Oil Groups in the Continental Margin and Onshore Israel- Geochemical Characterization

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Abstract

Discriminating genetic groups of oils from various reservoirs and the related source rocks from which they were originated are fundamental factors for identification of petroleum systems and their utilization for basin evaluation and petroleum exploration (Magoon and Dow, 1994; Peters et al., 2005 and references therein). We studied 26 oil samples from various exploration wells at the eastern Mediterranean margin onshore and continental shelf of Israel and neighboring N. Sinai (Egypt). We attempted to classify them into their genetic groups (oil-oil correlations) and postulate on the characteristics of their potential source rocks (oil-source rock correlations). We have conducted detailed geochemical characterization including bulk and elemental composition, molecular proxies and biomarkers and carbon stable isotopes of the saturates and aromatics fractions. Based on these analyses we classify the oil samples into four, and possibly five, genetic groups, which cluster in accordance with the samples geographic areas. Furthermore, these analyses enable us to evaluate their thermal maturation, infer the probable characteristics of their potential source rocks, and, based on variable secondary variations in composition, asses effective post-generation secondary modification processes which affected different sampled oils.

1 Introduction

Classification of different oil and gas discovered into genetic groups and demarcating their source rocks is among the fundamental criteria for identification of petroleum (oil and gas) systems and its utilization for basin evaluation and exploration. Genetic relation between oil and gas discovered in different reservoirs and between genetic groups to particular source rocks are defined based on correlation of detailed geochemical characteristics. The molecular and isotopic (C,H,S) composition of petroleum carries complex geochemical "fingerprints" which is unique for a given sample and developed in three major stages, the first two: 1) biogenic composition of the sedimentary organic matter accumulated in its source rock, and 2) its structural and isotopic modification through the diagenetic and thermal maturation processes, both during the pre-petroleum generation; and 3) post-generation (also called "secondary modification") processes ,e.g., further maturation, migrational-geochromatography, degradation (Peters et al., 2005). Compounds more resistant to secondary processes retain the pre-generation signature ("biomarkers"), and thus are used for oil-oil and oil-source rock correlation and genetic classification. On the other hand, the less stable compounds that are affected by secondary processes, which might gradually obscure the genetic signal inherited from the pre-generation composition of the organic matter in their source rocks, are used for reconstruction of post-generation and degradation processes. Additionally, biomarkers of various genetic groups are used for assessment of their source rock environment of deposition, lithology, and redox conditions during deposition and thermal maturity (Radke, 1988; Hughes et al., 1995; Chakhmakhchev and Suzuki, 1995; Peters et al., 2005; Li et al., 2014).

The application of stable carbon isotopes ($\delta^{13}C$) of bulk oil fractions allows the distinction of marine and terrestrial organic matter input to the source rock, which in turn aids the identification of the source rock in cases where only hydrocarbons are available for analysis (Amit and Bein, 1979b; Sofer , 1984).

1.1. Petroleum geochemistry in Israel- Gained knowledge and missing links

Earlier studies nominated 6 petroleum systems onshore- and offshore-Israel: Dead Sea, Helez, Yam, Yafo, Meged and Tamar (Gardosh and Tannenbaum, 2014) and occasional gas discoveries, mainly of biogenic source (Feinstein et al., 2002; Avrahamov et al., 2015). The most studied petroleum system in Israel is the Dead Sea system. Detailed geochemical characteristics of oils, asphalts and gases with subsequent oil-oil and oil-source rock correlations demonstrate that the Maastrichtian (Latest Cretaceous) oil shales of the Ghareb formation are the source rock for the Dead Sea oils and asphalts (Amit and Bein, 1979a; Amit and Bein, 1979b; Tannenbaum, 1983; Spiro et al., 1983; Tannenbaum and Aizenshtat, 1984; Tannenbaum and Aizenshtat, 1985; Rullkötter et al., 1985; Rosenberg et al., 2017).

The geology of the Helez petroleum system in the coastal plain was investigated by several studies (Tschopp, 1956; Cohen, 1976; Amit, 1978; Amit et al., 1979; Bein and Sofer, 1987; Gilboa et al., 1990). Bein and Sofer (1987) confirmed based on oil-oil and oil-potential source rocks correlations the classification of the coastal plain oils into a genetic group and suggested the Jurassic Barnea formation to had been their source. However, they also indicate the presence of impregnation by migrating external oil with a similar composition to that of the coastal plain in the Barnea rocks. Moreover, the ability of the Barnea formation to act as a source rock is unclear either as most measured total organic carbon (TOC) of Barnea formation samples is low (~≤0.5%) and might be insufficient to classify the Barnea as a petroleum source rock (Peters and Cassa, 1994).

Regarding Yam, Yafo, Meged and Tamar petroleum systems (Gardosh and Tannenbaum, 2014), only a handful of geochemical studies were performed, and relatively little had been published (Nissenbaum, 1984; Nissenbaum et al., 1985; Feinstein et al., 2002; Needham et al., 2017; Rosenberg et al., 2017). These studies mainly focused on gaseous hydrocarbons while only one (Nissenbaum et al., 1985) has dealt in detail with characterization of the hydrocarbons and biomarkers geochemistry. As of today, no source rocks were proposed to account for the oil and gas discovered in these systems. Other results of oil shows throughout the various petroleum systems were presented during the years in different scientific conferences (Feinstein et al., 1988; Feinstein et al., 1993; Feinstein et al., 2001; Tannenbaum and Lewan, 2003; Feinstein et al., 2013a; Feinstein, 2013b) but, for various reasons, never been published as a coherent regional assessment in the scientific literature.

2 Research goals

The main and general goal of the present proposal is to develop a biomarker and isotopic database to improve our understanding and utilization of the petroleum systems in Israel.

2.1. Specific aims:

1) Perform detailed geochemical characterization in the bulk level of oil samples from onshore and offshore boreholes in Israel. These analysis will include: elemental (C, H, S) analysis of the petroleum samples as well as separation, quantification and carbon isotope analysis of different petroleum fractions (SARA).

2) Detailed molecular and biomarker analysis of the saturate and aromatic fractions in the petroleum samples.

3) Use the detailed molecular and isotopic "fingerprints” to examine possible correlation to other oil and gas shows in the SE Levant Basin as well as their possible link to source rocks in known geological settings.

4) Combine the gained knowledge together with previously published results, and propose potential source rocks and migration pathways for the studied petroleum systems in Israel.

3 Samples and Methods

3.1. Samples

We studied 26 crude oil samples from exploration wells. Figure 1 shows the location of the wells from which the samples studied were obtained whereas Table 1 provides well name, samples depth and reservoir formation from which they were produced. Some of the samples were collected during drill stem testing (DST) while others were collected during production of the wells. The samples studied were collected gradually since the 1950's. Unfortunately, due to the long time elapsed and non-optimal storage conditions, some of the samples underwent various levels of weathering. However, in all the samples studied proxies preserved enables their correlation with other oil samples and discerning their geniting grouping.

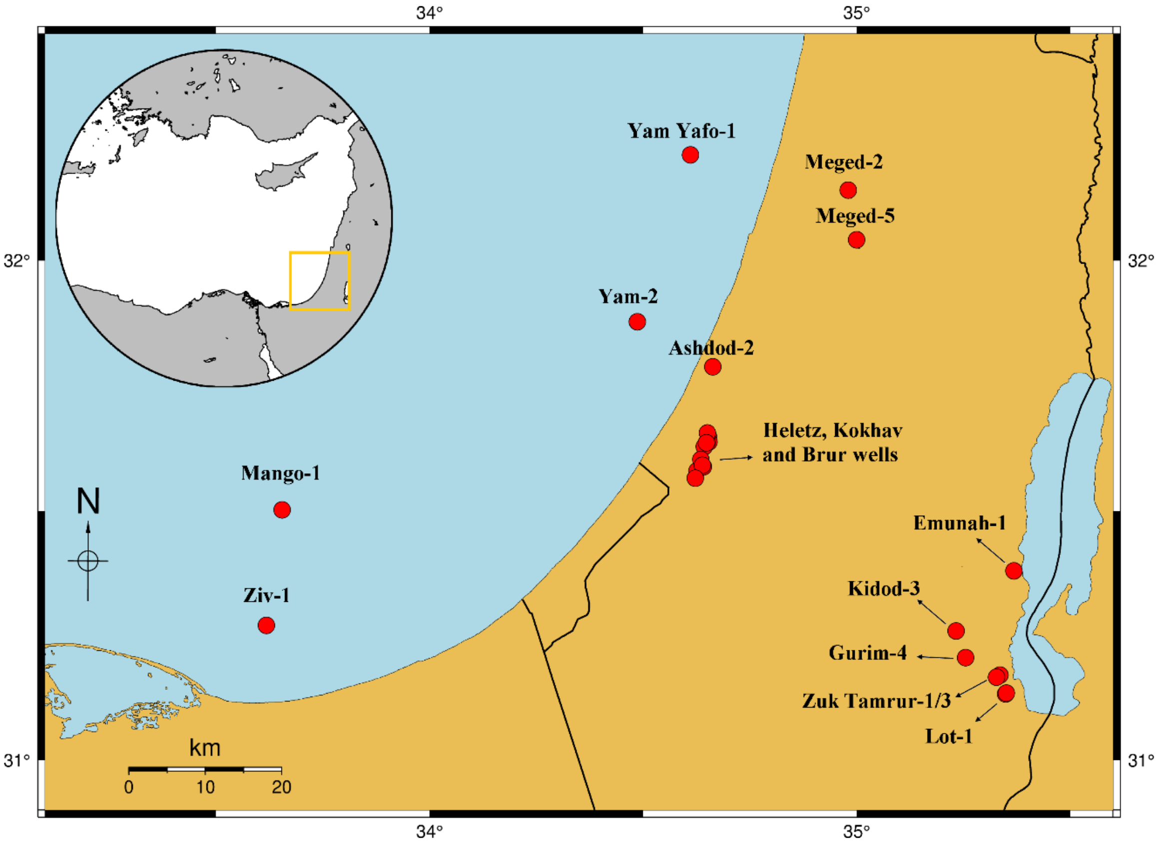


Figure 1. Location map of the various oil samples studied.

3.2.Polarity-based organic separation by liquid chromatography

The studied oils and samples were divided into four fractions according to their polarity: Saturates, Aromatics, Resins and Asphaltenes (known as "SARA"; Peters, et al., 2005; Bastow, et al., 2007). Asphaltenes precipitation was performed by mixing approximately 100 mg of sample with 50 times (by weight) *n*-pentane in a clean 20 ml vial. The vial was sealed, and its contents were ultrasonically mixed for 10 minutes. Following the mixing the vial was left overnight (at least 12 hours) to precipitate all asphaltenes. The remaining solution (maltene solution) comprising the saturate, aromatic and resin fractions was filtered and transferred for further separation by column liquid chromatography (LC). The column used was composed of pre-activated silica gel (2.5 g) and alumina (~0.2 g). The saturate fraction was eluted from the column with *n*-hexane (20mL), the aromatic fraction with *n*-hexane/dichloromethane (7:3 v/v) (20 mL), and the resins with methanol (20 mL). The solvent used for each fraction (i.e., saturate, aromatic, resins) was evaporated under gentle flow of nitrogen and the fractional weight was recorded.

3.3. Total sulfur analysis

Some of the oil samples (Lot-1, Zuk Tamrur-3, Gurim-4, Emunah-1, Meged 2, Meged-5, Yam-2) were analyzed for their total organic sulfur content. In this analysis, approximately 20mg of a given sample is placed in a porcelain crucible and combusted in a pure oxygen atmosphere at 1350°C in a LECO SC632 Sulfur-Carbon elemental analyzer (LECO Corporation, USA). Released sulfur dioxide is measured by an IR detector. Each analysis is be repeated 2-4 times to ensure reproducibility.

3.4. Gas chromatography and mass spectra analysis of molecular markers

Acyclic, *n*- and iso- alkanes (n-C_{15+}) were analyzed by Varian 3800 GC equipped with a flame ionization detector (GC-FID). A 30m·0.25mm·0.25μm DB-1 fused silica column was used. Helium was used as a carrier gas at a constant rate of 1.5 ml/min. The temperature program used is initial temperature of 60°C followed by a 6°C/min linear gradient up to 300°C with a hold at final temperature (300°C) for 30 minutes.

Oil hydrocarbons fractions (i.e., saturate and aromatic) were analyzed using an Agilent 7890A GC coupled with an Agilent 5975C mass selective detector (GC-MS). A 30m·0.25mm·0.25μm DB-5MS fused silica column was used. About 1 μL of was injected at varying split (10-100) and constant injector temperature of 320°C. Helium was used as a carrier gas at a constant rate of 1.5 ml/min. The temperature program used is: 50°C for 5 minutes, a 5°C/min linear gradient up to 320°C with a hold at final temperature (320°C) for 20 minutes. This analysis provides accurate data regarding the molecular distribution in steranes, hopanes, naphthalenes, phenanthrenes and other groups of biomarkers.

Additional analysis of biomarker was performed at the Geological survey of Canada in Calgary. The analysis was performed on Varian CP 3800 GC equipped with 1200L MS (GC-MS). A 30m·0.32mm·0.25µm DB-5MS fused silica column was used. About 1 µL of was injected at varying split (10-100) and constant injector temperature of 320°C. Helium was used as a carrier gas at a constant rate of 1.5 ml/min. The temperature program used is: 80°C for 3 minutes, a 40°C/min linear gradient up to 180°C followed by a 4°C/min linear gradient up to 320°C with a hold at final temperature (320°C) for 7 minutes.

Aromatic fractions of oil for benzo- and dibenzo-thiophenes data were also analyzed by Perkin Elmer, Clarus 580 GC that was equipped with a flame photometric detector (GC-FPD), a specific detector for sulfur compounds allowing the identification of sulfur bearing molecules. This GC used the same column and operational setup as described for the GC-MS above.

3.5. Gasoline fraction and acyclic alkanes analysis

The analysis of the gasoline fraction and the acyclic alkanes was performed at the Geological survey of Canada in Calgary. Analysis of the gasoline fraction was performed using an Agilent 7890A GC equipped with a flame ionization detector (GC-FID). A 60m·0.32mm·1.0µm DB-5MS fused silica column was used. Helium was used as a carrier gas at a constant rate of 1.5 ml/min. The temperature program used is 30°C for 10 minutes, a 1°C/min linear gradient up to 40°C with 25 minutes hold at 40°C followed by 50°C/min linear gradient up to final temperature of 200°C.

Acyclic alkanes (*n*- and *iso*-) were analyzed by Varian 3800 GC equipped with a flame ionization detector (GC-FID). A 30m·0.25mm·0.25µm DB-1 fused silica column was used. Helium was used as a carrier gas at a constant rate of 1.5 ml/min. The temperature program used is initial temperature of 60°C followed by a 6°C/min linear gradient up to 300°C with a hold at final temperature (300°C) for 30 minutes.

4 Results

4.1. Bulk oil properties and composition

The data obtained for bulk oil properties and composition in the oil samples studied are presented in Table 2. In general, it shows the lowest range API gravities from 9 to 31.4° are observed in the oil from the Dead Sea region. Mid-range API gravities of 30-40° are observed in oils from the coastal plain (Ashdod-2), Meged-2 and -5, and the oils from Mango-1 well. The highest range of API gravities of 44-47° is observed in the samples of Yam Yafo-1 and Yam-2 respectively. Sulfur content varies significantly between the different oils: the samples of the Dead Sea region display the highest S% with a range of 2.2-4.4%; the Helez-1 sample of the coastal plain display slightly lower S% of 1.6%; the samples of Meged display an S% range of 0.1-0.3% while the samples of the Mango-1 well display the lowest S% range of 0.06-0.07%. The sulfur content of the Yam samples was below the detection level.

The distribution of the Ni/V ratio is divided into two main groups: samples that had Ni/V≤1 which included the samples from the Dead Sea region (Lot-1, Zuk Tamrur-1, Gurim-4 and Kidod-3) and the samples of Mango-1 well; samples that had Ni/V>1 which include the samples of the coastal plain (Kokhav-26 a/b and Helez-1), samples of Yam (Yam-2 and Yam Yafo-1) and the sample of Ziv-1 from Sinai offshore.

The SARA analysis results demonstrate that most of the samples studied display dominance of the saturate fraction and is followed by the aromatic fraction (except for Zuk Tamrur-1 where saturate%=aromatic% and Kidod-3 where saturate%<aromatic%). The contents of the resins and asphaltenes fractions varied between the different samples irregularly with most having resin%≤asphaltene% while others (Yam Yafo-1 and the samples of Sinai offshore) displayed the opposite trend.

4.2. Molecular analyses

4.2.1. Gasoline fraction

Table 3 presents compositional ratios between compounds in the gasoline fraction range (C_5-C_8), the light-end hydrocarbons obtained in the investigated oils, and the most sensitive to secondary modification processes. The definition of the various ratios used is presented in the footnote of Table 3. In general, the various parameters exhibit differences in the distribution between the oil groups, as well as some variations also within the groups, particularly between the Dead Sea oils.

4.2.2. *n*- and *iso*-alkanes analysis

Gas chromatographic data for *n*- and iso-alkanes are summarized in Table 4 and chromatograms for representative samples for the genetic oil groups are presented in Fig. 2 A-E. The oils of Yam (Fig. 2E) and the Dead Sea region (Fig. 2A) display a smooth-unimodal distribution of their *n*-alkane envelope with peak at *n*-C_{15}. The oils of the Sinai offshore display a unimodal distribution *n*-alkanes distribution which peaks at n-C_{11} to n-C_{16} (Fig. 2D). The oils of Meged demonstrate a bimodal *n*-alkanes distribution, which peaks at n-C_{15} and n-C_{29} (Fig. 2C), with distinct dominance of low molecular weight *n*-alkanes and diminishing abundance of *n*-alkanes greater than C_{19}. The oils of the Coastal plain demonstrate irregular *n*-alkanes distribution with dominance of n-C_{15}, n-C_{18}, n-C_{26} and n-C_{28} (Fig. 2B). The varying distribution of n-alkanes between the different oils lead to variation in the carbon preference index (CPI; Peters et al., 2005): the oils of the Dead Sea region, the coastal plain and Yam have CPI<1 (0.86-0.99) while the oils of Meged and the Sinai offshore have CPI>1 (1.01-1.25). The pristane/phytane ratios (Pr/Ph) display distinctive variability between the different oil samples: oils of the Dead Sea region display Pr/Ph in the range of 0.29- 0.53 which is the lowest observed in this study. Oils of the Coastal plain display higher range of Pr/Ph of 0.72-1.09 (average 0.91). Oils of Meged display a narrower range of 0.88-0.92. Pr/Ph>1 is displayed by the oils of Yam (1.22-1.48) and by the oils of Sinai offshore which display the highest Pr/Ph of this study (1.63-2.24).

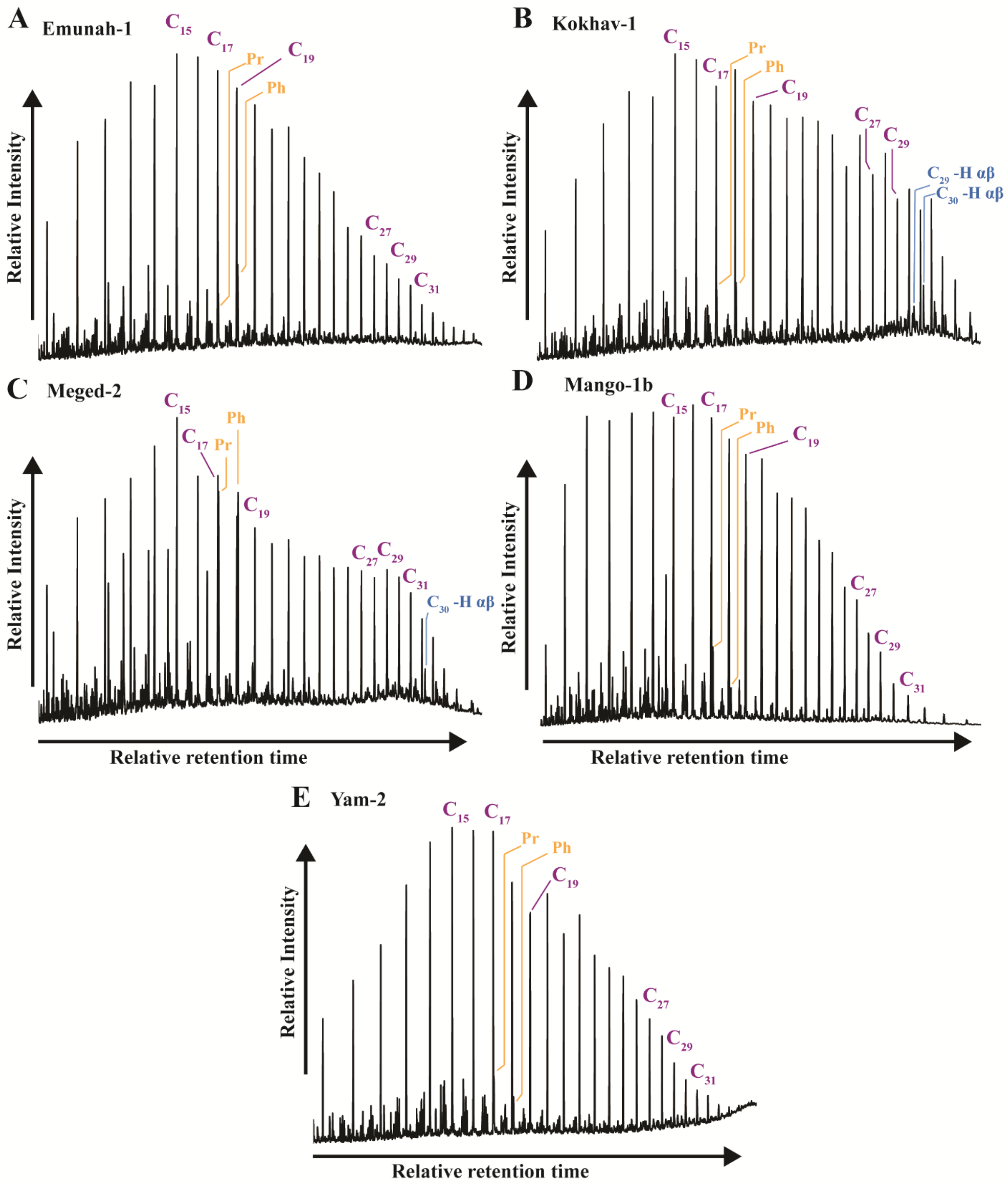


Figure 2. Total ion current (TIC) GC-MS chromatograms showing the distribution of *n*-alkanes, Pristane (Pr) and Phytane (Ph) in non-degraded oils. Emunah-1 oil of the Dead

Sea group (A), Kokhav-1 oil of the Coastal Plain group (B), Meged-2 of the Meged group (C) Mango-1b of the Sinai offshore group (D) andYam-2 of the Yam group (E).

4.2.3. Polycyclic alkanes and biomarker analysis

Selected gas chromatographic data for polycyclic alkanes and biomarkers is summarized in Tables 4 and 5. Chromatograms of hopanes and steranes for representative samples for the genetic oil groups are presented in Fig. 3 A-E.

Most studied samples display dominance of steranes relatively to hopanes as evident by the sterane/hopane ratio (Table 4). The samples of Yam display the highest sterane/hopane ratios of 1.12-1.90. The oils of the Dead Sea region and Meged display similar sterane/hopane ratios of 0.34-0.48; the samples of the coastal plain display slightly lower sterane/hopane ratios of 0.21-0.25 while the oils of the Sinai offshore display the lowest sterane/hopane ratios of 0.05-0.12.

The C_{29}/C_{30} 17α hopane ratio (C_{29}/H) of the Dead Sea region oils is >1 in all studied samples (1.17-1.49; Fig. 3A). In all other oils studied this ratio is <1: for the oils of the Sinai offshore display the lowest C_{29}/H of 0.34-0.43 (Fig.3D), the oils of the coastal plain region display slightly higher C_{29}/H ratios of 0.49-0.71 (Fig. 3B), the oils of Meged display C_{29}/H of 0.62-0.65 (Fig. 3C) while the oils of the Yam region had no identifiable hopanes (Fig. 3E).

