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ORGANIC GEOCHEMICAL CHARACTERISTICS OF MIOCENE OIL SHALE DEPOSITS IN THE ESKİŞEHİR BASIN, WESTERN ANATOLIA, TURKEY

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Abstract. *In the Eskişehir Basin, western Turkey, oil shale occurs in alternation with claystone, siltstone, conglomerate and coal (lignite) seams in lacustrine deposits of Early-Middle Miocene age. The thickness of oil shale seams drilled during the study varies between 20 and 30 m. Organic geochemical features of the shale were evaluated using TOC, pyrolysis, GC and GC-MS analyses.*

The Eskişehir oil shale is characterized by very high TOC contents (6.32–37.15 wt%), Hydrogen Index (HI = 392–777 mg HC/g TOC), Potential Yield (PY = 35.50–159.32 mg HC/g rock) and very low Oxygen Index (OI = 13–92 mg CO_2/g TOC) values. Organic matter in the studied oil shale is of Type II kerogen and shows S_2/S_3 ratio values between 5.49 and 56.79 and low T_{max} (421–435 °C) and PI (0.01–0.05) values.

Low Pr/Ph ratio of oil shale (0.17–0.96) is indicative of anoxic conditions. Dominant steranes are either C_{27} or C_{28}. Normal steranes are more abundant than iso- and diasteranes and diasterane abundances as well as 20S/(20S + 20R) and $\beta\beta/(\beta\beta + \alpha\alpha)$ sterane ratios are low.

While oil shale samples in general have low tricyclic terpane (C_{19}–C_{29}) abundance, their C_{30} (R + S) tricyclic terpane content is high. For all the oil shale samples studied C_{29}/C_{30} hopane, $C_{31}R$ homohopane/hopane and moretane/hopane ratios are high and Ts/(Ts + Tm) and $C_{29}Ts/(C_{29}Ts + C_{29}H)$ ratios are low. 22S homohopanes are recorded in lower quantities in comparison to 22R epimers and the 22S/(22S + 22R) homohopane ratio is low.

Keywords: *Eskişehir Basin, oil shale, maturity, biomarker, hydrocarbon potential.*

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1. Introduction

Turkey hosts 1.6 billion tonnes of oil shale reserves. Some of the most important oil shale deposits are located in Beypazarı (Ankara), Seyitömer (Kütahya), Himmetoğlu and Hatıldağ (Bolu), Gölpazarı (Bilecik), Ulukuşla (Niğde), Burhaniye (Balıkesir), Beydili (Ankara), Dodurga (Çorum) and Bahçecik (İzmit) regions. Geologic characteristics, organic and trace element geochemistry, chemical and thermal properties and economic value of the oil shales from these areas have been investigated in several studies [1–11].

In addition to the above-mentioned fields, an oil shale deposit was discovered during coal exploration initiated by the General Directorate of Mineral Research and Exploration (MTA) in 2008 in the Eskişehir Basin, western Turkey. In this basin, 350 boreholes were drilled for coal exploration and reserve improvement and about 1.5 billion tonnes of sub-bituminous coal and about 1 billion tonnes of oil shale reserve were discovered. The thickness of oil shale is between 5 and 60 m with an average of 20–30 m. Oil shale encountered in the basin is thin-layered and laminated, and light brown, gray and blackish in color.

In this contribution, the organic geochemical characteristics, thermal maturity, depositional environment and conditions as well as source rock potential of the oil shale discovered in the Eskişehir Basin are investigated.

2. Geological setting

The study area is located in the Eskişehir graben east of Eskişehir in western Anatolia, Turkey (Fig. 1). Regional geological work was first carried out by Siyako et al. [12], Gözler et al. [13] and Şengüler [16], followed by coal and oil shale studies by other researchers [14–15]. The basement of the region is composed of Paleozoic metamorphosed rocks and Mesozoic ophiolites. The metamorphic rocks are in tectonic contact with ophiolitic units in the northern part of the basin [13]. The metamorphic rocks consist of schist and marbles and ophiolitic mélange represented by radiolarite-bearing limestone, mudstone, serpentinite, diabase, limestone and gabbro.

The basement rocks are unconformably overlain by Miocene deposits which are developed in three different facies: m1, m2 and m3 series (Fig. 2). The m1 series at the base of the Miocene sequence is composed mainly of sandstone and claystone. Pebbles of conglomerate have been derived from the basement rocks of various types. The upper portion of the m1 series is a red, yellowish grey, gray, light gray but mostly brownish red thick to very thick bedded sandstone-claystone sequence [12].

This sequence is overlain by the m2 series which is, from bottom to top, composed of alternating, partly pebbly green claystone, coal, gray sandstone, dark gray-green siltstone, oil shale, claystone, coal and green claystone-sandstone fine-grained conglomerate. The sequence is mostly green and

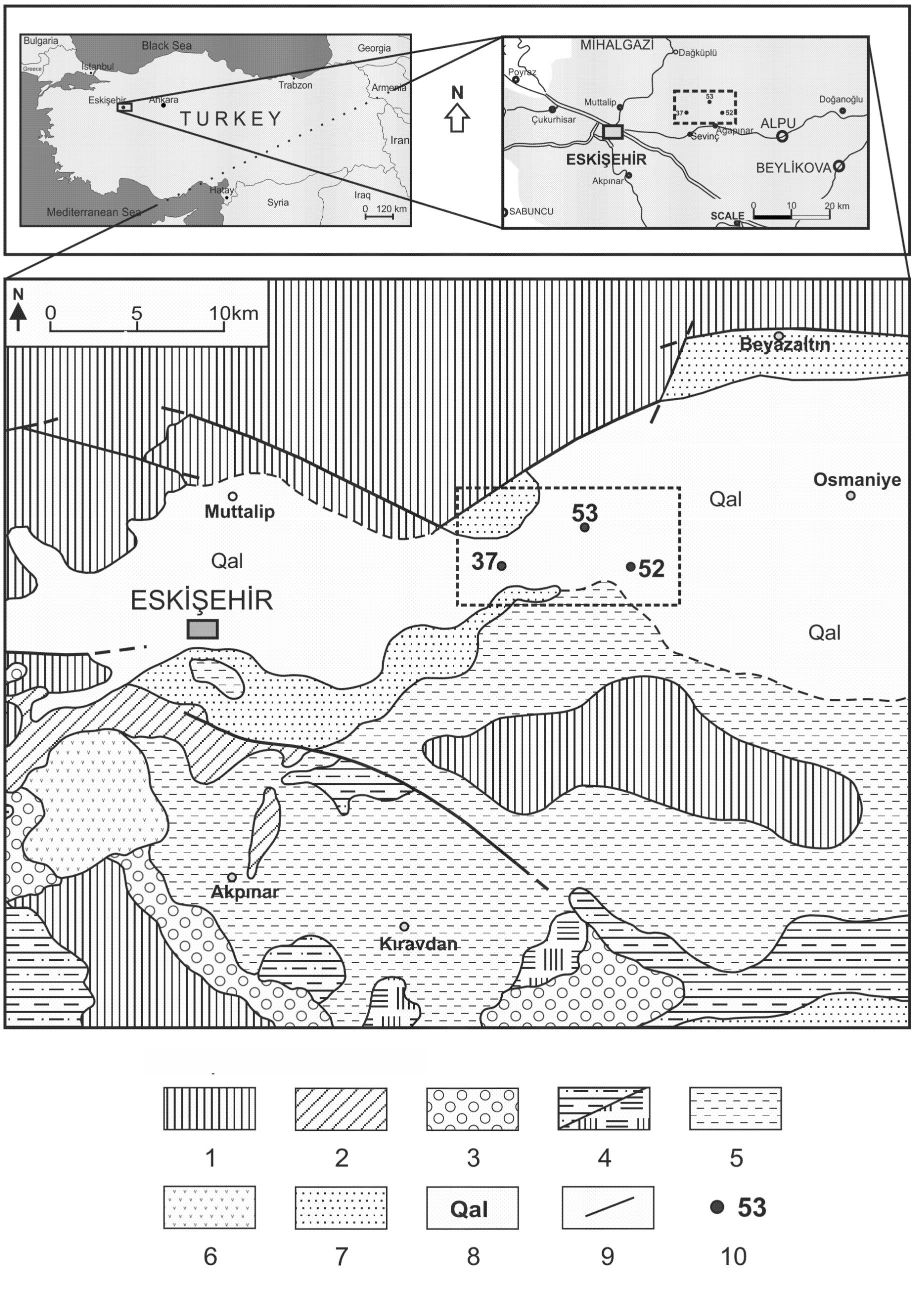

Fig. 1. Geological map of the Eskişehir Basin (simplified from [16]) and study area. Explanations: 1 – Paleozoic-Mesozoic (metamorphic and ophiolitic rocks); 2 – Eocene (sandstone, claystone, conglomerate); 3 – Miocene (conglomerate, claystone, gravel); 4 – Miocene (claystone, sandstone, lignite, oil shale); 5 – Miocene (sandstone, limestone, conglomerate); 6 – basalt; 7 – Pliocene (clayey limestone); 8 – Quaternary (alluvium); 9 – fault; 10 – drilling location.

