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Coal quality, mineralogy, petrography, and geochemistry of the high-strontium Bozburun lignite (Malatya, eastern Türkiye)

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Research Article

Keywords:

Malatya Basin, Miocene, Maceral, Celestine, Barite.

ABSTRACT

The Bozburun coalfield hosts a late Miocene 1.1 m thick coal seam. This study aims to determine coal quality, mineralogy, petrography and geochemistry, and controlling factors of elemental enrichments. The coals are generally black and greyish black in colour, and the low part of the seam commonly includes fossil shell remains. The ash yield displays a decreasing trend towards the upper part of the seam; in turn, gross calorific and total C values increase upwards. The total S content being generally higher than 5% (on dry basis), displays an increasing trend towards the upper part. In the entire seam, huminite is the most common maceral group, while inertinite and liptinite display variable proportions. The identified minerals by XRD are mainly quartz, clay minerals, calcite, pyrite, and aragonite (in fossil shell remains-bearing samples), whereas feldspars and marcasite determined in a few samples. Furthermore, in the coal samples, celestine and barite were identified by SEM-EDX. This study indicates that precipitation of celestine and Sr-bearing barite grains during diagenetic stage and Sr-uptake by mollusc within the palaeomire caused Sr enrichment in the entire seam. Overall, the water influx and redox conditions controlled the mineralogical and the elemental compositions of the coal seam.

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1. Introduction

The mineralogical and geochemical features of coal and coal combustion remains have been the subject of several studies because of the hazardous elements and critical elements contained (e.g., Dai et al., 2012a, 2020a, b, 2021; Dai and Finkelman, 2018; Hower et al., 2020, 2022). Besides, more recent studies show that these features of coal beds and partings in combination with coal petrography, palaeontological, and sedimentological data could provide significant information about the depositional conditions in the palaeomires (e.g., Finkelman et al., 2019; Dai et al., 2020a; Hood et al., 2020) for this purpose, indicative

elements, and element ratios have been used (e.g., Goodarzi and Swaine, 1994; Dai et al., 2015a, 2018, 2020a; Spiro et al., 2019). For example, distributions of As, U, and Mo contents, along with Th/U ratio, are used for the determination of palaeoredox conditions in palaeomires, while distributions of total S, B, and Mo contents and Sr/Ba ratio serves as palaeosalinity indicator in palaeomires (Goodarzi and Swaine, 1994; Spiro et al., 2019; Dai et al., 2020a; Goodarzi et al., 2020; Çelik et al., 2021). Nevertheless, these index elements and elemental ratios should be used with caution, since coal seams have heterogeneous elemental and mineralogical compositions and certain

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accessory minerals (e.g., barite, chromite, monazite) can increase the concentrations of certain indicator elements (Finkelman et al., 2019; Dai et al., 2020a, b; Karayiğit et al., 2020a, b).

The petrographical and geochemical features of Turkish low-rank coals, particularly of the early-middle Miocene coals in western and central Anatolia, are well documented as a result of their use as feed coals in power plants (Querol et al., 1997; Karayiğit et al., 2000, 2017a; Tuncalı et al., 2002; Palmer et al., 2004). However, the coalfields of eastern Anatolia, with the exception of Kangal and Afşin-Elbistan coalfields, have received less attention (Karayiğit and Gayer, 2000; Karayiğit et al., 2001, 2019; Sütçü and Karayiğit, 2015). The tectonic evolution of eastern Anatolia during late Cenozoic times resulted in the formation of several sedimentary basins (e.g., Afşin-Elbistan, Gölbaşı, Sivas-Kangal and Malatya), which host mineable late Miocene and Plio-Pleistocene coal seams (Tuncalı et al., 2002; Kaymakçı et al., 2006; Sütçü and Karayiğit, 2015; Karayiğit et al., 2016; Yılmaz, 2019; Seyitoğlu et al., 2022). Another result of the tectonic activity is the development of regional volcanic activity from the early Miocene to Pliocene (Figure 1a) (Kocaaslan and Ersoy, 2018; Di Giuseppe

et al., 2021). Hence, volcanic complexes (Yamadağ and Kepezdağ) and volcanic fields (Kangal and Sivas) were developed.

The Bozburun coalfield is located in the Malatya Basin (Figure 2) and hosts a 1.1 m thick economic coal seam. Previous studies have mostly focused on the sedimentological and palaeontological properties of the Cenozoic sedimentary rocks and the petrogenesis of Cenozoic volcanic rocks in the Malatya Basin (Ercan and Asutay, 1993; Türkmen et al., 2004, 2007, 2011; Ekici et al., 2007; Nazik et al., 2008; Koç-Taşgım, 2011). Although coal seam exploitation in the study area began in early 1990s (Önal, 1995), only one coal geology study from the western part of the Bozburun coalfield has been conducted to date. In there, the coal seam displays relatively small thickness, and coal beds-bearing outcrops are located in the northern part of the Malatya Basin (Yalçın-Erik and Ay, 2020). The results of the previous coal geology study show that the coal displays significantly high ash yield and total sulphur content, and the coal is of subbituminous rank. The biomarker data supports the previous palynological results from Önal (1995) and Türkmen et al. (2004), indicating that the peat-forming vegetation was a mix of herbaceous

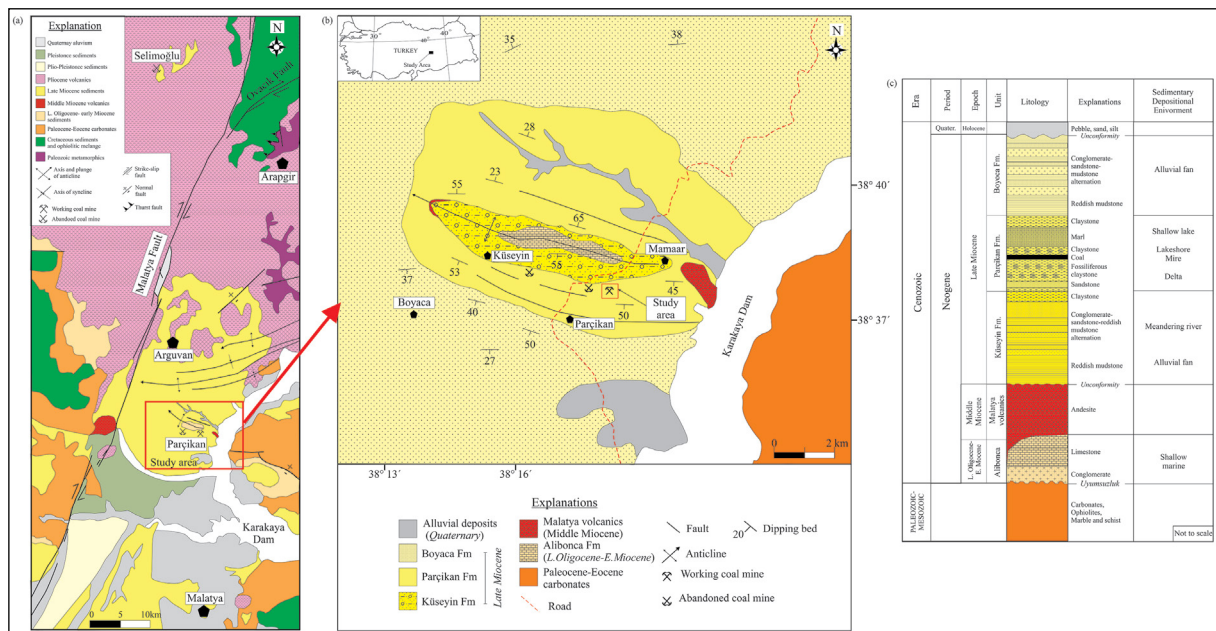


Figure 1- a) Regional geological map of the surrounding area of the Bozburun coalfield (modified from geological map of Türkiye, 1/500.000-scale), b) simplified geological map of the study area (modified from Türkmen et al., 2004; Sümengen, 2016), c) generalized stratigraphic column in the study area (modified from Türkmen et al., 2004).

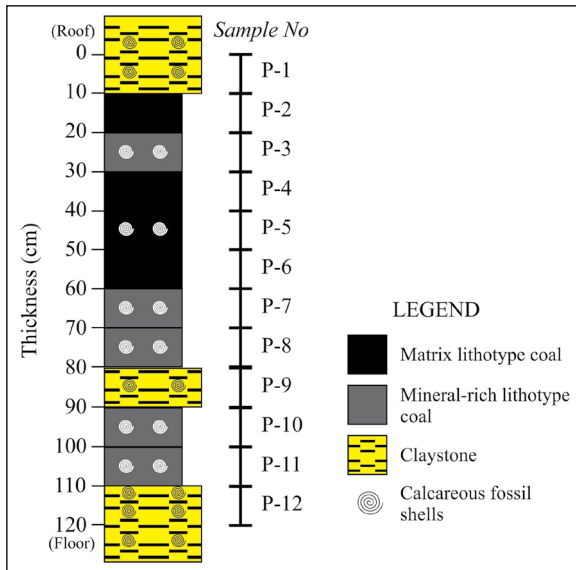


Figure 2- The sampled profile at the Bozburun coalfield.

and woody plants. Nevertheless, detailed elemental composition and paleoenvironmental reconstruction of the Bozburun coalfield are still lacking. Considering the volcanic activity in the Malatya Basin, the coal rank of the Bozburun coalfield might have differences from the northernmost of the Malatya Basin (Figure 1a). Therefore, this study focuses on determining the factors controlling the coal quality, the petrographical, mineralogical, and geochemical features of the late Miocene coal in the eastern part of the Bozburun coalfield and reconstructing the palaeoenvironment during the peat accumulation. The specific goal of the current study is to ascertain factors controlling coal rank variation in the Malatya Basin.

2. Geological Setting

The Bozburun coalfield is located in the southernmost of the NE–SW trending Malatya Basin, which is controlled by the Malatya Fault Zone (Figure 1a) (Kaymakçı et al., 2006; Sançar et al., 2019). The pre-Neogene basement consists of Permo-Triassic Keban metamorphics (marble and schist), middle Triassic-early Cretaceous Kuluncak ophiolite, late Cretaceous Elazığ magmatics (andesite, basalt, diorite, and gabbro), and Palaeocene to late Eocene marine carbonates with gypsum lenses and beds (Figure 1b-c) (Türkmen et al., 2007; Koç-Taşgın, 2011; Sümengen, 2016). The Malatya Basin began developing during early Miocene due to regional extensional tectonic

regime (Kaymakçı et al., 2006). Thus, the Neogene basinal infillings started with late Oligocene (?)–early Miocene shallow marine deposits (Alibonca Formation), and this unit is conformably overlain by middle Miocene Malatya volcanics (andesite and basalt) of the Yamadağ volcanic complex (Ercan and Asutay, 1993; Önal, 1995; Türkmen et al., 2004, 2007; Koç-Taşgın, 2011; Sümengen, 2016; Kocaarslan and Ersoy, 2018; Di Giuseppe et al., 2021). Terrestrial conditions became dominant in the Malatya Basin during the late Miocene and these units inequitably overlay early-middle Miocene units (Figure 1c). The total thickness of late Miocene basinal infillings in the study area is around 1200 m and is divided into three formations (Türkmen et al., 2004, 2007; Nazik et al., 2008; Koç-Taşgın, 2011), from bottom to top, Küseyin Formation, Bozburun Formation, and Boyaca Formation (Figure 1c).

The Küseyin Formation is composed of alteration of conglomerate, sandstone, and reddish mudstone with freshwater mollusc-bearing limestone (Türkmen et al., 2004, 2007; Nazik et al., 2008; Koç-Taşgın, 2011). The sedimentological features of Küseyin Formation imply that the formation was deposited under alluvial fan and meandering river conditions where small freshwater ponds and lakes were developed (Türkmen et al., 2004, 2007; Koç-Taşgın, 2011). The ostracod fauna hosted in sediments suggest freshwater to oligohaline conditions (Nazik et al., 2008). The coal-bearing Bozburun Formation overlies conformably the Küseyin Formation and commences with current- or wave-ripple cross-laminated sandstone, plant remains-bearing greyish green claystone, a coal seam, fossiliferous marl and limestone, and reddish mudstone (Türkmen et al., 2004, 2007; Sümengen, 2016) (Figure 1b). Previous sedimentological and palaeontological studies show that the Bozburun Formation was deposited in shallow lakes associated with peatlands and deltaic areas (Önal, 1995; Türkmen et al., 2004, 2007; Nazik et al., 2008). Furthermore, the identified palynoflora from the Bozburun coal seam implies that palaeomires were developed under freshwater lakeshore and floodplain conditions, while the ostracod and gastropod fauna from the Bozburun Formation show that freshwater and brackish conditions were developed during the late Miocene.

The Boyaca Formation is widely exposed in the study area and consists of reddish mudstone, mudstone, and an alternation of planar parallel-stratified conglomerate, planar cross-stratified sandstone, and reddish mudstone (Figure 1b), related to alluvial fan conditions (Türkmen et al., 2007; Koç-Taşgın, 2011). During late Miocene to Pliocene, a compressional tectonic regime caused the deformation of Miocene formations in the Malatya Basin, which could be observed as hydroplastic deformation horizons within the late Miocene formations (Kaymakçı et al., 2006; Koç-Taşgın, 2011) (Figure 1b). Even though late Pliocene basalt lava flows are common in the northern part of the Malatya Basin (Ercan and Asutay, 1993; Ekici et al., 2007; Kocaaslan and Ersoy, 2018; Di Giuseppe et al., 2021) Late Pliocene basalt lavas or volcanic rocks are not exposed within the Bozburun coalfield. Finally, all Neogene units are overlain by unconformably unconsolidated Quaternary sediments (pebbles, sand, and silt) (Figure 1c).

3. Samples and Applied Methodology

In this study, a total of twelve samples (nine coal, one floor, one roof, and one parting) were obtained from the working coal face of an underground mine in the eastern part of Bozburun coalfield (Figure 2). The lithotype descriptions of the coal samples were performed following the International Committee for Coal and Organic (ICCP) nomenclature (ICCP, 1993). Standard proximate, ultimate and petrographic analyses, as well as calorific determination were conducted at Hacetepe University. Coal petrography analyses were performed using polished blocks prepared according to the ASTM D2797/D2797M (2019) and examined under a coal petrography microscope. The maceral nomenclature followed ICCP System 1994 (ICCP, 2001; Sýkorová et al., 2005; Pickel et al., 2017). For rank determination, the mean random huminite reflectance measurements (%Rr) were exclusively performed on uliminite B following ISO 7404-5 (2009) standard.

For X-ray powder diffraction (XRD) analysis of raw coal and non-coal samples, a Bruker D8 equipment at the General Directorate of Mineral Research and Exploration (MTA) (Ankara, Türkiye) was used. EVA⁺ software (Bruker) was used for semi-

quantitative determination of the mineralogical composition of the samples. For a better detailed mineralogical composition and determining accessory phases selected six coal (P-4, -5, -6, -8, -10, -11) and two non-coal samples (P-1 and -9) examined using FEI Quanta 400 FEI-SEM-EDX at the MTA. For these examination polished blocs were coated with carbon. The powered raw coal and non-coal samples pellets with KBr mixture were examined using a Perkin Elmer Spectrum-II (Fourier transform-infrared spectrometry (FT-IR) instrument. The XRF, ICP-OES, and ICP-MS analyses of all samples were conducted at the MTA. The major oxide contents were determined from raw samples using XRF equipment. For determination of minor and trace elemental compositions using ICP-OES and MS analyses, all samples were firstly ashed at 550 °C, for complete the removing of organic fraction of samples, in a muffle furnace. The digested solutions were prepared from ashed samples using in perchloric acid, aqua regia, nitric acid and concentrated hydrochloric acid following Nadkarni (1980) methodology. Minor and trace elemental compositions were determined using ICP-OES and ICP-MS equipment. External and internal standards were used for checking the accuracy of the analyses.

4. Findings

4.1. Coal Quality

The coal samples are generally black and greyish black in colour. In the low part of the seam, calcareous fossil remains-bearing bands were identified. In the upper part of the seam, the matrix lithotype dominates, i.e., black-coloured gelified humic mass without any mineral impurities and/or with mineral impurities thinner than 1 mm, were identified. In the low part the mineral-rich lithotype prevails, i.e., greyish in colour and containing fossil shell remains-bearing thicker than 1 mm (Table 1, Figure 2). The roof rock sample is fossiliferous claystone, while the parting and floor rock samples are fossiliferous carbonaceous claystone (Figure 2). Furthermore, parting and roof rock samples also contain disseminated carbonized fossil plant litter remains.

Table 1- The results of proximate and ultimate analyses of coal and coal samples, as well as of the calorific value determination of coal samples ((VM: volatile matter, GCV: gross calorific value; asr: as-received basis; d: dry basis; daf: dry, ash-free basis; *oxygen content is calculated by subtraction [O = 100 – (C + H + S + N + ash)] on dry basis).

