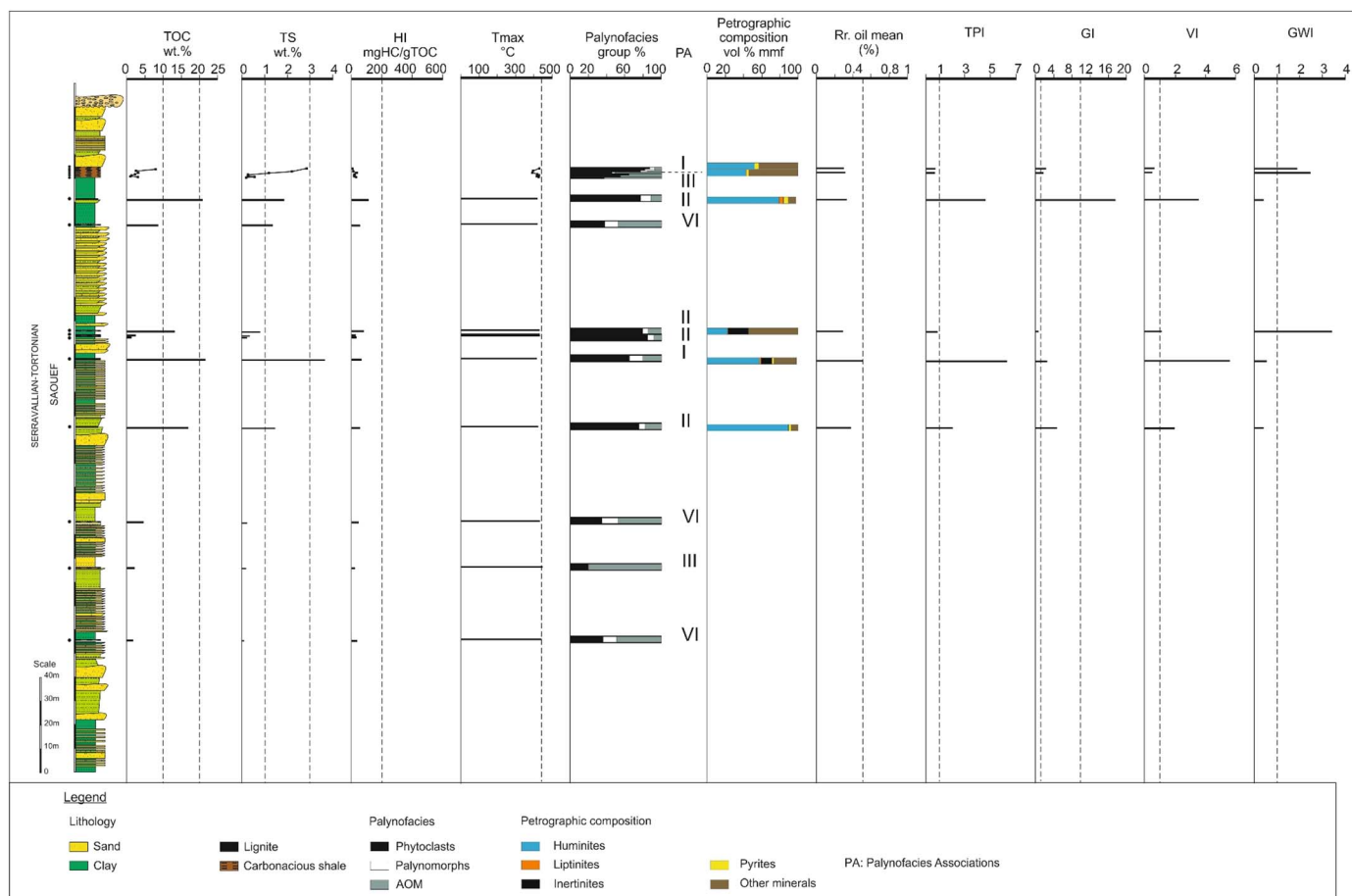


Fig. 4. Section profile including the TOC, TS, HI and T_{max} variations, palynofacies composition and different palynofacies associations, petrographic composition and the measured R_r, and the petrographic indices (TPI, GI, VI and GWI).

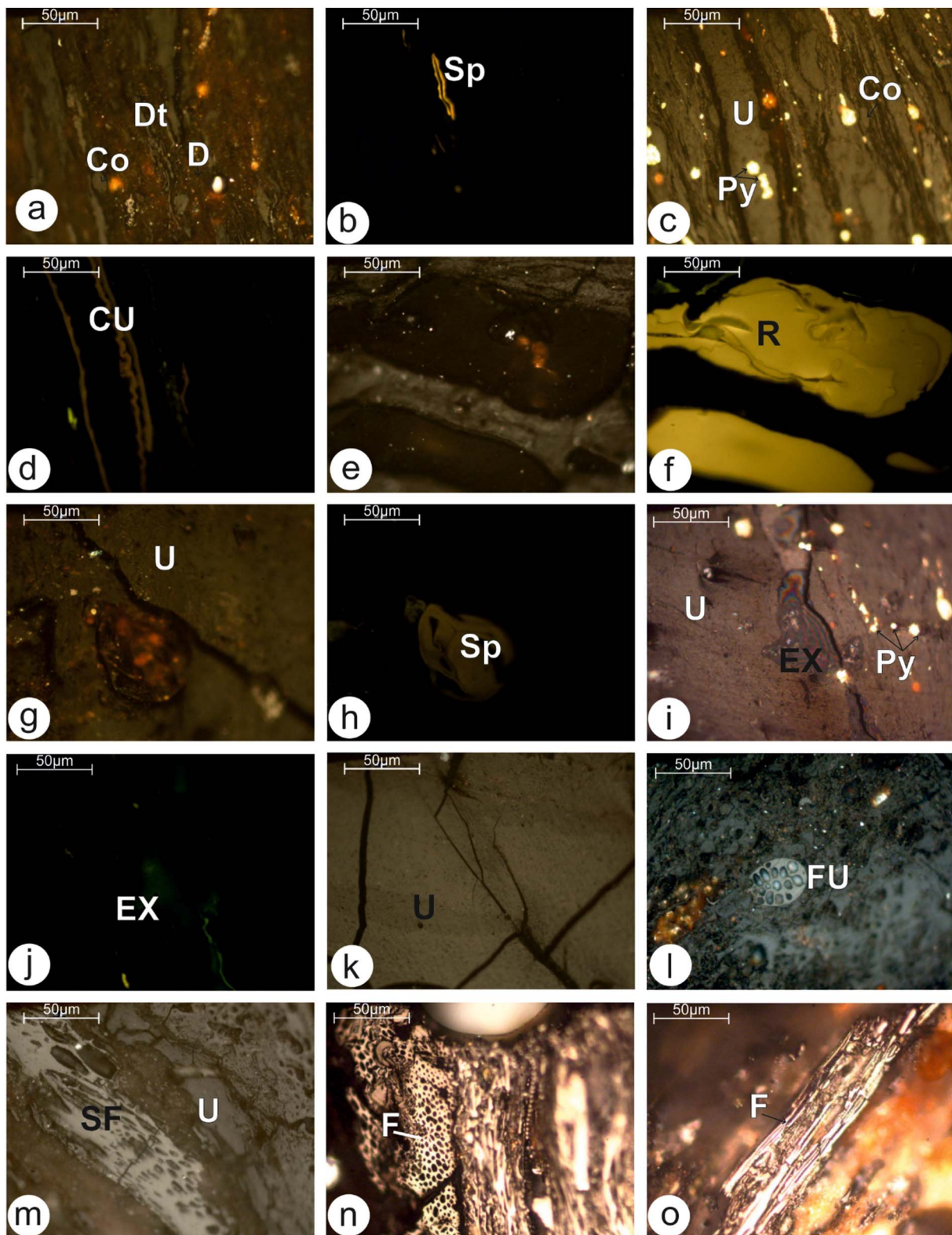


Fig. 5. Representative micrographs of macerals and associated minerals of the Saouef lignites: a) huminite group (Co: Corpohuminite, Dt: detrohuminite, U: ulminite), b) sporinite (Sp), c) huminites associated with framboidal pyrites (Py), d) cutinite (CU), e–f) resinite (R), g–h) sporinite, i–j) exsudatinite (EX), k) ulminite, l) funginite (FU), m) semifusinite (SF), n–o) Fusinite (F). Photomicrographs taken under incident white light (a,c,e,g,i–l) and blue light excitation (b,d,f,h). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

samples and 28 vol% in carbonaceous shale samples. Macerals of the detrohuminite subgroup (35.5 vol% on average) include attrinite (av. 20 vol%) and densinite (av. 15 vol%). Majority of the attrinite and densinite macerals show a weak brown fluorescence. In contrast to the

lignite samples, detrohuminites are present in higher percentages compared to telohuminites in the carbonaceous shales. Macerals of the gelohuminite subgroup are present in low contents with highest percentages of corpohuminite (av. 3 vol%).

