Full Length Research Paper

Spectral characterization of non-clay minerals found in the clays (Central Anatolian-Turkey)

Burhan Davarcioglu

Department of Physics, Faculty of Arts and Sciences, Aksaray University, Aksaray, Turkey.
E-mail: burdavog@hotmail.com. Tel: +90 382 2801237. Fax: +90 382 2801246.

Clays contain varying amounts of co-occurring non-clay minerals and lesser amounts of organic materials. Characterization of the clays in the Central Anatolian region (Turkey) was carried out using the spectroscopic techniques and results were qualitatively interpreted in terms of non-clay minerals found in the clays. The DTA-TGA measurements have been carried out for determinations of thermal behaviour of the clay samples. The FTIR spectra of clays known as standard clays such as illite, illite-smectite mixed layer, montmorillonite, Ca-montmorillonite, Na-montmorillonite, kaolinite, chlorite (ripidolite), palygorskite were first taken, and then the spectra of anhydrite, gypsum, illite+quartz+feldspar, quartz+feldspar were taken together with the standard clays. The minerals present in the samples were identified by comparing their FTIR spectra with those of the standard clay minerals and XRD results. Silica polymorphs, quartz being the most abundant, zeolites, feldspars, calcite, dolomite, and magnesite are the most common non-clay occurring in association with the clays. It is observed that bentonites are more frequently associated with silica, zeolites, feldspars, calcite, and dolomite, while kaolinites are often accompanied by silica, calcite and alunite. However, magnesite, dolomite and calcite co-occur commonly with sepiolite and palygorskite.

Key words: Non-clay minerals, FTIR, XRD, carbonates, zeolites, feldspars.

INTRODUCTION

Through understanding and correct interpretation of geological structures and soils covering the earth crust and their possible relations with the materials underlying them requires reliable quantitative and qualitative analyzing methods. Study of the clay minerals present in soils with varying quantities and types depending on the geological environment and discussion of the relations between the layer covering the surface of earth crust and the underlying layers have been utterly important. Clay is a general name for an important mineral group which is used for the production of great number products, encompasses every part of daily life, such as from soil to ceramics and from fine arts to advanced technological industry (Adams, 1987). Physical and chemical properties of the clays make them right material for different purposes in different fields (Murray, 1999). The past few decades have seen increasing use of clays in a wide range of fields such as production from paper industry to ceramics, bleaching of the vegetable oils, beer, wine and fruit juices, cleaning of the radioactive wastes and waste waters, and production of drugs, parfumes, soaps,

detergents, rubbers and plastics (Adams, 1987; Murray, 1991; Breen et al., 1997; Falaras et al., 2000).

Clays frequently contain varying amounts of non-clay minerals and lesser amounts of organic materials (Grim, 1968; Grim, 1988). In general, while more comprehensive investigations are available for the clays due to their obvious economic significance, associated non-clays are often overlooked (Grim and Guven, 1978; Murray et al., 1993; Murray, 1991; Murray, 1999). Whereas extent and quality of non-clay content of the clay minerals deteriorate their market value and quality. Clays with high purity rarely occur in the nature. High purity is achieved through various processes. However non-clay minerals often hamper the process. Therefore, certain similarities and differences in physico-chemical characteristics of both clays and non-clays should be well established.

Clay mineral characterization could be carried out employing spectroscopic methods for various purposes in the geological sciences (Heroux et al., 1979). In the literature, there is a voluminous research on determination of clay mineral chemistry using diverse

techniques. Today, one of the most preferred methods is the FTIR (Fourier Transform Infrared) Spectroscopy. There is a significant increase in number of studies using this method dealing with the clay characterization in Turkey (Akyuz and Akyuz, 2003; Davarcioglu et al., 2005; Davarcioglu and Kayali, 2007; Davarcioglu et al., 2007; Davarcioglu and Ciftci, 2009). One of such studies is on the quantitative and qualitative characterization of Central Anatolian clay deposits and diatomites by employing the spectroscopic methods (Kayali et al., 2005; Davarcioglu et al., 2008; Davarcioglu, 2009).

Clays, as one of the principle raw materials occurring in large deposits in Turkey, should be characterized well to improve their market value. Thus, considering the contribution to the industry, such characterization is significantly imperative. In this study, it is our objective to study clay samples acquired from various localities throughout the Central Anatolian using spectral techniques to determine non-clay components and if there is any characteristic association.

Non-clay minerals

Feldspars

A group name of silicate minerals. Feldspar minerals including albite, anorthite and orthoclase or mixture of these were found within the clays (Norton, 1974). These are feldspars with different chemical and crystallographic structures. Thus, they could easily be distinguished using characteristic FTIR and XRD (X-ray powder diffraction) spectra. In addition, they can be removed from the mixture easier than the zeolites due to their fairly larger sizes.

Carbonates

While bentonite and kaolin deposits often include calcite and sepiolite impurities, palygorskite contains dolomite and magnesite. Presence of numerous carbonates with diverse chemistry and mineralogy in the clays has been reported (Reeder, 1983). These can easly be resolved using their FTIR and XRD spectra. Carbonates can also be removed from clay suspensions buffered at pH 5 using acetic acid or sodium acetate by adding 0.1 N HCl droplet-wise to the mixture. This can also be achieved by straight heating the buffered solution without using dilute HCl solution (Jackson, 1969).

Zeolites

Zeolites occur in nature and have been known for almost 250 years as aluminosilicate minerals. Examples are faujasite, mordenite, natrolite, ferrierite, erionite and chabazite. Today, these and other zeolite structures are of great interest in catalysis, yet their naturally occurring forms are of limited value, because (i) they almost always contain undesired impurity phases, (ii) their chemical composition varies from one deposit to another and even from one stratum to another in the same deposit, and (iii) nature did not optimize their properties for catalytic applications.

The elementary building units of zeolites are SiO_4 and AlO_4 tetrahedra. Adjacent tetrahedra are linked at their corners via a common oxygen atom, and these results in an inorganic macromolecule with a structurally distinct three dimensional framework. It is evident from this building principle that the net formulae of the tetrahedra are SiO_2 and AlO_2, one negative charge resides at each tetrahedron in the framework which has aluminum in its center. The framework of a zeolite contains channels, channel intersections and/or cages with dimensions from 0.2 to 1 nm. Inside these voids are water molecules and small cations which compensate the negative framework charge.

Zeolites are hydrated alkaline- or alkaline earth-aluminum silicates and like the clay minerals they have high cation exchange capacity (CEC) (Breck, 1974; Barrer, 1978; Sakizci and Yorukoğulları, 2005). While clays are formed of silicon tetrahedrons and aluminum octahedrons (T-O or T-O-T), silicon and aluminum occur as tetrahedrons in the zeolite structures. While the building units in the clays occur as layers or fibers, they occur as three dimensional frameworks. Zeolites such as clinoptilolite, heulandite, and analcime occurring in association with the clays can be easily determined in their FTIR and XRD spectra of the clays due that they have different crystal structures. Zeolites behave more refractor to the heat treatments comparing with the clays. When they occur in clay size, removing them from the clays is not an easy task.

Sulfates, sulfides and phosphates

While gypsum occurs more frequently within bentonites, alunite is generally found in kaolinite. Sulfates, sulfides and phosphates occurring in the clays can be specified by utilizing their FTIR and XRD spectra. When gypsum is heated to 60°C, a new mineral called bassanite $CaSO_4 \cdot (1/2)H_2O$ emerges. Sulfur and iron-bearing non-clays are deleterious in the ceramic applications. Thus their presence and abundance is not desired in clays. Consequently, they should appropriately be characterized for their removal.