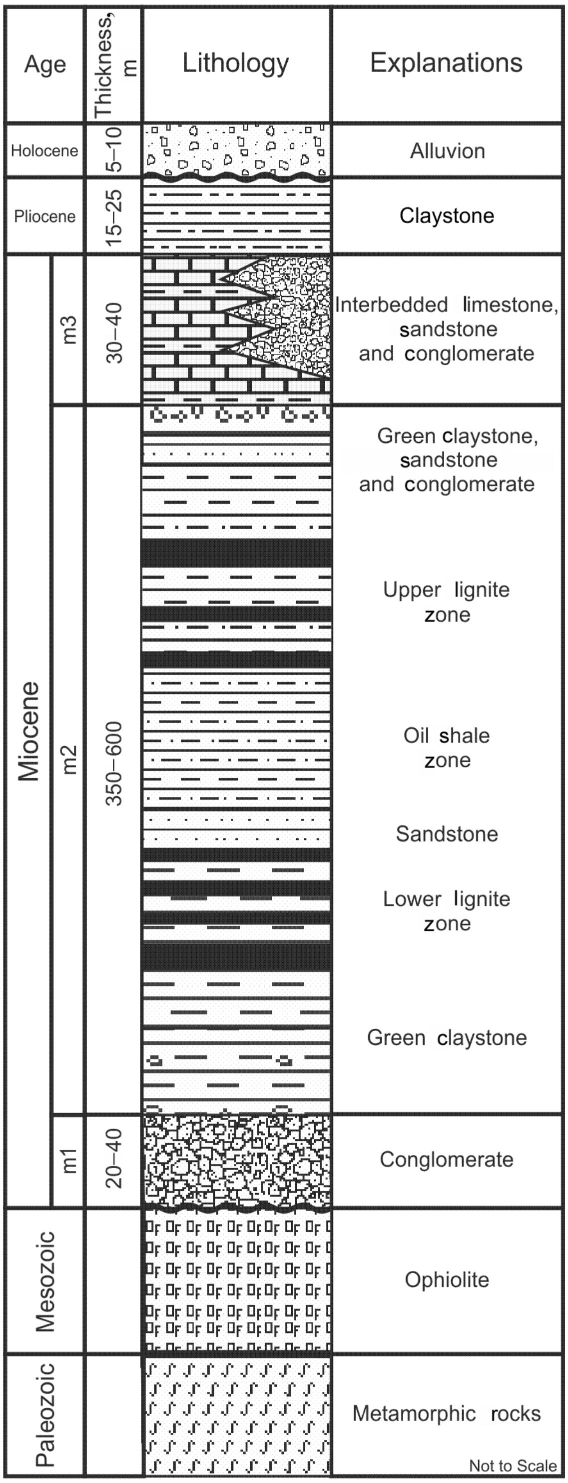

Fig. 2. Generalised columnar section of the Eskişehir Basin (from [16]).

yellow in color and partly multicolored. The lower levels of thin-bedded claystone and marls are reddish and purplish and change to green to the top. Yellow parts are generally the upper levels of claystone and marls. Very thin bedded limestone bands occur between marls and clays. North of Sevinç-Ağapinar coal and oil shale are found at depths between 250 and 450 m. In deeper parts of the basin the thickness of the m2 series is 350–600 m; however, in the study area its thickness reaches 400 m [16]. The upper parts of the Miocene sequence comprise the m3 series, which consists of limestone and conglomerate. Limestone is pale white and gray in color and occurs as lenses. In the study area, this unit has a thickness of 30–40 m.

Palynological analysis of the samples collected from the lower and upper levels of coal zones show that the coal and oil shale-bearing unit (m2) was deposited in the Lower-Middle Miocene. The amount of various forest trees and swamp-freshwater plants is high whilst river-side and open field plants are in low quantity. *Bortyococcus ovoidites* forms detected in the unit are in support of freshwater conditions. Palynological data indicate that the coal and oil shale-bearing unit in the Eskişehir graben was deposited under wet and hot conditions [17].

Pliocene deposits in the basin are composed of pale, light brown claystone and loosely compacted conglomerate. Conglomerate levels in the m3 series contain pebbles of all units older than conglomerate itself. This unit has a thickness of 15–25 m. Quaternary alluvium, modern deposits and slope wash unconformably cover all the underlying deposits.

3. Material and methods

In the current study, boreholes 37, 52 and 53 drilled in the central part of the basin (north of Ağapınar village) cut 20–30 m thick oil shale in the deeper sections of the Eskişehir Basin. The distance between boreholes 37–52 was 1 km, between boreholes 37–53 1.5 km and between boreholes 52–53 600 m. In borehole 37, 355 m claystone, siltstone, sandstone and conglomerate, 20 m oil shale (between 355 and 378 meters) and 20 m coal were cut and the borehole was completed at a depth of 410 m. In borehole 52, 295 m claystone, siltstone, sandstone and conglomerate, 25 m oil shale (between 295 and 321 meters), 10 m coal and 10 m claystone were cut and the borehole was completed at a depth of 340 m. In borehole 53, 355 m claystone, siltstone, sandstone and conglomerate, 25 m coal, 30 m oil shale (between 353 and 378 meters) and 10 m coal were cut and the borehole was completed at a depth of 430 m (Fig. 3).

Pyrolysis and TOC analyses were performed for 14, 15 and 16 samples selected respectively from boreholes 37, 52 and 53 drilled in the Eskişehir Basin. From borehole 37, one coal sample, one coaliferous claystone sample and 12 oil shale samples were taken. Two coal and 13 oil shale samples were

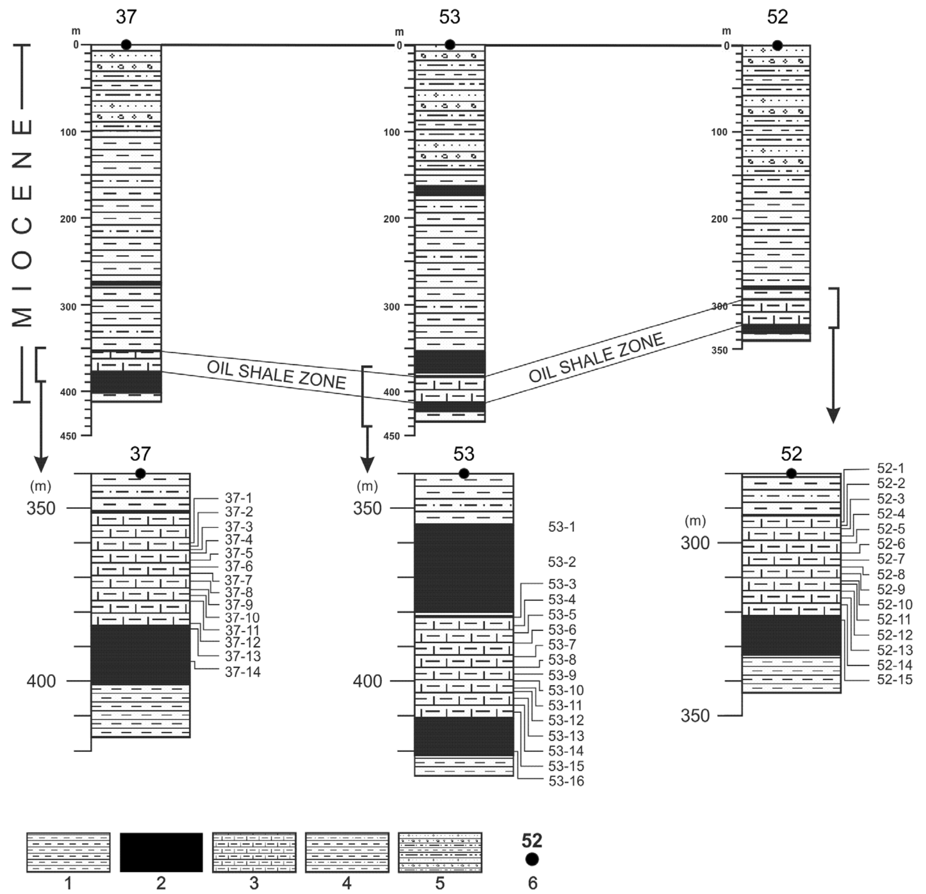

Fig. 3. Lithostratigraphic section of drillings and sample distributions. Explanations: 1 – claystone, sandstone, conglomerate; 2 – lignite; 3 – oil shale; 4 – claystone, siltstone; 5 – claystone; 6 – drilling section (log).

collected from borehole 52. From borehole 53, three were coal samples and 13 oil shale samples (Tables 1, 2 and 3).

