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THE GEOLOGY AND ORIGIN OF SEPIOLITE, PALYGORSKITE AND SAPONITE IN NEOGENE LACUSTRINE SEDIMENTS OF THE SERINHISAR-ACIPAYAM BASIN, DENİZLİ, SW TURKEY

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Abstract—The Serinhisar-Acıpayam basin of western Anatolia hosts a Neogene alkaline lake which formed in some graben and semi-graben depression zones as a result of N–S tension. The basin is filled with fluvial and lacustrine sediments dominated by clayey materials. The filling of the basin with fine sediments and associated water level changes caused the development of swampy and/or semi-swampy, alkaline-lake environments where sepiolite, palygorskite, saponite and dolomitic sepiolite or palygorskite precipitated periodically in the basin. Sepiolite is predominant in the Kuyucak section and is intercalated with saponite-dominated levels, whereas saponite accompanied palygorskite at Kocapınar where basaltic volcanism occurred. The contacts between sepiolite-palygorskite and saponite levels are more or less sharp, reflecting rapid changes in the physicochemical conditions of the depositional environment. Micromorphological images reveal that both sepiolite and palygorskite grew as interwoven fibers or fiber bundles and masses where dolomite was absent, indicating direct precipitation from solution, whereas fibrous networks grew authigenically on and out of dolomite in dolomitic sepiolite and dolomitic palygorskite. Saponite is either green or reddish brown due to its organic material-rich content and derivation from products of basaltic volcanism. Synsedimentary basaltic volcanism was the main source of Fe and Al, whereas Si and Mg were derived from surrounding ultrabasic and detrital units and partly from the volcanism. It can be concluded that sepiolite, palygorskite and saponite formed either by direct precipitation from alkaline lake water or authigenically from interstitial pore-water between dolomite rhombs as controlled by concentration of Si, Mg, Al and Fe, rather than by mutual transformation.

Key Words—Denizli, Lacustrine Environment, Palygorskite, Saponite, Sepiolite, Turkey.

INTRODUCTION

Although this is the first reported occurrence of sepiolite and palygorskite from the Denizli Province, sepiolite from the Eskişehir Province (central Anatolia) has been known since the 18th century. It occurs there as nodules and in beds in a lacustrine environment (Akıncı, 1967). Sepiolite in the Eskişehir region occurs predominantly in Lower Pliocene gypsum-bearing clays and in dolomite that occurs between fossiliferous limestone. Examples are authigenic sepiolite in white dolomitic sepiolite, and brown sepiolite which precipitated directly (Yeniyol, 1992; Gençoğlu *et al.*, 1993). The Denizli sepiolite and palygorskite do not contain gypsum, but are accompanied by saponite and volcanic emanations, in contrast to those of the Eskişehir district where they are often associated with gypsum. Sepiolite and palygorskite deposits lacking gypsum have also been observed in Spain and Portugal (Galán and Farrero, 1982; Dias *et al.*, 1997). The aim of this study was to determine the geology, depositional environment and origin of the sepiolite, palygorskite and saponite deposits that were discovered in Denizli during the course of this research. These deposits have reserves of ~200,000 tons.

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METHODS

A total of 110 clay-dominated samples from nine stratigraphic sections were collected for mineralogical and chemical analyses (Figure 1). The mineralogy of the samples was determined by X-ray powder diffraction (XRD-Rigaku Geigerflex) and scanning electron microscopy (SEM-EDX Jeol JSM 6400-Noran instruments Series II).

The XRD analysis was carried out using CuKα radiation with a scanning speed of 1°2θ/min. Bulk mineralogy was studied using unoriented air-dried samples. Clay minerals were determined on <2 μm clay fractions prepared by sedimentation followed by centrifugation of the suspension after being soaked in distilled water overnight. The clay particles were dispersed using a soil mixer and ultrasonic vibration for ~15 min. Four specimens from the <2 μm fractions of each altered sample were prepared by gravity settling onto glass slides that were air-dried, solvated with ethylene glycol at 60°C for 2 h, and heated at 350°C and 550°C, each for 2 h. Semi-quantitative mineralogical determinations were obtained by multiplying the intensities of the principal basal reflections of each mineral by appropriate factors according to an external method developed by Gündoğdu (1982) following the method of Brindley (1980).