Hydroxides and oxides

Hydroxides and oxides are rarest minerals occurring in the clays. When heated, they yield oxides. While mineral
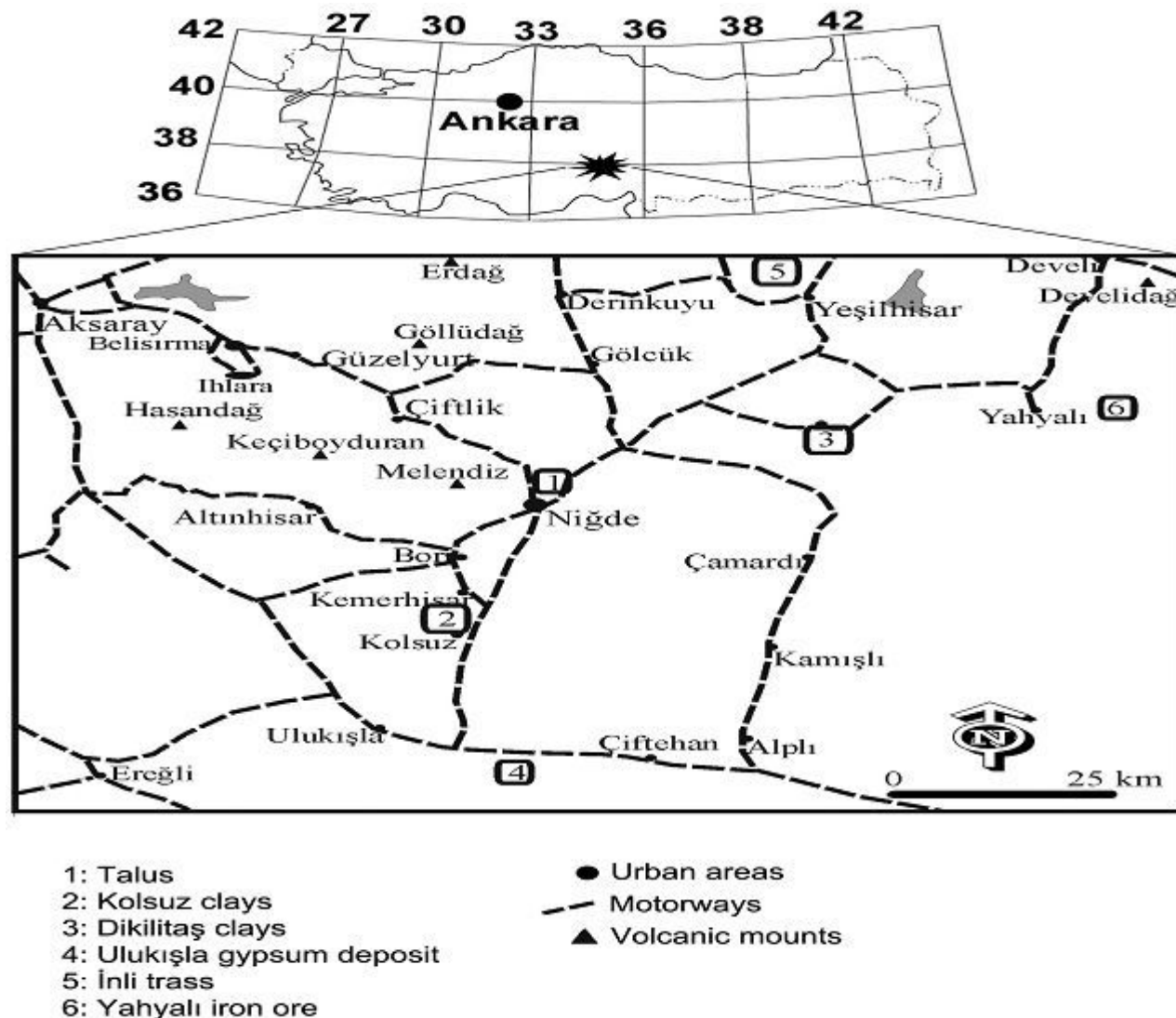
Figure 1. Generalized geological map of the study area and its near vicinity (adapted from Kayali et al., 2005).

chemistry remains the same, crystal structures are subjected to change depending on the temperature during this conversion. Particularly Al-oxide has a number of varieties with diverse physico-chemical characteristics (Gitzen, 1970).

MATERIALS AND METHODS

Characterization of selected clays in the Central Anatolian region (Turkey) including Kolsuz (Ulukisla-Nigde) (Davarcioglu and Ciftci, 2010), Dikilitas (Nigde) (Davarcioglu et al., 2005; Davarcioglu, 2010), Arapli (Yesilhisar-Kayseri) (Davarcioglu et al., 2008; Davarcioglu and Ciftci, 2009) and Guzelyurt (Aksaray) areas (Davarcioglu and Kayali, 2007; Davarcioglu and Ciftci, 2010) was carried out with respect to non-clay minerals found in association the clays. Localities of the profiles representing the constructed profiles chosen for this study and nearby area were shown in Figure 1. Samples were ground into powder. Powdered samples were then

alternately washed with pure water, ethyl alcohol, and ether. Subsequently, they were dried in an oven at 110°C for 24 h.

In general, the clay minerals contain significant amounts of water. Conversely, they contain less alkaline and alkaline earth elements. Absorption bands due to the water molecules occupy large spectral fields, the ones critical for identification of clay minerals. Thus in order to minimize this undesired overlap, samples for the FTIR measurements were prepared through clay concentration without employing a centrifuge. However for the chemical analyses, samples were analyzed as bulk samples without concentrating for clay fraction. Organic matter was removed through boiling in H_2O_2 and then samples were dried in an oven at 110°C for 24 h.

FTIR measurements

Samples collected from the clay sites were prepared applying the disc technique (mixing ~1 mg clay sample with 200 mg KBr) and put in molds. These intimate mixtures were then pressed at very high pressure (10 tons per cm^2) to obtain the transparent discs,

Table 1. Fundamental vibration frequencies of standard natural clays (I = illite, ISmML= illite-smectite mixed layer, Na-mont = Na-montmorillonite, C = chlorite, P = palygorskite).

Assignment	I	ISmML	Na-mont Wavenumber (cm^{-1})	C	P
ν(OH) stretching	-	3685 (shoulder)	-	-	-
Inner-layer OH, (Al-O...H) stretching	-	-	3680	-	-
ν(OH) stretching	-	-	-	3662	-
ν(OH) stretching	-	-	3627 (shoulder)	-	3627
ν(OH) stretching	3622	3622	3622	-	-
ν(OH) stretching	-	-	-	3565	3546
ν(OH) stretching	-	-	-	3434	-
δ(water-OH) stretching	-	-	-	-	3408, 3266
δ(water-OH) scissoring	-	-	-	-	1731
δ(water-OH) scissoring	-	-	-	-	1673, 1640
ν(Si-O) stretching	-	-	-	-	1163, 1114
ν(Si-O) normal to the plane stretching	1090	1090	-	-	-
ν(Si-O) planar stretching	1031	1031	-	-	-
ν(Si-O) stretching	-	-	-	-	1020
ν(Si-O) stretching	-	-	-	988	-
(Al-Al-OH) deformation	916	916	920	-	-
OH deformation	-	-	-	-	905
(Al-Fe-OH) deformation	-	-	890	-	-
(Al-Mg-OH) deformation	832	810	875	-	-
M-OH stretching	-	-	805	819	-
Si-O deformation	-	-	-	766	-
(Al-O-Si) inner surface vibration	756	-	-	-	-
(Al-O-Si) inner layer vibration	-	750	-	-	-
OH deformation	688, 622	622	620	667	-
(Si-O-Al) deformation	-	-	-	543	-
(O-Si-O) bending	525	525	520	-	528
(O-Si-O) bending	468	468	468	-	469
(Si-O-Mg) deformation	-	-	-	441	-
(O-Si-O) bending	-	-	-	-	426

Illite (Wilson, 1987), Illite-smectite mixed layer (Wilson, 1987), Na-montmorillonite (Farmer and Russell, 1964), Chlorite (Wilson, 1987), Palygorskite (Frost et al., 2001).

which were then placed in the sample compartment. Bruken Equinox 55 Fourier transform FTIR spectrophotometer (Department of Physics, METU, Ankara-Turkey) was used for the FTIR spectral measurements of these samples with standard natural clay and the spectra were recorded over the range of 5000-370 cm^{-1} (% transmission versus cm^{-1}). Before taking the spectra measurements of the samples, spectrophotometer was calibrated with polystryrenes and silicate oxide of thickness 0.05 nm.

