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Source Rock Potential and Oil to Source Rock Correlation of the Upper Cretaceous (Campanian-Maastrichtian)–Lower Paleocene Units in the Malatya Basin, East Anatolia, Turkey

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The hydrocarbon potential of possible shale source rocks from the late Cretaceous to early Paleocene (Sarıkız and Kapullu formations) of the Malatya Basin is evaluated using an integration of organic geochemistry. The TOC values for about 67 samples are between 0.03% and 1.32%, and hydrogen indices (HI) are almost below 100 mgHC/gTOC. They contain Type III/IV kerogen and most of the samples are thermally immature. The TOC values of limestone and coaly facies of the unit ranging from 0.28 to 1.28 wt% and 2.18 and 11.89 wt%, respectively; however, they have low S_2 except for the coaly samples. Nevertheless, high maturity samples, where T_{max} averages 543°C that could be resulted from local heat sources. According to the biomarker characteristics of oil seeps from the late Cretaceous carbonates and bituminous from the late Eocene limestones, they have the same origin and however, no oil-to-source rock correlation has been performed in the basin. A negative correlation and no having source rock potential of the Upper Cretaceous shales and biomarker results suggest that seep oils could be originated from the older carbonates source rock than Upper Cretaceous in the basin.

Keywords: Malatya basin, Neo-Tethys southern branch, Sarıkız and Kapullu formations

1. INTRODUCTION

The Malatya Basin is located between Sivas basin and Southeastern Anatolia petroleum province (Figure 1). Previous studies of the general geology, tectonic setting, and mineralogy–petrology in the basin have been published (e.g., Bozkaya and Yalcin, 1992; Gurer, 1994; Ayyildiz et al., 2009). However, there are scanty published studies (Ayyildiz and Önal, 2005; Önal, 2009) about petroleum geology Also, only the Akçadağ-1 well has been drilled by MTA in 1970 (Figure 1); however, could have not be discovered petroleum.

Due to containing oil seeps, the Upper Cretaceous deep marine shales are generally assumed to be the source of the oil seep at the basin. However, there is lack of good surface and subsurface data, including source rock samples to correlate with molecular fingerprints of oils. Therefore, there are many questions has been unanswered in the basin yet. Biomarkers studies are broadly and successfully used in the petroleum exploration to identify groups of genetically related oils, to correlate oils with source rocks, and to describe the probable source rock depositional environments

