

Full Length Research Paper

Spectral Characterization of Kolsuz-Ulukisla-Nigde Clays, Central Anatolian Region-Turkey and Petroleum exploration

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Accepted 31 July, 2010

Characterization of the Kolsuz clays in the Central Anatolian Region (Ulukisla-Nigde-Turkey) were carried out using the spectroscopic techniques and results were interpreted in terms of petroleum exploration. 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. Moreover, to see whether any changes occur or not in the structure of the clay samples which have been undergone to thermal processes, the FTIR spectrum of the sample (Kk1) belonging to the lower level has been taken. It has been found that Kolsuz clays have included illite, illite-smectite mixed-layer, Na-montmorillonite, chlorite, palygorskite, calcite, feldspar and quartz that silicate has a T-O-T smectite structure. During the diagenesis and metamorphism, changes in the clay structures due to the temperature increase will reflect degree of diagenesis and metamorphism. Factors including temperature, pressure, depth and burial that are all influential during these changes along with hydrocarbon formation and the primary migration of the hydrocarbons could be explained through the diagenesis of clay minerals and organic maturation. Required temperatures for these changes in the clay structures are in the same range with that required for petroleum formation (60 - 150 °C). Results acquired by using the organic maturation could be obtained through the spectral studies of the clay mineral structures.

Key words: Clay minerals, FTIR, petroleum exploration, Central Anatolian, Turkey.

INTRODUCTION

Clays are naturally occurring, fine-grained minerals under surface conditions mostly as alteration products with distinct crystal structures. They may show plastic behavior when mixed with sufficient water and become stiff when dried or cooked. They, having different physical properties, occur in three modes: (1) surface clays that may be old or very young sedimentary formations, as

suggested by the name, they occur near surface; (2) shales that have been subjected to pressures to become rigid and layered due to various reasons (e.g., tectonic or subsidence-related), and (3) fire clays that are mined out from deeper sites comparing to the other two and they behave refractory and include less impurities thus they are physically and chemically more uniform.

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 (Falaras et al., 2000). Clay-organic complex structures have been a research subject particularly since

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1930's. Results of these researches made beneficial contribution to the process of expanding their use in diverse areas (Smith, 1934). Besides, progresses in analytical techniques that made it possible to determine mineralogical and chemical compositions of the clays appreciably expedited this process.

Clay minerals are formed as a result of changes in temperature, pressure, geochemical, and physical conditions (Murray, 1999). Although clay minerals could be resulted from weathering, sedimentation, burial, diagenesis and hydrothermal alteration processes in general, occurrence of monomineralic clay deposits is scant. Even in an ordinary clay sample, several clay species could occur together. Clay minerals can be categorized in 4 subgroups in natural environments: (1) kaolinite group; (2) smectite group; (3) illite group, and (4) chlorite group.

The relationship between heat and pressure with the formation of clay minerals and its consequence on the formation of petroleum has been an imperative subject for research past 40 years (Perry and Hower, 1970; Dypvik, 1983). In the recent years one of the methods in the petroleum explorations is organic maturation and the other is clay mineral diagenesis. In both the clay mineral diagenesis and the organic maturation, clay minerals show structural changes with the changing temperature, which reveals the degree of metamorphism. The principal factors including pressure, temperature, depth and burial that are efficient during the conversion of the clay minerals and hydrocarbon formation and primary migration can be explained through clay mineral diagenesis and organic maturation (Dunoyer de Segonzag, 1970; Dypvik, 1983).

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). The Central Anatolia is one of the richest in occurrence of clay deposits in the world. Therefore, investigation of these deposits, their quantitative and qualitative characterization is highly important.

One of the geological studies in the Kolsuz area (Ulukisla-Nigde, Central Anatolian) deals with the clay profiles. In this study, using columnar sections and local observations, distribution of clay horizons and their

lithostratigraphic relations were investigated (Oktay, 1982). On the other hand, sedimentological, mineralogical and chemical properties of the clays of the same area were studied in depth later by Gurel (1999). The Kizilbayir Formation outcropping in the north of Ulukisla basin is the key formation due to its association with the clay occurrences. The formation starts with gravel-bearing red-green clays at the base, progressing upward, large-scale cross-bedded conglomerate, sandstone with clay intercalations occur and conglomerate with mudstone interbeds dominate towards the top (Demirtasli et al., 1986). Thickness of the formation in the area range from 10 to 250 m.

However, no comprehensive study on the qualitative and the quantitative characteristics of the clays occurring in this area was available to date. Thus, this study aims to investigate clays of the area using the spectroscopic method and observed structural changes in the clay structures were interpreted in terms of petroleum formation and their possible use in petroleum exploration in the area.

EXPERIMENTAL

Preparation of samples

A combined profile representing the constructed profiles chosen for this and nearby area was shown in Figure 1. The clay samples were taken from three different levels shown in the lithostratigraphic columnar section of a selected locality in the Kolsuz-Ulukisla region (Figure 2). The samples were taken from lower level, middle level and upper level labeled as (Kk1), (Kk2) and (Kk3), respectively. Samples were ground into powder. Powdered samples were alternately washed with pure water, ethyl alcohol, and ether. Then, they were dried in an oven at 110 °C for 24 h.

In general, the clay minerals contain significant amount 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 sample without concentrating for clay fraction. Organic matter was removed through boiling in H₂O₂ and then samples were dried in an oven at 110 °C for 24 h.

