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**The significance of 24-norcholestanes, 4-methylsteranes and dinosteranes in oils and source-rocks from East Sirte Basin (Libya)**

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## **Abstract**

The present paper involves a detailed evaluation of specific steroid biomarkers by gas chromatography- mass spectrometry (GC-MS) and GC-metastable reaction monitoring (MRM) analyses of several crude oils and source rocks from the East Sirte Basin. 24-*norcholestanes*, *dinosteranes*, 4 $\alpha$ -methyl-24-ethylcholestanes and triaromatic steroids have been identified in both source-rocks and crude oils of the East Sirte Basin. Diatoms, dinoflagellates, (including those potentially associated with corals) and/or their direct ancestors are amongst the proposed sources of these biomarkers. These biomarker parameters have been used to establish a Mesozoic oil-source correlation of the East Sirte Basin. Hydropyrolysis of an extant coral extract revealed a similar distribution (although immature) of *dinosteranes* and 4 $\alpha$ -methyl-24-ethylcholestanes also observed in the Sirte oils and source-rocks. This is consistent with the presence of dinoflagellates present during the deposition of the Mesozoic aged East Sirte Basin Formations.

A good data correlation for the rock extracts revealed a similar distribution of 3, 24-dimethyl triaromatic steroids, 3-methyl-24 ethylcholestanes, 4-methyl-24-ethylcholestanes and 2-methyl-24- ethylcholestanes observed in the one of the oil families and associated source-rocks for the East Sirte Basin.

**Keywords** Sirte Basin, *dinosteranes*, dinoflagellates, diatoms, corals, Mesozoic, Libya

## 1. Introduction

Eukaryotic steroids are the most commonly occurring polycyclic biomarkers in the geologic record. The most important components of Eukaryotic cell membranes include sterols (e.g. cholesterol, ergosterol and sitosterol). Eukaryotes biosynthesise a wide range of sterols that are characterised by the number and position of functional moieties (from double bonds, hydroxy- oxo- and alkyl groups to other complex, substituents) diagnostic to a wide range of algal assemblages (Volkman, 2003). There is however, a very limited range of diagenetically-altered steroids reported in sediments and petroleum with the most commonly reported steranes from the Late Neoproterozoic to the Cenozoic age being cholestane, 24*R*-methylcholestane (ergostane), 24*S*-methylcholestane and stigmastane. Natural product precursors of cholestane, ergostane and stigmastane are the most commonly occurring biomarkers found in almost every Eukaryotic assemblage (see Table 1 and Volkman, 1986; Volkman, 2003; Brocks and Grice, 2011) and are thus non-specific. Some steroids have also been reported in three independent groups of bacteria. These steroids include, Myxococcales, Methylococcales, and Planctomycetales (Pearson et al., 2003). Other steroids such as 24-*n*-propylcholestanes are diagnostic markers for marine algae of the order Sarcinochrysidales and brown tide algae (Moldowan et al., 1990). Dinosterane (4, 23, 24-trimethylcholestane) is uniquely derived from dinosterol and related compounds (Robinson et al., 1984) reported in many dinoflagellates. Dinosterane is thus a marker for dinoflagellates, although a diatom has been reported to contain similar sterols (Volkman et al., 1993). In addition, dinoflagellates are probably the main origin of aromatic steroids bearing a methyl group at C-4 (4-methylcholestane, 4-methylergostane, and 4-methylstigmastane). The source of

the 24-*norcholestane* is unknown, but diatoms have been suggested as the main source by Holba et al. (1998a). 24-*norcholestanes* have been found in crude oils associated with the proliferation of diatoms from the Jurassic to the Tertiary (Holba et al., 1998b) and 24-*norsterols* have been reported in both diatoms and dinoflagellates (Rampen et al., 2007). Other biomarkers for diatoms include the “highly branched isoprenoid” (HBI) alkanes (e.g., Volkman et al., 1994). HBI's are also identified in diatoms, consisting of the genus *Rhizosolenia* and the other of several genera (*Navicula*, *Haslea*, *Pleurosigma*) (Sinninghe Damsté et al., 2004) (Table 1).

Geochemical data of sedimentary organic matter (SOM) obtained by Burwood et al. (2003) from the East Sirte Basin (Libya) indicated the occurrence of hybrid oils comprising two or more end members and proposed several potential Palaeocene source rocks in addition to the already known Late Cretaceous source rocks. Recent studies of the East Sirte Basin oils established two main petroleum families with contrasting maturities, the more mature in family A from a predominant terrigenous source and family B derived from predominant sub-oxic marine shales (Aboglila et al. 2010a and b).

The present paper involves a detailed evaluation of specific steroid biomarkers by gas chromatography - mass spectrometry (GC-MS) and GC-metastable reaction monitoring (MRM) analyses of several crude oils and source rocks from the East Sirte Basin (Burwood et al., 2003; Aboglila et al., 2010a and b). In addition, a coral sample was obtained from the Great Barrier Reef, Australia in order to provide a chemical characterisation of the major pyrolysis products in the extant coral so as to determine if the same diagnostic components (representative of dinoflagellates in general) are evident in the pyrolysate of the Sirte Basin

samples. 24-Norcholestanes, dinosteranes, and 4 $\alpha$ -methyl-24-ethylcholestanes have been identified in crude oils, source-rocks of the East Sirte Basin as well as the extant coral sample. Diatoms, dinoflagellates (including those potentially associated with corals) and/or their direct ancestors are the proposed sources of these biomarkers. These biomarker parameters have been used to establish the genetic source and an age and oil-source correlation for the rocks from the East Sirte Basin.

## **2. Geological setting**

The Sirte Basin is located in the northeast of Libya, extending from the 2000<sup>th</sup> meters bathymetric contour offshore in the Gulf of Sidra and bordered by the Haruj Uplift in the west, the Cyrenaica Platform and Al jaghbub Low in the east, and the Tazirbu and Sirte Arches in the south (Ahlbrandt, 2001) (Fig. 1 ). The geology of the Sirte Basin has been described previously (Parsons et al., 1980; El-Alami et al., 1989; Gras, 1996; Macgregor, 1996; Ghori and Mohammed, 1996), and research is ongoing (Burwood et al., 2003; Aboglila et al., 2010a and b). The main evolution of the basin resulting in the current configuration occurred during the Cretaceous with the collapse of the Sirte arch (Rusk 2001; Hallett, 2002). Extensional faulting and subsidence of the basin continued into the Tertiary and maximum subsidence occurred in the Late to Middle Eocene. The Sirte Basin is divided into the West Sirte Basin and the East Sirte Basin by the Zelton Platform (Hallett, 2002). The main faults, which divide the Sirte Basin into a series of platforms and troughs, trend in a north-west to south-east direction except in the East Sirte Basin where fault trends occur in an east-west direction and it is this faulting which has contributed to the structural traps which have resulted in the

East Sirte Basin being most productive for the petroleum industry of Libya (Rusk 2001; Ahlbrandt, 2001; Hallett, 2002). The post-rift sediments in the Sirte Basin comprise sequences of lacustrine and alluvial deposition as well as marine clastics and carbonates which range in thicknesses between 1000 m- 1500 m, the deeper area being in the east (Hallett, 2002). The tendency for gas rather than oil to be produced in the northern part of the basin is thought to be depth related (Rusk 2001; Ahlbrandt, 2001; Hallett, 2002). Correlation of stratigraphic units between the sediments of the platform and troughs has proved to be difficult due to the rapid lateral changes in facies type and sediment thickness (Burwood et al., 2003).

The main petroleum system is the Sirte-Zelten located in the East Sirte Basin. The Cretaceous Sirte Shale comprises organic-rich beds and mudstones and is regarded as the major oil source rock for the East Sirte Basin (e.g. Barr and Wegner, 1972; Hallett, 2002; Burwood et al., 2003). Both oil and rock samples were taken from the East Sirte Basin for this study. A rich fauna of benthic and planktonic foraminifera has been recovered from these sediments as well as from the slightly older Rachmat Formation (Hallett, 2002). The dinoflagellates *Lagenorhysis* sp. and *Odontohina* sp. have been recorded from the Nubian Cretaceous that considered a minor source rock; however, this area is currently recognised as under-studied (Rusk, 2001; Hallett, 2002). Other potential source horizons have been recognised in Cretaceous, Triassic, Cambrian and Precambrian formations and have supplied a number of stratigraphically distinct oil reservoirs (Hallett, 2002, Burwood et al., 2003). Recent geochemical analyses of oils by Burwood et al. (2003) and Aboglila et al. (2010a) have indicated the presence of more source rocks than are currently identified.

## 4. Experimental

### 4.1 Samples

Oil and rock samples were collected by the National Oil Corporation (NOC) in Tripoli from eleven different wells (Fig. 1, Tables 2 and 3] from the East Sirte Basin. In total, twenty four petroleum samples were obtained from 7 oilfields (Fig. 1) and their depth and locations are shown in Table 3. Twenty one drill cuttings were provided from the following formations, 8 Sirte, 4 Tagrifet, 2 Rakb, 4 Rachmat, 1 Bahi and 2 from the Nubian Formation. Their depths and locations are shown in Table 2.

### 4.2. Rock extractions

The rocks were washed with double-distilled water to remove any surface contaminants. Rock samples were finely ground by a mechanical rock grinding machine (particle size of  $<150\ \mu\text{m}$ ), using a ring-mill (Rocklabs). All samples (10-20 g) were then extracted ultrasonically (2 hours), using a mixture of dichloromethane (DCM) and methanol (MeOH) (9:1 v/v). The solvent extract was filtered using a centrifuge and excess solvent was removed by heating on a sand bath at  $80^\circ\text{C}$ , to isolate the extract.

