Chapter 1

Petroleum Source Rocks Characterization and Hydrocarbon Generation

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.70092

Abstract

This chapter is proposed to give the principal learning on the application of the formation of petroleum source rocks and hydrocarbon generation to exploration activities. The evaluation of petroleum source rocks and hydrocarbon generation is a very important skill for explorationists to define the location and type of petroleum prospects in a region. In this chapter, subsurface samples from case study (Sayun-Masilah basin) were used to determine the source rock characteristics and petroleum generative potentials of prospective source rocks. Qualitative and quantitative evaluation of the source rock in this basin was done by means of geochemical and geophysical approaches for four rock units. It is clear that Madbi Formation is considered the main source, in which the organic carbon content reached up to more than 5.2 wt%. The types of organic matter from rock-eval pyrolysis data indicated that type I kerogen is the main type, in association with type II, and a mixture of types II and III kerogens. The study of the different maturation parameters obtained from rock-eval pyrolysis, such as T_{max} and vitrinite reflectance, reflects that the considered rock units are occurred in different maturation stages, ranging from immature to mature sources. One-dimensional basin modeling was performed to analyze the hydrocarbon generation and expulsion history of the source rocks in the study area based on the reconstruction of the burial and thermal maturity histories in order to improve our understanding of the hydrocarbon generation potential. Calibration of the model with measured vitrinite reflectance (%Ro) and borehole temperature (BHT) data indicates that the paleo-heat flow was high at Late Jurassic. The models also indicate that the early hydrocarbon generation in the Madbi source rock occurred during late Cretaceous and the main hydrocarbon generation has been reached approximately at Early Eocene. Therefore, the Madbi source rock can be considered as generative potentials of prospective source rock horizons in the Sayun-Masilah basin.

Keywords: source rocks, thermal maturity, basin modeling, hydrocarbon generation modeling, Sayun-Masilah basin, Yemen

1. Introduction

Petroleum source rock is defined as the fine-grained sediment with sufficient amount of organic matter, which can generate and release enough hydrocarbons to form a commercial accumulation of oil or gas [1]. Source rocks are commonly shales and lime mudstones, which contain significant amount of organic matter [2]. A petroleum source rock is defined as any rock that has the capability to generate and expel enough hydrocarbons to form an accumulation of oil or gas. Source rocks are classified according to oil generation into three classes [1], as follows:

1. Immature source rocks that have not yet generated hydrocarbons.
2. Mature source rocks that are in generation phase.
3. Post mature source rocks are those which have already generated all crude oil type hydrocarbons.

Waples [3] distinguished the petroleum source rocks into potential, possible, and effective, as follows:

A. Potential source rocks are immature sedimentary rocks capable of generating and expelling hydrocarbons, if their level of maturity were higher.

B. Possible source rocks are sedimentary rocks whose source potential has not yet been evaluated, but which may have generated and expelled hydrocarbons.

C. Effective source rocks are sedimentary rocks, which have already generated and expelled hydrocarbons.

The hydrocarbon source evaluation is generally based on the organic matter quantity (organic richness), quality (kerogen type), and the thermal maturation generation capability and of the organic matter disseminated in the rock [2–4]. Organic matter content can be determined directly from laboratory analyses of the source rock samples (shale, limestone, or marl), and through indirect methods based on wireline data offer the advantages of economic, ready availability of data, and continuity of sampling of vertically heterogeneous shale section.

This chapter displays how to evaluate source rocks and hydrocarbon generation using geochemical data, with an easy method and evaluate source rocks from gas chromatography for crude oil and extract bitumen. This chapter will be presented with case study and some examples for understanding petroleum source rocks and hydrocarbon generation. Also, in this chapter, quantitative one-dimensional basin modeling is performed for evaluating the thermal histories and timing of hydrocarbon generation and expulsion of the source rocks in the sedimentary basin.

2. Evaluation of petroleum source rocks using geochemical data

The source rock evaluation within any study area involved the recognition of petroleum source, which depends on the determination of its proportion of organic matter (organic matter quantity), which is usually expressed as total organic carbon (TOC wt%). It also depends on the type (or quality) of organic matter (kerogen) preserved in the petroleum source. The geochemical data such as total organic carbon (TOC wt%), rock-eval pyrolysis data, bitumen extraction, and vitrinite reflectance are presented and discussed for the proposed Upper Jurassic and Lower Cretaceous rock units in the Sayun-Masilah basin in Yemen. The total organic carbon, S2 and genetic potential from rock-eval pyrolysis and extractable organic matter (bitumen) from selected rock samples were used to identify the source-richness in terms of quantity and generation potential. Plots of T_{max} (C°) against hydrogen index (HI mgHC/gm of TOC) and hydrogen index (HI) against oxygen index (OI) from rock-eval pyrolysis are used to identify the kerogen type (quality) and depositional environment. Rock-eval T_{max} (C°) was used to evaluate source rock maturity stage, in conjunction with vitrinite reflectance pattern as a maturity tool.

Pyrolysis is almost the best routine tool for determining the kerogen type [5]. The rock-eval pyrolysis data are considered to be the most valuable geochemical exploration tool used to evaluate the type of organic matter, thermal maturity, and the generation capability of source rocks. The generated thermo-vaporized free hydrocarbons already present in the rock "S1" are released at temperatures lower than those needed to break down the kerogen, hence monitoring the hydrocarbons released by steadily increasing temperature, providing a way for obtaining the amount of generated hydrocarbons relative to the total potential. The "S2" peak represents the genetic potential of the sample, which is the hydrocarbon that would generate at optimum maturity. The "S1" and "S2" are expressed in milligrams of hydrocarbon per gram of rock (mg/g). The "S3" peak represents the quantity of evolved CO_2 expressed in milligrams of CO_2 per gram of rock (mg/g). The temperature (T_{max}) at which the pyrolysis peak S2 occurs has been used as a measure of maturity; it increases with increasing levels of maturity. Two useful parameters are obtained from rock-eval pyrolysis data: the hydrogen index (HI = S2/TOC wt%, equivalent to H/C atomic ratio in van Krevelen diagram) and the oxygen index (OI = S3/TOC wt%, equivalent to O/C atomic ratio in the kerogen).

2.1. Source rock generative potential

The organic matter richness and hydrocarbon generative potential of the source rocks in the Sayun-Masilah basin can be evaluated by bulk geochemical data such as TOC content and pyrolysis S1 and S2 yields (**Table 1**). The organic richness of a rock is usually expressed as the total organic carbon content (wt% TOC). The minimum acceptable TOC value for clastic type rocks indicating good source potential is 1.0% [1, 6]. The Upper Jurassic sediments samples have moderate to high TOC content (0.85–33.3 wt%), revealing organic-rich intervals within stratigraphic levels (**Figure 1**). The L. Qishn Member (Lower Cretaceous age) consists of sandstone and shale and with small intercalations of carbonates. The L. Qishn shale samples contain rich organic matter and have TOC content of 1.4–3% (**Figure 1**). Based on the classification proposed by [7], L. Qishn shale sample is considered to be a fair to good source rock (**Figure 1**). The amount of hydrocarbon yield (S2) expelled during pyrolysis is a useful measurement to evaluate the generative potential of source rocks [7, 8]. Most of the analyzed samples have more than 1.0 mg HC/g rock (**Figure 1**). Thus, pyrolysis S2 yields indicate that the L. Qishn shale samples are poor to fair generative potential (**Figure 1**).

Age	Rock Units	Depth (m)	TOC (wt%)	Rock-eval pyrolysis								Ro (%)
				S_1 (mg/g)	S_2 (mg/g)	S_3 (mg/g)	T_{max} (C)	HI (mg/g)	OI (mg/g)	PI (mg/g)	PY ($S_1 + S_2$)	
Lower Cretaceous	Harshiat Fm	900	3.47	0.0694	6.8706	0.3817	433	198	11	0.01	6.94	0.36
		1000	33.3	0.6963	68.931	2.664	428	207	8	0.01	69.6	0.36
		1100	34	0.5564	55.08	2.72	430	162	8	0.01	55.6	0.34
		1500	0.85	0.0201	0.3825	0.476	427	45	56	0.05	0.4	0.4
	L. Qishn Member	1860	1.87	2.1442	3.0855	3.927		165	210	0.41	5.2	0.39
		1875	17	23.803	37.23	24.99		219	147	0.39	61.0	
		1890	2.99	3.8757	5.3521	3.9767		179	133	0.42	9.2	
		1920	1.4	1.0478	1.946	3.024		139	216	0.35	2.9	0.41
Upper Jurassic	Nayfa Fm	2310	0.82	0.0306	0.5822	0.164	436	71	20	0.05	0.6	0.43
		2400	2.6	1.7967	6.37	4.264		245	164	0.22	8.1	0.5
		2430	0.83	0.0743	0.9877	0.1826	442	119	22	0.07	1.0	
		2457	1.01	0.114	1.515	0.2828	444	150	28	0.07	1.6	0.5
		2490	1.57	0.3072	3.5325	0.3454	444	225	22	0.08	3.8	
		2510	1.65	0.2359	3.696	0.396	442	224	24	0.06	3.9	0.5
		2540	1.62	0.2456	4.6656	0.2754	441	288	17	0.05	4.9	
		2555	1.29	0.3668	4.2183	0.4257	435	327	33	0.08	4.5	
		2570	2.23	0.5082	9.6559	0.4014	440	433	18	0.05	10.1	
	Madbi Fm	2585	8.37	5.5056	49.55	0.7533	443	592	9	0.1	55.0	0.74
		2586.4	6.1	6.9342	33.855	0.61	442	555	10	0.17	40.7	
		2587	4.07	4.4224	20.147	0.4477	439	495	11	0.18	24.5	
		2588	8.16	6.5111	43.574	0.5712	441	534	7	0.13	50.0	
		2589	11.8	7.3684	66.316	0.472	442	562	4	0.1	73.6	
		2590	6.85	4.9697	40.21	0.3425	441	587	5	0.11	45.1	
		2591	7.9	5.1359	41.554	0.869	443	526	11	0.11	46.6	0.87
		2591.3	8.82	5.3472	54.067	0.3528	438	613	4	0.09	59.4	
		2592.7	2.75	3.1625	12.65	0.55	437	460	20	0.2	15.8	
		2593.4	3.48	3.9917	17.017	0.3828	432	489	11	0.19	21.0	
		2595	7.37	5.265	42.599	0.6633	442	578	9	0.11	47.8	
		2597	7.41	5.507	40.385	0.8151	441	545	11	0.12	45.8	
		2598.5	5.92	5.9989	31.494	0.6512	442	532	11	0.16	37.4	
		2602	4.63	4.1098	23.289	0.5093	444	503	11	0.15	27.3	
		2605	4.08	3.3276	20.441	0.4896	440	501	12	0.14	23.7	0.78
		2606	5.96	4.3237	31.707	0.2384	442	532	4	0.12	36.0	0.81

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Age	Rock Units	Depth (m)	TOC (wt%)	Rock-eval pyrolysis								Ro (%)
				S_1 (mg/g)	S_2 (mg/g)	S_3 (mg/g)	T_{max} (C)	HI (mg/g)	OI (mg/g)	PI (mg/g)	PY ($S_1 + S_2$)	
		2606.5	4	4.5828	17.24	0.64	439	431	16	0.21	21.8	
		2610.7	4.05	4.2737	22.437	0.5265	440	554	13	0.16	26.7	0.73
		2615	1.24	0.7307	4.4888	0.2232	436	362	18	0.14	5.21	
	Shuqra Fm	2615.5	5.09	3.3802	24.788	0.7126	442	487	14	0.12	28.1	
		2625	5.94	3.9718	32.135	0.594	440	541	10	0.11	36.1	
		2665	1.47	0.3286	4.3659	0.4557	440	297	31	0.07	4.6	
		2680	1.13	0.163	3.0962	0.3729	442	274	33	0.05	3.2	0.82

S1: volatile hydrocarbon (HC) content, mg HC/g rock; TOC: total organic carbon, wt.%.
S2: remaining HC generative potential, mg HC/g rock; S3: Volatile carbon dioxide (CO2) content, mg HC/g rock; PI: production index = S1/(S1 + S2).
T_{max}: temperature at maximum of S2 peak; PY: potential yield = S1 + S2 (mg/g).
HI: hydrogen index = S2 × 100/TOC, mg HC/g TOC; OI: Oxygen Index = S3 × 100/TOC; Ro: Vitrinite reflectance.

