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Organic geochemical characteristics and depositional environment of Lower-Middle Miocene Küçükkuyu Formation, Edremit Gulf, NW Turkey

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Abstract: The Lower-Middle Miocene Küçükkuyu Formation crops out extensively in the Edremit Gulf area (NW Turkey). In this study, shale samples from this unit were investigated to evaluate source rock characteristics, depositional conditions, and hydrocarbon potential. Outcrop samples of the Küçükkuyu Formation were taken from different locations and analyzed by Rock-Eval pyrolysis, vitrinite reflectance (R_o), stable carbon isotope ($\delta^{13}C$), total sulfur (TS), gas chromatography (GC), and gas chromatography-mass spectrometry (GC-MS). The total organic carbon (TOC) values range from 0.23 to 6.1 wt.% with an average of 1.76 wt.% for the northern samples and 0.24 to 2.82 wt.% with an average of 1.66 wt.% for the southern samples around the Edremit Gulf. Hydrogen index (HI) values were up to 606 and 712 mg HC/g TOC in the north and south of the gulf, respectively. Organic matter type in the formation consists predominantly of Type II and III kerogen with a minor component of Type I kerogen. Tmax values ranging from 414 to 496 °C in the north and 423 to 446 °C in the south of the gulf indicate that most samples are at the beginning of the oil generation window and are thermally immature or early-mid-mature. Vitrinite reflectance (R_o) and biomarker maturity parameters support this result. Based on geological observations, biomarker distributions, and TOC/TS ratios, the Küçükkuyu Formation was deposited in a freshwater to slightly brackish water environment under anoxic-suboxic conditions with organic matter input from aquatic organisms and from terrestrial higher plants. According to Rock-Eval pyrolysis data, the Küçükkuyu Formation mostly has medium to good hydrocarbon-generation potential. However, as these potential source rocks are in general immature and/or early-mature, the hydrocarbon potential of the study area is very limited.

Key words: Küçükkuyu Formation, Lower-Middle Miocene, source rock, Edremit Gulf, NW Turkey

1. Introduction

The study area is the region to the north and south of the Edremit Gulf in northwestern Anatolia (Figure 1). The area is located between the Thrace basin in the north, the Prinos oil field of Greece in the northwest, and the western Aegean grabens to the south. Neogene sediments represented by lacustrine sedimentary rocks and volcanics are exposed around the Edremit Gulf. Sedimentary rocks such as shale, siltstone, tuff, and lignite were deposited contemporaneously with the Lower-Middle Miocene volcanics, deposited in small, isolated, fault-bounded lacustrine basins (Siyako et al., 1989). The shales are thin-bedded, laminated, and bituminous. The Küçükkuyu Formation, which has wide exposures and a certain source rock potential, is represented by these lacustrine sediments in the region.

The oil seeps observed in calcite-filled fractures of the Küçükkuyu Formation have been mentioned in previous studies (Saka, 1979; Siyako et al., 1989; Kesgin, 2001; Çiftçi et al., 2004, 2010). In these studies, possible elements of the hydrocarbon system in western Anatolia and around the Edremit Gulf were identified, but the Küçükkuyu Formation shales have not been investigated in detail according to their organic geochemical properties to date. Published investigations related to the source rock properties of the Küçükkuyu Formation are limited (Çiftçi et al., 2004, 2010; Bozcu, 2015). In this study, organic geochemical properties and hydrocarbon generation potential of the Küçükkuyu Formation at different outcrop locations are evaluated. In addition, depositional conditions of the formation were interpreted using $\delta^{13}C$ values, TOC/TS ratios, and biomarker distributions.

2. Geological setting

The Edremit Gulf and the adjacent area is a depression bordered by active faults between Kazdağ High in the north and Kozakdağ High in the south (Figure 1).

Kazdağ High geologically consists of tectonostratigraphic units of different origins and ages. These are: 1- Kazdağ Group (Bingöl, 1968, Bingöl et al.,

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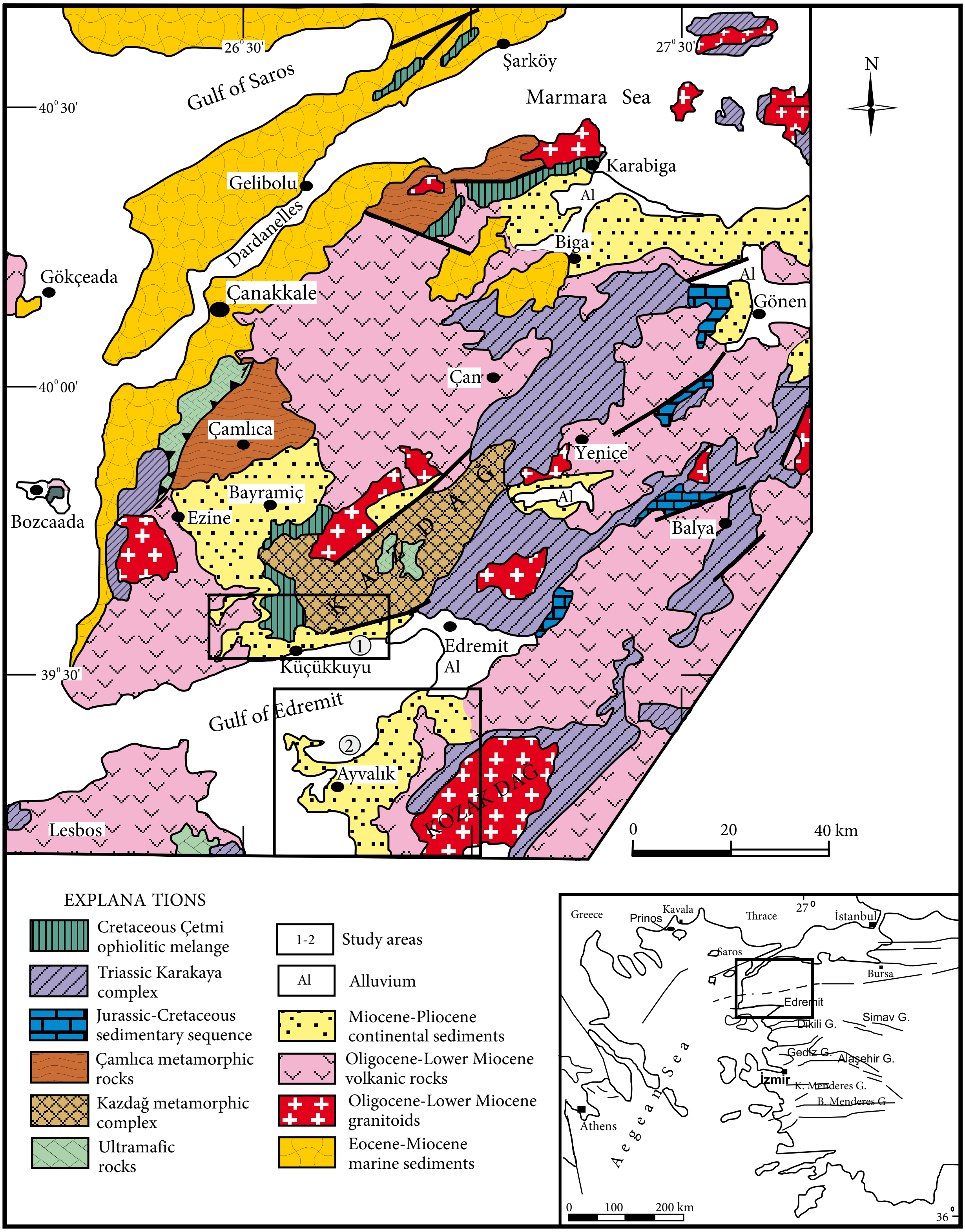

Figure 1. Location map of Biga Peninsula and generalized geological map of the Edremit Gulf and surroundings, northwestern Turkey, with the location of the studied areas (revised from Okay and Satır, 2000; Şengün et al., 2011).

1975; Okay et al., 1990a, 1990b; Okay and Satır, 2000); 2- Çamlıca Group (Çamlıca Metamorphics) (Okay et al., 1990a, 1990b); 3- Karakaya Complex (Bingöl et al., 1975; Okay et al., 1990a, 1990b); and 4- Çetmi Ophiolitic Mélange (Okay et al., 1990a, 1990b; Duru et al., 2004; Şengün and Çalık, 2007).

A very thick magmatic sequence (>2500 m) with various chemical compositions was formed in the Eocene-Pliocene interval. The sequence has an interfingering contact with sedimentary rocks (Siyako et al., 1989; Ercan et al., 1995). Magmatic activity was renewed in the Oligo-Miocene in the region and shallow intrusive rocks (Evciler and Kestanbol granites and granodiorites, Birkle and Satır, 1995; Karabiga and Kuşçayırı granites and granodiorites, Delaloya and Bingöl, 2000; Ilıca-Şamlı granites and granodiorites, Bingöl et al., 1982) were intruded into pre-Oligo-Miocene rocks during this period.

At the end of the Late Miocene, volcanic activity was renewed again and alkaline basalts were replaced along young faults formed by extensional tectonics (Yılmaz et al., 2001). E-W/NE-SW trending normal faults and/or oblique faults form the region's main tectonic framework, which is developing during the neotectonic period in relation to the N-S extensional regime in western Anatolia.

Terrestrial deposits (Küçükkuyu Formation) developed along with volcanic rocks in the Early-Mid Miocene. These are bituminous shales, claystones with intercalations of coal, siltstone, sandstone, and tuffs (Saka, 1979; Siyako et al., 1989). The Küçükkuyu Formation unconformably overlies the Kazdağ group and the Çetmi Ophiolitic Mélange or their contacts are faulted to the north of Edremit Gulf (Figure 2). In the Late Miocene-Pliocene, conglomerate, sandstone, shale, and clayey limestone levels were deposited and these associations reflect fluvial and lacustrine environments (İlyasbaşı Formation) (Saka, 1979). These sediments show lateral and vertical transition to shallow marine sandstone, conglomerate, shale, marl, and oolitic limestones (Bayramiç Formation) (Siyako et al., 1989).

