

## Organic geochemistry and element distribution in coals formed in Eocene lagoon facies from the Eastern Black Sea Region, NE Turkey

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**Abstract:** The amount and type, the inorganic element content, and the maturity of organic materials of Eocene coals, shaly coals, and coaly shales exposed in the Gümüşhane and Bayburt districts of the Eastern Black Sea Region of Turkey were investigated. The depositional environments and hydrocarbon potentials were also interpreted. The total organic carbon concentrations in the studied samples ranged from 0.50% to 63.08%. The samples from Özyurt, Kayadibi, and Tarhanas contained types II and III kerogen, and those from Sökmen and Manas contained type III kerogen. The samples contained Co, Cs, Ga, Hf, Th, U, Y, Mo, Be, Cd, Sb, and La, with average values similar to those of standard brown coals. The samples showed average contents of Co, Ga, Nb, Rb, V, Y, Cu, Pb, Zn, As, Be, and Se, similar to those of other Turkish coals. The sediment source of Eocene samples in the five areas was characterized by rocks with intermediate or mafic geochemical characteristics. The terrigenous/aquatic ratio of coal and shaly coal samples of the areas in question is  $>1$ . The sterane distribution was  $C_{29} > C_{28} > C_{27}$  and  $C_{29} > C_{27} > C_{28}$  for the Özyurt and Tarhanas areas, respectively. The average  $T_{max}$  values for samples are between 424 °C and 460 °C. For samples Oz-1 and Ta-2, 22S/(22S + 22R) homohopane ( $C_{32}$ ) ratios are 0.48 and 0.61, respectively; 20S/(20S + 20R) sterane ( $C_{29}$ ) ratios are 0.18 and 0.53, respectively; and Ts/(Ts + Tm) ratios are 0.015 and 0.64, respectively. The Pr/Ph ratios of the samples are  $>3$ . The studied samples have low sterane/hopane and high ( $C_{19}+C_{20}$ )/ $C_{23}$  ratios without anoxic biomarkers (17 $\alpha$ (H)-28,30-bisnorhopane). Based on these data, the coals, shaly coals, and coaly shales were probably deposited under an oxic-suboxic mixture of marine and terrestrial environment conditions; these materials contain terrestrial organic matter and cannot generate hydrocarbon.

**Key words:** Northeastern Turkey, Eocene coal, geochemistry, total organic carbon, rare earth elements and yttrium, gas chromatography-mass spectrometry, organic matter, paleoenvironment

### 1. Introduction

The total coal reserves of Turkey are estimated to be in the order of 13.4 billion tons of lignite and 0.4 billion tons of bituminous coal. Most of the lignite deposits are located in Tertiary basins, while Eocene lignite deposits are very limited.

Eocene aged clastic rocks of the eastern Pontides (NE Turkey) exhibit two different source characteristics. Volcaniclastic deposits are dominant in the northern section of Gümüşhane and siliciclastic deposits are dominant in the southern section (Kelkit, Köse). In Bayburt, deposition starting with basal conglomerate has volcaniclastic characteristics in the north of Varicna village and has siliciclastic characteristics in other sections (Saydam Eker, 2012, 2015). Eocene aged sedimentary rocks in the Gümüşhane region are composed of siliciclastic deposits. The rocks come over Cretaceous aged sedimentary rocks of this region with discordance. Eocene aged siliciclastic rocks lie with discordance over Late

Cretaceous aged limestones in the Bayburt region (Saydam Eker, 2012). The investigated coal occurrences are found within Eocene siliciclastic deposits in the Gümüşhane and Bayburt regions.

Prior to this publication, no record existed on the working details of the organic and inorganic geochemistry of the Eocene aged coals in the Eastern Black Sea Region (Gümüşhane and Bayburt fields). The aim of the present study was to determine organic matter contents and distributions of major, trace, and rare earth elements, and to interpret organic matter types and maturities, depositional environments, and hydrocarbon potentials of selected Eocene coals, shaly coals, and coaly shales in NE Turkey.

### 2. Geological background

The eastern Pontides belt in the Black Sea Region of Turkey is part of the Alpine metallogenic belt that has been subdivided into northern, southern, and axial zones,

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distinguished from north to south by different lithological units, facies, and tectonic characteristics (Bektaş et al., 1995; Eyuboglu et al., 2006). The northern zone contains Mesozoic–Cenozoic volcanic sequences associated with massive sulfide deposits, calderas, and granitic intrusions (Arslan et al., 1997; Şen et al., 1998; Kaygusuz et al., 2008, 2011; Sipahi, 2011; Temizel et al., 2012, Sipahi et al., 2014). The southern zone includes Mesozoic and Eocene sedimentary rocks, pre-Liassic ultramafic–mafic rocks, and metamorphic–granitic rocks (Figure 1A). Upper mantle peridotites and middle to upper Cretaceous olistostromal mélange occupy much of the axial zone (Eyuboglu et al., 2010). The basement rocks of the eastern Pontides are composed of metamorphic rock and granitoids (Yılmaz, 1972; Çoğulu, 1975; Okay and Şahintürk, 1997; Topuz et al., 2004, 2010; Dokuz, 2011). Liassic volcanics and volcanoclastic and clastic deposits lie unconformably on the basement rocks (Yılmaz, 1997; Şen, 2007). This unit is overlain by pelagic and neritic carbonates of Malm–Lower Cretaceous age. The Upper Cretaceous, largely represented by volcanics in the north, developed into turbiditic facies in the south (Saydam Eker and Korkmaz, 2011). Eocene aged rocks in the Gümüşhane region are composed of volcanics, volcanosediments, and coal interbedded with siliciclastic rocks in various places (Figure 1B). Eocene rocks in the Bayburt region are composed of volcanoclastics, basal conglomerate, and coal interbedded with turbiditic members (Saydam Eker, 2012) (Figure 1B). This sequence is widespread in the region and discordantly overlies the older rocks. Miocene and Pliocene deposits occurred in restricted areas and are characterized by clastic material (Saydam and Korkmaz, 2008; Figure 1A).

### 3. Samples and methods

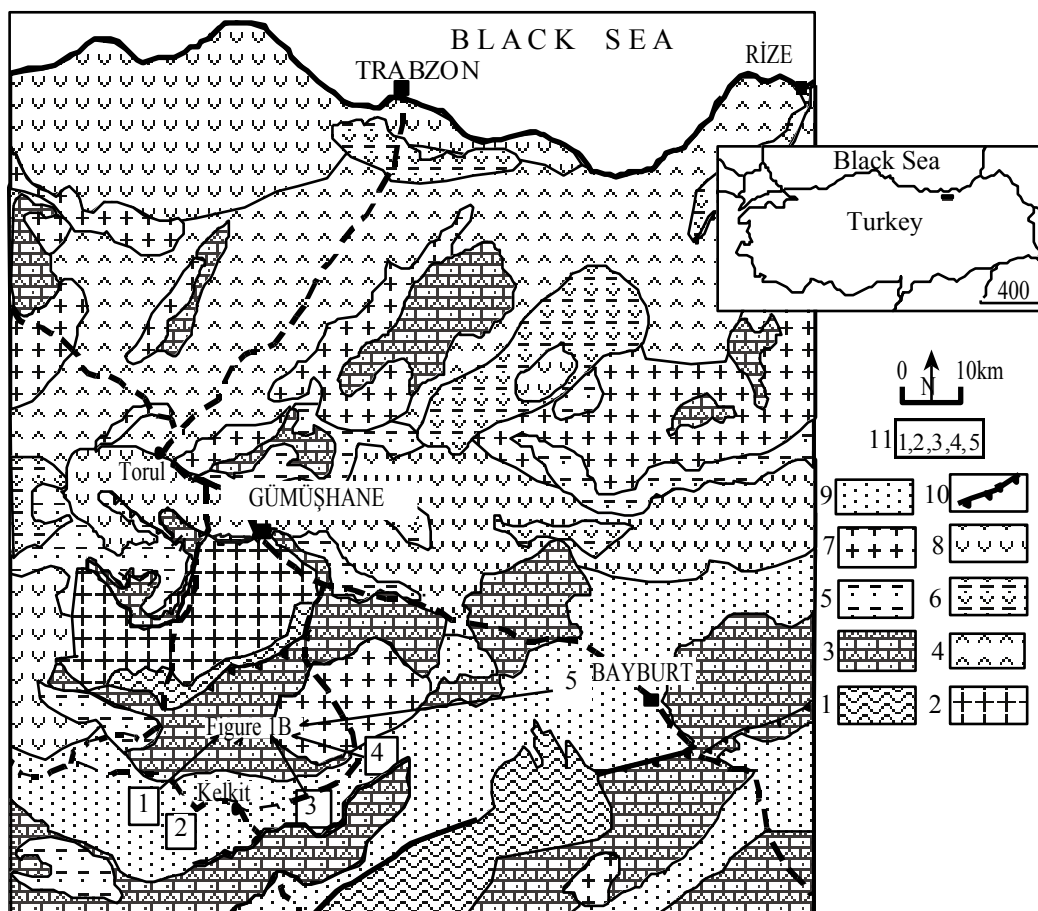
In this study, coal, shaly coal, and coaly shale samples were collected from five different areas [Tarhanas, Kayadibi, Özyurt, Sökmen (Gümüşhane), and Manas (Bayburt)]; total thicknesses of coal bearing claystones are ~10 m, 15 m, 50 m, 8 m, and 15 m, respectively (Figure 1B)] of the Eastern Black Sea Region. Rock-Eval/total organic carbon (TOC) analysis was applied to 22 chosen bulk samples (Özyurt: 6 samples, Kayadibi: 5 samples, Tarhanas: 4 samples, Manas: 4 samples, and Sökmen: 3 samples; Figure 1B). Whole rock major element, trace element, and rare earth element (REE) analyses were separately applied to 20 coal, shaly coal, and coaly shale samples (Özyurt: 6 samples, Kayadibi: 4 samples, Tarhanas: 4 samples, Manas: 4 samples, and Sökmen: 2 samples). Gas chromatography (GC) was used for four samples (one sample each from Özyurt, Tarhanas, Kayadibi, and Manas). Gas chromatography–mass spectrometry (GC-MS) analyses were also performed on one sample each from Özyurt and Tarhanas (labeled as Oz-1 and Ta-2, respectively).

### 3.1. Organic geochemistry analysis

Rock-Eval pyrolysis/TOC analyses of all the samples were done using a Rock-Eval 6 instrument equipped with a TOC module. The samples were heated from 300 °C (hold time: 3 min) to 650 °C at 25 °C/min. The crushed coal was heated from 400 °C (hold time: 3 min) to 850 °C (hold time: 5 min) at 25 °C/min for oxidation. Extracts were obtained from two coal samples (Oz-1, Ir-2), a shaly coal sample (Ta-2), and a coaly shale sample (Ma-2) by 40 h of Soxhlet extraction of the powdered rock with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). The whole extract was analyzed using an Agilent 6850 gas chromatograph equipped with a flame photometric detector and flame ionization detector. A fused capillary column (100 m, 0.25 mm i.d.) coated with cross-linked dimethylpolysiloxane (J&W, 0.50 µm film thickness) was used for separation and helium was used as the carrier gas. The oven temperature was programmed from 40 °C (hold time: 8 min) to 270 °C (hold time: 60 min) at 4 °C/min. The extract samples were separated into saturated hydrocarbon, aromatic hydrocarbon, and NSO-compound fractions by liquid chromatography. N-hexane, toluene, and methanol were used for eluting the fractions, respectively. GC-MS analyses were run on the two samples (Oz-1, Ta-2) having the highest levels of extract. The GC-MS analyses were conducted on saturated fractions of coal extracts. An Agilent 5975C quadrupole mass spectrometer was coupled to a 7890A gas chromatograph and 7683B automatic liquid sampler. The gas chromatograph was equipped with an HP-1MS fused silica capillary column of 60 m in 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 °C (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 the EI mode at ionization energy of 70 eV and source temperature of 300 °C. The biomarker contents were determined using single ion recording at m/z 191 (terpane) and m/z 217 (sterane). Compounds were identified by retention time and elution order matching. The analyses were carried out at the Oil and Organic Geochemistry Laboratory of the Turkish Petroleum Corporation (TPAO, Ankara).

### 3.2. Inorganic geochemistry analysis

Twenty samples were selected for whole rock major element, trace element, and REE analyses. Major and trace elements were determined by inductively coupled plasma (ICP)-emission spectrometry and ICP-mass spectrometry (MS) at ACME Analytical Laboratories Ltd., Vancouver, Canada, using standard techniques. Major and trace elements were analyzed by ICP using 0.2 g of rock powder fused with 1.5 g of LiBO<sub>2</sub> dissolved in 100 mL of 5% HNO<sub>3</sub>.



**Figure 1A.** Simplified geological map of the Eastern Black Sea Region (after Güven et al., 1993) and location map of the study area. 1- Paleozoic metamorphic basement, 2- Paleozoic granites, 3- Jurassic–Lower Cretaceous sequences, 4- Upper Cretaceous volcanics, 5- Upper Cretaceous sedimentary rocks, 6- Paleocene volcanosedimentary sequences, 7- Paleocene granites, 8- Eocene volcanic and volcanoclastic rocks, 9- Eocene sedimentary rocks, 10- thrust fault, 11- study area (1: Özyurt, 2: Sökmen, 3: Tarhanas, 4: Kayadibi, 5: Manas fields).