Table 1. Results of pyrolysis and TOC content analyses with calculated parameters with measured vitrinite reflectance of the source rocks in Sayun-Masilah basin.

L. Qishn shale samples have low hydrogen index (HI) values in the range of 139–219 mg HC/g TOC (**Figure 1**). The shale samples in the Nayfa Formation (Upper Jurassic age) contains a total organic carbon content ranging between 0.82 and 2.2 wt%; thus indicating a fair to good source rock (**Figure 1**). The pyrolysis yield S2 and petroleum potential yield ranging from 0.5 to 9.6 and 0.07 to 1.7 mg HC/g rock, respectively; **Figure 1**, consequently, is considered to be poor to good source generative potential. Total organic carbon (TOC) analysis showed high TOC values of the samples from the Madbi Formation (Upper Jurassic age) and ranging from 1.2 to 8.8 wt% (**Figure 1**). The TOC contents meet the accepted standards of a source rock with good to excellent hydrocarbon generative potential as suggested by [1]. This is confirmed by the pyrolysis S2 yield, petroleum potential yield S1, and extract of organic matter (EOM) (**Figure 1**) as a useful parameter to evaluate the generation potential of source rocks [7, 8].

The hydrocarbon yields (S2) are in agreement with TOC content, indicating that the shales of Madbi Formation are good to excellent source rock generative potential based on the classification by Peters and Cassa [6] (**Figure 2**). The shale samples could become the most promising source rock for hydrocarbon generation as reflected by high pyrolysis yield (S2) and total organic carbon (TOC wt%) content (**Figure 2**).

Overall, the relation between genetic petroleum potential yield (PY; S1 + S2) and TOC of the studied units in the Sayun-Masilah basin confirms the above results, where it suggests that most of the samples from Madbi source rocks locate in the zone of the potential source rocks for hydrocarbon generation (**Figure 3**).

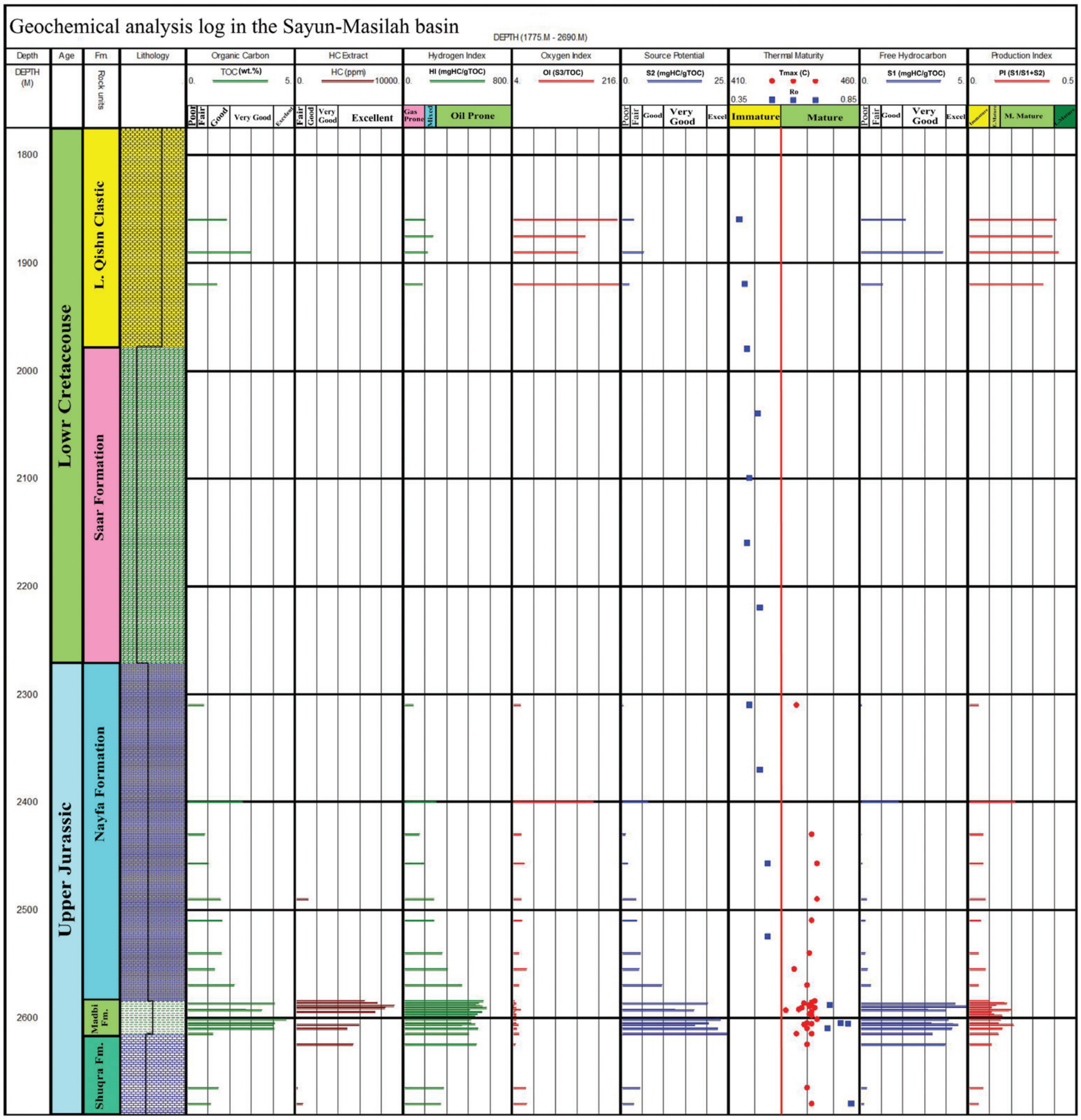

Figure 1. Organic geochemical log of the Upper Jurassic and Lower Cetaceous source rock samples according to Rock-eval pyrolysis and TOC content results.

2.2. Types of source rocks and depositional mechanisms of source rocks

One of the requirements needed for source rocks to generate commercial amounts of oil is that they must contain sufficient quantity of organic matter enough to generate and expel hydrocarbons [9]. Ronov (op.cit) also reported that the organic matter content in the open marine argillaceous sediments reaches about 1.1%, whereas that of the continental and lagoonal sediments reaches about 0.43%. Thomas [10] classified the potentiality of source rocks on the basis of their weight percentage of organic carbon; into poor source (<0.5 wt%), fair source

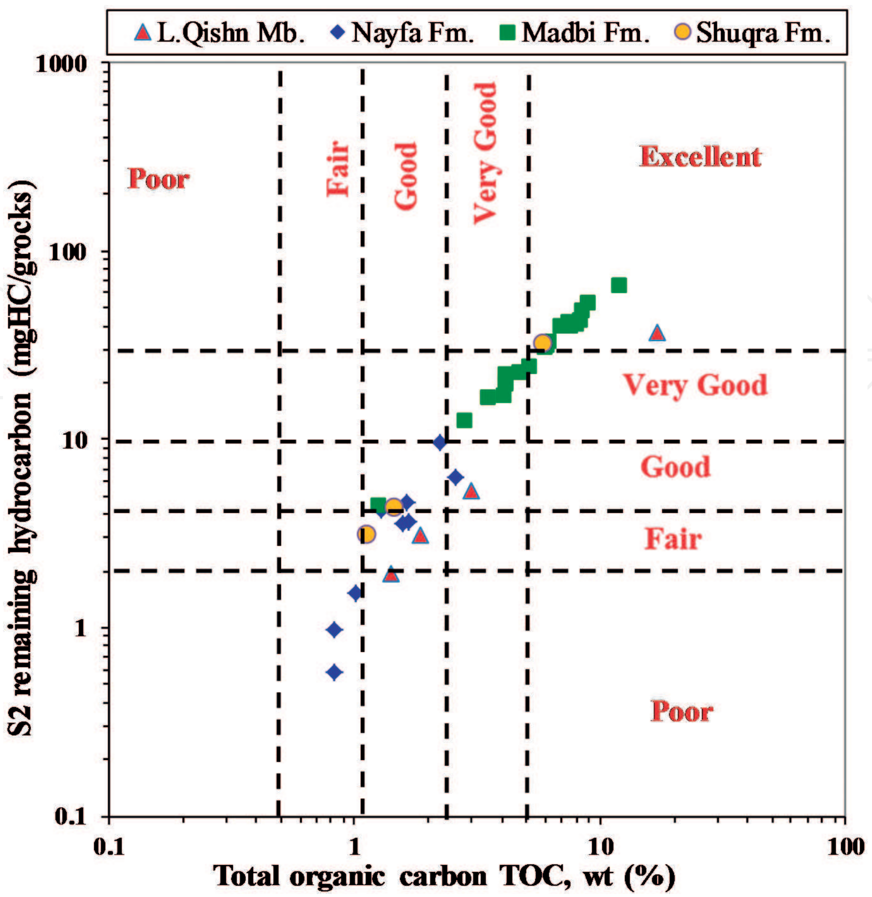

Figure 2. Pyrolysis S2 versus total organic carbon (TOC) plot showing generative source rock potential for the rock units in the study area.

(0.5–1.0 wt%), good source (1.0–2.0 wt%), and very good source (>2.0 wt%). Tissot and Welte [2] stated that, "clastic rocks, which are considered as source for petroleum contain a minimum of 0.5 wt% of the total organic carbon (TOC wt%), while good source rocks contain an average of about 2.0 wt% of TOC." The type of organic matter has important influence on the nature of generated hydrocarbons. Espitalie et al. [11] found that organic richness alone may not suffice to evaluate source rocks, where the organic matter is mainly inertinite, i.e., oxidized or biodegraded, is not capable of generating hydrocarbons, even if present at high concentrations. Peters and Cassa [6] presented a scale for the assessment of source rocks used in a wide scale and is applied in this work; a content of 0.5 wt% TOC as a poor source, 0.5–1.0 wt% as a fair source, 1.0–2.0 wt% as a good source, and more than 2.0 wt% TOC as a very good source rock, and also based on the rock-eval pyrolysis data, such S1 and S2, as shown in **Table 2**.

Pristane (pr) and phytane (ph) are usually the most important acyclic isoprenoid hydrocarbons in terms of concentration [12] and present in sediments and oil. Both are assumed to be diagenetic products of the phytyl side chain of chlorophyll 11 [13]. In certain restricted environments, for example, hypersaline, phytane can be derived from archae bacteria [14]. The pristane to phytane ratio (pr/ph) is similar for petroleum, which has resulted from material deposited under similar conditions [15]. Reducing conditions preferentially would lead to the formation of phytane.