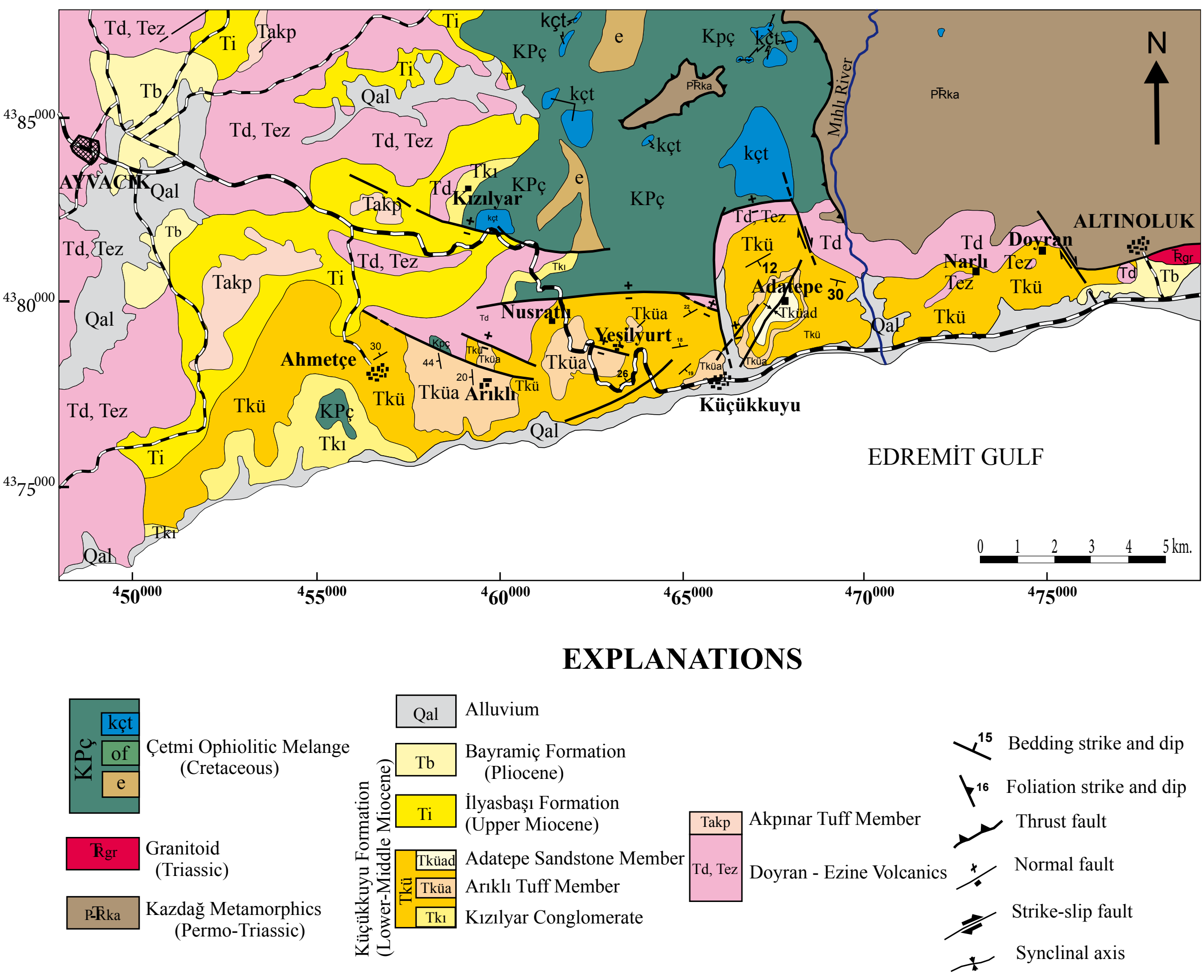

Figure 2. Geological map showing outcrops of the Küçükkuyu Formation in the north of the Edremit Gulf (revised from Okay et al., 1990b).

Kozakdağ High is located to the south of the Gulf (Figure 1). In this area Triassic units (Karakaya complex) form the basement. Oligo-Miocene plutonic and volcanic rocks (Kozak pluton and Yuntdağ volcanics) cut this basement. Miocene-Pliocene aged fluvial and lacustrine sediments (Küçükkuyu Formation, Mutlu Formation, Soma Formation) unconformably overlie these units (Figure 3).

2.1. Stratigraphy of the Küçükkuyu Formation

The stratigraphy of the formation is studied with the help of detailed lithological columns established from key areas in the north (Bozcu et al., 2014; Bozcu, 2015) and in the south (Aytepe, 2010; Bozcu et al., 2014). The Küçükkuyu Formation (Saka, 1979), which consists of alternating bituminous shale and sandstone, crops out extensively around the Edremit Gulf (Figures 1–3) The formation is Lower-Middle Miocene in age (İnci, 1984; Kesgin, 2001; Çiftçi et al., 2004).

In the north the Küçükkuyu Formation is divided into three members according to lithological and stratigraphic characteristics (Saka, 1979). The formation starts with a conglomerate level (Kızılyar conglomerate member), continues through sandstone-shale alternations, with observed tuff levels above (Arıklı tuff member), and ends with sandstone (Adatepe sandstone member).

Coal plant fragments, thin coal levels, and pyrite crystals are observed in sandstone-shale alternations of the formation. Sedimentary structures, including planar parallel stratification, lamination, grading, spheroidal nodules, ripple marks, slump structures, and mud dykes, are common in the formation (Bozcu, 2015). The formation is overlain unconformably by the İlyasbaşı Formation (Saka, 1979). The İlyasbaşı Formation starts with conglomerate and continues with sandstone-shale alternations (Figure 4).

The Kızılyar conglomerate consists of reddish, weakly cemented conglomerate and sandstone. The conglomerate is reddish, dark purplish-red, and purple colored, well rounded but poorly sorted, and consists of andesite, chert, alkaline lava pebbles, and coarse-grained sandstone layers around the Kızılyar village. The depositional environment of the unit was braided-river and/or steeply dipping alluvial fan (Beccaletto, 2004; Çiftçi et al., 2004). Lateral thickness change and geometry of the unit in a section near Kızılyar village reflects sedimentation as fan sediments (Bozcu, 2015).

The Arıklı tuff is white-beige in color on a fresh surface and yellow-brownish on weathered surfaces. It is thick-bedded, massive, and quite hard in unweathered areas. The tuff also contains thick-medium-bedded tuffite levels.

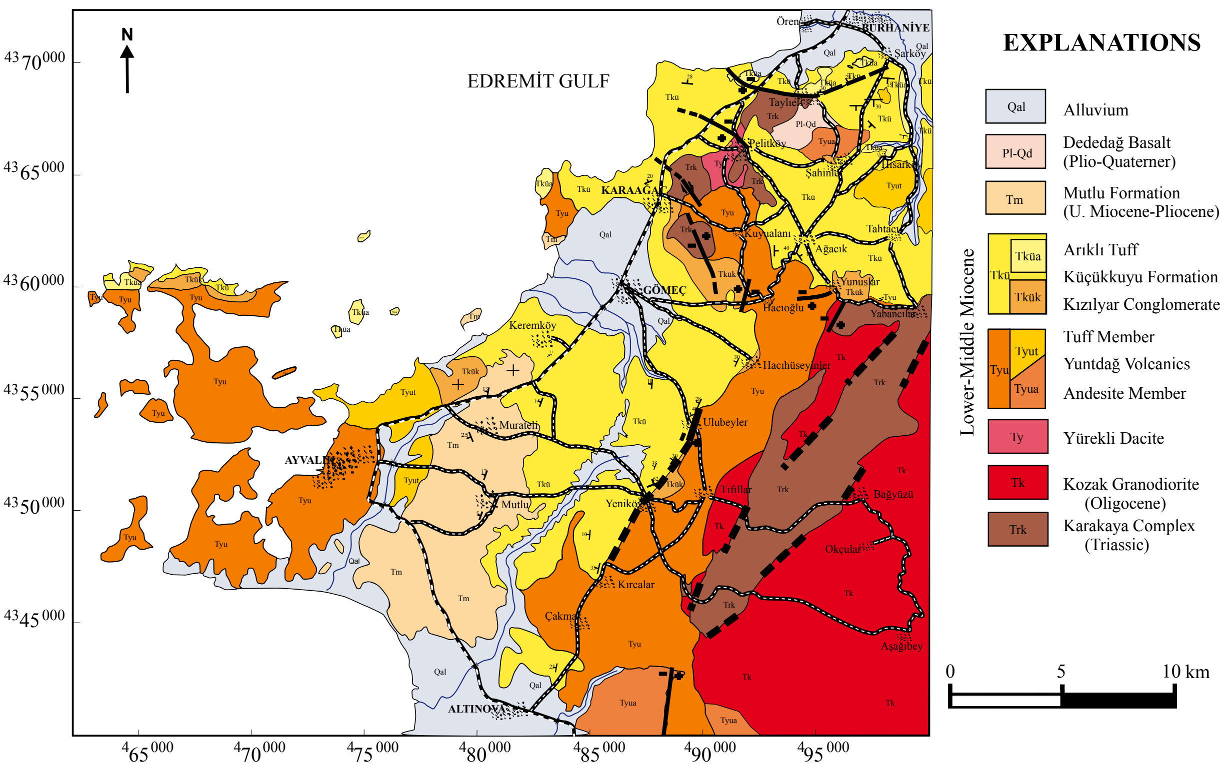

Figure 3. Geological map showing outcrops of the Küçükkuyu Formation in the south of the Edremit Gulf (revised from Akyürek and Soysal, 1983; Çiftçi et al., 2004, Aytepe, 2010).

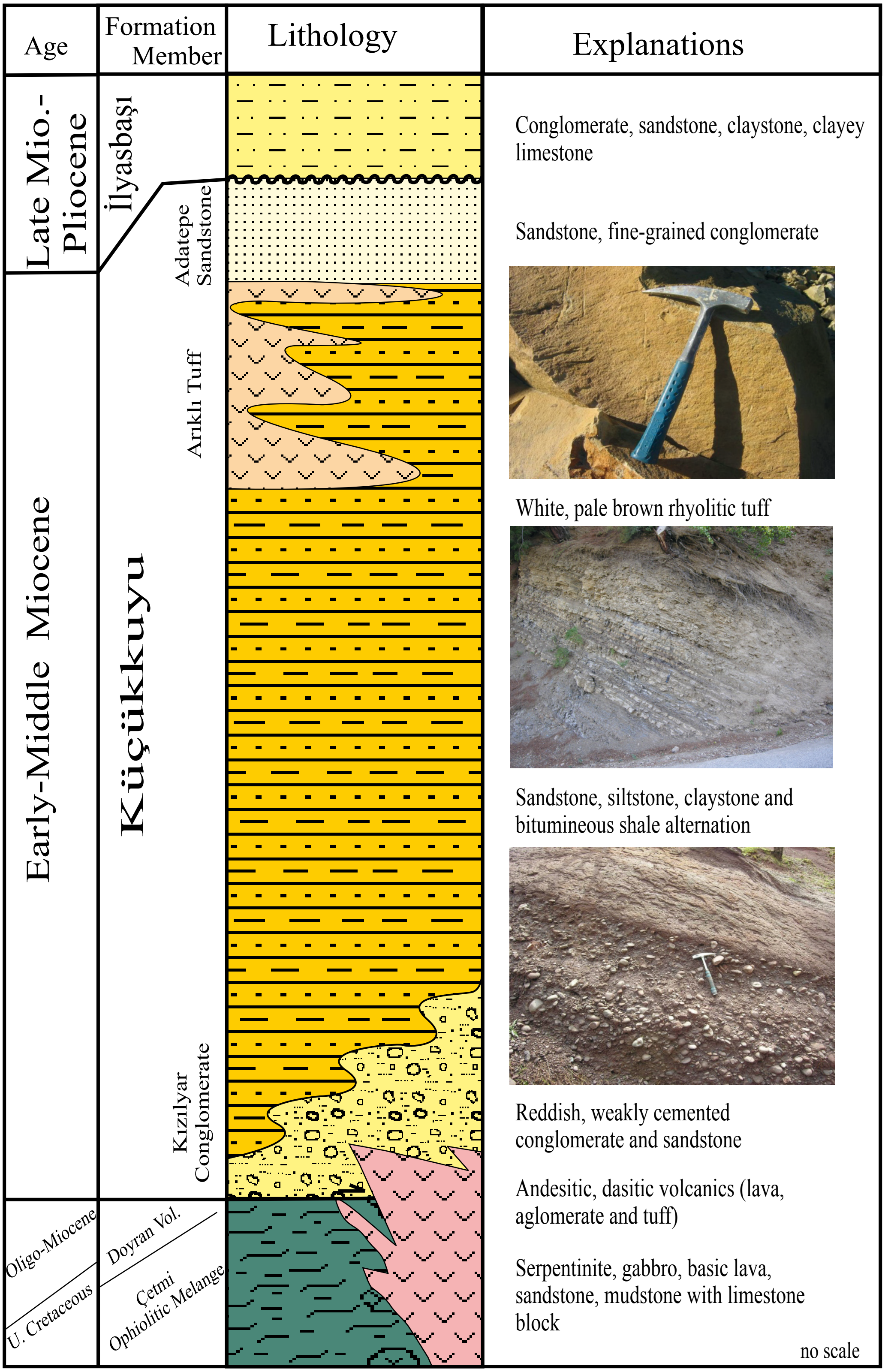

Figure 4. Stratigraphic column of the Küçükkuyu Formation in the north of the Edremit Gulf.

