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RESEARCH ARTICLE

MAJOR and TRACE ELEMENT GEOCHEMISTRY of the MALKARA (TEKIRDAĞ, TURKEY) COALS

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ABSTRACT

Coal, which contains various amounts of major and trace elements, has the feature of being a mineral deposit according to the accumulation rate of certain elements. The types and quantities of inorganic components are important to the chemical, geological and technological properties of coal. If the necessary precautions were not taken during the extraction, transportation, and coal combustion, some negative effects could occur to the environment and human health. A total of 54 coal, roof, floor, and parting samples were taken from 8 boreholes in the Tekirdağ, Malkara lignite field in the Northwest of Turkey. The samples were prepared in accordance with all the procedures of mineralogical and geochemical analyses. Quartz, ankerite, pyrite, calcite, mica, aragonite, dolomite, feldspar minerals and smectite, illite, cholinite, and chlorite among clay minerals were detected out. Trace elements, including V (8-212 ppm), Co (5.3-31 ppm), Ni (0.1-257 ppm), Cu (1.5-109.6 ppm), Rb (0.2-125.8 ppm), Sr (193.8-615.3 ppm), Y (5.4-28 ppm), Zr (13.6-495.1), Ba (120-436 ppm), and W (7.1-226 ppm) are enriched. The enriched elements in the coal are largely associated with inorganic matter. However, Be, Sr and W are related to organic and inorganic substances. Due to its high concentrations, Se, Be, Cu, Mo, Ni, Pb, Th, U, V, Zn, Ba, Co, and Sn might have negative effects on the environment and human health. Therein, Be, Co, Pb, Ni, and Se are potential air pollutants in the use of coal.

Keywords: *Coal, Enrichment Factor, Major and Trace Element, Malkara (Tekirdağ, Turkey)*

1. INTRODUCTION

China performed the largest coal production around the world in 2018 with a share of %44.7, while India ranked second, accounting for %9.7. In addition, almost half of the world’s coal consumption was also made by China. Germany is in the first place in lignite consumption, also with the effect of industrial development. Turkey is rich in coal resources, especially the lignite. The lignite reserve of Turkey reached up to 8.3 billion tons in 2005, and was further estimated to reach over 20 billion tons

JSR A
Journal of Scientific Reports

in 2022 with the exploration of new fields. The lignite production in Turkey accounts for %8.9 of the world's lignite production [1]. With the increasing energy demand, coal is intensively exploited in new fields and widely used in many fields, dominated by electricity generation. Coal combustion by power generation brings various negative results. The damages of coal come into view in its removal, transport and combusted. Although it cannot be prevented completely, it is necessary to keep this damage to a minimum. Coal quality parameters include the economic and technological importance of trace elements in the content of coal and their effects on the environment and human health [2-7]. The concentrations of trace element in coal are key parameters to evaluate the coal quality [8]. The Malkara lignites (with a reserve of 206 million tons) accounts large part of the Thrace Basin coals (639,17 million tons) [9]. The reason for choosing the research area in this study is that it is located in or near residential areas. The purpose of this study is to determine the element content of the Malkara coals, to interpret the sources of these elements, and to evaluate its possible environmental effects.

2. GEOLOGICAL SETTING

The Malkara coal mine is located in the Thrace Basin (Fig. 1). The Thrace Basin is the Tertiary intermontane basin, where the Middle Eocene-Pliocene strata is exposed [10,11]. The studied coal seams are hosted in the Danişmen Formation of Yenimuhacir Group, which is 300-1000 meters in thickness. It hosts three members of Armutburnu, Pınarhisar, and Taşlısekban. It is composed of limestone, sandstone, tuffite, siltstone, claystone, and is intercalated with coal. Above the Danişmen Formation and under the discordant Hisarlıdağ Formation is the Osmancık Formation which is a member of the same group as the Danişmen Formation (Fig. 2).

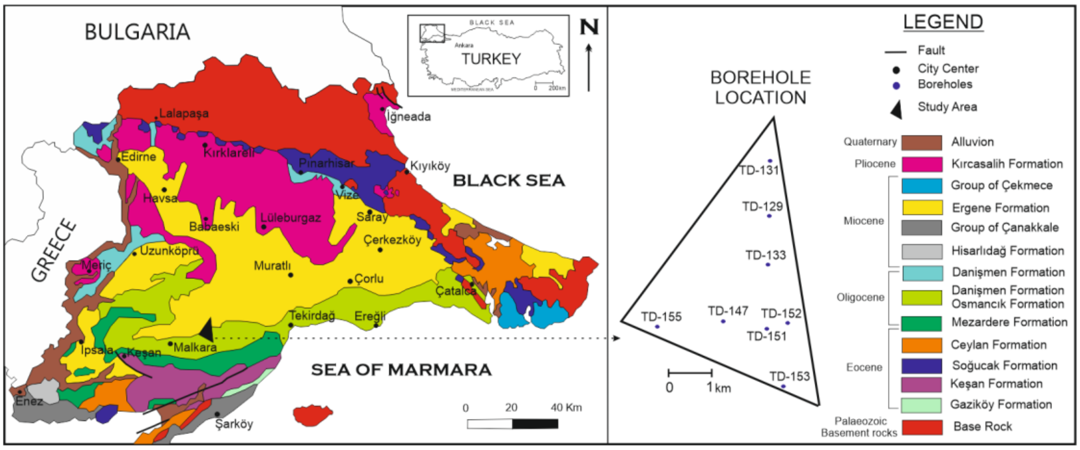

Figure 1. Geological map of the Thrace Basin in Turkey (modified from Perinçek et al. [11]) and location of study area.

JSR A
Journal of Scientific Reports

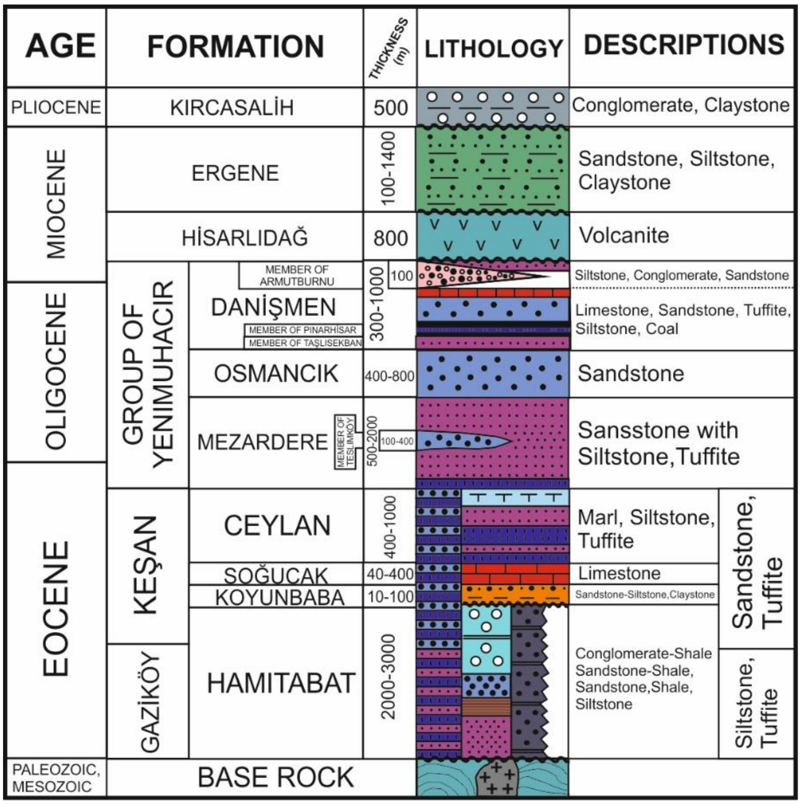

Figure 2. Generalized stratigraphic section of the Thrace Tertiary Basin (Modeified from [12]).

3. MATERIALS and METHODS

The major and trace element determination was conducted in a total of 54 samples, including 26 coal samples taken from 8 boreholes [TD-151 (n=2), TD-147 (n=4), TD-153 (n=2), TD-133 (n=3), TD-152 (n=3), TD-155 (n=4), TD-131 (n=3), and TD-129 (n=5)], 28 non-coal roof, floor, and parting rock samples [TD-151 (n=3), TD-147 (n=5), TD-153 (n=2), TD-133 (n=4), TD-152 (n=4), TD-155 (n=3), TD-131 (n=4), and TD-129 (n=3)] (Fig. 3). Lignite veins start at 25 meters and continue to a depth of 550 meters. The thicknesses of lignite veins vary between 25-100 centimeters. The measurement of major and trace elements were performed in the ACME laboratory (Canada). In a total of 25 samples (organic and inorganic), all XRD rock and clay fraction shots were performed in TPAO (Turkish Petroleum Corporation) Laboratory, being all XRD rocks and clay in 18 samples and all XRD rocks in 7 samples. The whole XRD rock and clay analyses were accredited with TÜRKAK (Turkey Accreditation Agency) TS EN ISO/IEC 17025: 2005 standards.