Sample No	Sampling Interval (cm)		Lithology for Non-coal samples/ Coal Lithotype	Moisture (wt.%, asr)	Ash yield	VM	GCV (MJ/kg, daf)	C	H	N	S	O*
					(wt.%, d)			(wt.%, d)				
P-1	0	10	Claystone	14.5	69.0	31.0	na	9.6	na	na	0.01	na
P-2	10	20	Matrix	25.6	30.6	40.9	28.4	49.9	5.4	1.2	6.8	6.1
P-3	20	30	Mineral-rich	24.4	48.3	35.0	26.2	36.5	4.3	0.8	6.3	3.8
P-4	30	40	Matrix	26.7	32.3	42.2	28.3	49.6	5.5	1.1	6.6	4.8
P-5	40	50	Matrix	22.3	32.0	43.4	28.5	50.5	5.4	1.1	6.4	4.5
P-6	50	60	Matrix	26.8	20.8	42.7	28.8	58.7	6.2	1.3	4.6	8.4
P-7	60	70	Mineral-rich	23.2	74.4	19.8	16.7	15.6	3.0	0.3	2.6	4.2
P-8	70	80	Mineral-rich	25.8	42.6	34.9	27.0	40.6	4.3	0.9	6.6	5.0
P-9	80	90	Carbonaceous claystone	17.1	62.0	38.0	na	12.8	na	na	0.1	na
P-10	90	100	Mineral-rich	19.6	60.6	39.4	8.6	17.4	1.5	0.1	0.3	20.1
P-11	100	110	Mineral-rich	19.4	62.7	37.3	6.7	15.6	1.4	0.1	0.4	19.8
P-12	110	120	Carbonaceous claystone	20.4	87.6	12.4	na	4.7	1.7	0.0	1.7	4.3

The ash yield displays a decreasing trend towards the upper part of the seam (Figure 3); in turn, the gross calorific value (GCV) and total C content are relatively high in this part. These trends are clearly related to the matrix lithotype in the upper part of the seam (Table 1). Furthermore, the total S content displays an increasing trend towards the upper part, where total S content is high (> 5%, on dry basis) (Table 1 and Figure 3). As expected, the volatile matter contents of fossil shell remain-bearing samples are deceptively higher than this in the other samples. This could be related

to the breakdown of the calcareous remains (Table 1). Similarly, relatively high volatile matter content is also generally reported from fossil shell-bearing Turkish Cenozoic coalfields such as Aşın-Elbistan, Soma, Kangal, Milas, and Karapınar coalfields (Karayığit et al., 2001, 2017a, 2019; Bückün et al., 2015; Oskay et al., 2016, 2019). The hydrogen content of the matrix samples is relatively higher (5.4-6.2%, on dry basis) than this of the mineral-rich ones (1.4-4.3%, on dry basis).

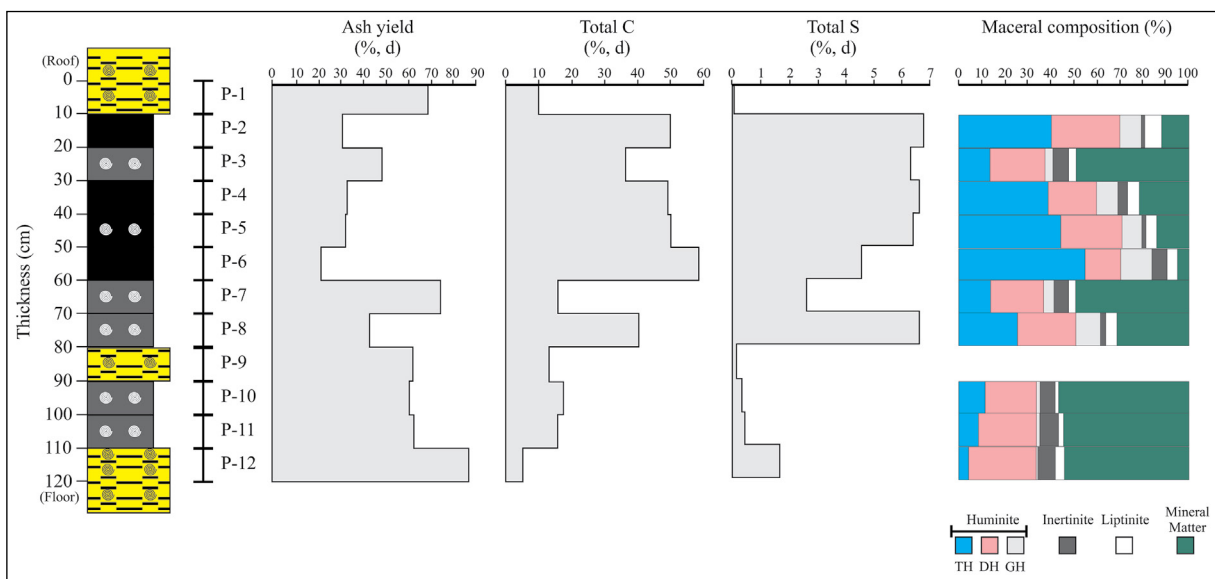


Figure 3- Vertical distribution of ash yield, total C and S, and maceral contents (on whole-basis) through the studied seam (for lithostratigraphic column, see Figure 2).

4.2. Maceral Composition and Huminite Reflectance

Huminite is the most common maceral group (34.1-84.5%, on a whole basis) in the studied samples, while inertinite (1.3-8.3%, on a whole-basis) and liptinite (1.5-6.7%, on a whole-basis) display variable proportions in the entire seam (Table 2 and Figure 3).

Telohuminite is the prevalent huminite maceral subgroup in the matrix lithotype samples, whereas detrohuminite displays generally higher proportions in the mineral-rich matrix samples (Figure 4). Textinite prevails generally in the matrix lithotype (Figures 4a-b) with telohuminite being mainly represented by ulminite (Figures 4a-c and e, and 5a). Porigelinite, resinite and corpohuminite commonly fill cell lumens of textinite (Figures 5a-b). The ulminite B variety is generally well gelified; however, the ulminite A variety exhibits very weak brownish fluorescence (Figures 5a-b). Densinite has higher proportions in the matrix samples, whereas in the mineral-rich ones, attrinite is more common. Inertinite (e.g., inertodetrinite and fusinite) and liptinite macerals (e.g., sporinite and liptodetrinite) are generally embedded within densinite (Figures 4d and 5c-d). Furthermore, attrinite appears generally within clay mineral aggregates (Figures 5c and f). Corpohuminite is the prevalent gelohuminite maceral in the coal samples and, as mentioned above, is mostly observed as cell-lumens infilling, as well as phlobaphinite (Figure 4a). The latter one could also be

an indicator of woody peat-forming plants (Sýkorová et al., 2005). As noted above, porigelinite is identified within telohuminite macerals (Figure 4b), while levigelite is identified in the entire seam (Figure 4d).

The inertinite content is generally higher than 10% (on a mineral matter-free basis) in the low part of the seam, and fusinite, inertodetrinite, and semifusinite are identified in the entire seam. Inertodetrinite, fusinite, and semifusinite macerals are mostly observed within clay aggregates and densinite (Figures 4d and 5c-d), while individual fusinite and semifusinite macerals are also identified in the coal samples (Figure 5f). Funginite is less common in the coal samples and is mostly identified within ulminite (Figure 4c). Liptinite proportions show an increasing trend towards the upper part of the seam (Figure 3), which resulted in increased H contents. Cutinite, liptodetrinite and sporinite are identified in all the samples (Figures 4e-f). The presence of fluorinite-variety resinite could also imply the existence of *Myrica* within the palaeomire, which is also supported by the presence of *Myrica* pollen according to Türkmen et al. (2004). The identified minerals under white-incident light are mostly clay mineral aggregates and framboidal pyrite grains and agglomerates, and rarely syngenetic carbonate bands (Figures 4b-d, and 5c and f). Furthermore, calcareous fossil shell fragments and possible diatom remains and/or sponge spicules are also included (Figure 5e).

Table 2- Maceral composition (vol%) and mean random ulminite reflectance (%Rr) of the studied coal samples and floor sample (P-12) (TH: telohuminite, DH: detrohuminite, GH: gelohuminite, H: huminite, I: inertinite, L: liptinite, MM: mineral matter, Stdv: standard deviation).

Sample No	Petrographic Composition (vol%)							%Rr ± Stdv	Maceral Indices (dimensionless)						
	TH	DH	GH	H	I	L	MM vol%, on whole basis		A	B	C	TPI	GI	VI	GWI
	vol%, on mineral-free basis														
P-2	46.0	33.6	10.9	90.5	1.9	7.6	11.9		56.1	42.0	1.9	1.4	2.3	1.3	0.8
P-3	27.0	46.3	7.7	81.0	12.6	6.4	49.1		31.9	55.5	12.6	0.6	0.9	0.6	1.9
P-4	49.0	27.0	12.0	88.0	5.2	6.8	21.1	0.31±0.01	55.5	39.4	5.1	1.4	2.3	1.7	0.9
P-5	51.7	30.7	10.2	92.6	1.5	5.9	13.4		58.0	40.5	1.5	1.5	3.1	1.5	0.6
P-6	57.9	16.6	14.2	88.7	6.7	4.6	4.7	0.32±0.01	66.5	26.8	6.7	2.6	4.0	2.9	0.6
P-7	27.2	46.2	7.7	81.1	12.5	6.4	49.0		32.0	55.4	12.5	0.6	0.9	0.6	1.9
P-8	37.2	36.9	15.9	90.0	3.1	6.9	31.2	0.32±0.01	42.6	54.3	3.1	0.8	2.8	1.0	1.5
P-10	27.6	52.0	2.2	81.8	14.8	3.4	57.0	0.32±0.01	29.6	55.6	14.9	0.5	0.4	0.5	1.8
P-11	19.0	55.6	3.0	77.6	18.1	4.3	54.4		21.4	60.4	18.2	0.3	0.3	0.4	1.7
P-12	9.1	64.4	1.0	74.5	16.7	8.8	54.1		13.1	70.1	16.8	0.1	0.1	0.2	1.6

The mean random huminite reflectance (%Rr) values ranges between 0.31-0.32% (Table 2). These values are generally lower than the reported measured ones (0.38-0.51%) from the western part of the coalfield by Yalçın-Erik and Ay (2021).

4.3. Mineralogy

4.3.1. Minerals in Coal Samples

The minerals identified by XRD in the bulk coal samples, are calcite, clay minerals (illite and smectite),

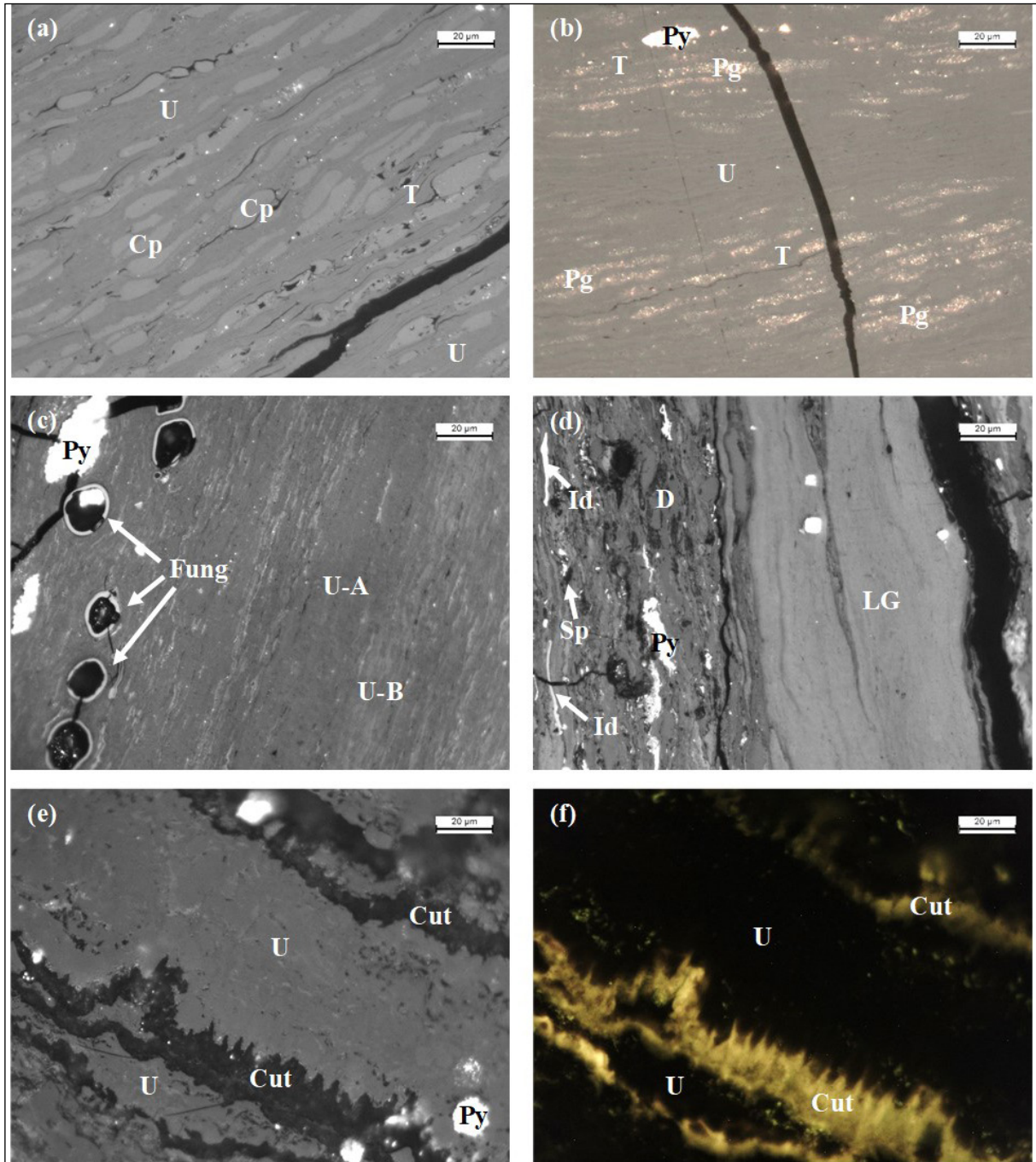


Figure 4- Selected photomicrographs of the Bozburun coal samples. All photomicrographs are taken under incident white light (a-e) or blue-light excitation (f), in oil immersion, 500× total magnification (Abbreviations: textinite (T), ulminite (U), ulminite-A (U-A), ulminite-B (U-B); densinite (D), corphuminite (Cp), porigelinite (Pg), levigelinite (LG), inertodetrinite (Id), funginite (Fung); sporinite (Sp); cutinite (Cut), and pyrite (Py)).