FTIR measurements

Samples collected from the study area 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 cm²) to obtain the transparent discs, which were then placed in the sample compartment. Bruker Equinox 55 Fourier transform FTIR spectrophotometer (Department of Physics, METU, Ankara-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, spectrophotometer was calibrated with polystyrenes 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.),

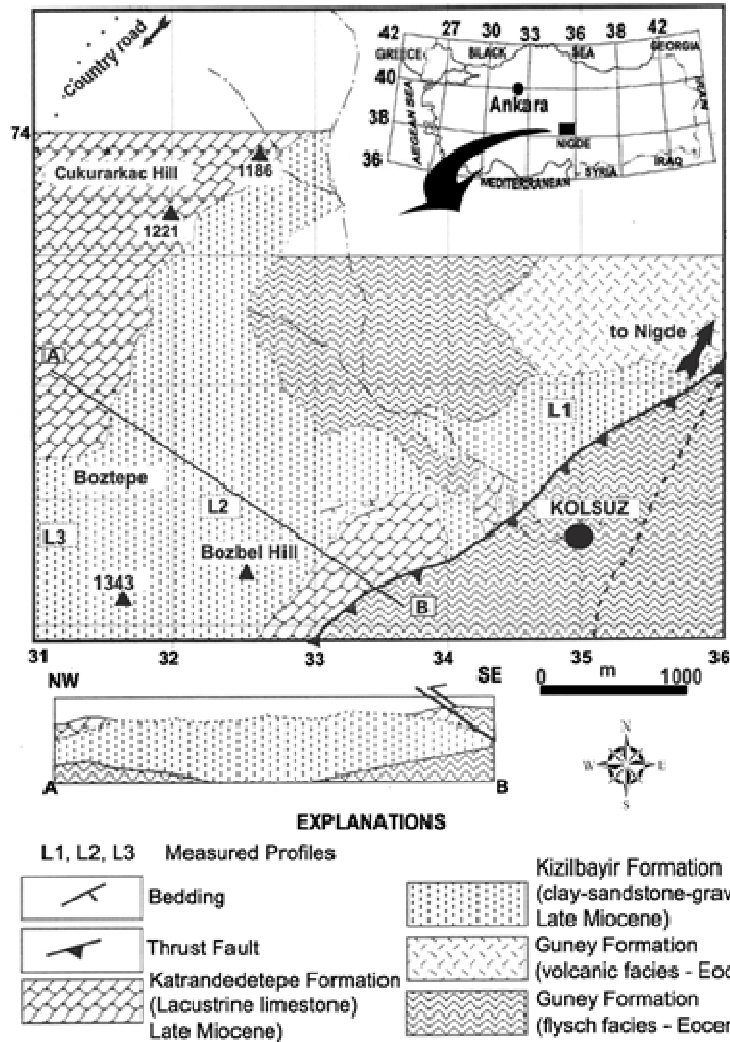


Figure 1. Generalized geological map of the Kolsuz-Ulukisla region and its around (adapted from Kayali et al., 2005).

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 (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 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.

A second treatment was employed only to the clay sample taken

from the lower level (Kk1) 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 sodiumdithionit ($\text{Na}_2\text{S}_2\text{O}_4$), and sodiumstrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) liquids were added to the sample to remove carbonates (mainly calcite and dolomite), amorphous materials and manganese oxides, which were expected to be present. This mixture was treated in an oven at 120°C for 24 h and washed using ethyl alcohol until complete removal of those unwanted components was achieved. The FTIR spectrum of the precipitate was then taken.

CHEMICAL AND MINEROLOGICAL ANALYSES

The chemical analyses of the Kolsuz-Ulukisla clay samples (dried in an oven at 110°C) were carried out at the ACME-Canada laboratories by means of XRF-ICP (X-ray fluorescence spectrometry-Inductively Coupled Plasma) technique. Major oxide composition of the samples representing the lower, middle and upper parts of the profile was given in Table 2. These data suggest that the clays of the region are essentially rich in SiO_2 , Al_2O_3 , and

