Palaeoecological and post-depositional changes recorded in Campanian–Maastrichtian black shales, Abu Tartur plateau, Egypt

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Abstract
The Upper Cretaceous black shales of Egypt are part of the worldwide belt of Late Cretaceous organic-rich shales. Black shales are particularly prominent in North Africa and the Middle East. In Egypt, these shales occur in an east-west trending belt extending from the Quseir-Safaga district along the Red Sea to the Kharga-Dakhla land-stretch passing through the Nile Valley. The black shales are hosted mainly in the Campanian to Maastrichtian Duwi and Dakhla formations. In order to reconstruct palaeoenvironmental conditions, the present work focuses on the distribution of organic matter including lipid biomarkers within the Abu Tartur borehole section, which was drilled in 2007 in the Maghrabi-Liffya area. The kerogen in the Abu Tartur section is of type III with the exception of sedimentary deposits at the Duwi/Dakhla transition. Low Tmax, odd-over-even predominance of n-alkanes with a commonly high Carbon Preference Index, good preservation of carboxylic acids and abundant 17β,21β-hopanes and -hopanoic acids indicate immaturity of the organic constituents in the bitumen. Although thermal maturation was only low, the preponderance of rearranged steranes (diasterenes) over regular steranes indicates enhanced clay catalysis. Significant allochthonous input typifies the Abu Tartur section deposits, which are characterized by high contents of long-chain n-alkanes and low carbonate contents. The high content of desmethyl steranes and diasterenes suggests that marine algae were the main marine primary producers. The presence of different isomers of hopanes (C27, C29–C31) and hopanoic acids (C31–C33) reveals input from various bacteria. The observed variation in the abundance of biomarkers corresponds to changes in planktic algal assemblages associated with sea level change and episodic photic zone anoxia, which are indicated by the occurrence of aryl isoprenoids, biomarkers of green sulphur bacteria.

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1. Introduction

Black shales are dark, finely laminated, fine-grained argillaceous, calcareous and sometimes siliceous deposits that formed under anoxic conditions. They are rich in organic matter, mainly preserved as kerogen, and contain abundant sulphide minerals (e.g., pyrite). Black shales commonly have high contents of redox-sensitive trace elements such as V, Cu, Cd, Ni, Co, Mo, U and rare earth elements (Brunnacker, 2006; Loukola-Ruskeeniemi and Lahtinen, 2013).

Black shales are deposited predominately in oxygen minimum zones, where depositional environments are characterized by low current speeds and low oxygen levels (Killops and Killops, 2005; Takashima et al., 2006), favouring the preservation of organic matter. On the other hand, high-energy systems can be considered as alternative settings for black shale deposition (Alexandre et al., 2012). The main environments of black shale deposition are classified according to Tourtelot (1979) into three categories, (1) the restricted circulation type, (2) the open ocean type and (3) the continental shelf type.

The Campanian–Maastrichtian was characterized by increased pCO2 from prominent global igneous activity and is known as a typical greenhouse period (Takashima et al., 2006) with moderate to high pCO2 levels from the Late Cretaceous until the early Eocene (Kent and Muttoni, 2013). Increased burial was accompanied by changes in the composition of the phytoplankton community (coccolithophores, dinoflagellates and diatoms), associated with
increased storage capacities caused by the opening of the Atlantic Ocean basin (Katz, 2005). Phytoplankton diversity was rapidly detached from the long-term sea-level trends at the Cretaceous–Palaeogene boundary (Falkowski et al., 2004).

In northern Africa and the Middle East, deposition of organic-rich black shales was widespread in the Late Cretaceous to Palaeocene. During this period, the sedimentation processes were influenced by greenhouse climate, favouring the establishment of anoxic conditions in many marine basins along a broad marine continental shelf across northeast Africa (Robinson and Engel, 1993). Apart from organic-rich shales, phosphorites, carbonates, glauconitic deposits and cherts dominate the shelf sequences (Bein and Amit, 1982; Tröger, 1984; Germann et al., 1985; Mikkel and Abed, 1985; Notholt, 1985; Ganz et al., 1987; Abed and Al-Agha, 1989; Glenn and Arthur, 1990; El-Kammar 1993). Black shales and marls reflect periods of high primary productivity on the shallow shelves, favouring the preservation of organic matter. As a consequence of the absence of a pronounced catagenesis, massive black shale successions have been preserved in Egypt and elsewhere in North Africa.

Some work on organic geochemical proxies in the Egyptian sequences of the Red Sea area has been conducted by Ganz et al. (1990). Apart from organic-rich shales, phosphorites, carbonates, glauconitic deposits and cherts dominate the shelf sequences (Bein and Amit, 1982; Tröger, 1984; Germann et al., 1985; Mikkel and Abed, 1985; Notholt, 1985; Ganz et al., 1987; Abed and Al-Agha, 1989; Glenn and Arthur, 1990; El-Kammar 1993). Black shales and marls reflect periods of high primary productivity on the shallow shelves, favouring the preservation of organic matter. As a consequence of the absence of a pronounced catagenesis, massive black shale successions have been preserved in Egypt and elsewhere in North Africa.

The present work focuses on the organic matter distribution within the Abu Tartur black shale sequence, analysing a complete core that was drilled in 2007 in the Maghrabi-Liffya area. We put particular emphasis on the lipid biomarker inventory of the strata at the transition from the Duwi to the Dakhla Formation, covering the transition from the Campanian to the Maastrichtian. This transition, changes in sedimentation, primary productivity and preservation of organic matter are observed based on the quantification of biomarkers including n-alkanes, n-fatty acids, steroids, hopanoids and isoprenoids. The overall palaeoenvironmental conditions during the deposition of the studied strata are finally reconstructed, combining the interpretation of lipid biomarker patterns and organic and inorganic bulk parameters.