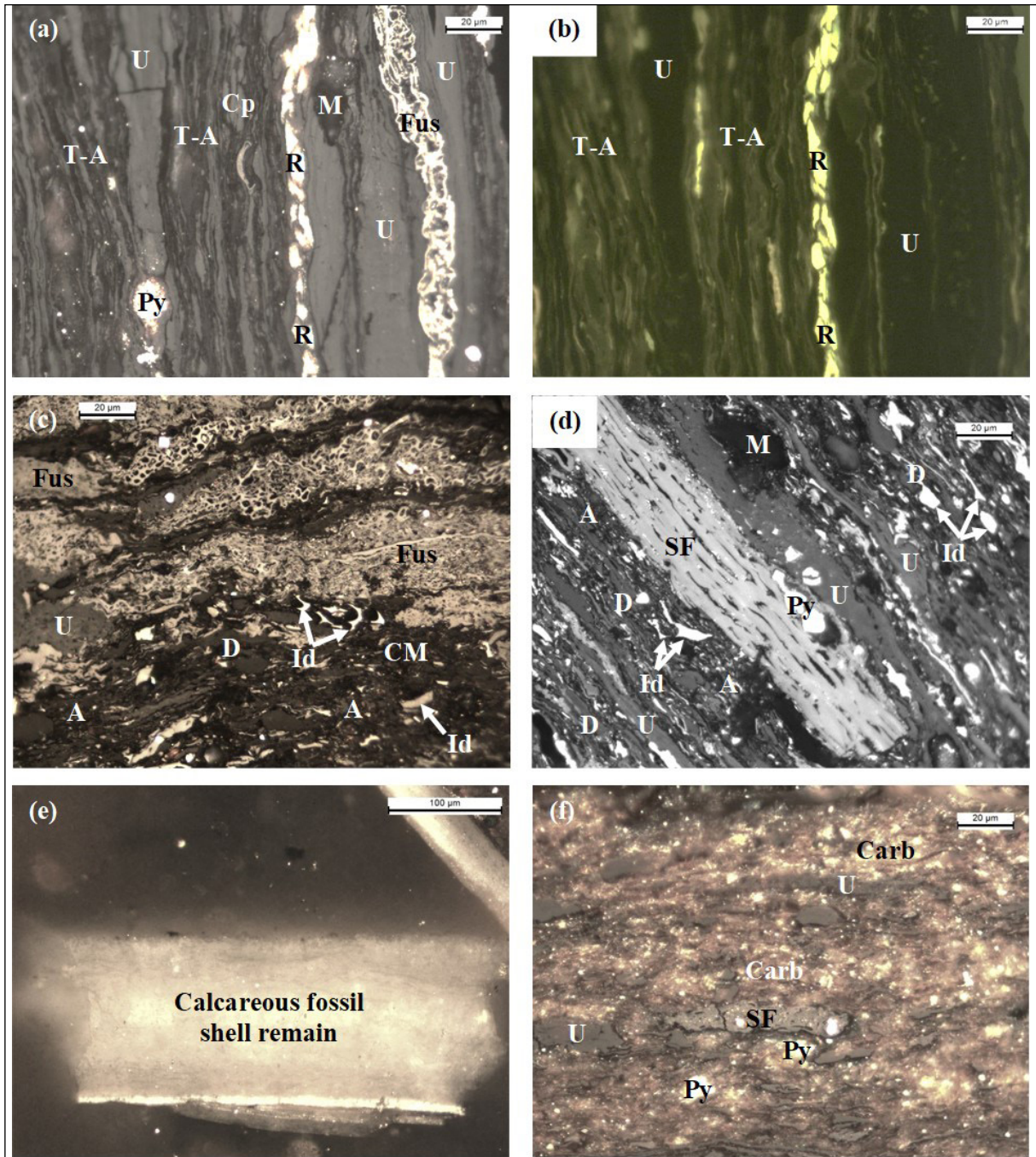


Figure 5- Selected photomicrographs of the Bozburun coal samples; a), c), d), e), f) all photomicrographs are taken under incident white light, b) blue-light excitation in oil immersion, 500× total magnification (Abbreviations: textinite-A (T-A), ulminite (U), attrinite (A), densinite (D), fusinite (Fus), semifusinite (SF), inertodetrinite (Id), resinite (R), pyrite (Py), clay mineral (CM), syngenetic carbonate (Carb), and mineral-matter (M)).

quartz, and pyrite (Table 3); a similar mineralogical composition is also obtained from the western part of the basin (Yalçın-Erik and Ay, 2021). Furthermore, in fossil shell-bearing samples, aragonite is also detected, and feldspars and marcasite are determined as minor phases (Table 3). Clay and carbonate minerals are

abundant to dominant phases, while quartz is generally a minor phase. The SEM-EDX data agrees with the XRD data, and chlorite (chamosite), Cl/F-apatite, celestine, dolomite, barite, sphalerite, titanite (sphen), and Ti-oxides, are identified as accessory phases (Table 3). In addition, pyritized calcareous fossil

Table 3- Semi-quantitative mineralogical composition of the Bozburun coal and non-coal samples based on XRD and SEM-EDX analyses (+++ = dominant phase (> 40%), ++ = abundant phase (10–20%), + = minor phase (< 10%) by XRD, a: accessory mineral detected by SEM-EDX).

Mineral	Sample											
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10	P-11	P-12
Quartz	+	+	+	+	+	+	+	+	+	+	+	+
Clay Minerals	+	+++	+++	+++	+++	+++	+++	+++	a	a	a	+++
Feldspar	a				+	a		a	a	a	a	+
Titanite	a					a						
Calcite	+++		+	++	++		+	+	+++	+++	+++	+
Aragonite			++		++						++	
Dolomite	a			a								
Pyrite	+	+++	++	++	++	+	+	+	+	a	+	+
Marcasite					a					+		
Sphalerite								a				
Celestine	a									a		
Barite	a											
Apatite						a			a	a		
Ti-oxides						a						

shell fragments and diatom/freshwater sponge spike remains, and fossil bone remains of Ca-phosphate composition were also identified using SEM-EDX.

4.3.2. Minerals in Non-coal Samples

According to XRD data, the minerals in the non-coal samples are similar to these of the coal samples. Calcite, clay minerals (smectite, illite and chlorite), quartz, and pyrite are identified in all non-coal samples (Table 3). Furthermore, feldspars are also detected from the floor sample. As expected, calcite is generally the dominant phase in the roof and parting samples in calcareous fossil remains-bearing samples, whereas in the floor sample clay minerals are predominant (Table 3). Quartz and pyrite are minor phases in the non-coal samples.

4.4. FT-IR Analysis

Selected FT-IR spectra are reported in Figure 6. The bands around wavenumbers 1030 and 530 cm^{-1} could be originated from clay minerals (Georgakopoulos et al., 2003; Madejova, 2003). Furthermore, the intense bands at 3400 cm^{-1} could also be attributed to clay minerals or more possibly with OH-stretching vibration (Madejova, 2003; Djowe et al., 2013; Jiang et al., 2021). The band around 470 cm^{-1} could be attributed to quartz/silica grains (Çetinkaya and

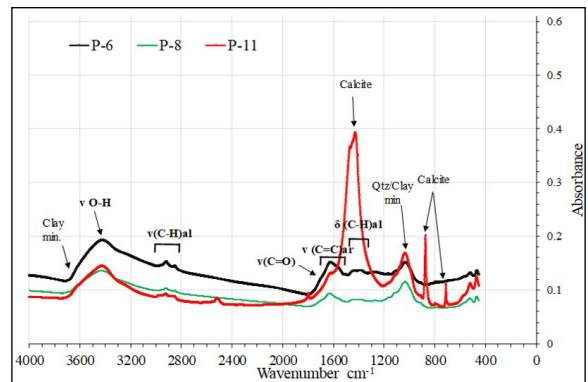


Figure 6- FT-IR spectra of selected Bozburun samples.

Yürüm, 2000; Georgakopoulos et al., 2003; Naik et al., 2021) however, the lack of intense bands at 1100 cm^{-1} might not imply a lack of quartz/silica in the samples. This may be caused by the strong absorption of clay minerals and the overlap of quartz peak at 1100 cm^{-1} . Strong and board peaks around 1425, 875, and 711 cm^{-1} , particularly in the sample P-11, clearly result from calcite and/or fossil shell remains; similar peaks were also reported from fossil shell remains bands-bearing Turkish Neogene coals (e.g., Soma and Muğla Basins) (Çetinkaya and Yürüm, 2000; Baysal et al., 2016). The peaks at 2851 cm^{-1} and 1385 cm^{-1} , and 2920 cm^{-1} could imply the existence of aliphatic CH_2 and CH_3 symmetric and aliphatic C-H asymmetric

stretching vibrations, respectively (Oikonomopoulos et al., 2013; Chen et al., 2015; Jiang et al., 2021; Naik et al., 2021). The oxygen-containing functional groups (e.g., C=O and C=C aromatic ring) in coal samples could be evident with the peaks between 1613-1630 cm^{-1} (Georgakopoulos et al., 2003; Chen et al., 2015; Çelik et al., 2021).

4.5. Geochemistry

The major oxide contents of studied samples are reported in Table 4. The SiO_2 (8.4-46.8%, on whole coal basis) and Al_2O_3 (3.1-11.6%, on whole coal basis) contents of the coal samples are generally higher than inorganic samples. The CaO contents of fossil shell-bearing coal samples (34.5-37.6%, on coal basis) in the low part of seam, floor and intercalation samples (33.3-36.8%, on whole rock basis) are significantly higher than coal samples in the upper part of seam (1.5-6.0%, on whole coal basis) (Table 4). The contents of SiO_2 , TiO_2 , Al_2O_3 , Na_2O , and K_2O display increasing trends towards the central part of the seam (Figure 7 and Table 4). As expected, the CaO content decreases towards the upper parts of the seam, and the Fe_2O_3 and MnO contents do not show any significant changes throughout the seam (Figure 7). The average concentrations of trace elements in analysed coal samples using ICP-MS do not exceed 100 ppm on a whole coal basis, except B and Sr concentrations (Tables 4 and 5). The average B concentration of coal samples is 161 ppm (Tables 4 and 5), whereas the average concentration of Sr is 1021 ppm, and the Sr concentration of sample P-10 is 6814 ppm on a whole coal basis (Tables 4 and 5). Like the coal samples, the average Sr concentration of non-coal samples exceeds 1000 ppm on a whole rock basis (Tables 4 and 6). In addition, the average Ba concentration of non-coal samples is higher than 100 ppm on a whole rock basis (Tables 4 and 6). The concentrations of trace elements in the coal samples are mostly less than 5 ppm, while the average concentrations of rare earth elements and Y (REY) contents do not exceed 1 ppm on a whole coal basis, except Y and La (Table 5).

The concentration coefficient (CC) of coal and non-coal samples was calculated for determining elemental enrichments (Tables 5 and 6). This calculation is based on dividing average concentrations of elements into

Clarke values for low-rank coals and sedimentary rocks (Ketriss and Yudovich, 2009; Dai et al., 2015b). Nickel (CC = 10.4) is the only significantly enriched element in coal samples, and the other enriched elements are Sr (CC = 8.5), As (CC = 5.8), Mo (CC = 5.4), and U (CC = 5.1). Furthermore, slightly enriched elements in coal samples are Cr (4.4), V (4.4), P (3.8), Ti (2.5), B (2.9), Rb (2.3), and Zn (2.1), whereas Ba and most of REY are depleted (CC<0.5) (Table 5). The remaining elements display concentrations close to the Clarke values of low-rank coals. In non-coal samples, the majority of elements are depleted (Table 6); nevertheless, the slightly enriched elements in non-coal samples are Sr (CC = 4.0), As (CC = 2.7), and Ni (CC = 2.2). The elements P, Ti, Cr, Mn, Co, Ba, Pb, and U have average concentration close to Clarke values of the sedimentary rocks (Table 6). Furthermore, outlook coefficient (C_{out}) of REY and ΣREY oxides values of coal and non-coal samples are within non-promising for REY recovery potential (Seredin and Dai, 2012). Of note, the ashing temperature might also cause the volatilization of As and B in coal samples; therefore, their CC might be higher than the measured concentrations.

5. Discussions

5.1. Coal Rank

The measured Rr values (0.31-0.32%) and the determined gross calorific values (6.7-28.8 MJ/kg, on dry, ash-free basis) of the coal samples imply that the Bozburun coal seam is of low rank C-B (lignite) according to ASTM D388-19a (2021), E.C.E-UN (1998) and ISO 11760 (2005) classifications. The coal samples are also classified as moderate to high ash yield coal and very low to moderate grade coal according to ISO 11760 (2005) and E.C.E-UN (1998) classification, respectively. Considering the ash yields of the mineral-rich lithotype samples from the low part of the seam, these samples could be classified as carbonaceous shale. Nevertheless, this identification could not be accurate since calcareous fossil shell remains-bearing bands are included in these samples.

In comparison with the reported measured Rr values (0.38-0.51%) from the western part of the Bozburun coalfield, and the northern part of the

Table 4- Elemental composition of coal and non-coal samples (all on whole rock-basis) in the Bozburun coalfield. All results in ppm, expect otherwise cited (LOI: loss on ignition, bdl: below detection limit).

Element	Sample											
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10	P-11	P-12
LOI (%)	31.0	72.4	55.1	70.6	70.7	81.6	26.7	60.6	37.2	38.7	37.0	37.0
SiO ₂ (%)	21.7	12.9	22.7	11.8	11.0	8.4	46.8	22.1	15.1	10.7	15.4	33.1
TiO ₂ (%)	0.2	0.3	0.3	0.2	0.2	0.2	0.7	0.4	0.1	0.2	0.2	0.7
Al ₂ O ₃ (%)	5.9	4.0	6.3	3.3	3.1	2.2	11.6	5.6	4.3	3.1	4.7	10.9
Fe ₂ O ₃ (%)	3.4	5.5	6.3	5.6	5.5	3.3	5.8	6.3	2.4	6.1	4.6	6.7
MnO (%)	0.11	0.05	0.07	0.06	0.07	0.04	0.08	0.07	0.09	0.09	0.07	0.09
MgO (%)	2.6	2.2	2.8	2.1	2.2	1.7	3.6	2.4	2.7	2.1	2.0	4.3
CaO (%)	33.3	1.5	4.8	5.1	6.0	1.4	2.2	1.0	36.8	37.6	34.5	4.3
Na ₂ O (%)	0.4	0.6	0.7	0.6	0.6	0.6	0.8	0.7	0.3	0.3	0.3	0.9
K ₂ O (%)	1.2	0.4	0.7	0.4	0.4	0.4	1.5	0.8	0.8	0.7	1.0	1.8
P ₂ O ₅ (%)	0.12	0.12	0.22	0.22	0.25	0.18	0.07	0.06	0.13	0.28	0.15	0.13
Li	bdl	10	12	6.0	7.2	5.5	14	14	bdl	bdl	bdl	8.4
B	15	216	146	234	235	297	87	170	17	37	28	30
Sc	3.4	2.6	2.9	2.2	2.6	2.2	7.6	4.5	2.2	2.1	2.4	5.9
V	20	70	142	81	89	110	82	152	21	69	74	43
Cr	63	57	66	45	55	47	126	104	41	45	49	108
Co	4.1	8.9	8.0	3.7	3.5	3.6	14	12	3.1	5.4	5.5	15
Ni	43	103	153	55	64	40	142	147	31	70	68	166
Cu	7.5	8.3	14	11	9.8	10	13	11	8.0	13	12	15
Zn	21	37	24	22	26	23	94	59	17	26	33	84
Ga	bdl	4.2	4.9	4.0	4.0	2.7	7.6	6.0	bdl	4.2	bdl	6.8
As	23	22	66	75	115	12	19	35	10	33	18	29
Rb	15	12	20	15	15	11	66	26	18	16	22	68
Sr	1794	244	239	329	269	240	162	216	1218	6813	679	244
Y	3.6	2.2	3.5	2.2	2.3	5.4	8.5	5.5	3.0	2.7	3.6	5.3
Cd	bdl	bdl	bdl	bdl	1.7	0.9	bdl	bdl	bdl	bdl	bdl	bdl
Mo	bdl	14.7	8.9	16.1	16.1	19.5	4.8	13.6	bdl	6.6	7.4	bdl
Sb	bdl	bdl	6.6	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Ba	478	32	33	33	26	16	56	35	126	181	97	47
La	4.6	3.1	5.3	3.1	3.6	4.7	16	6.6	3.2	3.0	4.5	13
Ce	8.5	6.5	11	5.6	6.3	7.9	30	12	5.6	5.4	7.8	24
Pr	1.1	0.7	1.3	0.7	0.8	1.0	4.0	1.6	0.7	0.7	1.0	3.2
Nd	3.5	2.4	4.2	2.2	2.6	3.5	13	5.0	2.4	2.4	3.4	10
Eu	0.3	0.1	0.2	0.1	0.1	0.2	0.7	0.3	0.2	0.2	0.2	0.4
Gd	0.7	0.4	0.8	0.4	0.5	0.8	2.3	1.1	0.6	0.5	0.7	1.9
Tb	0.14	0.08	0.13	0.09	0.09	0.15	0.4	0.2	0.06	0.06	0.12	0.3
Dy	0.6	0.4	0.7	0.3	0.4	0.7	1.8	1.0	0.4	0.4	0.6	1.3
Ho	0.14	0.08	0.13	0.09	0.09	0.16	0.3	0.2	0.06	0.06	0.12	0.3
Er	0.3	0.2	0.4	0.2	0.2	0.4	0.8	0.6	0.2	0.2	0.3	0.4
Tm	bdl	bdl	bdl	bdl	bdl	0.07	0.14	0.08	bdl	bdl	bdl	0.08
Yb	0.3	0.2	0.3	0.2	0.2	0.4	0.6	0.5	0.2	0.2	0.2	0.5
Lu	bdl	bdl	bdl	bdl	bdl	0.05	0.07	0.08	bdl	bdl	bdl	bdl
Hf	2.0	1.3	1.0	0.9	1.3	0.7	1.7	2.9	bdl	0.8	0.6	1.4
Pb	bdl	6.1	bdl	3.7	5.8	4.5	14.4	10.8	bdl	bdl	9.2	16.9
Th	1.6	1.9	2.8	1.3	1.6	1.3	6.9	3.3	1.1	1.0	1.4	5.7
U	0.7	10.9	15.5	16.7	19.6	20.4	9.5	19.2	2.0	9.8	10.0	4.4

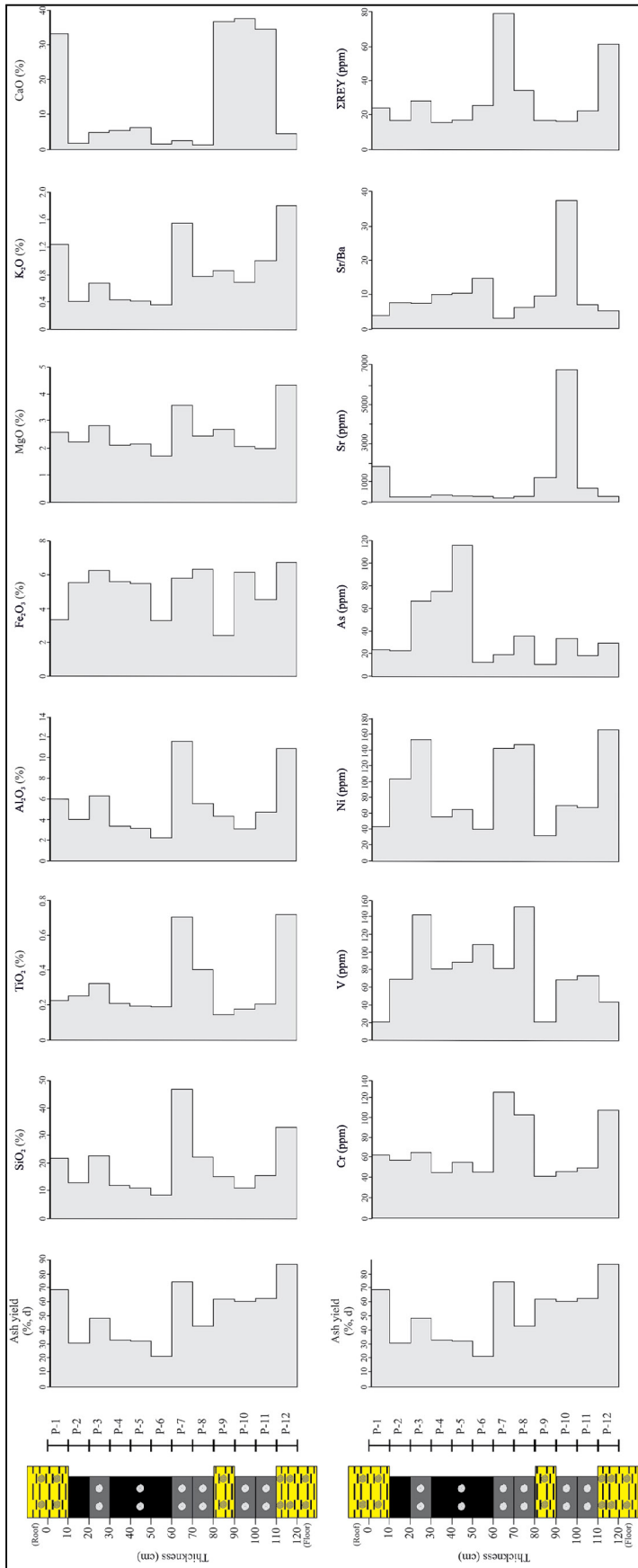


Table 5- Weighted average of the Ti, P, Mn, minor and trace elements (in ppm) for the Bozburun coal samples and their comparison with worldwide coals (a: from Swaine (1990); b: from Ketris and Yudovich (2009). Elements in bold are enriched.

