Biomarkers geochemistry of the Alpagut oil shale sequence: an evaluation of dispositional environments and source rock potential from Dodurga-Çorum basin (N-Turkey)

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Abstract

The Cenozoic Çankırı-Çorum basin, with sedimentary facies of varying thickness and distribution, contains raw matters such as coal deposits, oil shales and evaporate. Source rock and sedimentary environment characteristics of the oil shale sequence have been evaluated. The studied oil shales have high organic matter content (from 2.97 to 15.14%) and show excellent source rock characteristics. Oil shales are represented by very high hydrogen index (532–892 mg HC/g TOC) and low oxygen index (8–44 mgCO$_2$/g TOC) values. Pyrolysis data indicate that oil shales contain predominantly Type I and little Type II kerogen. The biomarker data reveal the presence of algal, bacterial organic matter and terrestrial organic matter with high lipid content. These findings show that organic matters in the oil shales can generate hydrocarbon, especially oil. High C$_{26}$/C$_{25}$, C$_{24}$/C$_{23}$ and low C$_{22}$/C$_{21}$ tricyclic terpane, C$_{31}$R/C$_{30}$ hopane and DBT/P ratios indicate that the studied oil shales were deposited in a lacustrine environment, and very low Pr/Ph ratio is indicative of anoxic character for the depositional environment. T$_{max}$ values from the pyrolysis analysis are in the range of 418–443 °C, and production index ranges from 0.01 to 0.08. On the gas chromatography, high Pr/nC$_{17}$ and Ph/nC$_{18}$ ratios and CPI values significantly exceeding 1 were determined. Very low 22S/(22S + 22R) homohopane, 20S/(20S + 20R) sterane, diasterane/sterane and Ts/(Ts + Tm) ratios were calculated from the biomarker data. Results of all these analyses indicate that Alpagut oil shales have not yet matured and have not entered the oil generation window.

Keywords Çankırı-Çorum basin · Oil shale · Biomarkers · Depositional environment · Hydrocarbon potential

Introduction

The Çankırı-Çorum basin which was filled with approximately 4 km thick Cenozoic deposits is noticeable in respect to its potential of hydrocarbon source rocks and evaporitic minerals (Kaymakçı 2000; Yavuz and Demirer 2018; Yavuz et al. 2017).

The Çankırı-Çorum basin is located in a complex region on the İzmir-Ankara-Erzincan suture zone which realized by the collision of Kırşehir and Sakarya continents in the Late Cretaceous (Ketin 1966; Birgili et al. 1975; Şengör and Yılmaz 1981; Kaymakçı 2000; Özçelik and Öztaş 2000; Uğuz et al. 2002; Yavuz and Demirer 2018). The northern

branch of Neotethys Ocean (İzmir-Ankara-Erzincan Ocean) began to subduct northward beneath the Sakarya continent in the early Cretaceous, and the Kırşehir and Sakarya continents were collided in the late Cretaceous (Şengör and Yılmaz 1981; Barrier et al., 2018). Following the collision, the Kırşehir continent started to rotate counterclockwise, and this rotation initiated a tectonic regime dominated by strike-slip faults during the Paleocene-Early Eocene. During this time, the basin was witnessed a marine transgression. Starting from the middle Eocene, south-vergent thrust faults developed around the basin and old units were pushed over the young units. This was followed by uplifting and shallowing of the basin. At the end of Middle Eocene, the sea was completely receded giving rise to formation of a terrestrial intermountain basin during late Eocene–Oligocene (Tüysüz and Dellaloğlu 1994; Kaymakçı 2000). Deposition in this closed basin, which resulted from vertical tectonic movements, continued uninterruptedly until the end of the Upper Miocene (Şenalp, 1981). The study area was inundated by

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an open semi-tropic lake with abundant organic matter during Early Middle Miocene. During this period, coal layers were deposited along the lakeshore. Evaporitic lacustrine units were deposited during the late Miocene–Pliocene depending on the changes in climatic conditions (Tüysüz and Dellaloğlu 1994; Varol et al. 2002; Zengin 2006).

The Alpagut coal and oil shale deposits occur in the Miocene sequences on the northeastern margin of Çankırı-Çorum basin covering a large area in the Central Anatolia having a basement comprising Paleozoic metamorphic and Upper Cretaceous ophiolitic rocks. Basement rocks are overlain locally by Upper Cretaceous clastic deposits and commonly by Paleogene–Neogene clastics, carbonates, evaporitic deposits and volcanics.

The Alpagut coal and oil shale field is situated 51 km northwest of Çorum city and 7 km west of Dodurga town (Fig. 1). Coal deposits in the region have been known for a long time and Blumenthal (1938), Kıpçak (1947), Bender (1955), Pekmezciler (1957), Wedding (1966) and Kara et al. (1990) conducted first geological studies on them. Following the drilling works in the basin, coal deposit became exploited. Micropaleontological, petrographic and organic geochemical characteristics of the coal sequence were carried out by Turnovsky (1964), Toprak (1996) and Yalçın-Erik et al. (2018), respectively. The coal level in the region is overlain by 141 m thick oil shale sequence. 138 million tons of probable oil shale reserve were discovered in the basin (Taka et al., 1982). Oil shales have ash ratio of 75.20%, water content of 0.90–16.15%, density of 2.32 gr/cm^3, bitumen ratio of 2.5% and calorific value of 70–870 kcal/kg (Taka et al. 1992). Taka et al. (1992) carried out the first geological study on the oil shale sequence. Khoitiyn (2016) examined the source rock potential of the sequence using the pyrolysis data.

Works in the studied basin were generally focused on coal deposits, and there are limited works on geological, fossil fuel and source rock characteristics and reserve estimation of the oil shales. However, organic geochemical features of these shales are not studied. Therefore, this study aims to clarify depositional environment, organic matter input, source rock and hydrocarbon potential of Alpagut oil shales using the pyrolysis/TOC, GC and biomarker data.

Geological setting

Geological characteristics of the study area, based on field observations and previous works by Birgili et al. (1975), Taka et al. (1992) and Toprak (1996), are summarized below (Figs. 1 and 2). The oldest exposed rocks are represented by Eocene rocks in the study area which are represented by three Eocene units, and the Hacıhalil Formation consists of dark–light gray, thick-bedded conglomerate, sandstone and siltstone alternation. It is conformably overlain by the Yoncalı Formation comprising gray, beige, light green colored turbiditic sandstone, siltstone, marl, shale, limestone and mudstone interlayers. The Narlı Volcanites were emplaced by cutting the Eocene aged Yoncalı Formation. The Narlı Volcanites consisting of basalt, andesite, agglomerates and tuffs represent the upper level of the Eocene units (Toprak, 1996).

Miocene lacustrine deposits in the basin unconformably overlie the Eocene units. Miocene aged Kızılırmak Formation represented by conglomerate, siltstone and reddish brown and light brown clays occurs at the lower part of the Miocene sequence. The clay unit contains lignite layers and lignite laminas of varying thickness. Miocene aged Dodurga Formation begins with lignite coal level and continues with
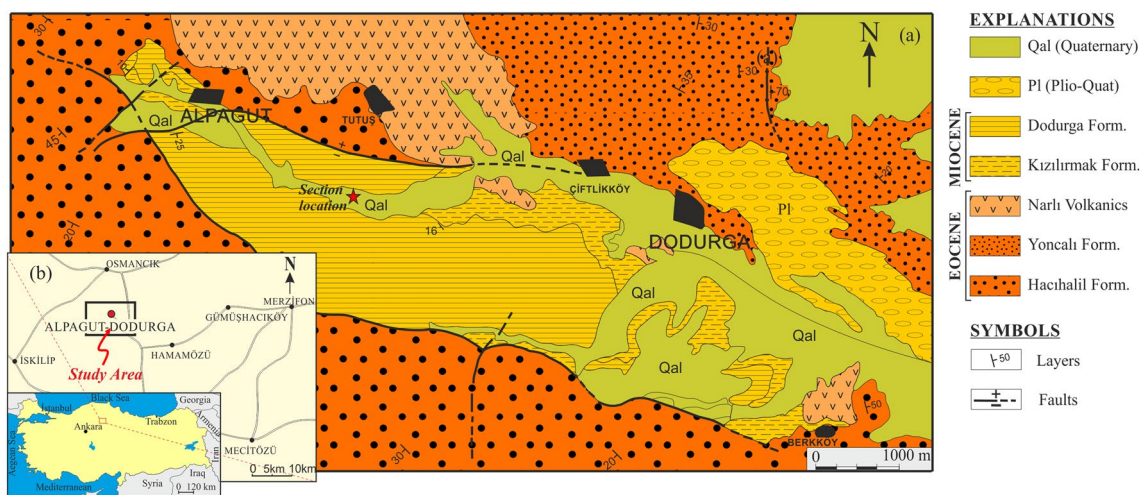

