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Use of petrological and organic geochemical data in determining hydrocarbon generation potential of coals: miocene coals of Malatya Basin (Eastern Anatolia-Turkey)

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Abstract With this study, the hydrocarbon generation potential of Miocene aged coals around Arguvan-Parçikan in the northern district of Malatya province was evaluated with the aid of petrological and organic geochemical data. According to organic petrography, coal quality data, and low thermal maturity, the Arguvan-Parçikan coals are of high-ash, high-sulfur subbituminous B/C rank. The organic fraction of the coals is mostly comprised of humic group macerals, with small percentages derived from the inertinite and liptinite groups. The mineral matter of the coals is comprised mainly of calcite and clay minerals. The total organic carbon (TOC, wt%) values of the shale and coal samples are between 2.61 wt% and 43.02 wt%, and the hydrogen index values are between 73 and 229 mg HC/g TOC. Pyrolysis (T_{max}, PI), huminite/vitrinite reflectance (R_o, %), and biomarker ratios (CPI, Pr/Ph ratio, $Ts/(Ts + Tm)$ ratio, C_{32} homohopane ratio (22S/22S + 22R) and C_{29} $\beta\beta/(\beta\beta + \alpha\alpha$ sterane ratio) indicate that the organic matter of the studied coals is thermally immature. When all these data are taken together, Miocene aged coals around Arguvan are suitable for hydrocarbon generation, especially gas, in terms of organic matter type (Type III and Type II/III mixed), organic matter amount (> 10 wt% TOC), however, low liptinitic macerals (< 15%–20%), low hydrogen index (< 200 mg HC/g TOC) and low thermal maturity values inhibit the hyrocarbon generation.

Keywords Arguvan · Malatya basin · Eastern Anatolia · Organic geochemistry · Organic petrography · Miocene coal

1 Introduction

Energy is one of the most fundamental and driving needs of the countries' social and economic development, and the concepts of "energy security" and "sustainable energy" are the main support for the stability of economic life and for ensuring national security in a global or regional significance. Although the energy consumed in the world today is derived from different sources, fossil fuels (oil, coal and natural gas) have the largest share in these resources, accounting for nearly 87% (TP Energy Report 2015) of all the sources. Turkey, though quite poor in terms of oil reserves, has different coal reserves in all its geographical regions, notably in Western Anatolia (Tuncalı et al. 2002). However, approximately 68% of the lignite/sub-bituminous coal in Turkey are of low calorific value (nearly < 1500–2000 kcal/kg) (Palmer et al. 2002; Tuncalı et al. 2002).

In Turkey, for which coal is so important in terms of meeting the energy needs, this resource needs to be re-evaluated in accordance with the industrial and energy sector development in the world as well as industrial and economic scope. In particular, the suitability of coals for liquefaction and gasification processes or the determination of their coal-derived hydrocarbon potential are important issues. Few geological studies have been carried out on the Tertiary coals of Anatolia (Artova, Zile-Tokat, Hafik-

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Sivas; Çayırlı-Erzincan, Oltu-Erzurum; Soma-Manisa; and Şarkikaraağaç-Isparta), and thus a limited number of and organic geochemical and petrographic evaluation has been made (Yalçın Erik and Sancar 2010; Hoş Çebi and Korkmaz 2013; Yalçın Erik and Ay 2013; Kara Gülbay 2015; Ünal et al. 2014; Hökerek and Özçelik 2015; Bechtel et al. 2016; Ünal and Özçelik 2017).

Although some geological and stratigraphic investigations have been made concerning the coals around Arguvan-Parçikan (Malatya) which are the subject of this study (Yoldaş 1972; Sun 1987; İçel 1988; Türkmen and Aksoy 1998; Erdoğan 2004; Türkmen et al. 2004; Koç-Taşgın 2011; Booth et al. 2014), there is not any study on the evaluation of petrology, organic geochemistry and hydrocarbon generation potentials.

This study focuses on the Miocene Arguvan-Parçikan (Malatya) coal bearing units located in the East Anatolian Fault Zone (EAFZ), Eastern Anatolia, Turkey. The principal aim of the study is to determine factors that control coalification environment and hydrocarbon generation potentials by means of bulk coal analyses (proximate-ultimate), mineralogical composition, coal petrography, and organic geochemistry.

2 Geological and stratigraphic properties

2.1 Regional geology

The formation of Central Anatolian basins between the two continental units, Sakarya continent and Kırşehir Massif, with the closure of the northern branch of Neo-Tethysin in the Cretaceous-Eocene time period is very important for the regional geological evolution of Turkey, (Şengör and Yılmaz 1981; Görür et al. 1998) (Fig. 1a, b). These basins, which indicate the paleotectonic period, are divided into two groups as magmatic arc (pre-arc and intra-arc) and collision-related interior basins (Görür et al. 1998). Malatya Basin, included in the study area, is the continuation of Hekimhan Basin and started to form in Late Cretaceous (Okay and Tüysüz 1999). The collision of Anatolian and Arabian plates during the Early Miocene completed its evolution with the closure of the Neo-Tethys. The coexistence of Neogene continental expansion and strike-slip tectonic movement in Eastern Anatolia caused the formation of limited intermountain basins such as Malatya Basin (Görür et al. 1998). Gravity tectonics in the study area are represented by growth faults that began in the early Miocene, and an anticlinal found in Middle Eocene sediments, and the Malatya fault, which cuts the Malatya Basin, with a NE–SW direction, with a left-directional pulse, and the rupture faults that cut the southern growth fault of the basin are structural elements that express neo-tectonic movements. (Okay and Tüysüz 1999; Önal 2009; Türkmen et al. 2004). This fault-controlled basin is an area where active tectonic activities still continue nowadays (The latest important earthquake occurred in the magnitude of 5.3 around Malatya-Elazığ on 24 January 2020). As a result of displacements between Eastern Anatolia Fault Zone (EAFZ) and Pliocene and Early Pleistocene, fluvial and lacustrine sediments occurred in these basins. There are also small economic coal deposits and/or coal layers as part of the basin development (Tuncalı et al. 2002; Türkmen et al. 2004; Önal 2009).

2.2 Stratigraphy

Stratigraphic sequence of the study area consists mainly of Paleozoic and Cenozoic aged sedimentary rocks and volcanics (Figs. 2a, 3). Paleozoic aged limestones are dark blue gray colored, medium-thick bedded limestones and calcschists. The Cenozoic sequence starts with Eocene series and is considered to be two lithostratigraphic units, Eocene (Lutetian) conglomerate and Limestone-Shale

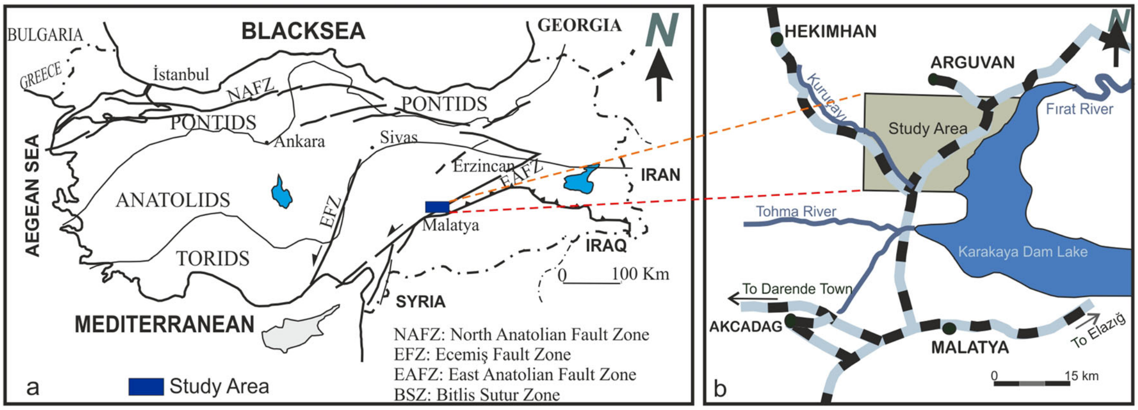

Fig. 1 **a** Turkey’s place in the tectonic units of the study area, **b** location map of investigated area

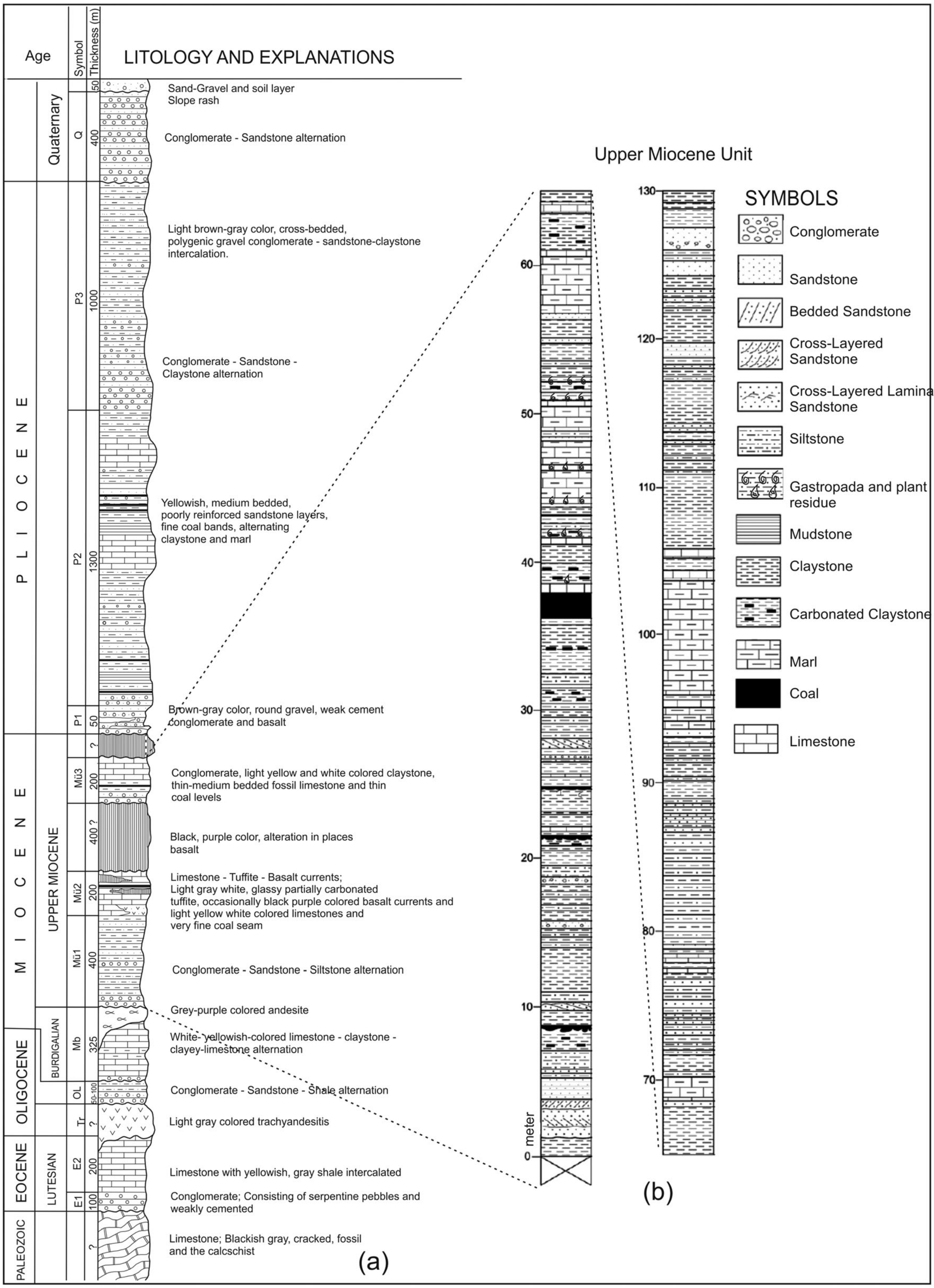

Fig. 2 **a** Stratigraphic columnar section of investigated area (modified from İçel 1988), **b** Columnar sections of Parçikan coal bearing units (modified from Koç-Taşgın 2011)

(Figs. 2a, 3) (İçel 1988). The polygenic conglomerates forming the base of the Eocene are approximately 100 m thick and consist of thick-bedded, brown colored, tightly cemented conglomerates (Fig. 2a).