Clay-rich representative samples were prepared for SEM-EDX analysis by adhering the fresh, broken

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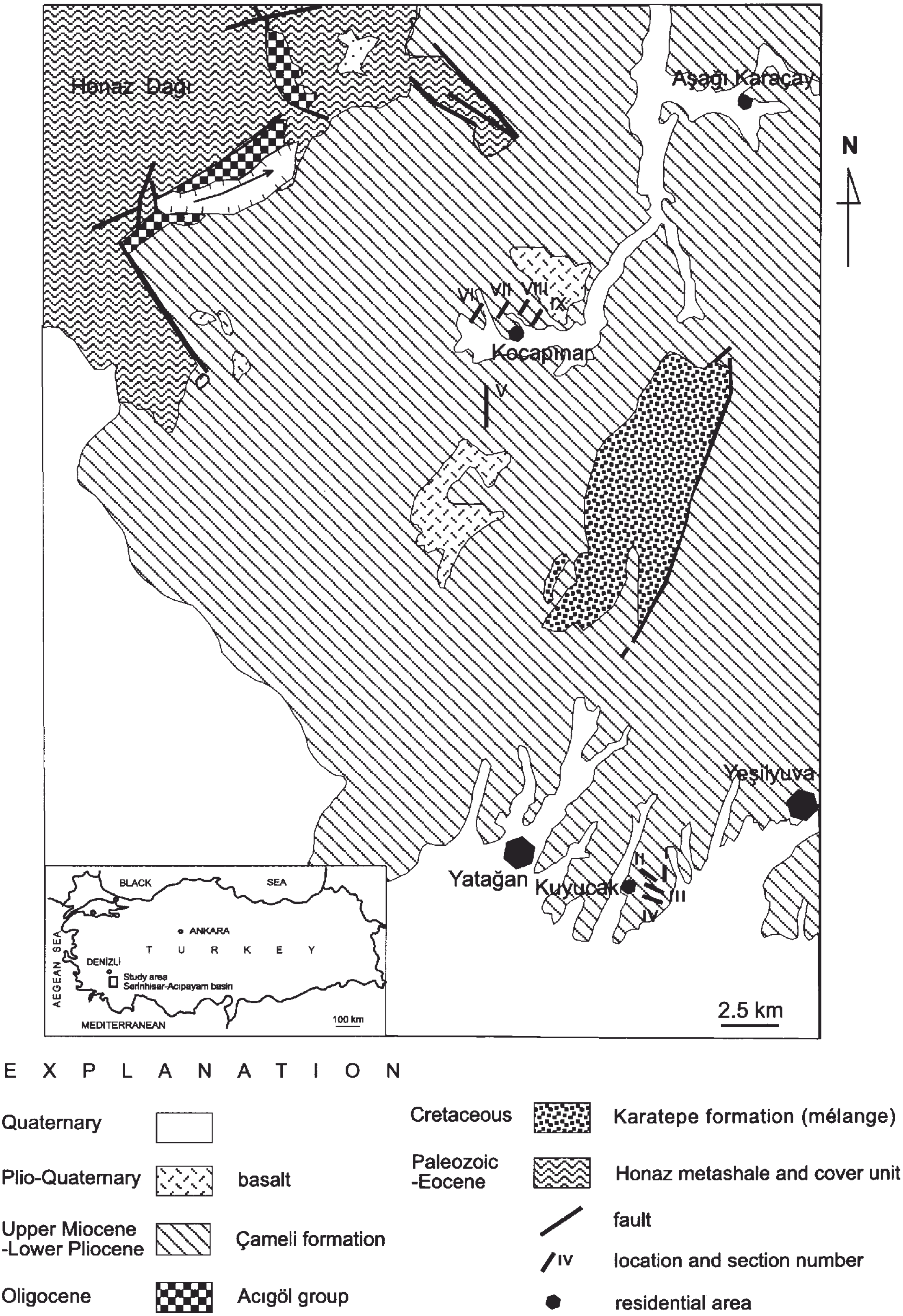

Figure 1. Geological map of the study area.