Fig. 1 Geological map of the Alpagut-Dodurga region (modified from Taka et al., 1992) (**a**) and location map of study area (**b**)
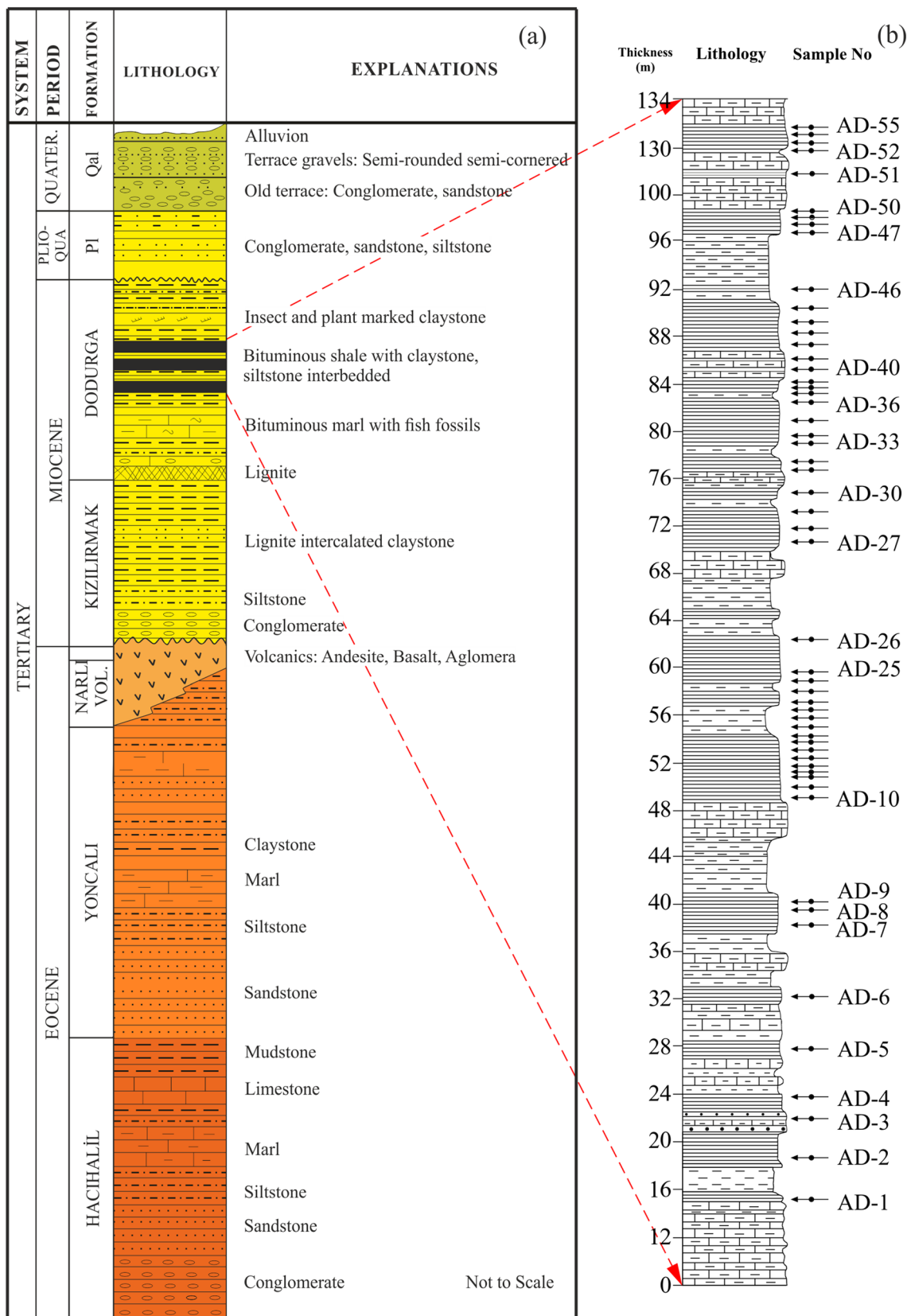
Fig. 2 Generalized stratigraphic section of the Alpagut-Dodurga region (Taka et al., 1992) (**a**) and measured stratigraphic section of the oil shale sequence (**b**)

siltstone and marls with abundant fish fossils and oil shales to the top. This level is not homogeneous and locally alternated with claystone, marl and siltstone. Plio-Quaternary units unconformably lie on the Miocene and Eocene units. They are characterized by loosely compacted conglomerates, fine-medium sandstones, and yellowish, gray, beige colored siltstones of 100 m thickness. Quaternary deposits that consist of loosely cemented conglomerates and sandstones unconformably overlie all the underlying units (Fig. 2).

The oil shale sequence in the study area occurs at the upper level of the Miocene Dodurga Formation. The stratigraphic section of oil shale sequence was measured in the Alpagut open-pit coal mine as 134 m and the sequence consisting of sandstone–limestone–siltstone–marl interlayers contains 17 different oil shale levels with thickness varying from 20 to 5.5 m (Figs. 2 and 3).

Materials and methodology

The stratigraphic section of oil shale sequence was measured in the Alpagut open-pit coal mine, and oil shale levels were systematically sampled from bottom to top along the sequence. Rock–Eval/TOC analysis was performed on 54 oil shale samples selected to represent oil shales at different levels. Taking into account the pyrolysis data obtained, samples AD-2 and AD-47 were selected to represent the bottom and upper levels of the succession, respectively, and GC and GC–MS analyzes were performed on these samples. Gas chromatography (GC) (bulk extract), gas chromatography–mass spectrometry (GC–MS) (saturated hydrocarbons-sterane and terpane/aromatic hydrocarbons-monoaromatic and triaromatic steroids, phenanthrene and methyl-phenanthrenes, dibenzothiophene, and methyl-dibenzothiophenes) analyses were conducted on extracts obtained from two oil shale samples (AD-2, AD-47). Rock Eval/TOC, GC and GC–MS analyses were carried out at the Geochemistry Laboratories of Turkish petroleum corporation (TPAO).

100 mg of 54 powdered samples which were systematically collected from oil shales of the Dodurga Formation was subjected to Rock–Eval pyrolysis/TOC analyses by using a Rock–Eval 6 instrument equipped with a TOC module. In the pyrolysis process, the sample was heated from 300 (hold time 3 min) to 650 °C at 25 °C/min. In the oxidation process, the sample was heated from 400 (holding time 3 min) to 850 °C (hold time 5 min) at 25 °C/min for oxidation.

The C_{15+} soluble organic matter (SOM) was isolated following Soxhlet extraction (40 h) of the powdered rock samples with dichloromethane (CH_2Cl_2). Whole shale extracts were analyzed using a Varian 3400 gas chromatograph equipped
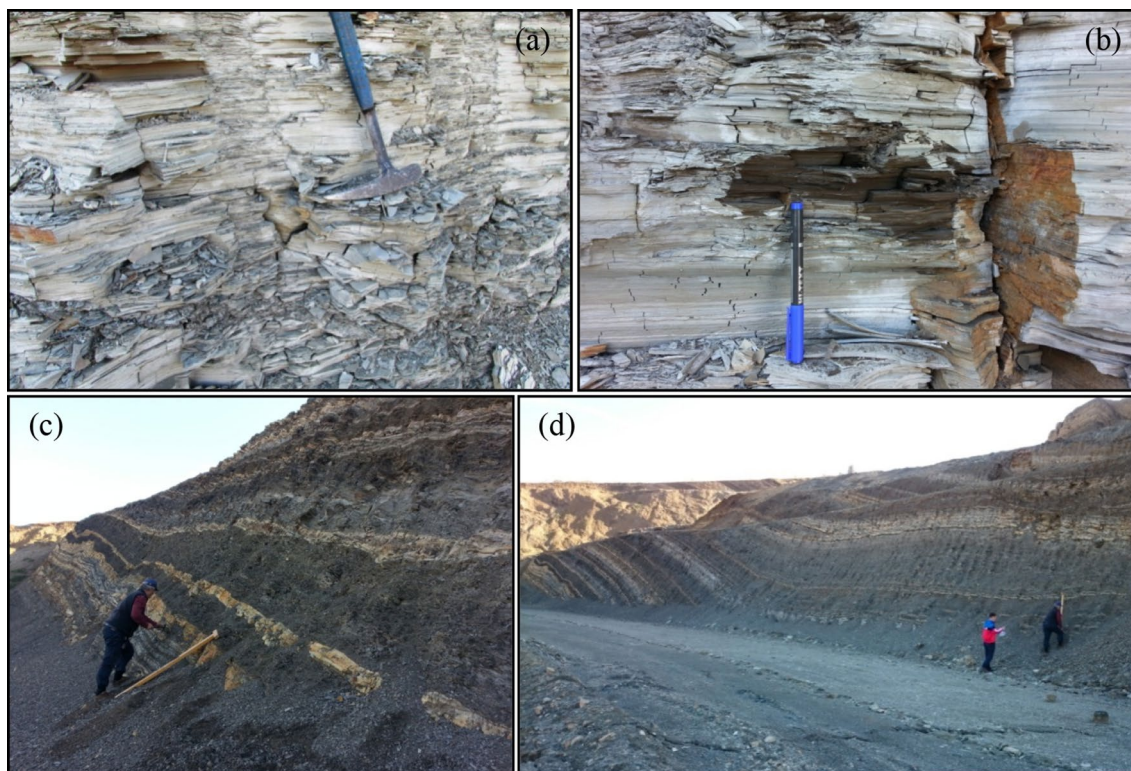

