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GEOCHEMICAL CHARACTERISTICS OF THE DILBI OILSHALES

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ABSTRACT. Geological survey and exploratory work for possible oilshale reserve investigation was conducted on 25 km^2 in Dilbi area, Jimma zone, Ethiopia. Potential oilshale reserves were estimated to be 100-120 million tonnes. 250 core samples from stratigraphically selected horizons and several outcrop samples from the eastern and western parts of the Dilbi area were chemically analyzed and geologically evaluated. The geochemical samples were studied using selective leaching, pyrolysis, and chemical methods. The presence and distributions of C_{30} steranes, rearranged steranes, monoaromatized steroids, diterpenes, triterpenes and demethylated triterpenes, carbon preference indexes (CPI), pristane/phytane (Pr/Ph) ratios were studied. Accordingly, the quality of the oilshale was determined and categorized as algal-rich fluvio-lacustrine sedimentation which has a source rock capacity of fair (3000 ppm) to good (20000 ppm) characteristics. The geochemical studies of the Dilbi-Moye Basin indicate an organic rich oilshales of potential source rock quality. The geological evidence also suggested that these oilshales occur within the regionally extending rift zone of south-western Ethiopia, which warrants exploration work for hydrocarbons.

INTRODUCTION

Oilshale is an organic-rich accumulation of rocks that has neither been buried deep enough nor subjected to temperature high enough to generate petroleum [1-4]. It has an organic origin derived from the remains of living organisms which were incorporated into sediments during deposition [5]. It is estimated by some authors [6-8] that organic rich shales have a potential yield of 2×10^{15} tonnes of oil [9]. When confronted with decreasing reserves of oil and natural gas, the abundance of oilshale and its potential as a source of hydrocarbons serve to emphasize its future economic importance. Understanding of the factors which influence the generation and expulsion of oil from these oil shales has improved significantly. Much of this progress has been a direct result of research focusing on kerogen and bitumen, which are the insoluble and soluble fractions of the organic matter in oilshales, respectively. In this regard, the role of source rocks evaluation for petroleum formation and favorable geological environments for the deposition of oilshale is attempted by several analytical and physical methods through kerogen and bitumen studies [10-11]. This paper intends to characterize the Dilbi oilshale by using geochemical and geological methods. The results of the study have assisted in the identification of the source rock characteristics, hydrocarbon potentials, organic matter types, and the degree of maturation levels [12]. Investigation of the bituminous materials also revealed their biological origin which offered considerable support for their prevailing aquatic and geological environment (i.e. lacustrine and fluviatile origins).

The study area (Dilbi) is located 50 km south of Jimma town, Ethiopia. It is bounded by the coordinates of 7°16' to 7°26' N and 36°18' to 36°53' E. A program of intensive explorations was conducted by the Ethiopian Institute of Geological Surveys (EIGS) since 1987. Based on this exploratory work, attempts have been made to investigate anomalous oilshale zones and potential accumulation areas in Dilbi [12].

GEOLOGICAL SETTING AND EXPERIMENTAL DATA

Geology. Dilbi is situated within the tertiary volcanic province of southwestern Ethiopia. The Basin has a structural as well as a depositional feature, preserving thick Cenozoic strata. Its evolution is perhaps closely related to an extentional tectonic phase of the Ashangie rift development during the early tertiary period. The graben follows an orientation of NE-SW directions. The boundary faults of the basin are well developed on either one or both sides, suggesting graben/semi-graben characteristics similar to other rift basins of the world. Systematic detailed mapping and subsurface studies [13] have disclosed at least four major basic to acidic volcanic cycles. Thick sequences of sediments are enclosed within the volcanic suits. They are mainly continental clastics of fluvio-lacustrine origin. The oilshales are contained within stratigraphic clusters of two horizons. These are, the upper oilshale unit of 12.5 to 17 m in thickness and the lower oilshale unit of about 50 m in thickness. The oilshale units are distinctly characterized by gray-olive brown beds. The commonly brownish colored beds apparently reflect abundant organic matter input during deposition. They are well developed at the eastern part of the basin. Age estimates based on paleontological studies gave a general agreement in the presence of middle/late eocene to upper miocene sedimentation in Dilbi Basin [13-18].