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surface of each sample onto an Al sample holder that had been covered with double-sided tape and coated with a thin film (350 Å) of Au using a Giko IB.3 ion coater.

Chemical analyses of the major oxides were carried out on 24 clay-dominated samples by X-ray fluorescence (XRF) spectrometry (Rigaku X-ray Spectrometer RIX 3000) using rock standards supplied by the MBH Reference Material and Breithlander companies, and by atomic absorption spectrophotometry (AAS) (Perkin-Elmer 2980 spectrophotometer) after dissolution by HF-$HClO_4$ acid. The error for these elements is <±2%. Loss on ignition (LOI) for each sample was also determined by drying the samples overnight at 105ºC, followed by calculation of their water and other volatile contents at 1050ºC.

Mineral chemistries were determined on the <2 µm fractions of sample KA-38 (pure sepiolite), and by sedimentation of samples A5-3 and A2-2 (those with the highest palygorskite and saponite contents, respectively), followed by centrifugation of the suspension at up to 15,000 rps for 10 min, after soaking overnight in distilled water.

GEOLOGY

The Acıpayam-Serinhisar basin is a N–S-oriented graben-like depression. A vertical fault at the west side of the basin is the contact between serpentinite that contains scarce lenticular magnesite bodies, and the Çameli formation that represents the margin of the basin.

The basement of the Serinhisar-Acıpayam basin consists of the Honaz Dağı units at whose base is metashale of uncertain age (Figure 1). This unit is overlain by slightly metamorphosed limestone of the Menderes Massif as well as by shale and ophiolitic rocks of the Lycian Nappes of Honaz Dağı (Okay, 1989). Another basement unit is the Cretaceous Karatepe formation (a tectonic mélange composed of ultrabasic rocks, limestone and chert blocks). In addition to Mesozoic dolomitic limestone and ultrabasic basement rocks on both sides of the basin, the Oligocene Karadere formation (Hakyemez, 1989) and the undifferentiated Acıgöl group (Şenel, 1997) are exposed as alluvial fan sediments containing detrital materials which were derived from ophiolite, dolomite, claystone *etc*., in the northern part of the basin.

The basin is filled with alternating conglomerate-sandstone-mudstone-limestone-dolomite-type fluvial and lacustrine sediments of the Çameli formation (Erakman *et al*., 1982). The Upper Miocene(?)–Lower Pliocene Çameli formation is characterized as a carbonate-rich detrital facies with conglomerate-sandstone, conglomerate-sandstone-limestone-intercalated mudstone, green claystone, sepiolite and palygorskite-bearing dolomitic claystone, and red palygorskite-bearing mudstone (Figures 2, 3). There are lateral and vertical transitions between all of these facies.

The green claystone facies

This is brown locally, and becomes sandy mudstone. This facies tends to be dominated by saponite and contains a small amount of dolomite and intercalated conglomerate, sandstone and dolomite layers. *Chara* spores and root imprints were observed locally.

