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DEPOSITIONAL ENVIRONMENT AND ORGANIC GEOCHEMICAL CHARACTERISTICS OF LOWER EOCENE BITUMINOUS ROCKS, IN THE KÜRNÜÇ/GÖYNÜK-BOLU AREA

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Research Article

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ABSTRACT

In this study, dark gray and dark brown colored, organic-carbon rich bituminous rocks (bituminous marl and bituminous shale) exposing around the Kürnüç area (Göynük, Bolu) are investigated by means of organic geochemical characteristics. In this respect, rock lithologies, depositional environments, rock source potential, kerogen and organic maturity types and hydrocarbon generation potentials of bituminous rocks were determined. For this reason, pyrolysis (Rock Eval–VI) analysis, gas chromatography (GC) and gas chromatography-mass spectrometer (GC-MS) analyses were carried out. In addition, spore color index (SCI) was determined with organic petrographic method and stable carbon analysis ($\delta^{13}C$) of the samples were also conducted. Lithology of the studied samples is of clastic source and the depositional environment is a lagoon with a partial connection to the sea. In bituminous rocks with excellent source rock potential TOC values are in the range of 2.52-8.38 wt % (average 6.08 wt %). With the exception of two samples (Type II) kerogen type of all samples is Type I. According to pyrolysis, GC and GC-MS organic maturity results, all the samples are in immature stage. Organic geochemical data indicate that bituminous rocks have an excellent oil generation potential and there is no organic contamination.

1. Introduction

The study area is located in Adapazarı H-24 d2 sheet, in southern part of Göynük, Bolu. In this respect, dark gray to dark brown colored, organic rich bituminous rocks (bituminous marl and bituminous shale) cropping out around Kürnüç (Göynük/Bolu) were investigated. To do that, the source rock potential kerogen type, organic maturity types and hydrocarbon generation potentials of bituminous rocks were determined. Besides, the source rock lithology and the depositional environment, which are important for the source rock potential, were also investigated.

In the vicinity of study area, the drilling explorations related to bituminous shales are conducted by MTA with the cooperation of Turkish Coal Enterprise (TKİ) and Turkish Petroleum Corporation (TPAO). Therefore; bituminous rocks around the study area has also been the subject of many investigators from the point of hydrocarbon and element enrichments view (Şeker and Kesgin, 1991; Sarı and Sonel, 1995; Şener and Şengüler, 1998; Büyükutku et al., 2005; Sarı and Aliyev, 2005; Aliyev et al., 2006; Sarı et al., 2007; Kara and Korkmaz, 2008; Sarı and Geze, 2008; Şengüler, 2012).

Bituminous rocks are deposited in the condition of reducing environment, which form as a result of the accumulation and decomposition of dead algae at the bottom. They die as highly dissolved oxygen in water and the algal productivity, which developed in the enrichment of nutrient (phosphates and nitrates necessary for algae), and in later stages the oxygen and nutrient needed by the high organic productivity is not satisfied by the source in water. Bituminous rocks are formed as; bituminous shale, bituminous claystone and bituminous marl according to lithological

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characteristics that develop based on geochemical conditions of the depositional environment. Gradually increasing oil prices in the world have impelled countries to explore new alternative energies. Within this context, the need for the alternative energy has again revived bituminous rocks. With this purpose, intensive exploration related to bituminous rocks (especially bituminous shales) and investigations related to hydrocarbon production are carried out in our country as well as in all over the world. Thus; drilling exploration and studies about reservoir estimation continue in Hatıldağ/Göynük (Ankara) and Beydilli/Nallıhan (Ankara) bituminous shale license areas within the scope of a project conducted by TKİ and TPAO. Considering mining costs, the oil is extracted either by excavating bituminous shale from surface (by retort method) or by in situ electrofrac process (Symington et al., 2008). In this process, the thickness of bituminous shales, the amount of organic material and especially the kerogen type to be in Type-I kerogen are significant.

In this study, the depositional environments of Lower Eocene bituminous rocks and source rock potentials were assessed in detail using pyrolysis analyses (TOC %, HI, OI, Tmax, S1, S2, S3), methods of gas chromatography (GC) and gas chromatography–mass spectrometer (GC-MS), stable carbon isotope analysis ($\delta^{13}C$) and organic petrographic analyses. Bituminous rocks have excellent source rock potential according to S1 (average 1.28 mg HC/g rock) and S2 (average 45.51 mg HC/g rock) hydrocarbons in addition to TOC values ranging between 2.52-8.38 %. According to hydrogen index (HI)/oxygen index (OI), Hydrogen Index (HI)/Tmax, S2/TOC diagrams, and Hydrocarbon Type Index (S2/S3) and Hydrogen Index limit values, the kerogen type is Type-I and Type-II (only in two samples). With respect to organic petrographic methods, samples are composed of 100% Algal+Amorph organic material. The organic material type is lacustrine algal considering the ternary diagram of C27, C28, C29 steranes. According to CV values estimated by $\delta^{13}C$ (saturated) and $\delta^{13}C$ (aromatic) hydrocarbon data the organic material type is terrigenous in some samples and is marine origin in others. However; it should be kept in mind that the results of isotope analysis present values in very large ranges. Nevertheless; these results show compatibility with Type I and Type II kerogen when it is considered that the depositional environment is lagoon partly connected with sea. It is seen that bituminous rock samples are still in immature stage based on biomarker studies, Tmax, production index (PI) and SCI values. Besides; it was determined that samples weer immature by m/z 191 triterpane and m/z 217 sterane biomarker data (Ts/(Ts+Tm), 22S/(22S+22R), αββ/(αββ+ααα), 29Ts/ (29Ts+norhopane), 20S/(20S+20R)). According to genetic potential values (S1+S2) (18400-70250 ppm) bituminous rocks have a good source rock potential. However; according to S2/S3 ratio, Hydrogen Index (HI) – TOC and S2 – TOC diagrams, the studied samples possess a hydrocarbon potential that can produce oil.

2. Material and Method

Pyrolysis analyses (Rock Eval-VI), gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS), stable carbon isotope analyses ($\delta^{13}C$) and Spore Color Index (SCI) studies were performed in Geochemistry Laboratories of TPAO Research Group. Pyrolysis estimations were carried out by IFP 160000 standard (Behar et al., 2001) using Rock Eval-VI type instrument (Institut Français du Pétrole). TOC % values were estimated automatically by TOC module mounted in the device. When applying the pyrolysis analysis (Espitalie et al., 1977; Peters, 1986) 100 g pulverized rock sample is heated 3 minutes under 300°C temperature under helium atmosphere in anoxic environment. Later on; the temperature is increased up to 600°C with 25°C increments each minute. During this heating period the peaks of S1 (mg HC/g rock), S2 (mg HC/g rock), S3 (mg CO_2/g rock), S4 (mg CO_2/gr rock) and Tmax come out. With these hydrocarbon peaks the following parameters are calculated;

Hydrogen Index [HI = (S2 / TOC) x 100]

Oxygen Index [OI = (S3 / TOC) x 100]

Production Index [PI = S1 / (S1+S2)]

Genetic Potential (S1 + S2)

Kerogen Type Index (S2 / S3)

Gas Chromatography (GC) analyses are carried out in Agilent 6850 instrument using the Norwegian Oil Standard. GC-MS analysis is performed in Agilent 5975C quadrupole mass spectrometer device using the Norwegian Oil Standard. This device is used as combined with 7890A gas chromatograph and 7683B automatic liquid sampler. Stable carbon isotope analysis was performed in GV instruments Isoprime EA-IRMS device.

