Biomarkers from Oil Shales in The Upper Cretaceous Amman Formation, NW Jordan

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Abstract

The presence of biomarkers such as hopanes in oil shales from the Upper Cretaceous Amman Formation of NW Jordan indicates the presence of immature organic matter. This is also suggested by the predominance of 17 trisnorneohopane over 18 hopane. Steranes, which are traced by GC/MS at m/z = 217, indicate a source input of organic matter derived predominantly from higher marine organisms such as fish. Also, the relatively high proportion of sterane compounds shows that the palaeoenvironment in which the formation was deposited was mainly estuarine to open marine.

Keywords: Biomarkers, Oil Shale, Sterane compounds, Jordan.

Introduction

The importance of biological markers in alkane stereochemistry relates to the fact that the chiral centres of structurally-specific natural products are isomerized during maturation. This isomerization occurs because hydrogen is removed from the centres at elevated temperatures [1]. The triterpane (hopanes) and sterane polycyclics decrease in abundance during the principal stages of hydrocarbon generation, either as a result of degradation or due to dilution by the newly-generated hydrocarbons [2].

For the hopanes, the configuration at the C22 location (either the 22R, or the more stable 22S epimer), which is represented by the ratio of 22S/(22S+22R) C32, is considered to be good evidence of maturity, and increases with increasing maturity [3].

In mature source rocks, 22S epimers predominate over 22R to reach an equilibrium ratio of 60:40. This means that the 22S/(22S+22R) ratio for mature source rocks must be 0.6 [4,5], because the 22S isomer is slightly more stable than the 22R isomer [6].

Tm [17 α (H)- trisnorneohopane] is unstable, while Ts [18 α (H) trisnorhopane] is stable and more resistant to subsequent degradation. With increasing maturity, Tm is converted irreversibly into Ts [7], and the Tm/Ts ratio tends towards zero [8]. This ratio is suitable as a maturity index.

Steranes are complex mixtures of C27, C28 and C29 stereoisomers. They are good indicators of source materials, since C27 steranes are derived predominantly from...
marine organisms, while C29 steranes are derived from higher plants [9], and from higher marine organisms [10]. In general, they are derived from steroids that are present in all organisms more advanced than Cyanobacteria [11].

The aim of the present study is to evaluate the maturity of oil shale deposits located in NW-Jordan, especially those of Kufr Asad and Deir Abu Sa'ed areas due to its high importance as possible source of energy and as possible mother rocks in Jordan and Wadi Sirhan grabens. A second purpose is to determine the depositional environment of this oil shale and the origin of the organic matter in order to help reconstructing the palaeogeography of the area.

**Geological Setting**

After not wide extended transgressions of the Tethys onto the NW and NE margins of Jordan during Triassic and Jurassic, predominated in Lower Cretaceous fluviatile environment covering almost the whole country with clastics, mainly sandstones and to lesser amount claystones.

Then at the beginning of Cenomanian transgressed the Tethys again covering large areas of Jordan and extending during Late Cretaceous and Palaeogene gradually southwards forming broad shallow shelf, in which deposited mainly limestone, marl, marly limestone, chert and phosphates.

The ground of the shelf was partly subdivided into long extended deeps and highs originated probably by synsedimentary tectonical movements during Coniacian to Campanian [12,13 and14].

In the deeps deposited in reducing environment during Campanian and Maastrichtian fine grained carbonates rich-in organic matter reaching values of 32%. These oil shales are concentrated in two horizons; one in the upper part of the Amman Formation, which is of Campanian to Early Maastrichtian age, and the other horizon in the Lower Muwaqqar Formation, which is of Maastrichtian-Eocene age [15].

The study area is located in N-Jordan at the eastern margin of the Jordan graben (Fig. 1). The exposed rocks in N-Jordan belong mainly to Upper Cretaceous and Palaeogene, beside the mainly fluviatile and Lacustrine Quaternary deposits and the basalt flows issued in Pliocene to Pleistocene.

