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CLAYS IN DENIZLI REGION (SOUTHWESTERN ANATOLIA), TURKEY

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Abstract: In this region, marine, continental and lacustrine clay deposits which are used as a raw material in the cement sector were investigated. It is seen that Upper Cretaceous-Upper Eocene shales representing marine deposition are found in Malidagi in economic quantities. However, their Na_2O % and K_2O % contents are higher than in other clays. The Oligocene aged Bayiralan clay representing marine deposition have abundant magnesian minerals. Because of its high MgO % content, this clay is not suitable cement standard. The areal extent of the Upper Miocene-Lower Pliocene Kizilburun clays represented fine sediments in the floodplain are widely situated. These may be used in cement sector, but they have reserve and environmental problems. The red coloured clays belonging to the Pliocene Sakizcilar Formation are sutitable for cement standard. To decreasing the transportation costs of the Denizli cement factory, the Malidagi clay and Sakizcilar clay may be used together in different proportions. If the Malidagi and Sakizcilar clays may be used, the contents of K_2O % and Na_2O % will decrease.

Key words: petrographic properties, different clay occurrences, suitable cement standard.

Introduction

The first studies related to a large part of the Denizli region (Nebert 1958) describe the geology of the region in general (Fig. 1). The stratigraphical features of the Denizli Neogene sediments were investigated by Taner (1973, 1974). Şimşek (1982) contributed the features of geothermal areas. The clay occurrences in the Neogene sediments were investigated by Ovayurt (1984) and Özpinar et al. (1995), Gürel (1997), Özpinar & Hançer (2000a,b,c) for possible use as a raw material in the cement sector. Sun (1990), Konak et al. (1990), Sözbilir (1994), Özpinar (1987, 1988, 1994) studied stratigraphical and structural features of Denizli and its surrounding areas. Altunel & Hancock (1993) studied the Quaternary tectonics of the Pamukkale travertine. Okay (1989) divided the Honaz Mountain into several tectonic units differing from each other in term of their depositional conditions, stratigraphy, metamorphism, rock types and structural positions.

Geological settings

At the basement of the studied area, the Upper Cretaceous-Upper Eocene Malidagi Formation is situated (Figs. 2, 3). The Malidagi Formation consists of laminated clay, laminated sandy clay, laminated silty clay, and intercalated sandstone and marl. This unit is autochthonous and is overlain by the Jurassic-Cretaceous Çökelez Limestone with a tectonic boundary (Fig. 4). The Çökelez Limestone is overlain by the Karetepe mélange with a tectonic boundary. The Karatepe mélange rocks are mainly composed of basic and ultrabasic rocks and huge blocks of crystalline limestones. The Karatepe mélange body was emplaced in this region in the Upper Cretaceous (Campanian).

All of these formations at the basement are overlain with angular disconformity by the Oligocene "Karadere Formation" represented by alluvial fan and deltaic deposits. This unit is represented by conglomerates, sandstone and siltstone. Karadere Formation is conformably overlain by the Oligocene

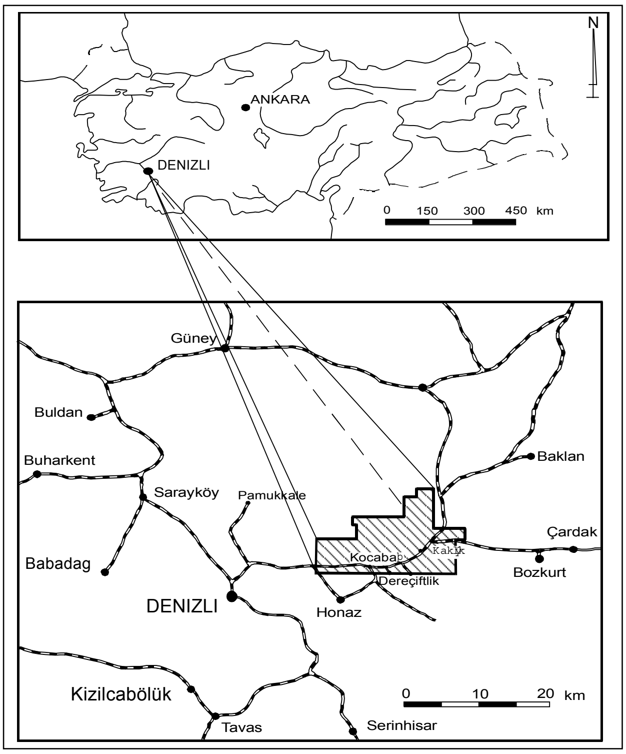

Fig. 1. Location map.