Fig. 3 Field photographs of Dodurga oil shale in Alpagut open coal mine site. Close up view of oil shale occurrence (**a**, **b**); General view of the oil shale sequence (**c**, **d**)

Table 1 Results of TOC and Rock–Eval analysis and calculated parameters for the oil shale samples analyzed (Khoitiyn, 2016)

Sample No	Kalnhk (m)	TOC (% wt.)	S$_1$ (mgHC/g rock)	S$_2$ (mgHC/g rock)	S$_3$ (mgHC/g rock)	Tmax (°C)	HI (mgHC/g TOC)	OI (mgCO$_2$/g TOC)	PI (S$_1$/S$_1$+S$_2$)	S$_2$/S$_3$	PY (S$_1$+S$_2$)	RC (%)	PC (%)	MINC (%)
AD-1	15.0	5.16	0.85	31.23	0.97	423	605	19	0.03	31.19	32.08	2.43	2.73	0.19
AD-2	18.5	12.45	2.47	97.23	1.91	430	781	15	0.02	50.90	99.70	4.04	8.41	0.28
AD-4	22.0	5.17	1.05	32.78	1.94	424	634	38	0.03	16.89	33.83	2.27	2.90	1.86
AD-5	23.5	5.89	1.16	34.60	1.23	423	587	21	0.03	28.13	35.76	2.84	3.05	3.37
AD-6	32.5	4.76	0.82	30.43	1.28	424	639	27	0.03	23.77	31.25	2.09	2.67	2.41
AD-7	38.5	9.11	1.44	71.54	1.20	431	785	13	0.02	59.61	72.98	2.98	6.13	1.74
AD-8	39.5	3.10	0.43	18.84	1.16	427	608	37	0.02	16.24	19.27	1.44	1.66	2.37
AD-9	40.5	4.87	0.69	35.84	1.06	431	736	22	0.02	33.81	36.53	1.77	3.10	2.20
AD-10	49.0	3.71	0.29	21.1	1.28	428	569	35	0.01	16.48	21.39	1.85	1.86	3.07
AD-11	50.0	5.81	0.56	39.34	1.65	431	677	28	0.01	23.84	39.9	2.39	3.42	3.13
AD-12	50.5	6.23	0.61	44.66	1.49	435	717	24	0.01	29.97	45.27	2.39	3.84	2.46
AD-13	51.0	3.90	0.42	24.00	1.07	424	615	27	0.02	22.43	24.42	1.79	2.11	3.55
AD-14	51.5	4.09	0.47	26.56	1.10	424	649	27	0.02	24.14	27.03	1.77	2.32	2.61
AD-15	52.0	2.97	0.20	15.81	0.99	423	532	33	0.01	15.97	16.01	1.58	1.39	1.71
AD-16	53.0	6.71	0.72	50.15	1.24	432	747	18	0.01	40.44	50.87	2.41	4.30	2.49
AD-17	54.0	6.95	0.73	51.89	1.28	434	747	18	0.01	40.53	52.62	2.50	4.45	2.26
AD-18	54.5	6.35	0.68	47.69	1.17	435	751	18	0.01	40.76	48.37	2.24	4.11	2.56
AD-19	55.0	4.90	0.45	32.99	1.11	429	673	23	0.01	29.72	33.44	2.05	2.85	2.36
AD-20	56.0	13.41	3.79	105.44	1.80	427	786	13	0.03	58.57	109.23	4.23	9.18	1.11
AD-21	56.5	13.54	3.04	104.33	2.08	427	771	15	0.03	50.15	107.37	4.49	9.05	1.05
AD-22	57.0	13.64	2.07	119.63	1.33	432	877	10	0.02	89.94	121.7	3.43	10.21	0.68
AD-23	58.0	15.14	2.35	132.4	1.31	434	875	9	0.02	101.07	134.75	3.83	11.31	0.54
AD-24	59.0	5.78	0.68	44.22	0.86	433	753	15	0.02	51.41	44.90	2.08	3.79	1.61
AD-25	59.5	4.47	0.52	27.38	1.04	419	613	23	0.02	26.32	27.90	2.07	2.40	1.70
AD-26	62.5	3.85	0.30	21.00	1.10	418	545	29	0.01	19.09	21.30	2.02	1.83	0.88
AD-27	70.5	6.35	0.65	39.82	1.38	424	627	22	0.02	28.85	40.47	2.89	3.46	1.48
AD-28	71.5	5.76	0.56	34.86	1.52	430	605	26	0.02	22.93	35.42	2.72	3.04	2.40
AD-29	73.5	5.16	0.55	33.04	1.16	429	640	22	0.02	28.48	33.59	2.29	2.87	2.28
AD-30	75.0	9.46	1.19	82.34	1.17	433	870	12	0.01	70.37	83.53	2.44	7.02	0.78
AD-31	76.5	11.05	3.24	82.08	2.02	422	743	18	0.04	40.63	85.32	3.84	7.21	1.82
AD-32	77.5	10.38	2.95	76.39	2.13	422	736	21	0.04	35.86	79.34	3.67	6.71	1.95
AD-33	79.0	7.13	1.29	52.76	1.39	426	740	19	0.02	37.95	54.05	2.56	4.57	2.77
AD-34	80.0	11.41	1.37	92.42	1.57	433	810	14	0.01	58.86	93.79	3.52	7.89	0.82
AD-35	81.0	10.20	1.04	88.52	1.02	434	868	10	0.01	86.78	89.56	2.68	7.52	0.80

Table 1 (continued)

Sample No	Kalınlık (m)	TOC (% wt.)	S_1 (mgHC/g rock)	S_2 (mgHC/g rock)	S_3 (mgHC/g rock)	Tmax (°C)	HI (mgHC/g TOC)	OI (mgCO$_2$/g TOC)	PI (S_1/S_1+S_2)	S_2/S_3	PY (S_1+S_2)	RC (%)	PC (%)	MINC (%)
AD-36	82.5	12.50	1.11	111.46	1.28	440	892	10	0.01	87.07	112.57	3.06	9.44	1.24
AD-37	83.0	11.32	1.06	80.56	3.35	434	712	30	0.01	24.04	81.62	4.37	6.95	0.58
AD-38	83.5	11.03	0.71	89.02	1.84	435	807	17	0.01	48.38	89.73	3.47	7.56	0.93
AD-39	84.0	11.49	0.76	91.98	1.53	435	801	13	0.01	60.11	92.74	3.68	7.81	0.50
AD-40	85.5	7.91	0.84	60.17	1.28	436	761	16	0.01	47.00	61.01	2.77	5.14	1.19
AD-41	86.0	7.53	2.84	57.70	1.27	440	766	17	0.05	45.53	60.54	2.41	5.12	3.08
AD-42	87.5	6.13	3.50	39.38	0.75	430	642	12	0.08	52.5	42.88	2.49	3.64	2.33
AD-43	88.5	7.13	3.97	42.85	1.09	433	601	15	0.08	39.31	46.82	3.15	3.98	2.08
AD-44	89.5	10.82	4.22	83.37	0.98	439	771	9	0.05	85.07	87.59	3.44	7.38	1.52
AD-45	90.5	6.82	2.41	48.75	0.56	436	715	8	0.05	87.05	51.16	2.51	4.31	2.10
AD-46	92.0	4.94	1.85	32.48	0.63	432	657	13	0.05	51.55	34.33	2.03	2.91	3.57
AD-47	96.5	11.56	3.59	77.77	2.52	438	673	22	0.04	30.86	81.36	4.61	6.95	0.19
AD-48	97.0	11.85	1.97	87.32	3.62	438	737	31	0.02	24.12	89.29	4.25	7.16	1.71
AD-49	97.5	4.51	1.21	24.14	1.04	431	535	32	0.05	23.21	25.35	2.34	2.17	1.23
AD-50	98.0	6.68	1.60	36.24	2.72	434	543	41	0.04	13.32	37.84	3.41	3.27	0.51
AD-51	130.0	10.23	1.72	72.02	4.52	434	704	44	0.02	15.93	73.74	3.89	6.34	1.12
AD-52	130.5	10.08	1.39	66.38	2.61	436	659	26	0.02	25.43	67.77	4.27	5.81	0.16
AD-53	131.0	13.03	1.98	103.8	1.85	436	797	14	0.02	56.10	105.78	4.11	8.92	0.28
AD-54	131.5	8.16	1.15	59.47	0.96	443	729	12	0.02	61.94	60.62	3.04	5.12	1.42
AD-55		5.93	0.79	38.96	0.78	438	657	13	0.02	49.94	39.75	2.57	3.36	1.36
Average		**7.90**	**1.45**	**58.28**	**1.50**	**430**	**705**	**20.66**	**0.02**	**42.25**	**59.73**	**2.88**	**5.05**	**1.67**

Fig. 4 Gas chromatograms of the oil shale extracts analyzed. **a** oil shale sample AD-2, **b** oil shale sample AD-47