3. Geological Setting

The study area is located along Sakarya Zone in the western part of Pontides. Sakarya Zone is surrounded by İzmir-Ankara-Erzincan suture belt in south and by Ankara-Erzincan suture zone in north (Şengör and Yılmaz, 1981). The zone consists of a metamorphic basement at the bottom and clastics overlying with an angular unconformity, carbonate rocks and volcanics. Volcanics, clastic rocks and carbonates of this zone are observed within formations located in the general geology map of the study area (Figure 1). The study area, which is situated between the Northwestern Anatolian Mountains rising with the effect of Alpine Orogeny and the Central Anatolian massive, and basins in its close vicinity were folded and faulted in several cases. As a result of these tectonical movements strike slip faults, thrust faults, anticlinal and synclinal structures and overturned layers are observed.

The oldest unit observed in the study area is Carboniferous aged Sarıcakaya granitoids (Csg). Bakırköy formation (Jba), which is composed of sandstone, mudstone, conglomerate and limestone, is Liassic in age and unconformably overlies Sarıcakaya granitoids. This formation is unconformably overlain by Callovian-Hauterivian neritic limestones of Bilecik formation (JKb) and by Callovian-Aptian aged limestones of Soğukçam formation. This formation is then overlain by Albian-Maestrichtian aged Yenipazar formation. Yenipazar formation in the study area is divided into three members as; Değirmenözü (Kyed), Bayat (Kyeb) and Taraklı (Kyet) members (Gedik and Aksay, 2002). Yenipazar formation, which is transitional with Soğukçam formation, consists of sandstone, shale, limestone and tuff units. Lower Paleocene Selvipınar formation, which is formed by reefal limestones, is overlain by Paleocene-Lower Eocene Kızılçay formation consisting of conglomerate, sandstone and mudstone units in nearby regions of the study area. However; the Lower Eocene Kabalar member (Tpekk) of the Kızılçay formation encountered in our study area is the member in which bituminous rocks are observed. Lutetian aged Güvenç formation (Teg), which is observed outside the study area and consists of sandstone, conglomerate and marl, unconformably overlies Kızılçay formation. This formation is then unconformably overlain by Upper Eocene-Lower Miocene Gemiciköy formation (Temg). The unit is generally composed of pale red, loosely consolidated, cross bedded conglomerate and sandstone. This formation is then unconformably overlain by Lower-Middle Eocene Hançılı formation

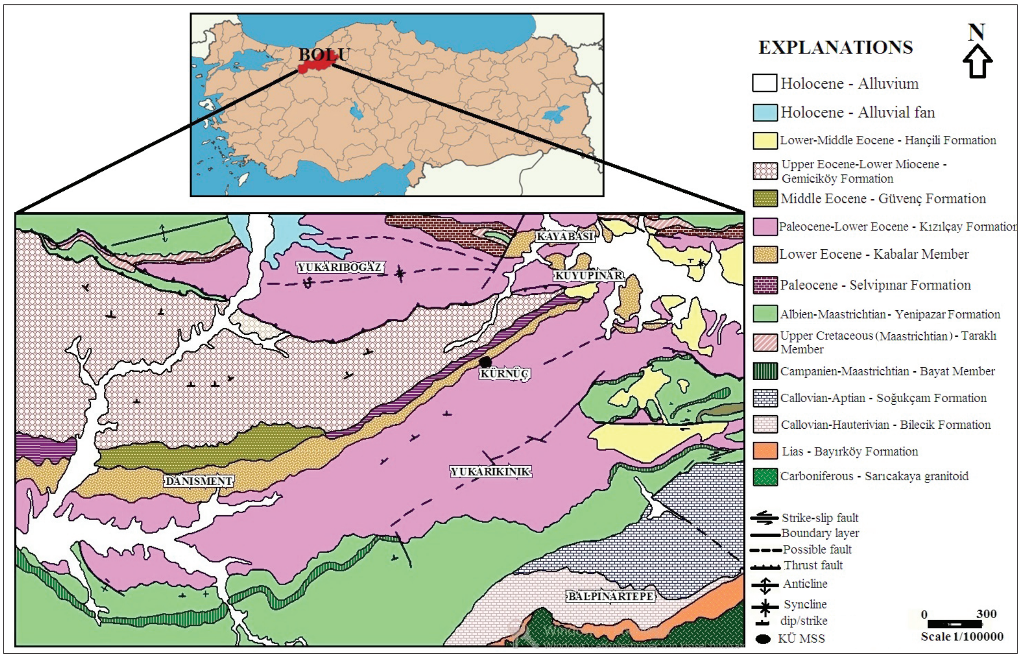

Figure 1- General geological map of the study area (modified from Gedik and Aksay, 2002).

(Tmh) (Gedik and Aksay, 2002). Hançılı formation is composed of sandstone, claystone, clayey limestone, diatomite, chert, tuffite and conglomerate units, and is unconformably overlain by Quaternary alluvial deposits (Qal) (Figure 2).

4. Findings and Discussion

4.1. Biomarker Studies

According to GC and GC-MS analyses significant data on organic material type, maturation, rock lithology and depositional environment are obtained. Within this scope, m/z 217 sterane and m/z 191 terpane lists defined in GC-MS analyses were given in table 1 and table 2, respectively.

In this study, GC analyses were carried out on 4 samples from which were subjected to pyrolysis analysis (Figure 3a.b), In each studied sample n-alkanes and prenoids were defined. N-alkanes in each studied sample range from n-C9 to n-C36. N-alkane peaks of n-C23, n-C-25, n-C27 and n-C31 are abundant in samples KÜ-19, KÜ-41 and KÜ-50. N-C27 is the n-alkane, which is the most abundant component belonging to terrigenous plants. Besides, fitan is the most abundant isoprenoid in samples. Slight increases from n-C15 to n-C25 in studied samples mainly indicate an increase in the biomasses of algae and planktons (Peters and Moldowan, 1993).

The aquatic source of n-alkanes is defined by carbon atoms varying from 16 to 18, because these are typically derived from aquatic algae and cyanobacteries. However, the terrigenous plant origin n-alkanes are defined as n-alkanes with n-C27 and n-C33 carbon atom, because these are typically derived from waxes' of terrigenous plants (Peters et al., 2005*a*).

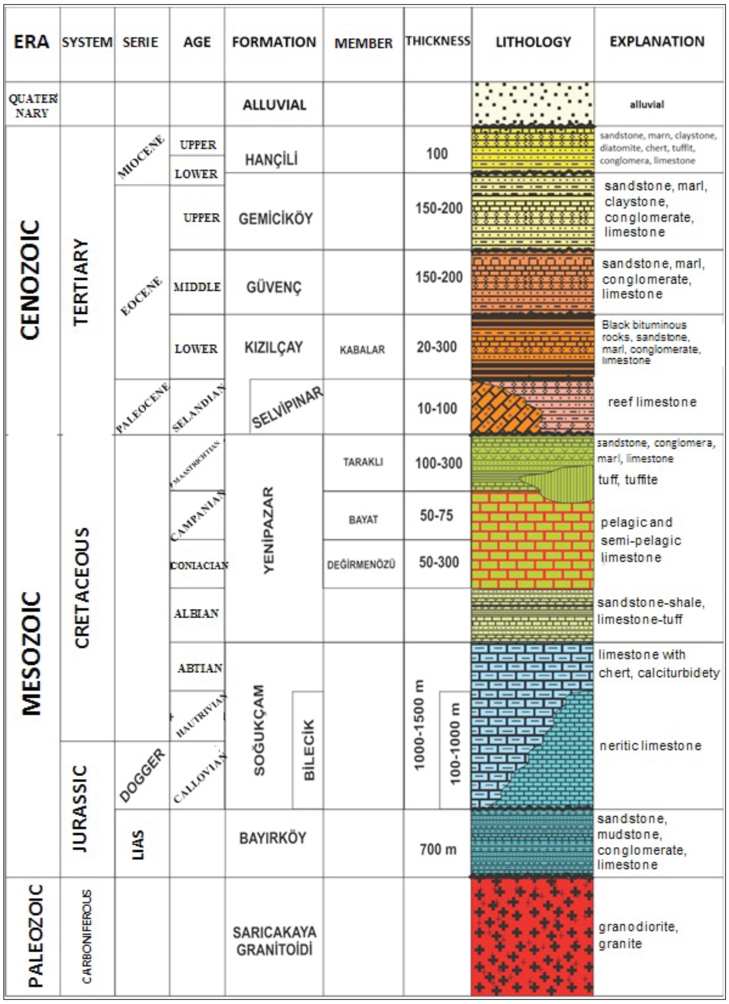

Figure 2- Generalized stratigraphic columnar section of the study area (modified from Gedik and Aksay, 2002).