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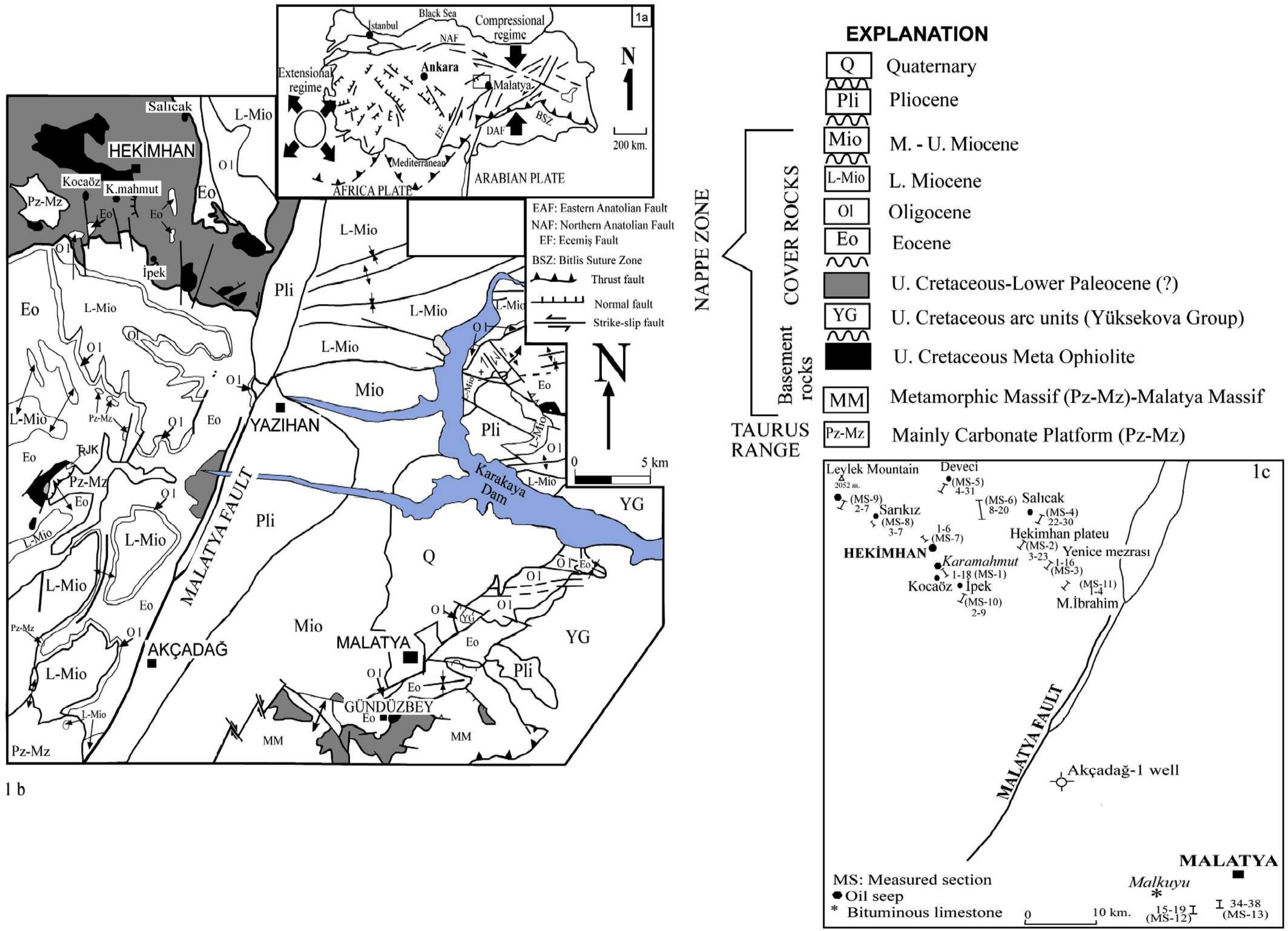


FIGURE 1 (a) Location map of the studied area. (b) Simplified geologic map of the study area (modified from Önal, 2009; used with permission). (c) Location map of stratigraphic measured sections.

for migrated oil of uncertain origin (Moldowan et al., 1985; Peters and Moldowan, 1993; Peters et al., 2005). There are lots of investigations about oil-oil and oil-source rock correlation in the different country (e.g., Roushdy et al., 2010; Asif et al., 2011). Therefore, some oil seeps (from Upper Cretaceous and Eocene aged rocks) and possible source rock shale samples were analyzed. Their geochemistry was studied to (a) evaluate their organic source and the depositional environment of the source rocks, (b) understand genetic relationships among these oil seeps and bituminous, (c) determine their thermal maturity, and (d) establish the oil–source rock correlations. This study is of significant importance for further petroleum exploration in the east Anatolia basins.

2. GEOLOGIC AND STRATIGRAPHIC SETTING

The Malatya basin is an Upper Cretaceous to Tertiary aged graben developed within the Neo-Tethys southern branch and as a whole is a major interior basin in East Anatolia, exposing Upper Cretaceous–Tertiary volcano-sedimentary rocks up to 4.5 km thick (Önal and Kaya, 2007; Figure 1). Due to sedimantological differences in Upper Cretaceous to lower Paleocene unit, it is suggested that the basin could be split into two sub-basins such as Hekimhan and Gündüzbey (Ayyildiz and Önal, 2006). The Upper Cretaceous–Lower Paleocene transgressive-regressive sequence shows a transition from terrestrial environments to reef carbonate and flysch-like deposits that were deposited in a fore-arc environment in the Gündüzbey subbasin (Kırmızıgüney, İnekpınarı, and Kapullu formations; Önal and Kaya, 2007), while it is represented by terrestrial, reefal, deep marine deposits with volcanics, shelf carbonates, and evaporites in the Hekimhan sub-basin (Medik, Tohma, and Sarıkız formations; Ayyildiz et al., 2009).