Sampling. Following the previous studies [19], attempts to characterize the nature of the Dilbi oilshale have been made. The core samples investigated comprise up to 250 samples from twenty five drill holes of the stratigraphically selected areas of the eastern and western parts of Dilbi. The samples were collected from the intervals of organogenic shales and claystones from various depths ranging from 0-300 m. They were carefully selected from composite sections of different wells and analyzed for geochemical characterization of the area. In the homogeneous formation of bituminous beds, intervals of one meter was selected, while for organogenic lean shales intervals of half a meter were chosen [20-22]. Prior to the chemical determinations, the samples were pulverized to pass through a 200 mesh sieve. Then, the average results were recorded for six consecutive replicates. Analyses for selective leaching, pyrolysis, chemical, and others were carried out on samples by the methods described elsewhere [19]. The results are presented in Tables 1 to 7.

Extraction and isolation. 25 g of the dried sample (105°) was Soxhlet-extracted in a ceramic thimble with dichloromethane (150 mL) for 24 h. Elemental sulfur was then removed from the extracts by percolating through a column of activated copper (15 g). The dichloromethane eluates were carefully evaporated to dryness, taken in 2 mL of benzene:methanol (1:1), concentrated in a stream of nitrogen to volumes of 0.1-0.2 mL [23-25], and subjected to gel permeation/adsorption chromatography. For this purpose Sephadex LH-20 (30 g) in benzene-methanol (1:1) was packed in a glass column (50 x 1.6 cm).

SEPARATION AND IDENTIFICATION

Gas chromatographic (GC) analysis. A Carlo Erba FV 2150, sigma 3B capillary gas chromatograph equipped with a FID was used. Sample components were separated using a 25 m x 0.2 mm id (0.52 μm film thickness) fused silica capillary column coated with a cross-linked methyl silicone liquid phase [GC program: 50-270° ramp rate, 5° min^{-1}; FID, H_2 (30 mL.min^{-1}); air, 30 mL.min^{-1}; attenuation, 1 x 32; carrier gas, He (15 psi); injector/detector temperature, 300°]. Individual n-alkane concentrations were calculated from standards [24-26].

Mass spectrometric (MS) analysis. For GC separation followed by MS separation and MS identification (GC-MS/MS) a S.N.G Nermag model MS/MS R30-10 triple quadruple mass spectrometer equipped with an EI/CI source combined with an on-line computer was used. The glass capillary column was directly coupled to the mass spectrometer by means of a platinum capillary. Helium was used as carrier gas. The MS operating conditions were: electron ionization energy, 70 eV; emission current, 350 μA; preamplifier sensitivity, 10^{-8} A/V; ion source temperature and pressure, 110° and 7 x 10^{-7} torr, respectively. Mass spectral data were acquired and edited using an INCOS 2300 data system scanning from *m/z* 50 to 600 in 1 s. Comparison of the mass spectra with standard spectra in the NBS library assisted in the identification of the compounds [27-29].

RESULTS AND DISCUSSION

Dilbi oilshales are characterized by high fixed carbon (0.2-50%) and mineral matter (50-87%), low moisture (2.3-7.3%), volatile matter (8-30%), sulfur (1.1-1.6%), phosphorus (0.3-0.8%), chlorine (0.3-0.8%), and low oil content (5-15%) with a calorific value of 540-5700 kcal/kg. The eastern Dilbi sub-unit is a swampy environment which favored the formation of coal/carbonaceous shale rather than the brown oilshales, found in the upper (western Dilbi) sub-unit. Long-chain aliphatic (saturates) and alicyclic compounds are abundant in the oilshale obtained from eastern Dilbi, while aromatic compounds are predominant in the oilshale obtained from western Dilbi (Table 1). Ratios of saturates to aromatics are less than one for western Dilbi, while they are greater than three for the eastern Dilbi oilshales. This shows that the eastern Dilbi oilshales are marginally mature, while the western Dilbi oilshales are immature with source interval of mature sediments [30]. The ratio of saturates to total organic carbon (TOC) and polars to TOC increase, while the ratio of aromatics to TOC decrease for oilshales that originated from both eastern and western Dilbi. This gives clues about the nature of reactions that take place deep in the sediments.

On the other hand, the residual kerogen in the western Dilbi oilshale contains 2.4% ash and that obtained from eastern Dilbi contains 1.4% ash (Table 1). The oilshales in boreholes 5, 6, 8 and 102 in the upper oilshale and in boreholes 1 and 2 in lower oilshale sub-units are interbedded with layers of coals. This may have resulted in the mean pH of about 8.6, indicating an alkaline nature of the shales deposited in Dilbi.