Element	Most world coals ^a	Clarke values for low-rank coals	Bozburun coal samples	Concentration coefficient (CC)
Li	1-80	10	7.7	0.8
B	5-400	56	161	2.9
P	10-3000	200	757	3.8
Sc	1-10	4.1	3.2	0.8
Ti	10-2000	720	1769	2.5
V	2-100	22	96	4.4
Cr	0.5-60	15	66	4.4
Mn	5-300	100	517	5.2
Co	0.5-30	4.2	7.2	1.7
Ni	0.5-50	9.0	94	10.4
Cu	0.5-50	15	11	0.8
Zn	5-300	18	38	2.1
Ga	1-20	5.5	4.2	0.8
As	0.5-80	7.6	44	5.8
Rb	2-50	10	23	2.3
Sr	15-500	120	1021	8.5
Y	2-50	8.6	4.0	0.5
Cd	0.1-3	0.24	0.3	1.2
Mo	0.1-10	2.2	12	5.4
Sb	0.5-10	0.84	0.7	0.9
Ba	20-100	150	57	0.4
La	1-40	10	5.6	0.6
Ce	2-70	7.2	10	1.4
Pr	1-10	3.5	1.3	0.4
Nd	3-30	11	4.3	0.4
Eu	0.1-2	0.5	0.2	0.5
Gd	0.1-4	2.6	0.8	0.3
Tb	0.1-1	0.32	0.1	0.5
Dy	1-4	2.0	0.7	0.3
Ho	0.1-2	0.5	0.1	0.3
Er	1-3	0.85	0.4	0.4
Tm	0.5-3	0.31	0.0	0.2
Yb	0.3-3	1.0	0.3	0.3
Lu	0.03-1	0.19	0.02	0.1
Hf	0.4-5	1.2	1.2	1.0
Pb	2-80	6.6	6.1	0.9
Th	0.5-10	3.3	2.4	0.7
U	0.5-10	2.9	15	5.0

Table 6- Weighted average of the Ti, P, Mn, minor and trace elements (in ppm) for the Bozburun non-coal samples and their comparison with worldwide coals [a: from Ketris and Yudovich (2009)].

Element	Clarke values for sedimentary rocks ^a	Bozburun non-coal samples	Concentration coefficient (CC)
Li	33	2.8	0.1
B	72	20	0.3
P	670	567	0.8
Sc	9.6	3.8	0.4
Ti	3740	2180	0.6
V	91	28	0.3
Cr	58	71	1.2
Mn	830	755	0.9
Co	14	7.4	0.5
Ni	37	80	2.2
Cu	31	10	0.3
Zn	43	41	0.9
Ga	12	2.3	0.2
As	7.6	20.7	2.7
Rb	94	33.4	0.4
Sr	270	1085	4.0
Y	29	4.0	0.1
Ba	410	217	0.5
La	32	6.8	0.2
Ce	52	13	0.2
Pr	6.8	1.7	0.2
Nd	24	5.4	0.2
Eu	0.94	0.3	0.3
Gd	4	1.1	0.3
Tb	0.69	0.2	0.3
Dy	3.6	0.8	0.2
Ho	0.92	0.2	0.2
Er	1.7	0.3	0.2
Tm	0.78	0.03	0.0
Yb	2	0.3	0.2
Hf	3.9	1.1	0.3
Pb	12	5.6	0.5
Th	7.7	2.8	0.4
U	3.4	2.4	0.7

Malatya Basin (0.68-0.79%) (Karayiğit and Whateley, 1997; Yalçın-Erik and Ay, 2021), the studied samples generally display relatively low R_r values (Table 3). Furthermore, the calculated R_r values using Rock-Eval pyrolysis data obtained from the western part of the Bozburun coalfield and coal beds outcropping north of Arguvan town (Yalçın-Erik and Ay, 2021), strongly vary from 0.20-0.69%. This parameter is proposed for organic-rich rock and/or bituminous shale samples by Jarvie et al. (2001), and its application to humic coals, particularly on Cenozoic low-rank coals, could be very problematic due to the presence of certain compounds (Zdravkov et al., 2006; Hazra et al., 2019; Çelik et al., 2021). For instance, the oxygenated functional groups in ulminite macerals (e.g., ulminite A or resin-impregnated ulminite A) or the breakdown of carbonate minerals could elevate S_3 peak values; hence, the T_{max} values are suppressed and calculated R_r values could be reduced. Considering the presence of oxygen-containing functional groups in the FT-IR spectra and the carbonate minerals in the coal samples, the calculated R_r values from Rock-Eval pyrolysis data should be used with caution as a rank parameter for the Bozburun coal. As mentioned above, the presence of H-rich compounds could also cause a reduction of the R_r values. The reported palynological and biomarker datasets from the Bozburun coalfield imply the existence of H-rich peat-forming plants (e.g., Taxodaeaceae-Cupressaceae) within the palaeomire (Önal, 1995; Türkmen et al., 2007; Yalçın-Erik and Ay, 2021). Thus, significantly low R_r values (e.g., 0.27) were calculated from coals according to Rock-Eval data. Nevertheless, the coal petrography data indicates that the potential influence of H-rich ulminite macerals on R_r values may be very limited, because ulminite B is the dominant telohuminite and ulminite A in the studied samples displays very weak fluorescence only (Figure 5b).

Another possibility controlling R_r differences within the Malatya Basin could be the tectonic deformation. Since the study area faced post-coalification regional tectonic deformation, the R_r values might have been affected (Hower and Gayer, 2002). This also seems to be not possible due to the lack of any deformed macerals in the coal samples. In the northern part of Malatya Basin, Pliocene basalts

and andesitic domes of the Yamadağ volcanics are widely exposed and overlay late Miocene coal-bearing sequences (Karayiğit and Whateley, 1997; Ekici et al., 2007). The measured R_r values of the coal seams in the Selimoğlu coalfield are around 0.70%, which indicates bituminous rank. Nevertheless, the elevated measured R_r values are obviously controlled by heat flow due to post-coalification andesitic domes in the Selimoğlu coalfield (Karayiğit and Whateley, 1997). Considering the presence of Pliocene volcanic rocks and lavas north of Arguvan town, the reported slightly high calculated R_r values of the coal beds outcropping in this area (Kuyudere and Akören locations in Figure 1a), could be related to increased heat flow in the northern part of Malatya Basin (Yalçın-Erik and Ay, 2021).

Since the Pliocene volcanic rocks are observed in the Bozburun coalfield, the relative differences on measured R_r values among the coalfield may not be related to influence of heat flow, like in the northern part of the Malatya Basin. Nevertheless, alkaline conditions within the palaeomire could cause biogeochemical gelification of organic matter; in turn, high gelification degree of organic matter could result in an increase of the R_r values (Dehmer, 1995). As can be seen in sections 5.2 and 5.4, gelification index (GI) values are different within the coalfield and carbonate minerals are more common in the western part of the Bozburun coalfield, the studied section and the western part of the Bozburun coalfield display relatively small R_r differences due to biogeochemical gelification and alkaline conditions within the palaeomire. Overall, coal-rank variations were developed from the northern (Selimoğlu coalfield) to the southern part (Bozburun coalfield) of the Malatya Basin due to post-coalification volcanic activity; biogeochemical gelification within the palaeomires caused variations in R_r values within the Bozburun coalfield.

5.2. Provenance of minerals

Quartz/silica is mostly identified as irregularly shaped individual grains during SEM-EDX examination (Figure 8a and d), which indicates a clastic origin. In some samples, partially pyritized siliceous skeletons of diatoms and/or sponge spicules are also detected (Figure 8e). Such remains suggest

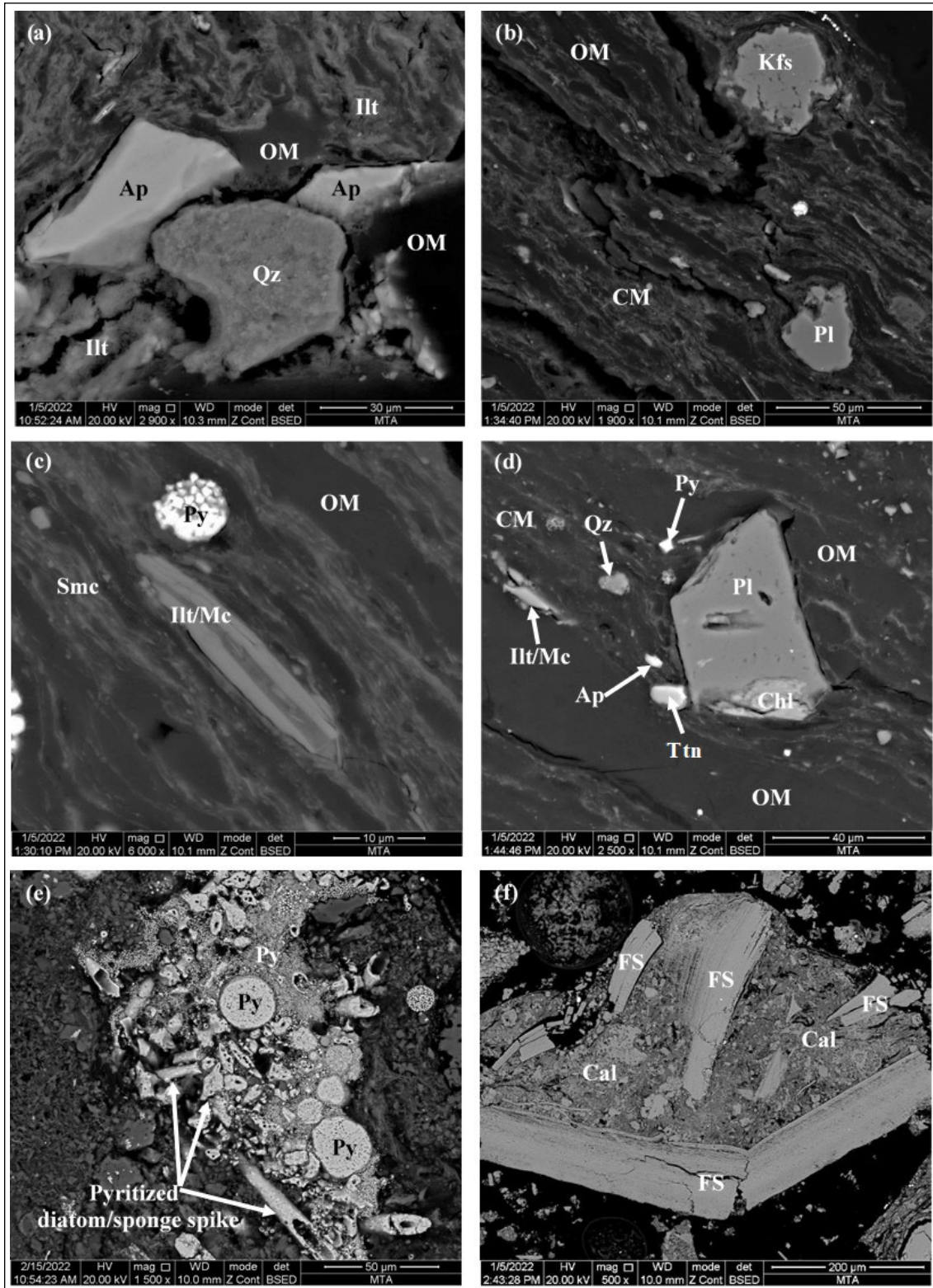


Figure 8- Selected SEM backscattered (BSE) images from the Bozburun samples: a) apatite (Ap), quartz (Qz) and organic matter (OM) associated with illite (Illt), b) K-feldspar (Kfs), plagioclase (Pl) and organic matter associated with clay minerals (CM), c) illite/mica (Illt/Mc) and organic matter associated with smectite (Smc) and framboidal pyrite (Py) grain, d) apatite (Ap), chlorite (Chl), quartz (Qz), plagioclase (Pl), titanite (Ttn), illite/mica (Illt/Mc) and organic matter (OM) associated with clay minerals (CM), e) pyritized possible diatom/sponge spike and framboidal pyrite (Py) aggregates, f) calcite (Cal) and fossil shell remains (FS).

that silica in coal samples is also biogenic in origin (Ward, 2002; Oskay et al., 2016; Çelik et al., 2021). Even though feldspar is a minor phase, K-feldspar and plagioclase grains are commonly observed during the SEM-EDX study. Like quartz, feldspar grains are identified as irregular shaped individual grains with sharp edges within clay mineral aggregates (Figure 8b and d). This implies short-distance transport of feldspar grains from the adjacent areas. The clastic sources for feldspars presumably are mainly the middle Miocene Malatya volcanics, and, in a lesser extent, the late Cretaceous Elazığ magmatics of the basements.

Clay minerals are identified as aggregates hosting also other mineral grains (e.g., Cl/F-apatite, quartz, feldspars, and titanite) and organic matter (Figures 8a-d). The clay aggregates mostly consist of smectite and subordinately illitic according to the SEM-EDX data. Illite components mostly derive as clastic input into the palaeomire (Siavalas et al., 2009), while smectite mostly originates from alteration of syngenetic or epiclastic volcanic input (Bohor and Triplehorn, 1993; Dai et al., 2017, 2020a; Karayiğit et al., 2020b). Since illitic aggregates are more common in the low part of the seam, illite aggregates in samples are syngenetic and clastic in origin. Furthermore, the individual illite/mica grains in the clay matrices could also be related to clastic input from the middle Miocene Malatya volcanic and/or magmatic rocks in the pre-Neogene basement (Figures 8c-d). The alterations of clastic input from the Malatya volcanics within the mires could result in syngenetic smectite formation under hydrogeologically closed system. During the SEM observations, lath-shaped Fe-rich chlorite (chamosite) grains are generally observed within the clay aggregates. Also, chlorite overgrowths are detected around feldspar grains (Figure 8d). These could indicate that chlorite is either derived from clastic inputs into palaeomires or alteration of feldspar grains within the paleomires and/or early diagenetic stages (Ward, 2002; Hower et al., 2015).

