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Mineralogical and Geochemical Properties of Clays to Associated with the Yarıkkaya (Yalvaç-Isparta) Coal Deposits

Oya CENGİZ[*1], **Ayhan Sinan UZUN**[2], **Maksat BEKİYEV**[3]

[1,2,3]Süleyman Demirel Üniversitesi, Mühendislik Fakültesi, Jeoloji Mühendisliği Bölümü, Isparta, Türkiye

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Yarıkkaya,
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Mineral composition,
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Occurrence

Abstract: This study contains the mineralogical and geochemical characteristics of clays associated with Yarıkkaya (Yalvaç-Isparta) lignite coals. The clays are located in three lignite coal sites in the Yarıkkaya Neogene basin. The claystone member mainly consisting of claystone, carbonated shale, marl and locally mudstone, is settled in the Miocene Yarıkkaya formation. The clay occurrence is generally at the bottom of coal and sometimes at the upper parts of coal levels or laterally transitive with clays. The clay deposits have gray, dark gray and khaki colour, and they are generally covered by brown or gray bituminous materials. Their thickness changes between 5-15 m, and has a maximum thickness of 40 m as intercalated with the other lithologies in the Yarikkaya-3 location. The mineral paragenesis of clay formation mainly consists of illite, kaolinite, chlorite, and to a lesser amount smectite. SiO_2/Al_2O_3 vs. Fe_2O_3/K_2O ratios indicated that Yarıkkaya clay samples are defined as mainly shale, less greywacke and quartz arenite. The average Al_2O_3/TiO_2 ratios suggest that Yarıkkaya clay samples show intermediate source rock. Cu, Ba, Pb, Zn, Co, Zr, Ga, Rb, V are considerably lower, only Ni contents are higher contents of with respect to PAAS. Geochemical contents of the investigated clays show that the clastics which are derived from the Seydişehir formation rocks could give a material to the Yarıkkaya lacustrine sediments.

Yarıkkaya (Yalvaç-Isparta) Kömür Yatakları ile İlişkili Killerin Mineralojik ve Jeokimyasal Özellikleri

Anahtar Kelimeler
Yarıkkaya,
Linyit kömürü,
Killer,
Mineral bileşimi,
Jeokimya,
Oluşumu

Özet: Bu çalışma, Yarıkkaya (Yalvaç-Isparta) linyit kömürleri ile ilişkili killerin mineralojik ve jeokimyasal özelliklerini kapsar. İncelenen killer Yarıkkaya Neojen havzasındaki üç linyit kömür lokasyonunda yeralmaktadır. Başlıca kiltaşı, karbonatlı şeyl, marn ve yer yer çamurtaşından meydana gelen kiltaşı üyesi Miyosen yaşlı Yarıkkaya formasyonunda bulunur. Kil oluşumu genellikle kömürün tabanında, bazen linyit kömür seviyelerinin üst kısmında yada geçişli olarak gözlenir. Kil çökelleri gri, koyu gri ve haki renklerdedir. Genellikle kahverengi yada gri bitümlü malzemeler ile örtülmektedir. Kalınlıkları 5-15 m arasındadır ve Yarıkkaya-3 lokasyonundaki diğer litolojiler ile arakatkılı olarak maksimum 40 m kalınlığa sahiptir. Kil oluşumunun mineral parajenezini başlıca illit, kaolinit ve klorit ve daha az miktarda smektit oluşturur. SiO_2/Al_2O_3 ve Fe_2O_3/K_2O oranları, Yarıkkaya kil numunelerinin başlıca şeyl, daha az grovak ve kuvars arenit olarak tanımlandığını gösterir. Ortalama Al_2O_3/TiO_2 oranları Yarıkkaya kil örneklerinin ortaç kaynak kaya olduğunu göstermektedir. İncelenen kil numunelerinin Cu, Ba, Pb, Zn, Co, Zr, Ga, Rb, V içerikleri oldukça düşüktür, sadece Ni içerikleri PAAS' a göre daha yüksektir. Yarıkkaya killerinin jeokimyasal içerikleri, Seydişehir formasyonundaki kayaçlardan türeyen kırıntılı materyallerin Yarıkkaya gölü tortullarına malzeme verebileceğini göstermektedir.

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*Corresponding author: oyacengiz@sdu.edu.tr

1. Introduction

The clays observed at the generally lower levels of coal deposits, sometimes at the top or at the transition of the coal beds, are called "sub-coal clays". In particular, refractory clays can be associated with hard coal, as well as with younger lignite coals. While hard coal and lignite contain a kaolinite-illite mixture or only illite mineral, anthracites include halloysite. Refractory clays contain mainly kaolinite and are of sedimentary origin. Kaolin has used in industry areas such as cement, paper, plastic, medicine, etc. These clays contain impurities such as calcite and pyrite. Refractory clays have low plastic properties and high aluminum content. Sub-coal clays have used in brick, tile, pottery, etc. ceramic industry and in the refractory industry such as cement and chemistry [1].

In order to determine the usage properties of sub-coal clays in industry, the mineralogical composition and geochemical properties of these clays should be known. For this reason, this study was carried out. The clays in the investigated area are located in the lignite coal situations in the Neogene aged Yarıkkaya lake basin (Figure 1). The lignite coal has been currently operated by a private company. Since coal outcrops are opened, the sub-coal clay beds are clearly observed in the field.

The purpose of this study is to investigate the mineralogical and geochemical properties of clays associated with lignite coals in an area of approximately 12 km^2 near surrounding Yarıkkaya (Yalvaç-Isparta) village (Figure 1).

The clay formations in the Neogene lake basin are observed in three coal quarry sites in the Miocene aged Yarıkkaya formation. In these locations, systematic clay samples were taken from the profiles of clay spread and mineralogical definitions (mineral contents and clay types) and geochemical analyzes (major oxide and trace elements) of these samples were made. By the results of the analyses, it was determined that could the usage of clays as brick soil and ceramic raw materials. In this study, only technological tests have not been performed to use clays in economy. However, it is known that the clays were used as washer clay by the local people.

2. Material and Method

The total eight clay samples were collected from certain clay profiles at three lignite coal locations. These are Y-1, Y-2, Y-3, Y-4 from Yarikkaya-1 Quarry, Y-5 from Yarikkaya-2 Quarry, and Y-8, Y-10 from Yarikkaya-3 Quarry. In order to examine the mineralogical characteristics of these samples, bulk rocks' mineral composition, air dried (AD), ethylene glycol (EG), heated at 350°C and 550°C were carried by X-ray diffractometer (XRD) detail clay analysis.

Figure 1. Google Earth location map of the investigated area.

Guided samples were prepared from clay-sized fractured samples to process these samples for XRD analysis. For this aim, approximately 20-30 grams of 250 µm grain size is put out a 1000 cc glass or polyethylene scale container and weighed. Then 55 cc of purified water is added and mixed with mechanical stirrer for about 10 min (1500 min-1) and left in a dust-free environment for 1 hour sedimentation at 20°C. The clear upper level is emptied. Then, 5-10 ml of the solution is pipetted at a depth of 5 cm from the surface of the suspension and stored for analysis. In this way, only <2µm grains are obtained and maximum richness is obtained in terms of clay minerals [2].

A series of standard secondary treatments were applied to the prepared specimens to create artificial changes in the basal diffraction of clay minerals, especially in the low 2θ° angle region. Distinction and exact definition of diffraction profiles and similar clay minerals were made by systematic examination of these artificial changes. XRD graphics were taken from after guided samples were subjected to the following standard procedures.

Treatment with ethylene glycol is carried out by waiting at least 1 hour in an oven (set to 60°C) in an open mouth container containing ethylene glycol (liquid or fraction). However, the most important factor to be considered during this process is to make XRD analysis of the sample taken from the oven in short and always same time interval. Heat treatment at 550°C is carried out by keeping the same sample subjected to ethylene glycol treatment in a temperature sensitive (± 5°C) oven for at least 1 hour. It is also important to perform XRD analysis immediately after the sample has cooled down for 15–20 minutes after heat treatment.

By using Shimadzu XRD-6000 model X-ray diffractometer with Ni filter, CuKα radiation, and Cu Kα X-ray with 1.544Å wavelength, XRD analyses of clay samples in the study area were performed in Afyon Kocatepe University Technology Application and Research Center (TUAM) Laboratory. In the analysis, 40 kV (voltage) and 30 mA (current) diffraction values were selected. Clay samples were scanned at 2° / min and analyzed at a peak intensity of 2000 cps (intensity) in the range of 2°-70° (2Φ) ganiometer diffraction angle.

By Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) method, major-oxide and trace element analyses were conducted on the same eight samples in Bureau Veritas Mineral (BVM) Canada laboratories. In this laboratory, samples were milled to 200mesh and then dissolved by lithium borate fusion and the element contents were measured by ICP-MS method.

3. Results

3.1. Geology of Yarıkkaya area

The study area is located in the inner part of the structure known as Isparta Angle in the southwestern Anatolia [3]. The region is surrounded by Sultandağları from the north and east and Anamasdağları from the south. The lithological units in the area are the rocks of Ordovician aged Seydişehir Formation epimetamorhics and Jurassic aged Hacıalabaz limestone. Hacıalabaz limestone unconformably overlies the Seydişehir Formation. The Seydişehir Formation contains slate, phyllite, meta-sandstone, and meta-conglomerate. These formations are unconformably overlaid by Neogene aged sediments. Neogene aged units consist of Miocene aged Bağkonak, Yarıkkaya and Göksöğüt formations, Pliocene aged Kırkbaş formation lacustrine sediments (Figures 2, 3).