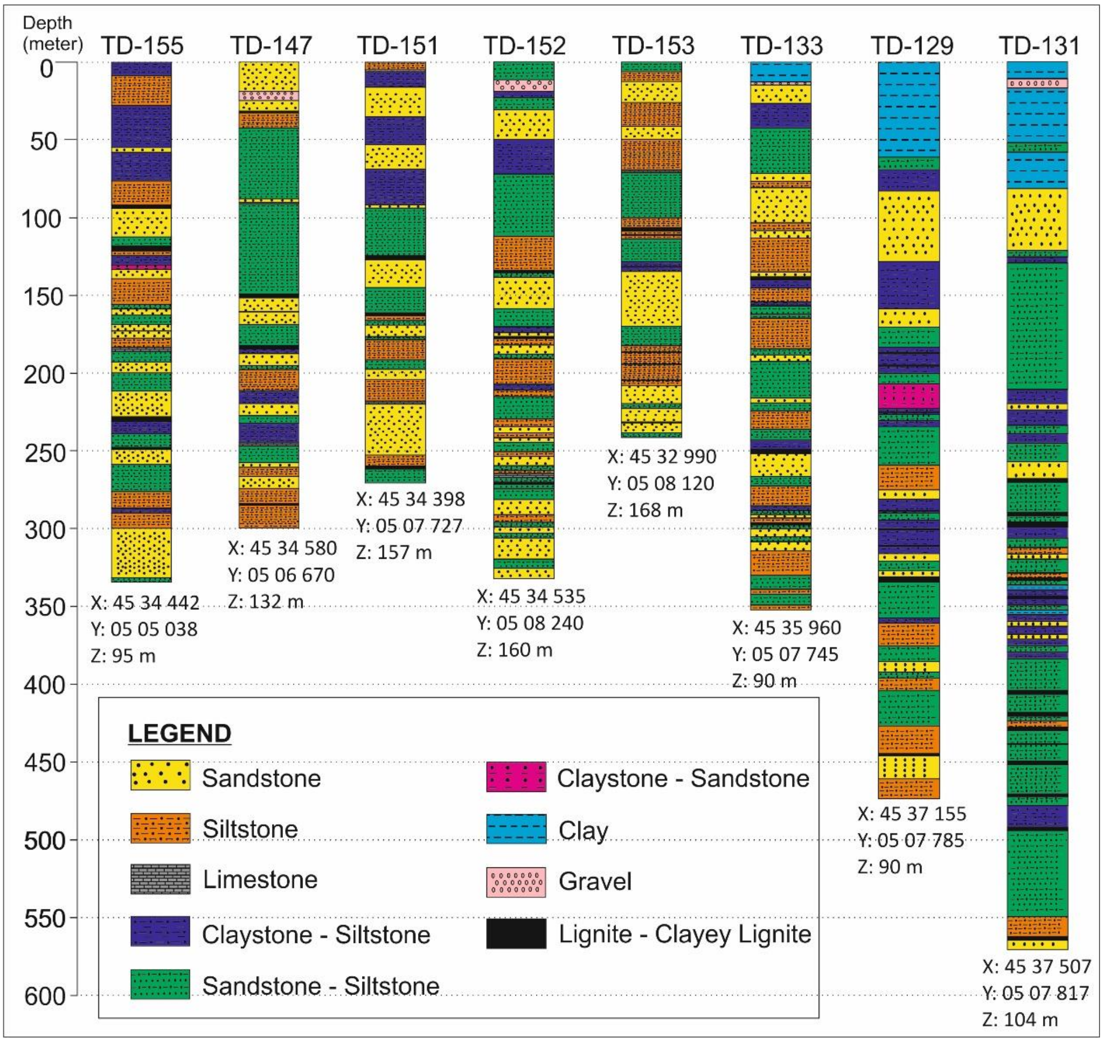

Figure 3. Changes of the lithology in the boreholes.

4. RESULT and DISCUSSION

4.1. Mineralogical Composition of Coal, Roof and Floor of the Coal Seams

The results of the analysis were evaluated in two parts as organic and inorganic materials. Similar mineral descriptions were found in both sample types. Clastic materials continue to be transported into the basin during sedimentation.

JSR A
Journal of Scientific Reports

The mica, quartz, clay minerals, calcite, dolomite, feldspar group minerals, ankerite, aragonite, pyrite and amorphous materials were found in the semi-quantitative XRD analysis. The clay minerals were abundant in these samples. The calcite, one carbonate mineral, is more abundant than that of dolomite and aragonite. Aragonite is more enriched than dolomite (Table 1).

The most abundant mineral in the analyzed coal and rock samples is quartz. Such a high content of quartz in samples at every seams that indicates the clastical of detrius material in the mine during peat-accumulation. Pyrite is detected at all seams. It can be concluded that pyrite occurs mostly syngenetically during burial and carbonization in the diagenesis phase. K-feldspar is available at almost all levels and in small quantities. Plagioclase is in small quantities and very rarely. Feldspars are of a detrital origin and usually weathered to clays. The presence of mica group minerals is also at a moderate level. The ankerite was present at all levels with a small amount.

As in the whole rock, in the clay fraction, a similar mineral type and abundance is observed in both coal and sandstone, siltstone, claystone samples. The dominant clay minerals are illite, and smectite, and the amount of smectite is higher than that of other clay minerals. Chlorite was rarely detected in few samples. Chlorite occurs only in a few examples, indicating that it was transported from source region (Table 2). The amount of smectite is very high, showing that it has not been transformed into illite. The coexistence of smectite with kaolinite and chlorite indicates that the feldspar was altered in a hot and semi-dry climates [13].

Table 1. Whole rock and clay components of the Malkara coal samples.

Sample Number	Group of Clayey Minerals				TCQ	Q	Ank	P	Cal	Mica	Arg	D	Felds	Pl
	Kln	I	Sm	Ch										
2152-20	#	#	###		XXX	XX	X	XX	XX		X	X		
152-42	#	#	##		XXX	XXX	X	XX	X	X	X			
133-21	#	#	###		XXX	XXX	X	XX	XX	X	X	X	X	X
133-30	#	#	##		XXX	XXX		XX	X	X	X		X	
129-18						XXX		XX	XX	X	X	X	X	
129-36						XXX	XX	XX	XX				X	X
147-14	#	#	##		XXX	XXX	X	XX	XX	X	X		X	X
147-26						XXX		XX	XX	XX			X	
153-6	#	#	##		XXX	XXX	X	XX	XX	X			X	
153-18						XXX	X	X	X	X	X		X	
151-13		#	###		XX	X	X		X	X		X	X	
151-30						XXX		X	XX	X			X	X
155-12						XXX	X	XX	XX	X	X	X	X	X
155-28	#	##	##		XX	XXX		XXX	XX	X			X	X
131-27		#	##	#	XXX	XXX	X	XX	XXX	X		X	X	
131-39		#	###		XXX	XX		XX	XXX	XX			X	

Kln (Kaolinite), I (Illite), Sm (Smectite), Ch (Chlorite), TCQ (Total Clay Quantity), Q (Quartz), Ank (Ankerite), P (Pyrite), Cal (Calcite), Arg (Aragonite), D (Dolomite), Felds (Feldspar), Pl (Plagioclase), “#”, “X” Relative abundance of minerals

Table 2. Whole rock and clay components of roof, floor, and parting samples of the Malkara coal measure.

Sample Number	Group of Clayey Minerals				TCQ	Q	Ank	P	Cal	Mica	Arg	D	Felds	Pl
	Kln	I	Sm	Ch										
152-19		#	#	##	X	XXX	X	XX	XX	X	X	X		
133-23	#	#	##		XXX	XXX	X	X	XX		X			
129-19	#	#	##		XXX	XX	X	X	XX	X	X		X	
147-15	#	#	##		XXX	XXX	X	X	XX	X	X	X	X	
153-7		#	##	#	XXX	XX	X	X	X	XX	X		X	X
151-12	#	#	##		XX	XX	X	X	XX	X	X		X	
151-14						XXX	X	XX	XXX	X	X	X	X	
155-13	#	#	#		XX	XX	X	X	XXX	X	X			
131-38	#	#	##		XXX	XX	X	X	XX	XX	X		X	

Kln (Kaolinite), I (Illite), Sm (Smectite), Ch (Chlorite), TCQ (Total Clay Quantity), Q (Quartz), Ank (Ankerite), P (Pyrite), Cal (Calcite), Arg (Aragonite), D (Dolomite), Felds (Feldspar), Pl (Plagioclase), “#”, “X” Relative abundance of minerals

4.2. Major Element Relations in Coal

The average contents of the major elements in the coal samples are below %1, except for Si, Al, Fe, Mg, and Ca (Table 3). All major elements presented comparable concentrations to the upper continental crust. Only Cr is at the same concentration as the upper continental crust. All major elements have higher concentrations than that of world coals. Compared to the Turkey and U.S. coals, only Ca, and P and Mn are at lower concentrations. Compared to the Chinese coals, Fe, P, and Mn are in low concentration. The statistical analysis was utilized to infer the major elements hosted in coal samples and the origin of these elements. Precision and relative standard deviation (RSD) values were calculated for the quality control elements. The statistical analysis was utilized to develop an approach about the main elements included in coal samples and the origins of these elements and the correlation matrix formed is given in Table 4.

