Organic geochemical characteristics and depositional environments of the Jurassic shales in the Masila Basin of Eastern Yemen

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ABSTRACT

In this paper, organic matter content, type and maturity as well as some petrographic characteristics of the Jurassic shales exposed in the Masila Basin were evaluated and their depositional environments were interpreted using organic geochemical and organic petrological studies. The total organic carbon (TOC) contents of shales in the Sunah, Wadi Taribah, and Kharir fields vary between 2.4% and 4.7% with high Hydrogen Index (HI) values. All shale samples display very low Oxygen Index (OI) values. The Sunah and Wadi Taribah shales contain Type II organic matter, while the Kharir shales contain Type II, with minor contributions from Type I organic matter.

$T_{max}$ values for the shales range from 428 °C to 438 °C and vitrinite reflectance values (%Ro) range from 0.52% to 0.80%. These values reveal that the Sunah and Kharir shales are at peak mature stage while the Wadi Taribah shales are early mature. This is supported by their biomarker maturity parameters.

The pristane/phytane (Pr/Ph) ratios range from 1.8 to 2.3. In addition, all shales show a homohopane distribution which is dominated by low carbon numbers, and $C_{35}$ homohopane index is very low for all shale samples. All these features may indicate that these shales were deposited in a suboxic environment. Sterane distribution was calculated as $C_{27}>C_{29}>C_{28}$ from the m/z 217 mass chromatogram for all shale samples.

The Sunah, Wadi Taribah and Kharir shales are believed to have good oil generating potential. This is supported by high total organic carbon content, hydrogen indices up to 400 mg HC/g TOC and early to peak mature oil window range.

INTRODUCTION

The origin of organic matter in sediments and crude oil has received much attention. Organic geochemistry is the study of the impacts and processes that organisms have had on the sediments. Hunt (1996) and Tissot and Welte (1984) discussed the concept and application of organic geochemistry principles in the study of the origin, migration, accumulation, and alteration of petroleum. Interpretation of depositional environment and thermal maturity based on biomarker distributions have also been widely applied (Peters and Moldowan, 1993; Peters et al., 2005).

The area that forms the scope of this study lies in Masila Basin (Figure 1). The basin is located in the Hadramaut region in East Central Yemen and has attracted the interest of numerous researchers, authors and oil companies for the exploration of hydrocarbons. The Masila Basin contains sediments of Jurassic and younger age. In Yemen, Jurassic shales are widespread, and are found in west Yemen and in the Masila Basin of Eastern Yemen. According to Beydoun et al. (1998), the age of these shales is Jurassic (Kimmeridgian).

In this study, organic geochemical analyses were performed on a selection of organic-rich Jurassic shales time in the Masila Basin to evaluate organic matter content, type and thermal maturity, as well as depositional environment conditions based on total organic carbon content, Rock-Eval pyrolysis, biomarker distributions and some petrographic characteristics.

STRATIGRAPHIC FRAMEWORK

The definition of the lithostratigraphic units in the Masila Basin has been studied by many authors, such as Haitham and Nani (1990); Bosence et al. (1996); Bosence (1997); Putnam et al. (1997); Beydoun...
Figure 1: Main sedimentary basins map in Yemen showing location of the Masila Basin and the study area.
et al. (1998, 1996 and 1993); Beydoun and Al-Saruri (1998); Watchorn et al. (1998); Cheng et al. (1999); Canadian Oil Company (1999); Total Oil Company (1999) and PEPA (2004, personal communication). The stratigraphic section of the study area ranges in age from Proterozoic to Tertiary (Figure 2) and can be classified into three megasequences: pre-rift, syn-rift and post-rift, as summarized below.

**Pre-Rift Megasequence**

This section ranges in age from Proterozoic to early Late Jurassic. It was penetrated by wells drilled in the Masila Basin (Figure 2). The basement of the Masila Basin consists mostly of igneous and metamorphic complex rocks of Proterozoic to early Cambrian age. This basement complex is overlain unconformably by the Jurassic sequence. In Early to Mid Jurassic time, sandstone was deposited widely across Yemen, where thick sedimentation developed in lows formed before Jurassic time. This thick sandstone deposit is known as the Kohlan Formation, and it is composed of siltstone and sandstone to conglomerate with some streaks of limestone and green clay. In Masila oilfields the sandstone of the Kohlan Formation is very fine- to medium-grained, well sorted, with good to poor porosity. Sediments within the Kohlan Formation were deposited during the transgression of the sea over the exposed and eroded igneous and metamorphic basement complex. Clastic sediments in this unit were deposited by subaerial to shallow water, near shore processes (Beydoun et al., 1998). After deposition of the Kohlan Formation, another marine transgression from the southeast reworked the sandstone and developed shallow marine carbonate (Shuqra Formation). The Shuqra Formation is Mid to Late Jurassic in age and it consists predominantly a platform carbonate (PEPA, 2004, personal communication). The Shuqra Formation is generally composed of limestone, including lime mudstone, wackestone and grainstone.