Rock-Eval pyrolysis and TOC analyses of all the samples were made using a Rock-Eval 6 instrument equipped with a TOC module. The samples were heated from 300 °C (hold time 3 min) to 650 °C at 25 °C/min. The crushed rock was heated from 400 °C (hold time 3 min) to 850 °C (hold time 5 min) at 25 °C/min for oxidation. Following Rock-Eval, TOC analysis, gas chromatographic (GC) (bulk extract) and gas chromatographic-mass spectrometric (GC-MS) (saturated hydrocarbons sterane and terpane) analyses of extracts obtained from three samples (37-9, 52-12, 53-9) were conducted.

The C_{15+} soluble organic matter (SOM) was isolated following Soxhlet extraction (40 hr) of the powdered rock with dichloromethane (CH_2Cl_2). Whole rock extracts were analysed using a Varian 3400 gas chromatograph equipped with flame photometric (FPD) and flame ionisation detectors (FID).

Table 1. Results of total organic carbon analyses (TOC) and Rock-Eval pyrolysis for oil shale, coal bearing claystone and coal samples from well 37 in the Eskişehir Basin

Sample	Depth, m	Lithology	TOC, %	S_1, mg HC/g rock	S_2, mg HC/g rock	S_3, mg CO_2/g rock	T_{max}, °C	HI, mg HC/g TOC	OI, mg CO_2/g TOC	PI, $(S_1/S_1 + S_2)$	S_2/S_3	PY, $(S_1 + S_2)$	RC, %	PC, %	Min C, %
37-1	360	Oil Shale	9.34	0.97	47.13	8.58	428	505	92	0.02	5.49	48.1	5.01	4.33	0.77
37-2	361	Oil Shale	9.09	1.57	45.91	3.42	426	505	38	0.03	13.42	47.48	4.93	4.16	0.99
37-3	362	Oil Shale	10.49	1.15	56.46	6.42	428	538	61	0.02	8.79	57.61	5.42	507	0.63
37-4	363	Oil Shale	12.36	1.21	67.96	4.19	428	550	34	0.02	16.22	69.17	6.34	6.02	0.73
37-5	365	Oil Shale	6.39	0.56	37.33	1.24	433	584	19	0.01	30.10	37.89	3.16	3.23	0.20
37-6	367	Oil Shale	9.39	1.02	47.80	7.88	429	519	84	0.02	6.07	48.82	4.95	4.44	0.90
37-7	369	Oil Shale	11.43	1.39	59.37	4..49	427	519	39	0.02	13.22	60.76	6.13	5.3	0.23
37-8	371	Oil Shale	10.27	0.76	74.96	1.32	460	730	13	0.01	56.79	75.72	3.86	6.41	0.23
37-9	373	Oil Shale	11.77	1.55	61.01	4.59	426	518	39	0.02	13.29	62.56	6.31	5.46	0.21
37-10	375	Oil Shale	21.01	1.57	151.77	3.86	435	722	18	0.01	39.32	153.34	7.97	13.04	1.38
37-11	377	Oil Shale	37.15	2.78	156.01	19.4	426	420	52	0.02	8.04	158.79	22.81	14.34	8.64
37-12	383	Oil Shale	7.63	0.62	36.42	2.46	425	477	32	0.02	14.80	37.04	4.35	3.28	1.54
37-13	385	Coal	49.07	0.90	72.05	26.94	427	147	55	0.01	2.67	72.95	41.20	7.87	5.58
37-14	394	Coal bearing claystone	34.17	1.52	52.13	21.27	426	153	62	0.03	2.45	53.65	28.40	5.77	1.09
		Average	17.11	1.26	69.02	8.29	430	492	46	0.02	16.48	70.28	10.77	42.19	1.65

Table 2. Results of total organic carbon analyses (TOC) and Rock-Eval pyrolysis for oil shale and coal samples from well 52 in the Eskişehir Basin

Sample	Depth, m	Lithology	TOC, %	S_1, mg HC/g rock	S_2, mg HC/g rock	S_3, mg CO_2/g rock	T_{max}, °C	HI, mg HC/g TOC	OI, mg CO_2/g TOC	PI, $(S_1/S_1 + S_2)$	S_2/S_3	PY, $(S_1 + S_2)$	RC, %	PC, %	Min C, %
52-1	294	Oil Shale	8.29	0.67	41.18	6.10	441	497	74	0.02	6.75	41.85	4.55	3.14	1.19
52-2	295	Oil Shale	9.69	1.05	49.42	8.06	429	510	83	0.02	6.13	50.47	5.17	4.52	0.83
52-3	296	Oil Shale	11.7	0.76	55.80	4.29	432	477	37	0.01	13.01	56.56	6.74	4.96	0.98
52-4	298	Oil Shale	6.32	0.37	36.42	1.13	432	576	18	0.01	32.23	36.79	3.18	3.14	0.11
52-5	300	Oil Shale	10.16	1.05	52.19	7.27	428	514	72	0.02	7.18	53.24	5.43	4.73	0.83
52-6	303	Oil Shale	7.61	0.55	45.14	1.46	431	593	19	0.01	30.92	45.69	3.71	3.90	0.44
52-7	305	Oil Shale	11.06	1.13	57.74	6.02	426	522	54	0.02	9.59	58.87	5.88	5.18	0.42
52-8	307	Oil Shale	7.36	0.48	43.15	1.54	432	586	21	0.01	28.02	43.63	3.63	3.73	0.21
52-9	309	Oil Shale	11.03	1.50	53.46	4.51	431	485	41	0.03	11.85	54.96	6.20	4.83	0.99
52-10	311	Coal	47.18	1.05	86.75	20.51	428	184	43	0.01	4.23	87.8	38.45	8.73	1.65
52-11	312	Oil Shale	11.49	1.08	59.88	5.51	424	521	48	0.02	10.87	60.96	6.14	5.35	0.48
52-12	314	Oil Shale	8.27	2.37	41.17	2.16	423	498	26	0.05	19.06	43.54	4.49	3.78	0.3
52-13	316	Oil Shale	7.26	0.40	40.56	1.77	430	559	24	0.01	22.92	40.96	3.73	5.53	0.40
52-14	318	Oil Shale	20.22	1.00	155.38	3.12	435	768	15	0.01	49.80	156.38	6.95	13.27	0.66
52-15	323	Coal	51.76	0.57	45.02	20.41	422	87	39	0.01	2.21	45.59	46.26	5.50	0.20
Average			15.29	0.94	57.55	6.26	429	492	41	0.02	16.98	58.49	10.03	5.35	0.65

Table 3. Results of total organic carbon analyses (TOC) and Rock-Eval pyrolysis for oil shale, coal bearing claystone and coal samples from well 53 in the Eskişehir Basin

Sample	Depth, m	Lithology	TOC, %	S_1, mg HC/g rock	S_2, mg HC/g rock	S_3, mg CO_2/g rock	T_{max}, °C	HI, mg HC/g TOC	OI, mg CO_2/g TOC	PI, $(S_1/S_1 + S_2)$	S_2/S_3	PY, $(S_1 + S_2)$	RC, %	PC, %	Min C, %
53-1	355	Coal	48.95	1.06	28.81	18.55	396	59	38	0.04	1.55	29.87	44.77	4.18	1.51
53-2	366	Coal	50.44	0.81	48.49	25.00	423	96	50	0.02	1.94	49.3	44.58	5.86	1.65
53-3	382	Coal bearing claystone	24.21	0.84	22.88	13.69	416	95	57	0.04	1.67	23.72	21.32	2.89	1.08
53-4	384	Oil Shale	8.82	0.71	40.09	5.53	421	455	63	0.02	7.25	40.8	5.16	3.66	0.73
53-5	386	Oil Shale	9.98	1.05	51.00	8.52	424	511	85	0.02	5.99	52.05	5.31	4.67	0.90
53-6	389	Oil Shale	9.20	0.73	36.11	4.65	424	392	51	0.02	7.77	36.84	5.89	3.31	0.49
53-7	393	Oil Shale	6.87	0.35	37.84	1.53	430	551	22	0.01	24.73	38.19	3.58	3.29	0.47
53-8	396	Oil Shale	11.04	1.06	58.82	5.97	426	533	54	0.02	9.85	59.88	5.76	5.28	0.75
53-9	398	Oil Shale	8.44	1.38	41.20	2.16	427	488	26	0.03	19.07	42.58	4.74	3.70	0.33
53-10	400	Oil Shale	20.37	1.07	158.25	3.06	437	777	15	0.01	51.72	159.32	6.86	13.51	0.66
53-11	402	Oil Shale	8.21	0.67	49.89	1.39	431	608	17	0.01	35.89	50.56	390	4.31	0.21
53-12	403	Oil Shale	6.92	0.90	34.60	1.57	425	500	23	0.03	22.04	35.5	3.85	3.07	0.18
53-13	405	Oil Shale	12.18	1.35	63.11	4.50	424	518	37	0.02	14.02	64.46	6.53	5.65	0.39
53-14	407	Oil Shale	7.94	0.71	44.72	1.40	428	563	18	0.02	31.94	45.43	4.05	3.89	0.22
53-15	409	Oil Shale	14.46	1.21	81.31	3.76	424	562	26	0.01	21.63	82.52	7.31	7.15	0.58
53-16	420	Coal	54.63	1.04	60.12	22.57	421	110	41	0.02	2.66	61.16	47.84	6.79	1.41
		Average	18.92	0.93	53.58	7.74	424	426	39	0.02	16.23	54.51	37.97	5.08	0.72

A fused capillary column (60 m, 0.20 mm i.d.) coated with cross-linked dimethylpolysiloxane (J&W, 0.25 µm film thickness) was used. Helium was the carrier gas. The oven temperature was programmed from 40 ºC (hold time 8 min) to 270 ºC (hold time 60 min) at 4 ºC/min.