Ignition loss was determined on dried samples heated to a temperature of 1050 °C for 15 min. REE analysis was conducted by ICP-MS at ACME.

## 4. Results and discussion

### 4.1. Rock-Eval pyrolysis and TOC

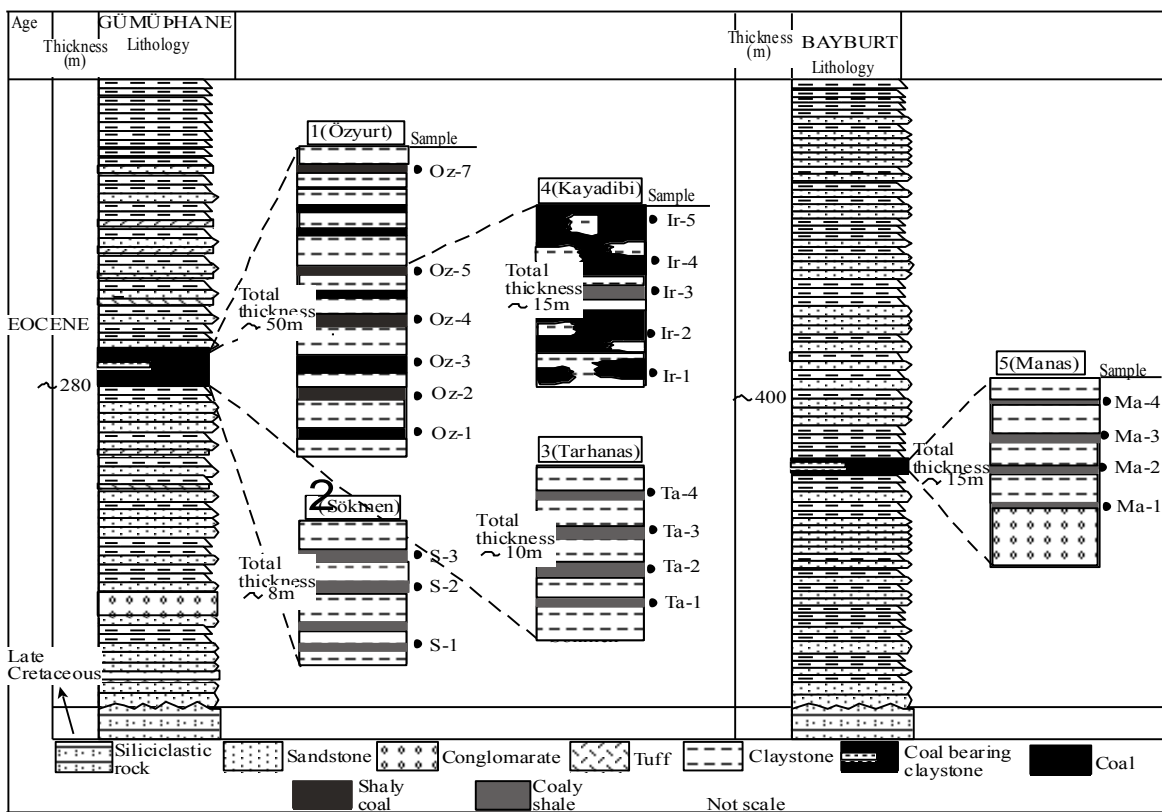
Table 1 lists our coal, shaly coal, coaly shale data from the Özyurt (6), Tarhanas (4), Sökmen (3), and Kayadibi (5) areas of the Gümüşhane region, as well as the Manas (4) area of the Bayburt region, including TOC and Rock-Eval pyrolysis analyses. The TOC concentrations in the study area ranged from 0.50% to 63.08%. In this paper, samples characterized by TOC concentrations of >50% are considered as coal, samples with concentrations ranging from 35% to 50% are considered as shaly coal, and samples with values of TOC <35% are considered as coaly shale.

The average highest PY value was calculated in Kayadibi coals and coaly shale (65.8 mg HC/g rock), the

average highest HI value was calculated in Tarhanas shaly coal and coaly shales (112 mg HC/g TOC), and the average highest  $T_{max}$  value was calculated in Manas coaly shales (460 °C). The average lowest PY, HI, and  $T_{max}$  values were calculated in Sökmen coaly shales (0.12 mg HC/g rock, 24 mg HC/g rock, and 424 °C, respectively) (Table 1).

### 4.2. Major, trace, and REY elements

Table 2 lists the percentages of major element oxides; concentrations of trace elements and REEs in the samples from Özyurt, Tarhanas, Sökmen, Kayadibi (Gümüşhane), and Manas (Bayburt); average values of major and trace elements of Eocene aged Sorgun coals (Karayigit, et al., 2000a); average values of major and trace elements of Turkish coals (Palmer et al., 2004); global average values of major elements of coal (Valkovic, 1983); and average values of trace elements and REEs of standard brown coal (Ketris and Yudovich, 2009). In the investigated samples from the five studied areas, Mg, K (except coals from



**Figure 1B.** Stratigraphy of the Eocene coals, coal beds, and positions of Eocene coals, shaly coals, and coaly shales in the Özyurt, Sökmen, Tarhanas, Kayadibi, and Manas fields.

Sökmen), Na, and Ti contents are generally close to one other, whereas Al, Fe, and Ca contents show remarkable differences. Sökmen area coaly shales show the highest average Al content (5.22%), whereas Özyurt coals and shaly coals exhibit the lowest value for Al content (0.75%). Coaly shales from Sökmen exhibit the highest average Fe content (4.56%), whereas the coals and shaly coals of Kayadibi show the lowest Fe value (0.97%). The average highest and lowest Ca contents are 14.9% and 0.08% for samples obtained from Tarhanas and Kayadibi, respectively.

The major element contents of the studied samples were compared with the average major element contents of Eocene aged Sorgun coals (Yozgat, Turkey) (Karayigit et al., 2000a). The Fe, Mg, and Ca contents of Özyurt; the Al, Mg, K, and Ti contents of Kayadibi; the Fe, Mg, Ca, K, and Ti contents of Tarhanas; and the Fe, Ca, K, and Ti contents of Manas are enriched. The remaining elements in the general area are depleted (except the Al contents of Manas samples). When the major element components of the investigated samples were compared with the average major element components of Turkish coals (Palmer et al., 2004), the Fe and Mg contents of Özyurt; the Al, Mg, K, and Ti contents of Tarhanas and Kayadibi; and the Al, Fe, Mg, K, and Ti contents of Manas show similarities.

The studied samples are depleted in Na (except Sökmen samples). All Sökmen samples contain low amounts of organic matter and only comprise coaly shale; therefore, the major element contents of the samples are enriched in Sorgun and Turkish coals. The major element contents of samples from the investigated areas were compared with the average major element contents of world coal (Valkovic, 1983). The Al, Na, and Ti contents of Özyurt; the Na content of Tarhanas; the Ca content of Sökmen; the Fe and Ti contents of Kayadibi; and the Na and Ti contents of Manas samples exhibit similarities to the average content of the major elements of the world's coals. The rest of the elements present are enriched (except the Na content of Kayadibi coals and shaly coal) (Table 2; Figure 2).

Generally, the average contents of W, Be, Cd, Hg, Sb, Se, and Tb in the examined samples show similarities. However, Be in Sökmen, Sb in Manas, and Se in Özyurt samples differed from those of the other samples. The lowest average contents of Co, Cs, Ga, Rb, V, and Zn values were calculated for Özyurt coals and shaly coals. The highest average Co, Cs, Ga, Rb, V, and Zn values were calculated in Sökmen coaly shales. Samples from Özyurt show the lowest average concentrations of Hf, Nb, Th, Zr, Cu, and Pb. Samples from Manas exhibit the highest

**Table 1.** TOC and Rock-Eval results.

Sample ID	TOC %Wt	S <sub>1</sub> mg HC/g rock	S <sub>2</sub> mg HC/g rock	S <sub>3</sub> mg CO <sub>2</sub> /g rock	PY (S <sub>1</sub> +S <sub>2</sub> ) mg CO <sub>2</sub> /g rock	PI (S <sub>1</sub> /S <sub>1</sub> +S <sub>2</sub> )	T <sub>max</sub> °C	HI (S <sub>2</sub> /TOC) mgHC/g TOC	OI (S <sub>3</sub> /TOC) mgCO <sub>2</sub> /g TOC	Lithology
Gümüşhane region										
Özyurt										
Oz-1	53.87	1.32	91.6	3.09	92.9	0.01	434	156	5	Coal
Oz-2	38.5	0.13	19.35	30.14	19.5	0.01	444	50	78	Shaly coal
Oz-3	55.03	0.51	45.57	20.74	46.1	0.01	440	83	38	Coal
Oz-4	35.46	0.25	16.57	26.22	16.82	0.01	445	47	74	Shaly coal
Oz-5	36.74	0.81	23.04	3.15	23.85	0.03	407	63	9	Shaly coal
Oz-7	43.74	0.16	21.55	34.08	21.71	0.01	442	49	78	Shaly coal
Average	43.89	0.53	36.28	19.57	36.8	0.013	435	74.7	47	
Tarhanas										
Ta-1	10.04	0.03	4.97	6.72	5	0.01	455	50	67	Coaly shale
Ta-2	35.2	1.32	38.27	14.31	39.6	0.03	451	111	41	Coaly shale
Ta-3	3.43	0.21	8.54	1.29	8.75	0.02	444	249	38	Coaly shale
Ta-4	4.52	0.02	1.66	0.18	1.68	0.01	472	37	4	Coaly shale
Average	13	0.4	13.4	5.6	13.8	0.02	456	112	38	
Sökmen										
S-1	0.50	0	0.14	0.26	0.14	0.02	439	35	65	Coaly shale
S-2	0.53	0	0.07	0.18	0.07	0.05	348	16	42	Coaly shale
S-3	0.60	0.01	0.13	0.08	0.14	0.09	485	22	13	Coaly shale
Average	0.54	0.004	0.118	0.178	0.12	0.05	424	24	40	
Kayadibi										
Ir-1	58.39	0.36	51.88	11.22	52.3	0.01	435	89	19	Coal
Ir-2	63.08	0.68	65.01	10.54	65.7	0.01	432	103	17	Coal
Ir-3	29.24	29.24	16.6	11.5	45.8	0.01	426	57	39	Shaly coal
Ir-4	62.24	62.24	52.26	17.15	114.5	0.01	429	84	28	Coal
Ir-5	53.83	0.35	50.37	0.71	50.7	0.01	468	94	1	Coal
Average	53.4	18.6	47.2	10.2	65.8	0.01	438	85	20	
Bayburt region										
Manas										
Ma-1	3.38	0.01	2.11	2.46	2.12	0	440	62	73	Coaly shale
Ma-2	7.85	0.02	4.4	5.7	4.42	0	440	56	73	Coaly shale
Ma-3	4.97	0.03	1.74	0.58	1.7	0.01	487	35	12	Coaly shale
Ma-4	3.13	0.01	0.09	0.61	0.1	0.01	473	32	19	Coaly shale
Average	4.80	0.02	2.10	2.30	2.12	0.005	460	46	44	

average concentrations of Hf, Nb, Th, Zr, Cu, and Pb. The lowest average values of Ba, Sr, and Ni are found in the Kayadibi area. Sökmen, Tarhanas, and Manas samples show the highest average values. The lowest average Y, Mo, and As values are observed for the Özyurt and Sökmen samples. Kayadibi, Manas, and Özyurt samples show the highest average values of Y, Mo, and As.

The average trace element contents of the studied coal samples (Oz-1, Oz-3, Ir-1, Ir-2, Ir-4) and shaly coal samples (Oz-2, Oz-4, Oz-5, Oz-7, Ta-2, Ir-3) from three locations and Eocene aged Sorgun coals (Karayigit et al., 2000a) were compared with those of standard brown coals (Ketris and Yudovich, 2009). The results showed high similarity to the coal samples (Table 2; Figure 3A). Ba and

**Table 2.** Concentrations of elements in the Gümtüşane and Bayburt coals, shaly coals, and coaly shales, as well as their comparisons with averages for Sorgun, Turkish, and world brown coals (major element oxides are in %; unit for trace and rare earth elements is µg/g).