"Bayiralan Formation", made up of sandstone, marl, limestone and claystones deposited in a shallow sea environment. These formations at the basement are overlain with angular disconformity by the Upper Miocene-Lower Pliocene "Kizilburun Formation" represented by conglomerate, sandstone, siltstone and clay formed in alluvial fan and lacustrinal fluvial environments. The Kizilburun Formation is conformably overlain by the Lower Pliocene "Sazak Formation" made up of limestone, travertine, sandstone and clay representing lacustrine environment sediments. The Sazak Formation is conformably overlain by the Pliocene Sakizcilar Formations made up of sandstone, marl, silty claystone and clay representing alluvium fan and lacustrine sediments. There are small clay deposits in Quaternary alluvium. One of these is found in the area of the southwesthern part of Karapinar village.

Method of study

The purpose of this paper is to report the results of detailed study of clay in the Belevi, Yokuşbaşi, Kaklik, Gürleyik and Kocabaş (Denizli regions) and its surrounding area (Fig. 1). In this study, an area of about 178 km^2 was mapped in detail (1 : 25,000 scale). Then about 8 km^2 of the Malidagi area was mapped on a scale of 1 : 500, an about 12 km^2 of the Kizilburun-Gürleyik, Kizilburun-Kaklik, Kizilburun-Belevi areas was mapped on a scale of 1 : 2000. 683 specimens obtained from drilling hole and opened channel were examined by microscope, XRD, DTA, XRF and SEM. The clay minerals were determined by XRD and DTA (26 samples) and electron microscope (8 sample). The chemical analyses of the clays were carried out by XRF in the Denizli Cement Factory Laboratories, Turkey. The raw mix prepared by iron ore, limestone and Malidagi shale was heated at different temperatures. At 1250 °C, 1350 °C and 1400 °C, the free lime amount was determined and mineralogical structure was obtained by X-ray patterns.

Results and discussion

In the clays the following petrographical properties were identified by microscope, XRD and DTA methods (Figs. 5, 6 and 7).

The laminated clay, laminated sandy clay and laminated silty clay of the Malidagi Formation investigated under the microscope contain quartz (3–15 %), calcite (2–10 %), albite (2–5 %), muscovite (0–2 %), opaque minerals (2–5 %), iron oxides (5 %), chlorite (5 %) and clay minerals (65–90 %). From one location to other, the shale includes silty and sandy material made up of quartz, calcite and albite. The results of XRD were the same with as results of polarizing microscope, which contains quartz, calcite, albite chlorite, montmorillonite and illite (Fig. 5a). In the laminated clay rocks, illite was obtained in abundance. Dark green laminated clay contains chlorite with illite and montmorillonite. In the gray laminated clay, chlorite was not obtained.

Oligocene Bayiralan clay contains abundant illite and a small amount of montmorillonite, as well as quartz, feldspar, dolomite, calcite, chlorite, clinochrysotile and opaque minerals (Fig. 5b). It can be seen that magnesian minerals such as chlorite, clinochrysotile have a negative effect on the chemical compositions of the clays.