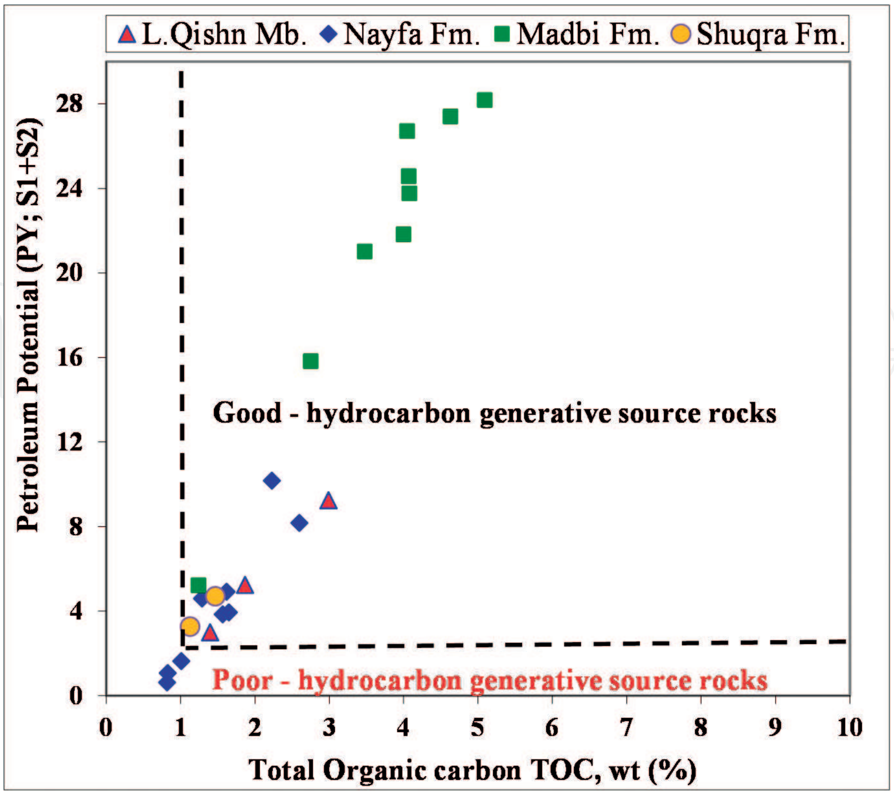

Figure 3. Source rock rating and hydrocarbon generative potential based on the plot of petroleum potential yield (PY) versus TOC for the analyzed rock samples.

Rowlands et al. [16] stated that, "the phytane carbon skeleton is extensively preserved under the condition, where H2S is available." Therefore, the pristane to phytane ratios of ancient sediments and oil reflect the paleoenvironmental conditions of source rock sedimentation [17] and are considered as potential indicators of the redox conditions during sedimentation and diagenesis [18]. Pristane/phytane ratio of less than 1 is ascribed to anoxic depositional environments, whereas ratios greater than 1 are ascribed to oxic depositional environments [17]. The use of the pr/ph ratio as an indicator, however, is not recommended to describe the paleoenvironment at low maturity levels [19]. Within the oil-generative window, the high pr/ph ratios (>3) indicate terrestrial organic matter input under oxic condition and low values typify anoxic, commonly under hypersaline environments. Hughes et al. [14] suggested that specific depositional environments and lithologies are associated with specific values for pr/ph ratios. Values less than 1 have associated with marine carbonates, between 1 and 3 with marine shales, and larger than 3 with

Quality	TOC (wt. %)	S_1 (mg HC/gm rock)	S_2 (mg HC/gm rock)
Poor	0.0–0.5	0.0–0.5	0.0–2.5
Fair	0.5–1.0	0.5–1.0	2.5–5.0
Good	1.0–2.0	1.0–2.0	5.0–10.0 >10
Very good	> 2	> 2	

Table 2. Source rock generative potential (after [7]).

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nonmarine shales and coals [20]. Lijmbach [21] proved that the ph/n-C17 ratio is less than 0.5 in environment with abundant aerobic bacterial activity and more than 1 in low aerobic bacterial activity environment. Shanmugam [22] made a combination between the isoprenoids and normal alkanes, which provides valuable information about the source of organic matter, organic facies, biodegradation, and maturation levels. These information are obtained from plotting the pristane /n-C17 versus phytane/n-C17. Abdullah [23], on the other hand, documented high pr/n-C17 and Ph/n-C18 values (1.5–1.6 and 1.2–1.6, respectively) in shallow marine shale and lower values (0.4–1.1 and 0.4–0.9, respectively) in deep marine shale conditions. Gas chromatography of the saturated hydrocarbons obtained from the extracted bitumen in the source rocks at Sayun-Masilah basin are used to identify the nature of organic matter present in these formations, preservation conditions, and depositional environments of the present organic matter. The isoprenoid pr/ph ratios of the studied rock units in the Sayun-Masilah basin (**Figure 4**) vary between 1.92 and 3.36, which point that the present organic matters were preserved under oxic to anoxic conditions in a deep marine environment as reflected from the lower values of pr/nC17 and ph/n-C18. The higher values of pr/ph ratio of >3 in some samples indicate a terrestrial input organic matter, i.e., presence of vitrinite macerals.

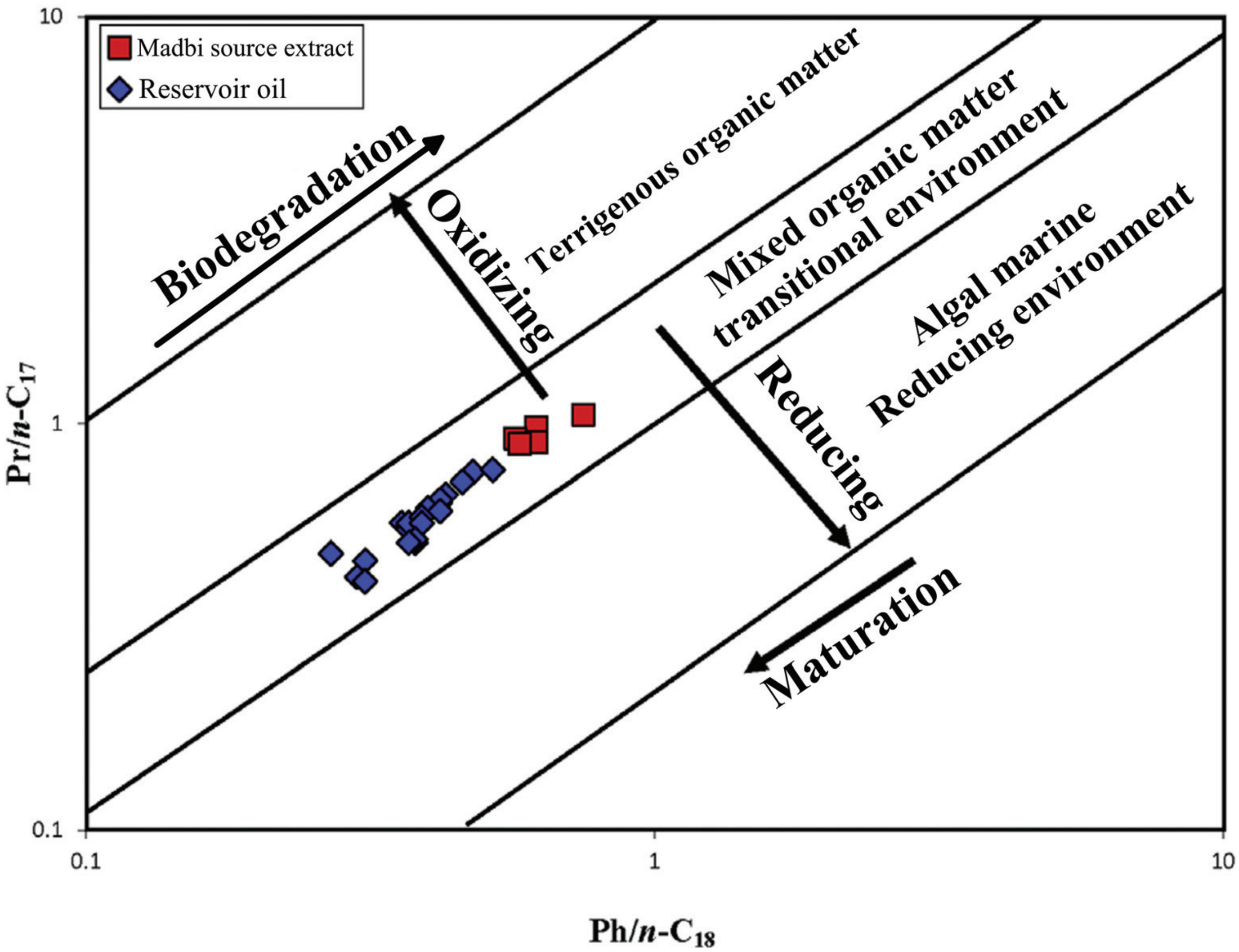

Figure 4. Phytane to n-C18 alkane (Ph/n-C18) versus pristane to n-C17 alkane (Pr/n-C17) ratios for reservoir crude oils and source rock extracts.

2.3. Types of organic matter (kerogen types)

The type of organic matter (kerogen) is considered the second most important parameter in evaluating the source rock. The kerogen type can be differentiated by optical microscopic or by physicochemical methods. The differences among them are related to the nature of the original organic matter. The organic matter in potential source rocks must be of the type that is capable of generating petroleum [2, 3]. It has been established that the organic matter is classified into three classes [24]:

1. (types I and II) equivalent Sapropelic type.
2. (type III) equivalent Humic type.
3. Mixed type from the two other types equivalent (II/III or III/II).

Espitalie et al. [5] used the pyrolysis yield to differentiate between the types of organic matter by plotting the hydrogen index versus the oxygen index on a modified Van Krevelen diagram, as follows:

1. Type I: mainly oil-prone organic matter with minor gas.
2. Type II: mixed oil and gas-prone organic matter.
3. Type III: mainly gas-prone organic matter.

The organic matter type is an important factor for evaluating the source rock potentiality and has important influence on the nature of the hydrocarbon products [2, 4]. Peters and Cassa [6] proposed that, for mature source rock, HI for gas-prone organic matter is less than 150, gas-oil-prone organic matter is between 150 and 300, whereas oil-prone organic matter is more than 300 HI. So, it is very important to determine the kerogen types, in order to detect the hydrocarbon products. The pyrolysis results can be used for the determination of the organic matter types. This can be achieved by drawing the relation between the hydrogen index (HI) and the oxygen index (OI).

In this study, the kerogen types present in the source rocks of the Sayun-Masilah basin identified from the modified Van Krevelen diagram (**Figure 5**) show that the Madbi shales interval contain kerogen of type I (algenite) oil prone, whereas type II (exinite) could be capable to generate mixed oil and gas. The hydrogen index (HI) value of Madbi Formation ranges from 362 to 613 mg/g with low oxygen index, indicating a capability of this formation to generate oil and mixed oil and gas hydrocarbons (**Figure 5**). The plots of the Naifa and L. Qishn Formations are characterized by the type II kerogen of lower hydrogen index (**Figure 5**), which could be capable to generate gases and oil, because they have higher (OI) than the Madbi Formation. Generally, most of the studied samples of Madbi source rocks of Sayun-Masilah basin are characterized by low OI, which reflect the capability of these sources to produce more oil than gases in type II kerogen.

