GEOCHEMICAL EVALUTION OF THE TANEZZUFT FORMATION IN THE JIFARAH TROUGH, NW LIBYA

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Abstract: The study area (Jifarah Trough) is bound to the north by a coastal fault system. To the south the Jifarah Trough is bound by the east-west trending Al Aziziyah Fault System and to the southwest by the Telmzane Arch; the Nafusah Uplift defines its eastern limit. The region lies at the intersection of two major structures the NNW trending Tripoli-Tibisti Arch formed in Caledonian times and the E-W trending Jifarah Uplift formed during the Hercynian Orogeny. The best expected hydrocarbon source rock in the area is the lower hot shale member of the Tanezzuft Formation. Several reservoirs can be targeted as hydrocarbon traps such as the Ordovician quartzitic sandstone in Tunisia and the sandstone of the Silurian Acacus Formation in Libya. The objectives of this study are to assess the source rock potential, measure the thermal maturity of the source rock (Silurian Tanezzuft Formation), and to recognize the sources of organic matter and probable depositional conditions for this formation.

A Rock-Eval 6 was used for bulk geochemical screening analysis. The analytical error of the system was assessed using an IFP standard sample. Seventeen samples were analysed by GC and GC/MS. The results gained during this study show that the TOC wt.%, S1 and S2 are high in the lower part of the formation and low in the upper part. Furthermore, all maturity parameters based on Rock-Eval, and biomarker maturity parameters give indicators to vertical variation of thermal maturity from late immature to early mature, although the aromatic hydrocarbons show higher ratios in the lower part than in the upper part of the Tanezzuft Formation. The Tanezzuft Formation is characterized by marine algae organic input with a bacterial contribution and that, dysoxic-anoxic conditions may be the most probable for the depositional environment of the lower Tanezzuft Formation with slightly more oxic conditions associated with some samples of the upper Tanezzuft Formation.

Keywords: Tanezzuft Formation, Jifarah Trough, aromatic hydrocarbons, dysoxic-anoxic conditions, thermal maturity.

INTRODUCTION

Geographic Location

The Jifarah region is at the eastern end of the South Atlas Lineament or Saharan Flexure which defines the southern margin of the Atlas fold belt (Dewey & Burke, 1973; Biju-Duval *et al.,* 1977). The flexure runs from Morocco ENE to ESE and extends into Tunisia, where it branches to northwest Libya as the Jifarah Axis (Anketell, 1981; Anketell & Ghellali, 1991). This Jifarah Axis forms the southern margin of the Pelagian Platform (Burollet, 1978) and the Jifarah Trough (Fig. 1).

Regional geophysical data suggest that the depth to basement in the trough ranges from 1820 to 6060 metres (Echikh & Suleiman, 1983). The trough is bounded to the north by a coastal fault system which separates it from the related offshore Tarabulus Basin (Swire & Gashgesh, 2000). To the south the Jifarah Trough is bounded by the east-west trending Jifarah Fault System and to the southwest by the Telmzane Arch and Dahar Uplift; the Nafush Uplift defines its eastern limit (Fig. 1). Sedimentary infill of the trough is predominantly of Carboniferous, Permian and Triassic age and its genesis is mainly related to tectonic movements associated with the Hercynian Orogeny. There was also an extensional tectonic phase in the Middle to Late Triassic and some younger tectonic activity which led to rejuvenation of old fault trends, folding and associated volcanic activity.

The structural history of the Jifarah region has been discussed by a number of authors. The region lies at the intersection of two major structures,

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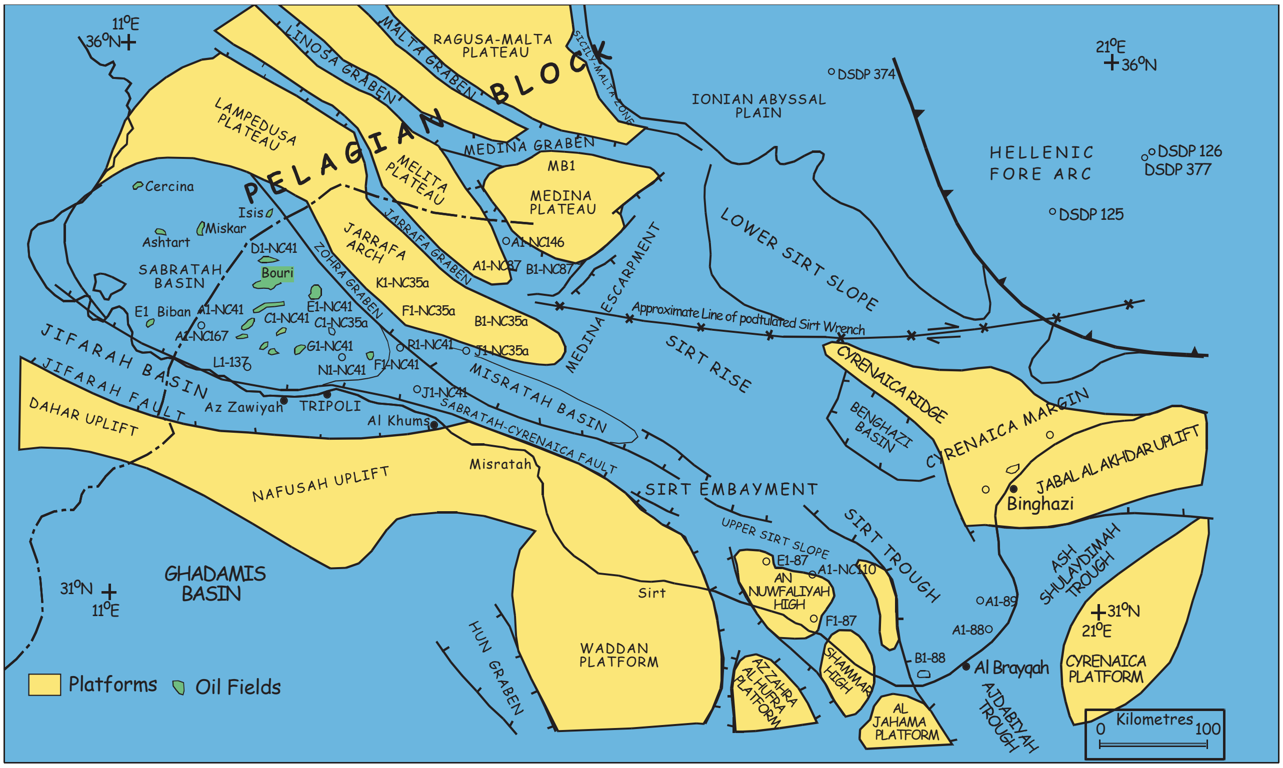


Fig. 1. Location Map of the Jifarah Trough, Libya.

the NNW trending Tripoli-Tibisti Arch formed in Caledonian times and the E-W trending Jifarah Uplift formed during the Hercynian Orogeny (Mikbel, 1977; Goudarzi, 1980).

Busson (1967) suggested that a subsidence zone, the Jifarah Flexure, occurred north of the Saharan Platform where thicker and more marine strata are characteristic.

Structure Components of the Jifarah Area

The Jifarah area can be distinguished by three main geomorphological units (El Hinnawy & Cheshitev, 1975) as follows:

1. The Jifarah Plain: This is nearly flat and is bounded in the north by the Mediterranean Sea and in the south by Jabal Nafusah. It is covered by Quaternary deposits with occasional outcrops of limestone hills belonging to the Al Azizyah Formation.
2. The Jabal: This is one of the dominant morphological features of northwestern Libya and is known as Jabal Nafusah (Jabal Gharyan). The Jabal runs in south-west to north-east direction from Al Khums and westwards to beyond the Libyan-Tunisian border. The Jabal is built by Mesozoic rocks which are made of limestone, sandstone, clay, dolomite, dolomitic limestone and gypsum.
3. The Plateau: This is made mainly of hard and resistant dolomitic limestone of Upper Cretaceous age. In the area southeast of Gharyan it is covered by basalt sheets forming a flat and broad plain.

Regional and Stratigraphic Geology

The stratigraphic sequence of the Jifarah Trough which extends from the basement to Quaternary is illustrated in (Fig. 2).

Basement and the Early History of the Jifarah Trough: The igneous basement was emplaced during the Pan-African Orogeny which took place during the late Precambrian to Middle Cambrian. This was as a result of continental collision and it established many of the fundamental tectonic patterns in North Africa. The only well to have penetrated the basement in the Jifarah Trough is the A1-9 well. Following the Pan African Orogeny there was a period of peneplanation of uplifted areas which led to deposition of siliciclastic sediments in the Late Cambrian and Ordovician periods. In the Jifarah Trough directly overlying the basement, transparent to white fine grained sandstones with thin interbeds of green shale (Hasaouna Formation) were deposited in subtidal to intertidal environment (Albani *et al*, 1991).