Sample	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	Ba	Co	Cs	Ga	Hf	Nb	Rb	Sr	Th	U	V	W	Zr	Y	Mo	Cu
Özyurt																							
Oz-1	0.44	1.48	0.23	10.8	0.007	0.07	0.04	37	6.3	0.7	3.3	0.5	2	7	140	1.7	5.7	67	0.9	16.4	11.4	3.2	14.2
Oz-2	0.64	3.4	0.62	5.96	0.011	0.11	0.06	56	16.8	0.9	4.1	1	2.7	11.3	255	2	4.8	91	0.9	28.6	18.1	3.4	24.2
Oz-3	0.27	1.54	0.14	1.31	0.004	0.02	0.02	10	6.1	0.5	0.7	0.3	0.6		80	0.9	1.6	24	0.7	8.6	6.3	2.1	6.6
Oz-4	0.85	2.96	0.77	5.29	0.03	0.12	0.07	54	12.4	1.2	3.8	0.9	2.9	12	369	1.5	7.8	53	0.5	227.8	8.7	2.5	12.8
Oz-5	0.26	2.59	0.11	5.64	0.004	0.04	0.02	16	6.8	0.5	1.2	0.3	1.2	2.9	89.5	1.1	2.2	43	0.5	10.5	7.2	4.6	6.9
Oz-7	2.03	2.36	0.85	3.79	0.045	0.41	0.15	141	3.8	2	9.3	1.8	6.3	49.2	250	4.4	7	74	0.5	60.4	11.8	1.6	16.8
Kayadibi																							
Ir-1	0.56	0.8	0.12	0.51	0.004	0.08	0.03	16	3.1	0.9	2.1	0.5	1.1	8.3	21.4	1.7	1.4	20	0.5	16.5	13.9	3.5	7.2
Ir-2	3.75	0.88	0.65	0.25	0.007	0.74	0.19	46	15.4	6.3	15.3	3.5	10.9	66	110	5.3	10.9	122	0.5	139.5	40.3	4.1	32.3
Ir-3	4.3	1.23	0.73	0.27	0.007	0.83	0.21	53	15.9	7	16.1	3.5	10.8	67.3	120	7.5	8.9	110	0.7	113.7	44	1.8	29.7
Ir-4	0.36	0.98	0.05	0.33	0.004	0.04	0.02	9	2.1	0.5	1.9	0.3	0.8	3.5	15.7	0.8	8	52	0.6	12.7	6.3	7.6	7.5
Tarhanas																							
Ta-1	3.08	4.72	0.4	4.5	0.096	0.58	0.18	110	26.7	3.3	11.7	3	7.1	44.9	264	4.2	5.1	210	0.6	126	14.6	6.6	59.3
Ta-2	1.2	1.45	0.35	18.5	0.015	0.25	0.07	239	7.8	1.6	4.1	0.9	3.4	18.8	656	8.9	2.6	94	0.5	35.6	6.5	2.9	14.3
Ta-3	0.23	0.67	0.49	36.6	0.007	0.05	0.01	56	1.9	0.5	0.5	0.2	0.3	2.8	2149	0.6	1.1	38	0.5	6.8	2.4	0.9	2.3
Ta-4	7.65	0.86	0.25	0.3	0.026	1.11	0.34	311	8	10	35.3	7	18.8	101	246	18.7	5.6	144	4.7	239.5	53.4	0.3	44.3
Sökmen																							
S-1	5.08	4.66	1.83	1.21	0.412	1.1	0.26	451	20.1	9.3	22	3.4	8.6	92	408	6	2.8	196	1.3	133	25	0.6	57
S-3	5.35	4.5	1.77	1.24	0.415	1.1	0.28	453	19.3	9.6	21.9	3.6	8.4	91.2	409	6.2	2.7	197	1.5	132.1	24.9	0.5	57.6
Manas																							
Ma-1	3.52	1.38	0.86	2.59	0.108	0.92	0.16	764	8.2	5.4	15.5	3.9	10.6	118	128	11.9	6.5	88	2.2	134.9	31.6	0.7	68.1
Ma-2	3.14	1.16	0.71	1.03	0.1	0.84	0.15	202	12	5.1	13.1	3.6	9.4	114	173	10.6	8.5	91	2.2	135.8	35.2	1.7	77.2
Ma-3	6.51	1.26	0.32	0.09	0.041	1.3	0.31	287	14.1	5.9	32.3	7.1	19.7	89.1	193	17.9	8.7	128	9.8	250.4	25.9	2.9	28.1
Ma-4	1.4	13.7	0.02	0.01	0.004	0.08	0.1	28	36.2	1	4	2.7	5.1	5.8	28.3	4.1	1.8	96	2.4	101.2	9.9	15.1	56.6
Sorgun Basin <sup>a</sup>	3.23	1.32	0.08	0.57	-	0.18	0.06	107	-	4.8	9.6	1.5	3.4	25	77	21	2.8	22	26	17	3.7	3.7	4.3
Turkey average <sup>b</sup>	2.1	2.3	0.53	1.8	0.11	0.32	0.097	130	10	4.9	5.8	-	4.0	25	210	-	13	65	-	-	8.3	9.8	20
World <sup>c</sup>	1	1	0.02	1	0.02	0.01	0.05																
World <sup>d</sup>								150	4.2	0.98	5.5	1.2	3.3	10	120	3.3	2.9	22	1.2	35	8.6	2.2	15

<sup>a</sup>Karayigit et al. (2000a).

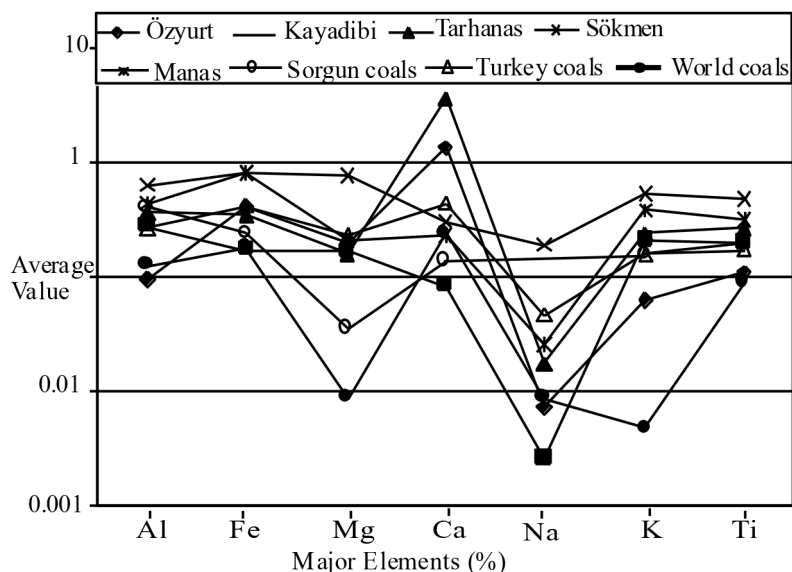
<sup>b</sup>Palmer et al. (2004).

<sup>c</sup>Valkovic (1983).

<sup>d</sup>Ketris and Yudovich (2009).

Table 2. (Continued).

Sample	Pb	Zn	Ni	As	Be	Cd	Hg	Sb	Se	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Özyurt																							
Oz-1	9.8	29	40.4	49.2	1	0.1	0.05	0.6	1.1	9.1	19.9	2.07	8.6	2.1	0.56	2.11	0.35	1.8	0.39	1.1	0.15	0.81	0.15
Oz-2	5.4	44	153.1	70.4	1	0.3	0.07	1.2	3.2	11.6	21.9	3.18	13.7	2.68	0.88	3.49	0.55	3.06	0.56	1.75	0.26	1.42	0.22
Oz-3	1.6	23	49	188.6	3	0.1	0.57	0.6	8.4	3.3	6.5	0.89	3.5	1.06	0.26	1.09	0.18	1	0.22	0.58	0.1	0.47	0.09
Oz-4	3.3	33	80.6	196	1	0.1	0.39	1.4	3	5.4	10.9	1.33	5.1	1.23	0.37	1.29	0.24	1.31	0.33	0.8	0.13	0.74	0.12
Oz-5	2.4	21	27.3	334.9	2	0.1	0.23	1.2	2.2	4.5	8.8	0.98	4.4	1.09	0.27	1.06	0.2	1.09	0.25	0.61	0.12	0.63	0.1
Oz-7	6.2	22	22.5	165.8	2	0.1	0.39	1	9.8	12.4	20.4	2.06	7.8	1.45	0.39	1.59	0.27	1.68	0.39	1.27	0.2	1.41	0.22
Kayadibi																							
Ir-1	4.1	55	8.8	19	3	0.2	0.06	0.1	1.4	12.4	22.6	2.42	9.3	2.01	0.53	2.09	0.33	1.9	0.39	1.14	0.17	0.99	0.16
Ir-2	13.1	118	35.1	7.9	1	1.2	0.1	0.4	2.3	29.7	54	6.83	26.5	6.53	1.64	7.16	1.21	7.32	1.37	4.12	0.59	3.81	0.55
Ir-3	8.1	139	31.1	7	1	0.7	0.06	0.2	1.1	30.7	54.9	7.1	28.2	6.24	1.67	7.27	1.28	7.53	1.58	4.23	0.62	3.95	0.63
Ir-4	5.3	22	6	28.8	1	0.2	0.1	0.1	2.2	4.6	8.9	1.03	4.1	0.79	0.25	0.98	0.16	0.92	0.2	0.49	0.08	0.53	0.09
Tarhanas																							
Ta-1	38.2	80	114.3	70.5	1	0.1	0.34	1.3	1.8	11.4	19.8	2.38	9	1.9	0.51	2.09	0.34	2.09	0.48	1.41	0.22	1.67	0.25
Ta-2	5.9	35	29.9	12.4	2	0.1	0.05	0.2	1.1	20.2	42.2	4.59	16.9	2.29	0.55	2.05	0.25	1.29	0.26	0.64	0.13	0.77	0.13
Ta-3	1.1	10	4.8	6.1	3	0.1	0.02	0.1	0.5	2.5	3.6	0.48	2	0.43	0.1	0.47	0.07	0.33	0.07	0.2	0.05	0.24	0.05
Ta-4	28	109	10.8	24	4	0.4	0.07	0.3	0.5	69.5	140.3	14.32	50.3	9.81	2.26	9.56	1.58	9.57	1.82	5.27	0.78	4.92	0.75
Sökmen																							
S-1	15.8	112	30.2	12.8	6	0.2	0.1	0.2	0.5	20.6	42.9	5.2	18.9	4.22	1.11	4.81	0.82	4.51	0.87	2.81	0.43	2.63	0.4
S-3	16.4	112	29.9	13.4	7	0.1	0.1	0.1	0.5	20.1	43.6	4.9	19.1	4.37	1.16	4.74	0.77	4.65	0.9	2.79	0.41	2.62	0.42
Manas																							
Ma-1	27.8	118	32.4	9.1	5	0.7	0.02	0.2	0.6	29.6	38.9	5.53	22.7	4.96	1.02	5.5	0.83	4.87	1.03	2.87	0.45	2.92	0.48
Ma-2	45.2	128	33.6	15.5	5	1	0.08	0.5	1.7	38.5	51.5	6.87	26.9	6.02	1.26	6.24	0.94	5.4	1.09	3.26	0.47	3.23	0.52
Ma-3	20.8	93	33.6	62.4	5	0.2	0.07	0.6	0.5	47.9	87.4	9.29	33.5	5.85	1.17	5.11	0.8	4.82	0.97	2.94	0.46	3.05	0.48
Ma-4	282	19	178.1	293.1	1	0.1	2.82	56.7	5.5	7.4	11.4	1.24	4.4	0.87	0.25	1.2	0.26	1.97	0.44	1.28	0.2	1.26	0.19
Sorgun Basin <sup>a</sup>	20	18	2.2	33	-	-	-	0.5	2.8	17	23	-	-	5.5	-	-	-	-	-	-	-	-	-
Turkey average <sup>b</sup>	9.3	40	150	65	1.3	-	0.11	2.7	2.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
World <sup>d</sup>	6.6	18	9	7.6	1.2	0.24	0.1	0.84	1	10	22	3.5	11	1.9	0.5	2.6	0.32	2	0.5	0.85	0.31	1	0.19



**Figure 2.** Diagram of average major element contents for Özyurt, Tarhanas, Sökmen, Kayadibi, and Manas samples; Sorgun (Karayigit et al., 2000a); Turkey (Palmer et al., 2004); and the world (Valkovic, 1983) coal averages.

Sb are depleted in the coal samples, with a concentration coefficient of  $<0.5$  (CC = ratio of element concentrations in studied samples vs. standard brown coals) (Dai et al., 2015a, 2015c). V, Zn, Ni, and Se are slightly enriched ( $2 < CC < 5$ ), and As is enriched ( $CC > 5$ ). The remaining elements ( $0.5 < CC < 2$ ) are close to the average values for standard brown coals. In shaly coal samples, W is depleted, whereas Co, Cs, Rb, Sr, V, Zr, Zn, Ni, Hg, and Se are slightly enriched. As is enriched, and other elements are close to the average values for standard brown coals (Figure 3B). In the Sorgun coal samples, Zr, Y, Cu, and Ni are depleted; Cs, Rb, Th, Pb, As, and Se are slightly enriched; W is enriched; and the remaining elements are relatively close to the average values for standard brown coals (Figure 3C). The depletion of Ba, Cs, Sr, U, Mo, Ni, Sb, and other elements in the coal samples is similar to the average values for Turkish coals (Figure 3D). The shaly coal samples show depleted contents of Cs, U, Mo, Ni, and Sb, whereas As is slightly enriched with amounts similar to that of Turkish coals in other elements (Figure 3E). Sorgun coals are fairly similar to Turkish coals in terms of Ba, Cs, Nb, Rb, As, and Se contents; the Sorgun coals are slightly enriched with Pb and depleted in other elements (Figure 3F). Accordingly, the studied coal and shaly coal samples are similar to Sorgun coals in Ga, Hf, Nb, Sr, U, Mo, and La, as well as Ba, Ga, Hf, Nb, Sr, U, Mo, Sb, and La samples, respectively.