In thin section it consists of fine-grained components and has vitric tuff characteristics. Quartz-plagioclase minerals and ferrous alteration are observed (Bozcu, 2015).

The Adatepe sandstone occurs at the upper level of the formation. It crops out in a restricted area along a synclinal structure to the north of Küçükkuyu near Adatepe village. The unit starts with sandstone-shale alternation at lower levels, passing into sandstone with pebbles. The dominant lithology is tuffite and carbonate-cemented sandstone (Bozcu, 2015).

In the south, the Küçükkuyu Formation starts with a conglomerate level and continues through sandstone-shale and carbonated siltstone alternations, with tuff levels above. The formation comprises two members. The lower is the Kızılyar conglomerate, consisting of chert, schist, and volcanic rock pebbles; the upper is tuff named Arıklı tuff. It is white-yellow in color, medium-thick-bedded, massive, and quite hard.

Sandstone content increases towards the upper part of the formation. The formation ends in medium-thick layered sandstone. Lamination, thin coal levels, and pyrite crystals are observed in the formation. The formation is overlain unconformably by the Mutlu Formation (Çiftçi et al., 2004). The Mutlu Formation (equivalent of İlyasbaşı Formation) starts with conglomerate, continuing to sandstone, clayey limestone, and marl (Figure 5).

3. Materials and methods

A total of 63 shale samples from the Küçükkuyu Formation outcrops in the north of the Edremit Gulf (44 samples) and to the south of the Edremit Gulf (19 samples) were analyzed. These shale samples were collected from measured sections systematically: around Narlı, Adatepe, Yeşilyurt, and Arıklı in the north from 10 measured sections, and around Burhaniye and Gömeç in the south from 6 measured sections.

Rock-Eval pyrolysis/TOC and Ro (vitrinite reflectance), GC (gas chromatography), GC-MS (gas chromatography-mass spectrometry), $\delta^{13}C$ isotope, and TS (total sulfur) measurements were performed. The analyses were carried out in the Turkish Petroleum Corporation Research Group laboratories (TPAO, Ankara).

Rock-Eval pyrolysis/TOC analyses of all the samples were carried out using a Rock-Eval 6 instrument equipped with a TOC module and results are presented in Table 1. The vitrinite reflectance measurements were performed on polished sections in reflected light. GC analyses were performed on 10 samples via Agilent 6850 whole-extract gas chromatographic analysis. GC-MS analyses were conducted on whole-rock extracts obtained from five samples. The saturated fractions were also analyzed using Agilent 7890A/5975C gas GC-MS equipment. Sterane and terpane distributions were defined in light of peak descriptions on m/z 191 and m/z 217 chromatograms.

Stable carbon isotope ($\delta^{13}C$) analyses were conducted on 8 samples using a GV Instruments Isoprime GC-C-IRMS device. The results are presented in ‰ versus (PDB).

4. Results

4.1. TOC content and Rock-Eval pyrolysis

Rock-Eval pyrolysis results of shale samples from north and south of the Edremit Gulf are given in Tables 1 and 2.

The TOC content of 44 shale samples from north of the Edremit Gulf ranges from 0.23 to 6.1 wt.% (mean: 1.76 wt.%). Rock-Eval S1 and S2 values are 0–1.07 and 0.03–33.08 mg HC/g rock, respectively. The HI varies from 8 to 606 mg HC/g TOC.

The TOC content of 19 shale samples from south of the Edremit Gulf ranges from 0.24 to 2.82 wt.% (mean: 1.66 wt.%). Rock-Eval S1 and S2 values are 0–0.28 and 0.05–22.07 mg HC/g rock, respectively. The HI varies from 21 to 712 mg HC/g TOC.

Rock-Eval pyrolysis results of the Küçükkuyu Formation were plotted in HI versus T_{max} (Espitalié et al., 1985) and HI versus OI diagrams (Espitalié et al., 1977) separately for the northern and southern areas of the Edremit Gulf. Although a few samples are in the Type I kerogen field, the majority of the samples are in Type II and Type III kerogen fields (Figures 6a and 6b).

Tmax values vary between 414 and 496 °C (except one, 607 °C) in the north and between 423 and 446 °C in the south. The production index (PI) values are 0–0.48 (average: 0.11) in the north and 0–0.19 (average 0.02) in the south (Tables 1 and 2).

4.2. Vitrinite reflectance

Vitrinite reflectance (R_o) is generally used as a maturity indicator (Dow, 1977). R_o data are given in Table 3. Measured vitrinite reflectance (R_o) values of the Küçükkuyu samples are 0.40%–1.73% R_o (average: 0.73% R_o).

4.3. Stable carbon isotopic composition

Stable carbon isotope ($\delta^{13}C$) values are listed in Table 4. $\delta^{13}C$ values are ranging from –26.15‰ to –30.50‰ with an average of –28.28‰.

4.4. Total sulfur

TS analysis was performed on 15 samples. Results for TOC and TS are shown in Table 5. Measured samples have TS values ranging from 0.0035% to 0.63%.

4.5. Molecular composition

4.5.1. *n*-Alkanes and isoprenoids

GC analyses were carried out for 10 samples (5 samples from the northern part and 5 samples from the southern part of the investigated area) and *n*-alkane distribution and isoprenoids were assessed based on gas chromatograms. Selected gas chromatograms of the total extracts are presented in Figure 7 and their parameters are given in

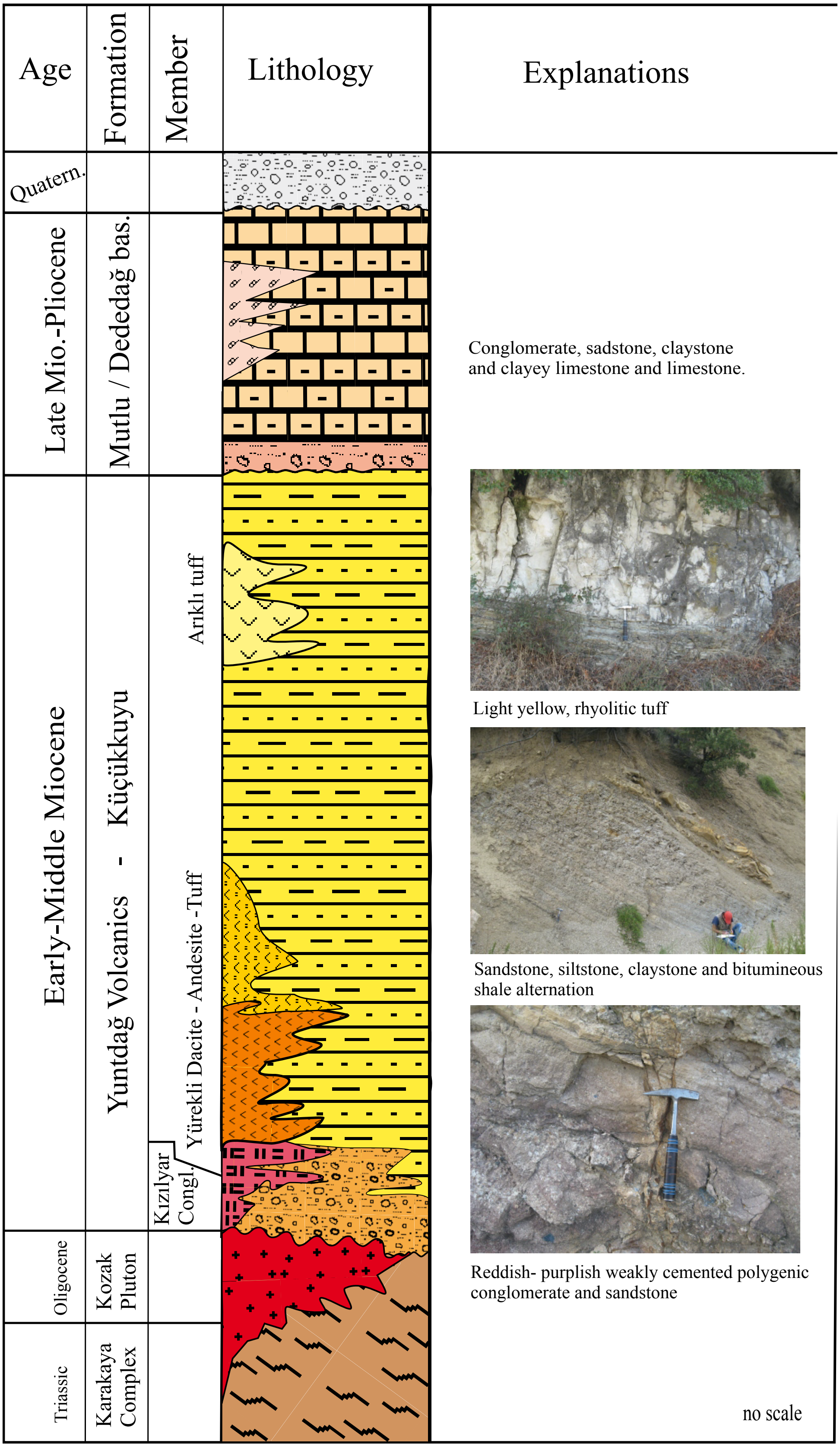

Figure 5. Stratigraphic column of the Küçükkuyu Formation in the south of the Edremit Gulf (revised from Aytepe, 2010).

Table 1. Rock-Eval pyrolysis results for Küçükkuyu Formation samples in the north of the Edremit Gulf (*: from Bozcu, 2015).