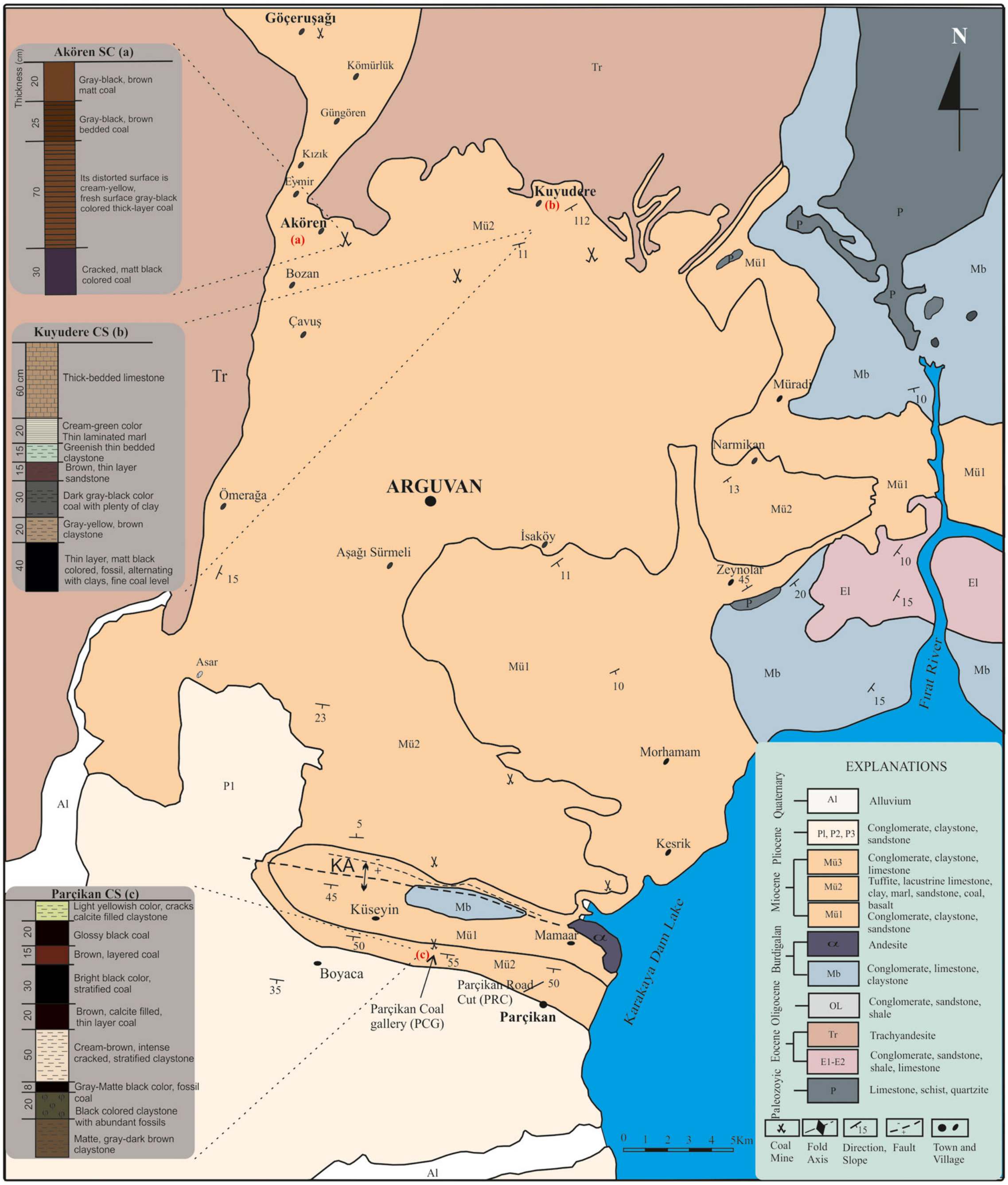

Fig. 3 Simplified geological map of investigated area and columnar sections of coaly areas

In the limestone-shale alternation, the limestones are yellow-light brown colored and highly fossiliferous. Oligocene aged unit, which is red, gray-green colored, generally consists of conglomerate-sandstone-shale intercalation, and the thickness is around 50–100 m (Figs. 2a, 3) (İçel 1988). The Burdigalian aged unit consists of red claystone, mudstone, siltstone-mudstone intercalation with coal levels, limestone and marls (Türkmen et al. 2004). This unit, which shows lateral and vertical transitions with Malatya volcanic, gives a sample in the Karaca Anticline (KA) core in the south (Fig. 3). It was described as the Alibonca Formation by Önal (2009). Volcanic rocks in the study area consist mainly of trachyandesite, andesite and basalts. The Late Miocene series with a lacustrine character consists of three levels: Mü1 (Conglomerate-Sandstone-Claystone), Mü2 (Limestone-Tuffite-Basalt Currents, coal layers), Mü3 (Conglomerate-Limestone-Claystone-coal layer) (Figs. 2a, 3) (İçel 1988).

Marl-Clayey Limestone-Claystone-Lignite (P2) The unit defined as Boyaca Formation by Önal (2009) is composed of clayey limestone-marl-claystone intercalations, and gravelly sandstone and coal bands are found occasionally. Conglomerate-Sandstone-Claystone (P3), which begins with conglomerates composed of distinctly layered basalt and limestone pebbles, and intercalation with sandstones continues approximately 1000 m, is very well rounded, (İçel1988). Quaternary aged units are comprised of conglomerate and alluviums and unconformably overlie all units (Fig. 2a) (İçel 1988).

3 Analysis methods

The properties of the coals in the study area (thickness, distribution area, lithotype changes and tectonic effects) were evaluated by field surveys and compared with other coal occurences in this basin. Thin coal veins are seen around Arguvan, mainly around Parçikan, Kuyudere, Göçeruşağı and Akören villages (Fig. 3). However, the only economically operating site is the Parçikan coal field. As the coal vein in this area is relatively thick (2 m) and the relationship between the floor and overlying rocks is more clearly seen, detailed investigations and sampling were made in the vicinity of Parçikan village (in the Arguvan-Parçikan road cut—Fig. 4a, d and Parçikan coal mining gallery—Fig. 4b).

Six channel samples of coal and other organic rich mudstones, coaly shales from all investigated areas were collected according to ASTM D-2234 and used for this study. A systematic sampling based on variation in lateral and vertical succession of the sedimentary facies was carried out. The samples were taken at about 1 m interval vertically after removing weathered surfaces. Lithological features of each of the studied coal sections (Fig. 4a–c) were macroscopically described and the lignite lithotype was determined according to guidelines established by the International Committee for Coal and Organic Petrology (ICCP 1994), as well as by Taylor et al. 1998.

Leitz MPV-SP reflective light microscope and 50X objective were used for petrographic evaluations. Leica DM2500 P and MSP200 windows-based program were used for random huminite/vitrinite reflection measurements and they were evaluated according to ICCP (1998), ISO 11760 (2005). Random reflectance measurements were performed using the Zeiss RS-III microscope with 40 × oil immersion objective according to ISO 7404-5 (2009) standards, and results have been presented as mean random reflectance values (R_o, %). The GI, TPI, WI, and GWI parameters were determined according to the formulas prepared for Tertiary aged lignites, by Kalaitzidis et al. (2004). The maceral nomenclature was based on the ICCP System1994 (ICCP 2001; Sýkorová et al. 2005; Pickel et al. 2017).

The standart proximate and ultimate analyses of the coal samples were conducted according to ASTM standards (ASTM D3174, 2004; D3302, 2004; D5373, 2004) in M.T.A. The analyses were carried out in the laboratories of the General Directorate of Mineral Research and Exploration MAT Department (MTA, Ankara). The gross and net calorific values of coal samples were determined using an IKA 4000 adiabatic calorimeter (ASTM D5865, 2004); also, sulfur, carbon, hydrogen and nitrogen contents were determined with LECO TGA 701 analyzer in the same laboratory.

Mineralogical composition was determined in the 28 powder coal samples and their clay fractions (Ø < 2 lm) using X-ray diffraction spectrometers with CuKa radiation (4–70 2H range in powder-samples and 0–30 2H range in clay-fractions) in the laboratories at Cumhuriyet University (Sivas) and the General Directorate of Mineral Research and Exploration (MTA, Ankara).

Rock–Eval/TOC analysis was made for ten coal and coaly shale samples that were collected systematically from measured sections in the Arguvan-Parçikan coal areas (Figs. 2b, 3). These analyses of all the samples were made 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 a rate of 25 °C/min. Using the TOC and Rock–Eval pyrolysis results as a basis for selection, ten samples were extracted in ASE 300 with Dichloromethane (CH_2Cl_2) for approximately 40 h in the TP AR-GE laboratory (Ankara). The whole extract was analyzed using an Agilent 6850 gas chromatograph equipped with a flame photometric detector and flame ionization detector. In addition, saturated portions were analyzed by Agilent 7890A/5975 °C GC–MS, terpane and sterane molecules were studied in SIM Scan mode using 191 and 217 *m/z* ratios, respectively (TP AR-GE Lab., Ankara).

4 Results and discussion

4.1 Coal geology investigations and macroscopic description

The investigated coals are found in the Upper Miocene units around the villages of Parçikan, Akören, Göçeruşağı and Kuyudere within the borders of Arguvan district (Figs. 2a–c, 4a–d). In the section (PCS; Figs. 2c, 4a) measured in the south side of the Karaca Anticline (KA), the thickness of the coal seam was determined to be around 1.85 m (Figs. 2c, 4a) but 2 m in the Parçikan coal gallery (Fig. 4b). Due to the relatively thick coal levels in the Parçikan region, a private coal company continues its mining operation for local needs. At the upper levels of the coal unit on the Arguvan-Parçikan road cut (PRC), there

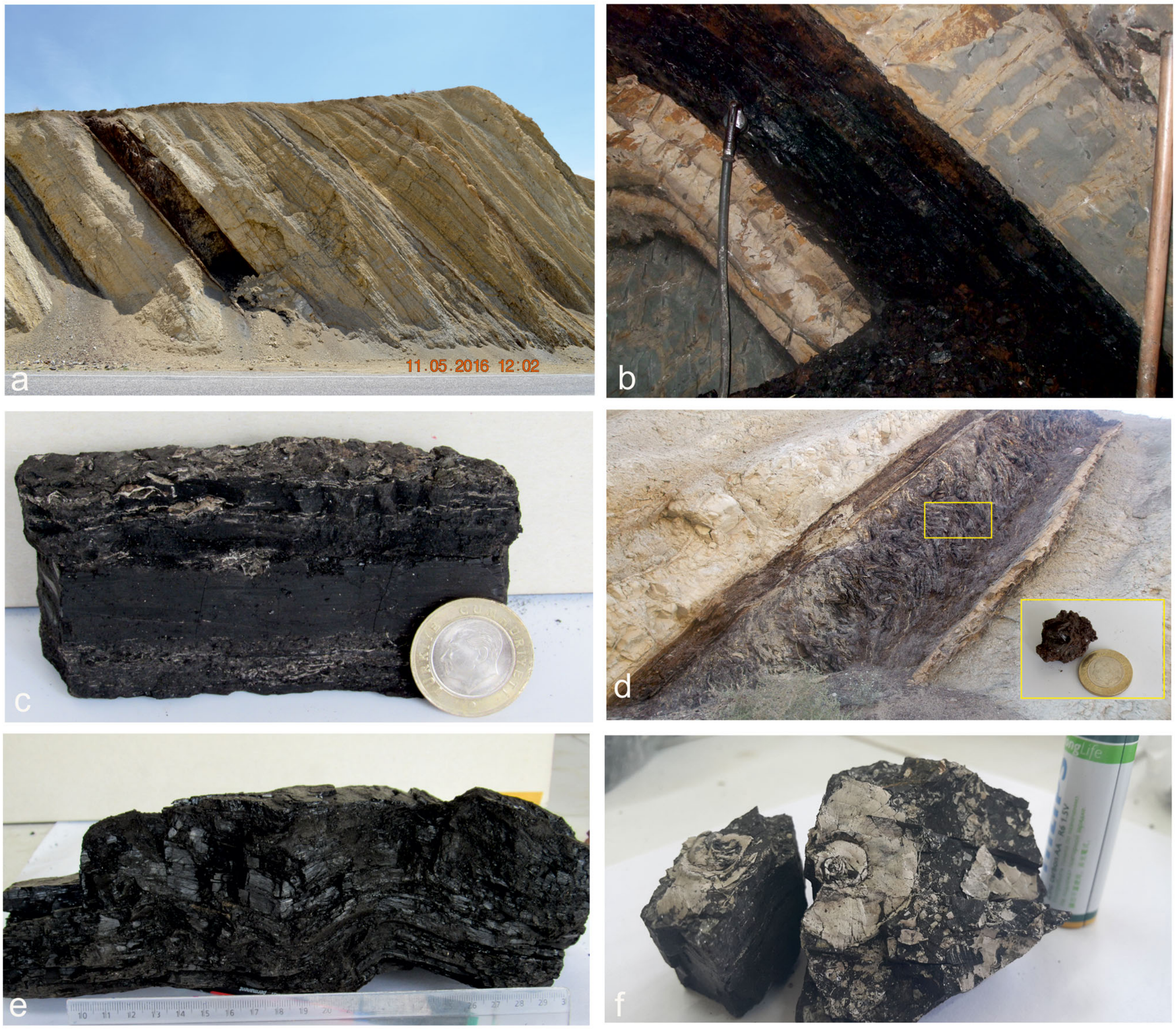

Fig. 4 Field views and some structural features of the coal in the study area. **a** The upper levels of the coal unit on the Arguvan-Parçikan road cut, **b** the view of the coal seam and side rocks in the coal mine gallery, **c**, **e** soft sediment deformation structure and macroscopic view of the studied coal, **d** Clayey coal levels showing soft sediment deformation under the influence of active tectonic movements **f** macroscopically, the coal section displaying blackish colour is dull and brittle, and contains gastropod shells at certain place

are bright, brittle coals about 30 cm thick (Fig. 4c, e). Macroscopically, the coal section displaying blackish colour is dull and brittle, and contains gastropod shells at certain places (Fig. 4f).

