Journal of Petroleum Exploration and Production Technology (2019) 9:141–157
https://doi.org/10.1007/s13202-018-0512-x

ORIGINAL PAPER - EXPLORATION GEOLOGY

# Basic geochemical characteristics of lacustrine rocks in the Neogene Kağızman–Tuzluca Basin, Northeastern Turkey

**Turhan Ayyıldız[1] · Baki Varol[1] · Zehra Karakaş[1] · Koray Sözeri[2]**

Received: 20 June 2017 / Accepted: 4 July 2018 / Published online: 27 July 2018


**Abstract**
The Neogene Kağızman–Tuzluca Basin is located in the NE Anatolia and extends eastward into Armenia Oktemberian Basin. The Halıkışlak (Late Oligocene), Turabi and Tuzluca formations (Lower–Middle Miocene) are time equivalents of the organic-rich Oligo-Miocene Maikop Series in the Caspian region. However, depositional conditions within the KBT are appreciably different and source rocks are not as richer as it. The Halıkışlak Formation has little source rock potentials, with very low values of TOC (0.04–0.25%), HI (14–90 mg HC/TOC) and genetic potential-GP (i.e. Rock–Eval $S_1+S_2=0.05$ to 0.22 mg HC/g rock). Although a peat facies sample has a relatively high TOC (6.78%), $T_{max}$ of 428 °C, HI values are very low (45 mg HC/TOC). TOC and GP values for the Tuzluca Formation are between 0.06 and 0.39 wt%, and 0.16–1.51 mg HC/g rock, respectively. Some levels of the Turabi Formation have TOC contents up to 6.14 wt%; however, mainly $T_{max}$ values are low 435 °C, and HI range from 25 to 54 mg HC/TOC. The extract of one low-maturity Turabi sample possesses biomarker distributions of an immature rock. Low relative abundance of tricyclic terpane and dominant C29 ααα (20R) are in accordance with the immature source rock. Some samples collected from the outcrops nearby Pliocene/Pleistocene lava series show localized maturation stage. We suggest that the Oligocene to Middle Miocene units could be more studied beneath the volcanic plateau.

**Keywords** Kağızman–Tuzluca basin · Turabi Formation · Intermountain basin · Oligo-Miocene units · Kömürlü Formation · Lacustrine source rock

## Introduction

In many parts of the world, organic-rich lacustrine sediments provide potential sources for the oil and/or gas (e.g., Paradox, Michigan and Uinta basins in USA; Tarim, Songliao, Junggar and Bohai Bay basins in China; Campos basin Brazil, Gongola Basin in Nigeria; Dong Ho and Song Hong basins, Vietnam). This depositional environment has received considerable attention in recent years for petroleum (e.g., Carroll and Bohacs 2001; Obaje et al. 2004; Petersen et al. 2005; Tian et al. 2014; Gao et al. 2016). Turkey has numerous lacustrine basins, mostly formed during the Paleogene and Neogene periods (e.g., Şengör 1987; Purvis and Robertson 2005a, b; Çiftçi and Bozkurt 2010). These basins have been widely explored for raw mineral materials such as trona, thenardite, (Central Anatolian) and borate (Western Anatolian) (e.g., İnci 1991; Helvacı and Orti 1998; García-Veigas and Helvacı 2013). Petroleum exploration has been largely limited to the Alaşehir (Gediz) graben (Ediger et al. 1996). The Kömürlü Formation of Ardahan Basin at the northwestern part of the study area (Uğur 2000; Sancay 2005) has been examined for unconventional properties (Aydemir 2010). However; the eastern Anatolian lacustrine basins have not been a target for the petroleum exploration. The Neogene Kağızman–Tuzluca Basin (KTB) is one of the main Upper Oligocene to Miocene lacustrine basins, located in the Eastern Anatolian plateau (Fig. 1) that formed as part of a Himalayan-type orogenic system (Dhont et al. 2006; Göğüş and Psyklywec 2008; Sharkov et al. 2015). Studies of the geology and tectonics of the KTB are reported in some workers (Eşder 1967; Yılmaz and Şener 1984; Şaroğlu and Yılmaz 1986; Sancay 2005; Yılmaz 2007; Varol et al. 2016). Petroleum and geothermal energy assessments have been

✉ Turhan Ayyıldız
ayyildiz@eng.ankara.edu.tr

[1] Department of Geological Engineering, Engineering Faculty, Gölbaşı Campus, Ankara University, 06830 Ankara, Turkey

[2] General Directorate of Mineral Research and Exploration, 06800 Ankara, Turkey

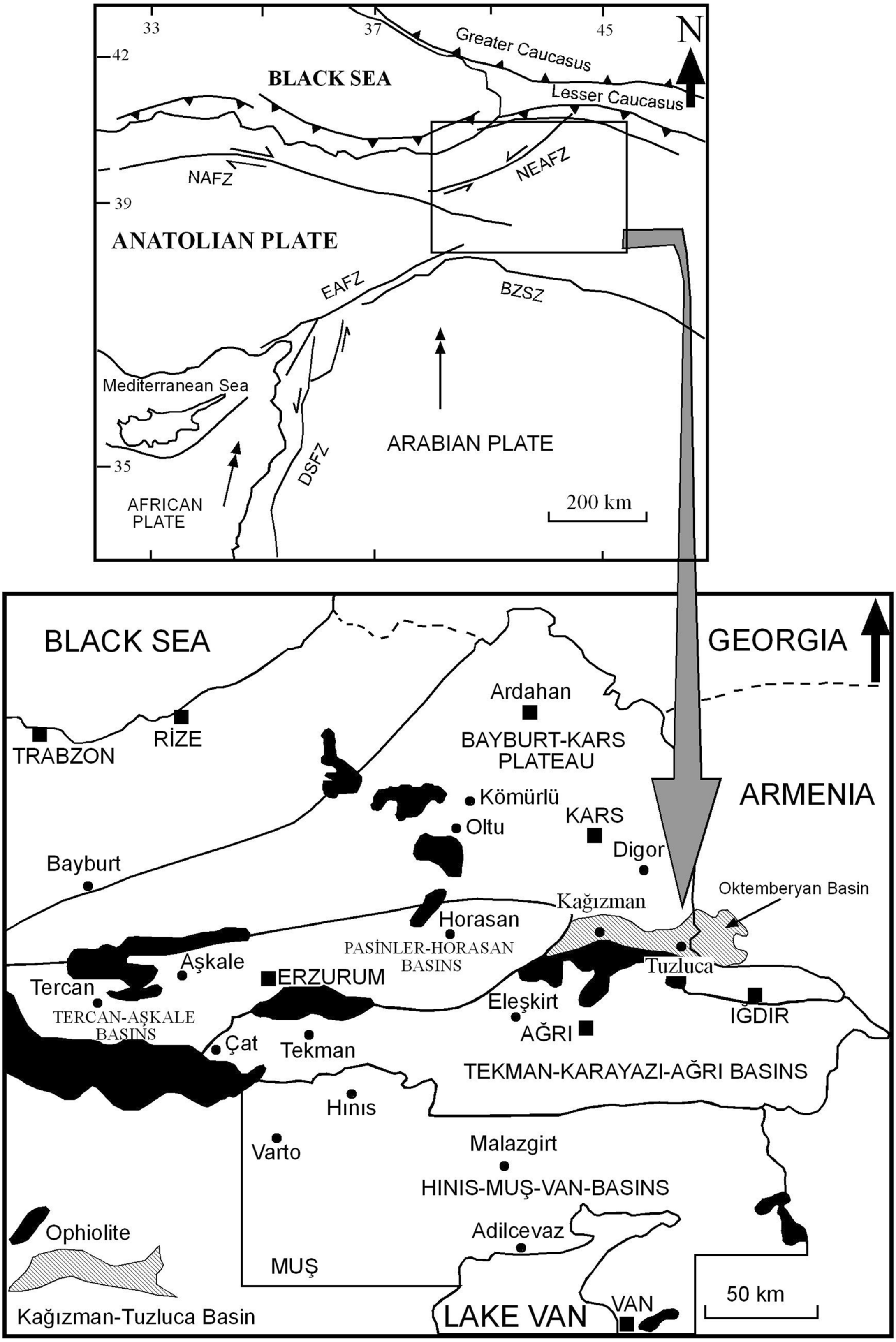


**Fig. 1** Location map of the Eastern Anatolian subbasins (*DSFZ* Dead Sea Fault Zone, *NAFZ* North Anatolian Fault Zone, *NEAFZ* Northeast Anatolian Fault Zone, *EAFZ* East Anatolian Fault Zone, *BZSZ* Bitlis-Zagros Suture Zone (modified from Bozkurt 2001; Şahintürk et al. 1998)

performed by a few workers (Şenalp 1966; Şenalp 1969a, b; Tanrıverdi 1971; Varol et al. 2009; Ayyıldız et al. 2011). However, there are no published data about the source rocks and their petroleum potential. This study is the first comprehensive investigation with analytical data based on sedimentology and basin evolution, and organic geochemistry of prominent lacustrine source rocks in the basin.