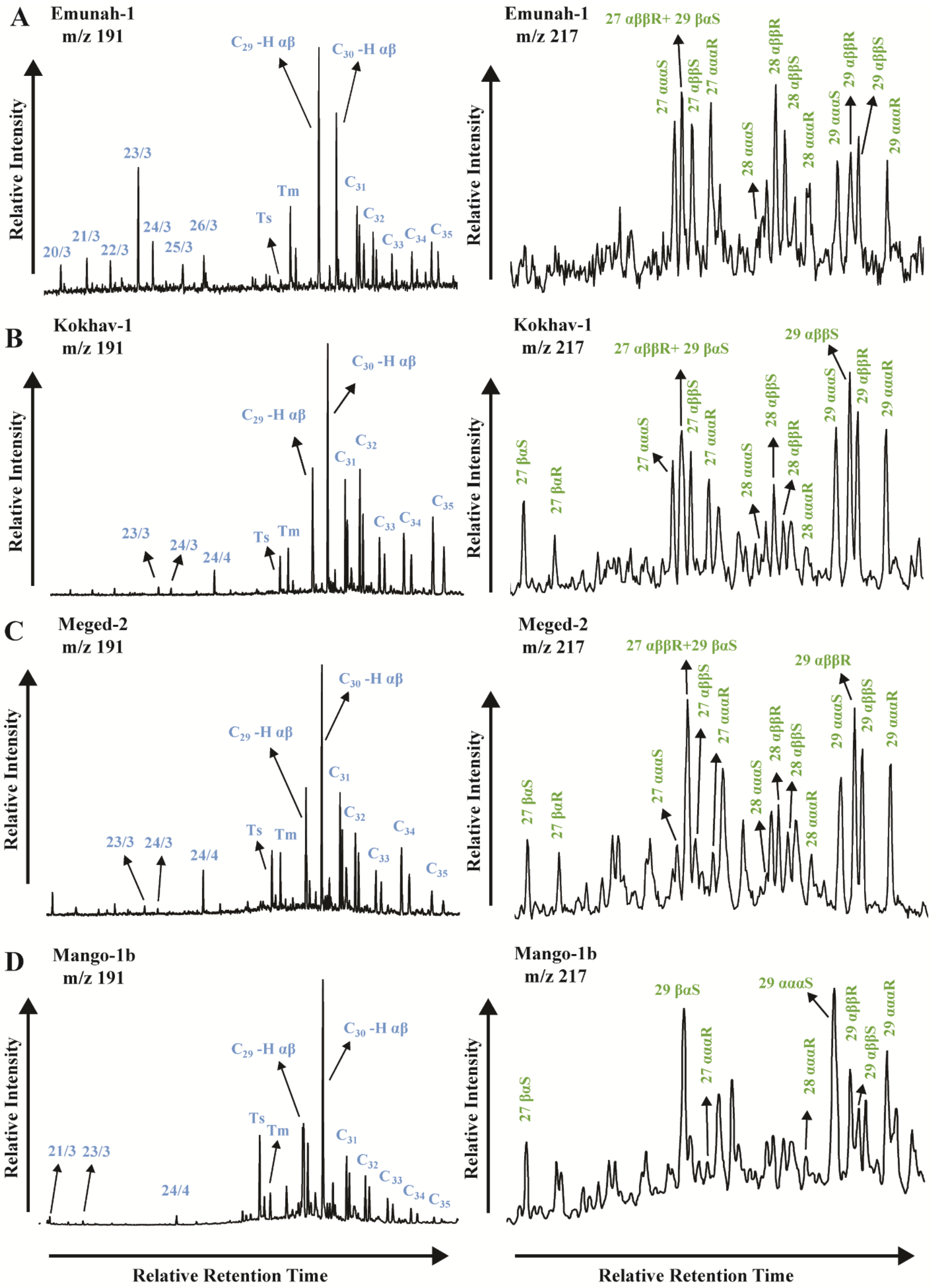
The C_{31}-C_{35} extended homohopane distributions of the oils studied is presented in Fig. 4. The oils of the Dead Sea region display gradual decrease of homohopane concentration from C_{31}-C_{34} with elevated C_{35} homohopanes ($C_{35}>C_{34}>C_{33}$). The Coastal Plain oils display a homohopane distribution with distinctive dominance of the C_{32} homohopanes

(C_{32}>C_{31}>C_{33}) and elevated C_{35} homohopanes (C_{35}>C_{34}>C_{33}). The homohopanes of the Meged oils display gradual decrease in abundance from C_{31} to C_{33} and are dominated by C_{34} homohopanes (C_{34}>C_{33}>C_{35}). The oils of the Sinai offshore display C_{31}-C_{35} homohopanes distribution with gradual decrease of concentration from C_{31} to C_{35}.

The variable abundance of C_{27} 18α- trisnorhopane (Ts) to C_{27} 17α- trisnorhopane (Tm) (Ts/(Ts+Tm)) is the highest in the samples of the Sinai offshore (0.65-0.77) and in sample Zuk Tamrur-1 (0.73) of the Dead Sea region. The oils of the coastal plain display Ts/(Ts+Tm) of 0.41-0.51, a range that is similar to that of the Meged oils (0.49-0.55). All samples of the Dead Sea region, excluding Zuk Tamrur-1, display the lowest Ts/(Ts+Tm) values of 0.09-0.24.

The presence of abundant tricyclic hopanes is distinctive in the oils of the Dead Sea region (Fig. 3A) while other oil groups show little to no tricyclic hopanes (Fig. 3B-E). In contrary, the presence of tetracyclic hopanes (in particular- C_{24} tetracyclic hopane) is minor in the oils of the Dead Sea region while being more abundant in the oils of the coastal plain (Fig. 3B), Meged (Fig. 3C) and Sinai offshore (Fig.3D) oils.

The sterane fraction of the oils display varying trends of C_{28}-C_{29} steranes distribution: The oils of the Dead Sea region display dominance of C_{28} steranes which are followed by C_{27} and C_{29} steranes respectively. The oils of the Coastal plain and Sinai offshore exhibit predominance of C_{29} steranes which are followed by the C_{27} and C_{28} steranes respectively. The steranes of the Meged oils show a V shape distribution where C_{27} and C_{29} steranes are in similar abundance. The Yam oils display sterane distribution which is dominated by C_{29} steranes and lacks any detectable C_{28} and C_{27} steranes.


A
Emunah-1
m/z 191
C29 -H αβ
C30 -H αβ
23/3
Tm
C31
Ts
C32
24/3
26/3
21/3
25/3
C33
C34
C35
20/3
22/3
Relative Intensity
Emunah-1
m/z 217
27 αββR+ 29 βαS
27 αααS
27 αββS
27 αααR
28 αααS
28 αββR
28 αββS
28 αααR
29 αααS
29 αββR
29 αββS
29 αααR
Relative Intensity
B
Kokhav-1
m/z 191
C30 -H αβ
C29 -H αβ
C32
C31
23/3
24/3
24/4
Ts
Tm
C33
C34
C35
Relative Intensity
Kokhav-1
m/z 217
27 αββR+ 29 βαS
29 αββS
27 βαS
27 βαR
27 αααS
27 αββS
27 αααR
28 αααS
28 αββS
28 αββR
28 αααR
29 αααS
29 αββR
29 αααR
Relative Intensity
C
Meged-2
m/z 191
C30 -H αβ
C29 -H αβ
C31
C32
C34
Ts
Tm
23/3
24/3
24/4
C33
C35
Relative Intensity
Meged-2
m/z 217
27 αββR+29 βαS
29 αββR
27 βaS
27 βαR
27 αααS
27 αββS
27 αααR
28 αααS
28 αββR
28 αββS
28 αααR
29 αααS
29 αββS
29 αααR
Relative Intensity
D
Mango-1b
m/z 191
C30 -H αβ
C29 -H αβ
Ts
Tm
C31
C32
C33
C34
C35
21/3
23/3
24/4
Relative Intensity
Relative Retention Time
Mango-1b
m/z 217
29 βαS
29 αααS
27 βαS
27 αααR
28 αααR
29 αββR
29 αββS
29 αααR
Relative Intensity
Relative Retention Time

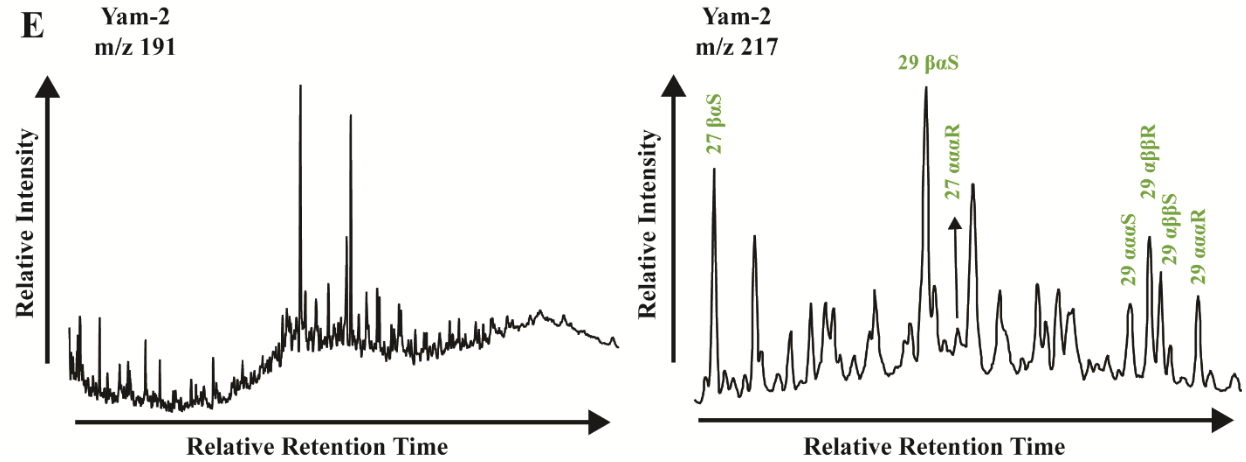


Figure 3. Partial GC-MS (SIM) chromatograms showing hopane (m/z 191) and sterane distribution (m/z 217) in oil samples of Emunah-1 oil of the Dead Sea group (A), Kokhav-1 oil of the Coastal Plain group (B), Meged-2 of the Meged group (C), Mango-1b of the Sinai offshore group (D) and Yam-2 of the Yam group (E)

4.2.4. Aromatic compounds

The aromatic fractions of oil samples studied were analyzed for their dibenzothiophene/phenanthrene ratio (DBT/Phen) and methyl-phenanthrenes and methyl-dibenzothiophenes distributions (Tables 4 and 5). The studied samples demonstrated DBT/Phen ratios in the range of 0.07 to 1.26. Analysis of methyl-phenanthrenes distribution by using the MPI-1 index (Radke, 1988) shows MPI range of 0.45 to 1.13 while the analysis of methyl-dibenzothiophenes distribution by using the MDR index (Radke, 1988) shows MDR range of 1.2 to 23.5.

4.2.5. Carbon isotopes analysis ($\delta^{13}C$) of saturate and aromatic fractions

Analysis of carbon stable isotopes ($\delta^{13}C$) in the saturate and aromatic fractions was performed by previous studies and reports (Tannenbaum, 1983; Bein and Sofer, 1987; Geomark research inc., 1994 and 2004; Geochem, 1999) and is compiled in table 6.

5 Discussion

5.1. Oil-oil correlations

Oil-oil correlations using bulk oil properties, and molecular and stable carbon isotopes parameters in oil samples from different wells drilled in Israel and offshore north Sinai (Egypt) their classification into four (or possibly five) genetic groups. In general, the clustering into genetic groups is concordant with the geographic distribution of the wells from which the samples were obtained (Fig. 1).

The oils of the Dead Sea region are distinctively different from the other oils by almost all the parameters used here for oil-oil correlation. These oils are characterized by high sulfur content of 2.2-4.4% unlike any of the other oils studied (Table 2). Their *n*-alkane envelope is the only one to displaying smooth-unimodal distribution (Fig.2A), and their Pr/Ph ratios range, 0.29 - 0.53, is the lowest observed in this study. Their distinct biomarker ratios include the highest concentration of tricyclic terpanes with the lowest C_{24} tetracyclic /C_{23} tricyclic terpanes (C_{24} Tet/C_{23} Tri), ratios, C_{29}/C_{30} hopane>1, and homohopanes distribution with $C_{35}>C_{34}$ (Table 4; Fig.3A, Fig. 4). Altogether, these unique geochemical properties suggest the Dead Sea group oils are genetically related thereby supporting similar conclusion of previous studies (Amit and Bein, 1979a; Nissenbaum and Goldberg, 1980; Spiro et al., 1983; Tannenbaum and Aizenshtat, 1984; Rullkötter et al., 1985; Aizenshtat and Amrani, 2004).

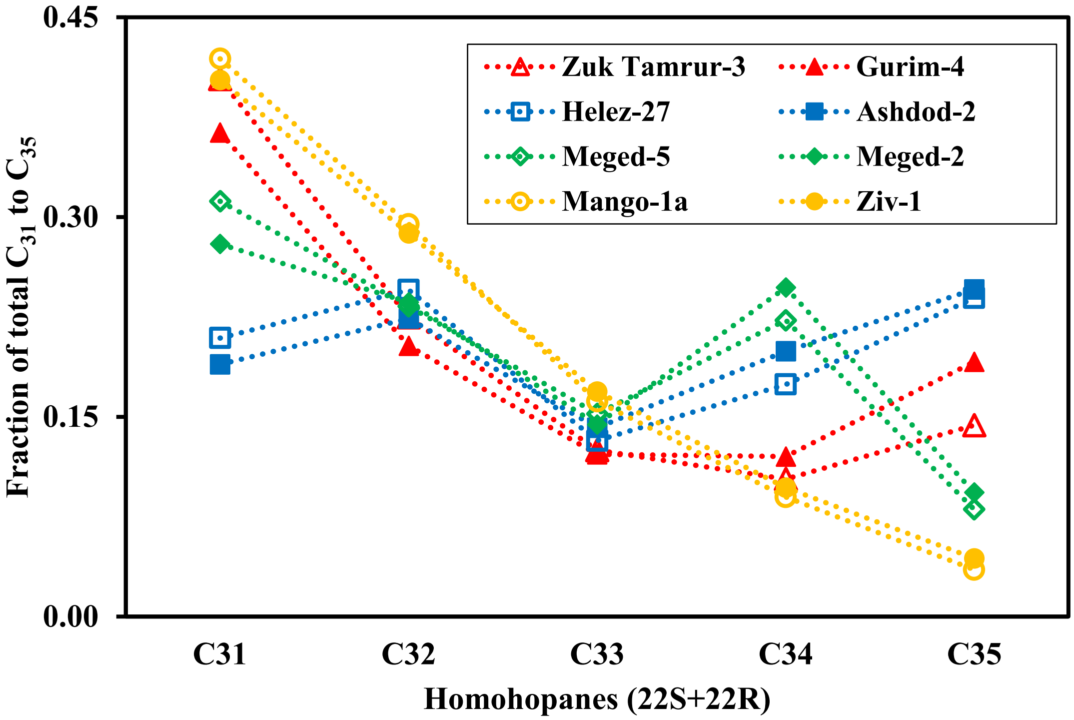


Figure 4. Homohopane distributions in selected oils. The different oil groups are represented by the following-colored dashed lines: Meged in green, Dead Sea in red, Coastal plain in blue, Sinai offshore in yellow.

The oils of the Coastal plain have CPI ratios that are similar to those of the Dead Sea oils, yet the former have elevated Pr/Ph ratios and their *n*-alkanes display an irregular distribution with dominance of *n*-C_{15}, *n*-C_{18}, *n*-C_{26} and *n*-C_{28} (Fig. 2B) which is different from that of the Dead Sea oils. The oils of the Coastal plain group display a unique C_{31}-C_{35} homohopanes distribution of $C_{31}<C_{32}>C_{33}$ and $C_{33}<C_{34}<C_{35}$ (Fig. 4), the elevated C_{32} homohopane is a unique feature of the coastal plain oils. The C_{24} Tet/C_{23} Tri-terpanes ratio of the Coastal plain group is >1, essentially different than in the oils of the Dead Sea group

(Fig. 3B). The steranes of the Coastal plain oils exhibit predominance of C_{29} steranes with low C_{28} steranes (Fig. 3B) which is the opposite distribution to that of the Dead Sea oils (Fig. 3A). Another distinctive property of the Coastal plain oils is their sulfur content of 1.5-3% (Tschopp, 1956; Carrales and Martin, 1975; Cohen, 1976; Gavrieli et al., 1994). Such elevated sulfur content is observed only in the oils of the Dead Sea group yet these have different hopane and sterane distributions. All in all, these observations suggest that the oils of the Coastal plain group are genetically related, further supporting previous studies of the Coastal plain oils (Bein and Sofer, 1987; Gilboa et al., 1990; Gardosh and Tannenbaum, 2014).

The Meged oils are characterized by *n*-alkane envelope with odd-over-even predominance in the *n*-C_{15}-*n*-C_{19} range which is not shared by any other oil. In addition, the Meged oils have high content of phytane and display Ph>*n*-C_{18} (Fig. 2C). Another feature exclusive to the Meged oils is their C_{31}-C_{35} homohopanes distribution which exhibits $C_{33}<C_{34}>C_{35}$ (Fig. 4). Such homohopanes distribution is rarely encountered (Peters et al., 2005) and is therefore a useful correlation parameter for oil-oil and oil-source rock correlations. Moreover, the C_{24} Tet/ C_{23} Tri terpanes ratio values of the group are significantly higher than those of the Dead Sea and Coastal plain groups (Table 4). The steranes of the Meged oils show a V shape distribution which is unlike the oils of the Dead Sea basin, yet it has some similarity to the sterane distribution of the Coastal plain oils (Fig. 3). Since the oils of Meged and coastal plain differ by many other parameters (e.g., *n*-alkanes envelope, homohopanes envelope, Pr/Ph ratio, S%, $C_{35}S/C_{34}S$ hopane ratio) we suggest the oils of Meged form genetically related group and are distinct from the oils of the Dead Sea and coastal plain groups.

The oils of Sinai offshore display the highest CPI and Pr/Ph ratios out of all studied samples (Table 4; Fig. 2D and Fig. 5). Among the distinctive molecular and biomarker features of the Sinai offshore oils are their high Ts/(Ts+Tm) ratio, high C_{24} Tet/C_{23} Tri terpanes ratio (although the C_{24} Tet is also very low, Fig. 3D), lowest C_{29}/C_{30} hopanes ratio (Table 4; Fig.3D) and the lowest sterane/terpane ratio of all studied samples (Fig. 5). High Ts/(Ts+Tm) is also demonstrated by the Zuk Tamrur-1 oil from the Dead Sea region (unlike all other oils from there - Table 4), and moderately high also in the Meged oils (0.49-0.55). On the contrary, the oils of the Dead Sea, Meged, and Sinai offshore exhibit distinctively different extended homohopane distribution and Ts/(Ts+Tm) (Fig. 4) which hints that the Sinai offshore oils are genetically related to each other while being distinctively different from oils of the other groups. The Sinai offshore oils have high API° of 36-38, low sulfur content of 0.6% and Ni/V ratio of 1.7 (Table 2). These bulk properties are similar to those of the Meged oils (API° of 37-40, 0.1-0.3% sulfur, Ni/V of 2-6) yet different from all other studied oils. The oils of Sinai offshore share no similarities with the oils of the Coastal Plain. Overall, based on the features described above we suggest the oils of Sinai offshore are genetically related.

The two samples of the offshore Israel (Yam-2 and Yam Yafo-1) have *n*-alkanes envelope with even-over-odd predominance in the range of C_{18}-C_{23}. The two oils display Pr/Ph values of 1.22-1.48 which are lower than the Sinai offshore oils yet higher than all other samples in this study. The Yam oils are the only oil group to be dominated by steranes (sterane/hopanes>1; Table 4, Fig. 5) and display sterane distribution which is dominated by C_{29} steranes and lacks any detectable C_{28} and C_{27} steranes. In addition, the two oils display the highest content of diasteranes relative to steranes (Fig. 3E). The hopane compounds in the Yam oils underwent significant modifications, probably due to the high thermal maturation and therefore were not used for defining weather they are genetically related and postulation on their characteristic potential source rock. Yet, the similarity of the acyclic alkanes, steranes and hopanes spectrum along with in several other parameters such as Pr/Ph ratio >1, sterane/hopane ratio >1, and the high maturity level in both Yam 2 and Yam Yafo 1 oil samples (Table 4 and 5) differentiate them from all other oils in this study and distinctly attest for the probability that they are related genetically. Previous study by Rosenberg et al., (2017) demonstrated compound-specific $\delta^{34}S$ of benzo- and dibenzo-thiophenes in the Yam-2 oils significantly different from those of the Dead Sea basin oils, which further suggest that they are not genetically related.

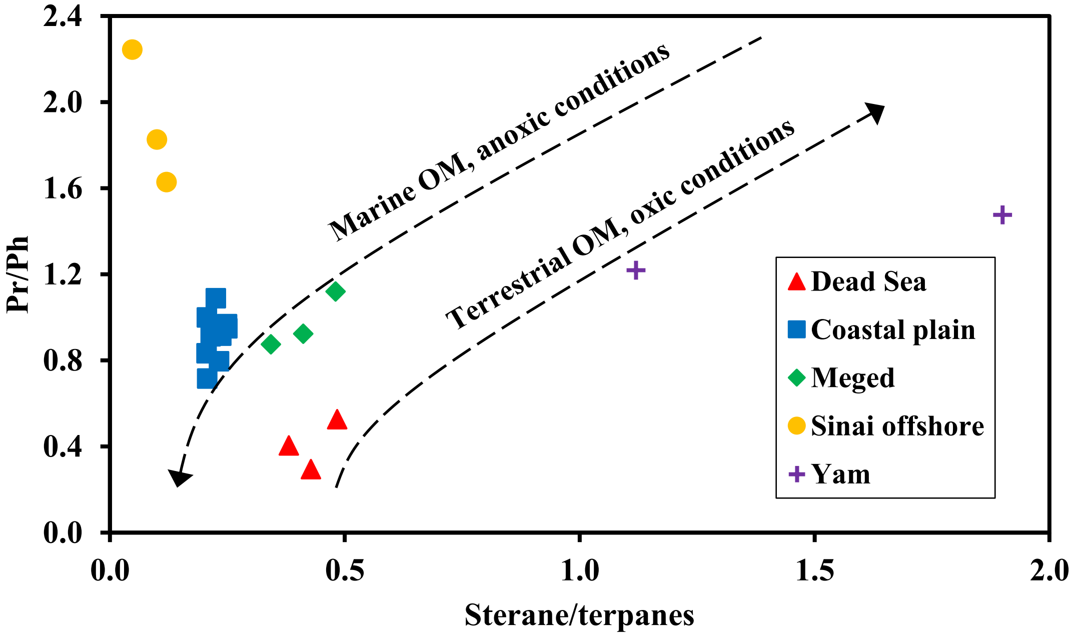


Figure 5. The ratio of steranes/terpanes vs pristane/phytane used to distinguish distribution of oil samples studied into separate clusters.

The $\delta^{13}C$ values measured in the saturate and aromatic fractions of the oils studied plotted onto the Sofer (1984) diagram (Fig. 6) further supports groups classification based on biomarkers discussed above. The Yam and the Dead Sea oils cluster into separate genetic groups as shown by the specific compound $\delta^{34}S$ by Rosenberg et al. (2017). Furthermore, the $\delta^{13}C$ data in Figure 6 demonstrate that the oils of Sinai offshore share the heaviest $\delta^{13}C$ of the aromatic fraction (~ -25‰) and the Dead Sea oils the lightest (< -28‰), which distinct them from all other samples studied and further supports our claim of them being genetically separate groups. The $\delta^{13}C$ values of the Yam, coastal plain and Meged oils plot in the marine-terrestrial mixed organic source strip, the Yam oils at a distinctively heavier $\delta^{13}C$ level whereas the Meged oils $\delta^{13}C$ cluster at the lighter part with slight overlap with the somewhat heavier coastal plain oils $\delta^{13}C$ (Fig. 6).