The infrared spectra of the illite (IMt-1; Silver Hill, Montana, USA), illite-smectite mixed layer (ISMt-1; Mancos Shale, Ord.), montmorillonite (SCa-3; Otay, San Diego Country California, USA), Ca-montmorillonite (STx; Gonzales Country, Texas, USA), Na-montmorillonite (SWy^{-1}; Crook Country, Wyoming, USA), kaolinite (KGa^{-1}; Washington Country, Georgia, USA), chlorite (ripidolite, CCa^{-1}; Flagstaff Hill, El Dorato Country, California, USA), and palygorskite (PFI; Gadsden Country, Florida, USA) known as standard natural clays ("The World Source Clay Minerals") were taken (Table 1), and then the spectra of anhydrite, gypsum, illite+quartz+feldspar, quartz+feldspar have been taken together with the standard clays since those spectra were necessary for the

analyses of subject samples.

Along with XRD, the FTIR investigation in clay mineral speciation could be regarded as useful and multipurpose application since some physical details of clay lattices and experimental qualitative correlation between the samples were made possible. Besides, for the minerals that were observed with the both techniques, functional groups could only be determined through the FTIR spectra. Therefore, qualitative and quantitative speciation of the minerals by employing the FTIR spectroscopy is very important and promising.

Chemical and minerological analyses

The chemical analyses of the Central Anatolian clay samples (dried in an oven at 110 ºC) were carried out at the Acme Labs (Canada) by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) technique. Major oxide composition of the samples representing Kolsuz, Dikilitas, Arapli, and Guzelyurt of the Central Anatolia were given in Table 2. The data suggest that Kolsuz,

Table 2. Major oxide composition of the samples from the studied profile (%).

	Kolsuz (Ulukisla-Nigde)	Dikilitas (Nigde)	Arapli (Yesilhisar-Kayseri)	Aksaray (Guzelyurt)
SiO_2	48.57	64.45	55.69	68.63
TiO_2	0.76	0.59	0.82	0.47
Al_2O_3	13.97	11.80	16.72	18.64
Fe_2O_3	8.10	5.83	6.57	0.22
MnO	0.14	0.16	0.04	0.01
MgO	5.09	2.22	1.80	0.06
CaO	6.94	1.22	1.40	0.26
Na_2O	1.10	1.63	0.34	0.07
K_2O	2.64	1.45	1.85	0.44
Cr_2O_3	0.027	0.102	0.014	0.003
P_2O_5	0.15	0.04	0.04	0.15
LOI	12.51	10.50	14.70	13.04
Total	99.997	100.00	99.98	99.993
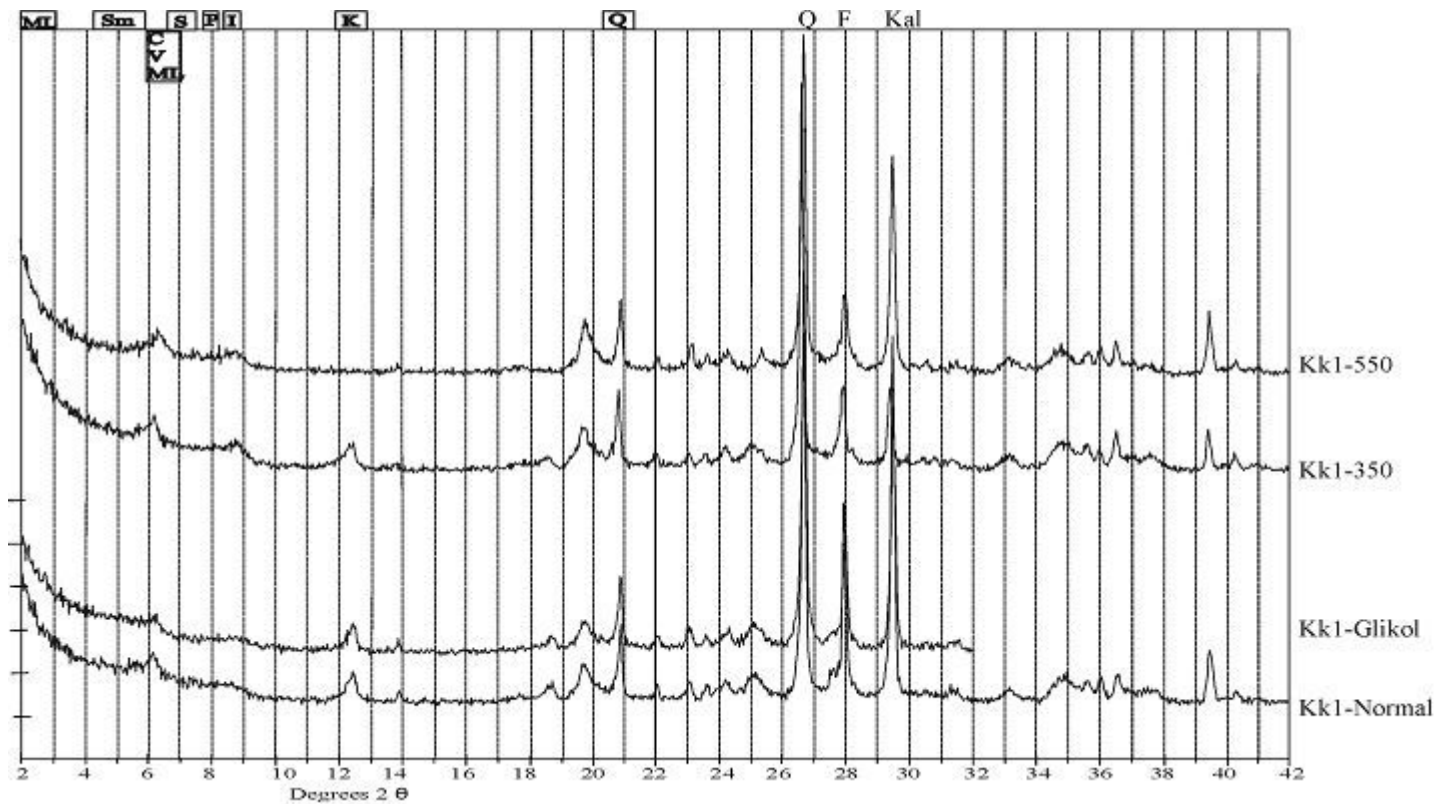
Figure 2. XRD spectrum of the Kolsuz clays (Ulukisla-Nigde) (Q = quartz, F = feldspar, I = illite, ML = mixed layer clay, C = chlorite, P = Palygorskite, S = smectite).

Dikilitas, and Arapli clays are essentially rich in SiO_2, Al_2O_3, and also CaO (Kolsuz clays only). Main cause of these enrichments was due to ascending briny and carbonated waters through capillary actions and precipitation due to transpiration in arid and semi-arid regions. Al^{3+} was the main cation of the octahedral sites.

The XRD measurements were employed to determine the mineral phases included in the same samples (Siemens D-5000 Diffract AT V 3.1 diffractometer, CuKα radiation λ=1.54056 A˚ and 0.03 steps; General Directorate of Mineral Research and Exploration laboratories-MTA, Ankara-Turkey). The XRD measurements are given in Figures 2 to 5, respectively.