The middle-upper Eocene (the Yıldıztepe, Suludere, and Gedik formations) and Oligocene (Dumanlar Formation) to lower Miocene (Akyar Formation) interval is represented by continental, shallow carbonate and deep-sea Flysch-like deposits. The basin was affected by an extensional and single-directional compressional tectonic regime during the middle Miocene and the upper Miocene and Pliocene time, respectively. During the middle Miocene time, the basin gave rise to uplift and subsidence, and resulted in the deposition of red clastics and lacustrine sediments (Karaca formation). The upper Miocene and the Pliocene rock units consist of alluvial and fluvial deposits (Önal and Kaya, 2007).

3. MATERIAL AND METHODS

Sampling was primarily focused on shale, limestone and coaly facies of the Sarıkız formation and oil seeps from the Hekimhan subbasin, and the Kapullu formation and the late Eocene bituminous bearing limestones (in the Gündüzbey sub-basin). Rock-Eval-6 analyzer, Gas Chromatography-Mass Spectrometry (GC-MS) and bulk δ^{13}C isotope analyses (GV Instruments Isoprime EA-IRMS instrument using the NBS22 standard) were performed at the TPAO-Research Center (Ankara) on the source rock samples and oil seeps (Espitalié et al., 1986). Organic matter types were determined from HI *vs.* T_{max} and HI *vs.* OI diagrams from TPAO Research Center.

4. ORGANIC GEOCHEMICAL INVESTIGATIONS

4.1. Source Rock Quality of the Upper Cretaceous Units and Distribution

The TOC and HI values of shale samples are between 0.03 and 1.32 and from 4 to 159 (mgHC/gTOC) in the basin, respectively (Table 1). The TOC and genetic potential values of

TABLE 1
TOC and Rock-Eval-6 Results of the Sarıkız and Kapullu Formations in the Malatya Basin

Formation (Age)	*Sample Location*	*Sample Number*	*Rock Types*	*TOC, %*	S_1, *ppm*	S_2, *ppm*	S_3, *ppm*	*Genetic Potential* ($S_1 + S_2$)	T_{max}, °*C*	*HI*	*OI*	*IP*
Sarıkız Formation (Campanian-Maastrichtian)	Karamahmut village (MS-3)	MS1-1	Shale	0.13								
		MS1-3	Shale	0.15								
		MS1-4	Shale	0.09								
		MS1-6	Shale	0.11								
		MS1-8	Shale	0.14								
		MS1-11	Shale	0.29	0	90	400	90	429	32	143	
		MS1-13	Shale	0.30								
		MS1-15	Shale	1.32	0	210	100	210	426	159	76	
		MS1-18	Shale	0.17								
	Hekimhan Plateau (MS-2)	MS2-3	Shale	0.14								
		MS2-9	Shale	0.16								
		MS2-12	Shale	0.07								
		MS2-16	Shale	0.05								
		MS2-18	Shale	0.10								
		MS2-22	Shale	0.11								
		MS2-23	Shale	0.14								
	Yenice Mezrası (MS-3)	MS3-1	Shale	0.16								
		MS3-3	Shale	0.09								
		MS3-7	Shale	0.10	20	20	320	40	422	20	230	0.5
		MS3-8	Shale	0.05								
		MS3-10	Shale	0.18								
		MS3-11	Shale	0.18								
		MS3-13	Shale	0.31	0	20	400	20	433	6	118	
		MS3-15	Shale	0.14								
		MS3-16	Shale	0.04								
	Salıcak village (MS-4)	MS4-22	Shale	0.16								
		MS4-27	Limestone	0.03								
		MS4-29	Shale	0.07								
		MS4-30	Shale	0.43	0	110	670	110	422	26	156	

(*continued*)

TABLE 1
(*Continued*)