### 4.3. Liquid chromatography

Crude petroleum and extracts were fractioned into saturate, aromatic, and polar fractions by using a small column (5.5 cm x 0.5 cm i.d.) of activated silica gel ( $120^\circ\text{C}$ , 8 h). Approximately 10 to 20 mg of sample was applied to the small



column. The saturated hydrocarbon was obtained by eluting with *n*-pentane (2 mL); the aromatic hydrocarbon was obtained by eluting with a mixture of *n*-pentane and DCM (2 mL, 7:3 v/v); and the polar (NSO) fraction was obtained by eluting with a mixture of DCM and MeOH (2 mL, 1: 1 v/v). The excess solvent was removed by heating the fractions on a sand bath at 80 °C following similar methodologies performed by Bastow et al. (2007); Dawson et al. (2007) and Maslen et al. (2011).

#### 4.4. *Hydropyrolysis (Hypy) of coral extract*

In order to aid the interpretation of the biomarker assemblage found in the samples from the East Sirte Basin an artificial maturation experiment of a representative coral (*Porites* sp.) from the Great Barrier Reef, Australia was performed to determine if the distribution of coral biomarkers formed under pyrolysis conditions were consistent with those of fossil dinoflagellates in general. The species was selected because it contained alga zooxanthellae of the phylum Dinoflagellata. This symbiotic relationship between corals and zooxanthellae first evolved in the mid Triassic (Moldowan et al., 1996).

The coral sample was finely ground and then extracted ultrasonically (2 hours), using a mixture of dichloromethane (DCM) and methanol (MeOH) (9:1 v/v). The solvent extract was filtered and excess solvent was removed by heating on a sand bath at 80°C, isolating the extract. The extract obtained was subjected to Hydropyrolysis (Hypy).

The instrumental procedure for fixed bed Hypy has been described by Love et al., 1995 and Meredith et al., 2006. Prior to Hypy, the coral extract was mixed with a dispersed sulfidic molybdenum catalyst  $[(\text{NH}_4)_2\text{MoO}_2\text{S}_2]$  (10 mg), dissolved

in a minimum of 20 % methanol in water], freeze dried and then placed into the pyrolysis reactor. The sample was then heated in a stainless steel tube (ambient temperature to 250°C at 300°C min<sup>-1</sup>, then to 500°C at 8°C min<sup>-1</sup>). A constant hydrogen flow of 5 L min<sup>-1</sup>, measured at ambient temperature and pressure, guaranteed rapid removal of the volatile products from the reaction vessel. The product was collected on a silica gel-filled trap chilled with dry ice (see Meredith et al., 2004).

#### 4.5 Biomarker analysis

GC-MS analysis was undertaken using a Hewlett Packard (HP) 5973 mass-selective detector (MSD) interfaced to a HP6890 gas chromatograph (GC). The GC oven was programmed from 40°C to 310°C at a rate of 3°C/min and *m/z* 50-500. A HP-5MS (J and W Scientific) GC column (5% phenylmethylsiloxane stationary phase) was used with helium as the carrier gas. Due to the low concentrations of the methylsterane isomers, GC-metastable reaction monitoring (MRM) mode was used. The GC-MRM was performed on a Hewlett-Packard 5890 GC interfaced with a VG Autospec Ultima mass spectrometer operated at 70 eV with a mass range of *m/z* 50-600 and a cycle time of 1.8 s. The MRM mode for full scan (TIC) and the following *m/z* transitions of 358→217, 372→217, 386→217, 400→217 and 414→217 were monitored to obtain the C<sub>26</sub>, C<sub>27</sub>, C<sub>28</sub>, C<sub>29</sub> and C<sub>30</sub> regular steranes in the saturated fractions respectively. The following *m/z* transitions of 358→217, 372→217, 386→231, 400→231, 414→231 and 414→98 were monitored to obtain the C<sub>26</sub>, C<sub>27</sub>, C<sub>28</sub>, C<sub>29</sub>, C<sub>30</sub> and dinosteranes, respectively. The C<sub>26</sub> steranes transitions were identified by their key fragment ions, their relative retention times and by comparison of their mass spectra with published data (Holba et al.,

1998b; Grice et al., 1998a; Peters et al., 2005; Grosjean et al., 2009). The 245 ion was monitored in single ion monitoring (SIM) mode for the triaromatic steroids present in the aromatic fractions. The triaromatic steroids were identified by their relative retention times reported by Wenzhi et al. (2005).

## 5. Results and Discussion

The oil samples analysed in this study have previously been characterised by a variety of organic geochemical analyses including stable carbon ( $\delta^{13}\text{C}$ ), hydrogen ( $\delta\text{D}$ ) isotopes of hydrocarbons (Aboglila et al., 2010a). From the study of Aboglila et al (2010a), two main oil families (A and B) were identified with respect to variations in their source inputs and relative thermal maturity levels. The family A oils included the Sarir-L, Nafoora, Faregh and Sarir-C fields and were found to be relatively more mature and have a relatively higher terrigenous input than the family B oils. The family B oils included the Amal, Gialo and Masrab fields and showed a higher contribution of marine-derived organic matter. In the East Sirte Basin, oils from the Nubian Formation (VV3-65 and 5I13-65 wells) are distinguished by a high relative abundance of hopanes to steranes. The oils from the Sahabi Formation (AA-01 and AA-03 wells) contained an abundance of extended tricyclic terpanes, whereas the other oils (see Table 3) contained a mixture of the various biomarkers identified in the two main groups (see Aboglila et al., 2010a for more details).

Biomarker and  $\delta^{13}\text{C}$  data was also obtained from a series of source rock extracts from the Sirte, Tagrifet, Rakb, Rachmat, Bahi and Nubian Formations (see Aboglila et al., 2010b for further details). The source rocks were found to contain Type II/III kerogen. The source-rocks from the Sirte Formation showed a relatively

higher thermal maturity than the Tagrifet, Rakb, Rachmat, Bahi, and Nubian Formations. Biomarker distributions supported an anoxic to a sub oxic depositional environment and varying contributions of OM from marine/lacustrine phytoplankton, green algae and/or land plants.

## 5.1. Crude oils

### 5.1.1. Sterane distributions

Representative parent-daughter ions of  $m/z$  358→217 ( $C_{26}$ ), 372→217 ( $C_{27}$ ), 386→217 ( $C_{28}$ ), 400→217 ( $C_{29}$ ) and 414→217 ( $C_{30}$ ) for crude oils from the East Sirte Basin are shown in the ion-chromatograms of Fig. 2. All oils contain a complex distribution of  $C_{26}$ – $C_{30}$  steranes, with the exception of oils from the 5I13-59 and VV3-65 wells, indicating a terrestrial depositional environment (Aboglila et al., 2010a). The oils obtained from AA-01 and AA-03 wells, contain a high abundance of tricyclic components, which is consistent with a marine depositional environment (Aboglila et al., 2010a). *Norcholestanes* are commonly present in crude oils and rock extracts in low concentrations, compared with the more common  $C_{27}$ ,  $C_{28}$  and  $C_{29}$  steranes, hence the need for GC-MRM analyses for identification. The following sub-sections describe the specific sterane distributions identified in the crude oils and source-rocks from East Sirte Basin in further detail.

### 5.1.2. *Norcholestanes ratios* ( $C_{26}$ )

The  $C_{26}$  steranes (24-*norcholestanes*, 27-*norcholestane*, and 21-*norcholestane* isomers) have been previously recognised in geological samples (Moldowan et al., 1991). Recently, 24-*Norsterols* have been reported in both

diatoms and dinoflagellates, considered as possible sources for the precursors of 24-*norsteranes* (Rampen et al., 2007 and references therein). All the oil samples analysed in this study contain *norcholestanes* (Fig. 2; C<sub>26</sub> steranes identified based on the work of Holba et al. (1998b) and an abundance of C<sub>28</sub> steranes, consistent with a diatomaceous facies (Grantham and Wakefield, 1988), except the oils from the 5I13-59, VV-65, AA-01 and AA-03 wells (Table 3). Holba et al. (1998b) observed a high abundance of 24-*nordiacholestanes* and 24-*norcholestanes* ratios in oils that were Cretaceous or younger compared with the abundance of their 27-*norcholestane* analogues. A high abundance of 24-*norcholestanes* to 27-*norcholestane* in oils has been attributed to algal groups, in particular diatom and a dinoflagellate species (Volkman, 2003; Rampen et al., 2007 and references therein), spanning the Jurassic to the Tertiary (Holba et al., 1998b). The *norcholestanes* have been reported to occur in varying quantities in crude oils. Therefore the 24-*nordiacholestane* ratios (24-NDR) and 24-*norcholestanes* ratios (24-NCR) were measured (Holba et al., 1998a, 1998b). The ratios of 24-NDR and 24-NCR vary between the Sirte oils (Table 3). For example, 24-NDR > 0.20 points to a Jurassic or younger source, whereas 24-24-NDR > 0.25 and 24-NCR ≥ 0.40 corresponds to samples derived from Jurassic to Tertiary-aged deposits, consistent with the evolution of diatoms during the Cretaceous Era (Holba et al., 1998b). The variations of relative concentrations of 24- to 27-*norcholestanes* between the Sirte oils (Table 3) can attribute to a difference in relative effect of thermal maturity between samples (Moldowan et al., 1991). The relative abundance of the 21-*norcholestanes* compared to the 24- and 27-*norcholestanes* (Moldowan et al., 1991) indicates that thermal maturity has had a negligible effect. Although, Rampen et al. (2007) suggested that high concentrations of 24- to 27-

*norcholestanes* in the Jurassic and the Cretaceous to Cenozoic oils are related to dinoflagellate expansion, whereas the increase in the Oligocene-Miocene is likely caused by diatom evolution. The distributions of the 21-*norcholestane* isomers are similar in all oil samples.

