Geochemical characteristics of some crude oils from Alif Field in the Marib-Shabowah Basin, and source-related types

Mohammed Hail Hakimi a,*, Wan Hasiah Abdullah b

a Geology Department, Faculty of Applied Science, Taiz University, 6803 Taiz, Yemen
b Department of Geology, University of Malaya, 50603 Kuala Lumpur, Malaysia

A R T I C L E   I N F O

Article info
Article history:
Received 12 December 2012
Received in revised form
29 April 2013
Accepted 14 May 2013
Available online 29 May 2013

Keywords:
Oil families
Biomarker
Depositional environment
Source inputs
Marib-Shabowah Basin
Yemen

A B S T R A C T

The Marib-Shabowah Basin is an important hydrocarbon province in western Yemen, but the origin of hydrocarbons is not fully understood. In this regard, geochemical characteristics are used to provide information on source organic matter input, depositional environment and the correlation between crude oils from different pay zones. Two oil families are present within the study area and classified based on biomarker and non-biomarker parameters. The family I oils are characterized by low API gravity, high sulfur and trace metal (Ni, V) contents and low Ph/Ph ratio < 1.0. These oils were derived from an algal organic matter that was deposited in a highly anoxic, hypersaline marine depositional environment and generated at low maturity.

Family II oils have medium to high API gravity, low sulfur and trace metal contents and relatively high Pr/Ph ratios (1.09 – 1.59). The family II oils were derived from mixed marine and terrigenous organic matter and deposited under sub-oxic conditions. These oils were generated from source rocks with a wide range of thermal maturity ranging from early to peak oil window. The oil characteristics suggest that family I oils may be derived from the Tithonian age Safer calcareous shales and family II oils from the deeper Kimmeridgian Madbi shales.

1. Introduction

Sedimentary organic matter and crude oils contain complex assemblages of biological marker compounds (biomarkers) that preserve the molecular structure of various compounds that constitute the organisms. Biomarkers are widely used in the petroleum industry to identify groups of genetically related oils, to correlate oils with source rocks and to describe the probable source rock depositional environments for migrated oil of uncertain origin and the degree of biodegradation (Moldowan et al., 1985; Peters and Moldowan, 1993; Peters et al., 2005).

Many oilfields have been discovered in the Marib-Shabowah Basin, an important hydrocarbon province in the western part of Yemen (Fig. 1), since oil was first discovered in the late 1980s. The Alif Field, located in the central portion of the Marib-Shabowah Basin (Fig. 1), is one of the most prolific oilfields. The Marib-Shabowah Basin has attracted the interest of numerous researchers, authors and oil companies for the exploration of hydrocarbons. The Marib-Shabowah Basin developed during the Jurassic and is related to rifting of the Arabian plate from the Gondwana supercontinent (Redfern and Jones, 1995; Beydoun et al., 1996). The stratigraphic section in the Marib-Shabowah Basin is dominated by a thick Mesozoic succession and ranges in age from Jurassic to Cretaceous (Fig. 2). The organic-rich shales of Madbi Formation (Kimmeridgian) and Safer Member (Tithonian) are the prolific oil prone source rocks in the Marib-Shabowah Basin (Bramlin et al., 1999; Csato et al., 2001; Hakimi and Abdullah, 2013). The Alif Member is considered the main reservoir in the Marib-Shabowah Basin (Fig. 2) and comprises over 90% of recoverable oil in the basin (JNOC, 2000 “personal communication”). Previous geochemical studies on the Marib-Shabowah Basin oils are unpublished. Within this perspective, we report the results of an organic geochemical investigation on crude oils from the Alif Field. The objective is to use biomarker distributions together with the bulk geochemical parameters to characterize the oil types and to assess the respective depositional environment and thermal maturity of their potential source rocks.

2. Samples and methods

The materials used in this study include 10 crude oil samples representing different petroleum reservoirs in the Alif Field, Marib-
Shabowah Basin (Table 1). The geographic locations of the wells chosen are shown in Figure 1.