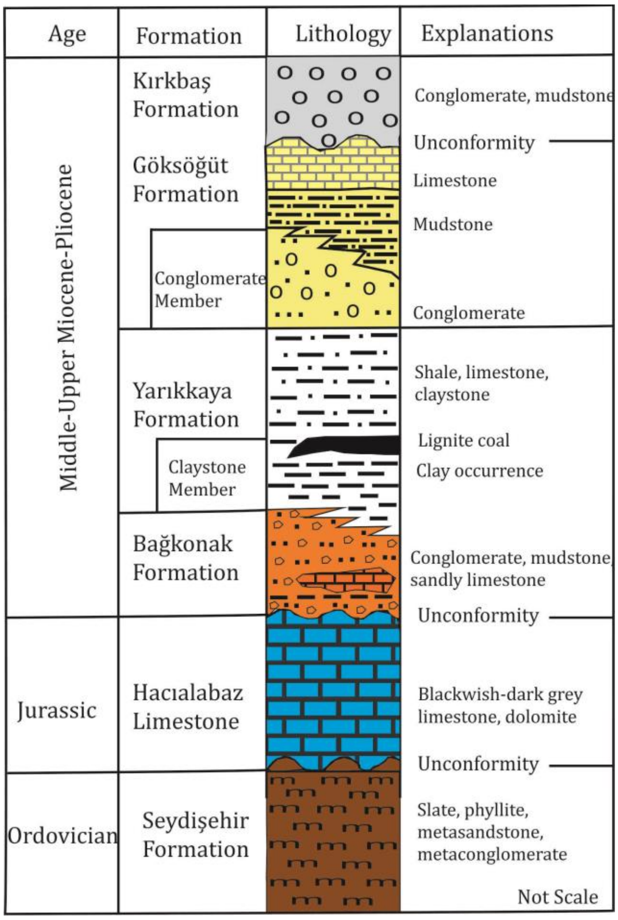

Figure 2. Tectono-stratigraphic column section of the study area modified from [4].

The dominant tectonic structures in the Yarıkkaya Neogene basin and surrounding areas are represented by normal and thrust faults. The thrust and reverse faults are generally developed between the Mesozoic and Paleozoic aged rock units before the Neogene period. The western and southern of the region are completely bounded by normal faults. The normal faults that delimit the basin are generally in the direction of N, NE and NW and show a stepped structure developed parallel to each other at the margins of the basin. Data such as the sudden increase in sediment thickness from the basin edge to the interior and the transgressive overlying of the old basement rocks in the edge of the basin are evidence that these faults are also active growth faults during the sedimentation period [4].

The N, NE trending and eastward sloping Sağır fault in the northern part of the basin is cut by NW trending and westward sloping Çakırcal fault in the northern part of Yarıkkaya. The Sağır fault is N, NW trending in the south of Sağır village, but NE trending in the northern part of the village. Sağır and Yarıkkaya faults and Çakırcal and Söğütdibi faults represent parallel stepped normal fault systems [4].

The Neogene aged rock units are outcropped in the Yarıkkaya Basin. They are generally discriminated from each other by lithofacies boundaries, which may be transitional in lateral and vertical directions. The basin is filled by the sediments in the time interval ranging from Middle Miocene to Pliocene. The clays are settled in the Yarıkkaya formation and indicate the lacustrine environment. The Yarıkkaya formation has reached a total thickness of 200 m. It has a lateral transition with Bağkonak formation in the northern and eastern parts of the basin and Madenli formation in the southern parts [4], [5].

Clay deposits in the study area are situated at three locations Yarıkkaya-1, Yarıkkaya-2, and Yarıkkaya-3. Yarıkkaya-1 clays have dark gray, khaki colored and light gray when dry. They have a moistly and easily adhering structure. The thickness of clay deposits in the outcrop is 10-12m, and the thickness of coal is approximately 40 cm. They include different sized pebbles at some levels. The clays are covered by yellowish beige sand, gravel, and block-sized grains (Figure 4. a, b, c, d).

In the Yarıkkaya-2 location, claystone is observed sometimes dark and light gray colored and their thickness varies between 5-15 m. The clay level could not be detected because coal level was underwater. Clay and gravel-sized grains overlie the clays. Sometimes fine-grained and brown bituminous materials were observed in the cover layer (Figure 4. e).

In the Yarıkkaya-3 area, clay formations display foliation and have dark gray in color. Due to the fault zone passing through the region, silicification and sulfurization have been detected in the area. The cover rocks are the rich in bituminous layers. The claystone can reach a maximum thickness of 40 m as intercalated with the other lithology's (Figure 4. f-g).

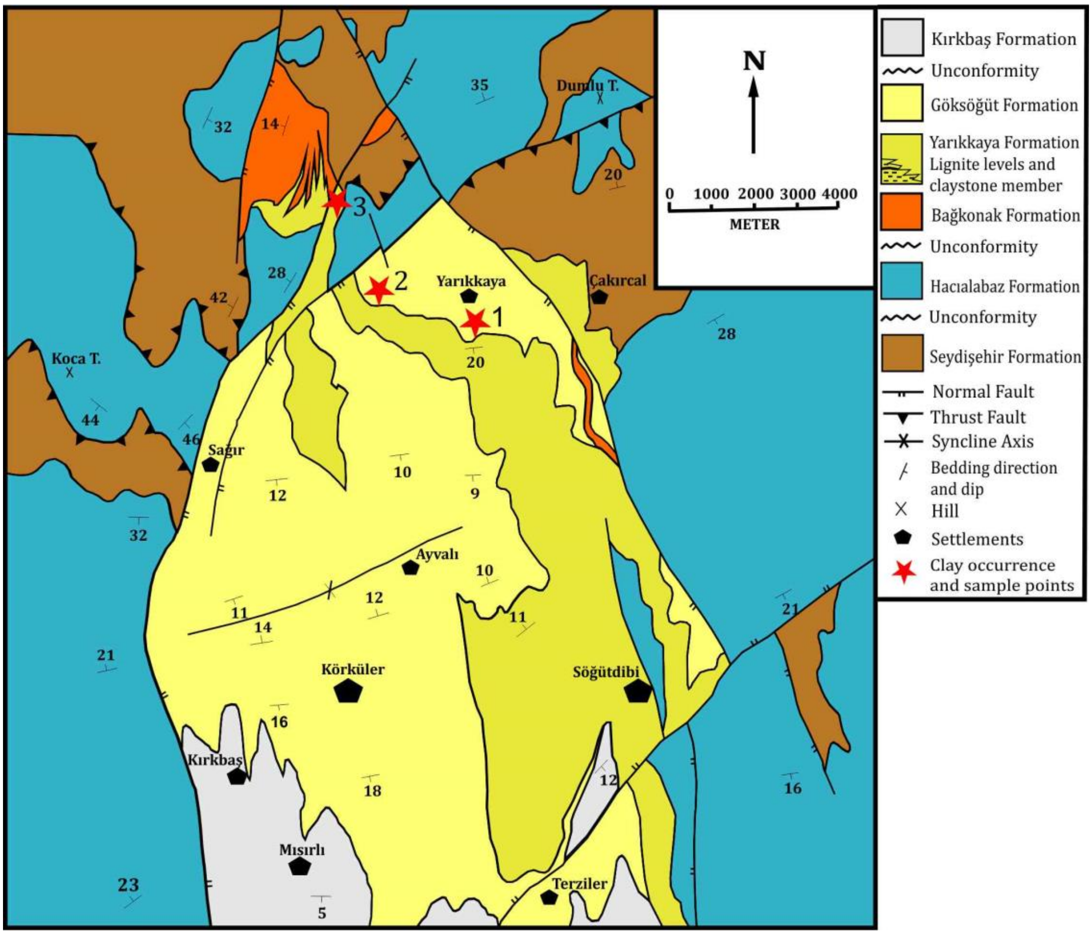

Figure 3. Geological map of the study area modified from [4].