## General petroleum assessment of the Kağızman–Tuzluca and nearby basins

The KTB is one of the important Tertiary basins in the eastern Anatolia. The basin is 40 km long and 10–15 km wide on average, extending eastwards across the river Aras (Araxes) into western Armenia where it is referred as Arexes and Oktemberian or Hoktemberian Basin (Balian 1969; Karakhanian et al. 2002; Hässig et al. 2013; Klett 2016) (Fig. 2). Although the basin consists of very thick (more than 2500 m), overfilled and underfilled lacustrine deposits, these sediments have not drawn much attention of petroleum explorations. Early exploration activities in the KTB started in the 1960s, commenced by MTA (General Directorate of Mineral Research and Exploration). MTA drilled two exploration wells about 2500 m deep to the NE of Tuzluca. Commercial volumes of petroleum were not discovered (Eşder 1968a, b, c). Only methane was reported to occur at different levels in the Tuzluca-1 well (Şenalp 1969a, b). Log determinations and preliminary reports concerning these wells are sealed; and samples are not currently available. Subsequently, we could not perform organic geochemical analysis on the cutting samples from these wells.

Oil shows from Oligocene units were reported in the Armenian (Oktemberian) Basin that was located in the NE extension of the KTB. However, locally generated hydrocarbon extracts suggest that these sediments are immature and hydrocarbon must have been generated at depth from more mature sediments beneath the ophiolite (Papworth and Aghabalyan 2002a, b). Transeuro Energy Corp., (2007) discovered the active Oligocene–Eocene petroleum system in the Oktemberian Basin. Fifteen wells was drilled in the basin and natural gas was tested from the well Oktemberian-13E over a 6-month period (Papworth 2002; Papworth and Aghabalyan 2002a, b). Petroleum exploration activities have been carried out by the SE Armenia Project Consortium. A 1995 study concluded that total in-place resources in the Oktemberian Basin may comprise 70 million bbl of oil (estimated 14 million bbl recoverable) in the Garni-Shorakhpur area, east of Yerevan (part of the Central Depression), together with 144 bcf gas in-place (110 bcf recoverable) (Papworth and Aghabalyan 2002a, b). These productive series (Oktemberian or Hoktemberian Suite—Lower Sand-Clay and Upper Multicolored Suite) are time equivalent of Halıkışlak and Turabi formations in the KTB (Fig. 3).

The Caspian region situated to the north of the study area has been studied in detail. The accumulation of organic-rich sediments occurred during an episode of isolation of the Paratethys Sea during Alpine–Himalayan collision (Golonka 2007), has made the south Caspian region one of the most productive oil-producing regions in the world (e.g., Guliyev et al. 2001; Feyzullayev et al. 2001; Bechtel et al. 2013). Therefore, there are numerous publications dealing with organic matter maturity and source rock potential of the Caspian basins, particularly Maikop series (e.g., Lerche et al. 1997; İnan et al. 1998; Guliyev et al. 2001; Feyzullayev et al. 2001; Bechtel et al. 2013).

## Geological setting and stratigraphy

The studied basin is surrounded by the Neogene Pasinler–Horasan Basin to the west, the Tekman–Karayazı–Ağrı Basin to the south, and the Miocene and younger volcanics of the Bayburt–Kars volcanic plateau to the north (Fig. 1). Previous studies based on the basin-fill deposits suggested that two different basin models are consistent with the tectonic constraints as a pull-apart basin (Şaroğlu and Yılmaz 1986; Koçyiğit et al. 2001; Varol et al. 2009) and intermountain basin (Şen et al. 2011; Ayyıldız et al. 2012). Dhont and Chorowicz (2006) suggest that KTB does not have a rhomb-shaped geometry and there are no dog-leg relays along the Tuzluca fault that would allow the opening of such a transtensional basin as pull-apart structure. The KTB was formed in the compressional zone extending across Azerbaijan, Iran and Armenia, resulting from the convergence of the Afro-Arabian and Eurasian plates (Adamia et al. 2011).

Şen et al. (2011) established a new Cenozoic stratigraphic scheme on the basis of recent discoveries of mammalian fossils, revealing sedimentologic aspects of marine–terrestrial mixed deposits in the basin in the range from Eocene (?)/Late Oligocene to Late Miocene age. This stratigraphic scheme nearly consisted of the contemporaneous deposits of the Oktemberian Basin in Armenia (Papworth and Aghabalyan 2002a, b). The basement rocks and basin-fill units are stratigraphically described in the below.

## Basement rocks

The basement rocks in the basin consist of serpentines, volcanics and marbles that are only exposed along the southern margin of the basin (Fig. 2) (Şahintürk and Kasar 1979; Şahintürk et al. 1998).