The ratios of transition metals (vanadium and nickel) in crude oil are useful in the determination of source rock type, depositional environment and maturation because they remain unchanged irrespective of diagenetic and in-reservoir alteration effects (Barwise, 1990; Udo et al., 1992). Absolute concentrations of vanadium and nickel can be used to classify and correlate oils. These metals are the major metals in petroleum (Boduszynski, 1987). The metals analysis was conducted at Geochem Laboratories Limited (USA).

Asphaltenes were precipitated from the crude oils by adding a 40 fold excess of n-hexane. The precipitated asphaltenes were filtered. The fractions of the hexane soluble organic matter were separated into saturated hydrocarbons, aromatic hydrocarbons and NSO compounds using liquid column chromatography. A chromatographic column (30 × 0.72 cm) was packed with equal volumes of alumina and silica (both activated for 2 h at 200 °C).

The saturated hydrocarbon fractions were then analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). A FID GC with HP-5MS column and helium carrier gas was used. A temperature program from 40 to 300 °C at a rate of 4 °C/min and then held for 30 min at 300 °C was used for GC analysis. GC–MS experiments were performed on a V 5975B inert MSD mass spectrometer with a GC attached directly to the ion source (70 eV ionization voltages, 100 mA filament emission current, 230 °C interface temperature with full scan).

3. Results and discussion

Biomarker distributions and bulk oil parameters were used to assess the genetic relationship between hydrocarbon generation and their source rock depositional environments. Based on bulk geochemical properties and fingerprints (GC and GC–MS), the investigated oils were classified into two genetic families. A description of the geochemical characteristics of the oil families follows.

3.1. Non-biomarker characteristics

3.1.1. Bulk properties of crude oils

The bulk crude oil properties and compositions for the studied oils are presented in Table 1. The crude oils from the Alif Field have a variety of API gravity values in the range of 15.0–58.7° (Table 1). Low API gravity is generally associated with either biodegraded oils or with immature sulfur-rich oils (Baskin and Peters, 1992). Biodegradation may occur in an oil reservoir, and the process dramatically affects the fluid properties of the hydrocarbons (e.g., Müllner et al., 1987). The early stages of oil biodegradation are characterized by the loss of n-alkanes or normal alkanes followed by loss of acyclic isoprenoids (e.g., pristane and phytane). Compared with those compound groups, other compound classes (e.g., highly branched and cyclic saturated hydrocarbons as well as aromatic compounds) are more resistant to biodegradation (Larter et al., 2005). In this respect, the analyzed oil samples contain a complete suite of n-alkanes in the low-molecular weight region and acyclic isoprenoids (e.g., pristane and phytane; Fig. 3). Therefore, there is no sign of biodegradation among the oil samples. This is also indicated by the oil samples generally containing more saturated hydrocarbons than aromatic hydrocarbons with saturate/aromatic hydrocarbons ratios >1 (Table 1). On the other hand, the relationship between API gravity and sulfur content reflects that the low API gravity is associated with sulfur-rich oils (Fig. 4). A wide range of bulk property values of the crude oils analyzed indicates that two oil families are represented (Table 1). Family I represent four crude oils, which have low API gravities corresponding to high sulfur content of 3.03–6.00 wt% (Fig. 4), suggesting that these oils were generated from clay-poor marine source rocks deposited under highly reducing conditions (Gransch and Posthuma, 1973; Moldowan et al., 1985). In contrast, family II represents six crude oil
Figure 2. Regional stratigraphic nomenclature in the Marib-Shabowah Basin, Republic of Yemen.

Table 1

Bulk organic geochemical properties of crude oil samples from Alif Field, Marib-Shabowah Basin.

