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Depositional environment, organic matter characterization and hydrocarbon potential of Middle Miocene sediments from northeastern Bulgaria (Varna-Balchik Depression)

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Abstract: The depositional environments and hydrocarbon potential of the siliciclastic, clayey and carbonate sediments from the Middle Miocene succession in the Varna-Balchik Depression, located in the south-eastern parts of the Moesian Platform, were studied using core and outcrop samples. Based on the lithology and resistivity log the succession is subdivided from base to top into five units. Siliciclastic sedimentation prevailed in the lower parts of units I and II, whereas their upper parts are dominated by carbonate rocks. Unit III is represented by laminated clays and biodetritic limestone. Units IV and V are represented by aragonitic sediments and biomicritic limestones, correlated with the Upper Miocene Topola and Karvuna Formations, respectively. Biogenic silica in the form of diatom frustules and sponge spicules correlates subunit IIa and unit III to the lower and upper parts of the Middle Miocene Euxinograd Formation. Both (sub)units contain organic carbon contents in the order of 1 to 2 wt. % (median: 0.8 for subunit IIa; 1.3 for unit III), locally up to 4 wt. %. Based on Hydrogen Index values (HI) and alkane distribution pattern, the kerogen is mainly type II in subunit IIa (average HI = 324 mg HC/g TOC) and type III in unit III (average HI ~ 200 mg HC/g TOC). TOC and Rock Eval data show that subunit IIa holds a fair (to good) hydrocarbon generative potential for oil, whereas the upper 5 m of unit III holds a good (to fair) potential with the possibility to generate gas and minor oil. The rocks of both units are immature in the study area. Generally low sulphur contents are probably due to deposition in environments with reduced salinity. Normal marine conditions are suggested for unit III. Biomarker composition is typical for mixed marine and terrestrial organic matter and suggests deposition in dysoxic to anoxic environments.

Key words: organic geochemistry, hydrocarbon potential, Euxinograd Formation, NE Bulgaria, Eastern Paratethys.

Introduction

The western Black Sea has long been recognized as a region with high petroleum potential. The Tyulenovo Field (Fig. 1b) was detected in the Bulgarian sector of the Black Sea in the 1950s. It contains significant oil (~30 Mbs) and gas reserves (~30 Bcf; Georgiev 2012). Additional potentially oil- and gas-bearing structures have been identified on and offshore Bulgaria in the 1990s. One of them, the Galata deposit, offshore cape Galata near Varna, already produced dry gas of about 55 Bcf (Georgiev 2012).

The question of active source rocks is an important issue for understanding petroleum systems. Georgiev (2012) considered the Middle to Late Jurassic shales from the Etropole and Provadia Formations, drilled in the Galata area, as the most likely source rocks for the formation of Tyulenovo oil. The same author, however, reports the presence of oleanane, which is an indicator for post-Jurassic source rocks, within this oil. Sachsenhofer et al. (2009) studied Oligocene clays of the Ruslar Formation and determined a good potential for hydrocarbon generation. Apart from Oligocene rocks, Eocene successions, which are of considerable thickness in the deeper parts of the western Black Sea may hold a source potential (Georgiev 2012).

No studies have been conducted so far on the Miocene succession, although there are some notes on the presence of organic matter-rich lenses within the diatomaceous clays of the Middle Miocene Euxinograd Formation (Koleva-Rekalova 1997). Thus, the limited knowledge on the amount and origin of the organic matter within the Miocene rocks leaves a gap in our understanding of the petroleum system in NE Bulgaria and its off-shore part.

Therefore, the main aim of the present paper is to study lithology, depositional environment, and hydrocarbon potential of the Miocene Euxinograd Formation and to explore vertical and partly lateral facies variations. To reach this goal, core material from Miocene rocks from borehole C-180a (Fig. 1b) was studied. Additional samples from the upper part of the Euxinograd Formation were taken from an outcrop near Albena resort. The present investigation is based on bulk geochemical parameters (inorganic and organic carbon, sulphur, hydrogen index), biomarker, and stable carbon isotope composition of the organic matter. Since the lower part of the Miocene succession, especially in the Balchik area, is not well

studied due to limited core material, we also investigate rocks underlying the Euxinograd Formation.

Geological setting

Miocene rocks are present in the southeastern part of the Moesian Platform in Bulgaria and Romania (Popov et al. 1986; Popov & Kojumdgieva 1987; Fig. 1) and have been studied intensively, because of their rich macro- and microfauna, as well as diatom flora (Kojumdgieva 1965; Kojumdgieva & Dikova 1978; Kojumdgieva & Popov 1987; Darakchieva 1989; Temniskova-Topalova 1990).

The Miocene succession, about 300 m thick, has been deposited in the relatively small, south-east widening Varna-Balchik Depression (Fig. 1c) of the Eastern Paratethys (Kojumdgieva & Popov 1981). The sediments overlie denudated Late Oligocene clays (Ruslar Fm) and represent the time span from the early Middle Miocene (Tarkhanian) to the middle Late Miocene (Khersonian) (Popov & Kojumdgieva 1987). Based on differences in sedimentary facies, Kojumdgieva & Popov (1981), Popov et al. (1986) and Popov & Kojumdgieva (1987) subdivided the Varna-Balchik Depression into the Varna part, dominated by shallow marine siliciclastic deposits, and the Balchik part, in which (sub-)littoral sandy to clayey sedimentation prevailed (Figs. 1c, 2).

The following summary of basin evolution is based mainly on Popov et al. (1986) and Popov & Kojumdgieva (1987), who subdivided the Miocene succession into seven formal and two informal lithostratigraphic units (Fig. 2).

The oldest Miocene rocks are biogenic limestones, 2 to 3 m thick, of Middle to Late Tarkhanian age (Karapelit Fm; not shown in Fig. 2). They were formed in a relatively narrow strait along the South Dobrudzha lowlands (Fig. 1c), which at that time connected the Eastern Paratethys with the Fore Carpathian Basin. Within the Varna part of the depression, Tarkhanian sediments are represented by a few meters of laminated clays near the base of Galata Formation. A ma-

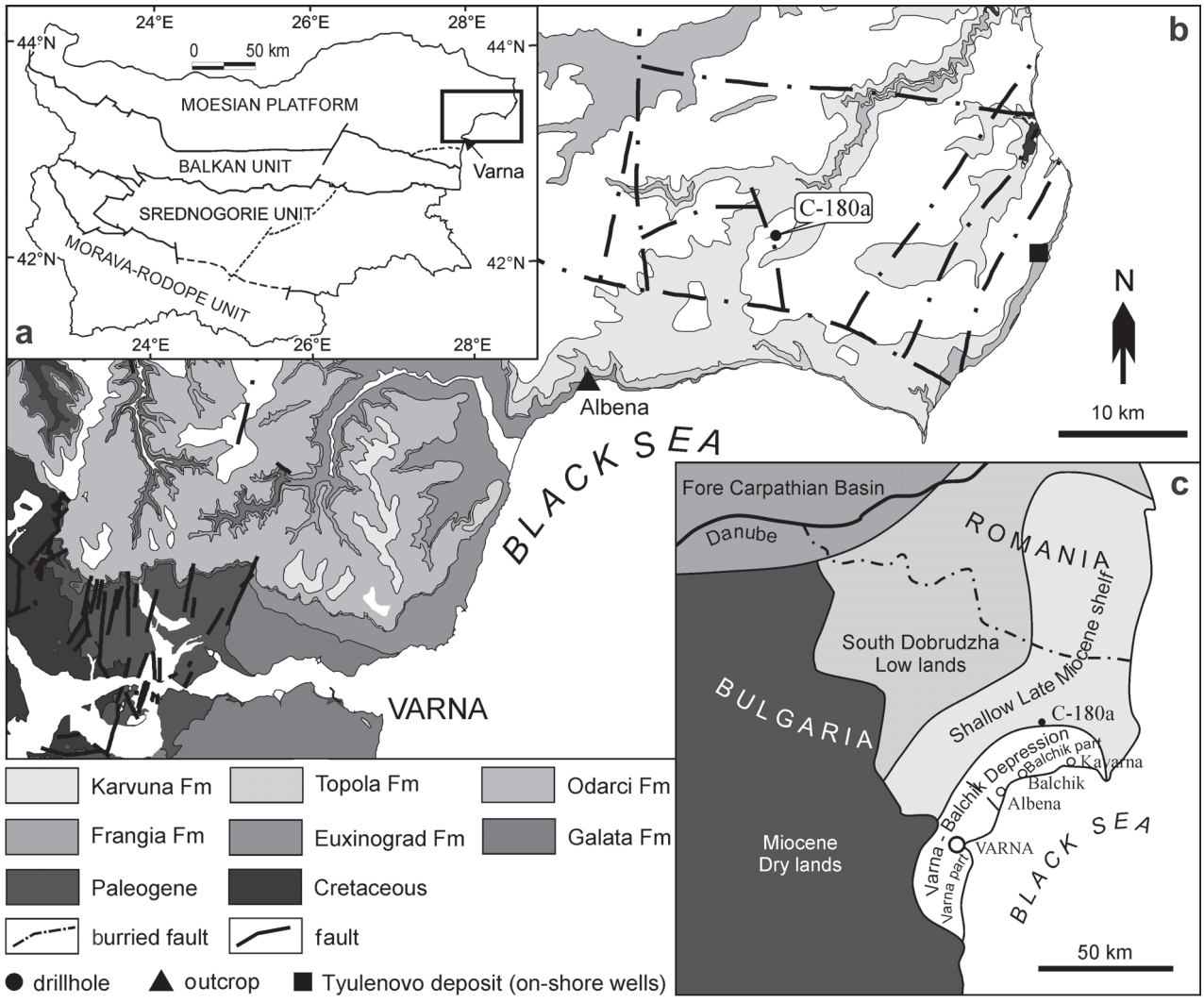

Fig. 1. a — Tectonic map of Bulgaria, showing the position of the study area within the south-eastern part of the Moesian Platform (simplified after Dabovski et al. 2002); **b** — Simplified geological map of the studied area (modified after Cheshitev et al. 1994a,b, 1995); **c** — Schematic scheme of the paleogeography of the studied area during the Miocene (modified after Popov & Kojumdgieva 1987).