Sample	TOC (%)	S1 (mg HC/ g rock)	S2 (mg HC/ g rock)	S3 (mg CO_2/ g rock)	Tmax (°C)	HI (mg HC/g TOC)	OI (mg CO_2/ g TOC)	PI (S1 / S1 + S2)	RC (%)	PC (%)	MINC (%)	PY (S1 + S2)
Do-1	0.96	0.44	0.46	0.62	447	48	65	0.48	0.86	0.1	0.22	0.90
Do-2	1.94	0.74	1.12	0.87	443	58	45	0.4	1.75	0.19	0.42	1.86
Do-3	0.87	0.08	0.29	1.16	442	33	133	0.22	0.79	0.08	1.38	0.37
Do-6	1.2	0.44	0.88	0.4	447	73	33	0.34	1.07	0.13	0.08	1.32
Na1	0.25	0.02	0.04	0.93	496	16	372	0.37	0.22	0.03	0.15	0.06
Na2	0.23	0.02	0.03	0.98	435	13	426	0.34	0.20	0.03	1.31	0.05
Na3	0.50	0.02	0.04	0.48	607	8	96	0.28	0.48	0.02	1.12	0.06
Na4	1.68	0.56	1.14	0.61	454	68	36	0.33	1.51	0.017	0.88	1.60
Kü-2*	2.43	0.17	5.36	1.47	440	221	60	0.03	1.91	0.52	0.19	5.53
Kü-5*	6.1	0.24	33.8	1.83	438	554	30	0.01	3.18	2.92	0.14	33.32
Kü-6*	0.56	0.01	0.21	0.74	450	38	132	0.06	0.51	0.05	0.58	0.22
Kü-10*	0.97	0.12	0.52	0.43	453	54	44	0.19	0.9	0.07	0.53	0.64
Kü-11*	1.34	0.16	1.14	1.00	448	85	75	0.12	1.2	0.14	0.85	1.30
Bd-2	2.7	0.4	8.84	0.53	441	327	20	0.04	1.9	0.8	0.29	8.92
Bd-3	0.92	0.18	1.18	0.38	445	128	41	0.13	0.79	0.13	0.51	1.36
Bd-4	2.41	0.74	5.4	0.91	441	224	38	0.12	1.86	0.55	1.3	5.78
Bd-6	1.63	0.26	1.82	0.86	450	112	53	0.12	1.42	0.21	0.38	2.08
Ad-1	0.37	0	0.15	0.22	462	41	59	0.02	0.35	0.02	0.8	0.15
Ad-3	1.44	0.44	1.96	0.91	444	136	63	0.18	1.21	0.23	0.81	2.4
Ad-5	1.42	0.4	1.97	0.6	446	139	42	0.17	1.19	0.23	0.43	2.37
A2-07*	0.93	0.23	1.63	1.03	445	175	111	0.12	0.74	0.19	2.73	1.86
A4-07*	1.54	1.07	2.74	0.73	443	178	47	0.26	1.2	0.34	0.19	3.81
Kç-4	0.47	0	0.15	0.77	447	32	164	0	0.43	0.04	0.79	0.15
Kç-5	2.18	0.22	8.99	0.86	443	412	39	0.02	1.37	0.81	0.64	9.21
Kç-6	1.2	0.07	2.3	0.59	439	192	49	0.03	0.98	0.22	0.15	2.37
Kç-7	1.88	0.18	7.57	0.18	444	403	10	0.02	1.22	0.66	0.65	7.75
Nu-2	1,76	0,02	4,74	1,01	436	269	57	0,01	1.31	0,45	0.47	4.76
N-6*	1.04	0.01	1.57	0.93	440	151	89	0.01	0.87	0.17	0.06	1.58
Ar-2	1.43	0.02	3.81	0.98	441	266	69	0.01	1.07	0.36	1.28	3.83
Ar-3	3.01	0.36	17.37	1.17	436	577	39	0.02	1.47	1.54	5.01	17.73
Ar-4	2.73	0.36	16.55	0.93	434	606	34	0.02	1.27	1.46	5.58	16.91
Ar-5	1.07	0.07	3.77	0.49	428	352	46	0.02	0.72	0.35	9.18	3.84
Ar-6a	4.29	0.7	24.28	1.25	425	566	29	0.03	2.14	2.15	0.14	24.98
Yk-1	1.98	0.12	6.08	0.9	440	307	45	0.02	1.42	0.56	0.22	6.2
Yk-2	2.83	0.32	10.93	1.11	440	386	39	0.03	1.84	0.99	0.16	11.25
Ye-1	1.99	0.17	6.31	1.13	441	317	57	0.03	1.4	0.59	0.22	6.48
Ye-2	1.66	0.23	5.02	0.74	436	302	45	0.04	1.19	0.47	0.08	5.25
Ye-3	2.15	0.15	8.38	0.79	429	390	37	0.02	1.4	0.75	0.11	8.53
Y-1*	4.18	0.26	11.8	1.89	438	282	45	0.02	3.1	1.08	0.34	12.06
Y-2*	2.08	0.42	11.4	1.39	439	548	67	0.04	1.04	1.04	0.14	11.82
Y-4*	1.7	0.2	9.6	1.22	440	565	72	0.02	0.84	0.86	0.46	9.8
Y-8*	1.55	0.19	6.47	1.08	423	417	70	0.03	0.95	0.6	0.12	6.66
B-1*	3.91	0.28	15.8	2.21	431	404	57	0.02	2.48	1.43	0.26	16.08
B-2*	0.27	0.02	0.11	0.58	414	41	215	0.12	0.24	0.03	0.52	0.13

Table 2. Rock-Eval pyrolysis results for Küçükkuyu Formation samples in the south of the Edremit Gulf.

Sample	TOC (%)	S1 (mg HC/ g rock)	S2 (mg HC/ g rock)	S3 (mg CO_2/ g rock)	Tmax (°C)	HI (mg HC/ g TOC)	OI (mg CO_2/ g TOC)	PI (S1 / S1 + S2)	RC (%)	PC (%)	MINC (%)	PY (S1 + S2)
Br-2	1.7	0.2	6.85	0.9	438	403	53	0.03	1.07	0.63	2.18	6.87
Br-5	2.82	0.2	13.78	0.53	439	489	19	0.01	1.62	1.2	1.19	13.80
Br-6	1.81	0.07	7.32	1	438	404	55	0.01	1.15	0.66	3.33	7.39
UL-2	0.73	0	0.56	0.44	431	77	60	0	0.66	0.07	0.47	0.56
UL-3	1.06	0.07	2.16	0.34	430	204	32	0.03	0.85	0.21	0.86	2.23
UL-5	0.24	0	0.05	0.51	446	21	212	0	0.22	0.02	0.38	0.05
Yn-1	0.28	0	0.06	0.54	445	21	193	0	0.25	0.03	3.89	0.06
Yn-3	1.13	0.06	3.66	0.57	426	324	50	0.02	0.79	0.34	4.95	3.72
Yn-4	0.35	0	0.13	0.38	445	37	109	0	0.32	0.03	1.28	0.13
Hi-01	2.73	0.18	18.61	0.52	438	682	19	0.01	1.13	1.6	3.91	18.79
Hi-02	1.56	0.07	6.58	0.68	437	422	44	0.01	0.97	0.59	5.56	6.65
Ul-02	0.77	0.1	0.44	1.55	423	57	201	0.19	0.66	0.11	0.32	0.45
Ul-07	0.57	0.07	0.79	1.08	442	139	189	0.08	0.46	0.11	1.92	0.86
Yu-03	2.01	0.28	8.22	0.95	433	409	47	0.03	1.25	0.76	2.69	8.50
Ş-02	1.32	0.13	6.18	0.57	436	468	43	0.02	0.76	0.56	7.17	6.31
Ş-07	2.09	0.15	8.58	1.68	440	411	80	0.02	1.3	0.79	4.49	8.73
Ş-12	1.52	0.09	5.01	1.07	436	330	70	0.02	1.05	0.47	3.46	5.10
Şr-06	3.1	0.4	22.07	0.54	437	712	17	0.02	1.19	1.91	1.07	22.47
Ao-09	0.84	0.06	2.21	0.7	436	263	83	0.02	0.62	0.22	2.86	2.27

Table 6. Küçükkuyu samples comprise *n*-alkanes in the range of C_{12}–C_{35}. The chromatograms show a dominance of mid chain (n-C_{21-25}) and long chain (n-C_{27-32}) *n*-alkanes. The Pr (pristane) and Ph (phytane), the main acyclic isoprenoids, also exist, with the Pr/Ph ratio ranging between 0.22 and 1.42 (Table 6).

The Pr/*n*-C17 and Ph/*n*-C18 values are given in Table 6, and the Pr/*n*-C17 versus Ph/*n*-C18 cross-plot is shown in Figure 8.

The carbon preference index (CPI) was computed from the gas chromatography data using the *n*-alkanes $C_{25-}C_{33}$ (Bray and Evans, 1961) (Table 6). The CPI values range between 0.96 and 1.69.

4.5.2. Steranes and terpanes

The sterane (m/z 217) and terpane (m/z 191) distributions in the Küçükkuyu samples are shown in Figure 9. The biomarker data calculated from the m/z 217 and 191 mass chromatograms are listed in Table 7. Peak definitions on m/z 217 and m/z 191 chromatograms are given in Tables 8 and 9.

5. Discussion

5.1. TOC contents

The TOC content of the Küçükkuyu Formation in the north and south of the Edremit Gulf (Tables 1 and 2) range from 0.23 to 6.1 wt.% (average: 1.76 wt.%) and 0.24 to 2.82 wt.% (average: 1.66 wt.%), respectively, and generally indicate a good source rock potential.

5.2. Type of organic matter (OM)

Figures 6a and 6b show that the organic matter in shale samples contains mainly Type II–III (oil- and gas-prone) kerogen, with a minor component of Type I (oil-prone) kerogen (Tissot and Welte, 1978).

The HI values of the Küçükkuyu shales from the north and south of the Edremit Gulf are in the range of 8–606 and 21–712 mg HC/g TOC (average: HI 238.95 and 309.10 mg HC/g TOC), respectively. These HI values indicate that the organic matter contains predominantly Type II–III (aquatic and terrestrial organic matter) kerogen. The Küçükkuyu samples are predominantly represented by long and mid-chain *n*-alkanes. Long chain *n*-alkanes are

