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Investigation of the paleodepositional environment of the Middle Miocene aged organic matter rich rocks (Tavas/Denizli/SW Turkey) by using biomarker parameters and stable isotope compositions (^{13}C and ^{15}N)

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Research Article

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Tavas (Denizli Basin), Organic Geochemistry, Biomarkers, Stable Isotopes (^{13}C and ^{15}N), Depositional Environment.

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ABSTRACT

The study area is located 45 km south of Denizli. The purpose of this study is to identify the organic geochemical properties and paleo depositional environment of organic matter rich rocks from Tavas (Denizli/SW Turkey). For this purpose, total organic carbon (TOC, wt.%) and pyrolysis, n-alkane, isoprenoid, sterane, terpane and aromatic hydrocarbon parameters have been investigated of the studied samples. In addition, scanning electron microscopy (SEM) and stable isotope (δ^{13}C and δ^{15}N) investigations were also carried out. Organic matter rich rocks which have type III kerogen have got 25.80 and 44.00 wt.% TOC content. Hydrogen index (HI, 73 and 120 mg HC/g TOC) and Oxygen index (OI, 34 and 59 mg CO_2/g TOC) values of samples are very low. The values of δ^{13}C and δ^{15}N show the terrestrial C3 ecosystem. The predominance of high molecular weight n-alkanes, degree of waxiness and less dibenzothiophene (DBT) concentrations indicate terrestrial organic matter. At the same time, biomarker and pyrolysis parameters indicate that the organic matter rich rocks (Tavas/Denizli) are in the immature stage. Pr/Ph, C_{35}/C_{34} homohopane biomarker ratios and C_{35} homohopane index values point out oxic-suboxic paleo depositional environment.

1. Introduction

The study area is within the boundaries of the district Tavas, which is located in 43 km south of Denizli, in the neighborhood of Avdan (Figure 1). Neogene sedimentary rocks have a wide distribution in Western Anatolia. Among the terrestrial and / or lacustrine lithologies observed in the depression basin called Denizli Graben, there are coaly levels with low spread and thickness. Although Tavas coals are not used for the coal need of the whole city like other coals in the region, they meet the energy needs of small scale enterprises in the vicinity. The calories of the coal, which are operated by a local company in the open pit method, are 2100-2400 Kcal / kg, and the reserve is 8-10 million tons. Moisture content is 45%, ash content is 15-20%, sulfur content is around 3%. To reduce the amount of moisture, a special drying oven is used in the coal mine. Before being offered for sale, the moisture content of the coals is reduced to 20% and the calorie is increased to 3000 calories. However, as a result of the drying process, 25% tonnage loss occurs in the coals. In the study area, starting from the bottom 90 cm, 1 m and 20 cm coal levels outcrop with intercalated claystones. Above this level, there is a cover unit consisting of sandstones approximately 4 m thick. The units below and above the Tavas clayey

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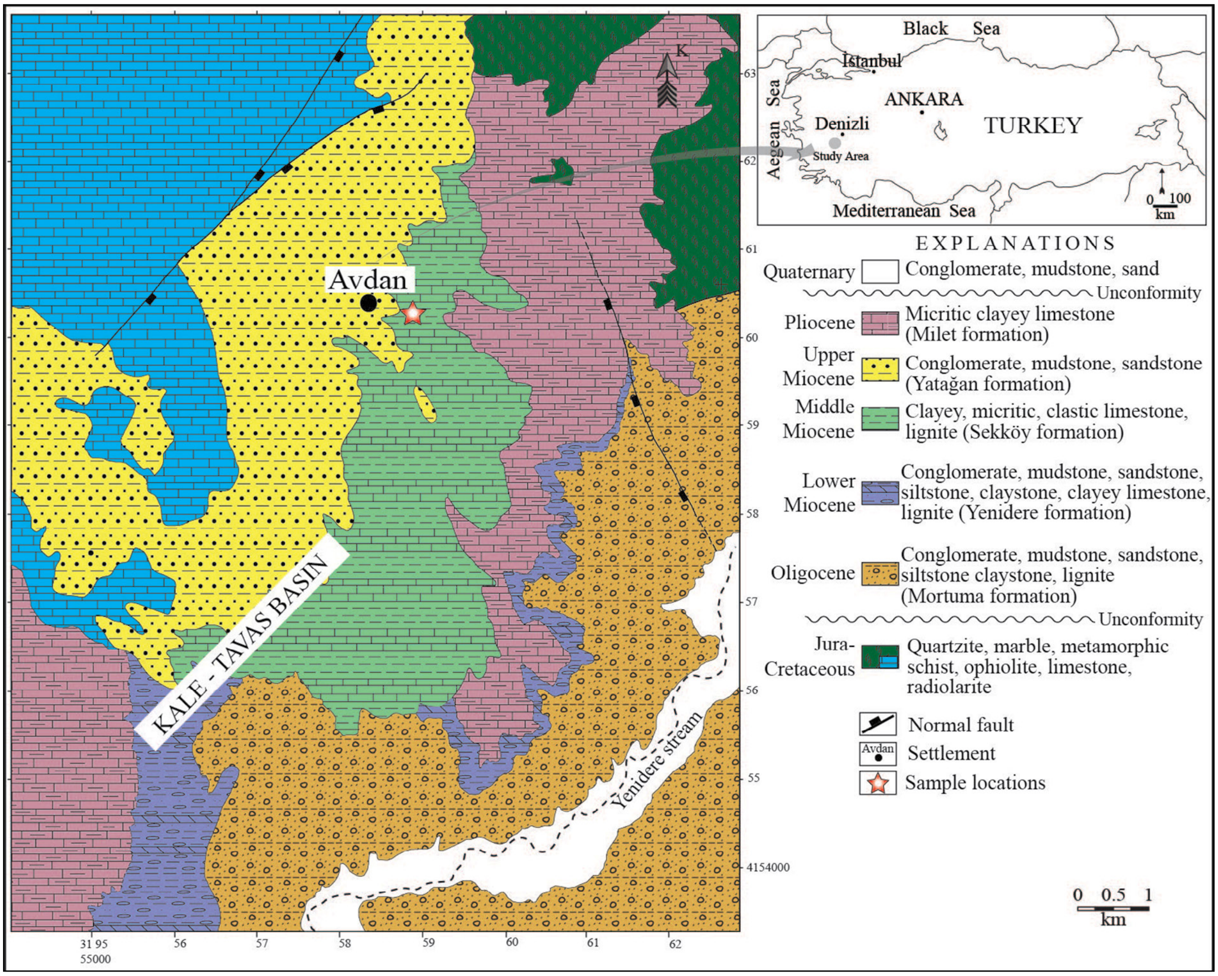

Figure 1- Geology and location map of the study area (Modified from Hakyemez, 1989).

coals belonging to the middle Miocene aged Sekköy formation is consisted of claystone, siltstone and marl lithologies.