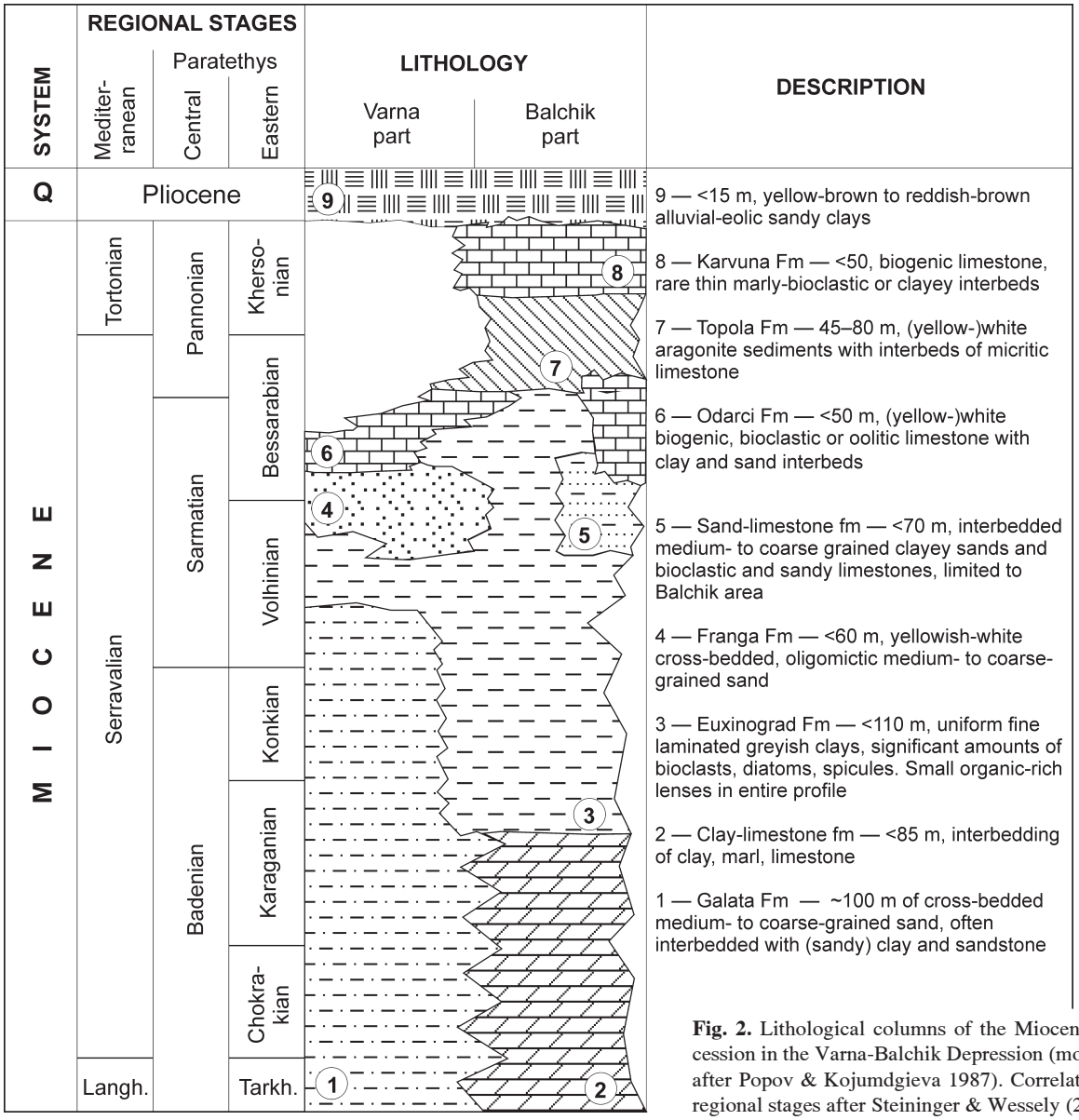

Fig. 2. Lithological columns of the Miocene succession in the Varna-Balchik Depression (modified after Popov & Kojumdgieva 1987). Correlation of regional stages after Steininger & Wessely (2000).

rine regression triggered by enhanced tectonic activity interrupted the connection with the Fore Carpathian Basin at the end of the Tarkhanian.

The overlying Galata Formation is limited to the Varna part of the depression (Fig. 2). It is composed predominantly of mid- to coarse-grained sands, intercalated by frequent clay and rare limestone and clayey sandstone beds. Ori (2004) investigated outcrops south of Varna and established a shallow marine environment with predominant beach sands, tidal deposits and deltaic channels. According to Popov & Kojumdgieva (1987), the southern part of the depression became dry land at the end of the Chokrakian shifting the area of maximum sedimentation northwards. North of Varna, deposition of the sediments of the Galata Formation continued until Early Volhynian time (Fig. 2), but the quantity of siliciclastic material was significantly reduced (Popov & Kojumdgieva 1987). At the same time up to 85 m of white-greenish calcareous clays, irregularly alternating with marls, and oolitic, biogenic, or bioclastic limestones were deposited in the Balchik part of the depression (Clay-limestone formation; Fig. 2). The rocks are known from few wells and poorly studied.

The overlying Euxinograd Formation (Fig. 2) is made up of finely laminated, diatomaceous pelites with frequent thin (2–20 mm) coquina intercalations composed of well-stratified shell fragments. Koleva-Rekalova (1997) also reported the presence of lenses, rich in plant remains. Thin interlayers of sandstone or limestone are very rare. Some rocks were described as diatomite (Popov & Kojumdgieva 1987). However, Koleva-Rekalova (1997) showed that opal sponge spicules prevail over diatom frustules. Studies performed by Koleva-Rekalova (1997, 1998), indicate deposition in a sublittoral low energy environment, influenced by surface water currents, introducing significant amounts of bioclastic material to the deeper zones of the depression. Based on the abundant fauna Kojumdgieva & Dikova (1978), estimate a water depth of less than 100 m, which is consistent with the predominance of

benthic foraminifera (Darakchieva 1989) and with high amounts of sponge spicules (Koleva-Rekalova 1998). The thickness of the Euxinograd Formation varies considerably and exceeds 100 m in the central part of the depression north of Varna (Popov & Kojumdgieva 1987). North and west of Balchik, the sand-limestone formation splits the Euxinograd Formation into a lower and an upper unit (Fig. 2 — Popov & Kojumdgieva 1987) and reduces its thickness significantly. Increased terrigenous input from the north (sand-limestone fm) and south (Franga Fm), was probably a result of late Volhynian uplift of surrounding areas (Fig. 2 — Popov & Kojumdgieva 1987), limited the area of deposition of the Euxinograd Formation to the central basin between Balchik and Albena resort. This situation lasted until the Early Bessarabian, when decreased terrigenous input allowed expansion of the area of clay deposition to the northern part of the depression.

After the Middle Bessarabian water salinity increased rapidly resulting in carbonate sedimentation. The area of the basin gradually diminished and was generally restricted to the Balchik part of the depression. Koleva-Rekalova (1994, 1997, 1998); Koleva-Rekalova & Darakchieva (2002) provide a comprehensive overview of the Sarmatian rocks. Porous bioclastic to oolitic limestones with micritic cement (Odarci Fm; Fig. 2) were deposited in shallow environments, followed by massive aragonitic sediments that in upper part show seasonal lamination (Topola Fm; Fig. 2). According to Koleva-Rekalova (1998) these rock formed due to chemical precipitation of needle-like aragonite crystals in shallow water under specific conditions. The youngest Miocene rocks are micritic limestones with varying abundance of bivalve shells (Karvuna Fm; Fig. 2).

Methods

The present study is based on 47 core samples from well C-180a drilled during the 1980s. The aim of the well was to study the Lower Cretaceous (Valanginian) carbonate succession, the main aquifer in north-eastern Bulgaria. Unfortunately there is no information on Miocene rocks. Therefore, we use geophysical data from well C-180, located about 20 m north of C-180a, to reconstruct the lithology of the missing parts of the studied core. Twelve additional samples were taken from an outcrop near Albena resort (Fig. 1b), representing about 5 m from the upper part of the Euxinograd Formation.

For microscopic investigations thin slides were prepared and studied under transmitted light using polarized microscope Leica DM 2500P.

Total carbon (TC) and sulphur (S) contents were determined with an Eltra Helios C/S analyser. Total organic carbon (TOC) content was determined on samples pretreated with phosphoric acid. Total inorganic carbon (TIC = TC–TOC) contents were used to calculate calcite equivalent percentages ($calcite_{eq}$ = TIC×8.34). Rock-Eval pyrolysis was performed using a Rock-Eval 6 instrument. S_1 and S_2 (mg HC/g rock) values were used to calculate Hydrogen index (HI = 100×S_2/TOC[mg HC/g TOC]) and Production index (PI = S_1/(S_1 + S_2); Espitalié et al. 1977). The temperature of maximum hydrocarbon generation (T_{max}) was recorded as a maturity parameter.

Biogenic silica contents were measured using the method proposed by Zolitschka (1998) and a Perkin-Elmer 3000 AAS spectrometer. The silica contents were used to calculate the opal percentages (= biogenic silica×2.4).

21 samples, mostly containing TOC greater than 1 wt. %, were chosen for biomarker analysis. Approximately 10 g of each sample were extracted for approximately 1 h using dichloromethane (DCM) in a Dionex ASE 200 accelerated solvent extractor. Asphaltenes were precipitated from a hexane-DCM solution (80 : 1) and separated by centrifugation. The hexane-soluble fractions were subdivided into saturated and aromatic hydrocarbons and NSO components using a Köhnen-Willsch MPLC instrument (Radke et al. 1980). No separation of the aliphatic and aromatic fractions was conducted only in the case of sample C-20, due to the low amount of extract. This sample was analysed by GC-MS as total fraction.

The saturated and aromatic hydrocarbons fractions were analysed by a gas chromatograph-mass spectrometer (GC-MS) Thermo Fisher Trace Ultra, equipped with a silica capillary column. Oven temperature was programmed from 70-300 °C with steps of 4 °C/min, followed by an isothermal period of 15 min. Helium was used as the carrier gas. The device was set in electron impact mode with a scan rate of 50–650 Daltons (0.7 sec/scan). Data were processed with Thermo-Fisher Xcalibur ® v. 2.0. Identification of biomarkers is based on retention time and comparison of mass spectra with published data. The determination of absolute concentrations of biomarkers was done using internal standards (deuterated *n*-tetracosane for the aliphatic fraction and 1,1'-binaphthyl for the aromatic fraction). The concentrations were normalized against the total organic carbon contents.

Carbon isotope determination of *n*-alkanes and isoprenoid hydrocarbons was performed on 11 samples using a Trace GC ultra attached to a ThermoFisher DELTA-V ir-MS via a combustion interface (GC Isolink, ThermoFisher). For calibration, a CO_2 standard was injected at the beginning and end of each analysis. The GC coupled to the ir-MS was equipped with the column described above and the temperature program was the same as for GC-MS analysis. Isotopic composition is reported in the δ notation relative to the PDB standard.

Results and discussion

The lithological profile of well C-180a is plotted together with the resistivity log in Fig. 3. Based on lithology, the Miocene succession can be divided into five units, which in general correspond to the lithostratigraphic units introduced by Popov & Kojumdgieva (1987).

Lithology

Unit I

Unit I discordantly overlies finely laminated Oligocene brownish clays and correlates with the Clay-limestone formation from the northern part of the Varna-Balchik Depres-

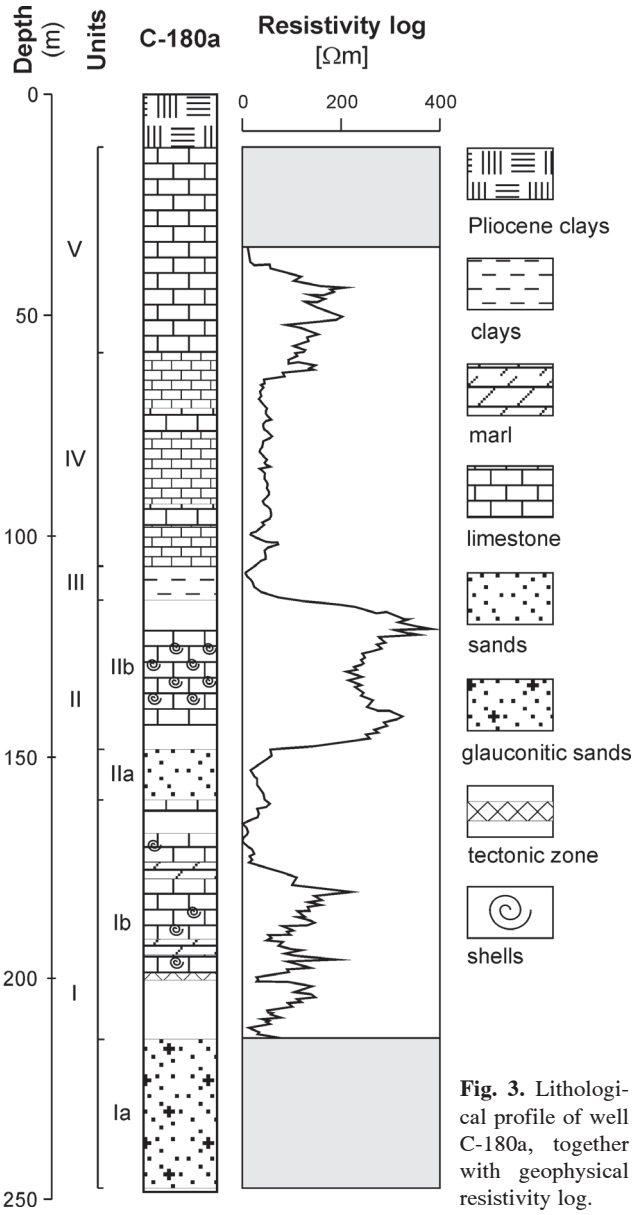

Fig. 3. Lithological profile of well C-180a, together with geophysical resistivity log.

sion and with the Galata Formation from its southern part (Popov & Kojumdgieva 1987). The unit is 87 m thick (Fig. 3) and can be subdivided into two subunits.