**Syn-Rift Megasequence**

During the syn-rift sequence, horsts and nested fault blocks were developed, where differential compaction and drape anticlines occurred over the Upper Jurassic to Lower Cretaceous with basement uplifting (Redfern and Jones, 1995; Canadian Oil Company, 2001, personal communication). Upper Jurassic sediments, known as the Madbi Formation, were penetrated by some wells drilled in the study area. This formation is generally composed of porous lime-grainstone to argillaceous lime-mudstone. The lithofacies of this unit reflects open-marine environments. This formation is divided into two members. The lower part of this formation is commonly argillaceous lime and basal sand, and forms a good reservoir in some oil fields of the Masila Basin (Canadian Oil Company, 2003, personal communication). The upper part of Madbi Formation is composed of laminated organic-rich shale (Mills, 1992). During latest Jurassic to Early Cretaceous time, the rifting system of the Masila Basin continued, but the subsidence became slower. It was accompanied by the accumulation of carbonates in shallow-marine shelf deposits (Naifa Formation). The Naifa Formation consists mainly of silty and dolomitic limestone and lime mudstone with wackestone. The upper part of this formation is composed of very porous clastic carbonate overlain by the Saar dolomite facies. In Early Cretaceous time, sea level rose on relatively flat ground, resulting in marine transgression and sedimentation of widespread shallow-marine carbonates (Saar Formation). The Saar Formation is composed mainly of limestone, dolomitic limestone with some mudstone, and sandstone. Oil companies classified this formation into lower Saar carbonate and upper Saar clastic. The lower unit of the Saar is characterized by the predominance of limestone, dolomite, mudstone, and marl. Meanwhile, the upper part is mainly sandstone and dolomitic limestone facies (Canadian Oil Company, 1999, personal communication).

**Post-Rift Megasequence**

This section represents late Early Cretaceous to Tertiary time and rests unconformably on the syn-rift section. Late Early Cretaceous sediments, known as the Qishn Formation, consist of braided plain to fluvial and shallow-marine sediments deposited in the Masila Basin. The Qishn Formation is divided into two members, Upper Qishn Carbonate and Lower Qishn Clastic Members. The Upper Qishn Carbonate Member consists of laminated to burrowed lime-mudstone and wackestone interbedded with terrigenous mudstone and black fissile shales. These sediments were deposited in deep water under alternating open and closed marine conditions (Beydoun et al., 1998). The Lower Qishn Clastic Member represents the main reservoir rock in the Masila Basin (Canadian Oil Company, 1991, personal communication).
| Rift Stage | Age     | Formation                  | Lithology                        | Legend |
|------------|---------|----------------------------|----------------------------------|--------|
|            |         |                            | Unconformity                      |        |
|            |         |                            | Sandstone                        |        |
|            |         |                            | Sandstone with high clay content |        |
|            |         |                            | Shale                            |        |
|            |         |                            | Limestone                        |        |
|            |         |                            | Marl                             |        |
|            |         |                            | Anhydrite                        |        |
|            |         |                            | Top Seal                         |        |
|            |         |                            | Source rock                      |        |
|            |         | Rus                        |                                  |        |
|            |         | Jiza’                      |                                  |        |
|            |         | Umm Er Radhuma              |                                  |        |
|            |         | Sharwayn                   |                                  |        |
|            |         | Mukulla                    |                                  |        |
|            |         | Fartaq                     |                                  |        |
|            |         | Upper Harshiyat            |                                  |        |
|            |         | Rays                       |                                  |        |
|            |         | Middle and Lower Harshiyat |                                  |        |
|            |         | Qishn Carbonates Mbr       |                                  |        |
|            |         | Red Shale                  |                                  |        |
|            |         | Upper Qishn Clastic Mbr    | R                                |        |
|            |         | Lower Qishn Clastic Mbr    | R                                |        |
|            |         | Clastics Carbonate         | R                                |        |
|            |         | Sa’ar                      | R                                |        |
|            |         | Naifa                      | TS                               |        |
|            |         | Madbi Shale                | S                                |        |
|            |         | Madbi Limestone            |                                  |        |
|            |         | Basal Sandstone            |                                  |        |
|            |         | Shuqra (?)                 | R                                |        |
|            |         | Kuhlan (?)                 | R                                |        |
|            |         | Basement                   | R                                |        |

Figure 2: Litho-stratigraphic column of the Masila Basin, Yemen (modified after Canadian Oil Company, 2003, personal communication).
Jurassic shales, Masila Basin, Eastern Yemen

During the late Early Cretaceous, alternating regression and transgression occurred. This pattern developed clastic (Harshiyat Formation) and carbonate rocks (Fartaq Formation) interbedded with each other. A similar pattern of sedimentation occurred in Upper Cretaceous time, where fluvial systems (Mukulla Formation) prograded southeastward in the Masila Basin. The Late Cretaceous Sharwayn Formation deposits are composed mainly of shale. In the Late Paleocene, sea level rose and resulted in the formation of transgressive shale deposits (Shammer Member) at the base of the Umm Er Radhuma carbonate formation. The Umm Er Radhuma Formation consists of limestone (hard to medium) interbedded with thin layers of white to brown microcrystalline dolomite, and is influenced by the unconformity between the Cretaceous and Tertiary sequences. It is overlain by shale (Jiza’ Formation). Jiza’ deposits are widespread in the Early Eocene followed by the deposits of the anhydrite rocks (Rus Formation).