Formation (Age)	Sample Location	Sample Number	Rock Types	TOC, %	S_1, ppm	S_2, ppm	S_3, ppm	Genetic Potential ($S_1 + S_2$)	T_{max}, °C	HI	OI	IP
	N of Hekimhan (MS-6)	MS6-08	Shale	0.19								
		MS6-09	Shale	0.17								
		MS6-12	Shale	0.14								
		MS6-13	Shale	0.16								
		MS6-19	Shale	0.11								
		MS6-20	Shale	0.06								
	Hekimhan-Kurşunlu road (MS-7)	MS7-01	Shale	0.29								
		MS7-02	Shale	0.12								
		MS7-03	Shale	0.11								
		MS7-06	Shale	0.22								
	Sarıkız village (MS-8)	MS8-03	Shale	0.09								
		MS8-04	Shale	0.09								
		MS8-06	Shale	0.12								
		MS8-07	Shale	0.14								
	S of Leylek M. (MS-9)	MS9-1	Coaly mudstones	2.18	60	800	290	860	380	36	13	0.06
		MS9-10	Coal	11.89	120	1,460	5,930	1,580	385	12	49	0.07
		MS9-06	Limestone	1.2	0	220	350	220	555	18	29	0.07
		MS9-09	Limestone	0.44	0	50	180	50	554	7	14	
		MS9-02	Limestone	1.28	50	50	2,390	100	520	4	187	0.5
		MS9-03	Limestone	0.49								
		MS9-04	Limestone	0.67	0	100	260	100	554	15	39	
		MS9-07	Limestone	0.28								
	İpek town (MS-10)	MS10-02	Shale	0.32								
		MS10-04	Shale	0.66	100	410	810	510	422	62	123	0.19
		MS10-05	Shale	0.42	50	160	660	210	427	38	157	0.23
		MS10-07	Shale	0.22								
		MS10-09	Shale	0.29								
Kapullu Formation (late Cretaceous to early Paleocene)	Kapullu (MS-12)	MS12-15	Shale	0.37	90	350	290	440	427	94	78	0.20
		MS12-18	Shale	0.08								
		MS12-19	Shale	0.57	50	370	350	420	425	64	61	0.11
	Yeşilyurt (MS-13)	MS13-34	Shale	0.05								
		MS13-36	Shale	0.23								
		MS13-38	Shale	0.13								

coaly (MS 9-1, MS 9-10) samples are 2.18–11.89 wt% and 860–1,580 ppm, respectively. The sample has bituminous with fractures, showing high values (44.52 wt%); however, its HI value is very low (35 mgHC/gTOC). For coaly mudstones and coal samples, S_1 and S_2 range from 60 to 120 ppm and from 800 to 1,460 ppm, respectively. A plot of HI versus T_{max} (Figure 2a) show that five samples are in the "over mature" ($T_{max} = 520$–$555°C$ and $R_0 > 1.3\%$), while the others are within the "immature" but close to threshold maturity for Type III kerogen. The HI versus OI diagram show that they contain mainly type IV and some type III kerogens (Figure 2b). All samples of genetic potential (GP) values are lower than 2,000 ppm (Table 1).

4.2. Geochemical Characteristics of the Source Rock and Oil Seeps

Because the degraded natures of these oils from GC (Figure 3, Table 2), Carbon Preference Index (CPI) and Pr/Ph values could not be used for maturation and depositional environment interpretation. It has been commonly assumed that a predominance of C_{27} steranes in an oil or rock extract would signify an algal or marine input; however, C_{29} steranes signified the presence of higher plant or terrestrial input. C_{27} steranes of the Karamahmut oil seeps are not visible due to degradation. However, the bituminous samples of the Malkuyu and Leylek-05 samples show both C_{27} and C_{29} steranes (Figures 4 and 5).