Table 1. Analysis of organic richness.

WDB	E (ppm)	RB to TOC	S (%)	A (%)	P (%)	POC (%)	OCR (%)	CK (%)	AK (%)
102	3200	30.5	11.5	50.0	38.5	1.8	8.7	8.2	1.8
101	3300	60.1	10.4	51.0	39.0	2.4	3.1	12.3	0.5
5	3900	162.5	9.8	51.5	39.7	1.7	5.9	12.5	2.4
8	4600	20.7	8.8	50.7	40.5	5.5	16.8	20.8	0.8
6	10500	77.3	8.5	49.5	42.0	1.2	2.2	7.9	1.9
Total	5100	105.6	9.8	50.5	39.9	2.5	7.4	12.3	1.5
EDB									
4	5700	84.4	52.9	9.6	37.5	3.0	3.7	19.0	0.5
2	5200	45.4	52.0	8.5	39.5	3.1	8.4	25.0	0.5
1	5000	1000	51.5	8.0	41.0	1.8	7.0	9.9	1.4
11	14200	206.3	58.5	7.5	34.0	1.4	5.5	30.3	1.1
7	6540	91.9	54.3	8.0	37.7	2.2	6.8	30.3	0.8
Total	7328	105.6	53.8	8.3	37.9	2.3	9.3	22.9	0.9

WDB = western Dilbi borehole; E = extractables; RB = ratio of bitumen; S = saturates; A = aromatics; P = polars; POC = pyrolyzed organic carbon; OCR = organic carbon residue; CK = content of kerogen; AK = ash of kerogen; EDB = eastern Dilbi borehole.

Furthermore, geochemical studies revealed that the TOC content of the oilshales from western Dilbi are 1.5-40%, while that from eastern Dilbi has TOC content of 0.8-50% (Table 2). The maximum amounts of free hydrocarbons (HC) generated from one gram of rock at 200-250° (S1), and HC generated by pyrolytic degradation of the kerogen in one gram of rock at 445° (S2), are 2.4 and 61.4 mg HC/g of rock, respectively, in the western Dilbi samples, and 2.8 and 83 mg HC/g of rock, respectively, in the eastern Dilbi samples (Table 2). On the other hand, the ratio of total extractables to TOC range from 20-163 mg/g and 45-206 mg/g in the upper and lower oilshales of Dilbi, respectively. The hydrogen index (HI) averages 546 mg HC/g of organic carbon (C_{org}) for eastern Dilbi samples. The organic matter preserved during deposition in this part of Dilbi is hydrogen-rich and capable of forming nearly type I and II kerogen, which are considered as good qualities for source rock. The HI of the western Dilbi oilshale samples range from 150-580 mg HC/g of C_{org} and these samples are known to contain substantial amounts of type II and III kerogen and are considered to be good potential sources for liquid HC and gas [12]. Source rock characteristics of these samples, i.e. TOC, S1, S2, maximum temperature of the pyrolysis of the residual organic matter (T_{max}), HI (Table 3), and the ratio of total extractables to TOC (Table 1), indicate that the oilshales have a good source rock potential. Even though geochemical log data obtained through pyrolysis (Table 2), ultimate analyses (Table 4) and chemical analyses, indicate lower free hydrocarbons and the immaturity of the source rock, the observed distribution of the TOC, and S2 (Table 3) data shows the organic richness of the samples obtained from both the western and eastern parts of Dilbi.

Table 2. Pyrolysis of Dilbi oilshale.