The dolomitic-claystone, sepiolite-palygorskite facies

White dolomitic claystone is intercalated with conglomerate, sandstone and dolomite, as well as a few sections of brown-beige sepiolite-palygorskite that occurs as distinguishable layers. Saponite and, in some places, palygorskite and sepiolite, are the dominant clay minerals. Saponite-dominated dolomitic claystone containing (locally) white dolomitic palygorskite is exposed at Kocapınar, and continues upward as greenish-white dolomitic claystone, pale purple dolomitic sepiolite and brown, nodular sepiolite-palygorskite. Ultimately, these facies continue upward as a pure, green saponite bed and white dolomitic claystone and dolomite bed. Basaltic and vitric tuff and synsedimentary emanations cut and enclose sepiolite, dolomite and dolomitic claystone clasts in the Kocapınar area. These volcanic units were determined to be shoshonitic basalt by Ercan *et al.* (1983). There is no sintering at the contact between the ash flow tuff and the host sediments on the floor of the lake, except that the outer parts of dolomitic to magnesitic clasts, that were enclosed by tuffs which were still internally hot, are covered by 1–2 cm thick polygonal columns sintered as cracked shells. These facies, laterally and vertically, change upwards into red mudstone in the Kocapınar area, and upwards into green sandstone-conglomerate in the Kuyucak area.

The red mudstone-palygorskite facies

These facies start with a few accumulated oncolitic mounds of partially siliceous clayey dolomite and continue with an alternation of red mudstone, clayey sandstone and conglomerate that changes laterally into dolomitic claystone-clayey dolomite and palygorskite facies. Palygorskite predominates in the dolomitic claystone, while red, soapy saponite-dominated claystone appears as brown and green-brown clay layers with root imprints in these facies. Also, locally a single, lenticular, coarse debris-flow bed immediately overlies a red mudstone.

The general features of the lacustrine detrital, clay and carbonate precipitation in the area reflect three main sub-environments: (1) fan delta; (2) shallow littoral; and (3) open lake and/or swamp (Figure 4).

Fan delta. Sandy-cemented, blocky para-conglomerate-type detritus comprises a debris flow of poorly sorted, angular–semiangular pebbles. The pebbles are similar in size to those of fan-delta sediments of the Baise basin (Changsong *et al*., 1991).

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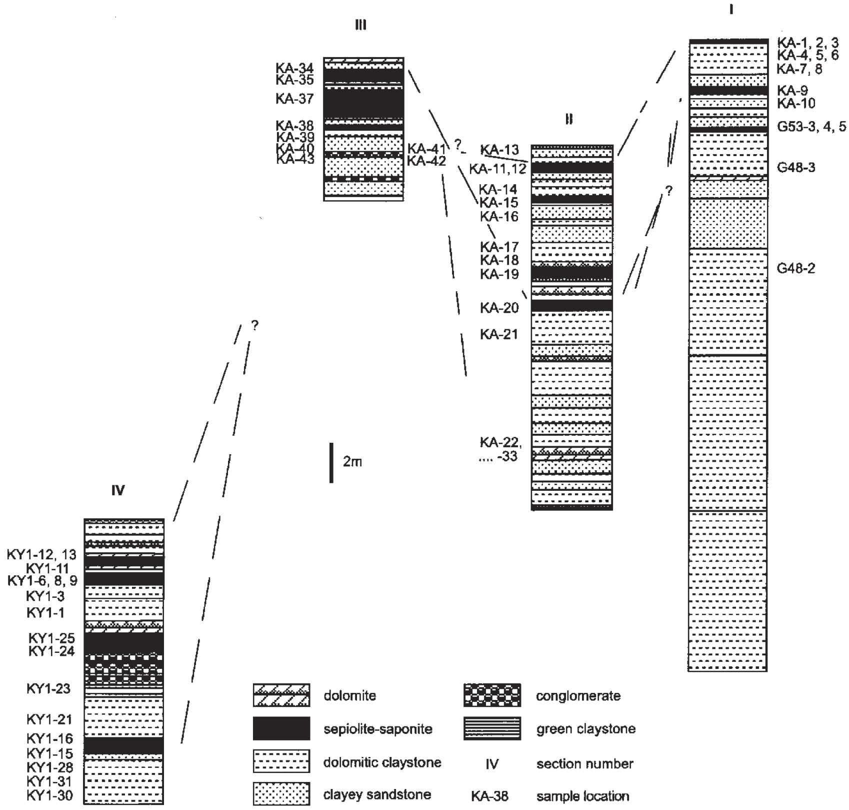

Figure 2. Distribution of the principal lithologies in the Kuyucak section (see Figure 1 for section location, and Table 1 for mineralogical compositions of the samples).