REE and yttrium (Y) are not significantly affected by sedimentary processes (Taylor and McLennan, 1985; Bhatia and Crook, 1986; Wronkijewicz and Condie, 1987, 1989, 1990; Saydam Eker, 2012). REE and Y are used as

geochemical indicators of the sedimentary environment and postsedimentary history of coal deposits (Hower et al., 1999; Seredin and Dai, 2012; Dai et al., 2015b).

The studied coals, namely shaly coals and coaly shales, exhibit similar REE and Y (REY) distribution patterns. The light REY (LREY = La, Ce, Pr, Nd, and Sm) elements are slightly depleted in Kayadibi, Tarhanas, Sökmen, and Manas samples. Medium REY (MREY = Eu, Gd, Tb, Dy, and Y) elements and heavy REY (HREY = Ho, Er, Tm, Yb, and Lu) elements are slightly enriched in Kayadibi, Sökmen, and Manas samples but slightly depleted in the Tarhanas sample. LREY elements are highly depleted in Özyurt samples, whereas MREY and HREY are moderately depleted compared with the upper continental crust (Taylor and McLennan, 1985; Figure 4). Eu in all samples shows slight or no anomalies. Mafic rocks exhibit low LREE/HREE ratios and contain nonanomalous Eu. However, silicic rocks show high LREE/HREE ratios and contain negative Eu anomalies (Cullers and Graf, 1983; Bauluz et al., 2000). In this study, the mean  $La_N/Lu_N$  ratios of the samples are  $<1$ . The  $La_N/Lu_N$  ratios range from 0.38 to 0.58 in Özyurt samples, 0.56 to 0.81 in Kayadibi samples, 0.47 to 0.96 (except  $Ta_2 = 1.6$ ) in Tarhanas samples, 0.50 to 0.54 in Sökmen samples, and 0.40 to 0.77 (except  $Ma-3 = 1.04$ ) in Manas samples. Based on these results, the studied samples were characterized by MREY and HREY enrichment types. Moreover, the  $Al_2O_3/TiO_2$  ratio is a generally useful provenance indicator for sedimentary rocks (Hayashi et al., 1997; He et al., 2010) and sediments associated with coal deposits (Dai et al., 2015a, 2015b). The characteristic  $Al_2O_3/TiO_2$  ratios are 3–8 for sediments



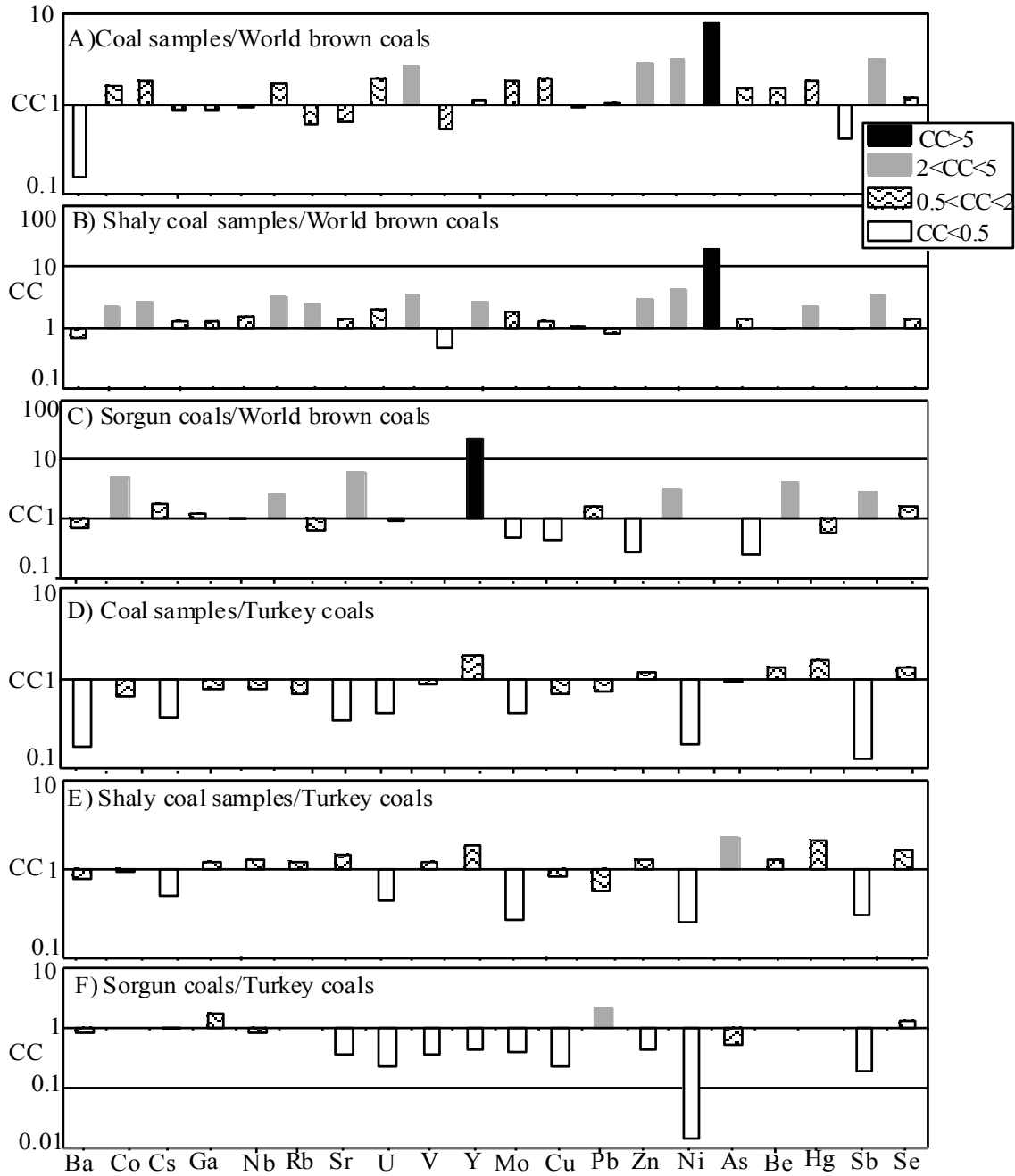
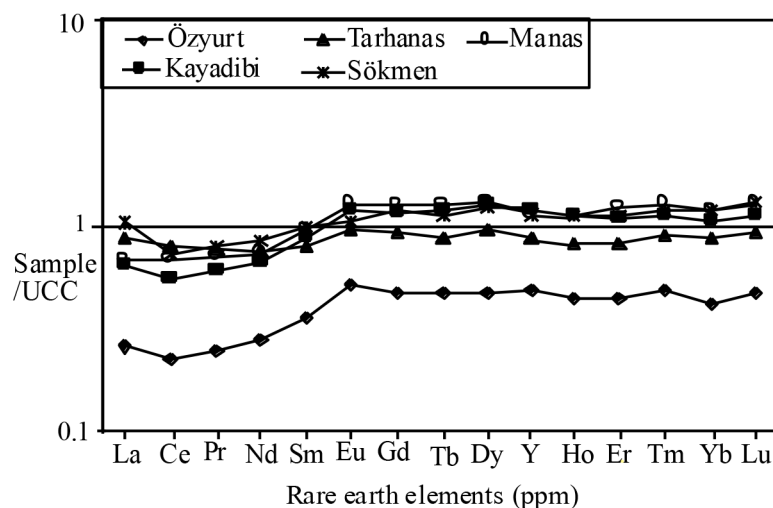


Figure 3. Concentration coefficient (CC) of trace elements in the samples and Sorgun coal samples.

derived from mafic, 8–21 for sediments derived from intermediate, and 21–70 for sediments derived from felsic igneous rocks (Hayashi et al., 1997; Dai et al., 2015a). The  $Al_2O_3/TiO_2$  ratios range from 12.3 to 19.9 in the studied samples (the average  $Al_2O_3/TiO_2$  ratios are 12.3, 19.2, 19.9, 19.3, and 19.5 for Özyurt, Kayadibi, Tarhanas, Sökmen, and Manas, respectively). This result indicates that the sediment source regions for Eocene coals, shaly coals, and coaly shales in the Gümüşhane and Bayburt regions

are characterized by rocks with intermediate or mafic geochemical properties.

In the analyzed samples from the Özyurt area, a weak negative correlation ( $r = -0.46$ ,  $P < 0.05$ ) and a strong negative correlation ( $r = -0.62$ ,  $P < 0.05$ ) were detected between As and Cd as well as between As and Zn, respectively. However, a strong positive correlation ( $r = 0.85$ ,  $P < 0.05$ ) exists between Cd and Zn. Shaly coal and coaly shales from Tarhanas demonstrate a weak positive



**Figure 4.** Distribution patterns of rare earth elements and yttrium in the Özyurt, Kayadibi, Tarhanas, Sökmen, and Manas samples. REY elements are normalized by Upper Continental Crust (UCC) (after Taylor and McLennan, 1985).

correlation ( $r = 0.55$ ,  $P < 0.05$ ) between As and Zn and a strong positive correlation ( $r = 0.76$ ) between Cd and Zn; however, no relationship was observed between As and Cd. In Kayadibi samples, a strong negative correlation ( $r = -0.82$ ,  $P < 0.05$ ) and a very strong negative correlation ( $r = -0.98$ ,  $P < 0.05$ ) were observed between As and Cd and between As and Zn, respectively. In addition, a strong positive correlation ( $r = 0.80$ ,  $P < 0.05$ ) was observed between Cd and Zn. In the Manas area, a strong negative correlation ( $r = -0.74$ ,  $P < 0.05$ ) exists between As and Cd, a very strong negative correlation ( $r = -0.99$ ,  $P < 0.05$ ) was found between As and Zn, and a strong positive correlation ( $r = 0.83$ ) was found between Cd and Zn. In the studied samples from Özyurt, Kayadibi, and Manas, the negative correlation between As and Cd as well as between As and Zn indicates a possible organic origin for As and a mineral origin for Cd and Zn. Based on this assumption, all three elements (As, Cd, and Zn) in the Tarhanas samples exhibit inorganic origins. Copper in the investigated samples is generally assumed to be associated with chalcopyrite and pyrite (Swaine, 1990; Finkelman, 1995).

Nickel is associated with both organic (Swaine, 1990; Orem and Finkelman, 2003) and inorganic (Finkelman, 1995) materials as well as with sulfites (Querol et al., 1998; Spears and Zheng, 1999; Goodarzi, 2002; Ribeiro et al., 2010). In the samples of Özyurt, a weak positive correlation ( $r = 0.54$ ,  $P < 0.05$ ) was found between Cu and Ni, and a strong positive correlation ( $r = 0.70$ ,  $P < 0.05$ ) exists between Pb and Ni. In the Tarhanas area, Cu and Ni show a strong positive correlation ( $r = 0.72$ ,  $P < 0.05$ ), whereas Cu and Pb exhibit a very strong positive correlation ( $r = 1.00$ ,  $P < 0.05$ ). Very strong correlations were also observed between Cu and Ni ( $r = 1.00$ ,  $P < 0.05$ )

and between Cu and Pb ( $r = 0.89$ ,  $P < 0.05$ ) in Kayadibi samples. However, no correlation was observed between these element pairs in the Manas samples. These values indicate that Cu, Ni, and Pb elements in all coal, shaly coal, and coaly shale samples (except the Manas area) may have inorganic origins. Furthermore, the existence of a very strong correlation between Ni and As in samples from Tarhanas confirms that the latter has inorganic origin. In most cases, As in the studied samples is associated with epigenetic cleat and fracture-filling pyrite. In some cases, As is associated with fine-grained, syngenetic pyrite and occurs in arsenopyrite (Finkelman, 1994; Karayigit et al., 2000b). U (Finkelman, 1995) and V in the studied samples may have been derived from both organic materials and clays (Finkelman, 1995; Querol et al., 1996; Goodarzi, 2002; Ribeiro et al., 2010).