Table 2
Maceral composition (vol%, mineral matter-free), random reflectance (% R_r) and petrographic indices of the Saouef samples.

Sample	T	U	TH	A	D	DH	Co	Ge	GH	TH	Sp	Cu	Su	R	TL	Sf	F	Fu	ID	TI	Py	Om	TM	Rr	GI	TPI	GWI	VI
S-04	0.00	64.51	64.51	17.41	15.74	33.15	1.79	0.00	1.79	99.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.56	0.00	0.56	2.60	7.80	10.40	0.37	4.57	2.00	0.36	1.95
S-05	0.00	66.43	66.43	11.94	0.70	12.64	1.54	0.00	1.54	80.62	1.54	0.00	0.00	0.70	2.95	4.49	11.24	0.70	0.00	16.43	2.10	25.00	27.10	0.5	2.42	6.27	0.51	5.57
S-08	0.00	20.26	20.26	18.06	9.47	27.53	1.10	0.00	1.10	48.90	1.10	0.00	0.00	0.00	1.10	14.98	15.86	0.00	19.16	50.00	0.00	54.60	54.60	0.28	0.45	0.80	3.41	1.07
S-10	0.00	76.46	76.46	4.52	12.25	16.77	0.59	0.00	0.59	93.82	3.33	1.66	0.00	0.59	5.59	0.00	0.00	0.59	0.00	0.59	5.20	8.50	13.70	0.33	17.47	4.60	0.36	3.54
S-15	0.00	27.71	27.71	39.03	22.17	61.20	9.70	0.00	9.70	98.61	1.39	0.00	0.00	0.00	1.39	0.00	0.00	0.00	0.00	0.00	2.40	54.20	56.60	0.31	1.53	0.61	2.44	0.44
S-17	0.00	35.19	35.19	31.92	29.62	61.54	3.27	0.00	3.27	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.60	43.40	48.00	0.29	2.13	0.63	1.87	0.57
Total average	0.00	48.43	48.43	20.48	14.99	35.47	3.00	0.00	3.00	86.90	1.23	0.28	0.00	0.22	1.84	3.25	4.52	0.31	3.19	11.26	2.82	32.25	35.07	0.35	4.76	2.49	1.49	2.19

T = Textinite, U = Ulminite, TH = Telohuminitite, A = Attrinite, D = Densinite, DH = Detrohuminitite, Co = Corpohuminitite, Ge = Gelinite, GH = Gelohuminitite, TH = Total huminitite, Sp = Sporinite, Cu = Cutinite, Su = Suberinitite, R = Resinite, TL = Total liptinite, Sf = Semifusinite, F = Fusinite, Fu = Funginitite, ID = Inertodetrinite, TI = Total inertinite, Py = Pyrite, Om = Other mineral matter, TM = Total mineral matter.
 GI (Gelification Index) = Ulminite + Densinite + Corpohuminitite + Gelinite/Textinite + Attrinite (Kalaizidis et al., 2000).
 TPI (Tissue Preservation Index) = Textinite + Ulminite + Corpohuminitite + Fusinite/Attrinite + Densinite + Gelinite + Inertodetrinite (Kalaizidis et al., 2000).
 GWI (Ground Water Index) = Densinite + Corpohuminitite + Gelinite + mineral matter/Textinite + Ulminite + Attrinite (Kalaizidis et al., 2000).
 VI (Vegetation Index) = Textinite + Ulminite + Suberinitite + Resinite + Fusinite + Semifusinite/Attrinite + Densinite + Sporinite + Cutinite + Alginite + Bituminite + Liptodetrinite + Inertodetrinite (Kalaizidis et al., 2000).

Liptinite group macerals are important for characterizing the oil potential of a source rock. This maceral group is present in low relative abundances in the studied samples and ranges between 0 and 6 vol%. The group is represented by sporinite, cutinite, and resinite, derived from spores/pollen grains, leaves, and resins of land plants, respectively. The presence of few Exsudatinite grains (Fig. 5i,j) was noticed within ulminite cracks during the scanning of the sample S-10 (observed during reflectance measurement). This sample contains enhanced percentage of liptinite.

Macerals of the inertinite group are present in relative percentages between 0 and 50 vol%, with an average of 11 vol% of the macerals content. This group is mainly presented by fusinite (av. 4.52 vol%), which is characterized by bright and well-preserved cells. Semifusinite maceral (av. 3.25 vol%) is present in the form of grayish well-preserved cells.

There have been several suggestions to characterize coal facies on the basis of maceral ratios. For example, Diessel (1986, 1992) introduced a tissue preservation index (TPI), which emphasizes degrees of tissue preservation vs. degradation, and a gelification index (GI) contrasting gelified and ungelified macerals. This concept, originally developed for Permian coals, was adopted by Kalkreuth et al. (1991) and Kalaizidis et al. (2000) for the Cenozoic low rank coals. The TPI indicates the degree of humification of the OM, as well as the contribution of wood to the peat formation. The GI indicates the relative dryness or wetness of the peat-forming environment. TPI of the Saouef samples ranges from 0.6 to 6.27, whereas the GI ranges from 0.45 to 17.47 (Table 2, Fig. 4). The GI showing mostly high values except for S-08 sample.

Calder et al. (1991) defined the vegetation index (VI) and the ground water index (GWI). The VI provides information about the contribution of the forest vegetation versus the herbaceous and aquatic plants to peat-formation. However, the GWI define the water table by calculating the detrital macerals and mineral matter proportion compared to the structured macerals (Stock et al., 2016). The VI values of the Saouef samples range from 0.44 to 5.57 and indicate changing herbaceous to forest vegetation. The obtained values for the GWI vary between 0.36 and 3.41, reflecting significant changes in the water table (Fig. 4, Table 2).

4.3. Palynofacies composition

The palynofacies analysis revealed the presence of all three main groups of particulate organic matter– phytoclasts, amorphous OM, and palynomorphs (Fig. 6, Table 3). The phytoclasts group is dominating the kerogen, and range between 19.5% and 86.9% with an average of 59.5% of the total organic particles. Phytoclasts group is represented mainly by biostructured phytoclasts, non-biostructured phytoclasts, and pseudo-amorphous phytoclasts. Biostructured phytoclasts exhibit visible internal structures which change from a sample to another and appear in dark brown, orange to pale yellow color. Brown translucent particles with no internal structures are classified as non-biostructured components. Pseudo-amorphous phytoclasts show diffuse to irregular outlines, homogenous features, dark brown to dark orange color. Mycelium filaments classified as fungal hyphae show a minor contribution in the organic matter and are occasionally appear associated to AOM and pseudo-amorphous phytoclasts. Opaque phytoclasts of black color are present as lath, corroded shaped particles. Cuticles show as well a slight contribution to the organic matter and show a yellowish color and regular outlined cells.