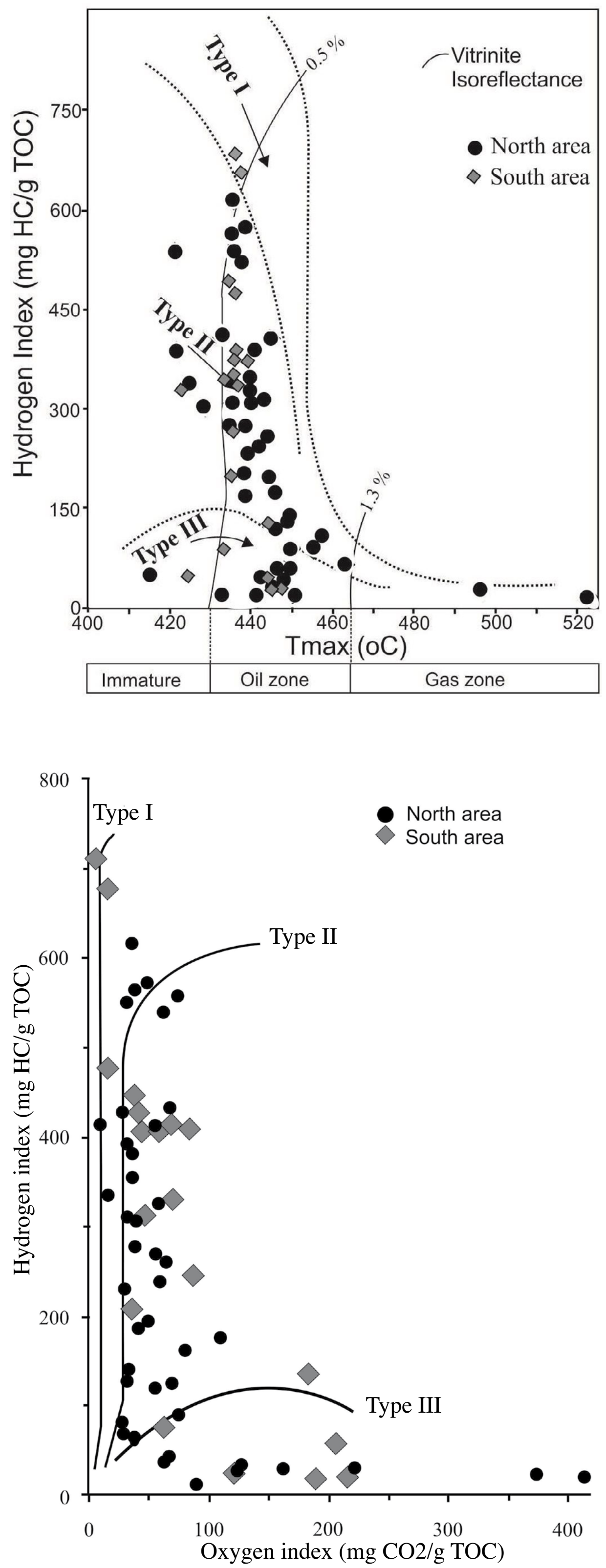

Figure 6. HI versus Tmax distribution (a) (Espitalié et al., 1985) and HI versus OI distribution (b) (Espitalié et al., 1977) for Küçükkuyu samples from north and south of the Edremit Gulf.

Table 3. Vitrinite reflectance (R_o%) analyses results of the Küçükkuyu Formation (*: from Bozcu, 2015).

Sample	R_o (%)
Do-2	1.35
Do-6	1.23
Kü-5*	0.50
Kü-10*	0.88
Bd-2	0.56
Bd-6	0.95
Ad-3	0.40
A2-07*	0.55
Kç-5	0.48
Kç-7	1.73
Ye-1	0.69
Ye-2	0.70
Ye-3	0.58
Br-2	1.66
Br-5	0.40
Ul-02	0.46
UL-3	0.67

Table 4. Stable carbon isotope values for Küçükkuyu Formation samples (*: from Bozcu, 2015).

Sample	$\delta^{13}C$
Kü-11*	–27.39
Y-2*	–29.26
B-1*	–26.15
Hi-01	–29.34
Yu-03	–30.50
Ş-02	–27.54
Ş-07	–26.97
Şr-06	–29.14

derived from terrestrial higher plant waxes (Eglinton and Hamilton, 1967; Tissot and Welte, 1984; Meyers, 1997). Mid chain *n*-alkanes are in general derived from aquatic macrophytes (Ficken et al., 2000). Short chain n-alkanes mainly present algae (Cranwell et al., 1987) and planktons (Meyers, 1997).

On a Pr/*n*-C17 versus Ph/*n*-C18 cross-plot, the Küçükkuyu Formation samples plot in the algal, mixed, and terrigenous Type I, II/III, and III fields (Figure 8).

Table 5. TOC, TS, and TOC/TS values of the Küçükkuyu Formation (*: from Bozcu, 2015).

Sample	TOC (%)	TS (%)	TOC/TS
Y-2*	2.08	0.041	50.73
Y-4*	1.7	0.12	14.16
Y-8*	1.55	0.077	20.12
A4-07*	1.54	0.012	128.33
N-6*	1.04	0.026	40
B-1*	3.91	0.062	63.06
Kü-2*	2.43	0.029	83.79
Kü-5*	6.1	0.63	9.68
Kü-10*	0.97	0.012	80.83
Na-1	0.25	0.067	3.73
Na-2	0.23	0.073	3.15
Na-3	0.50	0.024	20.83
Na-4	1.68	0.048	35
Do-2	1.94	0.014	138.57
Bd-2	2.7	0.029	93.10
Kç-5	2.18	0.027	80.74
Ad-3	1.44	0.015	96
Br-2	1.7	0.0174	97.70
Br-5	1.68	0.284	5.91
Br-6	1.81	0.0323	56.03
UL-2	0.73	0.2574	2.83
UL-3	1.06	0.455	2.32
Yn-1	0.28	0.0035	80
Yn-4	0.35	0.0229	15.28

Data related to type of organic matter indicate that it temporally and spatially changed according to conditions in the organic facies.

5.3. Maturity of organic matter

Organic matter maturity is defined based on Rock-Eval T_{max} data (Peters and Moldowan, 1993; Peters et al., 2005), on production index (PI) values (Tissot and Welte, 1984; Waples, 1985; Anders, 1991; Peters and Moldowan, 1993), and on vitrinite reflectance (R_o) measurements (Tissot and Welte, 1984; Espitalié et al., 1985).

Tmax values for Küçükkuyu samples range (except one, 607 °C) between 414 and 496 °C in the north and between 423 and 446 °C in the south. These values indicate that the level of organic maturity is in general immature or early-mid-mature (beginning of the oil window or probably within the oil window). Although most of the Tmax values of the Küçükkuyu Formation samples indicate early-mature to mature character, immature and overmature values were also measured. According to Çiftçi et al. (2004), this area is affected by an intense Neogene volcanism that is partly synchronous and postdates the deposition of the lacustrine Küçükkuyu Formation. Therefore, overmature values may be related to thermal stress caused by this volcanism.

The average PI values for the Küçükkuyu Formation are 0.11 and 0.02, respectively. PI values of less than 0.1 are indicators for the immature zone (Anders, 1991; Peters and Moldowan, 1993). Ro (vitrinite reflectance) values of analyzed samples vary between 0.40% and 1.73%. The average value is 0.78 % (Table 3), which indicates mostly an early-mature stage.

Based on the CPI for the *n*-alkanes, values around 1 are mature and values of <1 are early-mature. The CPI values for the Küçükkuyu samples are between 0.96 and 1.69. The maturation of the samples ranges from early mature to mature.

Other thermal maturity indicators based on biomarkers are 22S/(22S + 22R) homohopane and 20S/(20S + 20R) and ββ/(ββ + αα) sterane ratios (Seifert and Moldowan, 1986; Waples and Machihara, 1991; Peters and Moldowan, 1993; Hunt, 1995). Analyzed samples have C_{32} 22S/(22S + 22R) ratios in the range of 0.40–0.58 with an average of 0.50 (Table 7), suggesting that these samples are early-mature.

The moretane/hopane ratio can be also used as a maturity indicator. This ratio decreases from about 0.8 to 0.15–0.05 as the thermal maturity increases (Mackenzie et al., 1980; Seifert and Moldowan, 1980). Küçükkuyu samples have 0.13 to 0.37 moretane/hopane ratios with an average of 0.30, which also suggests that the samples are immature.

5.4. Depositional environment

According to previous studies the formation was deposited in a lacustrine environment (Saka, 1979; Siyako et al., 1989; Kesgin, 2001; Yılmaz and Karacık, 2001; Beccaletto, 2004; Çiftçi et al., 2004; Beccaletto and Steiner, 2005; Bozcu, 2015). It was argued by Siyako et al. (1989) and Yılmaz et al. (2001) that volcanism developed simultaneously with lacustrine sediments. Therefore, volcanic and lacustrine sediments have interfingering contacts. According to Yılmaz et al. (2001), magmatism related to collision took place in northwestern Anatolia in the Oligocene-Late Miocene period and the plutonics-volcanics widespread in the region are products of this magmatism. Lacustrine basins existed in depressions controlled by N-S faults, which were active simultaneously with the magmatism. On the other hand, Cavazza et al. (2009) stated that the Kazdağ Massif was exhumed in three stages as a result of N-S extension and the Küçükkuyu Formation was deposited during the first stage. Consequently, it was

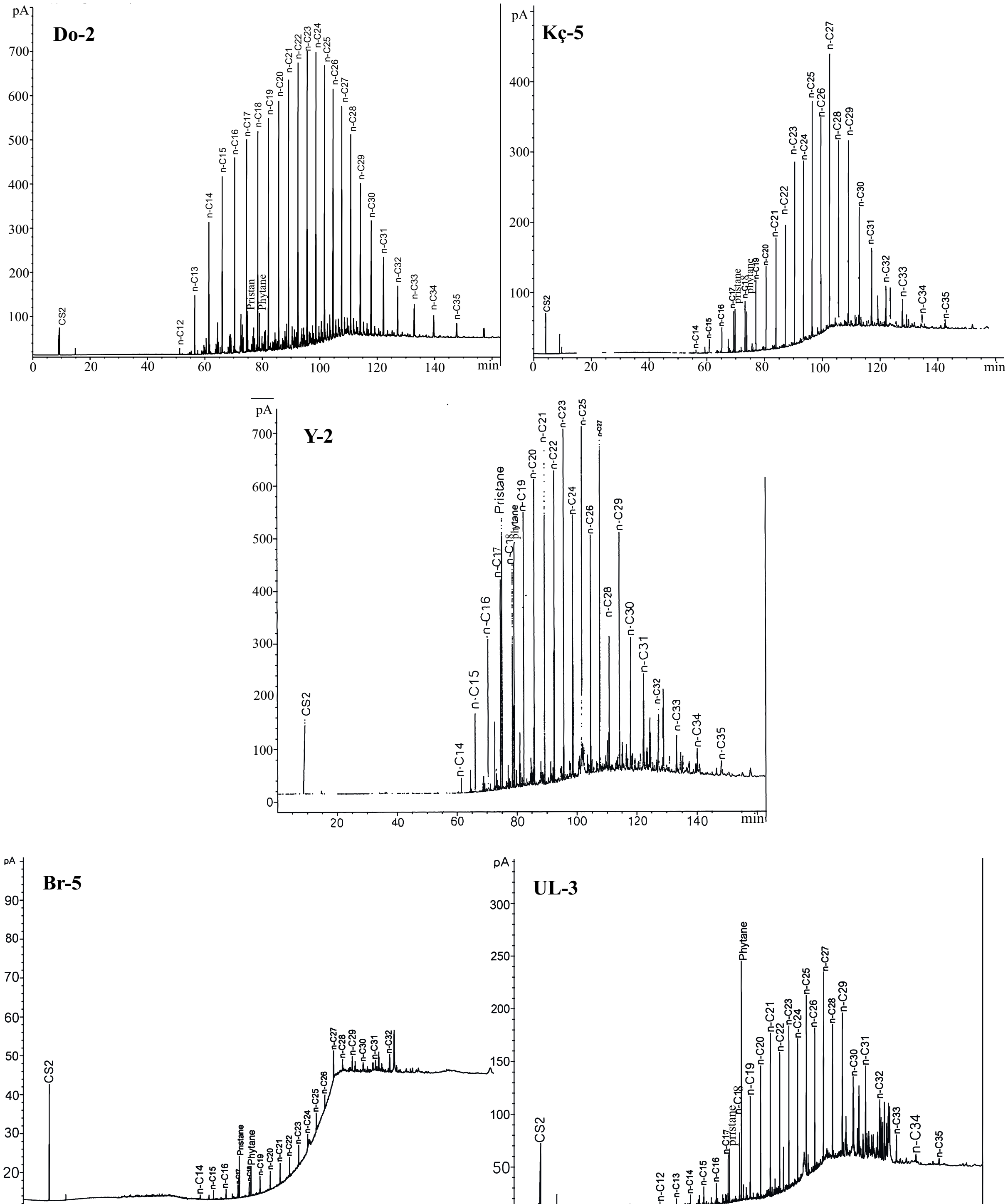

Figure 7. Gas chromatograms of selected shale samples from the Küçükkuyu Formation.

deposited in a lacustrine, fault-controlled basin. Field data also support this idea (Figure 10).