The oil shale extracts were deasphaltened using n-pentane and fractionated by thin-layer chromatography (MK-Iatroscan). n-Hexane, toluene and methanol were used for separation of extracts into saturated hydrocarbons, aromatic hydrocarbons and NSO fractions, respectively. GC-MS analyses of saturated fractions were performed using an Agilent 5975C quadrupole mass spectrometer coupled to a 7890A gas chromatograph and a 7683B automatic liquid sampler. The gas chromatograph was equipped with an HP-1MS fused silica capillary column of 60 m length, 0.25 mm i.d. and 0.25 µm film thickness. Helium was used as the carrier gas. The oven temperature was programmed from 50 ºC (hold time 10 min) to 200 ºC (hold time 15 min) at 10 ºC/min, to 250 ºC (hold time 24 min) at 5 ºC/min and then to 280 ºC (hold time 24 min) at 2 ºC/min. Finally, the oven temperature was increased to 290 ºC (hold time 40 min) at 1 ºC/min. The mass spectrometer was operated in EI mode at an ionisation energy of 70 eV and a source temperature of 300 ºC. The biomarker contents were determined using single ion recording at m/z 191 (190.7–191.7) for terpanes and tricyclic triterpanes, and at m/z 217 (216.7–217.7) for steranes and rearranged steranes. Compounds were identified by their retention time and elution order matching.

4. Results

4.1. TOC and pyrolysis analyses

Pyrolysis and TOC values of oil shale and coal samples from boreholes 37, 52 and 53 are given in Tables 1, 2 and 3. TOC values of oil shale samples from boreholes 37, 52 and 53 are 6.39–37.15% wt., 6.32–20.22% wt. and 6.87–14.46% wt., respectively (Tables 1, 2 and 3; Fig. 4a). The oil shale samples from these boreholes have very low S_1 (0.35–2.78 mg HC/g rock) and very high S_2 (34.60–158.25 mg HC/g rock) values as it is common for oil shale. In general, the Eskişehir oil shale is characterised by high to very high HI (392–777 mg HC/g rock) (Fig. 4b) and low OI (13–92 mg CO_2/g TOC) values (Tables 1, 2 and 3). In the oil shale samples, S_2/S_3 values are quite high (5.49–56.79) but in coal samples, very low (1.55–4.23). The residual carbon value is also high (21.32–47.84%) in coal and coal bearing claystone samples and low (3.16–7.97%, except one sample) in oil shale samples. Coal and coaliferous clay samples are distinguished from oil shale samples by their very high S_3 (13.69–26.94 mg CO_2/g rock) and low HI (59–184 mg HC/g rock) values. All the samples are characterized by very low PI (0.01–0.05), but very high PY (23.72–159.32 mg HC/g rock) values (Tables 1, 2 and 3).

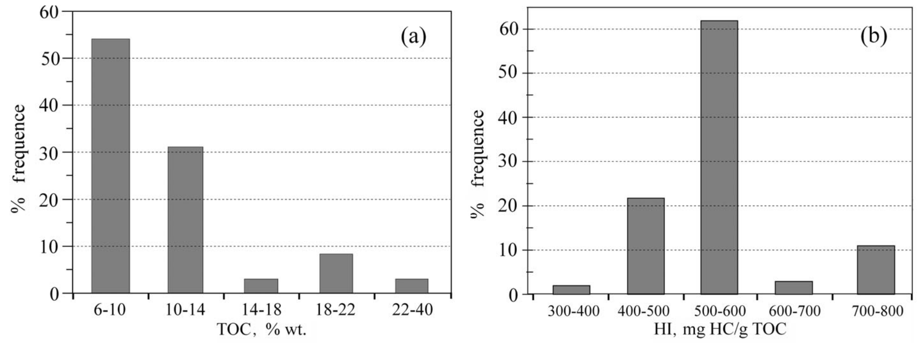

Fig. 4. Cumulative frequency diagrams for total organic carbon contents (a) and Hydrogen Index (mg HC/g TOC) (b) in the Eskişehir oil shale samples (n = 38).

Almost all oil shale samples with high HI values are plotted in Type II kerogen area which is close to Type I kerogen area, and only a few samples are found within the Type I kerogen field. Coal and claystone samples are within the Type II–Type III kerogen field (Figs. 5a–b). All the oil shale samples with high S_2 and TOC values show excellent source rock characteristics (Fig. 6).

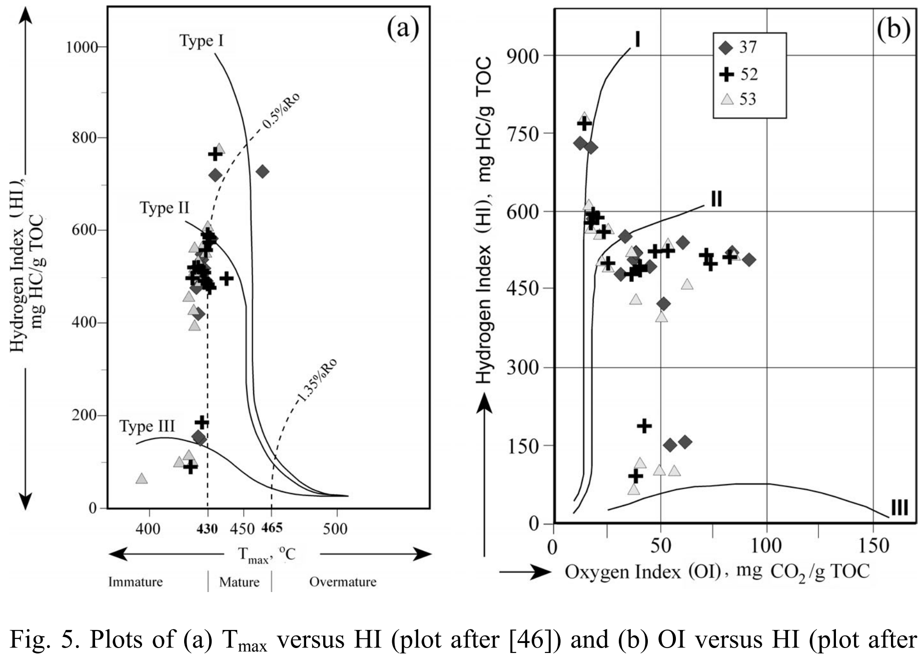

Fig. 5. Plots of (a) T_{max} versus HI (plot after [46]) and (b) OI versus HI (plot after [47]) for oil shale samples from the Eskişehir Basin.

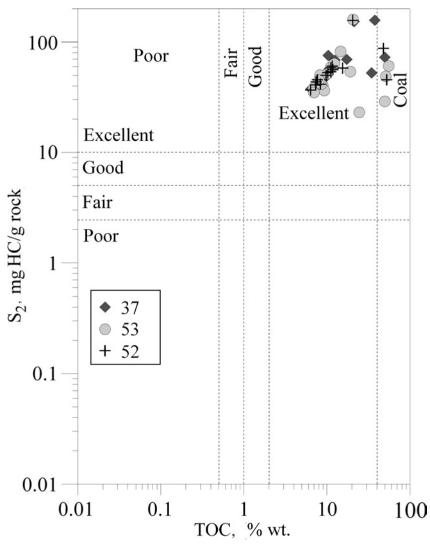

Fig. 6. The distribution of Eskişehir oil shale samples on the plot of TOC versus Rock-Eval S_2 (source rock classification diagram after [48]).