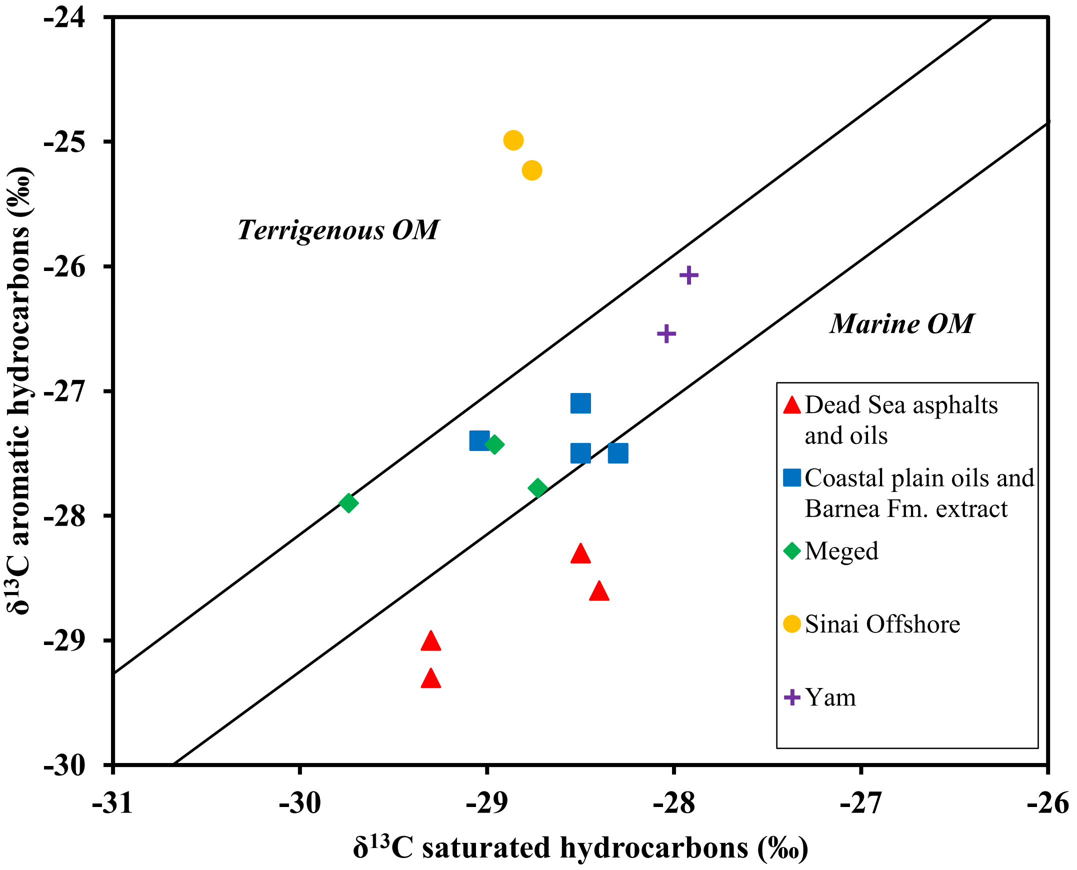


Figure 6. $\delta^{13}C$ values of saturated and aromatic hydrocarbon fractions of studied oils samples and additional oil samples from the literature. The border lines between marine (non-waxy) and terrigenous (waxy) organic matter are from Sofer (1984). Data sources include Tannenbaum (1983); Bein and Sofer (1987); Geomark research inc. (1994) and (2004); GeoChem, (1999).

5.2. Secondary alteration of oils

Upon expulsion from its source rock any oil sample is vulnerable to secondary alteration processes such as water washing, biodegradation, maturation and geochromatography (Peters et al., 2005). A trend of decreasing sulfur content with increasing API gravity is observed in many petroleum systems and related oil groups, often in relation to increase in thermal maturity whereas degradation processes can result in a decline of API gravity and increase in sulfur concentration (Orr, 1986; Baskin and Peters, 1992; Baskin and Jones, 1993; Hill et al., 2007; Lillis and Magoon, 2007). These trends reflect the thermal maturity experienced by the oil as early oils tend to be heavy, viscous, asphaltic and sulfur rich while mature oils are light and have much less sulfur as the sulfur rich fractions (asphaltenes and resins) crack preferentially during thermal maturation. In contrary, if a given oil sample has experienced degradation by either water-washing or biological processes its API gravity is expected to decrease while its sulfur content is expected to increase as the saturate and aromatic fraction, which are the lightest and typically contains the least sulfur, are prone to degradation. Oil gravity and sulfur concentration data show linear trend of decreasing sulfur content with increasing API gravity for the oils of the Dead Sea group (Table 2, Fig. 7). The relatively low API gravity with high sulfur contents of some of the oils may be interpreted as low thermal maturity, yet these have low contents of saturate and aromatic fractions, while the high gravity oils exhibit high content of these fractions (Table 2). Moreover, Dead Sea oil samples with low API gravity and high sulfur contents show considerable depletion of *n*-alkanes, particularly in the gasoline fraction range (Table 3) and light-end of the C_{10+} TIC chromatograms relative to those with high API and low S% (cf. Gurim 4 and (degraded) vs. Emuna 1 (not degraded) in (Tables 3 and 4, and Fig. 11). This trend (and other indications) hints that some of the Dead Sea oils experienced water washing and/or biodegradation as the saturate and aromatic fractions, particularly at the lighter end, contains the labile compounds for these weathering processes. While the oils of the Dead Sea area exhibit a large variation of both sulfur content and API gravity, the oils of the coastal plain are all concentrate around ~ 28° API gravity and sulfur content of 1.8% with relatively little variations. The clustering of the coastal plain oils indicates they experienced little degradation compared to the Dead Sea samples. The oils of the Meged, Sinai Offshore and Yam groups have very low amounts of sulfur (<0.3%) and high API gravities (between ~ 35°-47°), which suggest these oils have derived from highly mature source rocks and did not experience significant secondary alteration (non-degraded oils), as is also indicated by their rich saturate and aromatic fractions and light-end *n*-alkane and mono-aromatic compounds content (respectively, Tables 2 and 3).

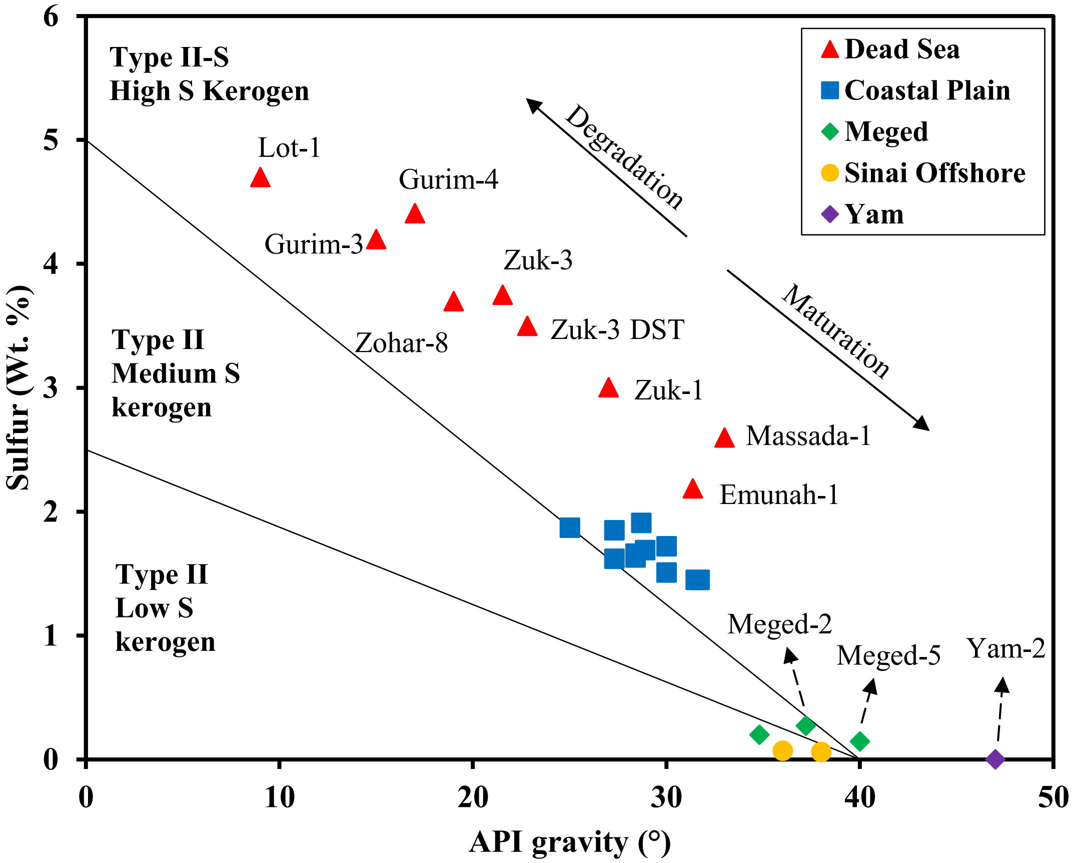


Figure 7. Plot of API gravity (°) versus sulfur content (%) of the oils studied. Kerogen type II and type II-S classification field are from Orr (2001). Data sources include Tschopp (1956), Nissenbaum and Goldberg (1980), Tannenbaum (1983), May and Goldberg (1984), National institute for Petroleum and Energy Research (1995), Gardosh and Tannenbaum (2014), Geomark research inc. (1994); GeoChem, (1999); Geomark research inc. (2004)

The susceptibility to alteration of different compound classes within the oils (i.e. *n*-alkanes, iso alkanes polycyclic alkanes, aromatic compounds etc.) to different alteration mechanisms varies so that variable compound groups and different compounds within the class might be differentially degraded depending on their resistance to the effective degradation mechanism(s) (Peters et al., 2005). In most cases, except for thermal maturation, resilience to weathering increases with compounds weight and structural complexity (Larter et al., 2012).

Compounds of the light hydrocarbons in the gasoline range fraction (C_5 – C_8 hydrocarbons, Table 3) are among the most susceptible to post-generation degradation processes, mainly water washing and microbial degradation (Peters et al., 2005). Water washing effects can be discern by analyzing ratios such as methylcyclohexane/toluene to 3-methylpentane/benzene ratio (parameters T and S, respectively; Fig. 8) since light mono-aromatic compounds are more water-soluble than normal- and iso-alkanes with the same carbon number. On the other hand, aromatic and iso-alkane hydrocarbons are more resistant to microbial biodegradation than normal alkanes and cycloalkanes (Obermajer et al., 2002). The relation between parameters T and S in Figure 8 indicate variable effects of water washing on the samples of the Dead Sea group where all samples, except for Emunah-1, display some degree of benzene and toluene depletion. The highest degree of water-washing was experienced by the Gurim-4 oil which experienced significant loss of both toluene and benzene (Table 3, Fig. 8), while the sample of Zuk Tamrur-3 experienced significant benzene loss with minor toluene loss. This observation can be attributed to the higher solubility of benzene, relatively to toluene, in brine (Keeley et al., 1988). However, the oils of Zuk Tamrur-1 and Kidod-3 appear to have experienced depletion of toluene with almost no depletion of benzene which is peculiar since benzene has higher solubility in brine than toluene. This observation may indicate variable degrees of benzene and toluene content among the initial, non-degraded, oils of the Dead Sea group. Water washing was also experienced by the Mango-1a sample which experienced significant toluene depletion with minor benzene depletion when compared to the slightly water-washed Mango-1b and the pristine Ziv-1. This observation likely indicates the non-degraded oils of the Sinai group had small benzene content in origin. Oils of the Coastal plain group show little signs of water washing while the oils of the Yam and Meged groups show no indication of water washing.

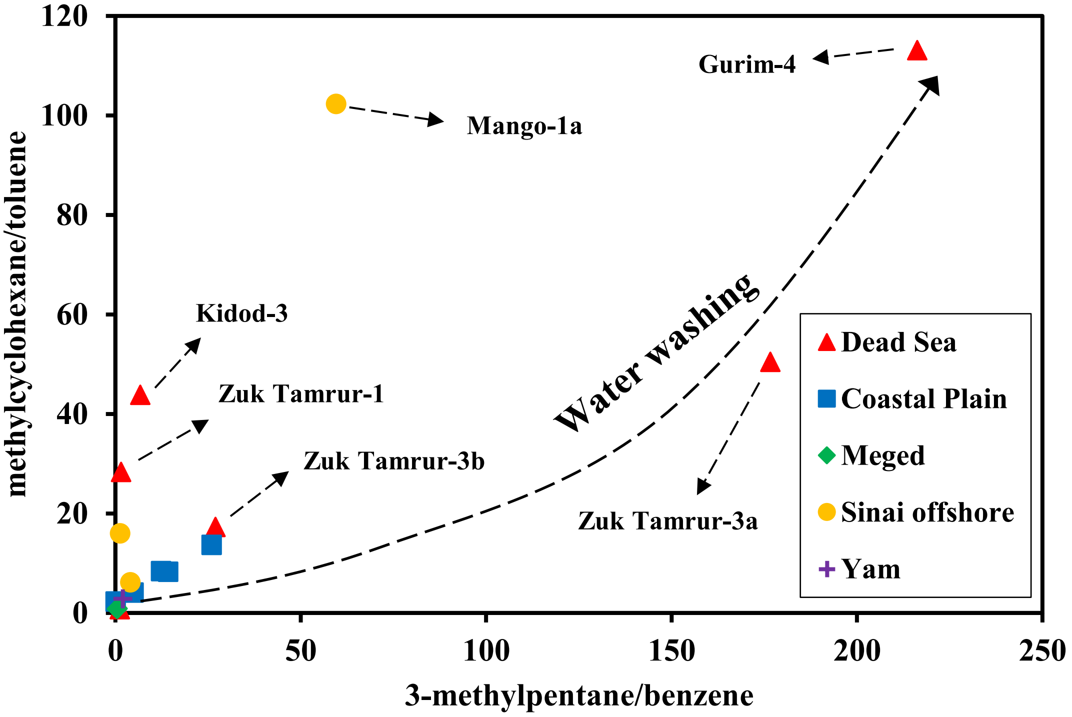


Figure 8. Light hydrocarbon parameters 3-methylpentane/benzene versus methylcyclohexane/toluene illustrating the effects of water washing.

Further investigation of post-generation alterations is possible by examining the ratio of *n*-heptane/methylcyclohexane versus toluene/*n*-heptane (Thompson, 1987) as demonstrated in Fig.9. Among the potential post-generation processes is evaporative-fractionation, a process where saturated gas phase is separated from the main oil as a result of pressure reduction in the reservoir or by introduction of new gas to the reservoir, and typically leads to removal of aliphatic compounds from the oil to the gas phase (Thompson, 1987). The presence of evaporative fractionation is marked by an increase of the toluene/*n*-heptane (Fig. 9A). It appears that all oil groups were affected, to some extent, by evaporative fractionation. The highest extent of evaporative fractionation was experienced by the Meged samples. Such observation is expected as the Meged oils are produced with wet gas (Geochem, 1999) from a reservoir at ~150°C. Additional group of oils which are produced from reservoirs with elevated temperatures are the Yam oils (Feinstein et al., 1993) which were suggested to have experienced some evaporative fractionation by Feinstein et al., (2002). Our results demonstrate that only Yam-2 oil sample experienced evaporative fractionation while the Yam Yafo-1 oil sample is likely pristine. Interestingly, the sample of Kokhav-29 seems to have experienced significant evaporative fractionation while the reservoirs of the Kokhav field are at current temperature of ~65°C (Gilboa et al., 1990), a temperature far lower than expected for evaporative fractionation, and are unlikely to have been subjected to considerably elevated reservoir temperatures in the past (Calvo et al., 2011). Moreover, the fact that only one sample (Kokhav-29) from the genetic group exhibits signs of evaporative fractionation suggests the depletion of toluene relative to *n*-C_7 is the result of a different mechanism of degradation. The samples of the Sinai and Dead Sea groups have experienced only minor evaporative fractionation.

The relation of *n*-heptane/methylcyclohexane versus toluene/*n*-heptane can also be used for identification of, respectively, biodegradation (Fig. 9D) and water-washing (Fig. 9C). According to the relation in Fig. 9, the Dead Sea group samples which experienced the most water washing are Zuk Tamrur-1 and Zuk Tamrur-3a while the samples of Gurim-4 and Kidod-3 show no signs of water-washing. Such observation is in contradiction of to the relation presented in figures 7 and 8. Therefore, we suggest that the depletion of toluene in the Zuk Tamrur samples is a genetic property rather than a sign of water-washing. In the Yam and Sinai offshore groups, the samples of Yam Yafo-1 and Mango-1a have likely experienced some water-washing. Assessment of biodegradation (Fig. 9D) is difficult as most studied oils are clustered and no clear trend that may be attributed to biodegradation is observed.

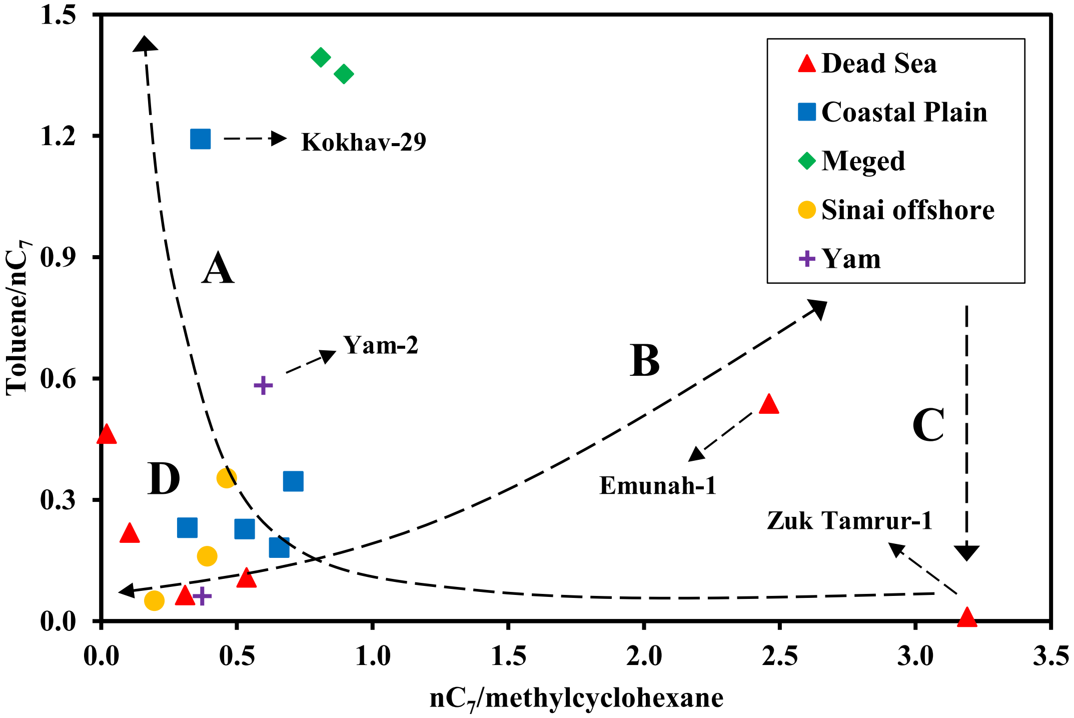


Figure 9. Light hydrocarbon parameters *n*-heptane/methylcyclohexane versus toluene/*n*-heptane illustrating changes in oil compositions as a result of evaporative fractionation (A), maturation (B), water washing (C) and biodegradation (D) (after Thompson, 1987).

The resistance of aromatic and iso-alkane hydrocarbons to biodegradation, relatively to normal alkanes and cycloalkanes could be used to estimate the degree of biodegradation experienced by the different oils. The relation of hexane/methylcyclopentane ratio (parameter Q, Table 3) to the paraffin index II (heptane value; "PI-2", Table 3; Thompson, 1983) is used to differentiate the degree of biodegradation experienced by the different oil samples (Fig. 10). As expected, the largest variability of biodegradation is demonstrated by the oils of the Dead Sea group where the samples of Zuk Tamrur-1 and Emunah-1 experienced the least, if any, biodegradation. On the other hand, the samples of Kidod-3 and Gurim-4 are clearly the most biodegraded in this group. Slight biodegradation may have affected the samples of Yam Yafo-1 and Kokhav-6. The sample of Sinai offshore show that sample Mango-1a may have experienced some biodegradation but more interestingly, the oil of Ziv-1 seems to be the least biodegraded and also does not fall on the general line expected for biodegradation, therefore hinting it may have experienced different post-generation processes when compared to the Mango-1 samples.

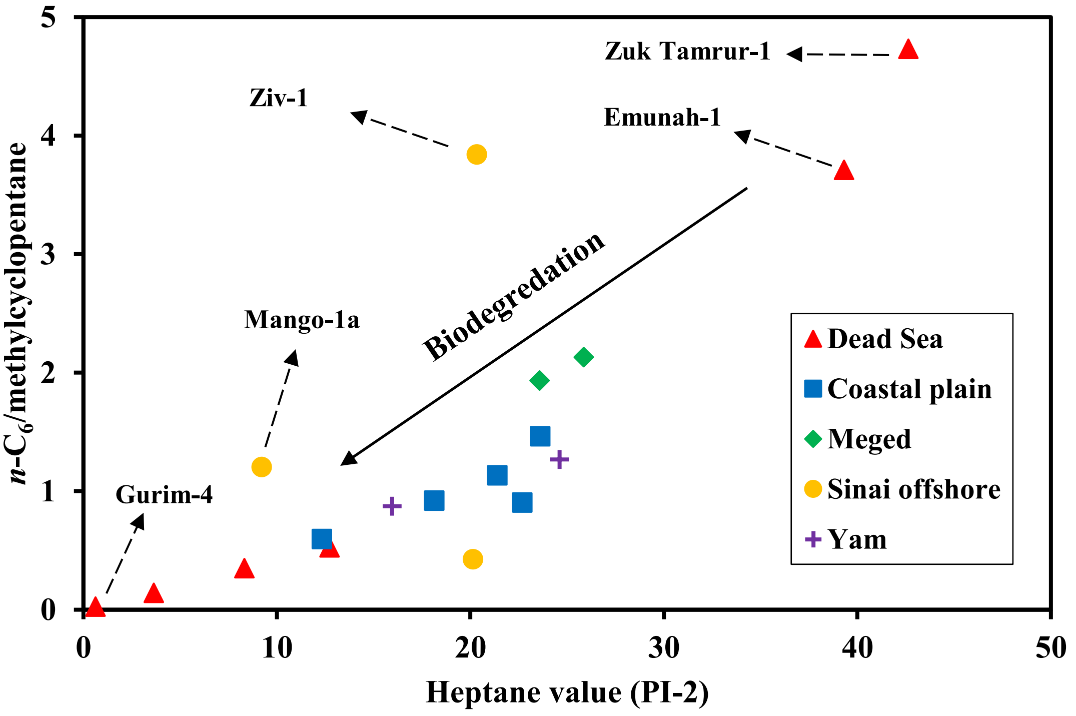


Figure 10. Light hydrocarbon parameters *n*-hexane/methylcyclopentane versus Heptane value (PI-2) (Thompson, 1983) illustrating the extent of biodegradation experienced by the different oil samples studied.