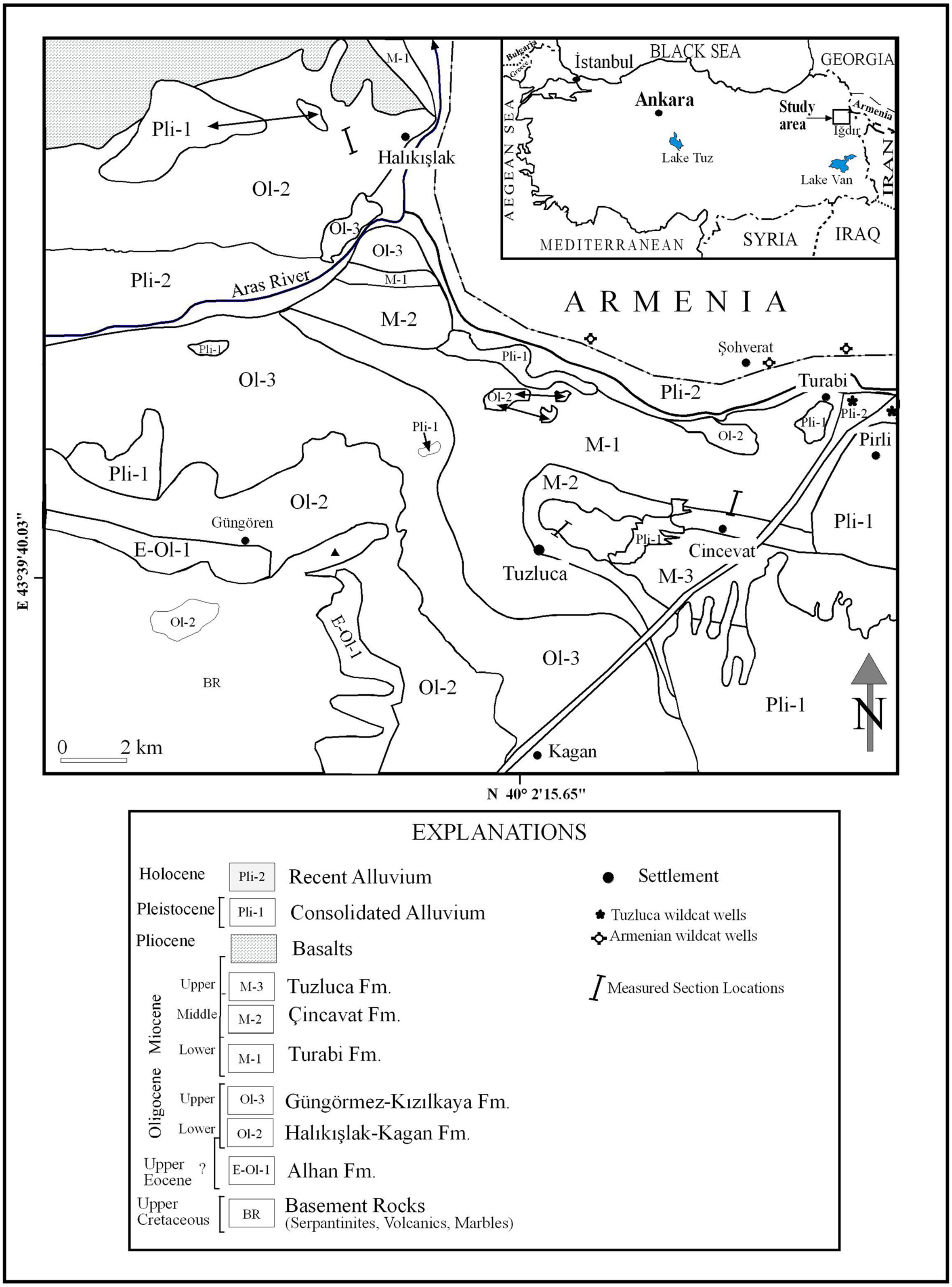


**Fig. 2** Geological map of the Tuzluca area (revised from Şen et al. 2011; Varol et al. 2016)

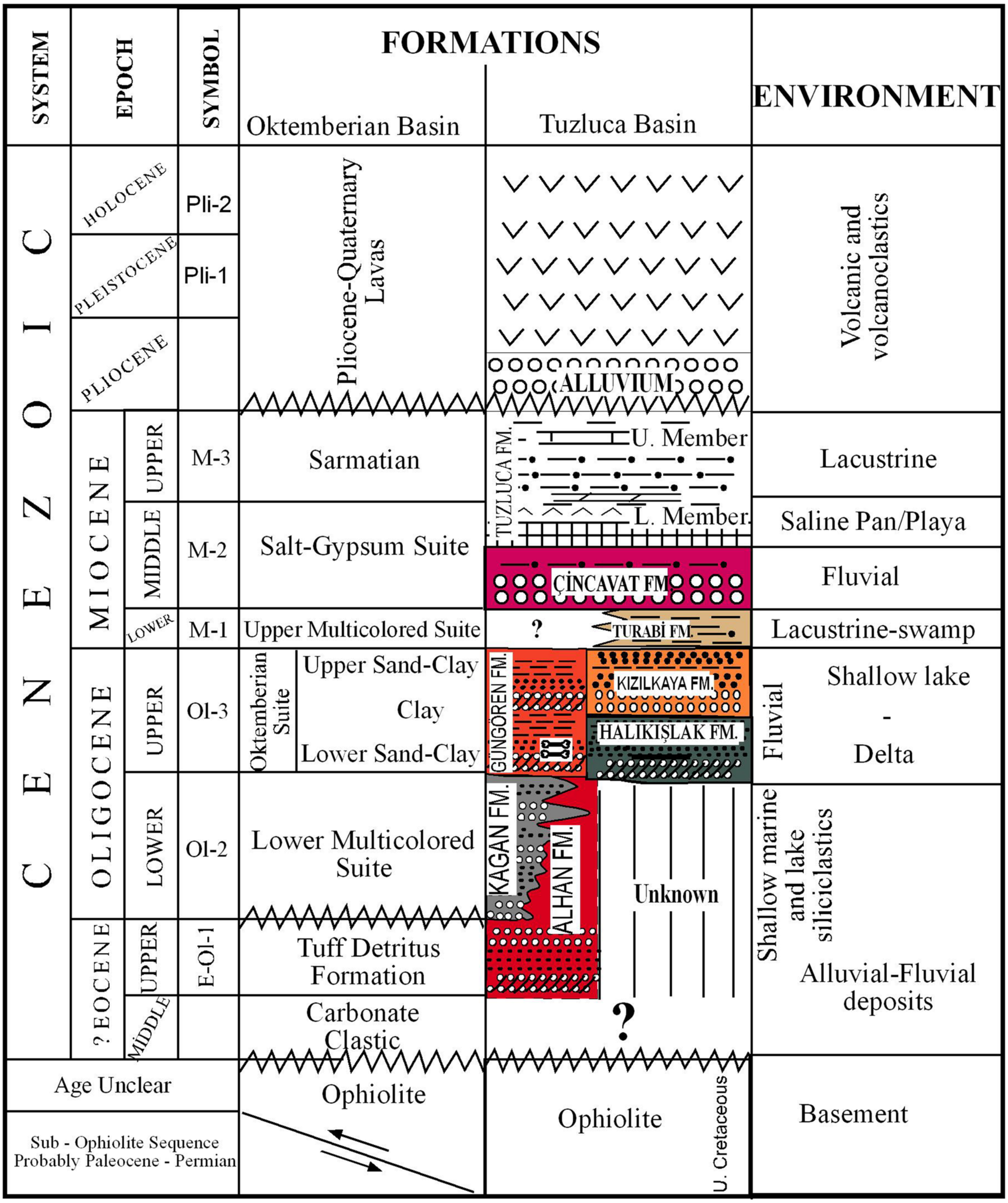


**Fig. 3** Comparative stratigraphic columnar section of the studied area and Oktemberian basin (modified from Papworth and Aghabalyan 2002a; Varol et al. 2016)

## Sedimentary units

Alhan Formation is the first stratigraphic unit over the basement, dominated by alluvial valley-fill deposits consisting of conglomerates, sandstones and mudstones with a thickness between 100 and 650 m. There is no paleontological dating for this formation. It assigned a Late Eocene–Early Oligocene age, and it is a lateral equivalent unit of the Kağan Formation with Early Eocene marine fossils, and conformably covering the Güngören Formation that includes Late Oligocene fossil mammal taxa (Şen et al. 2011; Métais et al. 2015; Varol et al. 2016). The Kağan Formation outcrops are observed in the SW of the basin (Hamurkesen, Güngören anticline), consisting of fluvial, coastal and alluvial deposits alternating with nummulite-bearing sandy limestones that resulted from an Early Oligocene transgression (Altınlı

1966; Varol et al. 2011). The Güngören Formation conformably overlies the Alhan Formation (Figs. 2, 3) and is composed of lacustrine and meandering river channels and overbank deposits, evidenced by the Late Oligocene rhinoceros bones (Şen et al. 2011). In the northern part of the basin, this formation is replaced with Halıkışlak and Kızılkaya formations dominated by fluvial/ fluvial fan, and lacustrine delta deposits. Its age was determined as Late Oligocene based on the dating of pollen and spores (Sancay 2005; Kayseri-Özer et al. 2017) and freshwater molluscs (Varol et al. 2011, 2016). The strata also are known as the Kömürlü Formation in the Kars and Ardahan area where its age ranges from Late Oligocene to Early-(Middle?) Miocene (Sungurlu 1971; Şahintürk and Kasar 1980). Swamp deposits within the deltaic sediments of the unit were sampled for organic content analysis (Figs. 3, 4, 5a). The Kızılkaya Formation consists of thick siliciclastic deposits ranging from red mudstones to coarse conglomerates with minor carbonates deposited in lacustrine and fluvial–lacustrine settings.

The Turabi Formation presents as basin-center setting and gradually overlies the Kızılkaya Formation (Figs. 2, 3, 4). The Turabi Formation is composed generally of two main depositional packages: The first package starts with alternations of sandstone, and gravelly sandstone, followed by a cream-colored carbonaceous mudstone (110 m), indicating a fluvial–lacustrine transition zone (Varol et al. 2016). The second package is interbedded organic-rich mudstones, peat/lignite, with siliciclastic components that are up to 30% in some layers (Fig. 5b, c). Single selenite gypsum crystals and minor framboidal pyrite (5–10%) within the organic-rich mudstones probably formed diagenesis processes via bacterially-reduced sulphate (Garcia et al. 2001; Scheiber and Baird 2001). The Turabi Formation is overlain by 800-m-thick red beds (Çincavat Formation), mainly composed of ephemeral stream, caliche and flood plain deposits (Fig. 4) with small mammalian fossils and terrestrial gastropods dated as Early Middle Miocene (Şen et al. 2011).