The Kolsuz clays are found to be composed of abundant quartz (19.45%), feldspar, calcite, smectite (3.1%), illite (32.21%), chlorite (45.24%), and trace quantities of palygorskite and Fe-oxide
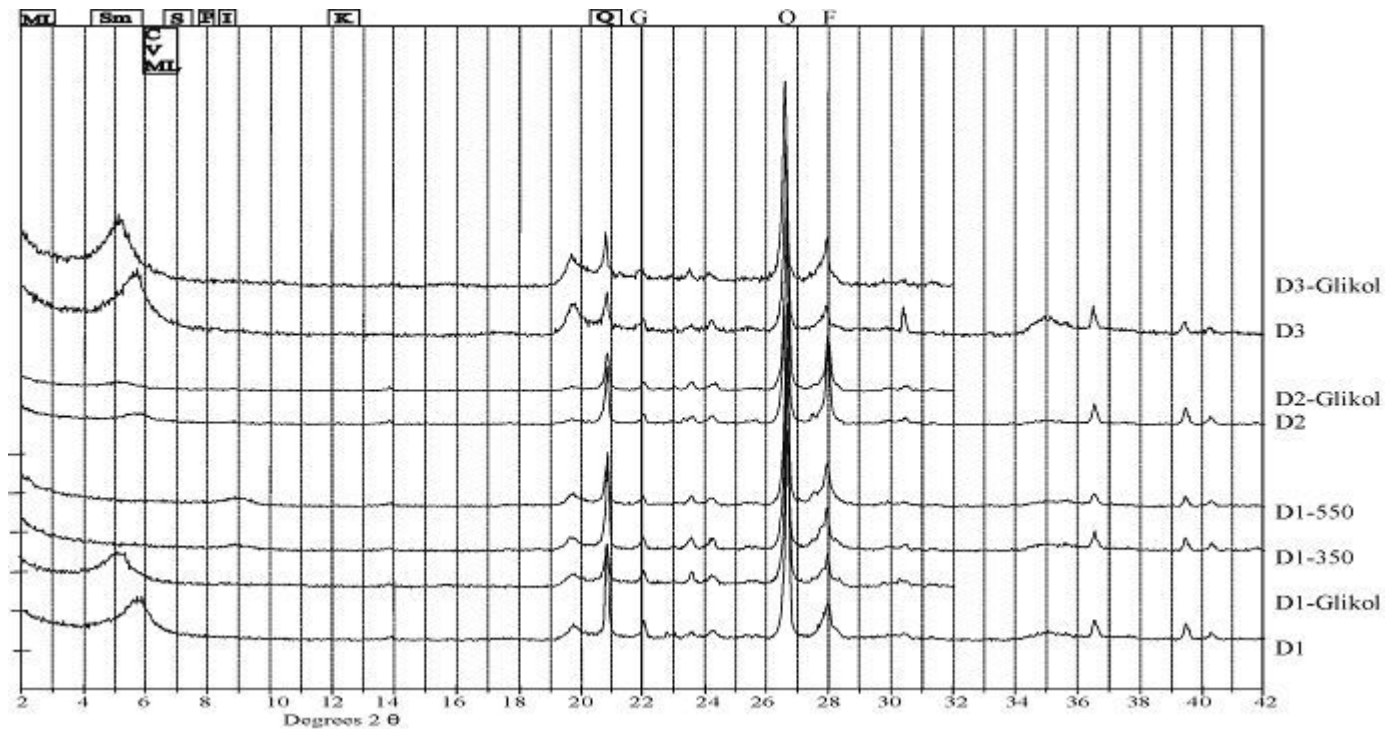
Figure 3. XRD spectrum of the Dikilitas clays (Nigde) (Q = quartz, F = feldspar, C = chlorite, S = smectite).
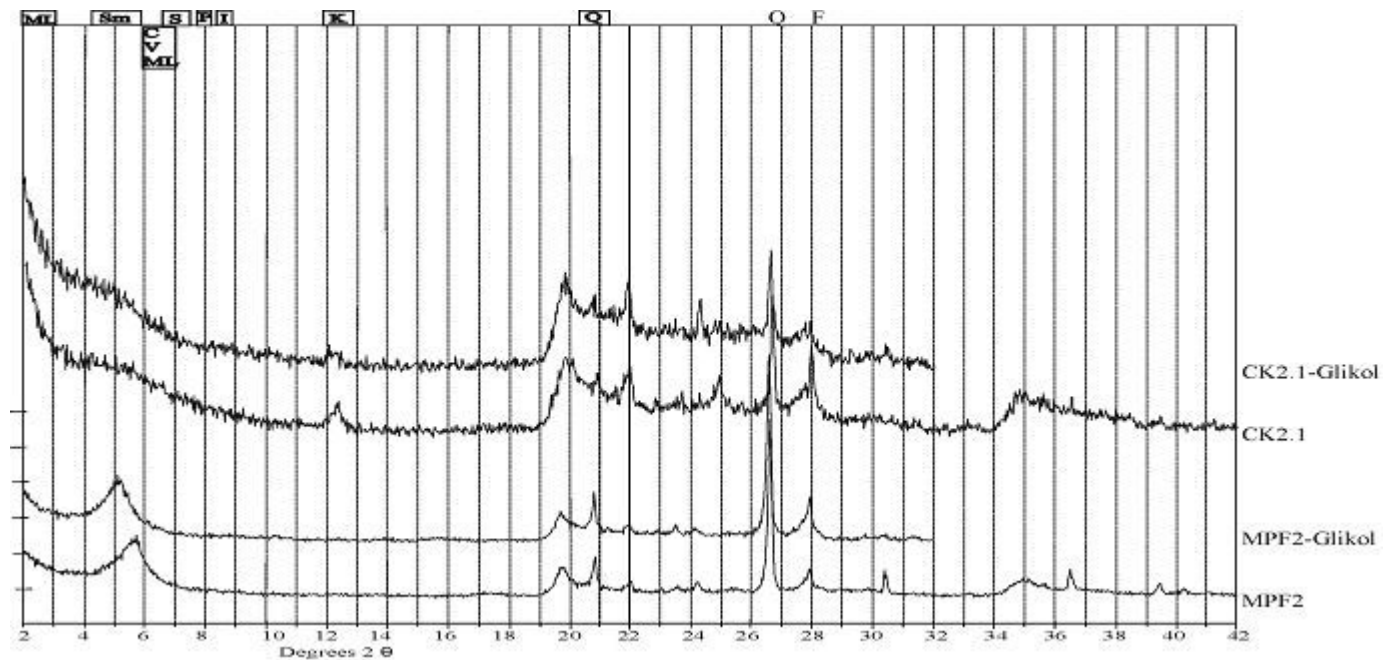

Figure 4. XRD spectrum of the Arapli clays (Yesilhisar-Kayseri) (Q = quartz, F = feldspar, I = illite, K = kaolinite, C = chlorite, S = smectite).

minerals. In the lower part, quartz tends to decrease while smectite, illite and chlorite show significant increase. Whereas in the top, just opposite of this abundance trend was observed and palygorskite was totally absent. In the study area, the Kolsuz clays are loosely
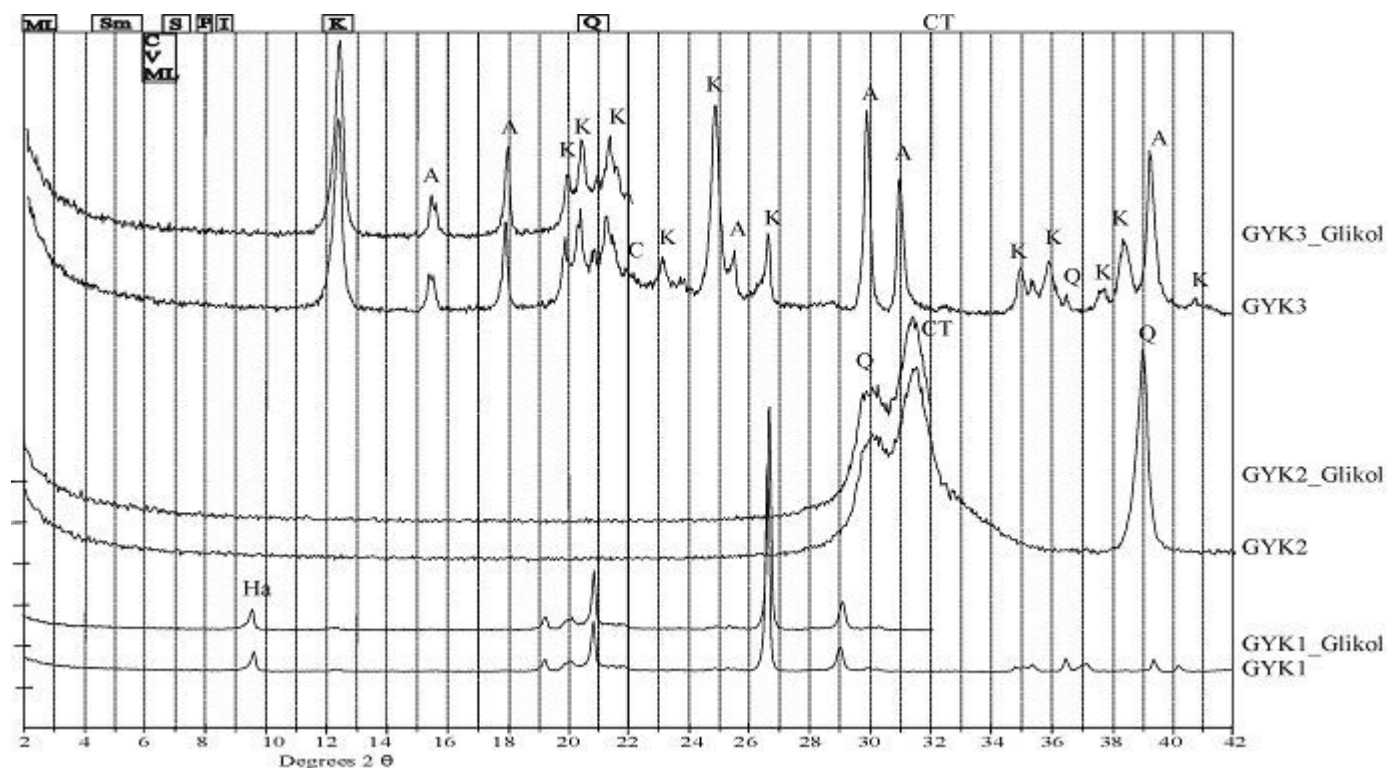
Figure 5. XRD spectrum of the Guzelyurt clays (Aksaray) (Q = quartz, I = illite, K = kaolinite, Ha = halloysite, CT = opal-CT, A = alunite).

