Investigation of Central Anatolian Clays by FTIR Spectrocopy (Arapli-Yesilhisar-Kayseri, Turkey)

Burhan DAVARCIOĞLU[1*"]   Emin ÇİFTÇİ[2]

[1"]Department of Physics, Aksaray University, 68100 Aksaray, Turkey

[2"]Department of Geological Engineering, Nigde University, 51245 Nigde, Turkey

ABSTRACT

The clay samples are taken from Arapli-Yesilhisar area, located in the southwest part of Kayseri province (Central Anatolia) have been investigated by the FTIR spectroscopy. The FTIR spectra of clays considered as standard natural clays including illite, illite-smectite mixed layer, beidellite, kaolinite, chlorite (ripidolite), nontronite, montmorillonite have been acquired first, and then the spectra of illite+quartz+feldspar, quartz+feldspar have been taken together with the standard natural clays. Minerals contained by the clay samples have been determined by comparing the both spectra. It is determined that the O-H, Si-O, Si-O-Al and Si-O-Fe groups prevail in the FTIR spectral measurements of the samples representing the lower, middle and upper levels of the Arapli-Yesilhisar profiles. In addition, chemical analyses of these clay samples indicated major presence of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, Cr_2O_3 and P_2O_5. It is found that the Arapli-Yesilhisar clay samples are mainly illite, kaolinite, feldspar and quartz, and they have T-O (tetrahedral-octahedral) or O-T (octahedral-tetrahedral) structure.

Key Words: Arapli-Yesilhisar-Kayseri, clay minerals, FTIR spectroscopy

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 [1]. Physical and chemical properties of the clays make them right material for different purposes in different fields [2]. 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 [1, 3, 4, 5].

The structure of the clay organic complexes has been the subject of many researches since 1930 [6]. Some clay minerals having large surface area, high ion exchange capacity and molecular grid properties have been pioneered for the development of many new products [5]. Subsequently, a great number of studies have been carried on the determination of chemical properties of the clays. One of the methods applied is the FTIR (fourier transform infrared) spectroscopy [7, 8].

Significant number of studies, generally on the geology of the study area is available in the literature. However, particularly one of them, which are more comprehensive study in terms of geology and mineralogy, deserves to be mentioned here. Pasquare [9] has investigated the Central Anatolian clays including the Arapli-Yesilhisar-Kayseri area by using geological columnar sections and field observations. In current study, distribution of clay-rich horizons and their litostragraphical relations have been investigated by constructing columnar sections (profiles) at type localities within the study area.

A combined profile representing the constructed profiles chosen for this and nearby area was shown in Fig. 1. It has been determined that the 20-25 m thick Kizilkaya ignimbrite generally occurs at the top the profile. The Kizilkaya ignimbrite is not lithologically homogenous in that varying from loosely-cemented with andesitic-basaltic-granitic gravels at the bottom and reddish color strongly-cemented, welded ignimbites towards the top. Underlying the ignimbrite, there is about 15 m thick, red colored unit consist of clay, tuff and paleosoil [9].

An earlier attempt to determine the chemical properties of the Anatolian clays using the FTIR spectroscopy was successful to certain extent [10]. In this study, the adsorption of 2,2'-biquinoline onto natural and ion-exchanged montmorillonite and saponite from Anatolia (Turkey) have been studied. In a similar study, the adsorption of 3-aminopyridine by natural sepiolite and montmorillonite from Anatolia (Turkey) have been investigated in the temperature range from 20 to 125 ^{o}C using a variable temperature unit [11]. They have also studied the adsorption of pyrimidine on natural montmorillonite and sepiolite from Turkey [12]. Another study carried on the area was about geological formation of the region's clays. It has been proposed that andesite, basalt and granite gravels have been transported into the ignimbrites as terresterial and lacustrine products [13]. But, no study on the quality and the quantity of the region's clays has been documented yet.