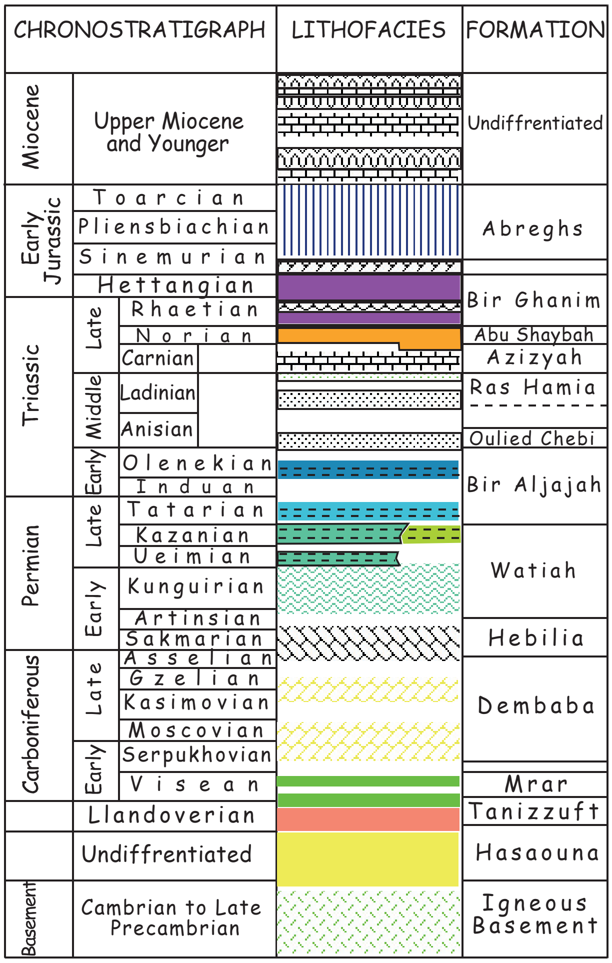


Fig. 2. Composite stratigraphical column, Concession 9, Jifarah Trough.

Ordovician System: A thick sequence of Ordovician age siliciclastic sediments was deposited to the south of the Jifarah Trough in the Ghadamis and Murzaq basins. The Ordovician section in the Jifarah Trough has been partly truncated by an unconformity. Erosion was associated with tectonic movements related to the Hercynian event.

Organic-rich black shales of the basal Tanezzuft Formation (Fig. 2) subcrop to the south of the Al Azizyah Fault Zone. The shales represent deposition during what was probably post-glacial flooding across much of the North African and Arabian platforms (Ref.).

The Tanezzuft Formation is a thick sequence of graptolitic, thinly laminated siltstones, shales and fine-grained sandstones. The type section is in the Wadi Tanezzuft near to the town of Ghat in the south west of Libya. The Tanezzuft Formation is of Early Silurian age.

In the Jifarah area of NW Libya the thickness of the Tanezzuft Formation is very variable. A thick sequence of the Tanezzuft Formation was penetrated by the MER-1 well on the Tunisian side of the Libyan-Tunisian Border (Swire & Gashgesh, 2000). The only well north of the Al Azizyah Fault Zone (and therefore in the Jifarah Trough) that has been recorded as penetrating the Tanezzuft Formation is the Tunisian well LG-1 (Swire & Gashgesh, 2000).

AIM AND OBJECTIVES OF THIS STUDY

In the Jifarah area, important oil shows have been observed in some drilled water and oil wells, but there has been no significant oil discovery in the region. Accordingly, this area is not classified as good for hydrocarbon prospection. Geochemical studies in neighbouring sedimentary basins emphasized that the shales of the Silurian Tanezzuft Formation have a high quantity of organic matter, which could generate significant amounts of hydrocarbons. Regarding previous geochemical correlations between oil samples and the potential source rocks, it is believed that the Tanezzuft Formation is the main source rock in the western part of Libya. The geological studies showed that the Tanezzuft Formation is present in considerable thickness in this region and there are good structures for the migration and accumulation of hydrocarbons.

There are 17 samples from the Tanezzuft Formation of Well (B1-23), comprising ditch cutting and core samples covering the interval from 1291 to 1431m. All samples from this interval are dark greenish to olive grey (95-100%) shale.

Therefore, the aim of this paper is to identify and evaluate the probable source rock (Tanezzuft Formation) of the study area, as well as to gain a better understanding of the petroleum potential of source rock within the Jifarah Trough. The objectives include the following: i) to assess the source rock potential of the Tanezzuft Formation using Rock-Eval 6. ii) to measure the thermal maturity of source rock samples, and any thermal maturity changes exhibited by the Tanezzuft Formation in the Jifarah Trough using biomarker-based maturity parameters as well as Rock-Eval (Tmax). iii) to recognize the sources of organic matter and probable depositional conditions for the source rock samples using biomarker distribution characterization with Gas Chromatography/Mass Spectrometry (GC/MS).

MATERIALS AND METHODS

Cutting and core samples of Tanezzuft Formation from B1-23 well were analyzed using Rock-Eval 6, gas chromatography (GC) and gas chromatography mass spectrometry (GC-MS). Rock-Eval 6 was used for bulk geochemical screening analysis at laboratories of the Libyan Petroleum Institute, Tripoli, Libya. The analytical error of system was assessed using an IFB standard sample. The source rock samples were progressively heated in an inert atomosphere (S1) and were thermally cracked (S2 & S3). Total organic carbon (TOC) was determined by oxidation under air, Tmax, HI, OI, and PI were also obtained.

All aliphatic and aromatic hydrocarbon fractions were analyzed by GC. The fractions were run on an HP5890 gas chromatograph with an auto-sampler and automatic split/splitless injector. Gas chromatography mass spectrometry (GC-MS) analysis of aliphatic and aromatic hydrocarbon fractions were carried out using a Hewlett-Packard 5890 II GC spilt/ spiltless injector (280 °C) linked to a Hewlett-Packard 5972 Mass Selective Detector.

RESULTS

Bulk Geochemistry

Geochemical analyses of rock samples from upper and lower part of the Tanezzuft Formation in well (B1-23) were used to evaluate their hydrocarbon potentials Table 1. The Total Organic Carbon (TOC) and hydrocarbon potential (S2) showed a broad variation with depth through the formation. The lowest value of TOC in the upper Tanezzuft is 0.36% at a depth of 1301m, while the highest value is 1.07% at 1360.93m depth. In the lower Tanezzuft the lowest value of TOC is 1.45% at 1401m deep, while the highest value is 12.35 % at 1431 m. The lowest value of S2 is 0.48mg HC/g rock recorded at a depth of 1301 m and the highest value is 2.37mg HC/g rock at depth 1360.93m in the upper Tanezzuft, while the lowest value of S2 is 3.59mg HC/g rock recorded at depth 1401m and the highest value is 34.90mg HC/g rock at depth 1431m of depth. The Tmax and PI values are very low and range from 433 to 437°C and 0.03 to 0.09 respectively in the upper Tanezzuft, and 426 to 436°C and 0.05 to 0.06 in the lower Tanezzuft. The samples show hydrogen indices (HI) values which range from 110 to 280mg HC/g TOC through the upper Tanezzuft and 284 to 379mg HC/g TOC through the lower Tanezzuft.

Molecular Geochemistry

Gas Chromatography (GC)

Table 2 provides a summary of the geochemical data for the upper and lower Silurian Tanezzuft Formation. The molecular distribution of saturated hydrocarbons is shown in fig. 3 and 4. The Upper and Lower Silurian Tanezzuft Formation show *n*-alkanes distribution dominated generally by short chain C_{14} to C_{25} and acyclic isoprenoids (pristane and phytane). The Pr/Ph ratios range from 0.81 to 1.48 through the upper part of the Tanezzuft, and 1.26 to 1.48 through the lower part of the Tanezzuft. The Pr/n-C_{17} and Ph/n-C_{18} ratios<1 through the whole formation which indicates that *n*-alkane (n-C_{17} and n-C_{18}) is more abundant than Pr & Ph. Generally, the distribution of *n*-alkanes shows no relative dominance of odd carbon numbers (CPI~1).

Gas Chromatography/Mass Spectrometry (GC/MS)

1- *Hopane*: The aliphatic fractions of both parts were analysed by GC-MS to obtain the percentage composition of hopane, sterane and diasterane. The hopane as monitored by the *m/z* 191, two selected samples are shown in Fig. 5 and 6. All Tanezzuft samples show similar distributions with predominance of $C_{30}\alpha\beta$ hopane. The doublets of $C_{29}\alpha\beta$ hopane and C_{29}Ts, series of $C_{31}\alpha\beta$ to $C_{35}\alpha\beta$ hopanes with two isomers (22S & 22R), $C_{29}\beta\alpha$, $C_{30}\beta\alpha$ (diahopane), C_{27} 18α (H) T_s (neohopane), and C_{27} 17 α (H)T_m are all present. The variation of hopanes biomarkers are represented by gradual changes in the relative concentration of some isomers with depth, with consequent effects on molecular parameters Table 3 and Table 5.