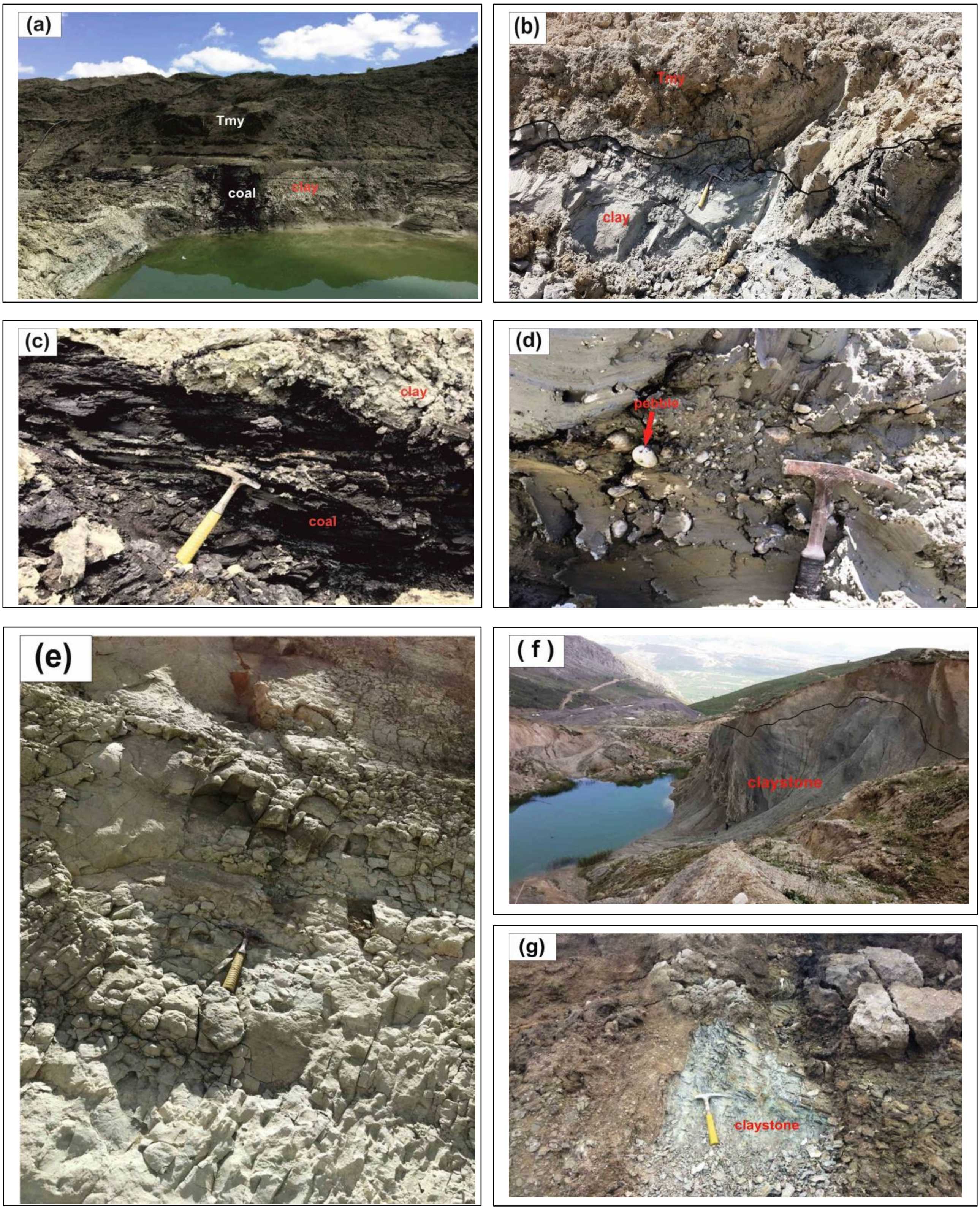

Figure 4. Field photographs of clay and coal deposits in the study area (a, b, c, d: Yarıkkaya-1 Quarry, e: Yarıkkaya-2 Quarry, f, g: Yarıkkaya-3 Quarry) [6].

3.2. Mineralogical determinations of Yarıkkaya clay

The X-ray diffractometer detail clay analysis results were presented in Table 1 and some samples' graphs are given below (Figure 5, 6, 7, 8, 9). In the mineralogical composition of the Yarıkkaya clays, illite is the main phase present in all clay samples. Kaolinite, smectite, and illite-smectite are the minor mineral phases in Yarıkkaya clay samples. Chlorite, feldspar, and calcite are abundant in clay samples. Silica polymorphs occur in the form of only quartz.

As seen in Table 1, hematite is not observed in Y-8, Y-10, and Y-11 samples. Also, chloride does not in Y-8 and Y-10 samples. Illite-chloride was observed only after heating at 350ºC in the Y-1 sample. Illite-smectite and smectite exist only in the Y-4 sample.

The air-dried clay fractions of Y-2 sample from the Yarıkkaya-1 clay quarry exhibit a d001 spacing of 9.83 A°, which slightly expanded to 9.93 A° after saturation with ethylene glycol, and slightly collapsed to 9.91 A ° after heating at 550ºC for 1 h (Figure 6).

The air-dried clay fractions of Y-5 sample from the Yarıkkaya-2 clay quarry display a d001 spacing of 9.98 A°, which is the same value (9.98 A°) after saturation with ethylene glycol, and slightly collapsed to 9.95 A ° after heating at 550ºC for 1 h (Figure 7).

The air-dried clay fractions of Y-10 sample from the Yarıkkaya-3 clay quarry exhibit a d001 spacing of 9.93 A°, which is the close values (9.94 A°) after saturation with ethylene glycol and (9.92 A°) after heating at 550ºC for 1 h (Figure 8).

The air-dried clay fractions of Y-11 sample from the Yarıkkaya-3 clay quarry exhibit a d001 spacing of 9.94 A°, which is the same value (9.94 A°) after saturation with ethylene glycol, and slightly collapsed to 9.89 A° after heating at 550ºC for 1 h (Figure 9).

Table 1. Mineral abundances of the investigated clay samples

Sample N	Phases	Mineral Composition								
		Illite	Quartz	Kaolinite	Feldspar	Chlorite	Calcite	Dolomite	Hematite	Smectite
Y-1	Standard	*****	*****	**	**		**	*	*	
	AD	***	**	*	*	**	*			
	EG	***	**	*	*	*	*			
	350ºC	**	**		*		*			
	550ºC	***	**		*	*	*			
Y-2	Standard	*****	****	*	**	**	****	*	*	
	AD	**	*	*	*	**	*			
	EG	**	**	*		*	*			
	350ºC	**	**	*		**	*			
	550ºC	**	**		*	*	*			
Y-3	Standard	****	****	*	*	***	****	*	*	
	AD	***	**	*	*	**	*			
	EG	**	**	*	*	***	*			
	350ºC	**	**	*	*		*			
	550ºC	**	**		*	*	*			
Y-4	Standard	*****	******	*	**		****	*	*	**
	AD	*	*			*				*
	EG	***	**	**	*		*			
	350ºC	**	**	*	*		*			
	550ºC		*							
Y-5	Standard	*****	****	*	**	***	****	*	*	
	AD	**	**	*	*	**	*			
	EG	***	**	*	*	**	*			
	350ºC	**	**	*	*	**	*			
	550ºC	**			**	*				
Y-8	Standard	******	******	*	***		*	*		
	AD	***	**							
	EG	**	**	*	*					
	350ºC	**	*	*						
	550ºC	**	**							
Y-10	Standard	*****	******	*	**		*	*		
	AD	***	**	**						
	EG	***	**	**	*		*			
	350ºC	****	*	**	*		*			
	550ºC	***	**							
Y-11	Standard	*****	******	*	***	**	*	*		
	AD	***	**	*	*	*	*			
	EG	**	**	*	*	**				
	350ºC	*	**	*	*		*			
	550ºC	***	**		*		*			

Standard mineral composition, AD: air dried, EG: ethylene glycolated, heated at 350ºC and 550ºC methods.
The relative abundances from XRD peak heights are indicated by *

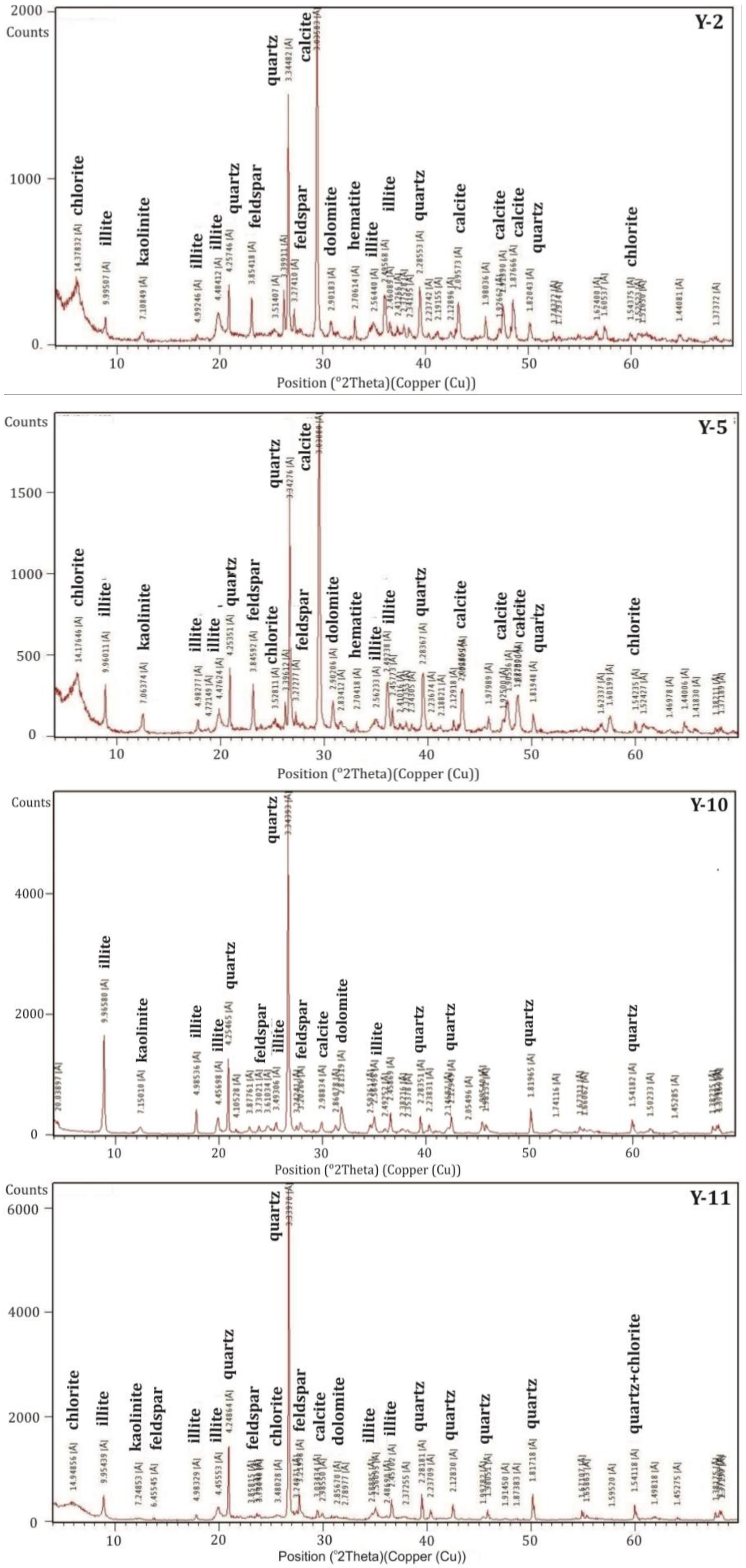

Figure 5. Representative XRD patterns of Yarıkkaya clay localities (bulk samples).