The AOM group contains structureless particles, including the amorphous products and the resins. Typical AOM are mostly derived from phytoplankton or is of bacterial origin (Tyson, 1995; Mendonça Filho et al., 2012). Resins occur as structureless round and homogeneous particles, produced by terrestrial higher plants. The amorphous products dominate the AOM group and exhibit diffuse outlines with structureless feature, light to dark brown in color. The studied samples

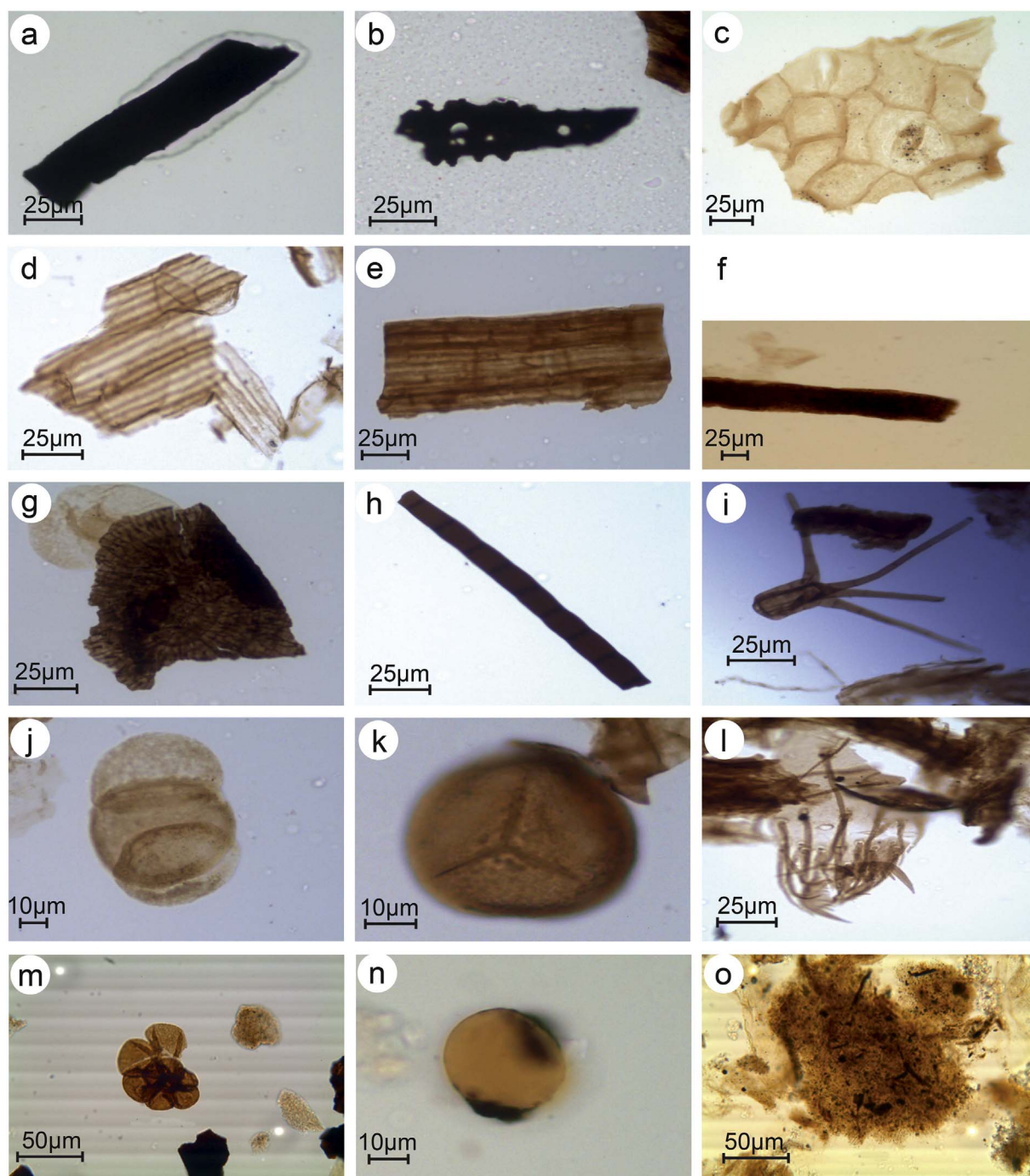


Fig. 6. Photomicrographs of palynofacies components: a–b) opaque phytoclasts, c) cuticle, d–e) biostructured phytoclasts, f) pseudoamorphous phytoclast, g–h–i) fungal, j–k) spore and pollen grains, l) zooclasts, m) zoomorph, n) resin, o) AOM terrestrially derived.

show that the AOM group is the subdominant group. AOM group percentages range between 7.7 and 97.7% (32.8% on average).

Organic-walled microfossils entirely composed of unmineralized proteinaceous material built up the group of palynomorphs (Mendonça Filho et al., 2012). Palynomorphs are minor constituents of the samples (7.39% on average) and constituted mainly by sporomorphs (spore and pollen grains) associated with a minor appearance of zoomorph like foraminiferal test linings besides the presence of some phytoclasts.

The statistical data were used to elaborate the AOM-Phytoclast-Palynomorph diagram (based on APP Tyson diagram, Tyson, 1995) in order to evaluate schematically the abundance of each group within samples (Fig. 12). Based on the kerogen associations and composition and the degree of similarity between the particulate organic

components, 4 palynofacies assemblages were determined.

Palynofacies assemblage I characterized by high phytoclast contents with an average of 77.62%. Structured phytoclast subgroup dominates the phytoclast group and shows large particles of light orange to pale yellow striped, banded and striated phytoclasts, as well as few, pitted biostructured phytoclasts. AOM and palynomorph group show a minor contribution with 13% and 9.31% averages respectively. The AOM group is composed mainly of amorphous products of light brown to orange color with diffuse outline and no internal structure.

Palynofacies assemblage II dominated also by phytoclasts (79.12%, average) with a minor contribution of palynomorphs (7.5% average) and AOM (13.34% average). However, the phytoclast group is dominated by non-biostructured and pseudo-amorphous phytoclasts

Table 3
Palynofacies composition of the studied samples from the Saouef section.

Samples	%Phytoclastes	%Palynomorphs	%AOM	Palynofacies association
S_01	36.44	14.98	48.58	VI
S_02	19.58	0.70	79.72	III
S_03	34.66	17.47	47.87	VI
S_04	75.14	6.74	18.11	II
S_05	64.79	14.52	20.69	I
S_07	84.52	6.74	8.74	II
S_08	79.78	5.29	14.93	II
S_09	37.80	14.34	47.86	VI
S_10	77.04	11.40	11.56	II
S_11	37.12	0.00	62.88	III
S_12	54.74	0.00	45.26	III
S_13	64.01	0.17	35.82	III
S_14	45.58	3.15	51.26	III
S_15	76.95	7.12	15.93	I
S_16	81.79	10.48	7.73	I
S_17	86.96	5.10	7.94	I
Total average	59.81	7.39	32.81	
Av. PA I	77.62	9.31	13.07	
Av. PA II	79.12	7.54	13.34	
Av. PA III	44.21	0.80	54.99	
Av. PA VI	36.30	15.60	48.10	

PA: palynofacies association.

subgroups. The non-biostructured phytoclasts show brown to dark brown color, lath to equant shape with no botanical structure. The pseudo-amorphous phytoclasts are homogenous in appearance with orange to brown color, show a subangular shape and diffuse outlines. The AOM group is composed of amorphous products of light brown to orange color with diffuse outline with no internal structure.

Palynofacies assemblage III display a subdominance between the phytoclasts group and the AOM group (44.21% and 55% averages respectively) with a minor contribution of palynomorphs (0.8% average). Phytoclasts are represented mainly by non-biostructure phytoclasts with brown to the dark brown color associated with pseudo-amorphous phytoclasts. AOM is essentially expressed amorphous products of brown to orange color, diffuse outline and shows no internal structure.

Palynofacies assemblage VI show a slight dominance of AOM (45% average) over phytoclasts (36.3%). Yet this assemblage differs from the previous one by the increase of the palynomorphs group contribution (15.6% average).

4.4. Molecular composition

Gas chromatography-Mass spectrometry revealed that the saturated hydrocarbons are dominated by *n*-alkanes, hopanes, and non-hopanoid triterpenoids, the latter derived from angiosperm precursors. Diterpenoids, sesquiterpenoids, and sterenes are present in lower amounts or absent in some samples. Sesquiterpenoids are more widespread in the aromatic fractions in comparison to hopanoids, diterpenoids, and angiosperm-derived triterpenoids.

4.4.1. *n*-alkanes, isoprenoids

The *n*-alkanes are present in the C₁₅ to C₃₅ range, and long chain *n*-alkanes with odd-carbon numbers (Fig. 7, Table 4) and maxima at *n*-C₂₉ or *n*-C₃₁ predominate. Mid-chain alkanes (*n*-C₂₁-C₂₅) are also present in high abundances in most of the samples. However, short chains *n*-alkanes ($\leq n$ -C₂₀) occur in low concentrations. The acyclic *n*-C₁₉ and *n*-C₂₀ isoprenoids pristane (Pr) and phytane (pH) are identified in all samples with an alternation of predominance from a sample to another. Pr/Ph ratios range between 0.63 and 1.32 (Table 4).