SAMPLES AND METHODS

A total of 30 samples from Jurassic Madbi shales were analyzed from boreholes (side wall core and drill cuttings) in the Sunah, Wadi Taribah and Kharir fields (Figure 1).

In this study, petrographic examinations were conducted on four shale samples from the Kharir field using a Leica CTR 6000-M microscope with white and ultraviolet (UV) light sources, photometer and oil immersion objectives. Vitrinite reflectance (%Ro) was measured in oil immersion. Pyrolysis/TOC analyses were performed on 30 samples (ten each from Sunah, Wadi Taribah and Kharir), extraction analyses were conducted on eight samples from various fields, GC analyses were performed on six samples and GC–MS analyses were carried out on one sample from each field.

Total Organic Carbon and Rock-Eval pyrolysis analysis were performed on 100 mg crushed rock sample which was heated to 600 °C in a helium atmosphere, using a TOC module equipped Rock-Eval II instrument.

Samples were subsequently extracted in a Soxhlet apparatus for 72 hours using an azeotropic mixture of dichloromethane and methanol (93:7). Extracts were separated into saturated hydrocarbon, aromatic hydrocarbon and NSO-compound fractions by liquid column chromatography. Saturated fractions were dissolved in hexane and analysed by gas chromatograph, equipped with a flame ionization detector (FID). A FID gas chromatograph with HP-5MS column, temperature programmed from 40–300 °C at a rate of 4 °C/minute, and then held for 30 minutes at 300 °C, was used for GC analysis. GC-MS experiments were performed on a V 5975B inert MSD mass spectrometer with a gas chromatograph attached directly to the ion source (70eV ionization voltage, 100 milliamps filament emission current, 230 °C interface temperature). For the analysis of biomarkers, the metastable ion transition for steranes (m/z 217) and triterpanes (m/z 191) was recorded at a dwell time of 25 ms per ion and cycle time of 1 second. Compounds were identified through retention time. Triterpane and sterane distributions were quantified by measuring peak heights in the m/z 191 and m/z 217 chromatograms.

RESULTS AND DISCUSSION

Palynomorphs and Macerals

On the basis of palynological determinations, the Kharir (Madbi Formation) shales are of Jurassic age. The main palynofacies identified in these shales are structured organic matter (SOM) and structureless (amorphous) organic matter (AOM). The structured organic matter contains phytoclasts (woody tissues) and palynomorphs. The organic residue is abundant in the studied shale samples and consists of AOM, well-preserved pollen, spores, woody fragments, as well as marine dinoflagellates (Figure 3).

Results of petrographic examinations and maceral determinations reveal that the shale samples (KH-1, KH-2, KH-3, and KH-4) possess low to medium levels of bitumen staining and contain abundant phytoclasts, which mainly consist of liptinitic constituents (particularly alginite), thin strands of cutinite, liptodetrinite and sporinite, and lesser amount of vitrinite. Pyrite and quartz are the main inorganic components observed in these samples (Figure 4).
Figure 3: Photomicrographs of palynofacies organic matter in Jurassic shales, Masila Basin under white transmitted light and oil immersion; (a) marine species of palynomorphs; (b) spore and pollen species; (c) amorphous organic matter (AOM; mostly brown-dark brown and black-opaque); and (d) structured woody tissue.
Figure 4: Photomicrographs of phytoclasts in Jurassic shales under visible white light (a and b) and plane polarized incident fluorescence (c, d, e and f); (a) bitumen staining associated with abundant phytoclasts; (b) showing high reflecting pyrite (Py); (c) alginite fluorescing bright yellow; (d) sporinite (SP); (e) thin strands of cutinite associated with liptodetrinite; and (f) dull yellow fluorescing liptodetrinite.
Total Organic Carbon and Rock-Eval Pyrolysis

Total organic carbon (TOC) analysis showed average TOC values of shale samples from the Sunah, Wadi Taribah and Kharir fields are 2.4, 2.9 and 4.7%, respectively (Table 1). Shale samples from the Sunah and Wadi Taribah fields have very similar TOC values, while the Kharir shales have TOC values higher than those of other fields.

In the Rock-Eval pyrolysis analysis, free hydrocarbons (S1) in the rock and the amount of hydrocarbons (S2) and CO2 (S3) expelled from pyrolysis of kerogen are measured (Table 1).