### 5.1.3. *Dinosteranes and 4 $\alpha$ -methyl-24-ethylcholestanes*

Dinosterol and associated sterols have been proposed as natural lipid precursors of dinosteranes and triaromatic dinosteroid biomarkers. They are produced by dinoflagellate organisms (Withers, 1987; Volkman et al., 1990; Moldowan and Talyzina, 1998). Biogeochemical evidence for dinoflagellate ancestors have been reported in the early Cambrian (Withers, 1987) and molecular evidence has provided a link of cyst-forming dinoflagellates with pre-Triassic ancestors (Moldowan and Talyzina, 1998), although other organisms have also been proposed since the Middle Triassic (Volkman et al., 1990). These include, bacteria (*Methylococcus capsulatus*) (Bird et al., 1971), some prymnesiophyte microalgae (Volkman et al., 1990) and diatoms (*Navicula*) have been reported to produce dinosterol and related sterols (Volkman et al., 1993). In this study GC-MRM analyses representative parent-daughter ( $m/z$ )  $\rightarrow$  ions of 386 $\rightarrow$ 231 (C<sub>28</sub>), 400 $\rightarrow$ 231 (C<sub>29</sub>), 414 $\rightarrow$ 231 (C<sub>30</sub>) and 414 $\rightarrow$ 98 (dinosteranes) for oils from the East Sirte Basin are shown in Figure 3. The 4 $\alpha$ -methyl-24-ethylcholestanes and dinosteranes are abundant in all of the Sirte oils with the exception of four oils from the 5I13-59, VV3-65, AA-01 and AA-03 wells. The presence and abundance of dinosteranes and 4 $\alpha$ -methyl-24-ethylcholestanes in the Sirte oils can be considered as evidence for dinoflagellates deposited during the Middle Triassic to Cretaceous (Mesozoic).

The hydrolysis products of the extant coral extract was analysed in this study by GC-MRM analyses and also revealed a similar distribution of dinosteranes and 4 $\alpha$ -methyl-24-ethylcholestanes as observed in the Sirte samples (Fig. 4) above supporting a general source from dinoflagellates. However, the dinosteranes and 4 $\alpha$ -methyl-24-ethylcholestanes show isomers with their original biological configuration (dominated by the  $\alpha\alpha\alpha$  C<sub>28</sub>R sterane). This is one of the unique features for the original biological configuration being retained during the pyrolysis process (c.f. Love et al., 1995).

The triaromatic dinosteroids derived from dinoflagellate precursors have also been considered as age diagnostic markers (Moldowan and Talyzina, 1998). On  $m/z$  245 mass fragmentograms, the ratios of triaromatic cholestane derivatives with the methyl substituents in the Sirte oils range between 0.31 and 0.46 (Table 2). This range indicates organic matter produced during the Mesozoic age and consistent with the presence of dinoflagellate cysts in the Nubian Formation of Lower Cretaceous age (Hallett, 2002).

## 5.2. Source rocks

### 5.2.1. Sterane distributions

Representative parent-daughter ( $m/z$ )  $\rightarrow$  ions of  $m/z$  358 $\rightarrow$ 217 (C<sub>26</sub>), 372 $\rightarrow$ 217 (C<sub>27</sub>), 386 $\rightarrow$ 217 (C<sub>28</sub>), 400 $\rightarrow$ 217 (C<sub>29</sub>) and 414 $\rightarrow$ 217 (C<sub>30</sub>) for source-rock extracts from the East Sirte Basin are shown in Fig. 5. All of the extracts contained steranes, diasteranes, norcholestanes and 4 $\alpha$ -methyl-24-ethylcholestanes and dinosteranes.

### 5.2.2. Norcholestanes ratios (C<sub>26</sub> steranes)

All of the measured bitumens contain abundant C<sub>26</sub> steranes (Fig. 5). The NDR and NCR ratios (2) are much higher than NDR and NCR ratios in the oils (Table 3). In the highly mature sediments the 21-*norcholestane* strongly dominates the 24- and 27-*norcholestanes* in contrast to the other steranes in thermally mature extracts (Moldowan et al., 1991). The NDR and NCR ratios vary between the formations (Table 2). The Sirte Formation show high abundances of 24-*norcholestanes* relative to 27-*norcholestanes*, which is in agreement with a higher thermal maturity for the Sirte Formation comparing to the other formations except the Tagrifet Formation as observed previously see Aboglila et al. (2010b).

The NDR ratios range from 0.25 to 0.37 and NCR ratios range from 0.33 to 0.48 consistent with a Mesozoic age (Holba et al., 1998a and b). Depositions of the Sirte Cretaceous source-rocks are coincident with the evolution of diatoms (Holba et al., 1998b) and/or coincident with the expansion of dinoflagellates (Rampen et al., 2007). C<sub>30</sub> 4-desmethyl cholestanes were identified in all extracts (Fig. 6), indicating a source of OM from a marine environment (c.f. Peters et al., 2005)

### 5.2.3. 4 $\alpha$ -Methyl-24-ethylcholestane and dinosteranes

TIC and parent-daughter ( $m/z$ )  $\rightarrow$  ions of 386 $\rightarrow$ 231 (C<sub>28</sub>), 400 $\rightarrow$ 231 (C<sub>29</sub>), 414 $\rightarrow$ 231 (C<sub>30</sub>) and 414 $\rightarrow$ 98 (dinosteranes) for the bitumens from the East Sirte Basin are shown in Fig. 7.

All measured samples contain 4 $\alpha$ -methyl-24-ethylcholestane and dinosteranes, derived from 4-methyl-24-ethylsterol and dinosterol precursors produced by dinoflagellate organisms in marine or lacustrine environments (e.g. Summons et al., 1992). The enrichment of such biomarkers throughout the East Sirte shale supports a Cretaceous aged-source. Triaromatic dinosteroids (Table 2)



were observed in some of the extracts analysed from the studied Sirte formations. The triaromatic ratios varied between 0.22 and 0.37, which are consistent with a Mesozoic age contribution to the source rock (Hallett, 2002).

### 5.3. *Oil-source rocks correlations*

Oils from the East Sirte Basin show abundant and similar distributions of 3, 24-dimethyl triaromatic steroid, 3-methyl-24 ethylcholestanes, 4-methyl-24-ethylcholestanes and 2-methyl-24- ethylcholestanes to the bitumens extracted from various formations of the East Sirte Basin providing evidence for a source contribution from dinoflagellates and diatoms deposited during the Mesozoic. The presence of specific steroid biomarkers of oils and bitumens and their fractions permit the genetic correlation between the analysed oils and the Cretaceous source rocks. The genetic oil families in Tables 2 and 3 show good correlation among family B oils and condensates based on biomarker data evaluated from 3, 24-dimethyl triaromatic steroid, 3-methyl-24 ethylcholesteranes, 4-methyl-24-ethylcholesteranes and 2-methyl-24- ethylcholesteranes. Despite the absence of these steroids in oils from the 5I13-59, VV3-65, AA-01 and AA-03 wells may suggest that these oils can attribute a different genetic correlation. A various correlation between hydrocarbons from the East Sirte Basin is interesting, further geochemical research should be carried out to identify additional correlations.

## **6. Conclusions**

All oils and source rocks from the East Sirte Basin analysed contain a complex distribution of C<sub>26</sub>–C<sub>30</sub> steranes with the exception of oils from the 5I13-59, VV 65 AA-01 and AA-03 wells. All the samples were found to contain

*norcholestanes* consistent with a diatomaceous facies and/or a dinoflagellate-origin. The ratios of NDR and NCR varied between the Sirte oils.  $NDR > 0.20$  supports a Jurassic or younger source, whereas  $NDR > 0.25$  and  $NCR > 0.40$  corresponds to samples derived from Jurassic to Tertiary-aged deposits, consistent with the evolution of diatoms during the Cretaceous. Abundant dinosteranes, 4 $\alpha$ -methyl-24-ethylcholestanes and various triaromatic steroids provided evidence for a source contribution from dinoflagellates deposited during Mesozoic. This is consistent with the presence of dinoflagellate cysts in the Numbian Formation of Lower Cretaceous age. An excellent association between family B oils and condensates based on 3, 24-dimethyl triaromatic steroid, 3-methyl-24-ethylcholesteranes, 4-methyl-24-ethylcholesteranes and 2-methyl-24-ethylcholesteranes being an exception has been observed in steroids in oils from the 5I13-59, VV 65 AA-01 and AA-03 which indicates to further oil-source rock correlations. The 24-*norcholestanes*, 4-methylsteranes and dinosteranes considered important biomarkers can provide a significant geochemical knowledge about genetic source, an age and oil-source correlation of the oils and rocks from the East Sirte Basin.

### **Acknowledgements**

The authors thank Geoff Chidlow for his assistance with GC-MS and GC-MS MS analysis, respectively. We are grateful to the staff of the National Oil Corporation (NOC) in Tripoli, and staff of the Libyan Petroleum companies (Waha – Veba - Gulf) for providing samples. K.G. acknowledges ARC for a Discovery grant.