WDB	Depth (m)	S1*	S2*	S4*	T_{max} °C	GOGI	TPI	TOC (%)	HI**
102	10-18	1.0	28	100	435	0.11	0.02	13	616
	19-26	0.8	24	94	436	0.12	0.02	12	584
	27-35	0.6	16	85	437	0.13	0.03	9.9	478
	36-43	0.5	15	70	438	0.14	0.03	8.3	353
101	23-29	0.8	24	20	437	0.09	0.01	3.5	460
	30-37	0.7	22	25	438	0.12	0.03	4.4	480
	38-45	0.7	22	30	439	0.14	0.04	5.4	412
	46-53	1.1	33	40	437	0.15	0.05	7.2	580
	55-65	2	37	42	438	0.17	0.08	7.4	644
5	28-39	0.6	16	87	436	0.12	0.05	9.9	225
	40-50	0.5	20	85	438	0.12	0.04	11	236
	51-60	0.4	12	75	437	0.13	0.04	8.6	207
	61-70	0.5	23	19	436	0.14	0.03	3.1	709
	71-80	0.6	31	22	436	0.15	0.03	4.1	563
	81-90	0.7	20	69	434	0.16	0.05	9.4	620
8	45-55	1.1	56	168	432	0.13	0.02	22	290
	56-65	2.2	36	141	433	0.15	0.06	17	450
	140-150	4.7	78	107	434	0.17	0.09	18	569
	151-160	4	81	258	434	0.19	0.07	32	1100
6	180-188	1.0	10	20	443	0.18	0.03	5	320
	189-198	0.8	12	27	436	0.19	0.03	3.7	310
	199-207	0.5	19	14	434	0.20	0.03	3	450
	208-215	0.5	12	28	442	0.22	0.04	2.4	220
4	6-17	0.8	30	120	435	0.14	0.03	15	650
	18-28	0.8	26	95	436	0.15	0.03	12	600
	29-39	0.5	16	90	438	0.17	0.03	10	580
	40-50	0.5	17	86	438	0.20	0.03	10	550
	51-61	0.3	25	76	438	0.19	0.03	9.7	450
2	60-70	0.5	16	26	436	0.16	0.03	3.2	720
	71-90	0.8	25	38	436	0.16	0.03	5.9	625

WDB	Depth (m)	S1*	S2*	S4*	T_{max} °C	GOGI	TPI	TOC (%)	HI**
2	91-100	1.1	64	162	437	0.18	0.04	22	580
	101-110	1.6	42	69	438	0.18	0.04	11	520
	111-120	0.9	17	26	442	0.20	0.05	4.1	450
	121-131	0.7	15	20	443	0.20	0.06	3.3	450
	131-140	0.6	13	15	443	0.22	0.06	2.6	500
	200-210	0.5	9.3	13	444	0.24	0.07	2.1	550
1	60-90	2.4	63	138	437	0.55	0.03	19	390
	91-120	1.7	41	125	437	0.55	0.04	17	500
	121-150	1	31	100	435	0.60	0.05	13	540
	151-170	1.2	35	90	438	0.65	0.06	12	510
	171-180	1.4	38	70	440	0.70	0.05	10	610
	181-190	1	26	40	441	0.70	0.05	6.2	500
	191-215	0.8	16	25	442	0.80	0.04	3.9	450
7	140-165	0.9	21	77	441	0.7	0.05	7.5	280
	166-176	1.4	23	46	442	0.8	0.06	5.3	205
	177-197	1	16	41	442	0.8	0.04	4.5	200
	200-214	0.8	15	31	443	0.9	0.04	3.5	195
	215-225	0.6	12	80	443	0.9	0.07	6	190
	226-235	0.5	11	75	444	1	0.07	10	180
	236-245	0.4	9.3	39	444	1.2	0.07	10	160

*mg HC/g rock; **mgHC/g C_{org}.

The oilshales in the study area are diverse in lithological association and composition. Their organic matters are also derived from a variety of sources which include precursors of terrestrial and algal origin. The dominant kerogen is described as having an amorphous and algal origin, with great amounts of higher land-derived plant material. However, the T_{max}, the main maturation indicator, is compatible with the immaturity condition for western Dilbi ($T_{max} \leq 430°\text{-}435°$) oilshales. The T_{max} values for the eastern Dilbi oilshales suggest marginal maturity ($430°\text{-}435° < T_{max} \leq 465°$) [31] (Table 3).

The most widely used classification of kerogen is based on atomic hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios [31]. Accordingly, the western Dilbi kerogen has H/C ratio of 0.73 and O/C ratio of 0.12, which has typical characteristics of humic kerogen belonging to type III organic matter. On the other hand, the eastern Dilbi kerogen assemblages have H/C ratios of 1.3, and O/C ratios of 0.08, which suggests a mixture of algal and other liptinitic kerogen characteristics [9, 31].