The carbon preference index (CPI, according to Bray and Evans, 1961) ranges between 3.46 and 7.47. The P_{wax} or proxy wax is a ratio proposed by Zheng et al. (2007) in order to rate the waxy hydrocarbons derived from land plants relative to *n*-alkanes from macrophytes plus

terrestrial plants. P_{wax} shows values between 0.63 and 0.95 (Table 5, Fig. 9), and confirm the important contribution of land plants. Ficken et al. (2000) defined the P_{aq} for submerged/floating aquatic macrophyte input versus emergent and terrestrial plant input. P_{aq} ranges from 0.09 to 0.42. The ratio of terrigenous vs. aquatic *n*-alkanes (TAR defined by Bourbonniere and Meyers (1996) shows values higher than 1 (Table 5).

4.4.2. Steroids, hopanoids

Steroids are present in low abundances in all the studied samples. The C₂₉-(Δ^4 , Δ^5)-sterenes predominate by far over the C₂₇ homologues. The corresponding diasterenes (C₂₇, C₂₉) are also found in low quantities. The TOC-normalized amounts of the sum of steroid compounds identified are given in Table 6. The concentration ratios of diasterenes over sterenes are lower than 1 in most samples.

While algae are the biological source of C₂₇ sterols, the predominant primary producers of C₂₉ sterols are photosynthetic organisms, including land plants (Volkman, 1986). Also, freshwater microalgae like ulvophytes and early diverging freshwater prasinophyte produce high abundances of C₂₉ sterols. Other plausible candidates include the glaucocystophytes and early divergent red algae (Kodner et al., 2008).

Hopanoids are important constituents of the non-aromatic cyclic triterpenoids of the lignite and shale samples (Table 7). The hopanoid patterns are characterized by 17 β , 21 β -, and minor 17 α , 21 β -type hopanes from C₂₇ to C₃₂, with C₂₈ absent (Fig. 7). The predominant hopanoid in the samples is the $\alpha\beta$ -C₃₀ hopane and the hop-17(21)-ene, respectively. Furthermore, the neohop-13(18)-ene is present as well as minor amounts of trisnorhop-17(21)-ene. In the aromatic hydrocarbon fractions, a series of C₃₂- to C₃₄-benzohopanes cyclised at C-20 (Hussler et al., 1984) is identified in several samples (Fig. 8).

The main biological precursors of the hopanoids are the bacteriohopanepolyols (Ourisson et al., 1979; Rohmer et al., 1992) identified in bacteria and some cryptogames like moss and ferns. The occurrence of saturated hopanes and of the C₃₂ to C₃₄ benzohopanes in the aromatic fractions, suggest a significant contribution of the microbial biomass to the OM of the peat. The hop-17(21)-ene is present in most of the samples. Its precise biological precursor is still a matter of controversy. However, hop-17(21)-ene generally occurs in immature coal samples (Bechtel et al., 2003, 2005).

4.4.3. Sesquiterpenoids, diterpenoids, angiosperm-derived triterpenoids

Sesquiterpinoids occur in very low concentrations in the hydrocarbon fractions (Table 8). Saturated hydrocarbons include cadinane type, drimane, homodrimane, cedrane and eudesmane. Aromatic fractions contain sesquiterpenes of the cadalene-type in slightly higher abundances (Simoneit and Mazurek, 1982; Figs. 7 and 8). In all samples, diterpenoids occur in variable abundances. The saturated diterpenoids consist of compounds of the pimarane-, phyllocladane- and kaurane-type (Hagemann and Hollerbach, 1979; Noble et al., 1985; Philp, 1985). Pimarane and norpimarane are present in all the samples, whereas beyerane, 16 α (H)-phyllocladane, 16 β (H)-phyllocladane, and 16 α (H)-kaurane appear occasionally in some samples. The corresponding aromatic diterpenoids occur in the gas chromatograms of the aromatic hydrocarbon fractions, and consist of compounds of the abietane type (e.g. norabietatriene, dehydroabietane). Diterpenoids are important markers for the contribution of gymnosperms (Otto and Wilde, 2001).

The non-hopanoid triterpenoids occur in considerable amounts (Table 8). Saturated and mono-unsaturated compounds consist of des-A-oleanenes, des-A-urs-12-ene, des-A-lupane, olean-12-ene, and olean-13(18)-ene. Aromatic fractions include mainly tetramethyl-octahydrochrysenes and trimethyl-tetrahydrochrysenes, and minor tetramethyl-octahydricenes.

Sample S-09

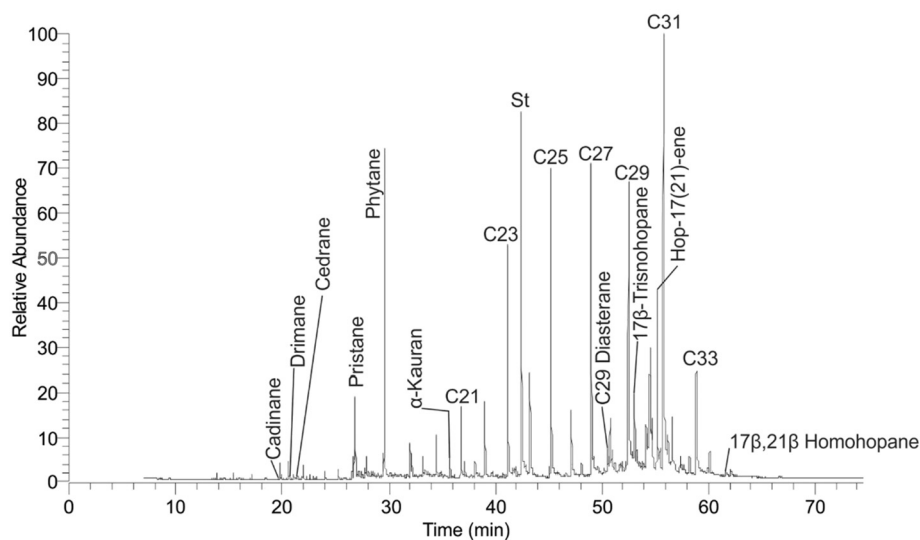


Fig. 7. Gas chromatographs (total ion current) of the saturated hydrocarbon fractions of the samples S-09 and S-06. *n*-alkanes are labeled according to their carbon numbers; Std. = Tetracosane.

Sample S-06

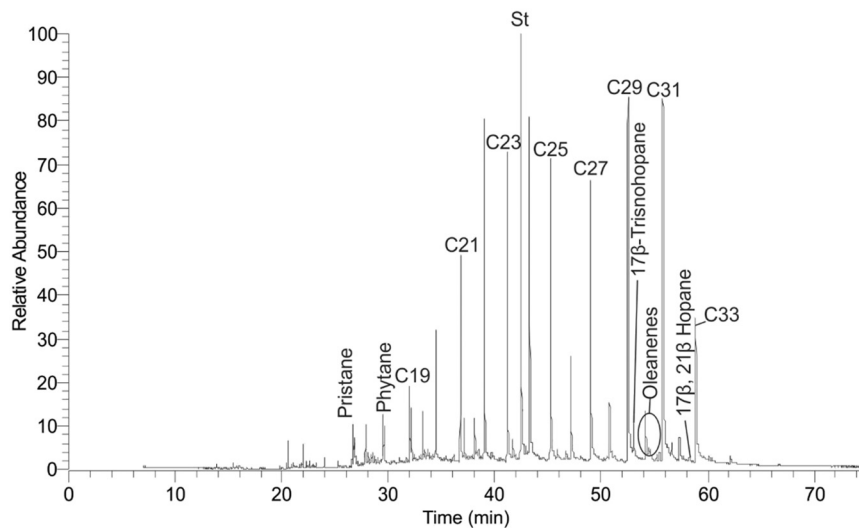


Table 4
n-alkanes and isoprenoid data of the studied samples.