Carbonate minerals generally appear in form of carbonate bands and calcareous fossil shell remains, and rarely as individual calcite and dolomite grains (Figures 8f, 9a-b). These observations might imply

that the carbonates are clearly syngenetic originating from clastic input from the Permo-Triassic Keban metamorphics (e.g., marbles) or the pre-Neogene carbonates. Besides, calcareous fossil fragments, which are partially pyritized, are commonly observed in fossil shell remains-bearing samples (Figures 9a-b). Aragonite is generally detected as an abundant phase in the XRD patterns in a few fossil shell remains-bearing samples. However, aragonite was not detected in some calcareous fossil remains-bearing samples, whilst calcite is detected instead of aragonite (Table 3). This could be related to the conversion of aragonite to its polymorph calcite within the palaeomire or during a diagenetic stage (Querol et al., 1999; Ward, 2002). The predominance of carbonate minerals and the presence of partially pyritized calcareous fossil shell remains could indicate neutral to weak alkaline conditions (Kortenski, 1992; Karayiğit et al., 2017a;). However, the lack of carbonate minerals and the existence of framboidal pyrite grains and siliceous fossil remains (e.g., diatom) in the upper seam part point to low pH values of mire water or the Ca contents of influenced water into palaeomires was decreased (Kortenski, 1992; Dai et al., 2020a). Thus, syngenetic carbonate formation was limited due to increased acidity of palaeomire during late stages of peat accumulation in the Bozburun coalfield. Overall, syngenetic carbonate formation in the Bozburun palaeomire was controlled by the Ca-rich water influx along with clastic influx.

Pyrite is generally observed as individual framboidal aggregates within organic matter (e.g., ulminite), and framboidal and euhedral pyrite grains aggregate during coal petrography and SEM studies (Figures 4b, c, e, 5a, f, 8c, e, 9a). Additionally, cleat/fracture pyrite-infillings, and pyritized plant tissues, siliceous skeletons of diatoms and/or sponge spicules, and fossil shell remains, as mentioned above, are contained in coal samples (Figure 8e, f, 9c). These findings suggest that framboidal pyrite grains were precipitated within the palaeomire and/or early diagenetic stages as a result of sulphate-reducing bacteria and sulphate-rich water influx into palaeomires (Querol et al., 1989). The cleat/fracture pyrite-infillings are presumably controlled by precipitation of sulphate-rich porewaters during coalification. Another sulphide mineral identified by XRD is

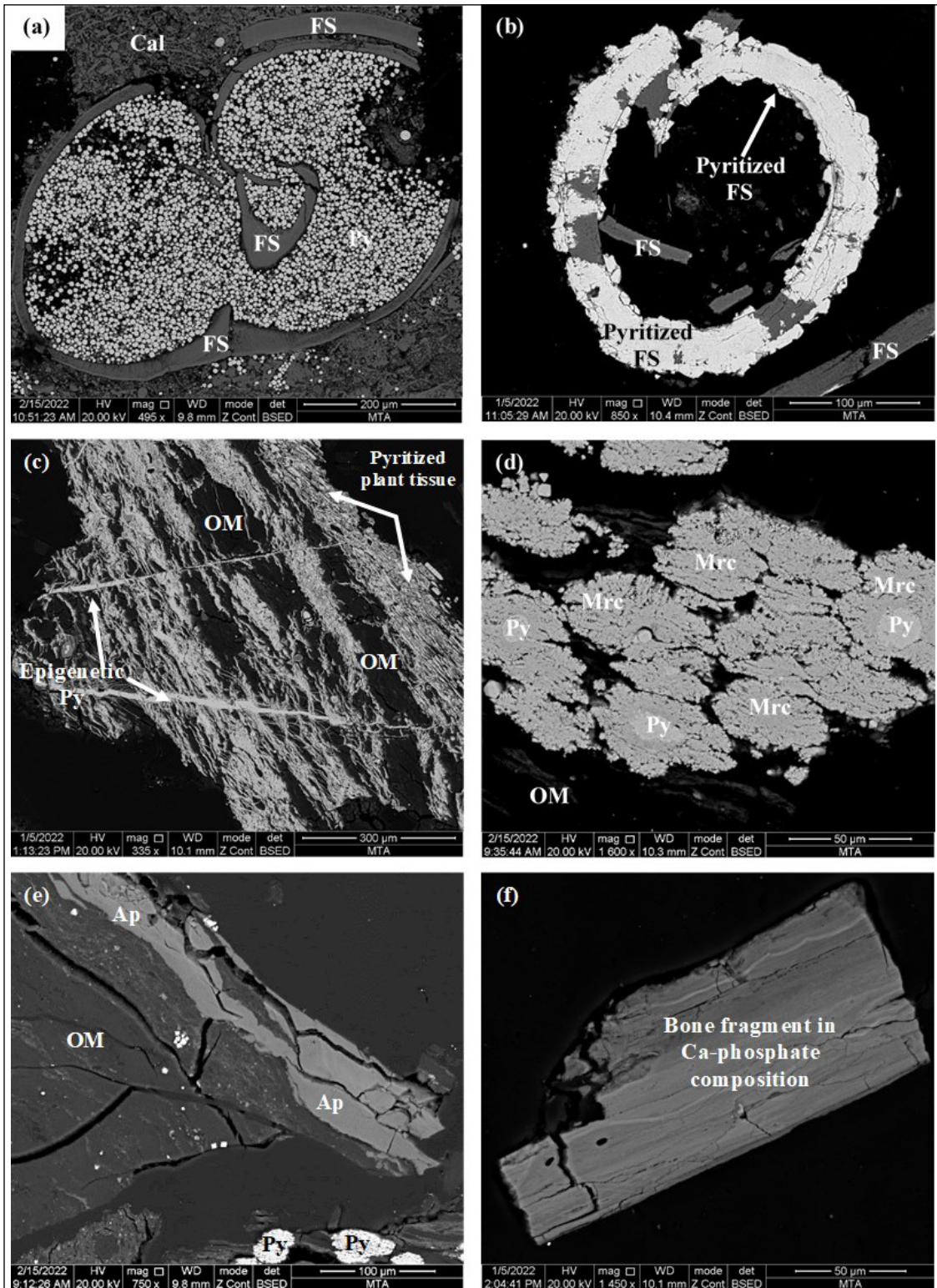


Figure 9- Selected SEM-BSE images from the Bozburun samples: a) calcite (Cal), fossil shell remains (FS) and euhedral pyrite grains, b) fossil shell remains (FS) and pyritized fossil shell remain, c) marcasite (Mrc) overgrowths around framboidal pyrite (Py) grains within organic matter (OM), d) epigenetic cleat/fracture pyrite infillings (Py) with organic matter and pyritized plant tissue, e) cleat/fracture apatite infillings (Ap) within organic matter (OM) and framboidal pyrite (Py) grains and f) fossil bone remain in Ca-phosphate composition.

marcasite (Table 3), and dendritic-like marcasite was identified as overgrowths around framboidal nucleated pyrite grains in a few samples by SEM-EDX (Figure 9d). Marcasite in coal is sometimes thought to be an indicator of marine influence in palaeomires and/or hydrothermal solution penetration (Querol et al., 1989; Rieder et al., 2007); however, both cases can be ruled out based on palaeontological data from the seam and the lack of cleat/fracture marcasite-infillings. Marcasite overgrowths around nuclei of framboidal pyrite grains; on the other hand, it forms replacing early diagenetic framboidal pyrite grains during the late diagenetic stages (Querol et al., 1989; Ruppert et al., 2005; Kolker, 2012). For such marcasite formation, pH should be lower than 5.0 (Ruppert et al., 2005); despite the fact that the co-existence of syngenetic pyrite grains and carbonate bands in these samples could indicate that marcasite formation was developed under weak acidic to neutral conditions. Other sulphide mineral that was identified by SEM-EDX in coal samples is sphalerite (Table 3), and its presence within clay mineral aggregates indicates a clastic origin. These micron-sized sphalerite grains are presumably derived from volcanic and/or magmatic rocks in the adjacent areas as clastic inputs into the palaeomire.

Apatite is the only identified phosphate mineral in the Bozburun coalfield by SEM-EDX, and apatite grains are identified within the clay mineral aggregates and/or syngenetic carbonate bands (Figures 8a, d, 9e, f, 10a), which indicate detrital origin for apatite. The presence of measurable Cl, F, and Sr (Figure 10a) in these grains could also imply that apatite grains have volcanogenic origin (Bohor and Triplehorn, 1993; Dai et al., 2020a). Beside individual apatite grains, cleat/fracture apatite-infillings (Figure 9e) and Ca-phosphate fossil bone remains (Figure 9f) are also observed during SEM-EDX analysis in a few samples. Cleat/fracture apatite-infillings are mostly derived from reactions between liberated P from decay of plant matter and dissolved CaO in porewater during coalification, while Ca-phosphate fossil bone remains are related to biogenic activities within the palaeomire (Ward, 2002). Hence, apatite has both syngenetic (clastic and biogenic) and epigenetic origin.

The identified sulphate minerals in the samples are barite (BaSO_4) and celestine (SrSO_4). Celestine grains are identified as euhedral individual grains within the syngenetic carbonate bands in coal samples and roof rock samples (Figure 10b-f). In addition, individual euhedral barite grains and barite-celestine (Ba, SrSO_4) solid solution overgrowths associated with syngenetic carbonate bands and rarely feldspar grains are also observed in the roof sample (Figure 10e-f). Barite is a common sulphate mineral in coal, while celestine in coal is less common. Both sulphate minerals generally originate from the precipitation of sulphate-rich solutions during coalification and/or leached solutions overlying marine sediments, and syngenetic barite in coal seams is very rare (Finkelman et al., 2019; Dai et al., 2020a, 2021; Karayiğit et al., 2020a). The authigenic formation of celestine is generally related to evaporation of seawater or reactions between Sr-bearing hypersaline fluids with gypsum/anhydrite (Honar, 2004). However, the identified mollusc fauna from the Bozburun coalfield implies freshwater to oligohaline conditions during the late Miocene. Therefore, any influence of marine and/or hypersaline water influence on the palaeomire and/or onset of geochemical coalification could be ruled out for the study area. Celestine and Sr-bearing barite have been found within cavities of syngenetic framboidal pyrite grains in Turkish Neogene coals, as well as Sr-bearing barite overgrowths around feldspars (e.g., Kangal/Sivas and Keles and Orhaneli/Bursa) (Karayiğit et al., 2019, 2021; Çelik et al., 2021). In these coalfields, altered tuff layers are located in the coal seams, and liberated Sr and Ba from alteration of volcanogenic minerals (e.g., Sr-/Ba-bearing feldspars) and/or air-fall ash (tephra) within paleomires were reacted with sulphuric acid in the palaeomire. As a result of sulphate-reducing bacteria activity in the palaeomire, celestine and Sr-bearing barite were precipitated along with syngenetic framboidal pyrite grains. Furthermore, the geochemical data from the Yamadağ volcanic complex reported high Ba and especially high Sr contents of Miocene andesite and basalt (Kocaaslan and Ersoy, 2018; Di Giuseppe et al., 2021). In the roof rock samples, the presence of barite grains and overgrowth barite-celestine solid solution associated with feldspar grains could explain the source of Ba and Sr in the roof rock samples. The presence of Sr-

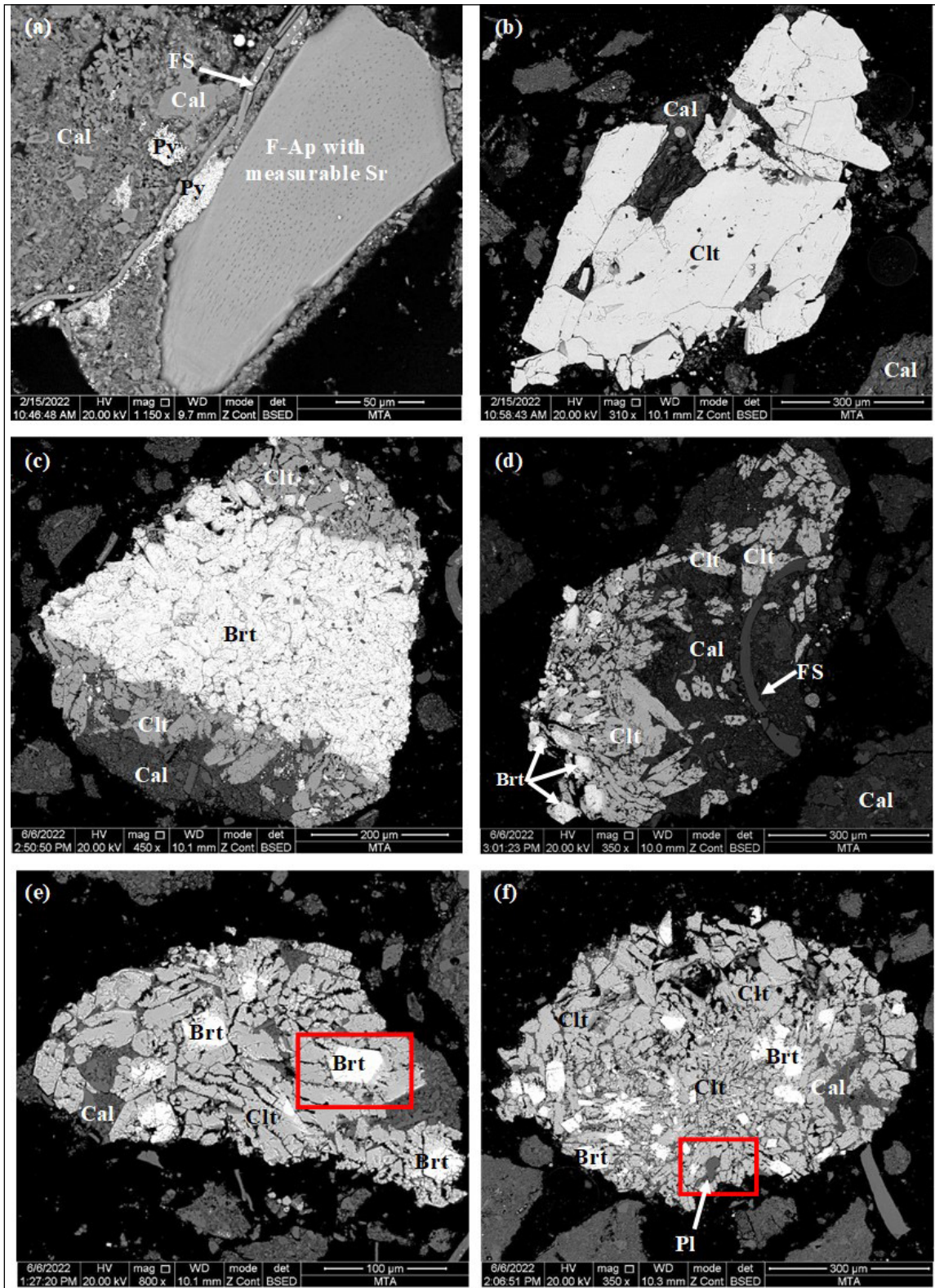


Figure 10- Selected SEM-BSE images from the Bozburun samples; a) fluorapatite (F-Ap) with measurable Sr and fossil shell (FS) remains within syngenetic carbonate bands (Cal) and framboidal pyrite (Py) grains, b) authigenic celestine (Clt) grains and syngenetic carbonates (Cal), c), f) celestine (Clt) and barite (Brt) within syngenetic carbonates and clastic plagioclase (Pl) grains and fossil shell (FS) remains. (Highlighted area in images e and d are reported in Figures 13 and 14, respectively).

bearing volcanogenic apatite grains could be another evidence of a clastic volcanogenic mineral source for Sr in the samples. Even though Ba and Sr could be derived from alteration of volcanogenic minerals in the Bozburun palaeomire, no altered tuff layer was identified in the coal seam and/or volcanic rocks were not observed from the overlying units in the coalfield. Therefore, the necessary Ba and Sr ions should have derived from another main source instead of clastic feldspar grains from middle Miocene volcanic rocks in the basin.

Economic gypsum and celestine deposits are found in late Cretaceous, Eocene, and early Miocene marine carbonates in the neighbouring Sivas Basin (Tekin et al., 2002). Similarly, Palaeogene-late Eocene marine carbonates in the basement rocks of the Malatya Basin contain gypsum layers and lenses like those in the Sivas Basin (Sümengen, 2016). Strontium is more soluble in aquatic environments than Ba (Hanor, 2004), and additional Sr could be introduced into the Bozburun palaeomire by dissolved sulphate-rich water from the gypsum-bearing Palaeogene-late Eocene marine carbonate. Therefore, alteration of clastic Ba-and Sr-rich feldspars from the middle Miocene Malatya volcanics and/or sulphate-rich water influx from the gypsum-bearing pre-Neogene units could be a source for Ba and Sr ions in the Bozburun palaeomire. Besides, Sr could display a high concentration in aragonitic mollusc shells, and this element could be essential for biogenic aragonite precipitation in the aquatic system (Hanor, 2004; Böning and Bard, 2009; Brisset et al., 2017) as well as Sr-bearing calcareous fossil shell remains were reported from some Turkish Neogene coalfields (Karayığit et al., 2000). Hence, introduced Sr from alteration of clastic feldspar grains in the palaeomire and/or sulphate-rich water influx could be uptaken by molluscs. With this assumption, a measurable amount of Sr should be traced by SEM-EDX from calcareous fossil shell remains in the studied samples. During the SEM-EDX observation, Sr was rarely detected from these remains (Figure 11); nevertheless, Sr could also be released from aragonitic fossil shell remains during calcination in the depositional environment at an early diagenetic stage (Querol et al., 1999; Hanor, 2004; Marcano et al., 2015). Furthermore, Sr could not be incorporated

into calcite due to its bigger ionic radius than this of Ca^{2+} (Langston et al., 1998; Finch and Allison, 2008). Thus, liberated Sr ions from calcination of fossil remains also seem having reacted with dissolved sulphate ions in the mire water. Overall, authigenic barite and celestine, and barite-celestine solid solution formation took place during diagenetic stages.