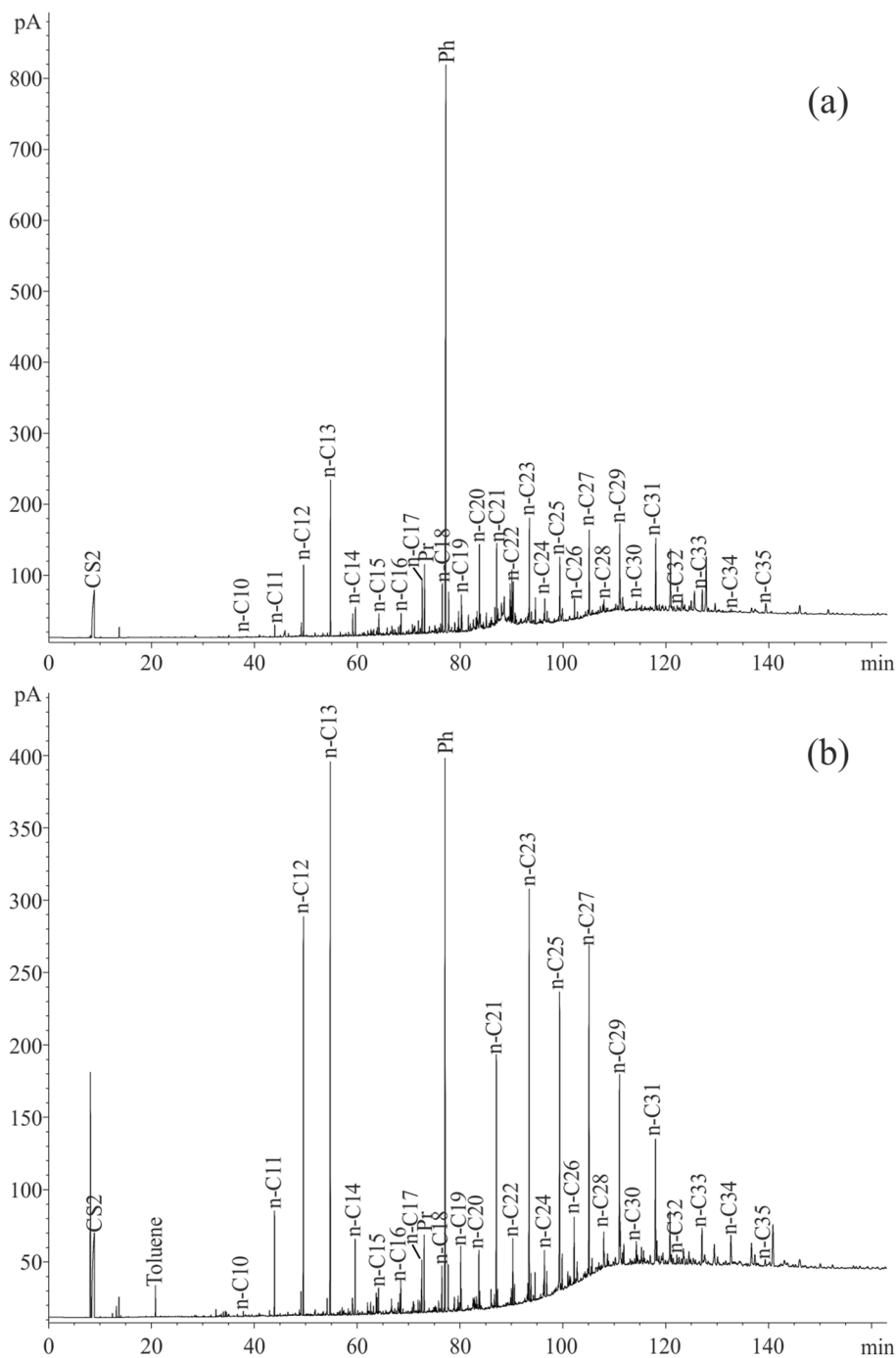**Table 2** Parameters calculated from gas chromatograms of the oil shale extracts analyzed

Sample No	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	CPI $_{(24–34)}$	TAR
AD-2	0.12	1.48	11.82	6.20	2.33
AD-47	0.12	1.25	11.76	5.73	4.47

with flame photometric (FPD) and flame ionization detectors (FID). 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 (hold time 8 min) to 270°C (hold time 60 min) at 4°C/min.

Shale extracts were de-asphaltened using *n*-pentane and were fractioned by thin-layer chromatography (MK-Iatroscan). *n*-hexane, toluene, and methanol were used for extract separation into saturated hydrocarbons, aromatic
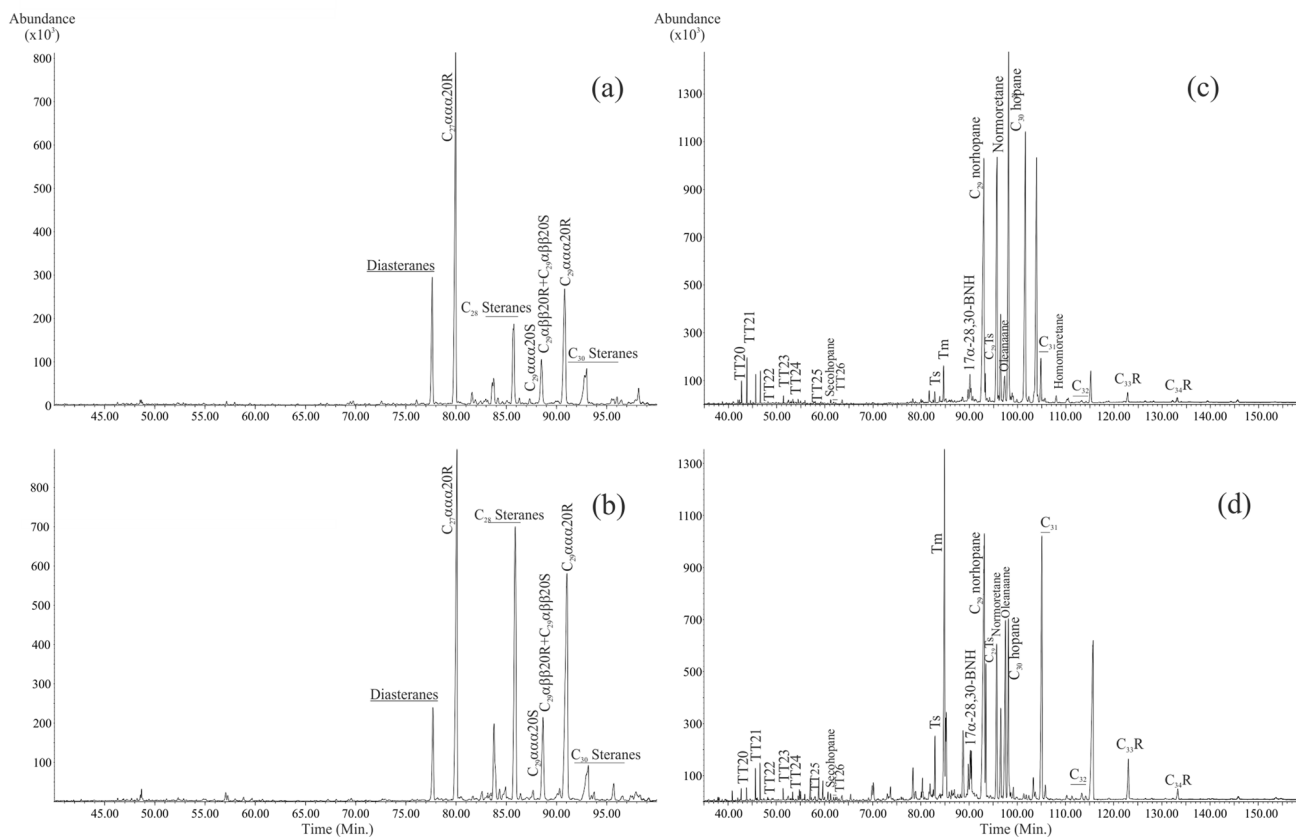
Fig. 5 m/z 217 mass chromatograms showing the distribution of aliphatic steroid (**a**, **b**) and m/z 191 mass chromatograms showing the distribution of the aliphatic hopanoid (**c**, **d**) of Alpagut oil shale samples (AD-2 and AD-47, respectively)

hydrocarbons, and NSO fractions, respectively. GC–MS analyses were performed on the saturated, aromatic and NSO fractions using an Agilent 5975C quadruple 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 (hold time 10 min) to 200°C (hold time 15 min) at 10°C/min, to 250°C (hold time 24 min) at 5°C/min and then to 280°C (hold time 24 min) at 2°C/min. Finally, the oven temperature was increased to 290°C (hold time 40 min) at 1°C/min. The mass spectrometer was operated in EI mode at ionization energy of 70 eV and a source temperature of 300°C. The biomarker contents were determined using single-ion recordingly at *m/z* 191 for tri-, tetra- and pentacyclic triterpanes, at *m/z* 217 for steranes and rearranged steranes, at *m/z* 253 for monoaromatic steranes, at *m/z* 231 for triaromatic steranes, at 178 and 192 for phenanthrene and methyl-phenanthrene, and at *m/z* 187 and 198 for dibenzothiophene and methyl-dibenzothiophenes. Compounds were identified by their retention time and elution order matching.