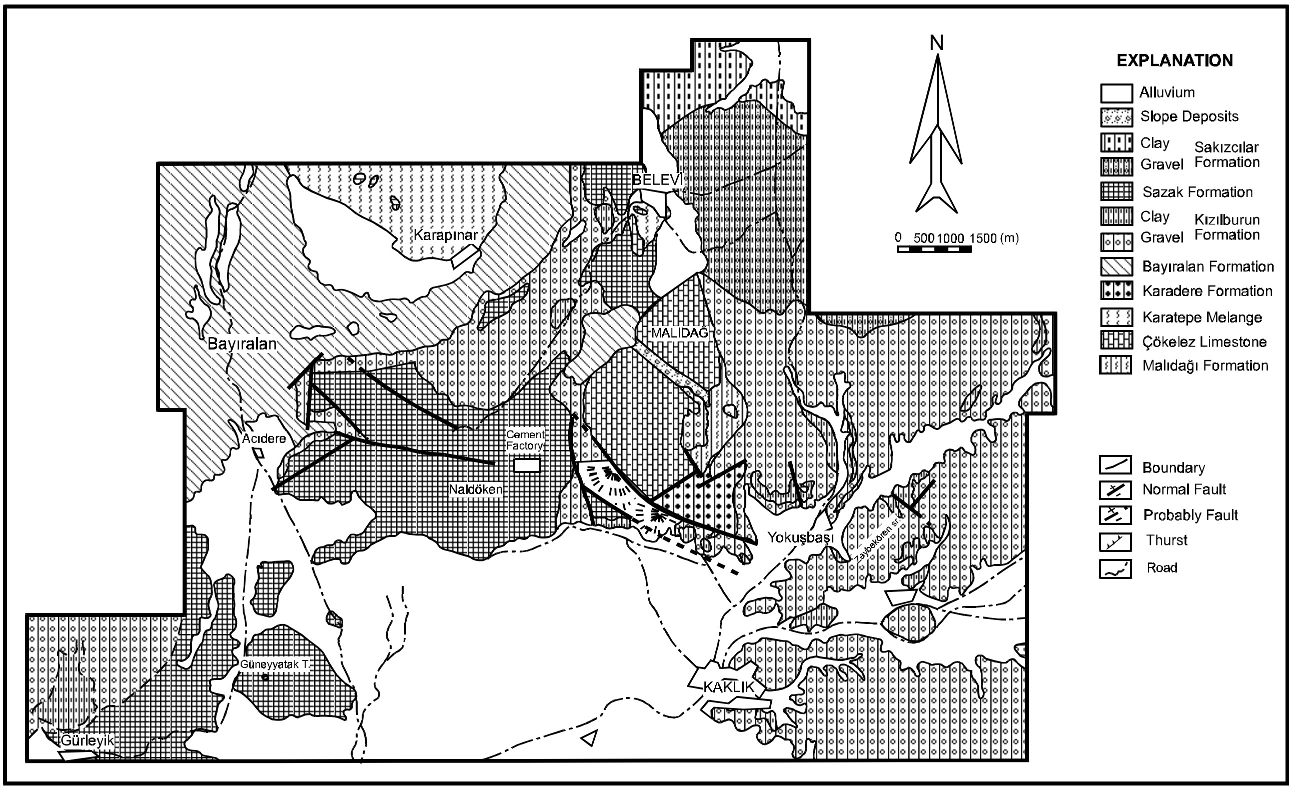

Fig. 2. Simplified geological map of investigated area.

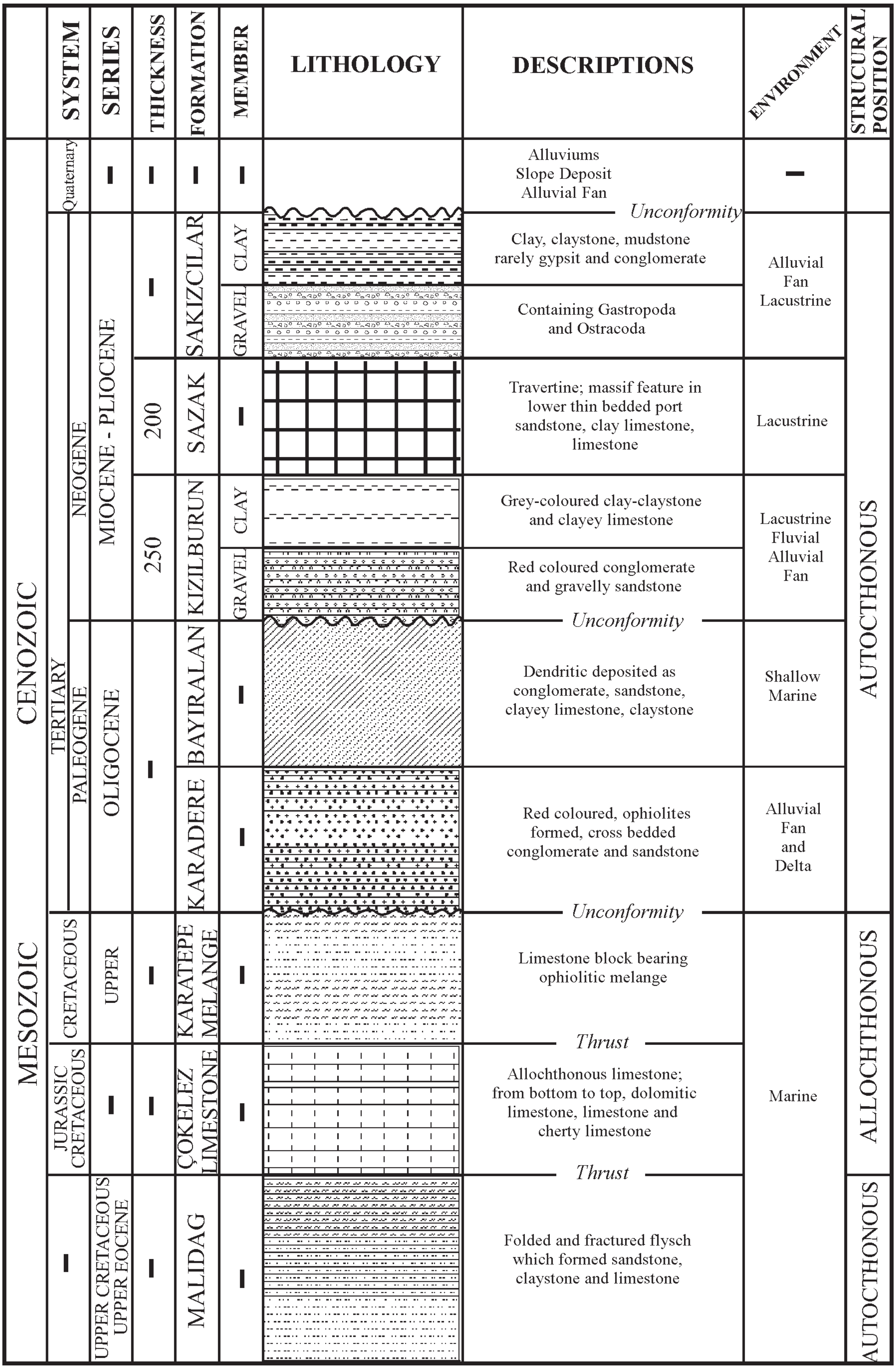

Fig. 3. Generalized tectono-stratigraphic section of the investigated area.