Along with XRD (X-ray powder diffraction), 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. In this study, the clay samples taken from the Arapli-Yesilhisar-Kayseri located in the Central Anatolia (Turkey) have been investigated by using the FTIR spectroscopy.
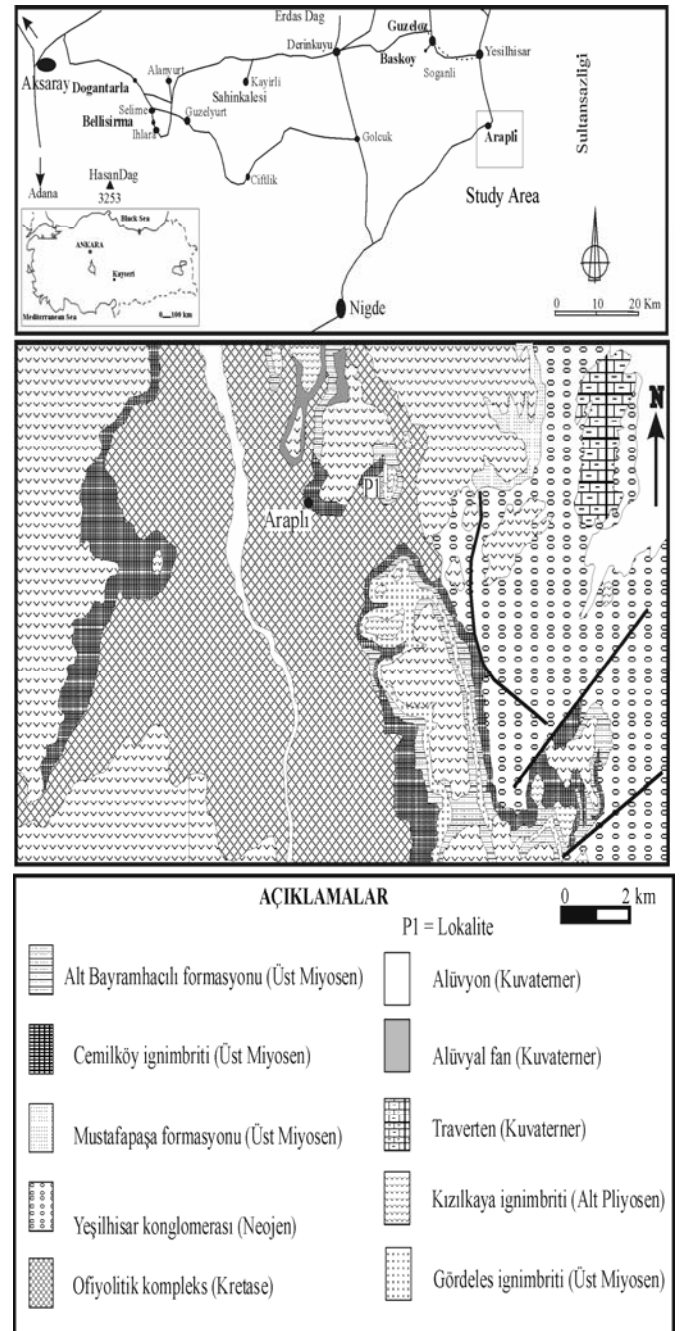

Figure 1. Generalized geological map of the study area (adapted from Pasquare [9] by rescaling from a 1/75000-scaled geological map).

MATERIALS AND METHODS

The clay samples were taken from three different levels shown in the litostratigraphic columnar section of a selected locality in the Arapli-Yesilhisar region (Fig. 2). The samples taken from lower level, middle level and upper level were labeled as MPF 1.2, MPF 1.1, and CK 2.3, and CK 2.2, CK 2.1, respectively. The following processes were applied to prepare the samples for the FTIR measurements.

Samples were ground into powder. Powdered samples were alternately washed with pure water, ethylealcohol, and ether. Then, they were dried in an oven at 110 °C for 24 hours. These samples 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, which were then placed in the sample compartment. Bruken Equinox 55 Fourier transform FTIR spectrometer (Department of Physics, METU, Turkey) was used for the IR 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, spectrometer was calibrated with polystryrene and silicateoxide of thicknes 0.05 nm.

On the other hand, the infrared spectra of the illite (IMt-1; Silver Hill, Montana, USA), illite-smectite mixed layer (ISMt-1; Mancos Shale, Ord.), beidellite (SBId-1; Idoha, USA), kaolinite (KGa-1; Washington Country, Georgia, USA), chlorite (ripidolite, CCa-1; Flagstaff Hill, El Dorato Country, California, USA), nontronite (NAu-2; Uleynine, South Australia), and montmorillonite (SCa-3; Otay, San Diego Country California, USA) known as standard natural clays were taken, since those spectra were necessary for the analyses of subject samples.