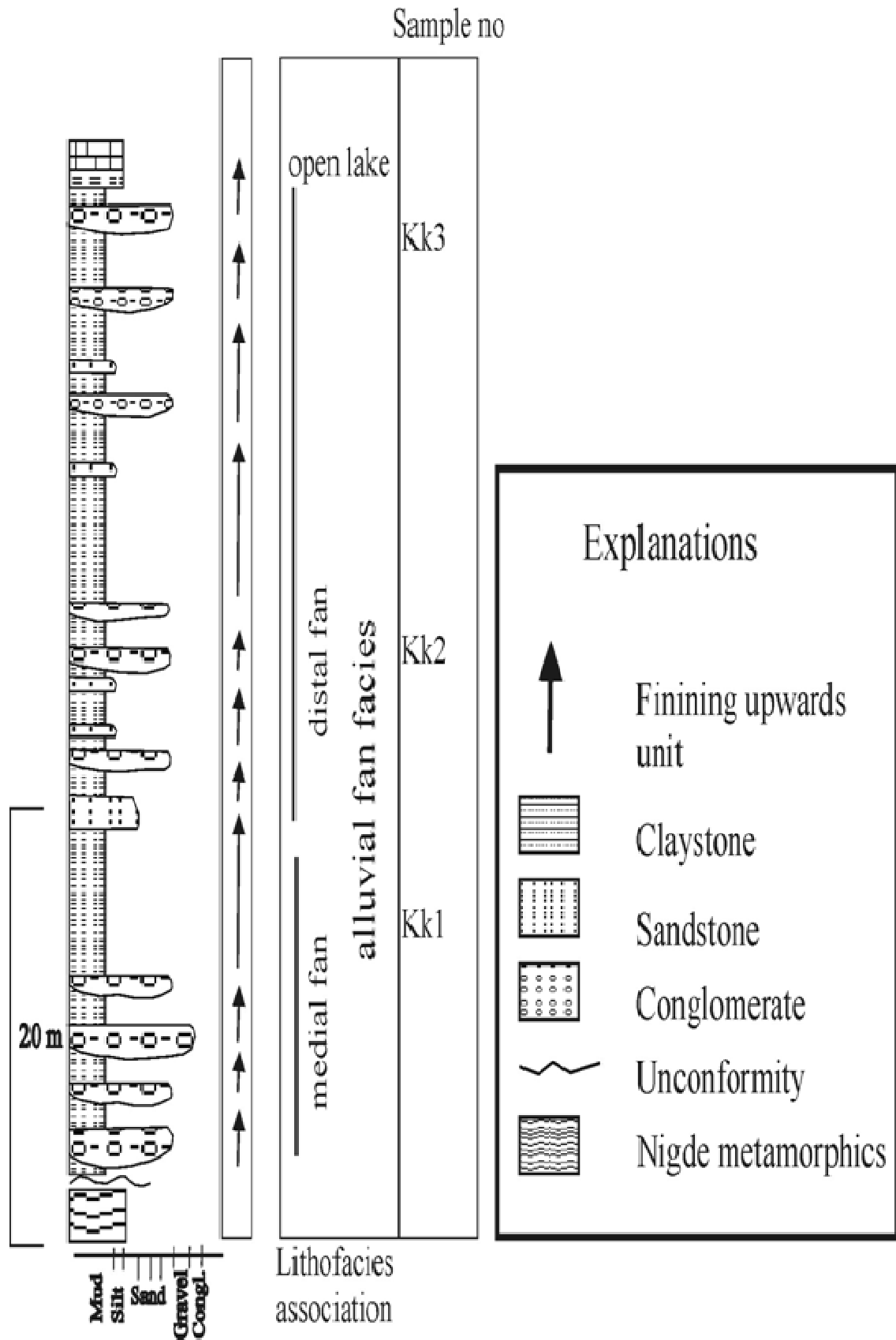


Figure 2. Generalized lithostratigraphic columnar section of the Kolsuz-Ulukisla region (adapted from Kayali et al., 2005).

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	C	P
	Wavenumber (cm ⁻¹)				
v(OH) stretching	-	3685 (shoulder)	-	-	-
Inner-layer OH, (Al-O...H) stretchin	-	3680	-	-	-
v(OH) stretching	-	-	-	3662	-
v(OH) stretching	-	-	3627 (shoulder)	-	3627
v(OH) stretching	3622	3622	3622	-	-
v(OH) stretching	-	-	-	3565	3546
v(OH) stretching	-	-	-	3434	-
δ(water-OH) stretching	-	-	-	-	3408, 3266
δ(water-OH) scissoring	-	-	-	-	1731
δ(water-OH) scissoring	-	-	-	-	1673, 1640
v(Si-O) stretching	-	-	-	-	1163,1114
v(Si-O) normal to the plane stretching	1090	1090	-	-	-
v(Si-O) planar stretching	1031	-	-	-	1031
v(Si-O) stretching	-	-	-	-	1020
v(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).

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

	Lower part (Kk1)	Middle part (Kk2)	Upper part (Kk3)
SiO ₂	46.50	48.57	49.12
TiO ₂	0.66	0.76	0.47
Al ₂ O ₃	12.74	13.97	9.46
Fe ₂ O ₃	7.28	8.10	4.24
MnO	0.14	0.14	0.15
MgO	4.68	5.09	2.90
CaO	9.37	6.94	15.04
Na ₂ O	0.96	1.10	1.72
K ₂ O	2.31	2.64	1.65
Cr ₂ O ₃	0.028	0.027	0.029
P ₂ O ₅	0.06	0.15	0.10