cemented with calcite, silica and Fe-oxides. Gravels are of various origins including sandstone, greywacke, claystone, limestone, marl, volcanics, granodiorite, gabbro, quartzite, chert, and serpentinite (Kayali et al., 2005). Petrographic investigations on thin-sections for 12 samples from the Kolsuz area indicated prevalent presence of feldspars, quartz, calcite, lithic fragments of volcanic, magmatic and metamorphic rocks, of carbonates (example, limestone and marl) and clastic sedimentary rocks (example, sandstone, claystone and greywacke) cemented chiefly by calcium carbonate (Gurel, 1999; Kayali et al., 2005).

The Dikilitas clay samples are composed of quartz (25.26%) and smectite (74.74%). Clay, silt, sand and/or gravel are poorly cemented with finer clay and Fe-oxides.

The Arapli clays indicated common presence of quartz (34.64%), feldspar, smectite (63.62%), kaolinite (1.74%), and iron-oxide (<1%). Likewise, the Arapli clays are also poorly cemented with finer clay and Fe-oxides.

According to the XRD results (Figure 5), the Guzelyurt clay samples are composed of quartz (66.51%), illite (26.23%), kaolinite (7.26%), and trace opal-CT, biotite and iron oxides. In the clay profile, kaolinite content is very high at the base, and tends to decrease towards the top. Quartz content is always significant (57.60 to 68.63%).

DTA (Differential Thermal Analysis) and TGA (Thermogravimetric Analysis) measurements have been carried out for the determinations of the thermal behaviour of the clay samples (Figures 6 to 9, respectively). Measurement were carried out in the MTA Labs (Ankara-Turkey) using a Rigaku Thermal Analyzer Ver. 2.22EZ (SN#39421).

Here smectite peak falls in the same field with the one of chlorite (Figure 6). Minute endothermic peak of smectite occurs in between 100 to 250°C, and second endothermic peak appears at 700°C and shallow endothermic/exothermic peak is observed at 800 to 900°C.

Best observed endothermic peak of chlorite in the DTA-grams is the one observed between 500 to 600°C. This peak may shift toward 700°C due to the iron content. Subsequently this peak may fall in the same interval with smectite's peak at 700°C. Chlorite's exothermic peak occurs at 750°C.

As can be seen in Figures 7 and 8, thermal behaviors of two smectite-rich clay samples are shown. In Figure 7, two major endothermic peaks: one at 150°C (15% weight loss) and the other at 820°C (7.7% weight loss) were determined. The first major peak is generally resulted by loss of absorbed or interlayer waters and the second was due to the structural water. In the Figure 8, two major endothermic peaks, one at 141°C (9% weight loss) and the other at 531°C (4% weight loss) along with an exothermic peak (at 894°C) were determined. The clay minerals in the sample are subjected to the structural changes towards the end of the DTA-TGA which will be manifested by the exothermic peaks. It is because there is a minute amount of quartz that results in an overlap with the second endothermic peak representing smectite.

In the DTA-TGA graph (Figure 9) of the sample representing kaolinite-rich zone (lower level), endothermic peak at 521.2°C and an exothermic peak at 977.9°C were observed (Paterson and Swaffield, 1987). Presence of a minor peak at 64.1°C could be associated with disappearance of absorbed water (in crystal structure) and consequently about 11.3% weight loss was measured at 512.2°C (Brindley, 1978; Kok, 2006; Kok and Smykatz-Kloss, 2008).