2.4. Bitumen bulk geochemical parameters

The amounts of extractable organic matter (EOM), total hydrocarbon yield as well as the relative proportions of saturated, aromatic fractions, and nitrogen/sulfur/oxygen (NSO) compounds. The saturated and aromatic fractions together create the petroleum-like hydrocarbon fraction; thus,

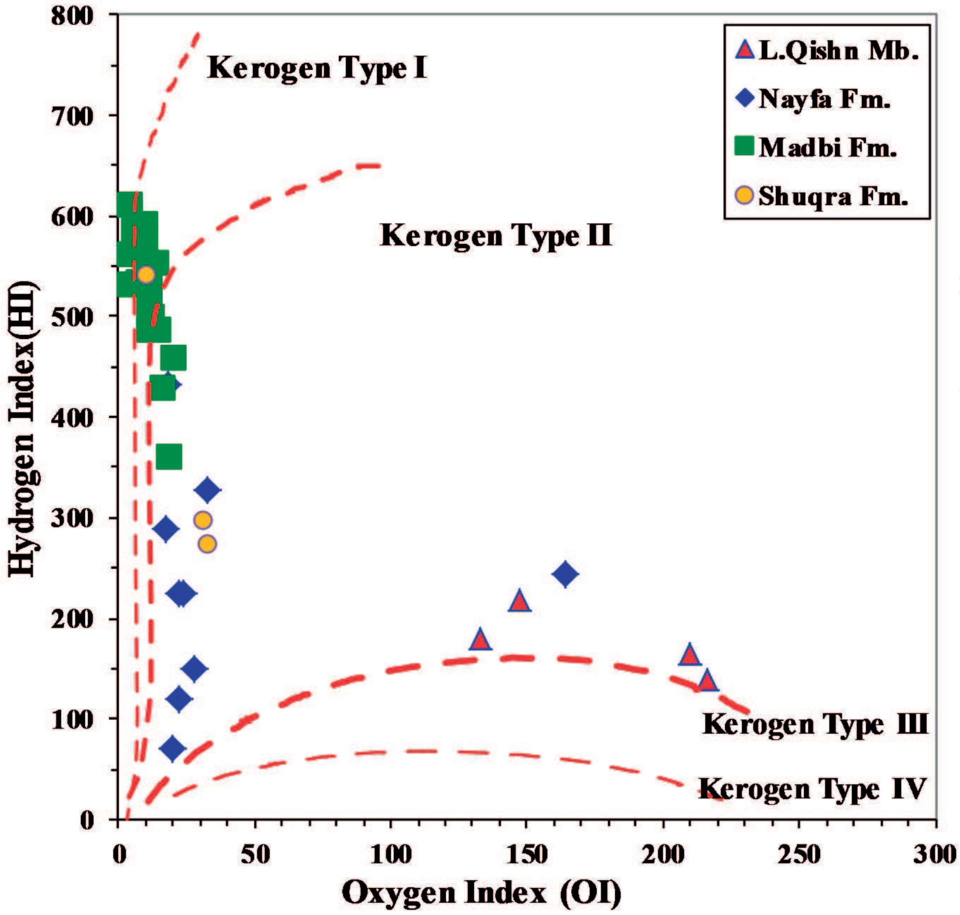

Figure 5. Plots of Hydrogen index (HI) versus Oxygen index (OI), showing kerogen quality of the Upper Jurassic samples in the Sayun-Masila basin, Yemen.

the sum of these two fractions is referred as hydrocarbons (HCs) [25]. Since the hydrocarbon portion of the bitumen extracted from sediment is the petroleum-like portion, it is used as an important parameter in the source-rock evaluation [26, 27]. These parameters are very important in petroleum source-rock evaluation (e.g., [26–28]). In this respect, most of the Upper Jurassic samples in Sayun-Masilah basin appear to be prolific petroleum sources where abundant naphthenic oils might be expected to be generated. The plots of TOC content versus extractable organic matter (EOM) and hydrocarbon yields (**Figure 6**) show the Upper Jurassic sediments in the study area as good to very good source rocks with good to very good potential for oil generation potential (e.g., [6]).

2.5. Thermal maturity of organic matter

As a rock containing kerogen and is progressively buried in a subsiding basin, it is subjected to increasing temperature and pressure. A source rock is defined as mature when it is reached to generate hydrocarbons. A rock that does not reach to the level of generation of hydrocarbons is defined as an immature source, and that which passed the time of significant generation and expulsion, it is considered as over-mature source rock. Generally, various parameters have been used for estimating source rock maturation. These parameters include vitrinite reflectance (Ro) and rock-eval pyrolysis data such as T_{max} and

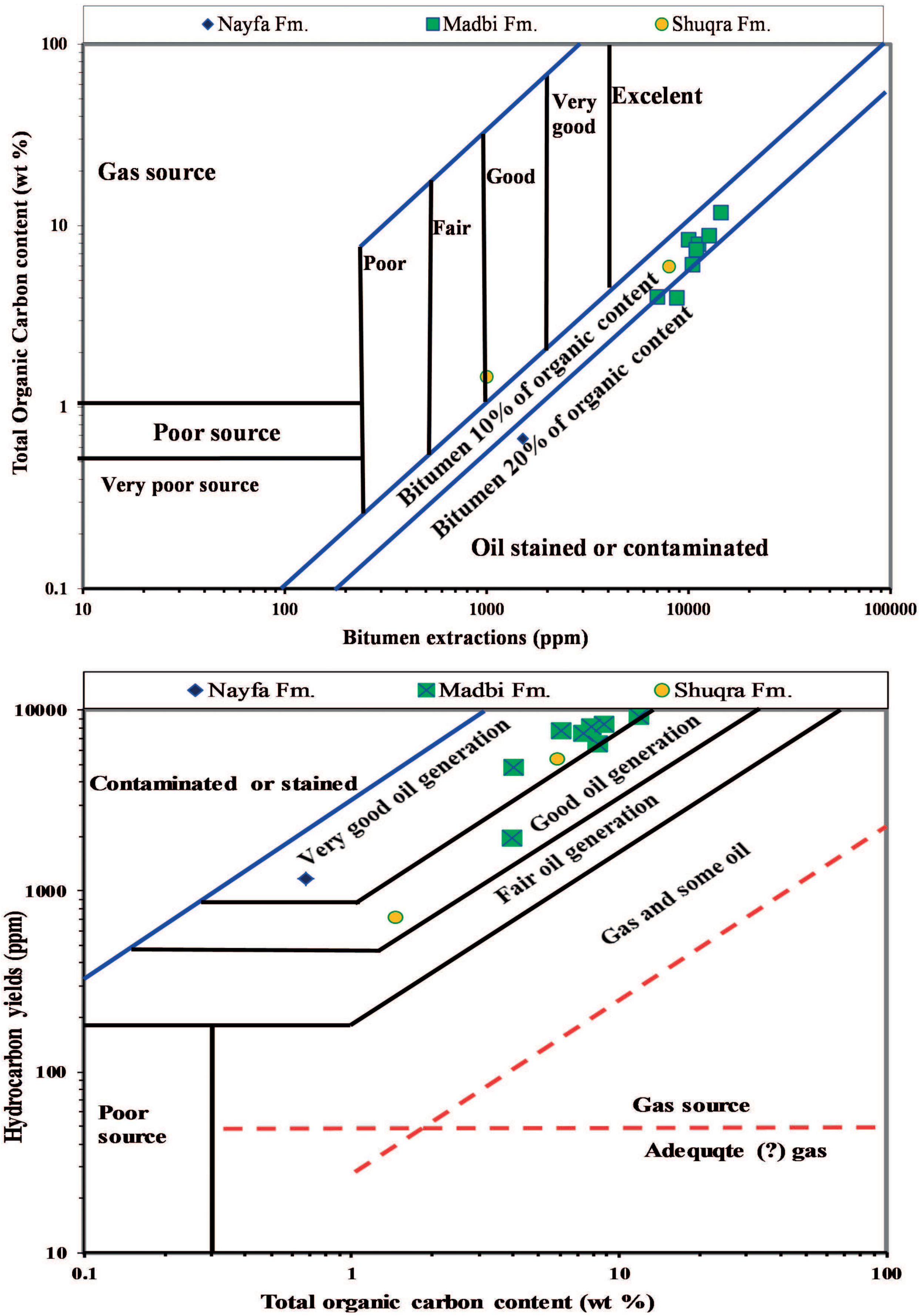

Figure 6. Plots of TOC content versus bitumen extractions and hydrocarbon yields, showing source potential rating and hydrocarbon source-rock richness for the selected samples.

production index (PI). The study of thermal maturation of source rocks is one of the main steps in the source rocks evaluation in the study area. This is because it is possible from the maturation stage to determine the position of the sediments with the respect to the oil generation. It can also help in oil exploration from knowing the relation between hydrocarbon generation, migration, and accumulation with the tectonics, which lead to the development of the structural traps in the study area.

A. Vitrinite reflectance (Ro %)

The most common method used for determining the stage of maturation is the vitrinite reflectance (Ro), which was discussed by several workers. Hood et al. [29] noted that one of the most useful measures of organic metamorphism is the reflectance of vitrinite. Tissot and Welte [2] considered the vitrinite reflectance as the most powerful tool for detecting maturation of organic matter. Waples [30] considered that a vitrinite reflectance (Ro%) of 0.6% mark the early stage of oil generation, while the peak of oil generation is at Ro ≈ 0.8%, and the late stage or the end of oil generation is marked at Ro ≈ 1.35%. The Ro% is considered as the most powerful maturation measure tool. It measures the ability of tiny vitrinite particles (called macerals) in kerogen to reflect incident light. This method depends on the separation of the organic macerals and measuring its vitrinite reflectance in oil immersion lens using a reflecting polarizing microscope connected with a photometer. The vitrinite macerals are increased in its reflectivity, as the maturation of their host rocks increases. Tissot and Welte [2] detected the onset, peak, and end of oil generation for the different types of kerogen according to Ro% (**Table 3**). In the Sayun-Masilah basin, the vitrinite reflectance values ranges from 0.32 to 0.87 Ro%. These reflect that Madbi and Shuqra Formations are mature stage, whereas the samples in L. Qishn Member and Nayfa Formation lie mainly in the mature stage (**Figure 7**). The lowering of the values of vitrinite reflectance in the studied samples from Sunah field, in spite of their occurrence at greater depths, may be related to the presence of high content of unstructured lipids of the type II kerogen [31]

B. Rock-eval pyrolysis

The relationship of the T_{max} with depth for the studied intervals in the Sayun-Masilah basin (**Figure 1**) shows values ranging from 432 to 443C°; this reflects that Madbi Formation is in the mature stage. The values in the Nayfa and Shuqra Formations reflect immature to mature stages. The production index (PI) data plotted against depth in (**Figure 1**) indicate that the phases of maturation of kerogen of these rock units are in the immature to mature stages. Most of the studied samples in the Madbi Formation at Sayun-Masilah basin lie in the mature stage (**Figure 1**). Reversely, the L. Qishn and Nayfa samples reveal a marginal mature stage. The types of organic matter ranges from oil- and gas-prone (HI ranged from >200 to 625) to oil-prone organic matter in Madbi Formation, and gas-prone kerogen in L. Qishn and Nayfa formations.

Generation	Type I	Type II	Type III
On set of oil generation	0.65	0.5	0.55 Ro%
Peak of oil generation	1.1	0.8	0.9 Ro%
End of oil generation	>1.4	>1.4	>1.4 Ro%

Table 3. The generation for the different types of kerogen with Ro%.