2- *Sterane and diasterane*: The selected mass chromatogram *m/z* 217 (steranes) and *m/z* 259 (diasteranes) are shown in Fig. 7, 8, 9 and 10. Generally, the diasteranes and sterane have similar distributions in all Tanezzuft samples, with some gradual changes in the relative abundance of some isomers with the depth. The distribution includes:

i) The C_{27} to $C_{29}\beta\alpha$ diasterane (20S & 20R).

ii) The C_{27} to $C_{29}\alpha\alpha\alpha$ and αββ steranes with two isomers (20S & 20R).

iii) The $C_{30}\alpha\alpha\alpha$ 20R sterane is present in all lower Tanezzuft Formation samples but low or absent in upper Tanezzuft Formation samples.

Table 1. Rock-Eval Pyrolysis Results for Selected Core and Cutting samples from well B1-23.

Depth (m)	**Formation**	**S1 mg HC/g rock**	**S2 mg HC/g rock**	**S3 mg HC/g rock**	**PI**	**S2/S3**	**TOC wt %**	**Tmaxº C**	**HI mg HC/g TOC**	**OI mg CO_2/g TOC**
1291	U.Tanezzuft	0.04	0.64	0.47	0.06	1.36	0.48	435	134	91
1301	U.Tanezzuft	0.02	0.48	0.64	0.04	0.75	0.36	434	134	179
1315	U.Tanezzuft	0.03	0.55	0.94	0.05	0.59	0.50	435	110	188
1325	U.Tanezzuft	0.02	0.58	0.83	0.03	0.69	0.48	434	121	174
1335	U.Tanezzuft	0.02	0.68	0.70	0.03	0.97	0.52	434	131	135
1345	U.Tanezzuft	0.03	0.86	0.50	0.03	1.72	0.61	435	140	82
1352.70	U.Tanezzuft	0.18	1.78	0.59	0.09	3.02	0.89	436	201	66
1356.36	U.Tanezzuft	0.17	2.25	0.25	0.07	9.00	0.80	437	280	31
1360.93	U.Tanezzuft	0.08	2.37	0.13	0.03	1.82	1.07	435	222	12
1361	U.Tanezzuft	0.04	0.74	0.77	0.05	0.96	0.61	435	122	127
1371	U.Tanezzuft	0.08	0.98	1.16	0.08	0.84	0.72	433	136	161
1381	U.Tanezzuft	0.07	1.11	1.05	0.06	1.06	0.68	434	162	154
1391	U.Tanezzuft	0.03	0.63	0.44	0.05	1.43	0.45	434	141	99
1401	L.Tanezzuft	0.21	3.59	0.49	0.06	7.33	1.45	436	248	34
1411	L.Tanezzuft	0.55	8.35	0.68	0.06	12.28	2.74	433	305	25
1421	L.Tanezzuft	1.05	15.93	0.81	0.06	19.67	4.20	432	379	19
1431	L.Tanezzuft	1.85	34.90	2.12	0.05	16.46	12.35	426	283	17

Table 2. The Geochemical data (acyclic isoprenoid and *n*-alkanes ratio) in well B1-23.

Depth (m)	**Formation**	Pr/Ph	CPI	Pr/nC_{17}	Ph/nC_{18}	(Pr+nC_{17})/(Ph+nC_{18})
1291	U.Tanezzuft	0.83	1.09	0.32	0.33	0.85
1301	U.Tanezzuft	0.83	1.09	0.27	0.33	0.97
1315	U.Tanezzuft	0.81	1.09	0.34	0.34	0.81
1325	U.Tanezzuft	0.86	1.09	0.33	0.33	0.86
1335	U.Tanezzuft	1.07	1.09	0.33	0.30	0.99
1345	U.Tanezzuft	1.04	1.12	0.34	0.32	1.00
1352.70	U.Tanezzuft	1.03	1.09	1.14	0.99	0.97
1356.36	U.Tanezzuft	1.48	1.09	0.95	0.74	1.29
1360.93	U.Tanezzuft	1.38	1.00	0.96	0.75	1.20
1361	U.Tanezzuft	0.83	1.07	0.31	0.29	0.79
1371	U.Tanezzuft	1.03	1.09	0.35	0.32	0.96
1381	U.Tanezzuft	1.00	1.10	0.31	0.30	0.97
1391	U.Tanezzuft	1.00	1.08	0.34	0.30	0.90
1401	L.Tanezzuft	1.26	1.08	0.41	0.37	1.18
1411	L.Tanezzuft	1.38	1.03	0.56	0.46	1.20
1421	L.Tanezzuft	1.36	1.00	0.37	0.36	1.34
1431	L.Tanezzuft	1.48	1.10	0.32	0.32	1.48

Some common maturity parameters such % $C_{29}\alpha\alpha\alpha$ (20S/20S+20R), % C_{29} ($\alpha\beta\beta$/ $\alpha\beta\beta$+ $\alpha\alpha\alpha$), and % diasteranes/steranes and environment parameters such as $C_{27}\alpha\alpha\alpha/C_{28}\alpha\alpha\alpha$ 20R and $C_{27}\alpha\alpha\alpha/C_{29}\alpha\alpha\alpha$ 20R ratios were calculated using peak area from *m/z* 217 chromatogram, as shown in Table 4 & Table 5 respectively.

3- *Aromatic*: GC/MS was used to analyse the aromatic hydrocarbon fractions for seventeen selected samples. Five ions were detected (*m/z* 142 methylnaphthalenes, *m/z* 156 dimethylnaphthalenes, *m/z* 170 trimethylnaphthalenes, *m/z* 178 phenanthrene and *m/z* 192 methylphenanthrenes) to calculate some aromatic maturity parameters and *m/z* 134 which indicate an environmental condition: examples of these mass chromatograms are shown in Fig. 11, 12, and 13. Table 6 shows calculated aromatic maturity parameters. These ratios were

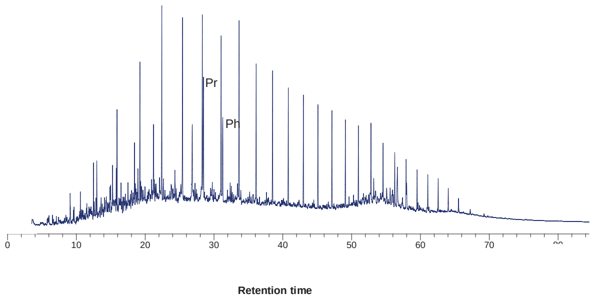


Fig. 3. Gas chromatogram showing the normal alkane distribution for the sample 1356.36m.

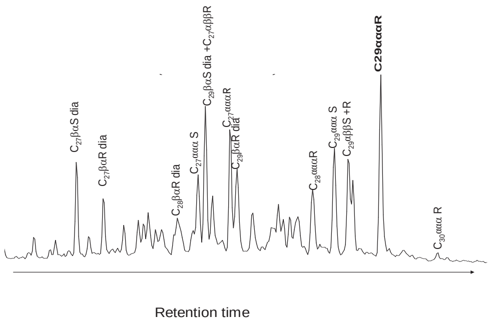


Fig. 7. m/z 217 mass chromatogram showing the sterane and diasterane distributions for the sample 1391m.

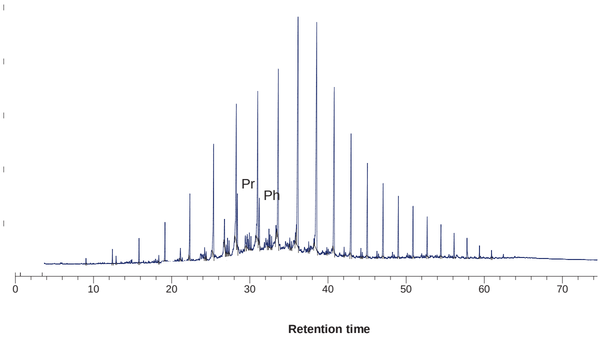


Fig. 4. Gas chromatogram showing the normal alkane distribution for the sample 1381m.

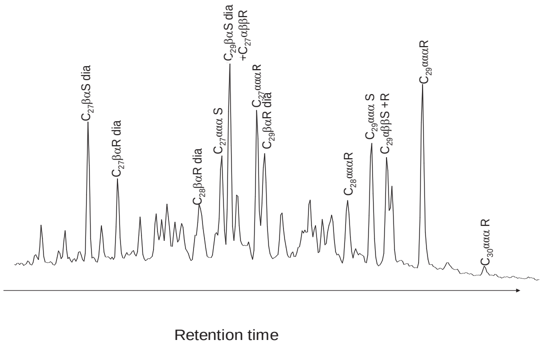


Fig. 8. m/z 217 mass chromatogram showing the sterane and diasterane distributions for the sample 1421m.

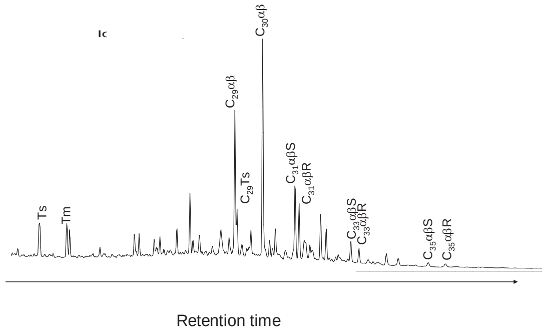


Fig. 5. m/z 191 mass chromatogram showing the hopane distribution for the sample 1352.70m.