Samples	Sum <i>n</i> -alkane (mg/g TOC)	<i>n</i> -C _{15–19} / <i>n</i> -C _{15–33}	<i>n</i> -C _{21–25} / <i>n</i> -C _{15–33}	<i>n</i> -C _{27–31} / <i>n</i> -C _{15–33}	Pr/ <i>n</i> -C ₁₇	Ph/ <i>n</i> -C ₁₈	Pr/Ph
S-01	234.87	0.03	0.41	0.33	1.28	1.52	0.63
S-02	93.39	0.07	0.29	0.46	0.90	1.03	1.30
S-03	60.02	0.09	0.19	0.51	1.15	1.11	1.06
S-04	44.59	0.05	0.25	0.54	3.65	1.56	1.32
S-05	25.42	0.05	0.28	0.51	3.10	3.80	0.76
S-06	189.45	0.05	0.43	0.37	1.34	1.02	1.06
S-07	138.36	0.03	0.41	0.34	2.86	1.70	0.88
S-08	281.52	0.02	0.09	0.82	3.89	3.88	0.81
S-09	60.93	0.04	0.32	0.51	10.02	9.99	0.72
S-10	32.13	0.02	0.07	0.83	0.82	2.24	0.78
S-11	429.73	0.02	0.09	0.77	0.41	1.49	0.77
S-12	251.21	0.18	0.18	0.50	0.90	0.80	1.11
S-13	139.53	0.03	0.15	0.72	1.14	1.95	0.84
S-14	131.65	0.06	0.21	0.60	1.56	1.39	1.11
S-15	131.65	0.06	0.21	0.60	1.56	1.39	1.11
S-16	53.30	0.05	0.32	0.53	1.38	1.35	0.99
S-17	17.59	0.03	0.31	0.54	3.13	2.73	1.31
Total average	136.20	0.05	0.25	0.56	2.30	2.29	0.97

Pr = Pristan; Ph = Phytane.

Table 5
Calculated parameters from the distributions of *n*-alkanes and isoprenoids.

Samples	CPI	TAR	P _{aq}	P _{wax}
S-01	4.64	22.6	0.42	0.63
S-02	3.55	13.99	0.33	0.74
S-03	4.12	16.11	0.19	0.82
S-04	5.44	17.07	0.24	0.8
S-05	5.63	14.13	0.28	0.77
S-06	3.83	13.34	0.42	0.66
S-07	4.53	15.16	0.40	0.66
S-08	6.61	56.16	0.07	0.93
S-09	4.91	17.25	0.38	0.69
S-10	7.47	88.22	0.05	0.95
S-11	4.27	90.13	0.09	0.91
S-12	3.46	4.12	0.22	0.82
S-13	4.58	64.25	0.15	0.88
S-14	4.04	13.13	0.27	0.78
S-15	4.04	13.13	0.27	0.78
S-16	4.15	15.2	0.42	0.69
S-17	4.87	27.24	0.35	0.7
Total average	4.71	29.48	0.27	0.78

CPI (Carbon preference index) = $1/2 \left(\frac{(n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31} + n-C_{33})}{(n-C_{26} + n-C_{28} + n-C_{30} + n-C_{32} + n-C_{34})} + \frac{(n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31} + n-C_{33})}{(n-C_{26} + n-C_{28} + n-C_{30} + n-C_{32} + n-C_{34})} \right)$.

TAR (terrestrial/aquatic ratio) = $(n-C_{27} + n-C_{29} + n-C_{31}) / (n-C_{15} + n-C_{17} + n-C_{19})$.

P_{aq} (submerged/floating aquatic macrophyte input versus emergent and terrestrial plant input) = $(n-C_{23} + n-C_{25}) / (n-C_{23} + n-C_{25} + n-C_{29} + n-C_{31})$.

P_{wax} (wax proxy) = $(n-C_{27} + n-C_{29} + n-C_{31}) / (n-C_{23} + n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31})$.

4.5. Carbon isotope composition

The $\delta^{13}C$ values of TOC of the studied samples vary from -24.9 to -26.5‰ , with an average of -25.6‰ (Table 1). The data fall within the range of $\delta^{13}C$ values obtained from the late middle Miocene lignite of the Lower Rhine Embayment in Germany (-26.7 to -24.5‰ ; Lücke et al., 1999). The $\delta^{13}C$ values show a slight tendency towards higher values with increasing depth.

5. Discussion

5.1. Organic matter sources and paleovegetation

Maceral analysis revealed that the lignite and carbonaceous samples are dominantly composed of macerals of the huminite group, reflecting the contribution of woody terrigenous OM to the peat-formation. As these samples were collected from the lignite layers separated by sediments of a prograding delta, the heterogeneity of petrographic indices revealed changes in vegetation and depositional environment, as noticed on the proposed models of Diessel and Calder. Samples S-04, S-05 and S-10 show TPI indices higher than 1 indicating a good preservation of plant tissues probably derived from forest trees. In contrast, samples S-08, S-15 and S-17 show low TPI indicating the advanced destruction of the woody organic tissues or the dominance of herbaceous plants. The uppermost samples S-15 and S-17 show $VI < 1$ providing evidence towards the significant contribution of herbaceous and marginal aquatic plants to peat-formation. However, the rest of samples show $VI > 1$ reflecting a trend towards forest vegetation. The overall dominance of phytoclasts OM also point towards the wood dominated forest vegetation.

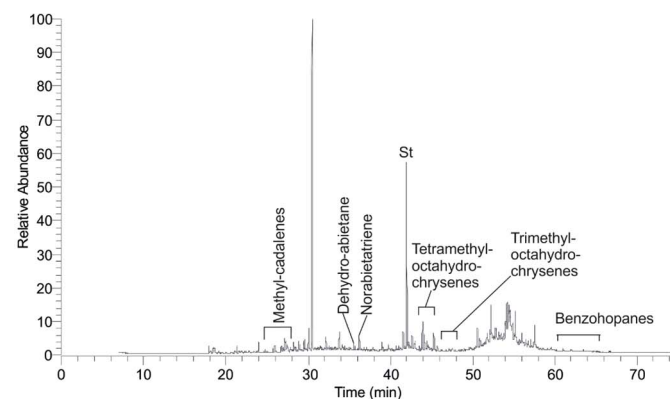
The *n*-alkane patterns reflect the dominant contribution of higher land plants to OM, testified by the high proportion of odd-numbered long-chain (C_{27} – C_{31}) homologues, as they constitute a main component of the epicuticular plant waxes (Eglinton and Hamilton, 1967). The relative proportions of the intermediate *n*-alkanes ($n-C_{21}$ – C_{25}), reported to be originated from Sphagnum and/or aquatic macrophytes (Nott et al., 2000; Ficken et al., 2000), range from 0.07 to 0.43 with 0.25 average (Table 4, Fig. 9). The alternation of the intermediate *n*-alkanes proportions indicate an alternative contribution of Sphagnum and/or

Table 6
Distribution of steroids in the Saouef samples and calculated parameters.

Samples	Sterenes (mg/g C _{org})	Diasterenes (mg/g C _{org})	Diasterenes/ Sterenes	Steroids (Sat.) (mg/g C _{org})
S-01	0.36	1.68	4.63	2.04
S-02	0.90	0.00	0.00	0.90
S-03	0.75	0.00	0.00	0.75
S-04	0.62	0.98	1.58	1.60
S-05	1.10	2.92	2.67	4.01
S-06	0.83	0.75	0.89	1.58
S-07	1.06	0.48	0.45	1.54
S-08	9.66	2.66	0.28	12.32
S-09	0.63	1.12	1.77	1.75
S-10	0.27	0.05	0.19	0.33
S-11	5.19	0.00	0.00	5.19
S-12	2.00	0.00	0.00	2.00
S-13	1.49	0.00	0.00	1.49
S-14	5.15	4.11	0.80	9.26
S-15	5.15	4.11	0.80	9.26
S-16	0.48	1.61	3.35	2.09
S-17	0.70	1.07	1.54	1.77
Total average	2.14	1.27	1.11	3.40

aquatic macrophytes like reed grasses in a temperate environment as well as of vascular plants (Bechtel et al., 2007a,b). The values for P_{wax} between 0.63 and 0.85 confirm the important contribution of land plants and macrophytes to OM. The P_{aq} ratios (0.05–0.42) indicate the important role of emerged macrophytes (e.g. reed grasses) in peat-formation (Ficken et al., 2000). High TAR values (> 4) confirm the minor abundance or the absence of algal derived biomass (Bourbonniere and Meyers, 1996). Thus, the palynofacies and petrographic data do not

Sample S-09



Sample S-10

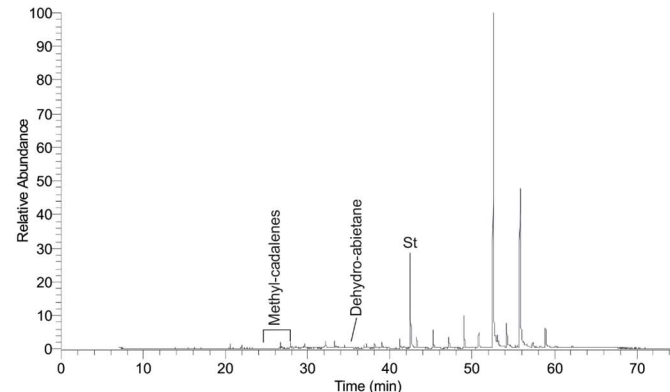


Fig. 8. Gas chromatographs (total ion current) of the aromatic hydrocarbon fractions of the samples S-09 and S-10; Std. = 1,1-binaphthyl.