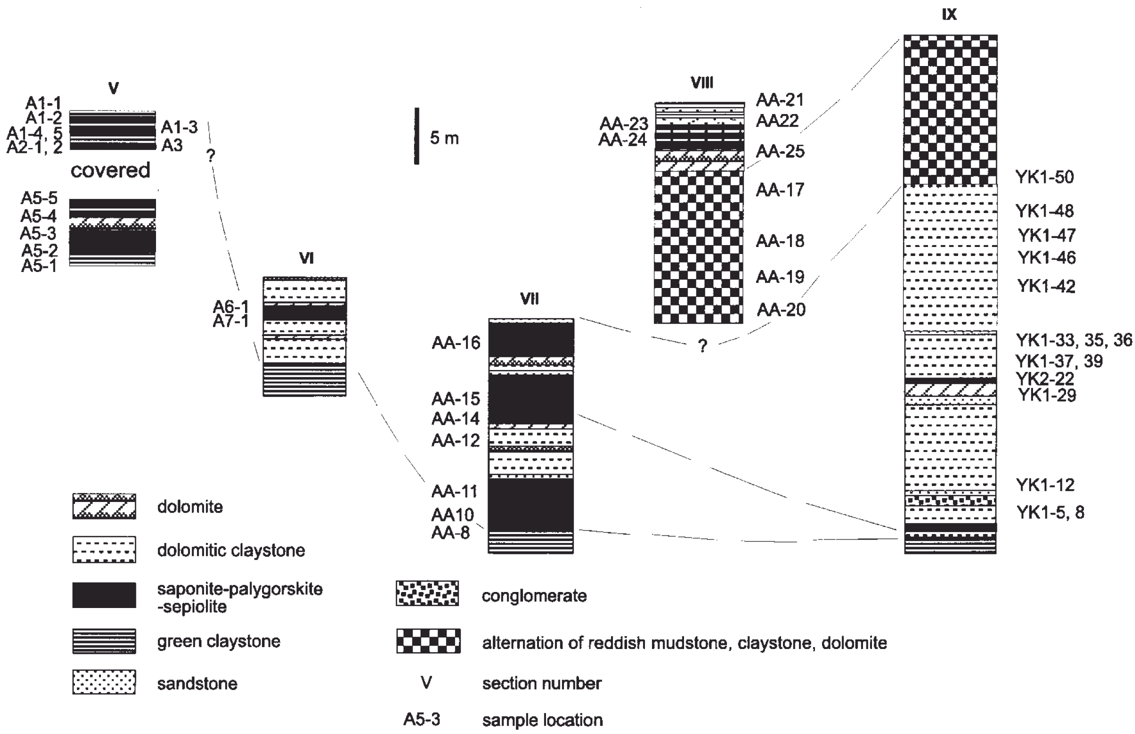

Figure 3. Distribution of the principal lithologies in the Kocapınar section (see Figure 1 for section location, and Table 1 for mineralogical compositions of the samples).