2. Geologic setting

The black shales of the Upper Cretaceous to lower Palaeocene in Egypt occur in an east-west trending belt from Quseir-Safaga in the east along the Red Sea to the Kharga-Dakhla land-stretch toward the west, passing through the Nile Valley (Fig. 1; see also Baioumy and Tada, 2005; El-Azabi and Farouk, 2010 for detailed maps). The organic-rich shales are hosted in two formations. The Duwi Formation is a phosphorite-bearing formation with intercalations of marls, chert-rich deposits along the Red Sea, and glauconite–bearing horizons in the Kharga-Dakhla area including the Abu Tartur plateau. The Duwi Formation is well known for its numerous phosphorite mines, which have been active since the beginning of the Miocene. The superjacent Dakhla Formation is characterized by abundant foraminifera-rich shales and marls with limestone and rare silstone intercalations.

According to Glenn and Arthur (1990), two major modes prevailed during the deposition of these Upper Cretaceous strata: (1) shallow hemipelagic deposition, representing the initial stages of marine transgression conducive for the formation of organic carbon-rich shales and massive phosphorites; (2) high energy deposition, representing regressive stages with advancing deltas, seawards reworked glauconites and prograding brackish oyster banks in the Red Sea area.

According to Baioumy and Tada (2005), the Duwi Formation in the Red Sea, Nile Valley and Abu-Tartur areas can be subdivided into four subunits: lower, middle, upper and uppermost members. The Duwi Formation ranges in age from late Campanian—late Maastrichtian, in the Red Sea (Zalat et al., 2008) to late Campanian in the Kharga-Dakhla area. The Duwi Formation has been suggested to be unconformably overlain by the Dakhla Formation, which is early Maastrichtian to early Thanetian in age in the Dakhla-Kharga region (El-Azabi and Farouk, 2010). The inferred unconformity was believed to have been caused by a tectonic movement coupled to a regression that took place during the latest Campanian, resulting in a hiatus in the Kharga-Abu Tartur district (Barthel and Herrmann-Degen, 1981). This area was probably a palaeohigh at that time. Sedimentation has been suggested to commence again in the early late Maastrichtian, resulting in the deposition of Dakhla shales overlying the Duwi Formation (Mansour et al., 1982; Hendriks et al., 1984; El-Azabi and Farouk, 2010).

The Dakhla Formation in the Dakhla-Kharga area has been subdivided by Awad and Ghobrial (1965) into Mawhoob, Baris and Kharga members in ascending order. The Kharga shale member has been further subdivided by Luger (1985) into two subunits, the lower and upper Kharga shales. These subunits are separated by an unconformity representing the Cretaceous/Palaeocene boundary. On the Abu Tartur plateau, the lower part of the upper Kharga shale is replaced laterally by limestones with shale interbeds named the Kurkur Formation (Issawi, 1968).

3. Material and methods

Black shales weather readily and weathering may have a significant effect on chemical composition, introducing artefacts in samples collected in outcrops (e.g., El-Kammar and El-Kammar 1996). Accordingly, the black shales studied here were taken from a drilled core that was not affected by surficial weathering. The borehole was drilled by the Egyptian Mineral Resources Authority (EMRA). Ten cores were drilled in the course of a project aiming to evaluate the potential of Egyptian black shales as unconventional source rocks. Among these cores, only one core was drilled in the Western Desert of Egypt. This study focuses on this drill core taken on the Abu Tartur plateau (Maghrabi-Liffya sector) in the Western Desert (Fig. 1). Drilling was done in cooperation of the Ministry of Petroleum and DanaGas® Egypt.

3.1. Sampling

Two sampling strategies were applied during the present study. First, down-core samples were collected every 10 cm and subsequently 10 successive samples were mixed and homogenized to obtain representative bulk samples for homogeneous 1 m transects for routine analyses. However, additional samples were taken in case of lithology changes in the transects. The obtained rock pieces were ground to a suitable mesh size for bulk analyses (TOC% and Rock Eval). Secondly, lower resolution sampling (every 2–6 m) was made to monitor lithology or facies changes. These samples were used for biomarker and XRD analyses.

3.2. X-ray diffraction

About 35 X-ray diffraction (XRD) analyses were performed on bitumen-free samples to determine the bulk mineralogy. The X-ray
diffraction was done on a Bruker D8 Advance diffractometer equipped with a Cu-tube ($\lambda_{\text{Cu}}$ 1.541, 45 kV, 40 mA), a fixed divergence slit of 0.2°, a 8 × 15 samples changer, a receiving slit of 0.1 mm, a secondary graphite monochromator and the Lyneye detector system. The measurements were made at the Geosciences Department of Bremen University, Germany. Mineral identification was done by means of the Philips software X’Pert HighScore™, and quantification has been performed using the full-pattern software package QUAX (cf. Vogt et al., 2002).

3.3. Total organic carbon and Rock Eval analysis

Aliquots of about 130 representative homogenized samples were measured for total organic carbon (TOC) contents (wt %) and Rock Eval pyrolysis in the laboratories of StratoChem® in Egypt. For the TOC contents, rock material was ground and sieved through a 40 mesh. 200 mg of the ground rock was weighed into a Pyrex beaker and reacted with hydrochloric acid to dissolve any inorganic carbon that may have been present in the samples. Thereafter, the samples are transferred to a microfiber filter paper using a Millipore filter apparatus. The samples were combusted in a LECO C230 or LECO EC-12 combustion furnace, where the resulting carbon dioxide was quantitatively measured using an infrared detector. For the Rock Eval measurements, approximately 60–100 mg of the ground rock material was weighed and placed into an auto-sampler crucible. During isothermal heating (300°C), S1 hydrocarbons (free hydrocarbons) were volatilized and detected by a flame ionization detector (FID), and were quantified as milligrammes of hydrocarbon per gram of rock (mg/g). A temperature increase to 600°C caused the release of additional hydrocarbons (S2) and simulated the pyrolytic degradation (i.e. cracking) of kerogen in the rock. This is roughly equivalent to the hydrocarbon potential of the rock. The carbon dioxide that was released up to approximately 400°C is reported in milligrammes per gram of sediments (S3). The amount of S3 is a measure of the amount of oxygen in the kerogen.