Table 3. Maturation parameters

Quality	TOC (%)	S1	S2	T_{max} (°C)	HI	Ref.
Poor	<0.05	<0.05	0-3	$\leq$430-435	0-150	32
Fair	$0.5<TOC<1$	$0.5<S1<1$	3-6	$\leq$430-435	0-150	32
Good	$1<TOC<2$	$1<S1<2$	6-20	$430\text{-}435 \leq T_{max} \leq 465$	$\geq$150	32
Very good	>2	>2	>20	$430\text{-}435 \leq T_{max} \leq 465$	$\geq$150	32
Western Dilbi	13	1.4	35.7	435.2	361	
Eastern Dilbi	16.9	1.8	44.4	439.4	530	

Another way of evaluating the Dilbi source rock is the examination of its organic extracts. Geochemical fossils from both parts of Dilbi include long-chain n-alkanes, a large number of aromatics, naphthenes containing 4- and 5-membered rings (steranes and triterpenes), and a number of isoprenoids including pristane (pr) and phytane (ph). Biomarker distributions obtained from GC/MS/MS data produced fragmentograms for *m/z* 85 (alicyclic alkanes), 123 and 163 (diterpenes), 177 (demethylated triterpenes), 149, 151, 217 and 218 (steranes), 191 (triterpenes), 231 (triaromatic steranes), 239 and 253 (monoaromatic steranes) and 259 (rearranged steranes or diasteranes). Data displayed in Tables 5-7 show that an immature type I/II kerogen of eastern Dilbi, and immature type III kerogen of western Dilbi extracts, contain predominantly non-marine organic matter. For both, western and eastern Dilbi oilshales, the ratio $(n\text{-}C_{24} + n\text{-}C_{26})/(2 \times n\text{-}C_{25})$ is less than one. This shows that the Dilbi oilshale is from ancient sediment of primitive plants, bacteria, and algae, ranging from $n\text{-}C_{31}$ to $n\text{-}C_{35}$, generally showing a maximum between $n\text{-}C_{23}$ and $n\text{-}C_{30}$, with low preference of odd to even carbon chain homologs (Table 5). Moreover, n-alkanes greater than $n\text{-}C_{24}$, with a high preference of odd carbon number chains, maximizing at $n\text{-}C_{27}$ - $n\text{-}C_{29}$, are characteristics of terrestrial plants [33]. The $n\text{-}C_{23}$, $n\text{-}C_{25}$, $n\text{-}C_{27}$ and $n\text{-}C_{29}$ alkane abundances show that Dilbi oilshales are derived from higher plant lipids and cuticular waxes, while the two alkanes ($n\text{-}C_{15}$ and $n\text{-}C_{17}$) are derived from the lipids of algae [34]. A moderate concentration of these latter two alkanes in the extracts of eastern Dilbi oilshale samples, indicates traces of planktonic algal component in the source of organic material of eastern Dilbi oilshale.

Thus, from the five categories of source rocks that prevail [35], the paralic depositional environment in the western part of Dilbi and lacustrine characteristics in the eastern part are more expressed. A pronounced quantitative expression for the odd-even carbon preference ($CPI > 1$) in both the western and eastern Dilbi oilshales speaks in favor of the odd numbered n-alkanes and a non-marine source (Table 6). Extracts of the Dilbi oilshale display a tendency toward $n\text{-}C_{31}/n\text{-}C_{17}$ ratio greater than 0.5 (Table 6) indicating a non-marine source, too [36].

Odd carbon and pristane ($pr/ph > 1$) predominance (Table 6) show the less reducing environments. The relations $pr/n\text{-}C_{17} > 1$ and $ph/n\text{-}C_{18} \leq 1$ may give an indication that the depositional origin of Dilbi samples are from inland environments. These ratios decrease significantly with depth showing increase of thermal stress [34]. In addition, odd carbon and pristane predominance in the extracts of Dilbi samples shows the immaturity of the sediments containing mostly kerogen of terrestrial plant origin. Long chain n-alkanes are abundant in the higher plant-derived incursion of western Dilbi oilshale, whereas, short chain n-alkanes are dominant in the eastern Dilibi oilshale (Table 6). Although the naphthene bulge between C_{25} and C_{30} indicate sterane and triterpene abundance, sterane distributions in Dilbi oilshale extracts are sparse (*m/z* 217 and *m/z* 218 in mass chromatograms) and barely detectable. Only the biological isomer of the C_{29} sterane was identified with any degree of confidence. The absence of C_{30} steranes in the oilshale was found to be a definitive indication of a contribution to the source from a non-marine-derived organic matter [37].