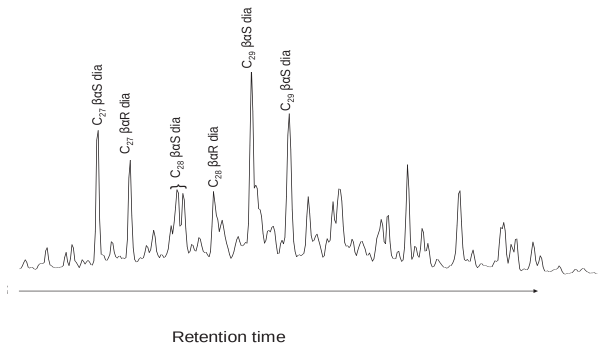


Fig. 9. m/z 259 mass chromatogram showing the diasterane distribution for the sample 1356.36m.

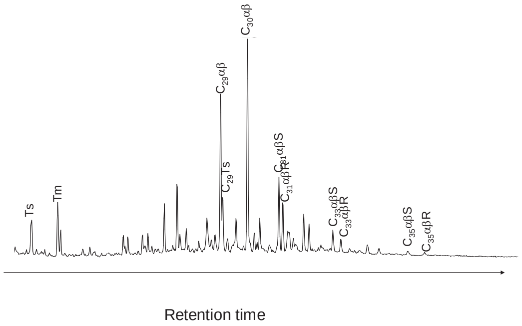


Fig. 6. m/z 191 mass chromatogram showing the hopane distribution for the sample 1361m.

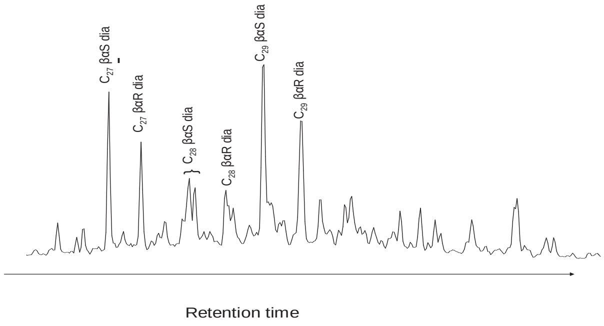


Fig. 10. m/z 259 mass chromatogram showing the diasterane distribution for the sample 1381m.

Table 3. Selected maturity parameters using *m/z* 191 hopane biomarker peak areas.

Depth (m)	**Formation**	**T_s%**	**%$C_{29}T_s$**	**%C_{31}αβ22S/(22S+22R)**	**%C_{30}βα/βα+αβ**
1291	U.Tanezzuft	41	17	61	20
1301	U.Tanezzuft	37	20	61	15
1315	U.Tanezzuft	41	15	60	20
1325	U.Tanezzuft	38	20	62	17
1335	U.Tanezzuft	37	23	59	16
1345	U.Tanezzuft	41	24	61	13
1352.70	U.Tanezzuft	55	23	62	11
1356.36	U.Tanezzuft	29	30	58	13
1360.93	U.Tanezzuft	29	30	61	12
1361	U.Tanezzuft	46	22	62	13
1371	U.Tanezzuft	45	25	62	13
1381	U.Tanezzuft	43	32	59	13
1391	U.Tanezzuft	41	32	59	15
1401	L.Tanezzuft	48	32	59	14
1411	L.Tanezzuft	52	29	58	14
1421	L.Tanezzuft	57	28	60	13
1431	L.Tanezzuft	59	22	64	11

Table 4. Selected maturity parameters using *m/z* 217 sterane biomarker peak areas.

Depth (m)	**Formation**	**%C_{29}ααα 20S**	**%C_{29}αββ/ αββ+ ααα**	**%Diasteranes/ steranes**
1291	U.Tanezzuft	32	29	35
1301	U.Tanezuft	32	36	31
1315	U.Tanezzuft	33	31	36
1325	U.Tanezzuft	30	27	41
1335	U.Tanezzuft	30	29	48
1345	U.Tanezzuft	32	30	52
1352.70	U.Tanezzuft	36	35	32
1356.36	U.Tanezzuft	29	27	27
1360.93	U.Tanezzuft	29	27	26
1361	U.Tanezzuft	33	32	33
1371	U.Tanezzuft	32	32	41
1381	U.Tanezzuft	35	33	63
1391	U.Tanezzuft	39	37	47
1401	L.Tanezzuft	38	31	53
1411	L.Tanezzuft	40	33	53
1421	L.Tanezzuft	42	36	58
1431	L.Tanezzuft	45	41	65

calculated by using absolute peak areas of the respective compounds. The MNR parameter in the upper part of the Tanezzuft Formation does not show considerable variation. The values range from 0.90 to 1.50, whereas, in the lower part they range from 1.14 to 1.77, with slight increase with increasing of depth Table 6. DNR1 shows wide variation in both the upper and in the lower parts of the formation. The ratio ranges from 1.64 to 8.23 and from 3.31 to 6.36 in the upper and the lower parts of the Tanezzuft Formation respectively (Table 6).

The rest of maturity parameters (TNR1, MPI-I, MPR and Rc) do not show a great variation in the upper and in the lower parts of the Tanezzuft Formation (Table 6).

INTERPRETATION AND DISCUSSION

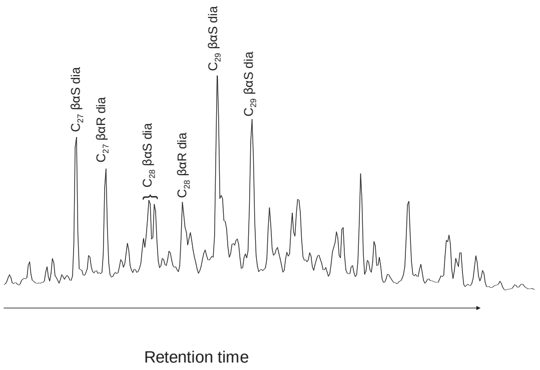
Source Rock Potential

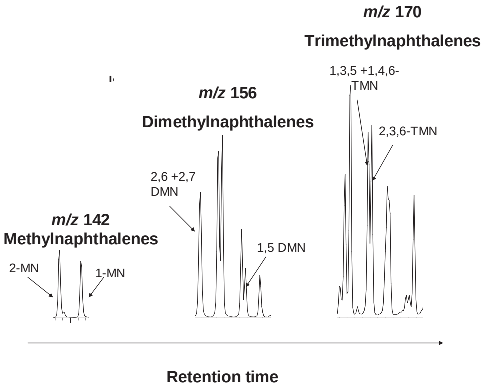
Organic Richness

According to bulk geochemistry (Table 1), the Tanezzuft Formation in Jifarah Region is a potential

Table 5. Selected depositional environment parameters calculated using *m/z* 217, 191 peak areas.

Depth (m)	Formation	C_{27}ααα(20R)/ C_{28}ααα(20R)	C_{27}ααα(20R)/ C_{29}ααα(20R)	Homohopane Index
1291	U.Tanezzuft	1.64	0.88	3.10
1301	U.Tanezzuft	1.34	0.74	3.42
1315	U.Tanezzuft	1.66	0.89	3.21
1325	U.Tanezzuft	1.65	0.87	2.47
1335	U.Tanezzuft	1.68	0.88	C_{35} hopanes are absent
1345	U.Tanezzuft	1.52	0.75	2.73
1352.70	U.Tanezzuft	1.22	0.53	4.11
1356.36	U.Tanezzuft	1.26	0.65	3.97
1360.93	U.Tanezzuft	1.23	0.64	3.26
1361	U.Tanezzuft	1.48	0.76	3.87
1371	U.Tanezzuft	1.48	0.70	C_{35} hopanes are absent
1381	U.Tanezzuft	1.37	0.64	3.24
1391	U.Tanezzuft	1.41	0.64	3.14
1401	L.Tanezzuft	1.63	0.67	3.53
1411	L.Tanezzuft	1.65	0.65	3.29
1421	L.Tanezzuft	1.79	0.76	4.06
1431	L.Tanezzuft	1.51	0.71	C_{35} hopanes are absent





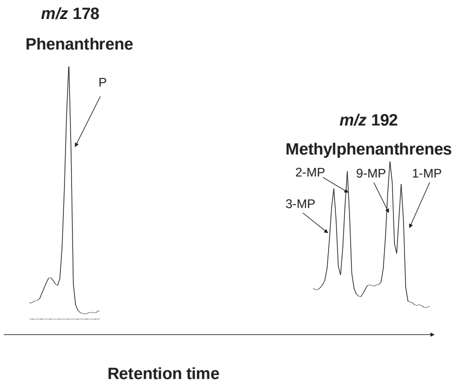


Fig. 11. GC/MS mass chromatograms for the aromatic hydrocarbon in sample 1356.36m.