The Kızılyar Conglomerate at the lower level of the unit consists of fault scarp fan (debris flow) and braided river sediments on basement rock (Figure 10a). The geometry of the unit and arrangement with sorting and rounding of the gravels indicate a high-energy environment. Alternating sandstone-shale in the middle part of the formation

Table 6. Parameters of gas chromatography for the Küçükkuyu Formation samples (*: from Bozcu, 2015). CPI was calculated using the equation of Bray and Evans (1961).

Sample	Pr/Ph	Pr/n-C17	Ph/n-C18	CPI_{25-33}
Do-2	1.01	0.21	0.19	1.00
Kü-11*	1.42	0.25	0.16	1.24
Ad-3	1.18	1.25	0.90	-
Kç-5	1.02	1.27	1.04	1.3
Y-2*	1.13	1.70	1.39	1.67
Br-5	1.30	3.30	2.35	0.96
UL-3	0.22	1.07	3.70	1.19
Hi-01	0.97	3.37	3.66	1.33
Ş-07	1.32	2.21	1.29	1.26
Şr-6	1.08	1.19	0.96	1.69

includes turbiditic current structures. The basin in which the formation was deposited had a slope that allowed turbidity currents to occur. Slump structures, boudinaged sandstone layers, and mud dykes frequently exist in the unit and indicate tectonic activity during deposition of the unit (Figure 10b).

Subsequent to the end of the regressive deposition of the formation, an extensional tectonic regime (development of detachment: Okay and Satır, 2000; Cavazza et al., 2009), causing the exhumation of Kazdağı, began during the Late Miocene-Early Pliocene. In this period volcanic activity was renewed and new depositional environments are formed. The İlyasbaşı Formation was deposited synchronously with volcanic activity in this period (Figure 10c). Sediments from this basin are presently observed in grabens bounded by E-W trending faults (Figure 10d).

The depositional environment of the Küçükkuyu Formation is also evaluated using the organic geochemical data, namely $\delta^{13}C$ values, TOC/TS ratios, and biomarker distributions.

According to Meyers (1997), carbon isotopic ratios can be used to distinguish between marine organisms and continental plants as sources of sedimentary organic matter and to identify organic matter from different types of land plants. Organic matter produced from atmospheric CO_2 by land plants using the C3 pathway has an isotopic composition of –34‰ to –24‰, averaging –27‰, $\delta^{13}C$ (PDB) value, and by those using the C4 pathway has –19‰ to –6‰, averaging –14‰, (O'Leary, 1988; Meyers and Ishiwatari, 1993; Meyers, 1994, 1997). Freshwater algae use dissolved CO_2, which is usually in isotopic equilibrium with atmospheric CO_2, whereas under saline water conditions, plants use the C_4 photosynthetic pathway. $\delta^{13}C$ values of typical lake algae in fresh water range from –30‰ to –25‰. Therefore, organic matter derived from algae in lakes is isotopically indistinguishable from organic matter derived by C_3 plants in the surrounding watershed (Meyers, 1997, 2003). Marine organic matter typically has $\delta^{13}C$ values between –20‰ and -22‰ and organic matter in lacustrine sediments is mainly derived from terrestrial and aquatic primary production (Meyers, 1994, 2003). The $\delta^{13}C$ values of organic matter in Küçükkuyu samples range

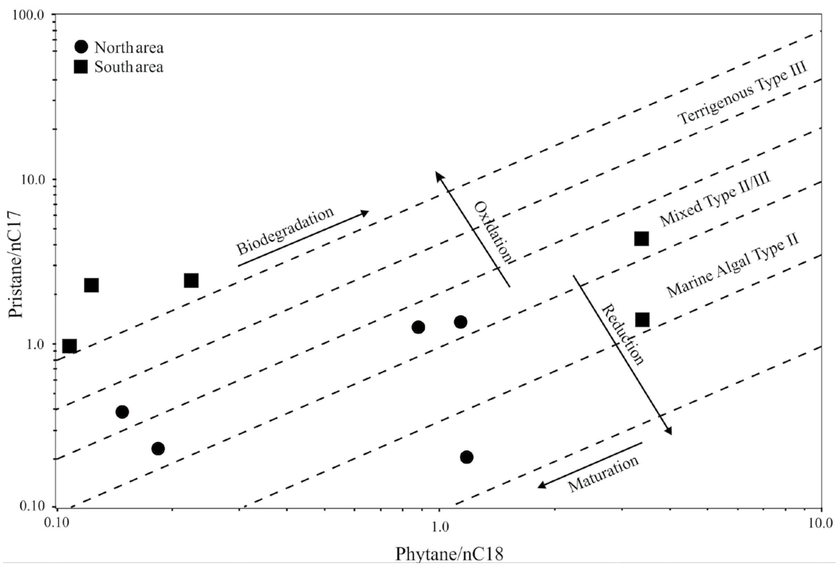

Figure 8. Cross plot of Pr/nC17 versus Ph/nC18 for the Küçükkuyu shale samples (fields after Peters et al., 2005).

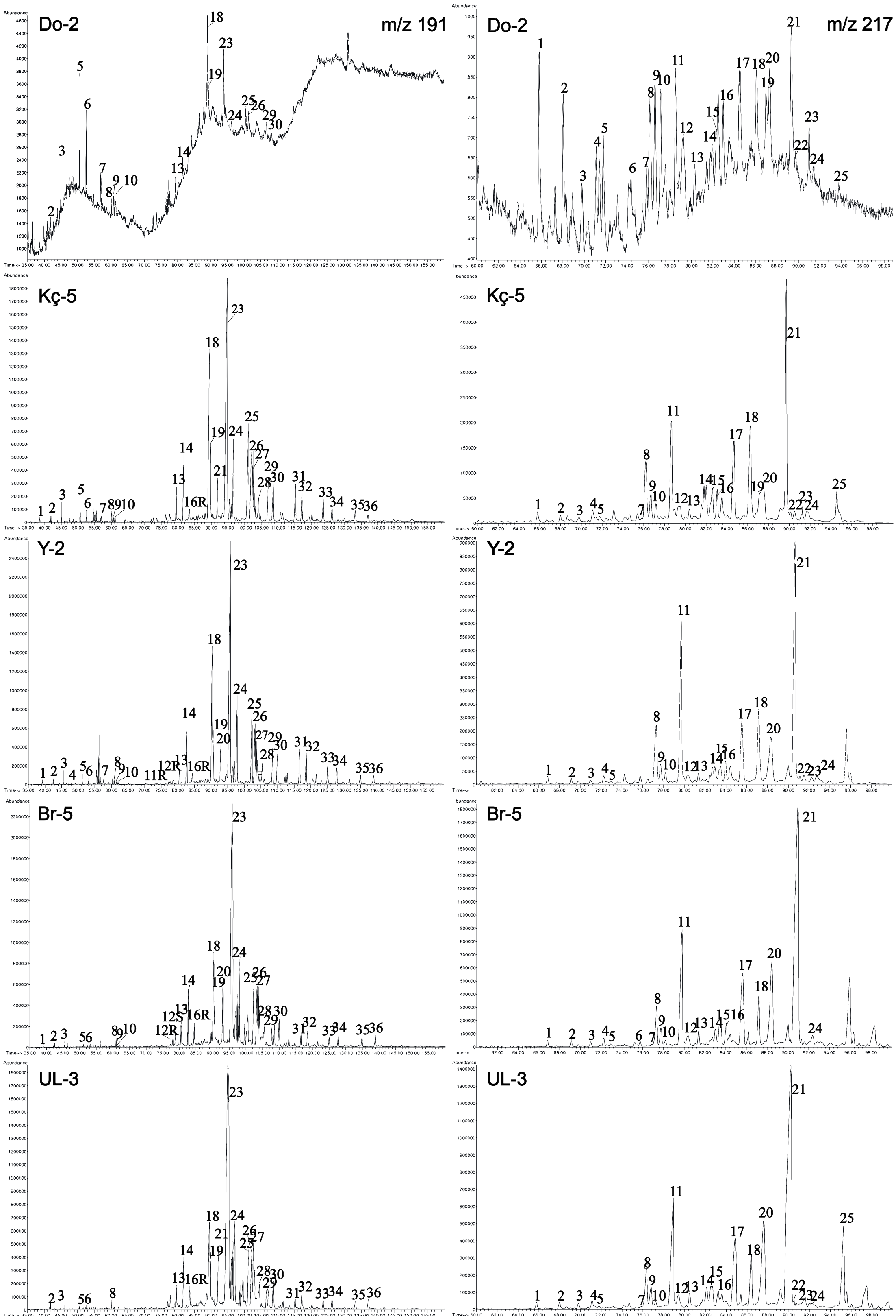

Figure 9. m/z 191 and m/z 217 fragmentograms showing the distribution of terpanes and steranes for selected shale samples from the Küçükkuyu Formation.

Table 7. Biomarker composition based on m/z 191 and m/z 217 mass chromatograms and calculated parameters.

Sample	1	2	3	4	5	6	7	8	9	10
Do-2	0.4	1.4	1.6	0.22	0.13	-	0.58	1.07	0.45	1.09
Kç-5	0.86	0.71	0.10	0.26	0.33	0.49	0.57	0.50	0.28	0.35
Y-2	0.82	0.57	0.04	0.25	0.37	1.06	0.53	0.23	0.02	0.39
UL-3	-	0.33	0.01	0.22	0.35	0.97	0.40	0.40	0.17	0.92
Br-5	0.75	0.21	0.01	0.27	0.35	1.01	0.43	0.46	0.92	0.77

1- C_{24}/C_{26}(S+R): C_{24} tetracyclic/[C_{26}tricyclic(S+R)]; 2- NH/H:C_{29} norhopane/C30 hopane; 3- C_{23}/C_{30}H:C_{23} tricyclic terpane/C_{30} hopane; 4- C_{31}22R/H: C3122R/C_{30}hopane; 5- moretane/hopane ratio; 6- C35(R+S)/C34(R+S); 7- C_{32} 22S/(22S+22R); 8- Ts/Tm; 9- C_{29}20S/(20S+20R); 10- sterane/hopane ratio.

from –26.15‰ to –30.50‰ and indicate that organic matter may have been derived from both terrestrial plants and aquatic organic matter (Table 4).