Table 3. Arithmetic means of the major elements’ concentrations of in the Malkara coal, UCC (Upper Continental Crust), world, Turkey, U.S. and China coals.

Malkara Coals	UCC [14]	World [15]	Turkey [17-19]	U.S. [20]	China [21]

JSR A
Journal of Scientific Reports

Element (%)	RSD %	Min.	Max.	Avr.					
Silicium	13.25	0.16	19.49	10.09	31.10	-[16]	5.10	2.40	3.96
Aluminum	4.14	0.19	33.40	5.26	8.15	1.00[16]	2.10	1.50	3.16
Ferrum	3.45	0.52	6.10	3.17	3.92	1.00[16]	2.30	1.30	3.39
Magnesium	0	0.28	2.19	1.22	1.50	0.02[16]	0.50	0.11	0.13
Calcium	0.92	0.55	6.65	1.41	2.57	1.00[16]	1.80	0.46	0.88
Natrium	1.91	0.10	0.96	0.46	2.43	0.02[16]	0.10	0.08	0.12
Kalium	0	0.01	1.95	0.77	2.32	0.01[16]	0.30	0.18	0.16
Titanium	0	0.02	0.38	0.21	0.38	0.05[16]	0.10	0.08	0.20
Phosphorus	0	-	0.32	0.03	0.07	-[16]	-	0.04	0.04
Manganum	0	-	0.05	0.02	0.08	0.05[16]	-	0.05	0.01
Chromium	12.86	-	0.06	0.01	0.01	-[16]	-	-	-
TOT-C	-	10.12	55.85	31.28	-	-	-	-	-
TOT-S	-	-	7.01	1.88	-	-	-	-	-

TOT-C: Total Carbon, TOT-S: Total Sulfur.

Table 4. Major element correlation of Malkara coals [22].

	Si	Al	Fe	Mg	Ca	Na	K	Ti	P	Mn	Cr	TOT C	TOT S	TOC
Si	1	,831**	,618**	,895**	-,199	0,177	,919**	,968**	0,348	,543**	,634**	-,977**	-0,2	-0,3
Al		1	,388*	,759**	-0,207	0,054	,718**	,864**	0,172	0,3	0,383	-,812**	-0,194	-0,095
Fe			1	,587**	-0,072	-0,148	,660**	,575**	0,21	,684**	,662**	-,697**	,511**	-0,303
Mg				1	0,054	-0,059	,920**	,848**	,441*	,654**	,525**	-,911**	0,999	-,438*
Ca					1	0,036	-0,129	-0,178	0,362	0,283	-0,031	0,11	0,182	-0,297
Na						1	-0,024	0 ,16	0,24	-0,164	0,01	-0,11	0,053	0,012
K							1	,873**	,516**	,631**	,669**	-,902**	0,061	-0,379
Ti								1	0,308	,507**	,547**	-,956**	-0,243	-0,25
P									1	,452*	0,31	-0,367	0,156	-,582**
Mn										1	,494*	-,647**	0,334	-,403*

Cr											1	-,662**	0,286	-,521**
TOT C												1	-0,075	0,361
TOT S													1	-,077
TOC														1
** Correlation is significant at 0,01 level														
* Correlation is significant at 0,05 level														

The high availability rate of the Si is a clastic source indicator and indicates diagenetic silica precipitation. Thus, Si may be associated with silica with biological origin or detritic quartz. The positive correlation between Al - Si (r=0.831), Si -Ti (r=0.968) and Al - Ti (r=0.864) indicates a terrestrial origin of these elements and the presence of detritic clays into the basin. The presence of illite accounts for the high positive correlation between Al and K (r=0.718) [24]. Fe is found in the structure of clay and iron minerals. The positive correlation to elements with a detritic source, such as Al (r=0.388), Si (r=0.618) and Ti (r=0.575), suggests that Fe is related to clay minerals (Table 4). Its positive correlation with total sulfur (r=0.511) and the presence of pyrite minerals in almost all samples show that Fe may also associated from pyrite.

Mg is found in clay minerals and dolomite. In addition, it can also be found in a small amount of organic matter [24]. Dolomite was only detected in a small amounts in certain samples. When evaluated together with the negative correlation relationship it has with TOC (r=-0.438), the presence of Mg mineral in the study area is thought to be related to clay minerals rather than organic matter. K in coal is usually associated with aluminosilicate minerals. K, Na, and Al are mostly associated with phases containing Al-Si (analcime, clay minerals, feldspar) and are rarely associated with halite [25]. The absence of analcime and halite minerals in the coals in the study area suggests that most of K is related to clay minerals and less of it is related to feldspar. Mn is mostly found in the structure of organic matter but can also be found together with carbonate, clay and pyrite minerals. When the correlation between the presence of Mn in the study area and TOC (r=-0.403) was evaluated, it was determined that it points to inorganic origin. Cr can be adsorbed on iron and manganese oxides, clays, apatites and organic matter [26]. There is a negative correlation between Cr and TOC (r=-0.521) in the samples in the study area. When XRD analyzes are also evaluated, Cr's source is thought to be clay minerals. When all the data are evaluated together, considering the positive correlation between Si, Al, Fe, Mg, K, Ti, Mn and Cr, it was determined that these elements come from the same origin and represent the clastic origin.

In the study area, a significant correlation relationship between Ca and Na and other main elements and TOC, TOT S, TOT C could not be established. Ca can be found in different forms such as clay minerals, sulphate, carbonate and organic origin in coals [27, 28]. It is thought that the source of Ca is largely calcite in the study area, and also that the fossil shells observed in the coal samples may be a source of some Ca. Although the Na in the coal samples is known to be related to clay minerals and feldspars, no significant relation was found with the elements pointing to clastic origin such as Al, Si, and T. While P had a negative correlation with TOC (r=-0.582), it showed a positive correlation with

JSR A
Journal of Scientific Reports

Mg (r=0.441), K (r=0.516) and Mn (r=-0.452). No significant relationship was found between TOT C and TOT S and other major elements. Although a certain amount of P is present in organic matter, apatite mineral can also be a source of phosphorus [29]. Considering its negative correlation with TOC, the source of element P in the study area is largely calcite mineral.

4.3. Mode of Occurrence and Element Enrichment

Trace elements in coals occur both in organic and inorganic matter [4]. In coals with low ash content, elements are generally found in relation to organic matter [2]. As the ash yield increases, the amount of elements associated with organic material decreases, while the amount of elements associated with minerals increases [30]. Concentrations of the elements Be, Sc, V, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Au, Hg, Tl, Pb, Bi, Th, U were presented (Table 5). The concentration of Ag was below the detection limit in most of the samples. Correlation coefficients were calculated in order to determine the relationship of trace elements with each other and TOC contents and to evaluate them in terms of their origin. Cluster analysis was performed to classify the elements according to their similarities in the ungrouped data matrix (Fig. 4).

Table 5. Arithmetic means of trace elements' concentrations of the Malkara coals, UCC, World, lignite, Turkey, U.S. and China coals.

Element (ppm)	RSD %	Malkara Coals			UCC[14]	World[15]	Lignite[16]	Turkey[17-19]	U.S. [20]	China[21]
		Min.	Max.	Avr.						
Be	12.86	-	7.00	2.68	2.10	1.60	1.20	1.30	2.20	2.10
Sc	0	-	21.00	10.56	14.00	3.90	4.10	4.80	4.20	4.38
V	2.12	8.00	212.0	109.7	97.00	25.00	22.00	65.00	22.00	35.10
Co	2.32	5.30	31.00	15.83	17.30	5.10	4.20	10.00	6.10	7.08
Ni	5.94	-	257.0	116.9	47.00	13.00	9.00	150.0	14.00	13.70
Cu	-	1.50	109.6	36.69	28.00	16.00	15.00	20.00	16.00	17.50
Zn	-	2.00	77.00	41.04	67.00	23.00	18.00	40.00	53.00	41.40
Ga	2.6	0.70	41.50	9.78	17.50	5.80	5.50	5.80	5.70	6.55
As	-	0.80	24.50	8.88	4.80	8.30	7.60	65.00	24.00	3.79
Se	-	-	6.00	1.64	0.09	1.30	1.00	-	2.80	2.47
Rb	-	0.20	125.8	52.37	84.00	14.00	10.00	25.00	21.00	9.25
Sr	2.45	193.8	615.3	351.2	320.0	110.0	120.0	210.0	130.0	140.0
Y	9.26	5.40	28.00	15.25	21.00	8.40	8.60	8.30	8.50	18.20
Zr	0.04	13.60	495.1	83.18	193.0	36.00	35.00	-	27.00	89.50
Nb	2.14	0.40	10.50	4.55	12.00	3.70	3.30	4.00	2.90	9.44
Mo	-	-	4.50	1.56	1.10	2.20	2.20	9.80	3.30	3.08