A second treatment was employed only to the clay sample taken from the upper level to see whether there is a change in the structure of the samples or not due to FTIR spectrum measurements. For this procedure, HCl, bicarbonate (Na_2CO_3), and sodiumdithonit ($Na_2S_2O_4$), and sodiumstrate ($Na_3C_6H_5O_7$) liquids were added to the sample to remove carbonates (mainly calcite and dolomite), amorph materials and manganese oxides, which were expected to be present. This mixture was treated in an oven at 120 °C for 24 hours and washed using ethylalcohol and eter until complete removal of those unwanted components was achieved. The FTIR spectrum of the precipitate was then taken.

The chemical analyses of the clay samples were carried out at the General Directorate of Mineral Research and Exploration (MTA, Ankara) laboratories. Major oxide composition of the samples representing the lower, middle and upper parts of the profile was as follows; for the lower part: 54.32% SiO_2, 0.57% TiO_2, 12.56% Al_2O_3, 6.70% Fe_2O_3, 0.07% MnO, 2.16% MgO, 1.44% CaO, 0.67% Na_2O, 1.08% K_2O, 0.105% Cr_2O_3, 0.03% P_2O_5; for the middle part: 55.69% SiO_2, 0.82% TiO_2, 16.72% Al_2O_3, 6.57% Fe_2O_3, 0.04% MnO, 1.80% MgO, 1.40% CaO, 0.34% Na_2O, 1.85% K_2O, 0.014% Cr_2O_3, 0.04% P_2O_5;

and for the upper part: 55.71% SiO_2, 0.70% TiO_2, 16.81% Al_2O_3, 8.67% Fe_2O_3, 0.04% MnO, 1.21% MgO, 1.31% CaO, 0.69% Na_2O, 1.55% K_2O, 0.007% Cr_2O_3, 0.05% P_2O_5. These data suggest that the clays of the region are essentially rich in SiO_2 and Al_2O_3.

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; MTA laboratories, Ankara). These measurements indicated common presence of quartz (34.64%), feldspar, smectite (63.62%), kaolinite (1.74%), and iron-oxide (<1%).
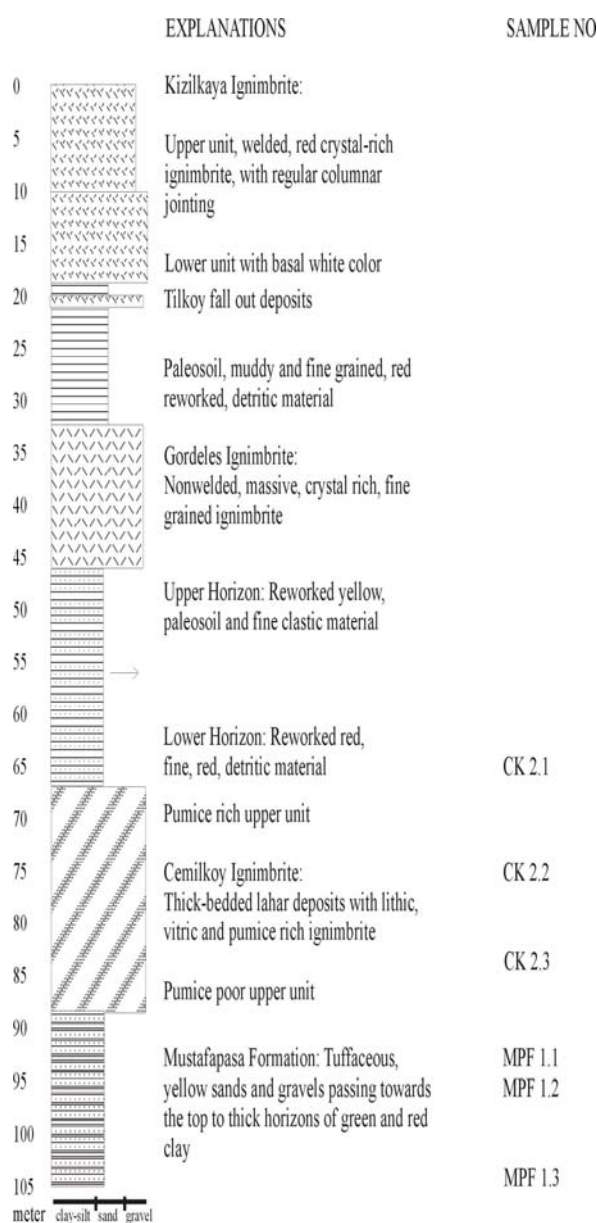

Figure 2. Generalized litostratigraphic columnar section of the Arapli-Yesilhisar region.