5.3. Factors Controlling the Elemental Distribution

The statistical approach is commonly applied for determining mode of occurrence of elements in coal (Dai et al., 2021). Nevertheless, recent studies denoted that the statistical approach should be cooperated with SEM-EDX or other direct methods in order to eliminate misinterpretations (Dai et al., 2021; Xu et al., 2022; Eminağaoğlu et al., 2022). Therefore, both statistical and SEM-EDX analyses were here applied in order to accurately identify the controlling factors of elemental distribution. The major oxides, such as SiO_2 , TiO_2 , MgO , and K_2O , display positive correlations with ash yield and Al_2O_3 content (Table 7); which indicates aluminosilicate mineral affinity. The SEM-EDX data also agrees with this observation, and the contents in TiO_2 , MgO , K_2O , and Na_2O are determined from clay minerals. Besides clay minerals, feldspar grains in the samples are another source of K_2O and Na_2O . In addition, Al_2O_3 contents of the samples show positive correlations with elements like Ga, Rb, Ni, and the REY (Table 7), which also imply an aluminosilicate affinity. Since aluminosilicate minerals in the samples are clastic in origin, clastic influx from volcanic and metamorphic rocks into the palaeomire could control their distributions and enrichment. This might also explain why P_2O_5 concentrations are high in clastic apatite-bearing samples (Figures 8a and 10a, and Table 4). Additionally, measurable Mg is also determined from fossil shell fragments (Figure 11). Furthermore, TiO_2 displays a moderate positive correlation with Fe_2O_3 , which could be related to the accessory Ti-oxide and/or titanite in the samples (Figure 8d). The lack of correlation among Fe_2O_3 , ash yield, total S, Al_2O_3 , and SiO_2 contents could imply an intermediate affinity for Fe_2O_3 ; however, Fe is also detected in clay minerals, sulphides, and sulphates in the samples. Therefore, iron seems having an inorganic affinity in the samples.

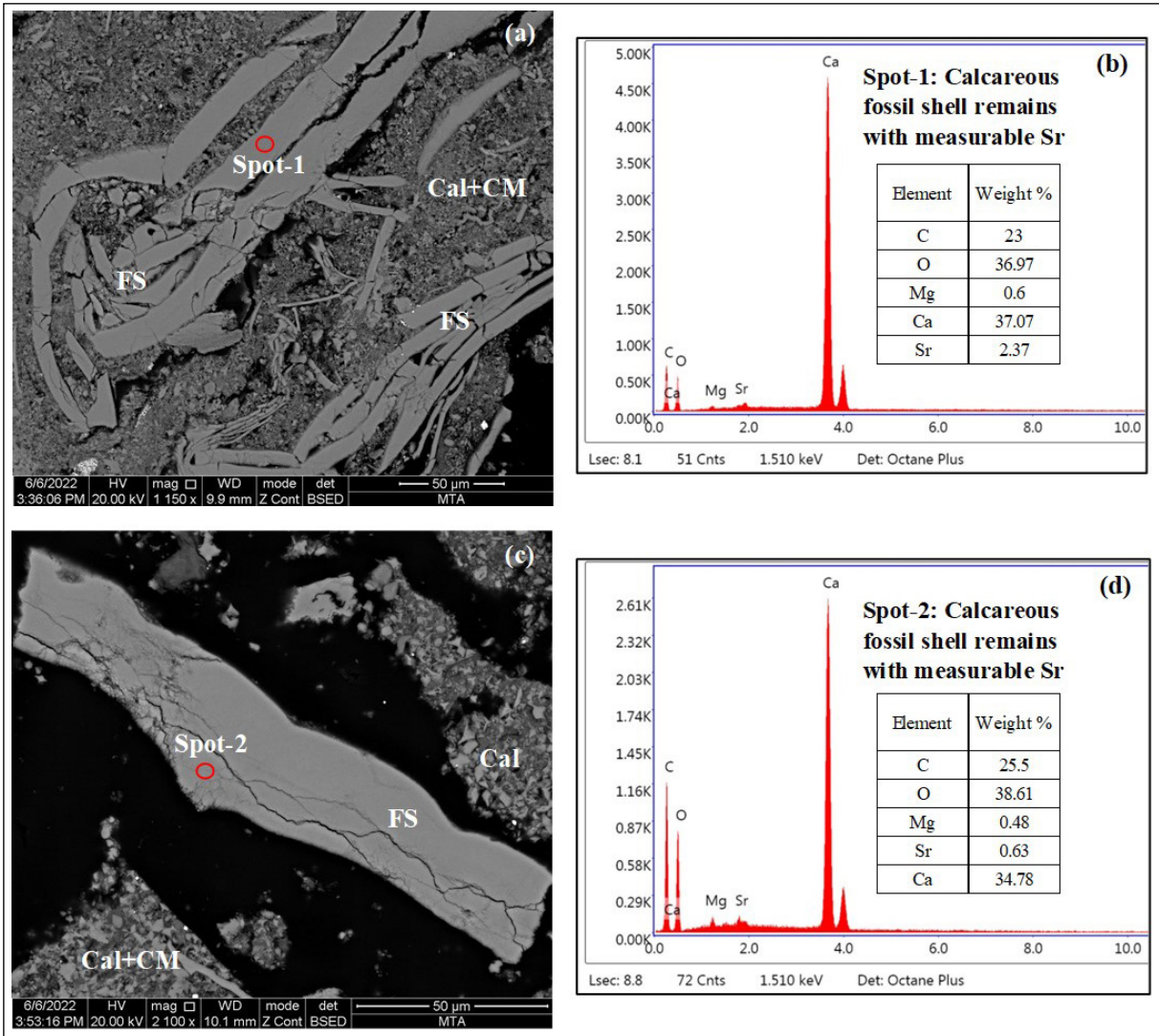


Figure 11- SEM-BSE images; a), c) SEM-EDX spectra of fossil shell (FS) in syngenetic carbonate (Cal), b) and d) SEM-EDX spectra of clay mineral (CM) matrix.

Table 7- Element affinities with ash yield (%), d) deduced from the calculation of Pearson's correlation coefficients.

Correlation with ash $0.70 \leq r < 1.0$
Al_2O_3 , MgO, K_2O , Ga
Correlation with ash $0.40 \leq r < 0.70$
SiO_2 , TiO_2 , MnO, Sc, Cr, Rb, La, Ce, Eu, Gd, Tb
Correlation with ash $r \geq -0.40$
B, V, Mo, U, total S
Correlation with Al_2O_3 $0.70 \leq r < 1.0$
SiO_2 , TiO_2 , MgO, K_2O , Sc, Cr, Co, Ni, Zn, Ga, Rb, Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Yb, Th
Correlation with Al_2O_3 $0.40 \leq r < 0.70$
Na_2O , Li, Cu, Pb
Correlation with Fe_2O_3 $0.50 \leq r < 1.0$
Li, Ga, Co, Cu, Ni, Pb, Zn, total S
Correlation with CaO $0.50 \leq r < 1.0$
Ba, Sr
Correlation with total S $0.50 \leq r < 1.0$
B, Mo, V, As

The CaO displays a weak positive correlation with ash yields. The organic matter contains measurable by SEM-EDX amounts of Ca and S. This data implies an organic affinity for CaO. In Turkish Neogene coals, sulphate minerals, particularly gypsum/anhydrite, are reported as minor phases due to the evaporation of porewater during storage or reactions between liberated sulphuric acid from pyrite oxidation and CaO in porewater or organic matter (Karayığit et al., 2017a, 2021). In contrast, gypsum/anhydrite are lacking from XRD and are also not identified during SEM examination. Although additional high-resolution analysis should be needed, measurable Ca and S in the organic matter might be an indicator for sub-micron sized gypsum/anhydrite grains (Finkelman et al., 2019; Dai et al., 2020b). Therefore, Ca seems to have an inorganic rather than organic affinity. Supporting this assumption, the CaO concentrations are generally high in fossil shell fragments and syngenetic carbonate-bearing samples. Thus, the CaO in samples has a carbonate affinity. Furthermore, the CaO displays moderate positive correlations with Ba ($r_{CaO} = 0.67$) and Sr ($r_{CaO} = 0.65$). These correlations again imply the sulphate affinity for CaO, which is supported by measurable Ca from barite and celestine by SEM-EDX (Figures 12-14). Although CaO does not show any meaningful correlations with Al_2O_3 and P_2O_5 , CaO in the samples could also be partially affiliated with apatite, Ca-phosphate fossil bone remains, and feldspar grains in the samples. Hence, CaO is mainly derived from carbonate minerals, and to a lower degree with sulphates, apatite and feldspars.

The Sr-enrichment in coal is related to epigenetic sulphate (e.g., celestine and Sr-bearing barite and gypsum/anhydrite) minerals, carbonate minerals (e.g., strontianite); and/or clastic feldspar grains, biogenic aragonite, and syngenetic phosphate and zeolite minerals (Pollock et al., 2000; Dai et al., 2012b, 2021; Karayığit et al., 2020b; Spiro et al., 2019; Çelik et al., 2021; Du et al., 2021). In the studied samples, Sr, as mentioned above, only displays a positive moderate correlation with CaO. This correlation and the presence of measurable Sr in fossil shells could easily imply a carbonate affinity for Sr (Figure 11). However, this could be only applicable for some samples due to the presence of celestine and

Sr-bearing Cl/F-apatite grains in coal and roof rock samples (Figure 10a). In the roof rock sample, Sr is also measured from barite grains (Figures 13 and 14). Therefore, significantly high Sr concentrations in samples are mainly controlled by sulphate minerals. Furthermore, measurable Sr is not traced by SEM-EDX from organic matter, which indicates a clear inorganic affinity for Sr.

The B concentrations of the Bozburun coal samples are generally higher than 110 ppm (Table 4). Such concentrations could be evidence of paralic conditions (Goodarzi and Swaine, 1994; Goodarzi et al., 2020). The reported palynoflora and mollusc fauna from the Bozburun Formation suggest that freshwater conditions have been common (Türkmen et al., 2004; Nazik et al., 2008). The B-enrichment in coal was not always controlled by seawater and the presence of clay minerals or certain detritus accessory minerals (e.g., tourmaline). Boron uptake by peat-forming plants could cause B-enrichment (Boyd, 2002; Karayığit et al., 2020a, b, 2021; Dai et al., 2021). The Turkish Neogene coals have B concentrations higher than 110 ppm despite their formation under freshwater conditions (Karayığit et al., 2000; Tuncalı et al., 2002; Palmer et al., 2004). Boron has been derived from the wash-out from the volcanic rocks in the adjacent areas. Since middle Miocene volcanic rocks are close to the Bozburun coalfield, similar controlling parameters seem to have been developed for B enrichment. The strong negative correlation between B and ash yield ($r_{ash} = -0.933$) could easily indicate an organic affinity for B and possible B uptake by plants in the mires. Boron, however, could easily be incorporated into clay minerals in the palaeomires, and the presence of clay minerals and illite/mica grains could also imply that B enrichment in the samples is also partially controlled by aluminosilicate minerals.

Chromium enrichment in Turkish Neogene coals is mostly related to clastic chromite grains derived from ophiolites in the basement (Karayığit et al., 2000, 2020a, 2021; Palmer et al., 2004; Çelik et al., 2021). Ophiolites, like in other Turkish Neogene coalfields, are found in the Bozburun coalfield's adjacent areas (Figure 1a), and chromitites reported from these ophiolites (Uysal et al., 2007). However,

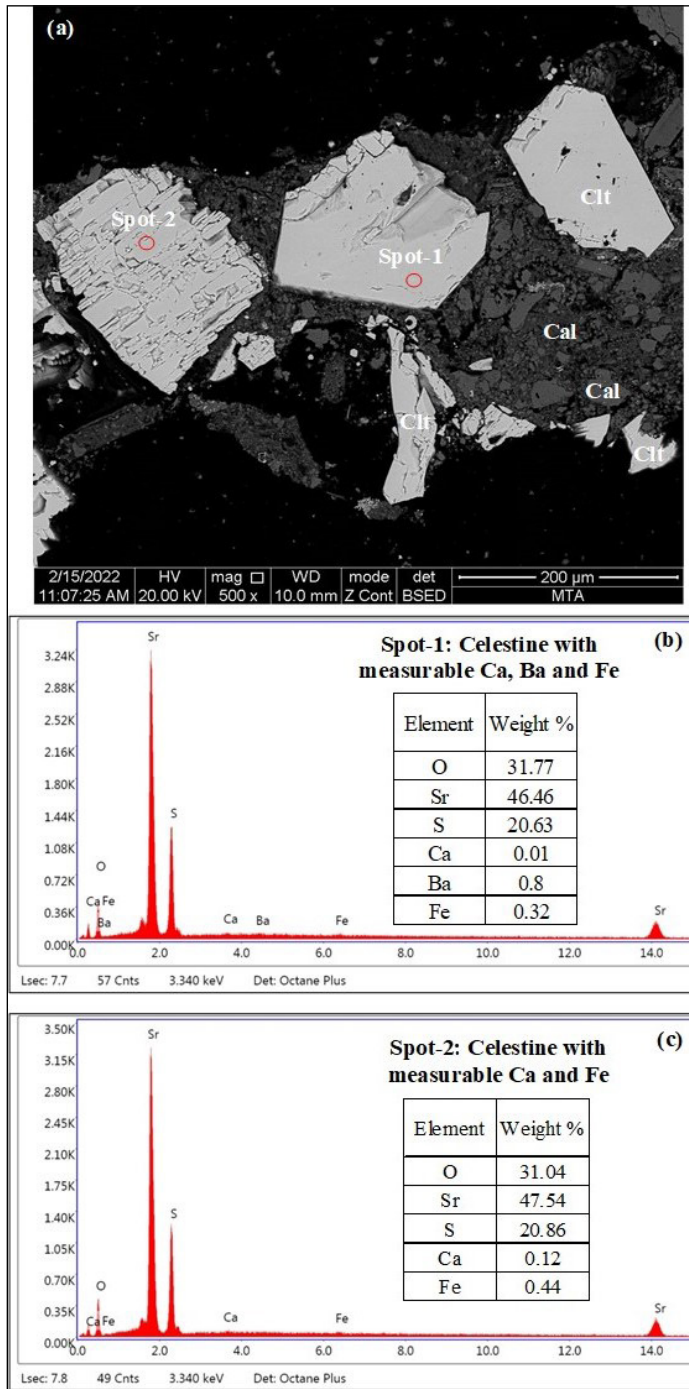


Figure 12-SEM-BSE images; a) SEM-EDX spectra, b), c) of authigenic celestine (Clr) grains within syngenetic carbonate (Cal) band.

chromite grains were not found in the samples during the SEM observations. Apart from clastic chromite grains, clastic input from ophiolitic rock within the palaeomire and their alteration by-products could control Cr enrichment of coal (Ruppert et al., 1996; Dai et al., 2021). In such cases, chlorite (chamosite)

may contain Cr^{3+} and/or Fe^{3+} which could be partially replaced by Cr^{3+} . Considering the presence of clastic chlorite (chamosite) in the samples and strong positive correlations among Cr, Al_2O_3 , SiO_2 and MgO (Table 7), it is possible that Cr enrichment was controlled by clastic chlorite grains. Nickel is another element