In addition, the T_max value, which represents the temperature at the point where the S2 peak is the maximum is also determined (Espitalié, 1985). Potential Yield (PY) values for the Kharir shale samples are higher than others. Shale samples from the Kharir field show HI values (average 574 mg HC/g TOC) higher than those of other fields. Average T_max values of shale samples from the Sunah, Wadi Taribah and Kharir fields are 438, 429 and 433 °C, respectively. Therefore, these Jurassic shales are good to excellent oil-prone source rocks at early to peak oil maturity.

| Samples | Depth (m) | TOC (%wt) | % Ro | S1 (mg HC/g rock) | S2 (mg HC/g rock) | S3 (mg CO2/g rock) | S2/S3 | PY (S1+S2) | Tmax (°C) | HI (mg HC/g TOC) | OI (mg CO2/g TOC) | PI (S1/(S1+S2)) | S1/(S1+S2) |
|---------|----------|-----------|------|------------------|------------------|------------------|-------|------------|----------|-----------------|-----------------|----------------|------------|
| Sunah Field | | | | | | | | | | | | | |
| SUN-1 | 2981 | 3.4 | 0.65 | 1.88 | 17.61 | 0.15 | 115 | 19.50 | 438 | 518 | 4.5 | 0.10 |
| SUN-2 | 2983 | 1.7 | 0.75 | 0.79 | 7.41 | 0.15 | 48.4 | 8.20 | 438 | 436 | 9.0 | 0.10 |
| SUN-3 | 2988 | 3.0 | 0.75 | 2.46 | 12.84 | 0.26 | 50.4 | 15.30 | 437 | 428 | 8.5 | 0.16 |
| SUN-4 | 2997 | 1.1 | 0.75 | 0.49 | 4.29 | 0.13 | 32.5 | 4.78 | 437 | 390 | 12.0 | 0.10 |
| SUN-5 | 3011 | 2.4 | 0.83 | 1.89 | 12.11 | 0.35 | 34.6 | 14.00 | 438 | 365 | 9.0 | 0.13 |
| SUN-6 | 3013 | 2.6 | 0.82 | 1.66 | 9.54 | 0.36 | 26.2 | 11.20 | 441 | 367 | 14.0 | 0.15 |
| SUN-7 | 3033 | 3.5 | 0.85 | 1.34 | 8.76 | 0.22 | 40.6 | 10.10 | 438 | 390 | 9.0 | 0.16 |
| SUN-8 | 3043 | 1.7 | 0.86 | 0.97 | 5.02 | 0.43 | 11.8 | 5.98 | 439 | 295 | 25.0 | 0.16 |
| SUN-9 | 3053 | 1.1 | 0.75 | 0.49 | 4.29 | 0.13 | 32.5 | 4.78 | 437 | 390 | 12.0 | 0.10 |
| Mean | | 2.40 | 0.80 | 1.60 | 9.50 | 0.27 | 41.50 | 11.10 | 438 | 386 | 11.8 | 0.14 |
| Wadi Taribah Field | | | | | | | | | | | | | |
| WTH-1 | 2295 | 4.4 | 0.51 | 1.18 | 19.65 | 0.92 | 21.4 | 20.83 | 428 | 447 | 21.0 | 0.06 |
| WTH-2 | 2298 | 3.1 | 0.51 | 1.08 | 14.64 | 0.84 | 17.4 | 15.14 | 429 | 472 | 27.0 | 0.03 |
| WTH-3 | 2303 | 3.5 | 0.52 | 1.08 | 14.81 | 1.02 | 14.5 | 15.89 | 425 | 423 | 29.0 | 0.07 |
| WTH-4 | 2307 | 3.1 | 0.52 | 0.62 | 17.21 | 0.90 | 19.1 | 17.83 | 428 | 559 | 29.0 | 0.03 |
| WTH-5 | 2310 | 3.2 | 0.52 | 1.02 | 15.19 | 1.09 | 13.9 | 16.21 | 429 | 475 | 34.0 | 0.06 |
| WTH-6 | 2316 | 2.9 | 0.52 | 0.39 | 13.26 | 0.81 | 16.4 | 13.65 | 429 | 457 | 28.0 | 0.03 |
| WTH-7 | 2322 | 1.9 | 0.53 | 0.25 | 8.04 | 1.01 | 8.0 | 8.29 | 430 | 432 | 53.0 | 0.03 |
| WTH-8 | 2335 | 2.3 | 0.53 | 0.31 | 10.66 | 0.78 | 13.7 | 10.97 | 431 | 464 | 34.0 | 0.03 |
| WTH-9 | 2337 | 2.2 | 0.53 | 0.18 | 6.84 | 0.70 | 9.8 | 7.02 | 435 | 360 | 37.0 | 0.03 |
| Mean | | 2.40 | 0.52 | 0.58 | 12.86 | 0.88 | 14.6 | 13.44 | 429 | 445 | 33.0 | 0.03 |
| Kharir Field | | | | | | | | | | | | | |
| KHA-1 | 2410 | 1.9 | 0.69 | 2.70 | 7.37 | 0.72 | 10.2 | 10.10 | 432 | 380 | 37.0 | 0.27 |
| KHA-2 | 2425 | 4.2 | 0.73 | 5.30 | 23.44 | 0.69 | 34.0 | 28.70 | 430 | 557 | 16.0 | 0.18 |
| KHA-3 | 2465 | 3.3 | 0.76 | 1.90 | 16.12 | 0.97 | 16.6 | 18.00 | 433 | 494 | 30.0 | 0.11 |
| KHA-4 | 2510 | 3.9 | 0.79 | 2.81 | 28.95 | 1.13 | 25.6 | 31.80 | 432 | 744 | 29.0 | 0.09 |
| KHA-5 | 2545 | 7.0 | 0.81 | 5.90 | 52.32 | 1.17 | 44.7 | 58.20 | 435 | 752 | 17.0 | 0.10 |
| KHA-6 | 2550 | 5.9 | N/P | 5.53 | 40.67 | 1.03 | 39.5 | 46.20 | 433 | 691 | 17.0 | 0.12 |
| KHA-7 | 2560 | 6.4 | 0.83 | 5.10 | 36.33 | 0.74 | 49.1 | 41.40 | 433 | 569 | 12.0 | 0.12 |
| KHA-8 | 2600 | 8.2 | 0.83 | 7.70 | 58.95 | 0.94 | 62.7 | 66.70 | 434 | 719 | 11.0 | 0.12 |
| KHA-9 | 2660 | 3.4 | 0.89 | 2.39 | 15.16 | 1.26 | 12.0 | 17.60 | 432 | 446 | 37.0 | 0.14 |
| KHA-10 | 2670 | 2.5 | 0.90 | 2.60 | 9.54 | 0.73 | 13.1 | 12.10 | 436 | 385 | 29.0 | 0.21 |
| Mean | | 4.70 | 0.80 | 4.19 | 28.89 | 0.94 | 30.8 | 33.10 | 433 | 574 | 24.0 | 0.15 |
Table 2
Amount of extractable bitumen and total organic carbon (TOC) and bitumen/TOC ratio of selected shale samples