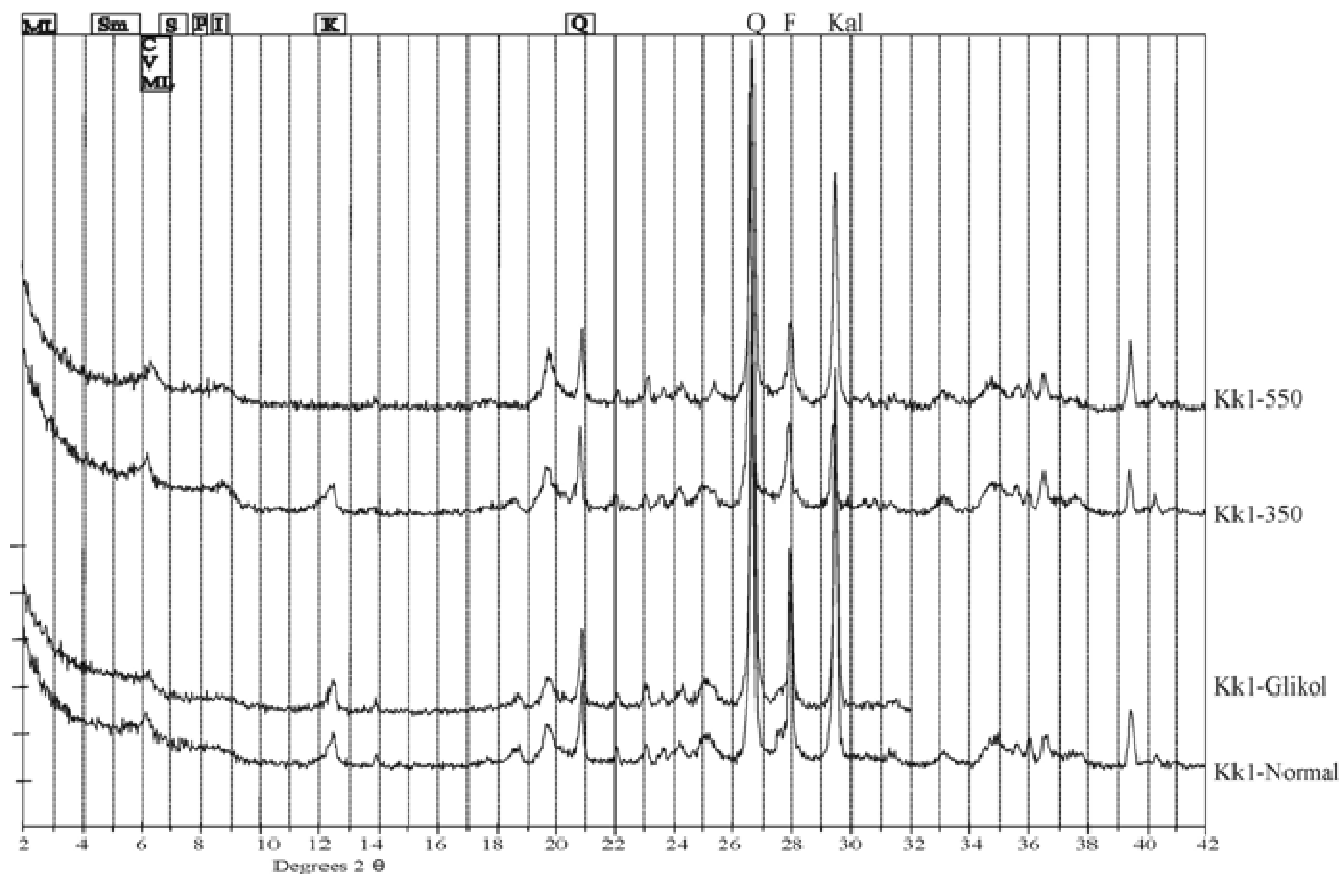


Figure 3. XRD spectrum of the clay sample belonging to the lower level (Kk1) of Kolsuz-Ulukisla clays (Q=quartz, F=feldspar, I=illite, ML=mixed layer clay, C=chlorite, S=smectite).

CaO. 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.

XRD measurements were employed to determine the mineral phases included in the same samples (Siemens D-5000 Diffract AT V 3.1 diffractometer, $CuK\alpha$ radiation $\lambda = 1.54056 \text{ \AA}$ and 0.03 steps; General Directorate of Mineral Research and Exploration laboratories-MTA, Ankara-Turkey). According to the XRD measurements (Figures 3 and 4), subject clays are found to composed of abundant quartz (20%), feldspar, calcite, smectite (3%), illite (32%), chlorite (45%) and trace quantities of palygorskite and Fe-oxide minerals. In the lower part of the clay profile (Figure 2), quartz tend 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.

DTA (Differential Thermal Analysis) and TGA (Thermogravimetric Analysis) measurements have been carried out for the determinations of the thermal behaviour of the clay samples (Figure 5). 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. Minute endothermic peak of smectite occurs in between $\sim 100 - 250^\circ\text{C}$, and second endothermic peak appears at $\sim 700^\circ\text{C}$ and shallow endothermic/exothermic peak is observed at $\sim 800 - 900^\circ\text{C}$. Best observed endothermic peak of chlorite in the DTA-grams is the one observed between $500 - 600^\circ\text{C}$. This peak may shift toward $\sim 700^\circ\text{C}$ due to the iron content. Subsequently this peak may fall in the same

interval with smectite's peak at $\sim 700^\circ\text{C}$. Chlorite's exothermic peak occurs at 750°C .

PETROLEUM FORMATION

In the recent years, one of the methods used in petroleum explorations is organic maturation and the other diagenesis of clay minerals. Results acquired through the first approach could be attained using the second method. Fundamental nature of the second approach can be explained as follow: Clays that immature or recently deposited may contain smectite (montmorillonite), illite and kaolinite depending on the source area. With subsidence, these minerals lose their water content and are subjected to mineralogical transformations. Smectite converts to illite within the range of oil formation temperature ($60 - 150^\circ\text{C}$). When the upper limit of this range was approached, kaolinite and illite convert to mica; if ferromagnesian minerals are available in the environment, these minerals transform to chlorite instead (Figure 6). Consequently, clays can give an idea about be the degree of maturation of a sample of interest. For the fields where oil explorations are carried out, clays can be used to answer following questions: (1) which layers has source rock potential, their regional coverage and relationship with the paleogeography; (2) source rocks occurs in what part and depth of the basin and which time interval have enough maturation; (3) when and how the oil migration occurred, and (4) the relationship with oil formation and oil migration (Hunt, 1995). However, time and duration plays an