Table 1- List of defined m/z 217 steran ions used in GC-MS analyses.

COMPONENT NO	COMPONENT NAME
9	C27 5α (H), 14β (H),17β (H)-Steran (20R)+C29 13β (H), 17α (H)-Diasteran (20S)
10	C27 5α (H), 14β (H),17β (H)-Steran (20S)+C28 13α (H), 17 β (H)-Diasteran (20R)
11	C27 5α (H), 14α (H),17α (H)-Steran (20R)
12	C29 13β (H), 17α (H)-Diasteran (20R)
13	C29 13α (H), 17β (H)-Diasteran (20S)
14	C28 5α (H), 14α (H),17α (H)-Steran (20S)
15	C28 5α (H), 14β (H),17β (H)-Steran (20R)+C29 13α (H), 17β (H)-Diasteran (20R)
16	C28 5α (H), 14β (H),17β (H)-Steran (20S)
17	C28 5α (H), 14α (H),17α (H)-Steran (20R)
18	C29 5α (H), 14α (H),17α (H)-Steran (20S)
19	C29 5α (H), 14β (H),17β (H)-Steran (20R)
20	C29 5α (H), 14β (H),17β (H)-Steran (20S)
21	C29 5α (H), 14α (H),17α (H)-Steran (20R)
22	C30 5α (H), 14α (H),17α (H)-Steran (20S)

Table 2- List of defined m/z 191terpan ions used in GC-MS analyses.

COMPOUND NO	COMPOUND NAME
1	C_{19} TRICYCLICTERPANE
2	C_{20} TRICYCLICTERPANE
3	C_{21} TRICYCLICTERPANE
4	C_{22} TRICYCLICTERPANE
5	C_{23} TRICYCLICTERPANE
6	C_{24} TRICYCLICTERPANE
7	C_{25}(22S+22R) TRICYCLICTERPANE
8	C_{24} TETRACYCLICHOPANE (SECO)
9	C_{26} 22 (S) TRICYCLICTERPANE
10	C_{26}22(R) TRICYCLICTERPANE
11R	C_{28} TRICYCLICTERPANE (R)
11S	C_{28} TRICYCLICTERPANE (S)
12R	C_{29} TRICYCLICTERPANE (R)
12S	C_{29} TRICYCLICTERPANE (S)
13	C_{27}18α(H)-22,29,30-TRISNORHOPANE (Ts)
14	C_{27}17α (H)-22,29,30-TRISNORHOPANE (Tm)
15	17 α (H)-29,30-BISNORHOPANE
16R	C_{30} TRICYCLIC TERPANE (R)
16S	C_{30} TRICYCLIC TERPANE (S)
17	17 α (H)- 28,30- BISNORHOPANE
18	C_{29} 17α (H), 21β(H)-30- NORHOPANE
19	C_{29} Ts (18α (H)-30-NORHOPANE
20	C_{30} (17α (H)-DIAHOPANE)
21	C_{29} 17β (H), 21α (H)-30 NORMORETANE
22	OLEANANE
23	C_{30} 17α (H), 21β (H)-HOPANE
24	C_{30} 17β (H), 21α (H)-MORETANE
25	C_{31} 17α (H), 21 β (H)-30-HOMOHOPANE (22S)
26	C_{31} 17α (H), 21 β (H)-30-HOMOHOPANE (22R)
27	GAMMACERANE
28	HOMOMORETANE
29	C_{32} 17 α (H), 21β (H)-30,31-BISHOMOHOPANE (22S)
30	C_{32} 17 α (H), 21β (H)-30,31-BISHOMOHOPANE (22R)
31	C_{33} 17α (H), 21β (H)-30,31,32-TRISHOMOHOPANE (22S)

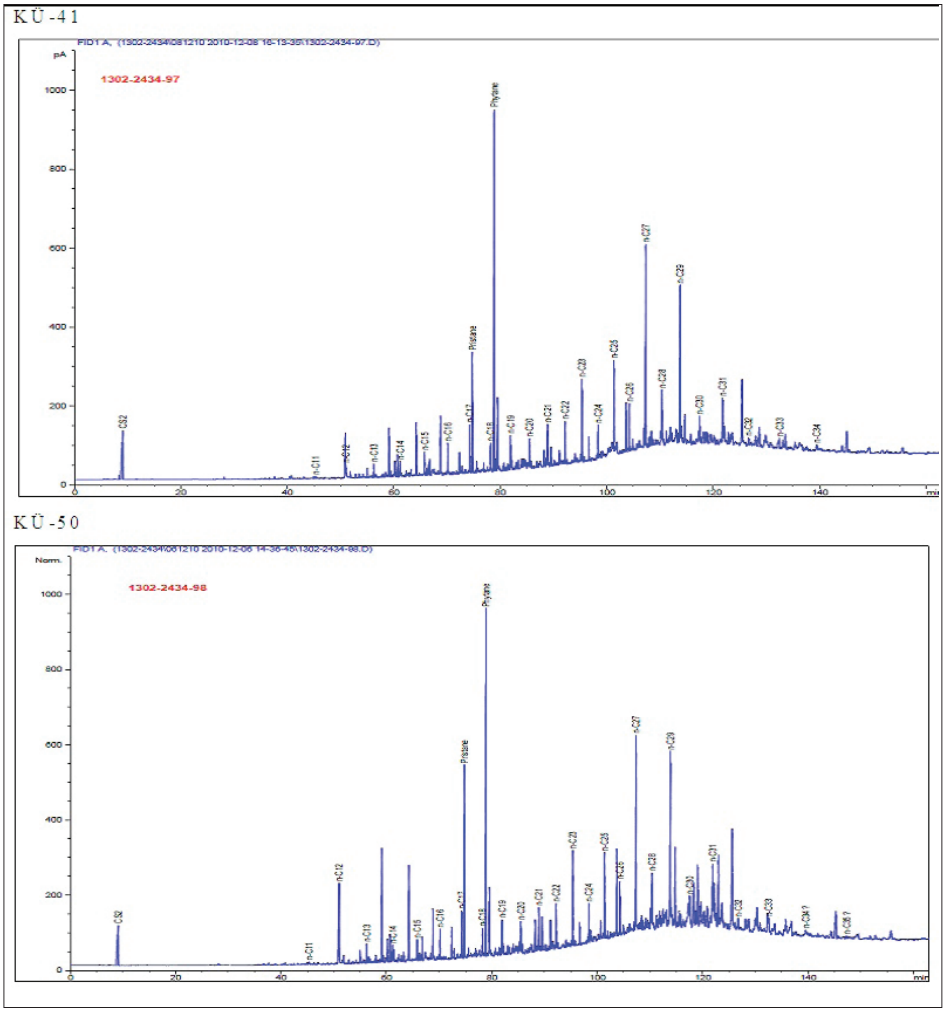

Figure 3a- Results of gas chromotography (GC) analysis.