<table>
<thead>
<tr>
<th>Wells</th>
<th>Crude oils</th>
<th>Oil family (ft)</th>
<th>Depths</th>
<th>Reservoir rocks</th>
<th>Lithology</th>
<th>API gravity (°)</th>
<th>Sulfur (wt%)</th>
<th>Ni (ppm)</th>
<th>V (ppm)</th>
<th>V + Ni (ppm)</th>
<th>Saturate</th>
<th>Aromatic</th>
<th>Resins + asphaltenes</th>
<th>Saturate/ aromatic</th>
<th>Waxiness degree</th>
<th>S(n-C_{21}−n-C_{31})</th>
<th>S(n-C_{15}−n-C_{20})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alif-9</td>
<td>SFCU-2</td>
<td>1</td>
<td>4367</td>
<td>Safer-sandstone</td>
<td>Tawilah Formation</td>
<td>14.0</td>
<td>3.03</td>
<td>3.80</td>
<td>36.3</td>
<td>40.1</td>
<td>33.4</td>
<td>24.1</td>
<td>42.5</td>
<td>1.39</td>
<td>0.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SFCU-3</td>
<td>5893</td>
<td>Safer-sandstone</td>
<td>5893</td>
<td>Safer-sandstone</td>
<td>Qishn Clastic</td>
<td>19.4</td>
<td>5.86</td>
<td>5.50</td>
<td>20.8</td>
<td>26.3</td>
<td>26.7</td>
<td>12.0</td>
<td>59.3</td>
<td>2.39</td>
<td>0.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alif-16</td>
<td>SFCU-4</td>
<td>1</td>
<td>4193</td>
<td>Safer-sandstone</td>
<td>Qishn Clastic</td>
<td>15.0</td>
<td>6.00</td>
<td>6.10</td>
<td>42.5</td>
<td>48.6</td>
<td>33.5</td>
<td>21.3</td>
<td>45.2</td>
<td>1.57</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alif-2</td>
<td>SFCU-1</td>
<td>1</td>
<td>5370</td>
<td>Safer-sandstone</td>
<td>Safer-sandstone</td>
<td>16.3</td>
<td>5.90</td>
<td>4.20</td>
<td>39.0</td>
<td>43.2</td>
<td>33.0</td>
<td>20.8</td>
<td>46.2</td>
<td>1.59</td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SFCU-2</td>
<td>5700</td>
<td>Alif-sandstone</td>
<td>5700</td>
<td>Alif-sandstone</td>
<td>Safer-sandstone</td>
<td>40.1</td>
<td>0.31</td>
<td>0.11</td>
<td>1.44</td>
<td>0.44</td>
<td>0.55</td>
<td>68.3</td>
<td>23.9</td>
<td>2.86</td>
<td>0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MECU-1</td>
<td>8080</td>
<td>Meem-sandstone</td>
<td>8080</td>
<td>Meem-sandstone</td>
<td>Meem-sandstone</td>
<td>35.8</td>
<td>0.17</td>
<td>0.11</td>
<td>1.60</td>
<td>1.71</td>
<td>34.0</td>
<td>27.9</td>
<td>38.1</td>
<td>1.27</td>
<td>0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MECU-2</td>
<td>8510</td>
<td>Meem-sandstone</td>
<td>8510</td>
<td>Meem-sandstone</td>
<td>Meem-sandstone</td>
<td>38.8</td>
<td>0.80</td>
<td>0.14</td>
<td>1.05</td>
<td>1.19</td>
<td>35.6</td>
<td>30.5</td>
<td>33.9</td>
<td>1.17</td>
<td>0.95</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
samples, which exhibit medium to high oil API gravities between 35.8° and 58.7°. These oils have a variety of sulfur contents, ranging from 0.11 to 1.13 wt% (Fig. 4), suggesting they have been generated from clay-rich source rocks (Hedberg, 1968; Gransch and Posthuma, 1973; Moldowan et al., 1985).

The degree of waxiness \( S(\text{n-C}_{21} - \text{n-C}_{31})/S(\text{n-C}_{15} - \text{n-C}_{20}) \) is used to categorize the amount of land derived organic material in oil, assuming that terrigenous material contributes a high molecular weight normal paraffin component to the oil (Connan and Cassou, 1980; Johns, 1986). The calculated ratio of \( S(\text{n-C}_{21} - \text{n-C}_{31})/S(\text{n-C}_{15} - \text{n-C}_{20}) \) generally indicates a low degree of waxiness <1 (Table 1), suggesting that these oils have been derived from algal and/or bacterial organic matter (Brooks et al., 1969; Tissot and Welte, 1984). The correlation between the degree of waxiness and sulfur content also reflects two different oil families (Fig. 5). The family I oil samples have low waxiness values (<0.6) and high sulfur content (>3 wt. %) suggesting that they have been derived from mainly