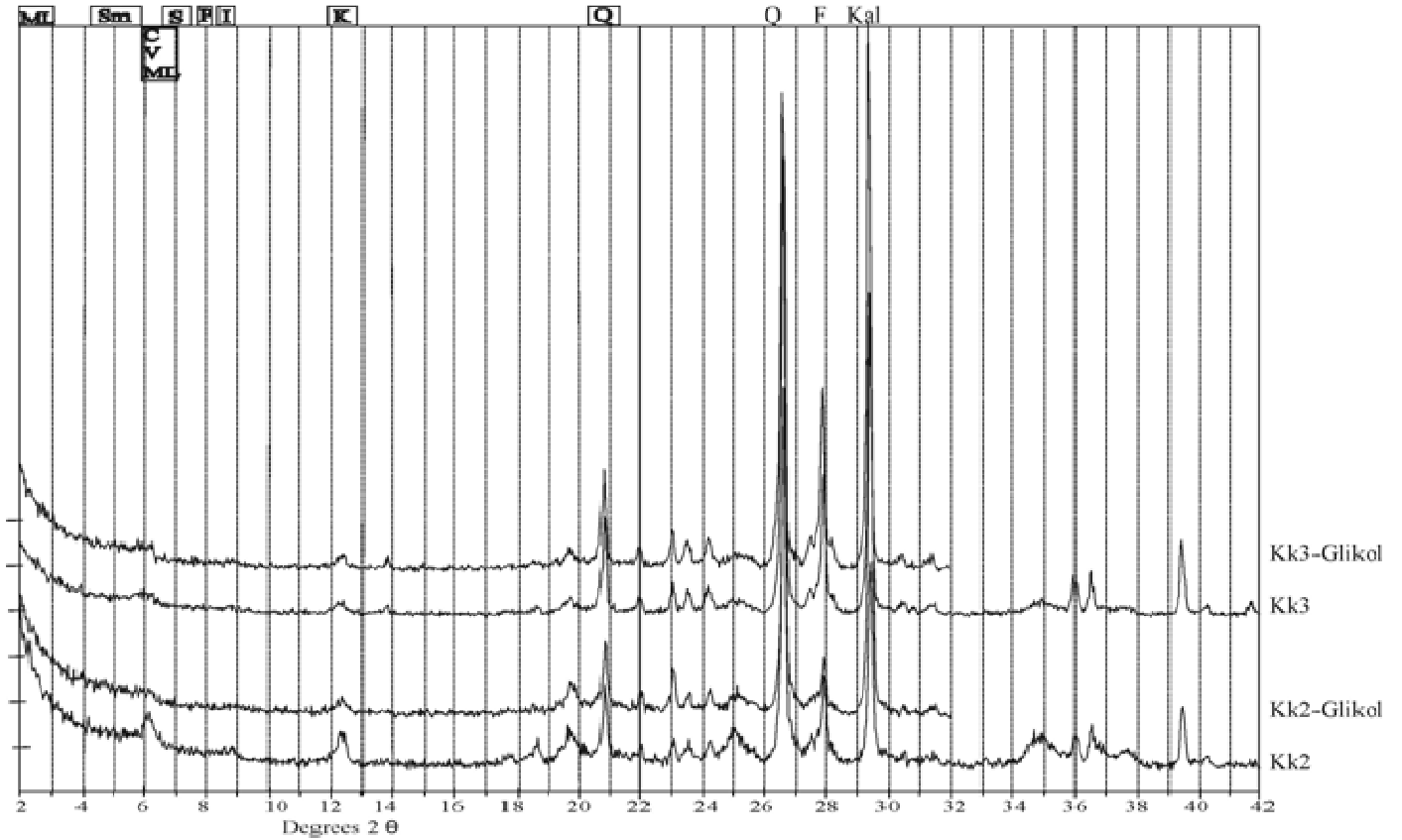


Figure 4. XRD spectrum of the clay sample belonging to the lower level (Kk2) and the upper level (Kk3) of Kolsuz-Ulukisla clays (Q=quartz, F=feldspar, I=illite, ML=mixed layer clay, C=chlorite, S=smectite).

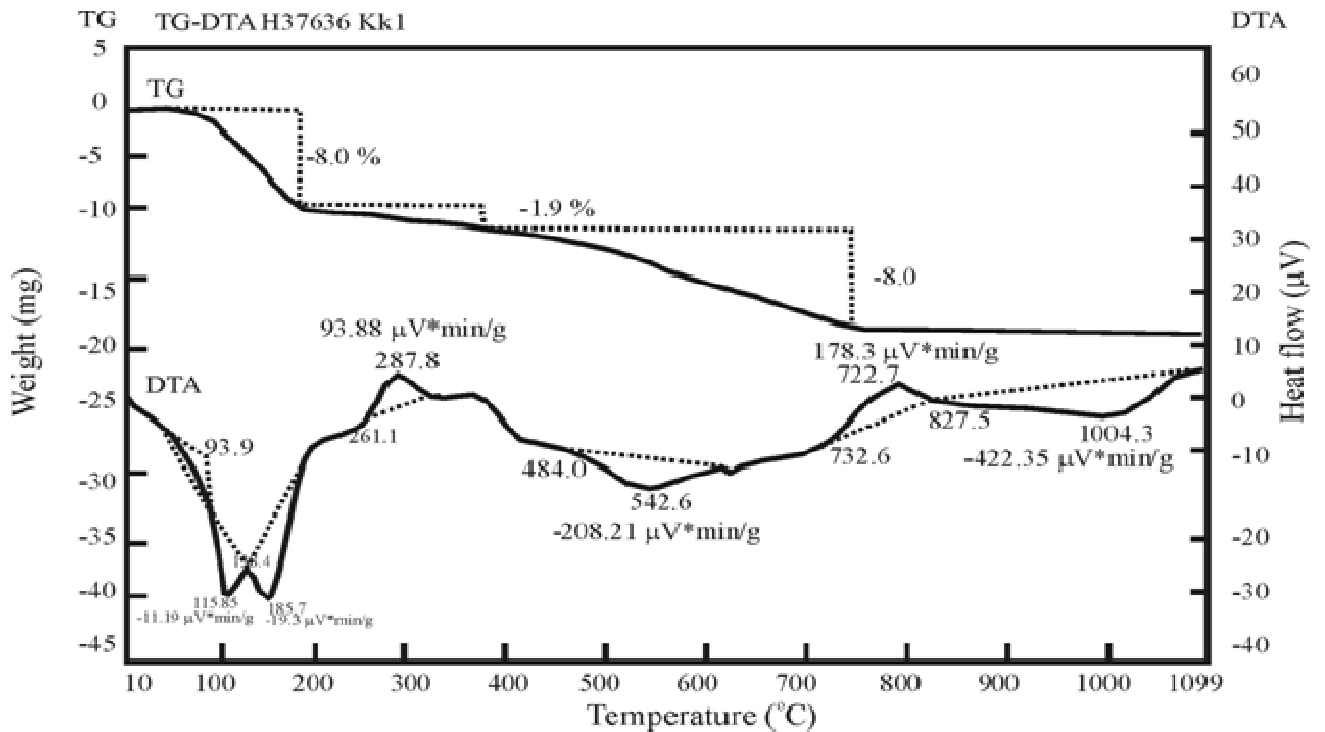


Figure 5. DTA-TGA measurements of the Kolsuz-Ulukisla clays.