Analysis of the C_{10}+ alkanes envelope on the total ion count (TIC) of oils (Fig. 11) provides more insights to oil alteration in the Dead Sea and Coastal Plain groups. The *n*-alkanes envelope of the Dead Sea group samples reveals several degrees of biodegradation: The sample of Zuk Tamrur-3 which showed high degree of water washing, demonstrates removal of short *n*-alkanes up to *n*-C_{16} (Fig. 11A). The sample of Gurim-4 which also experienced significant water washing demonstrates much greater *n*-alkanes removal which affected up to *n*-C_{21} (Fig. 11B), thus supporting the extent of biodegradation suggested by the parameters of the gasoline fraction (Fig. 10). Moreover, a bulge of the baseline where unresolved complex mixture (UCM hump), made of non-amenable to GC and biodegradation resistant compounds, is observed in both Zuk Tamrur-3 and Gurim-4, the extent of UCM increases with increasing degree of biodegradation (Fig. 11A-B).

The n-alkanes envelope of the coastal plain samples reveals low degree of biodegradation: the Kokhav-6 (Fig.11C) and Kokhav-14 (Fig. 11D) samples both show partial removal of *n*-alkanes shorter than *n*-C_{14}. The alteration of *n*-alkanes in the Kokhav oils did not affect heavier *n*-alkanes as evident from the CPI ratio values which are similar for both degraded and non-degraded samples of the group (Table 4). Further analysis and comparison of saturate fraction biomarkers that are more resistant to biodegradation than *n*-alkanes, such as iso-alkanes, steranes and hopanes, did not reveal any distinct signs of degradation.

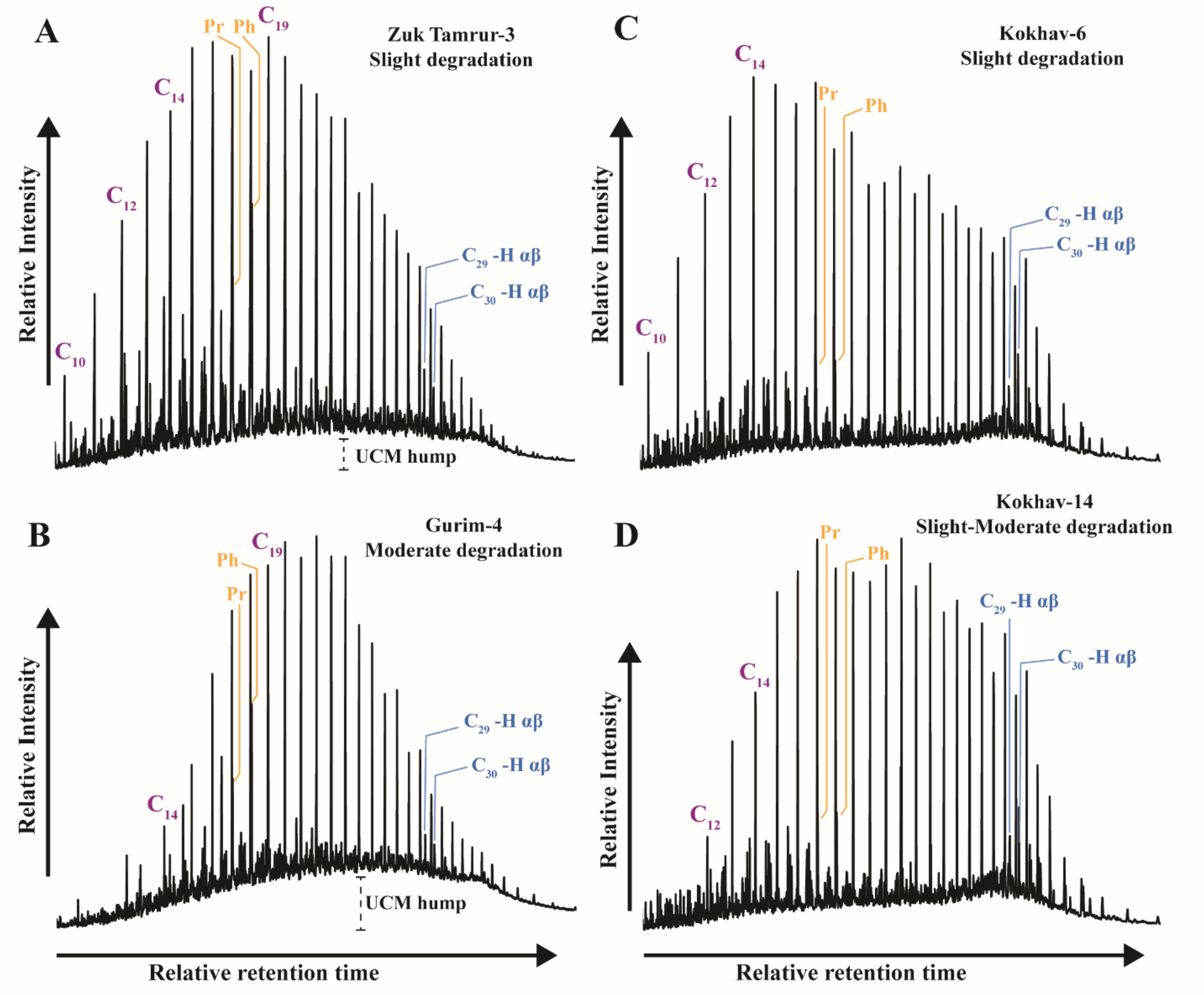


Figure 11. Total ion current (TIC) GC-MS chromatograms of two different oil groups: The Dead Sea basin (A-B) and Coastal Plain Kokhav field (C-D). Note the difference in the light ends (left) between A and B; C and D, illustrating an increasing degree of degradation.

Analysis of the aromatic fraction in the studied oils revealed further signs of post-generation alteration. Water washing has significant effect on the dibenzothiophene/phenanthrene (DBT/Phen) ratio as DBT is more water soluble than Phen (Kuo, 1994; Huang and Pearson, 1999). Indeed, the sample of Gurim-4 demonstrates low ratio of DBT/Phen relatively to non-degraded samples of the group such as Emunah-1 (Table 4, Fig. 14). The degraded oils of the Coastal plain group also show relatively low values of DBT/Phen, therefore suggesting they were affected by water-washing but were mostly altered by biodegradation.

The impact of water-washing and biodegradation observed in the analyzed samples are in agreement with previous studies of oils in the Dead Sea area (Amit and Bein, 1979a, 1979b; Spiro et al., 1983; Rullkötter et al., 1985). The degradation observed in the oils of the coastal plain group is likely of microbial origin as many of the oils are produced from close to the oil-water-contact (Gilboa et al., 1990). The microbial process likely responsible for the alteration of oils Helez and Kokhav reservoirs is probably microbial sulfate reduction (MSR) (Gavrieli et al., 1995). These authors suggested that the extent of MSR is limited, our results support their hypothesis of microbial degradation and its minor impact on the chemistry of the coastal plain oils.

5.3.Thermal maturation

Thermal maturity of crude oil was assessed by indices in the gasoline range, saturate and aromatic fractions.

5.3.1. Thermal maturation indices in the gasoline range fraction

In the gasoline fraction, the relation of paraffin indices I (isoheptane value; “PI-1”) and II (heptane value; “PI-2”) is used to differentiate the degree of thermal maturity of oil samples according to Thompson (1983). Apart from two Dead Sea group samples (Gurim-4, Kidod-3) which are affected by biodegradation, all the oil samples studied are thermally mature (Fig. 12). The samples of the coastal plain have intermediate values of isopheptane and heptane (1.1-1.6 and 12.3-23.6 respectively) which suggests these oils are of moderate thermal maturity. The oils of Meged, Yam and the non-degraded members of the Sinai offshore and Dead Sea groups display high PI-1 and PI-2 values of >2 and >30 respectively, which indicates these samples are of high thermal maturity.

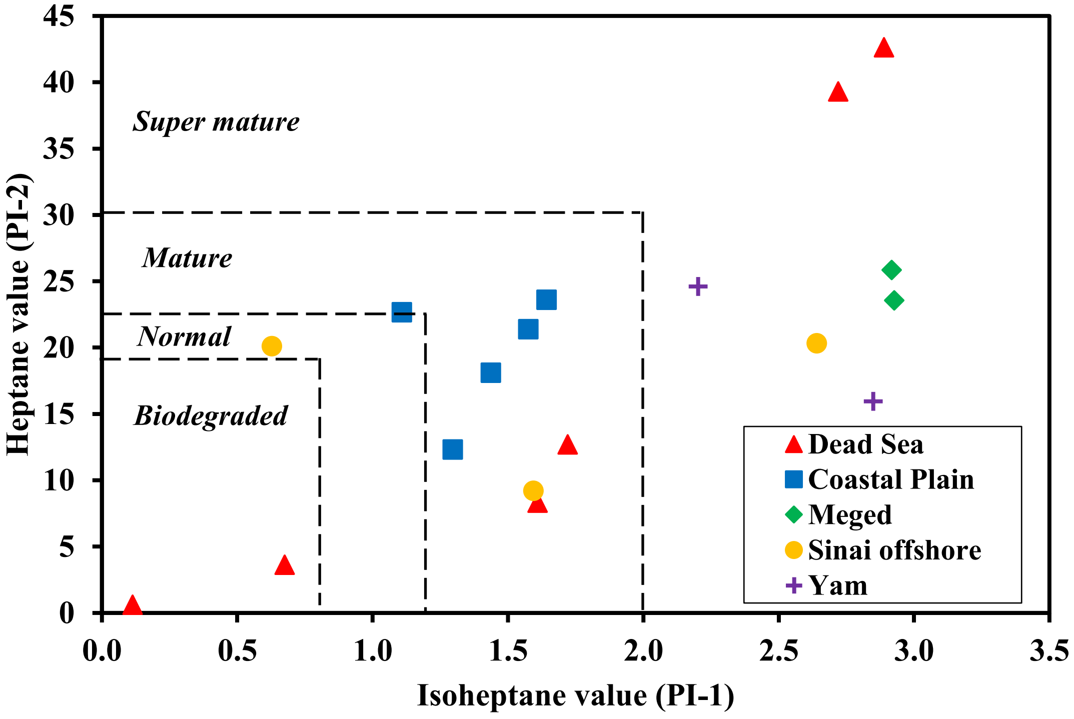


Figure 12. Heptane value (PI-2) versus isoheptane value (PI-1) for crude oil samples from the different groups studied. Border line of the different thermal maturities are from Thompson (1983).

5.3.2. Thermal maturation indices in the saturate fraction

Analysis of hydrocarbons in the saturate fraction allows further, in depth, assessment of the thermal maturity state of the oil samples. The conversion of the C_{31} hopane 22R epimer to the thermally more stable 22S epimer takes place during thermal maturation of organic matter and is typically expressed by the C_{31} hopane 22S/(22S+22R) ratio which rises from 0 to ~0.6 at the early stage of the oil window (Peters et al., 2005). All oils of the Dead Sea group show C_{31} hopane 22S/(22S+22R) ratio of 0.57 to 0.60 indicating they have a maturity of at least early oil window (Table 5). The Meged and Coastal Plain groups oils had C_{31} hopane 22S/(22S+22R) ratio of 0.57-0.59 and 0.57-0.62 respectively, indicating these oils have reached thermal maturity of the oil window and were generated during the main phase of oil generation (Peters et al., 2005). The samples of the Sinai offshore group display C_{31} hopane 22S/(22S+22R) ratios of 0.56-0.57 which suggest it is slightly less mature than the oils of Meged and the Coastal Plain.

Analysis of thermal maturity markers of the sterane group is used to further supports the thermal maturity indices previously described: The C_{29} sterane 20S/(20S+20R) and ββ/(ββ+αα) stereoisomer ratios are used for higher thermal maturities than the endpoint of the C_{31} hopane 22S/(22S+22R) ratio. The endpoints of C_{29} sterane 20S/(20S+20R) and ββ/(ββ+αα) stereoisomer ratios occurs at ~0.50-0.55 and 0.67-0.71 respectively and represents the peak of the oil window (Peters et al., 2005) yet these could be influenced by presence of clay minerals in the source rock which may lead to biased thermal maturity assessment (van Kaam-Peters et al., 1998). The Dead Sea group oils show 20S/(20S+20R) and ββ/(ββ+αα) ranges of 0.45-0.57 and 0.50-0.58 respectively (Fig. 13), thereby confirming these oils reached the oil window but did not surpass its peak. The Meged oils show 20S/(20S+20R) and ββ/(ββ+αα) ranges of 0.47-0.50 and 0.51-0.52 while the Coastal plain oils show 20S/(20S+20R) and ββ/(ββ+αα) ranges of 0.46-0.53 and 0.50-0.56, indicating both groups reached the oil window but did not surpass its peak. Interestingly, the oil of the Sinai offshore display two degrees of thermal maturity: the sample of the Ziv-

1 well shows ββ/(ββ+αα) of 0.42 and 20S/(20S+20R) of 0.51 thereby indicating it have reached the oil window. In contrast, the samples of the Mango-1 well show conflicting trend of low ββ/(ββ+αα) values of 0.30-0.32 with high 20S/(20S+20R) values of 0.60-0.67 which are beyond the maximal value at equilibrium. Based on the ββ/(ββ+αα) values the oils are of early oil window thermal maturity while the 20S/(20S+20R) suggest it passed the peak of the oil window. There are several reasons that could lead to such observation including an analytical error, sample quality, different thermal history at the studied wells or perhaps different level of interaction with clays in the source rock or the reservoir (Peters et al., 2005).

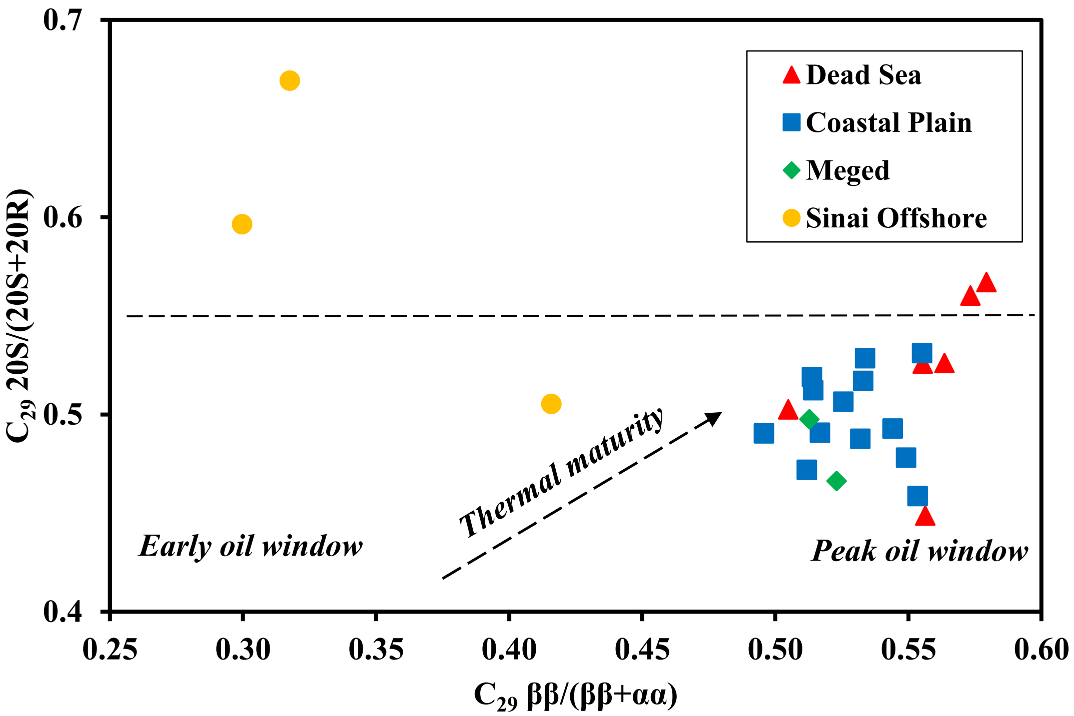


Figure 13. Themral maturity range of the studied oil samples based on two C_{29} sterane stereoisomer ratios (20S/(20S+20R)) and (ββ/(ββ+αα)). Border line between early to peak oil window is from Peters et al., (2005).

The oils of the Yam group display the highest content of diasteranes relative to regular steranes of all oils studied. Such high diasteranes content is common in oils of high degree of thermal maturity as diasteranes are more stable than regular steranes (Peters et al., 2005). The Yam oils lack detectable hopanes yet displayed no signs of degradation which may account for their absence. Such observation is typical of oil samples of very high thermal maturity and therefore assessment of thermal maturity for such samples is mainly limited to maturity proxies in the aromatic fraction.

5.3.3. Thermal maturation indices in the aromatic fraction

In the aromatic fractions, the distribution of the methyl dibenzothiophenes (MDBT) and methyl phenanthrenes (MP) isomers varies with the degree of thermal maturation (Radke et al., 1986; Radke, 1988; Radke and Willsch, 1994). Out of the MDBTs the 1-methyl isomer is the least thermally stable and 4-methyl is the most thermally stable, whereas in the MP group the 1-methyl and 9-methyl isomers are the least thermally stable while the 2-methyl and 3-methyl are the most thermally stable (Radke et al., 1986). Consequently thermal maturity proxies such as methylphenanthrene index (MPI) and methyldibnzothiophene ratio (MDR) are commonly used (often their corresponding calculated vitrinite reflectance equivalent values) as maturity parameters (Radke, 1988; Radke and Willsch, 1994; Budzinski et al., 1995; Huang and Pearson, 1999). Moreover, the concentration of MDBTs and MPs in oil is usually much higher than that of biomarkers used for maturity assessment. This feature makes maturity parameters based on MDBT useful in cases of high level of maturity or in situations where biomarkers are absent or are insufficient in concentration for maturity assessment (Chakhmakhchev et al., 1997).

The results of the MPI-I index and its calculated corresponding vitrinite reflectance (%R_C 1) obtained for the samples in this study are presented in Table 5. The MPI-I results indicate that most oils of the Dead Sea, Coastal Plain and Meged groups have reached a similar degree of thermal maturity of 0.7-0.9%R_{C1}, which implies their classification as oils expelled during the peak of the oil window (Peters and Cassa, 1994).

The oils of Sinai offshore display slightly lower degree of thermal maturity with 0.65 for the Ziv-1 oil sample, a very early stage of the oil window, and 0.82%R_{C1} the peak generation level for the two Mango-1 oil samples (Table 5).

The Yam Yafo-1 and Yam-2 samples of the Yam group display much higher MPI-I values of 0.98 and 1.13 which correspond to 0.98 and 1.07%R_{C1}, indicating thermal maturity of the late oil window which is consistent with their very high API gravity (Table 2, Fig. 7). The level of thermal maturity of the Yam-2 oil is slightly higher than the ~0.9-1% R_O proposed by Feinstein et al., (2002) for a gas sample associated to the oil studied. Additionally, these authors suggested the maturity of the Yam Yafo-1 oil to be lower than 1.1% R_O which is further supported by our results.

The use of the MDR index allows estimation of the T_{max} thermal maturity parameter of each sample by using the relation proposed by Radke (1988). The oils of the Dead Sea group demonstrate large range of MDR values from 0.2 to 2.5 with Emunah-1 being the most thermally mature sample of the group at calculated T_{max} of 438°C. The oil samples of Lot-1, Gurim-4 and Zuk Tamrur-3 are likely of a similar thermal maturation degree to that of Emunah-1 as suggested by steranes and terpanes maturation indices, yet these samples exhibit significantly lower MDR values than expected. This discrepancy is likely the result of biodegradation experienced by these samples as 4-mDBT is more susceptible to biodegradation compared to 1-mDBT (He et al., 2019) thereby lowering the MDR of biodegraded samples.

The MDR values of the Coastal Plain oils cover a narrow range of 1.9-2.6 which is corresponding to calculated T_{max} of 435-437°C. The oils of the Meged group have MDR values of 4.5 and 6.1 which correspond to calculated T_{max} of 445-450°C. The oils of the Sinai offshore group have MDR values of 1.9 to 3.9 which correspond to calculated T_{max} of 434-441°C. The calculated thermal maturity (T_{max} calc.) based on MDR is in agreement with thermal maturities estimated based on indices in the saturate fraction, suggesting that the Dead Sea, Sinai offshore and Coastal Plain groups is at the early-mid oil window level whereas the Meged samples are at the peak of the oil window (Peters and Cassa, 1994). Interestingly, the low maturity sample of the Sinai offshore group, Ziv-1, has calculated T_{max} similar to that of most Coastal plain oils and few of the Dead Sea oils yet its maturity indices in the saturate fraction suggest this sample is of lower thermal maturity than the samples of the Dead Sea and Coastal plain groups (Fig. 13). Both samples of the Yam group display very high values of MDR of 11.6 and 23.5. The correlation of Radke (1988) does not go to such high MDR values yet if a linear relation of MDR and Tmax is assumed at these high MDR values the corresponding Tmax is 482 and 543°C for Yam-2 and Yam Yafo-1 respectively. These high MDR values further support the high degree of thermal maturity experienced by the source of the Yam oils.

5.4. Sources of organic matter and molecular indicators of depositional environment

5.4.1. n-alkanes and acyclic isoprenoids

The *n*-alkanes distributions may be used to distinguish terrigenous organic matter input from that of marine origin as *n*-alkanes with high carbon numbers of C_{27}, C_{29} and C_{31}

typically occur in terrigenous organic matter while shorter *n*-alkanes of C_{15}, C_{17} and C_{19} are indicators of aquatic organic matter (Peters et al., 2005). Representative chromatograms of the saturate fraction of oils are presented in Fig. 2. The oils of the Yam, Dead Sea and Sinai offshore groups display unimodal distribution of *n*-alkanes with peak which centers around short alkanes (C_{11}-C_{15}), such pattern is normally attributed to marine algae and cyanobacteria organic matter which was deposited under anoxic conditions (Brassell et al., 1978). The oils of the Coastal plain group demonstrate an irregular, multi-modal, *n*-alkanes distribution (Fig. 2B) that is typical of mixed marine and terrigenous organic matter as the short *n*-alkanes are typically contributed by marine source while the longer *n*-alkanes are usually sources from higher plants and trees. The oils of the Meged group demonstrate a bimodal *n*-alkanes distribution with distinct dominance of low molecular weight *n*-alkanes (Fig. 2C) and diminishing abundance of *n*-alkanes greater than C_{19}. The dominance of short chain *n*-alkanes ($<C_{20}$) in the samples is typical of sedimentary OM dominated by autochthonous algal input. The bimodal distribution observed suggests mixed organic matter input with main marine origin (centered at *n*-C_{13} to *n*-C_{17}) and perhaps minor terrigenous contribution (centered at *n*-C_{23} and *n*-C_{28}). On the other hand, the *n*-C_{24} to *n*-C_{35} alkanes show a slight even-over-odd preference of 1.1 which is known to occur with marine organic matter from hypersaline or evaporitic conditions (Peters et al., 2005). Additional feature of the Meged oils is a strong odd-carbon preference which produce a "sawtooth-pattern" in the range of *n*-C_{14} to *n*-C_{18}. Similar "sawtooth-pattern" is typically attributed to oils derived from source rocks rich with *Gloeocapsomorpha prisca* – a marine algae which was widespread during the Ordovician but rarely occurred in later geological periods (Fowler, 1992; Fowler et al., 2004).

Pristane to phytane ratio (Pr/Ph) is used to estimate the redox conditions at the water-sediment interface zone during deposition of the source rock with Pr/Ph<1 indicating anoxia (Didyk et al., 1978). The ratio is also affected by thermal maturity as it increases with increasing thermal maturity (ten Haven et al., 1987). Another issue involving the use of the Pr/Ph ratio is noted for source rocks deposited under anoxic-sulfidic conditions where selective preservation of phytane over pristane occurs as result of sulfurization which in turn can lead to wrong assessment of the redox conditions (Kutuzov et al., 2020). The Pr/Ph ratio of all samples studied is presented in Table 4. The Pr/Ph ratio of the Dead Sea oils is well below 1 and indicates the source rock for these oils was deposited under anoxic conditions. This observation agrees with previous studies thar focused on the oils of the Dead Sea region (Tannenbaum, 1983; Tannenbaum and Aizenshtat, 1985). The oils of the Coastal plain have Pr/Ph ratio range close to 1 (0.72-1.09; average 0.91), similar to the range of 0.74-1.29 in the study of Bein and Sofer (1987). This range of Pr/Ph may suggest alternating anoxic-oxic conditions during deposition (Didyk et al., 1978). The large variability may be explained by either oil degradation, significant variation of the redox conditions during deposition of the source rock or as an effect of preferential phytane sulfurization as significant sulfur content was observed for the oils. The Pr/Ph ratio of the Meged samples is close to 1 (0.88-0.92) which suggest anoxic-dysoxic conditions during deposition. The oils of Sinai offshore and Yam groups show 1<Pr/Ph<3 which could indicate oxic water column conditions (Didyk et al., 1978) or could be the result of very high degree of thermal maturity (Peters et al., 2005). Since the oil samples of Sinai offshore are of low-moderate degree of thermal maturity their Pr/Ph ratio may hint the organic matter that comprised their source rock was exposed to oxic conditions during deposition.