![Figure 3. Gas chromatography traces of whole crude oil for representative two oil families in this study.](image)

![Figure 4. Plot of the API gravity versus the sulfur content (wt%) for crude oils from various reservoir rocks in the Alif Field, Marib-Shabowah Basin.](image)

![Figure 5. Relationship between sulfur content (wt%) and degree of the waxiness for the investigated crude oils in the Alif Field, Marib-Shabowah Basin.](image)

![Figure 6. Relationship between total concentration of (V + Ni) and degree of waxiness \( S(\text{n-C}_{21} - \text{n-C}_{31})/S(\text{n-C}_{15} - \text{n-C}_{20}) \) for investigated crude oils from Alif Field, Marib-Shabowah Basin.](image)
Figure 7. Gas chromatography traces of saturated hydrocarbons for representative oil samples in this study, showing two oil families.
Table 2
Selected biomarker parameters of the crude oil samples illustrating source and maturity differences between the two oil families.

<table>
<thead>
<tr>
<th>Crude oils</th>
<th>Oil family</th>
<th>n-alkane and isoprenoids</th>
<th>Triterpanes and terpanes (m/z191)</th>
<th>Steranes and diasteranes (m/z217)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-C18</td>
<td>n-C17</td>
<td>Ph/C17</td>
<td>Ph/C18</td>
</tr>
<tr>
<td>SFCU-2</td>
<td>I</td>
<td>0.42</td>
<td>0.43</td>
<td>1.47</td>
</tr>
<tr>
<td>SFCU-3</td>
<td>I</td>
<td>0.59</td>
<td>0.71</td>
<td>2.68</td>
</tr>
<tr>
<td>SFCU-4</td>
<td>I</td>
<td>0.27</td>
<td>0.23</td>
<td>1.10</td>
</tr>
<tr>
<td>SECU-1</td>
<td>I</td>
<td>0.30</td>
<td>0.82</td>
<td>3.24</td>
</tr>
<tr>
<td>SECU-2</td>
<td>II</td>
<td>1.09</td>
<td>0.64</td>
<td>0.66</td>
</tr>
<tr>
<td>SECU-1</td>
<td>II</td>
<td>1.53</td>
<td>0.03</td>
<td>0.46</td>
</tr>
<tr>
<td>AFCU-1</td>
<td>II</td>
<td>1.24</td>
<td>0.52</td>
<td>0.43</td>
</tr>
<tr>
<td>AFCU-2</td>
<td>II</td>
<td>1.52</td>
<td>0.59</td>
<td>0.44</td>
</tr>
<tr>
<td>MECU-1</td>
<td>II</td>
<td>1.59</td>
<td>0.40</td>
<td>0.29</td>
</tr>
<tr>
<td>MECU-2</td>
<td>II</td>
<td>1.36</td>
<td>0.40</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Pt: pristane.
Ph: phytane.
CPI: carbon preference index (2(C23 + C25 + C27 + C29)/[(C22 + 2(C24 + C26 + C28) + C30)].
Ts: (C27 18s(H)-22,29,30-trisnorhopane).
Tm: (C27 17s(H)-22,29,30-trisnorhopane).
C29(2S)/C29(2R) norhopane/C29 hopane.
MC30/HC30: C30 moretane/C30 hopane.
H Index: (C35/(C31 + C33)) homohopane.
G/C30: Gammacerane/C30 hopane.

The gas chromatograms of saturated hydrocarbon fractions from representative oil samples are shown in Figure 7 and derived parameters are listed in Table 2. The saturated gas chromatograms of the oil samples display a full suite of saturated hydrocarbons between C13–C35 n-alkanes and isoprenoids pristane (Pr) and phytane (Ph) (Fig. 7). The differences in the distribution patterns of n-alkanes and acyclic isoprenoids suggest that the investigated oils are derived from two different sources.