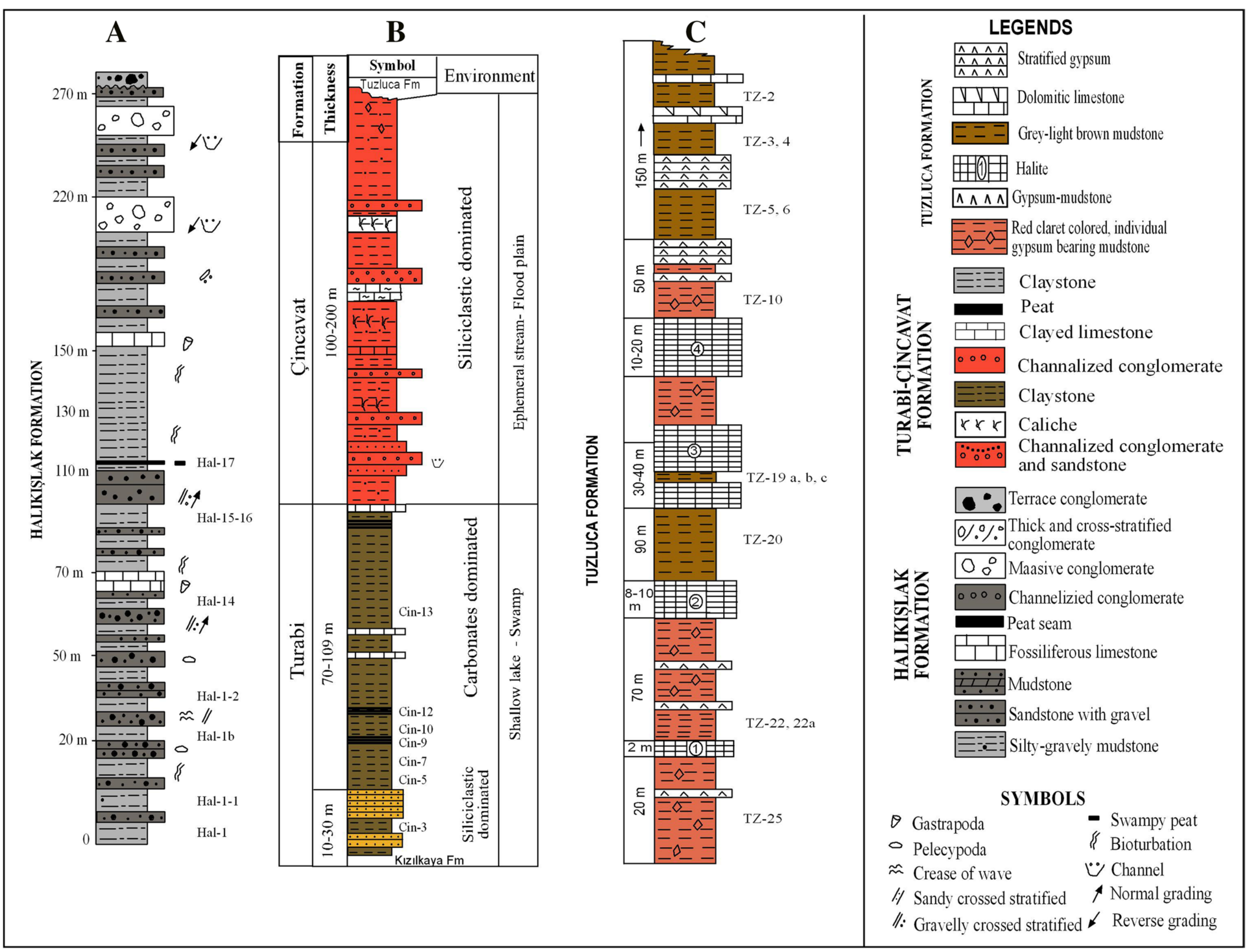


**Fig. 4** Sedimentologic logs of the Tertiary units in the Kağızman–Tuzluca Basin

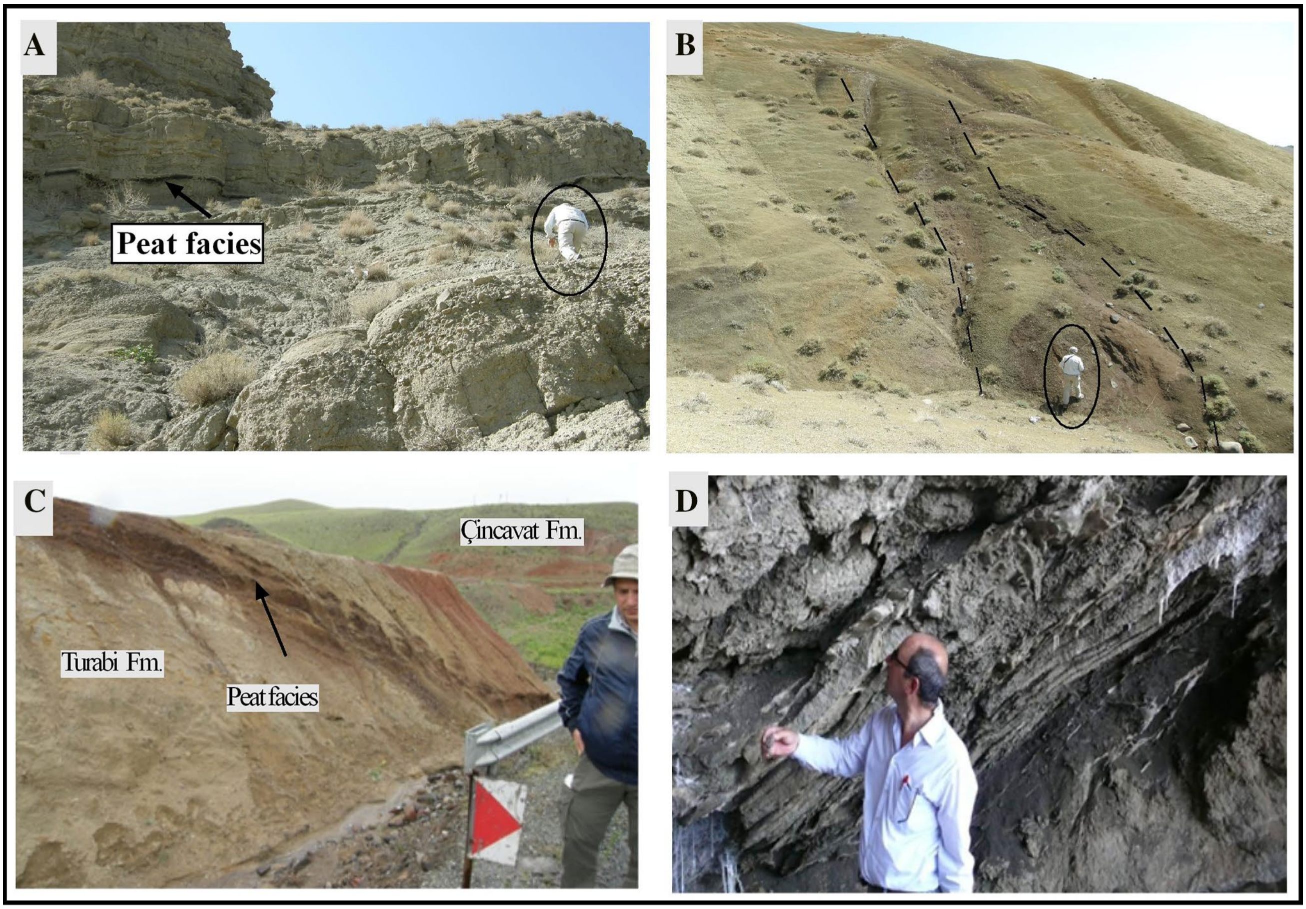


**Fig. 5** **a** Small fan delta clastics bearing peat facies at the Halıkışlak section, **b** panoramic view of organic rich mudstone and thick peat facies within the Turabi Formation, **c** close view of peat and mudstone in the Turabi lacustrine facies (Tuzluca–Iğdır high way); **d** black mudstone alternation with halite layers in the Tuzluca Formation at the Tuzluca salt

These units gradually turn into the evaporite-dominated Tuzluca Formation, deposited in shallow lake environment or saline pans and consisting of halite and dark-colored mudstones (Figs. 3, 4, 5d) overlain by gypsum and greyish-brown mudstones and dolomite. These units are interpreted as the Tuzluca Formation and an Undifferentiated Unit by Varol et al. (2016). In this study, we consider this unit as Tuzluca Formation, which is divided into Lower Member and Upper Member (Fig. 3). Its stratigraphic position and equivalence to the Salt-Gypsum Suite and Sarmatian in the Oktemberian Basin (Middle to Upper Miocene) suggests a Late Middle to Late Miocene age (Varol et al. 2011). Commercial salt deposits are present in the Tuzluca Formation and 11 salt mines are located to the east of Tuzluca. Cenozoic basins in Eastern Anatolia experienced intensive volcanism between the Middle/Late Miocene and the Holocene (Fig. 3). Ağrı Mountain (known as Mount Ararat), located on the eastern margin of the KTB, is one of the main eruption centers (Ercan et al. 1987; Karakhanian et al. 2002).

## Materials and methods

A total of 36 rock samples from three measured sections (Fig. 2) was obtained for organic geochemical analysis from the Kağizman–Tuzluca Basin. Eight samples were taken from the Halıkışlak Formation at the Halıkışlak Measured Section (40°08′46.36″ N; 43°38′44.60″ E; top at 40°08′55.53″ N; 43°38′25.26″ E) and consist of grey mudstones and silts; one sample was a peat-bearing mudstone facies. Thirteen samples were selected from the Turabi Formation at Köprübaşı (Çincavat) (N 40°03′17.82″–E 43°44′2.18″; top at N 40°06′51.77″–E 43°37′38.42″). Fifteen samples came from the Tuzluca Formation from extensive outcrops around the Tuzluca. The section was measured at 40°2′59.50" K–43°39′59.21" E; top at: 40°2′57.14" K–43°40′9.43" E.

Bulk geochemical parameters were obtained by Rock-Eval pyrolysis (Lafargue et al. 1998) at the Turkish Petroleum Corp., (TPAO) Research Center in Ankara using a Rock Eval-6 (RE-6) instrument with IFP 160,000 (Institut

**Table 1** TOC and Rock Eval data for the Halıkıslak, Turabi and Tuzluca formations in the KTB

| Formation/sample number | | TOC (%) | Lithology | $S_1$ (mg HC/g rock) | $S_2$ (mg HC/g rock) | S3 (mg $CO_2$/g rock) | $T_{max}$ ($^0$C) | HI | OI | PI $S_1/(S_1+S_2)$ | S1/TOC | $\%R_{eqv}$ [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tuzluca (Middle–Upper Miocene) | Tz-2 | 0.16 | LM | | | | | | | | | |
| | Tz-3 | 0.19 | LM | | | | | | | | | |
| | Tz-4 | 0.18 | LM | | | | | | | | | |
| | Tz-5 | 0.32 | LM | 0.05 | 0.11 | 1.90 | 307 | 34 | 594 | 0.33 | 0.15 | |
| | Tz-6 | 0.09 | LM | | | | | | | | | |
| | Tz-10 | 0.33 | LM | 0.02 | 0.22 | 1.21 | 432 | 67 | 367 | 0.08 | 0.06 | 0.64 |
| | Tz-19c | 0.16 | LM | | | | | | | | | |
| | Tz-20 | 0.06 | LM | | | | | | | | | |
| | Tz-22 | 0.21 | LM | | | | | | | | | |
| | Tz-22a | 0.11 | LM | | | | | | | | | |
| | Tz-23 | 0.10 | LM | | | | | | | | | |
| | Tz-25 | 0.13 | LM | | | | | | | | | |
| | Tuz-4 | 0.39 | LM | 0.44 | 1.07 | 3.08 | 382 | 274 | 790 | 0.29 | 1.13 | |
| | Tuz-5 | 0.33 | LM | 0.15 | 0.49 | 1.58 | 417 | 148 | 479 | 0.24 | 0.45 | 0.35 |
| | Tuz-8 | 0.27 | LM | | | | | | | | | |
| Turabi (Middle Miocene) | Cin-3 | 0.12 | LM | | | | | | | | | |
| | Cin-5 | 0.24 | LM | | | | | | | | | |
| | Cin-7 | 0.07 | LM | | | | | | | | | |
| | Cin-9 | 3.33 | CM | 0.19 | 1.80 | 6.30 | 422 | 54 | 189 | 0.10 | 0.06 | 0.45 |
| | Cin-10 | 0.27 | LM | | | | | | | | | |
| | Cin-12 | 2.68 | CM | 0.12 | 0.68 | 4.84 | 421 | 25 | 181 | 0.15 | 0.04 | 0.43 |
| | Cin-13 | 0.09 | LM | | | | | | | | | |
| | Cin-15a | 6.14 | CM | 0.19 | 3.20 | 11.17 | 432 | 52 | 182 | 0.06 | 0.03 | 0.64 |
| | Cin-15b | 4.17 | CM | 0.11 | 1.07 | 6.87 | 420 | 26 | 165 | 0.09 | 0.03 | 0.41 |
| | Cin-16 | 0.12 | LM | | | | | | | | | |
| | Cin-Y-9 | 1.30 | CM | 0.07 | 0.38 | 2.34 | 462 | 29 | 180 | 0.15 | 0.05 | 1.22 |
| | Cin-Y-10 | 0.67 | CM | 0.11 | 0.25 | 1.22 | 432 | 37 | 182 | 0.29 | 0.16 | 0.64 |
| | Cin-Y-11 | 0.03 | LM | | | | | | | | | |