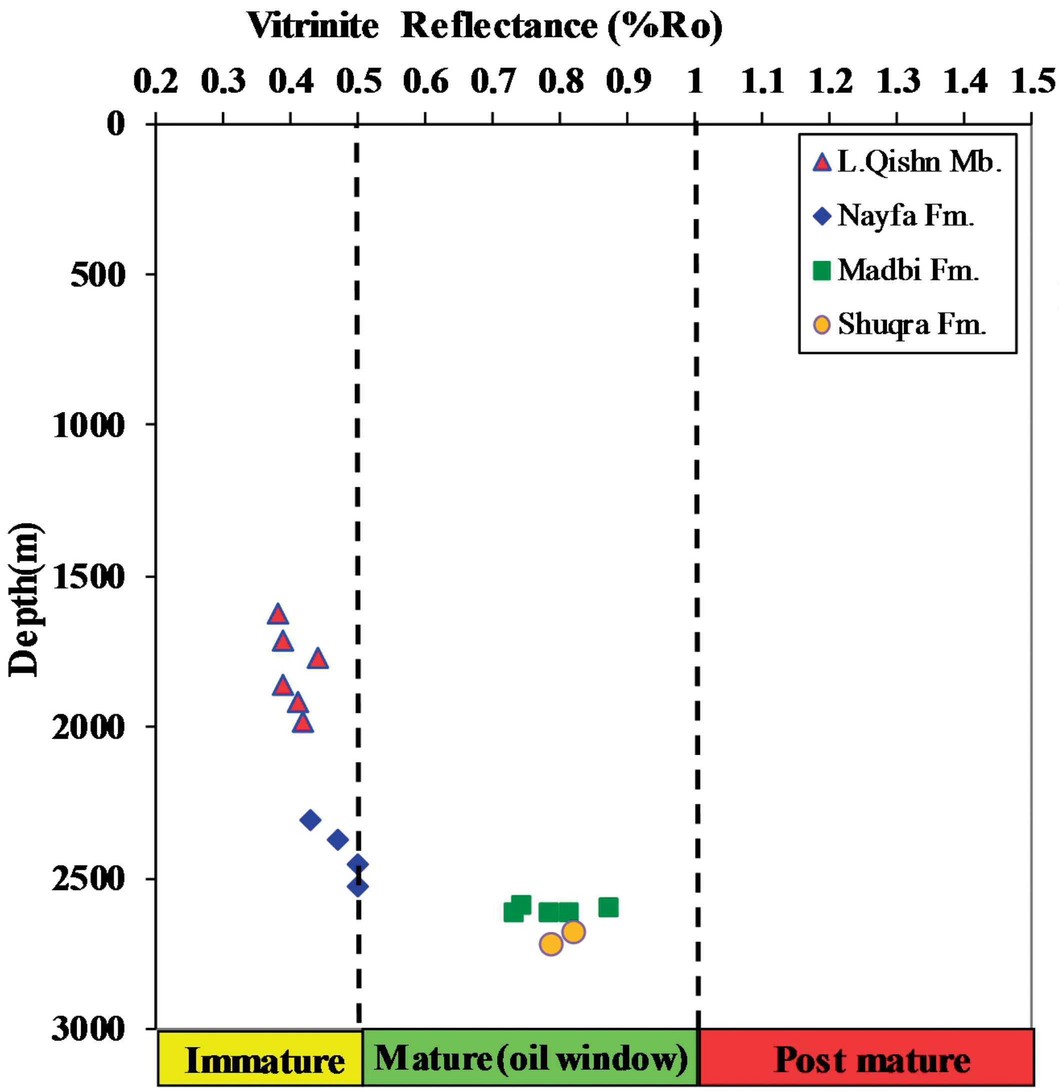

Figure 7. Plot of vitrinite reflectance data (Ro) versus depths showing thermal maturity stages of the Source rocks samples in the study area.

3. Basin modeling procedure

Geohistory diagrams [32] and similar diagrams have been widely used in geology, particular in hydrocarbon exploration. These diagrams were adapted to perform numerical modeling of burial, erosion, and thermal histories in sedimentary basins, e.g., [33, 30, 34, 35]. This method has become an important tool and successfully applied to search for new petroleum plays or for the evaluation of exploitable oil and gas accumulations around the world (e.g., [31, 36, 37]). In this chapter, quantitative one-dimensional basin modeling is performed for evaluating the thermal histories and timing of hydrocarbon generation and expulsion of the Nayfa, Madbi, and Shuqra source rocks in the Sayun-Masilah basin. The reconstruction of the burial, thermal, and maturity histories were modeled in order to evaluate the remaining hydrocarbon potential using Schlumberger's PetroMod (1D) modeling software. Sunah exploration well was created as a result of geochemical, well log, and further geologic data were used. The geologic model consisting of the depositional, nondepositional, and erosional events in absolute ages was compiled using stratigraphic data that were provided from well reports and previous stratigraphic studies, e.g., [38]. Hydrocarbon generation modeling was based on TOC and HI of the Nayfa, Madbi, and Shuqra source rocks in the Sayun-Masilah basin as example, and the maturity modeling was calculated using the EASY% Ro model of Sweeney and Burnham [39].

3.1. Subsidence and burial history

The tectonic evolution of the region has significantly influenced burial and thermal history of the study area. The burial (subsidence) and thermal histories are necessary in order to predict the timing of hydrocarbon generation and expulsion. To describe the resulting models clearly, we review first the results of our reconstruction of the subsidence curves [40]. Based on well profile, subsidence curves (**Figure 8**) were first constructed for the studied well by decompacting the sedimentary section using formation thicknesses (present day thickness) and lithologies assigned from mud logs and composite well log. The subsidence curves and basin history filling of one representative well is shown in **Figure 8**, it illustrate that the Upper Jurassic section have a long burial history although it has thin sedimentary cover (400 m), due to thick sedimentary sections (2300 m) precipitated during the Cretaceous and Tertiary epoch (**Figure 8**),which help oil generation in this area. However, the Madbi source rocks during that time were buried deeply, and the petroleum generation can be generated in this time.

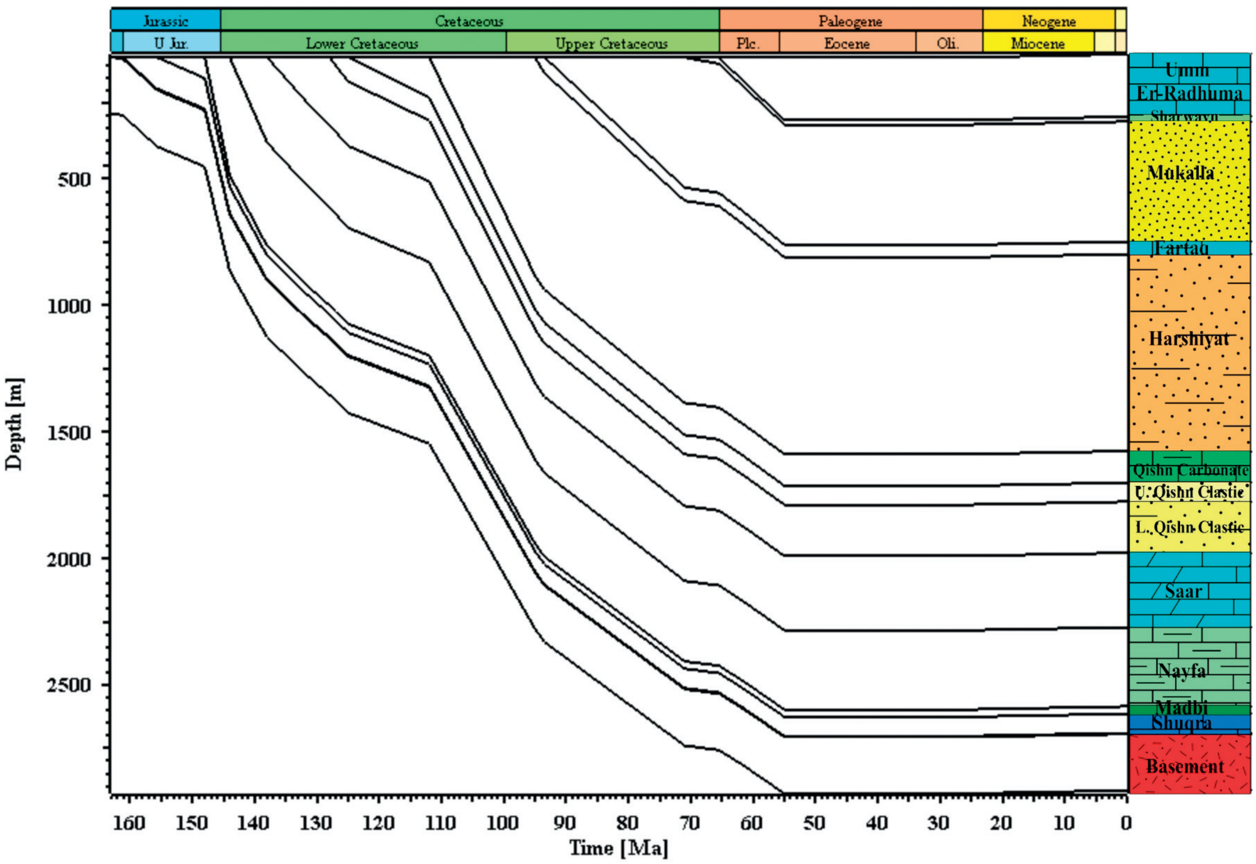

Figure 8. Burial history modeling for investigated well in the Sayun-Masilah basin.

3.2. Thermal history and paleo-heat flow

The thermal history of the source rocks in the sedimentary basins can be evaluated based not only on the deposition and erosion history but also on the heat-flow evolution [41, 42]. The borehole temperatures increase systematically with depth in the Earth and were used to calibrate the present day heat-flow regime. The increase of temperatures, indicating that heat is transferred through sediment layers to the surface. The transfer of heat is mainly controlled by thermal conductivity of the formations and geothermal gradient. Therefore, the thermal conductivity and geothermal gradient need to be determined to estimate the heat-flow history [43, 44, 45]. The present day geothermal gradient of borehole location was calculated using BHTs that were corrected for the circulation of drilling fluids. The maximum temperatures were reached at Upper Jurassic and Oligocene and Miocene time (**Figure 9**). The heat-flow is an important value in the input of the basin modeling, but needs to be determined for the geological past [45, 46]. Therefore, the reconstruction of the thermal history of the basin is simplified and calibrated with thermal maturation measurements (e.g., temperatures and vitrinite reflectance) (**Figure 10a**). Vitrinite reflectance was measured from maturity measurements of three stratigraphic units (Upper Jurassic), including Naifa, Madbi, and Shuqra formations (**Table 1**), and used to predict paleo-heat flow. Heat-flow model (**Figure 10b**) is used to calculate maturity, which is generally calibrated with a thermal maturity parameter such as vitrinite reflectance, e.g. [31, 47–49]. In the Sayun-Masilah basin, paleo-heat flow was affected