4.2. Molecular compounds

4.2.1. n-Alkanes and isoprenoids

On the gas chromatograms of oil shale samples, n-alkanes are more abundant than isoprenoids (Fig. 7). Pr/n-C_{17} and Ph/n-C_{18} ratios are very low (Table 4). n-Alkanes are more dominant than neighboring isoprenoids and only in one sample Pr is slightly more predominant than n-C_{17}. For all oil shale samples phytane (Ph) is more dominant than pristane (Pr) and Pr/Ph ratios are between 0.17 and 0.96 (Fig. 7; Table 4). On the gas chromatograms oil shale samples show high peaks in the biomarker area (Fig. 7).

4.2.2. Steranes and terpanes

On m/z 217 mass chromatograms pregnanes were recorded in all the oil shale samples. These compounds are quite abundant in one sample from borehole 37, low in one sample from borehole 52 and moderately abundant in one sample from borehole 53 (Fig. 8). Diasteranes were recorded in low quantities in three oil shale samples. The diasterane/sterane ratio was calculated to be very low (0.42–0.14) (Table 5). For all the oil shale samples n-steranes are more abundant than iso- and diasteranes. 20S/(20S + 20R) and $\beta\beta/(\beta\beta + \alpha\alpha)$ C_{29} sterane ratios were computed to be very low (0.46–0.18 and 0.14–0.04, respectively) (Table 5).

On m/z 191 mass chromatograms C_{19}–C_{29} tricyclic terpanes were recorded in very low abundance and in this range C_{23} is the dominant tricyclic terpane (Fig. 9). Contrary to low-numbered tricyclic terpanes, C_{30} tricyclic terpane (S + R) was measured in high concentrations, being

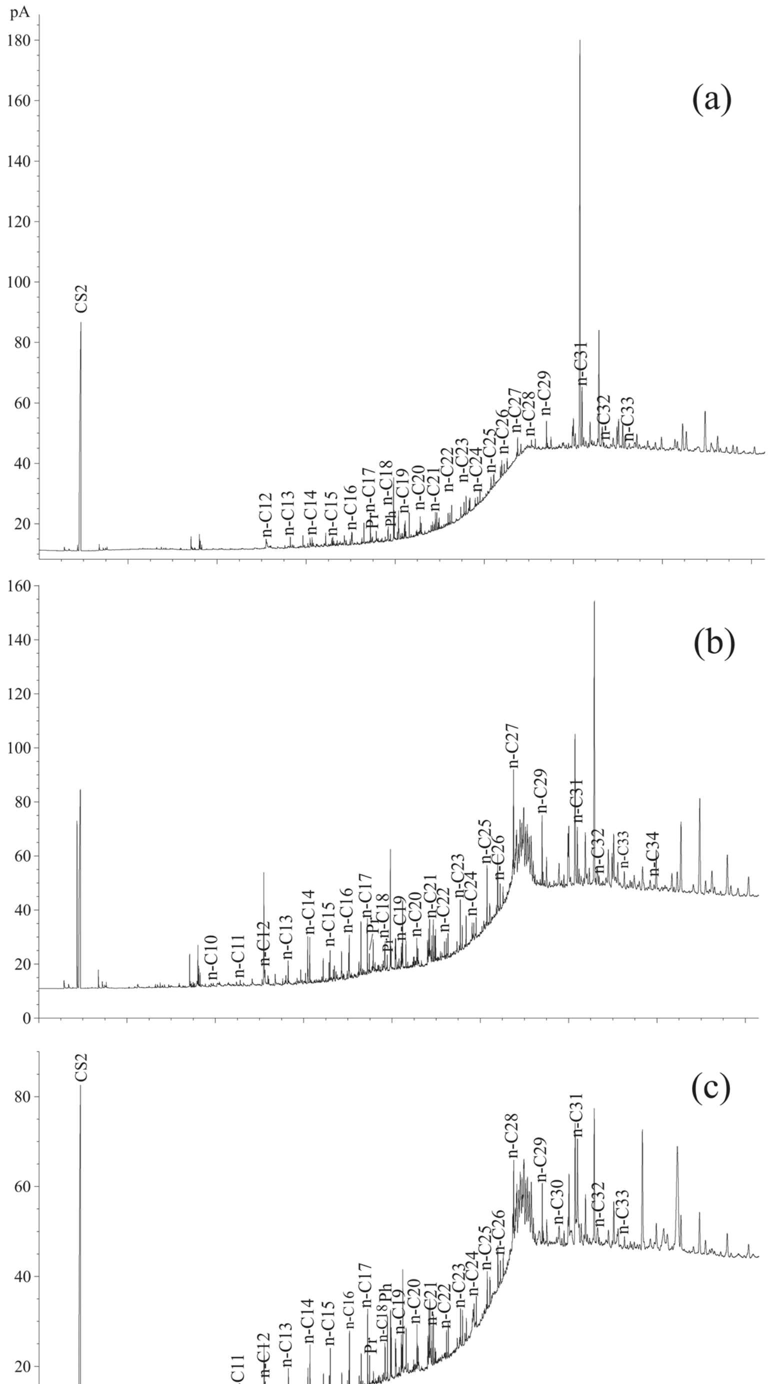

Fig. 7. Gas chromatograms for oil shale samples from (a) well 37, (b) well 52, (c) well 53 in the Eskişehir Basin.

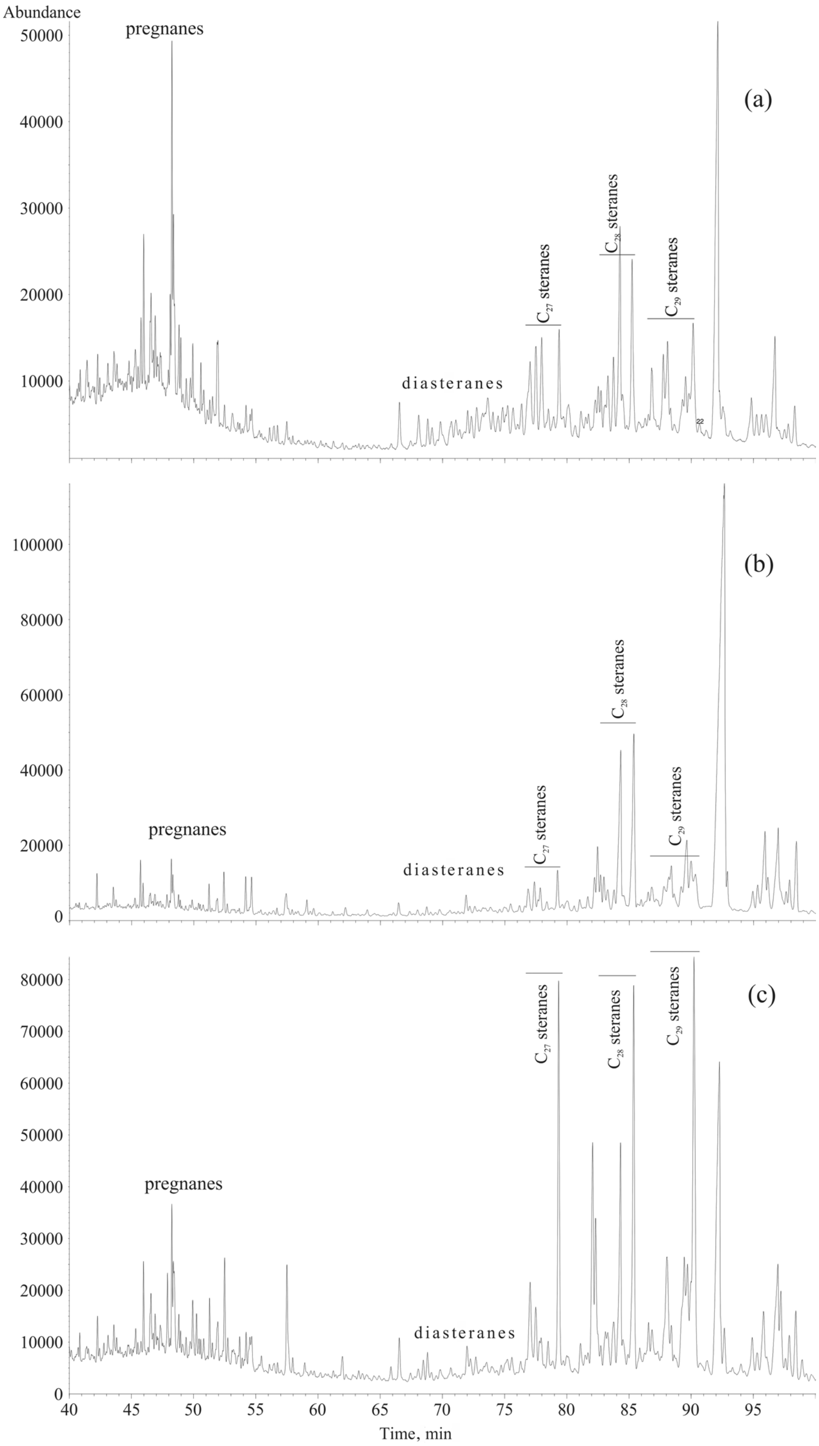

Fig. 8. Mass chromatograms (m/z 217) for oil shale samples from (a) well 37, (b) well 52, (c) well 53 in the Eskişehir Basin.