Due to the increase in investments in the mining and energy sectors in recent years, coal research and production in our country has gained importance and brought along detailed research on Neogene aged lignites. In addition, a large part of the power generation from the thermal power plant comes from clayey, and lignites have gained importance due to the abundance of reserves. From this point of view, Tavas clayey coals reveal the difference of this study. Considering the thermal power plant project planned to be established in the region, in this study it is aimed to examine the organic geochemical properties and hydrocarbon (oil and / or gas) potential of the coals spreading in Tavas district of Denizli, Avdan neighborhood. In addition to the stable isotope and biomarker examinations performed in coals, (Rigby and Batts, 1986; Dehmer, 1989; Whiticar, 1996; Fabiańska and Kruszewska, 2003; Bechtel et al., 2008; Xiao and Liu, 2011; Adedosu et al., 2012; Warwick and Ruppert, 2016; Ayinla et al., 2017) the literature gap in our country is considered to be closed by using these analysis techniques in Tavas clayey coals. There are some national and international researches on general geology, petrography, tectonism and prospecting in the study area and its surroundings (Hakyemez, 1989; Ercan et al., 1983; Okay, 1989; Göktaş et al., 1989; Akgün and Sözbilir, 2001; Gedik and Tunç, 2004; Büyükmeriç, 2017; Helvacı and Yağmurlu, 1995). Studies on Tertiary coals are quite limited (Özçelik and Altunsoy, 2005; Atalay and Karayiğit, 2010; Kara-Gülbay, 2015; Koralay, 2018*a*, *b*, *c*, *d*; Koralay and Gedik Vural, 2018; Koralay and Koralay, 2018; 2019). For coals outcropping in Tavas, organic geochemical properties of clayey coals belonging to the middle Miocene Sekköy formation, its hydrocarbon potential and paleoenvironment were determined by conducting total organic carbon and pyrolysis analysis, gas chromatography and gas chromatography mass spectrometry analysis, stable isotope (^{13}C and ^{15}N) scanning electron microscope studies.

2. Material and Methods

Clayey coals that make up the working materials were taken from the coal quarry where the production was made in 2018 by a private company located in Avdan neighborhood of Tavas district in the south of Denizli province (Figure 2a). Gas chromatography-

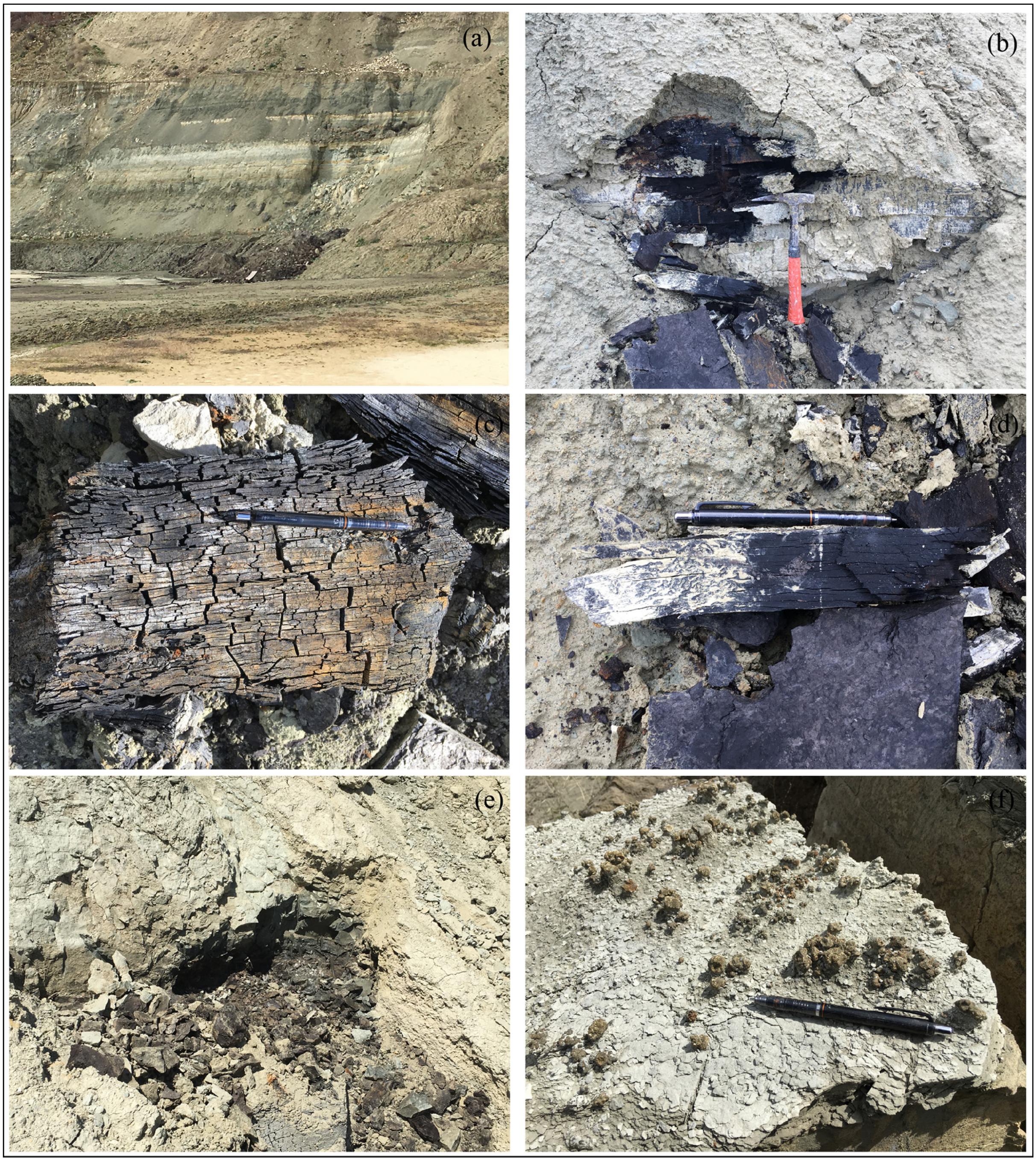

Figure 2- a) General view of open pit with organic matter-rich level, (b, c and d) Clayey coals and e) Organic matter-rich claystone, f) Pyrite crystals observed in clayey coals.

mass spectrometry (GC-MS) analysis of saturated and aromatic fractions of samples with total organic carbon (TOC, wt %), pyrolysis, gas chromatography (GC) analysis were performed in Applied Petroleum Technology Laboratories (Norway). GC and GC-MS analyzes are performed to see the general distribution of hydrocarbon compounds in extracts from coal samples and to determine the maturity level of organic matter. In addition to obtaining information about the type and maturation of organic matter by looking at the peak sizes and distributions in the chromatograms, the paleo deposition environment of the coals can be determined. Total organic carbon (TOC, wt%) and pyrolysis analyzes of three samples were performed on Leco and CS-632 Hawk devices, respectively. In order to remove carbonate in TOC measurement, diluted hydrochloric acid (HCl) was added to the sample, placed in the Leco furnace and the amount of carbon was measured with an IR detector. In pyrolysis analysis, measurements were checked according to NIGOGA standards (Espitalié et al., 1985). In the HP7890 A device, GC analysis was performed on two samples, and the analysis was performed using a 30 m long CP-Sil-5 CB-MS column, 0.25 µm film thickness and C20D42 internal standard. During the GC analysis, a temperature program was applied at 50 °C (1 min) - 4 °C / min - 320 °C (25 min). GC-MS analysis of saturated and aromatic hydrocarbons of two samples was performed on Thermo Scientific DFS device. The device is set to 3000 resolution and the data is taken in the selected ion recording (SIR) mode. The device has a 60 m CP-Sil-5 CB-MS column with a film thickness of 0.25 µm. The internal standards D4-27ααR were used to obtain the quantitative results of saturated compounds, and the internal standards D8-Naphthalene, D10-Biphenyl, D10-Phenanthrene and D12-Chrysene were used to obtain the quantitative results of aromatic compounds. During the GC-MS analysis, a temperature program of 50 °C (1 min) - 20 °C / min -120 °C - 2 °C / min - 320 °C (20 min) was applied.