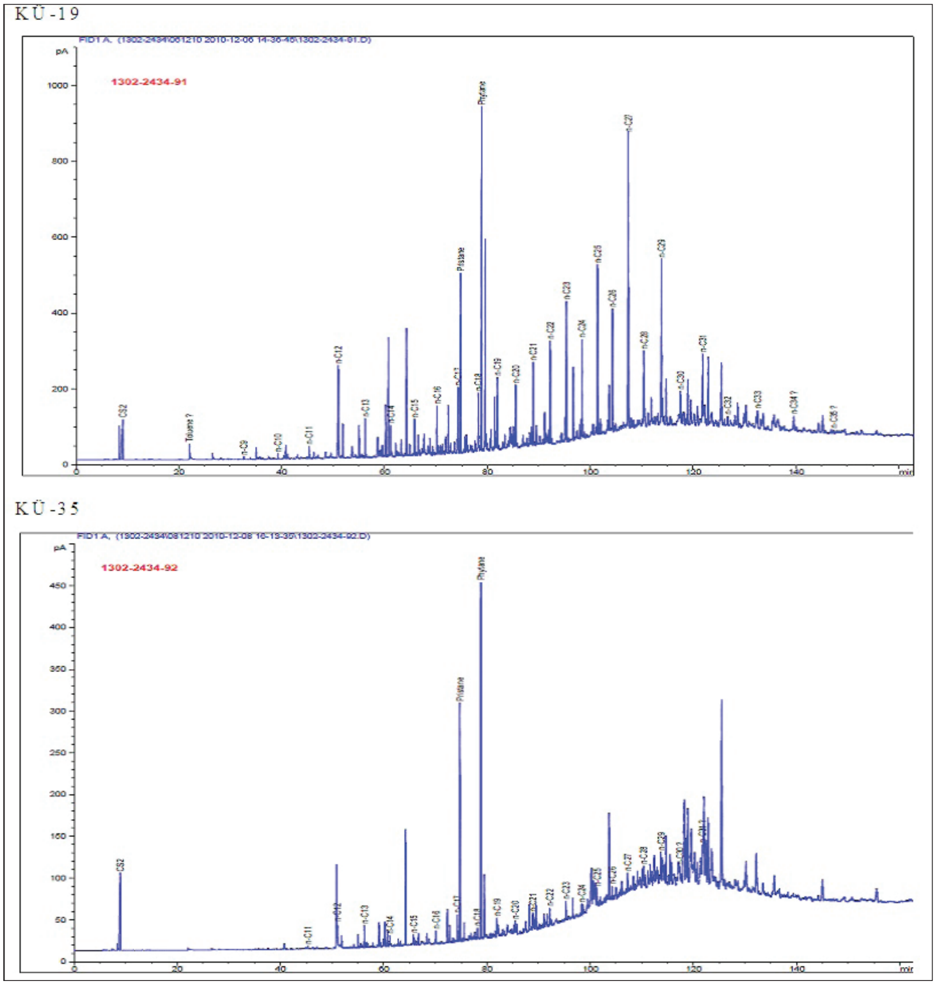

Figure 3b- Results of gas chromatography (GC) analysis.

Pr/Ph ratios for bituminous samples of KÜ-19, KÜ-35, KÜ-41 and KÜ-51 are 0.4, 0.6, 0.25 and 0.45, respectively. The depositional environment of samples according to isoprenoid ratios reflects anoxic reducing conditions (Didyk et al., 1978; Tissot and Welte, 1984; Leythaeuser and Schwarzkopf, 1986). Again, according to Pr/n-C17 and Ph/n-C18 ratios from isoprenoid/n-alkane ratios, the redox conditions of the depositional environment is reducing, organic material type is Type I and Type II kerogen and samples are yet in immature stage (Tissot and Welte, 1984, Moldowan et al., 1985, Hunt, 1995) (Figure 4).

The ratio of n-C17/n-C31 indicates that the source of organic material is marine algal or terrigenous plant. Values higher than 2 (>2) indicate terrigenous plant source is more than marine algae (Forster et al., 2004). However; the alteration of organic material within sedimentary system breaks down the n-alkane distribution and causes the increase of some more stable terrigenous n-alkanes and the loss of algal based n-alkanes. This situation may cause errors in n-C17/n-C31 ratio. The ratio of n-C17/n-C31 in samples KÜ-19, KÜ-41 and KÜ-50 changes between 0.7-0.9 and indicates terrigenous organic materials. According to pyrolysis analyses and organic petrographic data the kerogen types of the samples KÜ-19, KÜ-41 and KÜ-50 are Type-I, Type II and Type I, respectively. Accordingly; the organic materials to be terrigenous material according to n-C17/n-C31 can be concluded as the alteration of the organic material within sedimentary system.

Sterane mass chromatography (m/z 217) of the bituminous shale sample KÜ-35 is seen in figure 5. In order to determine the source of organic material a regular sterane distribution from C27 to C29 is used too. C27 steranes mostly are derived from marine

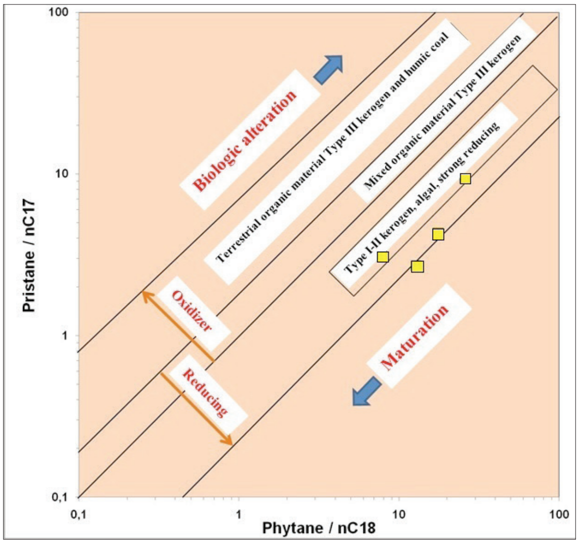

Figure 4- Kerogen type according to Pr/n-C17 and Ph/n-C18 values (Hunt, 1995).

algae, however; C28 steranes are derived from barm, fungi, bacterial plankton and algae; and C29 steranes are derived from terrigenous plants (Peters et al., 2005*b*).

The abundancy percentages of C27, C28 and C29 steranes in sample KÜ-35 were determined as 21.5%, 41.3% and 37.2%, respectively (Figure 6). C29/C27<1 indicates that marine algae are more dominant than terrigenous plants (Peters et al., 2005*b*). When studied in this manner, it can be said that the rational value of terrigenous plants in sample KÜ-35 are more dominant than marine algae. The dominancy of C29 steranes against C27 and C28 steranes in sterane distribution indicates that terrigenous organic material income into depositional environment is much despite the marine organic material contribution. However; C29 steranes may also come from blue-green algae and marine diatoms (Nichols et al., 1990).

Terpane mass chromatography (m/z 191) of bituminous shale sample KÜ-35 was given in figure 7. According to C29NH/C30H ratio (0.31), the bitumen was derived from a clastic clayey source rock (Mello et al., 1988, Clark and Philip, 1989). C24 tetracyclic/C26 tricyclic (S+R) ratio is 0.25, and indicates shale source rock. Also, the mineralogical data of the sample KÜ-35 show that the studied sample is bituminous shale. Gammacerane index value of the same sample was found as 0.17. Therefore; the salinity of water in a depositional environment cannot be talked about, even the presence of gammacerane molecule can be associated with an algal growth in a lacustrine environment (Hunt, 1995, Sinninghe Damsté et al., 1995, Peters et al., 2005*a*). In general, the presence of gammacerane may indicate the marine, lacustrine, near shore or a deltaic depositional environment (Waples and Machihara, 1991).

The distribution from C27 to C29 can also be used to determine the changes of sedimentary depositional environments from deep marine (>150 m) to shallow marine and to lacustrine depositional environments. Thus, the abundancy percentages of C27 and C29 steranes in sample KÜ-35 are 21.5% and 37.2%, respectively, and C29 steranes are dominant. This situation indicates that Kürnüç basin depositional environment cannot be a deep marine.