### **References**

- Aboglila, S., Grice, K., Trinajstic, K., Dawson, D., Williford, K., 2010a. Use of biomarker distributions and compound specific isotopes of carbon and hydrogen to delineate hydrocarbon characteristics in the East Sirte Basin (Libya). *Organic Geochemistry* 41, 1249-1258.
- Aboglila, S., Grice, K., Trinajstic, K., Dawson, D., Williford, K., 2010b. A geochemical evaluation of thermal maturity and depositional palaeoenvironments of seven Cretaceous formations from the East Sirte Basin (Libya). *LPI Petroleum Research Journal*. In press.
- Ahlbrandt, T.S., 2001. The Sirte Basin Province of Libya – Sirte-Zelten Total Petroleum System. US Geological Survey Bulletin 2202-F. <<http://geology.cr.usgs.gov/pub/bulletins/b2202-f/>> (accessed 20.4.2009).
- Audino M., Grice K., Alexander R., and Kagi R. I., 2002. Macrocyclic alkanes in crude oils from the algaenan of *Botryococcus braunii*. *Organic Geochemistry* 33, 979–984.
- Barr, F.T., Wegnar, A.A., 1972. Stratigraphic Nomenclature of the Sirte Basin, Libya. Petroleum Exploration Society of Libya, Tripoli. p. 179.
- Bastow, T.P., van Aarssen, B.G.K., Lang, D., 2007. Rapid small-scale separation of saturate, aromatic and polar components in petroleum. *Organic Geochemistry* 38, 1235–1250.
- Bird, C.W., Lynch J.M., Pirt F.J., Reid W.W., Brooks C.J.W., Middleditch B.S., 1971. Steroids and squalene in *Methylococcus capsulatus* grown on methane. *Nature* 230, 473-474.
- Blokker, P., Van Bergen, P.F., Pancost, R.D., Collinson, M.E., Sinninghe Damsté, J. S., De leeuw J.W., 2001. The chemical structure of *Gloeocapsomorpha prisca*

microfossils: implication for their origin. *Geochimica et Cosmochimica Acta* 65, 885-900.

Bode, H.B., Zeggel B., Silakowski B., Wenzel S.C., Hans, R., Müller R., 2003. Steroid biosynthesis in prokaryotes: identification of myxobacterial steroids and cloning of the first bacterial 2,3(S)-oxidosqualene cyclase from the myxobacterium *Stigmatella aurantiaca*. *Molecular Microbiology* 47, 471–481.

Brassell, S.C., Eglinton, G., Marlowe, I. T., Pflaumann, U., Sarnthein, M., 1986. Molecular stratigraphy: a new tool for climatic assessment. *Nature* 320, 129-133.

Brocks J.J., Grice K., 2011. Biomarkers (Ancient biomolecules end evolution) *Encyclopedia of Geobiology*. In: (eds. V. Thiel, J. Reitner), *Encyclopedia of Earth Science Series*. Springer. 167-182.

Burwood, R., Redfern, J., Cope, M., 2003. Geochemical evaluation of East Sirte Basin (Libya) petroleum systems and oil provenance. In: (eds. T. Burnham et al.), *Petroleum Geology of Africa: New Themes and Developing Technologies*, 207. Geological Society Special Publication, London. 203–214.

Dawson, D., Grice, K., Edwards, D.S., Alexander. R. 2007. The effect of source and maturity on the stable isotopic compositions of individual hydrocarbons in sediments and crude oils from the Vulcan Sub-basin, Timor Sea, Northern Australia. *Organic Geochemistry*. 38, 1015-1038.

El-Alami, M., Rahouma, S., Butt, A., 1989. Hydrocarbon habitat in the Sirte Basin northern Libya. *Petroleum Research Journal* 1, 17–28.

Fowler, M.G., 1992. The influence of *Gloeocapsomorpha prisca* on the organic geochemistry of oils and organic-rich rocks of Late Ordovician age from Canada. In: (eds. M. Schidlowski et al.), *Early Organic Evolution: Implications for Mineral and Energy Resources*. Springer. 336-356.

- Ghori, K.A.R., Mohammed, R.A., 1996. The application of petroleum generation modelling to the eastern Sirte Basin, Libya. In: (eds. M.J. Salem et al.), The Geology of Sirte Basin II. Elsevier, Amsterdam, 529–540.
- Grantham, P.J., Wakefield, L.L., 1988. Variations in the sterane carbon number distributions of marine source rock derived crude oils through geological time. *Organic Geochemistry* 12, 61–73.
- Gras, R., 1996. Structural style of the southern margin of the Messlah High. In: (eds. M.J. Salem et al.), The Geology of Sirte Basin II. Elsevier, Amsterdam, 201-210.
- Grice K., Schouten S., Peters K.E., Sinninghe Damsté J.S., 1998a. Molecular isotopic characterisation of hydrocarbon biomarkers in Palaeocene-Eocene evaporitic, lacustrine source rocks from the Jiangnan Basin, China. *Organic Geochemistry* 29, 1745-1764.
- Grice K., Klein Breteler, W.C, Schouten, S., Grossi, V., De Leeuw, J.W., Sinninghe-Damste, J.S., 1998b. The effects of zooplankton herbivory on biomarker proxy records. *Paleoceanography*. 13, 686-693.
- Grice, K., Schouten, S., Nissenbaum, A., Charach, J., Sinninghe Damste, J.S., 1998c. A remarkable paradox: freshwater algal (*Botryococcus braunii*) lipids in an ancient hypersaline euxinic ecosystem. *Organic Geochemistry* 28, 195-216.
- Grice, K., Audino, M., Alexander, R., Boreham, C.J., Kagi, R.I., 2001. Distributions and stable carbon isotopic compositions of biomarkers in torbanites from different palaeogeographical locations. *Organic Geochemistry* 32, 1195-1210.

- Grosjean, E., Love, G.D., Stalvies, C., Fike, D.A., Summons, R.E., 2009. Origin of petroleum in the Neoproterozoic–Cambrian South Oman Salt Basin. *Organic Geochemistry* 40, 87–110.
- Hallett, D., 2002. *Petroleum Geology of Libya*. Elsevier, Amsterdam, V, 1.
- Holba, A.G., Dzou, L.I.P., Masterson, W.D., 1998a. Application of 24-norcholestanes for constraining source age of petroleum. *Organic Geochemistry* 29: 1269-1283.
- Holba, A.G., Tegelaar, E.W., Huizinga, B.J., Moldowan, J.M., Singletary, M.S., McCaffrey, M.A., Dzou, L.I.P., 1998b. 24-Norcholestanes as age-sensitive molecular fossils. *Geology* 26, 783–786.
- Huang, Z., Poulter C.D., Wolf, F.R., Somers, T.C., White J.D., 1988. Braunicene, a novel cyclic C<sub>32</sub> isoprenoid from *Botryococcus braunii*. *Journal of American Chemical Society*, 110, 2959-3964.
- Kohl, W., Gloe, A., Reichenbach, H., 1983. Steroids from the myxobacterium *Nannocystis exedens*. *Journal of Genetic Microbiology* 129, 1629-1635.
- Love, G.D., Snape, C.E., Carr, A.D., Houghton, R.C., 1995. Release of covalently-bound alkane biomarkers in high yields from kerogen via catalytic hydrolysis. *Organic Geochemistry* 23, 981–986.
- Macgregor, D.S., 1996. The hydrocarbon systems of North Africa. *Marine and Petroleum Geology*, 13, 32-340.
- Maslen E., Grice K., Dawson D., Le Metayer P., Edwards D., 2011. Stable carbon isotopic compositions of individual aromatic hydrocarbons as source and age indicators in oils from Western Australian Basins. *Organic Geochemistry* (in press).

- Meredith, W., Russel, C.A., Snape, C.E., Fabbri, D., Vane, C.H., Love, G.D., 2004. The thermal desorption of hydropyrolysis oils from silica to facilitate rapid screening by GC-MS. *Organic Geochemistry* 35, 73-89.
- Meredith, W., Sun, C.G., Snape, C.E., Sephton, M.A., Love, G.D., 2006. The use of model compounds to investigate the release of covalently bound biomarkers via hydropyrolysis. *Organic Geochemistry* 37, 1705-1714.
- Metzger P., Casadevall E., Pouet M.J., Pouet Y., 1985. Structures of some botryococenes: branched hydrocarbons from the B-race of the green alga *Botryococcus braunii*. *Phytochemistry* 24, 2995-3002.
- Metzger P., Largeau C., 1999. Chemicals of *Botryococcus braunii*. In *Chemicals from Microalgae* (ed. Z. Cohen), pp. 205-260. Taylor and Francis
- Moldowan J.M., Fago F.J., Lee C.Y., Jacobson S.R., Watt D.S., Slougui N.E., Jeganathan A., Young D.C., 1990. Sedimentary 24-*n*-propylcholestanes, molecular fossils diagnostic of marine algae. *Science* 247, 309-312.
- Moldowan, J.M., Lee, C.Y., Watt, D.S., Jeganathan, A., Slougui, N.E., Gallegos, E.J., 1991. Analysis and occurrence of C<sub>26</sub>-steranes in petroleum and source rocks. *Geochimica et Cosmochimica Acta* 55, 1065-1081.
- Moldowan, J. M., Dahl, J., Jacobson, S.R., Huizinga, B.J., Fago, F.J., Shetty, R., Watt, S., Peters, K.E., 1996. Chemostratigraphic reconstruction of biofacies: Molecular evidence linking cyst-forming dinoflagellates with pre-Triassic ancestors. *Geology* 24, 159-162.
- Moldowan, J.M., Talyzina, N.M., 1998. Biogeochemical evidence for dinoflagellate ancestors in the Early Cambrian. *Science* 281, 1168-1170.
- Nichols, P.D., Volkman, J.K., Palmisano, A.C., Smith, G.A., White, D.C., 1988. Occurrence of an isoprenoid C<sub>25</sub> diunsaturated alkene and high neutral lipid

content in Antarctic sea-ice diatom communities. *Journal of Phycology* 24, 90-96.