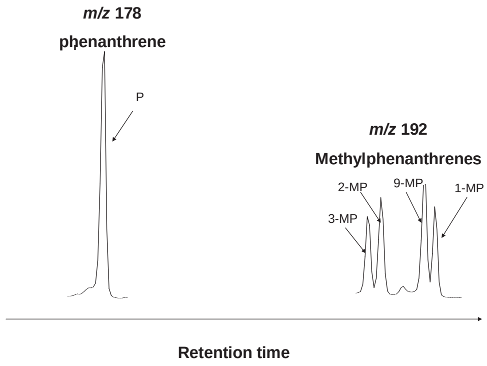


Fig. 12. GC/MS mass chromatograms for the aromatic hydrocarbon in sample 1401m.

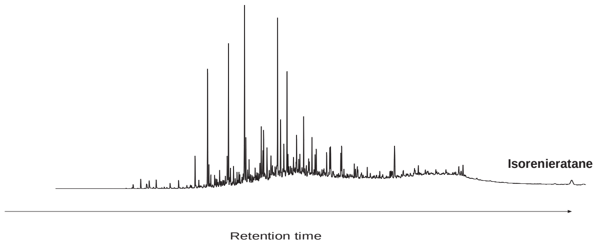


Fig. 13. *m/z* 134 mass chromatogram showing the isorenieratane distribution for the samples 1401m.

source rock in Well B1-23 because the upper part of this formation has a mean TOC value greater than 0.63 wt. %, which indicates good source potential. The mean of residual hydrocarbon (S2) is >1.05 mg/g HC indicating poor residual potential. The lower part of the Tanezzuft Formation has mean TOC values greater than 5 wt %, which indicates very rich source rock, and mean residual hydrocarbon (S2) value of around 15 mg/g HC indicating very good residual potential (Table 7; Peters, 1986). Figure 14 shows the linear relationship between TOC and S2 in the Tanezzuft Formation. This diagram can be used as an indicator of petroleum potential and the type of kerogen by calculating the average HI (Langford & Blanc-Valleron, 1990). The HI calculated from the slope of TOC and S2 is greater than the mean of measured HI by about 100 (Cornford, 1998). The regression slope of lines for upper Tanezzuft samples give an average HI of 301mg HC/g TOC indicating type II oil prone kerogen. The slope for lower Tanezzuft samples represent mean HI value of 277mg HC/g TOC, this line indicates kerogen type II/III (Fig. 14 a). In contrast figure 14b shows that the regression slope of lower part of Tanezzuft Formation indicates a mean HI of 450mg HC/g TOC (one sample with a TOC 12.35% excluded). This suggests that the lower part of Tanezzuft Formation is type II kerogen and good oil prone.

In summary, TOC value and residual hydrocarbon of the upper part of the Tanezzuft Formation indicate poor potential source rock. The same parameters indicate that the lower part of this formation is very rich potential source rock.

Organic Matter Maturity

Bulk geochemical data: The Production Index (PI) together with Tmax values were used to evaluate maturity level. Table 8 shows how to use the production indicators (PI) and Tmax to estimate maturity.

Table 6. Maturity parameters based upon aromatic hydrocarbons.

Depth (m)	Formation	MNR	DNR 1	TNR 1	MPI-1	MPR	Rc
1291	U.Tanezzuft	0.96	2.85	0.97	0.54	1.16	0.73
1301	U.Tanezzuft	1.09	3.45	0.85	0.59	1.33	0.75
1315	U.Tanezzuft	1.45	3.72	0.80	0.56	1.26	0.73
1325	U.Tanezzuft	0.91	1.46	1.00	0.60	1.22	0.76
1335	U.Tanezzuft	1.10	2.98	0.70	0.53	1.25	0.72
13459	U.Tanezzuft	1.14	3.20	0.81	0.52	1.22	0.71
1352.70	U.Tanezzuft	1.29	5.06	0.61	0.64	1.10	0.79
1356.36	U.Tanezzuft	1.50	8.23	0.43	0.77	1.17	0.86
1360.93	U.Tanezzuft	1.42	5.63	0.55	0.74	1.19	0.84
1361	U.Tanezzuft	1.05	3.33	0.82	0.64	1.35	0.79
1371	U.Tanezzuft	0.90	2.78	1.05	0.59	1.26	0.75
1381	U.Tanezzuft	1.22	3.71	0.79	0.63	1.25	0.78
1391	U.Tanezzuft	1.20	3.32	0.78	0.59	1.25	0.75
1401	L.Tanezzuft	1.29	3.36	0.61	0.66	1.25	0.79
1411	L.Tanezzuft	1.77	6.36	0.92	0.64	1.13	0.78
1421	L.Tanezzuft	1.46	5.66	0.69	0.69	1.19	0.81
1431	L.Tanezzuft	1.14	3.31	0.46	0.67	1.15	0.80

Methylnaphthalene Ratio (MNR) = 2-MN/1-MN
Dimethylnaphthalene Ratio (DNR 1) = (2, 6-DMN+2, 7-DMN)/1, 5-D
Trimethylnaphthalene Ratio (TNR 1) = 2, 3, 6-TMN/ (1, 3, 5-TMN+1, 4, 6-TMN)
Methylphenanthrene Index (MPI-1) = 1.5*(3-MP+2-MP)/ (P+9-MP+1-MP)
Methylphenanthrene Ratio (MPR) = 2-MP/1-MP
Vetrinite Reflectance (Rc) = (0.6*MPI 1) + 0.4

Table 7. Geochemical parameters describing source rock generative potential.

Quality	TOC (wt%)	S1 mg HC/g rock	S2 mg HC/g rock
Poor	0-0.5	0-0.5	0-2.5
Fair	0.5-1	0.5-1	2.5-5
Good	1-2	1-2	5-10
Very good	2+	2+	10+

Table 8. Geochemical parameters describing level of thermal maturation (after Peters *et al*, 2005).

Quality	TOC (wt%)	S1 mg HC/g rock	S2 mg HC/g rock
Poor	0-0.5	0-0.5	0-2.5
Fair	0.5-1	0.5-1	2.5-5
Good	1-2	1-2	5-10
Very good	2+	2+	10+

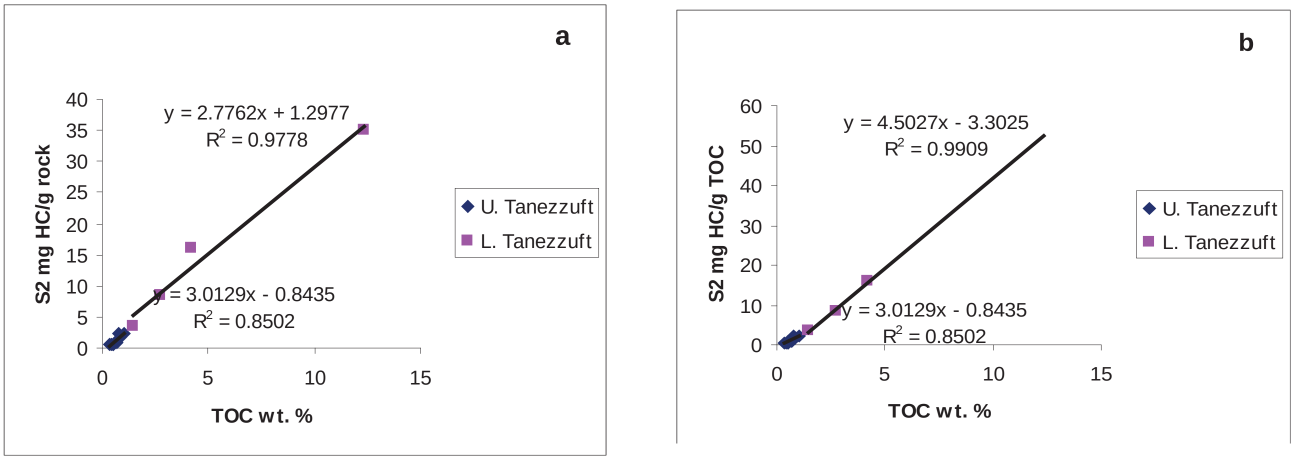


Fig. 14. Cross plot between TOC & S2 for the Tanezzuft Formation. a: with high TOC value, b: excluding high TOC value.

Tmax ranges in both parts, from 426-437°C, these values are very low which indicates late immature to early mature source rock. Production indices (PI) values throughout this formation are low (0.03-0.09), which correspond with the Tmax values (Fig. 15), and indicate the sediments are late immature to early mature. Figure 16 illustrates a cross plot between Tmax and HI. This diagram showing a vertical variation in HI may indicate kerogen variation. Most of the Tanezzuft samples are late immature (Tmax < 435), and kerogen is type II and II/III.