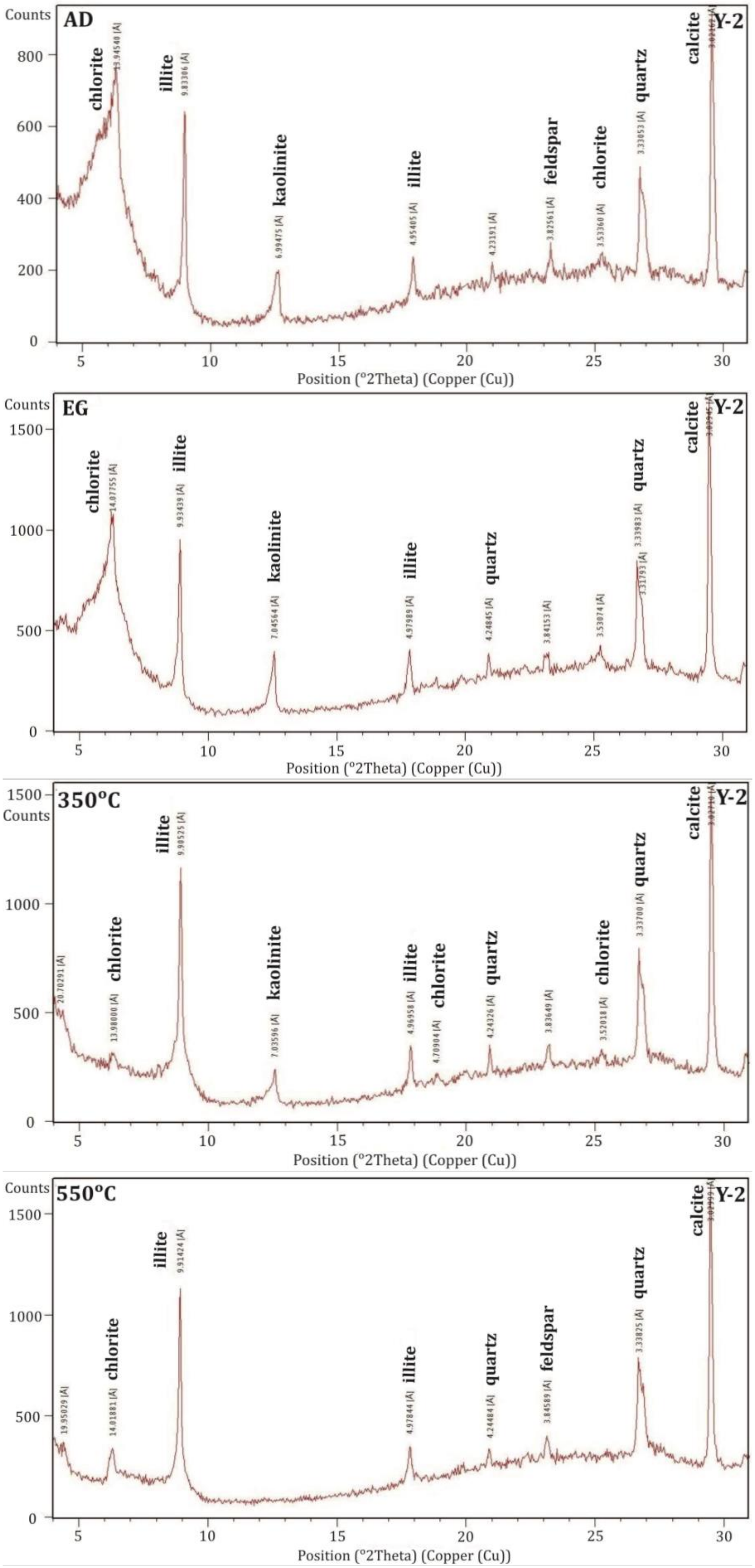

Figure 6. XRD patterns of Yarıkkaya-1 clay after treatment. AD: Air dried, EG: ethylene glycolated, and heated at 350 and -550°C.

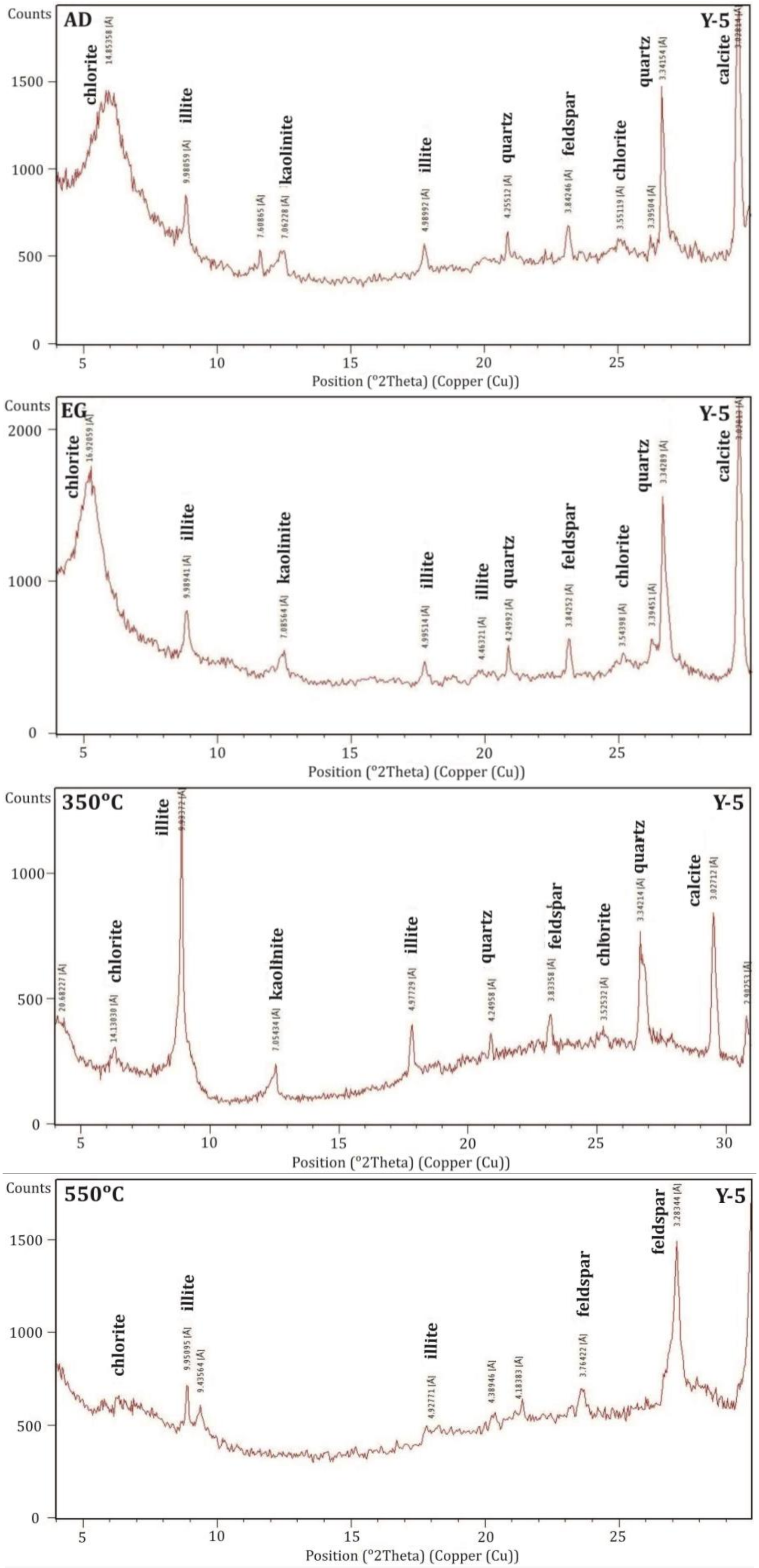

Figure 7. XRD patterns of Yarıkkaya-2 clay after treatment. AD: Air dried, EG: ethylene glycolated, and heated at 350 and-550°C.