Pearson, A., Budin, M., Brocks, J.J., 2003. Phylogenetic and biochemical evidence for sterol synthesis in the bacterium *Gemmata obscuriglobus*. *Proceedings of the National Academy of Science* 100, 15352–15357.

Parsons, M.G., Zagaar, A.M., Curry, J.J., 1980. Hydrocarbon occurrence in the Sirte Basin, Libya. *Canadian Society of Petroleum Geologists Memoirs*, 6, 723-732.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. *The biomarker guide vol 1: biomarkers and isotopes in the environment and human history*. Cambridge University Press, Cambridge, 488.

Rampen, S.W., Schouten, S., Abbas, B., Panoto, F.E., Muyzer, G., Campbell, C.N.,

Fehling, J., Sinninghe Damsté, J.S., 2007. On the origin of 24-*norcholestanes* and their use as age-diagnostic biomarkers. *Geology* 35, 419–422.

Robinson, N., Eglinton, G., Brassell, S.C., Cranwell, P.A., 1984. Dinoflagellate origin for sedimentary 4 $\alpha$ -methylsteroids and 5 $\alpha$ (H)-stanols. *Nature* 308, 439-442.

Rusk, D.C., 2001. Libya: Petroleum potential of the underexplored basin centers—A twenty-first-century challenge. In: (M.W. Downey et al.), *Petroleum Provinces of the Twenty-first Century*. American Association of Petroleum Geologists Memoir 74, 429–452.

Sinninghe Damsté, J.S., Muyzer, G., Abbas, B., Rampen, S.W., Massé, G., Allard, W.G., Belt, S.T., Robert, J.M., Rowland, S.J., Moldowan, J.M., Barbanti, S.M., Fago, F.J., Denisevich, P., Dahl, J., Trindade, L.A.F., Schouten, S., 2004. The rise of the rhizosolenid diatoms. *Science* 304, 584-587.



- Summons, R.E., Thomas J., Maxwell J.R., Boreham C.J., 1992. Secular and environmental constraints on the occurrence of dinosterane in sediments. *Geochimica et Cosmochimica Acta* 56, 2437-2444.
- Summons, R.E., Bradley A.S., Jahnke L.L., Waldbauer J.R., 2006. Steroids, triterpenoids and molecular oxygen. *Philosophical Transactions of the Royal Society B: Biological Sciences* 361, 951.
- Summons, R.E., Metzger P., Largeau, C., Murray A. P., Hope J.M., 2002. Polymethylsqualanes from *Botryococcus braunii* in lacustrine sediments and oils. *Organic Geochemistry* 33, 99-109.
- Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter. *Organic Geochemistry* 9, 83-99.
- Volkman, J.K., 2003. Sterols in microorganisms. *Applied Microbiology and Biotechnology* 60, 496-506.
- Volkman, J.K., Barrett, S.M., Dunstan, G.A., 1990. A new source of 4-methyl sterols and 5 $\alpha$ (H)-stanols in sediments: Prymnesiophyte microalgae of the genus *Pavlova*. *Organic Geochemistry* 15, 489-497.
- Volkman, J.K., Barrett S.M., Dunstan G.A., Jeffrey, S.W., 1993. Geochemical significance of the occurrence of dinosterol and other 4-methyl sterols in a marine diatom. *Organic Geochemistry* 20, 7-15.
- Volkman, J.K., Barrett, S.M., Dunstan, G.A., 1994. C<sub>25</sub> and C<sub>30</sub> highly branched isoprenoid alkanes in laboratory cultures of two marine diatoms. *Organic Geochemistry* 21, 407-413.
- Volkman, J.K., Barrett S.M., Blackburn, S.I., Mansour, M.P., Sikes, E.L., Gelin, F., 1998. Microalgal biomarkers: a review of recent research developments. *Organic Geochemistry* 29, 1163-1179.

- Wenzhi, Z., Shuichang, Z., Feiyu, W., Jianping, C., 2005. Gas accumulation from oil cracking in the eastern Tarim Basin: A case study of the YN2 gas field. *Organic Geochemistry* 36, 1602-1616.
- Withers, N., 1987. Dinoflagellate sterols. In: *The Biology of Dinoflagellates*. (ed. F.J.R. Taylor), *The Biology of Dinoflagellates*. Oxford: Blackwell Scientific, 316-359.

## Figures

**Fig. 1** Location of the Sirte Basin, the studied fields and selected oil wells in studied area (modified from Ahlbrandt (2001); Burwood et al. (2003); Aboglila et al. (2010a).

**Fig. 2** MRM chromatograms show distributions of C<sub>26</sub>–C<sub>30</sub> steranes of crude oils (oil from 6J1-59 well) from East Sirte Basin. βα, ααα and αββ indicate 13β (H), 17α (H)-diasteranes, 5α (H), 14α (H), 17α (H)- and 5α (H), 14β (H), 17β (H)-steranes, respectively. Identification obtained from Holba et al. (1998b) Grosjean et al. (2009).

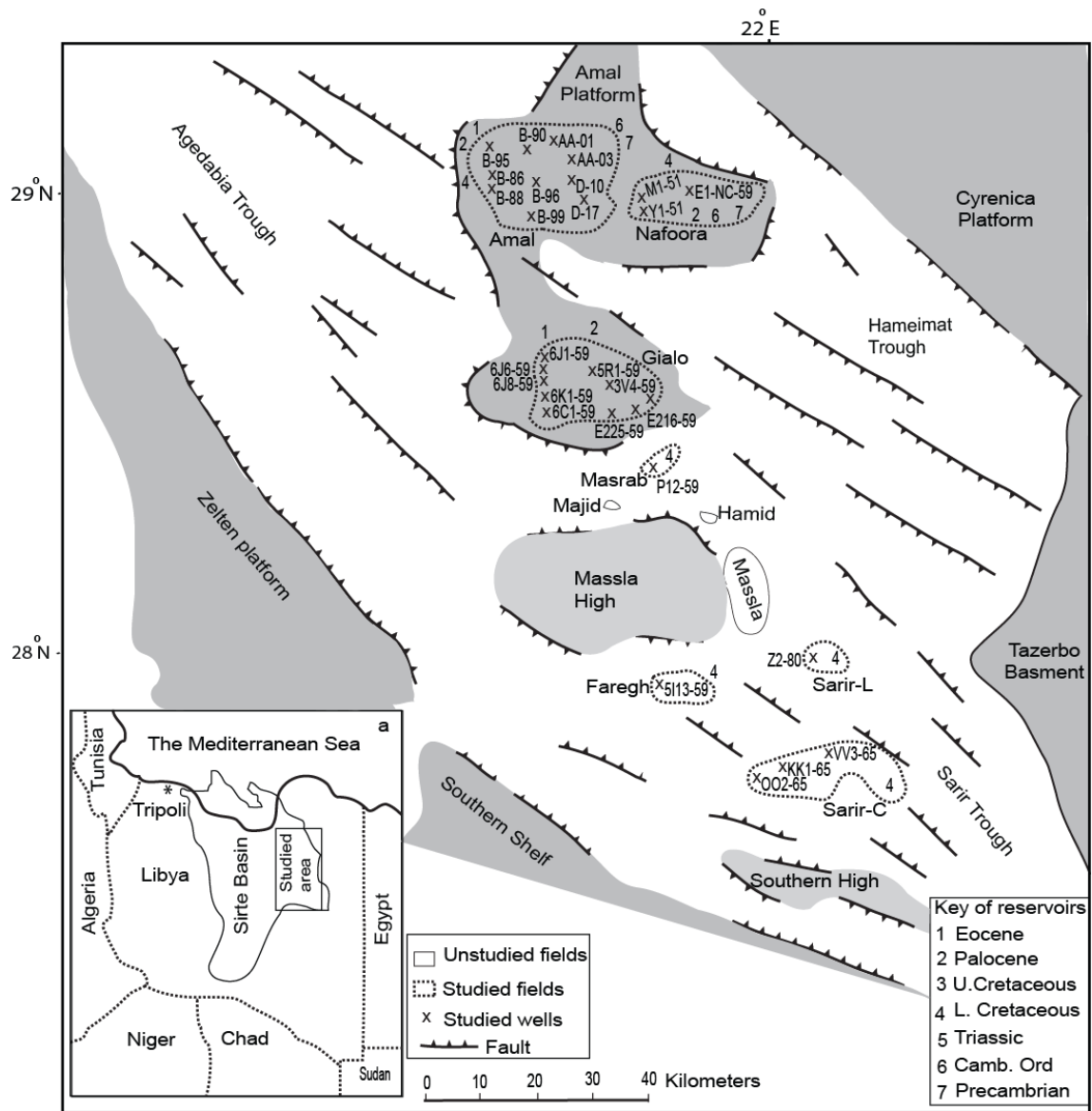
**Fig. 3** MRM chromatograms show desmethylsteranes distributions of C<sub>27</sub>–C<sub>30</sub>, including dinosteranes in crude oils (D-17) from East Sirte Basin. Identification from Grice et al. (1998a); Grosjean et al. (2009); Peters et al. (2005). Note that two additional dinosteranes have been tentatively proposed.