RESULTS AND DISCUSSIONS

FTIR spectra of the samples taken from lower level (MPF 1.2, MPF 1.1), middle level (CK 2.3), and upper level (CK 2.2, CK 2.1) of the Arapli-Yesilhisar soil profile are given in Figs. 3 thru 5, respectively.

The assignments of the vibration bands of the samples were carried out as stated in the materials and methods: using the fundamental vibration frequencies of the clays known as the World Source Clay Minerals (standard natural clay), each of the vibration bands corresponding to which clay species in the spectra of the samples were determined and results for the clay samples given below and the results obtained for each clay sample representing certain levels within the profiles were given in tables (Tables 1 thru 3).

Fundamental vibr   ational fre   quencies of illite standard natural clay (cm^{-1})

ν(OH) stretching	3622
ν(Si-O) normal to the plane stretching	1090
ν(Si-O) planar stretching	1031
(Al-Al-OH) deformation	916
(Al-Mg-OH) deformation	832
(Al-O-Si) inner surface vibration	756
OH deformation	688
OH deformation	622
(O-Si-O) bending	525
(O-Si-O) bending	468 [14]

Fundamental vibration   frequencies of   illite-smectite mixed layer standard natural clay (cm^{-1})

ν(OH) stretching (shoulder)	3685
ν(OH) stretching	3622
ν(Si-O) normal to the plane stretching	1090
ν(Si-O) planar stretching	1031
(Al-Al-OH) deformation	916
(Al-Mg-OH) deformation	810
(Al-O-Si) inner surface vibration	750
OH deformation	622
(O-Si-O) bending	525
(O-Si-O) bending	468 [14]

Fundamental vibr ational fre quencies of kaolinite standard natural clay (cm^{-1})

|	
Inner-surface OH, (Al-O...H) stretching	3679
Inner cage OH stretching	3655
Inner-layer OH, (Al-O...H) stretching	3623
ν(H-O-H) stretching	3433
ν(Si-O) normal to the plane stretching	1118
ν(Si-O) planar stretching	1027
ν(Si-O) planar stretching	1009
Inner-surface Al-OH deformation	942
Inner-layer Al-OH deformation	914
M-OH stretching	791
Si-O deformation	754
(Si-O-Al) deformation	546
(Si-O-Fe) deformation	470
(Si-O-Mg) deformation	428 [15]
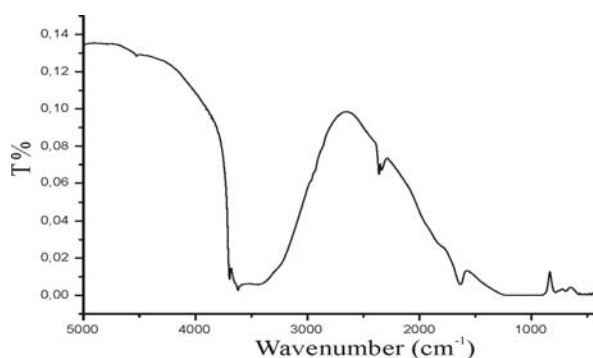
Figure 3. FTIR spectrum of the clay sample taken from the lower level (MPF 1.2) of Arapli-Yesilhisar profile.

Table 1. Results of the FTIR spectrum analyses of the clay sample taken from the lower level (MPF 1.2) of Arapli-Yesilhisar profile.

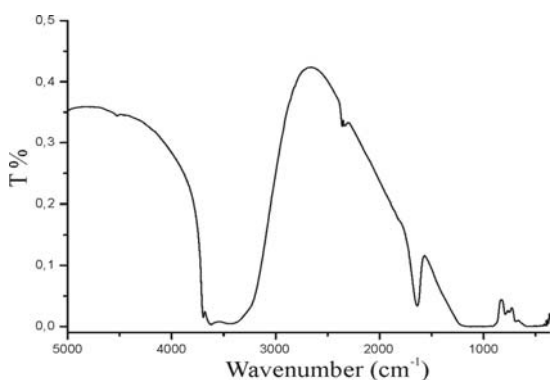| Wavenumber (cm^{-1})	Assignment	Clay Mineral Type
3679	Inner-surface OH, (Al-O...H) stretching	Kaolinite
3655	Inner cage OH stretching	Kaolinite
3623	Inner-layer OH, (Al-O...H) stretching	Kaolinite
3623	ν(OH) stretching	Illite
1120	ν(Si-O) normal to the plane stretching	Kaolinite
1010	ν(Si-O) planar stretching	Kaolinite
940	Inner-surface Al-OH deformation	Kaolinite
910	Inner-layer Al-OH deformation	Kaolinite
800	ν(OH) stretching	Feldspar
798	ν(OH) stretching	Quartz
790	M-OH strecthing	Kaolinite
788	ν(OH) stretching	Quartz
755	Si-O deformation	Kaolinite
697	ν(OH) stretching	Quartz
546	(Si-O-Al) deformation	Kaolinite
470	(Si-O-Fe) deformation	Kaolinite