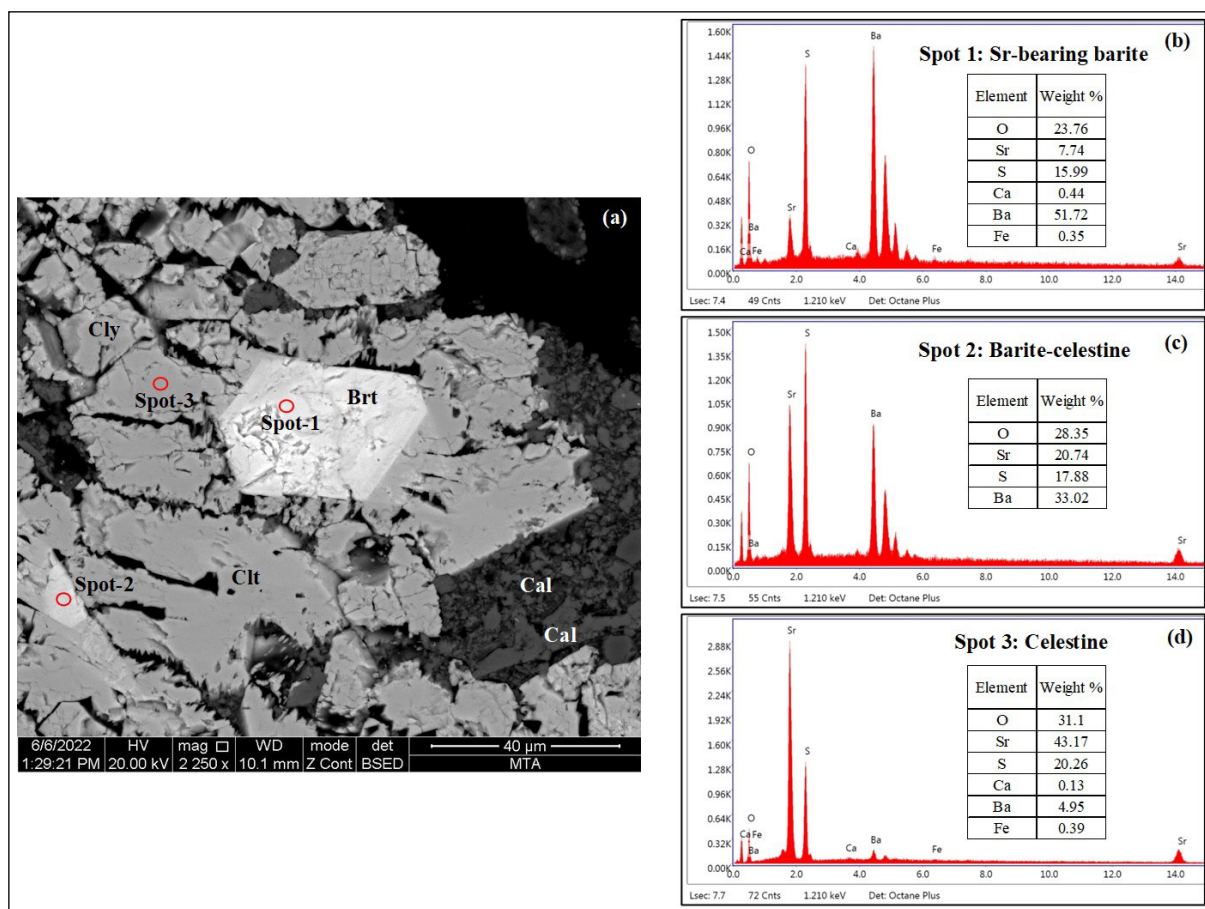


Figure 13- SEM-BSE images; a) SEM-EDX spectra, b), d) of barite (Brt) and celestine (Clt) within syngenetic carbonate (Cal) band.

which could be associated with clay minerals in coal or clastic input from the basement ophiolites (Ruppert et al., 1996). The positive moderate correlations among Ni, Al_2O_3 , and SiO_2 also suggest an aluminosilicate affinity for Ni (Table 7); however, the SEM-EDX indicates another affinity for Ni. During the SEM-EDX studies, measurable Ni and As contents were detected in matrices of framboidal pyrite aggregates and/or marcasite overgrowths around nuclei of framboidal pyrite (Figure 15). As the samples contain more Ni- and As-bearing marcasite overgrowths, Ni and As enrichments in the coal samples might be took place during the late diagenetic stages. The MnO does not display any significant correlation with ash yield, total S, or any other elements, which implies an intermediate affinity for MnO. In contrast, Mn is detected from euhedral framboidal grains (Figure 16). Hence, MnO shows a sulphide affinity. While elements Cu, Zn, and Pb were not detected in the framboidal pyrite grains, these elements generally display concentrations in

framboidal pyrite grains below the detection limit of conventional SEM equipment (Hower et al., 2008; Kolker, 2012). The moderate positive correlation between Fe_2O_3 and Zn can also be controlled by sphalerite grains in the samples (Figure 8b).

The elements V, Mo, and U also have negative correlations with ash yields (Table 7), which implies an organic affinity. Furthermore, V, Mo, and U elements show positive correlations with total S contents (Table 7), which are typical for Turkish Neogene coals. The enrichment of these elements in coal, on the other hand, could have been controlled by redox conditions (Arbuzov et al., 2011; Dai et al., 2021). These elements are generally enriched due to the development of anoxic conditions within the palaeomire and, in some cases, neutral to weak alkaline conditions. The latter one could be possible since fossil shell fragments and syngenetic carbonate bands are common in the samples. In the Turkish Neogene coals (e.g., Soma,

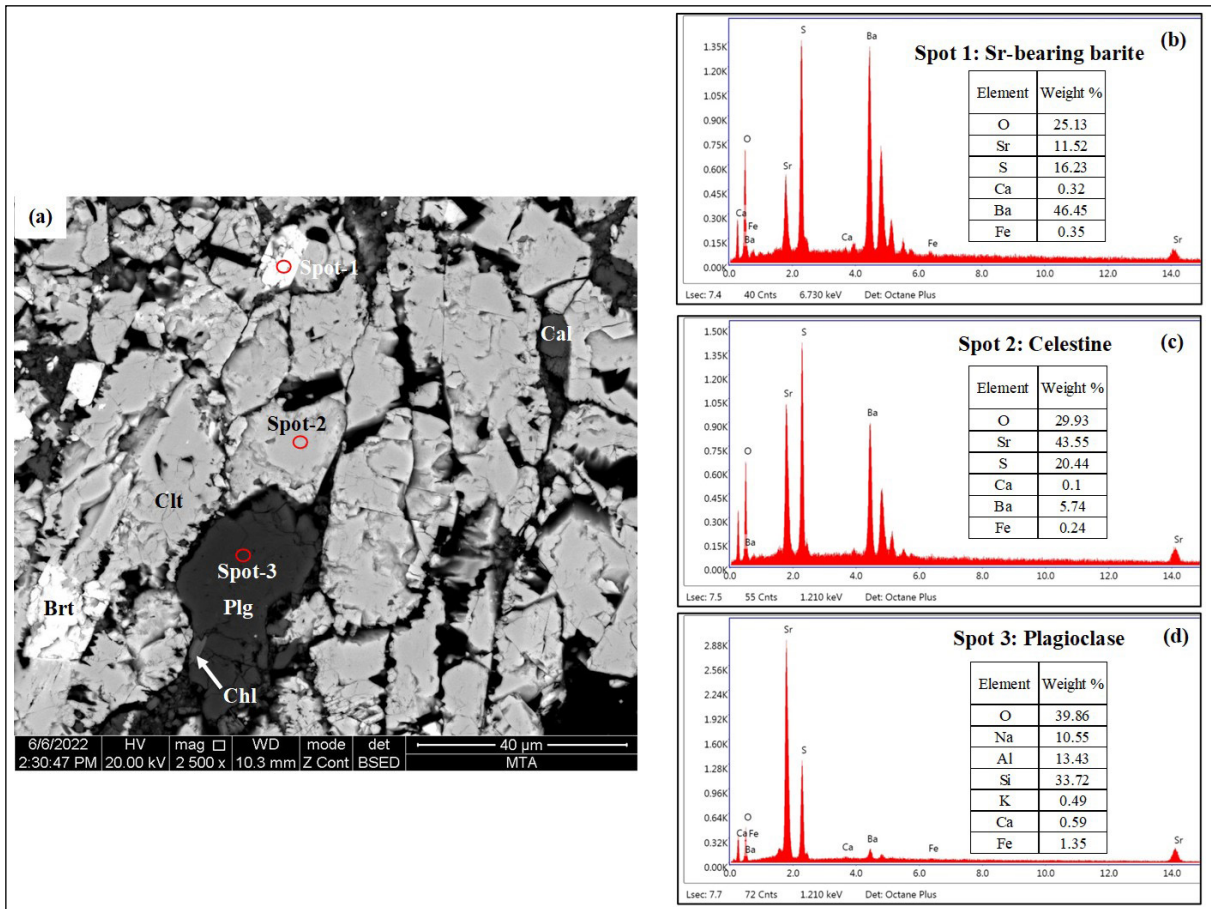


Figure 14- SEM-BSE images; a) and SEM-EDX spectra, b), d) of barite (Brt) and celestine (Clt) around clastic plagioclase (Plg) grain, and calcite (Cal) and chlorite (Chl).

Orhaneli, and Çayırhan coalfields), the alterations of synchronous volcanic input and/or clastic influx into the palaeomire could cause V, Mo, and U enrichment due to anoxic conditions (Querol et al., 1997; Palmer et al., 2004; Karayığit et al., 2017a, 2021b, 2022). Considering that the middle Miocene volcanic rocks are exposed in the eastern margins of the coalfield, the source of V, Mo, and U could have been related to clastic input. These elements could be taken by peat-forming plants, like B; thus, they are enriched in coal samples. This could also explain their positive correlation with B.

5.4. Depositional Environment

The coal facies diagrams are the most common approach for assessing the depositional conditions during peat accumulation; nevertheless, these diagrams should be supported by sedimentological, palaeontological, mineralogical, and geochemical

(e.g., biomarker) data from coal seams due to the complex nature of the peatlands and uncertainties about the origin of some macerals (Crosdale, 1993; Moore and Shearer, 2003; Oikonomopoulos et al., 2015; Dai et al., 2020a; Guo et al., 2020; Liu et al., 2020; Hower and Eble, 2022). Therefore, in this study, the coal facies data is interpreted along with elemental and mineralogical compositions of the studied samples, and published sedimentological, palaeontological, and organic-geochemical data from the Bozburun coalfield (Türkmen et al., 2004; Nazik et al., 2008; Yalçın-Erik and Ay, 2021). The coal samples are generally plotted close to the mid-point between the A and B apexes on Mukhopadhyay's (1989) ternary diagram (Figure 17). The presence of both woody and herbaceous peat-forming plants in the palaeomires resulted in such distribution. In addition, some mineral-rich samples from the low part of the seam are plotted close to apex B, which suggests the predominance of herbaceous

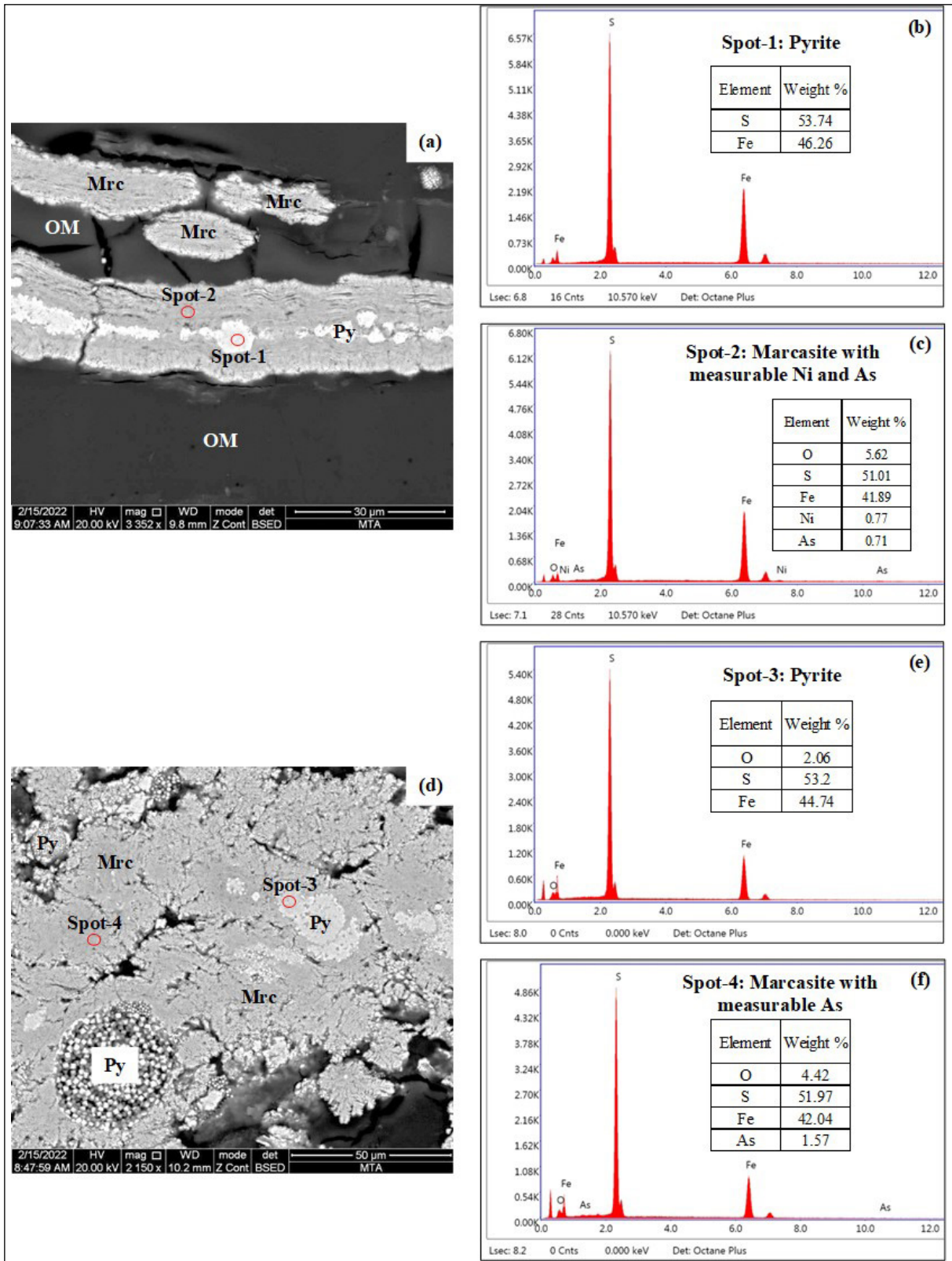


Figure 15- a, d) SEM-BSE images of pyrite (Py) and b), c, e) and f) SEM-EDX spectra (b, c, e and f) marcasite (Mrc).

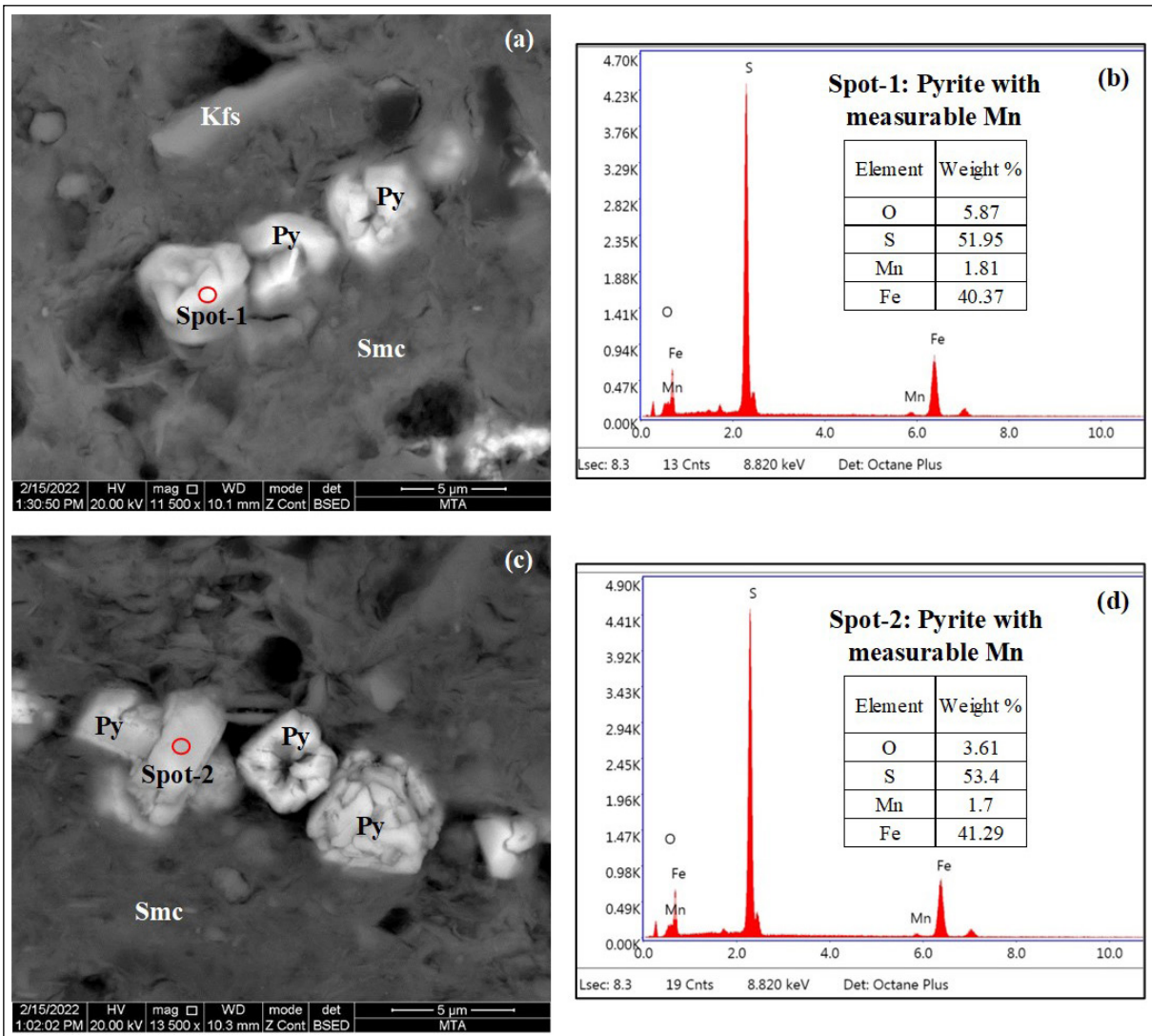


Figure 16- SEM-BSE images (a-c) and SEM-EDX spectra (b-d) of pyrite (Py) grains within smectite (Smc).

peat-forming plants and/or macrophyte in palaeomires. The relatively high total inertinite contents (> 10% on a mineral matter-free basis) of these samples could have been controlled by oxic conditions such as these caused by exposure of peat surface due to very low watertable and/or wildfires on palaeomire's surface or in the surrounding area (Figure 17). The presence of semifusinite and fusinite macerals in these coal samples are an indicator of wildfires within the palaeomire (O'Keefe et al., 2013; Hower et al., 2021). Char-rich lithotype should be observed in the studied coal seam a, if such thermal oxidation took place in the palaeomire (O'Keefe et al., 2013). In the studied profile, however, neither char-rich lithotypes nor char bands were observed. High inertinite contents do not

always relate to oxic conditions in the palaeomire, and the presence of allochthonous inertinite macerals could result in higher inertinite contents (O'Keefe et al., 2013; Oskay et al., 2019). In the coal samples, semifusinite, fusinite, and inertodetrinite macerals are mostly associated with clay mineral aggregates and/or detrohuminite macerals. Thus, the high inertinite content in the low part of the seam are due to inertinite transport by surface water/windblown or mechanical degradation and subsequent oxidation in the palaeomire.