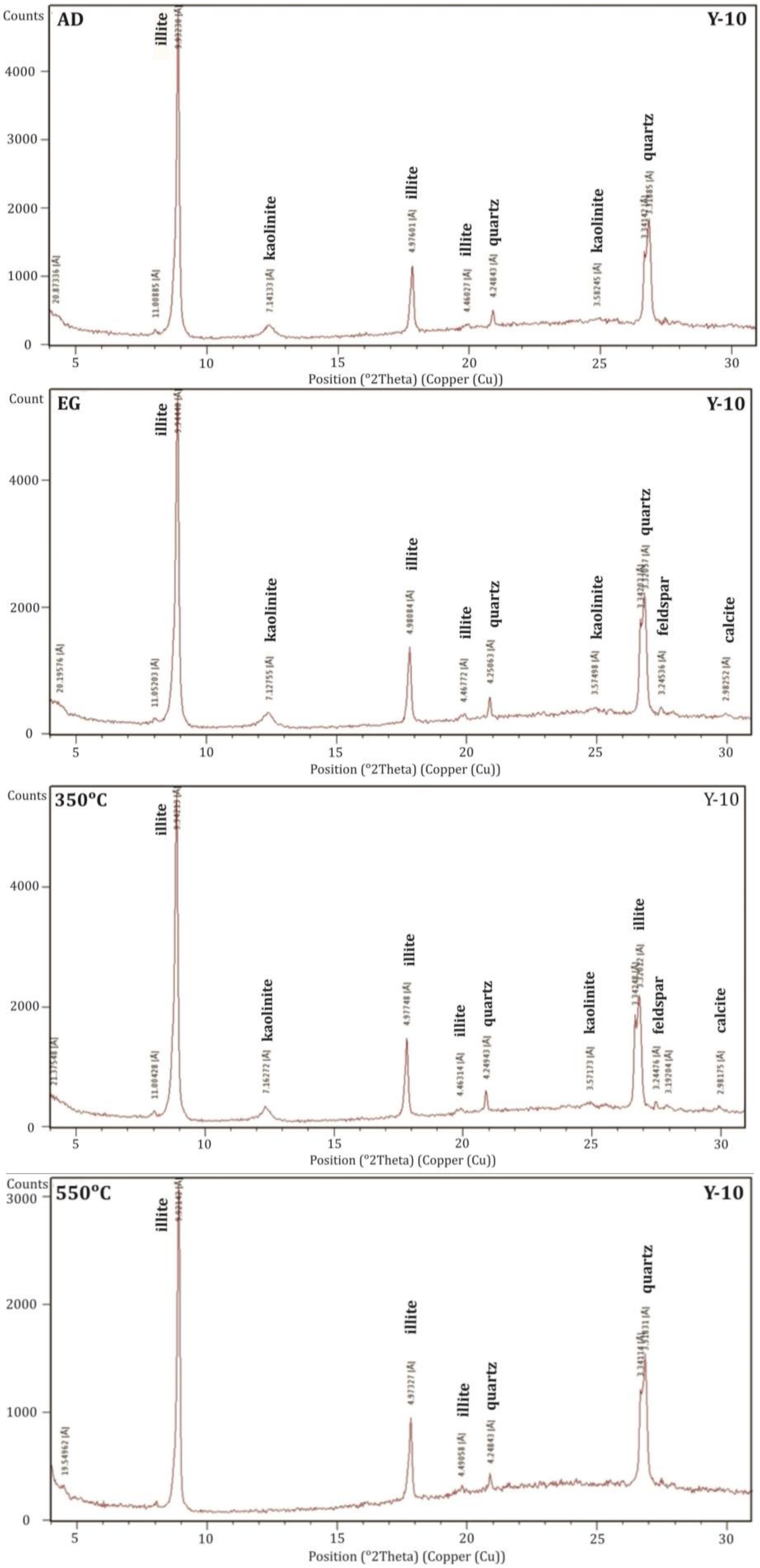

Figure 8. XRD patterns of Yarıkkaya-3 clay after treatment. AD: Air dried, EG: ethylene glycolated, and heated at 350 and-550°C.

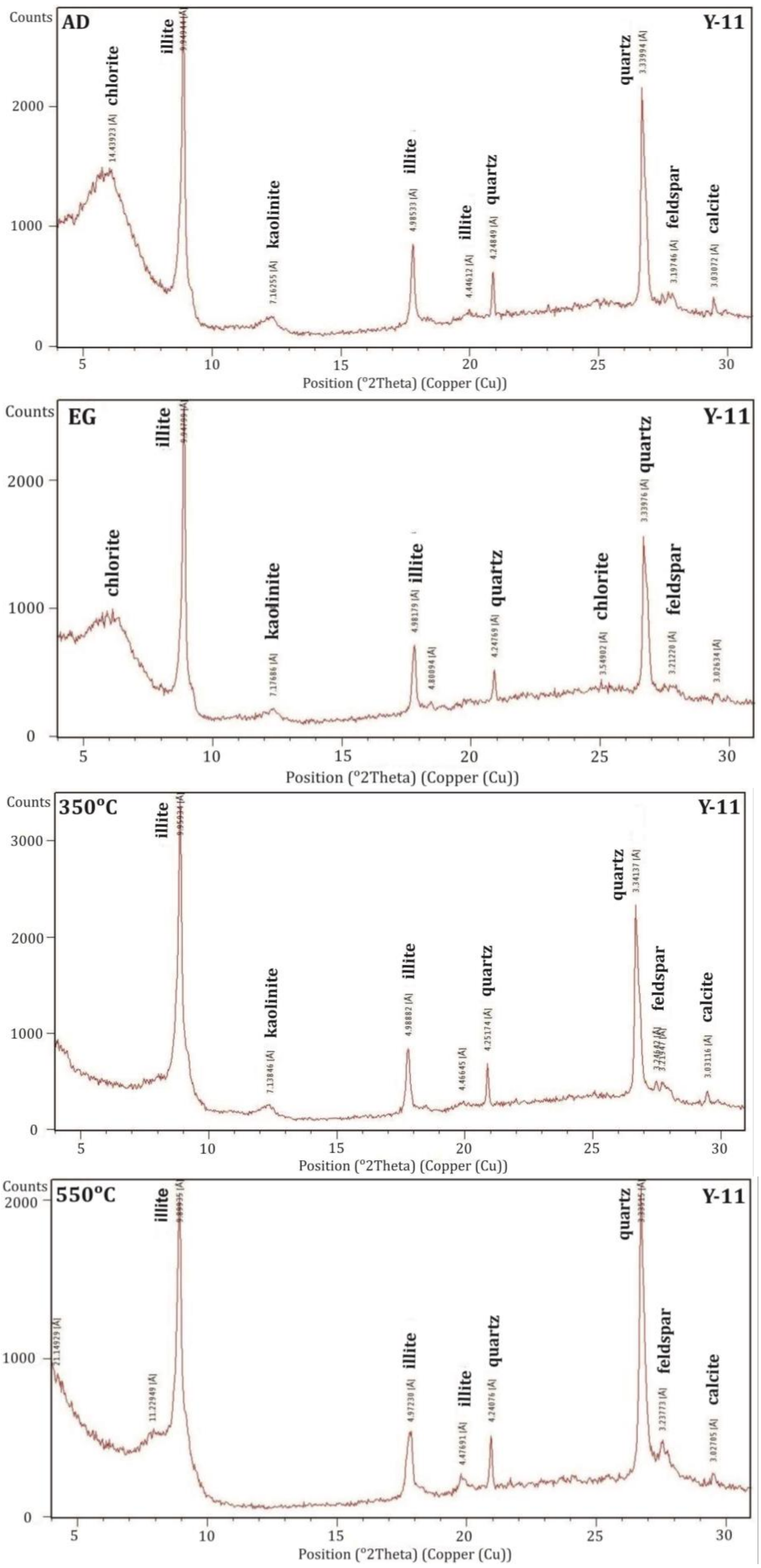

Figure 9. XRD patterns of Yarıkkaya-3 clay after treatment. AD: Air dried, EG: ethylene glycolated, and heated at 350 and 550°C.

3.3. Geochemical investigations

The results of the major-oxide analysis in the samples, taken from the clay formations in three coal quarries in the study area, are given in Table 2. SiO_2, Al_2O_3, K_2O, Fe_2O_3, and Na_2O are the most important oxides that make up the chemical composition of these clays associated with coals.

Clay samples of the Yarıkkaya-1 location have values between 30.81-33.36% SiO_2, 8.77-9.55% Al_2O_3, 1.32-1.51% K_2O, 4.01-5.30% Fe_2O_3, 2.49-2.90% MgO, 22.72-24.13% CaO. The clay sample of Yarıkkaya-2 area contains 31.92% SiO_2, 7.36% Al_2O_3, 1.18% K_2O, 3.55% Fe_2O_3, 2.51% MgO, and 25.87% CaO. Values of clay samples belonging to Yarıkkaya-3 area vary between 56.38 to 67.01% SiO_2, 14.10 to 25.24% Al_2O_3, 2.87 to 7.75% K_2O, 2.36 to 3.66% Fe_2O_3, 0.85 to 1.17% MgO, and 0.18 to 2.30% CaO. The concentrations of other oxides were measured below 1% in all three sites (Table 2). It is seen that the SiO_2, Al_2O_3 and K_2O values of the clay samples in the Yarıkkaya-3 quarry are higher than those of other locations and are rich in potassium clays. Fe_2O_3 contents of the samples taken from Yarıkkaya-1 quarry are higher than those of the other two quarries. In addition, it is remarkable that the CaO and MgO contents of clay samples in Yarıkkaya-1 and 2 quarries are very high compared to the values of Yarıkkaya-3 quarry (Table 2).

The total carbon content of clay samples taken from Yarıkkaya-1 and Yarıkkaya-2 Quarries (5.45-6.14%) is considerably higher than those of Yarıkkaya-3 quarry (0.14-0.46%). Total sulfur contents have similar values and low contents in three sites.

The variation in the abundance of Si, Fe, Mg, Ca, K, and Ti with the Al_2O_3 content in samples is shown in Figure 10. Fe, Mg and Ca elements display strong negative correlation with Al_2O_3. Si, K, and Ti elements show strong positive correlation with Al_2O_3. This shows that they are mainly concentrated in phyllosilicates (Figure 10. a, b, c, d, e, f).

Table 2. Major-oxide (%) and trace element (ppm) concentrations (%) of Yarıkkaya samples and Average Post Archean Australian Shales (PAAS; data from [8])