Clayey coal levels showing soft sediment deformation under the influence of active tectonic movements are present below this level (Fig. 4e). There are abundant fossiliferous, clayey limestones particularly on the floor and ceiling of the thick coal vein. Black colored very fossiliferous claystones with 8 cm thickness and gray-black colored fossiliferous coal levels are observed on matt, gray-dark brown colored claystones. Approximately 50 cm of cream colored, occasionally dark brown, claystones with abundant-cracks are followed by the main coal vein. At the base of this vein is a 20 cm brown, calcite filled thin coal layer followed by a bright black colored 30 cm coal vein and 15 cm brown colored, mostly clayey coals. The side rocks of the coal vein are composed of gray-dark yellow, brownish-green colored clayey and carbonated parts and alteration structures are intensely observed in places (Fig. 4a, d).

Coals around Akören village are seen as alternation of black, dark brown color, mostly calcite and claystone. The lower parts of the coal vein are matt black, with abundant cracks; medium levels are creamy-yellowish black, hard and layered, the top layer of coal is cracked and matt black

Table 1 Proximate analysis data of investigated samples

Coal section	Sample number	Sample type	Total moisture (wt%)	Ash (wt%, db)	Volatile matter (wt%, db)	Fixed carbon	Net calorific value (kcal/kg)	Gross calorific value (kcal/kg)
Parçikan	P06	Original	21.50	50.95	18.34	11.03	1394	1591
		Dry	–	69.90	23.36	14.56	1936	2027
	P11	Original	27.74	46.55	20.15	18.14	694	912
		Dry	–	64.42	27.89	21.09	1184	1282
Göçeruşağı	GC-1	Original	20.99	73.36	4.39	8.35	This analysis value could not be determined because the sample was not burned	
		Dry	–	92.85	5.56	6.91		
Akören	A-03	Original	29.65	62.69	6.84	13.74	28	224
		Dry	–	89.12	9.72	16.25	286	318
	Akb-2	Original	22.08	68.37	8.37	10.64	137	294
		Dry	–	87.74	10.74	6.48	342	377
		ASTM D7582					ASTM D 5865	

and 145 cm thick (Fig. 4a). The coal bearing section around Kuyudere village is approximately 200 cm thick and has a matt black and brown color, mostly carbonate host rock, clayey, and it has abundant cracks. Above the coal layer, there are abundant fractured and brittle claystones, and at the top are layered limestones (Fig. 4b). It is observed that coal layer thicknesses are around 30–40 cm and some carbonated and clayey levels are frequently intercalations. In the coal sample observed around the Göcerusagı, generally there are "mixed" levels with soil cover, irregular "thickness and diffuse", and dense clayey layers. There are coal levels with an approximate thickness of 195 cm. It was found that the matte black and brown coals, although the layer is difficult to follow, 0.3–0.85 cm thick coal layer, are mostly carbonate host rock and claystone intercalation due to the presence of a cover layer and a thin soil layer.

4.2 Mineralogical compositions

The coal bearing units in the studied areas are mainly composed of coal, organic-rich carbonated rock, coaly claystones and clayey levels (Figs. 2b, 4a, b, d). The investigated samples contain a variety of minerals at variable proportions. Identifiable mineral constituents include pyrite, quartz, clay minerals, calcite, and jarosite (Fig. 4d). The dominant component is carbonates (calcite; 4 wt%–96 wt%; dolomite; 7 wt%) and clay (11 wt%–82 wt%) in the mineralogical composition of the studied samples. In addition, sulphides (framboidal pyrite and cavity fillings; 4 wt%–7 wt%), quartz 3 wt%–48 wt%, feldspar 5 wt%–46 wt% are other minerals in the composition. The predominance of silicate minerals along with the high ash yields implies that the clastic input was high during peat depositions. The clay minerals are mostly aggregated with other clastic minerals (e.g., quartz, feldspars) and attrinite as well. Clay minerals determined by XRD-clay fraction diffractograms are illite (12 wt%–76 wt%), smectite (21 wt%–63 wt%) and chlorite (11 wt%–75 wt%). Framboidal pyrite crystals are common in the studied samples, whereas massive pyrite crystals are barely identified.

4.3 Proximate and ultimate analyses

Table 1 summarizes the results of proximate and ultimate analyses along with net calorific values of the investigated coal samples. The high ash yield of the samples on an air dry basis varies between 64.42% and 92.85% (av. 80.81%), total sulfur 0.02%–3.73% (av. 1.46%); the total moisture was determined as 20.99%–29.65% (av. 28.69%) as well as low net calorific values (Table 1). The ultimate analysis shows that the coal samples are characterized by moderate hydrogen (up to 1.67%, on an air dry basis) contents (Tables 1 and 2). Carbon values on dry basis were between 12.63% and 65.53% (av; 43.41% on an air-dry basis), hydrogen 4.18%–7.06% (av. 5.53% on an air-dry basis), nitrogen 0.13%–2.07% av. 1.23% (on an air-dry basis), H/C ratios vary between 0.91 and 6.71 and O/C ratios range between 0.06 and 0.90 (Table 2).

The gross calorific value varies between 318 and 2027 kcal/kg (av. 1001 kcal/kg), and the volatile matter yield is between 5.56% and 27.89% (av. 15.45%). 1282–2027 kcal/kg values were determined only from the hand piking samples taken from the coal bands operated in the Parçikan coal field. The calorie, total sulfur and fixed carbon values of the samples in the other sites were lower and the ash yields were higher in comparison with the Parçikan coal area samples (Table 1).

Table 2 Ultimate analysis data of investigated samples

Coal section	Sample number	Sample type	C	H	N	O	S	H/C	O/C	N/C
Parçikan	P-06	Original	18.06	1.38	0.57	5.91	2.93			
		Dry in the air	21.90	1.67	0.69	6.38	3.73			
		Dry ash free	**65.53**	**4.99**	**2.07**	**19.08**	1.58	**0.91**	**0.22**	**0.03**
	P-11	Original	13.22	1.07	0.53	11.81	2.18			
		Dry in the air	17.25	1.40	0.70	12.73	0.02			
		Dry ash free	**51.41**	**4.18**	**2.07**	**37.95**	0.02	**0.98**	**0.55**	**0.03**
Göçeruşağı	GC-1	Original	0.71	0.40	0.01	5.08	0.23			
		Dry in the air	0.85	0.47	0.01	5.47	0.33			
		Dry ash free	**12.63**	**7.06**	**0.13**	**81.37**	0.81	**6.71**	**0.06**	**0.01**
Akören	A-03	Original	3.31	0.43	0.09	4.97	1.04			
		Dry in the air	4.48	0.58	0.12	5.36	2.93			
		Dry ash free	**43.22**	**5.84**	**1.20**	**51.78**	3.73	**1.62**	**0.90**	**0.02**
	Akb-2	Original	4.23	0.53	0.06	5.01	1.58			
		Dry in the air	5.13	0.65	0.08	5.40	2.18			
		Dry ash free	**44.24**	**5.57**	**0.66**	**46.59**	0.02	**1.51**	**0.80**	**0.01**

4.4 Petrological properties

4.4.1 Lithotype characteristics

When broken, the sorfaces of the Parçikan coals appear blackish-brown, while the layer is seen to be darker black at some levels. After surface moisture is gone, prismatic cracks and concoidal fractures develop in the coal structure (Fig. 4c, e). The coals in the investigated locations are macroscopically different from each other due to their mainly seam thickness, and physico-chemical degradation processes. Coals in Akören, Göçeruşağı and Kuyudere sections are generally much more clayey; they are seen in the form of very thin bands or lenses and differ from Parçikan coals in macroscopic view. In the field observations of the coals and in the detailed macro examination of the samples in the laboratory, the durain level is clearly monitored with a few mm clarain band with vitrain bands of approximately 5–6 cm thickness (Fig. 4c, e). Plant tissues, fossil shells (gastrapods) and jarocyte minerals, which have remained intact in fine coal seam, have also been found (Fig. 4d, f).

4.4.2 Microlithotype and maceral composition

The quantitative distribution of different macerals (on mineral-free basis) and associated mineral matter from the coal samples are shown in Table 3. Representative microphotographs of various macerals are illustrated in Fig. 5.

Petrographic observations reveal that the Arguvan coals are rich in huminite (49 vol%–67 vol%, mean; 60.29 vol%), in which textinite and ulminite (telohuminite subgroup), attrinite, densinite (detrohuminite subgroup), and corpohuminite (gelohuminite subgroup) are more abundant than other macerals. (Table 3 and Fig. 5). The amount of the macerals of the liptinite group is very low (3 vol%–9 vol% (av. 5.86 vol%), and they are represented by sporinite, resinite suberinite and dominantly liptodetrinite. The color of sporinite in fluorescent light is yellow. Inertinite macerals are rare 1 vol%–4 vol% (av. 2.29 vol%) and represented by fusinite, funginite and inertodetrinite. The inertinite group macerals occur in low concentrations (av. 6.64 vol%), and inertodetrinite is the most common maceral of this group (Fig. 5). The distributions of the maseral groups of the studied coal samples in the triangular diagram are given in Fig. 6a, b.

The mineral matter content, as determined microscopically, ranges from 11 vol% to 42 vol%, and consists mainly of clay minerals, followed by carbonate (calcite), sulphate (gypsum) and iron (pyrite) minerals. The most common occurrence of pyrite in the form of crack and void filling or granular formations observed in the coals is framboidal pyrites and they have an average composition of 3.71 vol% (Table 3) (Fig. 5). Framboidal pyrite crystals are generally syngenetic and related to reducing conditions within the palaeomire (Kalaitzidis et al. 2004; Siavalas et al. 2009). Although the coal formations around Arguvan appear physically different from each other, there is no an important difference in petrographic composition. Only Akören coals can be said to have more inertodetrinites, except that the maceral composition properties are similar (Table 3).

Table 3 Maceral composition (vol%), mineral matter content (vol%), and petrological parameters (GI, TPI, GWI, VI) of Arguvan coals

Huminite group macerals (vol% on mineral matter free basis)										Liptinite group macerals (vol% on mineral matter free basis)					
Coal section	Sample No.	Tx	Tul	Eul	Den	At	Gel	Kr	$\sum$HUM	Sp	Al	Rz	Kt	Ldt	$\sum$LIP
Parçikan	PM-03	2	4	7	14	4	34	2	67	3	2	0	3	0	8
	P-06	3	4	9	11	2	30	0	59	2	1	0	0	0	3
	P-07	2	3	10	13	3	32	1	64	4	1	0	1	0	6
	P-08	3	3	10	10	3	29	0	58	2	2	0	0	0	4
	P-10	4	5	6	9	2	23	0	49	1	2	0	0	0	3
	P-11	2	4	7	8	1	44	0	66	3	3	0	1	0	7
Akören	A-01	3	1	4	8	4	44	0	64	3	2	0	0	0	5
	A-02	1	2	5	9	3	45	0	65	3	1	0	0	0	4
	A-04	2	2	3	9	6	45	0	67	2	2	0	0	0	4
	Akb-2	3	6	7	2	12	20	0	50	3	2	0	2	2	9
	Akb-3	2	5	6	3	11	27	0	54	2	1	0	3	2	8
Kuyudere	K-01	3	5	7	12	8	23	0	59	2	3	0	1	1	7
	K-02	2	7	8	11	10	25	0	63	1	3	0	2	2	8
	K-03	2	8	10	8	12	22	0	62	1	2	0	1	2	6

Coal section	Sample No.	Inertinite group macerals (vol% on mineral matter free basis)						Mineral matter (vol% on visible mineral matter free basis)		Petrographic indices			
		Mk	Fz	Sf	Mi	idt	$\sum$IN	PYR	V.S.	GI	TPI	GWI	VI
Parçikan	PM-03	2	1	0	0	0	3	4	18	2.56	0.23	6.15	0.38
	P-06	1	1	0	1	0	2	3	33	2.86	0.30	5.21	0.81
	P-07	1	2	0	1	0	4	3	23	2.67	0.31	3.87	0.64
	P-08	1	1	0	1	0	3	2	33	2.22	0.33	3.31	0.82
	P-10	2	1	0	0	0	3	3	42	1.67	0.32	3.92	0.79
	P-11	2	0	1	0	0	3	2	22	2.50	0.17	6.80	0.56
Akören	A-01	5	4	0	2	4	15	2	11	0.55	0.18	6.09	0.52
	A-02	6	6	0	1	5	18	2	10	0.64	0.19	8.22	0.57
	A-04	3	4	0	1	3	11	4	14	0.63	0.14	6.45	0.41
	Akb-2	3	2	0	0	4	9	6	26	0.38	0.32	2.27	0.48
	Akb-3	3	1	0	0	4	8	5	25	0.43	0.20	3.11	0.38
Kuyudere	K-01	3	1	0	0	2	6	6	22	1.12	0.24	2.94	0.39
	K-02	2	1	0	0	1	4	5	20	1.19	0.23	2.75	0.39
	K-03	2	1	0	0	1	4	5	23	1.00	0.30	2.00	0.52

Tx Textinite, Texto-ülminite, *Eul* Eu-ülminite, *Den* Densinite, *At* Attrinite, *Gel* Gelinite, *Kr* Corpohuminite, $\sum$*HUM* Hüminite, *Sp* Sporinite, *Al* Alginite, *Rz* Resinite, *Kt* Cutinite, *Ldt* Liptodetrinite, $\sum$*LIP* Liptinite, *Mk* Macrinite, *Fz* Füsinite, *Sf* Semifüsinite, *Mi* Micrinite, *Idt* Inertodetrinite, *Fg* Funginite, $\sum$*INT* Inertinite, $\sum$*Pir.* Total pyrite, *VS.* Clay and silicate minerals, *GWI* Groundwater index (gel + Kr + min.mat.)/(Tx + Eul + den), *VI* Vegetation index (Tx + Eul + Fz + Sf + Rz)/(den + idt + Al + ldt + Sp + Kt), *TPI* Tissue preservation index (Tx + Eul + Sf + Fz)/(den + Mk + idt), GI Gelification index (hum + Mk)/(Sf + Fz + idt)