Subunit Ia — is about 35 m thick and is represented by white-greenish, very soft fine-grained glauconitic sands. The rocks appear homogenous, but sedimentary structures within the non-lithified sands may have been obliterated during coring. Carbonate contents are typically low (<3 wt. %; Table 1), but reach up to 25 wt. % in the upper part of the section. Carbonate is exclusively represented by micrite crystals. No biogenic carbonate remains were detected. Microscopic investigations showed that the detrital material is predominantly of fine- and very fine sand-size fractions. The mineral composition is relative uniform and is dominated by quartz and glauconite. Rare feldspar (mostly orthoclase; rare microcline), as well as mica flakes, can also be found. Some samples contain lithic fragments, composed of polycrystalline quartz, and fine charcoal fragments. Irregular-shaped, subangular to subrounded quartz grains are the predominant detrital component. Significant amounts (15–30 wt. %) of light green glauconitic pellets with very fine sand sizes give the rocks a pale greenish colour. Under the microscope, most glauconite grains show red-brownish colours, indicating initial oxidation. Although an authigenic origin of glauconite is possible, we assume a detrital origin, because glauconite-bearing Cretaceous and Paleogene rocks exist in the hinterland.

Subunit Ib — about 52 m thick (Fig. 3), is composed of hard, but highly porous biomicritic limestone layers with randomly orientated intact and fragmented bivalve shells. These rocks alternate irregularly with marlstones, up to 1 m thick. A thin layer of oolitic limestone was observed in the upper part of the subunit. Although the core representing the lower part of subunit Ib is missing, a gradual upward increase in resistivity suggests a continuous transition from subunits Ia to Ib.

Popov et al. (1986) give a similar description for the rocks from the Clay-limestone formation in two other drill holes from the Balchik area. Considering the above data, we assume that deposition of subunit Ia commenced in a sand and mud dominated shallow marine environment, characterized by high terrigenous input. The small grain size indicates formation in a relatively low energy environment, probably within the inner shelf below the wave-dominated zone. According to Kojumdgieva (1965), the Chokrakian was a time of reduced salinity. Very low sulphur contents in sediments of unit Ia may support this interpretation.

During the later stages of subunit Ia sediment deposition, a gradual decrease of the terrigenous input enabled increased carbonate deposition. Apart from this, the sedimentary environment most probably did not change significantly. The dominance of biomicritic limestone with random orientation of the fossils in subunit Ib argues for deposition in shallow marine environments with bottom currents and/or waves. Oolitic limestone interbeds in the upper part of the subunit indicate a change to a very shallow, high energy environment (Tucker & Wright 1990).

Unit II

Unit II, about 47 m thick, follows above unit I with a sharp boundary. Similar to unit I, two subunits can be distinguished (Fig. 3).

Subunit IIa — is composed of 13-m-thick sandy limestone in transition to fine sand with micrite matrix. The rocks are white to white-grey, very soft and friable. The carbonate content varies significantly between 21 and 80 wt. % and is relative low in the middle part of the subunit (Table 1, Fig. 4). Carbonates are almost exclusively represented by micrite crystals. With the exception of few foraminifera, detected by light microscopy, no other organic remains were detected.

The siliciclastic component is composed of fine and very fine sand-sized quartz grains and rare feldspar and glauconite grains. The clastic fraction is further characterized by the presence of detrital mudstone fragments, often including small charcoal fragments. This shows that at least part of the organic matter is redeposited.

Table 1: Depth from surface, sulphur (S), total organic carbon (TOC), total inorganic carbon (TIC), calcite equivalent (eq.) percentages, biogenic silica (BSi), TOC/S ratio, Rock Eval parameters (S_1, S_2, T_{max}), hydrogen index (HI), production index (PI), soluble organic matter yield (SOM), and relative proportion of saturated (Sat. HC) and aromatic (Aro. HC) hydrocarbons, polar compounds (NSO) and asphaltenes (Asph.).

Sample	Depth	Unit	S	TOC	TIC	Calcite eq.	BSi	TOC/S	S_1	S_2	Tmax	HI	PI	SOM	Sat. HC	Aro. HC	NSO	Asph.
			(wt. %)						mg HC/g		(°C)			(mg/g TOC)	(wt. %, SOM)			
Drillhole C-180a																		
C-1	107.0		0.2	1.6	6.6	54.9	2.4	6.7	0.2	4.2	423	254	0.04	19	16	2	67	14
C-2	107.4		0.7	1.6	6.4	53.0	2.6	2.4	0.2	3.7	424	229	0.04					
C-3	107.9		0.0	0.7	9.9	82.3	1.2	93.6	0.1	1.6	429	210	0.05	29	18	0	71	10
C-4	108.2		1.0	2.6	4.2	35.3	6.5	2.6	0.4	7.9	422	301	0.05					
C-5	108.5		1.4	4.3	4.0	33.1	1.9	3.0	0.5	8.6	423	201	0.05	25	22	2	65	12
C-6	108.8		1.5	3.7	3.4	28.1	3.9	2.5	0.4	7.5	422	205	0.05					
C-7	109.0		1.0	3.2	5.2	43.4	2.4	3.1	0.3	6.5	422	203	0.04	21	12	0	72	15
C-8	109.3		1.2	2.9	4.7	39.4	1.7	2.4	0.3	5.2	424	176	0.05					
C-9	109.5		0.4	1.8	7.2	60.0	0.9	4.8	0.1	3.2	423	179	0.04	18	16	2	71	11
C-10	109.8	**Unit III**	0.4	1.2	7.3	60.6	1.0	3.4	0.1	2.8	425	227	0.04					
C-11	110.2		0.5	1.3	6.6	55.2	2.4	2.8	0.1	2.2	425	174	0.04	35	34	1	58	7
C-12	110.6		0.3	1.2	6.2	51.6	2.4	4.8	0.1	3.3	422	272	0.03	26	18	0	67	14
C-13	110.7		0.2	0.6	8.0	66.8	1.0	3.3	0.1	1.0	428	172	0.06					
C-14	111.5		0.7	1.1	6.0	49.7	1.9	1.7	0.2	3.8	425	333	0.04	35	14	0	74	12
C-15	112.0		0.5	1.3	5.1	42.5	1.9	2.5	0.1	1.7	426	129	0.05	30	16	1	74	9
C-16	113.0		0.0	0.6	8.6	71.6	1.0	49.8	0.1	1.3	429	213	0.05	51	42	0	55	2
C-17	113.7		0.0	0.6	8.8	73.4	2.0	80.9	0.1	1.2	429	194	0.05	37	12	0	84	3
C-18	114.0		0.0	0.6	8.3	69.0	1.7	94.6	0.1	0.9	428	136	0.06					
C-19	114.2		0.0	0.6	7.6	63.1	1.9	184.7	0.0	0.6	433	96	0.06					
C-20	114.5		0.0	0.2	10.4	86.4	0.9	146.7	–	–	–	–	–	41	–	–	–	–
C-21	148.7		0.0	1.7	8.1	67.7	0.5	63.1	0.2	3.8	420	223	0.06	16	31	18	37	14
C-23	149.4		0.0	0.7	5.6	47.0	9.0	37.3	0.2	2.2	419	318	0.06					
C-24	149.8		0.0	0.3	7.7	63.8	5.1	45.9	0.1	1.0	419	309	0.07					
C-25	150.3		0.0	0.8	8.0	66.3	2.1	48.4	0.2	2.5	419	318	0.07					
C-26	152.0		0.5	1.1	4.5	37.8	3.3	2.2	0.3	4.3	416	397	0.07	21	9	5	83	3
C-27	153.0		0.0	0.9	4.6	38.3	11.8	38.0	0.3	3.4	415	359	0.08					
C-28	153.9	**Unit IIa**	0.0	1.0	7.8	64.9	14.3	47.2	0.3	3.8	421	360	0.07	20	24	10	59	7
C-29	154.7		0.1	0.8	2.9	24.4	4.5	6.2	0.2	3.4	418	427	0.06					
C-30	155.2		0.0	0.5	6.6	55.0	8.7	27.3	0.1	1.4	418	287	0.07					
C-22	155.7		0.9	2.8	2.5	20.9	2.4	3.1	0.5	7.3	419	257	0.06	14	31	13	41	15
C-31	157.9		0.0	1.0	3.7	31.0	22.1	40.4	0.4	4.8	419	464	0.08	40	18	9	62	11
C-32	158.6		0.0	0.9	4.2	35.1	11.1	46.3	0.3	4.4	422	501	0.06					
C-34	159.7		0.0	0.2	6.7	55.5	1.5	260.2	0.0	0.3	423	186	0.08					
C-35	160.5		0.0	0.7	8.4	69.7	1.5	42.9	0.1	1.4	420	209	0.06	18	22	13	55	9
C-36	161.5		0.0	0.6	9.6	80.2	1.3	43.2	0.1	1.6	423	248	0.07					
C-37	214.3		0.3	0.1	0.3	2.3	–	0.2	–	–	–	–	–					
C-38	215.3		0.1	0.1	2.3	19.5	–	0.6	–	–	–	–	–					
C-39	216.4		0.2	0.1	2.4	19.6	–	0.4	–	–	–	–	–					
C-40	219.2		0.0	0.2	3.1	25.5	–	33.9	–	–	–	–	–					
C-41	221.0		0.0	0.0	0.9	7.1	–	11.0	–	–	–	–	–					
C-42	230.0	**Unit Ia**	0.0	0.1	0.1	0.5	–	18.7	–	–	–	–	–					
C-43	231.0		0.0	0.0	0.0	0.2	–	17.7	–	–	–	–	–					
C-44	232.0		0.0	0.0	0.0	0.4	–	11.2	–	–	–	–	–					
C-45	236.0		0.1	0.1	0.1	0.8	–	0.5	–	–	–	–	–					
C-46	238.0		0.0	0.0	0.2	1.5	–	13.4	–	–	–	–	–					
C-47	240.0		0.0	0.1	0.1	0.9	–	16.4	–	–	–	–	–					
C-48	241.0		0.0	0.1	0.3	2.6	–	44.2	–	–	–	–	–					
Outcrop near Albena resort*																		
A-1	3.7		0.0	0.1	0.2	1.4	8.2	1.9	–	–	–	–	–					
A-2	4.1		1.1	0.9	1.5	12.2	8.5	0.8	0.1	1.5	411	166	0.06					
A-3	4.4		0.8	1.1	1.8	14.7	12.8	1.4	0.2	2.4	414	216	0.06	21	11	5	53	31
A-4	4.8		1.0	1.2	1.9	16.2	1.4	1.2	0.2	2.5	417	213	0.06					
A-5	5.2		0.4	1.0	2.2	18.4	11.6	2.7	0.1	2.0	417	200	0.05					
A-6	5.6		0.3	0.7	3.0	25.0	7.3	2.2	0.1	1.3	413	171	0.06					
A-7	6.0	**Unit III**	0.6	1.1	2.5	21.1	10.6	1.8	0.1	2.4	412	207	0.02	15	12	6	51	31
A-8	6.4		0.4	0.7	3.4	28.2	3.7	1.7	0.2	0.6	419	77	0.22					
A-9	6.7		0.6	1.1	2.8	23.3	8.6	1.8	0.1	2.4	419	213	0.04					
A-10	7.1		0.5	1.0	3.5	29.1	9.9	2.0	0.1	2.5	415	256	0.05					
A-11	7.6		0.5	1.3	4.1	33.8	5.5	2.5	0.1	2.2	415	175	0.05	19	12	7	42	39
A-12	8.1		0.5	1.1	2.7	22.3	1.6	2.1	0.1	2.4	423	220	0.04					