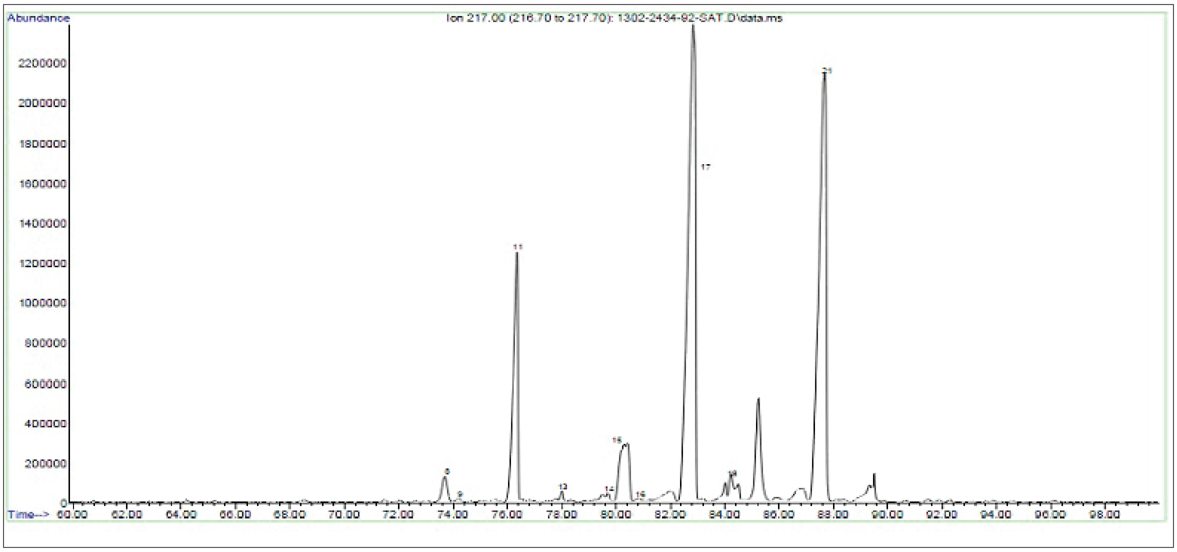

Figure 5- Sterane mass chromatograph of the sample number KÜ-35 (m/z 217).

And according to the ratio of C25/C26 tricyclic trepane (0.32), it is understood that the depositional environment of Kürnüç bituminous rocks is not marine environment (Burwood et al., 1992, Hanson et al., 2000). Besides; according to pyrolysis analyses and lithological data the investigated basin can be regarded as a lagoon partly connected with the sea.

4.2. Source Rock Potential

Results of pyrolysis analyses of Kürnüç (Göynük/Bolu) bituminous rocks (bituminous shale, bituminous marl) was given in table 3. TOC contents vary between 2.52-8.38% with a mean value of 6.13%. Considering TOC values of bituminous rocks they possess excellent source rock potential (Tissot and Welte, 1984; Peters, 1986; Jarvie, 1991; Peters and Cassa, 1994).

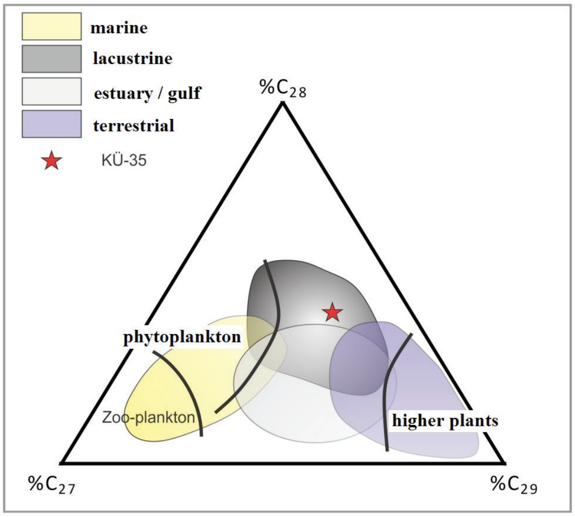

Figure 6- Basin determination by means of C_{27}, C_{28} and C_{29} steranes (Huang and Meinchein, 1979).

According to carbon average in medium shales (Wedepohl, 1971) the total organic carbon amounts of bituminous rocks in the study area is quite rich (Figure 8). When a frequency interval for the total organic carbon amount for studied bituminous rocks is formed, it is seen that most of the samples concentrate between 5-8% TOC values (Figure 9). S1 hydrocarbon values of Lower Eocene bituminous rocks is between 0.37-2.84 mg HC/g rock with a mean value of 1.28 mg HC/g rock. The source rock potential according to S1 hydrocarbon values is good (Petrs, 1986; Peters and Cassa, 1994). S2 hydrocarbon values range between 18.03-69.23 mg HC/g rock with a mean value of 45.51 mg HC/g rock. Source rock potential is good for S2 hydrocarbon value according to Espitalie (1982), very good according to Peters (1986) and excellent according to Peters and Cassa (1994).

4.3. Organic Material Type

The determination of organic material or kerogen type was assessed also using other parameters. Hydrogen Index values (HI) vary between 476-891 mg HC/g rock (Table 3) in studied samples, and the kerogen type is Type I and Type II according to Peters and Cassa (1994). However; according to Hydrogen Index (HI)–Oxygen Index (OI) diagram the organic material type is mostly Type I kerogen. When the kerogen type is assessed according to Hydrogen Index (HI)-Tmax diagram, Type I kerogen is mostly observed and only in 2 samples Type II kerogen is observed (Figure 10 a, b). According to S2-TOC diagram associated with Hydrogen Index (HI) values, the kerogen type is mostly Type I and in some samples it is Type II (Figure 11).

Table 3- Results of pyrolysis analysis.

Sample No	TOC %	$*S_1$	$*S_2$	$**S_3$	T_{max}, °C	HI	OI	PI	S_2/S_3	GP
KÜ-19	8,38	0,52	67,36	3	439	804	36	0,01	22,45	67.88
KÜ-35	5,61	0,67	48,77	1,1	437	869	20	0,01	44,34	49.44
KÜ-37	2,52	0,37	18,03	0,51	432	715	20	0,02	35,35	18.40
KÜ-38	7,77	1,02	69,23	1,08	430	891	14	0,01	64,10	70.25
KÜ-39	5,21	1,35	35,41	2,08	425	680	40	0,04	17,02	36.76
KÜ-40	4,78	1,61	30,45	1,25	419	637	26	0,05	24,36	32.06
KÜ-41	5,61	2.00	29,48	1,86	402	525	33	0,06	15,85	31.48
KÜ-50	6,15	1,22	53,99	0,84	438	878	14	0,02	64,27	55.21
KÜ-51	7,91	1,22	67,35	1,21	437	851	15	0,02	55,66	68.57
KÜ-52	7,36	2,84	35.00	4,55	403	476	62	0,08	7,69	37.84