Table 7

Distribution of hopanoids in the Saouef samples and calculated parameters.

Samples	$\alpha\beta$ Hopanes (mg/g C _{org})	$\beta\beta$ Hopanes (mg/g C _{org})	Hopenes (mg/g C _{org})	Benzohopanes (mg/g C _{org})	Hopanoids (mg/g C _{org})	20S/(20S + 20R) $\alpha\beta$ C31 Hopanes	Steroids/ Hopanoids
S-01	0.00	9.01	3.12	0.00	12.13	0,60	0.17
S-02	0.88	4.40	1.52	0.00	6.80	0,37	0.13
S-03	0.50	2.46	1.17	0.00	4.13	0,50	0.18
S-04	0.41	2.55	1.30	0.09	4.26	0,50	0.37
S-05	0.27	2.04	1.72	0.08	4.04	0,56	0.99
S-06	1.19	6.50	2.28	0.00	9.97	0,49	0.16
S-07	0.57	3.56	1.47	0.00	5.60	0,54	0.28
S-08	1.61	12.31	9.99	0.11	23.90	0,43	0.52
S-09	0.54	4.94	5.22	0.09	10.71	0,56	0.16
S-10	0.13	1.41	0.50	0.00	2.05	0,47	0.16
S-11	1.92	17.32	7.46	0.00	26.70	0,50	0.19
S-12	1.50	9.47	6.27	0.00	17.23	0,52	0.12
S-13	1.42	6.63	2.38	0.00	10.43	0,34	0.14
S-14	1.49	9.11	9.28	0.27	19.88	0,52	0.47
S-15	1.49	9.11	9.28	0.27	19.88	0,52	0.47
S-16	0.69	4.25	5.04	0.12	9.98	0,44	0.21
S-17	0.37	2.15	2.12	0.03	4.64	0,35	0.38
Total average	0,88	6,31	4,12	0,06	11,31	0,48	0,30

indicate any contribution of algae in the peat forming.

The predominance of C₂₉ steroids (sterenes, diasterenes) over C₂₇ and C₂₈ steroids correlates well with the calculated CPI and the high abundance of the long-chain *n*-alkanes proving a terrigenous origin of the OM. The identified sesquiterpenoid and diterpenoid biomarkers in the Saouef samples are frequently found in coal and lignite. These compounds are derived from the resinous material of higher land plants (Simoneit, 1986; Wang and Simoneit, 1990). Based on the diterpenoids present in the Saouef samples, a predominant role of species of the Coniferales families Pinaceae, and/or Cupressaceae/Taxodiaceae are concluded (Otto et al., 1997; Otto and Wilde, 2001). Non-hopanoid triterpenoids containing the structures typical of the oleanane skeleton, the ursane skeleton, or the lupane skeleton are known as biomarkers for angiosperms (Karrer et al., 1977; Dev, 1989). These compounds are significant constituents of leaf waxes, wood, roots, and bark (Karrer et al., 1977). Identified biomarkers are in accordance with the results of previous palynological studies of the same area (Moktar and Mannai-Tayech, 2014).

The ratios of diterpenoid hydrocarbons versus angiosperm-derived triterpenoids [Di/(Di + Triterpenoids)] vary considerably in the studied samples (Table 8, Fig. 9). High values indicate the significant contribution of conifers to the peat-forming vegetation, whereas low values indicate the predominance of angiosperms. Samples with TPI higher than 1 show generally higher Di/(Di + Tri)-terpenoid ratios than analyzed samples with TPI lower than 1.

As woody remains from gymnosperms are more resistant to degradation compared to angiosperm wood (Hatcher and Clifford, 1997), the TPI has been shown to be influenced by the type of vegetation (Bechtel et al., 2002).

5.2. Depositional environment

The 3rd unit of Saouef Formation is characterized by a stacking of parasequences (El Euch El Kondi, 2007; Moktar and Mannai-Tayech, 2014). Each sequence starts with greenish to brown greenish clay containing a silty to sandy fraction arranged into wavy beddings to flaser beddings structures. The clay is overlain by an upward coarsening parasequence. Clay intercalations dominating the sandy beds re-appear at the top of the parasequence. A lignite or carbonaceous layer marks the end of the prograding sequence.

Total sulphur contents in the samples are below 1.3 wt%, indicating a freshwater environment and neutral to slightly acidic pH values (Casagrande, 1987). The high ash yields of lignite and carbonaceous shales are intimately related to the inundation of the depositional

environment (mesotrophic) favoring the oxygenation of the basin and the degradation of the OM. The predominance of huminite macerals in the coaly sediments provides evidence for the anaerobic preservation of lignocelluloses material in the mire (Sýkorová et al., 2005). In carbonaceous samples (S-08, S-15, S-17), macerals detrohuminite and gelohuminite associated with clay minerals predominate over telohuminite, indicating physical degradation of the macerals during transportation (allochthonous origin (O'Keefe et al., 2013)). The degree of tissues destruction might be also related to the biochemical degradation by bacterial activity at low pH in an oxygenated environment (Diessel, 1992). However, the high GI values of the Saouef samples indicate a moderate to high water level for most of the samples, except of sample S-08. Thus, the lignite samples show the dominance of telohuminite over the detrohuminite and gelohuminite.

The GI versus TPI plot suggests a deposition of OM in terrestrial, limnic to the wet forest swamp, and in the telmatic environment (Fig. 10; Diessel, 1986). Samples with high TPI plot into the fields, characteristic for fen, telmatic, and wet forest swamp, are characterized by lower contents of mineral matter. Same latter samples fall into the ombrotrophic zone in the Calder diagram (Fig. 11) suggesting the transition to a bog forest. However, these facies diagrams should be interpreted with care and conclusions about the peat-forming environment require supporting additional data.

The predominance of OM (kerogen) particles by phytoclasts in the palynofacies assemblage I suggest a good preservation of the higher plants lignin in an oxygen deficient environment (Tyson, 1993, 1995; Mendonça Filho et al., 2012). The frequent large biostructured phytoclasts components reveal a close proximity to a fluvio-deltaic source and confirm a short transport distance (Tyson, 1995). The palynofacies II is also dominated by phytoclasts. Yet, the phytoclasts components show a moderate alteration features expressed by the high non-biostructured phytoclasts content which might be explained by a slight increase of the transportation distance of the organic matter. The palynofacies association III is made up of subequal dominance between AOM and phytoclasts group and display a dominance of pseudo-amorphous phytoclasts and might be explained by the enhanced degradation of the organic matter and suggests a sedimentary alteration promoted by the sub-aerial oxidation during a distant transport of the organic matter (Mendonça Filho et al., 2011, 2012; Tyson, 1995). The palynofacies assemblage VI suggest the promoting of the OM degradation expressed by the high pseudo-amorphous and amorphous product contents. Moreover, the rise of the palynomorphs content associated with the enhanced OM degradation endorses the evolution of the deposit environment towards a distal basin (Tyson, 1995).