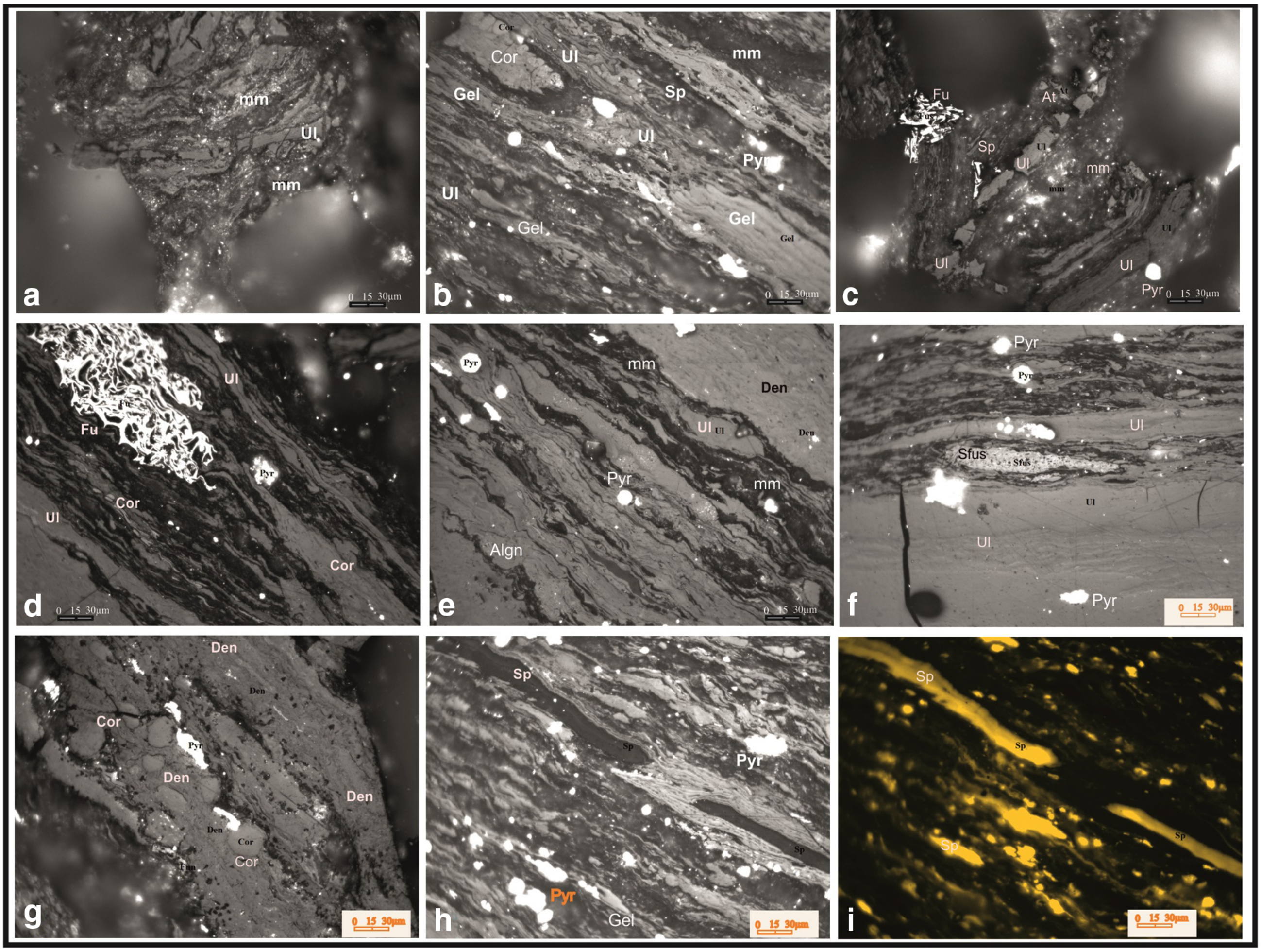

Fig. 5 Representative photomicrographs of macerals of the investigated coals

4.5 Bulk geochemical characteristics

Rock–Eval pyrolsis data were interpreted according to Peters (1986) and Lafarqué et al. (1998), on the amount of organic matter, organic matter type (kerogen type), diagenetic process (thermal maturity) and hydrocarbon generation potential of coal and coaly samples taken from the vicinity of Arguvan. Total organic carbon (TOC) values range from 2.61 wt% to 43.02 wt%. The total organic carbon and hydrogen index values are seen to be higher especially in the Parçikan and Akören area samples (Table 4). Coal samples are characterized by a low hydrogen index (HI = 73–229 mg HC/g TOC). T_{max} values ranging from 409 to 436 °C agree with the low rank of the coal.

4.6 Molecular geochemistry reviews

4.6.1 n-alkane and isoprenoid compound properties

The extract values of the investigated samples are generally low (Table 5), higher only in the Parcikan samples (260–5202 ppm; av.: 2294 ppm), despite relatively low values in samples of Akören, Göçeruşağı and Kuyudere sites (260–2269 ppm; av.1327 ppm). The total ion current chromatograms of the saturated hydrocarbon fractions of five samples are shown in Fig. 7.

In the studied samples, *n*-alkanes are the dominant peaks of gas chromatograms, and unimodal distribution is observed (Fig. 7a). The relative abundance of the odd-numbered ones in the *n*-alkanes in the C_{11}–C_{35} range and the *n*-C_{29} and *n*-C_{31} components is dominant (Table 5 and Fig. 7a). In particular, long chain *n*-alkanes (*n*-C_{27} to *n*-C_{32}) are typically found in the highest relative abundances in low-rank coals in Turkey (Yalçın Erik and Ay 2010, 2013; Ünal et al. 2014; Kara-Gülbay 2015). High molecular weight (> *n*-C_{27}) straight chain lipids, which are

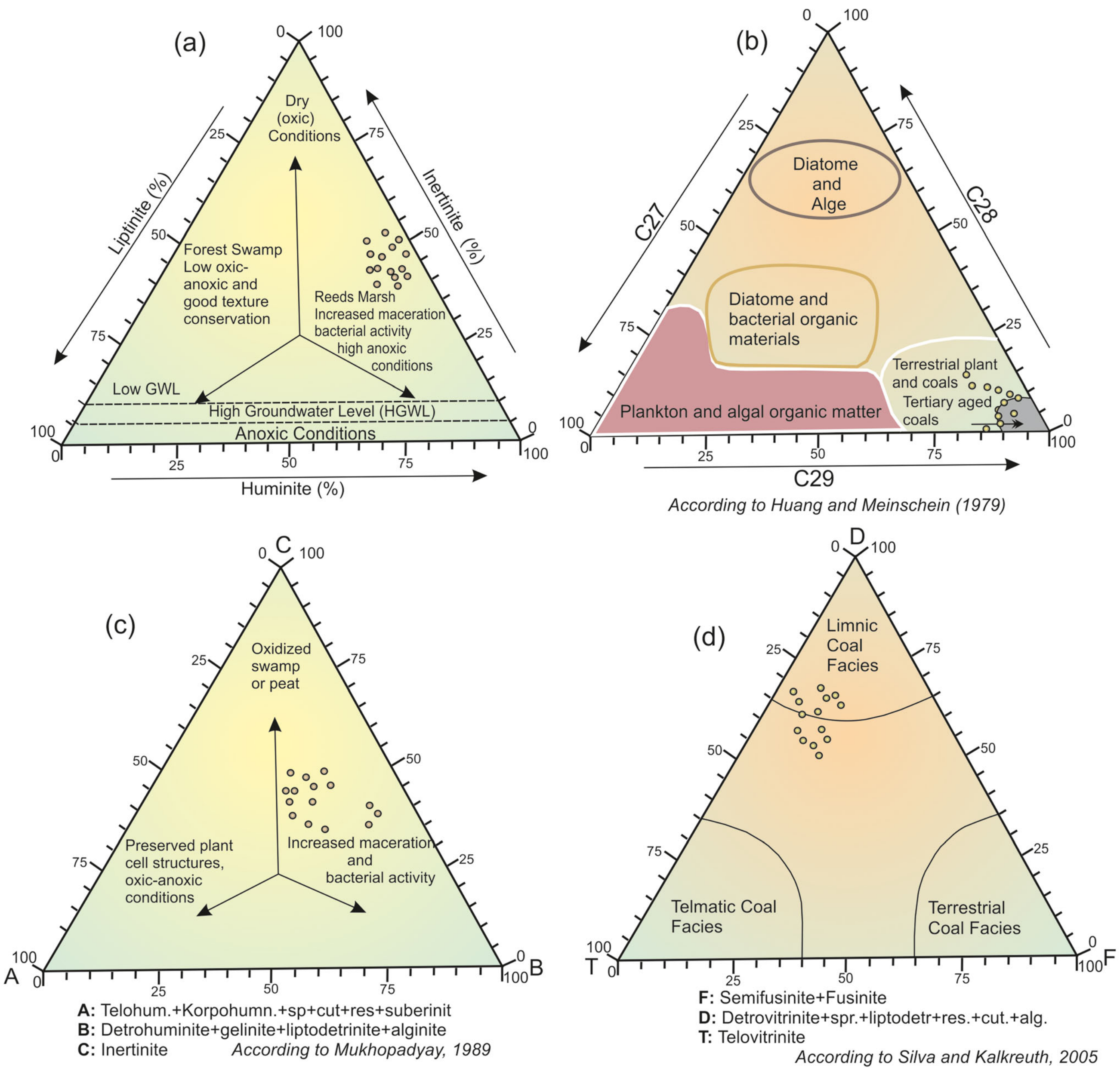

Fig. 6 Ternary diagrams expressing the sedimentation conditions and the organic matter type of the investigated coals

the main component of plant waxes, are characteristic biomarkers for higher terrestrial plants (plant wax) (Eglinton and Hamilton 1967). These data bring about a controversial issue in terms of the formation of long-chain *n*-alkanes from vascular plants, but they are suitable for the immature character of organic matter (Peters and Moldowan 1993). Low molecular weight *n*-alkanes ($< C_{20}$) consisting of major algae and microorganisms are found in very low relative ratios, such as 1% of total *n*-alkanes (Peters et al. 2005) (Fig. 7). The intermediate molecular weight *n*-alkanes (n-C_{21-25}), which are reported to be originated from aquatic macrophytes (Ficken et al. 2000), are found in studied samples in proportions between 19% and 29% relative to total n-alkane concentrations (Table 5 and Fig. 7a). The acyclic isoprenoids pristane (Pr) and phytane (Ph) are present in the saturated hydrocarbon fractions of all samples in low concentrations (Pristane; 0.09%–0.97%, and phytane; 0.12%–0.54%) (Table 5, Fig. 7a).

4.6.2 *Sterane and terpane compounds*

Detailed biomarker characteristics have been used to discern source input of organic matter, maturation degree and

Table 4 Total organic carbon (TOC) and Rock-Eval pyrolysis results of the studied samples

Coal section	Sample No.	TOC	S1	S2	T_{max}	HI	OI	PI	S2/S3	PY	QI	BI	R_o (%)	R_{o2} (%)
Parçikan	PM-03	8.61	0.57	7.83	436	91	97	0.07	0.94	8.40	0.98	0.07	0.38	0.69
	P-06	40.40	0.91	46.37	417	115	78	0.02	1.47	47.28	1.17	0.02	0.51	0.35
	P-07	35.76	1.13	42.61	419	119	122	0.03	0.97	43.74	1.22	0.03	–	0.38
	P-08	37.01	2.31	84.91	417	229	82	0.03	2.81	87.22	2.36	0.06	–	0.35
	P-10	43.02	1.28	78.46	424	182	72	0.02	2.53	79.74	1.85	0.03	0.39	0.47
	P-11	30.57	1.33	22.20	413	73	123	0.06	0.59	23.53	0.77	0.04	0.38	0.27
Akören	A-02	30.40	1.36	23.99	416	79	127	0.05	0.62	25.35	0.83	0.04	0.38	0.33
	A-04	2.61	0.32	5.25	409	201	78	0.06	2.59	5.57	2.13	0.12	–	0.20
Kuyudere	K-01	10.14	1.26	18.79	424	185	55	0.06	3.34	20.05	1.98	0.12	–	0.47
	Akb-2	7.48	0.77	12.32	420	165	64	0.06	2.56	13.09	1.75	0.10	–	0.40

TOC, Total Organic Carbon (%). S1, the amount of free hydrocarbons in the sample (mg HC/g rock). S2, Remaining HC generative potential (mg HC/g TOC). T_{max}, temperature at which maximum S2 pyrolyzate can generate (°C). HI, Hydrogen Index (mg HC/g TOC). OI, Oxygen Index (mg CO_2/g TOC). PI, Production Index (mg HC/g TOC). S2/S3, Hydrocarbon type index. PY, Potential yield (mg HC/g TOC). QI, Quality Index ((S1 + S2)/TOC). BI, Bitumen Index (S1/TOC). R_o (%), Measured vitrinite/huminite reflection value. R_{o2} (%),The vitrinite/huminite reflection value calculated according to Jarvie et al. (2001) (%)

depositional environmental conditions based on the distribution patterns of normal alkanes, isoprenoids, steranes and terpanes (Waples and Machihara 1991; Peters et al. 2005). Biomarker properties of saturated components of Arguvan coal samples are given in Table 6. The main steranes identified in the investigated coal composition are; C_{29} 5_{α} (H), 14_{α} (H), 17_{α} (H)-Sterane (20R) and C_{30} 5_{α} (H), 14_{α} (H), 17_{α} (H)-(20R) steranes. Terpenoid biomarkers, respectively, according to abundance rates are; C_{30} tricyclicterpane, homomoretane, $C_{29}17_{\beta}$(H), 21_{α}(H)-30-Normoretane, C_{29} 17_{α}(H), 21_{β}(H)-Norhopane, C_{30} 17_{α}(H), 21_{β}(H)-Hopane and C_{30} 17_{β}(H), 21_{α}(H)-morethane (Fig. 7b, c).