The Amman Formation crops out at the surface and in most wadis in North Jordan. Lithologically, it is mainly composed of interbedded marly limestone, marl, limestone and chert layers, bands, and nodules with intercalations of phosphates and locally mainly in the lower part carbonate oil shale. It is overlain by the Al-Hisa phosphorite Formation and underlain by the Umm Ghudran Formation.

This paper deals with the oil shales in the Amman Formation west of Irbid City, between latitudes 35° 38’ to 36° 14’ N, and longitudes 32° 47’ to 32° 57’ E, in two locations: Wadi Abu-Zeyad and Kufr Asad (Fig. 1).

They are generally hard, dark-brown to black in colour, and are present as beds and massive bodies within the grey fossiliferous limestones (Fig. 2). They contain abundant
fish remains, shells of gastropods and cephalopods, and phosphatic intraclasts [16,17 and 18].
The organic matter of these oil shales consists mainly of kerogen and to lesser amount of bitumen [16,17 and18]. The overburden is less than 700m. It is expected that under normal conditions the organic matter is immature. But in the Jordan graben, where since the beginning of its formation in Late Palaeogene to Early Neogene several thousand meters sediments are accumulated and along its margin, where the effect of the movements is highest the oil shale could have been more or less affected and become more mature than elsewhere. Therefore the samples have been obtained from exposures not far away from the margin of the Jordan graben.

Fig. 2: Columnar section of the Amman Formation in the study area.
Methods

More than 30 samples were collected systematically (one each 100 cm) from in deep incised wadis exposed rocks of the Amman Formation after removal of weathered parts. The samples were in the field enveloped by aluminium paper, then in the lab pulverized < 63m, treated with 20% HCl to remove inorganic carbon, and burned in Leco CS-244 computerized furnace to determine TOC (Fig.3). 7 samples were selected for further analyses (Fig.3), because of the high cost of these analyses; they are 2.2, 2.3 and 2.34 from section 1, 3.5, 3.9 and 3.11 from section 2 and 4.16 from section 3.

The bitumen has been extracted from these samples by Dichloromethane soxhlet apparatus, using silicate thimbles for 22 hours.

Free sulfur has been eliminated by using activated copper.

The extracted material is filtered and evaporated by a rotary evaporator at 70°C under reduced pressures until a constant weight was reached.

The isolated bitumen was chromatographed on alumina - silica gel, eluting successively with pentane, 1:1 mixture of pentane/dichloromethane and methanol to collect the saturated fraction, aromatic and the NSO fractions, respectively.

The samples were analyzed using a Hewlett-Packard 5995 GC/MS (30m X 0.25 m.i.d, cross-bonded 100% dimethylpolysiloxane; 90.52nm, film thickness; Split Ratio 30:1; temperature rate: 120 C-340°C).

The GC spectra were identified by comparison with previously-published data, especially those of Philp [11]. Detected compounds consisted of triterpanes with m/z = 191, and steranes with m/z = 217.
Fig. 3: Schematic flow chart for laboratory analysis. EOM: Extractable Organic Matter; GC: Gas Chromatograph; HC: Hydrocarbon; MS: Mass Spectrometer; NOS: Heterocompounds; TOC: Total organic carbon.
Results:

A number of hopane biomarkers were identified from the samples analyzed (Table 1, Fig. 4).

**TABLE 1: LIST OF HOPANES IDENTIFIED IN THE M/Z 191 ION CHROMATOGRAMS IN FIG. 4**

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18α (H)-22,29,30-trisnorhopone (Ts)</td>
</tr>
<tr>
<td>2</td>
<td>17α (H)-22,29,30-trisnorneohopone (Tm)</td>
</tr>
<tr>
<td>5</td>
<td>17α (H),21β (H)-30-norhopane</td>
</tr>
<tr>
<td>10</td>
<td>17α (H), 21β (H)-hopane</td>
</tr>
<tr>
<td>11</td>
<td>17β (H), 21α (H)-moretane</td>
</tr>
<tr>
<td>14 &amp; 15</td>
<td>22S &amp; 22R- 17α (H), 21β (H)-30,31- bishomohopane</td>
</tr>
</tbody>
</table>