Carbon and nitrogen isotope ($\delta^{13}C$ and $\delta^{15}N$) analyzes of two samples were performed in Iso-Analytical Limited (UK) Laboratories, Elemental Analyzer - Isotope Ratio Mass Spectrometry (EA-IRMS) instrument. The standards used during ^{13}C and ^{15}N isotope analysis are $d^{13}C_{V-PDB}$ = of -26,43 ‰ and $d^{15}N_{AIR}$ = 2,55 ‰, respectively. Stable isotope compositions are used effectively together with biomarkers to determine the type of organic matter and the depositional environment. It is possible to determine which ecosystem and plant species of the swamp environment where coals deposit, by using stable isotopes.

3. Geology of the Study Area

The study materials are clayey coals at the base of Sekköy formation in Kale-Tavas Basin (Figure 2b, c, d and e). Formations in the basin consist of shallow marine and terrestrial units from bottom to top. Basement rocks are arranged from bottom to top as follows Gneisses, schists and marbles, limestones at the top (Okay, 2001). Gneiss, schist and marble are the lithologies of the Menderes Massif. There are carbonate rocks called Lycian nappes, ranging from Permian to Paleocene on the schists and marbles. The marine sedimentary rocks covering the basement rocks unconformably are called Akçay Group at the bottom; It is defined as Karadere, Mortuma, Yenidere, Künar and Kale formations (Hakyemez, 1989; Yakupoğlu and Bayhan, 2017). Sekköy, Yatağan and Milet formations that overlie these units unconformably consist of terrestrial units and are called Muğla Group (Figure 3) (Göktaş et al., 1989). Tavas clayey coals which constitute the study material is placed in Miocene aged Sekköy formation. Sekköy formation overlies Kale formation unconformably and overlain conformably by Yatağan formation (Şafak, 2010; Yakupoğlu and Bayhan, 2017). The age of Sekköy formation was determined by *Zygolophodon turicensis*, a taxon found in clayey coals and well-known in Eurasia in the early-late Miocene (Erten and Koralay, 2020, https://doi.org/10.1007/s12549-020-00422-7). Sekköy formation starts with coal levels at the bottom and continues with clayey, micritic, clastic limestone and siltstone levels. Medium-thick bedding and parallel lamination are common in the limestones of Sekköy formation.

4. Results

4.1. *n*-Alkanes and Isoprenoids

Gas chromatography (GC) examinations revealed that high molecular weight (n-C_{20} +) n-alkanes were dominant in both samples. Long-chain n-alkanes, such as n-C_{27}, n-C_{29}, predominate peaks express the predominance of terrestrial tall plants (Figure 4)

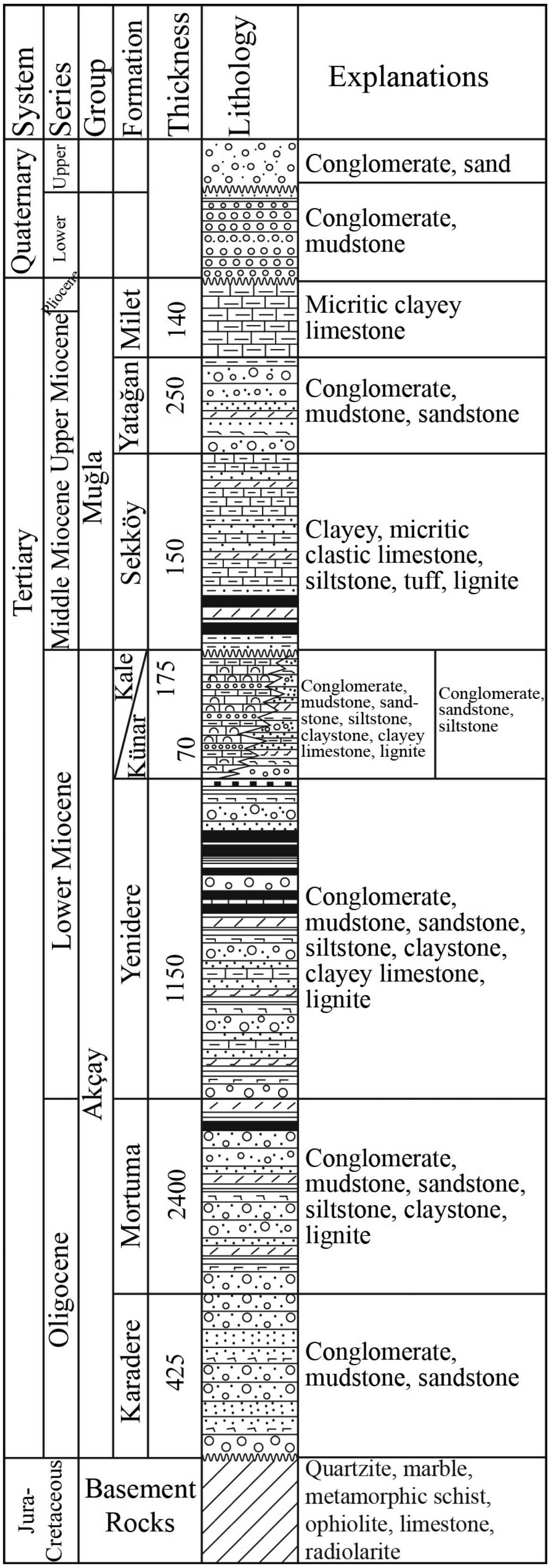

Figure 3- Generalized stratigraphic section of Kale-Tavas area (modified from Hakyemez, 1989).

(Meyers, 1997). The Pr / Ph ratio of Tavas clayey coals was calculated as 1.07 and 1.00, respectively. Its rank was determined as brown coal and subbituminous coal (Pr / Ph ratio between 1 and 3), and its paleo deposition condition was marshy environment are oxy-suboxic (Diessel, 1992).

In the ratio of n-C_{17} / n-C_{31} (0.13 and 0.04), since the n-C_{31} n-alkanes are more dominant, the samples examined contain organic matter originating from terrestrial plants (Hunt, 1996) (Table 1). Another way to determine the amount of terrestrial origin organic material is the degree of waxiness and is calculated by the ratio Σ (n-C_{21}-n-C_{31}) / Σ (n-C_{15}-n-C_{20}). The waxiness values in the TAV-3 and TAV-6 samples were calculated as 10.87 and 22.22 respectively, indicating the terrestrial input with mainly high plants in accordance with the above parameters (Hunt, 1996; Peters and Moldowan, 1993). High CPI (26-28) (4.63 and 4.76) and CPI (22-30) (4.25 and 4.80) values observed in TAV-3 and TAV-6 samples indicate that are deposited in relatively dry and cold paleo-climatic conditions, but it also points that terrestrial plants and low level of maturity depending on the high molecular weight n-alkane amount (Peters et al., 2005).