4.3. Maturation and Alteration Degree of the Oil Seeps

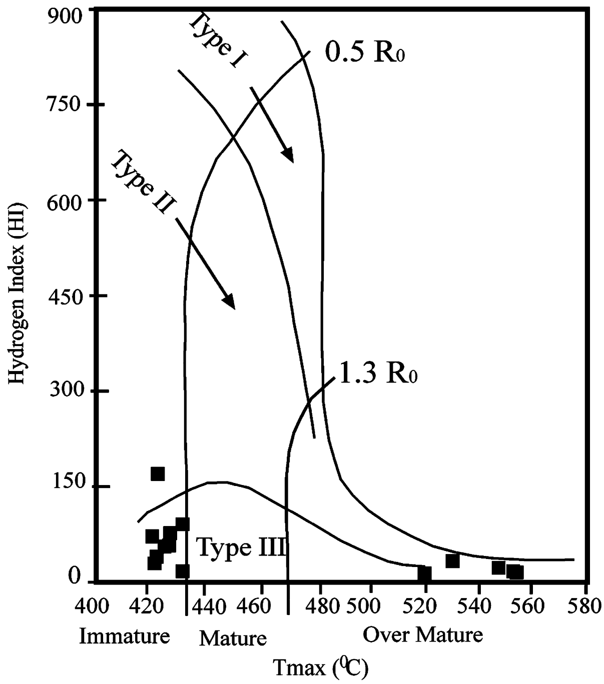
The maturation of crude oils is an important parameter for understanding their thermal history and is generally determined by several biomarker parameters (Seifert and Moldowan, 1978, 1981; Mackenzie 1984; Peters et al., 2000). Determination of maturation level of the oil seeps in the basin is very difficult due to the degraded characterizations. C_{32} 22S/22S + 22R values are the same for oil seeps; however, the Malkuyu bituminous shows lightly differences (Figure 5d and Table 2). A plot of regular sterane parameters C_{29} 20S/20S + 20R versus C_{29} $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ shows that the oil seeps and bitumen are slightly similar, and are in the mature level (Peters and Moldowan, 1993).

The GC of the oil seeps show that the samples are alterated (Figures 3a and 3b). n-Alkane ratio is low, and branch-cyclic alkanes are not differentiated each other. Some geochemical properties of the oil seeps; for examples: decreasing of C_{14}-C_{16} bicyclic alkanes, observing diterpanes, alteration of C_{21}-C_{22} sterane and decreasing of C_{27} ratios, presence of 30-norhopane and hexacyclic hopane series, and absence of 25-norhopane, indicating that alteration level is medium degree at least.

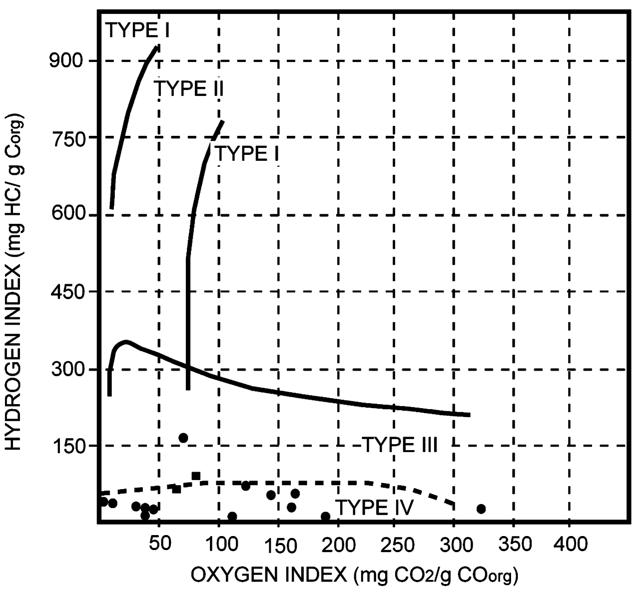
4.4. Organic Facies and Carbon Isotope Ratios

Oil to oil seep correlation has been investigated taking into consideration the degradation degree of seep oils samples. Alkanes with high molecular weight nC_{29}–nC_{31} are observed as low in the oil seeps. Tricyclic terpane distributions of the source rock and oil seep samples are shown in Figures 3 and 4. In the Malatya basin oil seeps contain a significant abundance of a C_{23} tricyclicterpane, indicating that oils yielded from carbonate sedimentary rocks. In addition to this, C_{19}-C_{21} tricyclic ratios are less than C_{23} indicate that the oil seeps were originated from marine organic matter. The ratio of C_{24} tetracyclic to C_{26} $(S + R)$ tricyclic (>1) also suggests that the oil was sourced from a carbonate (Rulkötter and Philip, 1981).

The carbon isotopic compositions of crude oils have been used to study depositional environments and types of organic matter (Sofer, 1984). An analysis of "Whole-bitumen" $\delta^{13}C$ composition of two seep samples (Upper Cretaceous) are −25.15 and −25.04‰.