***** — Sampling position in meters above sea level.

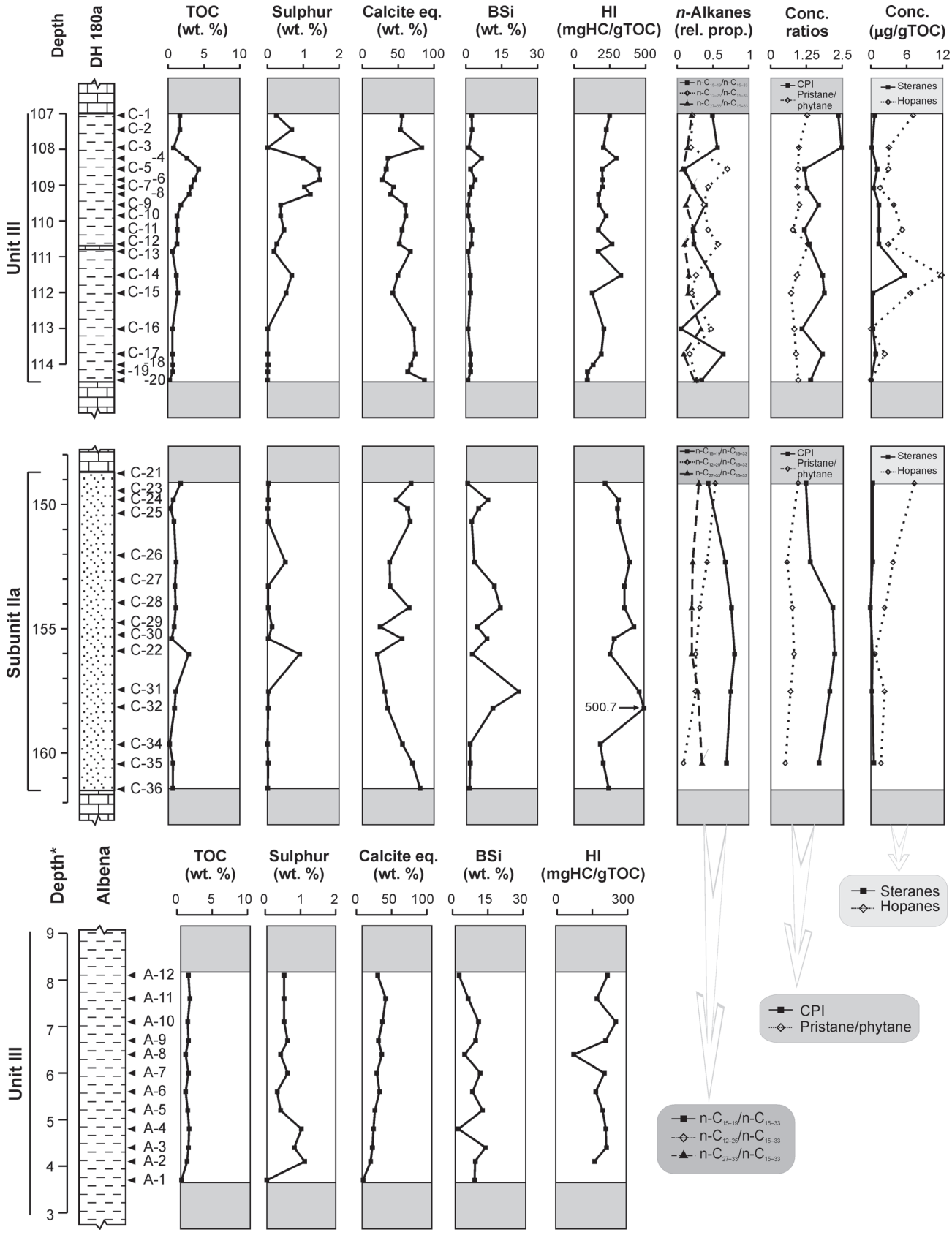

Fig. 4. Vertical distribution of total organic carbon (TOC), sulphur, calcite equivalent percentages, biogenic silica (BSi), hydrogen index (HI), relative proportions of *n*-alkanes, CPI, pristane/phytane ratio, sterane and hopane concentrations in core samples from subunit IIa and unit III, and outcrop samples.

Rocks from subunit IIa contain varying amounts of biogenic silica derived from diatom frustules (Table 1). Diatom remains were previously detected mostly within clays of the Euxinograd Formation (Popov & Kojumdgieva 1987; Temniskova-Topalova 1990). This suggests that subunit IIa is coeval with the lower part of this formation. Biogenic silica contents reach a maximum of 22 wt. % about 4 m above the base of the subunit (C-31) and decrease upwards (Fig. 4, Table 1). However, the biogenic silica content may significantly under estimated diatom contents. For example, microscopic inspection revealed that sample C-23 (9 wt. % silica) contains significantly more than 50 % of diatoms. The abundance of diatoms reflects a high nutrient supply and dissolved silica (DeMaster 2003). High nutrient supply is also supported by the frequent occurrence of calcareous nannoplankton assemblage rich in *Braarudosphaera bigelowii* (Gran & Braarud 1935) Deflandre, 1947 in sample C-31, which also argues for reduced salinity and cold water environment. High nutrient and silica supply may be related to rhyolitic volcanic activity, indicated by tephra layers within the Euxinograd Formation (Milakovska et al. 2001). The occurrence of *Cyclicargolithus floridanus* (Roth & Hay in Hay et al. 1967) Bukry, 1971 shows that sample C-23 is not younger than 13.33 Ma (Lourens et al. 2004).

Subunit IIb — is represented by white to grey-white biomicritic limestone, similar to that in subunit Ib. Although significant parts of the core are missing, the resistivity log suggests the presence of limestone within the missing intervals. The similarity of the lithologies of units I and II suggest that the rocks formed in similar sedimentary environments.

Unit III

Unit III in well C-180a is about 14 m thick and represents the upper part of the Euxinograd Formation (Figs. 2, 3). Its characteristics are similar to the 5-m-interval studied in the outcrop section. At both sites unit III is composed of a monotonous succession of fine-laminated clays and detritus of bivalve shells. With the exception of a few samples, the rocks contain no detrital sand-sized grains. Needle-shaped siliceous sponge spicules are extremely abundant in the upper part of the unit (samples C-10 to C-1) where biogenic silica contents reach up to 6.5 wt. % (Table 1).

The presence of sponge spicules proves deposition in a low energy sedimentary environment (Krautter 1998). A low energy environment and oxygen-depleted conditions are also supported by the lamination of the rocks (see also Kojumdgieva & Dikova 1978; Koleva-Rekalova 1998). The presence of ascidian spicules indicates shallow water conditions and enrichment in the nutrient supply (Toledo et al. 2007). Whereas sponge spicules are abundant in well C-180a, diatoms are more frequent in the outcrop samples, maybe due to different distance from the shoreline.

Redeposited coaly organic material is present, as in subunit IIa.

Units IV and V

Units IV and V correlate with the Upper Miocene Topola and Karvuna Formations (Popov & Kojumdgieva 1987), respectively. They are represented mainly by white massive and fine laminated aragonitic sediments (Topola Fm; Fig. 2 — Koleva-Rekalova 1994) and biomicritic limestones (Karvuna Fm; Fig. 2). Since the rocks do not contain organic matter, they are not considered in this study.

TOC and Rock-Eval parameters

Total organic carbon (TOC) contents are listed in Table 1 and are plotted versus depth in Fig. 4. TOC contents in subunit Ia are very low (<0.2 wt. %; Table 1) and vary between 0.2 and 4.3 wt. % in the rest of the samples. The highest TOC contents (1.8–4.3 wt. %) were detected in the upper part of unit III from well C-180a (Table 1, Fig. 4). Single samples with TOC contents up to 2.8 wt. % also exist in the middle and upper part of subunit IIa (Table 1, Fig. 4).

Fig. 5 shows the relationship between TOC and calcite eq. percentages. Whereas there is no linear relation for units Ia

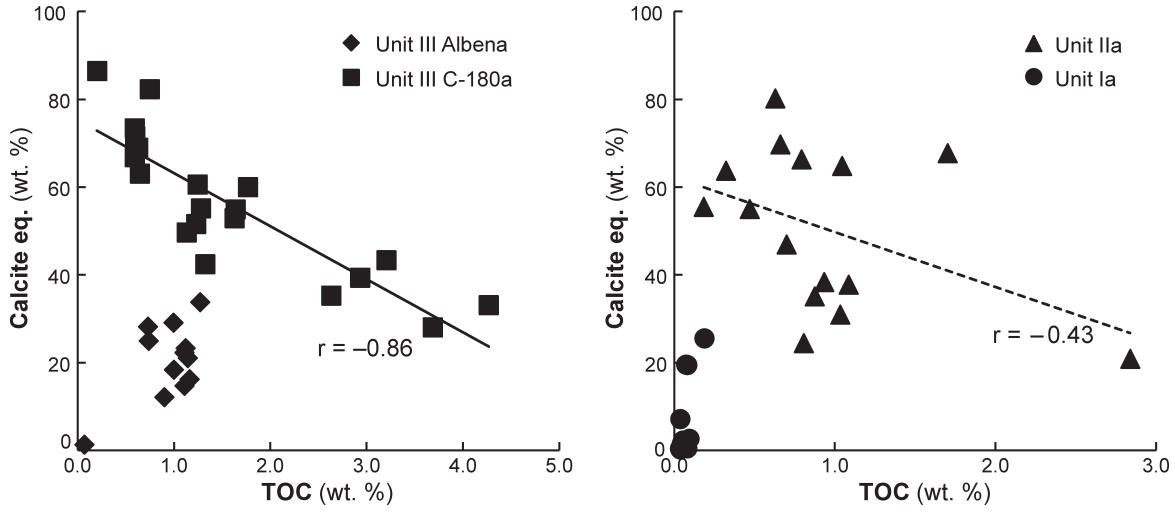

Fig. 5. Graphs of TOC versus calcite equivalent percentages.

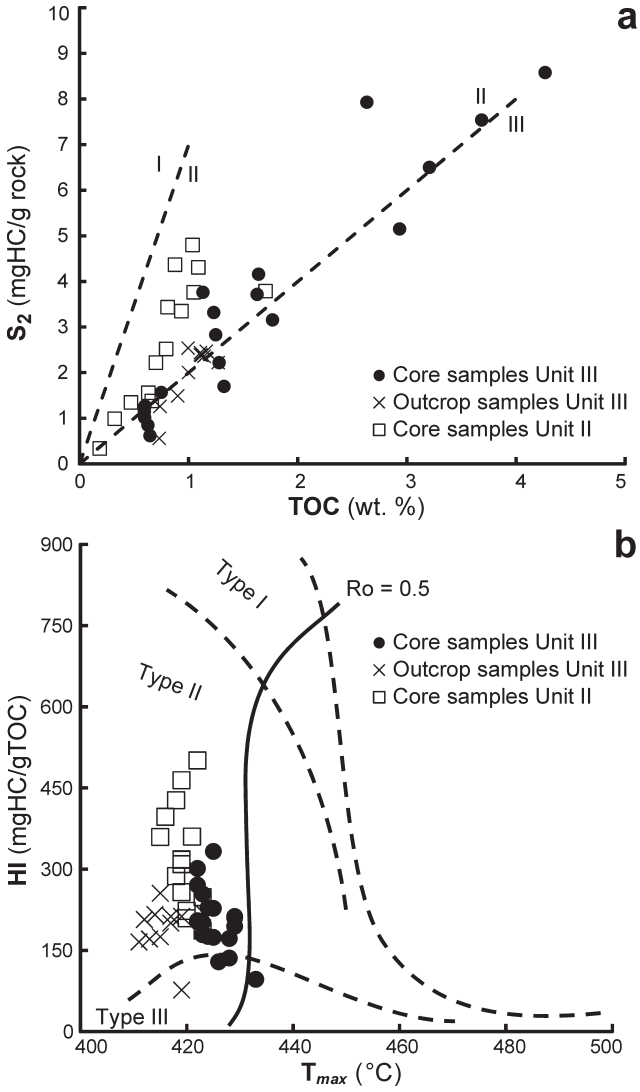

Fig. 6. Plots of S2 versus TOC (**a**) and HI versus T_{max} (**b**). Dashed lines in Fig. 6a represent HI values of 200 mgHC/gTOC (kerogen type III) and 700 mgHC/gTOC (kerogen type I).

and IIa, and the studied outcrop (unit III), a strong negative relation (correlation coefficient: –0.86) exists for samples from unit III from well C-180a. Ricken (1991) points out that a negative correlation is indicative for roughly constant organic matter production and dilution by varying amounts of calcite. Calcite in this unit is mostly derived from calcareous bivalve shell fragments.