4.2. Steranes and Terpanes

Saturated and aromatic hydrocarbon biomarker ratios obtained from gas chromatography mass spectrometry (GC-MS) examinations in saturated hydrocarbon compounds were investigated. Ts / Tm ratio is the maturity parameter. Ts / Tm ratio of both samples is determined as 0.17 (Ts / Tm <1) (Table 2), Tavas clayey coals are immature phase according to Ts / Tm ratio (Seifert and Moldowan, 1986). Moretane / hopane ratio generally decreases with increasing thermal maturity (Kvenvolden and Simoneit, 1990). Moretane / hopane ratio decreases from 0.8 to 0.15-0.05 with increasing thermal maturity (Hoffmann et al.,1984). This ratio was calculated as 0.85 and 0.53, respectively, in TAV-3 and TAV-6 samples and indicates the early mature stage. C_{23} tricyclic terpane / (C_{23} tricyclic terpane + C_{30} hopane) (C_{23} tt / (C_{23}tt + C_{30} H)) ratio increases with maturity. Very low C_{23} tt / (C_{23} tt + C_{30} H) ratios in TAV-3 (0.28) and TAV-6 (0.14) samples support low maturity (Aquino Neto et al., 1983). SC_{31} and SC_{32} homohopanes obtained by calculating 22S / 22S + 22R ratios increase from

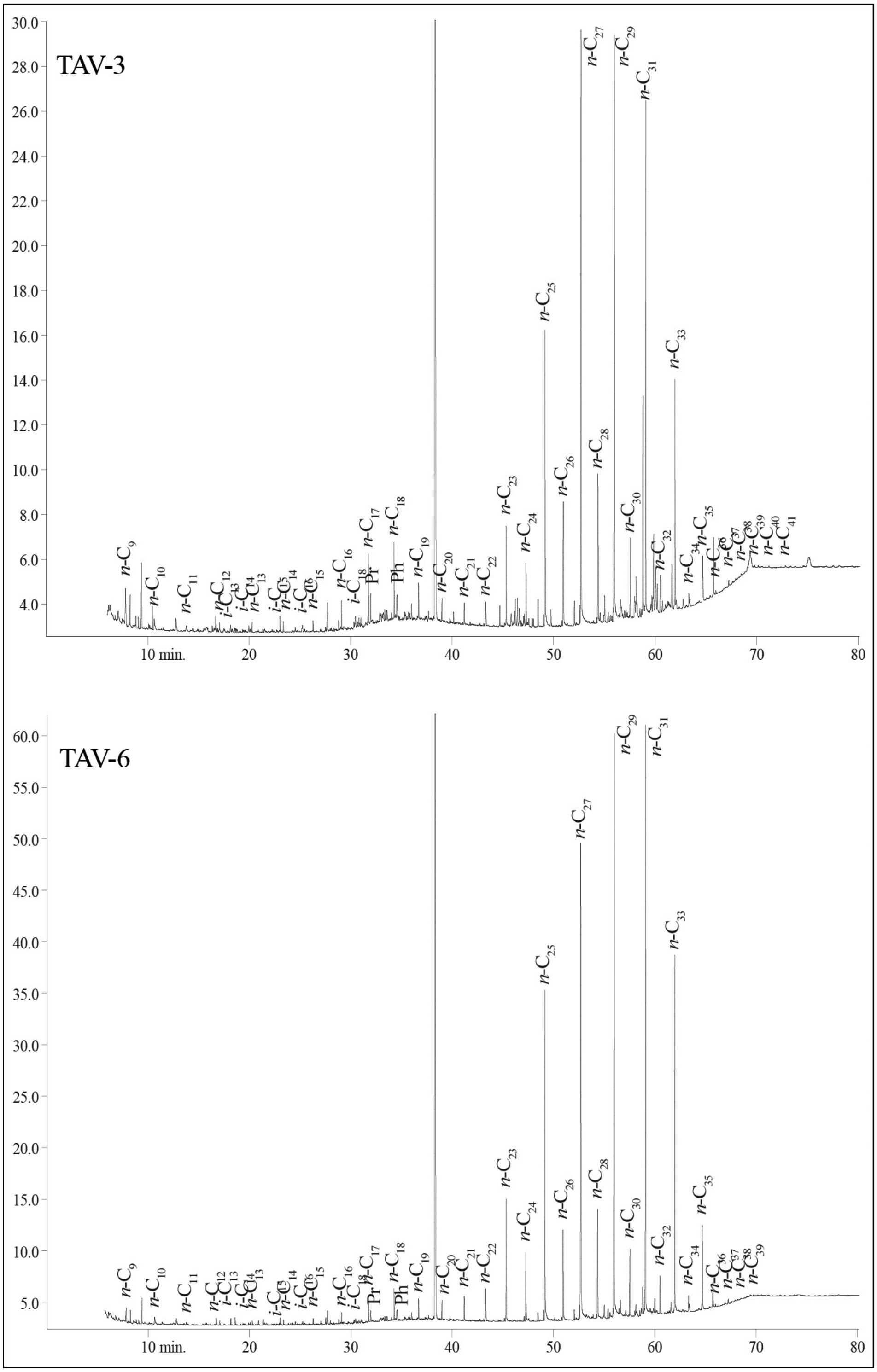

Figure 4- *n*-Alkane and isoprenoide distribution of the studied samples.

Table 1- Some parameters and general molecular composition (%) calculated from gas chromatograms of examined samples.

Sample No	Pr/Ph	n-C_{17}/n-C_{31}	n-C_{23}/n-C_{29}	n-C_{23}/n-C_{25}	Σ(n-C_{21}-n-C_{31})/ Σ(n-C_{15}-n-C_{20})	$CPI_{(26-28)}$	$CPI_{(22-30)}$
TAV-3	1,07	0,13	0,17	0,32	10,87	4,63	4,25
TAV-6	1,00	0,04	0,20	0,36	22,22	4,76	4,80

Pr: Pristane, Ph: Phytane, $CPI_{(26-28)}$: $2nC_{27}/(nC_{26}+nC_{28})$, $CPI_{(22-30)}$: $[2(nC_{23}+nC_{25}+nC_{27}+nC_{29})]/[nC_{22}+2(nC_{24}+nC_{26}+nC_{28})+nC_{30}]$.