Table 4. ,Ultimate analysis of Dilbi oilshale (%).

WDB	H	C	O	N	S	Cl	H/C	O/C	N/C	S/C
102	7.5	76	15	0.3	0.7	0.5	1.20	0.15	0.003	0.004
101	6.5	77.5	13.7	0.5	1.3	0.5	1.00	0.13	0.006	0.006
5	5.0	79	12.8	0.6	1.4	0.6	0.75	0.12	0.007	0.007
8	4.5	81	12.0	0.7	1.4	0.6	0.66	0.11	0.007	0.007
9	3.5	83	10.5	0.7	1.6	0.7	0.50	0.10	0.007	0.007
6	3.5	85	9.0	0.9	1.6	0.7	0.49	0.08	0.009	0.007
Total	5.08	80.3	12.2	0.6	1.3	0.6	0.75	0.12	0.006	0.006
EDB										
4	12.0	70	15.4	0.7	1.3	0.6	2.04	0.17	0.009	0.007
104	11.0	75	11.3	0.7	1.4	0.6	1.75	0.11	0.008	0.007
2	10.0	80	7.2	0.8	1.4	0.6	1.49	0.07	0.009	0.007
1	8.0	83	6.1	0.8	1.4	0.7	1.15	0.06	0.008	0.006
11	6.0	85	6.1	0.8	1.4	0.7	0.84	0.05	0.008	0.006
7	4.0	87	5.8	0.9	1.4	0.9	0.55	0.05	0.009	0.006
Total	8.5	80	8.6	0.8	1.4	0.7	1.3	0.08	0.009	0.007

A diagnostic C_{30} sterane pattern, C_{30}/C_{27}-C_{30}, and steranes/17α(H) hopanes ratios (Table 7) approaching zero, show the non-marine source of Dilbi oilshale. Differences in sterane distributions from eastern to western Dilbi indicate a predominance of 5α,14α,17α,20R- and 5ß,14α,17α,20R-steranes (Table 7). Besides, the steranes of relatively immature sediments of Dilbi basin consist predominantly of (20R)-5α,14α,17α(H) and (20R)-5α,14α,17α(H) components (Table 7) in a typical ratio of 1:3.4. Having increased amounts of the 20R isomers of the 5α,14α,17α-steranes, compared to the 20S isomer, can also be taken as an evidence of immaturity.

Table 5. Composition (%) of C_{15}+ hydrocarbons (HCs).

HCs	Composition	
	EDB	WDB
n-C_{12}	1.5	0.6
n-C_{13}	2.3	1.2
n-C_{14}	3.0	1.8
n-C_{15}	3.5	2.5
n-C_{16}	3.5	2.8
n-C_{17}	4.2	3.5
n-C_{18}	4.3	4.0
n-C_{19}	4.5	4.2
n-C_{20}	4.5	4.5
n-C_{21}	5.3	5.0
n-C_{22}	5.5	5.5
n-C_{23}	7.5	7.0
n-C_{24}	6.0	7.3
n-C_{25}	8.0	7.5
n-C_{26}	6.5	6.8
n-C_{27}	8.0	7.7
n-C_{28}	5.5	5.6
n-C_{29}	9.0	11.0
n-C_{30}	3.0	4.5
n-C_{31}	2.0	3.5
n-C_{32}	1.0	1.5
n-C_{33}	0.8	1.2
n-C_{34}	0.5	0.5
n-C_{35}	0.3	0.3
Paraffins	25.8	18.0
Saturates	42.6	9.9
Aromatics	10.1	49.6
Isoprenoid	13.0	15.0
Steranes	2.7	2.5
Terpenes	5.8	6.0