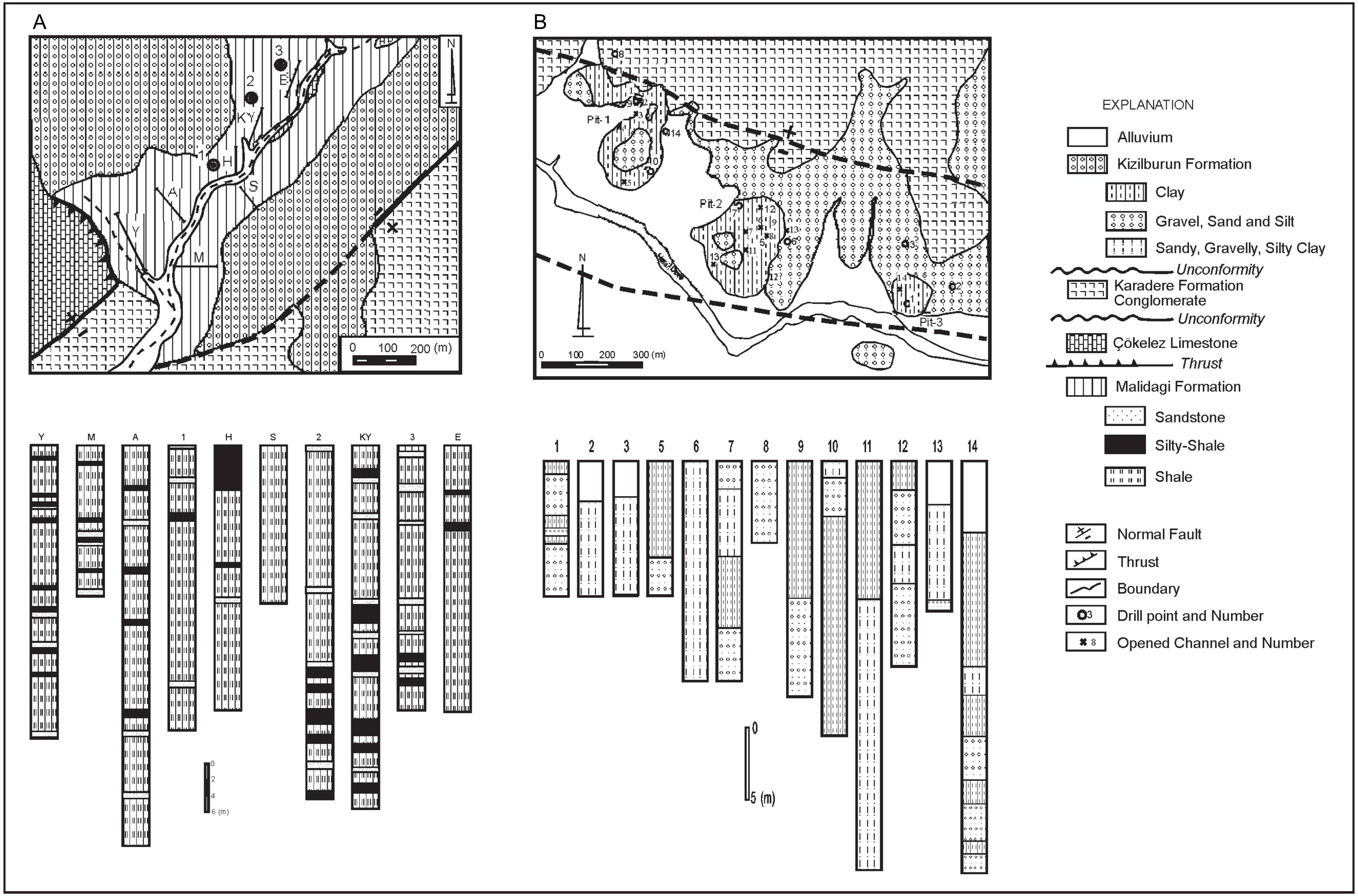

Fig. 4. Simplified geological maps and locations taking specimens and their columnar sections. Malidagi shale **(A)**, In the Denizli cement factory clay area, Kizilburun Kaklik-2 clay **(B)**.