3.4. Lipid biomarker analysis

Thirty-five biomarker samples were selected for extraction of easily soluble organic matter (bitumen). All samples were measured by coupled gas chromatography–mass spectrometry (GC–MS) as well as gas chromatography with a flame ionization detector (GC–FID) following the extraction procedures below:
Samples were homogenized by pestle and mortar avoiding contamination. 40 ml dichloromethane (DCM); methanol (3:1 v/v) was added prior each extraction step. The extraction was done by microwave extraction with a CEM MARS X for 15 min at 80°C and 600 W. Internal standards of various polarities (squalene, behenic acid methylster, 1-nonadecanol and 2-methyl-octadecanoic acid) were added to the samples prior to extraction. The samples were extracted several times until they became colourless (at least three times). The extracted organic phases were collected and dried with sodium sulphate. The combined total lipid extracts (TLE) were evaporated under a stream of nitrogen. Subsequently, separation of the DCM-soluble asphaltene from the n-hexane soluble maltenes was achieved. This procedure was applied as a clean-up procedure using 150 mm pasteur pipettes filled with glass wool and sodium sulphate. The maltenes were fractionated into four fractions with increasing polarity (1: hydrocarbons, 2: esters/ketones, 3: alcohols and 4: carboxylic acids) by means of a solid phase extraction column (Supelco DSC-NH2; 500 mg). The reagents used were (1) 4 ml n-hexane, (2) 6 ml n-hexane: DCM (3:1, v/v), (3) 7 ml DCM:acetone (9:1, v/v) and (4) 8 ml 2% formic acid in DCM, respectively. Carboxylic acids were transformed to methyl esters by adding 1 ml of boron trifluoride (BF3) in methanol to the dried fatty acid fraction. The reaction time was 1 h at 70°C. The hydrocarbon and fatty acid fractions were examined in all samples, whereas the alcohol fractions were found to lack pristine biomarker signatures.

Aliquots of the hydrocarbon and fatty acid fractions of each sample were injected into the GC–FID for quantification and a selection of samples was injected on the GC–MS for identification of compounds. The samples were measured on a Thermo Electron Trace GC–MS equipped with a 30 m Rxi-5MS fused silica capillary column (0.32 mm i.d., 0.25 µm film thickness) using helium as a carrier gas. The GC temperature program was 60°C (1 min) to 150°C at 15°C min⁻¹, then to 320°C at 4°C min⁻¹. The final temperature was held for 37 min. The analysed samples represent different lithologies including black shale, mudstone, marl, limestone (wacke-to-packstone) and phosphorite in order to identify possible variations of biomarker patterns with different lithologies.

4. Results

4.1. Stratigraphy and micropalaeanontology

A multistratigraphic framework for the Upper Cretaceous in the Western Desert, including the Abu Tartur-Dakhla area, was given by Tantawy et al. (2001). These authors assigned the top part of the Duwi Formation to the late Campanian CF8a planktonic foraminifera zone as well as nannofossil zones CC23a and the base of CC23b. The Duwi/Dakhla boundary corresponds to the base of CF8b planktonic foraminifera zone and was interpreted to represent the Campanian/Maasrichtian boundary, followed by CF7, which includes a thick interval barren of fossils, then CF6, CF4 and CF3 up to an unconformity around the Cretaceous/Palaeogene boundary. The TOC content varies between 0.2 and 3.5%; the highest contents are recognized at the Duwi/Dakhla transition including the uppermost member of the Duwi Formation and the lowermost part of the Mawhoob member of the Dakhla Formation. The TOC content, reflecting two peaks, coincide with the maximum hydrogen index (HI) values, reaching 575 mg HC/g TOC, indicating good preservation of marine organic matter. Elsewhere, the HI mostly varies between 30 and 200, but reaches approximately 300 mg HC/g TOC in places. The overall low Tmax values (less than 435°C) confirm that organic matter is characterized by low to intermediate maturity with regard to hydrocarbon generation.

With respect to the oxygen index (OI) to HI, the Tmax to HI and TOC to S2 ratios, the majority of samples from both the Duwi and Dakhla formations are located in the field of kerogen type III (Fig. 3), whereas the samples from the Duwi/Dakhla transition are in the field of kerogen type II. Additionally, two argillaceous limestone samples from the Baris member also plot in the kerogen type II field at 121 and 124 m depth with a HI of 293 and 299 mg HC/g TOC, respectively (Figs. 2 and 3). It can be inferred that the majority of the Duwi and Dakhla shales contains organic matter that is chiefly derived from land plants, whereas at the boundary between the two formations the rocks contain organic matter apparently...
derived from marine sources, which was deposited under anoxic conditions as indicated by high TOC contents, high HI, the absence of bioturbation, as well as lipid biomarkers (see Section 5.2). The majority of total sulphur (S\text{tot}) contents range from 0.22 to 10.00%, not correlating with TOC (Fig. 2). The lowest S\text{tot} contents (0.10%) are observed in the Mawhoob member of the Dakhla Formation, whereas the highest values are observed in the Baris member of the Dakhla Formation (Fig. 2). Interestingly, the samples with the highest TOC and HI contents at the Duwi/Dakhla transition do not show particularly high S\text{tot} contents (0.57–2.14). The

Fig. 2. Whole-rock organic geochemical data of the Abu Tartur section (TOC; Hydrogen Index; and total sulphur). The grey zone represents the strata with the highest TOC contents at the Duwi/Dakhla transition (Nanno zone CC20–23 at 156.7 m).