| Field name      | Sample Number | Total extract (%) | TOC (wt %) | Bitumen/TOC |
|-----------------|---------------|-------------------|------------|-------------|
| Sunah-Field     | SUN-2         | 0.32              | 1.7        | 0.18        |
|                 | SUN-9         | 0.30              | 1.7        | 0.18        |
|                 | SUN-10        | 0.31              | 2.0        | 0.16        |
| Wadi Taribah Field | WTH-1    | 0.44              | 4.4        | 0.10        |
|                 | WTH-8         | 0.30              | 2.3        | 0.13        |
| Kharir Field    | KHA-4         | 0.53              | 3.9        | 0.14        |
|                 | KHA-5         | 1.16              | 7.0        | 0.17        |
|                 | KHA-9         | 0.73              | 3.4        | 0.21        |

Molecular Composition

Extraction amounts obtained from the shale samples from Sunah, Wadi Taribah and Kharir fields are given in Table 2. In comparison to other fields, shale samples from the Kharir and Sunah fields yield higher bitumen/TOC ratios. This is most probably due to higher maturity of the Kharir and Sunah shales. Bitumen/TOC ratios of Wadi Taribah shales are low.

Biomarker Distributions

N-alkanes and Isoprenoids

The gas chromatograms of the Kharir, Wadi Taribah and Sunah samples, examples of which are shown in Figure 5, display abundant n-alkanes, particularly of low to medium molecular weight. n-C$_{14}$ to

![Figure 5: Gas chromatography showing saturate fraction distributions in the selected Jurassic shale samples in the Sunah, Wadi Taribah and Kharir fields, Masila Basin.]
n-C20 and Pr are the most dominant peaks in the saturate gas chromatograms of the studied shale samples. Acyclic isoprenoids are abundant in the samples with pristane being dominant prominent peak in all of the saturate gas chromatograms. The Pr/Ph ratios of samples from the Sunah, Wadi Taribah and Kharir fields are 1.8, 2.3 and 1.9, respectively (Table 3). CPI index is calculated here based on the formula proposed by Peters and Moldowan (1993), that is \( \frac{2(C_{23}+C_{25}+C_{27}+C_{29})}{[C_{22}+2(C_{24}+C_{26}+C_{28})+C_{30}]} \). On the basis of the gas chromatograms of the Kharir (KH-2 and KH-3) samples, the CPI value is 1.0.

**Triterpanes and Steranes**

In this study, sterane and triterpane distributions of bitumen were determined for shale samples of the Sunah, Wadi Taribah and Kharir fields (Figure 6). Peak identification on m/z 191 and m/z 217 chromatograms are given in Appendix 1. In addition, various parameters were computed (Table 4) using the sterane distribution recorded on the m/z 217 mass chromatograms and using the triterpane distribution recorded on the m/z 191 mass chromatograms.