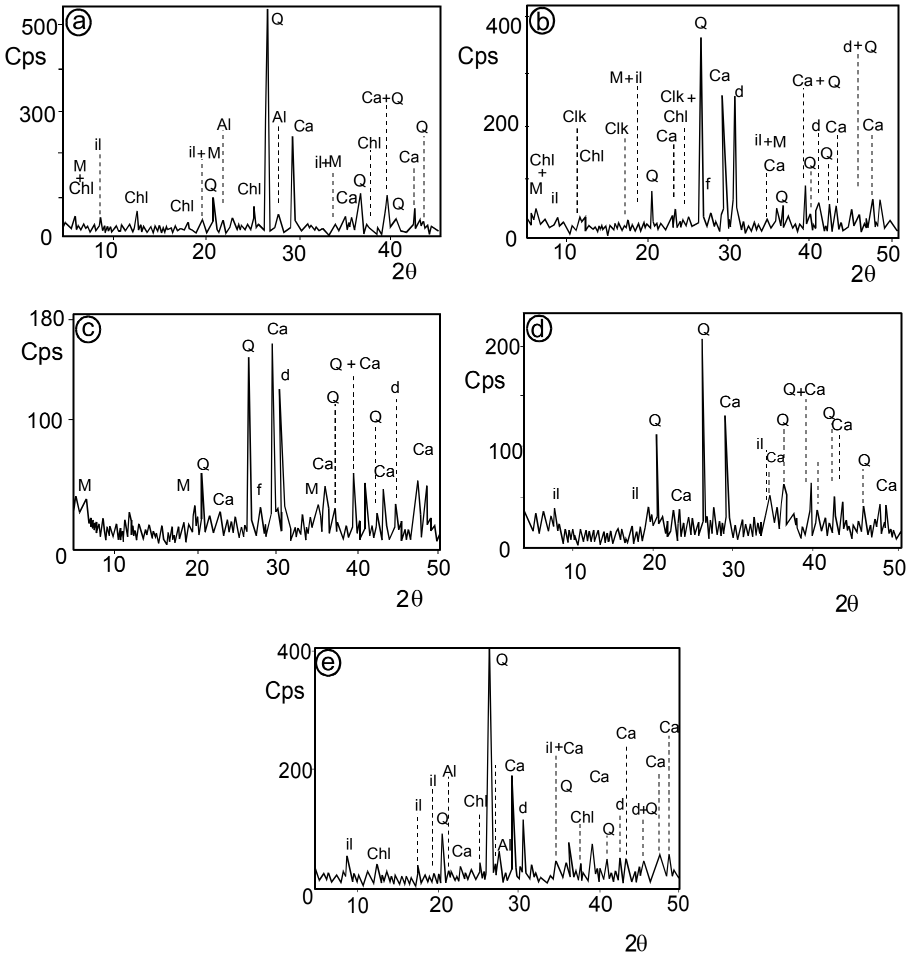

Fig. 5. X-Ray diffractograms of Malidagi shale **(a)**, Bayiralan clay **(b)**, Kizilburun clay **(c)**, red colour clay of the Sakizcilar Formation **(d)**, and Quaternary clay **(e)**. Chl — Chlorite, il — Illite, Al — Albite, Ca — Calcite, Q — Quartz, M — Montmorillonite, d — Dolomite, Clk — Clinochrysotile, f — Feldspar, S — Sanidine.

The Upper Miocene-Lower Pliocene Kizilburun clay contains illite, montmorillonite, quartz, feldspar (albite, sanidine), dolomite, chlorite (Fig. 5c). One of these clay occurrences named Kaklik-2 has been used in the Denizli cement factory since 1986, but it may be used up in one or two years. Silty, sandy and gravelly levels and grains in clay levels and/or beds cause changing of chemical compositions.

The mineralogical composition of the Pliocene Sakizcilar clay is same as the Kizilburun clay (Fig. 5d) but they are red in colour and they are found with intercalated thin limestone layers. On the other hand, the bottom of some locations of the Sakizcilar Formation has very thick marl levels. But owing to the fact that the marls have some problems such as high MgO%, they are not suitable for the cement sector (Table 1). Quaternary clays contain illite, quartz, calcite, dolomite, albite and chlorite (Fig. 5e).

Malidagi shale was examinated by DTA analyses method. According to differential thermal curves, illite shows a loss of adsorbed water at about 100 °C, montmorillonite and chlorite show a loss of adsorbed water at 100 °C (Fig. 6). The first endothermic peak shows between about 100 °C and 300 °C. These peaks appear after the loss of crystal water from the clay minerals. The dehydroxylations of illite, montmorillonite and chlorite begin at 400 °C. The loss of hydroxyls from illite begins at about 400 °C and may continue to about 900 °C. In illite dehydration appears at about 550 °C. In montmorillonite, a second endothermic peak appears at about 600 °C. The third endothermic peak appears between about 870 °C and 877 °C. The third endothermic peak shows the structural change. The last endothermic peaks between about 1197 °C and 1292 °C show the melting point. Both phases persist up to 1292 °C.

After doing detailed mapping of the promising areas such as the area of Kaklik-2, Belevi, Gürleyik, Malidagi (Figs. 5, 6, 7) were taken orderly specimens. A total of 683 specimens were taken from the whole studied areas for chemical and petrographical investigations. The results of average chemical analysis from the clay occurrences are given in Table 1.