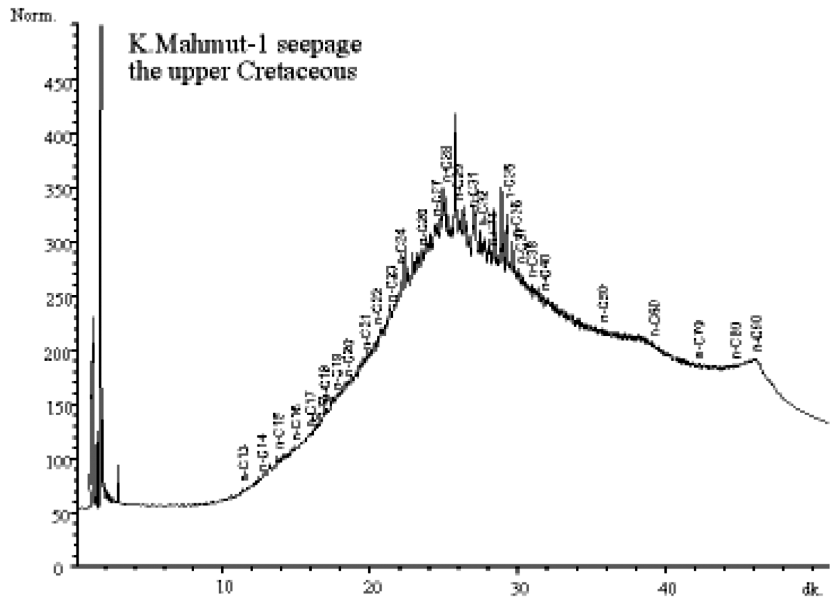


(a)

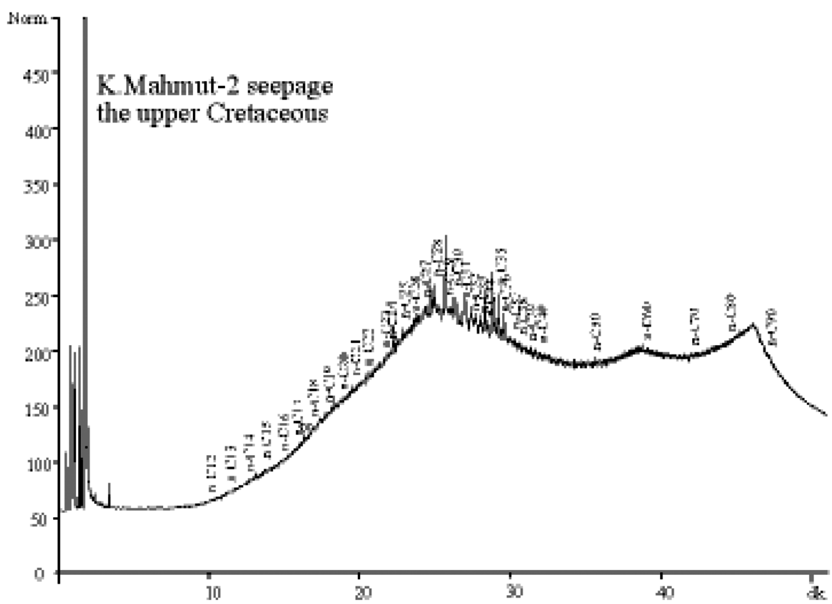


(b)

FIGURE 2 Results of rock-eval pyrolysis for the Sarıkız and Kapullu formations plotted on (a) hydrogen index (HI) vs. Tmax and (b) hydrogen index (HI) vs. oxygen index (OI) kerogen classification diagrams (Espitalié et al., 1986, used with permission).



(a)



(b)

FIGURE 3 Gas chromatogram of residue oil samples of the Karamahmut 1 and 2.

TABLE 2
Organic Geochemical Results for the Residue Oil Samples in the Malatya Basin

Geochemical Data	*Late Cretaceous*			*Late Eocene:*
	K.mahmut-1	*K.mahmut-2*	*Leylek-05*	*Malkuyu*
Pristane/Phytane	0.69 (?)	n.d	—	—
Ts/Tm	0.21	0.14	0.97	0.52
C_{29}/C_{30}	1.5	1.3	1.3	0.82
C_{29} 20S/20S + 20R	0.44	0.49	0.46	0.48
C_{29} $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$	0.42	0.33	0.48	0.18
C_{32} 22S/22S + 22R	0.58	0.58	0.57	0.45
CPI (C_{16}-C_{30})	0.60	0.71	—	—