Element (ppm)	RSD %	Malkara Coals			UCC[14]	World[15]	Lignite[16]	Turkey[17-19]	U.S. [20]	China[21]
		Min.	Max.	Avr.						
Ce	0	3.50	50.60	26.46	63.00	23.00	22.00	-	21.00	46.70
Pr	1.43	0.49	5.77	3.13	7.10	3.50	3.50	-	2.40	6.42
Nd	3.29	2.20	21.90	12.31	27.00	12.00	11.00	-	9.50	22.30
Sm	6.53	0.68	4.40	2.48	4.70	2.00	1.90	-	1.70	4.07
Eu	8	0.23	1.02	0.61	1.00	0.47	0.50	-	0.40	0.84
Gd	8.32	0.94	4.49	2.60	4.00	2.70	2.60	-	1.80	4.65
Tb	5.9	0.14	0.70	0.41	0.70	0.32	0.30	-	0.30	0.62
Dy	6.94	0.85	4.56	2.56	3.90	2.10	2.00	-	1.90	3.74
Ho	4.46	0.20	0.98	0.55	0.83	0.54	0.50	-	0.35	0.96
Er	4.47	0.55	2.87	1.64	2.30	0.93	0.90	-	1.00	1.79
Tm	6.15	0.08	0.41	0.23	0.30	0.31	0.30	-	0.15	0.64
Yb	1.71	0.52	2.68	1.51	2.00	1.00	1.00	-	0.95	2.08
Lu	0	0.08	0.44	0.24	0.31	0.20	0.20	-	0.14	0.38
Hf	6.15	0.30	3.60	1.80	5.30	1.20	1.20	-	0.73	3.71
Ta	0	-	0.60	0.32	0.90	0.28	0.30	-	0.22	0.62
W	4.3	7.10	226.0	42.98	1.90	1.10	1.20	-	1.00	1.08

Ag	-	-	-	-	53.00	0.10	0.10	-	-	-	Au*	-	-	2.70	1.81	1.50	3.70	3.00	-	-	-
Cd	-		0.40	0.20	0.09	0.22	0.20	-	0.47	0.25	Hg	-	0.02	0.31	0.08	0.05	0.10	0.10	0.10	0.17	0.16
Sn	0	-	3.00	1.50	2.10	1.10	0.80	-	1.30	2.11	Tl	-	-	0.50	0.18	0.90	0.63	0.70	-	1.20	0.47
Sb	-	-	2.00	0.40	0.40	0.92	0.80	2.70	1.20	0.84	Pb	-	1.80	19.20	10.10	17.00	7.80	6.60	9.30	11.00	15.10
Cs	0	-	7.90	3.62	4.9	1.00	1.00	4.90	1.10	1.13	Bi	-	-	0.50	0.26	0.16	0.97	0.80	-	<1.00	0.79
Ba	1.18	120.0	436.0	256.3	624.0	150.0	150.0	130.0	170.0	159.0	Th	-	0.40	10.70	6.09	10.5	3.30	3.30	-	3.20	5.84
La	0	1.70	26.80	13.82	31.00	11.00	10.00	-	12.00	22.50	U	0.92	0.20	8.30	4.12	2.70	2.40	2.90	13.00	2.10	2.43

**ppb*

The average concentration levels of the trace element contents of coal samples were compared with the World, Turkey, lignite, U. S. and China coals. Mo, Cd, Sb, Au, Hg, Tl, Bi elements presented low values, while Scandium, Vanadium, Cobalt, Cupric, Gallium, Rubidium, Strontium, Barium, Tungsten, Thorium elements presented high values, considering all coals of study area. While Be had close values with Chinese coals, it showed lower values than U. S. coals and higher values than other coals. Se, Zn and Pb are concentrations, which are lower than U. S. and Chinese coals and higher than the World and lignite coals. The average concentration of U, Cs and Ni elements is lower than Turkish coals and higher than other coal values. Y, Zr, Nb, Sn, Hf and Ta were measured at higher values than other coals, excluding Chinese coals. The median concentration of as element is below lignite, Turkey and U. S. coals. Rare earth elements (REE) are composed of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu trace elements, and they present higher values than U. S. coals and lower values than Chinese coals. All rare earth elements other than Pr, Gd and Tm are found in high concentrations in lignite and other world coals. No average values of rare earth elements were determined for Turkish coals. While Sb offers close values according to the upper continental crust averages, other elements except Beryllium,Vanadium, Nickel, Cupric, Arsenic, Selenium, Strontium, Molybdenum, Cadmium, Tungsten, Mercury, Bismuth and Uranium have low concentration values.

It was stated that Be is found in coals with quartz and clay minerals [31]. Based on the XRD analysis, it was determined that in wells numbered TD-131 and TD-133 where Be presented relatively higher values, clay minerals and quartz were also abundant. In addition, Be is largely associated with organic matter in coals, but no significant correlation was found between Be and TOC in the correlation matrix (Table 6). However, there is a close relationship between Be and TOC in the dendrogram (Fig. 4). It is reported that As [32], which is generally related to pyrite in coals and is seen in a small amount in organic structure, also originates from clay minerals and phosphates. Phosphate minerals were not found in XRD analyses. Clay minerals and pyrite determined in almost all coal samples constitute the source of As in the study area. Se formation is stated to be largely of organic origin [33, 34]. However, it has been reported that some Se originates from pyrite and accessory minerals, claustalite and galena [35]. The correlation between Se and TOC could not be established in the correlation matrix. Clausthalite and galena minerals were not found in XRD analysis. However, some Se may be caused by the pyrite mineral set at almost any level. Sr coals are generally together with sulphate, carbonate and phosphate minerals [35]. They have a less amount of organic associations [32]. Since no meaningful relationship was established with TOT S, it is not possible to make a definite judgement about its stemming from sulfates. The absence of phosphate minerals in the XRD analysis eliminates this possibility. When its relationship with carbonate related elements was examined, no significant increase or decrease was detected. However, the carbonate minerals observed in all coal samples may be a source of some Sr. Although there was no significant correlation between Sr and TOC in the correlation matrix, a close relationship was found between the two in the dendrogram. Mo has a strong relationship with organic and inorganic substances [35, 36, 37]. Increased anoxic conditions also causes the concentration of Mo to increase. Mo element is related to humic acids as well as sulphide [38]. The correlation between Mo and TOC could not be establised in the correlation matrix. It is stated that the element W is related to organic matter in coals, but some W can also be found in the wolframite and scheelite minerals [39]. W is also found in carbonate minerals [31]. In XRD analysis, wolframite and scheelite minerals could not be determined. In the study area, no relationship was detected with carbonates. In the correlation matrix, although a significant relationship could not be established between W and TOC, their close relationship in the dendrogram reveals the association of W with organic matter. Although U coals can have both organic and inorganic origin, they are generally related to organic matter [35, 36]. It is also stated that it is found in silicate, carbonate, oxide, vanadate and sulfate minerals. A small amount of U can also be found in clay minerals through adsorption [40, 35]. There is no data in the study area indicating that U may be of organic origin. U is thought to be largely inorganic in origin.

Ni is largely related to sulfides but can also be found in relation to organic matter [35, 2]. Since no significant relationship could be established with total sulphur, it is thought that the presence of Ni in the study area is not caused by sulphides. When evaluated together with XRD analysis, it was determined that Ni in the coals originated from clay minerals and carbonates. Co can be found in relation to pyrite, clay, linnaite, other sulphides and organic matter in coals [33, 41, 35]. When the amount of pyrite minerals determined in the wells where Co offers high values are evaluated, it is determined that Co in the study area is associated with inorganic matter, especially clay minerals and a small amount of pyrite. The association of the element Y with organometallics [42], organic matter [43] and mineral matter [35] are indicated. Its negative relationship with TOC (r=-0.527) decreases the possibility of organic matter association. The high concentration it offers in samples rich in elements associated with detritic minerals indicates that Y is associated with mineral material, and most probably clays, in the study area. REEs, whose organic association is very rare, are generally found in coals in relation to mineral substances [44, 45, 46, 47]. In the study area, the negative correlation between REEs and TOC reveals that REEs belong to inorganic fraction. Considering its similar tendency with elements indicating a detritic source such as AI, K and Ti, it was concluded that REEs originate from clay minerals. A negative correlation was found between Ni, Co, Y, REE and TOC. No relation was determined between these elements and TOC in the dendrogram, which confirms the relationship of Ni, Co, Y and REE with inorganic association.