Results

Bulk organic geochemical characteristics

TOC values of oil shales of the Dodurga Formation in the Alpagut area are in the range of 2.97–15.14% with average of 7.9% (Table 1). Oil shales have very high S_2, S_2/S_3 and PY values. They are characteristic with particularly very high HI (varying from 532 to 892 mg HC/g TOC with average of 705 mg HC/g TOC) and low OI values (varying from 8 to 44 mg HC/g CO_2 with average of 21 mg HC/g CO_2). T_{max} was measured 418-443°C (average T_{max} 430 °C). PI values are from 0.01 to 0.08 with average of 0.02 (Table 1).

Molecular geochemistry of organic matter

n-alkanes and isoprenoids

The n-alkanes in the C_{10}-C_{35} range were recorded from the gas chromatograms. A bimodal distribution, where C_{13} is the maximum peak and C_{23} is recorded at a significant rate (Fig. 4), was observed. Pyhtane was recorded as being in very high concentrations compared to pristane, and the Pr/

Table 3 Biomarker compositions based on m/z 191, 217, 231, 253, 178, 192, 187, 198 mass chromatograms and calculated parameters for the oil shale extract

Terpanes	Sample No		Steroids	Sample No	
	AD-2	AD-47		AD-2	AD-47
C_{22}/C_{21} tt	0.50	0.07	C_{27},C_{28},C_{29} MA steroid (%)	21, 48, 31	14, 65, 21
C_{24}/C_{23} tt	0.46	0.67	MA(I)/MA(I+II)	0.08	0.04
$(C_{19}+C_{20})/C_{23}$ tt	3.14	1.04	TA(I)/TA(I+II)	0.11	0.05
Ts/(Ts+Tm)	0.23	0.45	TA$[C_{20}/(C_{20}+C_{28}.$ 20R)]	0.80	0.25
C_{31} R HH./C_{30} H	0.01	0.07	C_{28}-TA/(C_{29}-MA+C_{28}-TA)		
C_{23} tt/(C_{23}tt+C_{30} H)	0.02	0.06	$C_{29}/(C_{28}+C_{29})$ MA	0.40	0.24
C_{26}/C_{25} tt	1.67	1.83	Phenanthrenes		
C_{29}/C_{30} hopane	0.69	1.44	MPI-1	0.24	0.13
C_{29}Ts/(C_{29}H+C_{29}Ts)	0.09	0.33	MPI-2	0.32	0.15
C_{30}*/C_{29}Ts	0.17	0.02	MPI-3 (β/α MP)	1.49	1.34
C_{30}*/(C_{30}H+C_{30}*)	0.01	0.01	MPR	2.31	1.40
(oleanane/ C_{30} hopane)*100	7	100	MPR1	0.05	0.04
22S/(22S+22R)(C_{32}) H	0.30	0.41	MPR9	0.07	0.03
sterane/hopane	0.87	0.46	MPR2	0.12	0.05
Steranes			MPR3	0.06	0.04
C_{27}, C_{28}, C_{29} ste. (%)	57, 16, 27	34, 35, 31	1-MP/9-MP	0.78	1.22
n-, iso-, diasterane (%)	8, 74, 17	15, 77, 8	*Dibenzothiophenes*		
20S/(20S+20R) C_{29}	0.04	0.03	MDR	4.25	3.31
ββ/(ββ+αα)	0.27	0.26	MDR'	0.81	0.77
			DBT/P	0.05	0.03

sterane/hopane = C_{27}. C_{28}. C_{29} αα/ββ (20S+20R)/C_{29}-C_{33} hopane; MPI-1 = 1.5(2MP+3MP)/(P+1MP+9MP); MPI-2 = 3(2MP)/(P+1MP+9MP);

MPI-3 = (2MP+3-MP)/(1MP+9MP); MPR = 2MP/1MP; MPR$_1$ = 1MP/P; MPR$_2$ = 2MP/P; MPR$_3$ = 3MP/P; MPR$_9$ = 9MP/P; MDR = 4MDBT/1MDBT; MDR' = 4MDBT/(1MDBT+4MDBT);

MA(I)/MA(I+II) = ($C_{21}+C_{22}$)/($C_{21}+C_{22}+C_{27}+C_{28}+C_{29}$); TA(I)/TA(I+II) = ($C_{20}+C_{21}$)/($C_{20}+C_{21}+C_{26}+C_{27}+C_{28}$

Ph ratio was calculated to be very low (mean 0.12) (Table 2). Pristane and pyhtane have been recorded at higher concentrations in comparison to C_{17} and C_{18} n-alkanes, especially the Ph/nC_{18} ratio is very high. Odd-numbered n-alkanes are very dominant over even-numbered ones and have a very high CPI (Table 2).

Biomarkers (saturated and aromatics)

In m/z 191 mass chromatographs, a distribution in which tricyclic terpane contents are very low, C_{26} tt is dominant over C_{25} tt and Tm dominant over Ts was determined. C_{31} R HH/C_{30} H ratio is estimated very low. C_{30}*(diahopane) was recorded to be in trace amount while C_{29} Ts in significantly high quantity. Oleanane has been recorded in oil shale samples. Especially for the sample AD-47, the concentration of olenane and oleanane/C_{30} hopane is very high (Table 1). C_{31} components are the most common homohopane, and other homohopanes are recorded either in trace amount or not recognized. 22S/(22S+22R) (C_{32}) homohopane ratio was calculated as 0.30 and 0.41 (Fig. 5c,d, Table 3). In m/z 217 mass chromatographs, diasteranes were recorded in very

low abundance. C_{27} sterane is dominant over others for AD-2 sample, while in the other samples (AD-47), C_{27}, C_{28} and C_{29} steranes have similar abundances. Iso-steranes are much more abundant than n- and dia-steranes. 20S/(20S+20R) C_{29}, ββ/(ββ+αα) ratios were calculated as being very low (Fig. 5c, d, Table 3). In the studied oil shales, C_{21} and C_{22} monoaromatic steranes described as MA(I) are recorded as being in lower abundance compared to C_{27}, C_{28} and C_{29} monoaromatic steranes described as MA(II). Similarly, C_{20} and C_{21} triaromatic steranes, defined as TA(I), were determined to be in lower abundances compared to C_{26}, C_{27}, C_{28} triaromatic steranes, known as TA(II) (Fig. 6). MA(I)/MA(I+II) and TA(I)/TA(I+II) ratios were determined as being very low (Table 3). In general, C_{28} monoaromatic steroids are dominant, while C_{27} MA steroids constitute the group with the lowest abundance. $C_{29}/(C_{28}+C_{29})$ MA ratios of the shale samples were found to be between 0.40 and 0.24 (Fig. 6, Table 3).

In m/z 178-m/z 192 mass chromatographs, P was recorded in very low abundance and MPs are in very low concentrations compared to Ps (Fig. 7a, b). MPR-1, 2, 3 and 9 ratios were calculated to be very low (Table 3). 2MP is more dominant than
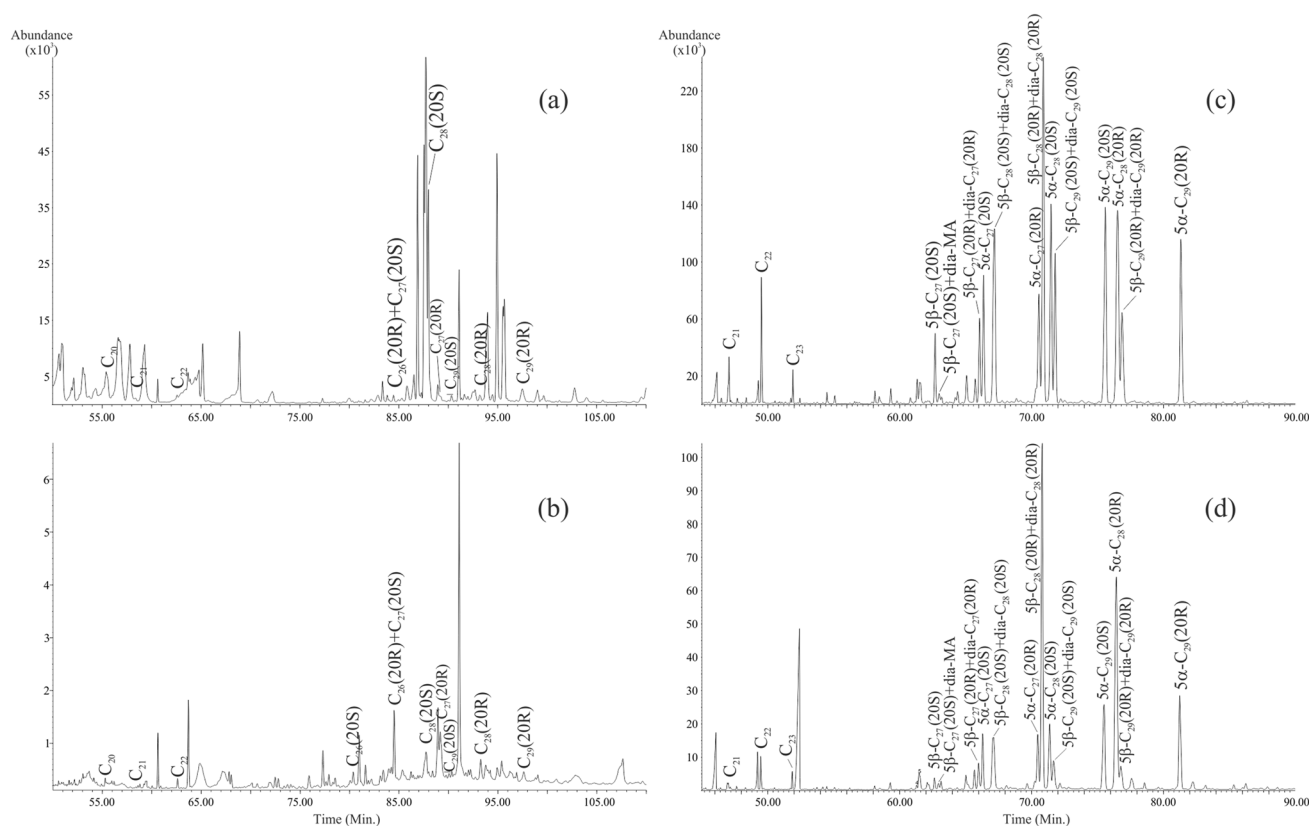
Fig. 6 Mass chromatograms (*m/z* 231) showing the distribution of monoaromatic steroid hydrocarbons (**a**, **b**), and mass chromatograms (*m/z* 253) showing the distribution of triaromatic steroid hydrocarbons (**c**, **d**) of Alpagut oil shale samples (AD-2 and AD-47, respectively)