**Table 1** (continued)

| Formation/sample number | | TOC (%) | Lithology | $S_1$ (mg HC/g rock) | $S_2$ (mg HC/g rock) | S3 (mg $CO_2$/g rock) | $T_{max}$ ($^0$C) | HI | OI | PI $S_1/(S_1+S_2)$ | S1/TOC | $\%R_{eqv}$ [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Halikişlak (Upper Oligocene) | Hal-1 | 0.24 | LM | 0.01 | 0.09 | 1.52 | 436 | 38 | 633 | 0.11 | 0.04 | 0.72 |
| | Hal-1-1 | 0.21 | LM | 0.03 | 0.19 | 0.47 | 436 | 90 | 224 | 0.12 | 0.14 | 0.72 |
| | Hal-1-1b | 0.09 | LM | | | | | | | | | |
| | Hal-1-2 | 0.22 | LM | 0.02 | 0.03 | 0.84 | 440 | 14 | 382 | 0.45 | 0.09 | 0.80 |
| | Hal-14 | 0.25 | LM | 0.01 | 0.11 | 0.57 | 436 | 44 | 228 | 0.10 | 0.04 | 0.72 |
| | Hal-15 | 0.06 | LM | | | | | | | | | |
| | Hal-16 | 0.04 | LM | | | | | | | | | |
| | Hal-17 | 6.78 | HC | 0.12 | 3.03 | 22.69 | 428 | 45 | 335 | 0.04 | 0.02 | 0.56 |

*LM* Cream-colored lacustrine mudstone, *CM* Coaly mudstone (dark colored), *HC* Humic coal

[a] $\%R_{eqv}$ calculated from $T_{max}$ according to the relation established by Petersen (2002)

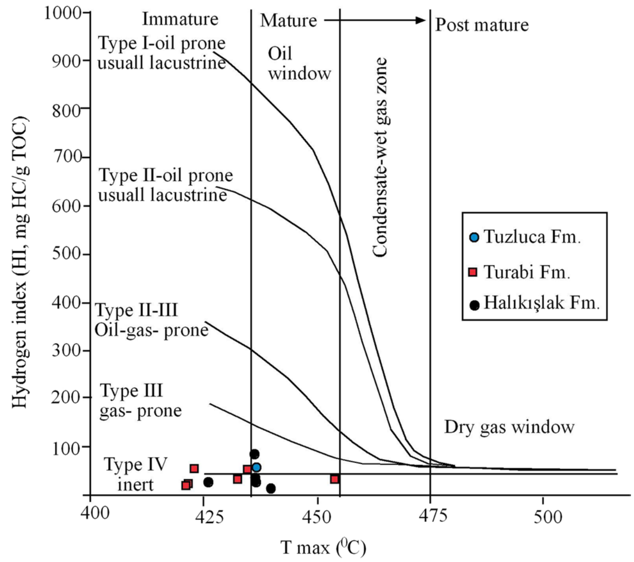


**Fig. 6** Plot of hydrogen index (HI) versus pyrolysis $T_{max}$ for the analyzed peat and shale sediments, showing kerogen quality and thermal maturity stages (modified after Mukhopadhyay et al. 1995)

Francais du Petrole) standards (Table 1). Additional parameters calculated from the pyrolysis data are the hydrogen index ($HI = S_2 \times 100/TOC$), oxygen index ($OI = S_3 \times 100/TOC$), and production index ($PI = S_1/(S_1 + S_2)$), normalized oil content ($S_1 \times 100/TOC$). Equivalent reflectance values (%Reqv) were derived from the measured $T_{max}$ values from the correlation $T_{max} = 51.96\%R + 398.39$ (cf. Petersen 2002). Organic petrographic analyses were performed with a Leica DM 2500P model microscope at the TPAO Research Center, Ankara.

Extracts from two shale samples from the Halıkışlak (Hal-17) and Turabi formations (Cin-15a) were analyzed by GC and GC–MS. GC analysis was conducted on an Agilent 6850 using a HP-1 SIMDIST column (15 m × 0.53 mm × 0.15 µm) equipped with a FID. GC–MS analysis is performed by Agilent 7890A GC–5975C MS instrument with Agilent 7683B auto sampler. HP-1 MS capillary column (60 m × 0.25 mm × 0.25 µm) is assigned. Helium is used as the carrier gas. Specify temperature program is used in the GC and GC–MS analyses.

## Geochemical results

The TOC values of the Halıkışlak Formation (Table 1) varied between 0.04 and 0.25 wt% (average: 0.15 wt%, except a single sample with 6.78 wt%) indicating as poor source rock potential. Hydrogen Index (HI) values for the Halıkışlak Formation, including the high TOC-bearing sample, are 14–90 mg HC/g TOC (× 100), and oxygen index values (OI) are 224–633 mg $CO_2$/g TOC (× 100), indicative of possibly oxidized organic matter. $T_{max}$ values ranging from 428 to 440 °C and vitrinite reflectance (%$R_{eqv}$) values ranging from 0.56 to 0.80% (Table 1) are in the immature to mature source rocks. A plot of HI versus $T_{max}$ (Fig. 6) shows that all the Halıkışlak Formation samples contain mainly kerogen Type III and IV. According to $S_2$ versus TOC wt% diagram, those samples are plotted in the poor source rock (Fig. 7).

The Turabi Formation possesses variable TOC values. Cream-colored mudstones samples of the lower part of Formation have relatively low TOC (ranging from 0.03 to 0.27 wt %), and coaly mudstones (CM) intervals indicate higher TOC values (up to 6.14 wt%). HI values of CM samples are between 29 and 54 mg $S_2$ HC/ g TOC (× 100), and oxygen index values are 165–189 mg $CO_2$/g TOC (× 100). The two organic matter rich mudstones were analyzed with organic petrographic method. Alginite organic matter is not found in sample CinY9, while it is present in minor proportions (% 5) in sample Cin-15a. They contain mainly herbaceous and woody organic materials (Table 2). Minor framboidal pyrite was observed in sample Cin-15a which is a huminite minor coal with a reflectance of 0.46%*R*o. Rock–Eval $T_{max}$ values, range between 420 and 432, and one sample is 462 °C. About 90% of the samples have $T_{max}$ < 435 °C (Peters 1986) indicating that they are mainly immature. In $S_2$ versus TOC wt% diagram, those samples are plotted in the good to excellent source rock potential (Fig. 7). Based on the $S_2$ yield, only a single sample is of poor quantity. The TOC wt% and $S_2$ (0.11–1.07) values for the Tuzluca Formation are very low, indicating no source rock potential (Table 1; Fig. 7). This is confirmed by the

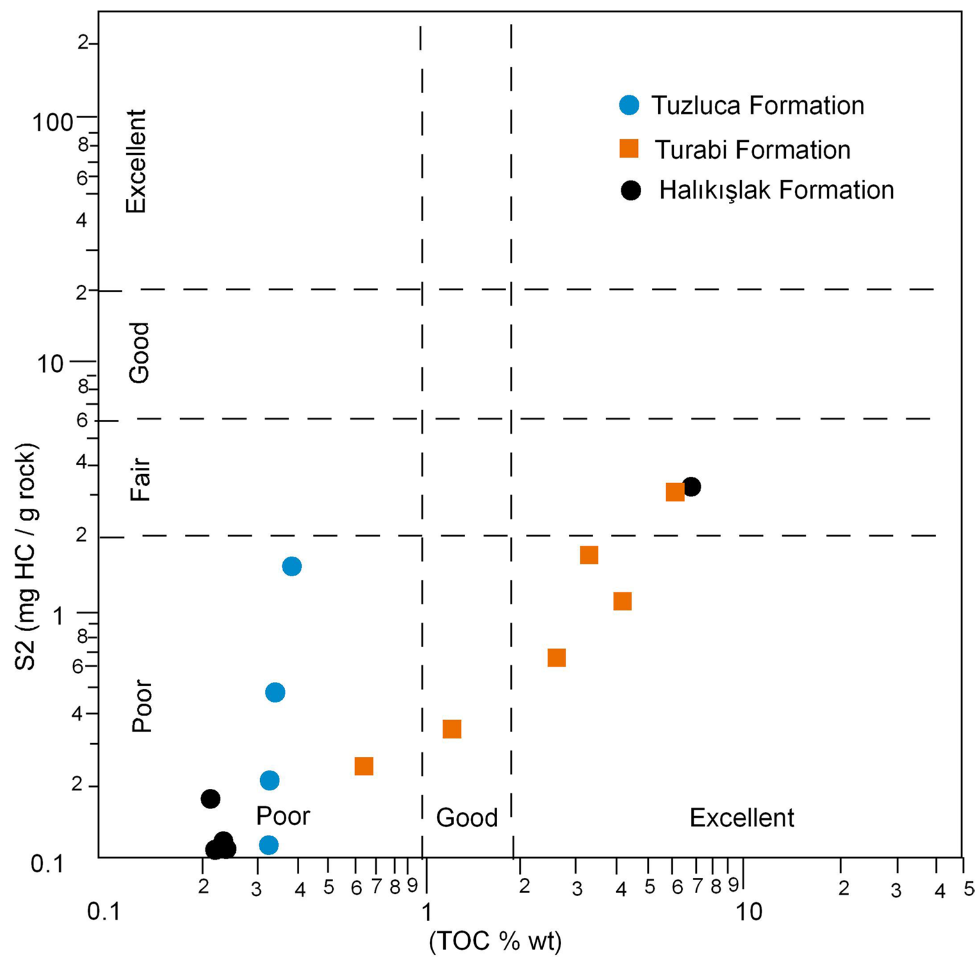


**Fig. 7** The distribution of the Halıkışlak, Turabi and Tuzluca shale samples on S2 vs. TOC wt% source rock classification diagram (after Dembicki 2009)

**Table 2** Organic petrographic and kerogen-type compositions (vol%) and mean vitrinite reflectance (random) values (*nd* not determined)

| Formation | Sample number | Amorphous | Herbaceous | Woody | Coaly | SCI | % $R_0$ |
|---|---|---|---|---|---|---|---|
| Turabi | Cin-15a | 5 | 25 | 65 | 5 | nd | 0.46 |
| | Cin-Y9 | n.d | 80 | 20 | nd | nd | nd |

$S_2$ versus TOC wt% diagram. $T_{max}$ values indicate the low thermal maturity (307–432 °C).