0 to approximately 0.6 with maturity (Waples and Machihara, 1991). SC_{31} (C_{31} 22S / 22S + 22R; 0,12 and 0,21) and SC_{32} (C_{32} 22S / 22S + 22R; 0,27 and 0,44) values of TAV-3 and TAV-6 samples are immature-early mature states that it is in the stage (Figure 5a, Table 2). The C_{27}, C_{28} and C_{29} ααα 20R isomers from the steranes, respectively, in the TAV-3 sample; While 31%, 17% and 52%, respectively, in TAV-6; It was calculated as 26%, 6% and 68%. The abundance of C_{29} ααα R isomers in both examples (C_{29}> C_{27}> C_{28}); While referring to immature organic matter, Tavas shows that clayey coals have a terrestrial origin (Figure 5b, Table 2), (Czochanska et al., 1988). Dia / (Dia + Reg) steran [Diasteranes / (Diasteranes + Regular Steranes)] ratios of TAV-3 and TAV-6 samples were calculated as 17% and 29%, respectively (Table 2), the samples examined have immature organic matter (Peters and Moldowan, 1993). C_{29} ααα 20S / (20S + 20R) and ββ / (ββ + αα) C_{29} steran ratios are used as an indicator of maturity at 0.52-0.55 and 0.67-0.71 balance values, respectively (Seifert and Moldowan, 1986). Although the examined samples are below the equilibrium value, it can be said that when the ββ / (ββ + αα) C_{29} steran (0,24) value in the TAV-6 sample is evaluated, the Tavas coals are in the immature-early mature stage (Table 2). Diasteranes / Hopane ratios are generally low in immature sediment extracts as in Tavas clayey coals (0.26 and 0.29) (Affouri et al., 2013).

As in TAV-3 (1.38) and TAV-6 (0.97) examples, the high (C_{19} + C_{20}) / C_{23} tt ratio can be explained by the abundance of terrestrial organic matter input into the depositional environment of Tavas coals (Peters and Moldowan, 1993). As in TAV-3 and TAV-6 samples, lacustrine sediments and coals are characteristic with high C_{24} / C_{23} tt (1.42 and 0.51, respectively) and low C_{22} / C_{21} tt (0.30 and 0.36, respectively) (Peters et al., 2005). The C_{29} norhopane / C_{30} hopane (C_{29} NH / C_{30} H) ratio is used to distinguish between carbonate and clastic lithologies. The ratio of C_{29} NH / C_{30} H less

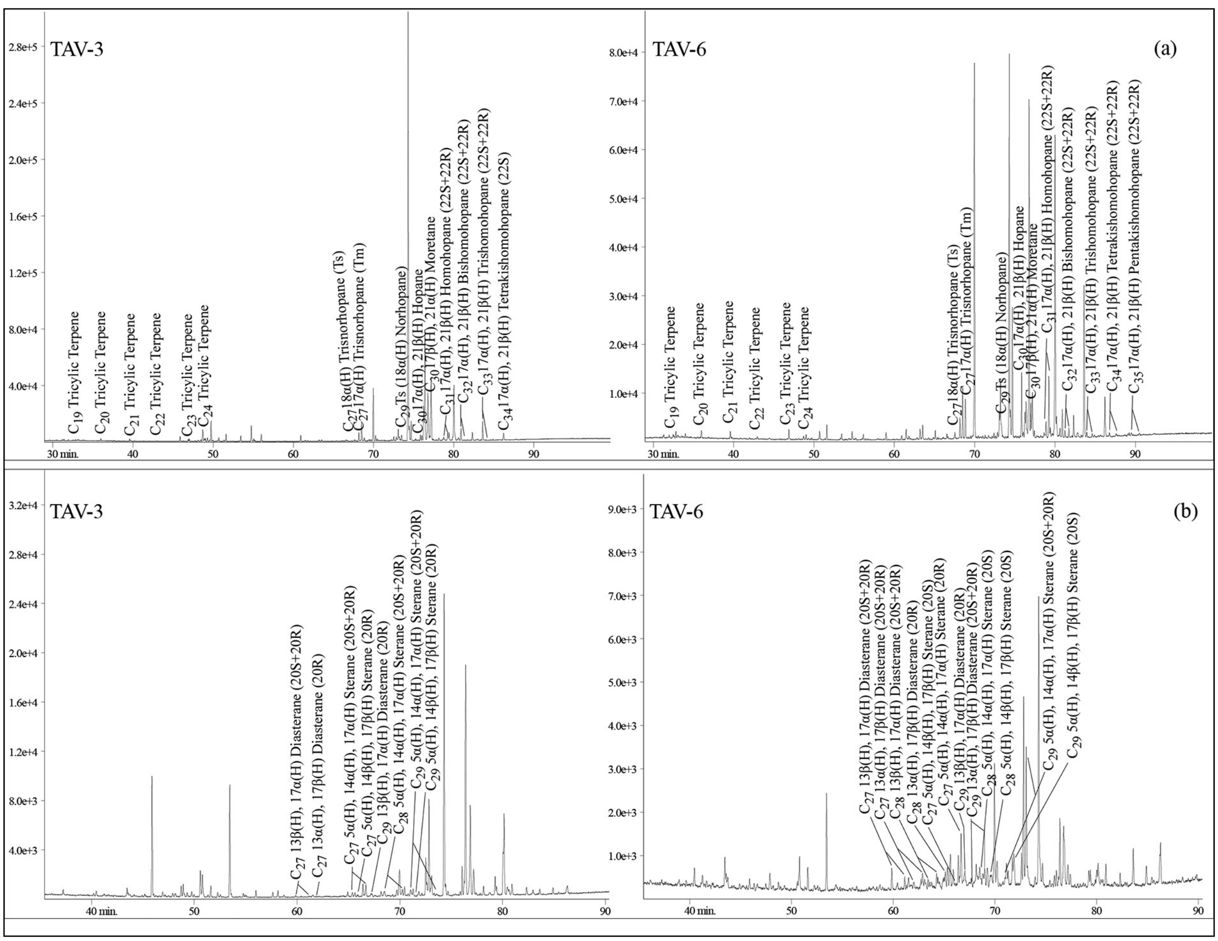

Figure 5- Distribution of the a) *m/z* 191 and b) *m/z* 217 molecules in the studied samples.

Table 2- Saturated and aromatic biomarkers ratios of Tavas (Denizli / SW Turkey) clayey coal *m/z* 191, 217, 178, 192, 184, 198, 231 and 253 determined from the mass chromatogram.

Saturated Hydrocarbon Molecules		TAV 3	TAV 6	Aromatic Saturated Hydrocarbon Molecules (ng/g)	TAV 3	TAV 6
m/z 191 Terpane	Ts/Tm	0,17	0,17	Dibenzothiophene (DBT)	362	166
	Moretane/Hopane	0,85	0,53	Phenanthrene (P)	2776	2139
	$C_{19}+C_{20}/C_{23}$ tt	1,38	0,97	DBT/P	0,13	0,08
	C_{23} tt/C_{23} tt+C_{30} H	0,28	0,14	C_{21} MA	34	46
	C_{24}/C_{23} tt	1,42	0,51	C_{22} MA	38	25
	C_{22}/C_{21}tt	0,30	0,36	C_{27} MA	32	83
	C_{29} NH/C_{30} H	0,70	0,90	C_{28} MA	17	97
	C_{31} 22R/C_{30} H	1,46	0,94	C_{29} MA	11	82
	SC_{31}	0,12	0,21	% MA(I)/MA(I+II)	0,55	0,21
	SC_{32}	0,27	0,44	1-MP	960	323
	$C_{35}/(C_{31}-C_{35})$HH index	-	0,05	2-MP	711	403
	C_{35}/C_{34} HH	-	0,76	3-MP	588	332
m/z 217 Sterane	$\%C_{27}$	31	26	9-MP	1859	613
	$\%C_{28}$	17	6	MPI-3	0,46	0,79
	$\%C_{29}$	52	68			
	% Dia/(Dia+Reg) Sterane	17	29			
	20S/(20S+20R) (C_{29} αα)	0,13	0,13			
	ββ/(αα+ββ) (C_{29})	0,14	0,24			
	Diasterane/Hopane	0,26	0,29			
	Sterane/Hopane	0,33	0,12			

tt: Tricyclic Terpane, NH: Norhopane; H: Hopane; HH: Homohopane; SC_{31} (22S/22S+22R) HH; SC_{32} (22S/22S+22R) BHH; Dia/(Dia+Reg) Sterane: Diasteranes/(Diasteranes+Regular Steranes); MA: Monoaromatic Steroid; MA(I)/MA(I+II): $(C_{21}+C_{22})/(C_{21}+C_{22}+C_{27}+C_{28}+C_{29})$; DBT/P: Dibenzothiophene/Phenanthrene; MPI-3: Methyl-phenantrene Index (β/α MP) = (2MP+3MP)/(1MP+9MP).