No significant relation was found between the elements of Barium, Scandium, Caesium, Hafnium, Niobium, Rubidium, Thorium, Vanadium, Cuprum, Zincum, Gallium, Stannum, Tantalum, Zirconium, Plumbum, Cadmium, Antimonium, Bisemutum, Aurum, Hydrargyrum, Thallium and TOC either in correlation matrix or in dendrogram. The source of these elements is also thought to be related to the inorganic material. Finkelman [36] stated that Ba is present in the barite minerals occurring in coal samples, while Goodarzi [48] showed its association with organic matter and clay. Since a significant relationship with TOC could not be determined, an approach regarding association with organic matter could not be made. Barite mineral was not found in XRD analysis. Swaine [35] reported that there is also Ba in ankerite mineral. It is thought that the Ba in the study area is related to clay minerals and ankerite. Although association with organic and inorganic materials in coals was stated, no relationship could be established with TOC in the study area; therefore, its relationship with organic matter could not be determined. Inorganically, it can be found in silicates, clays and phosphate minerals [31]. Phosphate minerals were not found in the study area and it was determined that the presence of Sc is related to silicate and clay minerals. In the evaluation of the correlation matrix of element V, it was found to have the same characteristics as Sc element. Dendrogram also shows the close relationship between Sc and V element. Since no significant relationship was established with TOC, V is thought to be related to clay minerals rather than organic matter. Cs is found in coals in clays, mica minerals, feldspars and organic matter. The presence of clay, mica and feldspar minerals detected in XRD analysis in wells numbered TD-133 and TD-153, where the Cs concentration is high, supporting this association. Zr is always present with a certain amount of Hf element [41]. When the correlation matrix and dendrogram are examined, it is seen that Zr has a high positive correlation with Hf (r=0.960), Nb (r=0.693) and Ga (r=0.684). Hf and Nb are considered indicative of detritic material input into the storage medium. Therefore, it was determined that Zr, together with Hf and Nb, originated from detritic minerals. Cd is generally observed in coals of inorganic origin and possibly sphalerite formation [35, 34, 36]. It can also be found to be related with carbonates, clays and organic matter [48]. It was stated that pyrite may also contain some Cd [35]. In the study area, no data could be determined indicating that Cd may be of organic origin. No sphalerite mineral was found in the XRD analysis. The positive relationship it presents with Hf (r=0.527) and Zr (r=0.475) in the correlation matrix was monitored in dendrogram and it was determined that Cd element was mostly caused by detritic minerals, especially clay minerals. It is stated that Rb stems from clay minerals in coals [45]. In the study area, clay minerals, which are intensely observed in most of the coal samples, are thought to be the source of Rb. Pb may be associated with organic matter in coals of low maturity [49, 35, 36]. However, Pb no significant relationship with TOC in the study area, and considering the correlation with W (r=0.602), which was found to be of organic origin, it was determined that it is not related to organic matter. Finkelman [32] states that Pb originates from sulphite minerals. Although no significant relationship was established with TOT S, it suggests that almost any level of pyrite minerals may be the source of Pb. Bi is found in coals in relation to sulfide minerals. The characteristics of Bi in the correlation matrix are similar to Pb. There is a close relationship between these two elements in the dendrogram. Like Pb, Bi is thought to be of inorganic origin. Th is thought to be found together with mineral material, mostly monazite and zircon [45], as well as xenotimel [41]. Swaine [35] also stated that Th can be found together with iron oxides and clay minerals. Monazite, zircon and xenotime were not detected in XRD analysis. Th is probably related to clay minerals in the study area. Pyrite in coals can contain some Au [35]. Very low amounts of Au can also be found in detritic origin. The pyrite mineral determined at almost all levels in the study area is thought to be the source of Au in coal. It is stated that Cu source in coals is related to sulphides, generally pyrite, chalcopyrite and organic matter [35, 50, 48]. When the correlation matrix is evaluated, no significant relationship is observed between Cu and TOT S. No significant relationship could be established with TOC either and a close relationship between Cu and TOC could not be found in the dendrogram. This shows that the presence of Cu is related to inorganic matter rather than organic matter. The source of Cu is thought to be mainly clay minerals. It was maintained that Zn [36], the organic associations of which is mentioned in low rank coals, is generally associated with sulfite minerals, sphalerite, carbonate and clay minerals [25, 48]. No sphalerite was found in the XRD analysis of coals. Since a significant relationship could not be determined with TOT S and TOC, a significant relationship could not be established with organic matter and sulfide minerals. Considering the XRD analyses in the well numbered TD-153, where Zn is the most intense, it is thought that the element in question largely stems from carbonate minerals and some clay minerals contribute. Ga element can be found in the structure of sphalerite, feldspar, clay and sulphite minerals. No sphalerite mineral was found in the XRD analysis. Since no meaningful relationship could be established with TOC, there is no organic association either. The Ga concentration in the study area is thought to be largely related to clay minerals and feldspar. Especially the high amounts of these minerals in the well numbered TD-133 support this view. It was reported that most of Sn in coal is found as Sn-oxides and Sn-sulfites such as disseminated cassiterite [3]. It is generally accepted that Sn is associated with minerals in coal. Ta is found in coal in relation to mineral matter, and possibly in relation to Ti, Zr and phosphates [41, 45]. Phosphate minerals could not be determined in the study area. In the well number TD-153, where the elements associated with the detritic input are concentrated, the Ta element shows its highest values. Therefore, when the correlation matrix and dendrogram are evaluated together, Ta is associated with detritic minerals in the study area. Sb is together with organic matter and sulfides in coals [35]. Since a meaningful relationship with TOC could not be determined, an original approach could not be developed. Sb is thought to be related to sulfites in the coals in the study area. In coals, Hg is generally related to selenite and sulfites [36, 48]. Pyrite is largely the source of Hg. Its positive correlation with TOT S (r=0.417) also confirms this. It is known that Tl is associated with pyrite in coals. Although no significant relationship could be established between Tl and TOT S in the correlation matrix, their close relationship in the dendrogram shows that the source of Tl is the pyrite mineral in the study area as well (Table 6).

Table 6. Trace element correlation matrix values of study area coals [22].

	Ba	**Ni**	**Sc**	**Co**	**Cs**	**Hf**	**Nb**	**Rb**	**Sr**	**Th**	**U**	**V**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Cu**	**Zn**
Ba	1,00	0,28	,520*	0,32	0,31	0,29	0,26	0,36	,416*	,530*	0,08	,419*	,510*	,546*	,569*	,599*	,611*	,651*	,646*	,612*	,578*	,541*	,509*	,495*	,495*	,490*	,641*	,594*
Ni		1,00	,737*	,758*	,797*	0,37	,749*	,798*	-0,24	,616*	,512*	,564*	,617*	,701*	,747*	,728*	,727*	,712*	,711*	,727*	,693*	,676*	,649*	,649*	,636*	,594*	0,29	,730*
Sc			1,00	,836*	,738*	,618*	,804*	,841*	-0,11	,682*	0,27	,850*	,542*	,785*	,829*	,825*	,830*	,811*	,769*	,761*	,708*	,658*	,661*	,634*	,653*	,637*	,558*	,868*
Co				1,00	,688*	,553*	,788*	,739*	-0,16	,505*	0,29	,705*	,409*	,627*	,687*	,658*	,667*	,619*	,582*	,574*	,549*	,515*	,506*	,509*	,536*	,515*	,414*	,751*
Cs					1,00	,454*	,818*	,950*	-0,34	,755*	0,18	,428*	,482*	,805*	,822*	,789*	,759*	,707*	,655*	,643*	,576*	,554*	,527*	,521*	,535*	,510*	0,21	,792*
Hf						1,00	,719*	,475*	-0,25	,540*	0,28	,611*	0,31	,502*	,512*	,524*	,515*	,468*	,444*	,446*	,427*	,440*	,447*	,462*	,488*	,478*	0,16	,515*
Nb							1,00	,869*	-	,672*	0,30	,586*	,543*	,772*	,794*	,770*	,751*	,698*	,684*	,682*	,649*	,640*	,640*	,644*	,666*	,653*	0,11	,745*
Rb								1,00	-0,33	,777*	0,14	,524*	,570*	,883*	,894*	,868*	,850*	,801*	,763*	,745*	,678*	,646*	,633*	,609*	,626*	,605*	0,27	,873*
Sr									1,00	-0,13	-0,01	-0,10	-0,08	-0,20	-0,16	-0,12	-0,09	-0,05	-0,02	-0,04	-0,05	-0,07	-0,09	-0,07	-0,11	-0,05	0,38	-0,14
Th										1,00	0,20	,502*	,491*	,906*	,900*	,908*	,888*	,841*	,752*	,708*	,599*	,569*	,515*	,496*	,497*	,476*	0,37	,851*
U											1,00	,399*	,443*	0,24	0,28	0,29	0,30	0,33	,395*	,438*	,482*	,511*	,480*	,528*	,511*	,511*	0,12	0,23
V												1,00	0,35	,570*	,616*	,632*	,643*	,653*	,576*	,570*	,525*	,469*	,473*	,445*	,459*	,439*	,694*	,703*
Y													1,00	,706*	,707*	,715*	,734*	,790*	,891*	,921*	,959*	,978*	,974*	,967*	,959*	,938*	0,18	,582*
La														1,00	,991*	,988*	,979*	,954*	,910*	,877*	,803*	,767*	,734*	,712*	,723*	,706*	0,38	,929*
Ce															1,00	,996*	,989*	,969*	,923*	,894*	,821*	,779*	,745*	,724*	,734*	,712*	,425*	,941*
Pr																1,00	,996*	,979*	,935*	,904*	,831*	,788*	,753*	,730*	,738*	,720*	,463*	,945*
Nd																	1,00	,986*	,949*	,920*	,850*	,805*	,771*	,748*	,753*	,735*	,486*	,945*
Sm																		1,00	,974*	,953*	,895*	,849*	,817*	,789*	,793*	,769*	,514*	,912*
Gd																			1,00	,993*	,967*	,937*	,912*	,892*	,891*	,873*	,431*	,849*
Tb																				1,00	,985*	,961*	,944*	,927*	,922*	,902*	,390*	,811*
Dy																					1,00	,989*	,978*	,968*	,965*	,945*	0,33	,730*
Ho																						1,00	,991*	,987*	,984*	,968*	0,25	,675*
Er																							1,00	,992*	,990*	,977*	0,22	,641*
Tm																								1,00	,994*	,986*	0,19	,609*

JSR A
Journal of Scientific Reports

Yb																									1,00	,991*	0,18	,629*
Lu																										1,00	0,19	,612*
Cu																											1,00	,587*
Zn																												1,00

Table 6 continues.