Arguvan coal samples generally had $C_{29} > C_{28} > C_{27}$ ααα (20R) sterane values, but in the sample K-01, the rates higher than the general average ones were determined, C_{28} 5α (H), 14α (H), 17α (H) -Sterane (20R). In the sample of A-03, C_{27} and C_{29},5α (H), 14α (H), 17α (H) -Sterane (20R) components are in equal proportion, and there are approximate values of C_{28} 5α (H), 14α (H), 17α (H) -Sterane (20R) (Table 6). As is common in Tertiary aged coal samples, steranes are more abundant than hopanes (sterane/hopane ratio 1.67–7.79) (Stefanova et al. 2013, Yalçın Erik 2011; Yalçın Erik and Ay 2013). Norhopane/hopane values generally > 1, moretane/hopane ratios vary between 0.36 and 2.70 (Table 6). Hopanoids are important constituents of the non-aromatic cyclic triterpenoids of the Arguvan coal samples (Table 6, Fig. 7c). The hopanoid patterns are characterized by the occurrence of 17β,21β (H)-type hopanes from C_{27} to C_{31} with the C_{28} hopane being absent. The ratio of the 17β,21β (H)-C_{31} hopane to (17β,21β (H) + 17α,21β (H))-C_{31} hopanes is in the range generally measured in coals (0.5–0.6; Table 6). The most probable biological precursor of the hopane derivatives found in the samples are bacteriohopanepolyols (Peters et al. 2005; Singh et al. 2017b).

5 Discussion and results

5.1 Coal type and rank

Physical and chemical properties of coal are crucial for the classification of coal, quality determination and definition of the potential economic value. Rank (maturity) of the Arguvan coals are specified by reflectance measurement on ulminite (huminite) maceral. The mean random reflectance (Ro) value ranges between 0.38% and 0.51% (Table 4) across the seams, suggesting that the studied coals have attained 'Brown coal' (German Standard) or 'Sub-bituminous' stage/rank (ASTM) and are of low rank B/C (ISO: 11760, 2005), and fall in the early diagenetic zone of methane generation (Taylor et al. 1998). It is consistent with other maturation parameters and indicates that the units studied have not matured yet.

5.2 Evaluation of hydrocarbon generative potential of coals with petrological and biomarker data

5.2.1 Type of organic material

In the Van Krevelen (HI-OI) and HI-T_{max} diagrams prepared according to the Rock–Eval pyrolysis data of the studied samples, most of the samples were scattered in Type II-III (terrestrial and marine) and Type III kerogen (terrestrial, residual organic matter) in the area (Fig. 8a, b).

Table 5 Gas chromatographic results and some determined parameters of Arguvan samples

Sample number parameter	Akb-2	K-01	A-02	A-03	P-03	P-11	P-10	P-06	P-07	P-08
Pristane (Pr) %	0.09	0.25	0.97	0.19	0.36	0.21	0.37	0.40	0.39	0.21
n-C_{17} %	0.26	0.42	0.42	0.73	0.15	0.33	0.31	0.33	0.29	0.17
n-C_{18} %	0.41	0.75	0.47	0.83	0.34	0.49	0.44	0.47	0.35	0.24
Phytane (Ph) %	0.12	0.54	0.32	0.23	0.22	0.35	0.46	0.48	0.50	0.29
Pr/n-C_{17}	0.35	0.60	0.31	0.26	0.24	0.64	1.19	1.21	1.34	1.24
Ph/n-C_{18}	0.29	0.72	0.68	0.28	0.65	0.71	1.05	1.02	1.43	1.20
Pr/Ph	0.75	0.72	0.68	0.28	0.65	0.71	1.05	1.02	1.43	1.20
Pr/(Pr + Ph)	0.62	0.46	0.89	0.44	0.45	0.38	0.43	0.55	0.75	0.45
Short chain n-alkanes ($< n$-C_{20}) (%)	2.39	3.27	4.76	9.43	3.89	3.32	3.87	4.29	3.47	2.26
Medium chain n-alkanes (n-C_{21}-n-C_{25}) (%)	11.80	14.36	9.40	17.82	15.76	7.62	13.67	14.11	10.85	11.32
Long chain n-alkanes (n-C_{25}-n-C_{35}) (%)	85.81	82.37	85.83	72.75	80.35	89.06	82.46	81.60	85.68	86.42
Main n-alkane component	nC_{31}	nC_{27}	nC_{29}	nC_{31}, nC_{29}	nC_{29}	nC_{29}	nC_{29}	nC_{29}	nC_{29}	nC_{29}
n-C_{17}/n-C_{31}	0.01	0.05	0.02	0.07	0.02	0.02	0.03	0.04	0.02	0.01
CPI_{25-34}	2.66	2.64	4.60	2.64	2.51	4.36	3.84	3.75	4.27	5.06
OEP_2	3.20	5.62	4.78	5.63	5.60	5.84	3.69	5.56	5.20	2.82
TAR	42.88	47.21	61.64	103.25	52.24	50.22	47.11	32.67	44.58	12.28
Wax ratio	16.92	14.52	18.67	8.6	21.06	25.40	22.40	20.40	26.78	25.47
P_{aq}	0.16	0.17	0.12	0.13	0.16	0.08	0.20	0.34	0.10	0.34
P_{wax}	0.85	0.86	0.90	0.88	0.87	0.93	0.84	0.79	0.92	0.85
Q_w/p	0.55	0.79	0.72	0.60	0.76	0.72	0.84	0.84	0.75	0.78
Q_g/p	0.45	0.21	0.28	0.40	0.24	0.28	0.16	0.16	0.25	0.22
Amount of extract (ppm)	1057	1723	2269	260	410	1973	5202	2449	3458	4143

CPI: $(nC_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{24} + C_{26} + C_{28} + C_{30} + C_{32}) + (C_{24} + C_{26} + C_{28} + C_{30} + C_{32})/(C_{26} + C_{28} + C_{30} + C_{32} + C_{34})$ (Bray and Evans 1991)

OEP_2: $(nC_{25} + 6nC_{27} + nC_{29})/4(nC_{26} + nC_{28})$ (Scalan and Smith 1970)

TAR: (Terrestrial/Aquatic Organic matter ratio); $(C_{27} + C_{29} + C_{31})/(C_{15} + C_{17} + C_{19})$ (Bourbonniere and Meyers 1996)

Wax ratio (WR): $\sum(nC_{21}\text{-}nC_{31})/(nC_{15}\text{-}nC_{20})$ (Zheng et al. 2007)

P_{aq}: Aquatic plant rate $(nC_{23} + nC_{25})/(nC_{23} + nC_{25} + C_{29} + C_{31})$ (Ficken et al. 2000)

P_{wax}: Waxy plant rate $(C_{27} + C_{29} + C_{31})/(C_{23} + C_{25} + C_{27} + C_{29} + C_{31})$ (Zheng et al. 2007)

Q_w/p: Wood/plant ratio $(C_{27}/C_{29})/(C_{27} + C_{29} + C_{31})$ (Bourbonniere and Meyers 1996)

Q_g/p: Herb/plant ratio $(C_{31}/(C_{27} + C_{29} + C_{31})$ (Bourbonniere and Meyers 1996)

This data is consistent with the results obtained in the petrographical evaluation of coal samples, and shows the dominance of terrestrial organic matter (Table 3, Fig. 6a).

N-alkane and isoprenoid ratios are also used so as to determine the type of organic matter (Peters and Moldowan 1993; Peters et al. 2005). In the studied samples, the n-alkane distributions are in the range of n-C_{11} and n-C_{35} and the long chain hydrocarbons in the range of nC_{25}–nC_{31} are the dominant peaks (72.75%–89.06%). Medium chain hydrocarbons in the range nC_{21}–nC_{25} in the total n-alkane composition are 7.62%–17.82% and short-chain n-alkanes are found in the ratio of 2.26%–9.43% (Table 5). Short-chain n-alkanes are formed from algae and microorganisms and as shown in Table 3; the low rate of alginite in the composition (1%–3%) is also supported by low hydrogen index and high oxygen index values (Ficken et al. 2000) (Table 4).

The abundance of long-chain n-alkanes in immature coals indicates that the primary organic material is terrestrial plant waxes (leaves) rich in cuticular and waxy constituents of long-chain fatty fatty acids, alkanoids and their esters (Eglinton and Hamilton 1967; Tissot and Welte 1984; Zdravkov et al. 2011; Yalçın Erik 2011; Fabianska et al. 2012). According to Schwark et al. (2002), the increase in nC_{27} and nC_{29} components in long chain n-alkanes indicates high terrestrial plants in forests, and nC_{31} indicates herbaceous components.

As in the studied examples, high nC_{31} in the composition (8.89%–18.34%) (Fig. 7a) indicates the waxy constituents (wax) of either grass/weed or temperate climate plants such as the ones in Bourgas and Maritza East

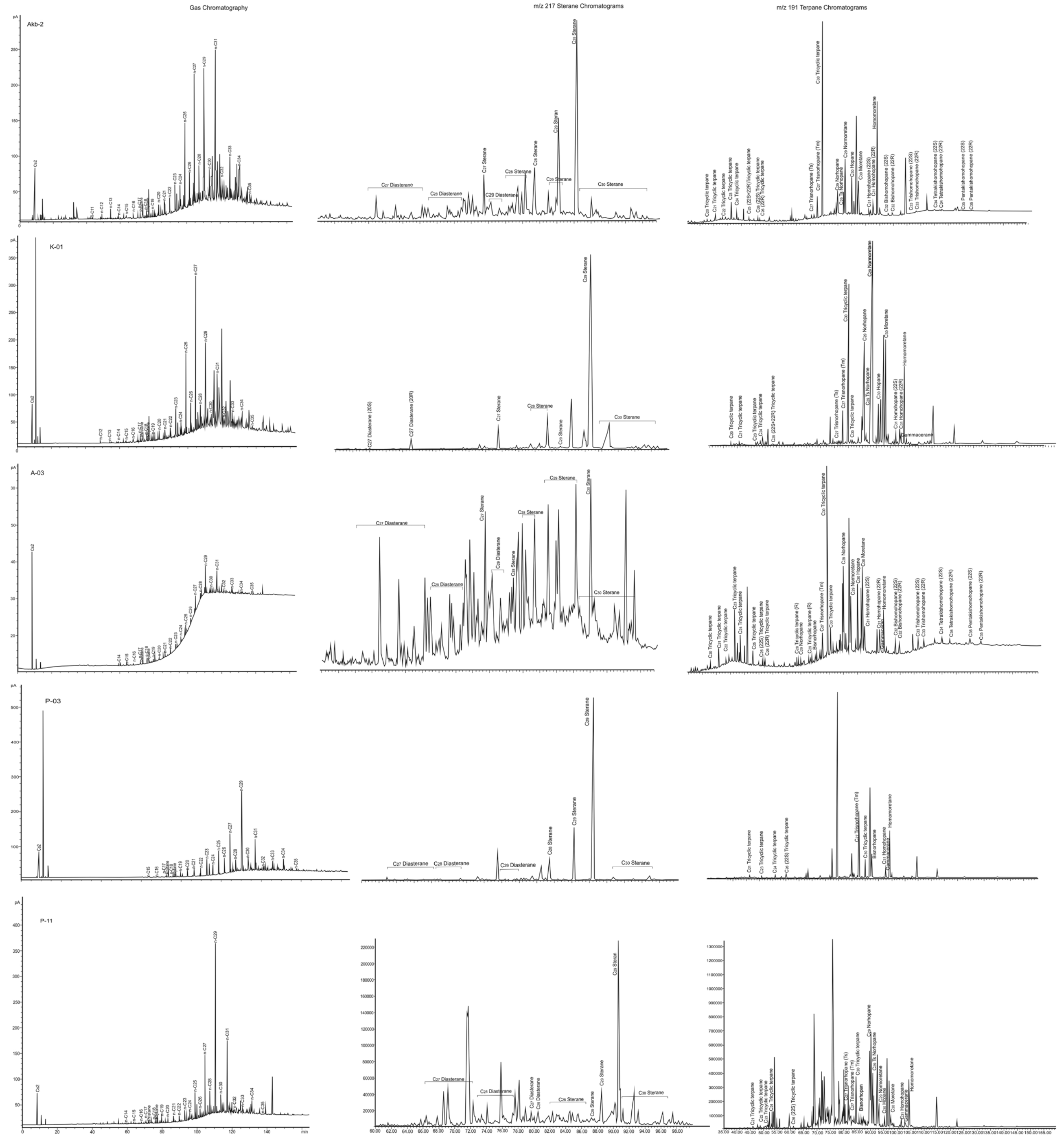

Fig. 7 Gas chromatographic (**a**) and gas chromatography–mass spectrometry chromatograms (**b**, **c**) of the investigated coals

(Bulgaria) coals (Schwark et al. 2002; Bechtel et al. 2005). In varying proportions of the composition, medium-chain n-alkanes are composed of vascular plants, microalgae, cyanobacteria, Sphagnum spp (algae) and aquatic plants (Ficken et al. 2000; Nott et al. 2000).