than 1 indicates the clastic origin rock (Waples and Machihara, 1991). In the TAV-3 and TAV-6 samples, this ratio is 0.70 and 0.90, respectively, confirming the fact that clayey coals deposition together with clastic lithologies such as claystone and siltstone (Figure 5a, Table 2). However, the C_{31} 22R / C_{30} Hopane ratio is the depositional environment parameter, which is calculated as 1.46 and 0.94 in TAV-3 and TAV-6 samples. According to the C_{31} 22R / C_{30} Hopane ratios less than 0.25, the samples analyzed show lacustrine origin rock characteristics (Table 2) (Peters et al., 2005). According to the C_{31} 22R / C_{30} Hopane ratios less than 5, the samples analyzed show a lacustrine origin rock feature (Table 2) (Peters et al., 2005). The C_{35} Homohopanes index (C_{35} (S + R) / [$C_{31}+C_{32}+C_{33}+C_{34}+C_{35}$ (S + R)]) ratio determined only in TAV-6 sample is 0.05. This ratio shows that the length of the side chains in hydrocarbon molecules decreases with oxidation and suboxic paleo deposition conditions are predominant (Hunt, 1996). In addition, low sterane / hopane ratios (0.33 and 0.12) reflect the terrestrial and / or microbial reworked organic matter, as in the examples studied (Espitalié et al., 1985). The C_{35} / C_{34} homohopanes ratio was calculated as 0.76 in TAV-6 sample and points to suboxic depositional conditions in accordance with the homohopanes index and Pr / Ph ratio (Peters and Moldowan, 1993). In addition to the above findings to determine paleo depositional conditions; As a result of SEM studies, framboidal pyrites and fine grained pyrites were identified in Tavas coals (Figure 2f and figure 6). This indicates the presence of relatively reducing conditions (Rimstidt and Vaughan, 2003) in the deposition environment during peat formation, but also supports biomarker data.

4.3. Aromatic Hydrocarbons

As in the studied samples, terrestrial facies are generally dominant in the depositonal environment

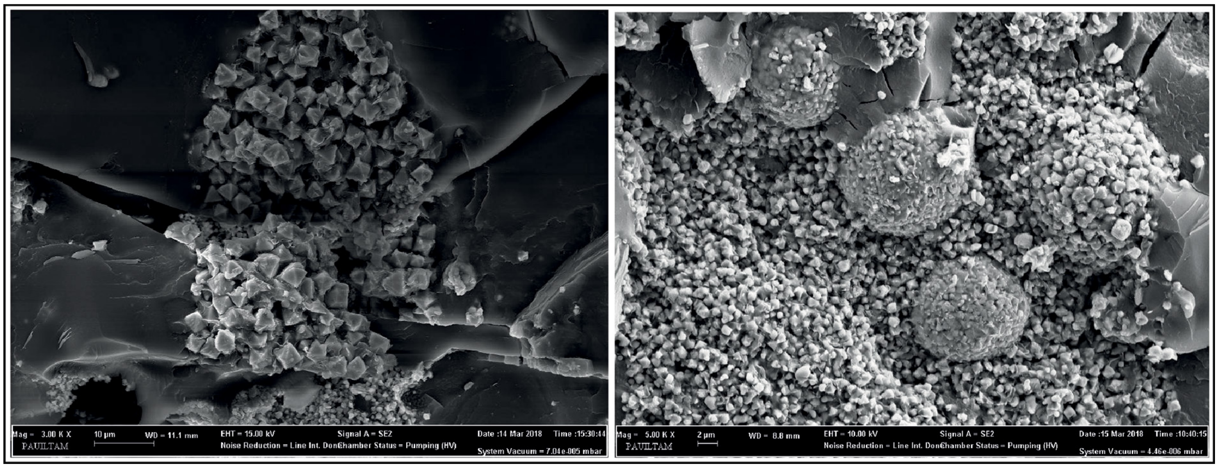

Figure 6- SEM images of framboidal pyrite in Tavas clayey coal samples.

due to low dibenzothiophene (DBT, 166 ng / g and 362 ng / g) concentrations (Radke et al., 1991). In coals, the dibenzothiophene / phenanthrene (DBT / P) ratio should generally be between 0.06 and 0.2 (Requejo, 1994). DBT / P ratio of Tavas coals was calculated as 0.08 and 0.13 (Table 2). Reten determined in TAV-6 sample; aromatic biomarker molecule derived from a typical gymnosperm (Figures 7a and b), (Izart et al., 2015).

Monoromatic (I) (MA (I)) value increases with thermal maturity compared to monoaromatic (II) (MA (II)) (Hunt, 1996). The MA (I) / MA (I + II) ratio results in a complete conversion to MA (I) at the end of the extremely mature stage. In TAV-3 and TAV-6 samples, MA (I) / MA (I + II) ratios are calculated as 55% and 21%, and the TAV-3 sample indicates the early mature stage and the TAV-6 sample indicates the immature stage (Peters and Moldowan, 1993). Methylphenanthrene index-3 (MPI-3) value; it is greater than 1 in mature organic matter and less than 0.8 in immature organic matter (Radke, 1987). MPI-3 values of the samples examined were calculated as 0.46 and 0.79, and it was determined that the organic matter was in the immature-early mature stage (Table 2).