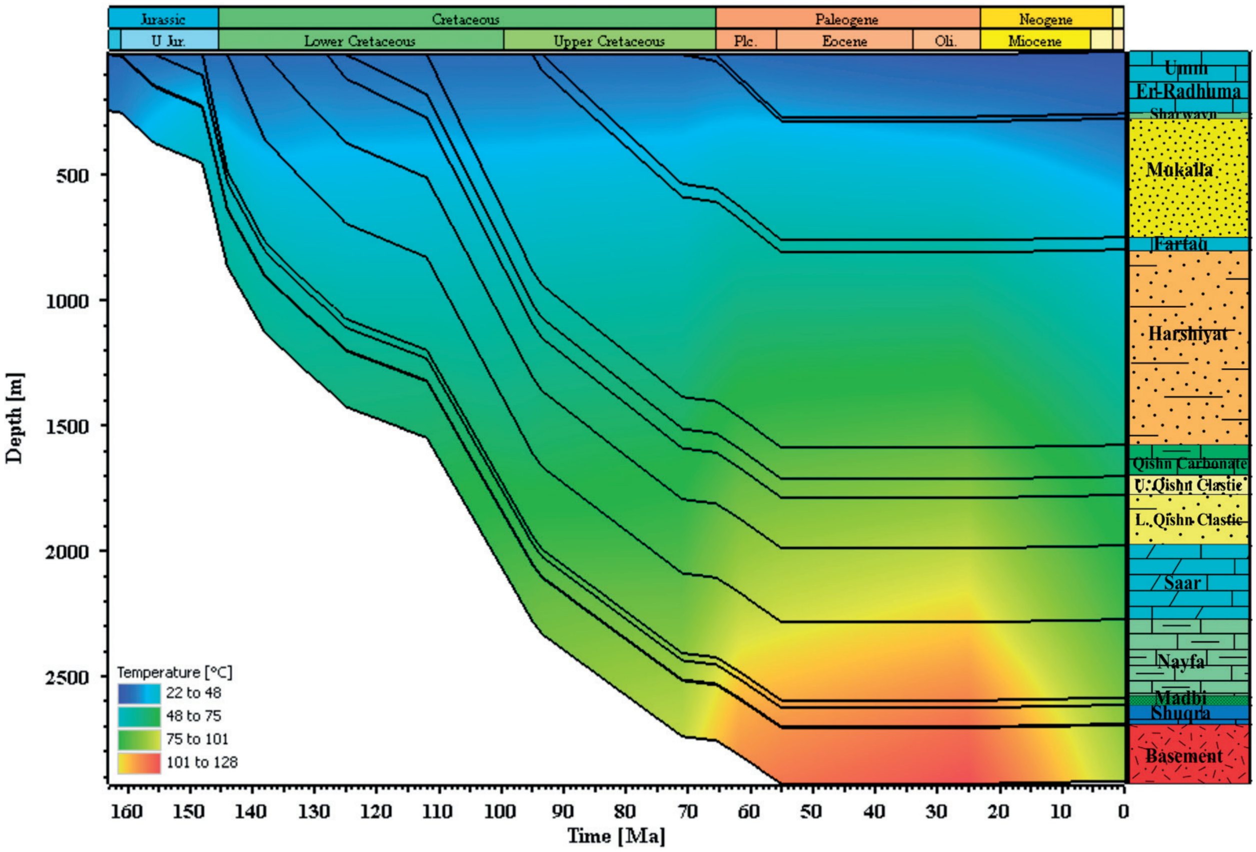

Figure 9. Paleo-temperature modeling in well calibrated using borehole temperature.

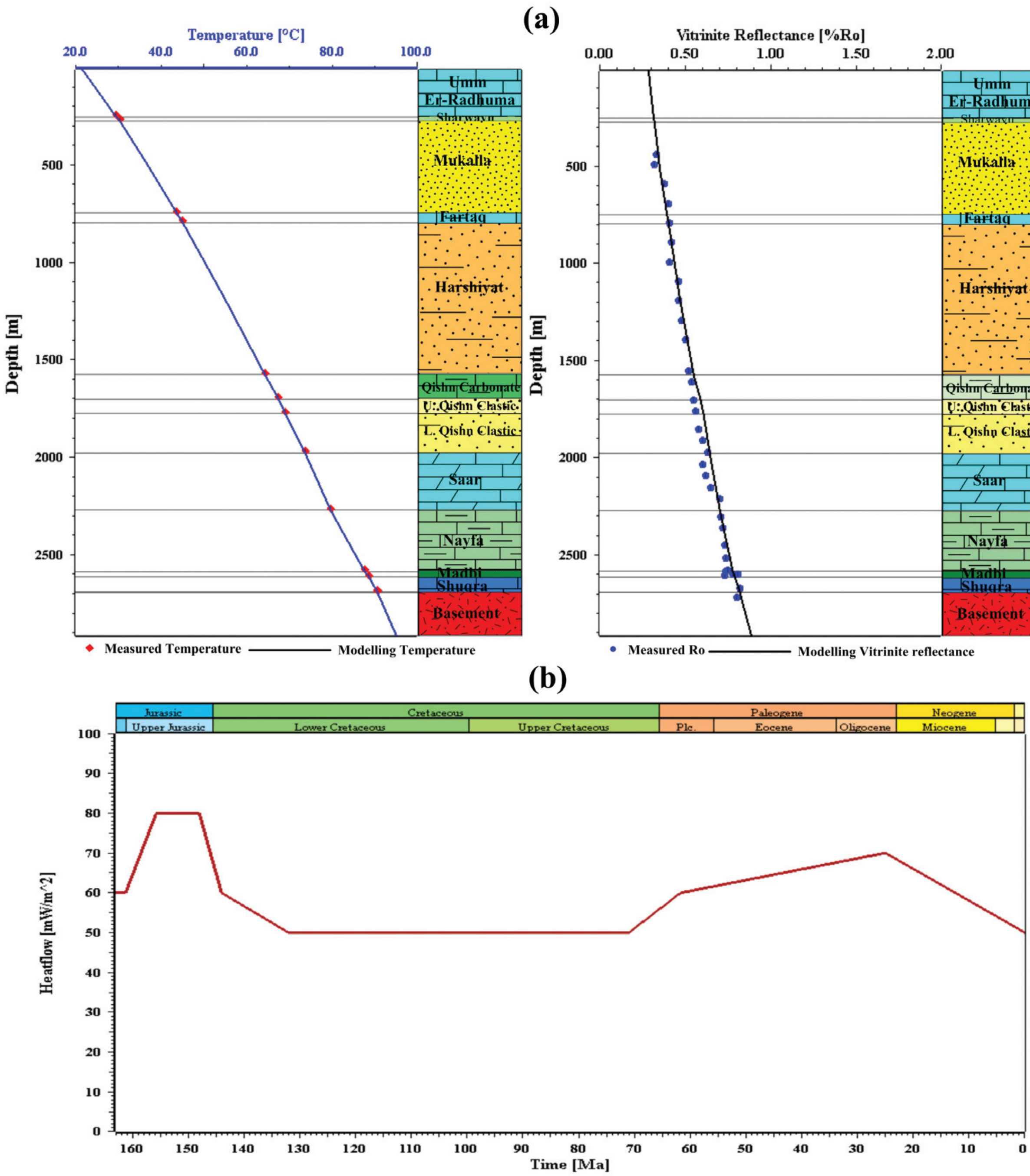

Figure 10. (a) Calibration of the thermal and maturity modeling in the studied in the Sayun-Masilah basin. Notice that there is a good correlation between measured data and calculated curves of temperature and measured vitrinite reflectance. (b) Heat flow through time in the investigated well, which were used to model the most probable scenario for hydrocarbon generation and expulsion in the Upper Jurassic source rocks.

by the tectonic evolution and rifting phase. The rift influenced heat-flow model, which incorporates a higher heat flow episode during the rift phase and an exponential reduction during the post-rift phase [50]. Based on the geological evolution of the Sayun-Masilah basin, the two rifting phases were incorporated in the heat flow model by peaks of heat flow during the periods of rifting (**Figure 10b**).

3.3. Source rocks maturity history model

In thermal history reconstructions of the study area, the influence of the tectonic evolution on the heat-flow distribution through time was applied. Thermal maturity levels of the Upper Jurassic source rocks are calculated based on the Easy% Ro routine [39] using one-dimensional modeling of single well. The detailed maturity history model of source rocks was used to determine the time when source rocks passed through the oil window. The detailed maturity history of source rocks in the Upper Jurassic source rocks is modeled for the representative well in the Sayun-Masilah basin (**Figure 11**). Based on the thermal maturity model, the hydrocarbon generation history of the source rocks in the model are different because of the variation in thermal and buried history (**Figure 11**). Assigning a heat-flow value of 80 mW/m^2 during 155.7 Ma gives the best fit between measured and calculated vitrinite reflectance and bottom hole temperatures (**Figure 10**). The Madbi Formation has reached the required levels of maturity in the model probably due to the temperatures (**Figure 11**). The model also shows that the source rock in this unit has reached the required levels of thermal maturity to onset of the oil window (0.64–0.87% Ro) from about 77 Ma at a depth 2315 m (**Figure 11**).

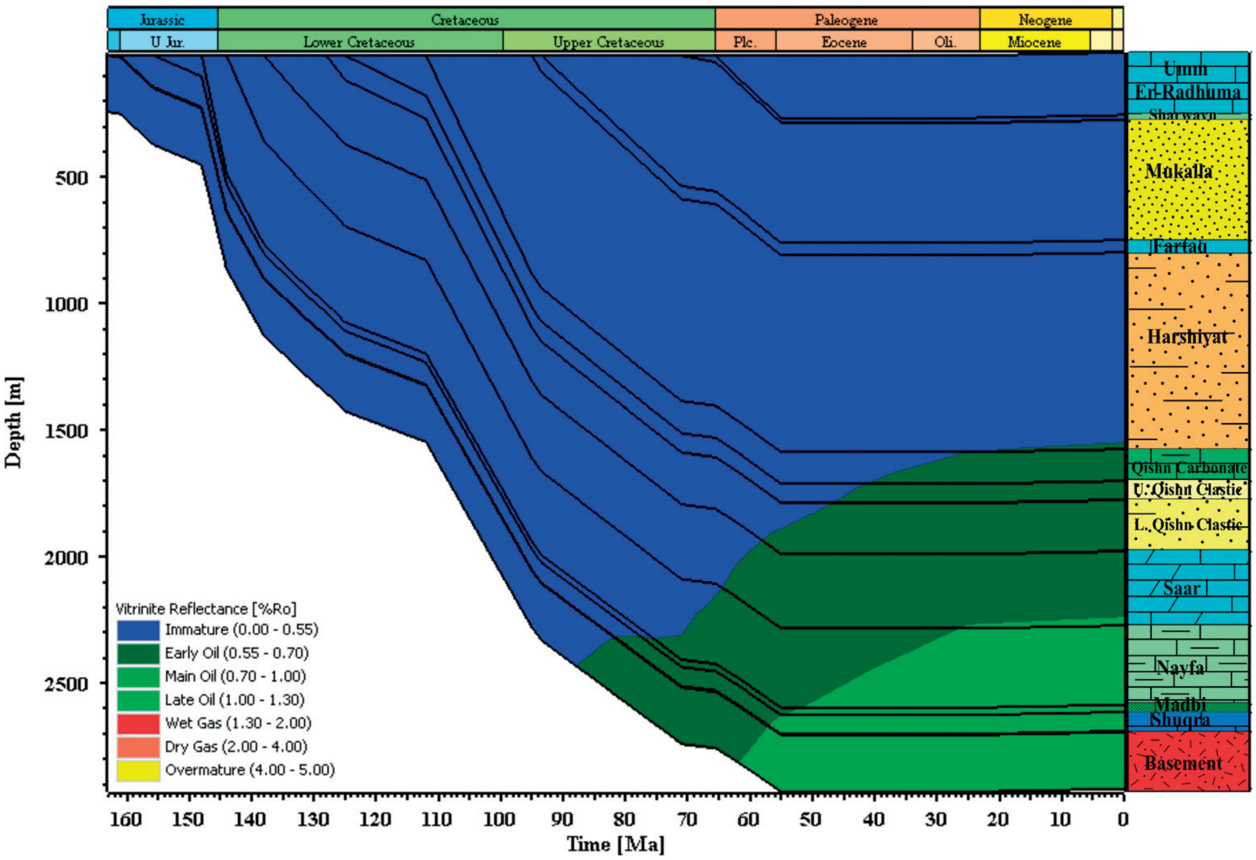

Figure 11. Burial and thermal maturity histories of the Upper Jurassic source rocks for the studied well showing the positions of the oil window.