The analysis of these biomarkers and the interpretation of their ratios show, that the oil shales in the study area are deposited in an estuarine or bay to open-marine environment and that the organic matter is mainly derived from zoo- and phytoplanktons beside partly from land-plants or brown algae and partly probably from higher marine animals. They show also that the oil shales did not reach maturity, but may be possible source rocks.
Fig. 4. M/z 191 (Hopane) mass fragmentograms of the saturated hydrocarbon fractions of seven representative samples from the study area(2.2, 2.30, 2.34, 3.5, 3.9, 3.11, 4.16). Peaks identification are listed in Table 1.
Discussion

As shown in Table 2, the relative amounts of \( \frac{22S}{22S+22R} \) C32 are less than 0.6. This indicates that source rocks are immature, and the ratio of \( \frac{Tm}{Ts} \) is very high, relative to the supposed mature value. Also, the ratio of \( C29/C30 \) 17\(^\alpha\) (H)-hopane strongly indicates immaturity in the studied samples; it is around 0.35, while the "mature" level, according to Rulkotter et al., [19], requires a ratio of greater than 1.0.

**Table (2):** Hopanes biomarkers from 7 analyzed samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>( \frac{22S}{22S+22R} )C32</th>
<th>( \frac{Tm}{Ts} )</th>
<th>( C29/C30 )</th>
<th>( C30/C30+Mor )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>0.55</td>
<td>10.35</td>
<td>0.31</td>
<td>0.89</td>
</tr>
<tr>
<td>2.30</td>
<td>0.51</td>
<td>16.29</td>
<td>0.40</td>
<td>0.87</td>
</tr>
<tr>
<td>2.34</td>
<td>0.51</td>
<td>8.35</td>
<td>0.42</td>
<td>0.86</td>
</tr>
<tr>
<td>3.5</td>
<td>0.58</td>
<td>7.00</td>
<td>0.42</td>
<td>0.89</td>
</tr>
<tr>
<td>3.9</td>
<td>0.57</td>
<td>12.71</td>
<td>0.30</td>
<td>0.90</td>
</tr>
<tr>
<td>3.11</td>
<td>0.58</td>
<td>10.74</td>
<td>0.35</td>
<td>0.88</td>
</tr>
<tr>
<td>4.16</td>
<td>0.53</td>
<td>8.18</td>
<td>0.29</td>
<td>0.88</td>
</tr>
</tbody>
</table>

The presence of 17\(\alpha\)(H), 21\(\beta\)(H) hopanes indicates that the sediments may be a possible source rock. With increasing thermal stresses, the concentrations of 17\(\alpha\) hopane and its isomer moretane will increase [9]. Also with increasing maturity to the level of oil generation, the moretane concentration decreases and the hopane concentration increases, so that the ratio of hopane/(hopane+moretane) reaches nearly unity [20,1].

From the previous discussions of hopane biomarker distribution, it can be seen that the source rock has not reached maturity. This can be clearly observed in Fig. 4, where trisnorneohopane (Tm) greatly exceeds trisnorhopane (Ts). Also, there is the influence of bacterial input which can be traced, according to Waples [11], on the C35 of chromatograms.

The sterane distribution monitored by m/z= 217 (Fig. 5) shows the occurrences of C27-C29 rearranged (diasterane) and regular steranes for all steranes in the examined samples. Peak identifications are listed in Table 3.