Both monoaromatic (C-ring) and triaromatic (ABC-ring) steroid hydrocarbons are present in significant quantities in Dilbi oilshale. Monoaromatic steroid hydrocarbons, eluting with the aliphatic hydrocarbon fraction, are typified by the *m/z* 239 and 253 in the mass spectrogram. Hopanes with the 17ß(H),21ß(H) skeleton are found in the pyrolysate in high amounts relative to the 17α(H),21ß(H)-hopanes. This shows that the kerogen and its pyrolysate are at an early stage of maturation. The presence of significant amounts of thermally mature 17α,21ß(H)-hopanes (*m/z* 217, 218) and triaromatized steranes (*m/z* 231) as well as diasteranes (*m/z* 259) indicate that some portion of the HC mixture in the Dilbi oilshale was generated at much higher temperatures than that of their present site of occurrence. The ratios of the C_{28} 20R triaromatic sterane to C_{28} 20R triaromatic sterane + C_{29} 20R monoaromatic sterane and that of the C_{20} triaromatic sterane to C_{20} triaromatic sterane + C_{29} 20R monoaromatic sterane (Table 6) are less than one for the Dilbi oilshale samples showing the weathering degree of the biomarkers. These low ratios have been suggested to reflect intense weathering and that the materials are largely of residual origin in the Dilbi source areas. The 20S/20R ratio (0.04) (Tables 6 and 7) suggests that the Dilbi oilshales analyzed are thermally immature.

Table 6. Source indicative parameters of Dilbi Basin.

Indicative parameters	EDB	WDB
CPI	1.6	1.4
Pr/Ph	4.4	4.0
Pr/n-C_{17}	2.4	2.0
Ph/n-C_{18}	1.2	0.8
n-C_{31}/n-C_{19}	0.9	0.9
long-chain/short-chain	2.7	3.9
C_{30}/C_{27}-C_{30}	0.02	0.01
steranes/17α-hopane	0.1	0.06
20S/20R$\alpha\alpha\alpha$ C_{29} steranes	0.8	0.7
20S/(20S+20R) steranes	0.3	0.3
$C_{28}/(C_{28} + C_{29})$	0.06	0.02
Ts/(Ts+Tm)	0.4	0.4
C_{28}/20R Tas./(C_{28} 20R Tas+C_{29} Mas)	0.4	0.5
C_{20} Tas/(C_{20} Tas+C_{29} 20R Mas)	0.4	0.5
ßα-steranes/all steranes(%)	37	25

Indicative parameters	EDB	WDB
hopanes/(hopanes + steranes) (%)	56	60
Ts/Tm	0.8	1.2
normoretane/norhopane	0.9	0.6
moretane/hopane	0.2	0.1
C_{26}/(Tm+Ts) tricyclics	0.2	0.3
Tm/Ts hopanes (%)	1.3	1.2
C_{30} hopanes (%)	81	75
C_{31}/C_{30} hopanes	0.01	0.08
22S(C_{31}) hopanes (%)	62	57
diasteranes (C_{29}) (%)	51	37
22S/22R C_{31}-$_{33}$ triterpene	1.6	0.8
$\alpha\alpha\alpha$ C_{29}/C_{27} sterane	1.0	0.6
αßß /$\alpha\alpha\alpha$ C_{29} sterane	0.6	0
C_{27}:C_{28}:C_{29} $\alpha\alpha\alpha$ steranes (%)	28:22:50	31:20:49
22S/(22S+22R)	0.4	0.6

Tas = Triaromatic steranes; Mas = Monoaromatic steranes.

The sterane patterns in both Dilbi oilshale extracts examined are characterized by a very low concentration of rearranged steranes (the so called diasteranes, *m/z* 259), 20S/20R-ethylcholestane ratios, and a $C_{28}/(C_{28} + C_{29})$ methyl aromatic steroid ratio (< 0.5) (Table 6), indicating that the Dilbi oilshale is of non-marine source. The carbon number distribution of 5α,14α,17α,20R-steranes is similar for all extracts of eastern and western Dilbi, regardless of depth or basin location, and is suggestive of land-lacustrine depositional conditions for the source matrix involved. The C_{29} ethylcholestanes are more abundant than their C_{27} and C_{28} counterparts in the extracts of Dilbi oilshale. Rearranged C_{29} sterane content indicates that the source rocks received organic matter from terrestrial plants, whilst the strong diasteranes indicate that they are siliclastic in nature. The naphthene bulge between C_{30} and C_{35} would indicate a strong pentacyclic triterpene component. The occurence of ion peaks at *m/z* 177 and 191 in mass spectrograms indicate the presence of tricyclic and pentacyclic terpenes. The eastern Dilbi oilshale appears to have slightly greater concentrations of pentacyclic (C_{27}-C_{32}) terpenes than tricyclic terpenes.