Fig. 3. Plots of the samples of the Abu Tartur section on (A) a van Krevelen diagram, (B) a \( T_{\text{max}} \) versus hydrogen index diagram and (C) a Langford and Blanc-Valleron (1990) diagram.
majority of the sulphur is most likely present as pyrite and not associated with the organic matter, as suggested by XRD data, where pyrite was found to average 1.2% (0.2–4.2%) in the Duwi Formation and 1.7% (0.3–5.3%) at the Duwi/Dakhla transition, and reaches its highest abundance in the Baris member averaging 2.3% (0.2–10.4%) from the total mineralogical composition.

4.3. Lipid biomarkers

4.3.1. Hydrocarbons

The $n$-alkanes range from $n$-C$_{14}$ to $n$-C$_{32}$ (Fig. 4) with quite variable distributions through the entire section. In general, there is an odd over even $n$-alkane preponderance in all samples. Long chain $n$-alkanes are usually maximizing at $n$-C$_{27}$, $n$-C$_{29}$ and $n$-C$_{31}$, whereas short chains maximize at $n$-C$_{15}$, $n$-C$_{17}$ and $n$-C$_{19}$. The short chain $n$-alkanes are typically derived from aquatic algae and microorganisms (Blumer et al., 1971; Cranwell et al., 1987), whereas long chain $n$-alkanes derive from epicuticular waxes of vascular land plants (e.g., Eglington and Hamilton, 1967). The Carbon Preference Index (CPI), calculated after Marzi et al. (1993), is >3 on average for all samples (Table 1). The CPI values are variable but generally significantly higher than 1, except for the limestone interbeds of the Dakhla Formation (Baris member), where the CPI is around 1 (Table 1). The CPI typifies the organic matter and its maturity (Tissot and Welte, 1984). The obtained high CPIs indicate a significant input of terrigenous organic matter. This is also confirmed by the positive relation between the CPI and the Terrestrial/Aquatic Ratio (TAR; $R^2 = 0.31$). The TAR for $n$-alkanes is used as an indicator for vascular land plant input into marine environments (cf. Bourbonniere and Meyers, 1996). The determined TAR is variable but generally $\geq 1$ with the exception of phosphorite and limestone samples of the Duwi Formation and the limestone intervals in the Dakhla Formation where the TAR is $<0.5$ (Fig. 5). Both the TAR and CPI values are not correlating with TOC ($R^2 = 0.01$ and 0.001, respectively). The most prominent acyclic isoprenoids are phytane (Ph), pristane (Pr) and in some samples farnesane (Fig. 4). The Pr/Ph ratio of the majority of samples is $\leq 1$, most likely indicating anoxic conditions during deposition. Samples of the lower and middle Duwi Formation have ratios $>1$, whereas the samples from the upper and uppermost members have relatively low Pr/Ph ratios (up to 1.7; Fig. 5). The Dakhla Formation shows significantly lower Pr/Ph ratios, especially the Baris member and lower Kharga members ($<0.5$).

In contrast to the desmethyl steranes, rearranged C$_{27}$–C$_{29}$ diaster-enes (characterized by m/z 257) were observed in nearly all samples (see Appendix II for structures). Only in the middle and upper members of the Duwi Formation, diasterenes occur in lower abundance than elsewhere (Fig. 6). Diasterenes are predominantly present as 5α,14α,17α(H) 20R isomers, whereas the 5α,14β,17β(H) 20R isomers are only present in minor amounts (Fig. 4). Diasterenes...
The distribution of hopanoids in the Abu Tartur sequence is maximized at the Duwi/Dakhla transition (up to 81 μg/g TOC; Fig. 6) and within the Baris member (up to 80 μg/g TOC). The C27 diasterenes show maximum contents in the phosphorite samples compared to the others (C28 and C29). Not all of the extracted bitumen contains desmethyl steranes. Desmethyl steranes were found with low amounts at the Duwi/Dakhla transition (up to 170 μg/g TOC). The dominant compounds are C27 hopanoic acids (H.A.) found with low amounts at the Duwi/Dakhla transition (up to 50 μg/g TOC). The C27 hopanoic acids are overall abundant (Fig. 6). Highest proportions of ββ-hopanoids were found in the Mawhoob member. Apart from the saturated hopanes, a number of hopanes was found including 29-norneohop-13(18)-ene, neohop-13(18)-ene as well as hop-17(21)-ene (see Appendix II for structures). These hopanes are present in almost all samples, but only in minor amounts compared with saturated hopanes (maximum content: 30 μg/g TOC; Fig. 6). Generally, 29-norneohop-13(18)-ene is the most abundant hopane (Fig. 4).

Aryl isoprenoids were observed in the free lipid extracts of the hydrocarbon fraction in some samples. Raney nickel-desulfurization was not applied, although aryl isoprenoids were found in some samples at different depths. It seems that aryl isoprenoids are not or at least not entirely bound to sulphurized organic matter. Anyway, overall contents of aryl isoprenoids are low. The trace amounts of aryl isoprenoids represent contents below detection limit when measured in full scan mode (Fig. 6). Only when measured in single ion monitoring (SIM; m/z 133/134) mode, the aryl isoprenoids were identified by comparison with retention times in full scan mode. Isorenieratane (C40; Appendix II) was found only in few samples, reaching its maximum abundance at the top of the Baris member, where the Pr/Ph ratios are very low, too. Some samples yielded diagenetic products of isorenieratane and other aryl isoprenoids (cf. Summons and Powell, 1987; Koopmans et al., 1996; Sinninghe Damsté et al., 2001). Short-chain aryl isoprenoids (including C13, C14, C15 and rarely C19 chains; Figs. 4 and 6) are particularly abundant in the Abu Tartur section, where isorenieratane was only found in minor amounts. At the Duwi/Dakhla transition the contents of short-chain aryl

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isoprenoids are higher than elsewhere in the section (Fig. 6). C33 aryl isoprenoid (Fig. 4) reaches its highest abundance at depths between 125.5 and 108.5 m within the Baris member (Fig. 6).