	TOC	**TOT/C**	**TOT/**	**Be**	**Ga**	**Sn**	**Ta**	**W**	**Zr**	**Eu**	**Mo**	**Pb**	**As**	**Cd**	**Sb**	**Bi**	**Au**	**Hg**	**Tl**	**Se**
Ba	-0,16	-,576**	-0,11	-0,20	0,20	0,34	,454*	-0,15	,511*	,727*	0,12	,594*	-0,02	0,33	-0,24	0,37	-0,12	0,27	0,15	0,20
Ni	-,443*	-,754**	0,19	-0,05	,709*	,591*	,698*	-,399*	0,37	,702*	0,12	,674*	,490*	0,31	,517*	,669*	0,17	0,22	0,34	0,13
Sc	-0,34	-,859**	0,02	-0,11	,803*	,724*	,775*	-,452*	,566*	,793*	-0,01	,705*	0,27	,526*	0,22	,663*	0,28	0,08	0,16	0,00
Co	-,437*	-,725**	-0,04	0,00	,759*	,662*	,702*	-0,28	,516*	,597*	-0,12	,545*	0,26	,486*	0,31	,588*	,445*	-0,04	0,12	-0,08
Cs	-0,37	-,854**	0,14	-0,31	,628*	,621*	,782*	-,419*	0,37	,646*	0,04	,646*	0,24	0,30	0,16	,733*	0,03	0,10	0,34	0,00
Hf	0,07	-,544**	-0,22	-0,20	,793*	,558*	,750*	-0,14	,960*	,514*	-0,06	,519*	-0,01	,527*	0,09	,525*	0,14	0,14	0,12	-0,27
Nb	-0,25	-,788**	0,05	-0,19	,833*	,691*	,843*	-0,27	,693*	,595*	-0,06	,587*	0,35	,395*	0,34	,614*	0,15	0,06	0,27	-0,25
Rb	-0,38	-,908**	0,13	-0,31	,676*	,699*	,767*	-,475*	0,37	,723*	0,00	,681*	0,28	0,30	0,18	,751*	0,08	0,00	0,26	-0,07
Sr	-0,05	0,06	0,23	0,08	-,492*	-0,22	-0,29	0,22	-0,20	-0,01	0,20	-0,10	-0,13	-,420*	-0,08	-0,25	0,05	0,37	-0,27	0,34
Th	-0,19	-,865**	-0,11	-0,39	,639*	,598*	,757*	-	,552*	,754*	0,18	,888*	-0,01	0,31	0,03	,882*	-0,07	0,14	,419	-0,01
U	-0,26	-0,22	0,25	0,28	,473*	0,15	0,18	-0,37	0,22	,453*	,645*	,456*	,629*	,394*	,690*	0,37	0,06	,395*	,413	0,35
V	-0,11	-,628**	-0,09	-0,04	,684*	,566*	,551*	-,433*	,459*	,577*	0,05	,539*	0,16	,553*	0,23	,491*	0,37	0,07	0,19	0,11
Y	-	-,575**	-0,02	0,09	,519*	,542*	,489*	-0,34	0,37	,859*	0,18	,686*	,431*	0,29	,416*	,514*	-0,19	0,20	0,29	0,19
La	-0,36	-,917**	-0,09	-0,32	,676*	,699*	,750*	-	,528*	,888*	0,14	,865*	0,12	,411*	0,07	,854*	-0,04	0,05	0,33	-0,04
Ce	-,390*	-,927**	-0,07	-0,25	,681*	,734*	,775*	-	,531*	,917*	0,15	,884*	0,16	,414*	0,12	,825*	-0,03	0,10	0,33	0,05
Pr	-0,38	-,931**	-0,06	-0,27	,687*	,722*	,755*	-	,507*	,923*	0,15	,883*	0,16	,428*	0,11	,825*	-0,02	0,06	0,32	0,05
Nd	-,402*	-,924**	-0,08	-0,25	,669*	,734*	,755*	-	,512*	,939*	0,12	,883*	0,16	,421*	0,11	,809*	0,01	0,10	0,31	0,06
Sm	-,416*	-,884**	-0,06	-0,25	,602*	,641*	,667*	-	,434*	,973*	0,21	,865*	0,22	,418*	0,14	,744*	-0,09	0,13	0,37	0,17
Gd	-,469*	-,832**	0,00	-0,13	,595*	,603*	,600*	-	,430*	,986*	0,24	,829*	0,35	,407*	0,28	,689*	-0,07	0,18	0,36	0,19
Tb	-,476*	-,797**	0,01	-0,09	,625*	,617*	,605*	-	,445*	,980*	0,22	,823*	0,37	,396*	0,32	,664*	-0,03	0,21	0,34	0,19
Dy	-	-,716**	0,03	-0,01	,637*	,603*	,564*	-,393*	,470*	,942*	0,18	,725*	,449*	,407*	,389*	,562*	-0,04	0,19	0,29	0,15
Ho	-	-,671**	0,02	0,03	,622*	,571*	,523*	-0,35	,477*	,901*	0,22	,689*	,462*	0,38	,453*	,525*	-0,08	0,19	0,27	0,14
Er	-,485*	-,642**	-0,02	0,05	,627*	,603*	,516*	-0,35	,499*	,880*	0,17	,663*	,440*	0,36	,444*	,496*	-0,05	0,15	0,20	0,09
Tm	-	-,620**	-0,02	0,06	,596*	,580*	,496*	-0,31	,471*	,855*	0,18	,630*	,454*	0,34	,457*	,463*	-0,08	0,16	0,22	0,09
Yb	-	-,630**	-0,03	0,06	,636*	,591*	,515*	-0,32	,503*	,840*	0,17	,618*	,444*	0,38	,458*	,455*	-0,07	0,14	0,23	0,04
Lu	-	-,622**	-0,01	0,07	,624*	,627*	,505*	-0,35	,472*	,847*	0,16	,615*	,438*	0,32	,465*	,460*	-0,02	0,12	0,16	0,03
Cu	-0,18	-,517**	0,01	-0,19	0,32	,473*	0,38	-,489*	0,18	,626*	0,20	,599*	0,02	0,39	-0,06	,579*	0,21	0,11	0,23	,412*
Zn	-0,37	-,958**	-0,09	-0,31	,658*	,688*	,759*	-	,436*	,841*	0,07	,855*	0,10	,495*	0,03	,811*	0,18	0,01	0,28	0,06
TOC	1,00	0,36	-0,08	-0,19	-0,23	-0,29	-0,18	0,31	0,17	-,428*	-0,08	-0,22	-0,29	0,00	-0,36	-0,23	0,09	0,08	-0,14	-0,17
TOT/C		1,00	-0,07	0,30	-	-	-	,465*	-	-	-0,05	-	-0,14	-0,38	-0,11	-	-0,15	-0,12	-0,24	0,01
TOT/S			1,00	0,25	-0,03	-0,28	-0,06	0,20	-0,20	-0,03	0,36	-0,06	,602*	-0,07	0,31	-0,04	0,03	,417*	0,15	0,38
Be				1,00	-0,03	-0,15	-0,29	0,16	-0,14	-0,15	0,09	-0,16	,447*	0,08	,449*	-0,16	0,13	0,15	-0,08	0,19
Ga					1,00	,638*	,738*	-,399*	,684*	,557*	-0,08	,589*	0,30	,490*	,433*	,636*	0,30	-0,04	0,17	-0,31
Sn						1,00	,699*	-	,449*	,615*	-0,24	,539*	-0,03	0,23	0,08	,521*	0,20	-0,18	-0,03	-0,36
Ta							1,00	-0,33	,648*	,585*	-0,19	,691*	0,05	0,35	0,09	,643*	0,14	0,18	0,19	-0,19
W								1,00	-0,01	-	-0,31	-	0,06	-0,17	-0,11	-	0,02	0,29	-0,15	0,00
Zr									1,00	,445*	-0,02	,455*	0,00	,475*	0,04	,408*	0,10	0,14	0,04	-0,29
Eu										1,00	0,22	,835*	0,26	,390*	0,18	,684*	-0,05	0,18	0,30	0,21
Mo											1,00	0,23	0,31	0,19	0,25	0,20	-0,38	0,25	0,36	,512*
Pb												1,00	0,18	0,35	0,15	,840*	0,03	0,24	,396	0,21
As													1,00	0,19	,762*	0,14	0,12	0,38	0,30	0,31
Cd														1,00	-0,01	,391*	0,08	0,05	0,28	0,15
Sb															1,00	0,18	0,18	0,25	0,23	0,10
Bi																1,00	-0,01	0,11	,416	0,09
Au																	1,00	-0,03	-0,22	-0,24
Hg																		1,00	,463	,568*
Tl																			1,00	0,35
Se																				1,00