$S_1$/TOC values for the Halıkışlak, Turabi and Tuzluca formations range from 0.02 to 0.14, 0.03 to 0.16 and 0.06 to 1.13 mg oil/g TOC, respectively, and the production index range from 0.04 to 0.45, 0.06 to 0.29 and 0.08 to 0.33, respectively (Table 1). Though some samples belonging to the Turabi Formation are in the good area in Fig. 7, based on low $S_1$/TOC and PI values are less than 0.2 except one sample (Peters 1986; Hunt 1996), it seems that HC generation has not occurred from the Turabi Formation.

## GC analysis

Specific parameters were calculated from GC chromatograms of samples Cin-15a and Hal-17 (Fig. 8) and are presented in Table 3. Pr/Ph ratios of samples are determined as 3.33 and 2.0, respectively (Table 3). Oil and condensates derived from organic matter rich in lakes, fluvial and deltaic sediments of Pr/Ph ratio is greater than 3 (Connan and Cassou 1980). Evenick (2016) compared the XRD results with the Pr/Ph ratios and suggest that Pr/Ph ratio is greater than 2.5, indicating terrestrial organic facies. Pr/Ph > 1 and high odd–even carbon dominance ratio (CPI > 1) indicate terrestrial components (Peters et al. 2000). CPI is also used as the maturity parameter. For example, CPI > 5 indicates immature resource rocks containing terrestrial high plants (Bray and Evans 1961). As a maturity parameter, it is about 1 for mature shale and petroleum, while it is high values (from 5 to 10) in immature sediments.

Isopronoid ratios (Pr/nC17-Ph/n-C18) are used to interpret the depositional conditions of the source rocks (Shanmugam 1985). On the Pr/nC17-Ph/nC18 graph, petroleum derived from terrestrial materials is represented by a pink-colored area, a purple-colored area on a reduced marine environment, and a mixed organic matter yellow-colored area (Fig. 9). The high Pr/Ph and CPI ratios in the samples indicate an immature terrestrial dominant-mixed organic matter.

**Table 3** Pr/Ph ratios and CPI values of the studied samples

| Sample number | Pr/Phy | Phy/Pr | Pr/n-C17 | Phy/n-C18 | CPI 16–32 |
|---|---|---|---|---|---|
| Cin-15a | 3.33 | 0.30 | 0.37 | 0.25 | 2.35 |
| Hal-17 | 2.00 | 0.50 | 2.33 | 1.40 | 2.20 |

## Biomarkers

Ion chromatograms of the shally and coaly samples from the Turabi (Cin-15a) and Halıkışlak formations (Hal-17) and are presented in Fig. 10. Low tricyclic terpane concentration in both samples in *m/z* 191 chromatograms and dominant C29 ααα (20R) in the *m/z* 217 chromatograms indicate an immature source rock. The dominant 16R peak in the *m/z* 191 chromatogram of Turabi samples indicate that the formation was deposited in a clastic-dominated environment. The same maturation and depositional environments are indicated by similar biomarker ratios: Tm/Ts > 1, $C_{29}$ Nor/$C_{30}$ Hop < 1 ratios in the *m/z* 191 chromatograms and also % $C_{29}$ ααα (20R) peak are higher than % $C_{27}$ ααα (20R) and % $C_{28}$ ααα (20R) in the *m/z* 217 chromatograms (Fig. 10; Tables 3, 4).

According to Mello et al. (1988), the Ts/Tm ratio is below 1.0 in lacustrine/saline, marine evaporitic or marine carbonates, while it is above 1 in lacustrine, freshwater or marine-deltaic environments. The lower of Ts/Tm ratio for Cin-15a number sample and not having Ts but the presence of gammacerene for the Hal-17 number sample showed that these samples may have precipitated in the lake/saline environment (Table 4). In

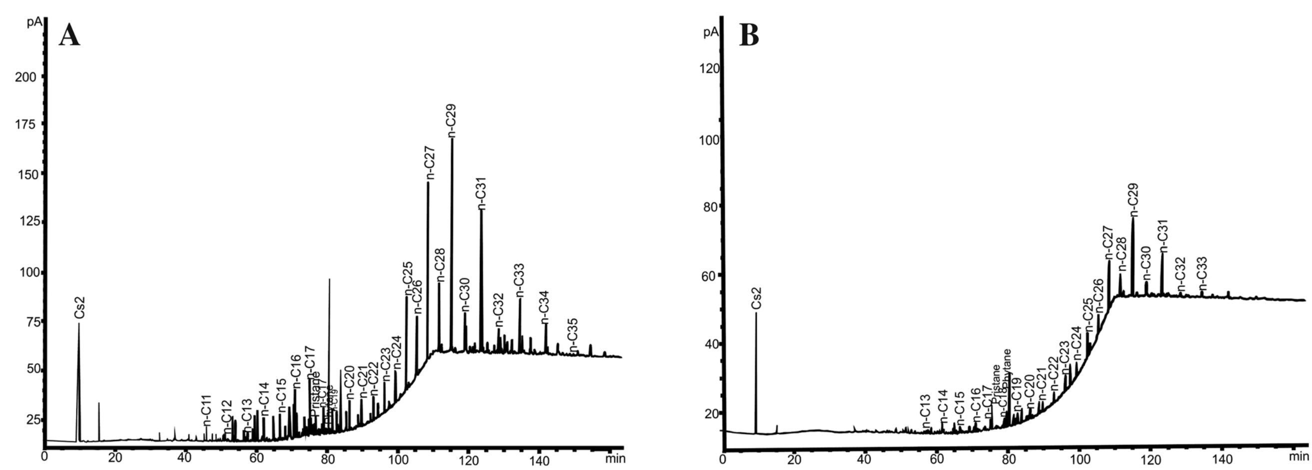


**Fig. 8** Gas chromatograms for the whole extract from the shale samples and humic coal from Turabi and Halıkışlak formation, **a** Turabi and **b** Halıkışlak formation's samples