Figure 4. FTIR spectrum of the clay sample taken from the middle level (CK 2.3) of Arapli-Yesilhisar profile.

Table 2. Results of the FTIR spectrum analyses of the clay sample taken from the middle level (CK 2.3) of Arapli-Yesilhisar profile.

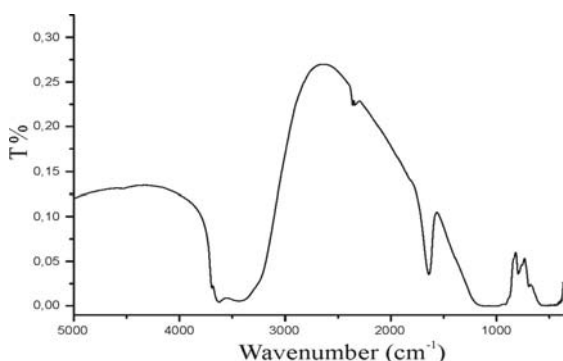| Wavenumber (cm⁻¹)	Assignment	Clay Mineral Type
3679	Inner-surface OH, (Al-O...H) stretching	Kaolinite
3655	Inner cage OH stretching	Kaolinite
3623	Inner-layer OH, (Al-O...H) stretching	Kaolinite
3623	ν(OH) stretching	Illite
1120	ν(Si-O) normal to the plane stretching	Kaolinite
1010	ν(Si-O) planar stretching	Kaolinite
940	Inner-surface Al-OH deformation	Kaolinite
910	Inner-layer Al-OH deformation	Kaolinite
800	ν(OH) stretching	Feldspar
798	ν(OH) stretching	Quartz
790	M-OH strecthing	Kaolinite
788	ν(OH) stretching	Quartz
750	Si-O deformation	Kaolinite
697	ν(OH) stretching	Quartz

Figure 5. FTIR spectrum of the clay sample taken from the upper level (CK 2.1) of Arapli-Yesilhisar profile.

Table 3. Results of the FTIR spectrum analyses of the clay sample taken from the upper level (CK 2.1) of Arapli-Yesilhisar profile.

Wavenumber (cm⁻¹)	Assignment	Clay Mineral Type
3679	Inner-surface OH, (Al-O...H) stretching	Kaolinite
3655	Inner cage OH stretching	Kaolinite
3623	Inner-layer OH, (Al-O...H) stretching	Kaolinite
3623	ν(OH) stretching	Illite
1120	ν(Si-O) normal to the plane stretching	Kaolinite
1010	ν(Si-O) planar stretching	Kaolinite
940	Inner-surface Al-OH deformation	Kaolinite
910	Inner-layer Al-OH deformation	Kaolinite
800	ν(OH) stretching	Feldspar
798	ν(OH) stretching	Quartz
790	M-OH strecthing	Kaolinite
788	ν(OH) stretching	Quartz
750	Si-O deformation	Kaolinite
697	ν(OH) stretching	Quartz
546	(Si-O-Al) deformation	Kaolinite
470	(Si-O-Fe) deformation	Kaolinite