Sample Location	Yarıkkaya-1				Yarıkkaya-2	Yarıkkaya-3				PAAS
Sample N.	Y-1	Y-2	Y-3	Y-4	Y-5	Y-8	Y-10	Y-11	Average	
SiO_2	33,11	30,81	32,45	33,36	31,92	56,38	63,56	67,01	43,57	62,80
Al_2O_3	9,55	9,05	8,77	8,77	7,36	25,24	19,68	14,10	12,82	18,90
Fe_2O_3	4,01	4,14	4,11	5,30	3,55	2,36	2,94	3,66	3,76	6,50
MgO	2,65	2,49	2,90	2,61	2,51	0,89	1,17	0,85	2,01	2,20
CaO	22,81	24,13	23,12	22,72	25,87	0,18	0,66	2,30	15,22	1,30
Na_2O	0,23	0,16	0,16	0,21	0,19	0,17	0,14	0,57	0,23	1,20
K_2O	1,51	1,32	1,35	1,44	1,18	7,75	6,01	2,87	2,93	3,70
TiO_2	0,54	0,52	0,48	0,52	0,47	1,08	0,94	0,84	0,67	1,00
P_2O_5	0,08	0,10	0,08	0,12	0,08	0,08	0,43	0,02	0,12	0,16
MnO	0,06	0,04	0,07	0,10	0,09	0,01	0,01	0,01	0,05	0,11
Cr_2O_5	0,023	0,030	0,033	0,025	0,029	0,018	0,015	0,012	0,023	0,01
LOI	25,20	27,00	26,30	24,60	26,60	5,60	4,20	7,60	18,39	-
Total	99,77	99,79	99,82	99,78	99,85	99,76	99,76	99,84	99,80	-
Total C	5,45	6,14	5,58	5,57	6,14	0,18	0,14	0,46	3,71	-
Total S	0,07	0,04	0,02	0,12	0,02	0,25	0,03	0,02	0,07	-
Al_2O_3/TiO_2	17,68	17,40	18,27	16,86	15,66	23,37	20,94	16,79	19,13	18,90
Ba	256	273	260	252	257	737	406	333	346,75	650
Ni	133,7	225,1	150,9	240,3	145,1	7,5	34,4	15,7	119,09	55
Co	18,1	20,8	17,6	20,2	19,8	3,9	9,2	5,9	14,44	23
Cs	5,2	5,2	7,4	5,1	3,9	9,7	11,7	9,3	7,19	15
Ga	12,0	11,3	10,5	10,4	8,5	32,5	24,7	16,9	15,85	20
Hf	2,8	2,6	2,7	3,1	3,2	5,6	6,5	12,4	4,86	5
Nb	12,6	11,5	10,9	11,8	10,0	26,1	22,9	20,5	15,79	19
Rb	70,2	67,7	70,8	67,1	53,0	215,0	189,6	137,7	108,89	160
Sr	283,1	265,3	291,1	219,6	234,9	26,5	36,4	112,8	183,71	200
Th	9,2	8,1	8,2	8,6	7,2	17,2	22,2	22,0	12,84	14
U	2,6	2,2	2,2	2,1	2,0	3,0	3,9	3,2	2,65	3,1
V	89	89	102	85	67	150	136	94	101,50	150
Zr	109,5	93,1	102,0	116,4	123,8	213,8	248,0	477,0	185,45	210
Y	20,3	20,1	18,4	21,3	18,2	34,3	86,2	27,4	30,77	30
Sc	10	11	10	10	8	21	17	11	12,25	16
Cu	23,2	21,0	17,2	21,3	20,0	3,7	30,8	13,5	18,84	50
Pb	11,3	9,8	10,4	11,4	9,4	4,5	7,1	15,9	9,97	20
Zn	40	43	39	41	34	11	63	42	39,12	85

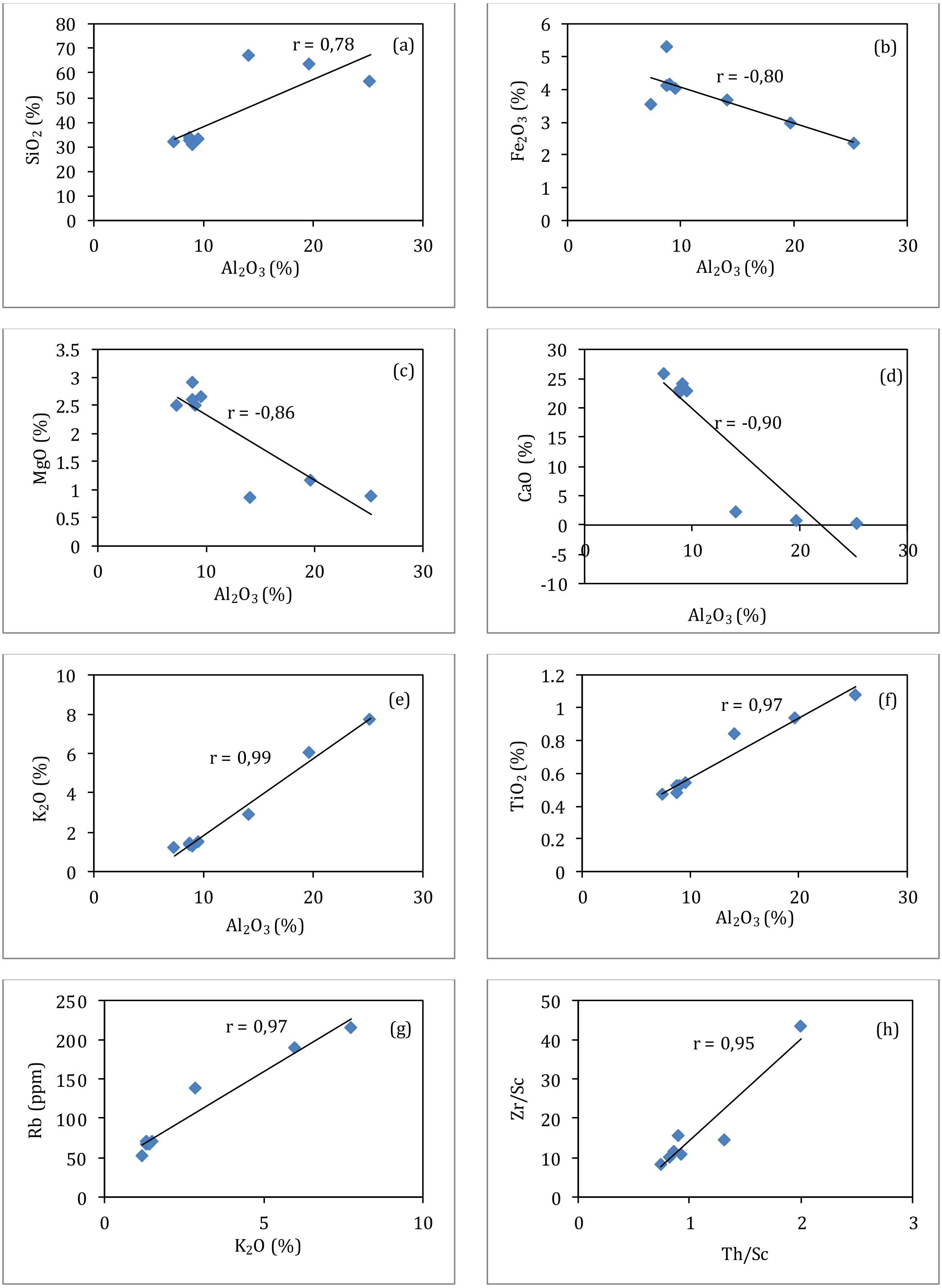

Figure 10. a, b, c, d, e, f. Correlation graphics between some major elements and Al_2O_3. g. K_2O-Rb correlation, h. Correlation graphic between Th/Sc and Zr/Sc ratios.

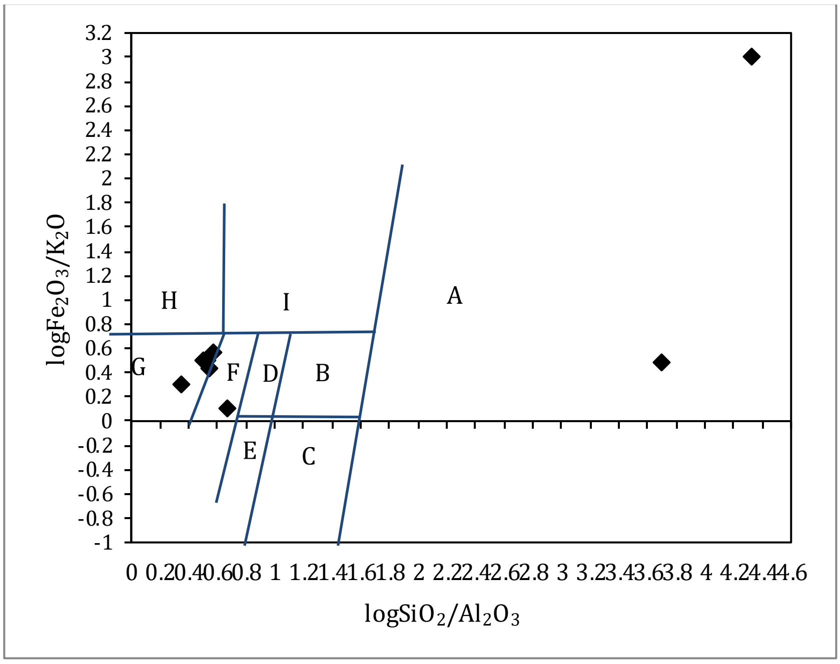

Figure 11. Chemical classification schema for Yarıkkaya clay samples after [7]. A. quartz arenite, B. sublitarenite, C. subarkose, D. litharenite, E.arkose, F. greywacke, G. shale, H. Fe-shale, I. Fe-sand.

In log SiO_2/Al_2O_3 vs. log Fe_2O_3/K_2O of chemical classification schema modified from [7], major oxide compositions of clastic sedimentary rocks have been used to indicate the rocks of Yarıkkaya clays. According to SiO_2/Al_2O_3 vs. Fe_2O_3/K_2O ratios in the diagram the rocks of Yarıkkaya samples are defined as mainly shale, except two quartz arenite sample and one greywacke sample (Figure 11).

In Figure 12, major oxide elements were compared in Yarıkkaya samples and Post Archean Australian Shale (PAAS; data from [8]). Fe_2O_3, SiO_2, Al_2O_3, Na_2O, TiO_2, and K_2O values in Yarıkkaya clay samples are quite low compared to PAAS. MgO has approximately similar values, but CaO contents are quite high compared to PAAS. High calcium values are due to the fact that lacustrine sediments contain high amounts of calcite. All elements, except CaO, show compatible patterns with each other (Figure 12).

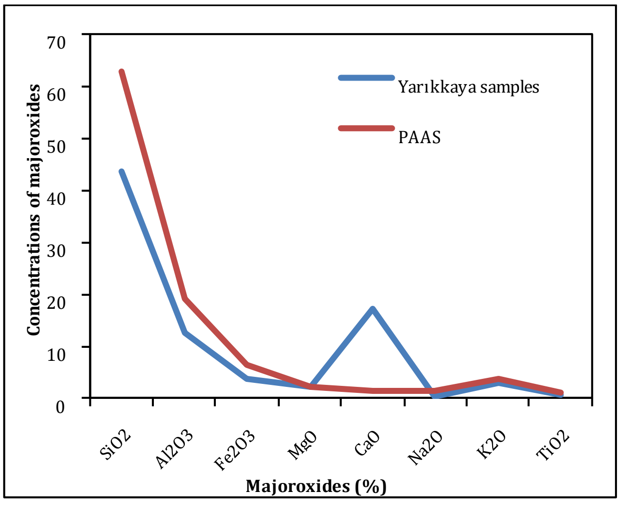

Figure 12. Major-oxide elements comparison of Yarıkkaya samples and Post Arcean Australian Shales (PAAS).