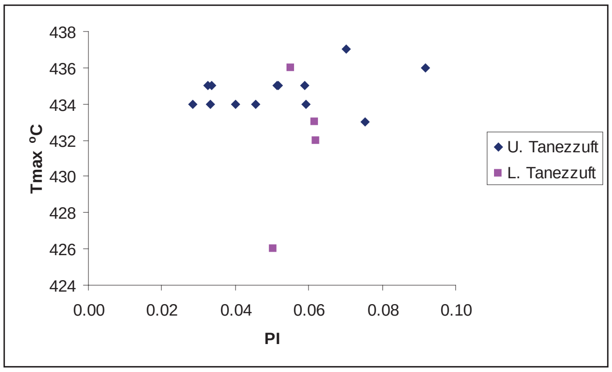


Fig. 15. Cross plot between PI and Tmax for Tanezzuft Formation.

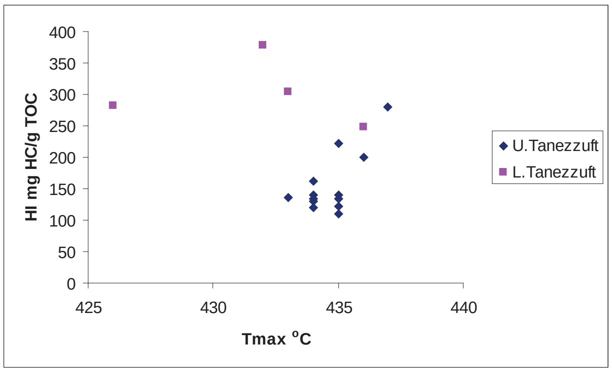


Fig. 16. Tmax plotted against HI for the Tanezzuft samples.

***Molecular Maturity Parameters*:** The relative abundance of odd even carbon-numbered n-paraffins can be used to obtain a crude estimate of thermal maturity of petroleum. These measurements include the carbon preference index [(CPI) (Bray & Evans, 1961)]. CPI values significantly above (odd preference) or below (even preference) 1.0 indicate low thermal maturity. Values of 1.0 do not prove that an oil or rock extract is thermally mature (Peters & Moldowan, 1993). Based on this, most Tanezzuft samples showed a CPI value > 1.0 which suggest immature to low mature samples.

Maturity parameters based on hopane and sterane ratios were shown in Table.3 and Table 4 respectively. The C31αβ %22S/22S+22R parameter is the most widely applied of the hopane maturity parameters, and records the relative enrichment of the more thermally stable 22S isomer compared to the biologically-derived 22R stereochemistry. The increases in 22S% is initially the result of a greater proportional increases of 22S isomer, followed by the earlier and more rapid decreases in abundance of 22R isomer. Therefore, the main two factors controlling this parameter are the relative rate of generation and thermal degradation (Farrimond *et al*, 1998). Bishop and Abbott (1993) also reported that 22S/22S+22R being to increase as a result of release/generation of 22S which increases more rapidly relative to its initial concentration than 22R. This parameter shows equilibrium values throughout two parts of the Tanezzuft Formation, the upper part ranging from 58 to 62%, whereas, the lower part ranges from 58 to 64% (the equilibrium value of 55-60%; Seifert & Moldowan, 1986). These values of %22S indicate that the Tanezzuft Formation is at early mature level. The T_S/T_S+T_m parameter is commonly used for maturity assessment, although it is known to be very dependent on organic facies (Moldowan *et al*, 1986). This parameter increases with maturity, just before and within the oil window. The T_S parameter increases with maturation when T_m decreases in abundance, and T_S concentration continues to increase; the main increases in this parameter is controlled by earlier and faster thermal degradation of T_m (Farrimond *et al*, 1998). In the present study there is a slightly noticeable variation in this ratio through the upper and lower Tanezzuft Formation, it remains constant due to the early mature level. Furthermore, $\%C_{29}T_S$ parameter behaves in a similar way to $\%T_S$ parameter (Farrimond *et al*., 1998). The relative loss of 17 β-hopanes occurs in the early stages of thermal maturity (Farrimond *et al*., 1998). The maturity sensitive sterane isomers ratios are based on the percentage of C29ααα 20S/20S+20R. This ratio increases from zero to equilibrium at 50 -55% (Mackenzie *et al*, 1980). It is based on the relative enrichment of 20S isomers compared with 20R isomers. An increases in 20S/20S+20R is concomitant with a loss in concentration of 20S, the rate of loss of which is less than that of 20R, hence 20S continuous to increase relative to 20R (Bishop & Abbott, 1993). Abbott *et al* (1990) noted that release or generation of 20R and 20S from extracted vitrinite kerogen occurred in the laboratory, concluding from this the control on the maturity dependent variations of 20S/(20S+20R), is composite of empire release or generation from components followed by sterane loss. The Tanezzuft Formation has %20S parameter range from 29 to 39% at the upper part of the section which increases to range from 38 to 45% at the lower part, it is considered as late immature to early mature. The %C29αββ parameter reaches to equilibrium at 67 to 71% (Seiferd & Moldowan, 1986). This ratio is effective at higher level maturity, due to being slower to reach equilibrium than %20S parameter (Peters & Moldowan, 1993). In the upper part of Tanezzuft Formation the ratio ranges from 27 to 37%, from 31 to 41% in the lower part of Tanezzuft Formation which is considered as an immature formation. Moreover, Figure 17 illustrates the relationship between %C29ααα and C29%αββ which indicates that not all samples have reached their end point values. Figure 18 represents the variation of thermal maturity biomarker parameters of sterane and diasterane with depth. This plot shows that the maturity increases gradually with depth.

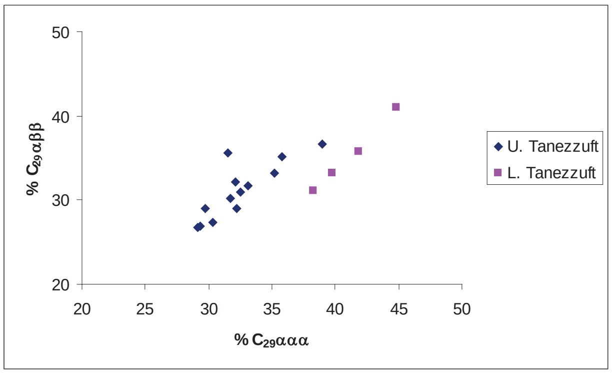


Fig. 17. Cross plot between $\%C_{29}\alpha\alpha\alpha$ and $\%C_{29}\alpha\beta\beta$

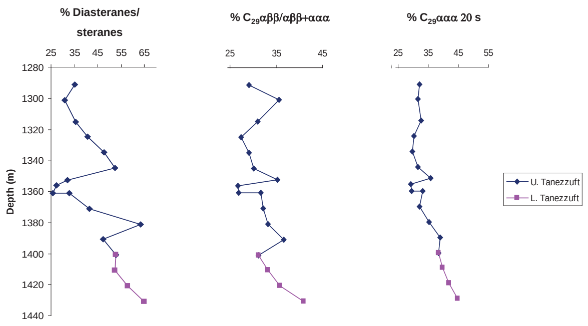


Fig. 18. Displays the variation of sterane and diasterane thermal maturity parameters within the Tanezzuft Formation.

From Tmax, the production indices (PI), and biomarker data it can be seen that the section of the Tanezzuft Formation in the well B1-23 is at late immature to early mature level.

Maturity parameters based on alkylphenanthrene and alkylnaphthalene are displayed in Table 6 and Figure 19. The methylphenanthrene index (MPI-1) appears to be useful as vitrinite reflectance to determine the thermal maturity of source sediments in late oil window and gas prone. It increases with maturity due to the relative thermal stabilities of methylphenanthrene isomers (α & β) and methylation of phenanthrene, which represent stable (β) methylphenanthrene isomers (2-MP & 3-MP) relative to less stable (α) methylphenanthrene isomers (1-MP & 9-MP) and phenanthrene (P).

The MPI-1 parameter within the two parts of the Tanezzuft Formation shows values that range from 0.52 to 0.77, indicating mature formation. Calculated vitrinite reflectance (VRc%) estimates, using the formula proposed by Radke *et al* (1984), shows values ranging from 0.71 to 0.86 within the whole Tanezzuft section, again considered as a mature section. Methylphenanthrene ratio (MPR) is also used as a maturity parameter in late oil window and gas zone, and increases with maturity due to the relative stabilities of β & α. MPR ratio within the study section shows a range from 1.10 to 1.35, and this given an indication to mature section. Methylnaphthalene ratio (MNR) is also used as maturity parameter at a higher maturity level than MPI-1; it increases with maturity due to the thermal stabilities of β methyls and α methyls. The MNR within the Tanezzuft section shows a range from 0.90 to 1.77, indicating mature section

Based on aromatic parameters the Tanezzuft sediments seem to be mature. This conclusion is in contradiction with all other parameters (Rock-Eval data, CPI, hopane & sterane ratios), which conclude that the Tanezzuft samples used in this study are late immature to early mature. This contradiction can be explained by that the aromatic ratios e.g. MPI are good parameter within oil window as a hydrocarbon internal maturity parameter (Radke *et al*, 1981). Moreover, this contradiction also can be related to organic facies; at the maturity stage onset of intense *n*-alkane generation has been found in coals (Radke *et al*, 1980) and sediments predominantly terrestrial organic matter (Radke *et al*, 1981), and the sediments of Tanezzuft Formation found to be kerogen type II amorphous (AOM).