**Table 3**: List of steranes identified in the M/z = 217 ion chromatograms in Fig. 5

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13(\beta), 17(\alpha) -diacholestane (20S)</td>
</tr>
<tr>
<td>2</td>
<td>13(\beta), 17(\alpha) -dicholestane (20R)</td>
</tr>
<tr>
<td>10</td>
<td>14(\alpha),17(\alpha) -cholestane (20R)</td>
</tr>
<tr>
<td>16</td>
<td>24-methyl - 14(\alpha),17(\alpha) -cholestan(20R)</td>
</tr>
<tr>
<td>17</td>
<td>24-ethyl-14(\alpha) -cholestan(20S)</td>
</tr>
<tr>
<td>18</td>
<td>24-ethyl-14(\beta), 17(\beta) -cholestane (20R)</td>
</tr>
<tr>
<td>19</td>
<td>24-ethyl-14(\beta), 17(\beta) -cholestane (20S)</td>
</tr>
<tr>
<td>20</td>
<td>24-ethyl-14(\alpha), 17(\beta) -cholestane (20R)</td>
</tr>
</tbody>
</table>
The configuration at the C20 chiral centre, especially for C29 steranes, has an important application for the assessment of the thermal maturity of sedimentary rocks and crude oils [1]. As maturity increases, the 20R epimer is isomerized into the 20S epimer [21, 9]. In mature source rocks, the amount of 20S relative to 20R is approximately 1:1 [21]. For the studied samples, the 20S/20R ratio of C29 steranes ranges from 0.23 to 0.75, with an average of 0.52 (Table 4), which indicates immaturity. Therefore, the rocks in the study area were not exposed to sufficient thermal stress and have not reached equilibrium.

![Fig. 5. Sterane mass fragmentograms of the saturated hydrocarbon of seven selected samples (for peak identification, see Table 3).](image)
Also, the regular 20R epimer can be converted into a mixture of 20R and 20S configurations with increasing temperature, while the rest of the molecules retain their biological configuration [10]. The ratio of 20S/(20S+20R)-C29 steranes is commonly used as a thermal maturity indicator; it rises from zero to 0.5-0.6 in the mature stage [13]. However, it does not exceed 0.43 for the examined samples (Table 4), indicating that the thermal history of these samples was inadequate for petroleum generation.
The configuration of C20 in diasteranes (13, 17, \( \text{C}_{27} \) (20S) and (20R)) depends on increasing maturity. The concentration of these rearranged steranes (diasteranes) increases in relation to the concentration of regular C27 steranes with increasing thermal stress or burial depth [22].

The relative abundance of C27-C29 regular steranes can be considered to be an important indication of the source of organic matter in oil and sediments [23], as well as a correlation tool for oil [24].

Regular C27 and C28 steranes are mainly derived from autochthonous aquatic organisms, such as zoo-and phytoplankton. Regular C29 steranes may be derived from continental higher-plant wax or from brown algae and phytoplankton [2,10 and25].

Therefore, the content of regular steranes can be used as a palaeoenvironmental indicator. In the present study, the C27, C28 and C29 contents of seven samples were plotted in a ternary diagram according to Huang and Meinschein [22] and Waples [11], to interpret the origin of the organic source material. The distribution (Fig. 6) shows a close grouping within the centre, indicating, according to this diagram, an estuarine or bay to open-marine depositional setting.