In contrast, the Yam samples are of high degree of thermal maturity which makes the use of Pr/Ph ratio unreliable.

The Pr/Ph ratio could be used in parallel with the dibenzothiophene/phenanthrene (DBT/Phen) to determine the source rocks depositional environments and lithologies (Fig. 14) according to the correlations proposed by Hughes et al., (1995). The Dead Sea area oils fall mostly with the marine-carbonate zone with the altered sample of Gurim-4 falling within the lacustrine zone as a result of DBT depletion by the water washing the samples experienced (i.e., diagenetic artifact). The Coastal plain oils are indicated of originating from a source rock of mixed environment of deposition ranging from marine carbonate to lacustrine. The Meged group oils show very low values of DBT/Phen (0.08-0.17) and Pr/Ph of less than 1 which suggest they have originated from a lacustrine source rock. The Yam group oils have even lower DBP/Phen of 0.07-0.1 and have Pr/Ph>1 (probably due to elevated thermal maturity) which may indicate they have originated from a marine shale or a lacustrine source rock.

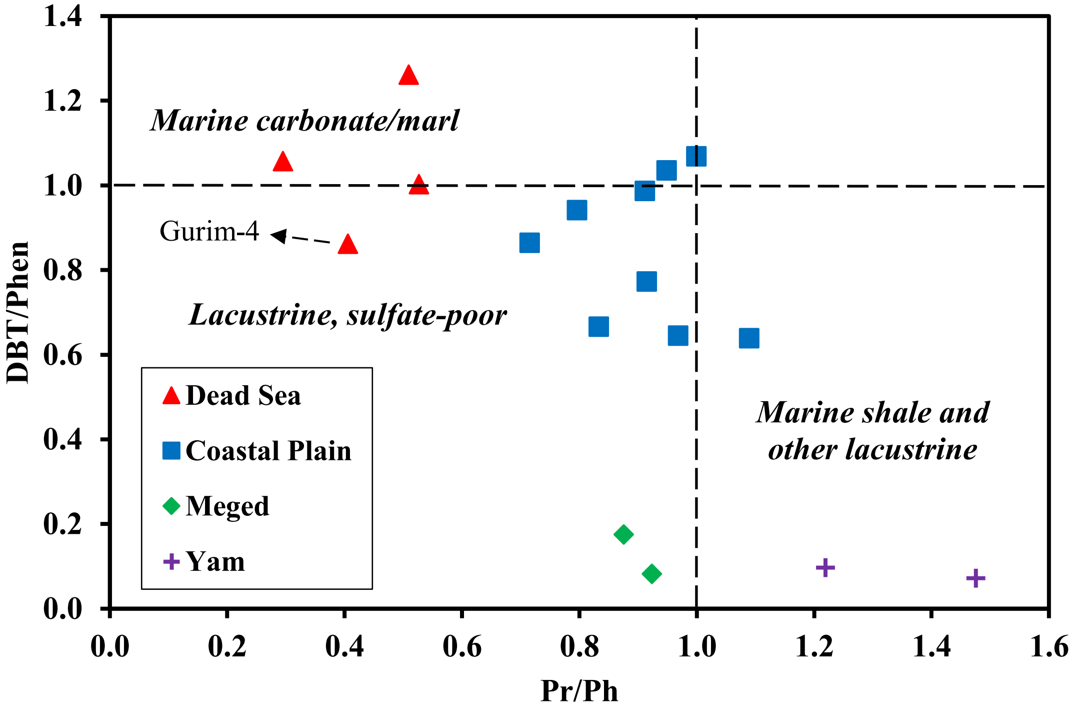


Figure 14. Relationship of pristane/phytane (Pr/Ph) to dibenzothiophene/phenanthrene (DBT/Phen) ratios. Field boundaries of the various lithologies are from Hughes et al., (1995).

5.4.2. Steranes and diasteranes

Steranes are derived from sterols which are widely dispersed in plants, animals and other organisms. Marine organisms tend to contain abundant C_{30} sterols (Moldowan et al., 1985) and exhibit enhanced amounts of C_{27} steranes relative to C_{29} steranes (Mackenzie et al., 1982). Presence of C_{29} sterane in high concentration in oil may be interpreted as an input from higher land plants or from certain primitive green algae containing mainly C_{29} sterols yet these are limited to samples from the Early Paleozoic (>350 m.y) (Moldowan et al., 1985; Volkman, 1986). Predominance of C_{28} steranes is typically attributed to lacustrine algae and diatoms input (Rampen et al., 2010). The oils of the coastal plain and Meged display a V-shape sterane distribution profile with C_{29}>C_{27}>C_{28}, their enrichment in C_{29} steranes is especially evident with $C_{29}\alpha\alpha\alpha$ (20R) > $C_{27}\alpha\alpha\alpha$ (20R) in these groups (Fig. 3). This observation suggests the source rocks for the oils of these groups received input of both marine and terrestrial organic matter. Such mixed origin of organic matter is also supported by the $\delta^{13}C$ values of their aromatic and saturate fractions (Fig. 6). The oils of the Sinai offshore group display sterane distribution profile dominated by C_{29} which is typical of oils generated from source rocks containing mainly organic matter of terrestrial origin, this observation is further supported by the $\delta^{13}C$ values of their aromatic and saturate fractions (Fig. 6). Dominance of C_{27} steranes is evident in the samples of the Dead Sea group which display $C_{27}>C_{28}\geq C_{29}$ sterane distribution profile (Fig. 3), thereby suggesting their source rocks contain OM of marine origin. The oils of the Yam group show little steranes, mainly of C_{29} with minor content of C_{27} steranes. Such distribution may suggest the oils originated from source rock containing organic matter from terrestrial sources with minor contribution of organic matter from marine origins.

The presence of diasteranes in oil samples is governed by both clay/TOC ratio of the source rock (van Kaam-Peters et al., 1998) and the degree of thermal maturation (Peters et al., 2005). Since the oil samples of the Coastal plain, Dead Sea and Meged groups are of comparably moderate thermal maturation degree the notable presence of diasteranes in the samples of Coastal plain and Meged groups (Fig. 3) suggests these oils originated from a clay-containing source rock. On the other hand, the complete lack of diasteranes in the samples of the Dead Sea group suggests their source rock was likely a carbonate with little to no clays present (El Diasty and Moldowan, 2012). The presence of diasteranes in the samples of the Sinai offshore, which are of low thermal maturity, likely indicates these oils were generated from a clay-containing source rock. The high content of diasteranes in the samples of the Yam group is likely the result of the samples high degree of thermal maturity rather than their source rock properties.

5.4.3. Terpanes

The C_{29}/C_{30} 17α hopane ratio (C_{29}/H) in anoxic carbonate or marly source rocks and their associated oils is generally >1 (Palacas et al., 1984; Peters et al., 2005). The oils of the Dead Sea group are the only to exhibit $C_{29}/H>1$ while all groups exhibit C_{29}/H of <0.7 (Table 5). Therefore, suggesting the oils of the Dead Sea group have originated from a carbonate or marly source rock deposited under anoxic conditions.

The C_{22}/C_{21}, C_{24}/C_{23} and C_{26}/C_{25} tricyclic terpane ratios of the oil samples studied could indicate the lithology of their source rock as high C_{22}/C_{21} (~ >0.5) and low C_{24}/C_{23} (~ <0.5) occur in oils derived from carbonate source rocks while lacustrine source rocks typically have C_{26}/C_{25} ratio of at least 1.3 (Peters et al., 2005). The Dead Sea group samples have high C_{22}/C_{21} and low C_{24}/C_{23} ratios (Fig. 15) which suggest their source rock is a carbonate. Coastal plain, Meged and Sinai offshore oils have lower C_{22}/C_{21} and higher C_{24}/C_{23} ratios than that of the Dead Sea oils, suggesting these oils may have originated from a non-carbonate source rock. The exception to this observation is Ziv-1 oil which has high C_{24}/C_{23} ratio and abnormally high C_{22}/C_{21} ratio, we could not provide an explanation for such observation. Based on empirical results presented in Peters et al., (2005) it is conceivable that the source-rock depositional environment of the Coastal plain, Meged and Sinai offshore oils is that of a marl, lacustrine or a marine shale. Furthermore, the Mango-1 oils of the Sinai offshore group display high C_{26}/C_{25} tricyclic terpane of >2 (Table 4) which suggest they have originated from a lacustrine source rock. Interestingly, the sample of Ziv-1 from the same group display low C_{26}/C_{25} ratio of 0.84 which suggests it have originated from a non-lacustrine source rock.

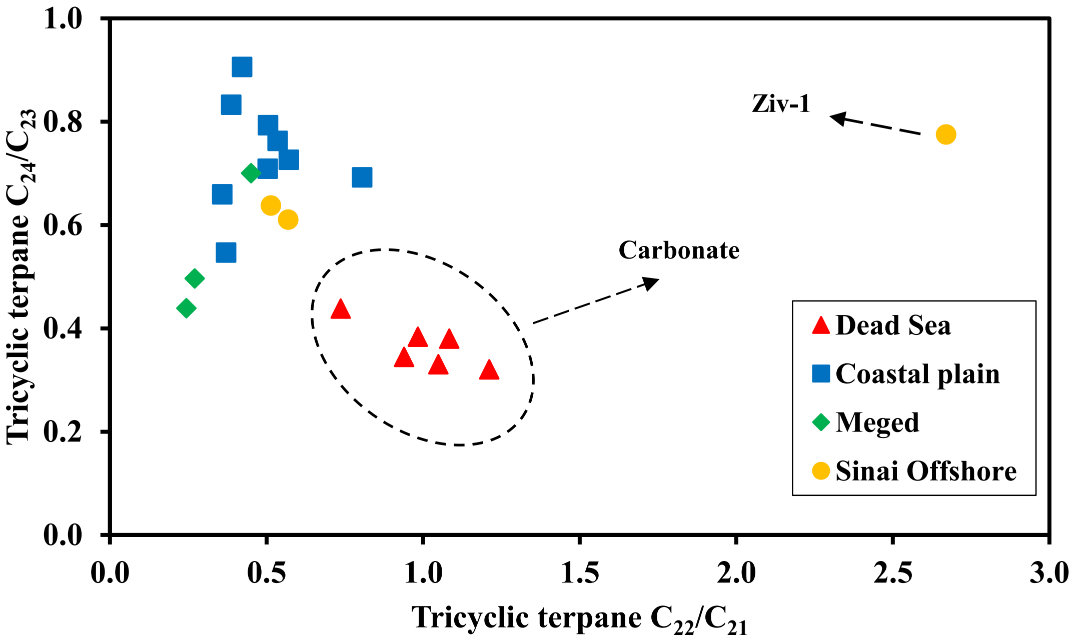


Figure 15. C_{24}/C_{23} versus C_{22}/C_{21} of tricyclic terpanes for the studied oils used to infer source rock lithology from oil composition (Peters et al., 2005).

The environment of deposition and lithology of the oils source rocks can be further investigated by tandem use of C_{29}/C_{30} and $C_{35}S/C_{34}S$ homohopane ratios or the Ts/(Ts+Tm) ratio (Fig. 16 and 17, Table 4 and 5) as most oil from marine carbonate source rocks show high $C_{35}S/C_{34}S$ (>0.8) coupled with high C_{29}/C_{30} (>0.6) (Peters et al., 2005). The oils of the Dead Sea group do indeed exhibit C_{29}/C_{30} and $C_{35}S/C_{34}S$ ratio of marine carbonate (Fig. 16) further supporting indices discussed above. The $C_{35}S/C_{34}S$ ratios of the coastal plain oil samples is similar to those characterizing the Dead Sea samples, but their C_{29}/C_{30} hopanes ratio is considerably lower, yet for most samples it is ≥ 0.6 (Table 4). Comparison to empirical C_{29}/C_{30} versus $C_{35}S/C_{34}S$ ratios presented in Peters et al., (2005) and their relation to source rock lithologies suggests that the source-rock of the Coastal Plain oils is likely a marl. The oils of Meged and Sinai offshore display low C_{29}/C_{30} hopanes and $C_{35}S/C_{34}S$ ratios which may suggest their source rock is a marine shale or a lacustrine source rock. The high C_{26}/C_{25} tricyclic terpane of the Mango-1 oils differentiate them from the Meged oils and further supports the possibility of lacustrine origins yet the low C_{26}/C_{25} tricyclic terpane of Meged suggests they are not lacustrine and therefore likely of a marine shale origin.

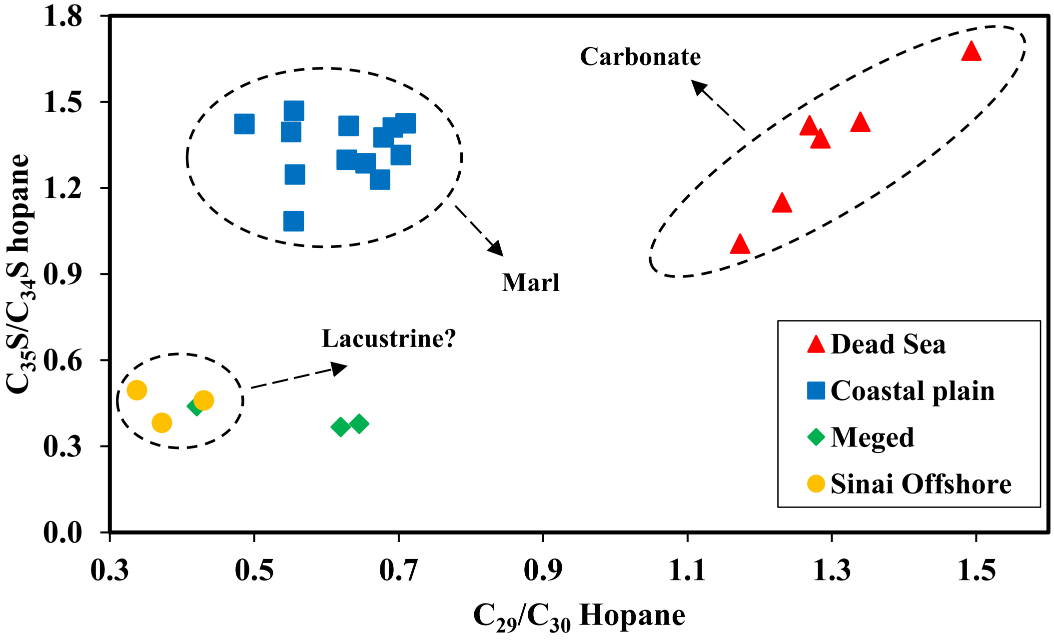


Figure 16. $C_{35}S/C_{34}S$ hopanes ratio versus C_{29}/C_{30} hopane ratio for the studied oils. Identification of the potential source-rocks lithofacies fields follows Peters et al., (2005)

The Ts/(Ts+Tm) ratio is sensitive to clay-catalyzed reactions and so oils from an anoxic-carbonate source rock typically have Ts/(Ts+Tm)<0.25 while oils from clay rich settings will have Ts/(Ts+Tm)>0.4 (Peters et al., 2005). The main drawback of the Ts/(Ts+Tm) ratio is it sensitivity also to thermal maturation as Ts/(Ts+Tm) typically approaches 1 at the end of the oil window and onset of the gas window (Seifert and Moldowan, 1978). Nonetheless, since almost all samples of the Dead Sea and Coastal plain groups are of similar level of thermal maturity (Tmax$_{calc.}$ of 430-438°C; Table 5) differences in the Ts/(Ts+Tm) ratio can be attributed to influence of lithology and conditions at the depositional environment. Cross plot of C_{29}/C_{30} hopanes vs. Ts/(Ts+Tm) (Fig. 17) exhibit very low Ts/(Ts+Tm) of 0-0.15 and high C_{29}/C_{30} hopane ratio of above 1 for all the oil samples of the Dead Sea group, except Zuk Tamrur-1. The distinct ratios displayed by Zuk Tamrur-1 are unclear and may perhaps be the result of an analytical or data-interpretation error. The oils of the Coastal plain group exhibit Ts/(Ts+Tm) of 0.41-0.51 with C_{29}/C_{30} hopane ratio below 0.8. This observation supports the presence of clays in the source rock of the Coastal Plain group. The oils of the Meged and Sinai offshore groups display Ts/(Ts+Tm) of above 0.5 and C_{29}/C_{30} hopane ratio of below 0.7 which suggests its source rocks likely contain clays.

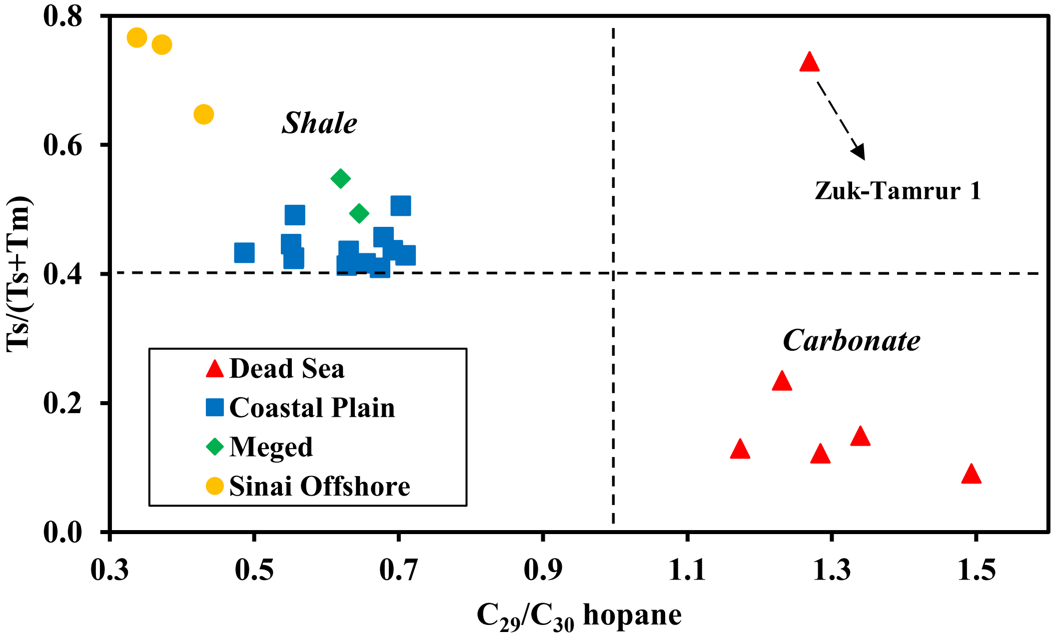


Figure 17. Ts/(Ts+Tm) ratio versus C_{29}/C_{30} hopane ratio for the studied oils. Identification of the potential source-rocks lithofacies fields follows Peters et al., (2005)

The presence of Gammacerane was noted in the oils of the Dead Sea (Rullkötter et al., 1985) and Meged groups (Geochem, 1999; Geomark research inc., 2004). This compound, when present, is usually characteristic for samples deposited under hypersaline or anoxic conditions and stratified water body (Sinninghe Damsté et al., 1995).

The C_{31}-C_{35} extended homohopane distributions of the oils studied is presented in Fig. 4. The oils of the Dead Sea display elevated C_{35} homohopanes (C_{35}>C_{34}), indicating anoxic source rock depositional conditions with restricted water circulation (Peters and Moldowan, 1991; Sinninghe Damsté et al., 1995). The Coastal Plain oils display dominance of the C_{32} homohopanes and elevated C_{35} homohopanes (C_{35}>C_{34}). The dominance of the C_{32} homohopanes may be the result of free oxygen availability in the waters of the deposition basin during diagenesis which led to oxidation of bacteriohopanetetrol to C_{32} acid, followed depletion of all available oxygen and preservation of the C_{32} homohopanes (Peters and Moldowan, 1991). The depletion of oxygen up to the state of anoxia is supported by the elevated C_{35} homohopanes relative to C_{34} homohopane for all oil of this genetic family, which are indicative of deposition under anoxic conditions (Peters and Moldowan, 1991). This peculiar observation of both dysoxic and anoxic markers in a large set of oils suggests the source rock of the Coastal plain oils was initially deposited under dysoxic conditions, as organic matter continued to accumulate it led to consumption of all the free oxygen in the water column and subsequently to formation of anoxic conditions. Alternatively, it is plausible that the mixed redox signature is a combination of two different organic matter inputs- while the anoxic OM is most likely of marine origin and represents the basin of deposition, the dysoxic OM could be of terrigenous origin where the dysoxic condition could have occurred in swamps or stagnant lakes from which OM could have been carried to the final deposition basin. Similar homohopane dominance of C_{32} and C_{35} was observed in two source rock samples from the Late Permian Zechstein formation in Poland (Słowakiewicz et al., 2018) where the authors concluded the environment of deposition for these samples was lower slope/ shallow basin facies deposited under reducing conditions.

The homohopanes of the Meged oils are dominated by C_{34} homohopanes ($C_{34}>C_{33}>C_{35}$) (Fig. 4). This uncommon homohopanes distribution is rarely encountered in mature oil samples and is typically attributed to carbonate lagoonal and evaporitic environment during deposition of the source rock (Waples and Machihara, 1991 in Slowakiewicz et al., 2018). Several studies (Köster et al., 1997; Snowdon et al., 1998; Marynowski et al., 2000) on source rocks (mainly dolostones) with $C_{34}>C_{33}$ homohopanes, abundant aryl isoprenoids and presence of gammacerane suggested the environment of deposition is shallow water lagoons with elevated salinity and anoxic bottom waters.

5.4.4. *Stable carbon isotopes of hydrocarbon fractions*

The cross plot of $\delta^{13}C_{SAT}$ versus $\delta^{13}C_{ARM}$ hydrocarbon fractions of crude oils was introduced by (Sofer , 1984) for correlation and to discriminate oils derived from predominantly marine or non-marine source rocks. The relationship proposed by Sofer (1984) which seperates waxy oils from nonwaxy oils. Waxy oils are usually derived from terrigenous organic matter, whereas nonwaxy oils are usually derived from marine organic matter. C isotopes ratio obtained for the hydrocarbon fractions in the samples studied are presented on $\delta^{13}C_{SAT}$ versus $\delta^{13}C_{ARM}$ diagram Fig. 6 following the method of Sofer (1984). All the Dead Sea oils fall below the “Sofer line” indicating their source rock contained organic matter of marine origin. The Meged, Yam and coastal plain oils fall in the transition zone between marine and terrigenous origin of oils, suggesting these oils originated from a source rock containing organic matter from both marine and terrestrial origins. The Sinai offshore oils are the only samples that fall above the “Sofer line” which indicates they originated from a source rock containing predominantly terrestrial organic matter.

5.5. Potential source rocks

Since no source-rock samples were analyzed in this study, direct oil-source correlation is not possible. However, based on biomarkers indication of biogenic precursors, depositional environment, and thermal maturity level, it is possible to postulate on the characteristics of potential source rocks for each group of oils.

A geological time frame for the deposition of source rocks of various oils can, sometimes, be estimated from the C_{28} sterane content tends to increase with geological time due to diversification and proliferation of phytoplankton assemblages (Grantham and Wakefield, 1988). When applied to organic matter of marine origin, source rocks of Jurassic age and younger typically have $C_{28}/C_{29}>0.7$ while lower values are associated with Triassic and Paleozoic organic matter. Nevertheless, the C_{28}/C_{29} sterane ratio is not uniquely related to the depositional time and can be affected by other factors.