In the Özyurt samples, a strong positive correlation was observed between V and Ba ( $r = 0.60$ ,  $P < 0.05$ ), and a weak positive correlation exists between the element pairs of V-U, V-K, and V-Al ( $r = 0.59$ ,  $r = 0.47$ , and  $r = 0.49$ , respectively). Strong positive correlations are also observed between U-Ba, U-K, and U-Al, with  $r = 0.70$ ,  $r = 0.67$ , and  $r = 0.62$ , respectively. In the Tarhanas samples, weak positive correlations ( $r = 0.54$ ,  $P < 0.05$ ) were observed between V and Al, a strong positive correlation ( $r = 0.64$ ,  $P < 0.05$ ) was found between V and K, and a very strong positive correlation ( $r = 0.89$ ,  $P < 0.05$ ) exists between V and U; however, no correlation was detected between V and Ba. In these samples, weak positive correlations were observed between U and Ba ( $r = 0.55$ ,  $P < 0.05$ ) and between U and Al ( $r = 0.54$ ,  $P < 0.05$ ). In the Kayadibi samples, very strong positive correlations were found between element pairs of V-Ba, V-U, V-K, and V-Al, with  $r = 0.89$ ,  $r = 0.90$ ,  $r = 0.93$ ,

and  $r = 0.93$ , respectively. In these samples, strong positive correlations were observed between U and Ba ( $r = 0.60$ ,  $P < 0.05$ ), U and K ( $r = 0.68$ ,  $P < 0.05$ ), and U and Al ( $r = 0.68$ ,  $P < 0.05$ ). In the Manas samples, a very weak positive correlation was detected between V and U ( $r = 0.35$ ,  $P < 0.05$ ), a weak positive correlation was found between V and K ( $r = 0.53$ ,  $P < 0.05$ ), and a strong positive correlation was determined between V and Al ( $r = 0.81$ ,  $P < 0.05$ ); conversely, no correlation exists between V and Ba. In the Manas area, V and Ba show a weak positive correlation ( $r = 0.35$ ,  $P < 0.05$ ), V and Al exhibit a strong positive correlation ( $r = 0.78$ ,  $P < 0.05$ ), and V and K demonstrate a very strong positive correlation ( $r = 0.93$ ,  $P < 0.05$ ). These results indicate that U and V in the investigated samples have silicate origins.

### 4.3. Molecular geochemistry of coal extracts

#### 4.3.1. Isoprenoids and n-alkanes

In the Gümüşhane region, n-alkanes are recorded within the  $C_{14}$ – $C_{35}$  range in the gas chromatogram of the Oz-1

coal sample from the Özyurt area. Among n-alkanes,  $C_{29}$  n-alkane has the maximum peak value. However, the highest peak pristane (Figure 5A) Pr/Ph value of the Oz-1 coal sample was calculated as 13.05 using gas chromatograms (Table 3). The carbon preference index (CPI) was calculated using n-alkanes in the range of  $C_{25}$ – $C_{30}$  (Tissot and Welte, 1984; Barker, 1986; Marzi et al., 1993; Peters and Moldowan, 1993) and  $C_{23}$ – $C_{29}$  (Bray and Evans, 1961) of the gas chromatograms. Accordingly, CPI values 1 and 2 of coal sample Oz-1 were determined as 1.64 and 1.38, respectively (Table 3).

N-alkanes in the range of  $C_{14}$ – $C_{35}$  are recorded in gas chromatograms of the Ta-2 shaly coal sample from the Tarhanas area. Maximum peak values belong to  $C_{21}$ ,  $C_{22}$ , and  $C_{23}$  n-alkanes (Figure 5B). The Pr/Ph ratio of coal sample Ta-2 is calculated as 3.6; the CPI values (1.05 and 1.02; Table 3) indicate that n-alkanes with odd carbon numbers and n-alkanes with even carbon numbers have almost the same values. In gas chromatograms of the Ir-2

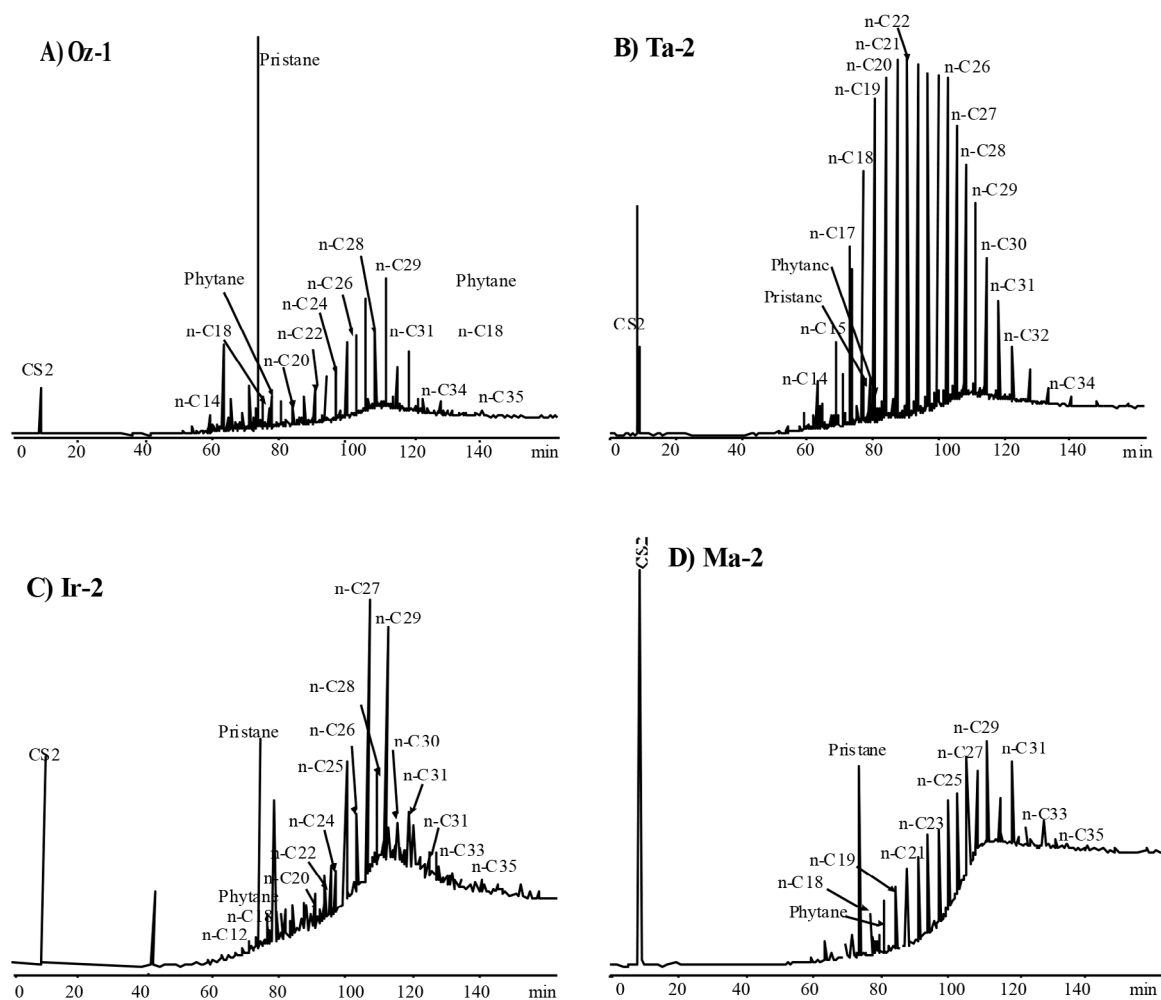


Figure 5. Gas chromatograms of extracts from the selected samples.

**Table 3.** The parameters calculated from gas chromatograms for selected samples.

Sample ID	CPI1	CPI2	Pr/Ph	Pr/n-C <sub>17</sub>	Ph/n-C <sub>18</sub>	TAR
Gümüşhane						
Ir-2	3.155	2.687	8.557	13.18	1.21	15.86
Oz-1	1.644	1.379	13.053	19.44	2.13	5.59
Ta-2	1.054	1.02	3.615	0.99	0.21	1.5
Bayburt						
Ma-2	1.332	1.208	12.902	0	0.42	4.32

$$CPI1 = \frac{1}{2} * \{ [(C_{25}+C_{27}+C_{29})/(C_{24}+C_{26}+C_{28})] + [(C_{25}+C_{27}+C_{29})/(C_{26}+C_{28}+C_{30})] \} \text{ (Tissot and Welte, 1984).}$$

$$CPI2 = \{ [(C_{23}+C_{25}+C_{27}) + (C_{25}+C_{27}+C_{29})] / [2 * (C_{24}+C_{26}+C_{28})] \} \text{ (Bray and Evans, 1961).}$$

$$TAR = (C_{27}+C_{29}+C_{31})/(C_{15}+C_{17}+C_{19}) \text{ (Bourbonniere and Meyers, 1996).}$$

coal sample from the Kayadibi area, n-alkanes in the range of C<sub>16</sub>-C<sub>35</sub> are recorded. NC<sub>27</sub> forms the maximum peak value (Figure 5C). The Pr/Ph ratio of the Ir-2 sample was calculated as 8.56. In this coal sample, CPI1 and CPI2 values were determined as 3.16 and 2.69, respectively (Table 3).

In the Bayburt region, n-alkanes were recorded in the range of C<sub>18</sub>-C<sub>35</sub> in gas chromatograms of the Ma-2 coaly shale sample from the Manas area (Figure 5D). The maximum peak value belonged to alkane C<sub>29</sub>. The Pr/Ph ratio of the Ma-2 coaly shale sample was calculated as 12.9. Using gas chromatograms, CPI values 1 and 2 were calculated as 1.3 and 1.2, respectively (Table 3), indicating that n-alkanes with odd carbon numbers are slightly more dominant compared with n-alkanes with even carbon numbers.

### 4.3.2. Biomarkers

#### 4.3.2.1. Terpanes

The relative abundance and distribution of terpanes obtained from m/z mass chromatograms of investigated coal and shaly coal samples are given in Figures 6A and 6B, and their calculated parameters are presented in Table 4. Whereas tricyclic terpanes are insufficiently recorded in sample Oz-1, tricyclic terpanes with lower numbers were recorded as more dominant in sample Ta-2. Accordingly, the C<sub>25</sub>/C<sub>26</sub> tricyclic terpane ratio cannot be calculated

in sample Oz-1, but this value was calculated as 0.72 in sample Ta-2. In sample Oz-1, Tm (C<sub>27</sub> 17a(H)-22,29,30-trisnorhopane) is more abundant compared with Ts (C<sub>27</sub> 18a(H)-22,29,30-trisnorhopane); in sample Ta-2, Ts is more abundant than Tm. The C<sub>29</sub>/C<sub>30</sub> hopane ratios in samples Oz-1 and Ta-2 are calculated as 0.76 and 0.62, respectively. The C<sub>31</sub>R homohopane/C<sub>30</sub> hopane ratio was calculated as 0.36 in sample Oz-1 and as 0.16 in sample Ta-2. In samples Oz-1 and Ta-2, C<sub>31</sub> homohopane is more dominant compared with C<sub>32</sub>-C<sub>35</sub> homohopanes. A steady decrease is observed in peak height from the C<sub>31</sub> member toward C<sub>35</sub> (Figures 6A, 6B, and 7). The C<sub>35</sub>/C<sub>31</sub>-C<sub>35</sub> homohopane ratios of samples Oz-1 and Ta-2 were determined as 0.011 and 0.039, respectively. The C<sub>35</sub>/C<sub>34</sub> homohopane ratio was calculated as 0.39 in sample Oz-1 and as 0.55 in sample Ta-2. The moretane/hopane ratio was determined as 0.50 in sample Oz-1 and as 0.10 in sample Ta-2. In the Ta-2 sample, the (oleanane/C<sub>30</sub> hopane) × 100 rate is calculated as 11.9%, but the ratio is unmeasurable in sample Oz-1.

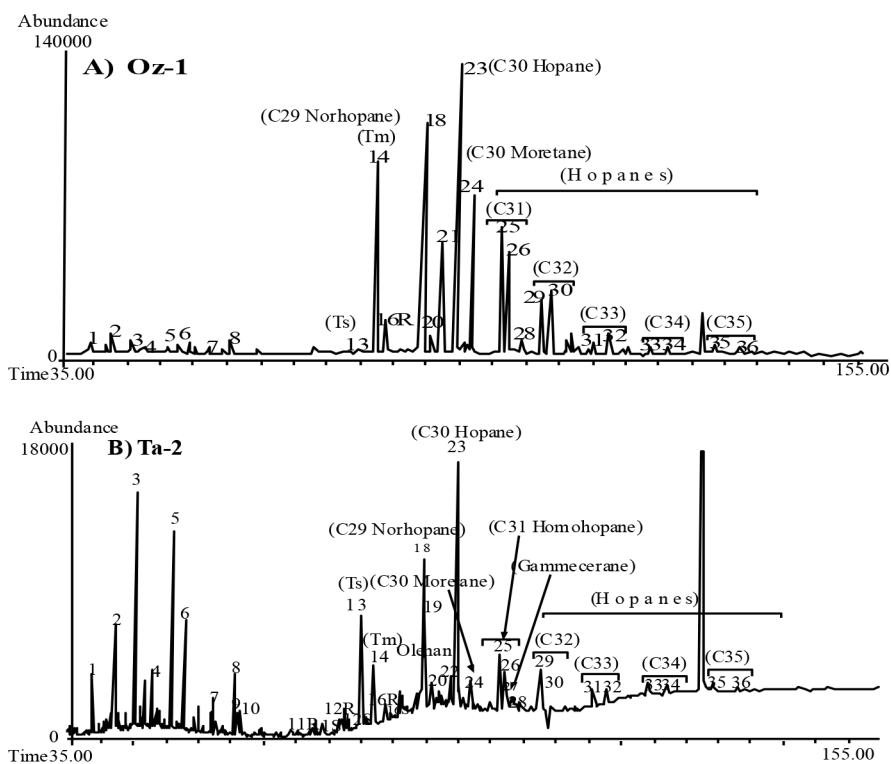
#### 4.3.2.2. Steranes

The distributions and relative abundances of steranes obtained from m/z 217 ion chromatograms are given in Figure 8; the parameters calculated using these chromatograms are presented in Table 5. Based on their relative abundances, C<sub>27</sub>-C<sub>28</sub>-C<sub>29</sub> steranes of sample Oz-1

**Table 4.** Calculated parameters from m/z 191 mass chromatograms for selected samples.

Sample ID	1	2	3	4	5	6	7	8	9	10
Oz-1	0.76	0.36	4.55	0.39	0.48	0.015	0.50	ND	ND	ND
Ta-2	0.62	0.16	0.81	0.55	0.61	0.64	0.10	0.50	11.9 %	0.72

1) C<sub>29</sub>/C<sub>30</sub> hopane, 2) C<sub>31</sub> R homohopane/C<sub>30</sub> hopane, 3) (C<sub>19+</sub>-C<sub>20</sub>)/C<sub>23</sub> tricyclic terpane, 4) C<sub>35</sub>/C<sub>34</sub> homohopane, 5) 22S/(22S+22R) homohopane (for C<sub>32</sub>), 6) Ts/(Ts+Tm), 7) moretane/hopane (for C<sub>30</sub>), 8) (gammacerane/C<sub>30</sub> hopane) × 100, 9) (oleanane/C<sub>30</sub> hopane) × 100, 10) C<sub>25</sub>/C<sub>26</sub> tricyclic terpane.