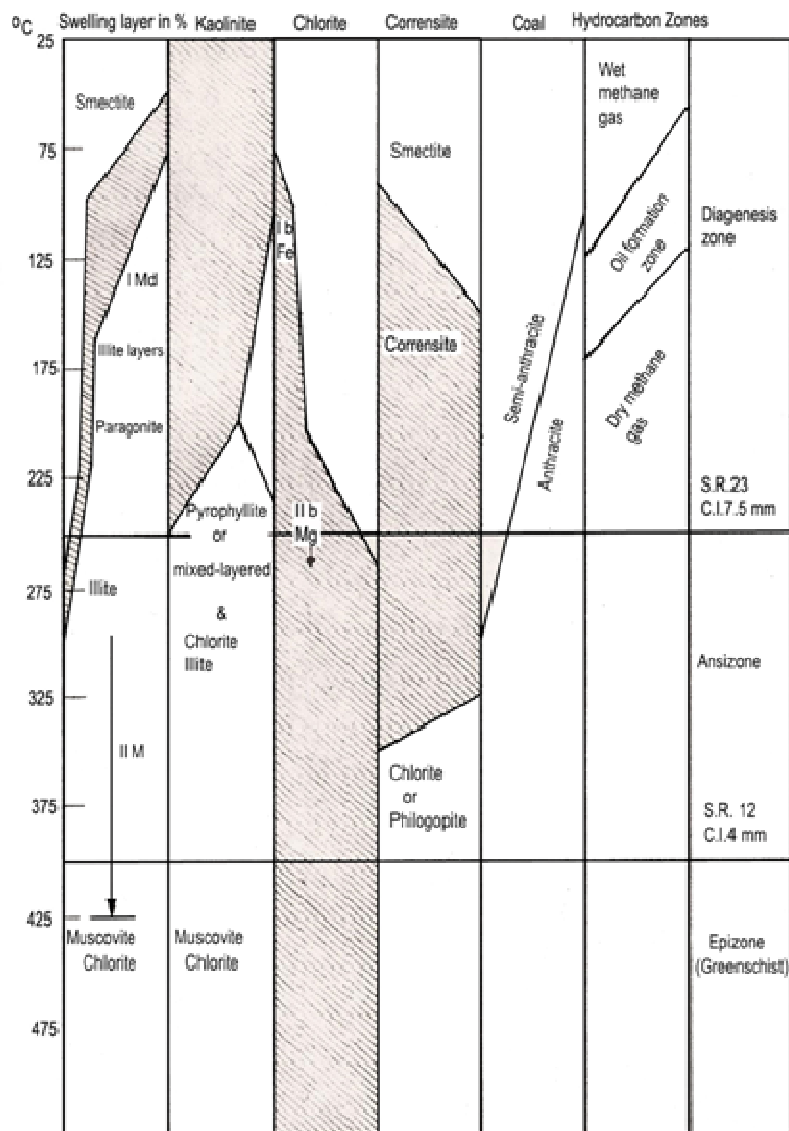


Figure 6. Diagenesis of clay minerals and oil formation zones in terms of temperature (adapted Weaver, 1960; Suchy et al., 2007).

important role in this process accompanying the mineralogical transformations.

Mineralogical changes of the clay minerals are closely related to the temperature and water chemistry of the environment. Thus, they reflect better and more precise transformation temperature (paleotemperature) of the clay minerals. Reflectance degree of vitrinite, a major organic component of coals, shows increase with increasing degree of metamorphism (Teichmuller, 1987). In diagenesis stage, reflectance degree of vitrinite is 5%. In this stage, organic matter is not mature enough to produce oil and the second stage is catagenesis (boundary is 2%). While oil formation takes place between 0.7 and 1.3%, wet gas occurs between 1.3 and 2%. Lower boundary of metagenesis is 4%, under which metamorphism starts (Bozkaya and Yalcin, 1996).

During diagenesis and metamorphism, mineralogical changes occurring in the clay structures give extent of such events of the sedimentary rocks. Structural characteristics and parameters of the

clay minerals are not unique for all depositional environments. However, depositional environments are characteristic to formation of certain clay minerals. Major parameters of sedimentary environment including pressure, temperature, subsidence, time, proton-electron concentration and metal-ion concentration greatly affect the clay mineral structures (Bozkaya and Yalcin, 1996). Most of the petroleum source rocks contain various clay minerals. Source rock properties like porosity and permeability vary depending on variety, abundance and distribution of the clay minerals (Bayar et al., 1987).

In the study area, the Kolsuz clays are loosely 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 of 12 samples from the Kizilbayir Formation indicated prevalent presence of feldspars, quartz, calcite, lithic fragments of volcanic, magmatic and

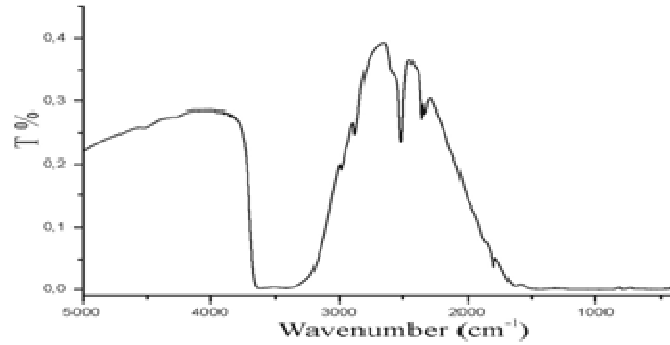


Figure 7. FTIR spectrum of the clay sample taken from the lower level (Kk1) of Kolsuz-Ulukisla.

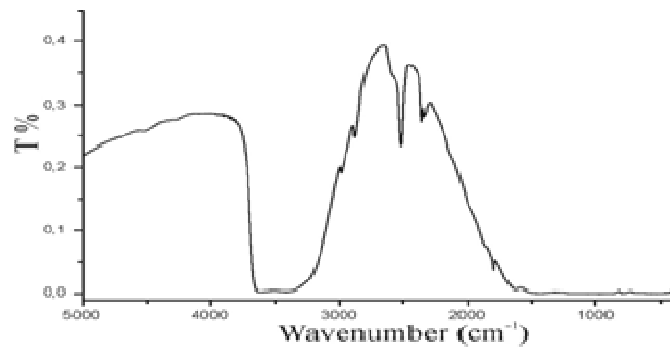


Figure 8. FTIR spectrum of the clay sample taken from the middle level (Kk2) of Kolsuz-Ulukisla.