4.3.2. Carboxylic acids

Straight-chain saturated fatty acids were observed in the majority of samples, ranging from \( n-\text{C}12 \) to \( n-\text{C}33 \) and maximizing at \( n-\text{C}16 \) and \( n-\text{C}18 \). They are characterized by a preponderance of even over odd numbered carbon chains (Fig. 7). CPI\text{even} average values calculated according to Marzi et al. (1993) fall between 3.25 and 4.44 for the Duwi and Dakhla formations, respectively, indicating immature organic constituents with significant input of terrigenous organic matter. No unsaturated \( n \)-fatty acids were observed. \( \text{i} \)\)-\( \text{C}14 \) to \( \text{i} \)-\( \text{C}17 \) as well as \( \text{ai} \)-\( \text{C}15 \) and \( \text{ai} \)-\( \text{C}17 \) fatty acids were recognized. Pristanoic and phytanoic acids were found in some samples only (Fig. 7). Pentacyclic triterpenoic acids (hopanoic acids), including 17\( \beta \)-(H),21\( \beta \)-(H) and 17\( \alpha \)-(H),21\( \beta \)-(H) bishomohopanoic acids with 31–33 carbon chains, were found to be abundant (Fig. 7). Like with hopanes, the \( \beta \beta \) isomers dominate over the \( \alpha \beta \) isomers (Fig. 7 and Table 1).

5. Discussion

5.1. Implications of Rock-Eval analysis

It has been suggested that the Duwi Formation is separated from the overlaying Dakhla Formation by an unconformity (El-Azabi and Farouk, 2010 and references therein). However, this study resulted in new evidence that calls a hiatus between the Duwi and Dakhla formations into question. The circumstance that the highest organic carbon content was observed at the Duwi/Dakhla transition along with the recording of a complete foraminiferal biozonation succession at the Campanian/Maastrichtian boundary (e.g., Tantawy et al., 2001) argues against a hiatus, which would necessarily have resulted in prolonged exposure, reworking, and remineralization of organic matter in proximity to the hiatal surface. At the studied site, the variations in the TOC profile (Fig. 2) are gradual and smooth, which is in sharp contrast to what would be expected in case of a hiatus. The high TOC contents at the Duwi/Dakhla transition, thus, reflect enhanced preservation of organic matter, confirmed by the absence of bioturbation at the Duwi/Dakhla transition. The association of these high TOC values with low sulphur contents suggest anoxic rather than euxinic environments. As Rock Eval pyrolysis revealed organic matter composition reflecting type II kerogen (marine algal-derived), increased marine primary production rather than input of terrestrial organic matter typifies this transition.

5.2. Implications of redox-sensitive isoprenoids

High contents of both phytane and pristane in the entire section probably reflect input from oxygenic phototrophs (eukaryotic algae and cyanobacteria; cf. Didyk et al., 1978; Sepúlveda et al., 2009), with possible contributions from anoxic phototrophs (e.g., Brooks et al., 1969). Although additional input from Archaea cannot
be excluded, the overall biomarker patterns rather point to phototrophic prokaryotes and eukaryotes. In the Baris member for example, high phytane contents are accompanied by abundant isorenieratane and C\textsubscript{33} aryl isoprenoids, indicating that indeed anoxygenic phototrophs may have contributed to the phytane input. Aryl isoprenoids are robust indicators for water column anoxia within the photic zone (e.g., Kuypers et al., 2004; Kolonic et al., 2005; Sepúlveda et al., 2009). Such compounds are not restricted to the Baris member. Isorenieratane, C\textsubscript{33} and also short-chain aryl isoprenoids were also detected close to the Duwi/Dakhla transition, suggesting the former presence of Chlorobiaceae along with the occurrence of photic zone anoxia (cf. Summons and Powell, 1987; Grice et al., 1997; Brocks et al., 2005; Knoll et al., 2007). Although no \(\beta\)-carotane was detected in the studied

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**Fig. 6.** Down-core variations of biomarkers in the Abu Tartur section including desmethylated steranes, rearranged diasterenes, C\textsubscript{30} hopanes, aryl isoprenoids and distribution of (nor-neo)-hopenes (all in \(\mu\)g/g TOC).

**Fig. 7.** Representative gas chromatogram (FID) of a sample from Baris member (116 m depth), showing the distribution of fatty acids (methyl esters). FID = flame ionization detector.
samples, it seems feasible that the short-chain aryl isoprenoids were accessorily derived from sources other than isorenieratane including β-carotene (Schouten et al., 2000).

It has to be noted that aryl isoprenoids were not only found in the maximum TOC intervals, but also in other facies of the Duwi and Dakhla formations. Highest contents of these compounds were encountered in the Baris member, where the TOC values are actually rather low compared to the Duwi/Dakhla transition. It has been suggested that a marine incursion led to the deposition of the deep sub-tidal shales alternating with shallow sub-tidal wackestones and floatstone of the Baris member (El-Azabi and Farouk, 2010). The occurrence of C33 aryl isoprenoid together with isorenieratane in this member indicates an anoxic and possibly even euxinic water column, the latter agreeing with high sulphur contents. The rather low TOC contents of the Baris member are probably best explained by lower productivity or only episodic oxygenation as indicated by the presence of bioturbation in some layers among otherwise well-stratified beds. Apart from the Baris member, some samples of the Mawhoob and Kharga members yielded trace amounts of aryl isoprenoids, similarly indicating anoxic conditions. To sum up, the discontinuous distribution of aryl isoprenoids in the Abu Tartur section indicates the episodic occurrence of photic zone anoxia.