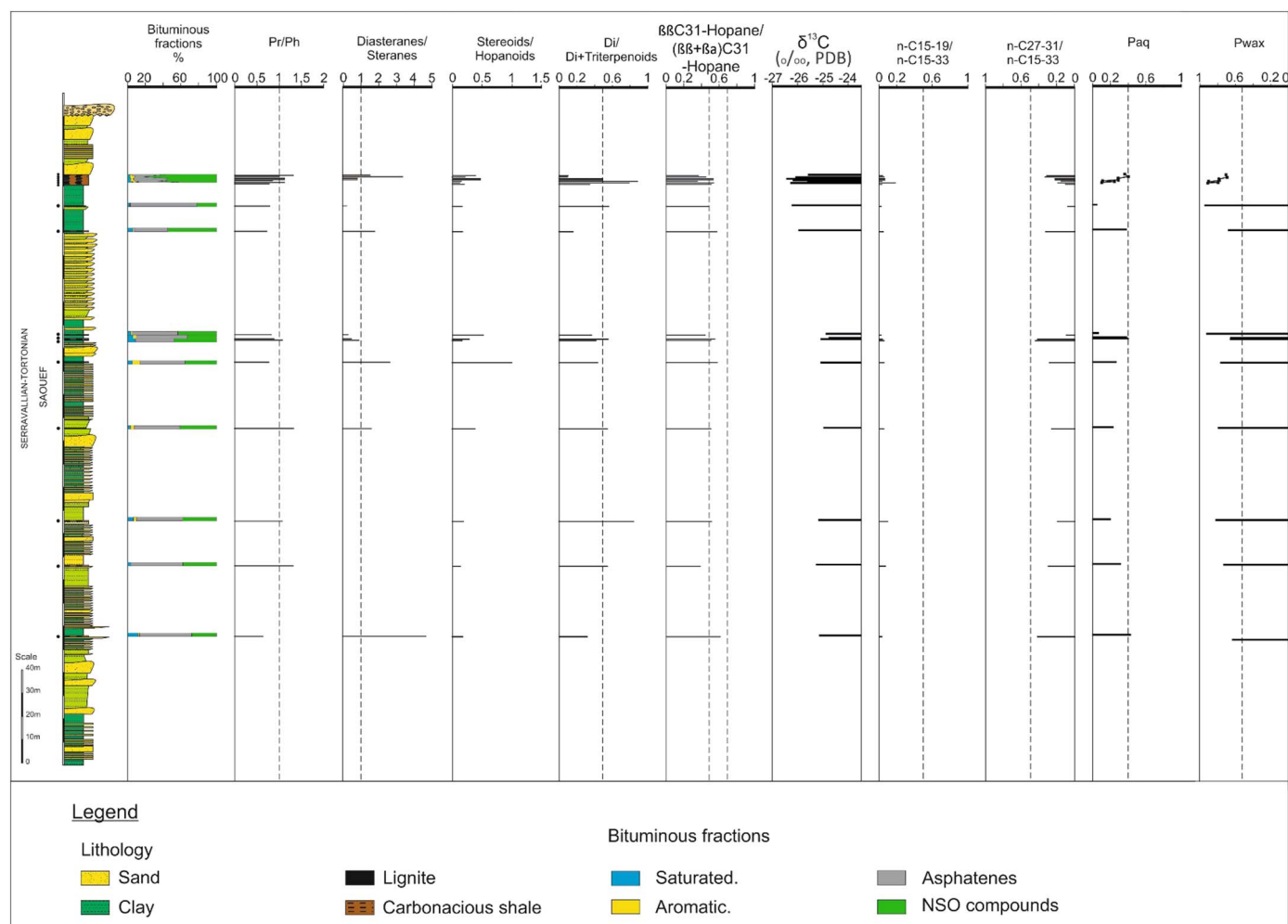


Fig. 9. Section profile including the bituminous fractions composition, Pr/Ph ratios variation, steraneoids/hopanooids ratios variation, Di/(di + triterpenoids) ratios variation $\beta\beta$ C31/ ($\beta\beta + \alpha\beta$) C31 – hopanes variation, $\delta^{13}\text{C}$, $n\text{-C}_{15-19}/n\text{-C}_{15-33}$ and $n\text{-C}_{27-31}/n\text{-C}_{15-33}$, P_{aq} and P_{wax} variation.

The Pr vs. Ph ratio provides evidence about the redox conditions of the depositional environment. According to Didyk et al. (1978) a ratio < 1 indicates anaerobic conditions during early diagenesis, whereas ratios > 1 are observed in dysaerobic environments. However, this ratio should be used with precaution as different precursors were

noted, like the bacterial origin of Ph (Volkman and Maxwell, 1986; Ten Haven et al., 1987), and the production of pristane from tocopherols or chromanes (Goossens et al., 1984). The analyzed samples show a repetitive alternation of the aerobic and anerobic conditions according to the Pr/Ph. In other words, Pr/Ph ratios point to an alternation between

Table 8
Terpenoids distribution in the Saouef samples and calculated parameters.

Samples	Sesquiterpenoids (Sat.) (mg/g C _{org})	Diterpenoids (Sat.) (mg/g C _{org})	Triterpenoids (Sat.) (mg/g C _{org})	Sesquiterpenoids (Arom.) (mg/g C _{org})	Diterpenoids (Arom.) (mg/g C _{org})	Triterpenoids (Arom.) (mg/g C _{org})	Di –/(Di- + Tri-)) Terpenoids
S-01	1.25	2.81	6.59	0.00	0.27	0.22	0.31
S-02	0.56	3.34	2.76	0.00	0.16	0.22	0.54
S-03	1.14	3.98	1.15	0.00	5.62	0.73	0.84
S-04	0.42	1.30	2.24	0.72	3.12	1.53	0.54
S-05	0.18	1.66	4.01	0.34	1.96	0.77	0.43
S-06	0.00	3.51	5.08	0.40	0.39	0.53	0.41
S-07	0.18	2.05	1.87	0.36	0.74	0.44	0.55
S-08	2.65	1.31	9.15	0.30	5.61	3.02	0.36
S-09	0.39	0.80	5.79	0.00	0.43	1.15	0.15
S-10	0.11	0.39	0.48	0.05	0.31	0.09	0.55
S-11	0.00	9.81	17.33	0.00	0.26	2.20	0.34
S-12	4.97	7.04	0.92	0.00	5.94	2.66	0.78
S-13	0.00	3.16	0.00	0.00	0.48	0.50	0.88
S-14	1.06	9.32	9.78	0.32	0.92	1.28	0.48
S-15	1.06	9.32	9.78	0.32	0.92	1.28	0.48
S-16	0.15	0.35	4.30	0.08	0.19	1.28	0.09
S-17	0.15	0.29	1.35	0.10	0.12	2.60	0.09
Total average	0,84	3,56	4,86	0,18	1,61	1,21	0,46

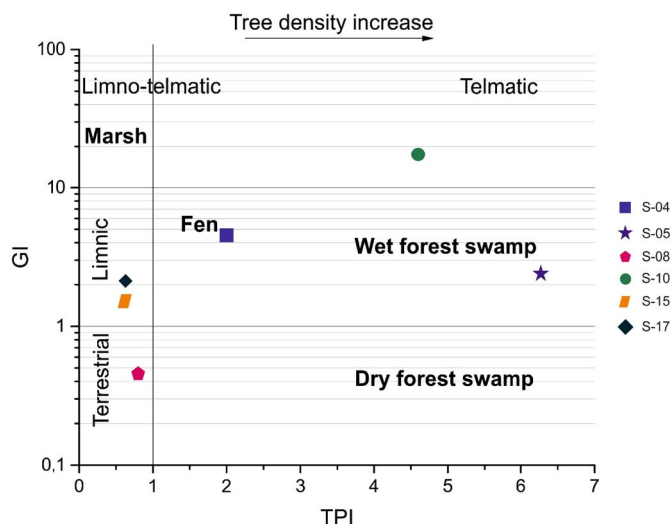


Fig. 10. GI vs. TPI plot of the studied Saouef lignite.