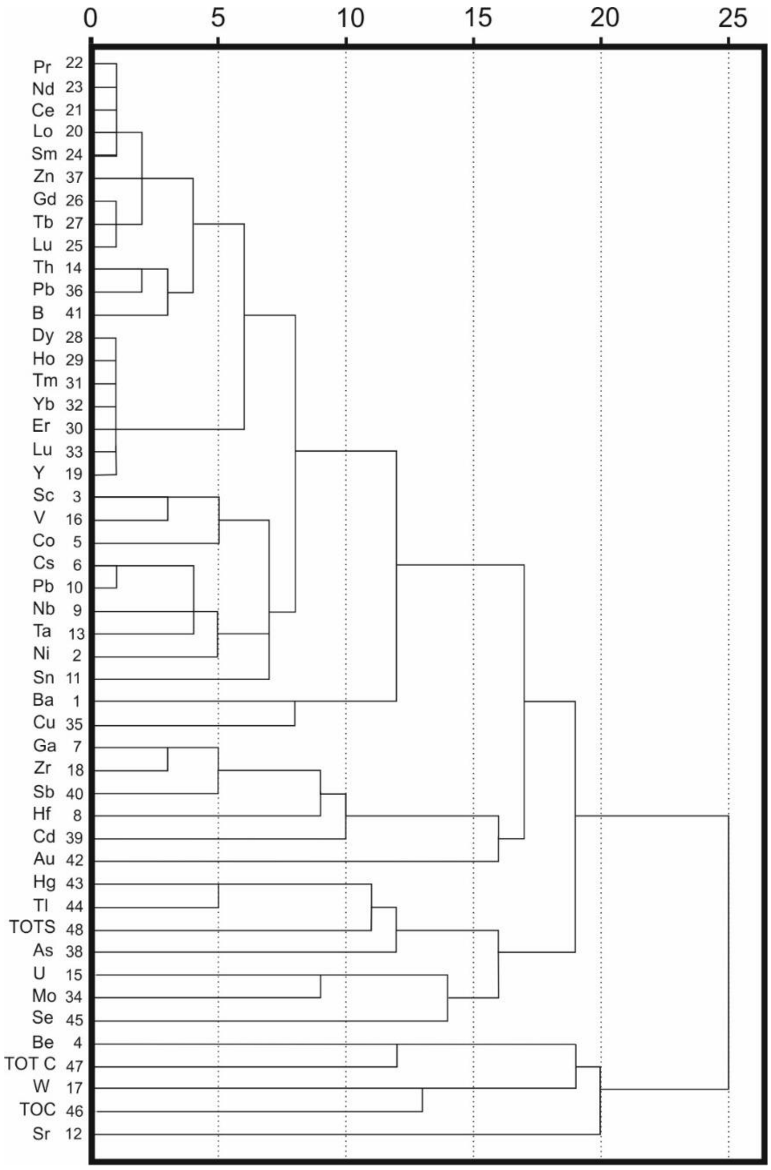

Figure 4. Dendrogram of trace elements in the Malkara coals.

4.4. Element Enrichment

The enrichment factors of the main and trace elements of Malkara coals were calculated according to the average UCC values [51] with the formula given below, values less than 1 were depleted, and values greater than 1 were considered enriched. While the main elements Si, Na, K and Mn were

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consumed in all coal samples, Fe, Mg and Cr were enriched in all samples except for the samples taken from the well numbered TD-151. Ca was enriched in the samples taken from the wells numbered TD-155 and TD-129; Ti was enriched in the wells other than the samples taken from the wells numbered TD-151 and TD-131 and P was only enriched in the samples taken from the well numbered TD-129 and consumed in all the other wells (Fig. 5).

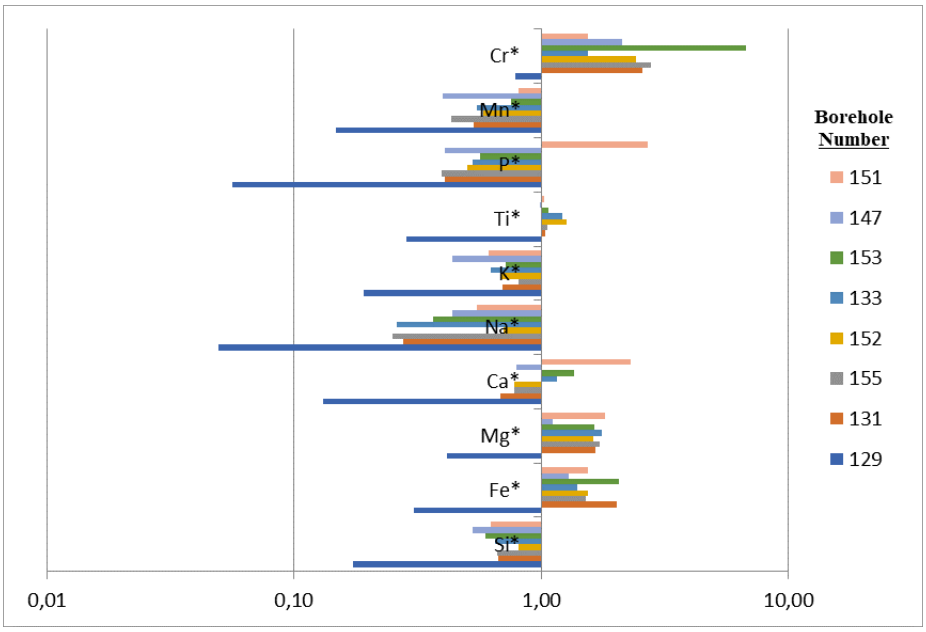

Figure 5. Well-based enrichment factors of major elements relative to the UCC. (Enrichment Factor (EF) = (element/Al)sample / (element/Al)average shale [52], *Major elements)

In trace elements, Barium, Beryllium, Cobaltum, Caesium, Gallium, Hafnium, Niobium, Rubidium, Stannum, Strontium, Tantalum, Thorium, Uranium, Vanadium, Zirconium, Yttrium, REE, Molybdenum, Cuprum, Plumbum, Zincum, Antimonium, Bisemutum, Aurum, Hydrargyrum and Thallium elements were found to be consumed both in the averages taken on the basis of wells and in general average (Fig. 6). W and Se elements were enriched in all coal samples both on general average and on a well basis. Ni was enriched in the samples taken from wells numbered TD (151,147 and 153), and consumed in samples taken from the wells numbered TD (133, 152, 155, 131 and 129). While As was enriched only in the samples taken from the well numbered TD-153, Cd was enriched only in the samples taken from the wells numbered TD (131 and 133). When the enriched elements were evaluated throughout the study area, it was found that the enrichments in question are related to organic matter.

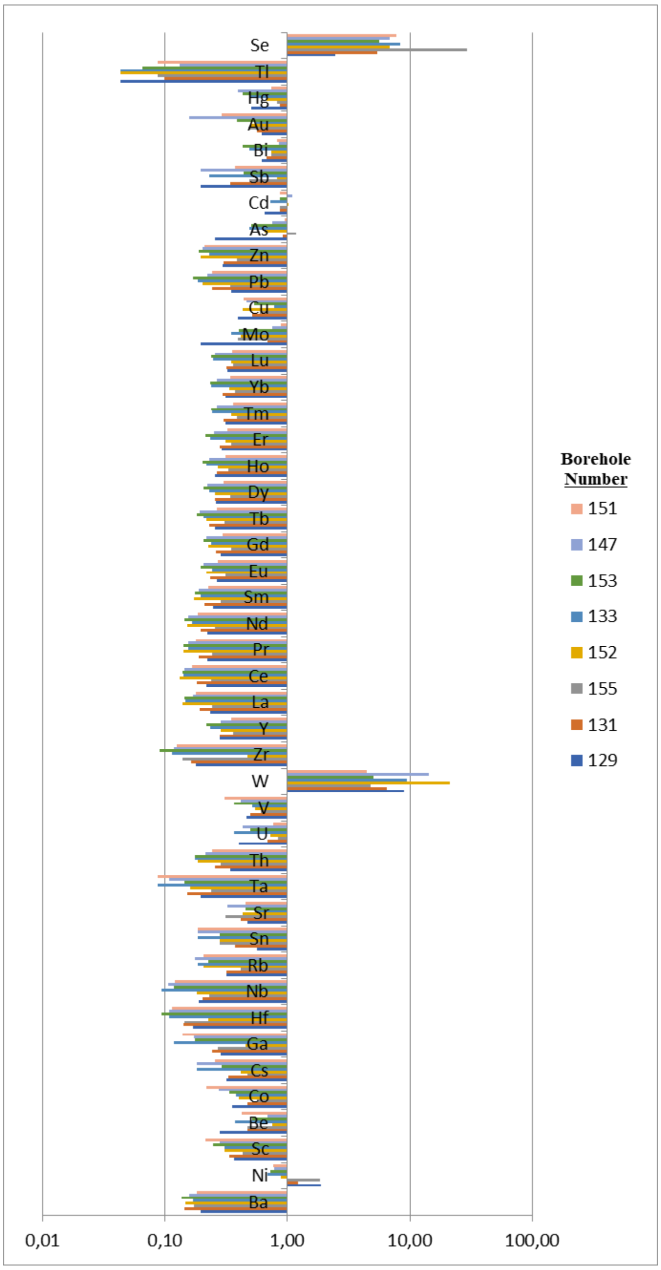

Figure 6. Well-based enrichment factors of trace elements relative to the UCC.