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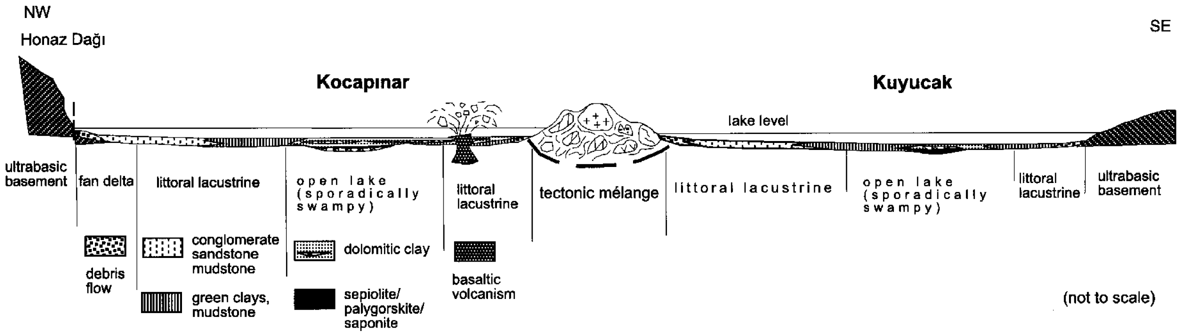

Figure 4. Schematic model of the sedimentation environment in the study area.

Shallow littoral. Dolomite and conglomerate-sandstone are intercalated with green silty clay that is massively nodular and sometimes laminated. These clays, which are lake sediments of low- to middle-energy shallow littoral facies, contain *Chara* spores. The conglomerate and sandstone in the area between the littoral and central parts of the basin show changes in water levels by means of beach sediments having planar and trough cross-bedding that is attributed to movement of the shoreline (Calvo *et al.*, 1995). The interlayered dolomite precipitated when the detrital supplement ceased. Root imprints, *Chara* spores and plant-stem imprints have been observed in the dolomite and green claystone, also suggesting a littoral lacustrine environment. The association of sepiolite, palygorskite and saponite with carbonates indicates that the lake had an alkaline character. The local soapy appearance and nodular structure of the clays are probably related to shallowing of the lake water level as well as to rapid changes in water composition. The predominant red siltstone-mudstone, interbedded with similar colored dolomite, locally hosts basaltic vitric tuff flows and channel fills that contain some penecontemporaneous dolomite, claystone, basaltic tuff blocks and pebbles. This situation indicates synsedimentary basaltic volcanic activity, with lava being extruded from the floor of the lake especially in the vicinity of present-day Kocapınar. This volcanism caused the emanation of hot springs, rich in silica and Fe, which probably influenced certain parts of the basin. The development of algae-covered dolomite pebbles and the formation of red, siliceous oncolitic algal accumulations mark the vents of the springs (Dean and Fouch, 1983) on the lake floor where it was slightly domed or shallowed. Detrital rock-dominated sandstone represents the shallow littoral facies of the lake, while palygorskite, saponite and dolomite were precipitated relatively offshore, in an area which was periodically shoaly and even swampy.

Open lake and/or swamp. This facies is represented by a predominance of dolomite and dolomitic claystone. Locally, micritic and siliceous dolomite as well as root imprints are typical features. This facies is characterized by rather shallow, alkaline open-lake units. Brown sepiolite and beige dolomitic sepiolite were precipitated in the local shoal hollows in the central part of closed alkaline lake where concentrations of Si, Mg and $CaCO_3$ increased by feeding from parent rocks. Furthermore, silt and carbonized plant remnants in brown sepiolite-palygorskite indicate some sporadically swampy environments due to the regression of Mg-rich waters towards the central part of the lake in the present-day Kocapınar area for a certain period. The nodular texture of the dolomitic sepiolite and palygorskite developed during low-level dehydration of sepiolite, as reported by Hay and Stoessell (1984).

A few areas of interlayered green saponite, also rich in Fe and Mg, may have developed in an alkaline lake fed by detritus-free and oxygenated fresh-water springs originating from areas of basaltic volcanism, whereas brown saponite always formed in a swampy lake environment, rather than an oxygenated one, due to volcanic activity.

MINERALOGICAL AND CHEMICAL RESULTS

XRD determinations

The XRD results for the bulk samples and clay fractions are presented in Table 1. Sepiolite, palygorskite and saponite are the dominant clay minerals in the basin, associated with dolomite, calcite and detrital minerals such as feldspar, quartz, serpentine, amphibole and illite.