The n-alkane distribution of family I oils shows a predominance of low to medium molecular weight compounds (n-C14–n-C20), suggesting a significant contribution of algal derived organic source input and reflects two different oil families. However, the latter figure shows that the family II oils considered to be derived from source rock contain a higher terrigenous organic matter contribution compared to family I oil samples.

3.2. Biomarker characteristics

3.2.1. Normal alkanes and isoprenoids

The gas chromatograms of saturated hydrocarbon fractions from representative oil samples are shown in Figure 7 and derived parameters are listed in Table 2. The saturated gas chromatograms of the oil samples display a full suite of saturated hydrocarbons between C13–C35 n-alkanes and isoprenoids pristane (Pr) and phytane (Ph) (Fig. 7). The differences in the distribution patterns of n-alkanes and acyclic isoprenoids suggest that the investigated oils are derived from two different sources.

The n-alkane distribution of family I oils shows a predominance of low to medium molecular weight compounds (n-C14–n-C20), suggesting a significant contribution of algal derived organic source input and reflects two different oil families. However, the latter figure shows that the family II oils considered to be derived from source rock contain a higher terrigenous organic matter contribution compared to family I oil samples.

Figure 9. Cross plot of dibenzothiophene/phenanthrene (DBT/Ph) versus pristane/phytane (Pr/Ph) ratios provides a powerful way to infer crude oil source rock depositional environments and lithologies (Hughes et al., 1995).
matter from a marine environment, whereas family II oils also show a predominance of low to medium molecular weight compounds (\(n\)-C\(_{14}\)–\(n\)-C\(_{20}\)) with the presence of significant waxy alkanes (+\(n\)-C\(_{23}\)) thus gave moderate CPI values (Table 2), suggesting a higher contribution of marine organic matter with minor terrigenous organic matter contribution (Brooks et al., 1969; Powell and McKirdy, 1973; Tissot et al., 1978; Ebukanson and Kinghorn, 1986; Murray and Boreham, 1992).

Acyclic isoprenoids occur in a significant amount in all studied oil samples (Fig. 7) and diagnostic biomarker ratios are listed in Table 2. The phytane being the most dominant peak in the saturated gas chromatograms of the family I oil samples studied (Fig. 7); phytane concentration is always higher than \(n\)-C\(_{18}\), thus giving distinctively high phytane/\(n\)-C\(_{18}\) ratios of 3.24–1.10. Comparatively lower values for these ratios (0.29–0.66) were displayed by family II oil samples, which generally possess relatively, lower amounts of acyclic isoprenoids (compared to \(n\)-alkanes) than the family I oil samples (Fig. 8). The pristane/phytane (Pr/Ph) ratio is also one of the most commonly used geochemical parameters and has been widely invoked as an indicator of the redox conditions in the depositional environment and source of organic matter (Didyk et al., 1978; Powell, 1988; Chandra et al., 1994; Large and Gize, 1996). Organic matter originating predominantly from land plants would be expected to contain high Pr/Ph > 3.0 (oxidizing conditions), low values of (Pr/Ph) ratio (<1.0) indicate anoxic conditions and values between 1.0 and 3.0 suggest intermediate conditions (sub-oxic conditions) (Philp, 1985; Amane and Hideki, 1997). The Pr/Ph ratios of the investigated oil samples range from 0.27 to 1.59 (Table 2), suggesting two oil types and derived from different source rocks. The family I oils have Pr/Ph ratio values <1.0, whereas family II oils have moderately Pr/Ph ratios in the range of 1.09–1.59. The Pr/Ph ratios indicate that the family I oils considered to be

---

**Figure 10.** The distributions of triterpanes m/z 191 mass fragmentograms of saturated hydrocarbons representative of the two oil families in the Alif Field, Marib-Shabowah Basin, showing two oil families.
derived from source rocks containing mainly marine algal-derived organic matter which was deposited in a more reducing environment compared to family II oil samples (sub-oxic). This is consistent with the observed of high phytane/n-C18 ratios of family I oil samples compared to family II oil samples (Fig. 8). Furthermore, the ratios of dibenzo[ghi]phenanthrene and pristane/phytane can be also used to infer crude oil source rock depositional environments and lithologies (Hughes et al., 1995). The cross plot of dibenzo[ghi]phenanthrene versus pristane/phytane indicates that Alif oils have been derived from two different source rock (Fig. 9). The family I oils were derived from marine carbonate and marl sediments whereas the family II oils were derived from marine shales (Fig. 9).