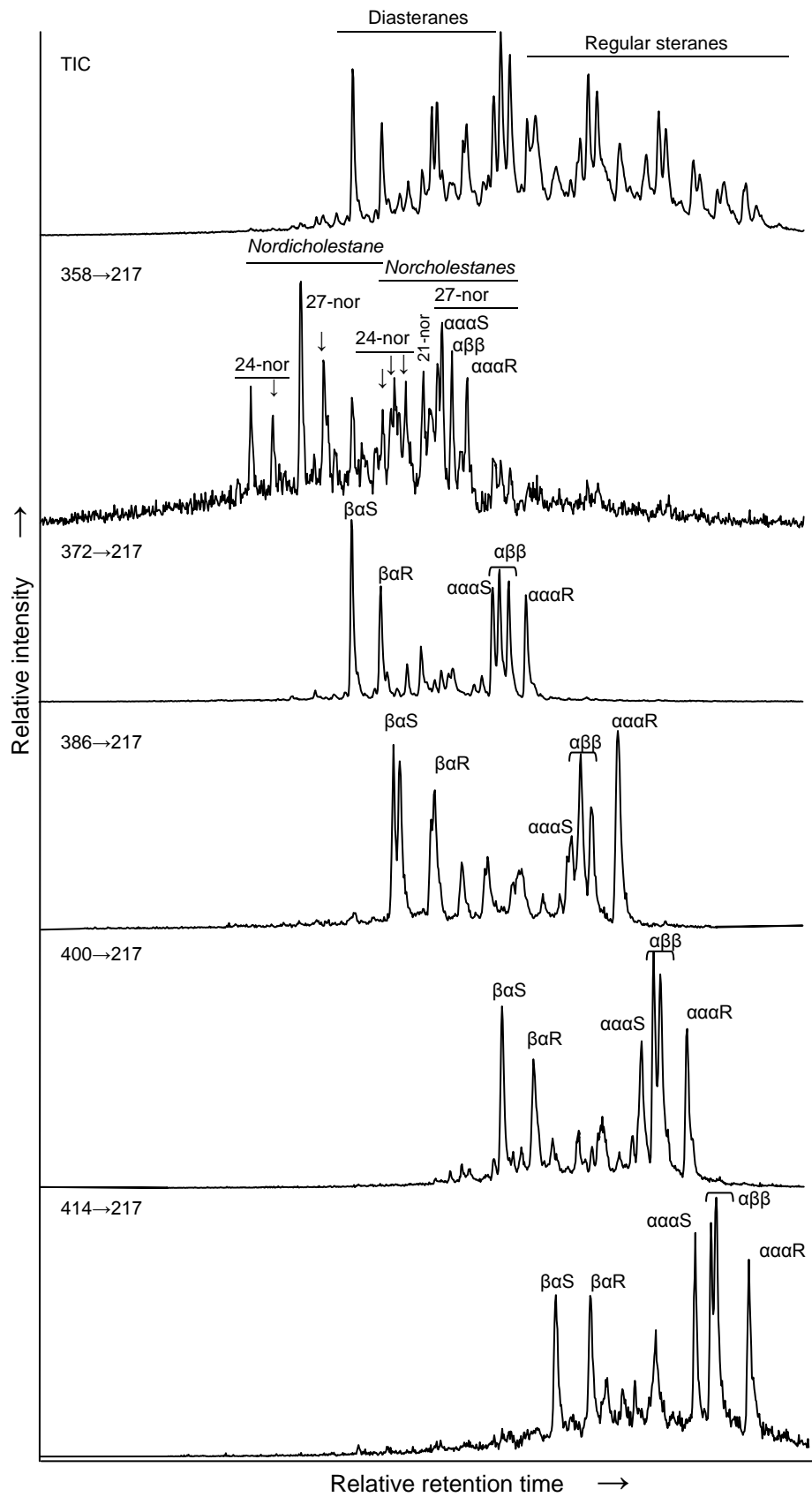
**Fig. 4** The coral extract analysed by MRM analyses, includes dinosteranes and 4α-methyl-24-ethylcholestanes. Identification from Grice et al. (1998b); Grosjean et al. (2009); Peters et al. (2005).

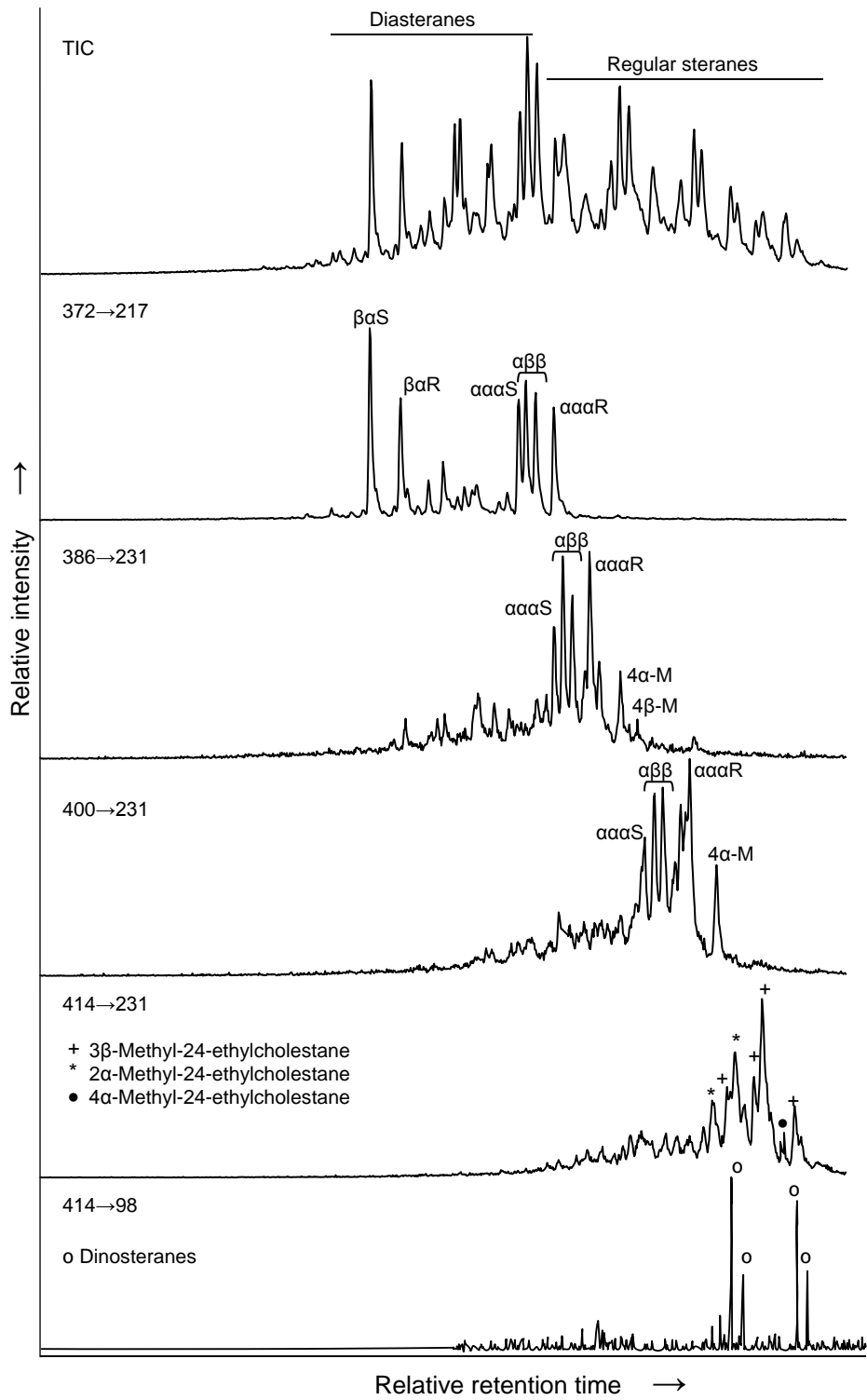
**Fig. 5** MRM chromatograms show distributions of C<sub>26</sub>–C<sub>30</sub> steranes in source rock (e.g. Rachmat Fm; M1-51; 3015 m). Identification obtained from Holba et al. (1998b) Grosjean et al. (2009).