The values of high SiO_2 %, Al_2O_3 %, Fe_2O_3 % and total alkali (Na_2O % + K_2O %) are seen in the Malidagi shale (Table 1) and the values of low SiO_2 %, Al_2O_3 %, Fe_2O_3 % and total alkali (Na_2O % + K_2O %) in Kizilburun-Kaklik-2 clay. On the other hand, the value of high CaO % is seen in the Kizilburun Kaklik-1 clay (Table 1) and the value of low CaO % seen in the Malidagi clay. It can be seen that sandstone and siltstone intercalated beds in the shale have a negative effect on the chemical composition of the shale.

Table 1: The results of chemical analyses of total 683 clay specimens from different clay occurrences in studied area.

Channel and drilling	Spe. Numb.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI	TOT.	SM	AM
Malıdağı clay	299	53.54	13.19	6.51	8.19	3.37	0.01	0.99	2.46	9.41	98.07	2.78	1.99
Bayıralan clay	11	35.24	5.72	5.8	17.9	10.46	1.21	0.50	0.77	21.05	98.70	3.22	0.99
Kızılburun Belevi	44	36.31	8.20	5.14	21.35	5.09	0.07	0.29	1.34	21.86	99.84	2.72	1.59
Kızılburun Kaklık-2	55	35.19	7.31	4.29	23.94	3.74	0.01	0.39	1.01	23.82	99.72	3.03	1.70
Kızburun Kaklık-1 (Yokuşbaşı)	77	39.15	7.85	5.25	19.19	4.16	0.01	0.55	0.93	19.90	99.71	2.90	1.49
Kızılburun Gürleyik	159	49.95	7.93	5.88	13.13	3.41	0.48	0.99	1.51	13.85	97.13	3.61	1.34
Sakızcılar clay	17	46.64	10.29	6.10	13.90	3.54	0.02	0.48	1.37	14.39	96.78	2.86	1.64
Sakızcılar Marl	13	41.37	6.62	5.77	17.37	7.23	0.3	0.38	0.84	19.83	99.54	3.37	1.14
Alluvium clay	8	41.93	9.50	5.76	15.02	4.93	0.37	0.96	1.84	15.79	96.13	2.80	1.64
Total	683												

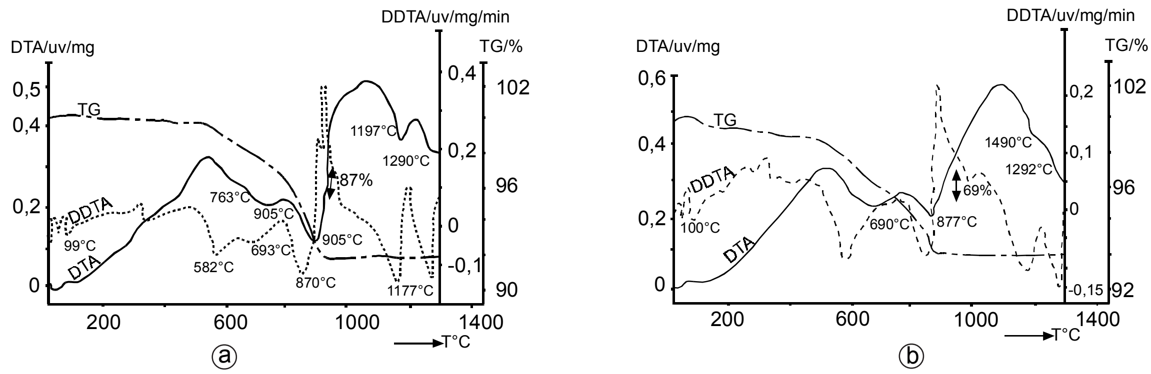

Fig. 6. Differential thermal curves of shale (Malidagi) samples. TG curves show the changing weight % of the samples dependent on the increase of temperature (disappearing weight % on the sample up to 1000 °C shown on the thermograms). DDTA curve show the derivative of DTA curve.

Because of the marine deposits, decrease and increase of the chemical composition of the Malidagi shale is regular. Whereas cross bedding of gravel and sand is found in the Kizilburun clays. Owing to the thickness and length of gravel and sand cross bedding, the chemical composition of the Kizilburun clays changes from one location to the other in an irregular way (Fig. 4).

The average value of MgO % in the Bayiralan clay is higher than in the other clays and the average value of MgO % is 10.46 %. In the Kizilburun Belevi clay and Sakizcilar marl, the values of MgO % are 7.23 and 5.09 % respectively and these values are higher than the Portland cement standard. The modulus of silica is between 2.72 and 3.61. The high values of the modulus of silica are seen in the Kizilburun Gürleyik clay, Sakizcilar marl and Bayiralan clays (Table 1). These are 3.61 %, 3.37 % and 3.22 %, respectively. They are higher than the Portland cement standard values (the modulus of silica values is suitable between 1.9 and 3.2 and accepted values are between 2.2 and 2.6 at Turkish cement factories).