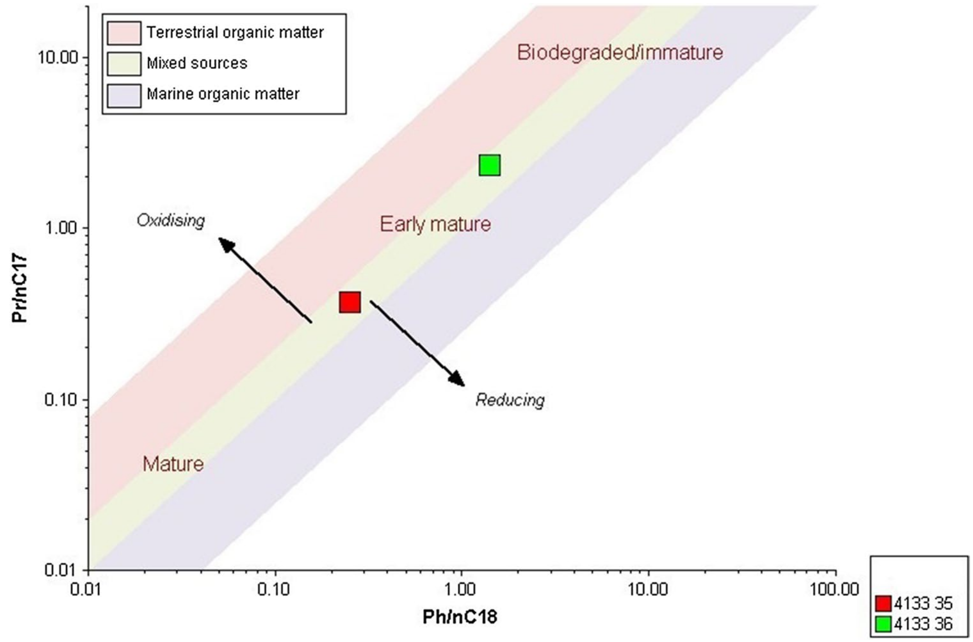


**Fig. 9** Pristane/nC17 versus Phytane/nC18 diagram. (4133 35: Turabi Fm., 4133 36: Halıkışlak Fm.)

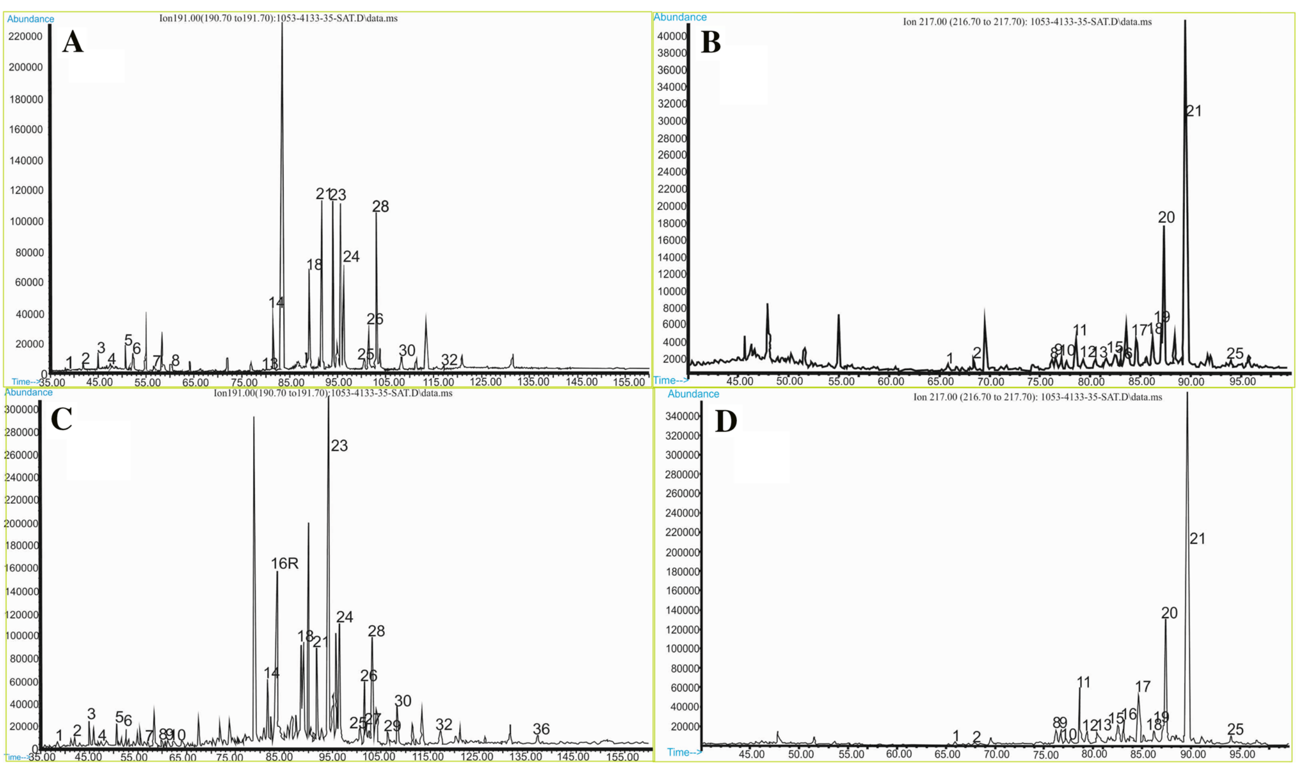


**Fig. 10** *m/z* 191 and 217 mass chromatograms of Turabi shale sample (Cin-15a) (a, b), (c, d) *m/z* 191 and 217 mass chromatograms of Halıkışlak peat samples (a, b) (Hal-17)

addition, dominance of hopan to norhopan also pointed to terrestrial materials (Peters and Moldowan 1993). The low number of terpans in the distribution of terpenes is probably due to the very low maturation. The low rates of C29 ββ/αα + ββ (0.27–0.28) and diasteran values show immature source rock (Fig. 11).

**Table 4** GC-MS results of Halıkışlak and Turabi formations samples

| Terpan Parameters | | Steran Parameters | |
|---|---|---|---|
| 1053-4133-35 (Turabi Fm.–Cin-15a) | | | |
| $C_{19}$ Tri/$C_{23}$Tri | 0.10 | DiaStr (%) | – |
| $C_{23}$ Tri/ $C_{24}$ Tet | 3.57 | NorStr (%) | – |
| $C_{23}$ Tri/ $C_{30}$ Hop | 0.16 | IsoStr (%) | – |
| $C_{24}$ Tri/$C_{23}$ Tri | 0.61 | % $C_{27}$ ααα (20R) | 7.56 |
| $C_{24}$ Tet/$C_{23}$ Tri + $C_{24}$ Tet | 0.22 | % $C_{28}$ ααα (20R) | 7.56 |
| $C_{24}$ Tet/$C_{26}$ | – | % $C_{29}$ ααα (20R) | 84.88 |
| $C_{24}$ Tet/$C_{30}$ Hop | 0.05 | $C_{27}$ ααα 20(S/R) | 0.24 |
| Tm/Ts | 24.00 | $C_{28}$ ααα 20(S/R) | 0.35 |
| Ts/Tm | 0.04 | $C_{29}$ ααα 20(S/R) | 0.09 |
| Ts + Tm/$C_{29}$ Nor | 0.34 | $C_{27}$ RegStr (%) | – |
| Ts + Tm/$C_{28}$–$C_{29}$ Tri | 0.68 | $C_{28}$ RegStr (%) | – |
| $C_{28}$–$C_{29}$ Tri/Tri + Hop | 0.00 | $C_{29}$ RegStr (%) | – |
| $C_{29}$ Nor/$C_{30}$ Hop | 0.61 | $C_{27}$/$C_{29}$ | 0.09 |
| Oleanene Index | 0.00 | $C_{28}$/$C_{29}$ | 0.09 |
| Moretane Index | 0.38 | DiaStr/RegStr | 0.06 |
| $C_{30}$ Hop/$C_{31}$ Homohop | 2.90 | $C_{27}$βα DiaStr/RegStr ααα 20R | 0.05 |
| Gammacerane Index | 0.00 | $C_{27}$ ββ/αα + ββ | 0.39 |
| $C_{32}$ 22S/C32 22S + 22R | 0.00 | $C_{28}$ ββ/αα + ββ | – |
| $C_{35}$/$C_{34}$ | – | $C_{29}$ ββ/αα + ββ | 0.32 |
| $C_{27}$ DiaStr (%) | | | 55.56 |
| $C_{28}$ DiaStr (%) | | | 0.00 |
| $C_{29}$ DiaStr (%) | | | 44.44 |
| 1053-4133-36—(Halıkışlak Fm. Hal-17) | | | |
| $C_{19}$ Tri/$C_{23}$Tri | 0.15 | DiaStr (%) | 3.63 |
| $C_{23}$ Tri/ $C_{24}$ Tet | 2.67 | NorStr (%) | 68.72 |
| $C_{23}$ Tri/ $C_{30}$ Hop | 0.06 | IsoStr (%) | 27.65 |
| $C_{24}$ Tri/$C_{23}$ Tri | 0.63 | % $C_{27}$ ααα (20R) | 12.20 |
| $C_{24}$ Tet/$C_{23}$ Tri + $C_{24}$ Tet | 0.27 | % $C_{28}$ ααα (20R) | 11.59 |
| $C_{24}$ Tet/$C_{26}$ | 0.50 | % $C_{29}$ ααα (20R) | 76.22 |
| $C_{24}$ Tet/$C_{30}$ Hop | 0.02 | $C_{27}$ ααα 20(S/R) | 0.20 |
| Tm/Ts | 0.43 | $C_{28}$ ααα 20(S/R) | 0.00 |
| Ts/Tm | 2.33 | $C_{29}$ ααα 20(S/R) | 0.04 |
| Ts + Tm/$C_{29}$ Nor | 2.16 | $C_{27}$ RegStr (%) | 13.11 |
| Ts + Tm/$C_{28}$–$C_{29}$ Tri | 0.70 | $C_{28}$ RegStr (%) | 13.11 |
| $C_{28}$–$C_{29}$ Tri/Tri + Hop | 0.00 | $C_{29}$ RegStr (%) | 73.77 |
| $C_{29}$ Nor/$C_{30}$ Hop | 0.30 | $C_{27}$/$C_{29}$ | 0.16 |
| Oleanene Index | 0.00 | $C_{28}$/$C_{29}$ | 0.15 |
| Moretane Index | 0.26 | DiaStr/RegStr | 0.04 |
| $C_{30}$ Hop/$C_{31}$ Homohop | 4.35 | $C_{27}$βα DiaStr/RegStr ααα 20R | 0.01 |
| Gammacerane Index | 0.05 | $C_{27}$ ββ/αα + ββ | 0.22 |
| $C_{32}$ 22S/C32 22S + 22R | 0.24 | $C_{28}$ ββ/αα + ββ | 0.41 |
| $C_{35}$/$C_{34}$ | 1.50 | $C_{29}$ ββ/αα + ββ | 0.28 |
| $C_{27}$ DiaStr (%) | | | 16.67 |
| $C_{28}$ DiaStr (%) | | | 0.00 |
| $C_{29}$ DiaStr (%) | | | 83.33 |

C27 sterane dominance refers to marine phytoplankton, while C29 sterane dominance indicates strong terrestrial origin. The relative presence of at least C28 sterane in these three sterols indicates the contribution of lacustrine algae. According to Volkman (2003), C27 sterans predominantly dominate marine plankton, while C28 sterans are yeast, fungus, plankton and algae. In addition, C29 sterans may originate from higher plants (Volkman 1986) and brown-green algae (Volkman 2003).

In the samples, high % C29 ααα (20R) indicates terrestrial organic matter contribution (Table 4). In addition, 20R and 20S epimeric forms 20S/(20S + 20R) ratio of αα sterans are the most important parameters used for maturity measurement. In the biological configuration, while the ααα forms are 20R, the maturity increases with the change in the configuration of the 20S–20R residues. The maturity ratio of C29αα (S/(S + R)) reaches the equilibrium value in the oil generation window at ~ 0.52. However, this value and little above this value can cause misunderstanding and misinterpretation (Petersen et al. 2005).