FTIR spectrum of the clay sample taken from the lower level of Arapli-Yesilhisar (Fig. 3) was compared with the fundamental vibration frequencies of the clays known as standard natural clay and the assignments of the band components of the samples, minerals corresponding to each of the vibration bands in the spectra were determined and the results for each clay sample were presented in Table 1. There are 10 fundamental vibration frequencies of illite mineral in the spectrum of standard natural clay. But, there is only a ν(OH) stretching vibration frequency of this sample at 3623 cm⁻¹. Although Si-O deformation of kaolinite in standard natural clay is seen at 754 cm⁻¹, it was observed at 755 cm⁻¹ for the sample. There is a little shift. ν(Si-O) planar stretching vibration frequency, ν(H-O-H) stretching frequency, and Si-O-Mg deformation frequency are not observed at 1027 cm⁻¹, 3433 cm⁻¹, and 428 cm⁻¹, respectively. But, Si-O-Al and Si-O-Fe deformation bands are observed at 546 cm⁻¹ and 470 cm⁻¹, respectively. The bands corresponding to 1010 cm⁻¹ and 910 cm⁻¹ are the vibration bands of kaolinite mineral. These are in a good agreement with the fundamental vibration frequencies of standard natural kaolinite clay. On the other hand, ν(OH) stretching vibrations of quartz were observed at 798 cm⁻¹, 788 cm⁻¹, and 697 cm⁻¹ and ν(OH) stretching vibration of feldspar was observed at 800 cm⁻¹. These results show that the samples taken from the lower level include illite, kaolinite, feldspar, and quartz minerals.

The FTIR spectrum of the clay sample taken from the middle level of Arapli-Yesilhisar clays (Fig. 4) was compared with the fundamental vibration frequencies of the clays known as standard natural clay and the assignments of the band components of the samples were performed as given in Table 2. Only one ν(OH) stretching vibration frequency band was observed for illite mineral at 3623 cm⁻¹ as it was observed for the sample taken from lower level.

Although Si-O deformation frequency of kaolinite was observed at 755 cm^{-1} for the lower level sample, it was observed at 750 cm^{-1} for the middle level sample being different from the lower level sample. In addition, the ν(Si-O) planar stretching vibration, ν(H-O-H) stretching, and Si-O-Mg deformation frequencies belonging to 1027 cm^{-1}, 3433 cm^{-1}, and 428 cm^{-1}, respectively, are not observed for this sample and also Si-O-Al and Si-O-Fe deformation bands have not been observed and at 546 cm^{-1} and 470 cm^{-1} in the spectrum of middle level sample. The assigned bands observed for lower level samples at 1010 cm^{-1} and 910 cm^{-1} were observed for the middle level samples. The observed vibration bands for both quartz and feldspar are the same for the middle level sample. Although, there are little shifts from the fundamental vibration frequencies, 11 of all the fundamental frequencies of the kaolinite mineral were observed. These very small frequency shifts are caused by the water going into among the layers of kaolinite mineral [16].

For the upper level sample, results given in Table 1 and Table 3 have been compared. All the assignments on these two tables are the same and only Si-O deformation band belonging to the kaolinite was observed at 750 cm^{-1} for the upper level sample as being the same for middle level and being different from lower level sample. Since all the clay samples include illite, kaolinite, feldspar, and quartz minerals, it means that these clays have the framework of slicate structure, such as T-O (tetrahedral-octahedral) or O-T (octahedral-tetrahedral). On the other hand, it was observed O-H, Si-O, Si-O-Al and Si-O-Si groups in their FTIR spectra. This situation is attributed to the substitutions of different atoms having different valance values displaying in clay samples. Kaolinite minerals are formed of one octahedral and one tetrahedral layer overlying on each other. In this case, unit layer 1:1 and this structure are named as T-O or O-T. Octahedral layer forms jips like structure layer (hydroxil planar) and tetrahedral layer forms silicate like structure (oxygen planar) in kaolinite mineral. Organic molecules enforce the silicate layers and may be penetrated into the vacancies among them. They form H-bonding with the surface hydroxyles breaking the strong electrostatic and van der Waals forces between the layers. This hydroxyle planes are weak proton donors, so they can form hydrogen bonds with the strong bases [15, 17]. Bipolar molecules which behave as both powerly proton donor and acceptor place on the tetrahedral surface giving protons to the oxygens while placing on the octahedral surface taking protons from hydroxyles [18]. Formed hydrogen bonds are very weak since oxygen plane is very weak electron donor. Therefore, the atoms having different valances and substituting on the octahedral layer form H-bonding with inner-surface hydroxyles. On the other hand, different ions and water molecules also go into among the layers since bonding forces between them are very weak. Some small organic molecules and ions take place straightforward among the layers forming H-bonding with the inner surface hydroxyles or oxygen plane of kaolinite mineral. In this case, this causes frequency shifts as mentioned above.