The C_{28}/C_{29} steranes ratios obtained for the oil samples in this study are presented in Table 4 and in representative m/z 217 mass fragmentograms in Figure 3 (right hand side). The mature, non-degraded, sample of Emunah-1 which represents the Dead Sea group has C_{28}/C_{29} of 0.77 (Table 4), which is consistent with Cretaceous age. The C_{28}/C_{29} regular sterane ratio of the Meged samples (Table 4) obtained in this study and in previous report by Geochem (1999) is 0.43-0.5. Similar values of C_{28}/C_{29} sterane ratio, lower than 0.55, were attributed to algal organic matter of Ordovician to Upper Devonian age (Schwark and Empt, 2006), which might be pertinent in this case. The samples of the Coastal Plain have C_{28}/C_{29} ratio of 0.24-0.38 (Table 4) which could assign them to Ordovician-Devonian age. Nevertheless, we suggest these very low C_{28}/C_{29} values are the result of substantial input of terrestrial organic matter, which is evident from the elevated C_{29} steranes content of the group samples therefore, creating a bias towards older geological age for the oils source rock and making the C_{28}/C_{29} sterane ratio inapplicable. We believe that this is also the case with the samples of the Sinai offshore oils where the recorded C_{28}/C_{29} sterane ratio of 0.39-0.64 (Table 4) is affected by an input of terrestrial organic matter to their source rock (as is also reflected by other parameters) and disrupts its application as an age proxy.

The biomarkers analysis of the oils suggests the following depositional setting for the source rock of each oil group:

5.5.1. The Dead Sea group

Proxies such as relatively high C_{27} sterane, C_{29}/C_{30} hopane>1, low Pr/Ph, low CPI, high C_{35}/C_{34} homohopanes ratio and gammacerane presence suggest that the Dead Sea group source rock is likely a marine carbonate, which was deposited in anoxic, possibly euxinic(?), possibly hypersaline stratified water column (Sinninghe Damsté et al., 1995; Peters et al., 2005). The high DBT/Phen and the high sulfur content of the oils further suggest that the source rock for this oil group contained a type IIS kerogen (Orr, 2001).

Previous studies used various oil-source rock and oil-oil correlation techniques to show that the source rock for the oils in the Dead Sea region is the Maastrichtian (Latest

Cretaceous) organic-rich carbonate Ghareb Formation with a type IIS kerogen (Spiro et al., 1983; Tannenbaum and Aizenshtat, 1984; Rullkötter et al., 1985). More recently, compound-specific sulfur isotope ratio analysis, for oil-oil correlation and correlation to oil produced by semi-open pyrolysis experiments of Ghareb rocks, supports the earlier conclusion (Rosenberg et al., 2017).

5.5.2. The Coastal Plain group

The oils of the coastal plain group were most likely generated from a marine shale or a mixed carbonate containing marine organic matter with significant input of terrestrial organic matter. The elevated C_{35}/C_{34} homohopane ratios along with relatively high S content and low Pr/Ph and CPI indicate that considerable portion of the organic matter in the source rock of the coastal plain oil was deposited in a marine anoxic, sulfidic, and possibly hypersaline conditions (Bray and Evans, 1961; Didyk et al., 1978; Peters et al., 2005). But on the other hand, bi-modal *n*-alkanes distribution, C_{29} sterane dominance, presence of diasteranes, elevated C_{32}/C_{31} homohopane ratios, low C_{29}/C_{30} hopane coupled with high $C_{35}S/C_{34}S$ and $\delta^{13}C$ of the aromatic and saturate fractions all suggest also a terrigenous input, probably terrestrial organic matter washed from the land along with some clays. The deposition basin of the source rock was likely characterized by low energy sedimentation regime with limited water circulation that allowed the formation of anoxic bottom waters which aided the formation of a sulfur rich, type IIS, kerogen. The most likely mechanism for accumulation of clays and terrestrial organic matter within a marine basin is transport by rivers from the land to the marine shelf. Moreover, a river could end in a submerged canyon, within the shelf itself, which may act as a deep- restricted basin.

Deposition within several, disconnected, shelf canyons may explain the patched nature of the source rock and its seemingly small area.

Previous petrographic study of the Helez reservoirs by Calvo et al. (2011) suggested that hydrocarbons were introduced to the reservoirs during the Late Cretaceous, therefore implying the source rock of the oils must be older than Late Cretaceous. Previous geochemical studies of the coastal plain oils suggested, based on oil-source rock correlation, that the Bajocian- Bathonian Barnea formation is the source rock for the oils (Bein and Sofer, 1987; Tannenbaum, 1995a and b). The Barnea formation and its equivalent formations of Shederot and Daya are composed mainly of marine carbonates with some interbedded shales (Gardosh et al., 2011), they were deposited in shallow marine inner- to outer shelf settings (Derin, 1974) and seem to fit the lithology criteria suggested by biomarker analysis of the oils. However, the Barnea samples analyzed by Bein and Sofer (1987) are thermally immature and yet contain relatively high amount of solvent extractable bitumen with higher thermal maturity. They infer that this discrepancy indicates staining, likely by a more mature Barnea-type oil migration through the Barnea formation in the study area. Moreover, most of the Barnea samples analyzed to date are characterized by very low TOC, e.g., out of 17 samples analyzed by Bein and Sofer (1987) only 5 had TOC>0.5 while out of 50 samples analyzed by Tannenbaum (1995a) only 12 had TOC>0.5 and the average TOC value was 0.4. Such a TOC level appears to be insufficient to generate the amount of the bitumen extracted (and thus further corroborate the implied presence of staining), and too low to classify the known Barnea samples as a source rock (Peters and Cassa, 1994). Out of all Barnea samples with TOC>0.5 analyzed by Tannenbaum (1995a) most have hydrogen and oxygen values which would classify then as a mixed type II and III kerogen which classifies them as oil and gas prone, unlike the oils studied (Fig. 18).

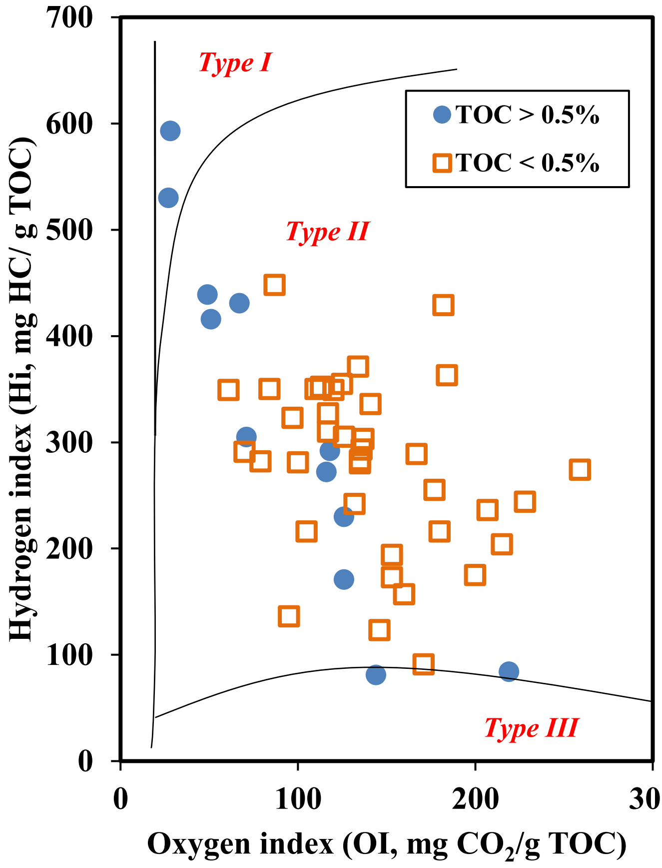


Figure 18. Pseudo van-Krevelen plot of hydrogen index (HI) versus oxygen index (OI) for the Barnea formation samples analyzed by Tannenbaum, (1995a).

The above observations lead to one of two conclusions: either the bitumen analyzed in the Barnea formation is not indigenous and is actually an oil staining or that the Barnea formation has another, TOC rich, facies which is located west of the modern coastline and was not drilled yet. This puzzle regarding the Barnea Fm. might be solved by performing hydrous pyrolysis experiment on few of its more organic-rich samples and analysis of the evolved oil biomarkers to provide decisive oil-source rock correlation.

The regional extent of the Coastal plain source rock is unclear. However, it was suggested to extend further to the south-west based on a report of a kerogen with similar composition to the Barnea fm. in the Late Jurassic-Early Cretaceous carbonates of the “Masajid Formation Equivalent” in the El Mazar-1 well in the north of Sinai (Keeley et al., 1990).

5.5.3. The Meged group

The Meged oil, with its Pr/Ph<1, unique C_{34} homohopane prominence relative to both C_{33} and C_{35} homohopanes and the gammacerane contained, indicates it originated from a marine source rock which was probably deposited in anoxic, stratified, hypersaline water (Moldowan et al., 1985; Sinninghe Damsté et al., 1995). The bimodal distribution of *n*-alkanes and dominance of C_{29} sterane indicate of some terrigenous organic material input. The low values of DBT/Phen, low C_{24}/C_{23} and C_{22}/C_{21} tricyclic terpanes ratios, very high C_{24} tetracyclic/C_{23} tricyclic terpanes, and the low C_{29}/C_{30} hopane ratio indicate the source rock of the Meged oils is a marine shale, probably mixed with terrigenous terrestrial organic matter.

The only known marine source rock in the study area that was deposited under hypersaline conditions is the Maastrichtian Ghareb formation which is a distinct marine-carbonate and shares no similarities in biomarkers distribution and therefore not the source of the Meged oils. A litho-facially suitable candidate for a source rock, which was deposited in a saline to hypersaline basin that contain notable amount of shale is the Upper Triassic Mohilla formation (Bialik et al., 2012), that happens to be the reservoir formation and the seal rock of the Meged oils. Unfortunately, no geochemical data of the organic matter in the Mohilla formation is available to perform oil-source rock correlation (Bein et al., 1984) but, based on the C_{28}/C_{29} sterane ratio discussed above we can reject the Mohilla formation as the source rock for the Meged oils. Alternative hypothesis for the Meged source rock was raised by Luskin et al., (1997) who suggested, based on a presence of C_{26} sterane in Meged 2 oil sample (Geomark research inc., 2004), that the source rock of the oils is Paleozoic, probably the Silurian “hot” shales (Lüning et al., 2000). The C_{28}/C_{29} sterane ratio discussed above consists with the possibility of Paleozoic origin for the Meged oils and suggests Ordovician to Upper Devonian age.

The unique coupling of *n*-alkanes distribution (dominant *n*-C_{15} and *n*-C_{17}) and markedly greater C_{34} than C_{33} and C_{35} homohopanes contents, as exhibited by the Meged oils, is known mainly in mature Paleozoic oils from various locations, e.g. Silurian to Mid. Devonian sourced oils of the Timan-Pechora Basin in Russia (Requejo et al., 1995; Abrams et al., 1999; He et al., 2012); Mid. Devonian sourced oils in the Williston (Osadetz et al., 1992; Obermajer et al., 1999) and Alberta (Snowdon et al., 1998) basins in Canada; Oils of mixed Ordovician and Silurian sources at the Michigan basin in Canada (Obermajer et al., 1998; Obermajer et al., 2000). The unique C_{34} homohopane predominance alone was identified in several examples of thermally-mature oil from the Paleozoic including Mid. Ordovician sourced oil in the Williston Basin in USA (Geomark, 1999 in Peters et al., 2005; pg.782), Pennsylvanian reservoired oils from central Montana (Obermajer et al., 2002), Paleozoic oils of the Canning basin in Australia (Spaak et al., 2018) and in the Permian basin of Poland and Germany (Słowakiewicz et al., 2018). Thus, there are distinct similarities to oils which were generated by Ordovician and Devonian source rocks. Nevertheless, the origin and mechanisms responsible for such molecular patterns are unclear and they all may be coincidental and therefore cannot either support or reject the Paleozoic source rock theory.

An attempt to compare the biomarkers and bulk properties of the Meged oil to Silurian "hot" shales sourced oils from North Africa (Hodairi and Philp, 2012; El Diasty et al., 2017), Middle East (Cole et al., 1994; Lüning et al., 2005; Armstrong et al., 2009) and Western-Iraq (Alkhafaji et al., 2015) showed little to no resemblance. Moreover, kerogen analysis of the Silurian "hot shale" equivalent in the north of Saudi-Arabia (Qusaiba Shale formation) revealed it is a type III kerogen (Abouelresh et al., 2020) which is gas prone and unlikely to generate oil similar to that of the Meged group. An attempt to correlate the Meged oils to other oils produced from Triassic reservoirs in Syria and Iraq (Abboud et al., 2006; English et al., 2015) showed no resemblance.

If we take all the observations into account, the most likely source for the Meged oils is a marine source rock with terrestrial contribution which was deposited in a restricted basin under hypersaline and anoxic conditions during either Ordovician or Devonian age.

Luskin et al., (2012) suggested the source rock of the Meged oils is in the Palmyrides Basin in Northern Syria and that the oils migrated to their current reservoir from the Palmyra trough prior to the Miocene sinistral displacement on the Dead Sea transform. Such hypothesis suggests the oils have migrated long distance (~ tens of km) from source to trap. Upon such long migration oil tend to geochemically homogenize (Obermajer et al., 1998 and 2000) yet the two oil samples of Meged show some geochemical differences (especially in their *n*-alkanes envelope) and have relatively high contents of water-soluble toluene and benzene which suggest the migration distance of the oils from their source to trap was likely not very long (Palmer, 1993; Obermajer et al., 2002). Based on this geochemical constrains we suggest the source rock of the Meged oils is buried closer to the reservoirs, perhaps it is buried in the deep section of the Judea Graben which is <10 km from the reservoirs (Cohen et al., 1990; Gardosh et al., 2010). Unfortunately, the presence of organic rich, Paleozoic strata, in the Judea Graben was not proven yet.

5.5.4. The Yam group

The results in the present study of the Yam oils indicate that the saturate hydrocarbon biomarkers conventionally used for oil-source rock correlation are not fully diagnostic, probably due to their very high levels of thermal maturity as is indicated by their MDBTs and MPhen isomerization ratios and high API which is past the oil window and would classify the Yam oils as gas-condensate. The $\delta^{13}C$ of the oils saturate and aromatic fractions indicate the organic matter in their source rock is likely of a mixed terrigenous and marine origin. The input of organic matter form marine origin is also supported by the unimodal *n*-alkanes envelope. In contrast, the oils show dominance of C_{29} steranes which strengthens the possibility of terrestrial input to its source rock. The oils Pr/Ph and DBT/Phen ratios suggest the oils have originated from a marine shale or lacustrine source rock. The oils have Pr/Ph>1 which could indicate the organic matter in their source rocks was deposited under dysoxic conditions but could also be the result of their elevated degree of thermal maturity.

5.5.5. The Sinai offshore group

The results of the current study suggest the source rock for the Sinai offshore oils is likely a shale, perhaps from lacustrine depositional settings. Based on $\delta^{13}C$ of the oils saturate and aromatic fractions, CPI larger than 1, Ts/Tm>1 and high C_{24} Tet/C_{23} Tri terpanes the source rock of the Sinai offshore oils experienced significant contribution of terrestrial OM. Our attempt to correlate the geochemical characteristics of Mango-1 and Ziv-1 with potential source rocks in previously published studies (Mostafa and Younes, 2001; Sharaf, 2003) was not successful.

6 Conclusions

We have conducted a detailed geochemical study of oil samples obtained from exploration wells at the eastern Mediterranean margin onshore and continental shelf of Israel and N. Sinai (Egypt). We attempt to classify them into genetic groups (i.e., oil-oil correlations) and postulate on the characteristics of their potential source rocks (i.e., oil-source rock correlations). The main conclusions of this study are:

1. There is a clear classification of the oils studied into five different genetic groups, which cluster in accordance with their geographic distribution, i.e., Dead Sea, Meged, Coastal plain, Yam (Israel continental shelf), and Sinai offshore (Egypt, N. Sinai continental shelf).
2. Internal differences in composition of samples within distinct groups are mostly shown by relatively unstable proxies. These compositional differences indicate their attribution to compositional modifications due to variable post-generation and diagenetic processes, mainly biodegradation, water washing, and thermal maturation.
3. Thermal maturation of the oils in four of the groups (Dead Sea, Meged, Coastal plain, and Sinai offshore) is in the main range of oil generation, with little differences of samples within each group. The thermal maturation of the Yam oils is considerably higher, at the highly-mature to over-mature level.

4. The identification of five different oil genetic groups insinuate probable existence of five different active source rocks and pods of generation in the study region within a plausible migration radius.

5. The oils of the Dead Sea group have originated from a source rock deposited in marine, anoxic (perhaps euxinic) depositional environment while the other four different source rocks were deposited in marine or lacustrine depositional environments with variable input of terrigenous organic matter.

a. The geochemical characteristics of the coastal plain oils indicate their source rock was deposited under anoxic conditions, likely euxinic. The origins of organic matter for this source rock were both marine and terrigenous. The fraction of terrigenous organic matter experienced exposure to oxic conditions, probably during transport from the land to the marine deposition basin. The most likely lithology for this source rock is marl while its age is older than Late Cretaceous. The current study does not support or reject the hypothesis of the Barnea formation being the source rock for the coastal plain oils.

b. The geochemical characteristics of Meged oil imply an origin from a marine source rock deposited in an anoxic depositional environment, with possibly stratified and exceedingly saline water column, and some input of terrigenous organic matter. Some of the geochemical data characterizing the Meged oil (e.g., unique bi-modal *n*-alkanes distribution and C_{34} dominance relative to C_{33} and C_{35} homohopanes) correlate the source rock of Meged oils to Paleozoic (Ordovician-Mid. Devonian) source rocks previously described in the literature.

c. The geochemical characteristic of the oils in the northern Sinai continental shelf (Egypt) suggests an origin from lacustrine or marine shale with a considerable input of terrigenous organic matter. We could not correlate the geochemical characteristics of Mango-1 and Ziv-1 with published potential source rocks.

d. The Yam oils were modified by high thermal maturity and their applicability for oil-oil correlation, and characterization of potential source rocks, is restricted. From the limited information available, the source rock of the Yam oils is likely a marine shale that may have been deposited in dysoxic conditions and probably contains considerable input of terrigenous organic matter.

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8 References

Abboud, M., Philp, R.P., Allen, J., 2006. Geochemical correlation of oils and source rocks from central and NE Syria. Journal of Petroleum Geology 28, 203-216. https://doi:10.1111/j.1747-5457.2005.tb00080.x.

Abouelresh, M., Babalola, L., Bokhari, A., Omer, M., Koithan, T., Boyde, D., 2020. Sedimentology, geochemistry and reservoir potential of the organic-rich Qusaiba Shale, Tabuk Basin, NW Saudi Arabia. Marine and Petroleum Geology 111, 240-260. https://doi.org/10.1016/j.marpetgeo.2019.05.001.

Abrams , M.A., Apanel , A.M., Timoshenko, O.M., Kosenkova , N.N., 1999. Oil Families and Their Potential Sources in the Northeastern Timan Pechora Basin, Russia. AAPG Bulletin 83, 553-577. https://doi.org/10.1306/00AA9BF6-1730-11D7-8645000102C1865D.

Aizenshtat, Z. and Amrani, A., 2004. Significance of δ34S and evaluation of its imprint on sedimentary organic matter: I. The role of reduced sulfur species in the diagenetic stage: A conceptual review. The Geochemical Society Special Publications 9, 15-33. https://doi.org/10.1016/S1873-9881(04)80004-X.

Alkhafaji, M.W., Aljubouri, Z.A., Aldobouni, I.A., Littke, R., 2015. Hydrocarbon potential of Ordovician–Silurian successions in Akkas field, western desert of Iraq. AAPG Bulletin 99, 617-637. https://doi.org/10.1306/10221413197.

Amit, O., 1978. Organochemical Evaluation of Gevar'am Shales (Lower Cretaceous), Israel, as Possible Oil Source Rock. American Association of Petroleum Geologists Bulletin 62, 827-836.

Amit, O., Aizenshtat, Z., Pinski, I., 1979. The role of kerogen constituents in oil generation in the Gevar'am Formation (Lower Cretaceous), Israel. Organic Geochemistry 1, 237-241. https://doi.org/10.1016/0146-6380(79)90026-3.

Amit, O. and Bein, A., 1979a. The genesis of the asphalt in the Dead Sea area. Journal of Geochemical Exploration 11, 211-225. https://doi.org/10.1016/0375-6742(79)90001-3.

Amit, O. and Bein, A., 1979b. The Genesis of the Zohar Gas as Deduced from its Chemical and Carbon Isotope Composition. Journal of Petroleum Geology 2, 95-100.

Armstrong, H.A., Abbott, G.D., Turner, B.R., Makhlouf, I.M., Muhammad, A.B., Pedentchouk, N., Peters, H., 2009. Black shale deposition in an Upper Ordovician–Silurian permanently stratified, peri-glacial basin, southern Jordan. Palaeogeography, Palaeoclimatology, Palaeoecology 273, 368-377. https://doi.org/10.1016/j.palaeo.2008.05.005.

Avrahamov, N., Gelman, F., Yechieli, Y., Aizenshtat, Z., Nissenbaum, A., Sivan, O., 2015. Proposed sources of methane along the Dead Sea Transform. Chemical Geology 395, 165-175. https://doi.org/10.1016/j.chemgeo.2014.11.026.

Baskin, D.K. and Jones, R.W., 1993. Prediction of Oil Gravity Prior to Drill-Stem Testing in Monterey Formation Reservoirs, Offshore California. AAPG Bulletin 77, 1479-1487. https://doi.org/10.1306/BDFF8EB6-1718-11D7-8645000102C1865D.

Baskin, D.K. and Peters, K.E., 1992. Early Generation Characteristics of a Sulfur-Rich Monterey Kerogen. AAPG Bulletin 76, 1-13. https://doi.org/10.1306/BDFF874A-1718-11D7-8645000102C1865D.

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. https://doi.org/10.1016/j.orggeochem.2007.03.004.

Bein, A., Feinstein, S., Aizenshtat, Z., Weiler, Y., 1984. Potantial source rocks in Israel: a geochemical evaluation, Israel Geological Survey.

Bein, A. and Sofer, Z., 1987. Origin of Oils in Helez Region, Israel—Implications for Exploration in the Eastern Mediterranean. AAPG Bulletin 71, 65-75. https://doi.org/10.1306/94886D49-1704-11D7-8645000102C1865D.

Bialik, M.O., Korngreen, D., Benjamini, C., 2012. Lithofacies and cyclicity of Mohilla evaporite basins on the rifted margin of the Levant in the Late Triassic, Makhtesh Ramon, southern Israel. Sedimentology 59, 2097-2124. https://doi.org/10.1111/j.1365-3091.2012.01336.x.

Brassell, S.C., Eglinton, G., Maxwell, J.R., Philp, R.P., 1978. Natural Background of Alkanes in the Aquatic Environment, In: Hutzinger, O., Van Lelyveld, I.H. and Zoeteman, B.C.J. (Ed.), Aquatic Pollutants. Pergamon, Amsterdam, pp. 69-86.

Bray, E.E. and Evans, E.D., 1961. Distribution of n-paraffins as a clue to recognition of source beds. Geochimica et Cosmochimica Acta 22, 2-15. https://doi.org/10.1016/0016-7037(61)90069-2.

Budzinski, H., Garrigues, P., Connan, J., Devillers, J., Domine, D., Radke , M., Oudin, J.L., 1995. Alkylated phenanthrene distributions as maturity and origin indicators in crude oils and rock extracts. Geochimica et Cosmochimica Acta 59, 2043-2056. https://doi.org/10.1016/0016-7037(95)00125-5.