The biomarker parameters calculated for the Arguvan samples are listed in Table 5. The carbon preference index (CPI) and Odd-to-even predominance (OEP) may be used as an indicator of the source of the OM (Misra et al. 2020). The carbon preference index (CPI_{24-34}; Bray and Evans 1961) values range between 2.51 and 5.06, and indicate higher plant source for the organic matter. In studied samples, even though the values are in accordance with the low rank, the slightly low values could be caused by high

Table 6 Biomarker parameters calculated from *m*/*z* 217 and *m*/*z* 191 mass chromatograms

Bıomarker parameters		P-03	P-06	P-07	P-08	P-10	P-11	Akb-2	K-01	A02	A03
Steranes	Sterane/17α Hopane ratio	7.79	3.24	3.17	3.90	1.67	2.31	5.37	4.9	2.05	1.99
	C_{29} 20S/(20S + 20R) Sterane ratio	–	–	0.03	1.44	0.03	0.03	0.10	1	0.07	0.47
	$\beta\beta/(\beta\beta + \alpha\alpha)$ Sterane ratio (C_{29})	0.23	0.20	–	0.21	0.20	0.15	0.34	0.97	0.21	0.45
	C_{28}/C_{29} Sterane ratio	–	0.27	3.53	4.57	3.65	1.78	1.87	23.07	0.92	1.06
	C_{29}/C_{30} Sterane ratio	1.51	5.24	4.31	5.21	6.46	17.78	0.67	3.27	2.67	1.43
	Diasterane/(Diasterane + Regular Sterane) ratio ı, C_{27}	0.04	1.18	0.15	0.94	1.44	0.98	0.58	–	0.55	0.96
	% C_{27} Sterane ratio	11.87	8.22	8.34	10.16	9.37	5.15	14.26	35.17	7.42	35.60
	% C_{28} Sterane ratio	9.18	6.23	6.35	10.55	7.22	4.26	16.74	51.84	6.16	29.13
	% C_{29} Sterane ratio	78.94	85.55	85.31	79.28	83.41	90.60	69.0	12.03	86.43	35.27
Terpanes	C_{24} Tetracyclic terpane/C_{26} Tricyclic terpane	0.71	0.21	0.38	0.31	0.26	0.31	1.02	0.25	–	0.41
	C_{31} Homohopane/C_{30} Hopane ratio	0.47	1.60	0.83	0.91	1.61	0.63	0.32	0.39	0.48	0.36
	$C_{35}/(C_{31}–C_{35})$ Homohopane Ind.	–	–	–	–	–	–	0.07	–	–	0.08
	Moretane/Hopane ratio	1.27	2.22	1.13	1.33	2.70	1.12	0.90	2.62	0.68	0.36
	22S/(22S + 22R) Homohopane ratio (C_{31})	–	–	–	–	–	–	0.42	–	0.56	0.59
	$Ts/(Ts + Tm)$ ratio	–	0.44	0.30	0.41	0.48	0.69	0.11	0.06	–	0.22
	Gammacerane index	0.06	0.37	0.27	0.35	0.42	0.40	–	0.20	0.18	0.10
	C_{23}/C_{24} Tricyclic terpane ratio	2.52	1.00	1.92	0.51	1.25	0.31	2.16	0.86	0.77	1.89
	C_{22}/C_{21} Tricyclic terpane ratio	0.46	0.74	0.41	0.51	0.88	1.14	0.41	–	1.31	0.26
	C_{24}/C_{23} Tricyclic terpane ratio	0.40	1.0	0.52	1.97	0.80	3.27	0.46	1.16	1.30	0.53
	C_{27}/C_{29} Tricyclic terpan rate	0.19	0.33	0.29	0.46	0.33	0.20	0.95	0.27	0.22	0.35
	C_{25}/C_{26} Tricyclic terpane ratio	–	0.2	0.4	0.42	–	–	0.89	0.25	–	0.74
	C_{23} Tricyclic terpane/C_{30} Hopane	0.13	0.26	0.24	0.30	0.36	0.17	0.32	0.06	0.47	0.44
	ETR$(C_{28} + C_{29})/(C_{28} + C_{29} + Ts)$	1.0	0.89	0.90	0.82	0.86	0.70	0.98	–	1.0	0.88
	Tm/Ts ratio	6.99	1.30	2.31	1.42	1.10	0.46	8.37	15.22	4.40	1.52
	Norhopane/Hopane ratio	1.3	4.24	3.08	3.92	5.54	11.44	0.61	2.51	1.66	1.27

microbial activity on the organic matter (Hunt 1995; Peters et al. 2005; Yalçın Erik and Sancar 2010; Yalçın Erik 2011; Yalçın Erik and Ay 2013; Hos-Çebi and Korkmaz 2013).

However, it is stated in recent studies that $CPI_{24–34}$ value also affects petrographic composition. For example, in Poland (Konin and Turolszow coals), in the Czech Republic and some coals in Greece, it was observed to be different in organic geochemical evaluations, and $CPI_{24–34}$ values were also different because of lithotype differences (Siavalas et al. 2009; Zdravkov et al. 2011; Fabianska et al. 2012; Havelcova et al. 2012). In general, the average CPI value of xylitic coals 2.8, in detritic and 4.2 in detoxylitic coals and fusinitic lignites were found to be 1.88–1.78 on average (Fabianska et al. 2012). Possible reasons for this can be the changes in the amount of low fatty acid containing mainly n-alkanes with a single carbon number in cuticular waxy constituents rather than changes in environmental conditions or maturity (Fabianska et al. 2012).

Odd even preference index (OEP 2, for long-chain n-alkanes) is calculated (OEP 2 = $1/4[(nC_{25} + 6\ n\text{-}C_{27} + n\text{-}C_{29})/(n\text{-}C_{26} + n\text{-}C_{28})]$, Stojanović et al. 2012) in between 1.90 and 2.62. The odd-numbered/even-numbered *n*-alkan ratios (OEP), which are used to determine the organic matter type by using n-alkanes, are between 2.82 and 5.84 in the examined samples (Table 5). The terrigenous/aquatic ratio (TAR; Bourbonniere and Meyers 1996) for the samples varies from 10.67 to 72.5. The higher ratio (> 1) indicates the relative variation in the terrigenous against aquatic input (Peters et al. 2005) and immature sediments composed of terrestrial plants (Bourbonniere and Meyers 1996; Peters et al. 2005).

The Paq determines the input of submerged/floating aquatic macrophytes relative to emergent and terrestrial organic matter. The proxy aqueous (Paq; Ficken et al. 2000) index of the samples varies from 0.24 to 0.35. In modern plants, these values correspond to the emergent

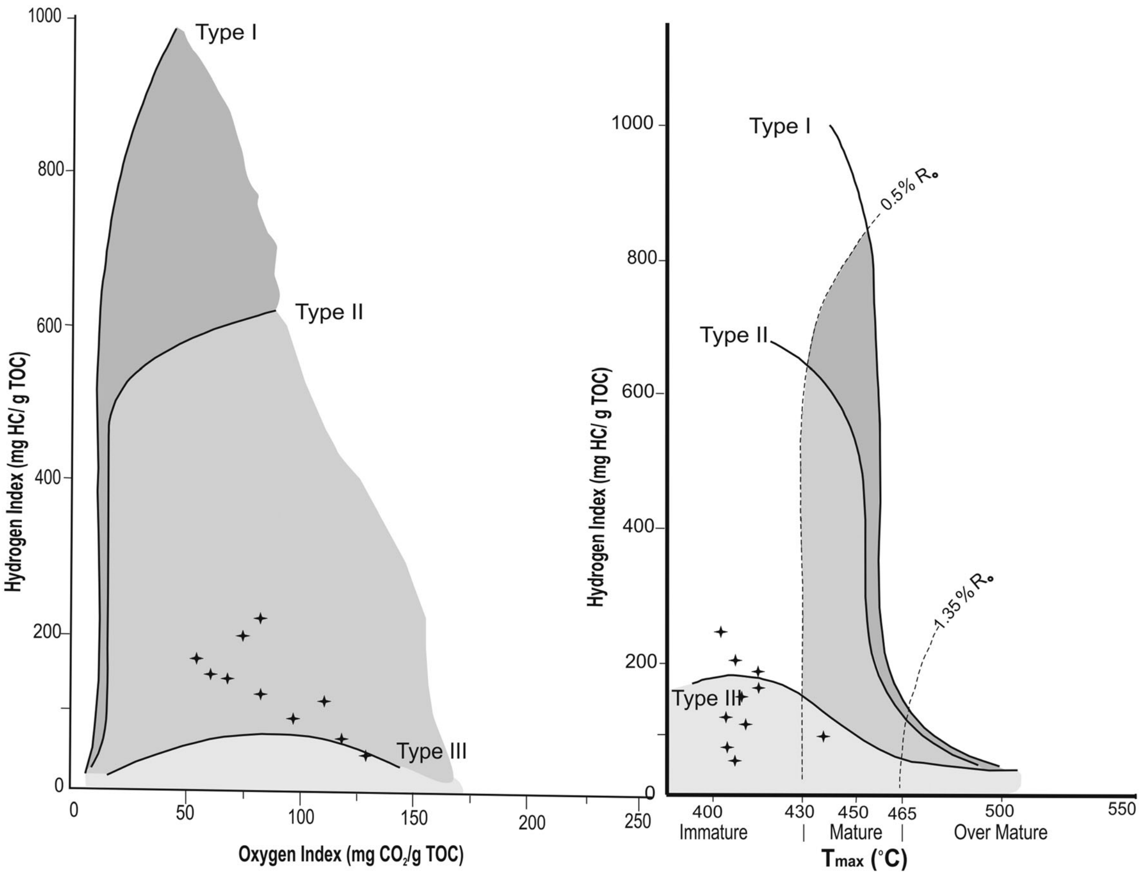

Fig. 8 Van Krevelen (hydrogen index vs. oxygen index) and hydrogen index versus T_{max} (°C)

macrophytes. However, in sediment extracts these values can indicate a mixed organic matter source.

In the studied samples, the $n\text{C}_{17}/n\text{C}_{31}$ ratio (0.02–0.11) (Bray and Evans 1961; Hunt 1995) and degree of wax (Connan and Cassou 1980), $P_{\text{wax}} > P_{\text{aq}}$ and $n\text{C}_{23}/(n\text{C}_{27} + n\text{C}_{31})$ values also support the result of domination of terrestrial organic matter. However, although the terrestrial plants are dominant, wood/plant ratio (Q_{w}/p) and weed/plant ratio (Q_{g}/p) of grassy and grass type short, low cellulose ratio of plants living around the lake show the enrichment (Peters et al. 2005) (Table 5).

The acyclic isoprenoids pristane (P_{r}) and phytane (P_{h}) are observed in relatively low concentration. The pristane/phytane ratio ranges between 0.28 and 1.43.

In addition, sterane and terpan distributions reflect the types of organic matter (Tissot and Welte 1984; Peters et al. 2005). The presence of $\text{C}_{29} > \text{C}_{28} > \text{C}_{27}$ ααα (20R) sterane in the Arguvan coal samples indicates that mainly high terrestrial plants and later herbaceous plants are dominant in peat formation and small amounts of lacustrine algae are added to the composition (Peters et al. 2005) (Fig. 6b).

However, terpane compositions and paleoenvironment indexes may also indicate the type of organic matter as well as the maturation value (Peters and Moldowan 1993; Peters et al. 2005). The Arguvan coal samples are characterized by the high relative abundance of pentacyclic triterpenes with a maximum abundance of hopanoids. Very low concentrations of C_{21}, C_{23} and C_{28} tricyclic terpane in coal samples from Arguvan, and the high amount of C_{19}-C_{21} tricyclic relative to C_{23} ($\text{C}_{19} + \text{C}_{20}/\text{C}_{23}$ tricyclic terpan ratio) refer to the input of terrestrial organic matter (Peters et al. 2005) (Table 6). Furthermore, the presence of the C_{29} Ts18α (H)-Norhopane (C_{29}Ts) component (Fig. 7b, c), and C_{29} Ts 18_{α}(H)-Norhopane/(C_{29}Ts18_{α}(H)-Norhopane + $\text{C}_{29}17_{\alpha}$(H), 21_{β}(H)-Norhopane ($\text{C}_{29}\text{Ts}/\text{C}_{29}\text{Ts}$ + Norhopane) with ratios, and the presence of $\text{C}_{29}17_{\beta}$(H),21_{α}(H)-30Normoretane and $\text{C}_{30}17_{\beta}$(H), 21_{α}(H)-Moretane show that organic matter is of terrestrial origin (Philip and Gilbert 1986). Abundance of hopanoids in the studied samples indicates the considerable contribution from bacterial source to these sediments. Abundance of 17_{α}(H), 21_{β}(H)-homohopane (R) has been reported previously from low rank coals (Singh et al. 2017a).