The trace element concentrations of the investigated samples are given in Table 2. Yarıkkaya 1 clay samples have 252-273 ppm Ba, 133,7-240,2 ppm Ni, 17,6-20,8 ppm Co values. Cs, Ga Hf contents of clay samples in this location are 5,1-7,4 ppm, 10,4-12 ppm, 2,6-3,1 ppm, respectively. At the same location, Rb contents ranged from 67,1 to 70,8 ppm. Sr values in the Yarıkkaya 1 quarry varied from 219,6 to 291,1 ppm. In this location clay samples, V and Zr ranged from 85 to 102 ppm, 93,1 to 116,4 ppm, respectively (Table 2).

In the Yarikkaya-2 quarry, one clay sample contains 257 ppm Ba, 145,1 ppm Ni, 19,8 ppm Co, 3,9 ppm Cs, 8,5 ppm Ga, 3,2 ppm Hf, 10 ppm Nb, 53 ppm Rb, 234,9 ppm Sr, 7,2 ppm Th, 2 ppm U, 67 ppm V. Zr, Y, Cu, Pb, and Zn in one clay sample in the same quarry have values of 123,8 ppm, 18,2 ppm, 20 ppm, 9,4 ppm, 34 ppm, respectively (Table 2).

Ba has a wide range of values between 333-737 ppm in Yarikkaya-3 quarry. At the same location, Sr displays values between 26,5-112,8 ppm. The Ni and Co contents of the clay samples in this location are 7,5-34,4 ppm and 3,9-9,2 ppm, respectively. The clays in Yarıkkaya-3 location contain 9,3-11,7 ppm Cs, 16,9-32,5 ppm Ga, 5,6-12,4 ppm Hf, and 20,5-26,1 ppm Nb. Clays at this location include 137,7-215 ppm Rb, 17,2-22,2 ppm Th, 3-3,9 ppm U, and 94-150 ppm V. Zr, Y, Sc, Cu, Pb, and Zn values in the Yarıkkaya-3 clay samples ranged from 213,8 to 477 ppm, 27,4 to 86,2 ppm, 11 to 21 ppm, 3,7 to 30,8 ppm, 4,5-15,9, and 11-63 ppm, respectively (Table 2).

Ba values are higher in the Yarıkkaya-3 quarry samples than the other two sites. Sr has very high values in clay samples from Yarıkkaya 1 and 2 localities compared to Yarıkkaya 3 quarry. Zr shows very high values in the Yarıkkaya-3 quarry compared to those of clay samples in the other two sites. According to those of samples in the other two locations, clay samples in the Yarıkkaya-3 location are more than twice for Nb and Th, and three times for Rb. Ni and Co contents have similar values in Yarıkkaya 1 and 2 quarries clay samples. Yarıkkaya 3 clay samples have very low Ni values. Th values have similar values in clay samples in Yarıkkaya 1 and 2 sites. The concentrations of Cs, Hf, U, and Y are slightly higher in Yarıkkaya-3 than in other sites. The vanadium contents of the samples in all three clay sites also differ (Table 2).

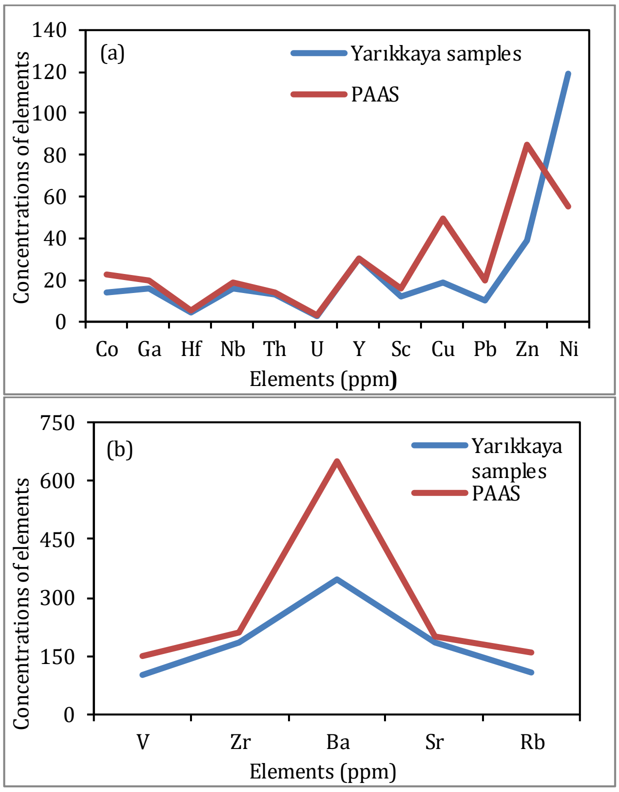

Figure 13. a, b. Trace element comparison of Yarıkkaya samples and Post Archean Australian Shales (PAAS).

In summary, when the clay samples in three fields are evaluated for trace elements they generally show similar values to the trace elements of the clay samples from Yarikkaya 1 and 2 locations. However, the trace element contents of the clay samples from the Yarıkkaya 3 location generally provide different values from the trace element contents of the clay samples from the Yarıkkaya 1 and 2 quarries.

In Figure 10.g, Rb displays strong positive correlation with K_2O showing a similar geochemical behavior, K_2O and Rb are probably supplied by detrital components in samples [9]. There is also positive correlation between Zr/Sc and Th/Sc ratios (Figure 10.h).

In Figure 13, trace elements were compared in Yarıkkaya samples and Post Archean Australian Shale (PAAS; data from [8]). Cu, Ba, Pb, Zn, Co, Zr, Ga, Rb, and V values in Yarıkkaya clay samples are considerably lower than those of PAAS. Hf, Nb, Sr, Th, U, Y, and Sc contents of Yarıkkaya samples and PAAS are approximately in similar amounts. Ni concentrations in Yarıkkaya clay samples have higher values compared to those of PAAS. High values of nickel were probably caused by ophiolites in the near field. All elements except Ni display compatible patterns (Figure 13.a, b).

3.4. Usage properties of the clays

The SiO_2, Al_2O_3, Fe_2O_3, CaO, and K_2O values of the investigated clay samples were correlated with the standard values which are usage as brick-tile raw materials and the major oxide contents of other sub-coal clay deposits in our country (Table 3).

As shown in Table 3, only Fe_2O_3 and K_2O values of clay samples in Yarıkkaya 1 and 2 locations are suitable as raw materials for the ceramic industry and brick-tile. Besides, in the Yarıkkaya-3 field, it is seen that other major oxide contents of clay samples except for potassium oxide values can be used as a ceramic industry and brick-tile raw material. In other words, the potassium oxide values of clay samples in Yarıkkaya-3 quarry are higher than those of clay to be used for ceramic and brick raw materials.

Table 3. Comparison of major-oxide values (%) of Yarıkkaya clay samples with those of some sub-coal clay areas and brick-tile material standard values

Deposit Location		SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Literature
Şile, Kilyos (İstanbul)		57,0-65,0	25,0-28,0	1,8-2,2	0,3	2,2	[10]
Söğüt (Bilecik)		56,0-67,0	15,0-26,0	1,0-5,5	0,1-1,5	0,1-2,5	
Ukraina		56,05	29,76	0,88			[11]
Ilgın (Konya)		63,46	19,41	2,86			[1]
Tavşanlı (Kütahya)		39,74-69,42	9,72-29,61	2,70-10,57	0,21-9,63	0,31-2,70	[12]
Seyitömer (Kütahya)		44,62-63,11	15,84-24,86	1,69-9,25	0,59-5,75	0,40-3,43	[12]
Malkara (Tekirdağ)		45,90-53,62	14,74-16,52	5,22-8,67			[13]
Yarıkkaya (Yalvaç)	1 Quarry	32,43	9,04	4,39	23,20	1,41	
	2 Quarry	31,92	7,36	3,55	25,87	1,18	
	3 Quarry	62,32	19,67	2,99	1,05	5,54	
Brick-Tile Standard		42-64	15-20	2,80-7,00	0,70-9,50	0,60-1,70	[11]

The studied clay samples are geochemically compared to some sub-coal clay occurrences in Turkey. As a result of this comparison, the major oxide concentrations of clay samples in Yarıkkaya-1 and Yarıkkaya-2 locations are not compatible with both standard values and values of some clay fields for industry use. The values of samples in only Yarıkkaya-3 quarry clays, excluding potassium oxide values, resemble Ilgın and Söğüt clay formations (Table 3).

3.5. Yarıkkaya Clay Formation

There are various opinions about the formation of sub-coal clays which are the product of a swamp environment. According to an idea, these clays are formed by the precipitation of the ashes of a fire in the coal forming forest. However, this idea does not explain the fact that the sub-coal clays have a very wide horizontal spread. According to the other idea, clays are fossil leaves. The layer seen just below the lignite veins is a vegetative soil produced by the coal vein forming forests. These soils are covered with peat formed by rotting plants. Covering them with top sediments, bottom clays are formed by diagenesis and partially altered during carbonization [14]. According to [15], the sub-coal clay layers are formed by the transformation of jelly-like clays resulting from the alteration of the deposited rocks.

Many researchers have emphasized that the sub-coal clays have a volcanic character. According to this idea, the rocks, which occurred as a result of volcanic activities undergo alteration, and deposit on stagnant waters to form sub-coal clays. According to [16], kaolinitic soils formed in swamps with the effect of acidic waters are more easily occurred than those formed on land. Based on this idea, occasionally, kaolinitic rocks occur on the shores of swamps which are inundated. The rocks dry out completely by surfacing with their movements in the basin. They have transported away after the destruction of the vegetation and formed sub-coal clays by sedimentation. In the opinion of [17], although the covered pyroclastic materials are rare, sub-coal clays have an in-situ formation in a lacustrine environment under a deep layer of water, which are precipitated from after being subjected to an insignificant move and clays have a volcanic origin.