Calvo, R., Ayalon, A., Bein, A., Sass, E., 2011. Chemical and isotopic composition of diagenetic carbonate cements and its relation to hydrocarbon accumulation in the Heletz-Kokhav oil field (Israel). Journal of Geochemical Exploration 108, 88-98. https://doi.org/10.1016/j.gexplo.2010.10.008.

Carrales, M. and Martin, R.W., 1975. Sulfur Content of Crude Oils, U.S. Government Printing Office.

Chakhmakhchev, A. and Suzuki, N., 1995. Saturate biomarkers and aromatic sulfur compounds in oils and condensates from different source rock lithologies of Kazakhstan, Japan and Russia. Organic Geochemistry 23, 289-299. https://doi.org/10.1016/0146-6380(95)00018-A.

Chakhmakhchev, A., Suzuki, M., Takayama, K., 1997. Distribution of alkylated dibenzothiophenes in petroleum as a tool for maturity assessments. Organic Geochemistry 26, 483-489. https://doi.org/10.1016/S0146-6380(97)00022-3.

Cohen, Z., 1976. Early Cretaceous Buried Canyon: Influence on Accumulation of Hydrocarbons in Helez Oil Field, Israel. AAPG Bulletin 60, 108-114. https://doi.org/10.1306/83D9228F-16C7-11D7-8645000102C1865D.

Cohen, Z., Kaptsan, V., Flexer, A., 1990. The Tectonic Mosaic of the Southern Levant: Implications for Hydrocabon Prospects. Journal of Petroleum Geology 13, 437-462. https://doi.org/10.1111/j.1747-5457.1990.tb00858.x.

Cole, G.A., Abu-Ali, M.A., Aoudeh, S.M., Carrigan, W.J., Chen, H.H., Colling, E.L., Gwathney, W.J., Al-Hajji, A.A., Halpern, H.I., Jones, P.J., Al-Sharidi, S.H., Tobey, M.H., 1994. Organic Geochemistry of the Paleozoic Petroleum System of Saudi Arabia. Energy & Fuels 8, 1425-1442. https://doi.org/10.1021/ef00048a034.

Derin, B., 1974. The Jurassic of central and northern Israel. Ph.D. thesis., The Hebrew University of Jerusalem.

Didyk, B.M., Simoneit, B.R.T., Brassell, S.C., Eglinton, G., 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. Nature 272, 216-222. https://doi.org/10.1038/272216a0.

El Diasty, W.S., El Beialy, S.Y., Anwari, T.A., Peters, K.E., Batten, D.J., 2017. Organic geochemistry of the Silurian Tanezzuft Formation and crude oils, NC115 Concession, Murzuq Basin, southwest Libya. Marine and Petroleum Geology 86, 367-385. https://doi.org/10.1016/j.marpetgeo.2017.06.002.

El Diasty, W. and Moldowan, J.M., 2012. Application of biological markers in the recognition of the geochemical characteristics of some crude oils from Abu Gharadig Basin, north Western Desert – Egypt. Marine and Petroleum Geology 35, 28-40. https://doi.org/10.1016/j.marpetgeo.2012.03.001.

English, J.M., Lunn, G.A., Ferreira, L., Yacu, G., 2015. Geologic evolution of the Iraqi Zagros, and its influence on the distribution of hydrocarbons in the Kurdistan region. AAPG Bulletin 99, 231-272. https://doi.org/10.1306/06271413205.

Feinstein, S., 2013b. Oil and gas shows in the eastern Levant Basin, Israel: genetic groups and their distribution in the basin; how many "systems" are there? he Bat Sheva De Rothschild Seminar: Hydrocarbons Exploration and Development in the Levant Offshore: Perspectives and Challanges, Caesarea.

Feinstein, S., Aizenshtat, Z., Miloslavski, I., Gerling, P., Slager, J., McQuilken, J., 2001. Gas plays in the east Mediterranean offshore southwestern Israel. 20th International Meeting of Organic Geochemistry, Nancy, pp. 437-438.

Feinstein, S., Aizenshtat, Z., Miloslavski, I., Gerling, P., Slager, J., McQuilken, J., 2002. Genetic characterization of gas shows in the east Mediterranean offshore of southwestern Israel. Organic Geochemistry 33, 1401-1413. https://doi.org/10.1016/S0146-6380(02)00184-5.

Feinstein, S., Aizenshtat, Z., Miloslavski, I., Slager, J., Gerling, P., Snowdon, L.R., 1993. Migrational stratification of hydrocarbons in the eastern Mediterranean basin. AAPG International Conference and Exhibition, The Hague.

Feinstein, S., Aizenshtat, Z., Miloslavski, I., Slager, J., Gerling, P., Snowdon, L., 1993. Migrational stratification of hydrocarbons in the Eastern Mediterranean Basin. AAPG International Conference. American Association of Petroleum Geologists, The Hague, p. p.48.

Feinstein, S., Aizenshtat, Z., Miloslavsky, I., Goldberg, M., Obermagher, M., 2013a. Oil Groups in the East Mediterranean Continental Margin and Onshore, Israel. AAPG European Regional Conference. American Association of Petroleum Geologists, Barcelona.

Feinstein, S., Brooks, P., Fowler, M., Snowdon, L., Goldberg, M., Aizenshtat, Z., 1988. Oil families in the eastern Mediterranean offshore and southern Israel: biomarkers and trace elements analysis. Mediterranean Basins Conference. American Association of Petroleum Geologists, Nice.

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: Schidlowski, M., Golubic, S., Kimberley, M.M., McKirdySr, D.M. and Trudinger, P.A.

(Ed.), Early Organic Evolution. 1st ed. Springer, Berlin, Heidelberg, Heidelberg, pp. 336-356.

Fowler, M.G., Stasiuk, L.D., Hearn, M., Obermajer, M., 2004. Evidence for Gloeocapsomorpha prisca in Late Devonian source rocks from Southern Alberta, Canada. Organic Geochemistry 35, 425-441. https://doi.org/10.1016/j.orggeochem.2004.01.017.

Gardosh , M.A., Garfunkel , Z., Druckman, Y., Buchbinder, B., 2010. Tethyan rifting in the Levant Region and its role in Early Mesozoic crustal evolution, In: Homberg, C. and Bachmann, M. (Ed.), Evolution of the Levant Margin and Western Arabia Platform since the Mesozoic. 341st ed. Geological Society, London, pp. 9-36.

Gardosh, M.A. and Tannenbaum, E., 2014. The Petroleum Systems of Israel, In: Marlow, L., Kendall, C. and Yose, L. (Ed.), Memoir 106: Petroleum Systems of the Tethyan Region. American Association of Petroleum Geologists, Tulsa, pp. 179-216.

Gardosh, M., Weimer, P., Flexer, A., 2011. The sequence stratigraphy of Mesozoic successions in the Levant margin, southwestern Israel: A model for the evolution of southern Tethys margins. AAPG Bulletin 95, 1763-1793. https://doi.org/10.1306/02081109135.

Garfunkel, Z. and Ben-Avraham, Z., 1996. The structure of the Dead Sea basin. Tectonophysics 266, 155-176. https://doi.org/10.1016/S0040-1951(96)00188-6.

Gavrieli, I., Starinsky, A., Spiro, B., Aizenshtat, Z., Nielsen, H., 1995. Mechanisms of sulfate removal from subsurface calcium chloride brines: Heletz-Kokhav oilfields, Israel. Geochimica et Cosmochimica Acta 59, 3525-3533. https://doi.org/10.1016/0016-7037(95)00229-S.

Gavrieli, I., Starinsky, A., Spiro, B., Nielsen, H., Aizenshtat, Z., 1994. Sulfur Isotopes Evidence for Sulfate Removal Processes from Subsurface Brines, Heletz Formation (Lower Cretaceous), Israel (conference abstract), The Geological Society of Israel.

Geochem, 1995. Geochemical evaluation of samples from the Yam Yafo-1 and Bessor-1 wells. Report 95/9630/9631/001; prepared for Isramco inc., Geochem group limited.

Geochem, 1999. Geochemical data for the CHDST#7 gas and oil samples from the well Meged-2. Report 99/1427/001/01, Geochem Group Limited.

Geomark research inc., 1994. O.I.L.S report for Mango-1 well. Unpublished confidential report, Geomark research inc.

Geomark research inc., 2004. O.I.L.S reports for Meged wells 2 and 4. Unpublished report, Geomark research inc.

Gilboa, Y., Fligelman, H., Derin, B., 1990. Helez-Brur-Kokhav Field-Israel Southern Coastal Plain, In: Beaumont, E.A. and Foster, N.H. (Ed.), The Atlas of Oil and Gas Fields and the Treatise of Petroleum Geology. The American Association of Petroleum Geologists, Tulsa, pp. 319-345.

Grantham, P.J. and 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. https://doi.org/10.1016/0146-6380(88)90115-5.

He , M., Moldowan, M.J., Nemchenko-Rovenskaya , A., Kenneth, P.E., 2012. Oil families and their inferred source rocks in the Barents Sea and northern Timan-Pechora Basin, Russia. AAPG Bulletin 96, 1121-1146. https://doi.org/10.1306/10181111043.

He, N., Grice, K., Greenwood, P.F., 2019. The distribution and δ34S values of organic sulfur compounds in biodegraded oils from Peace River (Alberta Basin, western Canada). Organic Geochemistry 128, 16-25. https://doi.org/10.1016/j.orggeochem.2019.01.005.

Hill, R.J., Jarvie, D.M., Zumberge, J., Henry, M., Pollastro, R.M., 2007. Oil and gas geochemistry and petroleum systems of the Fort Worth Basin. AAPG Bulletin 91, 445-473. https://doi.org/10.1306/11030606014.

Hodairi, T.A. and Philp, R.P., 2012. Biomarker characteristics of crude oils from the Murzuq Basin, SW Libya. Journal of Petroleum Geology 35, 255-272. https://doi.org/10.1111/j.1747-5457.2012.00529.x.

Huang, H. and Pearson, M.J., 1999. Source rock palaeoenvironments and controls on the distribution of dibenzothiophenes in lacustrine crude oils, Bohai Bay Basin, eastern China. Organic Geochemistry 30, 1455-1470. https://doi.org/10.1016/S0146-6380(99)00126-6.

Hughes, W.B., Holba, A.G., Dzou, L.I.P., 1995. The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. Geochimica et Cosmochimica Acta 59, 3581-3598. https://doi.org/10.1016/0016-7037(95)00225-O.

Hughes, W.B., Holba, A.G., Dzou, L., , 1995. The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. Geochimica et Cosmochimica Acta 59, 3581-3598. https://doi.org/10.1016/0016-7037(95)00225-O.

Jarvie, D.M., 2001. Williston Basin petroleum systems: inferences from oil geochemistry and geology. The Mountain Geologist 38, 19-41.

Keeley, M.L., Dungworth, G., Floyd, C.S., Forbes, G.A., King, C., McGarva, R.M., Shaw, D., 1990. The Jurassic System in Northern Egypt: I. Regional stratigraphy and implications for hydrocarbon prospectivity. Journal of Petroleum Geology 13, 397-420. https://doi.org/10.1111/j.1747-5457.1990.tb00856.x.

Keeley, D.F., Hoffpauir, M.A., Meriwether, J.R., 1988. Solubility of aromatic hydrocarbons in water and sodium chloride solutions of different ionic strengths: benzene and toluene. J. Chem. Eng. Data 33, 87-89. https://doi.org/10.1021/je00052a006.

Koopmans, M.P., Schouten, S., Kohnen, M.E.L., Sinninghe Damsté, J.S., 1996. Restricted utility of aryl isoprenoids as indicators for photic zone anoxia. Geochimica et Cosmochimica Acta 60, 4873-4876. https://doi.org/10.1016/S0016-7037(96)00303-1.

Köster, J., Van Kaam- Peters, H.M.E., Koopmans, M.P., De Leeuw, J.W., Sinninghe Damsté, J.S., 1997. Sulphurisation of homohopanoids: Effects on carbon number distribution, speciation, and 22S/22R epimer ratios. Geochimica et Cosmochimica Acta 61, 2431-2452. https://doi.org/10.1016/S0016-7037(97)00110-5.

Kuo, L.-C., 1994. An experimental study of crude oil alteration in reservoir rocks by water washing. Organic Geochemistry 21, 465-479. https://doi.org/10.1016/0146-6380(94)90098-1.

Kutuzov, I., 2017. Study of the early stage immature oil produced from the Israeli oil shale. M.Sc. Dissertation, Ben Gurion University of the Negev.

Kutuzov, I., Rosenberg, Y.O., Bishop, A., Amrani, A., 2020. The Origin of Organic Sulphur Compounds and Their Impact on the Paleoenvironmental Record, In: Wilkes, H. (Ed.), Hydrocarbons, Oils and Lipids: Diversity, Origin, Chemistry and Fate. Springer, Cham.

Larter, S., Huang, H., Adams, J., Bennett, B., Snowdon, L.R., 2012. A practical biodegradation scale for use in reservoir geochemical studies of biodegraded oils. Organic Geochemistry 45, 66-76. https://doi.org/10.1016/j.orggeochem.2012.01.007.

Lillis, P.G. and Magoon, L.B., 2007. Petroleum systems of the San Joaquin Basin Province, California-geochemical characteristics of oil types. Chapter 9 in Petroleum systems and geologic assessment of oil and gas in the San Joaquin Basin Province, California, U.S. Geological Survey.

Li, M., Wang, T.G., Shi, S., Zhu, L., Fang, R., 2014. Oil maturity assessment using maturity indicators based on methylated dibenzothiophenes. Petroleum Science 11, 234-246. https://doi.org/10.1007/s12182-014-0336-3.

Loydell, D.K., Butcher, A., Frýda, J., 2013. The middle Rhuddanian (lower Silurian) 'hot' shale of North Africa and Arabia: An atypical hydrocarbon source rock. Palaeogeography, Palaeoclimatology, Palaeoecology 386, 233-256. https://doi.org/10.1016/j.palaeo.2013.05.027.

Lüning, S., Craig, J., Loydell, D.K., Štorch, P., Fitches, B., 2000. Lower Silurian `hot shales' in North Africa and Arabia: regional distribution and depositional model. Earth-Science Reviews 49, 121-200. https://doi.org/10.1016/S0012-8252(99)00060-4.

Lüning, S., Shahin, Y.M., Loydell, D., Al-Rabi, H.T., Masri, A., Tarawneh, B., Kolonic, S., 2005. Anatomy of a world-class source rock: Distribution and depositional model of Silurian organic-rich shales in Jordan and implications for hydrocarbon potential. AAPG Bulletin 89, 1397-1427. https://doi.org/10.1306/05250505014.

Luskin, T., Shteingolts, V., Leifman, I., 1997. Paleozoic petroleum system of the Middle East - A new potential in Israel. Abstract. AAPG International Conference and Exhibition, Vienna.

Luskin, T., Shteingolts, V., Soferstein, M., 2012. The Meged Oil Field – Introduction. Abstract. Israel Geological Society Annual Meeting, Ashkelon, p. 93.

Mackenzie, A.S., Brassell, S.C., Eglinton, G., Maxwell, J.R., 1982. Chemical Fossils: The Geological Fate of Steroids. Science 217, 491-504. https://doi.org/10.1126/science.217.4559.491.

Magoon, L.B. and Dow, W.G. (Ed.), 1994. The Petroleum System-From Source to Trap, 60th ed.. American Association of Petroleum Geologists, Tulsa, Oklahoma.

Marynowski, L., Narkiewicz, M., Grelowski, C., 2000. Biomarkers as environmental indicators in a carbonate complex, example from the Middle to Upper Devonian, Holy Cross Mountains, Poland. Sedimentary Geology 137, 187-212. https://doi.org/10.1016/S0037-0738(00)00157-3.

May, P.R. and Goldberg, M., 1984. Oil and Gas Developments in Israel in 1983. AAPG Bulletin 68, 1430-1432. https://doi.org/10.1306/AD461949-16F7-11D7-8645000102C1865D.

Moldowan, M.J., Seifert, W.K., Gallegos, E.J., 1985. Relationship Between Petroleum Composition and Depositional Environment of Petroleum Source Rocks. AAPG Bulletin 69, 1255-1268. https://doi.org/10.1306/AD462BC8-16F7-11D7-8645000102C1865D.

Mostafa, A.R. and Younes, M.A., 2001. Significance of organic matter in recording paleoenvironmental conditions of the Safa Formation coal sequence, Maghara Area, North

Sinai, Egypt. International Journal of Coal Geology 47, 9-21. https://doi.org/10.1016/S0166-5162(01)00022-2.

[dataset] National Institute for Petroleum and Energy Research, 1995. Crude Oil Analysis Database: Department of Energy, 1st. https://catalog.data.gov/dataset/crude-oil-analysis-coa-database-9e839.

Needham, D.L., Pettingill, H.S., Christensen, C.J., Ffrench, J., Karcz, Z.K., 2017. The Tamar Giant Gas Field: Opening the Subsalt Miocene Gas Play in the Levant Basin, In: Merrill, R.K. and Sternbach, C.A. (Ed.), Memoir 113: Giant Fields of the decade 2000-2010. The American Association of Petroleum Geologists, Tulsa, pp. 221-256.

Nissenbaum, A., 1984. Methane derived organic matter and carbonates. Organic Geochemistry 5, 187-192. https://doi.org/10.1016/0146-6380(84)90005-6.

Nissenbaum, A. and Goldberg, M., 1980. Asphalts, heavy oils, ozocerite and gases in the Dead Sea Basin. Organic Geochemistry 2, 167-180. https://doi.org/10.1016/0146-6380(80)90007-8.

Nissenbaum, A., Goldberg, M., Aizenshtat, Z., 1985. Immature Condensate from Southeastern Mediterranean Coastal Plain, Israel. American Association of Petroleum Geologists Bulletin 69, 946-949.

Obermajer, M., Fowler, M.G., Snowdon, L.R., 1998. A Geochemical Characterization and a Biomarker Re-Appraisal of the Oil Families from Southwestern Ontario, Canada. CSPG Bulletin 43, 350-378.

Obermajer, M., Fowler, M.G., Snowdon, L.R., Macqueen, R.W., 2000. Compositional variability of crude oils and source kerogen in the Silurian carbonate–evaporite sequences of the eastern Michigan Basin, Ontario, Canada. CSPG Bulletin 48, 307-322. https://doi.org/10.2113/48.4.307.

Obermajer, M., Osadetz, K.G., Fowler, M.G., Silliman, J., Hansen, W.B., Clark, M., 2002. Delineating compositional variabilities among crude oils from Central Montana, USA, using light hydrocarbon and biomarker characteristics. Organic Geochemistry 33, 1343-1359. https://doi.org/10.1016/S0146-6380(02)00118-3.

Obermajer, M., Osadetz, K.G., Fowler, M.G., Snowdon, L.R., 1999. Geochemistry and Familial Association of Crude Oils From the Birdbear Formation in Southeastern Saskatchewan, Williston Basin. CSPG Bulletin 47, 255-269.

Orr, W.L., 1986. Kerogen/asphaltene/sulfur relationships in sulfur-rich Monterey oils. Organic Geochemistry 10, 499-516. https://doi.org/10.1016/0146-6380(86)90049-5.

Orr, W.L., 2001. Evaluating kerogen sulfur content from crude oil properties: cooperative Monterey organic geochemistry study, In: Isaacs, C.M. and Rullkötter, J. (Ed.), The Monterey Formation—from Rocks to Molecules. Columbia University Press, New York, pp. 348-367.

Osadetz, K.G., Brooks, P.W., Snowdon, L.R., 1992. Oil Families and Their Sources in Canadian Williston Basin, (Southeastern Saskatchewan and Southwestern Manitoba). CSPG Bulletin 40, 254-273.

Palacas, G., Anders, E., King, J., 1984. South Florida Basin-A Prime Example of Carbonate Source Rocks of Petroleum, In: Palacas, J.G. (Ed.), Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks. The America Association of Petroleum Geologists, Tulsa, pp. 71-96.

Palmer, S.E., 1993. Effect of Biodegradation and Water Washing on Crude Oil Composition, In: Engel, H.M. and Macko, S.A. (Ed.), Organic Geochemistry: Principles and Applications. Springer, Boston.

Peters, K.E. and Cassa, M.R., 1994. Applied Source Rock Geochemistry, In: Magoon, L.B. and Dow, W.G., The Petroleum System—From Source to Trap. American Association of Petroleum Geologists, Tulsa, pp. 93-120.

Peters, K.E. and Cassa, M.R., 1994. Applied Source Rock Geochemistry, In: Magoon, B.L. and Dow, G.W. (Ed.), The Petroleum System- From source to Trap. The America Association of Petroleum Geologists, Tulsa, pp. 93-120.

Peters, K.E. and Moldowan, J.M., 1991. Effects of source, thermal maturity, and biodegradation on the distribution and isomerization of homohopanes in petroleum. Organic Geochemistry 17, 47-61. https://doi.org/10.1016/0146-6380(91)90039-M.

Peters, K.E., Walters, C.C., Moldowan, M.J., 2005. The Biomarker Guide, 2nd ed.. Cambridge University Press, New York.

Peters, K.E., Walters, C.C., Moldowan, M.J., 2005. The Biomarker Guide, 2nd ed.. The Press Syndicate of the University of Cambridge, Cambridge.

Radke, M., 1988. Application of aromatic compounds as maturity indicators in source rocks and crude oils. Marine and Petroleum Geology 5, 224-236. https://doi.org/10.1016/0264-8172(88)90003-7.

Radke, M., Welte, D.H., Willsch, H., 1986. Maturity parameters based on aromatic hydrocarbons: Influence of the organic matter type. Organic Geochemistry 10, 51-63. https://doi.org/10.1016/0146-6380(86)90008-2.

Radke, M. and Willsch, H., 1994. Extractable alkyldibenzothiophenes in Posidonia Shale (Toarcian) source rocks: Relationship of yields to petroleum formation and expulsion. Geochimica et Cosmochimica Acta 58, 5223-5244. https://doi.org/10.1016/0016-7037(94)90307-7.

Rampen, S.W., Abbas, B.A., Schouten, S., Sinninghe Damsté, J.S., 2010. A comprehensive study of sterols in marine diatoms (Bacillariophyta): Implications for their use as tracers for diatom productivity. Limnology and Oceanography 55, 91-105. https://doi.org/10.4319/lo.2010.55.1.0091.

Requejo, A.G., Sassen, R., Kennicutt II, M.C., Kvedchuk, I., McDonald, T., Denoux, G., Comet, P., Brooks, J.M., 1995. Geochemistry of oils from the northern Timan-Pechora Basin, Russia. Organic Geochemistry 23, 205-222. https://doi.org/10.1016/0146-6380(94)00127-M.

Rosenberg, O.Y., Meshoulam, A., Said-Ahmad, W., Shawar, L., Dror, G., Reznik, J.I., Feinstein, S., Amrani, A., 2017. Study of thermal maturation processes of sulfur-rich source rock using compound specific sulfur isotope analysis. Organic Geochemistry 112, 59-74. doi.org/10.1016/j.orggeochem.2017.06.005.

Rullkötter, J., Spiro, B., Nissenbaum, A., 1985. Biological marker characteristics of oils and asphalts from carbonate source rocks in a rapidly subsiding graben, Dead Sea, Israel. Geochimica et Cosmochimica Acta 49, 1357-1370. https://doi.org/10.1016/0016-7037(85)90286-8.

Schwark, L. and Empt, P., 2006. Sterane biomarkers as indicators of palaeozoic algal evolution and extinction events. Palaeogeography, Palaeoclimatology, Palaeoecology 240, 225-236. https://doi.org/10.1016/j.palaeo.2006.03.050.

Seifert, W.K. and Moldowan, M.J., 1978. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. Geochimica et Cosmochimica Acta 42, 77-95. https://doi.org/10.1016/0016-7037(78)90219-3.

Sharaf, L.M., 2003. Source rock evaluation and geochemistry of condensates and natural gases, offshore Nile delta, Egypt. Journal of Petroleum Geology 26, 189-209. https://doi.org/10.1111/j.1747-5457.2003.tb00025.x.