From the m/z 217 mass chromatograms (Figure 6) of the Sunah, Wadi Taribah and Kharir samples, relative abundance of C_{27}-C_{28}-C_{29} regular steranes is calculated as 39-20-41, 43-18-38 and 41-20-38\%, respectively. Distributions of C_{27}^{25}C_{28}^{27}C_{29}^{29} steranes for all shale samples are very similar (C_{27}^{27}C_{28}^{28}C_{29}^{29}). The C_{29}/C_{27} sterane ratio for the Sunah, Wadi Taribah and Kharir shales are 41/36, 38/43, and 38/41, respectively. Diasterane/sterane ratios are calculated as 90, 34 and 44\%. The 20S/(20S+20R) regular steranes and αββ(αββ+ααα) for C_{29} are also calculated (Table 4).

The m/z 191 mass chromatograms of the saturated hydrocarbon fractions (Figure 6) show high relative abundance of pentacyclic triterpanes with low relative abundance of tricyclic terpanes. In the Wadi Taribah and Kharir samples, Tm (C_{27}^{17}-(H)-22,29,30-trisnorhopane) is more abundant than Ts (C_{27}^{18}-(H)-22,29,30-trisnorneohopane). On the other hand, in the sample from the Sunah field, Ts is more abundant than Tm. In all shale samples, C_{29} norhopane is less than C_{30} hopane. C_{29}/C_{30} hopane ratios for the Sunah, Wadi Taribah and Kharir samples are 0.44, 0.49 and 0.53, respectively. Moretane/hopane ratio for the Sunah, Wadi Taribah and Kharir shale samples are 0.14, 0.15 and 0.13, respectively. Extended hopanes are dominated by the C_{31} homohopane and decreasing towards the C_{35} homohopane (Figure 6). The concentrations of C_{35} homohopanes are low and the C_{35} Homohopane Index for the Sunah, Wadi Taribah and Kharir shale samples are 0.04, 0.05 and 0.04, respectively. The homohopane distributions of the shale samples in the Sunah and Kharir fields are very similar. Sterane/hopane ratios for the Sunah, Wadi Taribah and Kharir shale samples are 0.82, 0.80 and 0.70, respectively. The significance of biomarker parameters will be discussed in the organic maturation and depositional environment sections.

**Type of Organic Matter**

Shale samples collected from different fields were plotted in the pyrolysis S2 yield versus TOC diagram (Langford and Blanc Valleron, 1990). All shale samples from the Sunah, Wadi Taribah and Kharir

| Sample Number     | isoprenoids/n-alkanes | Pr/Ph | Pr/C_{17} | Ph/C_{19} |
|-------------------|------------------------|-------|-----------|-----------|
| Sunah (SUN-2)     |                        | 1.64  | 1.38      | 0.79      |
| Sunah (SUN-9)     |                        | 2.00  | 1.30      | 0.81      |
| Wadi Taribah (WTH-1) |                      | 2.50  | 1.45      | 0.82      |
| Wadi Taribah (WTH-8) |                      | 2.00  | 1.24      | 0.77      |
| Kharir (KHA-4)    |                        | 1.94  | 1.52      | 0.82      |
| Kharir (KHA-9)    |                        | 1.88  | 1.50      | 0.82      |
Jurassic shales, Masila Basin, Eastern Yemen

**Figure 6:** Selected mass fragmentograms (m/z 191, right) and (m/z 217, left) of saturate fraction from Jurassic shale samples.

**Table 4**

| Biomarker distribution parameters                      | Sunah (SUN-2) | Wadi Taribah (WTH-1) | Kharir (KHA-4) |
|---------------------------------------------------------|---------------|----------------------|----------------|
| 22S/(22S+22R) C₃₂ homohopane                           | 0.58          | 0.56                 | 0.58           |
| 20S/(20S+20 R) sterane ratio (C₂₉)                      | 0.49          | 0.47                 | 0.47           |
| ββ/[(ββ+αα) sterane ratio (C₂₉)]                        | 0.52          | 0.53                 | 0.55           |
| C₂₉/C₃₀ hopane ratio                                   | 0.44          | 0.49                 | 0.53           |
| Ts/(Ts+Tm) ratio                                        | 0.81          | 0.48                 | 0.46           |
| C₃₀, C₂₉, C₂₈ sterane abundance                        | 39, 20, 41    | 43, 18, 38           | 41, 20, 38     |
| C₃₀/C₂₉ sterane ratio                                  | 1.07          | 0.91                 | 0.97           |
| Moretane/hopane ratio                                  | 0.14          | 0.15                 | 0.13           |
| Diasterane/ sterane ratio                              | 0.84          | 0.45                 | 0.56           |
| Sterane/hopane ratio                                   | 0.82          | 0.80                 | 0.70           |
| C₂₅/C₂₆ tricyclic terpane                              | 1.60          | 1.53                 | 1.90           |
| C₃₅/(C₁₇-C₃₅) homohopane index                         | 0.041         | 0.047                | 0.042          |
fields are in the Type II area and two samples from the Kharir field are in the Type I area, while another sample from the same field plots in the Type II area (Figure 7).