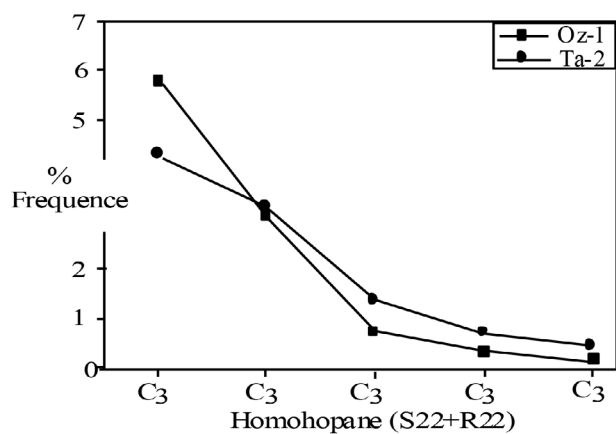
Peak	Compound	Peak	Compound
1	C <sub>19</sub> Tricycliterpane	19	C <sub>29</sub> Ts (18 α(H)-30-Noneorhopane
2	C <sub>20</sub> Tricycliterpane	20	C <sub>30</sub> (17 α(H)-Diahopane)
3	C <sub>21</sub> Tricycliterpane	21	C <sub>29</sub> 17 β (H), 21α (H)-30 Normoratene
4	C <sub>22</sub> Tricycliterpane	22	Oleanane
5	C <sub>23</sub> Tricycliterpane	23	C <sub>30</sub> 17 α(H), 21β(H)-Hopane
6	C <sub>24</sub> Tricycliterpane	24	C <sub>30</sub> 17 β (H), 21α (H)-Moretane
7	C <sub>25</sub> (22S+22R) Tricycliterpane	25	C <sub>31</sub> 17 α (H), 21β (H)-30-Homohopane (22S)
8	C <sub>24</sub> Tetracyclichopane (Seco)	26	C <sub>31</sub> 17 α (H), 21β (H)-30-Homohopane (22R)
9	C <sub>26</sub> 22(S) Tricycliterpane	27	Gammacerane
10	C <sub>26</sub> 22(R) Tricycliterpane	28	Homomoretane
11	C <sub>28</sub> Tricycliterpane	29	C <sub>32</sub> 17 α (H), 21β (H)-30,31-Bishomohopane (22S)
12	C <sub>29</sub> Tricycliterpane	30	C <sub>32</sub> 17 α (H), 21β (H)-30,31-Bishomohopane (22R)
13	C <sub>27</sub> 18α(H)-22,29,30-Trisnorneohopane (Ts)	31	C <sub>33</sub> 17 α (H), 21β (H)-30,31,32-Trishomohopane (22S)
14	C <sub>27</sub> 17α(H)-22,29,30-Trisnorhopane (Tm)	32	C <sub>33</sub> 17 α (H), 21β (H)-30,31,32-Trishomohopane (22R)
15	17 α(H)-29,30-Bisohopane	33	C <sub>34</sub> 17 α (H), 21β (H)-30,31,32,33-Tetrakishomohopane (22S)
16	C <sub>30</sub> Tricycliterpane	34	C <sub>34</sub> 17 α (H), 21β (H)-30,31,32,33-Tetrakishomohopane (22R)
17	17 α(H)-28,30-Bisohopane	35	C <sub>35</sub> 17 α (H), 21β (H)-30,31,32,33-Pentakishomohopane (22S)
18	C <sub>29</sub> 17 α(H)-21β(H)-30-Norhopane	36	C <sub>35</sub> 17 α (H), 21β (H)-30,31,32,33-Pentakishomohopane (22R)

Figure 6. The m/z 191 mass chromatograms of selected extracted samples.

are ranked as C<sub>29</sub> > C<sub>28</sub> > C<sub>27</sub>, and those of sample Ta-2 as C<sub>29</sub> > C<sub>27</sub> > C<sub>28</sub> (Figures 8A, 8B, 9A, and 9B). The C<sub>28</sub>/C<sub>29</sub> sterane ratios in samples Oz-1 and Ta-2 are calculated respectively as 0.44 and 0.36. Diasterane/sterane ratios of samples Oz-1 and Ta-2 were calculated as 0.3 and 1.3, respectively.

#### 4.4. Type of organic matter

HI-T<sub>max</sub> (Mukhopadyay et al., 1995) and HI-TOC (Subroto et al., 2010) diagrams were used to determine organic material types of coal, shaly coal, and coaly shale samples from Özyurt, Tarhanas, Sökmen, Kayadibi, and Manas (Figures 10 and 11). In the HI-T<sub>max</sub> diagrams, two samples



**Figure 7.** C<sub>31</sub>-C<sub>35</sub> (22R-22S) homohopane distributions of two of the studied coal and shaly coal samples.

from Tarhanas and one sample each from Özyurt and Kayadibi fall within the type II area, and the other samples fall within the type III area. In the HI-TOC diagram, one sample from the Tarhanas area is classified as type II and the remaining sample plots fall in the type III area. N-alkane distribution of samples is bimodal, and n-alkanes with high carbon numbers are dominant compared with n-alkane with low carbon numbers. Accordingly, the depositional environment may be dominated by terrestrial organic matter input (Tissot and Welte, 1984; Waples, 1985). The calculated CPI > 1 values in Ir-2, Oz-1, and Ma-2 samples as well as CPI ≥ 1 in the Ta-2 sample (Table 3) confirm the presence of terrestrial organic matter (Tissot et al., 1987). A high Pr/nC<sub>17</sub> ratio (>0.6) is observed in the samples (Table 3), thereby confirming the presence of terrigenous organic matter (Peters and Moldowan, 1993). In addition, the TAR results show the ratio of terrestrial organic matter to aquatic organic substance (Bourbonniere and Meyers, 1996; Peters et al., 2005; Varandas da Silva, 2008). TAR values were determined as TAR > 1 in four samples (Ir-2, Oz-1, Ta-2, and Ma-2) (Table 3). The oleanane amount of Oz-1 from Özyurt is immeasurable. However, the oleanane index of Ta-2 from Tarhanas was calculated as 11.9% (Table 4), confirming the terrestrial organic matter input (Hunt, 1995). The relative proportions of C<sub>27</sub>-C<sub>29</sub> regular steranes in living organisms are related to particular environments and show that steranes in sediments may supply valuable paleoenvironment information (Huang and Meinschein, 1979). A powerful terrestrial contribution is exhibited by a predominance of C<sub>29</sub> steranes because the marine effect is indicated by the domination of C<sub>27</sub> sterols. C<sub>28</sub> occurs less frequently than C<sub>27</sub> and C<sub>29</sub> and generally characterizes lacustrine environments (Huang and Meinschein, 1979). Nishimura (1982) emphasized that some C<sub>28</sub> and C<sub>27</sub> steranes can be derived from plankton or algae in lacustrine

environments. The C<sub>29</sub> sterane is abundant in Oz-1 and Ta-2 samples compared with C<sub>27</sub> sterane. Accordingly, the investigated samples are mainly composed of higher terrestrial plant forms (Figures 9A and 9B). Humic and waxy coals often indicate a strong predominance of C<sub>29</sub> (Farhaduzzaman et al., 2012).

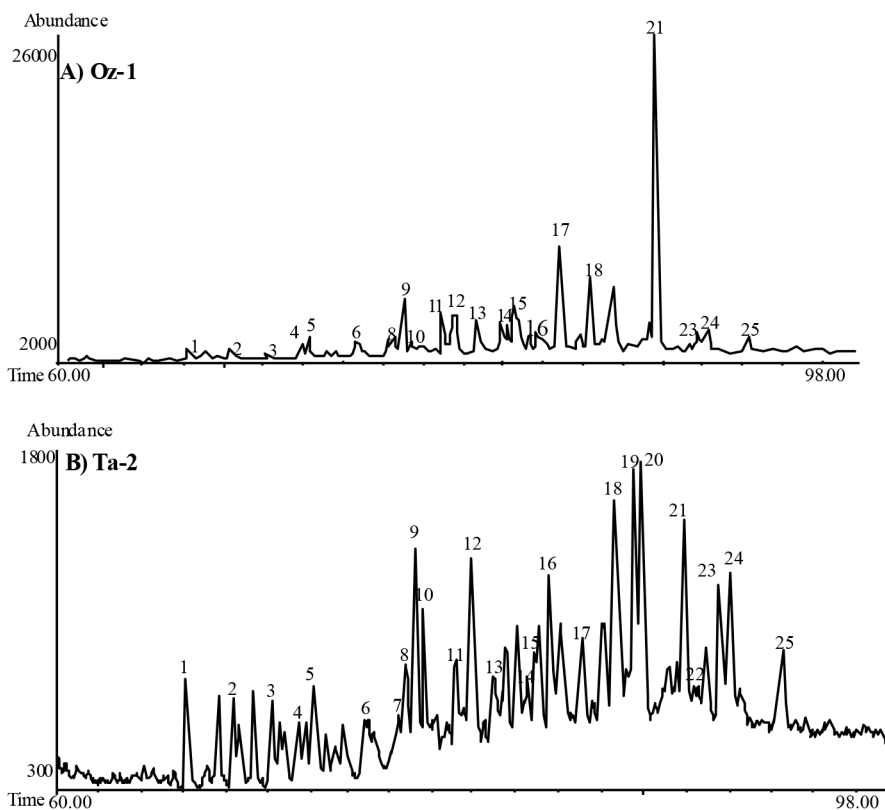
#### 4.5. Maturity of organic matter

Depending on T<sub>max</sub> values, coal and shaly coal samples from Özyurt thermally change from immature to mature. The coaly shale samples from Sökmen and the coal and shaly coal samples from Kayadibi change from immature to extremely mature. The shaly coals and coaly shales from Tarhanas and Manas change from mature to extremely mature (Figure 10).

Thermal maturity was determined by calculating the isoprenoid/n-alkane ratios obtained from the gas chromatograms of coal, shaly coal, and coaly shale samples of Ir-2, Oz-1, Ta-2, and Ma-2 (Table 3). The Pr/n-C<sub>17</sub> ratio could not be calculated because the n-C<sub>17</sub> of the Ma-2 sample cannot be measured, but the Ph/n-C<sub>18</sub> ratio is 0.42. The Pr/n-C<sub>17</sub> and Ph/n-C<sub>18</sub> ratios of sample Ta-2 are 0.99 and 0.21, respectively. These findings confirm that both samples are mature. The calculated Pr/n-C<sub>17</sub> ratios of samples Ir-2 and Oz-1 are 13.18 and 19.44, respectively, and their respective Ph/n-C<sub>18</sub> ratios are 1.21 and 2.13. The T<sub>max</sub> values are within the limit of maturity (i.e. 432 °C and 434 °C), depending on the oxidative nature of the deposition environment; thus, high Pr/n-C<sub>17</sub> ratio can be related to increase in Pr value.

The 22S/(22S + 22R) homohopane (C<sub>32</sub>) was used as a maturity parameter because the 22S isomer is more resistant to temperature increase than the 22R isomer (0.57, 0.62 = equilibrium; Seifert and Moldowan, 1986). The calculated 22S/(22S + 22R) homohopane (C<sub>32</sub>) ratios of samples Oz-1 and Ta-2 are 0.48 and 0.61, respectively. These values show that the homohopane conversion does not fully reach equilibrium in sample Oz-1, in contrast to sample Ta-2 (Seifert and Moldowan, 1986). The 20S isomer increases compared with the 20R isomer with increasing maturity of the 20S/(20S + 20R) sterane (C<sub>29</sub>) ratio; the 20S/(20S + 20R) reaches equilibrium (0.55) as the maturity continues to increase. This equilibrium value corresponds to the petroleum formation peak (Gürgey, 1999). The bb/(bb+aa) sterane (C<sub>29</sub>) ratio of sample Oz-1 could not be calculated, but its 20S/(20S + 20R) sterane (C<sub>29</sub>) ratio is 0.18. When the 20S/(20S + 20R) sterane (C<sub>29</sub>) ratio is considered, the sample in question is not thermally mature. The calculated 20S/(20S + 20R) sterane (C<sub>29</sub>) and bb/(bb+aa) sterane (C<sub>29</sub>) ratios of sample Ta-2 are 0.53 and 0.56, respectively; these values are approximate to the equilibrium value.