3.2.2. Triterpanes

The distributions of terpanes are commonly studied using GC–MS by monitoring the ions m/z 191 (Brooks et al., 1969; Peters et al., 2005) as a legend to Figure 10. For peak assignments see Table A1 in Appendix 1. Individual components were identified by comparison of their retention times and mass spectra with published literature (Philp, 1985; Peters and Moldowan, 1993).

The differences in the distribution patterns of m/z 191 mass fragmentograms suggest that the investigated oils are classified into two oil families (Fig. 10). The m/z 191 mass fragmentograms of the saturated hydrocarbon fractions of all the oil samples analyzed show high proportions of hopanes relative to tricyclic terpanes as shown in Figure 10. The relative abundance of C30 hopane in most of the studied samples (Fig. 10), with C29/C30 0.70 (Table 2). The predominance of C30 hopane is frequently associated with clay-rich source rocks (Gürgey, 1999).

The investigated oils possess a wide range of Ts/Tm ratio values and ranging from 0.18 to 5.00 (Table 2). Values of Tm (C27 17α(H)-22,29,30-trinsorhopane and Ts (C27 18x(H)-22,29,30-trisnorhopane) are well known to be influenced by maturation, type of organic matter, and lithology (Moldowan et al., 1985). In the present study, the main difference is controlled by organic facies and lithology, with a maturation overprint within each oil family. Furthermore, the ratio of diastereane/sterane is plotted against Ts/Tm ratio, suggesting that family I oils have been associated with more carbonate lithology compared to family II oil samples (Fig. 11) as indicated by dibenzothiophene/phenanthrene and pristane/phytane ratios (Fig. 9). Extended hopanes are dominated by the C31 homohopane and generally decreasing toward the C35 homohopane (Fig. 10). The αβ hopanes are more prominent than the βα hopanes while the S isomers are more dominant than the R isomers among the homohopane (C31–C35). The distribution of the extended hopanes or homohopanes (C31–C35) has been used to evaluate redox conditions based on homohopane index (Peters et al., 2005). This, in turn, suggests that the family I oils were derived from source rock deposited in a more reducing environment than the family II oil samples source rock. In support, relatively higher homohopanes index were obtained for family I oils compared to the family II oil samples (Table 2). High C35/C34 hopanes ratios have been reported in highly reducing marine oils (Moldowan et al., 1985; Peters and Moldowan, 1991). This is consistent with the observed of high C35/C34 hopanes ratios of family I oil samples (Fig. 10).

In addition, gammacerane has been recorded in family I oil samples (Fig. 10), is a strong indicator of high-salinity conditions and water column stratification during deposition of the source rocks (Moldowan et al., 1985; ten Haven et al., 1989; Sinninghe-Damsté et al., 1995; Peters et al., 2005). The occurrence of gammacerane in the family I oils is also consistent with Safer shales association with interbedded evaporites (refer to stratigraphic section in Fig. 2) (Rohrback, 1981; Mello et al., 1988).

3.2.3. Steranes

The distributions of diasteranes and the steranes (C27, C28 and C29) are characterized by the m/z 217 ion chromatograms (Fig. 12). Peaks labels are listed on Table A1 in Appendix 1 and the derived parameters are listed in Table 2. The relative amounts of C27/C28 and C29 steranes can be used to give indication of source differences (Seifert and Moldowan, 1979). The relative distribution of C27, C28 and C29 steranes is graphically represented in the form shown for a regular steranes in a ternary diagram (Fig. 13, Huang and Meinschein, 1979). The original classification of Huang and Meinschein (1979) related C27 steranes to strong algal influence and C29 steranes to stronger plant influence. The differences in the distribution of regular steranes (C27–C29) suggest that the oils are derived from different types of organic matter (Fig. 13). The family I oil samples display a strong predominance of C27 steranes (Table 2), which suggest a dominance of marine algal organic matter (Fig. 11), while the family II oils that composed of C27–C29 steranes which is an indicator of the mixed marine/terrigenous origin for the oil as indicated by Pr/n-C27 and Ph/n-C18 ratios (Fig. 8). This is consistent with the observed of low C29/C27 sterane ratios of family I oil samples compared to family II oil samples (Table 2).