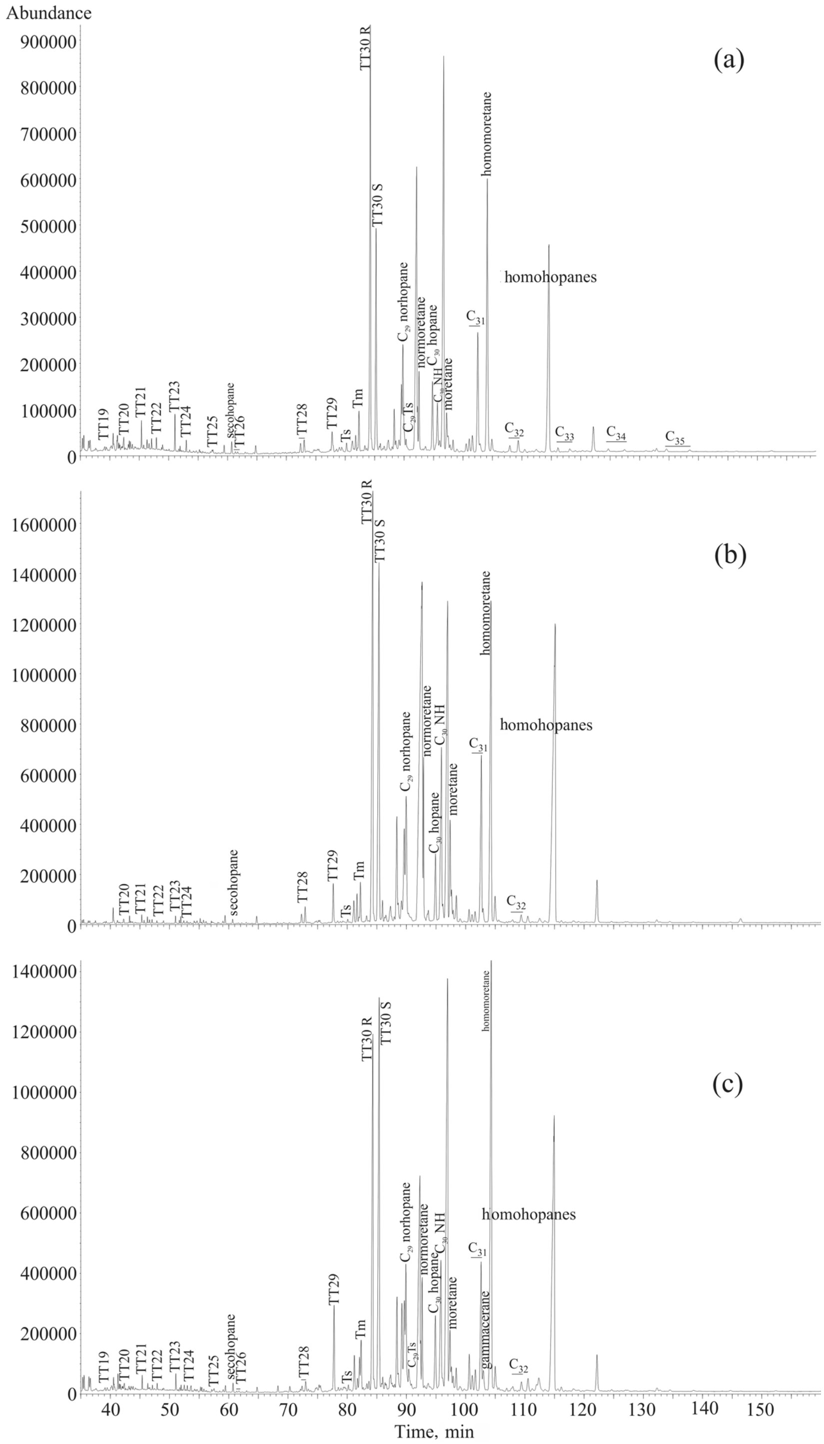

Fig. 9. Mass chromatograms (m/z 217) for oil shale samples from (a) well 37, (b) well 52, (c) well 53 in the Eskişehir Basin.

Table 4. Parameters calculated from gas chromatograms for oil shale from the Eskişehir Basin

Sample ID	Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}
37-9	0.67	1.30	0.47
52-12	0.17	0.35	0.38
53-9	0.96	0.97	2.20

Table 5. Biomarker composition based on m/z 217 mass chromatograms and calculated parameters for oil shale samples from the Eskişehir Basin

Sample ID	$C_{27,28,29}$ steranes	Iso-, normal and diasterane	20S/(20S + 20R)	ββ/(ββ + αα)	Diasterane/sterane	Regular sterane/hopane
37-9	36, 34, 30	35, 44, 21	0.40	0.46	0.42	0.17
52-12	27, 59, 14	22, 62, 16	0.31	0.39	0.37	0.08
53-9	36, 30, 34	14, 76, 10	0.05	0.18	0.14	0.20

Remark: 20S/(20S + 20R) sterane (for C_{29}), ββ/(ββ + αα) sterane (for C_{29}), diasterane/sterane (for C_{27}), regular sterane/hopane = [$C_{27,28,29}$ αα/ββ (20S + 20R) steranes]/C_{29-33} hopanes.

a major component on the m/z 191 mass chromatogram. Ts was recorded in trace quantities whilst Tm in high concentrations. The concentrations of C_{29} norhopane and C_{30} hopane are generally low and C_{29} norhopane is slightly dominant over C_{30} hopane. C_{30} norhopane was recorded in high concentrations in two samples and in low quantity in one sample. In all the oil shale samples the homomoretane abundance is quite high, whilst that of homohopanes is low. Only the C_{31} homohopane abundance is slightly higher and high-numbered homohopanes are either present in trace amounts or their existence was never recorded (Fig. 9). 22R homohopanes are more abundant than 22S epimers and the 22S/(22S + 22R) homohopane ratio of oil shale samples is very low (Table 6).

Table 6. Biomarker composition based on m/z 191 mass chromatograms and calculated parameters for oil shale samples from the Eskişehir Basin

Sample ID	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
37-9	1.24	1.69	0.34	0.19	0.52	0.43	0.33	0.47	0.35	0.07
52-12	1.47	2.45	0.29	0.08	1.28	0.27	0.32	0.52	0.10	–
53-9	1.25	1.69	0.33	0.13	0.62	0.46	0.34	0.54	0.19	0.14

(1) – C_{29}/C_{30} hopane; (2) – C_{31} R homohopane/C_{30} hopane; (3) – 22S/(22S + 22R) homohopane (for C_{32}); (4) – Ts/(Ts + Tm); (5) – moretane/hopane (for C_{30}); (6) – C_{22}/C_{21} tricyclic terpane; (7) – C_{24}/C_{23} tricyclic terpane; (8) – (C_{19} + C_{20})/C_{23} tricyclic terpane; (9) – C_{23} tricyclic terpane/(C_{23} tricyclic terpane + C_{30}hopane); (10) – C_{29}Ts/(C_{29}Ts + C_{29} H).

5. Discussion

The TOC content of oil shale in the Eskişehir Basin is high to very high (Tables 1, 2 and 3), ranging from 6.32 to 37.15% wt. TOC consists mostly of pyrolysable carbon and shows correspondingly high PY values (35.50–159.32 mg HC/g rock), which implies that the Eskişehir oil shale has quite high hydrocarbon generation potential (Tables 1, 2 and 3). HI values of oil shale samples from all boreholes are relatively high (392–777 mg HC/g TOC) and the S_2/S_3 ratio, which defines the type of organic matter and the variety of hydrocarbon to be derived, was computed to be high as well (5.99–56.79). High HI and S_2/S_3 values and the dominant Type II (to a lesser degree, Type I) kerogen indicate that when exposed to excessive temperature, the organic matter in the Eskişehir oil shale can generate a significant amount of oil.

The Pr/Ph ratio of oil shale samples from boreholes 37, 52 and 53 is rather low (0.17–0.96) showing that oil shale was deposited under anoxic conditions. Palynological analysis of oil shale and coal performed by Şengüler et al. [17] indicates that the oil shale and coal were deposited in a freshwater swamp and lacustrine environment when the climate was predominantly humid and hot. On the m/z 191 mass chromatograms of oil shale samples, gammacerane, which is indicative of salinity [18–22], is practically absent, implying that the environment was of a freshwater type.