other MPs (Fig. 7a, b). 9MP and 1MP generally have similar abundances, and for sample AD-2, 9MP was recorded in higher quantity than 1MP, and for sample AD-47, 1MP dominates over 9MP (Fig. 7a, b). MPI-3 and MPR ratios are very high (Table 3). In m/z 184-m/z 198 mass chromatographs, 4MDBT is more dominant one, and 1MDBT constitutes the lowest abundant MDBT (Fig. 7c, d). For sample AD-47, DBT dominates over MDBTs, and for sample AD-47, DBT was recorded in lower quantity than 4MDBT (Fig. 7c, d) and MDR and MDR' ratios are very high (Table 3).

Discussion

TOC values varying from 2.97 to 15.14% indicate that the organic matter content of Alpagut oil shales is very high and has "excellent" source rock characteristics (Table 1, Fig. 8). High hydrogen index values ranging from 532 to 892 mg HC/g TOC (average 705 mgHC/gTOC) and high S_2 (21.0–132.4 mg HC/mg rock) and low OI values indicate that oil shales contain predominantly Type I kerogen and little Type II kerogen (Table 1, Fig. 9). These characteristics

reveal that organic matter of studied oil shales can generate hydrocarbon, dominantly oil (Table 1).

The n-alkane distribution with very high concentrations of high carbon numbers (in the range of C_{21}-C_{31}), which is observed in gas chromatograms of the studied oil shale samples and indicates terrestrial organic matter input, and TAR values calculated at very high values (2.33–4.47) contradict the predominant Type I kerogen content interpretation done by pyrolysis data (Fig. 4, Table 2). High carbon numbered n-alkanes implying terrestrial organic matter are shown to be also associated with lacustrine algae (Gelpi et al. 1970; Peters et al. 2005; Riboulleau et al. 2007; Wang et al. 2011). Very high concentrations of Ph and very low estimated Pr/Ph ratio (0.12) indicate that oil shales deposited under anoxic conditions (Table 2). Very high Pr/n-C_{18} and lower Ph/C_{17} ratios estimated for the studied oil shales imply algal organic matter, reducing deposition conditions and low maturity values (Fig. 10a, Table 2). C_{30}* is recorded in high quantities particularly in clay-rich rocks deposited under suboxic and oxic conditions and in source rocks with high terrestrial organic matter input (Philp and Gilbert 1986; Volkman et al. 1983). Trace amount of C_{30}* recorded in
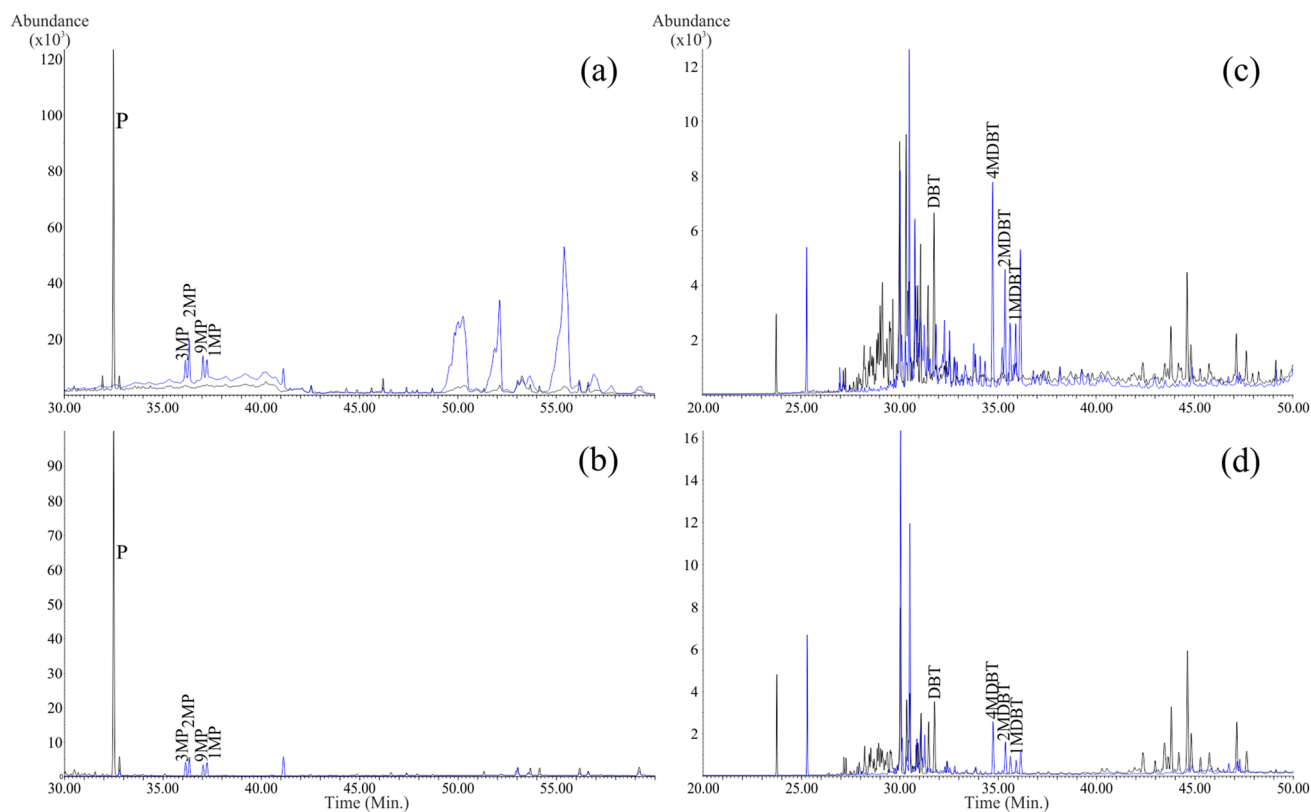
Fig. 7 **a**, **b** mass chromatograms (m/z 178 and 192) showing the distribution of phenanthrene and alkylphenanthrenes (P = phenanthrene; MP = methylphenanthrene); **c**, **d** mass chromatograms (m/z 184, 198) showing the distribution of dibenzothiophene and methyldibenzothiophene (DBT = dibenzothiophene, MDBT = methyldibenzothiophene) of Alpagut oil shale samples (AD-2, AD-47, respectively)

the oil shales supports the interpretation anoxic deposition conditions revealed from Pr/Ph (Fig. 5c, d).

In studied oil shales, C_{26} tricyclic terpane is much more abundant than C_{25} and C_{26}/C_{25} ratios are in the range of 1.67 to 1.83. In addition, oil shales have very low $C_{31}R/C_{30}$ hopane ratio (0.01–0.07) (Fig. 10b, Table 3). In general, the C_{22}/C_{21} ratios are low, and the C_{24}/C_{23} tricyclic terpane ratios are much higher (Fig. 10c). High C_{26}/C_{25}, C_{24}/C_{23} and low C_{22}/C_{21} tricyclic terpane ratios and having $C_{31}R/C_{30}$ hopane ratios less than 0.25 indicate that studied oil shales were deposited in a lacustrine environment (Peters et al. 2005; Kara-Gülbay et al. 2012, 2019; Şengüler et al. 2014). High DBT and ADBT concentrations are characteristic for marine shales and carbonates, and their abundance is very low in terrestrial facies (Radke et al. 1991). DBT content lower than phenanthrene implies organic matter accumulated either in lacustrine or fluvial deltaic environments (Hughes et al. 1995). High P and much lower DBT concentrations in the studied oil shales support the interpretation of lacustrine environment and in the DBT/P-Pr/Ph diagram, shales

samples with their very low DBT/P and Pr/Ph ratios are plotted in the "lacustrine sulphate-poor" field (Fig. 10d).