The moretane/hopane ratio of sample Oz-1 is higher than 0.15, but that of sample Ta-2 is lower than 0.15 (Table 4).



Peak	Compound	Peak	Compound
1	C <sub>27</sub> 13β (H)- 17 α(H)-Diasterane (20S)	14	C <sub>28</sub> 5α (H), 14α (H), 17α (H) - Sterane(20S)
2	C <sub>27</sub> 13β (H)- 17 α(H)-Diasterane (20R)	15	C <sub>28</sub> 5α (H), 14β (H), 17β (H) - Sterane(20R)+C <sub>29</sub> 13α (H), 17 β (H)-Diasterane (20R)
3	C <sub>27</sub> 13α (H)- 17 β (H)-Diasterane (20S)	16	C <sub>28</sub> 5α (H), 14β (H), 17β (H) - Sterane(20S)
4	C <sub>27</sub> 13α (H)- 17 β (H)-Diasterane (20R)	17	C <sub>28</sub> 5α (H), 14α (H), 17α (H) - Sterane(20R)
5	C <sub>28</sub> 13β (H)- 17 α(H)-Diasterane (20S)	18	C <sub>29</sub> 5α (H), 14α (H), 17α (H) - Sterane(20S)
6	C <sub>28</sub> 13β (H)- 17 α(H)-Diasterane (20R)	19	C <sub>29</sub> 5α (H), 14β (H), 17β (H) - Sterane(20R)
7	C <sub>28</sub> 13α (H)- 17 β (H)-Diasterane (20S)	20	C <sub>29</sub> 5α (H), 14β (H), 17β (H) - Sterane(20S)
8	C <sub>27</sub> 5α (H), 14α (H), 17α (H) - Sterane(20S)+C <sub>28</sub> 13α (H), 17 β (H)-Diasterane (20S)	21	C <sub>29</sub> 5α (H), 14α (H), 17α (H) - Sterane(20R)
9	C <sub>27</sub> 5α (H), 14β (H), 17β (H) - Sterane(20R)+C <sub>29</sub> 13β (H), 17 α (H)-Diasterane (20S)	22	C <sub>30</sub> 5α (H), 14α (H), 17α (H) - Sterane(20S)
10	C <sub>27</sub> 5α (H), 14β (H), 17β (H) - Sterane(20S)+C <sub>28</sub> 13α (H), 17 β (H)-Diasterane (20R)	23	C <sub>30</sub> 5α (H), 14β (H), 17β (H) - Sterane(20R)
11	C <sub>27</sub> 5α (H), 14α (H), 17α (H) - Sterane(20R)	24	C <sub>30</sub> 5α (H), 14β (H), 17β (H) - Sterane(20S)
12	C <sub>29</sub> 13β (H)- 17 α(H)-Diasterane (20R)	25	C <sub>30</sub> 5α (H), 14α (H), 17α (H) - Sterane(20R)
13	C <sub>29</sub> 13α (H)- 17 β (H)-Diasterane (20S)		

**Figure 8.** The m/z 217 mass chromatograms of selected extracted samples.

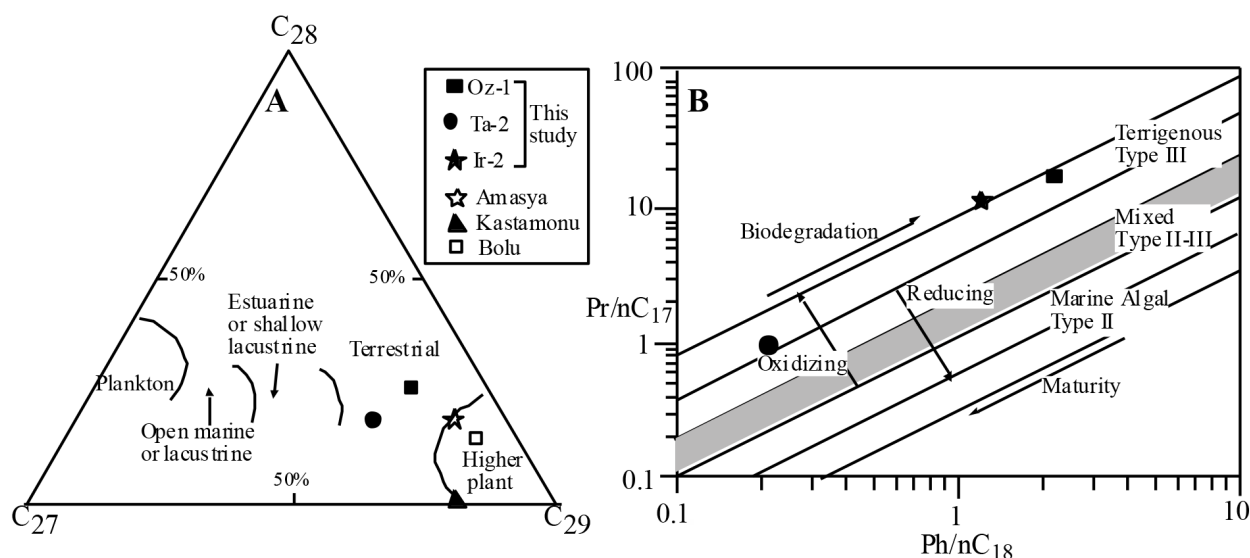
Accordingly, sample Ta-2 is thermally mature (Waples and Machihara, 1991). In addition, the high diasterane/sterane ratio of sample Ta-2 (Table 5) confirms its thermal maturity (Peters et al., 2005b), which is interpreted using the Ts/(Ts + Tm) rate. The Ts/(Ts + Tm) ratios of samples Oz-1 and Ta-2 are 0.015 and 0.64, respectively (Table 4). The high Ts/(Ts + Tm) ratio of sample Ta-2 confirms that the sample is thermally mature.

Hanson et al. (2001) identified upper Oligocene lacustrine oils from the northern Qaidam Basin of Northwest China, with C32, C33, and C34 22S/(22S + 22R) of < 0.50; low C29 sterane 20S/(20S + 20R); and low Ts/Tm support with considerably low maturity (Peters et al., 2005b). Thus, the thermal maturity of all parameters should be interpreted. In this context, Pr/n-C<sub>17</sub> and Ph/n-C<sub>18</sub>, moretane/hopane and diasterane/sterane ratios

**Table 5.** Calculated parameters from m/z 217 mass chromatograms for selected samples.

Sample ID	1	2	3	4	5	6
Oz-1	15.5, 25.9, 58.6	0.18	ND	0.44	0.34	0.17
Ta-2	26.7, 19.5, 53.8	0.53	0.56	0.36	1.30	0.24

1)  $C_{27}$ ,  $C_{28}$ ,  $C_{29}$  steranes (%); 2) 20S/(20S+20R) sterane (for  $C_{29}$ ); 3) bb/(bb+aa) sterane (for  $C_{29}$ ); 4)  $C_{28}/C_{29}$  sterane; 5) diasterane/sterane (for  $C_{27}$ ); 6) sterane/hopane.



**Figure 9.** A) Relationship between sterane compositions, source input, and depositional environment, by which two samples (Oz-1, Ta-2) are shown to be dominated by terrigenous organic matter input (after Farhaduzzaman et al., 2012). B) Pr/nC<sub>17</sub> vs. Ph/nC<sub>18</sub> for three samples infer oxicity and organic matter type of the source rock depositional environment (after Peters et al., 2005a, 2005b; Koeverden et al., 2011).

as well as the  $T_{max}$  value confirm the thermal maturity of sample Ta-2.

In the studied region, volcanic activity and sedimentation occur at various locations during the Eocene (Saydam Eker, 2012). This volcanic activity could be due to differences in the thermal maturity of the samples.

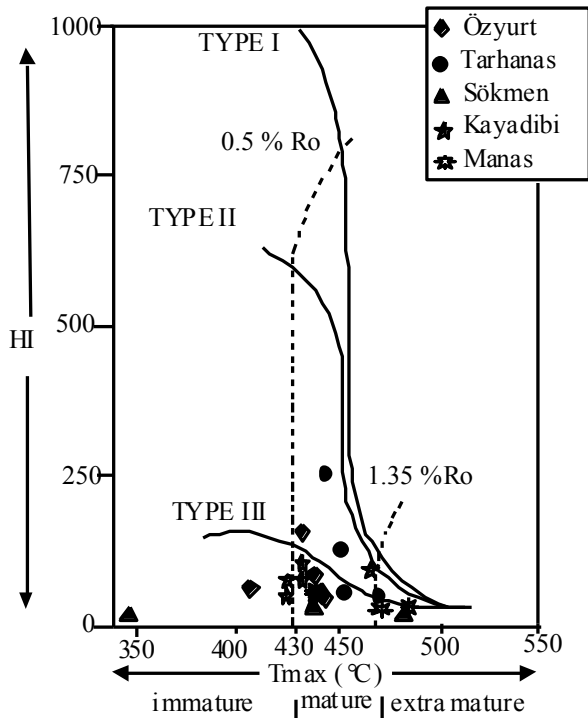
#### 4.6. Depositional environment

Eocene aged coals, shaly coals, and coaly shales exposed in the Gümüşhane and Bayburt regions have high Pr/Ph ratios, with values between 3.615 and 13.053. The high value of Pr/Ph indicates the presence of an environment with overall oxygen atmosphere during the deposition of organic material (Mello and Maxwell, 1990; Philp, 1994; Huang et al., 2003). Peters and Moldowan (1993) reported that samples with high Pr/Ph ratios (>3) within the oil-generative window exhibit terrestrial organic matter input under oxic conditions. Coals with a Pr/Ph ratio of >4 are characteristically precipitated under a peat-swamp depositional setting and oxic depositional conditions (Wan Hasiah and Abolins, 1998). These findings are consistent

with the depositional environments of the studied coal, shaly coal, and coaly shale samples, three of which have Pr/Ph > 4 and one of which has Pr/Ph > 3.

In addition to hopane/sterane and Pr/Ph diagrams (Subroto et al., 2010), sample Oz-1 falls into highly oxidizing terrestrial areas, whereas sample Ta-2 falls into anoxic-suboxic areas with active terrestrial influence (Figure 12). The absence of the anoxic biomarker (17 $\alpha$ (H)-28,30-bisnorhopane) indicates that the studied coals are deposited in an oxic-suboxic environment (Katz and Elrod, 1983; Peters et al., 2005b; Hoş-Çebi and Korkmaz, 2015). The high sterane/hopane ratio for coals would likely characterize a marine environment (Mann et al., 1998). The sterane/hopane ratios of the analyzed coal and shaly coal are very low at 0.17 and 0.24 for the Oz-1 and Ta-2 samples, respectively. The ratios are indicative of dominantly terrestrial and microbial organic matter input in depositional environments. Peters and Moldowan (1993) suggested that a high ( $C_{19}+C_{20}$ )/ $C_{23}$  tricyclic terpane ratio indicates terrestrial organic matter input.