Because of very low TOC contents, TOC/S ratios have not been calculated for samples from subunit Ia. For samples from units IIa and III TOC/S ratios range between 1.7 and 260.2. In general, the ratios are higher in subunit IIa (median: 42.9) than in unit III (3.4). High values in subunit IIa are consistent with a salinity-reduced environment. The TOC/S trend in unit III suggests an upward increase of salinity to normal marine conditions during deposition of the uppermost part of the Euxinograd Formation. Anoxic conditions indicated by TOC/S ratios below 2.8 (Berner 1984; Raiswell & Berner 1986) are not reflected by the data.

Hydrogen index (HI) values are summarized in Table 1. Their vertical distribution is shown in Fig. 4. Peters (1986) points out that pyrolysis experiments usually give erroneous results in samples with low TOC contents. For that reason HI was not calculated for samples, containing less than 0.2 wt. % TOC. These are mostly from subunit Ia, but also samples C-20 and A-1 from unit III. HI values vary significantly between 77 and 501 mg HC/g TOC.

Surprisingly, the sandy subunit IIa exhibits higher HI values (Fig. 6a; average: 324 mg HC/g TOC), than the clayey unit III (205 and 192 for core and outcrop samples, respectively). This is also reflected in plots of S_2 versus TOC (Langford & Blanc-Valleron 1990) and HI versus T_{max} (Fig. 6b — Espitalié et al. 1984). Whereas kerogen types II-III prevails in unit III, kerogen type II predominates in subunit IIa. Because biomarker data (see below) argue against a higher contribution of landplants to the organic matter in unit III, the difference might reflect enhanced microbial alteration of the organic matter in unit III.

Hydrocarbon potential

Peters (1986) proposed a classification scheme for source rocks based on TOC, S_2 and HI values. The respective average values for subunit IIa (TOC: 0.9 wt. %; S_2: 3.0 mg HC/g rock; HI: 324 mg HC/g TOC) show that it holds a fair to good hydrocarbon generative potential for oil. The upper 5 m of unit III (TOC: 1.7 wt. %; S_2: 3.5 mg HC/g rock; HI: 205 mg HC/g TOC) show that this thin interval holds a good to fair potential with the possibility to generate gas and minor oil.

The low maturity and the relatively low thickness of both diatom-bearing intervals, which are considered equivalents of the Euxinograd Formation, prevent significant hydrocarbon generation in onshore areas. However, both, thickness and maturity may increase towards the east in offshore areas.

Molecular composition of the hydrocarbons

The normalized yields of the soluble organic matter (SOM) are presented in Table 1 together with the contents of saturated and aromatic hydrocarbons, hetero-compounds (NSO) and asphaltenes. The contents of SOM are generally low (14–51 mg/g TOC), which is in accordance with a low maturity of the organic matter. In all samples, the SOM is mainly represented by polar compounds (37–84 wt. %; Table 1). It is noticeable, that most borehole samples show increased contents of saturated hydrocarbons and are depleted in aromatics and asphaltenes, in relation to outcrop samples. This finding might be an indication of the presence of free hydrocarbons in these samples. However, very low PI values (Table 1) are not consistent with the presence of mobile products.

n-Alkanes

The total ion current (TIC) chromatograms of the saturated hydrocarbon fractions of eight samples are shown in Fig. 7. The vertical trends of the *n*-alkanes and CPI (Carbon Preference Index after Bray & Evans 1961) in units IIa and III in well C-180a, are presented in Fig. 4.

All samples are characterized by the presence of *n*-alkanes in the range of *n*-C_{15} to *n*-C_{33} (Fig. 7). However, their distributions vary justifying the definition of three groups.

(i) Most samples from subunit IIa and six samples from unit III are characterized by a predominance of short-chain *n*-alkanes (*n*-C_{15-20}; Table 2, Fig. 7) and contain minor amounts of mid- and long-chain hydrocarbons. Typically, the dominant *n*-alkane is *n*-C_{17}, accompanied by appreciable amounts of *n*-C_{16} and *n*-C_{18}, with no odd-over-even predominance.

(ii) Outcrop samples from unit III show distributions dominated by mid- (*n*-C_{21-25}) and long-chain *n*-alkanes (*n*-C_{27-33}; e.g. sample A-7 in Fig. 7), with maximum concentrations of *n*-C_{29} or *n*-C_{31}. The CPI is moderately high (1.7–2.2; Table 2), and short-chain hydrocarbons are usually absent.

(iii) Another six borehole samples from unit III are dominated either by *n*-C_{20-22}, with a maximum at *n*-C_{21}(e.g. C-5, C-9) and a CPI of 1.2 to 1.7, or by *n*-alkanes in the range of *n*-C_{23-33} with a low CPI (1.1–1.3; e.g. C-11; Fig. 7).

Short-chain *n*-alkanes originate mostly from algae and microorganisms (Blumer et al. 1971; Cranwell 1977). Han et al. (1968) and Han & Calvin (1969) established a marked predominance of *n*-C_{17} in blue-green algae, and appreciable amounts of *n*-C_{16} and *n*-C_{18} in photosynthetic and non-photosynthetic bacteria. Considering the predominance of *n*-C_{17}, a significant contribution from phytoplankton and microorganisms can be suggested for samples with a type (i) distribution.

Mid-chain *n*-alkanes (*n*-C_{21-25}) are typical mostly for submerged aquatic plants and some moss species (Cranwell

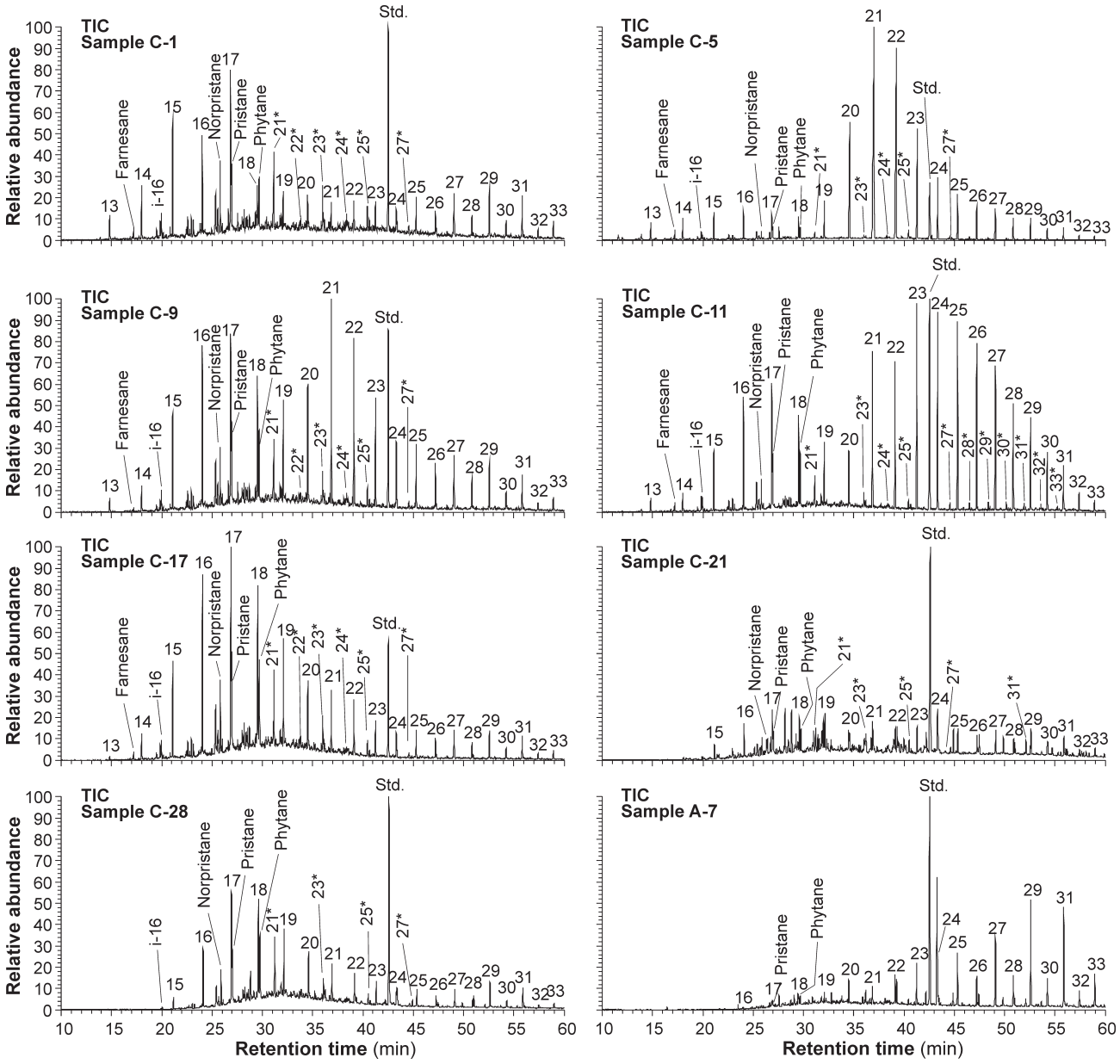

Fig. 7. Gas chromatograms of the saturated hydrocarbon fraction (Std. = standard). The numbers correspond to *n*-alkanes with the respective carbon atoms. Asterisk numbers correspond to iso-alkanes with the respective carbon atoms.

Table 2: Molecular composition of the organic matter.