5.3. Changes in the dominance of eukaryotes versus bacteria

5.3.1. Assessment of the sources of compounds

Sterols are mainly produced by eukaryotic algae, photosynthetic protists and higher plants (e.g., Volkman et al., 1998). Principally, sterols can be classified into groups including sterols with 27 carbons (e.g., cholesterol) produced by metazoans (Knoll et al., 2007) and various zooplankton (Huang and Meinschein, 1979; Killops and Killops, 2005). Sterols with 28 carbons are the main precursors of C28 steranes (ergostanes) and are predominantly found in algae and phytoplankton including diatoms, dinoflagellates and coccolithophorids (e.g., Knoll et al., 2007). Sterols with 29 carbons, including sitosterol and stigmastanol are produced by marine chlorophytes (Knoll et al., 2007) and land plants (Huang and Meinschein, 1979; Volkman et al., 1998; Killops and Killops, 2005).

Under slightly acidic conditions in the presence of catalytic clay minerals and a high geothermal gradient, steranes can undergo rearrangement to diasterenes upon dehydration and carbocation migration (Rubinstein et al., 1975; Sieskind et al., 1979; Mackenzie et al., 1982; ten Haven et al., 1989). Further reduction of diasterenes generates diasteranes (Gaines et al., 2009). The occurrence of diasterenes in the studied Upper Cretaceous shales of low thermal maturity is probably best explained by clay catalysis rather than thermal maturation (cf. Brassell et al., 1980).

Bacteriohopanepolys (BHPs) are the precursors of hopanoids and are exclusively derived from bacteria (Rohmer et al., 1984; Knoll et al., 2007). Most bacteriohopanepolys are bacteria aerobic, including methanotrophs, methylo trophs and cyanobacteria (e.g., Talbot and Farrimond, 2007 for a review). Only in recent years, anaerobic bacteria such as purple non-sulphur bacteria, sulphate reducers and iron reducers have been recognized to produce a great variety of BHPs (e.g., Blumenberg et al., 2006; Rashby et al., 2007; Eichkoff et al., 2013). Anyway, only less than 10% of all bacterial species are capable of producing hopanoids (Pearson et al., 2007).

Hopanoic acids found in sediments and sedimentary rocks are believed to be degradation products of BHPs (e.g., Farrimond et al., 2002). With increasing maturity, the concentration of hopanoic acids has been shown to decrease (Jaffé and Cardinalli, 1990). Like for hopanes, the hopanoic acids identified in the Upper Cretaceous strata are dominated by 17β[H]21β[H] 22R isomers, confirming that the sequence experienced little thermal alteration. Bacteria synthesize hopanoids with the 17β[H],21β[H]-configuration (ββ hopanoids). However, extracts of sedimentary rock are often typified by 17α[H],21β[H]-isomers (αβ hopanoids) and 17β[H],21α[H]-isomers (βα hopanoids), which formed by thermally induced isomerization (Peters et al., 2005). The ββC32 hopanoid acid versus ββC31 hopane ratio shows an intermediate correlation (R² = 0.5). The ratio between ββC31 hopanoid acid and ββC30 hopane shows an even better correlation (R² = 0.8), suggesting that hopanes derive from the corresponding parent hopanoid acids and, thus, derive from the same source. Such a relationship is best explained by decarboxylation of hopanic acids (cf. Bennett and Abbott, 1999).

5.3.2. Environmental implications derived from the distribution of compounds

The lowermost Duwi formation is typified by abundant phosphorite beds, along with C27 steroid predominance over other steroids (42.0% of diasterenes and 70.7% of desmethyl steranes). Such a pattern can be attributed to high contributions from meta zoans and zooplankton during phosphorite deposition. Similar observations have also been made for the Duwi Formation phosphorites of the Yoomis and Abu Shegela mines, for phosphorites along the Red Sea (Ganz et al., 1990), as well as for phosphorites from the Peruvian continental margin (Sanftleven, 1980). The content of all identified steroids (regular and rearranged) increases at the Duwi/Dakhla transition and reaches its maximum in the Mawhoob member of the lowermost Dakhla Formation, accompanied by low Terrestrial/Aquatic Ratios (TAR). At the same time when steroid contents reach their maximum, hopanoids decrease dramatically at the Duwi/Dakhla transition, suggesting a major change in the input of organic matter. The biomarker patterns at the Duwi/Dakhla transition suggest input of marine organic matter and the development of anoxia in the photic zone, indicated by type II kerogen and abundant aryl isoprenoids.

The carbonate to detritus ratio is a useful indicator for sea-level change. Increased carbonate contents are believed to reflect a more distant source of detrital material, suggesting greater water depth. An increase in detritus, on the other hand, is believed to reflect a more proximal source and shallower waters (e.g., Adatte et al., 2002). The carbonate to detritus ratio, calculated as calcite plus other carbonate minerals divided by quartz plus feldspars plus clay minerals (smectite, kaolinite, illite and chlorite), is negatively correlated with the input of terrestrial organic matter for the Abu Tartur section. This relationship is represented by the positive correlation of TAR of hydrocarbons with those of straight chain fatty acids (R² = 0.63), and the negative correlation with carbonate to detritus ratios (R² = −0.71).

Above the Duwi/Dakhla transition, in the Mawhoob member, diasterenes are present only in trace amounts and the content of all other steranes is dramatically decreased. Based on steroid distributions, Pr/Ph ratios and the relative abundance of hopanes, the Mawhoob member differs from the strata below and above. The high marine production and the development of photic zone anoxia that typified the Duwi/Dakhla transition had ceased abruptly. Interestingly, the decrease in steroid contents is mirrored by a strong increase in hopanoid contents in this member, suggesting the predominance of bacteria over algae during that time. Such a pattern may indicate that bacteria flourished at the expense of eukaryotes. This is at least not in conflict with more oxic conditions (Pr/Ph ratios of around 1 and lower contents of aryl isoprenoids) and the preponderance of land-derived organic material, reflected in a very low hydrogen index, high TAR values and low carbonate to detritus ratios in this member in comparison to the Baris member. Marine primary productivity was apparently relatively low following deposition of the Mawhoob member and the majority of organic matter was land-derived (kerogen type III). This land-derived
organic matter was then remineralised by various bacteria in the marine deposits of the Mawhoob member.