The modulus of aluminum is between 0.99 and 1.99. The high values for modulus of aluminum of 1.99 is seen in Malidagi clay. The low value for modulus of aluminum of 0.99 is seen in the Bayiralan clay. The standard values for modulus of aluminum are between 1.0 and 4.0. The suitable and accepted values in Turkish cement factories are between 2.2 and 2.6. Owing to their higher MgO % contents the Bayiralan clay and Sakizcilar marl were excluded. The values of modulus of the investigated area clays are within the Turkish Standard.

According to the results of the investigations, shales suitable as a raw material for the cement sector occur in Denizli (Turkey). They are found in abundance in the Malidagi and Honaz mountain region. So, in the Turkish cement manufacturers' association laboratory, the raw mix prepared by iron ore, limestone and Malidagi shale was heated at different temperatures such as 1250 °C, 1350 °C and 1400 °C. At these temperatures the free lime amount was determined and the mineralogical structures were obtained by X-ray patterns (Fig. 7). The amounts of free lime at 1250 °C, 1350 °C and 1400 °C are 24.11 %, 4.78 % and 2.56 %, respectively (Figs. 7, 8).

According to Fig. 7a, in normal clinker, the C_3S peak forms at 52 degree and the C_2S peak forms at 31–32 degrees. As can be seen in Fig. 7a, C_2S and C_3S peaks did not form, because clinkerization of the raw mix did not take place until 1250 °C. It is understood that the peak of free lime found at 37–38 degrees is higher than the normal clinker. As a result, it can be seen that clinkerization is not completed.

According to Fig. 7b, the peak of free lime found at 37–38 degrees is higher than the normal clinker. Respecting normal clinker, free lime is higher than 2 %. Because of high free lime, clinkerization was not completed at about 1350 °C.

According to Fig. 7c, free lime is still found in the clinker at a level of 2.65 %. It is understood that clinkerization had not

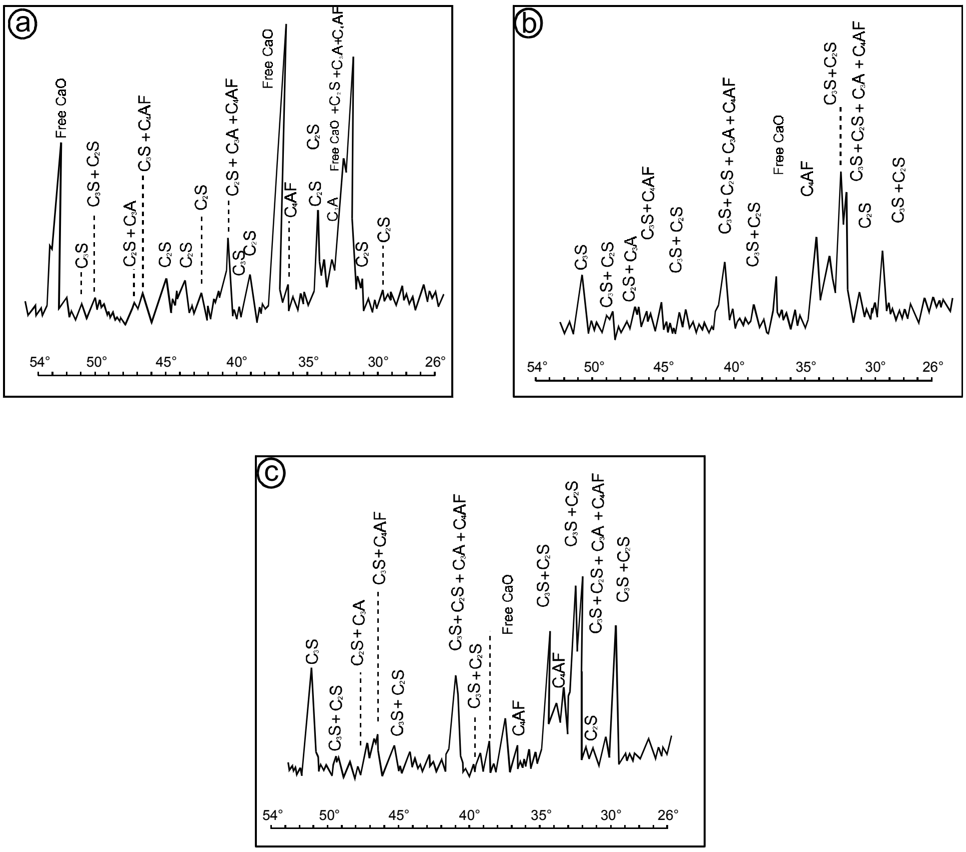

Fig. 7. X-ray diffractograms of clinker samples burnt at about 1250 °C **(a)**, 1350 °C **(b)** and 1400 °C **(c)**, respectively. C_3S — tricalcium silicate (Ca_3SiO_5), C_2S — dicalcium silicate (Ca_2SiO_4), C_3A — tricalcium aluminate ($Ca_3Al_2O_6$), C_4AF — tetracalcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$).