This also suggests that these sequences might have been deposited in a more oxic and acidic environment (Źivotić et al. 2014). Extended hopanes are represented by 17_{α}(H), 21_{β}(H)-homohopanes (both 22R and 22S epimers), 17_{β}(H),

21_β(H)-homohopane and 17_β(H), 21_β(H)-bishomohopane. Bacteriopolyhopanol, a compound present in the prokaryotic cell membrane is found to be the precursor of homohopanes (Waples and Machihara 1991; Peters et al. 2005).

The identified triterpenoids other than hopanoids include tetra- and pentacyclic compounds with oleanane, and lupane skeletons. Also, they are found to constitute very low amount in the composition of oleanane (Fig. 7c), and this indicates that plant material is denser by gymnosperm-derived plants rather than angiosperms (Peters et al. 2005). According to all these data, it can be said that terrestrial plants are dominant in the paleo-swamp environment. However, beginning from the reed plants, grasses near the water, herbaceous components near the marsh near the drier forest area, a developing vegetative accumulation, and to a lesser extent, woody components with high cellulose content, and high terrestrial plants and algae were also included in the composition (Peters and Moldowan 1993; Peters et al. 2005).

5.2.2 Organic maturity

As a result of the evaluation of Hydrogen Index (HI) and $T_{\max}$ (Mukhopadhyay et al. 1995), most of the samples are suitable for vitrinite/huminite reflection values ($R_{\max}$ values 0.38%–0.51%) and indicate the immature stage (Fig. 8b). Production index (PI) which is another maturity parameter obtained by pyrolysis analysis is in the range of 0.02–0.07 and together with the $T_{\max}$ data, and it indicates the diagenesis stage for immature sediments and hydrocarbon generation (Peters 1986; Hunt 1995; Wilkins and George 2002) (Table 4). Besides these data, low extracts of samples, $\beta\beta$ hopans, 17_β (H) trisnorhopane, presence of olefinic components and triterpanes, CPI_{24-34} values, C_{32} 22S/22S + 22R homohopane ratios, C_{23} tricyclic terpane/(C_{23}Tricyclic terpane + C_{30} hopane) $Ts/Ts + Tm$ ratio, moretane/hopane ratio, 20S/20S + 20R and $\beta\beta/\beta\beta + \alpha\alpha$, diasterane index values also indicate immature phase especially for hydrocarbon formation (Seifert and Moldowan 1986) (Tables 5 and 6).

5.2.3 Paleo-mire and coal facies characteristics

Facies analysis, palynology and sedimentological data are widely used in the determination of the coalification process and the characteristics of the depositional environment. The most common used petrological parameters in the paleo-environment and facies assessment of coals are tissue preservation index (TPI) and gelification index (GI), vegetation index (VI) and groundwater effect index (GWI). Changes have been made in this evaluation method by Calder et al. (1991) and Lamberson et al. (1991), in addition, some changes were made for coal with low carbonization degree by Kalkreuth et al. (1991).

Although there is a disagreement among the researchers regarding the interpretation of these data (Moore and Shearer 2003; Sen et al. 2016), TPI/GI and GWI/VI data continue to be used for paleo-depositional interpretation (Kalkreuth et al. 1991; Calder et al. 1991; Kalkreuth et al. 2000; Flores 2002; Siavalas et al. 2009; Singh and Singh 2000; Yalçın Erik 2011; Sia and Wan Hasiah 2012; Singh et al. 2013; Bechtel et al. 2014; Sen et al. 2016; Hoş Çebi and Korkmaz 2013). However, a more accurate interpretation can be obtained by multidisciplinary approaches (Scott 2002; Moore and Shearer 2003).

In Arguvan coal samples, TPI, GI, GWI and VI indices were calculated according to modifications introduced by Kalaitzidis et al. (2004) and Scott (2002) for Miocene low-rank coals. The TPI measures the degree of humification of the peatforming organic matter. A high TPI value (> 1) reflects equilibrium between the growth and accumulation of plant materials, rise of the water table, and domination of tree vegetation. A low TPI suggests either predominance of herbaceous plants in the mire or large-scale degradation of plant tissues as a result of advanced humification (Diessel 1992). The TPI also indicates the pH conditions of palaeomires because in a low pH conditions, microbial activity is weak and plants can be well preserved, and vice versa. Tissue Protection Index (TPI) value of Arguvan field samples ranged from 0.14% to 0.33% (Table 3).

The GI is the ratio of gelified versus non-gelified macerals and indicates the wetness in peat-forming environment. High GI value is indicative of a high moisture/water level and higher subsidence rate and vice versa. The gelification index (GI) value in the investigated samples ranges between 0.38% and 2.86%.

The VI is related to the type of vegetation that dominated the mire. It is dependent on the type of peat-forming plant communities (e.g. trees and bushes). VI generally indicates an aqueous environment in which herbaceous plants develop, as well as an area with woody plants.

Groundwater effect index (GWI) values were between 2.00% and 8.22%, while vegetation index (VI) values were determined between 0.38% and 0.82% (Table 3). This data generally indicates the dominance of herbaceous vegetation in the palaeomire (Kalaitzidis et al. 2004; Silva et al. 2008; Siavalas et al. 2009). This GWI values indicate ombrotrophic hydrological conditions (Fig. 9a).

TPI values are generally low; GWI is greater than 1 and VI is generally less than 1, also gastropod shells with high pyrite content indicate limnotelmatic environment (Fig. 9b). Low TPI and GI values were either dependent on the type of plant material (high angiosperm/gymnosperm ratio) or they developed according to low tissue protection conditions. As determined in the Arguvan coals, medium–

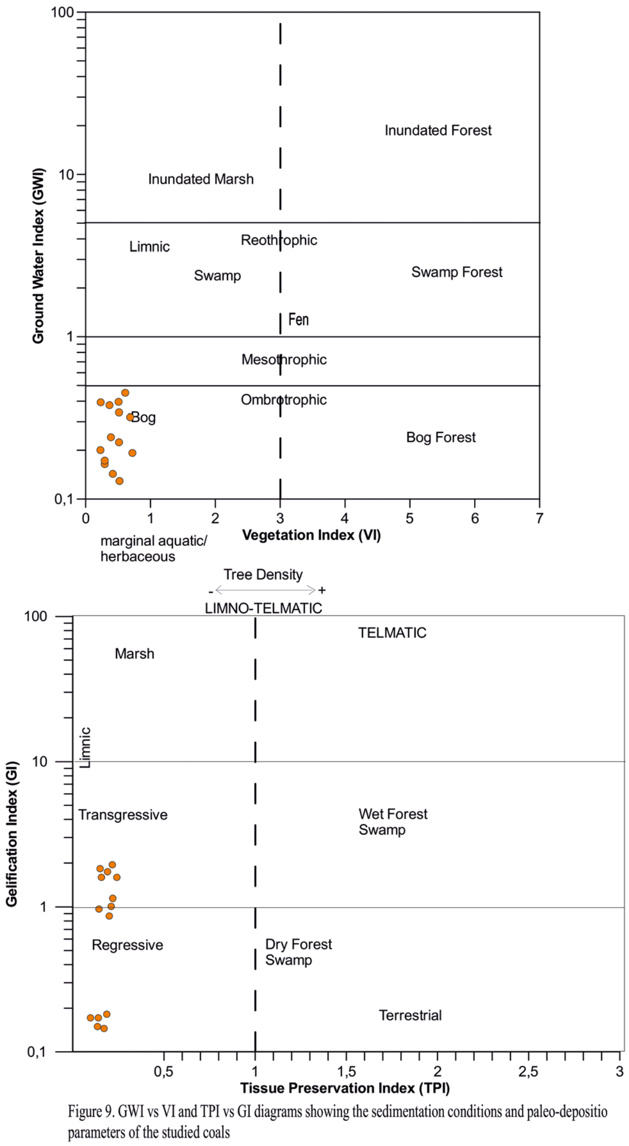

Fig. 9 GWI versus VI and TPI versus GI diagrams showing the sedimentation conditions and paleo-depositio parameters of the studied coals

high GI-GWI values indicate variable water level, and relatively medium–high sulfur content refers to alkaline, calcium-rich waters and changing P_h values (Casagrande 1987; Bechtel et al. 2003). In addition, according to Flores (2002) organic facies characteristics, the coals around Arguvan are rich in herbaceous plants and deposited in a wet forest and dry–wet mixed swamp environment.

In this environment, the water level usually covers the paleotopography and generally suboxic-anoxic conditions prevail. In wet forest facies, humotelinite ratio (ulminite) is abundant, and in mixed marshes, humodetrinites are dominant, and to a lesser extent, resinites and subberinites are accompanied. Abundance of inertinite macerals such as fusinite after humunite maceral group shows fires and decreasing water level in the marshes, thus surface oxidation (Flores 2002). The richness of the studied coals in terms of sporinite and clay minerals also indicates degradation due to reeds and underwater conditions as well as bacterial activity.

The medium–high sulfur content in the coals studied can be explained by the composition of the primary organic material or by marine or brackish water conditions affecting the depositional environment. Framboidal pyrites are related to the presence of sulfate-rich waters, and anaerobic bacterial activity during the formation of peat showed that the paleo temperature value could be between 100 and 125 °C (Rort, 0.38%–0.45%) according to the reflection value of Arguvan coals (Boggs 1987).

Isoprenoid and *n*-alkane data of the studied samples are also used in the interpretation of the precipitation medium. For example, the Pr/Ph ratio is directly related to the redox conditions of the precipitation medium (Didyk et al. 1978; ten Haven et al. 1987; Tissot and Welte 1984; Peters et al. 2005; Fabianska et al. 2012; Powell et al. 1991). High P_r/P_h ratio (> 3.0), oxidized, low rates (< 0.6) anoxic, values between 1.0 and 3.0 indicate suboxic conditions (Peters and Moldowan 1993). For example, in coal in SE Asia, it was reported that the P_r/P_h ratio was > 4 and it showed peat marsh in oxic conditions (Zulkifli et al. 2008). The same situation is laso valid for Pinangah coals (Malaysia) (Alias et al. 2012; Hakimi et al. 2013) and many Tertiary-aged Turkish coal gave similar results (Yalcin Erik and Sancar 2010; Yalcin Erik 2011; Yalcin Erik and Ay 2013; Bechtel et al. 2014; Hoş Çebi and Korkmaz 2013).

P_r/nC_{17} (0.26–2.4) and P_h nC_{18} (0.28–1.43) values were found to be similar to Tertiary coal in Bulgaria and Poland (Zdravkov et al. 2011; Havelcova et al. 2012). The P_r/nC_{17} and P_h/nC_{18} diagrams indicate oxidation–reduction conditions in the precipitation medium (Fig. 10). Fabianska et al. (2012) indicated the water washing effect of coals and stated that these results in Tertiary aged coal in Poland reflect the alteration effect and do not fully show the environmental characteristics. According to Fabianska et al. (2012), the water washing effect during or after carbonization is characterized by features such as low extract value in organic matter, destruction of methylnaphthalenes and sometimes removal of low carbon number *n*-alkanes. The low levels of nC_{17} in the organic composition are supported by the low amount of alginite in the petrographic composition, for this type of paleo bog wet, forest-reed bog sedimentation medium (in the lower delta plain) was determined. However, as in the Parcikan coal samples, P_r/nC_{17} ratios varying generally from moderate to high (greater than 1 or nearly 1) are related to coal formation in the continental and limnotelmatic environments. Similar results were obtained in Tertiary aged coal

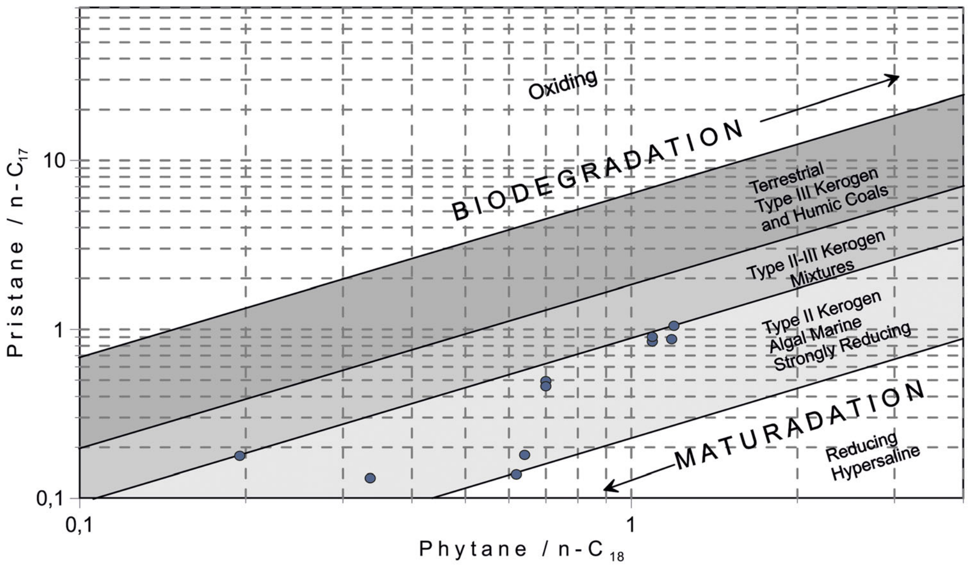

Fig. 10 P_r/nC_{17} versus P_h/nC_{18} diagrams showing the characteristics of sedimentation environment of the investigated coals P_r/nC_{17}–P_h/nC_{18} diagrams

in Sumatra basin (Indonesia) by Amijaya and Littke (2005).