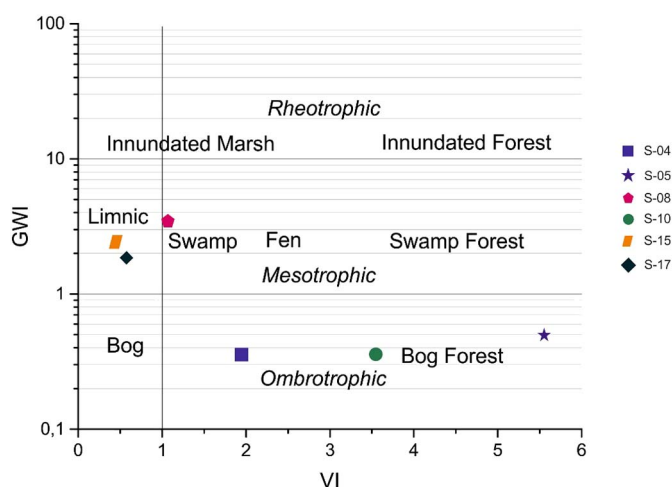


Fig. 11. GWI vs. VI plot of the studied Saouef lignite.

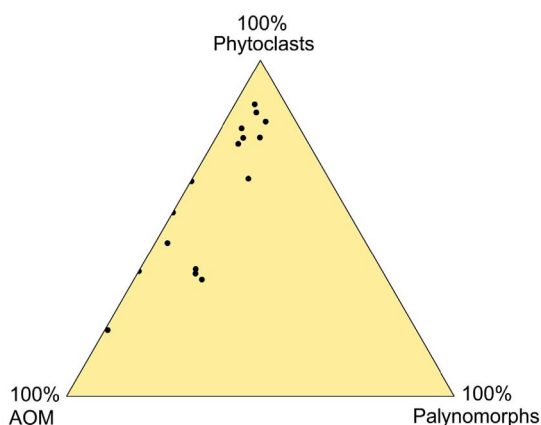
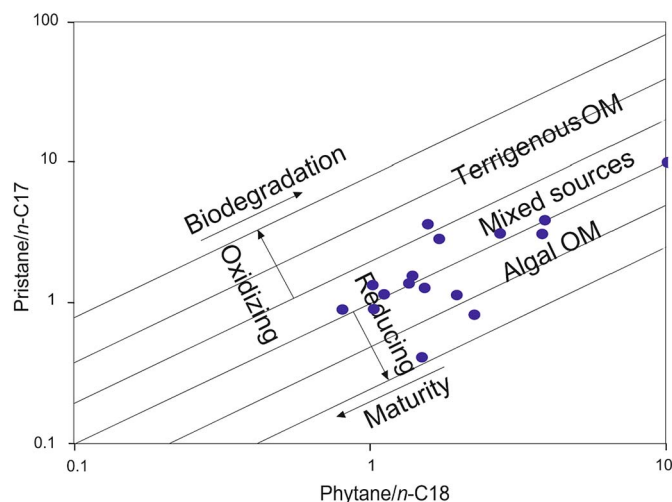


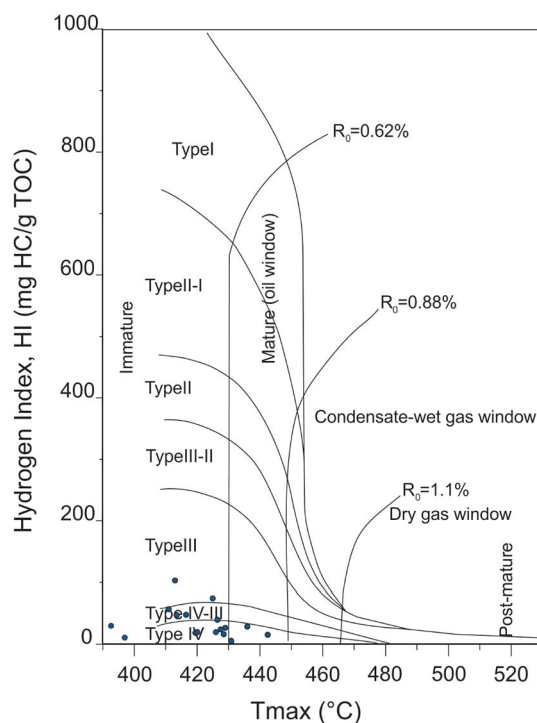
Fig. 12. AOM/Phytoclasts/Palynomorphs Ternary diagram showing the constitution of the kerogen of the lignites and carbonaceous layers of the Saouef formation (Based on Tyson, 1995).

suboxic to oxic environment. These results may partly be supported by the high proportion of amorphous products and pseudo-amorphous phytoclasts in most of the samples indicating a suboxic to anoxic deposit environment (Tyson, 1995). The $Pr/n-C_{17}$ vs. $Ph/n-C_{18}$ plot

Fig. 13. Pristane/ $n-C_{17}$ vs. Phytane/ $n-C_{18}$ plot of the studied Saouef samples.

indicates that the organic matter predominantly is derived from Mixed origins (Fig. 13). However, application of this diagram and of Pr/Ph ratio for the reconstruction of redox conditions is very limited in immature samples. In the immature OM, isoprenoid precursors are still incorporated into the macromolecular matrix either by esterification (Brooks et al., 1978) or by natural sulphurization (Brassell et al., 1986).

The high hopanoid contents and low steroids/hopanoids ratios (0.26 on average) indicate a high bacterial activity. The presence of AOM terrestrially derived associated with fungal remains testifies the high bacterial activity, most probably responsible for the gelification of plant tissues. Besides the influence of the peat-forming vegetation, climatic parameters like air temperature and humidity are probably responsible for the observed variability in $\delta^{13}C$ values of the lignite OM (Schleser, 1995; Kürschner, 1996; Lücke et al., 1999; Arens et al., 2000).

Fig. 14. HI vs. T_{max} plot of the studied Saouef samples. Total samples indicate Type IV-III and Type IV kerogens within 400–450 °C T_{max} range exhibiting immature state.

5.3. Maturity assessment and economic potential

The economic value of lignite/coal as fossil fuel depends on the amount of the deposited organic matter (TOC) and its thermal maturity (rank). Several proxies are used in order to assess the maturity of OM and to provide evidence for the hydrocarbon generative potential. The TOC values exceed 20 wt% in some of the studied samples. Rock-Eval pyrolysis yields show very low S1 (av. 0.19 mg HC/g), and low S2 values in the order of 3.6 mg HC/g in average. The data confirm the immature state of OM and the predominance of Type-IV-III kerogen (Fig. 14). The huminite reflectance ranges from 0.28 to 0.50% R_r (av. 0.34% R_r). The data confirm the widely designation of the Saouef coaly layers as “lignite” (Taylor et al., 1998). The sample S-10 shows some traces of exsudatinite providing evidence for the possibility of hydrocarbon expulsion, as supported by a higher S1 (0.6 mg HC/g) of the sample.

The average ratio of the $\beta\beta$ -C₃₁ hopane (22R) to the ($\beta\beta$ + $\alpha\beta$) C₃₁ hopanes (22R) (0.48) (Table 7) is slightly lower than generally measured within lignites (0.5–0.7; MacKenzie et al., 1981). The occurrence of 17 α ,21 β (H)-homohopane in low-rank coals has been explained by oxidation and subsequent decarboxylation reactions of bacteriohopantetrol with isomeric catalysation at position 17 achieved by the acidic environment in the mire (Van Dorselaer et al., 1975).

6. Conclusions

The sedimentary organic matter of the Saouef Formation in north-east Tunisia constitutes lignite/carbonaceous layers on top of each prograding parasequence of a river delta. The petrographic, palynofacies and geochemical results of the organic matter suggest a marginal dysoxic to anoxic basin. The *n*-alkanes and the steroids biomarkers data suggest the origin of OM predominantly from higher land plants and emerged macrophytes. Biomarker data further indicate the varying contributions of conifers and angiosperms to peat-formation. The high abundances of hopanoids indicate a high bacterial activity in the mire responsible for gelification of the plant tissues. The $\delta^{13}\text{C}$ data of TOC are consistent with values found in middle Miocene lignite deposits. The observed variation of $\delta^{13}\text{C}$ values might be related to the fluctuation of climatic parameters.

The palynofacies analysis, the Rock Eval and the biomarker (*n*-alkanes and terpenoids distributions) data suggest a kerogen (OM) Types III/IV with the potential to generate gas. However, T_{max} mostly doesn't exceed 435 °C and the huminite reflectance averages 0.34% R_r only characterizing the Saouef coaly layers as immature (“lignite”). Biomarker maturity parameters also confirm the immaturity of the Saouef organic matter.

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