*mg HC/g rock), **mg CO_2/g rock

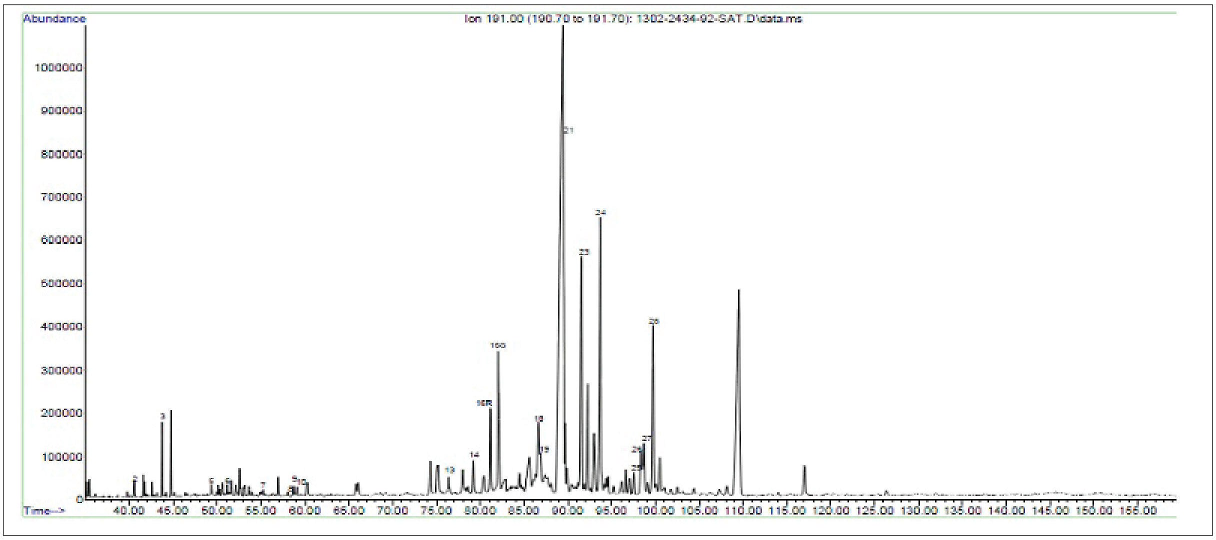

Figure 7- Terpane mass chromotograph of the sample number KÜ-35 (m/z 191).

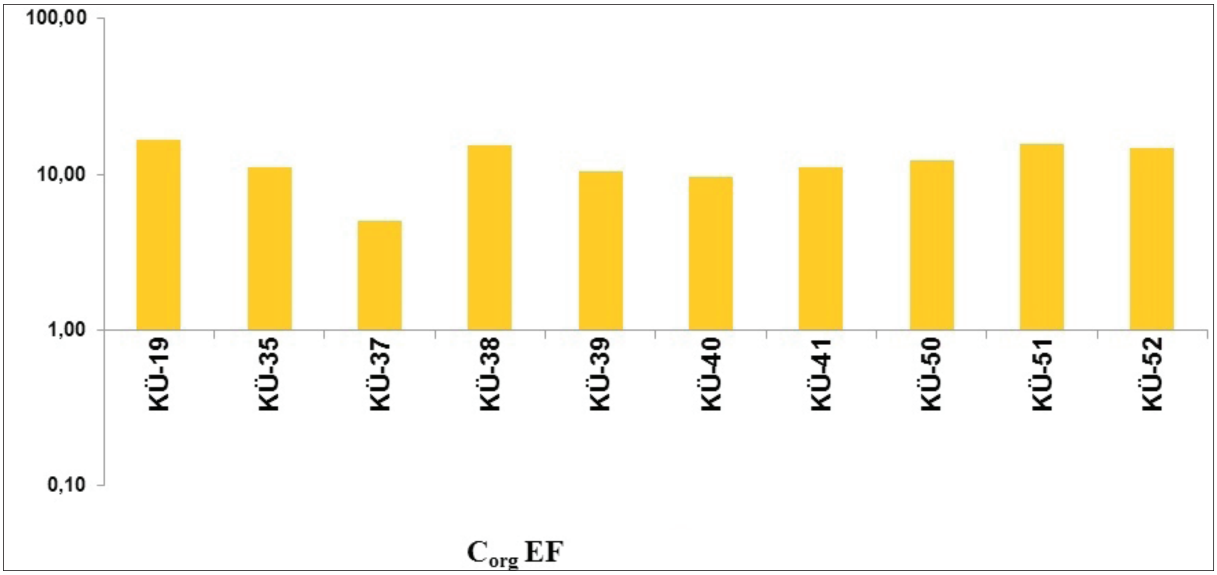

Figure 8- Total Organic Carbon (TOC) enrichments with respect to normal shales.

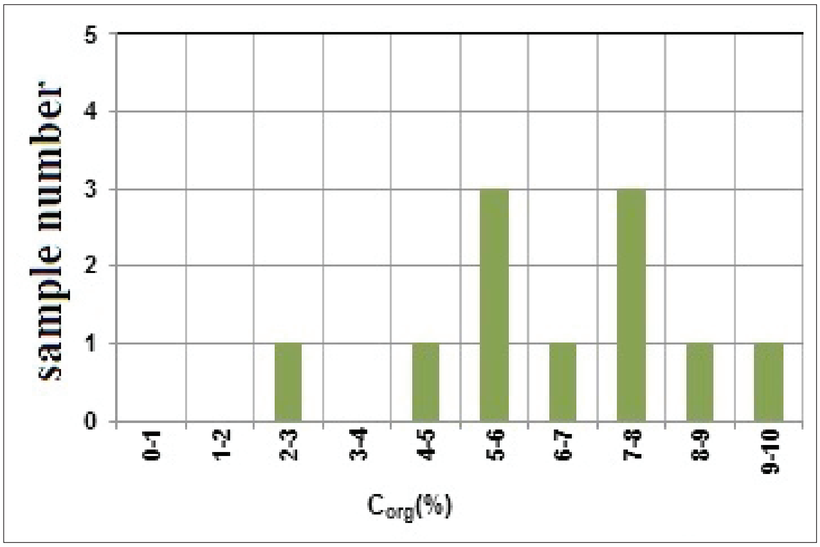

Figure 9- Total % organic carbon amount frequency interval.

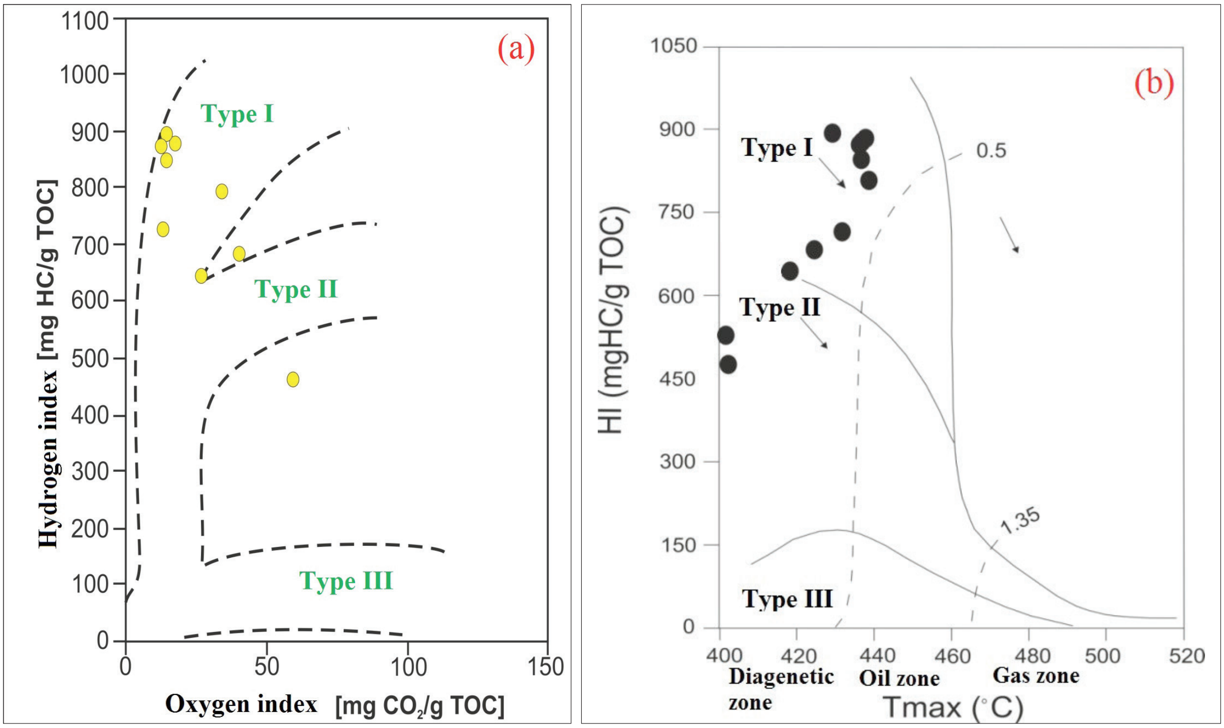

Figure 10 a, b- Kerogen types according to HI-OI and HI-Tmax diagrams (Pratt, 1984; Espitalie et al., 1977).