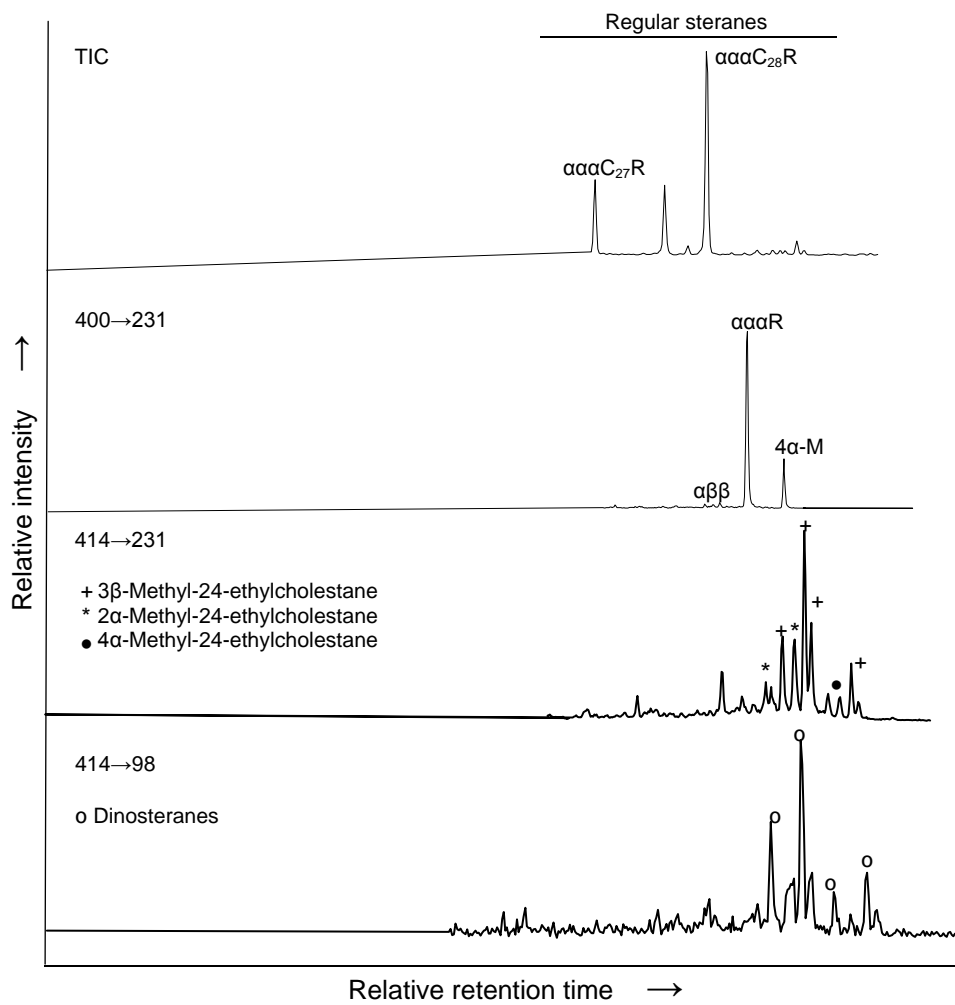
**Fig. 6** MRM chromatograms showing desmethylsteranes distributions of C<sub>28</sub>–C<sub>30</sub> (Sirte Fm; 002-65; 2478-81 m), based on transitions to *m/z* 231.

**Fig. 7** MRM chromatograms show methylsterane distributions including dinosteranes in source rocks (M1-51; Tagrifet Fm; 2882 m), based on transitions to *m/z* 231. Identification made from Grice et al. (1998a); Grosjean et al. (2009); Peters et al. (2005). Note that two additional dinosteranes have been tentatively proposed.



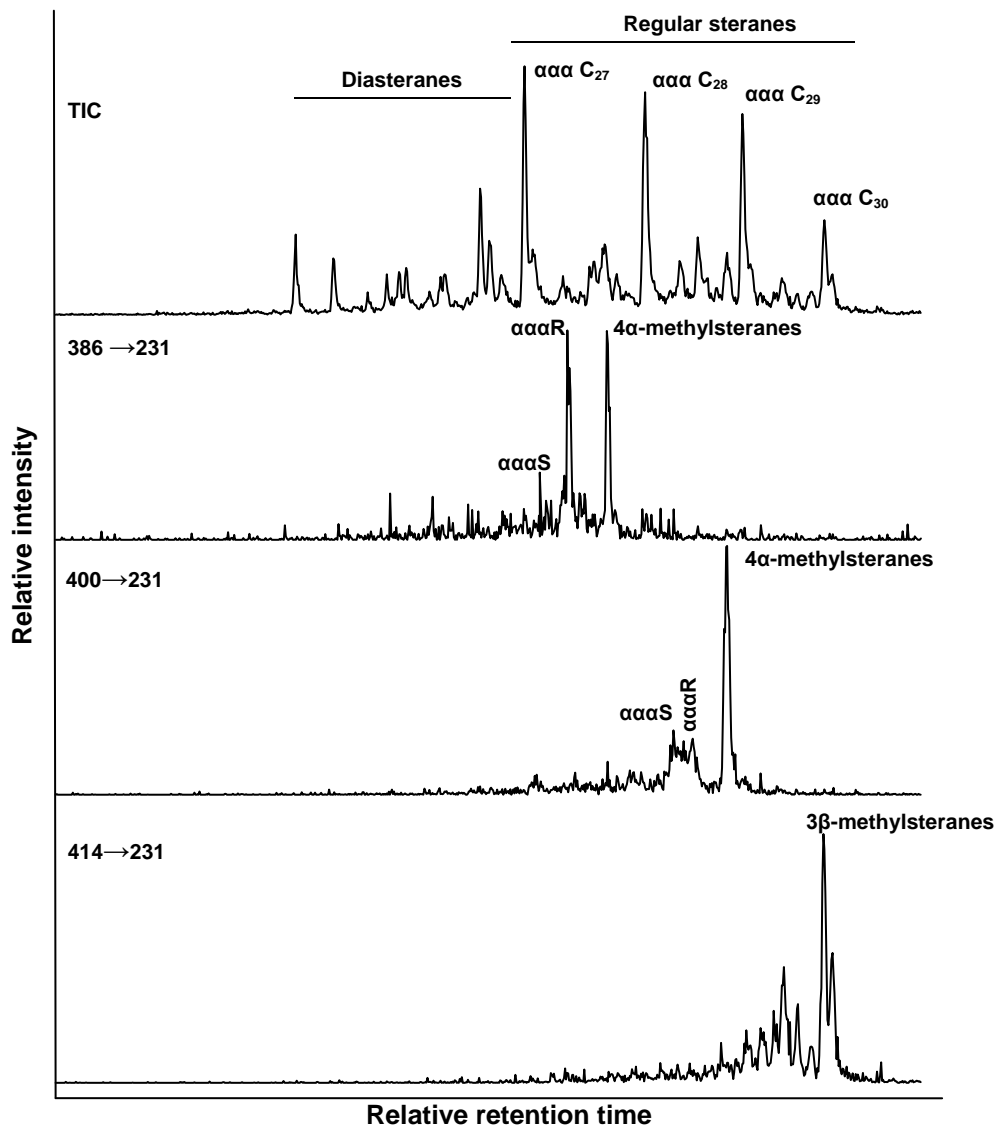


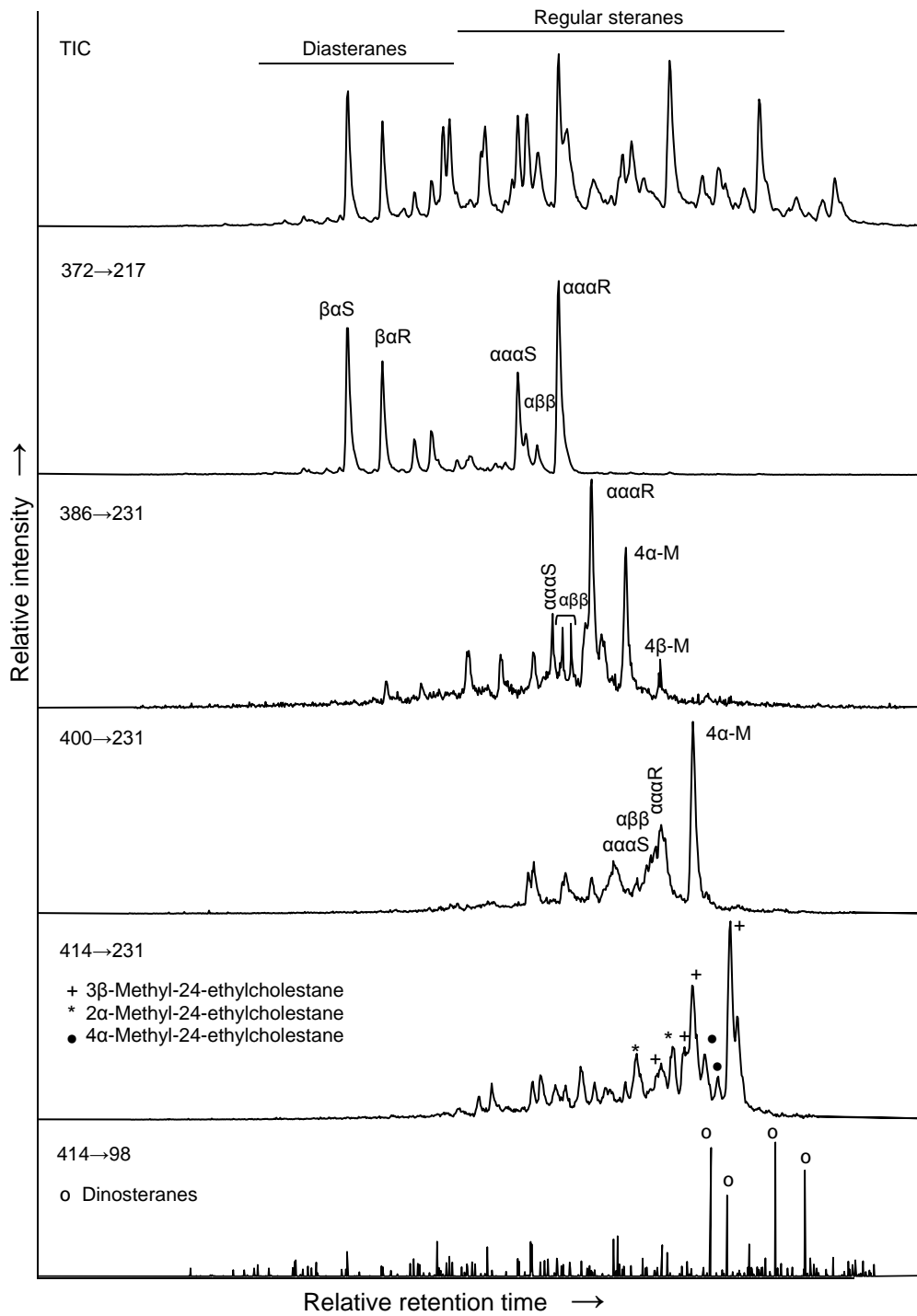












## **Tables**

**Table 1** Biomarkers associated with Eukaryotes and their environments of deposition (after, Brocks and Grice, 2011).

**Table 2** NDR= 24-Nordiacholestane ratio and NCR= 24-Norcholestane ratio calculated from peaks (C<sub>26</sub> steranes) of rock extracts (Holba et al., 1998a, 1998b).