	n-Alkanes					Isoprenoids		Steranes				Hopanespanes					Naphthalenes							
Sample	**Sum (µg/g TOC)**	***n*-C$_{15-20}$/*n*-C$_{15-33}$**	***n*-C$_{21-25}$/*n*-C$_{15-33}$**	***n*-C$_{26-31}$/*n*-C$_{15-33}$**	**CPI**	**Sum (µg/g TOC)**	**Pr/Ph**	**Sum (µg/g TOC)**	**C$_{27}$/Σsteranes**	**C$_{28}$/Σsteranes**	**C$_{29}$/Σsteranes**	**Sum (µg/g TOC)**	**Ts/(Ts+Tm)**	**22S/(22S+22R) C-31-Hopanes**	**Hop-17(21)-en (µg/g TOC)**	**Sat. Diterpenoids (µg/g TOC)**	**MN (µg/g TOC)**	**DMN (µg/g TOC)**	**TMN (µg/g TOC)**	**MP (µg/g TOC)**	**PAH (µg/g TOC)**	**Aryl Isoprenoids (µg/g TOC)**	**Chromans (µg/g TOC)**	**di-MTTC/tri-MTTC**
C-1	102.8	0.5	0.2	0.2	2.4	23.8	1.3	0.6	0.4	0.1	0.5	7.0	0.23	0.43	0.5	0.0	0.1	1.5	1.1	0.6	0.6	0.8	0.07	0.3
C-3	208.3	0.6	0.2	0.1	2.5	54.1	1.0	0.1	0.3	0.2	0.5	3.0	0.36	–	0.0	0.0	0.0	0.7	1.3	1.6	0.6	1.5	0.02	0.3
C-5	747.5	0.1	0.7	0.1	1.2	33.6	0.9	1.0	0.5	0.2	0.4	2.9	–	0.63	0.6	0.0	0.1	5.2	4.2	1.3	1.9	3.1	0.26	0.6
C-7	226.9	0.2	0.4	0.2	1.3	21.5	0.9	0.4	0.4	0.3	0.3	1.5	–	0.38	0.6	0.3	0.1	0.8	0.8	1.0	0.5	1.5	0.19	0.7
C-9	188.8	0.4	0.4	0.1	1.7	36.0	1.0	1.3	0.5	0.3	0.3	3.8	0.23	0.54	0.2	0.0	0.2	1.6	2.0	2.8	1.4	1.7	0.24	0.2
C-11	795.5	0.2	0.4	0.2	1.2	79.8	0.8	1.3	0.4	0.4	0.3	5.2	–	–	1.9	0.9	0.4	4.1	4.5	2.2	1.1	5.3	0.01	0.7
C-12	460.8	0.2	0.6	0.1	1.3	50.6	1.3	1.3	0.5	0.2	0.3	2.9	0.25	–	0.0	0.0	0.1	0.7	0.8	0.6	0.4	1.9	0.04	0.4
C-14	314.5	0.5	0.3	0.2	1.8	60.1	0.9	5.6	0.4	0.1	0.5	11.8	0.36	0.47	0.4	0.8	0.0	0.7	1.2	0.6	0.4	1.2	0.08	0.3
C-15	205.2	0.6	0.2	0.1	1.9	41.1	0.7	0.3	0.7	0.2	0.2	6.6	0.15	0.51	0.2	1.2	0.2	1.2	0.9	0.5	0.4	0.9	0.02	0.1
C-16	3132.8	0.1	0.5	0.3	1.1	70.1	0.8	0.3	0.4	0.1	0.5	–	–	–	–	0.0	0.0	0.7	1.2	1.0	0.7	1.5	0.09	0.1
C-17	253.2	0.6	0.2	0.1	1.8	68.9	0.9	0.8	0.5	0.3	0.2	2.3	0.25	0.59	0.2	1.3	0.5	4.4	3.2	1.3	1.3	1.9	0.03	0.1
C-20	469.8	0.3	0.3	0.3	1.4	84.3	1.0	–	–	–	–	–	–	–	–	–	–	–	–	8.7	–	–	–	–
C-21	71.5	0.3	0.4	0.2	1.2	12.2	0.9	0.4	0.4	0.2	0.4	7.4	0.80	0.65	0.8	0.8	0.0	0.0	0.0	0.6	0.4	0.0	0.00	–
C-26	368.2	0.5	0.3	0.1	1.4	40.2	0.6	0.4	0.4	0.2	0.4	3.8	0.50	0.57	1.2	1.2	0.0	0.3	0.5	0.5	1.0	0.0	0.00	–
C-28	42.2	0.5	0.2	0.1	2.1	13.2	0.7	0.0	0.4	0.2	0.4	2.4	0.50	0.63	0.2	0.2	0.0	0.1	0.1	0.2	0.2	0.0	0.00	–
C-22	27.5	0.6	0.2	0.1	2.2	8.0	0.8	0.4	0.5	0.2	0.4	0.8	0.34	0.66	0.2	0.2	0.0	0.1	0.1	0.1	0.4	0.0	0.00	–
C-31	155.2	0.4	0.2	0.2	2.0	36.1	0.7	0.3	0.2	0.2	0.6	2.4	0.54	0.65	0.2	0.2	0.1	0.7	0.8	0.6	1.7	0.0	0.00	–
C-35	86.3	0.4	0.3	0.2	1.7	11.9	0.5	0.6	0.4	0.2	0.4	1.8	0.66	0.66	0.0	0.0	0.0	0.2	0.6	0.1	4.0	0.0	0.00	–
A-3	164.1	0.1	0.4	0.4	2.0	2.8	0.6	0.4	0.4	0.2	0.4	1.5	0.57	0.57	0.2	0.2	0.2	0.0	0.0	0.1	0.1	0.0	0.01	0.2
A-7	163.8	0.0	0.4	0.4	2.2	1.3	0.6	0.1	0.4	0.2	0.4	2.0	0.36	0.41	0.1	0.1	0.2	0.0	0.0	0.1	0.2	0.0	0.01	0.2
A-11	154.5	0.0	0.4	0.4	1.7	0.9	0.7	0.2	0.4	0.2	0.4	2.7	0.54	0.51	1.3	1.3	0.2	0.0	0.6	1.0	4.7	0.0	0.07	0.1

$$\textbf{n-C}_{15-20}\textbf{/n-C}_{15-33} = \frac{\sum_{i=15}^{20}(n\text{-}Ci)}{\sum_{i=15}^{33}(n\text{-}Ci)}\ ;\ \textbf{n-C}_{21-25}\textbf{/n-C}_{15-33} = \frac{\sum_{i=21}^{25}(n\text{-}Ci)}{\sum_{i=15}^{33}(n\text{-}Ci)};\ \textbf{n-C}_{27-31}\textbf{/n-C}_{15-33} = \frac{\sum_{i=27}^{33}(n\text{-}Ci)}{\sum_{i=15}^{33}(n\text{-}Ci)}.$$

CPI – Carbon Preference Index (according to Bray & Evans 1961),

$$\text{CPI} = 0.5*\left(\frac{(n\text{-}C_{25}+n\text{-}C_{27}+n\text{-}C_{29}+n\text{-}C_{31}+n\text{-}C_{33})}{(n\text{-}C_{24}+n\text{-}C_{26}+n\text{-}C_{28}+n\text{-}C_{30}+n\text{-}C_{32})} + \frac{(n\text{-}C_{25}+n\text{-}C_{27}+n\text{-}C_{29}+n\text{-}C_{31}+n\text{-}C_{33})}{(n\text{-}C_{26}+n\text{-}C_{28}+n\text{-}C_{30}+n\text{-}C_{32}+n\text{-}C_{34})}\right).$$

Pri — Pristane, **Phy** — Phytane;

$$\textbf{C-27/steranes} = \frac{\Sigma\,\alpha\alpha\alpha C_{27}(20S+20R)}{\Sigma_{i=27}^{29}\,\alpha\alpha\alpha C_i(20S+20R)}\ ;\ \textbf{C-28/steranes} = \frac{\Sigma\,\alpha\alpha\alpha C_{28}(20S+20R)}{\Sigma_{i=27}^{29}\,\alpha\alpha\alpha C_i(20S+20R)}\ ;\ \textbf{C-29/steranes} = \frac{\Sigma\,\alpha\alpha\alpha C_{29}(20S+20R)}{\Sigma_{i=27}^{29}\,\alpha\alpha\alpha C_i(20S+20R)}$$

Ts — 18α-22,29,30-trisnorneohopane, **Tm** — 17α-22,29,30-trisnorhopane, **MN** — methyl naphtalenes, **DMN** — dimethyl naphtalenes, **TMN** — trimethyl naphtalenes, **P** — phenanthrene, **MPh** — methyl phenanthrenes, **PAH** — polyaromatic hydrocarbons (fluoranthrene + pyrene + benzo[a]pyrene + chrysene).

$$\textbf{Aryl Isoprenoids} = \Sigma_{i=13}^{21}C_i \text{ trimetyl (2,3,6)-alkylbenzol.}$$

$$\textbf{di-MTTC/tri-MTTC} = \frac{\text{dimethylated 2-methyl-2-(4´,8´,12´-trimethyltridecyl)chroman}}{\text{trimethylated 2-methyl-2-(4´,8´,12´-trimethyltridecyl)chroman}}.$$

1977; Ficken 2000). However, Han & Calvin (1969) established that mid-chain *n*-alkanes are typical components of bacterial lipids, especially in sulphate-reducing bacteria, thus indicating that microorganisms could also be a source of these hydrocarbons.

Long-chain *n*-alkanes with a high CPI are characteristic of waxes from vascular plants (Eglinton & Hamilton 1967). This suggests a major contribution of land plants for outcrop samples with a type (ii) distribution and a minor contribution for type (i) samples. However, other possible sources for long-chain *n*-alkanes have also been recognized. These include different bacterial communities, which produce mostly hydrocarbons with lower odd-over-even predominance (Albro & Dittmer 1967; Han & Calvin 1969; Johnson & Calder 1973; Volkman et al. 1980, 1983; Lichtfouse et al. 1994). Furthermore bacterial degradation of organic matter is known to reduce the CPI (Allen et al. 1971; Johnson & Calder 1973; Gagosian et al. 1983; Meyers 1994; Volkman & Tanoue 2002). Considering the partly high amount of long-chain *n*-alkanes with a low CPI in samples with a type (iii) distribution, a significant contribution of bacterial sources to the long-chain *n*-alkanes can be assumed. As seen in Table 3, the isotopic fractionation of the long- and short-chain *n*-alkanes do not differ significantly, which might be due to their similar origin. Nevertheless, the higher plant contribution to the long-chain alkanes is also noticeable by the slight depletion in ^{13}C (~0.5 ‰) of these compounds. On the other hand, redeposition of terrestrial organic matter might also

represent a substantial factor for the low CPI values, observed in the studied samples.

Isoprenoids

In the studied samples, the isoprenoids are represented by a series of compounds in the C_{14-20} range (Table 2). Among them, pristane and phytane are the most important, because of their ubiquity in sediments and oils of different maturity (Brooks et al. 1969). The relative proportions of isoprenoids depend on the Eh setting of the environment, since anoxic conditions favour the formation of phytane and more oxic conditions favour the formation of pristane (e.g. Volkman & Maxwell 1986). Hence, the pristane/phytane (Pr/Ph) ratio can be used to evaluate the Eh potential of the depositional environment (Didyk et al. 1978).

However, because pristane is formed during maturation of the organic matter, the Pr/Ph ratio is also influenced by thermal maturity (Goossens et al. 1984; Volkman & Maxwell 1986; Hughes et al. 1995; Koopmans et al. 1999). Moreover, pristane may be formed from the isoprenoidal side-chain of tocopherols (Goossens et al. 1984; ten Haven et al. 1987), phytoplankton and bacteria (Han et al. 1968; Han & Calvin 1969; Volkman 1988), and phytane may be formed from bacterial lipids (e.g. Volkman & Maxwell 1986; Volkman 1988).

Minor contributions from additional sources to both pristane and phytane cannot be completely discarded. However, since the low maturity of the rocks suppresses a significant contribution to pristane concentrations due to thermal maturity, the Pr/Ph ratio is considered an indicator of the oxic/dysoxic depositional conditions. Furthermore, the isotopic ratios of both pristane and phytane do not differ significantly (Table 3), which might be an indication for their common origin from chlorophyll-a. The Pr/Ph ratio is 1.3 for samples C-12 and C-1 from the middle and upper parts of unit III (Table 2, Fig. 4) indicating dysoxic conditions. The Pr/Ph of all remaining samples ranges between 0.5 and 1.0 (Table 2), which argues for deposition of organic matter in a strongly oxygen depleted environment.

Steroids and hopanoids

All the studied sediments are characterized by the occurrence of C_{27}–C_{29} regular steranes in very low concentrations. For the most samples, the steroid contents vary between 0.1 and 0.6 μg/g TOC (Table 2), although higher concentrations (0.8–1.3 μg/g TOC) were also found, mostly in the middle and upper parts of the core samples from unit III. Only sample C-14 is characterized by raised steroid contents (up to 5.6 μg/g TOC; Table 2). Interestingly, diasteranes or diasterenes were not detected, despite the high amounts of clay in the samples. Furthermore, the aromatic fraction is characterized by complete absence of aromatic steroids indicating the low maturity of the organic matter (Mackenzie et al. 1981).

In all samples, comparable steroid distribution patterns, composed of either nearly equal amounts of C_{27} and C_{29} steranes, or a slightly predominating C_{27} compounds, were detected (Table 2, Fig. 8). For most samples, the C_{28} steranes are present in very low amounts (10–20 %; Table 2). Slightly increased C_{28} concentrations (up to 40 %) exist only within the core samples from unit III. The steranes show very low 20S/(20S+20R) ratios of the ααα isomers (Fig. 8). In addition to the regular steranes, a series of C_{28}–C_{30} 4-methylsteranes in almost equal amounts were detected in sample C-14.