3.4. Hydrocarbon generation and expulsion modeling

The timing of petroleum generated and expelled from the Upper Jurassic source rocks were modeled (**Figure 12**). Oil generation is defined in this model by transformation ratios between 10 and 50%. Immature source rocks have transformation ratios less than 10% (no generation). Peak oil generation occur at a transformation ratio of 50% when the main phase of oil generation is reached [49]. The modeled hydrocarbon generation and expulsion of the studied well shows that the Madbi source rocks were generating hydrocarbon with oil as the main product (**Figure 12**). In general, the hydrocarbon generation and expulsion history of the Madbi source rock in the studied model was represented by only two stages (**Figure 12**). The first stage of hydrocarbon generation of the Madbi source rock was occurred during Late Cretaceous-Early Eocene time at 70–54.6 Ma (**Figure 12**). This stage is the early phase of oil generation without any expulsion. The transformation ratio of the source rock varied from 10 to 25% during this stage, with computed VR of 0.55–0.65% Ro. The second stage (approximately 25.12-0 Ma) is the main phase of the oil generation and no gas generation has been detected. The transformation ratio of the source rock in this stage varies from 25 to 36%, with calculated VR of 0.65–0.87% Ro (**Figure 12**).

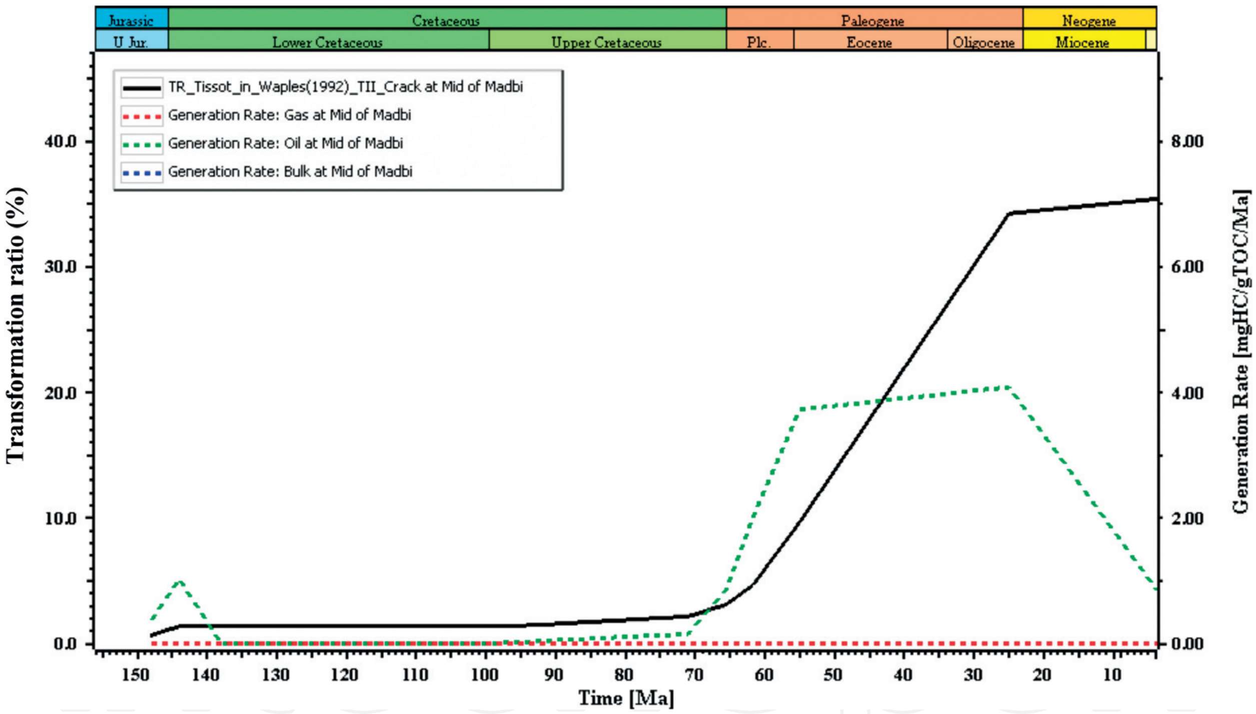

Figure 12. Plots of evolution of the transformation ratio and rate of hydrocarbon generation with age from the Madbi source rocks in the studied well.

4. Crude oil characterization

The petroleum was defined as a liquid substance referred to as "crude oil" or simply "oil" occurred in underground natural reservoirs, but the definition has been broadened to include hydrocarbon gases referred to as "natural gases" occurring in similar reservoirs. Oil is a complex mixture containing a large number of closely related compounds [2]. The compounds present and their relative amounts are controlled initially by the nature of the organic matter in the source rock. With more specific words, the relative amounts of normal alkanes, isoprenoids, aromatics, and sulfur compounds are characteristic of the source and should be essentially the same for all oil derived from a particular source rock. The fact that variations in crude oil composition are to a certain extent inherited from different source rocks. For instance, coaly material in general yields more gaseous compounds, whereas high wax crude oils are commonly associated with source material containing high proportions of lipids of terrestrial higher plants and of microbial organisms [2]. High-sulfur crude oils are frequently related to carbonate-type source rock. A side from the influence of source rock facies, the state of maturity of the source material is also of

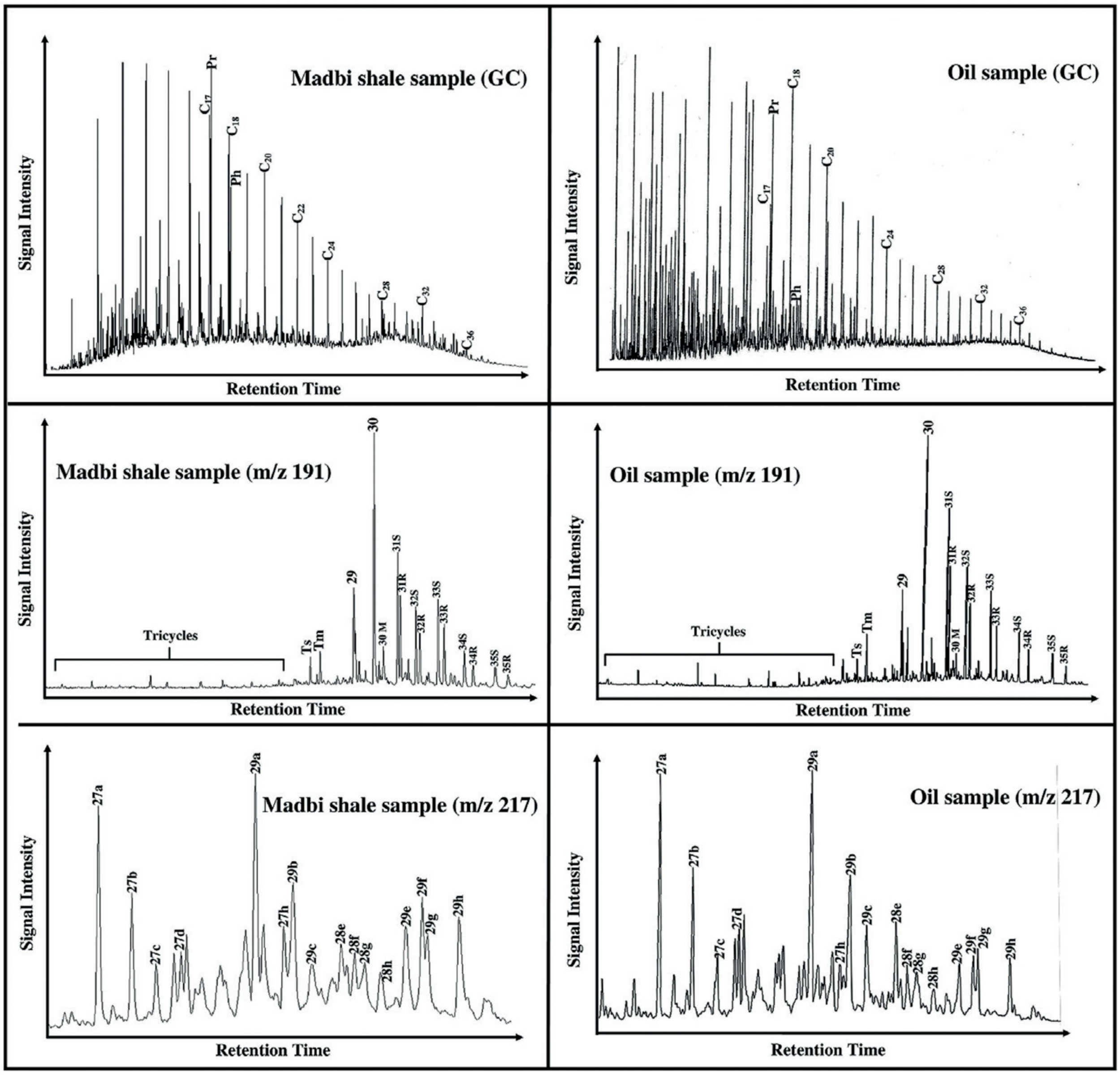

Figure 13. Gas chromatography traces and m/z 191, m/z 217 mass fragmentograms for the representative two oil samples.

importance. However, much larger variations in composition can cause processes operating in the reservoir. In other words, crude oil alteration processes (thermal alteration, deasphalting, biodegradation, and water washing) tend to obscure the original character of the oil, and therefore affects crude oil correlation, furthermore influence the quality and economic value of petroleum [2]. Therefore, the careful studying of the chemical compositions of the rock extracts, seeps, and produced oil can minimize the risk associated with finding petroleum accumulations.

The crude oils from the Sayun-Masilah basin have API gravity values in the range of 24.4–35.6 [51]. The crude oils have high saturated and aromatic fractions and ranging from 40.0 to 65.9% and 28.0 to 46.5%, respectively [51]. The high saturated and aromatic fractions with low amount of asphaltene and resin components indicate that these oils are naphthenic oils and have no sign of biodegradation. The similar bulk property and composition of the analyzed crude oils indicate that only one oil type is present. Biodegradation process may occur in an oil reservoir, and the process dramatically affects the fluid properties of the hydrocarbons, e.g., [52]. The early stages of oil biodegradation are characterized by the loss of n-alkanes or normal alkanes followed by the 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 [53]. In this respect, there is no sign of biodegradation among the studied oil samples, where the analyzed oils contain a complete suite of n-alkanes in the low-molecular weight region and acyclic isoprenoids (e.g., pristane and phytane); (**Figure 13**). This is also indicated by the analyzed oil samples generally contain more saturated hydrocarbons than aromatic hydrocarbons with generally saturate/aromatic ratios >1.