In the overlying Baris member, the content of steranes increases again with a slightly higher contribution of C28 ergostane (35.4%) followed by C27 cholestane (33.1%) and accompanied by abundant hopanoids. Diasterenes of different carbon numbers (C27–29) show a similar distribution in the Baris and Kharga members; proportions of C28 diasterene (35.9% and 39.7% from total diasterenes for Baris and Kharga members, respectively) are followed by C29 diasterene (34.6% and 35.3% for Baris and Kharga members, respectively). In the clay dominated Kharga member, steranes have disappeared while diasterenes and hopanoids are still present. The predominance of C29 steroids suggests a slightly higher contribution from phytoplankton containing chlorophyll c in the middle and upper members of the Dakhla Formation (cf. Knoll et al., 2007). In agreement with the prevalence of kerogen type III and high TAR, the dominant source of the C29 steroids were probably land plants (i.e. allochthonous organic matter), although no biomarkers of flowering land plants such as oleaneans were observed. Interestingly, in the uppermost Kharga member the greatly increased contents of bacterial-derived hopanes and low contents of eukaryote-derived diasterenes point to similar conditions as envisaged for the Mawhoob member.

5.4. Implications of the terrigenous input

The Carbon Preference Index (CPI) values of the samples from the Abu Tartur section, ranging from 1.09 to 4.84 and from 0.92 to 8.62 for n-alkanes and n-fatty acids, respectively, reveal no diagnostic trend and scatter over a wide range. Anyway, the obtained values are similar to those of extant vascular plants (cf. van Dongen et al., 2006), which are commonly $>3$, agreeing with significant contributions of organic matter derived from higher plants. The majority of this terrigenous organic matter was most probably derived from riverine transport. Although the overall composition of the organic matter (mostly type III kerogen) reflects terrestrial input, the great amounts of short-chain n-alkanes suggest additional contributions from marine sources. Short-chain lipids in marine deposits commonly reflect input of marine organic matter from photosynthetic algae and macrophytes (van Dongen et al., 2006; Carvajal-Ortiz et al., 2009).

Long-chain n-fatty acids and n-alkanes show some similarities in their distribution, pointing to a precursor-product relationship (cf. Peters et al., 2005). C16 and C18 fatty acids are commonly the most abundant n-fatty acids in deposits, partly because they are major lipids of phytoplankton, particularly diatoms and coccolithophorids (Uchida et al., 2005). In the Abu Tartur section long-chain n-alkanes display an odd-over-even predominance, which is best explained by significant input of organic matter from terrestrial plant leaves (cf. Eglington and Hamilton, 1967). Odd number long-chain n-alkanes are major components of plant cuticular waxes. Apart from n-alkanes, long-chain n-fatty acids are leaf wax components. Consequently, parts of the odd number long-chain n-alkanes may have formed as a result of decarboxylation from an even-numbered fatty acid precursor within the deposits (cf. Carvajal-Ortiz et al., 2009). The carbon number distribution in the n-alkanolic (fatty) acids strongly suggests that the acids may have generated some of the n-alkanes via decarboxylation during diagenesis.

The circumstance that TAR of n-alkanes and n-fatty acids are very similar over the entire section agrees with a common origin of n-alkanes and n-fatty acids. Generally, the obtained TAR of n-alkanes (average 1.5) is higher than the TAR of n-fatty acids (average 0.82). The TAR of n-alkanes and n-fatty acids follow parallel trends through the section, declining rapidly in the strata with the highest TOC levels. These patterns confirm that the interval with the highest TOC contents was characterized by an enhanced input of marine organic matter, which is in concert with the Rock Eval data and the abundance of steranes, reflecting input from algae. Likewise, the decline of TAR in the limestone horizon of the Baris member is in accord with an increase of the Pr/Ph ratio ($\sim 1.0$) and the increase of the carbonate to detritus ratio (up to 2.1). Summing up, these patterns suggest a marine incursion with little if any anoxic bottom water as evidenced by bioturbation in the foraminiferal limestone.

Apart from hopanes and hopanoid acids, hopenones were identified in the Abu Tartur section as well as in other Cretaceous rocks (e.g., Rullkötter et al., 1982; Simonet et al., 1984). The identified compounds 29-norneohop-13(18)-ene, neohop-13(18)-ene and hop-17(21)-ene have been suggested to be rearrangement products of diolopente, a common biohopanoid present in a variety of bacterial lineages (Rohmer et al., 1984). Interestingly, a positive correlation ($R^2 \sim 0.5–0.7$) between total hopanes and the TAR for both n-alkanes and n-fatty acids was found for the Abu Tartur section. This pattern suggests that the hopenes predominantly derived from terrestrial sources, probably soils. Accordingly, Simonet et al. (1984) and Saito and Suzuki (2007) attributed similar hopene distributions from Cretaceous and Miocene to recent sedimentary rocks and sediments from the Moroccan continental margin and the Nankai Trough to input from soil bacteria.

5.5. Reconstruction of water column anoxia

The detection of isorenieratane and its diagenetic derivatives in the Abu Tartur section indicates the former presence of Chlorobioaceae. The presence of ary isoprenoids in the rocks at the Duwi/Dakhla transition and further up-section in the Mawhoob and Baris members points to a stratified water column with a shallow chemocline located within the photic zone for prolonged time periods. A scenario for the deposition of organic-rich sediments in the study area is shown in Fig. 8, suggesting the episodic establishment of photic zone anoxia.