Steranes originate from sterols present in living organisms (Mackenzie et al. 1982; Waples & Machihara 1991; Meyers 1997; Volkman 2003, 2005). The main sources of C_{29} sterols are photosynthesizing organisms, including terrestrial plants, while C_{27} sterols are more characteristic for marine phytoplankton (Brassell & Eglinton 1981; Volkman 1986; Barrett et al. 1995; Volkman et al. 1998). However, numerous results from biomarker studies indicate that phytoplankton and microalgae also produce high proportions of C_{29} sterols (Volkman et al. 1998; Volkman 1999, 2003). The

Table 3: Compound-specific carbon isotopic composition of selected samples ($\delta^{13}C$, ‰; PDB).

Sample	A-7	C-1	C-5	C-7	C-11	C-14	C-16	C-21	C-22	C-26	C-35
***n*-C_{15}**		–28.3	–28.2	–28.7	–29.1	–29.3					
***n*-C_{16}**		–28.6	–28.3	–28.8	–29.4	–29.1	–29.5	–29.0	–29.5	–28.6	
***n*-C_{17}**		–28.5	–28.7	–28.7	–29.5	–29.4	–29.9	–29.6	–29.4	–29.1	–29.1
Pristane		–30.1	–29.8	–29.8	–30.2	–30.1	–30.4	–29.9	–30.2	–30.4	–29.9
***n*-C_{18}**		–29.0	–28.7	–28.7	–29.5	–29.3	–29.4	–29.1	–29.3	–28.5	–29.4
Phytane		–29.9	–29.8	–30.1	–30.7	–30.5	–30.2	–30.1	–30.2	–30.1	–30.2
***n*-C_{19}**		–28.5	–28.6	–28.5	–28.4	–29.0	–28.7	–28.8	–28.8	–28.7	–29.2
***n*-C_{20}**		–28.1	–28.3	–28.7	–28.5	–28.0	–28.3		–29.2	–27.9	–29.0
***n*-C_{21}**			–27.9	–28.2	–28.1	–28.8	–27.7			–28.6	–28.5
***n*-C_{22}**	–28.3		–28.1	–27.7	–27.2	–28.1	–27.4			–27.6	–28.0
***n*-C_{23}**	–27.5		–28.3	–28.1	–27.0	–28.3	–27.6			–28.5	–27.9
***n*-C_{24}**	–28.0		–27.5	–26.9	–26.8	–27.8	–26.9	–27.8		–28.1	–27.7
***n*-C_{25}**	–27.7	–28.6	–28.0	–27.2	–26.6	–28.1	–27.0	–28.6	–28.8	–28.7	–28.1
***n*-C_{26}**	–27.7	–28.7	–27.8	–27.4	–26.5	–28.4	–26.9	–28.2	–27.9	–28.0	–27.8
***n*-C_{27}**	–28.1	–28.1	–28.6	–27.6	–27.0	–29.2	–27.1	–28.8	–29.2	–28.8	–28.8
***n*-C_{28}**	–28.3	–27.6	–29.1	–28.2	–26.7	–28.7	–27.0	–28.6	–28.0	–28.4	–27.9
***n*-C_{29}**	–28.8	–28.9	–28.6	–28.1	–27.5	–29.1	–27.1	–28.9	–28.9	–29.3	–28.9
***n*-C_{30}**	–29.5	–28.4	–28.5	–27.8	–27.7	–29.1	–26.9	–28.7	–28.5	–28.3	–28.1
***n*-C_{31}**	–29.7	–28.7	–28.5	–28.4	–28.2	–29.3	–26.9	–29.1	–29.4	–29.2	–28.9
***n*-C_{32}**	–29.1						–26.4	–28.5	–27.8	–28.2	–28.5
***n*-C_{33}**	–29.2						–27.2	–27.6		–27.6	–27.8

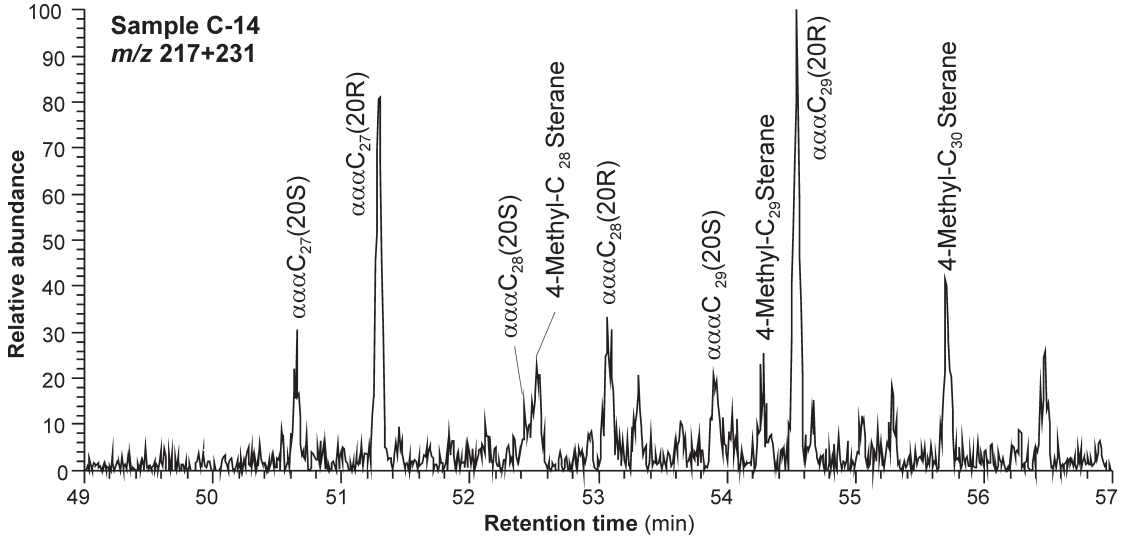

Fig. 8. Typical mass chromatogram (*m/z* 217+231) of the steroids and their methyl substituted derivatives.

most probable source of C_{28} steranes are marine microalgae, as suggested by the presence of significant amounts of C_{28} sterols in marine diatoms (Kates et al. 1977; Barrett et al. 1995; Volkman et al. 1998; Volkman 2003). Methyl steroids are also related to marine and lacustrine microalgal precursors (Volkman et al. 1990, 1998). A specific class of C_{30} 4-methyl steranes with dinosterol structure is a biomarker for dinoflagellates (Robinson et al. 1984; Mansour et al. 1999).

Considering these facts, the steranes distribution patterns argue for mixed organic matter, composed predominantly of marine phytoplankton, but with significant contributions from terrestrial plants. Enhanced contributions of C_{29} steranes are observed in few core samples from unit III (e.g. C-1, C-3, C-14; Table 2), as well as in sample C-31 from unit IIa, (Table 2). None of these samples shows increased concentration of long-chain *n*-alkanes. Therefore, the slight predominance of C_{29} steranes in these samples might reflect a change in the phytoplankton communities. It is noticeable that in contrast to *n*-alkanes distribution, the steranes distributions are similar in outcrop and core samples from unit III. Therefore, significant compositional changes in the short-chain hydrocarbons, possibly due to weathering, can be assumed.

Hopane concentrations range from 1.5 to 11.8 μg/g TOC (Table 2, Fig. 4). Two set of samples can be separated based on the hopane composition. The first set comprises the core samples from unit III, in which hopanes are represented by 17α,21β(H)-, 17β,21α(H), and 17β,21β(H) compounds with 27–32 carbon atoms (Fig. 9a). C_{28} hopanes are missing. An overall positive correlation in these samples exists between the hopane and sterane concentrations (r = 0.76), suggesting a proportional increase of bacterial activity together with the increase of organic matter input (see also Fig. 4). The second set comprises samples from subunit IIa and the outcrop samples, in which hopanes are represented by 17α,21β(H)-, 17β,21α(H) and 17β,21β(H) compounds with 27–35 carbon atoms, with the C_{28} hopane absent (Fig. 9b). For subunit IIa the vertical distribution of the hopanoids shows a marked upward increase (Fig. 4). However, no correlation exists between the hopane and sterane concentrations, suggesting that the increase of bacterial activity is probably related to a shift to a more oxygen-rich environment, as recent studies indicated aerobic bacteria as the main source of hopanes (Talbot et al. 2008; Rezanka et al. 2010).

For both sets the hopane distribution is characterized by a marked predominance of hopanoids in the 17α(H),21β(H) configuration (Fig. 9 — Ourisson et al. 1979). Dominant in all samples are 17α(H)-C_{29} and 17α(H)-C_{30} hopanes (Fig. 9), accompanied by 17β,21α(H)-C_{30} moretane and C_{27} hopanes. The core samples from unit III are characterized by low Ts/(Ts+Tm) ratios (0.2–0.4; Table 2). This ratio and appreciable amounts of hopanes with 17β,21β(H) configuration (Fig. 9a) argue for a low maturity of the organic matter. In contrast, Ts/(Ts+Tm) ratio is significantly higher (0.4–0.8; Table 2) for subunit IIa samples and the outcrop samples, indicating enhanced diagenetic changes. Furthermore, the ratio of 22S/(22S+22R) C_{31}-hopanes shows generally very high values (0.38–0.66), which are typical for marginal mature organic matter. However, both ratios are known to be influenced by facies variations (Waples & Machihara 1991; Peters et al. 2005).

The most probable biological precursors of hopanoid biomarkers are bacteriohopanepolyol derivatives, and to a lesser extent 3-desoxyhopanes (Ourisson et al. 1979; Rohmer et al. 1992), identified in the membrane of aerobic bacteria such as cyanobacteria, and heterotrophic and methanotrophic bacteria (e.g. Gibson et al. 2008; Talbot et al. 2008; Rezanka et al. 2010).

The extended hopanes with 31 to 35 carbon atoms are represented in relatively low amounts (data not shown) (Fig. 9). According to Van Dorselaer et al. (1975), the formation of 17α,21β(H)-homohopane (22R) implies complex reactions in acidic environments under oxic conditions. However, a direct bacterial input to the organic matter should also be considered, as Thiel et al. (2003) has proved the presence of homohopanoic acids with αβ configuration in living microbial mats.