5. Oil-source correlation

The correlation of crude oils with one another and with extracts from their source rocks provide valuable tools for helping the exploration geologist to answer production and exploration trends [2]. Are there one or more families of oils in a particular rock sequence? Each family of oils represents one element of distinct petroleum system. Oil-source rock correlations are more difficult than oil-oil correlation; this is because many problems are involved in both sampling and interpreting the data. Tissot and Welte [2] showed that source rock oil is not usually similar in composition to its corresponding reservoir oil for several reasons. First, there is an evidence for the oil fractionates during the process of leaving the source and migrating to the reservoir accumulation. Second, source rocks do not yield oils of the same composition throughout their generation history. Third, degradation processes can affect the reservoir oil. All these problems require that the correlation be made by parameters (e.g., gross composition of oil and source rock extracts, biomarker analyses… etc.) that are possibly unchanged by the preceding factors. These parameters solve most of problems in oil-source correlations, because the differences in the chemical composition of the oil and the organic matters retained in the source rock are a function of migration fractionation and post-migration alteration.

Various parameters have been used for oil-source correlation purposes. These parameters depend mostly on the pre-burial environments of living organisms, the depositional environments of the organic matter, and the diagenetic processes in the source rocks. In this respective study, the applied parameters used for oil-source correlation are the steranes ternary diagrams of oils and source rock extracts by gas chromatographic (GC) analysis of C_{27}, C_{28}, and C_{29} regular steranes distribution. The distribution of C_{27}, C_{28}, and C_{29} homologous sterols on a ternary diagram was first suggested by Tissot and Welte [2] as a source indicator.

The objective of this part in this study is to investigate the genetic link between the oils recovered from Sayun-Masilah oilfield and Upper Jurassic source rocks. In an attempt to develop an oil-source rock correlation, we extracted soluble bitumens from four samples of the Madbi shale and analyzed their biomarkers using GC and GC–MS analyses. Overall, the oil data closely match the Upper Jurassic source rock data. Key factors include biomarker parameters and the similar positions on the cross-plots (**Figures 14** and **15**) [51].

The results of the steranes ternary diagrams of the oil and source rock extract samples are illustrated in **Figure 14**. The steranes distribution shows composed of C_{27}–C_{29} regular steranes and relatively low C_{27}/C_{29} regular steranes ratios (**Figures 14** and **15**), suggest a combination of marine and terrestrial organic matter input [54, 55]. **Figure 14** shows that the C_{27}, C_{28}, and C_{29}

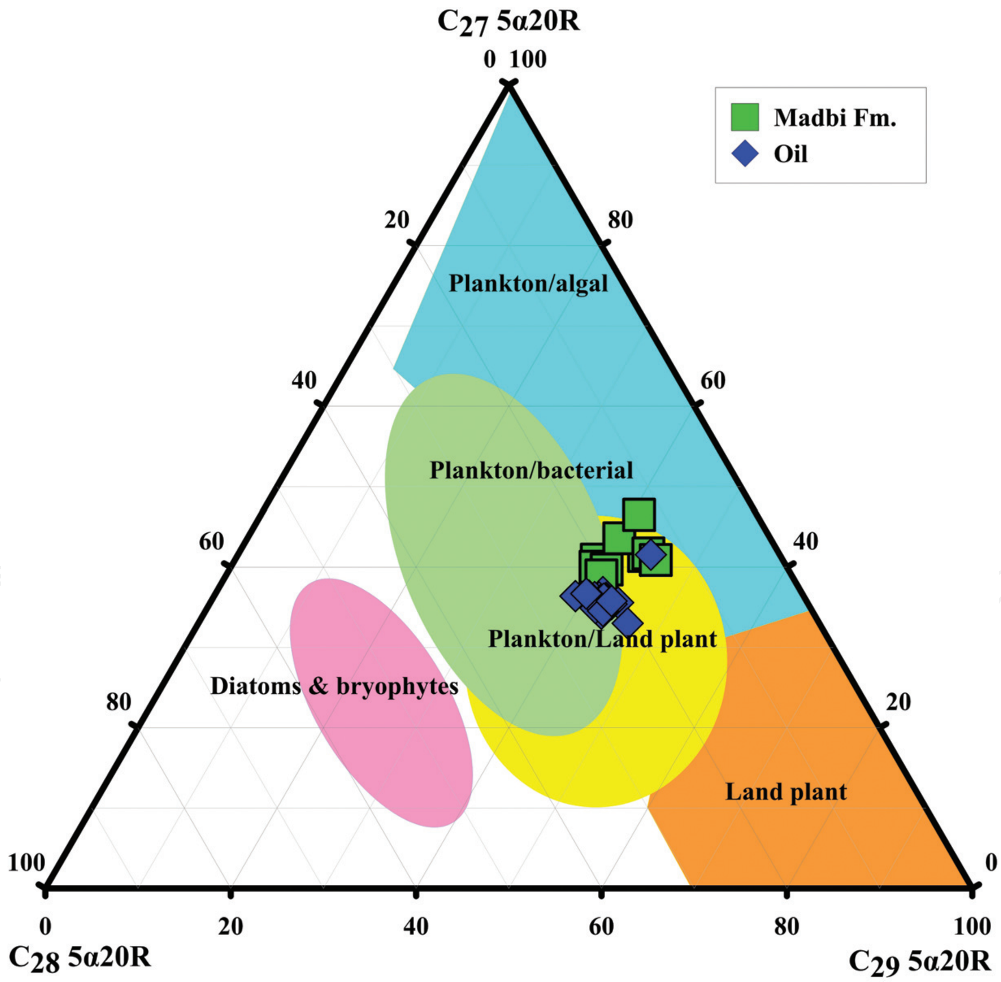

Figure 14. Ternary diagram of regular steranes (C_{27}–C_{29}) showing the relationship between sterane compositions, source organic matter input (modified after [56]).

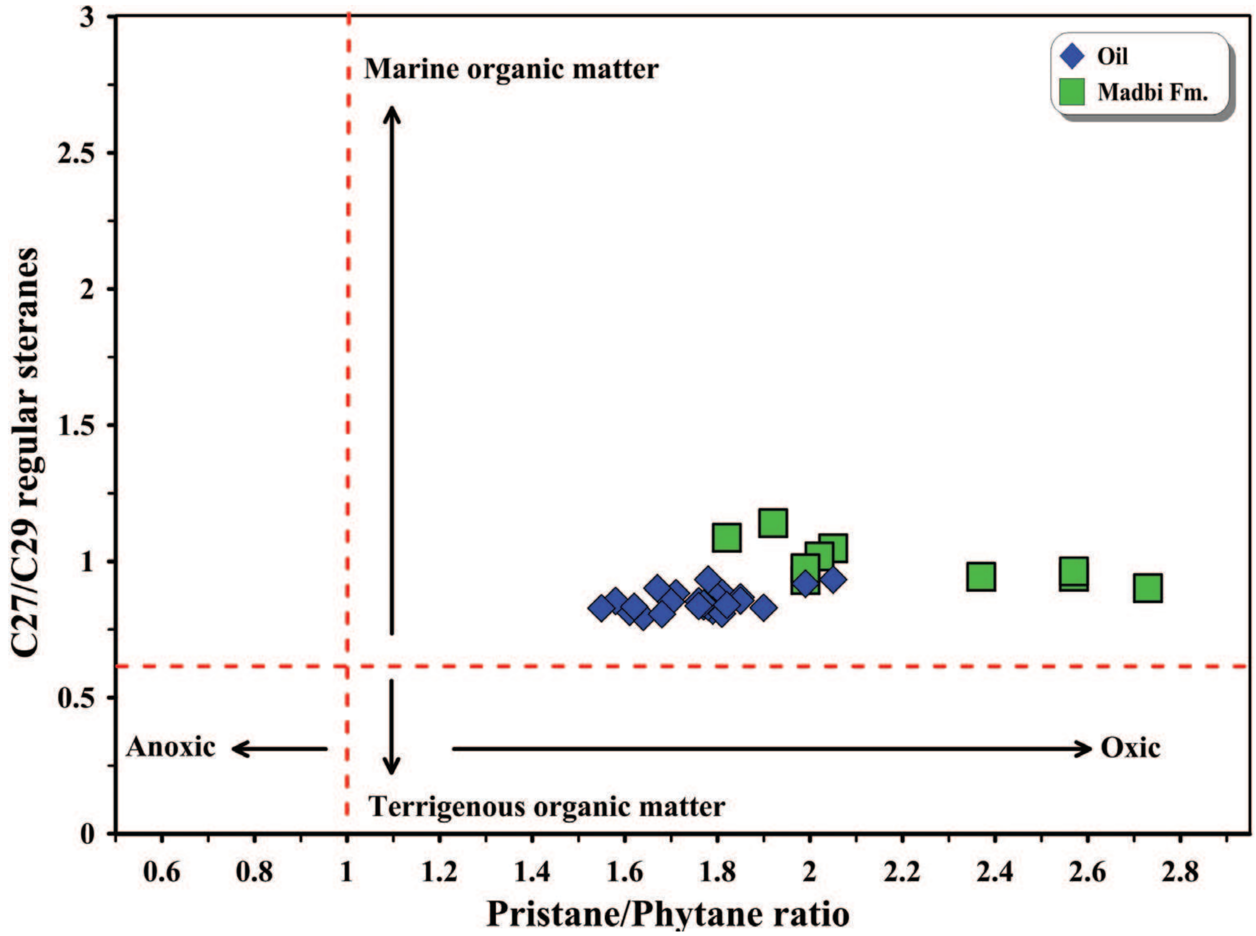

Figure 15. A plot of pristane/phytane versus C_{27}/C_{29} regular steranes, indicating organic matter input and depositional conditions [51].

are plotted in ternary diagram for oil extracts from the Madbi source rock, and the crude oils from the reservoir rocks, as shown in **Figures 14** and **15**, display the plotted points in the same area that mean the source oil in the Sayun-Masilah basin reflects that, the oils extracted from the source rock, and reservoir rocks are genetically have one family derived from the same basin.

6. Summary and conclusions

This chapter overviews the petroleum source rocks characterization and hydrocarbon generation, based on organic geochemical characteristics (e.g., total organic carbon content (TOC), rock-eval pyrolysis and bitumen extraction); in addition, burial and thermal histories and timing of petroleum generation/expulsion for petroleum source rock intervals using one-dimensional basin modeling software. The results obtained in this study give a strong indication as follows:

1. The organic geochemical data show that the Upper Jurassic sequence is the main source for hydrocarbon generation due to the high content of organic matter, which reached up

to more than 5.0 wt%, indicating a fair to very good source rock generative potential. The samples of Lower Cretaceous units vary between poor and fair source rocks.

2. The types of organic matter (kerogen) in these formations are of the type I and mixed types II and III, which were originally deposited in anoxic to suboxic depositional environment, as indicated from the low oxygen index OI, thus considered to be mainly oil- and gas-prone.

3. Maturity data such as vitrinite reflectance and pyrolysis T_{max} show that the Lower Cretaceous samples are thermally immature for hydrocarbon generation, whereas the Upper Jurassic samples are early-mature to peak-mature oil window mature stages for hydrocarbon generation.

4. The basin modeling study indicates that the source rocks in the Madbi Formation have entered the mature to peak-oil window mature stages for hydrocarbon generation and the mean-oil generation has been reached during Early Eocene (54.6 Ma), generating significant amount of oils with TR in the range of 25–36%.

5. In summary, results from the case study reveal that the Madbi Formation (Upper Jurassic) act as effective source rock and significant amount of hydrocarbons can be expected to generate in the study area.

6. From geochemical analysis, conclude the oils extracted from the source rock and reservoir rocks are genetically one family derived from the same basin.

Acknowledgements

The author would like to thank to Petroleum Exploration and Production Authority (PEPA), Ministry of oil and Minerals in Yemen for supplying the data and samples for this study. Schlumberger is acknowledged for providing the PetroMod Basin Modeling software.

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