4.4. Stable Isotope Analysis (^{13}C and ^{15}N)

In a total of three samples, ^{13}C and ^{15}N stable isotope analyzes were performed. $\delta^{13}C$ value ranges from 26 -26,43 to ‰ -19,77, and ^{15}N value ranges from ‰ 3.71 to ‰ 6.87 (Table 3). The $\delta^{13}C$ contents of the studied samples are very similar to the $\delta^{13}C$ content of coal (Figure 8a). Also, figure 8b shows the compatibility of $\delta^{15}N$ contents of Tavas samples with $\delta^{15}N$ contents of

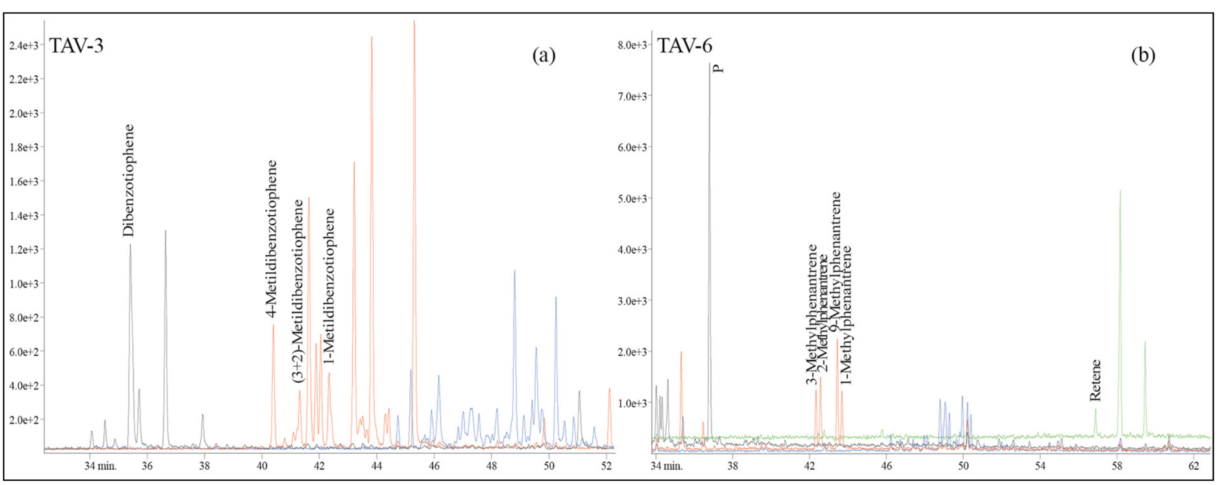

Figure 7- Mass fragmentograms of identifiable aromatic hydrocarbon molecules from the studied samples.

Table 3- C and N element (%) contents of ^{13}C (‰) and ^{15}N (‰) stable isotope of the samples examined.

Sample No	C (%)	$\delta^{13}C_{V-PDB}$ (‰)	N (%)	$\delta^{15}N_{AIR}$ (‰)	C/N
TAV-3	50,16	-26,43	1,55	3,71	32,36
TAV-4	3,50	-19,77	0,12	5,91	29,17
TAV-6	27,21	-25,90	1,03	6,87	26,42

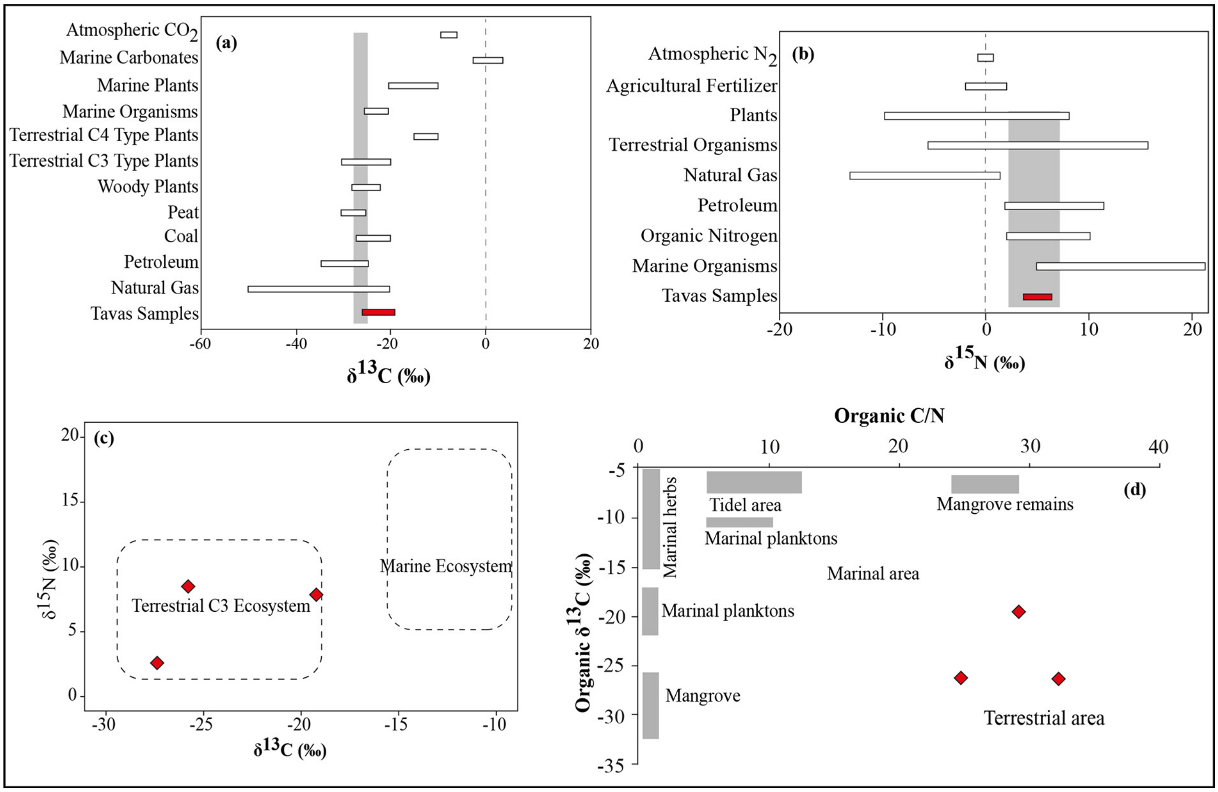

Figure 8- a) $\delta^{13}C$ and b) $\delta^{15}N$ concentrations according to some references c) $\delta^{15}N$ - $\delta^{13}C$ diagram of the studied samples (Coplen ve Shrestha, 2016) and d) Diagram of $\delta^{13}C$ values versus organic C/N ratio of the studied samples (Florentine, 2007).

some references such as terrestrial organisms, plants and organic nitrogen. As seen from the diagram $\delta^{13}C$-$\delta^{15}N$ Tavas (Denizli / SW Turkey) clayey coal of paleo vegetation it is designated as C3 terrestrial ecosystem (Figure 8c) (Coplin and Shrestha, 2016). C / N ratios of samples (between 26.42 and 32.36) are greater than 10 and are characterized by high terrestrial plants (Table 3) (Inoue et al., 2012). When C / N and $\delta^{13}C$ are evaluated together, it can be said that Tavas coals have the same origin and originate from a terrestrial source (Figure 8d), (Florentine, 2007).

4.5. Total Organic Carbon and Pyrolysis Parameters Analysis

The total organic carbon amount (TOC) of Tavas clayey coals belonging to Sekköy formation varies between 1,94-44,00%. Sample TAV-4 has very low S_2 (0.30 mg HC / g rock) and very high Tmax (528 °C) (Table 4). Tmax values determined by the device are not reliable when S_2 hydrocarbons are below 0.5 mg HC / g rock. In order not to cause misinterpretation, TAV-4 sample was excluded while evaluating pyrolysis parameters. TAV-3 and TAV-6 samples (Figure 9a), hydrogen index (HI, 120 and 73 mg HC / g TOC), T_{max} (414 °C and 413 °C) and S_2 / S_3 with very good source rock potential. According to the values (3,54 and 1,24), the gas contains type III kerogen suitable for hydrocarbon type (Figure 9b and c). Production index (PI) values, which are one of the maturation parameters, are 0,06 and 0,11. When T_{max} and PI are evaluated together, it is seen that the organic matter is in the immature stage (Peters and Cassa, 1994) (Figure 9d).