The TOC (%) to TS (%) ratio of fine-grained sediments is a proxy to distinguish oxic-anoxic and marine-freshwater depositional environments (Leventhal, 1983; Berner, 1984). Marine samples have low values (0.5–5), while samples deposited in fresh-water have high values (>10) (Berner and Raiswell, 1984). TS analysis was performed on 24 samples from the Küçükkuyu Formation (Table 5; Figure 11). The values for the samples here are generally >10, indicating that they were deposited in a lacustrine freshwater environment with slight marine input or occasionally brackish conditions.

GC analysis can also be used to assess depositional conditions and the organic matter origin of source rock (Tissot and Welte, 1984; Moldowan et al., 1985; Killops and Killops, 1993; Hunt, 1995). The pristane/phytane (Pr/Ph) ratio is commonly used. Low Pr/Ph ratios (<1) are considered to be indicative of anoxic environments, high values (>1) indicate oxic environments, and ratios between 1 and 3 are indicative of oxic to suboxic environments. The Pr/Ph ratio is low here (0.22–1.42). Hence, it can be interpreted that the depositional environment was anoxic to suboxic.

The Pr/n-C_{17} versus Ph/n-C_{18} cross-plot (Figure 8) for the Küçükkuyu samples shows that most of the samples consist of mixed or terrestrial organic matter inputs and were deposited in oxidizing conditions.

Biomarker characteristics also give information about source rock depositional environments (Tissot and Welte, 1984; Waples and Machihara, 1991; Peters and Moldowan, 1993; Hunt, 1995; Peters et al., 2005). Sterane and triterpene distributions recorded using m/z 217 and m/z 191 mass chromatograms (Volkman and Maxwell, 1986) were examined to determine depositional environment and parameters calculated from these distributions (Table 7).

The C_{27}, C_{28}, and C_{29} sterane distributions in analyzed samples are similar ($C_{29} > C_{27} > C_{28}$), except for one ($C_{27} > C_{29} > C_{28}$). The relative abundances of C_{27}, C_{28}, and C_{29} steranes are used to define the source of the organic matter (Huang and Meinschein, 1979; Moldowan et al., 1986; Peters et al., 2005). The C_{27} steranes mainly derive from phytoplankton (mainly algae), C_{28} steranes derive from specific phytoplankton types, and C_{29} steranes derive from terrestrial higher plants. Furthermore, C_{27} and C_{28} steranes may also derive from algae within lacustrine or marsh environments. Volkman (1986) stated that low C_{28} levels are typical of limnic environments. The dominance of C_{29} steranes shows mainly terrestrial OM contribution for the Küçükkuyu samples. The source of organic matter for one sample (Br-5) is dominantly algae, with less terrestrial plants.

The relative abundance of steranes to hopanes can be evaluated as an indicator for organic matter composition. Low sterane/hopane ratios suggest a terrigenous and/or microorganism-reworked organic matter source (Tissot and Welte, 1984), while high sterane/hopane ratios (>1) point to aquatic algae observed in many marine and evaporitic deposits (Moldowan et al., 1985; Fu et al., 1990). Sterane/hopane ratios of the Küçükkuyu samples range from 0.35 to 1.09, indicating mainly terrigenous with less aquatic algal organic matter source.

The C35 (R+S) / C34 (R+S) ratio is an indicator of depositional conditions. A C35 (R+S) / C34 (R+S) ratio of <1 indicates suboxic conditions; >1 indicates anoxic conditions (Peters and Moldowan, 1991). These ratios are 0.49 to 1.06 for the Küçükkuyu samples (Table 7), indicating mostly anoxic conditions. The Ts/Tm ratio may reflect oxic or anoxic environmental conditions during deposition. Low Ts/Tm (<1) may indicate anoxic conditions (McKirdy et al., 1983). This ratio in the Küçükkuyu Formation ranges from 0.23 to 1.07 and indicates mostly anoxic conditions.

Gammacerane is a biomarker pointing out reducing and hypersaline depositional conditions. It is commonly available in hypersaline marine and nonmarine depositional environments (Moldowan et al., 1985; Fu et al., 1986; Peters and Moldowan, 1993). However, high

Table 8. Peak definitions of steranes in the m/z 217 mass chromatograms.

Peak	Compound
1	C_{19} Tricyclic terpane
2	C_{20} Tricyclic terpane
3	C_{21} Tricyclic terpane
4	C_{22} Tricyclic terpane
5	C_{23} Tricyclic terpane
6	C_{24} Tricyclic terpane
7	C_{25} (22S+22R) Tricyclic terpane
8	C_{24} Tetracyclic hopane (Seco)
9	C_{26} 22(S) Tricyclic terpane
10	C_{26} 22(R) Tricyclic terpane
11R	C_{28}Tricyclic terpane (R)
11S	C_{28} Tricyclic terpane (S)
12R	C_{29} Tricyclic terpane (R)
12S	C_{29} Tricyclic terpane (S)
13	C_{27} 18α (H)-22,29,30-Trisnorhopane (Ts)
14	C_{27} 17α (H)-22,29,30-Trisnorhopane (Tm)
15	17α (H)-29,30-Bisnorhopane
16	C_{30} Tricyclic terpane
17	17α (H)-28,30-Bisnorhopane
18	C_{29} 17α (H), 21β (H)-30-Norhopane
19	C_{29} Ts(18α(H)-30-Norhopane
20	C_{30} (17α(H)-Diahopane)
21	C_{29} 17β (H), 21α (H)-30 Normoratene
22	Oleanane
23	C_{30} 17α (H), 21β (H)-Hopane
24	C_{30} 17_{β} (H), 21α (H)-Moretane
25	C_{31} 17α (H), 21β (H)-30-Homohopane (22S)
26	C_{31} 17α (H), 21β (H)-30-Homohopane (22R)
27	Gammacerane
28	Homomoretane
29	C_{32} 17α (H), 21β (H)-30,31-Bishomohopane (22S)
30	C_{32} 17α (H), 21β (H)-30,31-Bishomohopane (22R)
31	C_{33} 17α (H), 21β (H)-30,31,32- Trishomohopane (22S)
32	C_{33} 17α (H), 21β (H)-30,31,32- Trishomohopane (22R)
33	C_{34} 17α (H), 21β (H)-30,31,32,33 Tetrakishomohopane (22S)
34	C_{34} 17α (H), 21β (H)-30,31,32,33 Tetrakishomohopane (22R)
35	C_{35} 17α (H), 21β (H)-30,31,32,33,34 Pentakishomohopane (22S)
36	C_{35} 17α (H), 21β (H)-30,31,32,33,34 Pentakishomohopane (22R)

Table 9. Peak definitions of terpanes in the m/z 191 mass chromatograms.

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

gammacerane contents are also present in freshwater lacustrine sediments. Sinninghe Damsté et al. (1995) suggested that gammacerane is in fact an indicator for water column stratification. Gammacerane occurs in small amounts in the Küçükkuyu Formation samples.

The C_{31} R homohopane/C_{30} hopane ratio is also used to distinguish between marine and lacustrine source rock environments. In lacustrine source rocks, the ratio is <0.25 (Peters et al., 2005). This ratio is 0.22 to 0.27 for the Küçükkuyu samples (Table 7), indicating a mostly lacustrine depositional environment.

According to Katz (1990), paleoclimate and paleogeography are very important factors to control the distribution of lake bodies and influence the water chemistry. Palynomorph assemblages of the Küçükkuyu formation from the northern outcrops (det. Assoc Prof MS Akkıraz, Dumlupınar University, Turkey) are characterized predominantly by conifer Pinaceae forms indicating higher topography paleogeographically. *Pinus diploxylon* type, *P. haploxylon* type, *Cathaya*, *Picea*, *Abies*, *Larix*, *Tsuga*, *Keteeleria*, and *Fagus* plants are common in higher areas. In lower topographical areas Cyrillaceae-Clethraceae, *Engelhardia*, *Tilia*, Cycadaceae, and Oleaceae plants are present in minor percentages. *Carya*, Cupressaceae, Myricaceae (*Triatriopollenites rurensis* and *T. bituitus*), and Sparganiaceae plants are found in fresh-water swamp. Based on these results, intensive vegetation was at the edge of the basin in a mountain area. Intensive development of vegetation indicates that the climate was hot and rainy. Arid climate markers of *Artemisia*, *Ephedra*, and Chenopodiaceae forms are found in minor amounts. The presence of these forms shows that some local areas were arid in the region.

Beccaletto (2004) and Beccaletto and Steiner (2005) indicate that palynomorph assemblages from the base of the intermediate member of the Küçükkuyu Formation

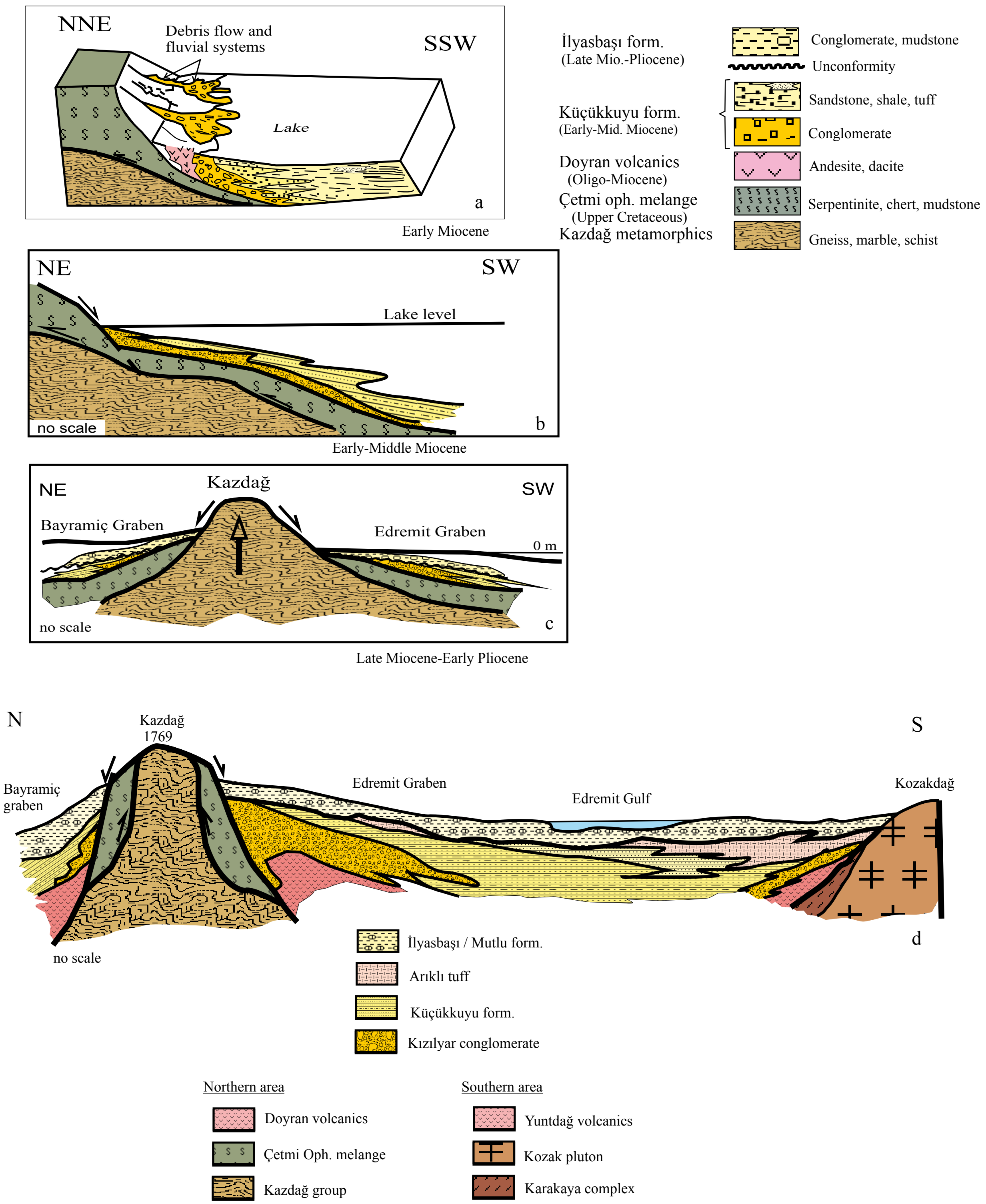

Figure 10. Depositional environment of the Küçükkuyu Formation. a) Schematic block diagram showing the basin in which the Küçükkuyu Formation was deposited; b) – c) Schematic geological cross-sections showing depositional model of the Küçükkuyu Formation and İlyasbaşı Formation; d) Schematic geological cross-section of the basin with Neogene-age units in the Edremit Gulf and surroundings (Early Miocene to present day).