Low sterane concentrations and low regular sterane/hopane ratio suggest terrigenous or microbial reworked organic matter [23]. According to Moldowan et al. [24], the sterane/hopane ratio in oils derived from non-marine sources is lower than that of marine sources. In the oil shale samples from all the boreholes, both the sterane abundance and sterane/hopane ratio are very low (0.08–0.20) (Fig. 8; Table 5). On the m/z 191 mass chromatograms of oil shale samples, no oleanane was recorded, which also supports terrigenous organic matter input [25–30] (Fig. 9). Typically, C_{27} sterane is a major component in lacustrine source rock or oils [19]. Indeed, C_{27} is dominant in the oil shale samples from boreholes 37 and 53 whilst C_{28} sterane is prevailing in those from borehole 52. On the other hand, C_{29} sterane which also reflects terrigenous organic matter input [19] was recorded in low quantities in all samples (Table 5). Moreover, the low tricyclic terpane abundance (except for C_{30}), and low $(C_{19} + C_{20})/C_{23}$ tricyclic terpane ratio show that terrigenous organic matter is almost absent (Fig. 9; Table 6). For all the samples C_{30} tricyclic terpane (S + R) was recorded in a surprisingly high abundance and is the most prevailing component as revealed on the m/z 191 mass chromatogram. Ourisson et al. [31] state that tricyclic terpanes were derived from prokaryotic membranes. In addition, high tricyclic terpane concentrations are indicative of algae in tasmanite-rich rocks deposited at high paleo-latitudes [32–34]. The unusually high C_{30} tricyclic terpane concentrations in the Eskişehir oil shale which was deposited in a lacustrine environment might be related to a high algal contribution to organic matter. In the shale Şengüler et al. [17] found *Bortyococcus ovoidites* forms which are indicative of a freshwater environment and in this respect, C_{30} tricyclic terpane abundance may have been derived from these algae.

Contrary to our expectations, the investigated oil shale samples show high C_{29}/C_{30} hopane and C_{31}R homohopane/C_{30} hopane ratios (Fig. 9; Table 6). The high C_{29}/C_{30} hopane ratio is suggested to be an indicator of carbonate presence, being especially characteristic of carbonate-rich rocks and oils [22, 35, 36]. Considering that oil shale has very low carbonate content, the high value of this ratio is confusing. The C_{31}R homohopane/C_{30} hopane ratio is also used to discriminate between the lacustrine and marine environments and its value < 0.25 is suggested to be typical of lacustrine deposits [22]. Although geological data indicate that the Eskişehir oil shale was deposited in the lacustrine environment, this ratio is quite high (1.69–2.45), which is in conflict with geological interpretation (Table 6).

Ts/(Ts + Tm) and diasterane/sterane ratios are affected by both maturity and lithology of source rock. It was shown that these two parameters are increased with increasing maturity [20, 19, 36]. Furthermore, the ratio of these two biomarkers tends to be higher in clay-rich source rocks and oils derived from these rocks in comparison with that in carbonate units [19, 20, 36]. Although oil shale has a high clay content, these two ratios are found to be very low in it (Table 6). Low Ts/(Ts+Tm) and diasterane/sterane ratios in oil shale are in contradiction with its lithology but are consistent with its low maturity level.

T_{max} values of oil shale samples from boreholes 37, 52 and 53 are between 421 and 435 ^{o}C, indicating that the rock is immature and did not enter into the oil window. Very low PI values of oil shale (0.01–0.05) also demonstrate its low maturity level and the very low rate of transformation of kerogen to hydrocarbon. On the gas chromatograms of oil shale samples from boreholes 37, 52 and 53, peaks with high concentrations particularly in the biomarker area are indicative of an immature character of organic matter [19]. 20S/(20S + 20R) and $\beta\beta/(\beta\beta + \alpha\alpha)$ sterane and 22S/(22S + 22R) homohopane ratios are used for analyzing the maturity of oil and source rock [19, 20, 36, 37]. The 22S/(22S + 22R) homohopane ratio of about 0.60 attains equilibrium at the beginning of the oil window [36]. 20S/(20S + 20R) and $\beta\beta/(\beta\beta + \alpha\alpha)$ sterane ratios of 0.55 and 0.70, respectively, attain equilibrium after a maturity level at which oil generation is maximum [37]. Very low 20S/(20S + 20R) and $\beta\beta/(\beta\beta + \alpha\alpha)$ sterane (for C_{29}) and 22S/(22S + 22R) homohopane (for C_{32}) ratios of oil shale indicate that it has not reached oil generation maturity. The moretane/hopane ratio is decreased with increasing maturity and it is an indicator of immature-early oil generation stages for oil and source rocks [22, 36, 38–40]. This ratio was computed to be very high for oil shale samples (0.52–1.28), implying an immature source rock. It has been suggested in several studies that C_{29}Ts is more stable to maturity in comparison with C_{29} norhopane and the

$C_{29}Ts/(C_{29}Ts + C_{29} H)$ ratio is increased with increasing maturity [41–45]. For oil shale samples this ratio is very low (0–0.35). Pyrolysis and biomarker data about oil shale samples from the study-area boreholes show that the shale levels cut in these boreholes are generally of similar maturity.

6. Conclusions

The very high values of TOC (6.32–37.15% wt.), PY ($S_1 + S_2$) (35.50–159.32 mg HC/g rock) and Hydrogen Index (392–777 mg HC/g TOC) of the Eskişehir Basin oil shale show its excellent source rock characteristics and high hydrocarbon generation potential. Oil shale samples with dominantly Type II and, to a lesser extent, Type I kerogen are characterised by organic matter with oil generation potential.

The extremely low Pr/Ph ratio implies that lacustrine shale was deposited under anoxic conditions. Based on biomarker data, the Eskişehir oil shale is characterized chiefly by algal and bacterial organic matter with scarce terrigenous organic matter input.

The very low T_{max} and Production Index values of oil shale samples reflect immature organic matter content. Biomarker data also indicate that oil shale contains organic matter with low maturity level (immature). Results of TOC and pyrolysis analysis and biomarker data imply that although the Eskişehir oil shale has a high hydrocarbon potential and oil generation capacity, it has not experienced any hydrocarbon generation due to not having attained sufficient burial and thermal maturity.

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REFERENCES

1. Talu, S. Oil shale of Bahçecik (İzmit). Report No. 4667, MTA, Ankara, 1967 (in Turkish).
2. Yanılmaz, E., İpeksever, M., Aslan, N. Report on Gölpazarı (Bilecik) oil shale field. Report No. 7060, MTA, Ankara, 1980 (in Turkish).

3. Taka, M., Şener, M. Oil shale facility of Himmetoğlu (Göynük-Bolu) field and their wells. Report No. 8533, MTA, Ankara, 1988 (in Turkish).
4. Şener, M., Şengüler, İ. Geology and economic usage of Beypazarı oil shale. Report No. 9202, MTA, Ankara, 1991 (in Turkish).
5. Şener, M., Şengüler, İ. Geology, usage facility and firing test results in fluid bed of Seyitömer oil shale. Report. No. 9441, MTA, Ankara, 1992 (in Turkish).
6. Şener, M., Şengüler, İ. Geology and technologic usage facility of Hatıldağ (Bolu-Göynük) oil shale. Report No. 9445, MTA, Ankara, 1992 (in Turkish).
7. Şener, M., Şengüler, İ., Kök, M. V. Geological considerations for the economic evaluation of oil shale deposits in Turkey. *Fuel*, 1994, **74**(7), 999–1003.
8. Kara Gülbay, R. Rhenium and molybdenum in Tertiary oil shale deposits in Northwestern Anatolia, Turkey. *Oil Shale*, 2007, **24**(3), 450–464.
9. Kara-Gülbay, R., Korkmaz, S. Element contents and organic matter–element relationship of the Tertiary oil shale deposits in northwest Anatolia, Turkey. *Energ. Fuel*, 2008, **22**, 3164–3173.
10. Kara Gülbay, R., Korkmaz, S. Organic geochemistry, depositional environment and hydrocarbon potential of the Tertiary oil shale deposits in NW Anatolia, Turkey. *Oil Shale,* 2008, **25**(4), 444–464**.**
11. Kök, M. V. Geological considerations for the economic evaluation of Turkish oil shale deposits and their combustion – pyrolysis behavior. *Energ. Source. Part A*, 2009, **32**(4), 323–335.
12. Siyako, F., Coşar, N., Cokyaman, S., Coşar, Z. Tertiary geology and coal possibilities of Bozüyük-İnönü-Eskişehir-Alpu-Beylikova-Sakarya areas. MTA Report No. 9281, Ankara, 1991 (in Turkish).
13. Gözler, Z., Cevher, F., Ergül, E., Asutay, J. H. Geology of the Central Sakarya and its southern area. MTA Report No. 9973, Ankara, 1996 (in Turkish).
14. Steffens, P. Sivrihisar Polatlı (Eskişehir, Ankara) region lignite report. MTA Technical Report No. 6386, Ankara, 1970 (in Turkish).
15. Ocakoğlu, F. A re-evaluation of the Eskişehir Fault Zone as a recent extensional structure in NW Turkey. J. Asian Earth Sc., 2007, **31**(2), 91–103.
16. Şenguler, İ. Geology and coal potential of Eskişehir-Sivrihisar Basin (Turkey). Technical Report No. 11473, MTA, Ankara, 2011 (in Turkish).
17. Şengüler, İ., Akkiraz, M. S., Yanık, G. Palynology, Palaeoecology and Clay Mineralogy of Miocene Deposits in the Eskişehir Basin. *Bulletin of Turkish Association of Petroleum Geologist* (in press), Ankara, 2013.
18. Connan, J. Molecular geochemistry in oil exploration. In: *Applied Petroleum Geochemistry* (Bordenave, M. L., ed.). Editions Technip, Paris, 1993, 175–204.
19. Peters, K. E., Moldowan, J. M. *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments*. Prentice-Hall, Englewood Cliffs, N. J., 1993.
20. Hunt, J. M. *Petroleum Geochemistry and Geology*. W. H. Freeman and Company, New York, 1995.
21. Sinninghe Damsté, J. S., Kenig, F., Koopmans, M. P., Köster, J., Schouten, S., Hayes, J. M., De Leeuw, J. W. Evidence for gammacerane as an indicator of water column stratification. *Geochim. Cosmochimic. Ac.*, 1995, **59**(9), 1895–1900.
22. Peters, K. E., Walters, C. C., Moldowan, J. M. *The Biomarker Guide. Biomarkers and Isotopes in Petroleum Exploration and Earth History*, vol. 2, 2nd ed. Cambridge University Press, Cambridge, 2005.