Table 4- TOC and pyrolysis analysis results of Tavas clayey coals.

Sample no	TOC (wt.%)	S_1	S_2	S_3	Tmax (°C)	PY	PI	HI	OI	S_2/S_3
TAV-3	44,00	3,29	52,83	14,94	414	56,12	0,06	120	34	3,54
TAV-4	1,94	0,05	0,30	2,61	528	0,35	0,14	15	135	0,11
TAV-6	25,80	2,45	18,92	15,29	413	21,37	0,11	73	59	1,24

S_1, S_2: mg HC/g rock, S_3: mg CO_2/g rock, PY(S_1+S_2): mg HC/g rock, PI: (S_1/(S_1+S_2)), HI(S_2/TOC): mg HC/g TOC, OI (S_3/TOC): mg CO_2/g TOC.

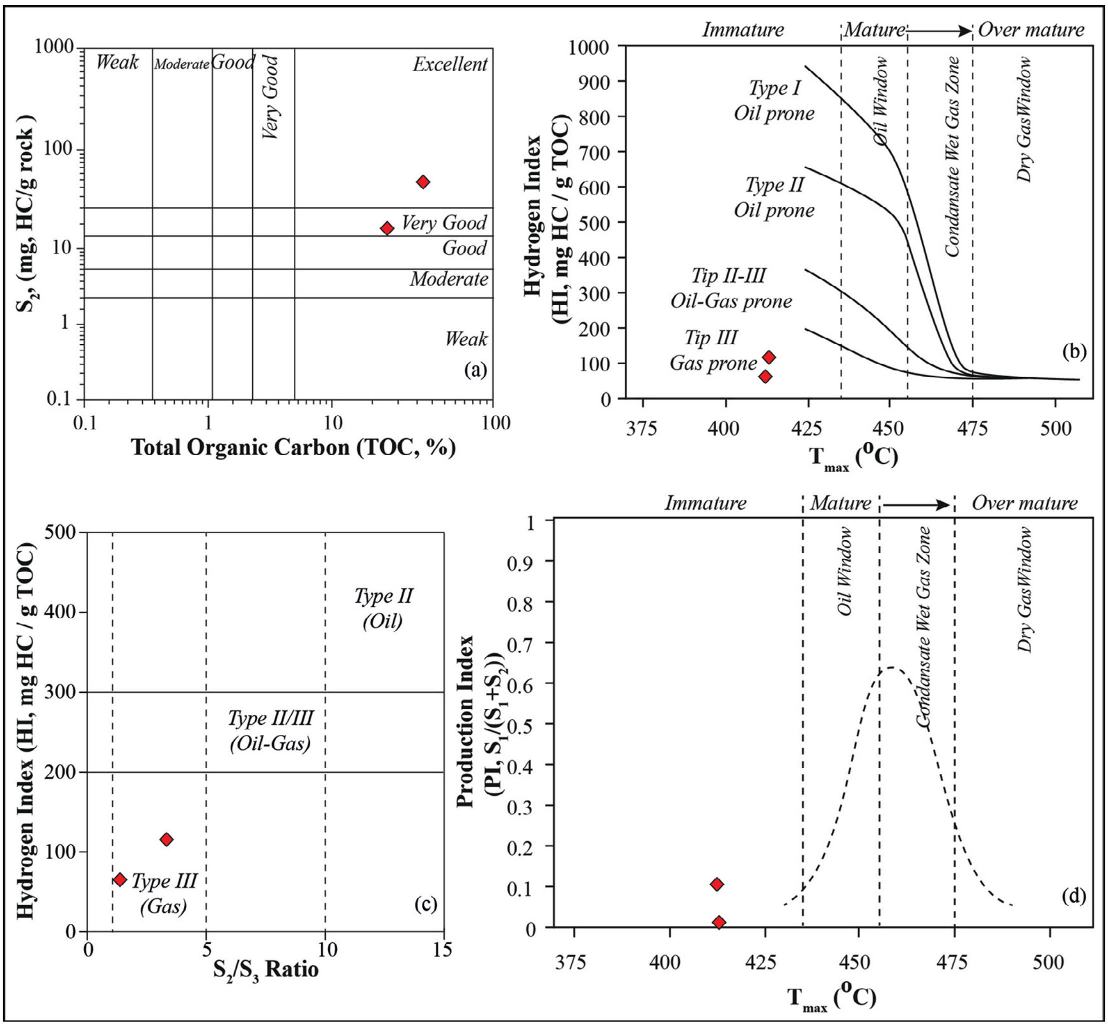

Figure 9- The positions of the data obtained as a result of pyrolysis analysis in a) S_2 – TOC, b) HI – T_{max}, c) HI – S_2/S_3 and d) PI – T_{max} diagrams.

4. Discussion

Tavas clay coals are located at the base of Sekköy Formation and the formation continues with clayey, micritic, clastic limestone and siltstone lithologies. As a result of organic geochemical investigations carried out within the scope of this study; Pr/Ph, C_{35}/C_{34} homohopanes ratio and C_{35} Homohopanes index values indicate oxic-suboxic depositional conditions (Diessel, 1992; Peters and Moldowan, 1993; Hunt, 1996). In addition, the sterane/hopane ratio and framboidal pyrites referring to the reworked organic matter in the samples examined; it supports the oxic-suboxic depositonal environment or the presence of relatively reducing conditions. While high molecular weight long chain *n*-alkanes indicate the presence of terrestrial plants, the concentration of dibenzothiophene from aromatic hydrocarbons indicates that the terrestrial facies are predominant in the depositonal environment. According to stable isotope studies ($\delta^{13}C$ and $\delta^{15}N$), paleo vegetation of coals is a terrestrial C3 ecosystem (Coplen and Shrestha, 2016). According to saturated and aromatic hydrocarbon molecules, which are observed to be compatible with isotope data; The predominance of high molecular weight *n*-alkanes, the degree of waxiness, $(C_{19}+C_{20})/C_{23}$ tt ratio and abundant C_{29} ααα R isomers indicate terrestrial source (Meyers, 1997; Hunt, 1996; Peters and Moldowan, 1993; Czochanska et al., 1988; Radke et al., 1991). In addition, the C_{29} NH/C_{30} H ratio supports paleo deposition in a clastic environment (Waples and Machihara, 1991). In addition to this information; the high C_{24}/C_{23} tt and low C_{22}/C_{21} tt rates and the C_{31} 22R/C_{30} Hopane ratio represent the lacustrine depositional environment (Peters et al., 2005). Coals containing type III kerogen suitable for gas hydrocarbon type are immature-early mature stage according to maturation parameters (Peters and Cassa, 1994).

5. Conclusion

According to all organic geochemical parameters and stable isotope data, terrestrial paleo vegetation, oxic-suboxic conditions and terrestrial facies predominate in the environment. As a result; in the light of site investigations, general geological information and organic geochemical investigations Tavas (Denizli / SW Turkey) clayey coals away from the marine influence of paleo-depositional environments, is thought to have marshes in the terrestrial environment in developing the lake shore facies.

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