Sinninghe Damsté, J.S., Kenig, F., Koopmans, M.P., Köster, J., Schouten, S., Hayes, J.M., de Leeuw, J.W., 1995. Evidence for gammacerane as an indicator of water column stratification. Geochimica et Cosmochimica Acta 59, 1895-1900. https://doi.org/10.1016/0016-7037(95)00073-9.

Sinninghe Damsté, J.S., Van Duin, A.C.T., Hollander, D., Kohnen, M.E.L., De Leeuw, J.W., 1995. Early diagenesis of bacteriohopanepolyol derivatives: Formation of fossil homohopanoids. Geochimica et Cosmochimica Acta 59, 5141-5157. https://doi.org/10.1016/0016-7037(95)00338-X.

Słowakiewicz, M., Blumenberg, M., Więcław, D., Röhling, H.-G., Scheeder, G., Hindenberg, K., Leśniak, A., Idiz, E.F., Tucker, M.E., Pancost, R.D., Kotarba, M.J., Gerling, J.P., 2018. Zechstein Main Dolomite oil characteristics in the Southern Permian Basin: I. Polish and German sectors. Marine and Petroleum Geology 93, 356-375. https://doi.org/10.1016/j.marpetgeo.2018.03.023.

Snowdon, L.R., Beauvilain, J.C., Davies, G.R., 1998. Debolt Formation Oil-Source Systems: 1. Crude Oil Families in the Dunvegan-Blueberry Area of Alberta and British Columbia. CSPG Bulletin 46, 266-275.

Snowdon, L.R., Davies, G.R., Beauvilian, J.C., 1998. Debolt Formation Oil-Source Systems: 2. Authigenic Petroleum Source Potential. Bulletin of Canadian Petroleum Geology 46, 276-287.

Sofer , Z., 1984. Stable Carbon Isotope Compositions of Crude Oils: Application to Source Depositional Environments and Petroleum Alteration. AAPG Bulletin 68, 31-49. https://doi.org/10.1306/AD460963-16F7-11D7-8645000102C1865D.

Spaak, G., Edwards, D.S., Allen, H.J., Grotheer, H., Summons, R.E., Coolen, M.J.L., Grice, K., 2018. Extent and persistence of photic zone euxinia in Middle–Late Devonian seas – Insights from the Canning Basin and implications for petroleum source rock formation. Marine and Petroleum Geology 93, 33-56. https://doi.org/10.1016/j.marpetgeo.2018.02.033.

Spiro, B., Welte, D.H., Rullkötter, J., Schaefer, R.G., 1983. Asphalts, Oils, and Bituminous Rocks from the Dead Sea Area—A Geochemical Correlation Study. AAPG Bulletin 67, 1163-1175. https://doi.org/10.1306/03B5B71D-16D1-11D7-8645000102C1865D.

Tannenbaum, E., 1983. Researches in the Geochemistry of Oils and Asphalts in the Dead Sea Area. Ph.D. Dissertation (In Hebrew, English abstract) , The Hebrew University.

Tannenbaum, E., 1995. Geochemical Characterization of Potential Source Rocks and Oils from the Southern Coastal Plain, Israel. Report submitted to Israel National Oil Company and Naphtha, Kimron Oil & Minerals.

Tannenbaum, E., 1995. Petroleum Evaluation of the Southern Coastal Plain, Israel. Report submitted to The Israel National Oil company and Naphta, Kimron Oil & Minerals.

Tannenbaum, E. and Aizenshtat, Z., 1984. Formation of immature asphalt from organic-rich carbonate rocks-ll. Correlation of maturation indicators. Organic Geochemistry 6, 503-511. https://doi.org/10.1016/0146-6380(84)90073-1.

Tannenbaum, E. and Aizenshtat, Z., 1985. Formation of immature asphalt from organic-rich carbonate rocks—I. Geochemical correlation. Organic Geochemistry 8, 181-192. https://doi.org/10.1016/0146-6380(85)90037-3.

Tannenbaum, E. and Lewan, M.D., 2003. Regional Upper Cretaceous (Senonian) petroleum source rocks in the Middle East and North America. AAPG International Conference. American Association of Petroleum Geologists, Salt Lake City.

ten Haven, H.L., de Leeuw, J.W., Rullkötter, K., Sinninghe Damsté, J.S., 1987. Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator. Nature 330, 641-643. https://doi.org/10.1038/330641a0.

Thompson, K.F.M., 1983. Classification and thermal history of petroleum based on light hydrocarbons. Geochimica et Cosmochimica Acta 47, 303-316. https://doi.org/10.1016/0016-7037(83)90143-6.

Thompson, K.F.M., 1987. Fractionated aromatic petroleums and the generation of gas-condensates. Organic Geochemistry 11, 573-590. https://doi.org/10.1016/0146-6380(87)90011-8.

Tschopp, H.J., 1956. The Oil find of Heletz, Israel. Bull. Swiss Ass. Pet.-Geol. & Eng. 22, 41-54. https://doi.org/10.5169/seals-188030.

van Kaam-Peters, H.M.E., Köster, J., van der Gaast, S.J., Dekker, M., de Leeuw, J.W., Sinninghe Damsté, J.S., 1998. The effect of clay minerals on diasterane/sterane ratios.

Geochimica et Cosmochimica Acta 62, 2923-2929. https://doi.org/10.1016/S0016-7037(98)00191-4.

Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter. Organic Geochemistry 9, 83-99. https://doi.org/10.1016/0146-6380(86)90089-6.

9 *Tables*

Table 1. Geographical area, reservoir depth and list of analysis performed on crude oil samples in this study

Group	**Sample name**	**Depth interval (m)**	**Reservoir formation**	**Sample type**
Dead Sea	Lot-1	1268-1278	Saharonim	Heavy oil
	Zuk Tamrur-3	1938-1950 (a); 1873-1934 (b)	Gevanim	Medium oil
	Zuk-Tamrur-1	1859-1863	Gevanim	Medium-light oil
	Gurim-4	993-1003	Hatira	Medium-heavy oil
	Emunah-1	1700-1720	Gevanim	Light oil
	Kidod-3	1251-1271	Zohar	Medium-heavy oil
Meged	Meged-2	4078-4093	Mohilla	Light oil
	Meged-5	4365-4380	Mohilla	Light oil
Coastal Plain	Kokhav-6	1648-1656	Helez	Medium oil
	Kokhav-1	????	Helez	Medium oil
	Kokhav-14	????	???	Medium oil
	Kokhav-5	????	???	Medium oil
	Kokhav-26	1325-1372 (a); 1567-1568 (b)	Helez and Talmey Yafe?	Medium oil
	Kokhav-29	1491-1516	Helez	Medium oil
	Helez-27	1487-1512	Helez	Medium oil
	Helez-2	1521-1522	Helez	Medium oil
	Helez-40	1500-1505	Helez	Medium oil
	Helez-1	1497-1499	Helez	Medium oil
	Ashdod-2	2562	Zohar	Medium oil
	Brur-5	????	????	Medium oil
Yam	Yam-2	5309-5317	Zohar	Light oil

	Yam-Yafo-1	4894-5034	Zohar and Karmon	Light oil
Offshore Sinai	Ziv-1	2979	Talmey Yafe	Light oil
	Mango-1	2387-2416 (a); 2638-2663 (b)	L. Createceous to Santonian shales and limestones	Light oil

Table 2. Results of bulk, elemental properties, and biodegradation parameters for the oil samples examined in this study.

Sample name	API gravity (°)	Oil %S	Ni/V	%Sat	%Arom	%Resin	%Asph	Evaporation loss %
Lot-1	9 [1]	4.2	0.9	24	23	8	45	0
Zuk Tamrur-3	21.5 [6]	3.8	n.d.	41	21	16	17	4
Zuk Tamrur-1	27 [1]	3.0 [6]	0.8	41	41	9	9	0
Gurim-4	17 [2]	4.4	0.8	67	18	6	12	2
Emunah-1	31.4 [6]	2.2	n.d.	69	19	4	8	0
Kidod-3	n.d.	n.d.	0.05	26	28	17	29	0
Meged-5	40 [6]	0.1	n.d.	47	28	1	1	23
Meged-2	37.8 [3]	0.3	n.d.	47	20	3	4	26
Kokhav-6	n.d.	n.d.	n.d.	38	28	3	14	20
Kokhav-1	n.d.	n.d.	n.d.	36	27	3	19	19
Kokhav-14	n.d.	n.d.	n.d.	32	18	12	29	12
Kokhav-5	n.d.	n.d.	n.d.	49	22	4	22	6
Kokhav-26 a	n.d.	n.d.	18	40	38	10	12	0
Kokhav-26 b	n.d.	n.d.	9	48	38	7	7	0
Helez-27	n.d.	n.d.	n.d.	39	26	3	20	16

Helez-2	n.d.	n.d.	n.d.	37	24	2	24	15
Helez-40	n.d.	n.d.	n.d.	63	24	6	8	0
Helez-1	28.4 [8]	1.6 [8]	20	51	36	6	7	0
Ashdod-2	33 [4]	n.d.	n.d.	59	25	4	12	0
Brur-5	n.d.	n.d.	n.d.	45	26	6	15	10
Yam-2	47	0	16	63	22	2	4	10
Yam Yafo-1	44 [4]	0[7]	5[7]	70	14	2	1	13
Mango-1a	36.0[5]	0.07[5]	0.75[5]	61[5]	26[5]	13[5]	0[5]	0
Mango-1b	38.0[5]	0.06[5]	1[5]	62[5]	25[5]	11[5]	2[5]	0
Ziv-1	n.d.	n.d.	7.1	78	13	7	2	0

Table references: [1] Tannebaum (1983), [2] Tippee (2001) or 18.5 at AAPG petroleum development in Israel for 1984 and 1983, [3] Geomark research inc. (2004), [4] Gardosh and Tannenbaum (2014), [5] Geomark research inc. (1994), [6] Kutuzov, (2017), [7] Geochem (1995), [8] Tschopp (1956). n.d.- not determined.

Table 3. Gasoline fraction range light hydrocarbons ratios in the investigated oils

Sample name	**PI-1** [a]	**PI-2** [b]	**Q** [c]	**R** [d]	**S** [e]	**T** [f]	**B** [g]
Kidod-3	0.67	3.64	0.14	0.10	6.70	43.84	0.22
Gurim-4	0.11	0.61	0.02	0.02	216.23	113.14	0.46
Zuk Tamrur-1	2.89	42.63	4.73	3.19	1.52	28.36	0.01
Zuk Tamrur-3a	1.61	8.31	0.35	0.31	176.58	50.47	0.06
Zuk Tamrur-3b	1.72	12.71	0.53	0.54	26.99	17.30	0.11
Emunah-1	2.72	39.30	3.71	2.46	1.19	0.76	0.54
Meged-2	2.93	23.57	1.93	0.81	0.58	0.89	1.39
Meged-5	2.92	25.86	2.13	0.89	0.34	0.83	1.35
Helez-1	1.58	21.38	1.13	0.66	12.24	8.40	0.18
Kokhav-6	1.30	12.32	0.60	0.32	25.88	13.67	0.23
Kokhav-26a	1.44	18.11	0.92	0.53	14.20	8.30	0.23
Kokhav-26b	1.64	23.61	1.46	0.71	4.89	4.09	0.35
Kokhav-29	1.11	22.66	0.90	0.37	0.00	2.30	1.19
Yam-2	2.20	24.60	1.27	0.60	1.98	2.87	0.58
Yam Yafo-1	2.85	15.94	0.87	0.37	n.d.	43.29	0.06
Ziv-1	2.64	20.33	3.84	0.46	3.97	6.13	0.35
Mango-1a	1.59	9.20	1.20	0.20	59.45	102.34	0.05
Mango-1b	0.63	20.12	0.43	0.39	1.22	15.98	0.16

a: PI-1-(Isoheptane value) =(2-methylhexane+3-methylhexane)/Σ1c3-, 1t3-, 1t2- dimethylcyclopentanes; b: PI-2-(Heptane value)=(n-heptane×100)/Σ compounds eluting between cyclohexane and methylcyclohexane; c:Q-normal hexane/methylcyclopentane ratio; d: R-normal heptane/methylcyclohexane ratio; e: S-3-methylpentane/benzene ratio; f: T-methylcyclohexane/toluene ratio; g:B- toluene/n-heptane;

Table 4. Saturate and aromatic fractions parameters used for analysis of secondary alteration and environment of deposition

Sample name	**CPI** [a]	**Pr/Ph** [b]	**DBT/Phen** [c]	**St C_{28}/C_{29}** [d]	**Ster/Hop** [e]	**C_{29}/C_{30} Hop** [f]	**C_{35}/C_{34} Hop** [g]	**$C_{35}S/C_{34}S$ Hop** [h]	**Tet/C_{23}** [i]	**C_{22}/C_{21}** [j]	**C_{24}/C_{23}** [k]	**C_{26}/C_{25}** [l]
Lot-1	0.96	0.51	1.26	1.18	n.d.	1.23	1.14	1.15	0.23	1.21	0.32	0.43
Zuk Tamrur-3	0.92	0.29	1.06	0.83	0.43	1.34	1.39	1.43	0.11	1.05	0.33	0.82
Zuk Tamrur-1	0.94	0.42	n.d.	1.15	n.d.	1.27	1.45	1.42	0.27	0.94	0.34	0.79
Gurim-4	0.95	0.41	0.86	0.87	0.38	1.49	1.59	1.68	0.31	1.08	0.38	0.85
Emunah-1	0.99	0.53	1.00	0.77	0.48	1.28	1.44	1.37	0.31	0.74	0.44	0.87
Kidod-3	0.95	0.49	n.d.	1.24	n.d.	1.17	1.04	1.01	0.26	0.98	0.38	0.88
Meged-5	1.04	0.92	0.08	0.50	0.41	0.62	0.36	0.37	4.05	0.24	0.44	n.d.
Meged-2	1.01	0.88	0.17	0.43	0.34	0.65	0.38	0.38	4.19	0.27	0.50	0.94
Kokhav-6	0.86	1.00	1.07	0.26	0.21	0.63	1.29	1.30	2.84	0.36	0.66	1.12
Kokhav-1	0.87	0.83	0.67	0.29	0.21	0.63	1.39	1.42	2.67	0.80	0.69	n.d.
Kokhav-14	0.87	0.91	0.99	0.24	0.21	0.65	1.31	1.29	2.98	n.d.	n.d.	n.d.
Kokhav-5	0.87	0.72	0.86	0.32	0.21	0.71	1.42	1.42	n.d.	n.d.	n.d.	n.d.
Kokhav-26 a	0.89	1.31	n.d.	0.35	n.d.	0.55	1.24	1.08	3.25	0.50	0.79	0.88
Kokhav-26 b	0.88	1.12	n.d.	0.40	n.d.	0.55	1.43	1.39	3.43	0.57	0.73	1.11
Kokhav-29	0.89	0.92	n.d.	0.38	n.d.	0.49	1.46	1.42	2.93	0.50	0.71	0.95
Helez-27	0.90	1.09	0.64	0.24	0.23	0.69	1.37	1.41	2.33	0.37	0.55	n.d.
Helez-2	0.90	0.91	0.77	0.35	0.24	0.68	1.33	1.38	2.44	0.39	0.83	0.41
Helez-40	0.90	0.80	0.94	0.38	0.23	0.67	1.32	1.23	2.10	n.d.	n.d.	n.d.

Helez-1	0.89	1.17	n.d.	0.35	n.d.	0.56	1.49	1.47	3.20	0.54	0.76	0.98
Ashdod-2	0.87	0.95	1.04	0.25	0.25	0.56	1.23	1.25	3.44	0.42	0.91	n.d.
Brur-5	0.91	0.97	0.64	0.31	0.25	0.70	1.37	1.31	1.53	n.d.	n.d.	n.d.
Yam-2	0.96	1.22	0.10	n.d.	1.12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Yam Yafo-1	0.98	1.48	0.07	n.d.	1.90	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mango-1a	1.13	1.63	n.d.	0.64	0.12	0.37	0.39	0.38	5.33	0.57	0.61	2.24
Mango-1b	1.13	1.83	n.d.	0.59	0.10	0.34	0.48	0.50	7.58	0.51	0.64	2.19
Ziv-1	1.25	2.24	n.d.	0.39	0.05	0.43	0.45	0.46	4.61	2.67	0.78	0.84

a: CPI- carbon preference index= $[\Sigma(nC_{25}\text{-}nC_{33})_{odd}/\Sigma(nC_{24}\text{-}nC_{32})_{even} + \Sigma(nC_{25}\text{-}nC_{33})_{odd}/\Sigma(nC_{26}\text{-}nC_{34})_{even}]/2.$, b: Pr/Ph=pristane/phytane c: DBT/Phen=dibenzothiophene/phenanthrene (Hughes et al., 1995), d: St C_{28}/C_{29}=C_{28} steranes (%)/ C_{29} steranes (%), e:Ster/Hop= Σsteranes/Σhopanes, f: C_{29}/C_{30} Hop= C_{29} 30-norhopane/hopane, g: C_{35}/C_{34} Hop= C_{35} homohopanes/C_{34} homohopanes, h: $C_{35}S/C_{34}S$ Hop= $C_{35}S/C_{34}S$ homohopanes, i: Tet/C_{23}= C_{24} tetracyclic terpane/ C_{23} tricyclic terpane, j: C_{22}/C_{21}= C_{22} tricyclic terpane/ C_{21} tricyclic terpane , k: C_{24}/C_{23}= C_{24} tricyclic terpane/ C_{23} tricyclic terpane , l: C_{26}/C_{25}= C_{26} tricyclic terpane/ C_{25} tricyclic terpane. n.d.- not determined.

Table 5. Saturate and aromatic fractions indices used for estimation of thermal maturation degree of oils analyzed

Sample name	**C_{31} hopane 22S/(22S+22R)** [a]	**Ts/(Ts+Tm)** [b]	**C_{29} sterane 20S/(20S+20R)** [c]	**C_{29} sterane ββ/(ββ+αα)** [d]	**MPI-1** [e]	**%Rc1** [f]	**MDR** [g]	**%Rc2** [h]	**Tmax (calc.)** [i]
Lot-1	0.60	0.24	0.57	0.58	0.76	0.84	1.2	0.65	430
Zuk Tamrur-3	0.57	0.15	0.53	0.56	0.75	0.84	1.8	0.70	434
Zuk Tamrur-1	0.52	0.73	0.45	0.56	n.d.	n.d.	n.d.	n.d.	n.d.
Gurim-4	0.60	0.09	0.50	0.50	0.87	0.91	2.1	0.72	435
Emunah-1	0.57	0.12	0.53	0.56	0.87	0.91	2.5	0.74	438
Kidod-3	0.59	0.13	0.56	0.57	0.82	0.88	1.7	0.69	433
Meged-5	0.59	0.55	0.50	0.51	0.74	0.83	6.1	1.21	450
Meged-2	0.57	0.49	0.47	0.52	0.87	0.91	4.5	0.85	445
Kokhav- 6	0.57	0.41	0.51	0.53	0.81	0.87	2.1	0.72	435
Kokhav-1	0.61	0.44	0.49	0.50	0.74	0.83	2.1	0.72	435
Kokhav-14	0.57	0.42	0.49	0.53	0.77	0.85	1.9	0.71	435
Kokhav-5	0.60	0.43	0.53	0.56	0.92	0.94	2.2	0.72	436
Kokhav-26a	0.59	0.42	0.51	0.51	0.54	0.71	1.5	0.67	432
Kokhav-26b	0.58	0.45	0.52	0.51	0.55	0.71	1.9	0.70	434
Kokhav-29	0.58	0.43	0.53	0.53	0.56	0.72	1.8	0.70	434
Helez-27	0.59	0.44	0.49	0.52	0.79	0.86	2.6	0.74	438

Helez-2	0.62	0.46	0.47	0.51	0.88	0.91	2.5	0.73	437
Helez-40	0.58	0.41	0.48	0.55	0.75	0.84	2.1	0.72	436
Helez-1	0.58	0.43	0.52	0.53	0.58	0.73	1.9	0.70	434
Ashdod-2	0.58	0.49	0.49	0.54	0.82	0.88	2.1	0.72	435
Brur-5	0.63	0.51	0.46	0.55	0.84	0.89	2.4	0.73	437
Yam-2	n.d.	n.d.	n.d.	n.d.	1.13	1.07	11.6	1.4	482
Yam Yafo-1	n.d.	n.d.	n.d.	n.d.	0.98	0.98	23.5	2.2	543
Mango-1a	0.56	0.76	0.60	0.30	0.72	0.82	3.4	0.76	441
Mango-1b	0.57	0.77	0.67	0.32	0.72	0.82	3.9	0.79	443
Ziv-1	0.57	0.65	0.51	0.42	0.45	0.65	1.9	0.70	434

a: C_{31} hopane 22S/(22S+22R) = C_{31}22S homohopane/ (C_{31} 22S homohopane+ C_{31} 22R homohopane), b: Ts/(Ts+Tm) = C_{27} 18α-trisnorneohopane/17α-trisnorhopane, c: C_{29} sterane 20S/(20S+20R) = ratio of epimers of 5α(H),14α(H),17αβ(H)-ethylsterane, d: C_{29} sterane ββ/(ββ+αα) = 5α(H),14β(H),17β(H)/[5α(H),14β(H),17β(H) + 5α(H),14α(H),17α(H) 20R ethylsteranes], e:MPI-1- Methylphenanthrene index= 1.5(2-MP + 3-MP)/(Phenanthrene + 1-MP + 9-MP) (Radke, 1988), f: %Rc1-Calculated vitrinite reflectance (%Rc)= 0.61 $\times$ MPI-1 + 0.38 (Radke, 1988), g: MDR- methyl dibenzothiophene ratio= 4-methyldibenzothiophene/1- methyl dibenzothiophene (Radke, 1988), h: %Rc2-Calculated vitrinite reflectance (%Rc)= $0.4+0.3\times$MDR-$0.094\times$(MDR^2)+$0.011\times$(MDR^3), note- the samples of Yam-2 and Yam Yafo-1 were calculated based on the liner relation (%Rc)= 0.51+($0.073\times$MDR) (Radke, 1988). ,i: Tmax(calc.)-Calculated Tmax= $419+10.9\times$MDR-$1.74\times$(MDR^2)+$0.13\times$ (MDR^3), note- the samples of Yam-2 and Yam Yafo-1 were calculated based on the liner relation Tmax(calc.)= 423+($5.1\times$MDR) (Radke, 1988). n.d.- not determine

Table 6. Carbon stable isotopes ($\delta^{13}C$) of saturate and aromatic fraction of various oils studied as reported in various studies and reports.

Sample name	**$\delta^{13}C$ saturate (‰)**	**$\delta^{13}C$ aromatic (‰)**	**Source of data**
Sample 907/1, Barnea extract	-29.0	-27.4	Bein and Sofer, 1987
Ashqelon 2 oil	-28.5	-27.5	
Ashdod 2 oil	-28.5	-27.1	
Helez 27 oil	-28.3	-27.5	
Sample 931, Gevaram extract	-27.9	-26.2	
Sample 930, Gevaram extract	-27.0	-24.8	
Sample 960, Jurassic extract (east)	-27.8	-24.3	
Ein Said 1 asphalt, 987m	-29.3	-29.0	Tannenbaum, 1983
Amiaz 1 asphalt, 3450m	-29.3	-29.0	
Floating DS asphalt block	-29.3	-29.3	
Massada surface Asphalt	-28.4	-28.6	
Massada 1 oil, 1940m	-28.5	-28.3	
Massada 1 oil, 2100m	-28.5	-28.3	
Meged 2	-28.73	-27.78	Geochem, 1999
Meged 2	-28.96	-27.43	Geomark research inc., 2004
Meged 4	-29.74	-27.90	
Mango 1b	-28.86	-24.99	Geomark research inc., 1994
Mango 1a	-28.76	-25.23	
Yam-2	-28.04	-26.54	Feinstein et al., 2013a
Yam Yafo-1	-27.92	-26.07	Feinstein et al., 2013a