SOURCE OF ORGANIC MATTER AND DEPOSITIONAL CONDITIONS

Source of Organic Matter

Rock-Eval 6 parameters suggest a kerogen type II and II/III. Type II kerogens are mainly dominated by well-preserved amorphous (AOM), but not all type III kerogen is derived from land plants as hydrogen indices of any kind of organic matter can be lowered

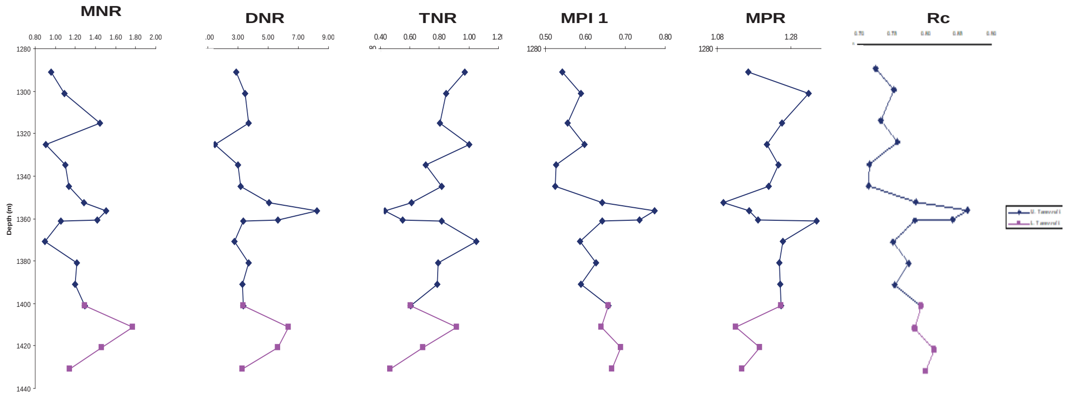


Fig. 19. Display the variation thermal maturity of aromatic parameter within upper and lower Tanezzuft Formation

by aerobic degradation, and thus its kerogen type increased e.g. II to III, III to IV. Original type II AOM partially degraded in depositional environment thus often end up with a type III gas prone composition. According to above type II/III in our samples which belong to Silurian do not mean land plants as to be known the diversity and distribution of terrestrial increased greatly during the Devonian (Killops & Killops, 1993). The source of the organic matter can be described using the Van Kervelen diagram (atomic O/C versus O/C) or a modified Van Kervelen diagram (OI versus HI), but the result should be supported by microscopy, element analysis or both (Peters, 1986). From the Rock-Eval data the observed linear relationship between the S2 and TOC values (Fig. 14) indicates that the organic matter within the Tanezzuft section in well B1-23 has generally the same origin (Espitalié *et al*, 1985) or is at least of the same source Type (II,III) with composition between type II and III. Gas fingerprints are indicative of certain types of source organic matter input (Peters *et al*, 1993). A representative gas chromatogram of saturated hydrocarbon fraction shows the normal alkanes distribution to have an abundance of the short-chain compounds within most of the upper and lower Silurian Tanezzuft samples which indicates an algal phytoplankton and/or bacterial input (Hunt, 1995). Gelpi *et al*, (1970) also reported that the high relative abundance of short-chain *n*-alkane suggested algal contribution. The Pr/n-C_{17} and Ph/n-C_{18} data points give a result indicating that the source rock samples are type II and III kerogen mixture and algal marine which agree with the Rock-Eval results. The sterane distribution of the whole of the Tanezzuft samples is largely dominated by C_{27} and C_{29} homologs, with the sterane carbon number predominance being $C_{29}>C_{27}>C_{28}$ at the beginning of upper part of the section and $C_{27}\sim C_{29}>C_{28}$ at the end of the Tanezzuft section and a predominance of C_{27} and C_{29} over $C_{28}\alpha\alpha\alpha$ 20R sterane. The relative abundance of $C_{29}\alpha\alpha\alpha R$ steranes in organic matter can often be associated with a predominant input of terrestrial land plants, where, the $C_{27}\alpha\alpha\alpha R$ steranes are often associated with marine organic matter (zooplankton), and $C_{28}\alpha\alpha\alpha R$ represent phytoplankton input (Huang & Meinschein, 1979). Caution needs to be implemented when interpreting the distribution of the relative abundance of C_{27}, C_{28}, and C_{29} steranes, as it has been reported that brown algae and many species of green algae contain predominantly C_{29} sterols (Moldowan *et al.*, 1985). Furthermore, previous studies showed oil and sediments having a high proportion of C_{29} sterane which is not related to land plants (Mickirdy *et al*, 1986). The concentration of C_{29} ααα steranes observed through the section of the Tanezzuft Formation in most of the samples must be predominantly phytoplankton algal in origin. Figure 20 illustrates the relationship between the C_{27} ααα20R/C_{29} ααα20R ratio and the C_{27} ααα20R/C_{28} ααα20R ratio as they are not dramatically influenced by maturity (Peters & Moldowan, 1993), and there are small distributions between these ratios in both parts, which indicate that the upper and lower Tanezzuft Formation have relatively the same source (algal input). Significant algal contribution in both parts of the Tanezzuft Formation is also suggested from the relative high abundance of diasteranes (Rubinstein *et al*, 1975), steroidal compounds (Volkman, 1986), and an absence of any obvious higher plant marker compounds (Peters & Moldowan, 1993). Bacterial contribution is clearly recorded in all Tanezzuft samples as evidenced by the high abundance of the hopanes (Ourisson *et al*, 1979). Moreover, homohopanes (C_{31}-C_{35}), which are derived from bacteriohopanetetrol and other polyfunctional C_{35} hopanoids common in prokaryotic microorganisms (Ourisson *et al*, 1984; Rohmer, 1987), are present through the upper and lower parts of the Tanezzuft Formation although these may be either bacterial or algal lipid source indicators.

The Rock-Eval, gas chromatogram, and biomarker results indicate a marine algae organic input, with additional abundance of bacterial contribution.

Depositional Conditions

The following Rock-Eval data point to an environmental condition at Tanezzuft Formation. The relationship between TOC and HI (Fig.21) represents a high variation in TOC and hydrogen

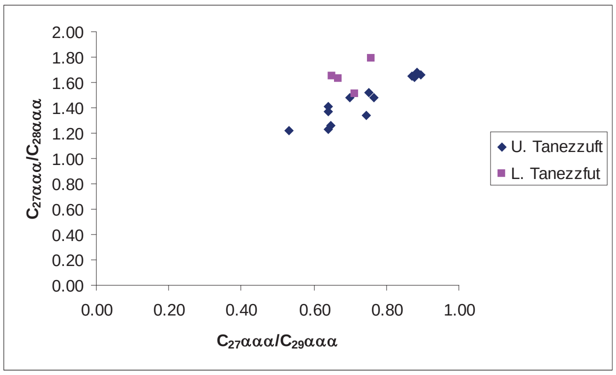


Fig. 20. Cross plot betweenC_{27}ααα /C_{29}α αα 20R and C_{27}ααα /C_{28}ααα20R

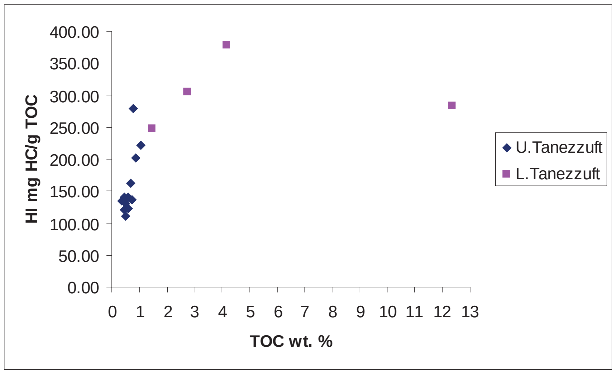


Fig. 21. Cross plot between TOC versus hydrogen indices

indices (HI) which may reflect changes in the degree of preservation through this formation. The TOC plot of HI indicates that the upper Tanezzuft Formation has lower TOC and HI values compared to the lower Tanezzuft Formation, which represent an increase of TOC due to an increase in the preservation of organic matter (HI); this may due to an enhancement of primary production and low dilution. According to the relationship between the TOC and HI, the samples that have high organic carbon content and hydrogen indices may indicate dysoxic-anoxic conditions. However, dysoxic-anoxic conditions 2.0-0.2 ml/l O_2; (Tyson & Pearson, 1991) may be the most probable for the depositional environment of the lower Tanezzuft Formation with slightly more oxic conditions associated with some samples of the upper Tanezzuft Formation that have low HI and TOC %.

Furthermore, Figure 22 shows a cross plot of the TOC and oxygen indices (OI) in both parts of the Tanezzuft Formation. This diagram illustrates an increase in TOC values with decreasing OI values which may also reflect the degree of preservation, and the change in sedimentary facies. The upper Tanezzuft Formation ($TOC \leq 1.07$ and high OI 12-188mg CO_2/g TOC) suggests that organic matter deposited under oxic conditions with a low sedimentation rate. The remaining samples of the Lower Tanezzuft Formation have $TOC \geq 1.45$ and low OI 17- 34mg CO_2/g TOC which indicate that sediments were probably deposited in anoxic facies. Therefore, the depositional environment of the Tanezzuft Formation may possibly have ranged from the suboxic to dysoxic-anoxic in some parts of the section.