The HI versus T\textsubscript{max} diagram (Mukhopadhyay et al., 1995) is used for determining the kerogen type (Figure 8). T\textsubscript{max} value may change with respect to not only maturity of kerogen but also kerogen type (Hunt, 1996). Shale samples from different fields were plotted in the HI–T\textsubscript{max} diagram, and it was determined that samples generally plot in the Type I and Type II kerogen areas (Figure 8). Four of the samples from the Kharir field plot in the Type I kerogen area, and other samples plot in the Type II kerogen area. Samples from the Sunah and Wadi Taribah fields plot in the Type II kerogen area. The HI–T\textsubscript{max} diagram also provides information on maturity of samples. As shown in Figure 8, the Sunah and Kharir shale samples are mature, while Wadi Taribah samples are immature. The organic matter type for Kharir, Sunah and Wadi Taribah shales was determined as Type II and this organic matter type agrees with the maceral type (dominantly liptinite) of these shale samples.

In the gas chromatogram of the shale samples, n-alkanes are found in the range of C\textsubscript{15}–C\textsubscript{34} (Figure 5). Such a distribution of n-alkanes reflecting an abundance of medium molecular weight material (n-C\textsubscript{13}–n-C\textsubscript{20}) is indicative of marine organic matter input when observed in source rock extracts (Tissot and Welte, 1984; Waples, 1985).

**Maturity of Organic Matter**

The average values of T\textsubscript{max} indicate that the samples from the Sunah and Kharir fields are early mature to mature. Shale samples from the Wadi Taribah field are immature (Tissot and Welte, 1984; Merrill, 1991). In addition, low bitumen/TOC ratios of these shale samples indicate immature character (Peters and Cassa, 1994). Bitumen/TOC ratios for Kharir shale samples are about the same as Sunah and much higher than Wadi Taribah samples (Table 2) in line with the relative maturities of the shales at these locations.

Average vitrinite reflectance (\%Ro) values of the Sunah and Kharir shales are 0.81% and 0.82%, respectively (Table 1). These vitrinite reflectance values indicate that the Sunah and Kharir shales are thermally mature.
Jurassic shales, Masila Basin, Eastern Yemen

Some biomarker ratios are used for evaluation of maturity (Table 4). For example, \(22S/(22S + 22R)\) homohopane ratios for Sunah, Wadi Taribah and Kharir shale samples are 0.58, 0.56 and 0.58, respectively (Table 4), and these values indicate that homohopane transformations are at equilibrium and therefore that the shales are at least at 0.7%-0.8% maturity. \(20S/(20S + 20R)\) and \(\alpha\beta\beta/\alpha\alpha\alpha\) sterane ratios and \(T_s/(T_s + T_m)\) ratios indicate the same interpretation, as do the moretane/hopane ratios (Waples and Machihara, 1991). On the basis of \(T_{max}\) and vitrinite reflectance values, the Sunah and Kharir shales yield early mature–mature character while the Wadi Taribah shales are of incipient maturity.

Depositional Environments of Shales

Biomarker distributions may provide information about organic facies and depositional environment (Waples and Machihara, 1991; Hunt, 1996; Peters et al., 2005). Using the organic geochemical data, depositional environment conditions for the shale samples can be evaluated. In this study, organic facies and depositional environments were examined with the use of sterane and triterpane distributions recorded at m/z 217 and m/z 191 mass chromatograms, respectively and parameters calculated from these distributions (Table 4).

The \(C_{25}/C_{26}\) tricyclic terpanes ratios >1 (Table 4) for the Sunah, Wadi Taribah and Kharir shales indicate a marine environment (Zumbringe, 1987; Burwood et al., 1992; Hanson, 1999; Hanson et al., 2000). In

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Figure 8: Distribution of shale samples in HI versus \(T_{max}\) plot.
addition, the sterane/hopane ratio is relatively high in marine organic matter, with values generally approaching unity (Tissot and Welte, 1984).

The Pr/Ph ratios of the shale samples of the Sunah, Wadi Taribah and Kharir fields are 1.8, 2.3 and 1.9 (Table 3) and suggest that these samples were deposited under suboxic conditions (Powell, 1988; Amane and Hideki, 1997; Sarmiento and Rangel, 2004; Basent et al., 2005). In addition, in cases of C_{31} and C_{32} dominancy, a low C_{35} homohopane index indicates a suboxic environment (Hunt, 1996; Murray and Boreham, 1992). On the basis of these data, the shale samples under investigation were deposited in a suboxic marine environment.

**Potential for Hydrocarbon Generation**

Rock-Eval/TOC analyses indicate that the best generative potential is found in the Jurassic shales (Collister, 2000; Simon Petroleum Technology, Robertson Research International, 1994). The shale samples in the Jurassic unit have high total organic carbon content (>2.0%) and pyrolysis S\textsubscript{2} yields are sometimes more than 20.0 mg HC/g rock. Therefore, these shales rate as very good potential source rocks for oil based on the total organic carbon content and pyrolysis S\textsubscript{2} yields (Figure 9).