RESULTS AND DISCUSSION

All clay and associated non-clay minerals in the subject samples were speciated. Silica polymorphs contained by the samples were attempted to be removed by employing
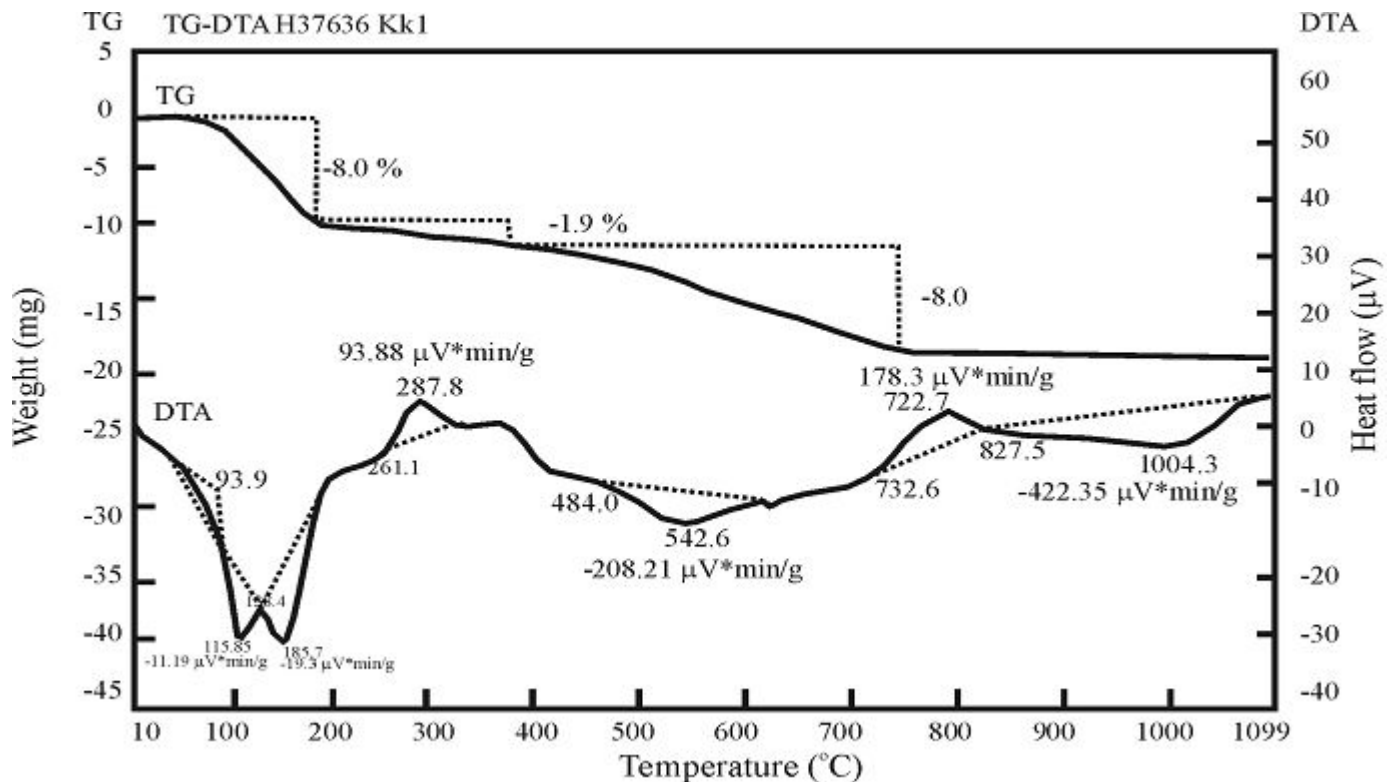
Figure 6. DTA-TGA measurements of the Kolsuz clays (Ulukisla-Nigde).
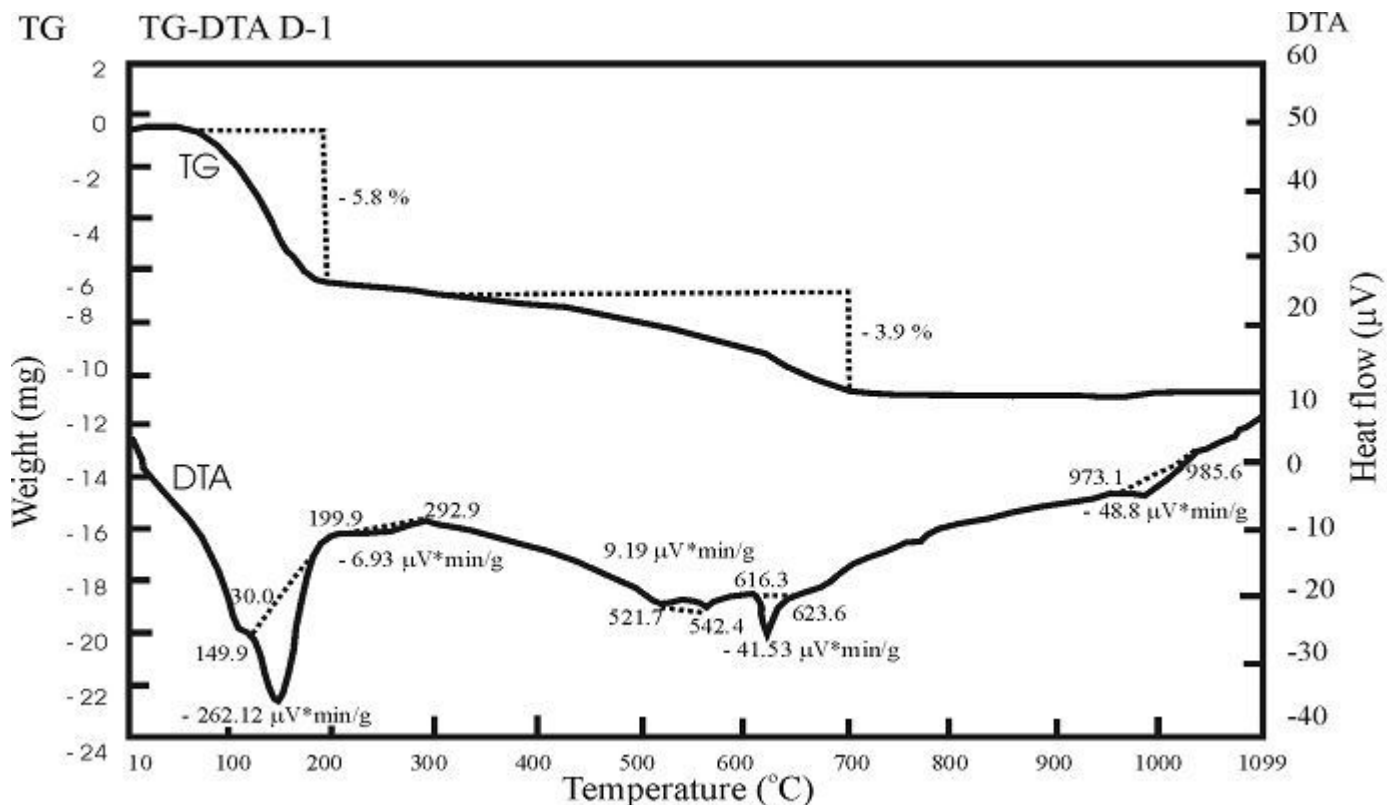

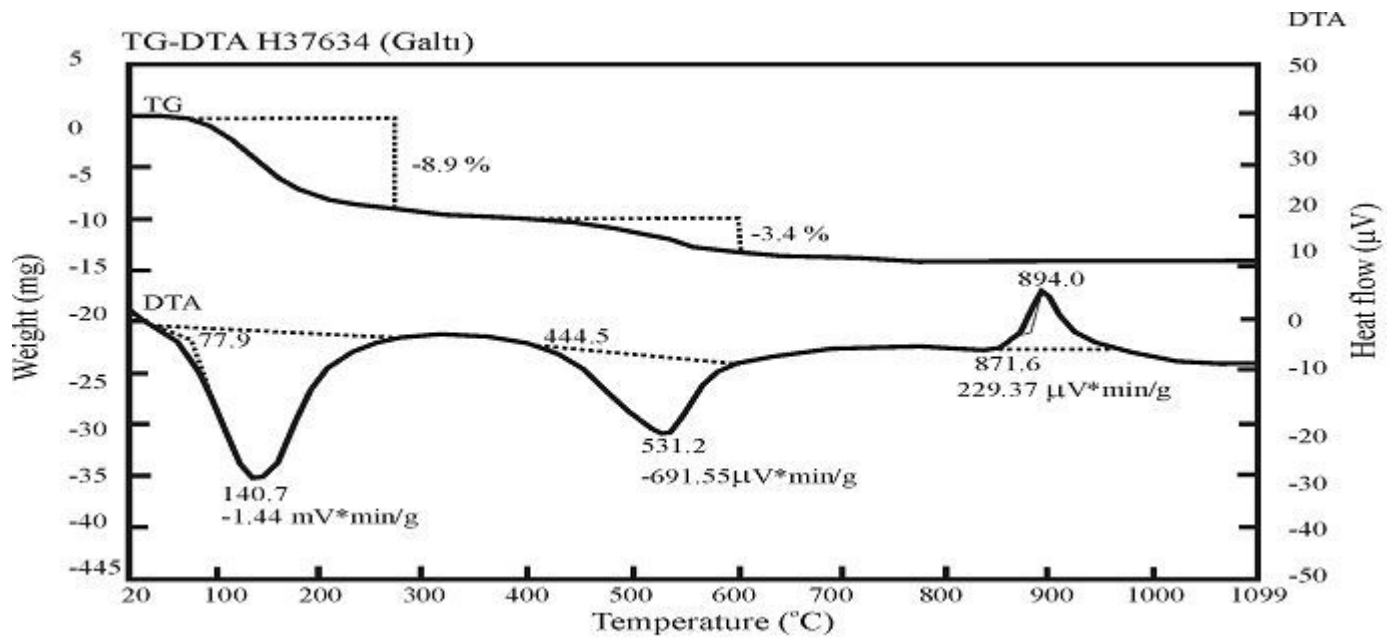**Figure 7.** DTA-TGA measurements of the Dikilitas clays.