5. DISCUSSION AND CONCLUSIONS

Analysis from outcropped shale samples, and oil seeps from reefal carbonates in the Malatya Basin, eastern part of Turkey, allowed the following conclusions to be drawn: the TOC, HI, $T_{\max}$, and GP values of shale samples are generally lower than 0.5 wt%, 300, 435°C and 2,000 ppm, respectively, and those values indicate that marine shales could not be source rocks potential in both

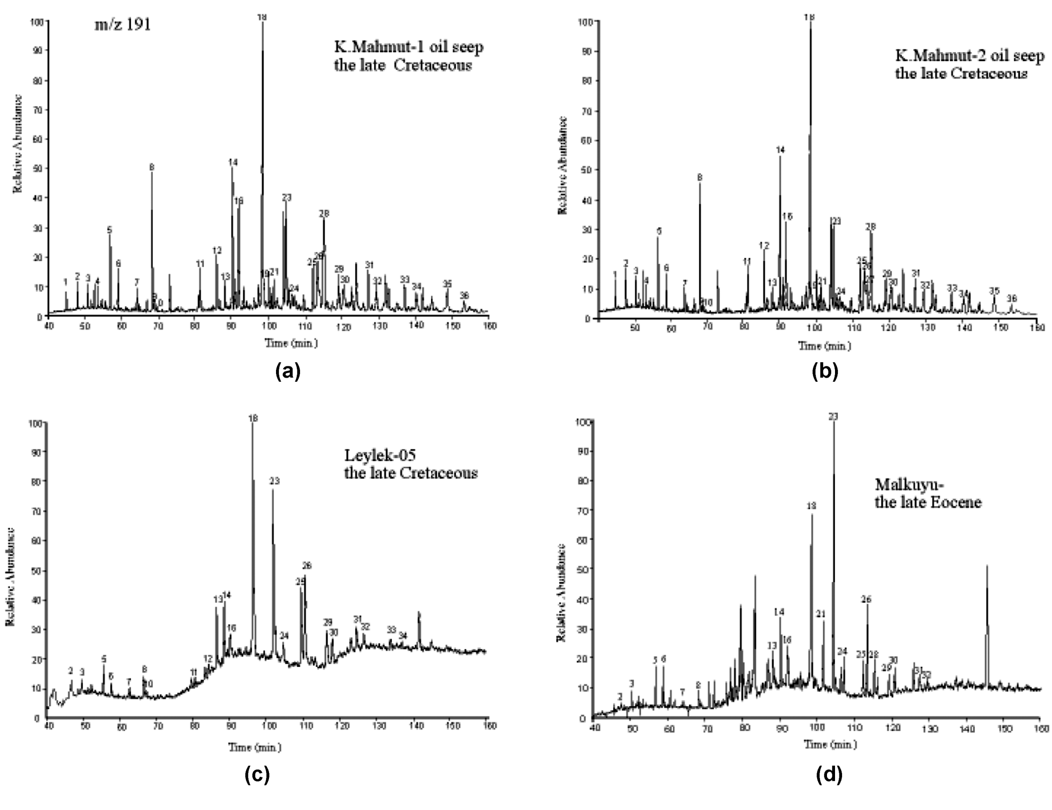


FIGURE 4 Terpane mass chromatogram (m/z 191) for the residue oil samples (a, b, c) and bituminous limestone (d).