As mentioned above, XRD analysis results have showed that our clay samples include 63.62% smectite and 1.74% kaolinite. On the other hand, vibration frequencies of the samples belonging to the lower, middle, and upper levels observed at 755, 750 and 750 cm^{-1}, respectively, have been assigned according to the Si-O kaolinite deformation (seen at 754 cm^{-1}) of kaolinite standard natural clay. 750 cm^{-1} vibration frequency is seen in the fundamental vibrations of illite-smectite mixed layer standard natural clay. This corresponds to Al-O-Si inner plane vibration. So, we can say that our samples include illite-smectite mixed mineral. In all tables, 3623 cm^{-1} vibration frequency was assigned for both kaolinite and illite or illite-smectite mixed layers. There is an uncertainty which of them this vibration frequency corresponds to. Therefore, 3623 cm^{-1} vibration frequency was assigned as ν(OH) stretching vibration of illite mineral and inner-layer OH, (Al-O...H) stretching vibration of kaolinite mineral.
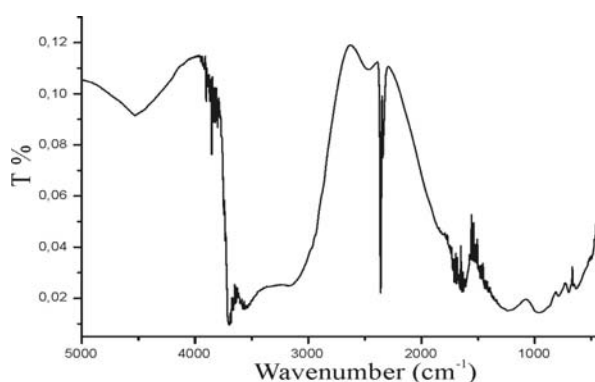

Figure 6. The FTIR spectrum of the clay sample taken from the upper level (CK 2.1) of Arapli-Yesilhisar profile after the heat treatment.

As summarized in the materials and methods, the FTIR spectrum of the sample representing upper level of Araplı-Yeşilhisar profile has been taken to see effects of the heat treatments on the structure of the subject samples (Fig. 6). The assignments of the vibration frequencies of this spectrum were carried out following the same procedure applied to the spectra of the other samples and the results are given in Table 4.

Table 4. Results of the FTIR spectrum analyses of the clay sample taken from the upper level (CK 2.1) of Arapli-Yesilhisar profile after the heat treatment.

Wavenumber (cm⁻¹)	Assignment	Clay Mineral Type
3679	Inner-surface OH, (Al-O...H) stretching	Kaolinite
3655	Inner cage OH stretching	Kaolinite
3622	ν(OH) stretching	Illite
1125	ν(Si-O) normal to the plane stretching	Kaolinite
940	Inner-surface Al-OH deformation	Kaolinite
915	(Al-Al-OH) deformation	Illite
832	(Al-Mg-OH) deformation	Illite
800	ν(OH) stretching	Feldspar
798	ν(OH) stretching	Quartz
788	ν(OH) stretching	Quartz
755	Si-O deformation	Kaolinite
695	ν(OH) stretching	Quartz
546	(Si-O-Al) deformation	Kaolinite
475	(Si-O-Fe) deformation	Kaolinite

It is found that this sample is consisted of illite, kaolinite, feldspar, and quartz. In the heat untreated samples, at 1010 cm⁻¹ ν(Si-O) planar stretching and 790 cm⁻¹ M-OH stretching of kaolinite mineral observed before heat treatment were not observed after the heat treatment. But, it is seen that (Al-Al-OH) and (Al-Mg-OH) deformation bands of illite mineral are observed at 915 cm⁻¹ and 832 cm⁻¹, respectively after the heat treatment. The formation of these bands was resulted from the displacements of Al and Mg atoms includeds in clay samples during the heat treatment [19]. Besides, M-OH stretching vibration (790 cm⁻¹) of kaolinite has not been observed. In addition, the reason of the disappearance of ν(Si-O) planar stretching vibration (1010 cm⁻¹) of the same mineral after the heat treatment is due to the penetrating of the organic molecules through the silicate layers by force them. ν(OH) stretching vibrations of quartz at 798, 788 and 697 cm⁻¹ and ν(OH) stretching vibration of feldspar at 800 cm⁻¹ remain the same after the heat treatment. As a result, it can be said that the framework of silicate (T-O or O-T) structures of the Arapli-Yesilhisar clay samples has not been destroyed.

ACKNOWLEDGEMENTS

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