The diasterane/regular sterane ratios and two different sterane thermal maturity parameters, C29 20S/(20S + 20R) and the C32 αββ/ (ααβ + ααα), are calculated and listed in Table 2. The higher diasterane/sterane ratios in the family II oil samples compared to family I oil samples correspond to the higher clay contents in the former (Gürgey, 1999).

3.3. Maturity of crude oils

The components in oil, NSO compounds, asphaltenes and saturated and aromatic hydrocarbons undergo increased cracking during thermal maturation. A variety of oil characteristics has been used to evaluate the level of thermal maturity of the investigated oils; these include biomarker and non-biomarker parameters. The biomarker and non-biomarker parameters are listed in Tables 1 and 2, and are discussed in more detail below. In gas chromatography–mass spectrometry (GC–MS), biomarker maturation parameters such as C25 22S/(22S + 22R) homohopane, moretane/hopane and 20S/(20S + 20R) and αββ/(ααβ + ααα) C29 sterane ratios, was used as
maturity indicators (Mackenzie et al., 1980; Waples and Machihara, 1991). The ratios of $22\text{S}/(22\text{R} + 22\text{S})$ for $C_{32} 17\alpha\ (H), 21\beta\ (H)$-hopanes are between 0.56 and 0.63 (Table 2) suggesting that they have reached equilibrium. The $20\text{S}/(20\text{S} + 20\text{R})$ and $\beta\beta/(\beta\beta + \alpha\alpha)$ $C_{29}$ sterane ratios of the oils are between 0.35 and 0.52, and 0.35–0.55, respectively (Table 2). These biomarker maturation parameters are indicating that the oils are expelled from source rocks that were exposed to thermal maturity level equivalent to the early to peak oil window stage of petroleum generation. The correlation between two biomarker maturity parameters is shown in Figure 14 (Peters and Moldowan, 1993). This correlation reflects that the family I oils are early mature, whereas the family II oils are early mature to peak oil window (Fig. 14). The relationship between isoprenoids $Pr/n-C_{17}$ and $Ph/n-C_{18}$ ratios (Fig. 8) reflects the same interpretation as do the moretane/hopane ratios (Waples and Machihara, 1991).

Non-biomarker parameters such as API gravity, sulfur and metal contents have also been used to evaluate the level of thermal maturity of the investigated oils (El-Gayar et al., 2002). The concentrations of Ni and V varied strongly with the maturity of oils and high maturity crude oils contained only small amounts of Ni and V elements (Barwise, 1990). This is consistent the observed of low Ni and V content of family II oil samples compared to family I oil samples (Table 1). The correlation between API gravity and sulfur content (Fig. 4), and between sulfur content and concentrations of $(V + Ni)$ values (Table 1) are indicated that the levels of metals and sulfur in crude oil decrease with increasing maturity, whereas the API gravity increase. This is consistent with previous biomarker observations.

Figure 12. The distributions of steranes $m/z$ 217 mass fragmentograms of saturated hydrocarbons for representative two oil families in the Alif Field, Marib-Shabowah Basin.
in the basin shows similar characteristics to these oils, suggesting that the family I oils are derived the interbedded Safer calcareous shales.

Family II oils have medium to high API gravity and low sulfur and metal contents. Oils from the family II display relatively high Pr/Ph ratios (1.09–1.59), relatively low C_{35} homohopane index and high diasteranes relative steranes, indicating a marine clay source rock deposited in sub-oxic conditions. These oils type are composed of C_{27}–C_{29} regular steranes suggest that these oils were generated from source facies contain a mixture of marine with land plant organic matter deposited in a marine or perhaps slightly restricted marine environment. This is consistent the observed of low trace metal (Ni, V) content and relatively high waxiness values. The characteristics of these oils are consistent with their sourcing from the Madbi shales as described by Hakimi et al. (2010).