Sterane and terpane data of coals are important to explain the paleoenvironment characteristics (Peters 1986; Peters et al. 2005; Alias et al. 2012). Homohopans are present in all samples of the Arguvan coals, and the decrease in the 17_{α} (H), 21_{β} (H)—homohopane ratios in the C_{31}–C_{35} range is typically observed for clastic facies (Waples and Machihara 1991; Peters and Moldowan 1993) (Fig. 7b, c). The presence of hopanoids indicates the presence of bacterial organisms (Simoneith 1986), which is especially typical of coals in Indonesia (Amijaya et al. 2006).

In Arguvan coals, α, β-C_{31} hopanes are at very low rates and 17_{α} (H), 21_{β} (H)-30 norhopane dominance is a characteristic for humotelinite rich coals (Amijaya et al. 2006). The hopane content is higher in detritic lignites (> 80%), increasing the hopane ratio with increasing gelification rate, which generally refers to the increase in ulminite content (Georgakopoulos and Valceva 2000; Sykorová et al. 2005).

*T*m/*T*s ratios may also reflect paleoenvironment properties; high values indicate oxic conditions during sedimentation (Peters et al. 2005). The high *T*m/*T*s values determined in the studied samples are consistent with the P_r/P_h ratios and indicate that the swamp formed by atmospheric precipitation (ombrogenous paleomire) is exposed to oxic conditions showing periodic change in the upper part (Ten Haven et al. 1987; Peters et al. 2005). A similar situation was also determined by Amijaya et al. (2006) in coal in Malaysia. However, it is seen that low proportional changes in *T*s and *T*m values may be related to maseral composition. The highest rates are in the coal rich in humocollinite (Amijaya and Littke 2005; Stojanović et al. 2012; Misra et al. 2020). In addition, high $C_{29}17\alpha$ (H), 21β (H)-30-Norhopane values accompanying, low “17α (H) -28,30-Bisnorhopane” deltaic deposition conditions and low rate of marine organic matter doped, refer to sovereign terrestrial organic matter accumulation, and low diasterane/sterane, low C_{23} tricyclic terpane/C_{23} tricyclic terpane + C_{30} hopane rates also support this data (Peters et al. 2005).

Also, gammacerans and pregnans are high salinity markers, βα-Moretane/αβ-hopane (moretane/hopane) ratio, low P_r/Ph (Ten Haven et al. 1987), and P_r/n C_{17} and Tm/Ts ratio and low–high norhopane/hopane ratios also indicate anoxic and refer to the low-moderate salinity conditions (Waples and Machihara 1991; Peters and Moldowan 1993; Hunt 1995; Peters et al. 2005; Alias et al. 2012; Stojanovic et al. 2012).

It can be said that the suboxic-anoxic conditions of Arguvan coals change periodically with high ash and sulfur content, topogenic, eutrophic swamp (in an elevated terrestrial area) and high mineral matter rate. It can also be said that there is an autochthonous-hypotoctonous coal formation that develops in limnotelmatic environment where there is not much intake of epigenetic clastic material. In addition, petrographic data of these coals are drawn in ternary diagrams. In these diagrams, the presence of mixed vegetation in the paleomire environment is indicated (Fig. 6c, d). Besides, the abundance of detrohuminite mixed up with liptodetrinite in some samples indicates significant contribution of reed/sedge vegetation. Appropriate pH and water-level conditions can be another explanation for the good preservation of cell structure. Almost all samples are projected on the lowest part of the Mukhopadhyay's diagram indicating relatively strong anoxic conditions in the northern part of the deposit in comparison to the eastern one; this suggests rather high and relatively stable water table in the palaeomire during peat accumulation (Fig. 6c) (Diessel et al. 2010; Silva et al. 2008).

5.3 Source rock potential

As in the examples in the study area, humic coals contain richer organic matter content (generally $< 10\%$ TOC) than conventional oil/gas source rocks, predominantly composed of type III and Type II/III kerogen, and have gas generation potential (Hunt 1995; Wilkins and George 2002; Petersen 2002). However, for Hedberg (1968), Sykes (2001), Petersen (2002) the hydrogen index (HI), which indicates the abundance of hydrogen in coals is more important than the total organic carbon (TOC) value. In general, they stated that values higher than > 200 mgHC/g (Hunt 1995) are necessary for generation. The TOC values of Arguvan samples evaluated within this scope vary between 2.61% and 43.02%, hydrogen index (HI) values between 73 and 229 mgHC/g and H/C values between 0.91 and 6.71. In addition, S2/S3 values are between 0.59 and 3.34, and production index (PY) is 5.57–87.22. S1 values are between 0.32 and 2.31, and S2 values are between 5.25 and 84.91 mgHC/gTOC. According to these values, it can be said that only P-08 and A-04 samples have gas generative potential (Tissot and Welte 1984; Peters 1986; Hunt 1995; Sykes and Snowdon 2002) (Fig. 11). However, as stated by Killops et al. (1998), the bitumen index of these samples is quite low for species $(\mathrm{BI} > 10)$ and removal $(\mathrm{BI} > 10)$ (0.02–0.12) (Table 4). Considering the rank related increase in HI of low-rank coals (Sykes and Snowdon 2002), none of the samples exceed the minimum HI of 300 mg HC/g TOC required for oil generation (Pepper and Corvi 1995) when their thermal maturity reaches the onset of oil expulsion (''effective HI'' of Sykes and Snowdon 2002) (Fig. 11).

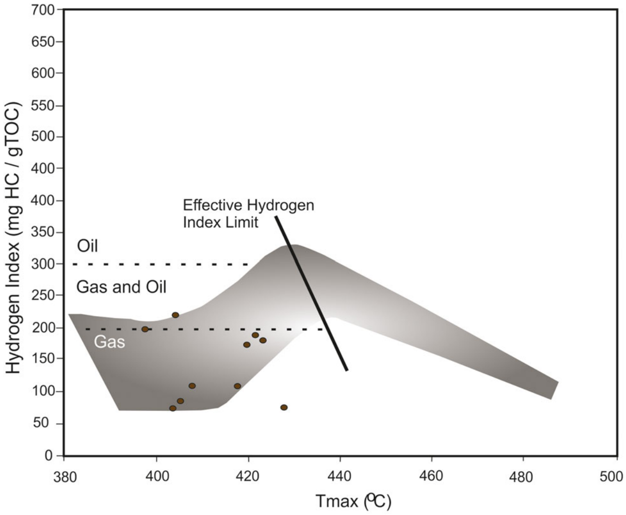

Fig. 11 HI-$T_{\max}$ diagram of Arguvan-Parçikan coals

The hydrocarbon potential in the samples was evaluated mainly by pyrolysis analysis data, and petrological data for coals are also important (Petersen 2002; Fabianska et al. 2012). Generally, the ratio of liptinite macerals $> 15\%$–20% has been found to be very important for hydrocarbon generation from coals (Stach et al. 1982; Petersen 2002; Sykes and Snowdon 2002; Wilkins and George 2002; Alias et al. 2012). For the humic coals of the Dong Ho Basin (Vietnam), which offer petrographic and chemical properties similar to Arguvan coals, and the oil window onset for Konin and Turszow coals in Poland are equal approximately to 1.03%–1.15% R_o. These coals have been mainly derived from oil and gas (Zdravkov et al. 2011; Fabianska et al. 2012). In Arguvan coals, maturation level is not sufficient for hydrocarbon generation according to biomarker maturity parameters and $T_{\max}$ and R_o values, and thus it was concluded that gas type generation could be possible at higher maturity values.

6 Conclusions

Concerning the significance of limited fossil fuel resources of Turkey, lignites/brown coals are of great economic importance as they represent the main source for energy production. A significant number of coal bearing basins with significant coal reserves formed during the Miocene especially in Western Anatolia of Turkey, as a result of different peat-forming conditions. Apart from the economical importance, the hydrocarbon generation potential and geochemical properties of coal-bearing strata have been intensely discussed all around the world. As a result of the floral evolution, especially Cenozoic coals and coaly sediments have higher potential to generate oil compared to older age counterparts.

During this research, the hydrocarbon potential and the paleo-depositional environment characteristics of the lignites from the places around Arguvan in Malatya Tertiary Basin were evaluated based on petrological, bulk organic geochemical parameters and biomarker analysis results. Samples were collected from Parçikan, Akören, Göçeruşağı and Kuyudere coal areas of Arguvan district. Investigated coaly units are composed of rich carbonated and coaly clay levels in coal, clay, organic matter.

Due to the regional intense tectonics, the coaly sequence is folded, broken, and easily fragmented. This lignites are typical humic coals. Calcite bands, pyrite, jarosite, and clay minerals are widely observed in the intermediate levels in the coal units or in veins, lenses, or scattered in the coal vein. The mineralogical composition of the studied samples is dominanted by mineral carbonate and clay (calcite, 4%–96%, dolomite, 7%). The clay minerals in the composition are illite (12%–76%), smectite (21%–63%) and chloride (11%–75%).

The ash yield of the samples is quite high (avr. 80.81 wt%). Total sulfur content is 1.46%, total moisture content 28.69%, volatile matter content 15.45%, and the gross heating value is between 318 and 2027 kcal/kg (avr, 1001 kcal/kg). High values such as 1282–2027 kcal/kg have been determined only for the Parçikan coal mining area samples. The carbon content in the dry basis determined by elemental analysis is 43.41% on average, 5.53% on hydrogen average, 1.23% on average nitrogen. According to ASTM (1983) standards, Arguvan coals are of low quality and low maturity ($R_{\max}$ %), low calorific, high ash, mineral matter and moisture values and potential for industrial use only as domestic fuel, of the type “lower bituminous B/C type coal.

The Arguvan coal is dominated by mixed xylitic/attrital and detritic lithotypes and by huminite macerals (gelinite) (avr. 60.29%) with secondary inertinite macerals (avr. 5.57%) and minor liptinite macerals (avr. 5.29%). Although the coals examined seem physically different from each other, they do not differ greatly as petrographic composition. Local and vertical variations in proportions of huminites and inertinites reflect frequent fluctuations in water levels, periodic flooding, dehydration and burning periods of the paleomire. According to the petrological and organic geochemical characteristics, the paleodepositional environment which formed the investigated coals around Arguvan developed more mixed forest marsh where the herbaceous and reed-crop plants cover wide areas, the water level decreases and the trees are concentrated in more distant areas. Peatification proceeded in a freshwater environment under variable redox conditions, from anoxic to slightly oxic.

Recently, detailed organic geochemical analyses in coal extracts have been used as an effecting tool for assessment of the reconstruction of paleobotanical characteristics and palaeoenvironmental conditions in peatlands during the formation of coal-bearing strata. In the examined samples, the n-alkane distributions are in the range of $n\mathrm{C}_{15}$ and $n\mathrm{C}_{35}$, with long and intermediate chain hydrocarbons being dominant. In addition, TAR, ETR, CPI, $P_{\mathrm{wax}} > P_{\mathrm{aq}}$ and n-$\mathrm{C}_{23}/(n\mathrm{C}_{27} + n\mathrm{C}_{31})$ values support the terrestrial organic matter dominance in paleomire. It can be said that sub-oxic-anoxic conditions are effective during the formation of peat according to n-alkane, isoprenoid and biomarker data. The major biomarkers are C_{30} tricyclic terpane, hopane, homohopane, moretane. In the studied samples, $\mathrm{C}_{29} > \mathrm{C}_{28} > \mathrm{C}_{27}$ steranes indicate the dominance of terrestrial and herbaceous plants, as well as the incorporation of lesser amounts of lacustrine algae. The environment with a high rate of sterane/hopane and a lacustrine or special bacterial activity and a low concentration of pentacyclicterpenes (C_{32}–C_{35}) indicates that biodegradation, and autochthonous/aquatic and allochthonous terrestrial organic materials have accumulated in paleomire during the formation of coals. In XRD and organic petrographical studies, it can be said that the tectonic movements in the swamp are influenced by the appearance of clay minerals and detrohuminites in high order and formation of coal. This situation is also clearly observed in units showing coarse and soft sedimentary deformation in the field.

The total organic carbon (TOC, wt%) values of the samples are between 2.61 and 43.02% and the hydrogen index values are between 73 and 29 mgHC/g TOC. The high TOC is corroborated by the hydrocarbon yield (S2) indicating excellent source rock generative potential for the samples. Based on HI, the Arguvan-Parçikan coal can be classified as being capable of generating gas/oil (> 200 mg HC/g TOC) at higher maturity. Vitrinite reflectance (R_o, %), $T_{\max}$ and biomarker ratios show that the organic matter of the studied samples are thermally immature. When all these data are considered together, Tertiary aged coals around Arguvan are have good hydrocarbon generation potential, especially gas, in terms of organic matter type (Type III and Type II/III mixed), organic matter amount (> 10 wt% TOC), however, low liptinitic macerals (< 15%–20%), low hydrogen index (< 200 mg HC/gTOC) and low thermal maturity values inhibit the hyrocarbon generation.

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