Volcanic tuffs horizontally kaolinized in the Carboniferous of Scotland and passed into sub-coal clays [18]. He reported that a kaolinitic material is formed by intense alterations of granitic rocks and covers large areas [19]. This material is deposited in a lake basin where carbonization occurs. This view can explain the wide horizontal extension of sub-coal clays, their fine grains, the smoothness of layers in which they occur and that they are always found with coal veins.

According to another view, decomposed and eroded material in the environment is transported to closed swamp basins by floods. Since they are transported at a very slow speed, the coarse-grained material remains around the basin. The relatively coarse grains of the material reaching the swamp are kept at the edges by the swamp plants and only colloid materials reach the basin. These materials, which reach into the basin, are altered by the circulation of the water during the sedimentation with CO_2 or organic acid waters or partly after the deposition. It is covered with a peat layer formed by swamp plants. They are compressed by other cover deposits and formed peat layer coal and clays in sediments. Although these are called bottom clays, clays of similar characteristics are also found in the top of coal layers [14].

At bottom of the Late Miocene aged three lignite coal levels in the Şile region, sub-coal clays were investigated [20]. They stressed that these clays are derived from Late Cretaceous calc-alkaline volcanic rocks (andesite). It was determined that the sub - coal clays were transported to the Miocene basin by primary decomposition processes of these volcanic rocks and after the transfer and storage, they underwent a second alteration in the swamp environment (organic system).

The composition of clay deposits is primarily controlled by the composition of the source rocks [21]. Provenance studies of clastic sedimentary rocks often reveal the composition and geological evolution of the sediment source areas and limit the tectonic setting of the depositional basin [22].

Al_2O_3/TiO_2 ratios of most sediments exhibit the average composition of the source area. Al_2O_3/TiO_2 ratios generally rise with increasing SiO_2 content. According to [23], the ratios range from 3 to 11 for mafic rocks, 11-21 for intermediate rocks and 21-70 for felsic rocks. The average Al_2O_3/TiO_2 ratios in Yarıkkaya clay samples show intermediate source rock for these samples.

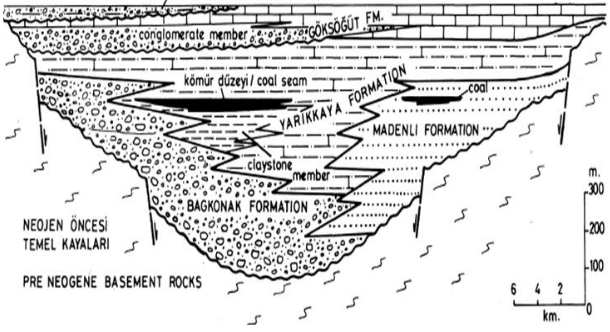

Figure 14. Lateral stratigraphic relations of Neogene rock units in the Yarıkkaya basin [5].

The Yarıkkaya clays associated with the coal deposits contain the clastics caused by the decomposition of lithologies of the Seydişehir formation in the basement stratigraphically, depending on their mineral composition and major-oxide contents. They probably occurred in relation to lacustrine sediments in the Yarıkkaya basin (Figure 14).

4. Conclusion

The Yarıkkaya clay deposits are outcropped in three locations where the coal mines are located in the Yarıkkaya Neogene basin. The investigated claystone member is found within the Miocene Yarıkkaya formation. The clay deposits are generally at the bottom of coal and sometimes at the upper parts of the lignite coal levels, or laterally transitive with clays. These clays are gray, dark gray and khaki. The thicknesses of the clays generally vary between 5-15 m and reach maximum 40 m thickness in the Yarıkkaya-3 coal mine field.

The clays in the study area contain mainly illite, kaolinite and chlorite, and less smectite. From the three clay locations in the field, only the Yarıkkaya-3 quarry clay samples are suitable for use as ceramic and brick-tile raw materials, based on the main oxide contents (56,38-67,01% SiO_2, 14,1-25,24% Al_2O_3 and 2,87-7,75% K_2O). In addition, Yarikkaya-3 quarry is rich in potassium clays.

According to SiO_2/Al_2O_3 vs. Fe_2O_3/K_2O ratios, Yarıkkaya clay samples are mainly defined as shale, less greywacke and quartz arenite.

According to the average Al_2O_3/TiO_2 ratios, Yarıkkaya clay samples show intermediate source rock.

Cu, Ba, Pb, Zn, Co, Zr, Ga, Rb, V are considerably lower, only Ni are higher contents of with respect to PAAS.

Yarıkkaya clays related to coal deposits contain the clastics resulting from the decomposition of lithologies of Seydişehir formation stratigraphically at the base according to their mineral composition and major-oxide contents. Then, the clastics from decomposited were transported to Yarıkkaya lake basin and the investigated clay deposits have probably occurred in association with lacustrine sediments.

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References

[1] Kuşcu, M., Yıldırımlar, Ş., 2016. Investigation of geological and economical properties of clays under llgın coal deposit. Afyon Kocatepe University Journal of Science and Engineering 16, 368-383.

[2] Brindley, G.W., Brown, G., 1980. Crystal structure of clay minerals and their X–ray identification. Mineralogical Society Monograph No. 5, Mineralogical Society, London, 485 p.

[3] Poisson, A., Akay, E., Dumont, J.F., Uysal, S., 1984. The Isparta Angle: a Mesozoic paleorift in the Western Taurides. In: Ö. Tekeli and C. Göncüoğlu (Editors), Geology of the Taurus belt, Institute of Mineral Research and Exploration, Ankara, 11-26.

[4] Yağmurlu, F., 1991b. Yalvaç-Yarıkkaya Neojen havzasının tektono-sedimanter özellikleri ve yapısal evrimi. Bulletin of the Mineral Research and Exploration 112, 1-12.

[5] Yağmurlu, F., 1991a. Stratigraphy and depositional environments of Yalvaç-Yarıkkaya Neogene basin, SW-Anatolia. Geological Bulletin of Turkey 34, 9-19.

[6] Uzun, A.S., Bekiyev, M., Cengiz, O., 2019. Yarıkkaya (Yalvaç - Isparta) çevresindeki kil oluşumlarının jeolojik ve ekonomik özelliklerinin araştırılması. TÜBİTAK-2209-A Üniversite Öğrencileri Yurtiçi Araştırma Projeleri Destek Programı, 70 p.

[7] Herron, M.M, 1988. Geochemical classification of terrigenous sands and shales from core or log data. Journal of Sedimentary Research 58 (5), 820-829.

[8] Taylor, S.R., McLennan, S.M., 1985. The continental crust: Its composition and evolution. Blackwell, Oxford, 312 p.

[9] Plank, T., Langmuir, C.H., 1998. The chemical composition of subducting sediment and its consequences for the crust and mantle. Chemical Geology 145 (3-4), 325-394.

[10] DPT, 1995. Seramik – Refrakter - Cam Hammaddeleri. D.P.T., VII. Five-Yearly Development Plan, Special Expertise Commission Report, 2418 ÖİK, Ankara, 477 p.

[11] Sazcı, H., 2001. Seramikte kullanılan killerin tanımı. 4. Industrial Raw Materials Symposium, İzmir, 28-42.

[12] Türkmenoğlu, A. G., Işık-Yavuz, N., 2008. Mineralogy, chemistry and potential utilization of clays from coal deposits in the Kütahya

province, Western Turkey. Applied Clay Science 42, 63-73.

[13] Özbay, O., 2014. Malkara (Tekirdağ) yöresindeki kömüraltı killerinin mineralojik - jeokimyasal incelemesi. Master Thesis, Balıkesir University Institute of Science 99 p.

[14] Gök, S., 1985. Kil mineralleri ve killerin jeolojisi. Institute of Mineral Research and Exploration Department of Industrial Raw Materials, 43 p.

[15] Hoehne, K., 1954. Zur Ausbildung und Genese der Kohlentonsteine im Ruhrkarbon. Chemie der Erde, 17 (1), 6-28.

[16] Erhart, H., 1956. La genèse des sols en tant que phénomène géologique, Paris: Masson et Compagnie, 90 p.

[17] Lombard, A., 1956. Géologie sédimentaire – Les séries marines, Paris: Masson et Compagnie, 722 p.

[18] Francis, W., 1961. Coal: Its formation and composition. 2nd Edition. Edward Arnold Ltd. London, 806 p.

[19] Nakoman, E., 1971. Coal. Institute of Mineral Research and Exploration, Education Series No. 8, Ankara.

[20] Çoban, F., Ece, Ö.I., Yavuz., O., Özdamar, Ş., 2002. Petrogenesis of volcanic rocks and clay mineralogy and genesis of underclays, Şile Region, İstanbul, Turkey. Neues Jahrbuch für Mineralogie-Abhandlungen: Journal of Mineralogy and Geochemistry 178 (1), 1-25.

[21] Armstrong-Altrin, J.S., Nagarajan, R., Madhavaraju, J., Rosalez-Hoz, L., Yong, L., Balaram, V., Cruz-Martınez, A., Avila-Ramırez, G., 2013. Geochemistry of the Jurassic and Upper source area weathering, provenance, and tectonic setting. C.R. Geoscience 345, 185-202.

[22] Zaid, S.M., Gahtani, F.A., 2015. Provenance, diagenesis, tectonic setting and geochemistry of Hawkesbury sandstone (Middle Triassic), southern Sydney Basin, Australia. Turkish Journal of Earth Science 24, 72-98.

[23] Hayashi, K.I., Fujisawa, H., Holland, H.D., Ohmoto, H., 1997. Geochemistry of 1.9 Ga sedimentary rocks from northeastern Labrador, Canada. Geochim Cosmochim Acta 61, 4115-4137.