The hopanes are more abundant than the steranes in these samples with C_{30} and C_{31}-C_{34} hopanes being dominant (Table 6). 17α,18α,21ß(H),22,28,30-Trisnorhopane is present in almost all samples of Dilbi oilshales. They contain a series of 25 norhopanes, including 25,28,30-trisnorhopane, a distinctive monoaromatic steroid hydrocarbon distribution, and aliphatic HC fraction devoid of n-paraffins. The triterpenes contain immature biomarkers as evidenced by relatively high concentrations of moretanes, the R isomers of the C_{31} hopanes, and hopanes (Table 6 and 7). The distribution of tricyclic terpenes in immature samples of

Dilbi oilshale revealed the presence of a series extending up to at least C_{28}, with major isomers for each homolog having the stereochemistries 13α(H),14α(H) and 13ß(H),14α(H) [38]. Besides, the abundance of the αα- components decrease with depth.

Table 7. Biomarker distributions of eastern Dilbi oilshale.

Biomarker	Scan No	Fragment ions (*m/z*, %)						
		149	191	177	217	218	259	231
18α(H)-triesnorhopane	1163	2	2.7	1.5				
17α-triesnorhopane	1194	6	3.4	3.2				
17α-bisnorhopane	1268		0.9					
17α-norhopane	1299		5.8	8.3				2.6
17α-hopane	1362		14					
17ß,21α(H)-moretane	1391		2.5					
17α,21ß,(22S)-homohopane	1436	3.7	8.2	3.5				2.8
17α,21ß,(22R)-homohopane	1445	2.5	5.2	5.6				6.1
rearranged sterane 13ß,17α,(20S)	1001 1069				6.5 8.5	4.8 1.8	4	
5α,14α,17α,(20S)- C_{29} sterane	1251				3.3			
5α,14α,17α,(20R) - C_{29} sterane	1298				4.5			
5α,14α,17α,(20R) - C_{23} sterane	1266				4.4		1.2	
5α,14ß,17ß,(20R+S)- C_{29} sterane	1270				3.2		8.2	
5α,14α,17α,(20R) - C_{28} sterane	1229				1			
5α,14α,17α,(20S) - C_{27} sterane	1111				5.6	1.7		
5α,14α,17α,(20R) - C_{27} sterane	1145				2.1	2		2.2

Lacustrine oils of eastern Dilbi are characterized by a greater relative abundance of C_{21} diterpenes (*m/z* 123 of *m/z* 163) and gammacerane (C_{32}, *m/z* 191), and paralic sources of western Dilbi by C_{19} and C_{20} diterpenes. The ratio of 30-norhopane/hopane (Table 6) appears to increase in depth. The strong ion at *m/z* 191 which arises from 25-norhopane is due to the ring D+E fragment. Thus only hopane (C_{30}) will provide a C-10 demethylated analog possessing a significant fragment ion at *m/z* 191. A C_{30} triterpene is observed (*m/z* 191) to elute just prior to regular hopane. The compound has been identified in the Dilbi oilshale and its occurrence suggest a contribution of land plant organic matter to the depositional environment. The 22S/22R homohopane and TS/TM ratio show immaturity (0.8) for the western Dilbi oilshale sample and marginal maturity (1.2) for the eastern Dilbi sample.

CONCLUSION

The Ethiopian rift is part of the East African rift and its history is a chapter in the evolution of ancient structural line, at weak points advocating genetic connection and parallelism of rift faults. This means that tectonic elements contain thicker accumulations of later tertiary sediments including potential organogenic source rocks. Extensive volcanics emplaced at the same localities could have raised the regional and local thermal gradients and improved the maturity condition of local source rocks. In the area of the study, the Dilbi-Moye Basin (i.e. Gojeb-Chida and others), thick and extensive oilshale deposits are preserved. These organic shales are of importance as potential source rock. The higher temperature gradient, thick sedimentation up to 500 m cumulative thickness, suitable stratigraphic and structural conditions, make these basins very good areas for petroleum exploration. This preliminary study concludes that all geochemical data derived from pyrolysis, ultimate, chemical, and GC/MS/MS analyses clearly indicate that extracts from Dilbi oilshales are immature for oil generation, but minor HC generation is occurring from claystones of the Dilbi Basin. The type of organic matter, TOC and HI values suggest that Dilbi oilshales are oil/oil-gas prone. In addition, they have a higher terrestrial plant incursion, a non-marine origin and are deposited in an environment of enhanced salinity.

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