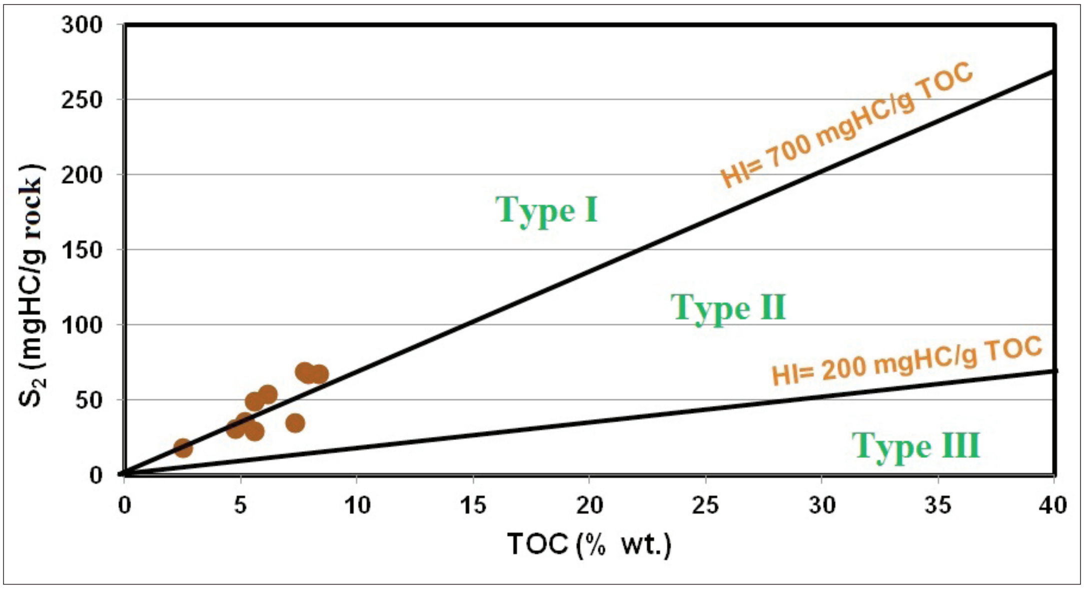

Figure 11- Kerogen types according to S2 and TOC values (Langford, and Blanc-Valleron, 1990).

The ratio of S2/S3 is 7.69 only in sample KÜ-52 and the kerogen type is Type II/III. The organic material type in the other samples according to S2/S3 ratio is Type I kerogen (Peters and Cassa, 1994). The organic material type of bituminous rocks according to organic petrographic studies is 100% Amorph+Algal (Table 4), and is compatible with results of pyrolysis analysis. The abundancy percentages of C27- C28-C29 steranes in sample KÜ-35 were determined as 21.5%, 41.3% and 37.2%, respectively (Figure 6). The dominancy of C28 steranes with 41.3% abundancy over C27 and C29 steranes indicate the presence of bacterial plankton and/or algae in this sample. C29/C27<1 shows that marine algae are more dominant than terrigenous plants (Peters et al., 2005*b*). Thus, it can be said that the rational value of terrigenous

Table 4- Results of organic petrography analysis

Sample No	% Amorp+ Alg	SCI
KÜ-19	100	2,5 - 3
KÜ-35	100	3
KÜ-37	100	3
KÜ-38	100	3
KÜ-39	100	-
KÜ-40	100	3
KÜ-41	100	-
KÜ-50	100	-
KÜ-52	100	-

plants in sample KÜ-35 is more dominant than marine algae. The dominancy of C29 steranes against C27 and C28 steranes in sterane distribution indicates that terrigenous organic material income into depositional environment is much despite the marine organic material contribution. However; C29 steranes may also come from blue-green algae and marine diatoms (Nichols et al., 1990).

4.4. Organic Maturation

The maturation assessments of organic materials in studied samples were examined in different methods. Tmax values vary between 402°C (min) and 439°C (max). According to Tmax values, bituminous rocks are not mature (Éspitalié et al., 1985). The Production Index (PI) values of the rocks are in between 0.01-0.08 mg HC/g rock and yet not mature (Peters and Cassa, 1994). Spore Color Index (SCI) values range in between 2.5-3.0 and are in immature stage.

17 α (H)-22, 29, 30-trisnorbopane (Tm) is biologically produced and turns into 18 α (H)-22, 29, 30 trisnorhopane (Ts) by burial and maturation (Peters et al., 2005*b*). Therefore; Ts/(Ts+Tm) ratio increases as thermal maturation rises. Ts/(Ts+Tm) ratio reaches 1.0 in late mature oil formation phase (Peters et al., 2005*b*). Ts/(Ts+Tm) ratio in studied sample KÜ-35 is 0.33, and can be regarded as immature.

R configuration is biologically produced in C-22 (22R) in 22S/(22S+22R) ratio, and gradually turns into 22R and 22S isomers by burial and maturation (Peters et al., 2005*b*). Therefore; 22S/(22S+22R) also increases by maturation. Thermal equilibrium value of 22S/(22S+22R) reaches 0.5 in oil formation zone (Peters et al., 2005*b*). 22S/(22S+22R) ratio to be 0.34 in the same sample indicates the beginning of immature/maturation.

Another maturation method is the ratio of 5α(H), 14β(H), 17β(H) isomers (αββ) to 5α(H), 14α(H), 17α(H) (ααα), and is expressed as; αββ/(αββ+ααα). As the thermal maturation increases (ααα) isomers are biologically produced and gradually turn into mixture of αββ and ααα isomers (Peters et al., 2005*b*). This ratio increases as the thermal maturation rises. The value of C28-αββ/(αββ+ααα) ratio indicates the thermal maturation and is 0.72 in oil formation zone (Peters et al., 2005*b*). Values lower and higher than 0.7 indicate early and late mature oil phase, respectively. In sample KÜ-35, αββ/(αββ+ααα) value is 0.02 and may indicate that the maturation has just started.

C30 17β (H), 21α (H)- moretan/ C 30 17α (H), 21β (H)- hopan ratio is again used as the maturity parameter. This value in the studied sample is 1.17 and may indicate that the immature/partly maturation has just started.

C29 Ts 18α (H)-30- norhopane/ C29 Ts 18α (H)-30- norhopane+ C29 17α (H), 21β(H)-30- norhopane ratio is again used as the maturity parameter. The stability of 29 Ts component is relatively higher than norhopane. It means that 29Ts/ (29Ts+norhopane) ratio will increase with rising temperature and maturation (Hughes et al., 1995). Again, this ratio for the sample KÜ-35 was determined as 0.49 and indicates immature stage.

The ratio of 20S/(20S+20R) starts to increase from 0 value with the increase in thermal maturation, and this increase continues with maturation until 0.52-0.55 interval (Seifert and Moldowan, 1981). This ratio is 0.44 in sample KÜ-35 and indicates that the maturation has just started.

According to all maturity assessment results, it is seen that the organic maturity in Lower Eocene bituminous rocks in Kürnüç area has not yet occurred.