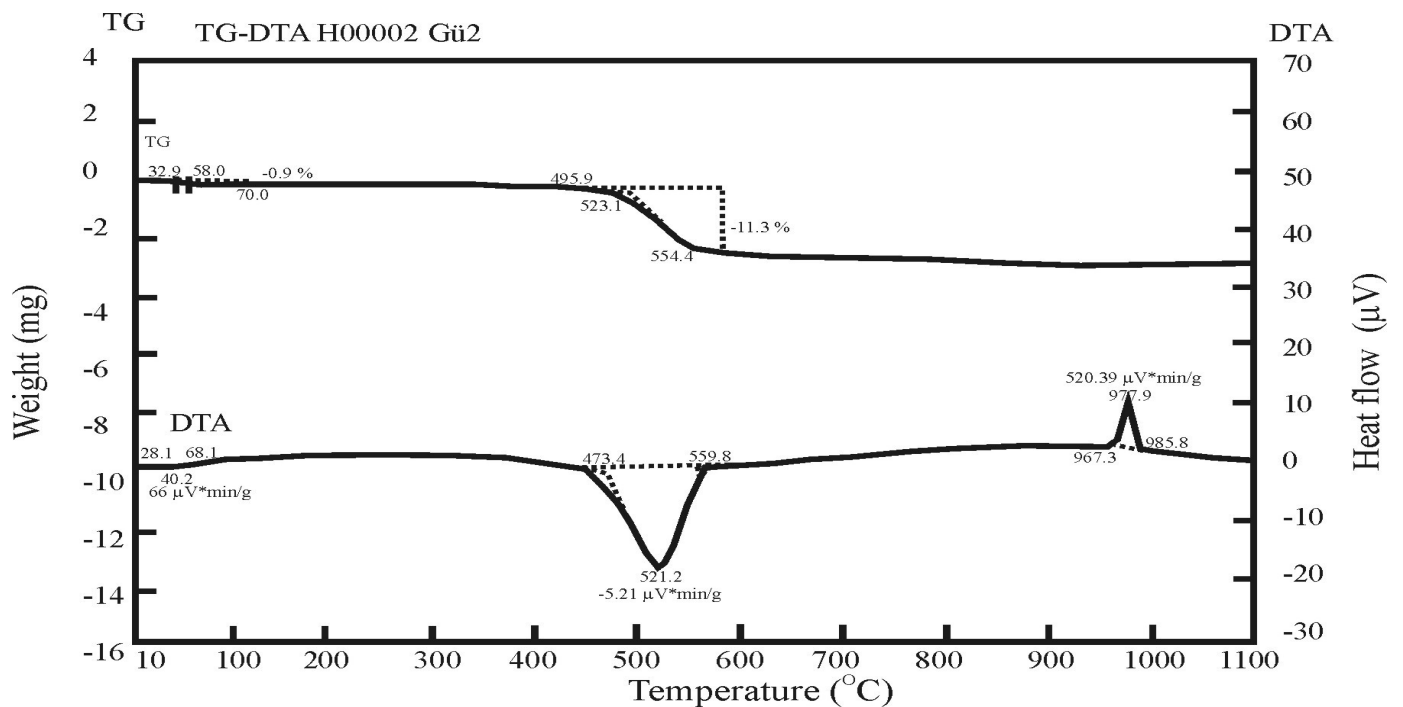**Figure 8.** DTA-TGA measurements of the Arapli clays.

Figure 9. DTA-TGA measurements of the Guzelyurt clays.

orthophosphoric acid fusion and thermal treatments (at 1050°C, for 24 h) (Sarikaya et al., 2000; Kahraman et al., 2005). Findings in combination with the literature were utilized to identify and to discuss non-clay minerals and their certain characteristics.

Only the clay mineral group's distribution of smectite, illite, kaolinite, chlorite and palygorskite were presented. The original XRD measurements of the clay sized fraction (< 2µm) contain much more information which might be useful in the determination of particular and distinct

Table 3. Some relevant basic information of feldspars, one of the common mineral occurring within clay samples as non-clay species (Sarikaya et al., 2000).

Feldspars	Formula	$2\theta^\circ$	d(hkl)/nm	100 I/I_o	t_{endo}/ C	t_{exo}/ C
Albite	$NaAlSi_3O_8$	27.95	0.319	-	-	-
Anorthite	$CaAl_2Si_2O_8$	26.75	0.333	-	-	-
Orthoclase	$KAlSi_3O_8$	26.75	0.331	-	-	-
Microcline	$KAlSi_3O_8$	27.5	0.326	-	-	-
Plagioclase	$NaAlSi_3O_8+CaAl_2Si_2O_8$	28	0.321	-	-	-

Table 4. Pertinent characteristics of non-clay minerals co-occurring with clays in the subject samples (Sarikaya et al., 2003; Kahraman et al., 2005).

Carbonates	Formula	$2\theta^\circ$	d(hkl)/nm	100 I/I_o	t_{endo}/ C	t_{exo}/ C
Calcite	$CaCO_3$	29.43	0.304	100	898	-
Aragonite	$CaCO_3$	26.249	0.34	100	965-970	-
Vaterite	$CaCO_3$	27.1	0.329	100	100	350
Magnesite	$MgCO_3$	32.75	0.274	100	625-643	-
Strontianite	$SrCO_3$	25.19	0.354	100	465, 860, 1250	-
Witherite	$BaCO_3$	23.9	0.372	100	830-840	-
Siderite	$FeCO_3$	32.02	0.28	100	540-555	571
Dolomite	$CaMg (CO_3)_2$	30.98	0.289	100	785, 990	-
Ankerite	$Ca(Fe,Mg)(CO_3)_2$	30.72	0.291	100	750, 820, 905	800

Table 5. Certain zeolite species occurring with clay minerals as non-clays and their significant properties (Sakizci and Yorukoguları, 2005).

Zeolites	Formula	$2\theta^\circ$	d(hkl)/nm	100 I/I_o	t_{endo}/ C	t_{exo}/ C
Clinoptilolite	$(Na,Ca)_{4-6}Al_6(Al,Si)_4$	22.3	0.398	61	120, 170	-
	$Si_{29}O_{72}.24H_2O$	22.7	0.391	63	-	-
Heulandite	$Na,Ca)_{4-6}Al_6(Al,Si)_4$	9.9	0.896	100	215	680
	$Si_{26}O_{72}.24H_2O$	17.4	0.510	70	-	-
Analcime	$NaAlSi_2O_6.2H_2O$	15.8	0.560	60	-	-
		26.0	0.343	100	376, 440	-

source regions. Here, data on the non-clay minerals in the clay fraction (quartz, feldspar, calcite, dolomite, and some heavy minerals) and the structural and chemical differences of the clay minerals will be presented. Non-clay minerals that were observed within the samples are listed in Tables 3 to 7. These were prepared by using our data in conjunction with the earlier findings reported in the literature (Bridnley and Brown, 1980; Smaykatz-Kloss, 1974).

Non clay minerals that were observed within the clay samples include feldspars, zeolites, sulfates, sulfides, phosphates, metal hydroxides, metal oxides, and silica polymorphs (quartz being the most abundant variety). In concentrating process of the clays, the most difficult task is separating identical sized non-clays. It is also observed that clays are not fast disseminated and precipitated

within the clay suspensions and it requires to be held for 24 h or more. Otherwise they are ideally concentrated due to the size effect of the non-clays. Removal of non-clays that are intimately associated and with similar densities with the clays is seldom accomplished. This can only be achieved if their distinctive chemical properties along with physical characteristics are taken into the consideration. For instance the carbonates can be removed by using an acetic acid/sodium acetate buffer solution with a pH 5 value which is heated while dilute hydrochloric acid is added in a controlled way (drop wise) until just before the bubbling initiates.

Non-clays may show subtle diversity depending on the prevalent clay types. It was observed that the bentonites are more frequently associated with silica, zeolites, feldspars, calcite, and dolomite, while kaolinites are often

Table 6. Sulfides, sulfates and phosphates observed within the samples as non-clay minerals and their relevant properties (Lagaly and Beneke, 1991).

Sulfates, Sulfids and Phosphates	Formula	$2\theta^{\circ}$	d(hkl)/nm	100 I/Io	t_{endo}/ C	t_{exo}/ C
Gypsum	$CaSO_4.2H_2O$	31.20	0.287	100	1225, 1385	-
Anhydrite	$CaSO_4$	25.46	0.350	100	1150, 1180 1200, 1280	-
Barite	$BaSO_4$	25.86	0.345	100	800-820	-
Celecite	$SrSO_4$	30.07	0.297	100	1175, 1200	-
Jarosite	$KFe_3(SO_4)_2(OH)_6$	29	0.308	100	-	600
Alunite	$KAl_3(SO_4)_2(OH)_6$	48	0.18	100	-	-
Pyrite	FeS_2	56.34	0.163	100	-	-
Apatite A	$Ca_5(PO_4)_3F$	32.97	0.272	100	-	-
Apatite B	$Ca_5(PO_4)_3F$	32.20	0.287	100	390	510

Table 7. Oxides and hydroxides that were found in the clay samples and their certain characteristics (Kahraman et al., 2005).