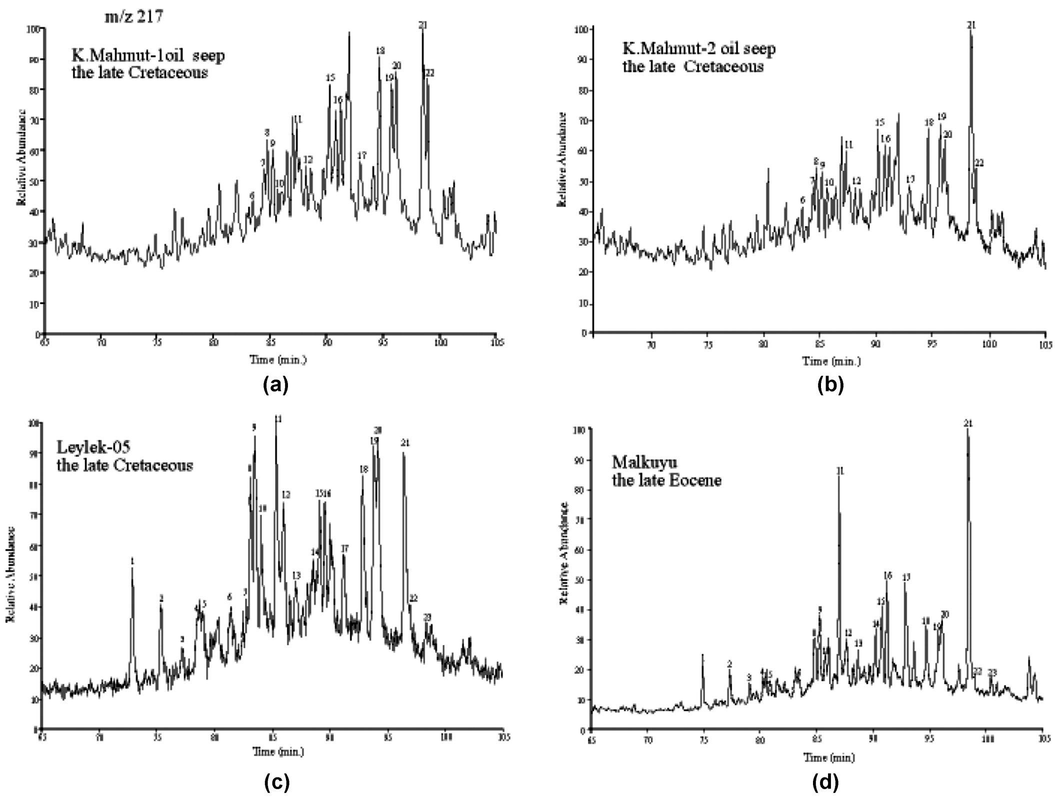


FIGURE 5 Sterane mass chromatogram (m/z 217) for the residue oil samples (a, b, c) and bituminous limestone (d).

sub-basin. Although $T_{\max}$ values below 435°C suggest that they are probably close to immature, some samples TOC wt% from the MS-9 show that from moderate to good with over mature source rock potential. High maturation might be related to the proximity of volcanic intrusive (Hasancelebi and Leylekdagi) in the Hekimhan subbasin. Therefore, we can say that limestone facies that have sufficient TOC wt% can be candidate source rock with a thickness of 50–100 m, where it is not attained over mature. Generally, shale samples are immature in the study area as stated previously. However, the immature source rock could be attained threshold maturation in the Malatya plain due to about 4 km extra sedimentary unit. Biomarker characteristics of the source rocks and oil seeps indicate that it was deposited in reducing environment, and oil seeps were yielded from the same carbonate and mature source rock from C_{29} 20S/20S + 20R versus C_{29} $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ diagram. The Malkuyu bituminous have little tricycles terpanes and pregnane/sterane, and separated from the others. Usually C_{31}- or C_{32}-homohopanes are used for calculations of the 22S/(22S + 22R) ratio. The 22S/(22S + 22R) ratio rises from 0 to about 0.6 during maturation. Sediments with the maturity level equivalent to Ro = 0.6% shows 22S/(22S + 22R) ratios in the range 0.50 to 0.54 (Peters and Moldowan, 1993). In this present study, that ratio of the C_{32} 17α-hopanes range from 0.45 to 0.58 (Table 2). The similarity of these values except the Malkuyu bituminous also suggested that the originated organic matter in the basin has reached a good stage of thermal maturity. According to the biomarker characteristics, they have the same origin and there has no correlation between GC and GC-MS results of oil to source rock samples. Those of δ^{13}C compositions are in the ranges of −25‰, suggesting a similar source rocks generation and deposited in a saline–hypersaline environment (Sofer, 1984; Peters et al., 2005). According to Chung et al. (1992), δ^{13}C values suggest that oils are from Mesozoic carbonates source rock interval. Generally, oil seeps are observed from reef facies over the ophiolitic and carbonates basement. Also, source rock potentials have not been yet identified within the Hekimhan subbasin could be indicate that the studied oil seeps could be originated from older carbonates source rock beneath the Upper Cretaceous in the basin.

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