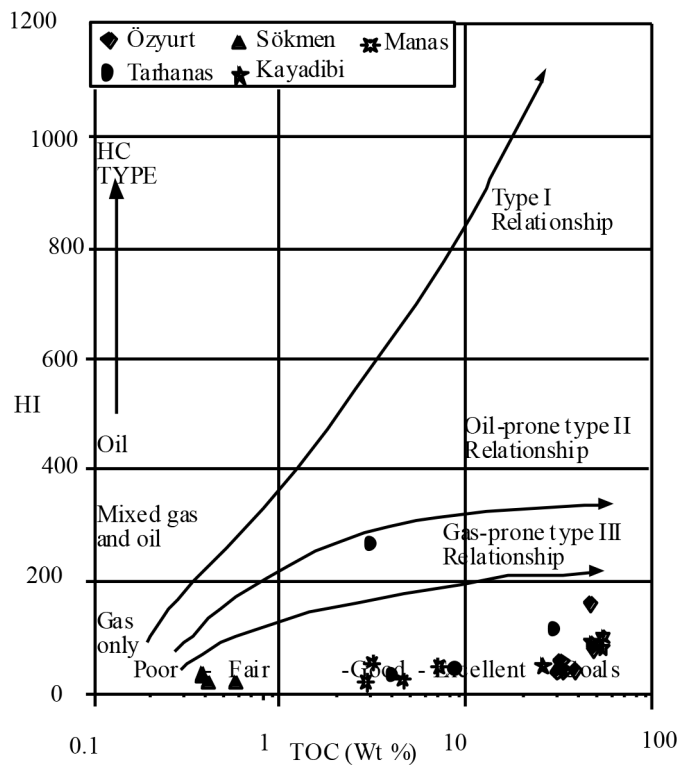


**Figure 10.** Distribution of HI vs.  $T_{max}$  for the studied samples (Mukhopadyay et al., 1995).

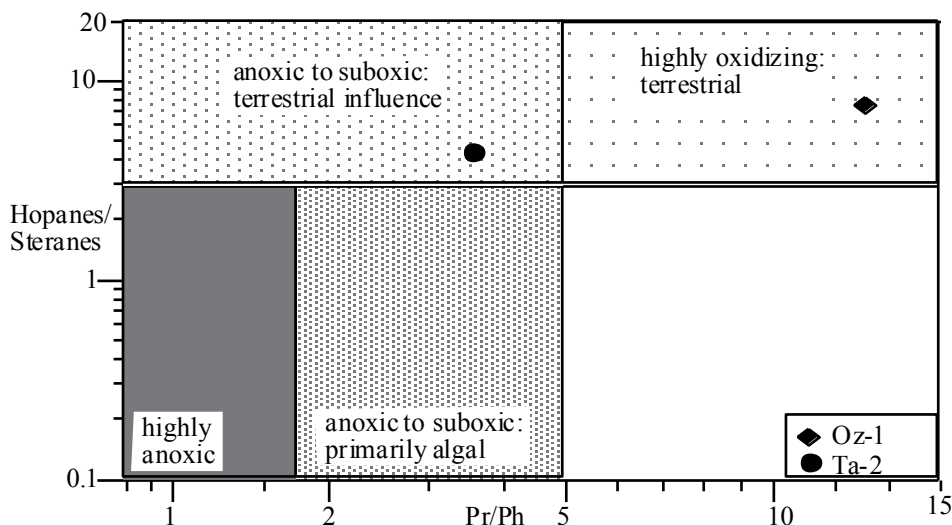
The  $(C_{19}+C_{20})/C_{23}$  tricyclic terpane ratios of the Oz-1 and Ta-2 samples (4.55 and 0.81, respectively) reflect terrestrial organic matter input. Additionally, the abundances of  $C_{27}$ ,  $C_{28}$ , and  $C_{29}$  are in the following order:  $C_{29} > C_{28} > C_{27}$  in Oz-1 and  $C_{29} > C_{27} > C_{28}$  in Ta-2. The dominance of  $C_{29}$  sterane indicates a terrestrial organic matter input (Huang and Meinschein, 1979; Robinson, 1987).

$C_{30}$  sterane was also recorded in both samples. This finding is a sign that both fields are influenced by marine conditions (Moldowan et al., 1985; Peters, 1986; Peters and Moldowan, 1993; Hunt, 1995; Mann et al., 1998). The gammacerane index is 0.50 in the Ta-2 sample. A low gammacerane index indicates the presence of at least some salts in the depositional environment of sample Ta-2 (Comet and Eglinton, 1987; Routh et al., 1999).

The high Pr/Ph ratios, high  $(C_{19}+C_{20})/C_{23}$  tricyclic terpane ratio (Oz-1), high abundance of  $C_{29}$ , high sterane/diasterane ratios, absence of an anoxic biomarker (17 $\alpha$ (H)-28,30-bisnorhopane), and low sterane/hopane ratios indicate that coaly organic matter is derived from higher land plants in terrestrial environments under oxic and suboxic depositional conditions. The presence of biomarkers such as  $C_{30}$  sterane (Oz-1 and Ta-2 samples) and gammacerane (Ta-2 sample) indicates the presence of a marine environmental influence on coal and shaly coal samples.



**Figure 11.** Distribution of the analyzed samples into HI vs. TOC plots (Subroto et al., 2010).



**Figure 12.** Distribution of the selected samples into total hopanes/steranes vs. Pr/Ph plots (after Subroto et al., 2010).

Ba and Sr concentrations are higher in seawater than in freshwater (Reimann and Caritat, 1998; Li et al., 2016). Furthermore, the Sr/Ba ratio (>1) suggests the involvement of a marine influence on coal formation (Shao et al., 1998). Moreover, Ba and Sr contents of the investigated samples range from 9 ppm to 764 ppm and from 15.7 ppm to 2149 ppm, respectively (Table 2). The Sr/Ba ratios of these samples fluctuate between 0.17 and 38.4. These results indicate that the depositional environment of marine and terrestrial conditions is effective.

Eocene aged clastic rocks of the eastern Pontides (NE Turkey) show two different source characteristics. Volcaniclastic deposits are dominant in the northern section of Gümüşhane, and siliciclastic deposits are dominant in the southern section (Kelkit, Köse) and the Bayburt region. The studied coaly sequences were measured from siliciclastic deposits, which likely are lagoon environments (Figure 13). However, Eocene aged Yeniçelttek-Amasya (Central Black Sea Region) and Salıpazarı-Bolu (Western Black Sea Region) coals are suboxic in lacustrine or lacustrine swamps, whereas Aspiras-Kastamonu (Western Black Sea Region) coals are in paralic and suboxic brack water swamps, and coals contain terrestrial organic matter (Hoş-Çebi and Korkmaz, 2013) (Figure 9A).

The investigated coals, shaly coals, and coaly shales were probably deposited in an environment dominated by marine and terrestrial settings with oxic or suboxic conditions. These samples comprise terrestrial organic matter.

#### 4.7. Hydrocarbon potential of Eocene aged coal

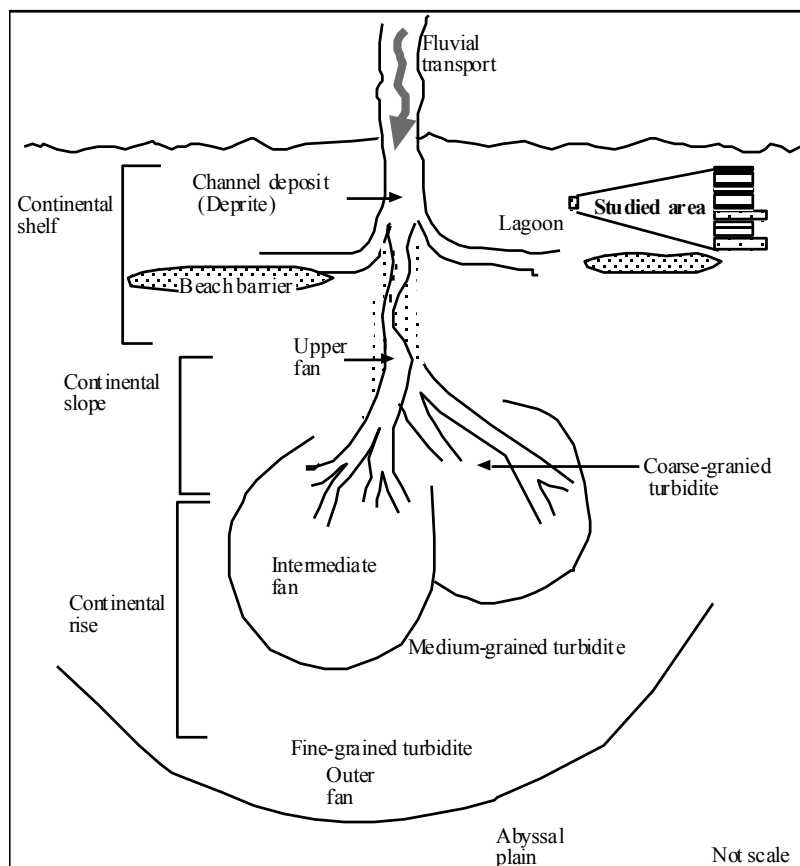
This study generally included coals, shaly coals, and coaly shales that belong to type III kerogen (Figures 10 and 11). The average PY values of Özyurt and Kayadibi coals and

shaly coals were high (36.8 mg HC/g rock and 65.8 mg HC/g rock, respectively), whereas the PY values of coals belonging to other areas were low. The average HI values of samples belonging to all areas were determined as <200 mg HC/g TOC. Based on these data, Eocene aged coals, shaly coals, and coaly shales exposed in the Gümüşhane and Bayburt regions do not have the potential to form liquid hydrocarbons, but they might be able to produce gas. Eocene aged coals in Yeniçelttek (Amasya) and Salıpazarı (Bolu) with type II kerogen can generate oil; in Aspiras (Kastamonu) with type III kerogen they can generate gas (Hoş-Çebi and Korkmaz, 2013).

#### 5. Conclusions

The average TOC values of Eocene aged samples from the Özyurt, Tarhanas, Sökmen, Kayadibi, and Manas areas were calculated to be 43.89%, 13%, 0.54%, 53.83%, and 4.80%, respectively. Coals and shaly coals from the Kayadibi area had the highest average PY value of 65.80 mg HC/g rock, whereas coaly shales from the Sökmen area had the lowest average PY value of 0.12 mg HC/g rock. The highest average HI value was calculated as 112 mg HC/g TOC for Tarhanas shaly coals and coaly shales, whereas the lowest average HI value was calculated as 24 mg HC/g TOC for Sökmen coaly shales.

The major element contents of the studied samples were compared with those of samples worldwide. Several similarities were demonstrated. Özyurt samples showed similarities in terms of Al, Na, and Ti; coaly shales from Sökmen in terms of Ca; Kayadibi samples in terms of Fe and Ti; and Manas shaly coals in terms of Na and Ti. Coaly samples from the abovementioned areas were enriched in terms of other major elements. Fe and Mg contents



**Figure 13.** Schematic diagram represents the paleodepositional environment of Eocene coals, shaly coals, and coaly shales in the Gümüşhane and Bayburt regions.

of Özyurt; Al, Mg, K, and Ti contents of Tarhanas and Kayadibi; and Al, Fe, Mg, K, and Ti contents of Manas show similarities to Turkish coals. In the studied samples, Co, Cs, Ga, Hf, Th, U, Y, Mo, Be, Cd, Sb, and La generally are similar to the average values for brown coals. The samples are close to the average values for Turkish coals in Co, Ga, Nb, Rb, V, Y, Cu, Pb, Zn, As, Be, and Se. As mean  $La_N/Lu_N$  ratios of studied samples were  $<1$ , these samples were characterized by MREY and HREY enrichment types. The  $Al_2O_3/TiO_2$  ratios of the coal samples indicated that the sediment source region for Eocene coals, shaly coals, and coaly shales in the Gümüşhane and Bayburt regions were likely characterized by rocks with intermediate or mafic geochemical characteristics.

As in the Özyurt, Kayadibi, and Manas samples is possibly of organic nature, whereas As in the Tarhanas samples possibly has inorganic origin. Cd, Zn, Cu, Ni, Pb (sulfide), V, and U (silicates, in particular clay minerals) were assumed to be derived from mineral substances.

N-alkanes with high carbon numbers were more dominant compared with n-alkanes with low carbon numbers. The calculated  $CPI > 1$  and  $TAR > 1$  values of

the analyzed samples indicated the presence of terrestrial organic material in the depositional environment. Moreover, the great majority of samples belonging to these five areas contain type III kerogen. The biomarker data indicated that the studied coal and shaly coal samples dominantly contained terrestrial and microbial organic matter.

According to  $T_{max}$  values, samples from the Özyurt, Sökmen, and Kayadibi areas changed from immature to mature, whereas the samples from Tarhanas and Manas changed from mature to extremely mature. The determined  $CPI > 1$  and  $TAR > 1$  values of samples Ta-2 and Ma-2 confirm that these shaly coal and coaly shales were thermally mature. Meanwhile, the calculated  $Ph/n-C_{18} > 1$  value of samples Ir-2 and Oz-1 showed that these coals were thermally immature. The calculated  $22S/(22S + 22R)$  homohopane ( $C_{32}$ ),  $20S/(20S + 20R)$  sterane ( $C_{29}$ ), and  $Ts/(Ts + Tm)$  ratios of sample Oz-1 were 0.48, 0.18, and 0.015, respectively. Given that these values did not reach equilibrium (0.55), the said coals were immature. The  $22S/(22S + 22R)$  homohopane ( $C_{32}$ ),  $20S/(20S + 20R)$  sterane ( $C_{29}$ ), and  $Ts/(Ts + Tm)$  of sample Ta-2 were calculated

as 0.61, 0.56, and 0.64, respectively, emphasizing that Tarhanas shaly coals were thermally mature.

The calculated Pr/Ph ratio (3.615) of sample Ta-2 showed that the environment was suboxic during the deposition of organic material. The determined Pr/Ph ratios for samples Ir-2, Oz-1, and Ma-2 were 8.557, 13.053, and 12.902, respectively; these values indicated that the environment was oxic. The absence of anoxic biomarkers indicated that the studied samples were deposited in a terrestrial environment under oxic-suboxic conditions. The low sterane/hopane ratios of the abovementioned samples indicated that the environment was terrigenous. However, the presence of  $C_{30}$  sterane and gammacerane in samples pointed out that the depositional environment was under the influence of the sea. In addition, the Sr/Ba ratios of the samples ranged from 0.17 to 38.4, indicating that the depositional environment of marine and terrestrial conditions were effective.

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- According to geochemical data, Eocene aged coals, shaly coals, and coaly shales exposed in the Gümüşhane and Bayburt regions exhibited similar properties; the coal samples were likely to be humic coals that were thermally immature-mature. The studied samples were probably deposited under an oxic-suboxic mixture of marine and terrestrial environment conditions, comprising terrestrial organic matter without the potential to form hydrocarbon.

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