The determination of oleanane in two samples reveals that the age of the studied oil shales is Cretaceous or younger and the presence of terrestrial organic matter input (Whitehead 1973, 1974; Ekweozor et al. 1979; Grantham et al. 1983; Riva et al. 1988; Udo and Ekweozor 1990) (Fig. 5c, d). Having different oleanane abundance and oleanane index [(oleanane/hopane) * 100] (Table 3) in both examples indicates that the amount of terrestrial input changes periodically. While the oleanane index of the sample taken from the lower levels of the sequence (AD-2) is 7 reflecting a weak terrestrial organic matter input, the oleanane index of the oil shale sample (AD-47) taken from the upper levels is 100 pointing to an important terrestrial organic matter input. Despite the high terrestrial organic matter content of the oil shale sample AD-47 (determined by the high oleanane content), the high HI value (673mgHC/gTOC) indicates the Type I kerogen characteristic. This situation, which develops due to the presence of oleananes, can be explained by the
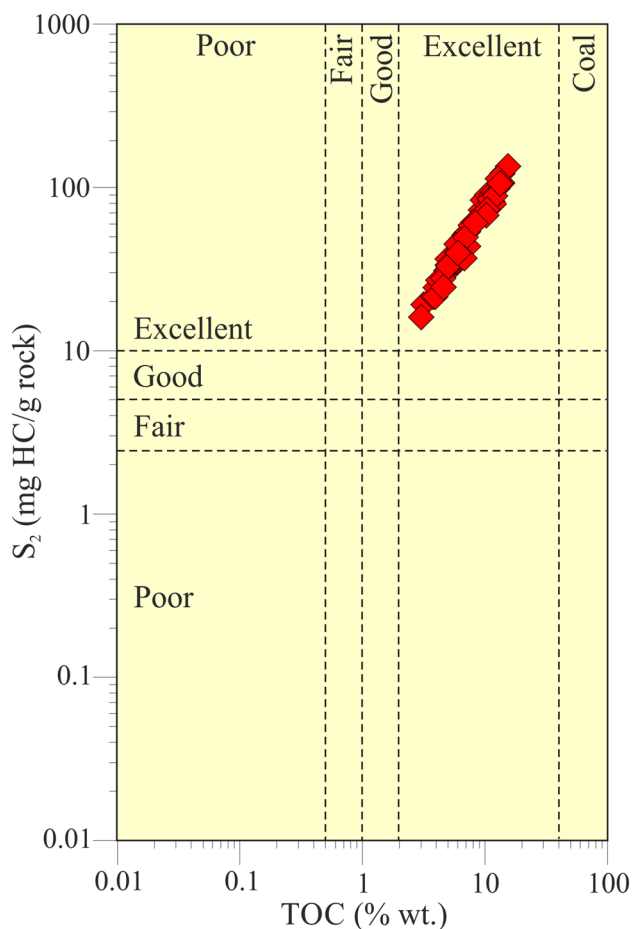
Fig. 8 Plot of Rock–Eval S_2 versus TOC (Dembicki, 2009) for the analyzed oil shale samples from Alpagut section, indicating the oil shales' excellent source rock potential

terrestrial organic matter input (Ekweozor and Udo 1988; Riva et al. 1988), which consists of angiosperms (belonging to Type I kerogen) having lipid-rich sections and producing abundant resin. Low regular sterane/hopane ratio is related to terrestrial and/or microbial organic matter (Tissot and Welte 1984). According to Moldowan et al. (1985), this ratio in non-marine oils is much lower than marine oils. The low sterane/hopane ratios calculated for studied oil shales (Table 3) might be related to their deposition in a lacustrine environment and their algal and significant bacterial organic matter contents as well.

T_{max} values of 418–443 ℃ (average 430 ℃) indicate that oil shales consisting predominantly of Type I kerogen and little of Type II kerogen are of immature in character that is

they do not reach in oil generation window yet. This is also supported by very low estimated PI values (average 0.02) (Table 1). CPI value of more than 1 and higher Pr and Ph concentrations with respect to n-alkanes imply that oil shales are not mature (Table 2). 22S/(22R + 22S) homohopane ratio increases with increasing maturity and attains equilibrium at the ratio of 0.57–0.62 which can be used for the immature-early maturity range (Peters and Moldowan 1993; Waples and Machihara 1991). 20S/(20R + 20S) sterane isomerization and **ββ/(αα+ββ)** sterane isomerization attain equilibrium at the ratios of 0.52–0.55 and 0.67–0.71, respectively, and these ratios can be used for the immature-maturity range (Seifert and Moldowan 1986). In addition, Ts/(Ts + Tm) and diasterane/sterane ratio also increases with increasing maturity. In a general sense, 22S/(22R + 22S) homohopane, 20S/(20R + 20S) sterane, Ts/(Ts + Tm) and diasterane/sterane ratios reflect immature character of oil shales (Table 3). The average **ββ/(αα+ββ)** sterane ratio of 0.27 indicates that oil shales are of early mature character and are at the oil generation window (Fig. 11). MA(I)/MA(I + II), TA(I)/TA(I + II) and TA[C_{20}/(C_{20} + C_{28} 20R)] steroid ratios increase from 0 to 100% with increasing maturity, and they can be used for describing early mature–late mature range (Seifert and Moldowan 1978; Mackenzie et al. 1981; Peters et al. 2005; Beach et al. 1989). MA(I)/MA(I + II) (0.08–0.04), TA(I)/TA(I + II) (0.11–0.05) and TA[C_{20}/(C_{20} + C_{28} 20R)] (0.80–0.25) steroid ratios of the studied oil shales reflect immature–mature range. 2-MP and 3MP isomers (**ββ/(αα+ββ)**-isomers) are thermally more stable than 1-MP and 9- MP (α-isomers) isomers, and **β/ α** MP ratio (MPI-3) can be used for maturity estimation (Radke et al 1982). For the studied oil shales, this value has been calculated to be very high (1.49–1.34), indicating mature organic matter. During the maturation, increase in 4-MDBT with respect to 1-MDBT is attributed to higher thermal stability (Radke et al. 1986; Dzou et al. (1995) . In the studied oil shales, the 4-MDBT content is higher than 1-MDBT content, and the calculated MDR is in the range of 4.25 to 3.31, reflecting mature organic matter. Maturity results obtained from MP and MDBT data are not compatible with immature source rock assessment using the pyrolysis, GC and other biomarker data. Budzinski et al. (1995) have shown that methyl-phenanthrene distributions vary with respect to deposition conditions. In their study on oil and condensate set, Chakhmakhchev et al. (1997) stated that MDR is not dependent on vitrinite reflectance. It has been revealed that the depositional environment and lithology have an effect on the distribution of ADBTs in coal samples at maturity levels below vitrinite reflectance
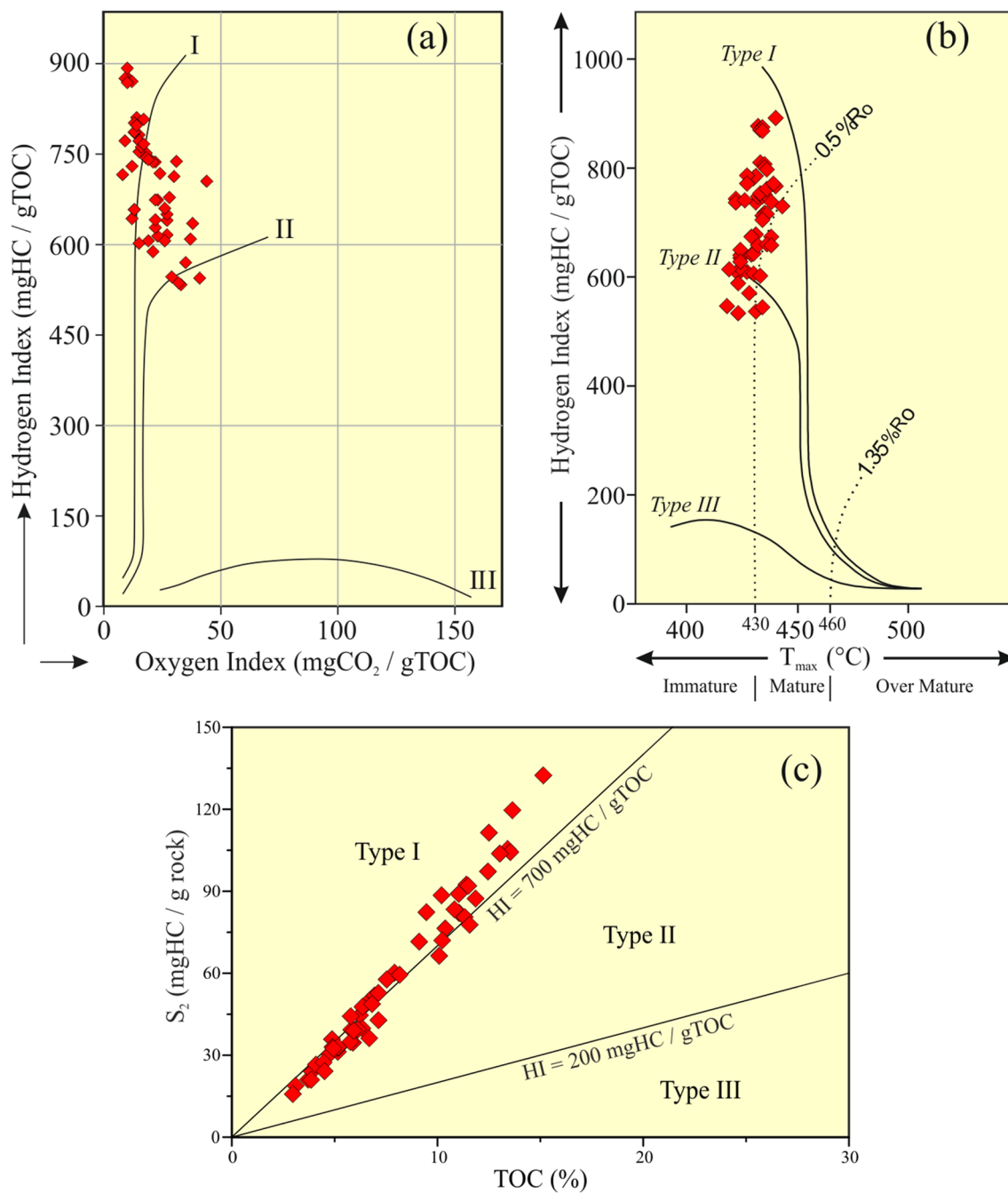
Fig. 9 Plots of (**a**) HI versus OI, (**b**) HI versus Tmax and (**c**) S_2 versus TOC for the analyzed oil shale samples from the Alpagut section
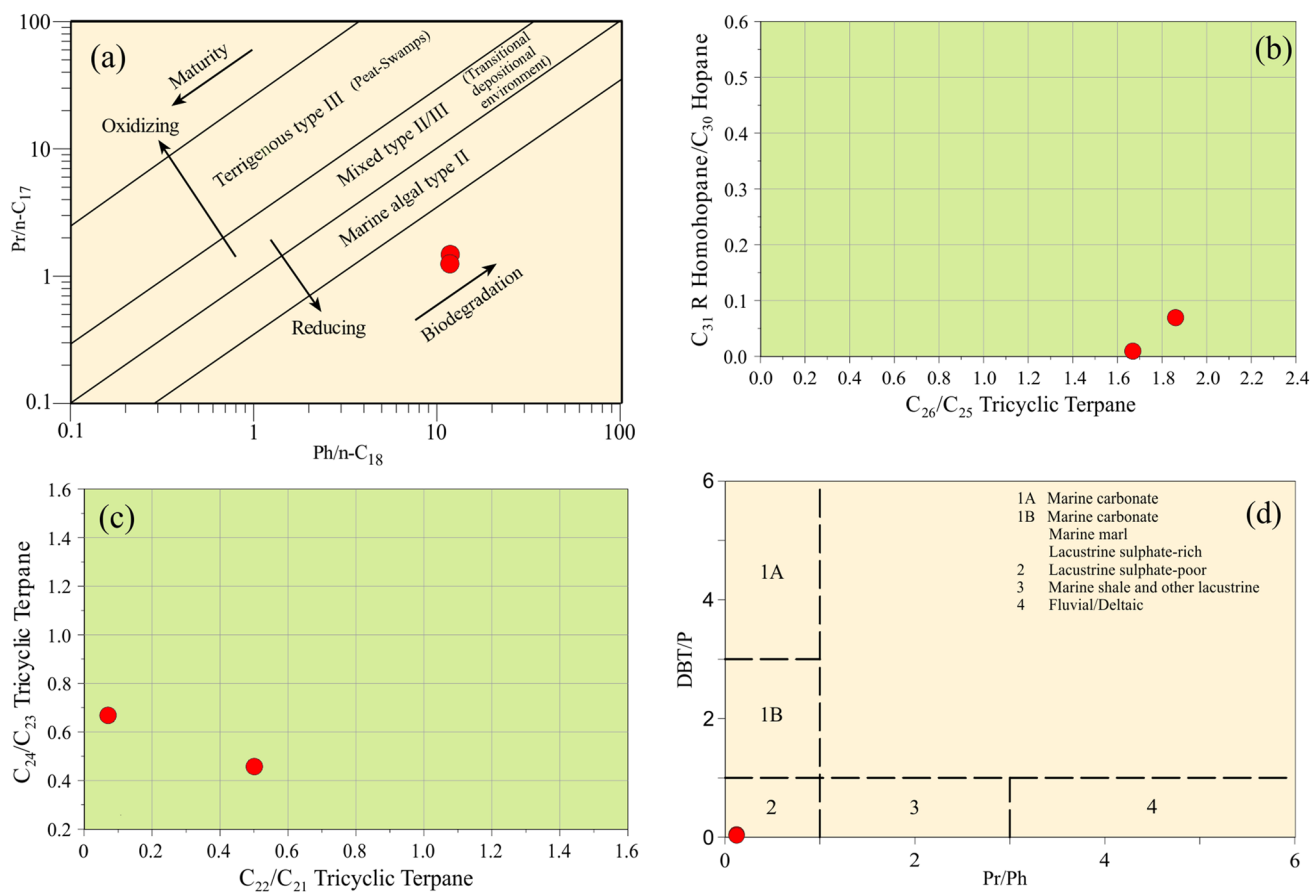
Fig. 10 Bivariate diagrams of Pr/n-C$_{17}$ versus Ph/n-C$_{18}$ (**a**), C$_{31}$R homohopane/C$_{30}$ hopane versus C$_{26}$/C$_{25}$ tricyclic terpane (**b**), C$_{24}$/C$_{23}$ versus C$_{22}$/C$_{21}$ tricyclic terpane (**c**) and DBT versus Pr/Ph for the oil shale extract samples from the Alpagut section