During the Late Cretaceous, Egypt was positioned near the palaeoequator (Smith et al., 1982; Tantawy et al., 2001; Baioumy, 2013), agreeing with the high abundance of kaolinite minerals in the Dakhla Formation, which suggests warm wet, tropical to subtropical conditions (Singer, 1984) with heavy rainfall and high concentrations of atmospheric carbon dioxide, resulting in deep chemical weathering. The Duwi Formation overlies fluvial shale of the Quseir Formation and is overlain by deeper marine shales and marls of the Dakhla Formation, reflecting a general deepening trend. A broad continental shelf developed in North Africa including Egypt as a result of Campanian to Maastrichtian transgressions (Baioumy and Tada, 2005). The initial stage of these Late Cretaceous marine transgressions in Egypt is represented by the deposition of the Duwi Formation. In this formation, two transgressive cycles were identified by Baioumy and Tada (2005); one in the lower member, another in the middle member when the maximum sea level was reached (High Stand System Tract; Fig. 8A). Importantly, a major regression occurred at the boundary between the middle and upper members (Low Stand System Tract; Fig. 8B). Interestingly, no steroids were detected in the samples of the middle and upper members. Hopanoids were detected in tiny amounts only and disappeared in the upper part of the upper member. The middle and the upper members have high Pr/Ph ratios, which, together with the absence of aryl isoprenoids, indicate poor preservation of organic matter in accord with very low hydrogen indices. The upper member of the Duwi Formation is characterized by the deposition of glauconite and iron-rich, land-derived deposits (Pestitschek, 2010). The occurrence of glauconite with both ferric and ferroan iron in its lattice indicates toxic to suboxic conditions, which hampered pronounced preservation of organic matter.
The second transgressive cycle was identified at the base of the uppermost member (Transgressive System Tract; Fig. 8C) and continued into the Mawhoob member (High Stand System Tract; Fig. 8D). This transgression was probably a major factor that favoured high primary productivity and the deposition of increased amounts of organic carbon at the Campanian–Maastrichtian transition. Additionally, the significant increase of short-chain aryl isoprenoids in these strata indicates the occurrence of photic zone anoxia, favouring the preservation of organic matter. This enhanced preservation is reflected in high TOC% contents, high contents of steroids and relatively low contents of hopanes as well as the absence of bioturbation.

According to El-Azabi and Farouk (2010), deposition of the lower Mawhoob member ceased after a minor eustatic sea level fall (Fig. 8E). Thereafter, marine invasion flooded the shelf and deep sub-tidal shale alternating with shallow sub-tidal wackestone and floatstone deposited (higher carbonate to detritus ratios and lower TAR; Transgressive System Tract; Fig. 8E). Notably, above its lower member, the Mawhoob member and the majority of Baris member are characterized by abundant aryl isoprenoids, indicating anoxia with good conditions for the accumulation of organic matter. However, there are obvious differences between the Mawhoob and Baris members. The former is characterized by an almost complete absence of marine steroids, abundant hopanoids and a very low hydrogen index, in accord with substantial remineralization of organic matter in bottom waters. The latter is characterized by an increase of steroids, a decrease of hopanoids and a medium to high hydrogen index, indicating higher marine productivity and better preservation of organic matter except for some levels with bioturbation.

Afterwards, low sub-tidal shale was deposited in the lower Kharga member (High Stand System Tract; Fig. 8F), pinpointing the beginning of regional uplift and relative sea level fall (cf. El-Azabi and Farouk, 2010) and the return to oxic water conditions reflected in the absence of aryl isoprenoids. However, the preservation of marine organic matter was still favoured based on high steroid contents and an intermediate to high hydrogen index. The relatively high TAR and low carbonate to detritus ratios together with the occurrence of type III kerogen indicate high supply of land-derived organic material during the deposition of the lower Kharga member.

6. Conclusions

With the aid of detailed organic geochemical analyses and based on lithological and stratigraphical examinations of a core drilled on the Abu Tartur plateau (Maghrabi-Liffiya sector) in the Western Desert of Egypt, the evolution of a shelf sea in the Late Cretaceous was reconstructed.

1. Type III kerogen, which is indicative of land-derived organic matter, was found to dominate the Campanian to Maastrichtian
Abu Tartur section with the exception of the deposits at the transition between the Duwi and Dakhla formations; these deposits reveal the highest TOC contents and contain type II kerogen, which is indicative of marine organic matter.

2. The studied succession on the Abu Tartur plateau is characterized by immature to marginally mature organic matter. The maturity is constrained by a low T_{\text{max}} (<445 {^\circ}\text{C}), odd over even predominance of n-alkanes and high Carbon Preference Indices, good preservation of carboxylic acids with even over odd predominance and the predominance of 17\beta,21\beta isomers of hopanes and hopanoid acids over 17a,21\beta isomers.

3. Terrestrial/Aquatic Ratios (TAR) of n-alkanes and n-fatty acids are positively correlated with carbonate to detritus ratios, indicating that sea level fluctuations greatly influenced palaeoecoproduction as well as the composition and accumulation of organic matter. The shelf was characterized by high input of allochthonous organic matter, reflected in the dominance of long-chain n-alkanes (high TAR) and low carbonate contents. Only at the Duwi/Dakhla transition autochthonous production of organic matter in the shelf sea became more significant, reflected in lower TAR (more algal biomass) and higher carbonate contents.

4. The preponderance of rearranged steranes (diasterenes) over regular steranes in the Abu Tartur section indicates that clay catalysis had a greater impact on sterane distribution than thermal maturity. The C_{28} (eukaritotic phytoplankton) and C_{29} (green algae or land plants) steranes are dominant in most parts of the section except for phosphorite layers, in which C_{27} steranes dominate.

5. The Campanian to Maastrichtian organic-rich sedimentary succession of the Abu Tartur plateau was deposited under the influence of the episodic occurrence of photic zone anoxia, fostering the preservation of organic matter. These episodes, which are documented by the occurrence of biomarkers of green sulphur bacteria (aryl isoprenoids including isorenieratane), preferentially occurred in the course of marine transgressions.

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