The Gelification Index (GI) vs Tissue Preservation Index (TPI) and the Groundwater Index (GWI) vs Vegetation (VI) diagrams were used in order to

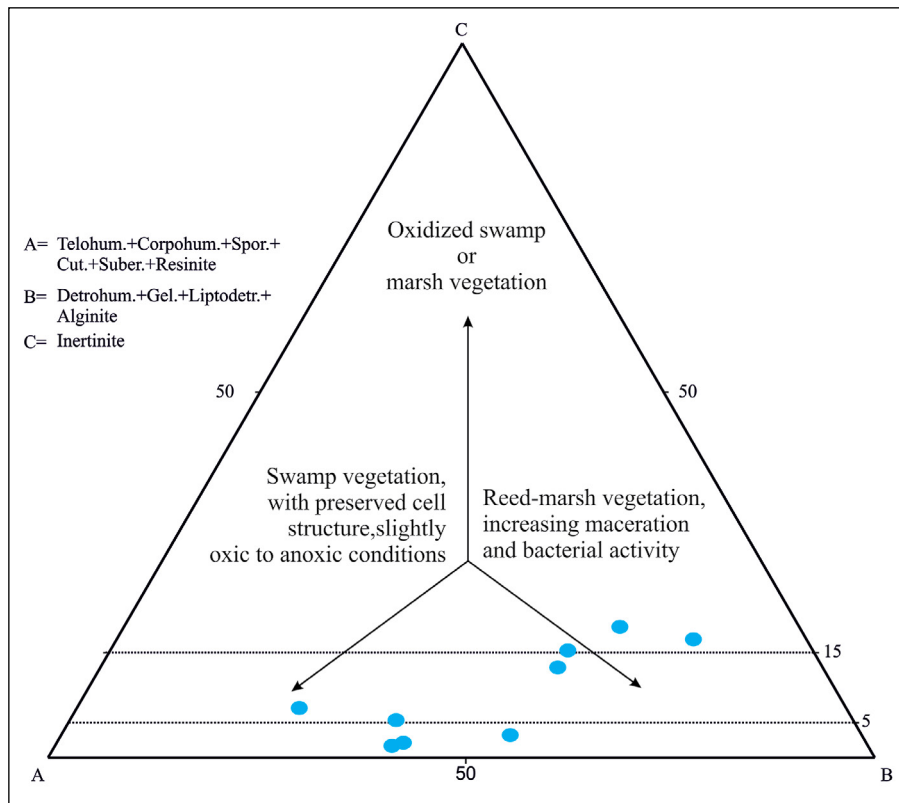


Figure 17- The Bozburun coal samples on Mukhopadhyay's ternary diagram (after Mukhopadhyay, 1989).

evaluate the preservation of organic matter and the vegetation type in the palaeomire (Figure 18). These diagrams were firstly proposed for late Palaeozoic coals of Canada and Australia by Calder et al. (1991) and Diessel (1992), respectively. Since the Cenozoic flora differs from the late Palaeozoic one, in this study the modifications proposed by Kalaitzidis et al. (2004) are applied. The TPI and VI values vary widely in the studied profile (Figure 18), which could imply variable preservation degree of organic matter and/or variations in the peat-forming vegetation. Additionally, the reported TPI (0.17-0.33) and VI (0.38-0.81) values from the western part of the Bozburun coalfield indicate vegetation variations in the palaeomire during the late Miocene (Yalçın-Erik and Ay, 2021). It is worth mentioning that the reported gelohuminitic contents are very high in the western part of the Bozburun coalfield, which in turn, reduces TPI and VI values. Despite this, increasing trends of TPI and VI values towards the upper part of the studied profile were calculated (Figure 18 and Table 2). The TPI and VI values from the low part of the seam are generally lower than 1.0, which indicates the predominance

of herbaceous peat-forming plants during the initial stages of peat accumulation (Oskay et al., 2016; Guo et al., 2020). The presence of palynomorphs related to reed and macrophyte plants, as well as the short-chain *n*-alkanes in the Bozburun coalfield also support this assumption (Türkmen et al., 2004; Yalçın-Erik and Ay, 2021). Furthermore, freshwater gastropod remains and syngenetic carbonate bands in coal seam could also be another evidence for lakeshore (limnetic) conditions and/or Ca-rich water influx into the palaeomire (Siavalas et al., 2009; Karayığit et al., 2017a). Hence, the Ca concentration of the coal samples is significantly higher in this part of the seam (Figure 7 and Table 4), and alkaline conditions seem to be more common. Gelification of organic matter is supposed to be high due to bacterial activity forced by the increased alkalinity (Dehmer, 1995; Zdravkov et al., 2006; Stock et al., 2016); however, the GI values are generally lower than 1.0 in this part of the seam. Fluctuating water tables might also cause mechanical degradation of herbaceous plant matter and allochthonous inertinite macerals (Mach et al., 2013; O'Keefe et al., 2013). Thus, the attrinite and

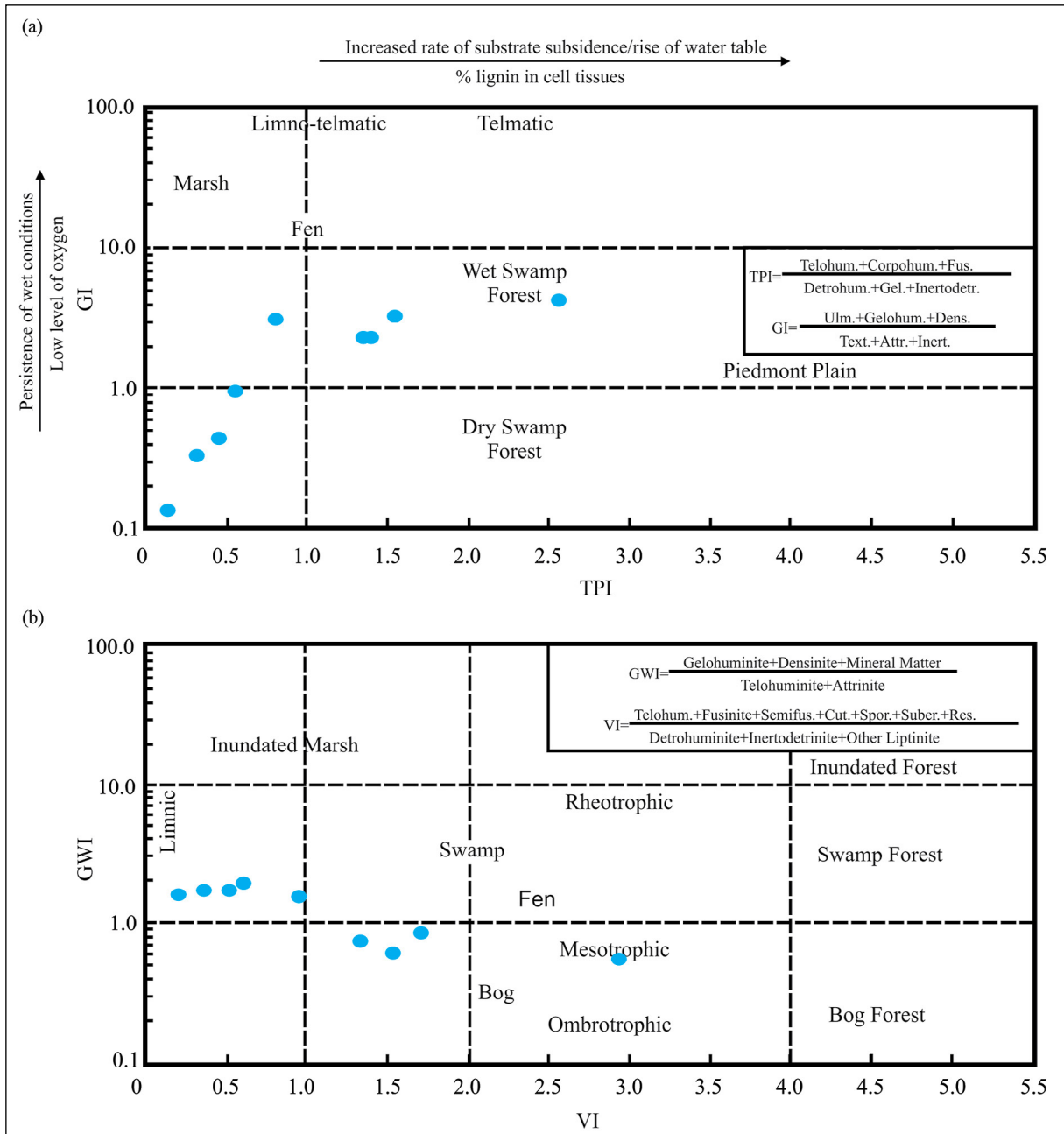


Figure 18- The distributions of the Bozburun coal samples on; a) GI vs. TPI plot of (after Diessel, 1992, modified from Kalaitzidis et al., 2004), b) VI vs. GWI plot of (after Calder et al., 1991, modified from Kalaitzidis et al., 2004).

inertodetrinite contents could be high; in turn, the GI values of the low part are low.

In contrast to the low profile part, the relatively higher TPI and VI values (Figure 18 and Table 2) in the central and upper parts of the seam imply an increased contribution of forested vegetation (Oikonomopoulos et al., 2015; Omodeo-Salé et al., 2017; Oskay et al., 2019; Karayığit et al., 2020a). Furthermore, the

reported existence of certain palynomorphs (e.g., *Inaperturopollenitis dubius*) and the long-chain *n*-alkanes point to coniferous peat-forming plants (Türkmen et al., 2004; Yalçın-Erik and Ay, 2021). This could also explain fluorescent ulminite A macerals in this part of seam, which is related to the presence of H-rich compounds in peat-forming plants and/or a coniferous peat-forming vegetation in the palaeomires

(Mastalerz et al., 2013; Karayığit et al., 2017*b*, 2020*b*; Oskay et al., 2019; Kus et al., 2020). Such vegetation is typical for wet-forest mires in flood and/or upper delta plains (Buillit et al., 2002). Supporting this assumption, previous sedimentological studies from the southern part of the Malatya Basin show that the Bozburun Formation was deposited under shallow lake and deltaic conditions. Furthermore, the watertable was generally stable and clastic influx could be low under such conditions; thus, anoxic conditions resulted in relatively good preservation of organic matter (Zdravkov et al., 2006; Mach et al., 2013; Kus et al., 2020). The anoxic conditions could be evident from the syngenetic framboidal pyrite grains and the decrease trend of ash yield upwards. The reported pristane/phytane (Pr/Rh) ratio from the Bozburun coalfield could also imply anoxic conditions (Yalçın-Erik and Ay, 2021). The GWI values of the coal samples from the upper part of the seam, however, are relatively low (Figure 18*b*), which is acceptable for telohuminitic-rich coals (Kalaitzidis et al., 2004; Oikonomopoulos et al., 2015; Karayığit et al., 2017*a*). The relatively high GI values and the syngenetic carbonate along with calcareous fossil remains could also imply that Ca-rich water influx and/or aquifer support into the palaeomire was continuous and gelification of organic matter is relatively high during the late stages of peat accumulation (Dehmer, 1995; Stock et al., 2016). Hence, the pH value of the mire water is alkaline, and concentrations of redox sensitive elements (e.g., Mo) are enriched in the upper part of the seam (Figure 7). The source of Ca-rich water could derive from the Palaeocene to late Eocene marine carbonates in the basement. As mentioned previously, these carbonates also contain gypsum layers; thus, the aquifer from these carbonates could also enrich the peat with sulphates. This supply could also cause the formation of authigenic sulphate minerals (e.g., celestine) since Sr is soluble in sulphate-rich waters (Honar, 2004). In general, the Sr/Ba ratios higher than 1 along with high total S content could be an indicator of marine influence during peat accumulation and/or penetrating solutions from the overlying marine sediments (Spiro et al., 2019; Medunić et al., 2020; Lui et al., 2021). Both cases seem to have been impossible for the Bozburun coalfield, since only terrestrial and lacustrine conditions were developed in the

Malatya Basin during the late Miocene. As mentioned previously, the alteration of clastic feldspar grains from the middle Miocene volcanic rocks could be also provided additional Sr²⁺ ions. In turn, Sr/Ba ratios and total S contents of coal samples are elevated and could be high like paralic coals. Nevertheless, sulphate-rich water influx into the palaeomire may also cause weak brackish conditions, and this could explain the presence of freshwater to oligohaline mollusc fauna in the Bozburun coalfield and the presence of salinity indicator biomarkers (Nazik et al., 2008; Yalçın-Erik and Ay, 2021). Besides, the significantly high Ba and Sr contents could also indicate subsidence ratio during the late Miocene in the study area was optimal for the fixation of Ba and Sr in sulphate minerals in the palaeomires (Hower and Eble, 2022). Moreover, the variations on clastic-influx ratio, common peat-forming vegetation and mire water chemistry between western and eastern parts of the Bozburun coalfield seem to cause differences on coal quality parameters and mineralogy.

6. Results

Changes in peat-forming environment, redox conditions, clastic influx, and chemistry of water supply in the palaeomire have implications for coal quality, mineralogical, and elemental composition of the late Miocene coal seam in the eastern part of the Bozburun coalfield. The low part of the seam was accumulated under limnotelmatic conditions, which were open to clastic influx and water table fluctuation, and Ca-rich water influx was high into the palaeomire. Hence, detrohuminitic, allochthonous inertinite, and calcareous fossil shell remains were commonly identified, and ash yields and volatile matter contents are relatively higher in this part of the seam. Furthermore, Ca-rich water influx resulted in the formation of neutral to weak alkaline conditions, which allowed authigenic formation of syngenetic carbonate minerals. Thus, CaO concentrations of the coal samples are significantly high in this part of the seam. The increasing trends of telohuminitic proportions, TPI, and VI values towards the upper part of the seam could imply the formation of pure telmatic (wet-forest mire) conditions during the late stages of peat accumulation. Low clastic influx and stable water table conditions led to the establishment of anoxic conditions, in which authigenic framboidal

pyrite grains and marcasite overgrowth formed. Thus, chalcophile elements were enriched in the coal. Furthermore, continuous Ca-rich water influx into the palaeomire seems to control gelification of organic matter. The co-existence of syngenetic framboidal pyrite grains and carbonate minerals in the palaeomire of the upper part also implies weak acidic to neutral conditions; in turn, V, Mo and U are enriched in this part.

The high Sr/Ba ratios, the high total S contents and the presence of authigenic marcasite in the coal samples might be an indication of marine influence and/or penetration of porewater from overlying marine sediments. All these are clearly inapplicable in the Bozburun coalfield due to the freshwater mollusc remains, and the freshwater peat-forming plants according to previously published palaeontological and biomarker data. The formation of celestine and Ca- and Sr-bearing barite during diagenetic stages could be related to Sr-bearing sulphate-rich water influx into the palaeomire from gypsum-bearing Palaeogene and late Eocene carbonates and clastic feldspar grains from middle Miocene volcanic rocks. In addition, Sr uptake by mollusc fauna within the palaeomire could also cause elevated Sr-concentrations in fossil shell fragments-bearing coal and non-coal samples. Overall, the chemical composition of the water supplied the palaeomire and the redox conditions controlled the mineralogical and the elemental compositions in the eastern part of the Bozburun coalfield.

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