values of 1.35 (Radke et al. 2000; Dzou et al. 1995). Therefore, very high MPI-3 and MDR ratios of the studied oil shales might be related to deposition environment, organic matter input and lithology rather than maturity.

Conclusions

The Miocene Alpagut oil shales in the Çankırı-Çorum basin with very high TOC contents have an excellent source rock character. Very high S$_2$ and HI values and very low OI values and biomarker data show that studied shales are represented by organic matters of predominantly Type I kerogen and little Type II kerogen (dominantly algal and bacterial). Oil shales are characterized by high organic matter content, dominantly Type I kerogen and very high HI, Potential Yield (PY) values and very high hydrocarbon potential, and they are capable of generating hydrocarbon and thus have a high oil potential. High C$_{26}$/C$_{25}$, C$_{24}$/C$_{23}$ and low C$_{22}$/C$_{21}$ tricyclic terpane, C$_{31}$R/C$_{30}$ hopane and DBT/P ratios indicate that studied oil shales were deposited in a lacustrine environment. Moreover, very low Pr/Ph ratios imply that deposition environment has an anoxic character.

Low T$_{max}$ and PI values obtained from pyrolysis analysis, high CPI and Pr/nC$_{17}$ and P/nC$_{18}$ ratios and very low 22S/(22S + 22R) homohopane, 20S/(20S + 20R) sterane, diasterane/sterane and (Ts/(Ts + Tm)) ratios obtained from GC
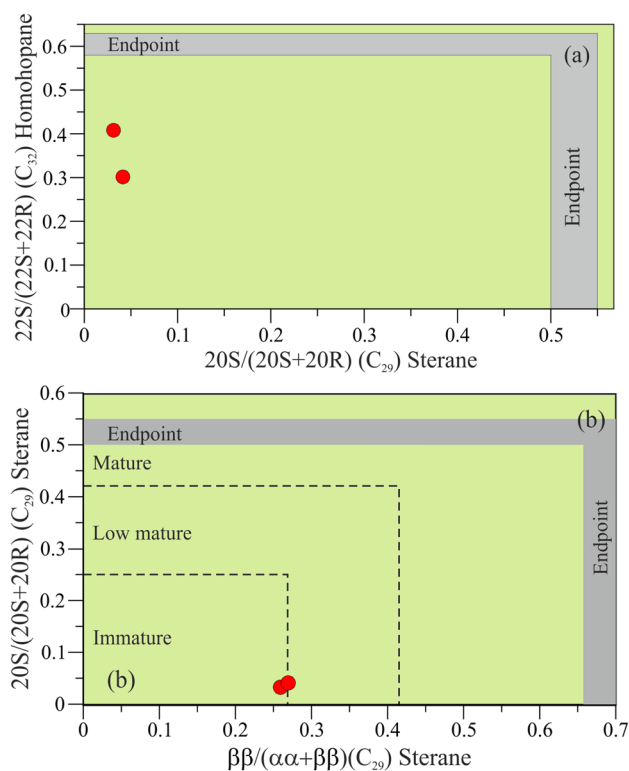
Fig. 11 Bivariate diagrams of 22S/(22S + 22R) homohopane versus 20S/(20S + 20R) sterane (**a**), and 20S/(20S + 20R) sterane versus $\beta\beta$/$(\alpha\alpha + \beta\beta)$ sterane (**b**) for the oil shale extract samples from the Alpagut section

analysis point out that studied oil shales are not mature yet and not regarded as being reached the oil generation window.

Although organic matter they contain may greatly transform to hydrocarbon (particularly oil), studied oil shales are considered as potential source rocks that have not been experienced any hydrocarbon generation.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical approval The article is an original article, and we declare that the article has not been published before and is not being submitted to any other journal for publication.

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