Hydroxides and Oxides	Formula	$2\theta^{\circ}$	d(hkl)/nm	100 I/Io	t_{endo}/ C	t_{exo}/ C
Lepidocrosite	γ-FeOOH	14.2	0.626	100	110, 305	512
Goethite	α-FeOOH	21.24	0.418	100	100, 120	-
Gibbsite	γ-Al(OH)$_3$	18.3	0.485	100	-	-
Anatasa	β-TiO$_2$	25.3	0.352	100	-	-

accompanied by silica, calcite and alunite. However, magnesite and the carbonates like dolomite and calcite co-occur with sepiolite and palygorskite.

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REFERENCES

Adams JM (1987). Synthetic organic chemistry using pillared, cation-exchanged and acid-treated montmorillonite catalysts-A review. Appl. Clay Sci., 2(4): 309-342.

Akyuz S, Akyuz, T (2003). FT-IR spectroscopic investigation of adsorption of pyrimidine on sepiolite and montmorillonite from Anatolia. J. Incl. Phen. Mac. Chem., 46(1): 51-55.

Barrer RM (1978). Zeolites and Clay Minerals. Academic Press, London., p. 657.

Breck DW (1974). Zeolite Molecular Sieves. Wiley, New York., p. 771.

Breen C, Watson R, Madejova J, Komadel P, Klapyta Z (1997). Acid activated organoclays: Preparation, characterization and catayptic activity of acid-treated tetraalkylammonnium exchanged smectites. Langmuir, 13(24): 6473-6479.

Bridnley GW, Brown G (1980). Crystal Structures of Clay Minerals and Their X-ray Identification. Monograph No. 5, Mineralogical Society, London., p. 495.

Brindley G.W (1978) Thermal reactions of clay and clay minerals. Ceramica, 24(102): 217–224.

Davarcioglu B (2009). Investigation of eastern black sea region clays by FTIR spectroscopy (Rize-Findikli-Camlihemsin, Turkey). Colloquium Spectroscopium Internationale XXXVI. August 30-September 3, Book of Abstract, 74, Budapest, Hungary.

Davarcioglu B (2010). Investigation of Central Anatolian region Nigde-Dikilitas (Turkey) clays by FTIR spectroscopy. Epitoanyag, 62(2): 55-60.

Davarcioglu B, Ciftci E (2009). Investigation of Central Anatolian clays by FTIR spectroscopy (Arapli-Yesilhisar-Kayseri, Turkey). Int. J. Nat. Eng. Sci., 3(3): 154-161.

Davarcioglu B, Ciftci E (2010). The clay minerals observed in the building stones of Aksaray-Guzelyurt area (Central Anatolia-Turkey) and their effects. Int. J. Phys. Sci., 5(11): 1734-1743.

Davarcioglu B, Gurel A, Kayali R (2007). Investigation of Eastern Black Sea Rize-Findikli-Camlihemsin region clays by FTIR spectroscopy. 6th International Industrial Minerals Symposium. Kemal, Batar, Kaya and Seyrenkaya (ed.), February 1-3, Izmir, Turkey, pp. 87-95.

Davarcioglu B, Gurel A, Kayali, R (2005). Investigation of Central Anatolia region Nigde-Dikilitas (Turkey) clays by FT-IR spectroscopy. Proceedings of 12th National Clay Symposium. Yakupoglu, Aclan and Kose (ed.), September 5-9, Van, Turkey, pp. 63-72.

Davarcioglu B, Kayali R (2007). Investigation of Central Anatolia Aksaray-Guzelyurt region kaolinitic clays by FT-IR spectroscopy. J. Fac. Eng. Arch. Selcuk Univ., 22(1-2): 49-58.

Davarcioglu B, Kayali R, Gurel A (2008). FT-IR spectroscopic study of Arapli-Yesilhisar-Kayseri clays from Central Anatolia region. J. Clay Sci. Technol., 1(3): 163-173.

Falaras P, Lezou F, Seiragakis G, Petrakis D (2000). Bleaching properties of alumina-pillared acid-activated montmorillonite. Clays Clay Miner., 48(5): 549-556.

Farmer VC, Russell JD (1964). The infrared spectra of layer silicates. Spectrochim. Acta., 20(7): 1149-1173.

Frost RL, Locos OB, Ruan H, Kloprogge JT (2001). Near-infrared and mid-infrared spectroscopic study of sepiolites and palygorskites. Vib. Spectrosc., 27(1-2): 1-13.

Gitzen WH (1970). Alumina as a Ceramic Materials. Am. Ceram. Soc.

Ohio, 253.

Grim RE (1968). Clay Mineralogy. Mc Graw-Hill, New York, 596.

Grim RE (1988). The history of the development of clay mineralogy. Clays Clay Miner., 36(2): 97-101.

Grim RE, Guven N (1978). Bentonites-Geology, Mineralogy, Properties and Uses: Developments in Sedimentology, Elsevier, New York, 24: 256.

Gurel A (1999). Determination of sedimentalogical, mineralogical and chemical properties of Ulukisla-Kolsuz area (Nigde-Turkey). Proceedings of 9th National Clay Symposium. Yeniyol, Ongen and Ustaomer (ed.), September 15-18, Istanbul, Turkey, pp. 31-37.

Heroux Y, Chagnon A, Bertrand R (1979). Compilation and correlation of major thermal maturation indicators. Am. Assoc. Pet. Geol. Bull., 63(12): 2128-2144.

Jackson ML (1969). Soil Chemical Analysis-Advanced Course. 2nd Ed., Published by the Auther, Madison, Wis., p. 895.

Kahraman S, Onal M, Sarikaya Y, Bozdogan I (2005). Characterization of silica polymorphs in kaolins by X-ray diffraction before and after phosphoric acid digestion and thermal treatment. Anal. Chim. Acta., 552(1-2): 201-206.

Kayali R, Gurel A, Davarcioglu B, Ciftci E (2005). Determination of qualitative and quantitative properties of industrial raw materials clays and diatomites in Central Anatolia by spectroscopic methods. TUBITAK-Turkey (project code: YDABCAG-1001Y067), p. 137.

Kok MV (2006). Effect of clay on crude oil combustion by thermal analysis techniques. J. Therm. Anal. Calor., 84(2): 361-366.

Kok MV, Smykatz-Kloss W (2008). Characterization, correlation and kinetics of dolomite samples as outlined by thermal methods. J. Therm. Anal. Calor., 91(2): 565-568.

Lagaly G, Beneke K (1991). Intercalation and exchange reactions of clay minerals and non-clay layer compounds. Colloid Pol. Sci., 269(12):1198-1211.

Murray HH (1991). Overview-clay mineral applications. Appl. Clay Sci., 5(5-6): 379-395.

Murray HH (1999). Applied clay mineralogy today and tomorrow. Clay Miner., 34(1): 39-49.

Murray HH, Bundy W, Harvey C (1993). Kaolin Genesis and Utilization. Clay Miner. Soc. Boulder, Colorada, p. 341.

Norton FH (1974). Elements of Ceramics. Addison-Wesley, Reading, Massachusetts, p. 311.

Paterson E, Swaffield R (1987). Thermal Analyses. In: Wilson MJ (ed), A Handbook of Determinative Methods in Clay Mineralogy, Blackie, pp. 99-133.

Reeder RJ (1983). Carbonates: Mineralogy and Chemistry, Reviewsin Mineralogy. Mineral. Soc. Am. Washington DC, 11: 394.

Sakizci M, Yorukogulları E (2005). Thermal properties of natural and modified zeolites. Proceedings of 12th National Clay Symposium. Yakupoglu, Aclan and Kose (ed.), September 5-9, Van, Turkey, pp. 662-668,

Sarikaya Y, Onal M, Baran B, Alemdaroglu T (2000). The effect of thermal treatment on some of the physicochemical properties of a bentonite. Clays Clay Miner., 48(5): 557-562.

Smykatz-Kloss W (1974). Thermal Analysis, Application and Results in Mineralogy. Springer Verlag, Berlin, pp. 185.

Wilson MJ (1987). A Handbook of Determinative Methods in Clay Mineralogy. Blackie-Son Ltd., London, p. 308.