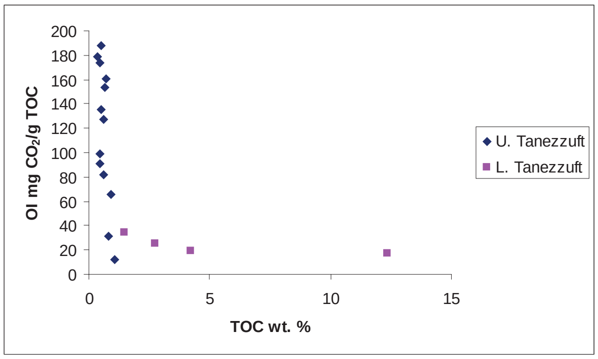


Fig. 22. Cross plot of TOC versus OI

Geochemical parameters based on *n*-alkane and acyclic isoprenoid alkane distributions are given in Table 2. The pristane/phytane ratios of oils and bitumens are commonly used as indicators of the redox potential of the source sediments. Pr/Ph ratios less than 1 generally indicate anoxic deposition, while Pr/Ph ratios more than 1 often indicate oxic deposition (Didyk *et al*, 1978). Pr/Ph for the Upper Tanezzuft Formation samples varies between 0.81-1.48 suggesting facies differences between samples.

The lower Tanezzuft Formation has a slightly higher Pr/Ph ratio varying between 1.26 to 1.48 suggesting changes in organic facies and depositional conditions. According to Volkman & Maxwell (1981), a Pr/Ph ratio between 0.6 and 2.5 is difficult to use as an indicator of the palaeoenvironment without corroborating data. Despite other evidence for low oxygen conditions, the relatively high Pr/Ph ratio in the Tanezzuft Formation may be due to additional sources of pristane, e.g. algal tocopherol (Goosens *et al*, 1984). Moreover, the relative distribution of C_{35} relative to total C_{31} to C_{35} $\alpha\beta$ 22S and 22R hopanes, measured by the homohopane index has been proposed as an indicator of the redox potential during and immediately after deposition of the source sediments (Peters & Moldowan, 1993). In the lower Tanezzuft Formation the homohopane index ratios are 3.29 to 4.09 suggesting reducing condition. In the upper Tanezzuft Formation the homohopane index ratios are 2.47 to 4.06, again suggesting a reducing marine environment with more oxidizing conditions. The relationship between the homohopane index and Pr/Ph ratio (Fig. 23) suggests some variability in oxygen concentration through the section of the Tanezzuft Formation.

A ternary plot of the relative distribution of C_{27}, C_{28} and C_{29} $\alpha\alpha\alpha$ 20S+20R steranes is shown in Figure 24. It is apparent from this figure that both parts of the Silurian Tanezzuft source rock samples have similar carbon number distributions of steranes, and

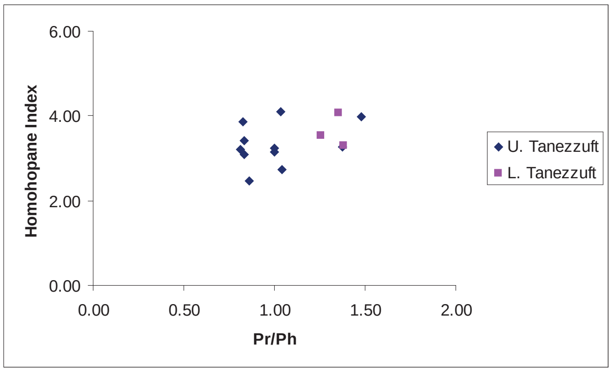


Fig. 23. Cross plot between Pr/Ph and Homohopane index.

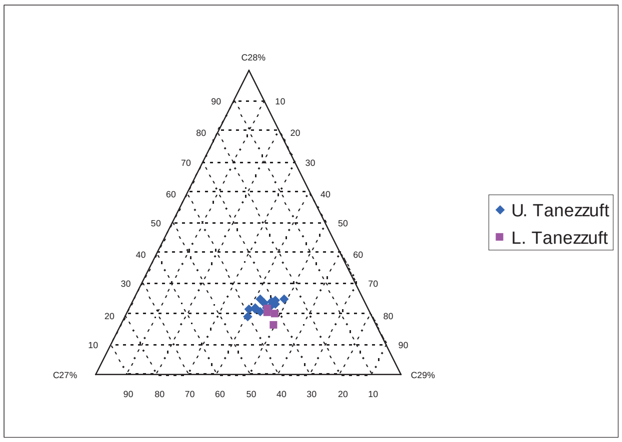


Fig. 24. Ternary diagram of C_{27}, C_{28}, & C_{29} ααα(20S+20R) steranes.

show a higher relative abundance of C_{27} and C_{29} than C_{28}. These mean they were derived from generally the same organic matter assemblages with high algal input. They plot in the area where most marine source rock samples are found to be located (Huang *et al*, 1979).

Moreover, the presence of C_{30} sterane is the most powerful parameter for identifying the input of marine organic matter to source rock (Moldowan *et a*l., 1985). The origin of C_{30} steranes suggests they arise from the marine sterols (Djerassi, 1981). The presence of C_{30} steranes within all of the Lower Tanezzuft Formation and most of the samples of the upper Tanezzuft Formation at Well B1-23, is considered as a good indicator for marine depositional setting. Furthermore, biomarker diagnostic for anoxygenic photosynthesis by Chlorobiaceae (green sulfur bacteria) was identified in Tanezzuft sediments. The anoxic conditions are favorable for Chlorobiaceae; these bacteria use a distinct light-harvesting pigment and require sulphide comprising bacteriochlorophylls, carotenoids isorenieratane and chlorobactene (Grice *et al*, 2005) and (Damsté *et al*, 2001). Isorenieratane is preserved in upper and lower part of Tanezzuft Formation (Fig. 13 & 25), reflecting intense green sulfur bacterial activity and, thus, provides unequivocal evidence for anoxic conditions.

We can conclude that, dysoxic-anoxic conditions may be the most probable for the depositional environment of the lower Tanezzuft Formation with slightly more oxic conditions associated with some samples of the upper Tanezzuft Formation.

CONCLUSION

Rock-Eval data (i.e. S2, TOC, & HI), indicate that the upper part of Tanezzuft retains fair source rock potential and mixed kerogen type II/III. Whereas, the lower part is very good source rock potential and kerogen type II. No commercial hydrocarbon can be expected from the upper part of this formation, but oil could be generated from the lower part.

Rock-Eval analysis (Tmax, PI) and molecular biomarker data (i.e. %20S/20S+20R, %22S/22S+22R), indicate that both parts of the Tanezzuft Formation are late immature to early mature, although the aromatic ratios indicate a mature source rock.

Based on the biomarker parameters, the Tanezzuft source rock in this locality is dominated by marine algae as evidenced by abundant of short

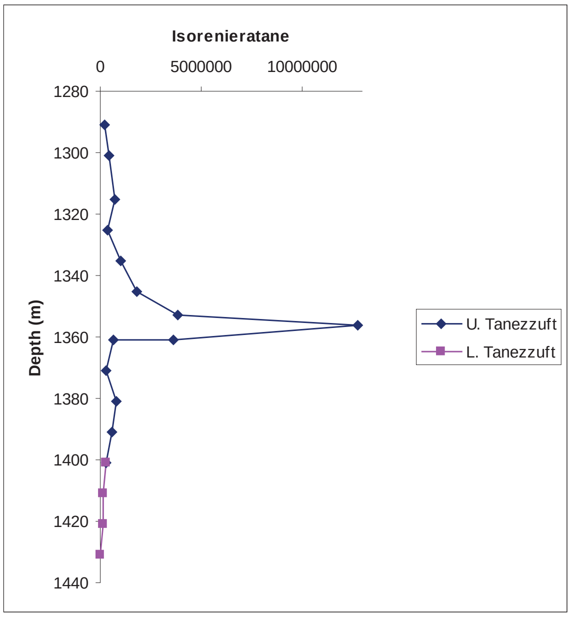


Fig. 25. Display the variation of isorenieratane within upper and lower Tanezzuft Formation.

chain *n*-alkanes with additional bacterial input, suggested from the abundance of hopanes.

Some combination of Rock-Eval, *n*-alkanes and biomarker data (such as the relative abundance of C27ααα , C28 ααα , C29 ααα20R , presence of C30 ααα 20R, and isorenieratane), suggest that both parts of the Tanezzuft succession were deposited in marine conditions, however, the upper part is relatively more oxidized. Furthermore, we can conclude that, dysoxic-anoxic conditions may be the most probable for the depositional environment of the lower Tanezzuft Formation with slightly more oxic conditions associated with some samples of the upper Tanezzuft Formation.

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