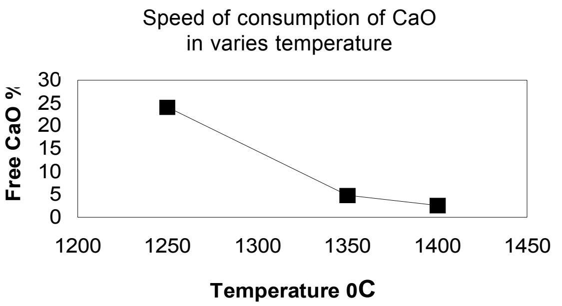

Fig. 8. Shown as a graphic of the speeds of consumption of CaO between 1250 °C and 1400 °C.

completely finished, at about 1400 °C. This situation may have happened to the various proportions of poorly heated material in the shale, which includes mineral such as quartz, albite and chlorite. As a result of investigation, it was found that the raw material mixing with the Malidagi shale had a clinkerization temperature of 1400–1450 °C.

At the end of this experimental study, the whole problems were kept in view. For production of clinker, the raw mixing material was prepared from iron ore, limestone and shale, in Denizli cement factory (Table 2). Clinker was formed after using light green laminated clay and grey laminated clay. The mixing ratio of raw materials and chemical analyses and the chemical conclusions of clinker are given in Tables 2 and 3.

Table 2: Chemical composition of raw materials (Modulus of silica — 2.3).

Oxide% Raw Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	LOI	MgO
Limestone	52.18	2.06	0.57	0.41	42.2	0.83
Clay	7.72	54.49	13.08	6.29	22.0	3.47
Iron ore	2.9	16.01	5.37	67.74	4.89	1.44

Table 3: Chemical composition of clinker (Standard of lime — 95.95, modulus of silica — 2.2, modulus of hydraulic — 2.1, modulus of aluminum — 1.33, C_3S — 64.83).

Oxide %	CaO	SiO_2	Al_2O_3	Fe_2O_3	LOI	MgO
Clinker	66.55	21.51	5.46	4.084	0	2.2

Conclusions

The following conclusions have been reached from the geological, petrographical and petrochemical investigation carried out in the Denizli region.

1. The average MgO % of Bayiralan clay is higher than in the other clay occurrences, because magnesian minerals such

as chlorite, clinochrysotile are abundantly found. In addition, the Sakizcilar marl has a high MgO % content. Both Bayiralan clay and Sakizcilar marl are not suitable for the cement standard.

2. In this study, it is seen that economic clay beds are found in Malidagi (Malidagi shale). The amount of their Na_2O % and K_2O % contents are higher than the other clays and they contain the various proportions of difficult to burn mineral such as quartz, albite and chlorite. As conclusion, the shale of the investigated area is suitable for use as a raw material for the cement sector. But, it is proposed that the shale may be used by mixing various proportions of the other clays found in the neighbouring area.

3. The areal extent of the Kizilburun Formation is widely spread over the Kaklik-1, Kaklik-2, Gürleyik and Belevi regions (Figs. 2, 3 and 4). The Kizilburun clay may be used in the cement sector, but its bedding sizes are small. The Kizilburun Belevi clay and clay marl contain intercaleted sand and gravel levels. The sand and gravels are generally include serpentinized harzburgite, dunite, gabbroic and doleritic materials, dolomitic limestone, quartzitic rocks and such as with quartz, calcite, albite, sanidine minerals. These situations effect the chemical compositions. The same problems are found in the Gürleyik region. It is proposed that the Kizilburun clays may be selectively worked. The gravel levels may be thrown away in the clay stock area. If the Kizilburun clays are selectively worked, they may be used in the cement sector.

4. Clay is produced for the Denizli cement factory in the Kaklik-2 region belonging to the Kizilburun Formation. The clay production in this area may be stopped within one or two years, because of limited reserves of clay. The Kaklik-1 Belevi and Gürleyik clays belonging to the Kizilburun Formation have sandy and gravelly levels like the Kaklik-2 clay which this situation effects to change of chemical composition were obtained.

5. The red coloured clays belonging to the Sakizcilar Formation are suitable for the cement standard so there is no reserve problem. Other clay occurrences are found long distances from the Denizli cement factory. The deviation of chemical composition is low. Thin limestone beds intercalated in clay may have caused the deviation of the chemical composition of the clay.

6. To decrease the transportation costs of the cement factory, the Malidagi shale and red coloured clay belonging to the Sakizcilar Formation located in the northern part of Belevi village may be used together in different proportions. If the Malidagi shale and Sakizcilar red coloured clays may be used, the contents of K_2O and Na_2O will decrease.

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