Marine shales that contain Type I and Type II kerogen can generate oil (Collister, 2000; Nani et al., 2000, personal communication). Shales with hydrogen index greater than 300 mg HC/gTOC that contain much more Type II organic matter can generate oil if they are subjected to sufficient burial and heating (Bordenave, 1993). In this respect, the Sunah, Wadi Taribah and Kharir shale samples have oil generation potential.
Jurassic shales, Masila Basin, Eastern Yemen

Bitumen/TOC ratio and production index (PI) can be used to show that the rock extracts and hydrocarbon yields represent indigenous rather than migrated hydrocarbons. High bitumen/TOC ratios of the Sunah and Kharir shales indicate mature character (Tissot and Welte, 1984; Peters and Cassa, 1994). In addition, one relationship (i.e. PI versus $T_{max}$) can be used to indicate the maturation and nature of the hydrocarbon products (i.e. indigenous or migrated; Figure 10). Based on this relationship, the Sunah and Kharir shale samples are thermally mature and the hydrocarbons are indigenous in these fields, while the hydrocarbons present in the Wadi Taribah field are low background amounts in low maturity (pre-generative) source rocks.

CONCLUSIONS

The combined organic geochemical analyses of the Jurassic shales in the Masila Basin indicate that the most organic-rich source rocks with the highest generative potential are the Jurassic Madbi shales. Based on this evaluation, the Madbi shale samples have very good source rock potential for oil generation as supported by high values of TOC, extractable organic matter, and hydrocarbon yield.

It was determined that the shales at Kharir Field contain dominantly Type II and lesser Type I kerogen, and the shales at Sunah and Wadi Taribah fields contain dominantly Type II kerogen. Moreover, on the basis of biomarker data, these shales contain organic matter of marine origin.

Overall evaluation of the maturity data implies that the Sunah and Kharir shales are early mature to mature, and Wadi Taribah shales are marginally mature. According to vitrinite reflectance values,
the shales at Sunah and Kharir are at peak mature stage. On the basis of these data, it is thought that
the shale sequences at Sunah and Kharir have attained sufficient burial depth and thermal effect for
significant oil generation.

The Pr/Ph ratios for the Sunah, Wadi Taribah and Kharir shales together with homohopane
distributions, in which C_{31} and C_{32} are dominantly observed while C_{35} homohopanes were recorded
in very low concentrations, indicate that all shales were deposited in a suboxic environment. The
presence of C_{30}/C_{29} tricyclic terpane ratios greater than one and sterane/hopane ratios imply that the
shales under investigation were deposited in a marine environment.

On the basis of all available data, Madbi shales exposed in the Sunah, Wadi Taribah and Kharir fields
are believed to be source rocks for oil generation and exhibit significant similarities in depositional
environments and conditions.

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APPENDIX 1

Peak assignments for alkane hydrocarbons (I) m/z 191 mass chromatograms and (II) m/z 217 mass
chromatograms.

| (I) peak No. | Compound | Abbreviation |
|-------------|----------|--------------|
| Ts          | 18α(H),22,29,30-trisnorneohopane | Ts |
| Tm          | 17α(H),22,29,30-trisnorhopane     | Tm |
| 29          | 17α,21β(H)-nor-hopane             | hopane |
| 30          | 17α,21β(H)-hopane                 | hopane |
| 3M          | 17 β,21α (H)-moretane             | C_{30}Mor |
| 31S         | 17α,21β(H)-homohopane (22S)       | C_{31}(22S) |
| 31R         | 17α,21β(H)-homohopane (22R)       | C_{31}(22R) |
| 32S         | 17α,21β(H)-homohopane (22S)       | C_{32}(22S) |
| 32R         | 17α,21β(H)-homohopane (22R)       | C_{32}(22R) |
| 33S         | 17α,21β(H)-homohopane (22S)       | C_{33}(22S) |
| 33R         | 17α,21β(H)-homohopane (22R)       | C_{33}(22R) |
| 34S         | 17α,21β(H)-homohopane (22S)       | C_{34}(22S) |
| 34R         | 17α,21β(H)-homohopane (22R)       | C_{34}(22R) |
| 35S         | 17α,21β(H)-homohopane (22S)       | C_{35}(22S) |
| 35R         | 17α,21β(H)-homohopane (22R)       | C_{35}(22R) |

| (II) peak No. | Compound | Abbreviation |
|---------------|----------|--------------|
| a             | 13β,17α(H)-diasteranes 20S | diasteranes |
| b             | 13β,17α(H)-diasteranes 20R | diasteranes |
| c             | 13α,17β(H)-diasteranes 20S | diasteranes |
| d             | 13α,17β(H)-diasteranes 20R | diasteranes |
| e             | 5α,14αα(H), 17αβ(H)-steranes 20S | δδδ | oxo20S |
| f             | 5α,14ββ(H), 17ββ(H)-steranes 20R | δββδ | oβo20R |
| g             | 5α,14ββ(H), 17ββ(H)-steranes 20S | δβδδ | oβo20S |
| h             | 5α,14αα(H), 17αβ(H)-steranes 20R | δδδδ | oxo20S |
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