4.5. Hydrocarbon Production Potential

It was assessed whether or not Lower Eocene aged bituminous rocks possess a hydrocarbon production potential using several parameters. S2/S3 ratio changes in between 7.69-64.27 and shows that rocks can produce oil (Clementz et al., 1979; Peters, 1986). Genetic Potential (S1+S2) values vary in between 18400-70250 ppm and bituminous rocks possess good source rock potential (Tissot and Welte, 1984). According to Hydrogen Index (HI)–TOC % diagram, again bituminous rocks indicate the excellent oil source (Figure 12). Also, according to S2-TOC diagram these rocks hold excellent oil generation potential except for one sample (Figure 13). Hydrocarbons were produced by Lower Eocene bituminous rocks according to S1-TOC diagram, and there is not any evidence showing that there had been any organic contamination in bituminous rocks (Figure 14). According to results of hydrocarbon production potential assessment, it is seen that Lower Eocene bituminous rocks in Kürnüç area have excellent oil production potential and the produced hydrocarbons are in situ.

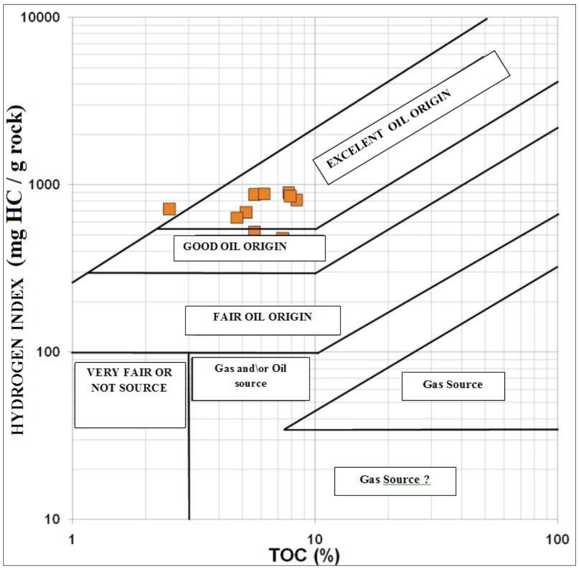

Figure 12- Hydrocarbon potential according to HI and TOC values (Jackson et al., 1985).

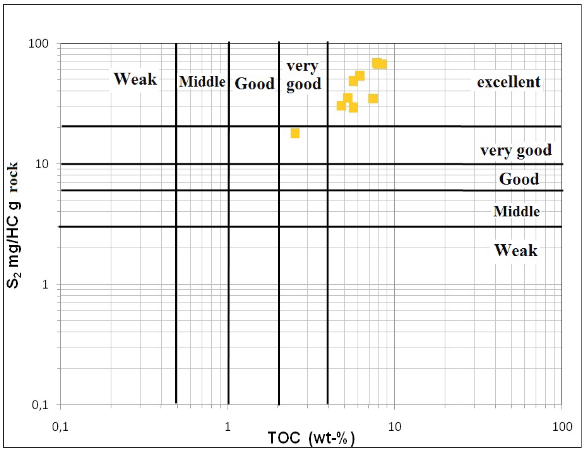

Figure 13- Hydrocarbon potential according to S2 and TOC values (Peters and Cassa, 1994).

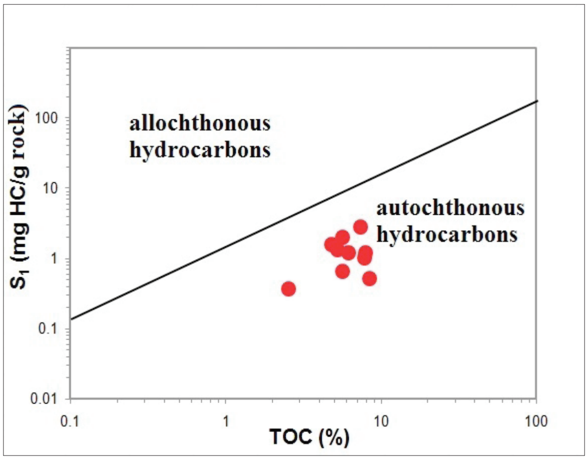

Figure 14- Hydrocarbon characterization according to S1-TOC values (Hunt, 1995).

4.6. Isotope Studies

In this study, pyrolysis analyses, GC and GC-MS analyses, and also the carbon isotope analyses were carried out. Carbon isotope analyses were performed on 3 samples selected from which organic petrographic investigations had been made. According to carbon isotope analyses carried out it was detected that δ13C (Saturated Hydrocarbon) isotope values and δ13C (Aromatic Hydrocarbon) ranged in between ‰(-) 32.07, (-)31.31 and ‰(-)32.59, (-)30.39, respectively (Table 5). If Canonical Variable (CV) value calculated from carbon isotope analyses is greater than 0.47, then it shows non-marine origin oil; if it is less than 0.47, then it shows marine origin oil (Sofer, 1984).

$$\text{CV (Canonical Variable)} = -\,2.53 * \delta^{13}\,\text{Csaturated} + 2.22 * \delta^{13}\,\text{Caromatic} - (11.65)$$

According to CV results, sample KÜ-35 falls into areas of non-marine and some lacustrine oils. However; samples KÜ-19 and 50 fall into areas of marine and other lacustrine oils (Figure 15).

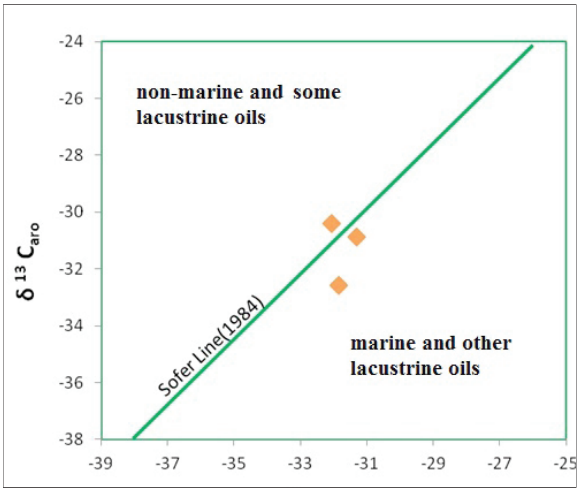

Figure 15- δ 13 C Aromatic and δ 13 C mature hydrocarbon diagram (Sofer, 1984).

Table 5- Saturated, aromatic δ 13C and CV values of bituminous rocks.

Sample No	$\delta\ ^{13}C$		
	Saturated Hydrocarbon	**Aromatic Hydrocarbon**	**CV**
KÜ-19	-31.85	-32.59	-4,3748
KÜ-35	-32.07	-30.39	1,0592
KÜ-50	-31.31	-30.88	-1,9286

5. Results

According to mean TOC % (6.13%) values and S1 (1.28 mg HC/g rock) and S2 (45.51 mg HC/g rock) hydrocarbon averages, the bituminous rocks have very good-excellent source rock potential. Kerogen types are Type I and very few Type II based on Hydrogen Index (HI) limit values. This result is also supported by Hydrogen Index (HI)-Oxygen Index (OI), Hydrogen Index (HI)-Tmax, S2–TOC diagrams and data of Hydrocarbon Type Index (S2/S3). Organic petrographic results imply 100% Algal+Amorph organic material. According to Tmax, PI, SCI, Pr/nC17 and Ph/nC18 ratios, all samples are in immature stage. Besides, m/z 191 triterpane and m/z 217 sterane biomarker data carried out in some samples [Ts/(Ts+Tm), 22S/(22S+22R)], αββ/(αββ+ααα), 29Ts/(29Ts+norhopane), 20S/(20S+20R) as well indicate that Lower Eocene bituminous rocks in Kürnüç area are immature.

Genetic potential (S1+S2) values show that samples possess good source rock potential. According to S2/S3 ratio, HI–TOC and S2–TOC diagrams, Lower Eocene bituminous rocks have excellent oil generation potential. According to S1–TOC diagram, hydrocarbons produced by Lower Eocene bituminous rocks are in situ and were not subjected to any contamination. According to C29 17α(H)-hopan and C24 tetracyclic/C26 tricyclic (S+R) ratio, source rock lithology is of clastic source and imply bituminous shale. Mineralogical data also support this result.

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