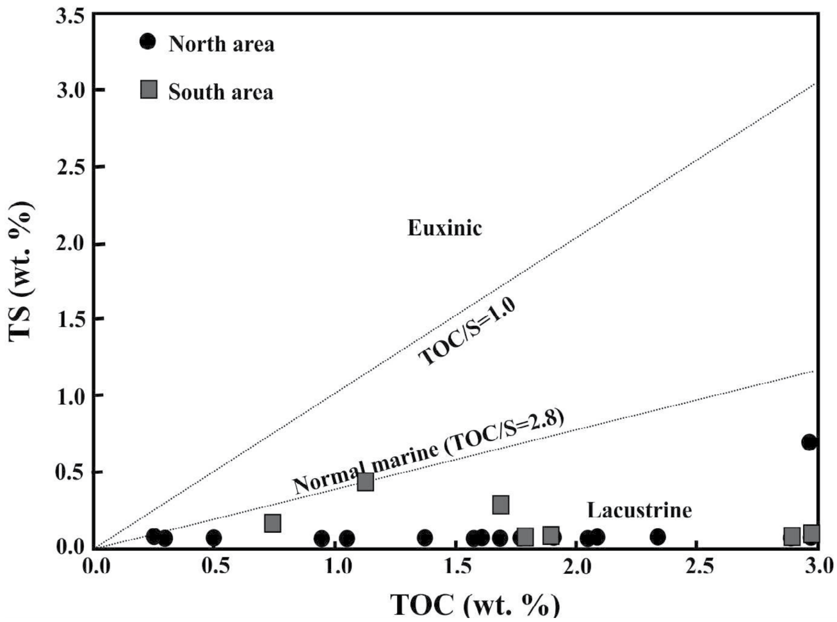

Figure 11. TOC (%) – TS (%) diagram (Berner, 1984).

demonstrate a fresh-brackish water environment representing a lacustrine environment. Conifers and deciduous forests (pollens of pine, cypress, oak, etc.) are present near the environment. This result is consistent with the palynomorph assemblages mentioned above.

Oleanane is a biomarker derived from angiosperms (Rullkötter et al., 1994; Bechtel et al., 2005). The absence of oleanane indicates that the source rocks were deposited far from angiosperm input (Moldowan et al., 1994). Oleanane has not been observed in the Küçükkuyu samples. This is consistent with the palynomorph assemblages that have been determined.

Carroll and Bohacs (2001) noted that no typical lacustrine source rocks and oils exist and lacustrine source rocks display a high degree of geochemical heterogeneity relative to marine facies. Powell (1986) stated that hydrocarbon lacustrine source rocks have organic carbon values ranging from <1% to >20% and Type I to Type III kerogen. The organic matter can be of land plant, algal, and bacterial origins.

Based on these data, it has been determined that the Küçükkuyu Formation was deposited in a fresh-water or slightly raised salinity (brackish-water) lacustrine environment indicating anoxic and suboxic conditions.

5.5. Hydrocarbon generation potential

Hydrocarbon source rock potential was evaluated using the pyrolysis data (TOC, HI, S1, S2, and PY). Based on Tissot and Welte (1984), rocks with TOC values higher than 0.5 wt.% can be regarded as potential source rock for oil and gas. In this study, the Küçükkuyu Formation shales have averages greater than 1% TOC, indicating a good generative potential.

S2 (pyrolyzed hydrocarbons) can also be used to evaluate hydrocarbon-generating potential of source rocks (Peters, 1986; Bordenave, 1993). S2 yields of more than 4.0 mg HC/g rock are generally accepted as a sign of good hydrocarbon source rocks (Bordenave, 1993). Most of the analyzed samples have S2 values greater than 4.0 mg HC/g rock. Thus, Rock-Eval pyrolysis S2 yields indicate that most samples have fair to good hydrocarbon generation potential.

The Rock-Eval pyrolysis parameters S1 and S2 can also be used to determine the source rock potential (Tissot and Welte, 1984). Most of the potential yield (PY = S1 + S2) values of the samples are >2.0 mg HC/g rock, which represents fair to good hydrocarbon generation potential. On a diagram of TOC versus S2 (Figure 12), the Küçükkuyu samples plot in fields representing poor, fair, good, and excellent hydrocarbon source rock potential. These differences are probably an indication that the source rock potential of the unit is varying depending on time and location. Considering the maturity (in general immature and/or early-mature), the hydrocarbon potential of the Küçükkuyu formation is limited. On a plot of HI versus TOC, the Küçükkuyu shale samples are dispersed in gas/oil sources and fair oil source areas (Figure 13).

6. Conclusions

Based on the geological and geochemical results, the source rock characterization, depositional conditions, and hydrocarbon potential of the Küçükkuyu Formation have been addressed.

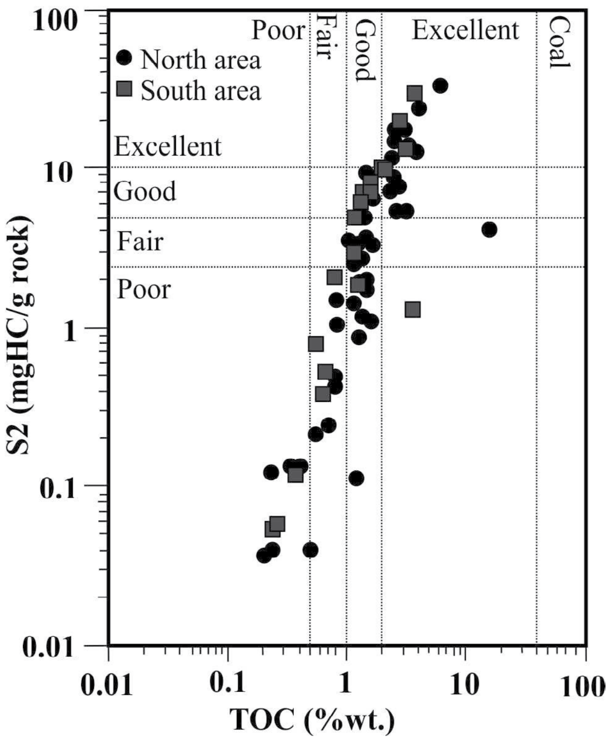

Figure 12. The distribution of the Küçükkuyu samples on a plot of TOC versus Rock-Eval S2 (source rock classification diagram after Dembicki, 2009).

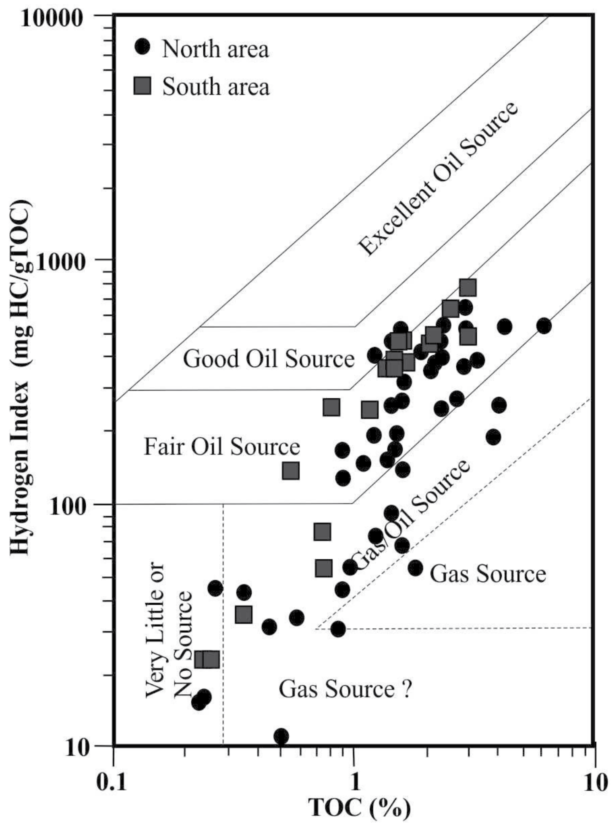

Figure 13. The distribution of the Küçükkuyu samples on a plot of TOC versus Rock-Eval HI (plot after Jackson et al., 1985).

The TOC content of the Küçükkuyu Formation in the north and south of the Edremit Gulf Basin ranges from 0.23 to 6.1 wt.% (average: 1.76 wt.%) and 0.24 to 2.82 wt.% (average: 1.66 wt.%) respectively and points to a generally fair to good source rock.

Rock-Eval pyrolysis data show that the organic matter in the Küçükkuyu Formation contains mainly Type II–III (oil- and gas-prone) kerogen, with minor Type I (oil-prone) kerogen. The C_{27}, C_{28}, and C_{29} sterane distributions of the samples are similar ($C_{29} > C_{27} > C_{28}$), except for one. This suggests that the organic matter sources are controlled by aquatic and terrestrial higher plants.

Tmax, PI, R_o, GC, and biomarker data suggest that the organic maturity level of the Küçükkuyu Formation samples correspond to immature or to an early-middle maturity stage.

Biomarker parameters, $\delta^{13}C$ values, and TOC/TS ratios suggest that the Küçükkuyu samples were deposited in a mainly freshwater lacustrine depositional environment indicating in general anoxic and suboxic conditions. The presence of gammacerane in the Küçükkuyu samples indicates slightly raised salinity or brackish-water conditions developing from time to time.

With regard to hydrocarbon-generating potential, most of the Küçükkuyu Formation shales have fair to good hydrocarbon potential based on TOC contents, S2, and PY values. According to the HI versus TOC plot, most of the Küçükkuyu shale samples have fair oil and less gas/oil sources. However, the hydrocarbon potential of the study area is limited because these potential source rocks are in general immature and/or early-mature.

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