23. Tissot, B. P., Welte, D. H. *Petroleum Formation and Occurrence*. Springer-Verlag, Heidelberg, 1984.
24. Moldowan, J. M., Seifert, W. K., Gallegos, E. J. Relationship between petroleum composition and depositional environment of petroleum source rocks. *Am. Assoc. Petr. Geol. B.*, 1985, **69**, 1255–1268.
25. Whitehead, E. V. The structure of petroleum pentacyclanes. In: *Advances in Organic Geochemistry* (Tissot, B., Biener, F., eds.), Editions Technip, Paris, 1974, 225–243.
26. Ekweozor, C. M., Okogun, J. I., Ekong, D. E. U., Maxwell, J. R. Preliminary organic geochemical studies of samples from the Niger delta (Nigeria): II. Analyses of shale for triterpenoid derivatives. *Chem. Geol.*, 1979, **27**(1–2), 29–37.
27. Grantham, P. J., Posthuma, J., Baak, A. Triterpanes in a number of far-eastern crude oils. In: *Advances in Organic Geochemistry* (Bjoroy, M. et al., eds.). J. Wiley and Sons, New York, 1983, 675–683.
28. ten Haven, H. L., Rullkötter, J. The diagenetic fate of taraxer-14-ene and oleanene isomers. *Geochim. Cosmochim. Ac.*, 1988, **52**(10), 2543–2548.
29. Riva, A., Caccialanza, P. G., Quagliaroli, F. Recognition of 18b(H) oleanane in several crudes and Tertiary-Upper Cretaceous sediments. Definition of a New Maturity Parameter. In: *Advances in Organic Geochemistry 1987* (Matte-velli, L., Novelli, L., eds.). Pergamon Press, Oxford, 1988, 671–675.
30. Udo, O. T., Ekweozor, C. M. Significance of oleanane occurrence in shales of Opuama Channel Complex, Niger Delta. *Energ. Fuel.*, 1990, **4**, 248–254.
31. Ourisson, G., Albrecht, P., Rohmer, M. Predictive microbial biochemistry – from molecular fossils to prokaryotic membranes. *Trends Biochem. Sci.*, 1982, **7**(7), 236–239.
32. Volkman, J. K., Banks, M. R., Denwer, K., Aquino Neto, F. R. Biomarker composition and depositional setting of Tasmanite oil shale from northern Tasmania, Australia. In: 14th *International Meeting on Organic Geochemistry*, September 22, 1989, Abstract No 168, Paris.
33. Azevedo, D. A., Aquino Neto, F. R., Simoneit, B. R. T., Pinto, A. C. Novel series of tricyclic aromatic terpanes characterized in Tasmanian tasmanite. *Org. Geochem.*, 1992, **18**(1), 9–16.
34. Simoneit, B. R. T., Schoell, M., Dias, R. F., de Aquino Neto, F. R. Unusual carbon isotope compositions of biomarker hydrocarbons in a Permian tasmanite. *Geochim. Cosmochim. Ac.*, 1993, **57**(17), 4205–4211.
35. Riva, A., Riolo, J., Mycke, B., Ocampo, R., Callot, H. J., Albrecht, P., Nalı, M. Molecular parameters in Italian carbonate oils: Reconstruction of past depositional environments. Abstract. In: *14th International Meeting on Organic Geochemistry*, Paris, September 18–22, 1989, pp. 335.
36. Waples, D. W., Machihara, T. *Biomarkers for Geologists: A Pratical Guide to the Application of Steranes and Triterpanes in Petroleum Geology*. AAPG Methods in Exploration Series, No. 9, 1991.
37. Seifert, W. K., Moldowan, J. M. Use of biological markers in petroleum exploration. In: *Methods in Geochemistry and Geophysics* (Johns, R. B., ed.), 1986, **24**, 261–190.
38. Seifert, W. K., Moldowan, J. M. The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. In: *Advances in Organic Ggeochemistry* (Douglas, A. G., Maxwell, J. R., eds.). Pergamon Press, Oxford, 1980, 229–237.

39. Grantham, P. J. Sterane isomerisation and moretane/hopane ratios in crude oils derived from Tertiary source rocks. *Org. Geochem.*, 1986, **9**(6), 293–304.
40. Kvenvolden, K. A., Simoneit, B. R. T. Hydrothermally derived petroleum examples from Guaymas Basin, Gulf of California, and Escanaba Trough, northeast Pacific Ocean. *Am. Assoc. Petr. Geol. B.*, 1990, **74**, 223–237.
41. Hughes, W. B., Holba, A. G., Mueller, D. E., Richardson, J. S. Geochemistry of greater Ekofisk crude oils. In: *Petroleum Geochemistry in Exploration of the Norvegian Shelf* (Thomas, B. M., Doré, A. G., Eggen, S. S., Home, P. C., Larsen, R. M., eds.). Graham and Trotman, London, 1985, 75–92.
42. Sofer, Z., Zumberge, J. E., Lay, V. Stable carbon isotopes and biomarkers as tools in understanding genetic relationship, maturation, biodegradation, and migration of crude oils in Northern Peruvian Oriente (Maranon) Basin. *Org. Geochem.*, 1986, **10**(1–3), 377–389.
43. Cornford, C., Christie, O., Endresen, U., Jensen, P., Myhr, M.-B. Source rock and seep oil maturity in Dorset, southern England. *Org. Geochem.*, 1988, **13**(1–3), 399–409.
44. Kolaczkowska, E., Slougui, N. E., Watt, D. S., Marcura, R. E., Moldowan, J. M. Thermodynamic stability of various alkylated, dealkylated, and rearranged 17α- and 17β-hopane isomers using molecular mechanics calculations. *Org. Geochem.*, 1990, **16**(4–6), 1033–1038.
45. Fowler, M. G., Brooks, P. W. Organic geochemistry as an aid in the interpretation of the history of oil migration into different reservoirs at the Hibernia K-18 and Ben Nevis I-45 wells, Jeanne d'Arc Basin, offshore eastern Canada. *Org. Geochem.*, 1990, **16**(1–3), 461–475.
46. Mukhopadhyay, P. K., Wade, J. A., Kruge, M. A. Organic facies and maturation of Jurassic/Cretaceous rocks, and possible oil-source rock correlation based on pyrolysis of asphaltenes, Scotian Basin, Canada. *Org. Geochem.*, 1995, **22**(1), 85–104.
47. Espitalie, J., Madec, M., Tissot, B., Mennig, J. J., Leplat, P. Source rock characterization methods of petroleum exploration. In: *Proc. Offshore Technology Conference*, **3**(9), 1977, 439–444.
48. Dembicki Jr., H. Three common source rock evaluation errors made by geologists during prospect or play appraisals. *Am. Assoc. Petr. Geol. B.*, 2009, **93**(3), 341–356.

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