### TABLE (4): BIOMARKERS RATIOS OF STERANES FOR 7 SAMPLES.

<table>
<thead>
<tr>
<th>SAMPLES NO.</th>
<th>( \text{C}<em>{27}/\text{C}</em>{29} )</th>
<th>( \text{C}<em>{28}/\text{C}</em>{29} )</th>
<th>( \text{C}<em>{28S}/\text{C}</em>{29S}+\text{C}<em>{29R}(\text{C}</em>{29}) )</th>
<th>( \text{C}<em>{28S}/\text{C}</em>{28R}(\text{C}_{29}) )</th>
<th>( \text{C}<em>{29 \text{REG.}}/\text{C}</em>{29 \text{REG.}} )</th>
<th>%C_{27}:</th>
<th>%C_{28}:</th>
<th>%C_{29}:</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>1.16</td>
<td>1.25</td>
<td>0.28</td>
<td>0.40</td>
<td>0.12</td>
<td>34.0</td>
<td>36.7</td>
<td>29.3</td>
</tr>
<tr>
<td>2.30</td>
<td>1.21</td>
<td>1.21</td>
<td>0.34</td>
<td>0.52</td>
<td>0.13</td>
<td>35.4</td>
<td>35.3</td>
<td>29.3</td>
</tr>
<tr>
<td>2.34</td>
<td>1.15</td>
<td>1.32</td>
<td>0.19</td>
<td>0.23</td>
<td>0.37</td>
<td>33.1</td>
<td>38.0</td>
<td>28.9</td>
</tr>
<tr>
<td>3.5</td>
<td>0.85</td>
<td>1.54</td>
<td>0.40</td>
<td>0.68</td>
<td>0.55</td>
<td>25.1</td>
<td>45.4</td>
<td>29.5</td>
</tr>
<tr>
<td>3.9</td>
<td>0.72</td>
<td>1.25</td>
<td>0.36</td>
<td>0.57</td>
<td>0.36</td>
<td>24.3</td>
<td>42.0</td>
<td>33.6</td>
</tr>
<tr>
<td>3.11</td>
<td>0.92</td>
<td>1.26</td>
<td>0.39</td>
<td>0.65</td>
<td>0.17</td>
<td>28.9</td>
<td>39.7</td>
<td>31.4</td>
</tr>
<tr>
<td>4.16</td>
<td>0.92</td>
<td>1.21</td>
<td>0.38</td>
<td>0.75</td>
<td>0.20</td>
<td>29.4</td>
<td>38.6</td>
<td>32.0</td>
</tr>
</tbody>
</table>
Fig. 6. Ternary diagram of regular steranes (after Waples, [11]). Distribution of the studied samples indicating estuarine or bay to marine ecosystem.

These palaeoenvironmental indications of the biomarkers are in conform with the field observations and with the analysis of the macerals of this oil shale, which contain cuticles, spores and xylem cells [18].

The discontinuous occurrences of the oil shales, which are separated from each other by mostly primarily reddish coloured marly rocks point to the subdivision of the basin into long extended reducing deeper and oxygenated higher zones. This is also indicated by the allochems (bioclasts and phosphatic clasts) found in the oil shale, which are transported from high energy to low energy environments. The accumulation of organic matter containing pyrite and fish remains beside other nektic organisms in the oil shales indicates reducing lower and oxidizing higher water horizons of the deeps.

As shown in Table 4, samples from Section 2 have relatively higher abundances of C27 and C28 steranes than C29 steranes, while samples from Sections 3 and 4 have higher C28 steranes than those of C29, and are depleted in C27 steranes. This depletion can be referred to the input of large quantities of higher marine organisms, or may be due to biodegradation which took place during exposure of the rocks, due to the fact that the area is highly jointed and fractured.
Conclusion

The studied oil shales are deposited in subdivided estuarine or bay to open marine environment.

These oil shales are as indicated by the 20S/20R ratio of C29 steranes strongly immature, and their thermal history as indicated by the ratio 20S/(20S+20R) - C29 steranes is inadequate for petroleum generation. But their richness in organic matter makes them good source of energy. They could be in areas, where they are deeply buried, mother rocks. Therefore, further investigation in such areas like the Jordan graben is needed.

Acknowledgement

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Kasafat عضوية من الصخور الزيتي في تكوين عمان-الكروتاني العلوي، شمال غرب الأردن

حاتم درويش وحكم مصطفى

ملخص

dل تواجد الكاسفات العضوية كالهوبيينات في الصخور الزيتي من تكوين عمان ( الكروتاني .. العلوي) في شمال غرب الأردن على أن المواد العضوية في هذا الصخور الزيتي غير ناضجة كذلك يشير إلى عدم التضخج هذا سبباً للتراسترئونيوبين17 على الهوبيين 18. كما تشير النتيجات المستند عليها من اخضاعات الكروستوبراف الغازى / ومقياس الطيف التشاجلي على أن الكاسفات العضوية البحرية المتطورة كالأسماك قد أسهمت بشكل كبير في تكوين المواد العضوية في هذا الصخور الزيتي .. وتشير النسبة العالية لمركبات الستيرينات كذلك إلى أن البيئة القديمة التي توضع فيها هذا التكوين، هي بشكل رئيسي مصابات أنهار إلى بحرية مفتوحة.
References