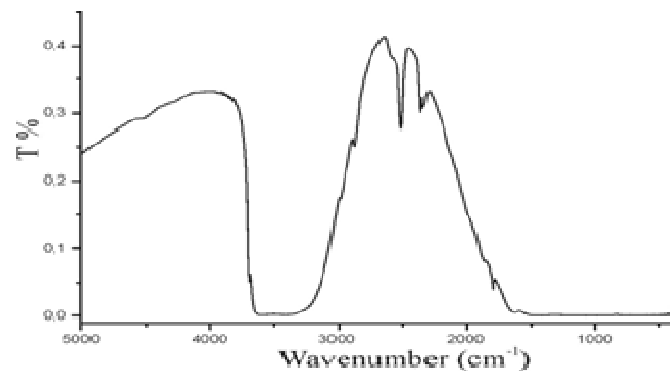


Figure 9. FTIR spectrum of the clay sample taken from the upper level (Kk3) of Kolsuz-Ulukisla.

metamorphic rocks, of carbonates (e.g., limestone and marl) and clastic sedimentary rocks (e.g., sandstone, claystone and greywacke) cemented chiefly by calcium carbonate (Gurel, 1999; Kayali et al., 2005).

RESULTS AND DISCUSSIONS

The clay samples were taken from three different levels

shown in the lithostratigraphic columnar section of a selected locality in the Kolsuz-Ulukisla region (Figure 2). The FTIR spectra of the samples taken from lower level (Kk1), middle level (Kk2), and upper level (Kk3) of Kolsuz-Ulukisla (Turkey) clay profile are given in Figures 7 - 9, respectively. Interpretation of the observed vibrational bands in these samples were carried out by comparing with those found in the world clay standards

Table 3. FTIR spectrum analysis results of Kolsuz-Ulukisla clay samples Kk1, Kk2, and Kk3 belonging to lower, middle, and upper levels, respectively.

Assignment	Kk1	Kk2	Kk3	Clay mineral type
	Wave number (cm ⁻¹)			
v(OH) stretching "shoulder"	-	-	3680	Illite
Inner-layer OH, (Al-O...H) stretching	-	-	3680	Na-Montmorillonite
v(OH) stretching	-	-	3660	Chlorite
v(OH) stretching	3622	3622	3622	Illite/Na-Montmorillonite
v(OH) stretching	2515	2515	2515	Calcite
δ(water-OH) scissoring	1731	1731	1731	Palygorskite
δ(water-OH) scissoring	1673	1673	1673	Palygorskite
v(Si-O) normal to the plane stretching	1090	1090	1090	Illite-smectite mixed layer
v(Si-O) planar stretching	1031	1031	1031	Illite-smectite mixed layer
v(Si-O) stretching	988	988	988	Chlorite
(Al-Al-OH) deformation	920	920	917	Na-Montmorillonite
OH deformation	905	905	905	Palygorskite
M-OH stretching	819	819	817	Chlorite
M-OH leaning	805	805	805	Na-Montmorillonite
v(OH) stretching	798	798	798	Quartz/Amorphous Silica/Feldspar
v(OH) stretching	788	788	788	Quartz
v(OH) stretching	697	697	697	Quartz
OH deformation	620	620	620	Na-Montmorillonite
(Si-O-Al) deformation	543	543	543	Chlorite
(O-Si-O) bending	520	520	520	Na-Montmorillonite
(O-Si-O) bending	468	468	468	Na-Montmorillonite/Palygorskite/Illite
(Si-O-Mg) deformation	441	441	441	Chlorite

with known fundamental vibration frequencies for illite, illite-smectite mixed layer, Na-montmorillonite, chlorite (ripidolite), palygorskite (Table 1) and the other clay standards. Results are listed in Table 3.

As seen from Table 3, all of the samples belonging to the lower, middle, and upper levels of Kolsuz-Ulukisla (Turkey) clay profiles Kk1, Kk2 and Kk3 respectively, include illite, illite-smectite mixed layer, Na-montmorillonite, chlorite, palygorskite, calcite, feldspar and quartz minerals. It means that these clays have the framework of silicate structure, such as T-O-T (Tetrahedral-Octahedral-Tetrahedral). On the other hand, H-O-H, Al-Al-OH, and Si-O-Si groups in their FTIR spectra was observed. This situation is attributed to the substitutions of different atoms in montmorillonite having different valance values displaying in clay samples.

The FTIR spectrum of the sample representing (as summarized in FTIR measurements) lower level (Kk1) of Kolsuz-Ulukisla profile has been taken to see effects of the heat treatments on the structure of the subject samples (Figure 10). 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. When results listed in Table 4 was interpreted with the one in Table 3, it was seen that the sample, Kk1, is composed of illite, calcite, chlorite, feldspar and quartz. Band assigned as vibrational frequencies for Na-montmorillonite and palygorskite were not observed after the thermal treatment. However, for illite at 916 and 833 cm⁻¹ (Al-Mg-OH) deformation and at 525 and 470 cm⁻¹ (O-Si-O) bending frequency bands were observed after the thermal treatment. This bands resulted due to re-arrangement of Al and Mg atoms within the crystal structure during the thermal treatment (Bishop et al., 2002).

Only v(Si-O) stretching at 988 cm⁻¹ among the vibrational frequencies of chlorite at 3660, 988, 819, 543 and 441 cm⁻¹ was not observed after the thermal treatment. This is because the organic molecules are forced into silicate layers during the thermal treatment. XRD data acquired from preheated sample (Kk1) between 350 - 550°C, indicated that chlorite and illite peaks were not shifted but smectite peak was shifted towards 10 Å. In the same sample, kaolinite should also be present, because the 7 Å peak disappears at 550°C.

Table 4. Results of the FTIR spectrum analyses of the clay sample (Kk1) from Kolsuz-Ulukisla (Turkey) after thermal treatment.