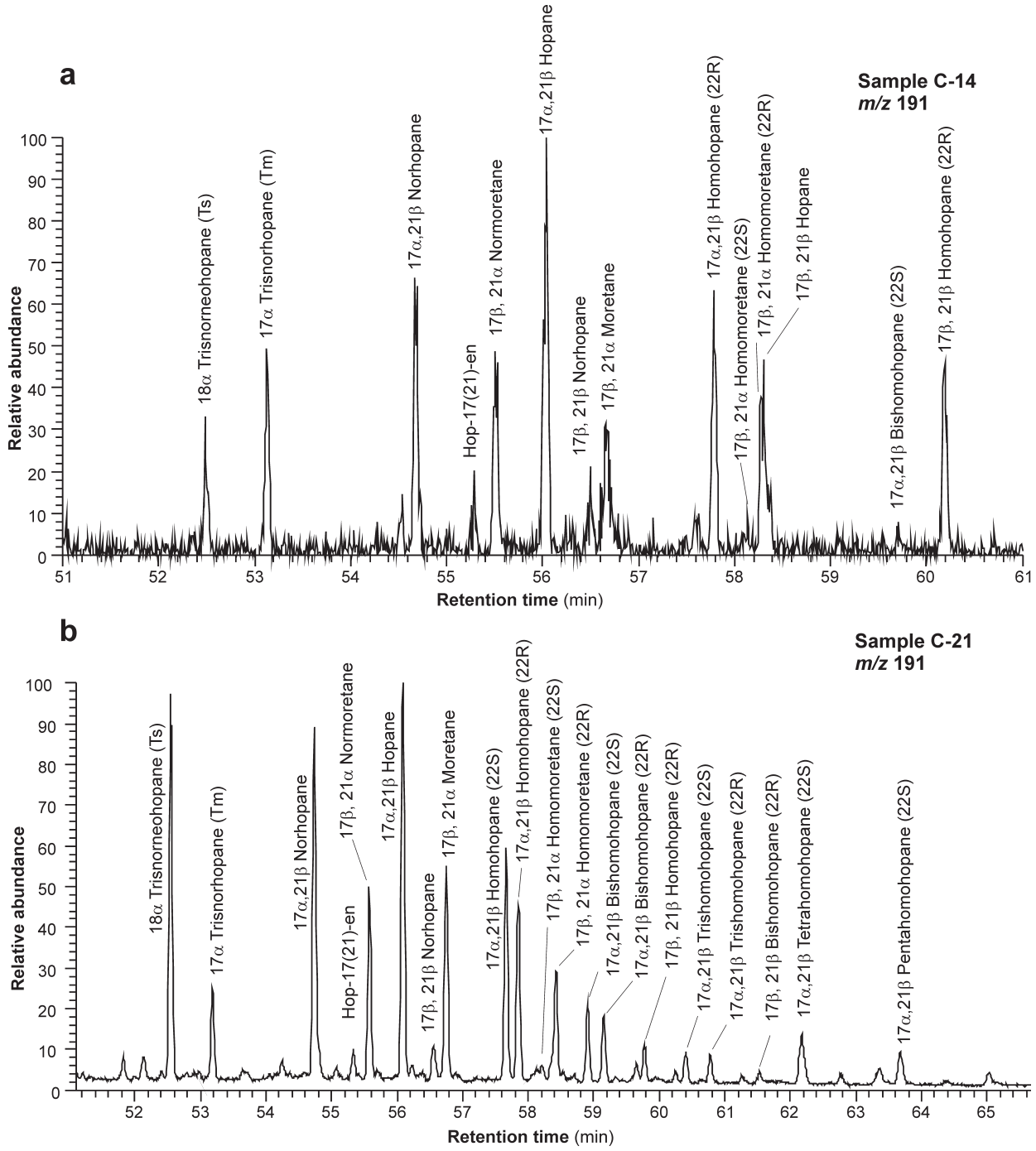

Fig. 9. Typical mass chromatograms (*m/z* 191) of the hopanoid hydrocarbons.

Hop-17(21)-ene was detected in small amounts (< 1.9 μg/g TOC; Table 2) in almost all samples. Its biological precursor has not yet been established (Bottari et al. 1972; Ourisson et al. 1979; Brassell et al. 1980; Volkman et al. 1986; Wakeham et al. 1980b; Wolff et al. 1992; Sabel et al. 2005).

Other terpenoids with non-hopanoid skeleton

Terpenoids are widespread in the geosphere (Thomas 1969) as part of the tissues of higher plants. Among them, di-and tri-terpenoids are valuable biomarkers for determining the type of precursor vegetation (Simoneit 1977, 1986, 1999). In most of the studied samples very low amounts (<1.3 μg/g TOC; Table 2) of diterpenoids were detected. They are represented by hydrocarbons with phyllocladane and pimarane type structure. The individual compounds identified are α-phyllocladane, occurring as a major component, whereas the samples from subunit IIa and the outcrop samples also contain trace amounts of β-phyllocladane and pimarane. Phyllocladanes are biomarkers for gymnosperms

(e.g. *Podocarpaceae*, *Taxodiaceae*, *Araucariaceae* and *Cupressaceae* — Noble et al. 1985; Sukh Dev 1989; ten Haven et al. 1992; Otto & Wilde 2001). Triterpenoids with oleanane, lupane and ursane type skeleton structure and their aromatic derivatives, derived from angiosperm plants (Philp 1985; Simoneit 1986), were not detected in the studied samples.

Aromatic hydrocarbons

The composition of the aromatic fraction in all the studied samples is relative uniform and comprises methyl-, dimethyl- and trimethyl-naphthalenes, phenanthrene and its methyl derivatives, as well as low amounts of polyaromatic hydrocarbons (PAHs), represented by fluoranthrene, pyrene, benzo[a]pyrene and chrysene (Table 2, Fig. 10a). PAHs may form due to diagenetic alteration of natural biolipids, but most authors accept an origin by wildfires (e.g. LaFlamme & Hites 1979; Wakeham et al. 1980a,b; Venkatesan & Dahl 1989; Killops & Massoud 1992; Yunker 2002, 2003). Considering this, we speculate that the detected PAHs are of terrestrial origin and were transported into the basin together with charcoal particles.

The aromatic hydrocarbon composition is further characterized by the occurrence of aryl isoprenoids in the range C_{13}–C_{21} with a 2,3,6-trimethyl substitution pattern for the aromatic ring and a tail-to-tail isoprenoid chain (Fig. 10b). They are present in low amounts in the core samples from unit III (Table 2). The aryl isoprenoids are derived from isorenieratene, which is known to be synthesized by photosynthetic green sulphur bacteria. These organisms are phototrophic anaerobes and require both light and H_2S for growth (Summons 1993; Pfennig 1997). Therefore, aryl isoprenoids are widely used as a biomarker for green sulphur bacteria and photic zone anoxia (e.g. Summons & Powell 1987; Sinninghe Damsté et al. 2001). However, Koopmans et al. (1996) found out that aryl isoprenoids with a 2,3,6-trimethyl substitution pattern can also form due to diagenetic transformation of the more ubiquitous carotenoid β-carotene, and, therefore, have only limited applicability as a biomarker. In the present case, isorenieratene itself has not been identified in the samples.

The aromatic fraction of the samples from unit III is further characterized by very low amounts of di- and trimethylated 2-methyl-2-trimethyltridecylchromans (MTTC; Table 2, Fig. 10b). Among them, tri-MTTCs predominate (di-/tri-MTTCs ratios: 0.1–0.4; Table 2). There are, however, samples (e.g. C-5, C-7, C-11), which also contain appreciable amounts of di-MTTCs (di-/tri-MTTCs ratios: 0.6–0.7).

The origin of the methyl substituted MTTCs is still unknown (e.g. Li et al. 1995). Sinninghe Damsté et al. (1987, 1993) suggest that MTTCs form in the upper parts of the water column, either from photosynthetic or non-photosynthetic organisms. On the contrary, Barakat & Rullkötter (1997) suggested that chromans are a result of cyclization of alkylated phenols. Despite this limitation, methyl-substituted chromans are widely used as a paleosalinity indicators (e.g. Schwark & Püttmann 1990; Sachsenhofer et al. 2009). Sinninghe Damsté et al. (1987, 1993) indicate that formation and preservation of mono-, di- and trimethyl substituted chromans require marine environments with normal to enhanced salinity and stratification of the water column. Furthermore, the authors observed increasing di-/tri-MTTC ratios with increasing salinity. Con-

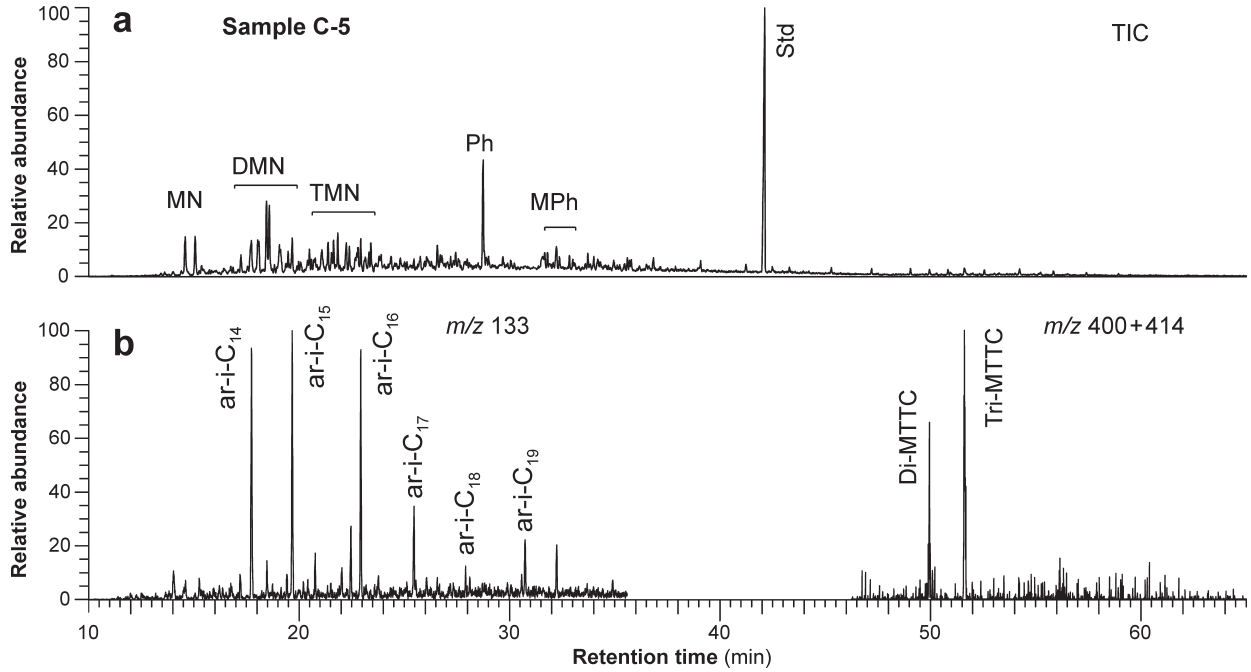

Fig. 10. a — Typical gas chromatogram of the aromatic fraction: MN — methyl naphthalenes, DMN — dimethyl naphthalenes, TMN — trimethyl naphthalenes, Ph — phenanthrene, MPh — methyl phenanthrenes; **b** — Gas chromatogram of the aryl isoprenoids (*m/z* 133) and chromans (*m/z* 400+414): ar-i-$C_{14\div19}$ trimethyl (2,3,6)-alkylbenzol, Di-MTTC — dimethylated 2-methyl-2-(4',8',12'-trimethyltridecyl)chroman; Tri-MTTC — trimethylated 2-methyl-2-(4',8',12'-trimethyltridecyl)chroman.

sidering this, fully marine conditions are suggested during the deposition of unit III, perhaps with a salinity stratified water column. This suggestion is supported by the lamination of the clays, as well as by the overall positive correlation between the concentrations of MTTC and sulphur (r = 0.51) as well as MTTC and aryl isoprenoids (r = 0.68).

Conclusions

The Middle to Upper Miocene succession in the Varna-Balchik Depression, located in the south-eastern part of the Moesian Platform, is up to 300 m thick and is represented by sandy, clayey and carbonate rocks. Based on lithology and resistivity log response, the succession is subdivided from base to top into five units.

Sedimentation of fine-grained siliciclastic material prevailed during deposition of the lower parts of units I and II (subunits Ia and IIa, respectively), whereas their upper parts (subunits Ib, IIb) are composed of biomicritic limestone. Based on high diatom contents, subunit IIa is considered coeval with the lower part of the Euxinograd Formation. Unit III represents the upper part of the Euxinograd Formation. It is composed of laminated clays with bioclastic layers and significant amounts of biogenic silica, which are mainly derived from sponge spicules in core samples and from diatom frustules in outcrop samples. Units IV and V are represented predominantly by carbonate rocks and are correlated with the Upper Miocene Topola and Karvuna Formations.

Whereas TOC contents in subunit Ia are negligible (<0.2 wt. %), TOC contents in subunit IIa and unit III (Euxinograd Fm) are generally between 1 and 2 wt. %, but can reach 4 wt. % in unit III. Sulphur contents are typically low (< 0.5 %) and exceed 1.0 % only in samples from unit III. Low sulphur contents may be due to deposition in environments with reduced salinity. Normal marine conditions are suggested for unit III.

The biomarker composition is typical for mixed marine and terrestrial organic matter, and shows no significant changes in subunit IIa and unit III. The molecular composition and biomarker ratios support the presence of immature organic matter, deposited in dysoxic to anoxic environments. Kerogen is mainly type II in subunit IIa (average HI = 324 mg HC/g TOC) and type III for unit III (average HI ~ 200 mg HC/g TOC).

Considering the classification scheme of Peters (1986), TOC and Rock Eval data show that subunit IIa holds a fair to good hydrocarbon potential for oil, whereas the upper 5 m of unit III holds a good to fair potential with the possibility to generate gas and minor oil. Both units are immature in onshore areas, but thickness and maturity may increase towards the east in offshore areas.

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