**Table 3** NDR= 24-*nordiacholestane* ratio and NCR = 24-*norcholestane* ratio calculated from peaks (C<sub>26</sub> steranes) of crude oils (Holba et al., 1998a, 1998b).

Organisms	Biomarkers	Depositional Environment and age	Other possible sources	References
<b>Eukarya</b>				
Eukaryotes (general)	Ergostane, stigmastane and their aromatic analogues	Most environments, Neoproterozoic to present		(Volkman et al., 1998; Volkman, 2003; Summons et al., 2006)
	Cholestane and aromatic analogues		Possible minor contribution from Myxococcales (myxobacteria)	(Kohl et al., 1983; Bode et al., 2003)
Pelagophyte algae ('brown tides' and Sarcinochrysidales)	24- <i>n</i> -propylcholestane	Common in marine environments		(Moldowan et al., 1990)
Dinoflagellates	4-Methylergostane, 4-methylstigmastane	Minor component in other eukaryotes		(Volkman, 2003)
	Dinosterane	Mostly Mesozoic and Cenozoic (minor concentrations in Paleozoic, possibly of 'protodinoflagellate' origin)	Rare in diatoms	(Robinson et al., 1984; Volkman et al., 1993; Moldowan and Talyzina, 1998; Grice et al., 1998a)
Diatoms and Dinoflagellates	24-Norcholestane (C <sub>26</sub> )	Cretaceous to Cenozoic		(Holba et al., 1998a; Holba et al., 1998b) ; (Rampen et al., 2007 and references therein)
Centric diatoms (genus <i>Rhizosolenia</i> )	Branched Isoprenoid	Marine environments, Upper Turonian to present	C <sub>25</sub> HBI in pennate diatoms	(Nichols et al., 1988; Volkman et al., 1994; Sinninghe Damsté et al., 2004)
Pennate diatoms (phylogenetic cluster including <i>Haslea</i> , <i>Pleurosigma</i> , <i>Navicula</i> )	C <sub>25</sub> HBI alkanes	Marine environments	Centric diatoms (genus <i>Rhizosolenia</i> )	(Nichols et al., 1988; Sinninghe Damsté et al., 2004 ; Volkman et al., 1994)
Prymnesiophyte algae	C <sub>37</sub> - C <sub>39</sub> di- to tetra-unsaturated alkenones		The degree of unsaturation changes with water temperature, and this is used in the photic zone temperature proxy Uk37	(Brassell et al., 1986; Grice et al., 1998b and references therein)
<i>Botryococcus braunii</i> (Chlorophyte alga)	Botryococcanes, cyclobotryococcanes, polymethylsqualanes	Fresh to brackish water, Tertiary		(Metzger et al., 1985; Huang et al., 1988; Metzger and Largeau, 1999; Summons et al., 2002; Grice et al., 1998c)
	Macrocyclic C <sub>15</sub> -C <sub>34</sub> alkanes without carbon number preference	Fresh to brackish water, Tertiary		(Grice et al., 2001; Audino et al., 2002)
<i>Gloeocapsomorpha prisca</i> (uncertain affinity, possibly an alga)	High concentrations of <i>n</i> -C <sub>15</sub> , <i>n</i> -C <sub>17</sub> and <i>n</i> -C <sub>19</sub>	Cambrian to Devonian		(Fowler, 1992; Blokker et al., 2001)

Field	Well	Formation	Depth (m)	NDR	NCR	3/3+4+6	3/3+5
Gialo	6C1-59	Sirte	3051-54	0.36	0.43	0.33	0.32
Gialo	6C1-59	Sirte	3600-03	0.29	0.47	0.35	0.34
Gialo	6C1-59	Sirte	3087-90	0.30	0.41	0.33	0.26
Gialo	6J1-59	Sirte	3528-31	0.27	0.42	n.d.	n.d.
Gialo	6J1-59	Sirte	3542	0.31	0.40	0.30	0.35
Gialo	6R1-59	Sirte	2967	0.34	0.44	0.33	0.26
Sarir-C	KK1-65	Sirte	2670	0.27	0.41	0.33	0.26
Sarir-C	002-65	Sirte	2478-81	0.26	0.39	n.d.	n.d.
Nafoora	M1-51	Tagrifet	2882	0.37	0.45	0.33	0.24
Sarir-C	KK1-65	Tagrifet	2745	0.26	0.46	0.31	0.24
Sarir-C	KK1-65	Tagrifet	2760	0.28	0.42	n.d.	n.d.
Sarir-C	002-65	Tagrifet	2612	0.29	0.48	0.32	0.28
Amal	B-96	Rakb	2786	0.26	0.42	0.36	0.36
Amal	B-95	Rakb	2725	n.d.	n.d.	0.37	0.35
Nafoora	M1-51	Rachmat	3015	0.33	0.45	0.34	0.22
Nafoora	M1-51	Rachmat	3000	n.d.	n.d.	0.33	0.24
Sarir-C	002-65	Rachmat	2681	0.29	0.43	0.34	0.23
Sarir-C	002-65	Rachmat	2660	n.d.	n.d.	n.d.	n.d.
Nafoora	M1-51	Bahi	3045	0.25	0.33	0.34	0.27
Nafoora	M1-51	Nubian	3120	0.25	0.36	0.33	0.28
Nafoora	M1-52	Nubian	3090-93	0.26	0.41	n.d.	n.d.

NDR= 24-nordiacholestane ratios; NCR= 24-norcholestanes ratios; n.d. not determined (i.e. samples were not analysed); Triaromatic dinosteroid ratios from peaks on  $m/z$  245 mass fragmentograms = 3/3+5 and 3/3+4+6 (Moldowan et al., 1996), 3= 3, 24-dimethyl triaromatic steroid, 4= 3-methyl-24 ethylcholesteroid, 5= 4-methyl-24-ethylcholesteroid and 6= 2-methyl-24-ethylcholesteroid.

Field	Well	Formation	Depth (m)	NDR	NCR	3/3+5	3/3+4+6	Family
Amal	B-90	Amal	3090	0.13	0.25	0.35	0.33	B
Amal	B-95	Amal	3092	0.15	0.25	0.34	0.35	B
Amal	B-99	Maragh	3053	0.16	0.26	0.37	0.31	B
Amal	D-10	-	824	0.08	0.12	0.36	0.34	B
Amal	D-17	-	808	0.20	0.28	0.34	0.32	B
Amal	B-86	Amal	2996	0.22	0.26	0.38	0.34	B
Amal	B-88	Amal	3000	0.11	0.16	0.36	0.35	B
Amal	B-96	Amal	3261	0.26	0.32	0.37	0.34	B
Galio	6J6-59	Nubian	3430	0.35	0.43	n.d.	n.d.	B
Galio	6J8-59	Nubian	3290	0.31	0.4	n.d.	n.d.	B
Galio	3V3-59	Lidam	3102	0.28	0.34	0.41	0.34	B
Galio	6K1-59	Lidam	3364	0.28	0.34	0.38	0.33	B
Galio	5R1-59	Lidam	3458	0.22	0.26	n.d.	n.d.	B
Galio	3V4-59	Nubian	3121	0.25	0.33	0.46	0.36	B
Galio	6C1-59	Galio	979	0.21	0.25	0.35	0.33	B
Galio	E225-59	Jakhira	3290	0.21	0.29	0.34	0.33	B
Galio	E216-59	Augila	3182	0.18	0.24	0.34	0.33	B
Masrab	P-12	Galio	3329	0.17	0.26	0.34	0.34	B
Nafoora	Y1-51	Nubian	3036	0.23	0.27	0.38	0.35	A
Sarir-L	Z2-80	Nubian	3167	0.18	0.25	0.41	0.35	A
Amal	AA-01	Sahabi	3824	n.d.	n.d.	n.d.	n.d.	B
Amal	AA-03	Sahabi	3848	n.d.	n.d.	n.d.	n.d.	B
Faregh	5I13-59	Nubian	3006	n.d.	n.d.	n.d.	n.d.	A
Sarir-C	VV3-65	Nubian	2667	n.d.	n.d.	n.d.	n.d.	A

NDR= 24-nordiacholestane ratios; NCR= 24-norcholestanes ratios; n.d. not determined; Triaromatic dinosteroid ratios from peaks on  $m/z$  245 mass fragmentograms = 3/3+5 and 3/3+4+6 (Moldowan et al., 1996), 3= 3, 24-dimethyl triaromatic steroid, 4= 3-methyl-24 ethylcholesteroid, 5= 4-methyl-24-ethylcholesteroid and 6= 2-methyl-24-ethylcholesteroid; Family A and B, based on study of Aboglila et al. (2010a).