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Element contents of coal base, ceiling and intercalation samples were compared with elemental contents of coal samples. As expected, the main elements increased in floor, ceiling and intercalation samples. In trace elements, an increase was determined in the amounts of Beryllium, Uranium, Vanadium, Molybdenum, Cuprum, Cadmium, Antimonium, Bisemutum, Hydrargyrum, Thallium and Selenium in coal samples. When the correlation matrix obtained by statistical analysis was evaluated, the elements Uranium, Vanadium, Cuprum, Cadmium, Antimonium, Bisemutum, Hydrargyrum and Thallium were associated with minerals content. However, the fact that these elements are found in coal samples in higher amounts reveals the relation of these elements to organic matters of sedimentation environment (Fig. 7).

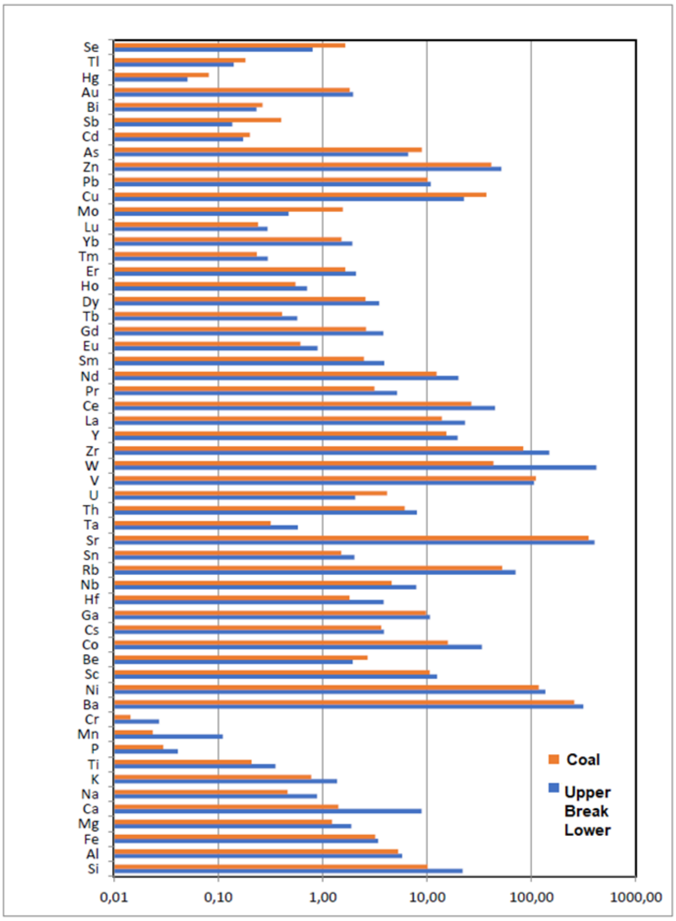

Figure 7. Comparison between the elemental contents of coal and rock samples.

4.5. Environmental Aspects of Trace Elements in the Malkara Coals
The environmental effects of the trace elements depend on their content and way of formation [53]. Toxic effects of trace elements may arise from the combustion of coal in domestic or industrial form [32]. Trace element content in coal has a great effect on the environment, economy and living beings [3].

Trace elements in coal are divided into three groups in terms of their environmental effects [2]. The elements in the first group consist of As, Cd, Hg and Se, and these elements are considered toxic. The elements in the second group consist of B, Be, Cu, Mo, Ni, Pb, Th, U, V and Zn, and these elements have environmental effects. The elements in the third group consist of Ba, Co, Sb, Sn and Tl and have the least environmental risk. Among the elements examined in the study area, Se in the first group, Be, Cu, Mo, Ni, Pb, Th, U, V, Zn in the second group, and Ba, Co, Sn elements in the third group presented values above the world coal averages. Due to the fact that especially Se element is a volatile element, due to its use in thermal power plants and for thermal purposes, it may have negative impact on environment and human health as a result of its emission to the atmosphere [54, 55, 56]. Although elements that may be environmentally hazardous such as Cd, Sb, Hg and Tl remain below world averages in coal samples, these elements also pose risks because there will be an increase in concentrations that will form in case of using coal due to the high amount of coal ceiling-floor and intercalation samples. On the other hand, As, Be, Cd, Cr, Co, Hg, Pb, Mn, Ni, Sb and Se elements are anthropogenic sourced air pollutants depending on coal use according to Clean Air Act Amendments. In the study area, Be, Co, Pb, Ni, and Se, which are among these elements offer values above the world average. Therefore, they are potential air pollutants in the use of coal.

5. CONCLUSIONS

As a result of the major and trace element analysis applied to 54 coal, coal ceiling base and intercalation samples taken from Malkara (Tekirdağ) region, XRD all rock and clay analyses, similar results were obtained from coal and roof, floor, and parting samples in mineralogical investigation of Malkara lignites. Quartz, ankerite, pyrite, calcite, mica, aragonite, dolomite, feldspar were detected. Smectite, illite, kaolinite, and chlorite were the clay minerals that are detected from big to small amounts.

In the value comparison of Malkara lignites, all elements other than Manganum, Molybdenum, Cadmium, Antimonium, Praseodymium, Gadolinium, Thulium, Aurum, Hydrargyrum, Thallium, Bisemutum were found to be above the world coal average; Vanadium, Nichelium, Cuprum, Arsenicum, Selenium, Strontium, Wolframium, Aurum, Hydrargyrum, Bisemutum, Uranium, above the upper continental crust average, Silicium, Aluminium, Ferrum, Magnesium, Natrium, Kalium, Titanium, Barium, Scandium, Vanadium, Cobaltum, Zincum, Cuprum, Gallium, Rubidium, Strontium, Yttrium, Niobium, Barium, Plumbum above the Turkey coal average, all elements other than Phosphorus, Manganum, Chromium, Zincum, Arsenicum, Selenium, Molybdenum, Cadmium, Antimonium, Aurum, Hydrargyrum, Thallium, Plumbum, Bisemutum above the U. S. coal average and Silicium, Aluminium, Magnesium, Calcium, Natrium, Kalium, Titanium, Manganum, Beryllium, Scandium, Vanadium, Cobaltum, Nichelium, Cuprum, Gallium, Arsenicum, Rubidium, Strontium, Caesium, Barium, Wolframium, Thorium is above the average of Chinese coals. All of the major elements other than Cr are below the UCC concentration. It was determined that the major elements largely stem from inorganic matter. It was found that Be, Sr and W which are related to trace elements are not only related to inorganic substances but also the organic origin and no relation was determined between other trace elements and organic matter.

Element enrichment factors were calculated and consumed and enriched elements were determined. Among the major elements, Silicium, Natrium and Kalium were consumed in all wells and Phosphorus was consumed in all the wells other than TD-129. Ferrum, Magnesium, Chromium were enriched in all wells except TD-151, and Ti was enriched in all wells except TD-151 and TD-131. Among the minor elements, Barium, Beryllium, Cobaltum, Caesium, Gallium, Hafnium, Niobium, Rubidium, Stannum, Strontium, Tantalum, Thorium, Uranium, Vanadium, Zirconium, Yttrium, REE, Molybdenum, Cuprum, Plumbum, Zincum, Antimonium, Bisemutum, Aurum, Hydrargyrum, Thallium were consumed in all wells, and Wolframium and Sulphurium elements were enriched in all wells.

Among the coal samples in the study area, Selenium, Beryllium, Cuprum, Molybdenum, Niccolum, Plumbum, Thorium, Uranium, Vanadium, Zincum, Barium, Cobaltum, Stannum, which are among the elements that may create an adverse environmental effect, offered values above the world coal averages. Among these elements, Beryllium, Cobaltum, Plumbum, Niccolum and Selenium are potential air pollutants in the use of coal. The average samples of coal, coal ceiling, floor and intercalation were compared. When the environmentally sensitive elements were examined, Chromium, Arsenicum, Manganum, Niccolum, Plumbum, Phosphorus, Zincum, Thorium, Titanium, Cobaltum, Stannum, Barium, roof, floor and parting samples exhibited an increase compared to coal.

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