## Discussion

Lacustrine petroleum source rocks are important for the production of large volume of hydrocarbons in many basins (e.g., Carroll and Bohacs 2001; Obaje et al. 2004; Petersen et al. 2005; Tian et al. 2014). While neighboring Oktemberian and Lesser Caucasus basins that consist of time-equivalent successions, are being explored, the Kağizman–Tuzluca basin has not attracted attention. Varol et al. (2016) suggest that this basin was filled by overfilled and underfilled lake units alternating with fluvial deposits which is similar depositional properties to Oktemberian basin. These are the fluvial–lacustrine (Halıkışlak Formation), fluctuating profundal lake (Turabi Formation) and evaporates (Tuzluca Formation).

The Halıkışlak Formation was deposited in a wide range of environments from fluvial/alluvial to deep and shallow lakes with local swamps. TOC wt% of analyzed samples indicates no source rock potential according to the classification of Peters (1986). A peat-bearing mudstone-deposited local swamps have high TOCs; but HI and $T_{max}$ values are quite low. The high Pr/Ph and CPI ratios of the samples indicate an immature terrestrial dominant-mixed organic matter. However, $T_{max}$ values for the other samples are between 436 and 440 °C (%$R_{eqv}$: ranging from 0.72 to 0.8) indicating slightly mature characteristics. The samples were generally collected around the margin of the lacustrine basin, and north of the Halıkışlak is mostly covered by volcanics. Ercan et al. (1987) identified electrically conductive layers beneath the volcanic plateau with a thickness of about 1.5–2 km that overlies basement, which is gradually shallower from North

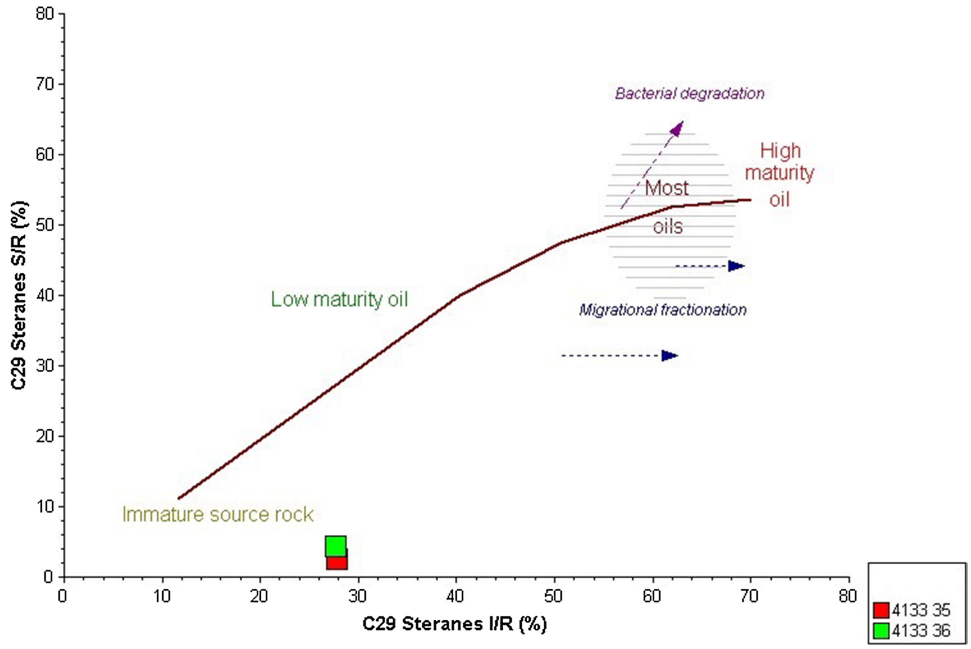


**Fig. 11** C29 sterane isomerisation: S/R versus I/R diagram. (4133 35: Turabi Fm., 4133 36: Halıkışlak Fm.)

to South. In addition to this, Kömürlü Formation, which is contemporary to the Halıkışlak Formation in the northern part (Ardahan Basin and Kars Plateau), has different lithology and organic geochemical properties. It is composed of conglomerates, sandstones, and shale intercalations in the lower part, grading into laminated shales, marls, and coal layers with thin gypsum layers at the top of sequence (Şahintürk and Kasar 1979; Uğur 2000). TOC (%) values of the Formation are very high (1.10–28.95 wt%), $T_{max}$ values vary between 436 and 442 °C and HI values are up to 827 mg HC/gTOC (Aydemir 2010, 2013). Aydemir (2010) also suggest that the Kömürlü Formation has great unconventional resources potential. Therefore, we suggest that the Halıkışlak Formation might be predicted as richer in organic matter under the volcanic area. However, an additional study clearly is needed to support this conclusion.

The Turabi Formation represents fresh water and alkaline lake units and it is divided into two sections: sandstone, coarse-grained sandstones and mudstone alternation, and a thick cream-colored mudstones facies composed of siltstone interbeds and organic matter-rich laminated mudstones (Varol et al. 2016). The formation is characteristic of the "fluvial–lacustrine facies association and algal organic facies" at lower and upper parts, respectively (Carroll and Bohacs 2001). The lower of Ts/Tm ratio and not having Ts value for Cin-15a number sample showed that the units may have deposited in the lake/saline environment. Organic petrographic results and $T_{max}$ versus HI diagram show that kerogen types are III and II origin. Upper part of the Turabi Formation has mainly terrestrial organic matter. Organic petrography of two samples (Cin-9 and Cin-15a) indicates that they are rich in herbaceous and woody material, and less coaly with pyrite, and support "algal–terrestrial organic facies". Carroll and Bohacs (2001) suggest that this type's lacustrine facies includes some of the world's richest source rocks. Organic-rich mudstones facies represents potentially could be good source rock with the TOC values. Reported Rock–Eval $T_{max}$ values for the Turabi samples vary greatly and are unreliable for samples with low $S_2$ yields. High $T_{max}$ values also can be the result of high oxidation. Considering only the $T_{max}$ of higher TOC samples, the organic petrography and the biomarker analysis, the studied Turabi Formation samples are mainly immature to marginally mature source rock potential.

Gas shows from the two wells (during 6 months) may support that petroleum system exists in the basin in the Oktemberian Basin next to KTB. However, maturation of the organic rich clay was determined as immature (Papworth and Aghabalyan 2002b). They concluded that it is likely that much of the observed gas was originated at depth from more mature sediments from beneath the ophiolite, which forms a floor to the tertiary sediments in the basin (Papworth and Aghabalyan 2002b). In addition, non- economic gas was detected from two wells in the KTB (Şenalp 1969b). However, there has not been any published study about gas origin in both basins.

The Halıkışlak and Turabi formations could be equivalent to Maikop Formation that is exposed in the Shmekha-Gobustan area in Azerbaijan (Guliyev at al. 2000; Feyzullayev et al. 2001). Bechtel et al. (2013) concluded that these Oligocene sediments have Type II (marine/brackish) organic matter with low to moderate Type III kerogen inputs, indicating different depositional properties from the KTB. Therefore, we could say that the lithostratigraphic units of the studied units are not equivalent to the Maikop and are not rich in TOC wt%.

The Tuzluca Formation is mainly composed of evaporites (halite, gypsum) with thin dark-colored mudstones in the lower part, and mainly green-colored claystone and dolomite alternation facies in the upper part. It is characterized by saline pan, sulphate lake and perennial lake units (Varol et al. 2016) and good seal rock properties in the basin. While TOC values are between 0.27 and 0.39 wt% for saline pan facies samples (Figs. 4c, 5d), that values are ranging from 0.06 to 0.33 wt% for the sulfate and perennial lake facies. Low HI and $T_{max}$ values indicate that the evaporate-bearing facies have poor petroleum potential. However, there are limited outcrops around Tuzluca, covered by recent alluvial conglomerate, extending to Armenian border. Therefore, deep evaporitic lacustrine units were not sampled and analyzed in this study. In addition, Br content of salt samples show saline pan environment in the Tuzluca, though salt samples belonging to Nakhichevan area have marine signature values. The data suggest that the Tuzluca Formation and its equivalent to the eastern part have marine source rocks. The authors suggest that evaporite units should be studied more detailed in the eastern areas.

## Conclusions

The Oligo-Miocene units in the KTB were deposited under different conditions from time equivalent to the Maikop Series. The studied basin has three types of lacustrine deposits. The Halıkışlak and Turabi formations have fluvial lacustrine facies and fluctuating profundal facies associations that could provide source rock beneath the volcanic cover at northern part of the study area. According to organic geochemical and sedimentological studies, non-economic gas shows in the Oligo-Miocene units in the studied basin might indicate that tertiary petroleum system exists for conventional resources. The Turabi and secondarily to the Halıkışlak formations should be tested in the future investigations when deeper boreholes become available from the proposed drilling program of the oil and gas exploration companies in KTB and beneath the Kars volcanic plateau.

**Acknowledgements** The study in the Kağızman–Tuzluca Basin was granted by Turkish Council for Scientific and Technical Research (TUBİTAK) under the Project number 108Y026. We are grateful to Ş. Şen, the DARIUS Research Program (France) (CNRS) for determination mammalian fossil in the terrestrial unit. Z. Dinçer Kırman (TPAO) for analyzing GC, GC-MS.



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