On the basis of the biomarker maturity and non-biomarker parameters, the investigated oils in the Alif Field are thermally mature and ranging from early mature to peak oil window. The family II oil samples were generated from source rocks with a wide range of thermal maturity and have entered early mature to peak oil window whereas the family I oil samples are early mature oils.

### Acknowledgments

The authors thank the Petroleum Exploration and Production Authority (PEPA) and Safer Oil Company, Yemen for supplying the data and samples for this study. The authors are more grateful to the Department of Geology, University Malaya for providing facilities to complete this research. Special thanks are offered to Dr. Lloyd R. Snowdon for his helpful comments and corrections on an earlier version of the manuscript.

### Appendix 1

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>Mass fragmentogram</th>
<th>Compound abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ts</td>
<td>18(2H),22,29,30-trisnorhopane</td>
<td>Ts</td>
</tr>
<tr>
<td>Tm</td>
<td>17(2H),22,29,30-trisnorhopane</td>
<td>Tm</td>
</tr>
<tr>
<td>29</td>
<td>17z,21t(H)-nor-hopane</td>
<td>C_{35} hopane</td>
</tr>
<tr>
<td>30</td>
<td>17z,21t(H)-hopane</td>
<td>Hopane</td>
</tr>
<tr>
<td>3M</td>
<td>17 [t,21t(H)-Moretane</td>
<td>C_{30}Mor</td>
</tr>
<tr>
<td>31S</td>
<td>17z,21t(H)-homohopane (22S)</td>
<td>C_{31}(22S)</td>
</tr>
<tr>
<td>31R</td>
<td>17z,21t(H)-homohopane (22R)</td>
<td>C_{31}(22R)</td>
</tr>
<tr>
<td>32S</td>
<td>17z,21t(H)-homohopane (22S)</td>
<td>C_{32}(22S)</td>
</tr>
<tr>
<td>32R</td>
<td>17z,21t(H)-homohopane (22R)</td>
<td>C_{32}(22R)</td>
</tr>
<tr>
<td>33S</td>
<td>17z,21t(H)-homohopane (22S)</td>
<td>C_{33}(22S)</td>
</tr>
<tr>
<td>33R</td>
<td>17z,21t(H)-homohopane (22R)</td>
<td>C_{33}(22R)</td>
</tr>
<tr>
<td>34S</td>
<td>17z,21t(H)-homohopane (22S)</td>
<td>C_{34}(22S)</td>
</tr>
<tr>
<td>34R</td>
<td>17z,21t(H)-homohopane (22R)</td>
<td>C_{34}(22R)</td>
</tr>
<tr>
<td>35S</td>
<td>17z,21t(H)-homohopane (22S)</td>
<td>C_{35}(22S)</td>
</tr>
<tr>
<td>35R</td>
<td>17z,21t(H)-homohopane (22R)</td>
<td>C_{35}(22R)</td>
</tr>
<tr>
<td>a</td>
<td>13z,17z(H)-diasteranes 20S</td>
<td>Diasteranes</td>
</tr>
<tr>
<td>b</td>
<td>13z,17z(H)-diasteranes 20R</td>
<td>Diasteranes</td>
</tr>
<tr>
<td>c</td>
<td>13z,17z(H)-diasteranes 20S</td>
<td>Diasteranes</td>
</tr>
<tr>
<td>d</td>
<td>13z,17z(H)-diasteranes 20R</td>
<td>Diasteranes</td>
</tr>
<tr>
<td>e</td>
<td>5z,14z(H), 17z(H)-steranes 20S</td>
<td>5z(20R)</td>
</tr>
<tr>
<td>f</td>
<td>5z,14z(H), 17z(H)-steranes 20R</td>
<td>5z(20R)</td>
</tr>
<tr>
<td>g</td>
<td>5z,14z(H), 17z(H)-steranes 20S</td>
<td>5z(20S)</td>
</tr>
<tr>
<td>h</td>
<td>5z,14z(H), 17z(H)-steranes 20R</td>
<td>5z(20S)</td>
</tr>
</tbody>
</table>
References