Kk1		
Assignment	Wave number (cm ⁻¹)	Clay mineral type
v(OH) stretching "shoulder"	3680	Illite
v(OH) stretching	3662	Chlorite
v(OH) stretching	3622	Illite
v(OH) stretching	3566	Chlorite
v(OH) stretching	3435	Chlorite
v(OH) stretching	2515	Calcite
v(Si-O) normal to the plane stretching	1090	Illite
v(Si-O) planar stretching	1031	Illite
(Al-Al-OH) deformation	916	Illite
(Al-MgI-OH) deformation	833	Illite
M-OH stretching	817	Chlorite
v(OH) stretching	798	Quartz//feldspar
v(OH) stretching	788	Quartz
v(OH) stretching	697	Quartz
(Si-O-Al) deformation	543	Chlorite
(O-Si-O) bending	525	Illite
(O-Si-O) bending	470	Llite
(Si-O-Mg) deformation	443	Chlorite

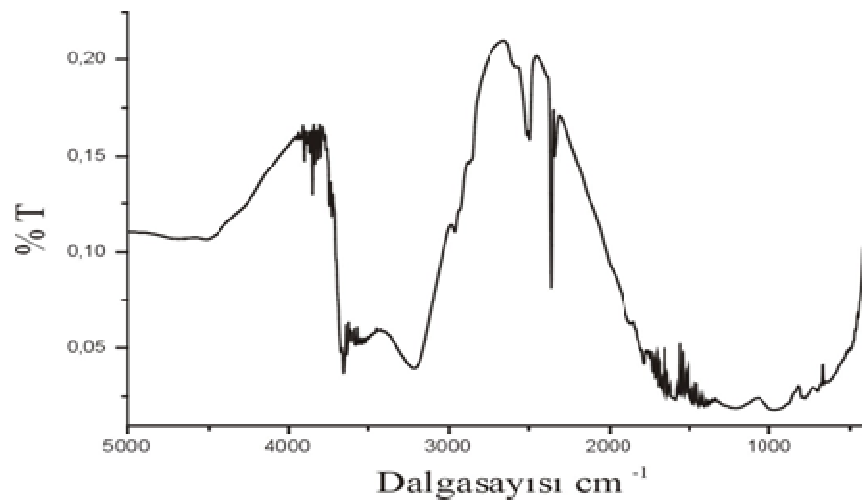


Figure 10. FTIR spectrum of the clay sample (Kk1) of Kolsuz-Ulukisla (Turkey) after thermal treatment.

Based on FTIR and XRD (even at slow scan) measurements, kaolinite was never observed. Thus we conclude that Kk1 does not include any kaolinite. v(OH) stretching vibrations of quartz at 798, 788 and 697 cm⁻¹ and v(OH) stretching vibration of calcite at 2515 cm⁻¹ remain the same after the heat treatment. As a result, we can say that the framework of silicate (T-O-T) structures of Kolsuz-Ulukisla-Nigde (Turkey) clay samples has not been destroyed.

Before the thermal treatment, in Kk1 and Kk3 samples, palygorskite's only bands including $\delta(\text{water-OH})$ scissoring vibrational bands at 1731 and 1673 cm⁻¹ (Frost et al., 2001), OH deformation bands at 905 cm⁻¹ and (O-Si-O) bending vibration band at 468 cm⁻¹ were observed. While illite's v(OH) stretching vibrational band appears as shoulder at 3680 cm⁻¹ in Kk3 clay samples, despite (O-Si-O) bending vibration band at 468 cm⁻¹ observed in Kk1 and Kk3 samples was assigned as belonged to

palygorskite, it could belong to Na-montmorillonite's (O-Si-O) bending vibration band. Similarly, vibration band observed at 3680 cm^{-1} in Kk3 sample was assigned as $\nu(\text{OH})$ stretching vibration band, it belongs to inner-layer OH, (Al-O...H) stretching band (Farmer and Russell, 1964). In samples Kk1 and Kk3, when bands assigned at 3622 , 920 , 805 , 620 , and 468 cm^{-1} were evaluated altogether; they appear well-matched with fundamental vibration bands of Na-montmorillonite standard. But vibration band at 920 cm^{-1} of the Na-montmorillonite standard clay was observed at 917 cm^{-1} in Kk3 sample.

In XRD measurements, characteristic peak of glycol-saturated montmorillonite is 17 \AA peak. As it disappears, mineralogical conversion of montmorillonite to illite becomes evident. As a consequence of chemical reactions depending on increasing depth and temperature, increase of Al and decrease of Si in montmorillonite's tetrahedral layers results in changes in tetrahedral structure and by taking-up K ions available in the environment due to feldspar alteration, montmorillonite converts to illite (Weaver, 1960; Suchy et al., 2007). Expelled water as result of this change results in an increase in salinity of connate water already present in shale. Mg, Si and Ca ions, products of such conversion, could form minerals like calcite and dolomite facilitated by increasing temperature and these new minerals deposit within shale. This in turn results in a decrease in porosity and permeability and an increase in density (Bishop et al., 2002; Dunoyer de Segonzac, 1970).

Montmorillonite, being very sensitive clay mineral to temperature and depth, play an important role in both oil formation and its migration. As a result of reactions occurring in association with increasing temperature and depth, montmorillonite converts to illite losing its structural water (smectite converts to illite in alkaline environment). This conversion occurs at about $2500 - 4500\text{ m}$ burial depth and at 100°C . In this process, K contents of pore waters show increase. Organic matter requires H ions to become hydrocarbon. H ions facilitate structural break-down (so-called cracking) of hydrocarbons with large organic molecules to smaller ones. During the loss of water from montmorillonite, H ion concentration of the environment raises. Water expulsion takes place at fairly steady and regular temperature. Some of the layers start losing water at $50 - 60^\circ\text{C}$ through 300°C . About $70 - 80\%$ of the water is expelled between $120 - 160^\circ\text{C}$ that corresponds to the formation of petroleum. This study suggests that results acquired from the organic maturation can be obtained through spectral analysis of structural changes occurring in clay minerals.

ACKNOWLEDGEMENTS

We would like to thank Turkish Scientific and Technological Research Council (TUBITAK-Turkey) for

the financial support (project code: CAYDAG 2005-101Y067). Professor Dr. Cigdem Ercelebi (Department of Physics, Middle East Technical University, Turkey) is also gratefully appreciated for the FTIR.

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