Sepiolite is dominant mainly in sections I, II, III and IV, but was also detected in samples AA-14, A1-1, -2 and A7-1, whereas palygorskite is dominant in sections V, VI, VII, VIII and IX (Figures 2, 3, Table 1). Thus, sepiolite is mostly concentrated in the Kuyucak area, as well as in some levels of the Kocapınar section, whereas palygorskite and saponite are dominant mainly in the Kocapınar section. The association of palygorskite with sepiolite is observed only in samples AA-14, A7-1, KA-16, G48-3 and KY1-12. Saponite is dominant in most of sections V, VI, VII, VIII and IX (Figure 3), and as intercalated layers in sections I, II, III and IV (Figure 2). Dolomite is generally dominant in the upper levels of the basin, whereas calcite was determined as an accessory

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Table 1. Mineralogical variation along stratigraphic sections in the study area.

	Sep	Pal	Sap	Chl	Dol	Cal	Fel	Qz	Srp	Amp	Il
KA-1	+		++		++				ac		
KA-2	++++				+		ac	ac	ac		
KA-3	+++				++			ac			
KA-4	++				+++						
KA-5	++++				+		ac		ac		
KA-6	++		+		++				ac		
KA-7	+++		+		+				ac		
KA-8	++++				+						
KA-9	++				+++				ac		
KA-10	+++				++						
G48-2	+		++		+				+		
G48-3	+	ac	+		+++				ac		
G53-3	++				+++				ac		
G53-4	+++++				ac			ac			
G53-5	+++				++			ac			
KA-11			++++					ac	+		
KA-12			++++					ac	+	ac	
KA-13	++		+		++				ac		
KA-14	++		++		+				ac		
KA-15	+++				++				ac		
KA-16	++	ac	+		++						
KA-17	+++				++				ac	ac	
KA-18	+++				++				ac		
KA-19			++++				ac	ac	+	ac	
KA-20	+++				++						
KA-21			+++		++				ac		
KA-22			++		+++						
KA-23	++++				+				ac		
KA-24	++++				+				ac		
KA-25	++				+++				ac		
KA-26	+		+		+++				ac		
KA-27	+++				++				ac		
KA-28	++++				+						
KA-29	+++				++						
KA-30	+++				++						
KA-31	+++				++				ac		
KA-32			++		++				+		
KA-33	++++				+					ac	
KA-34	+++++				ac						
KA-35	+++++				ac						
KA-37	+		+++		ac	ac		ac	+		
KA-38	+++++										
KA-39	+++				++				ac		
KA-40	+		+		+++						
KA-41	++				+++						
KA-42			++		++			ac	+		
KA-43			+++					ac	++		
KY1-1	+++				++			ac			
KY1-3	++				+++						
KY1-6	++++				+						
KY1-8	+				+++	+					
KY1-9	+++				++	ac					
KY1-11	++				+++						
KY1-12	++	ac	+		++				ac		
KY1-13	+		++		++				ac		
KY1-15	+++				++				ac		
KY1-16	++++				+				ac		
KY1-21				+++				ac	++	ac	
KY1-23			++	++				ac	+		
KY1-24			+++	+				ac	+		
KY1-25			++++					ac	+		
KY1-28			+++		+				+		

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Table 1 (*contd.*)

	Sep	Pal	Sap	Chl	Dol	Cal	Fel	Qz	Srp	Amp	Il
KY1-30			+++		++			ac	ac		
KY1-31			+++					ac	++	ac	
A1-1	+		+	+	++			ac			
A1-2	++		+++		ac			ac	ac		
A1-3		+	+++					ac	+	ac	
A1-4		+	+++	+				ac		ac	
A1-5		+	++++					ac	ac		
A2-1		+++			+		ac	ac	+		ac
A2-2			+++++					ac	ac		
A3			+++++		ac		ac	ac	ac		
A5-1		++	+		++			ac	ac		
A5-2		++	+		++			ac	ac		
A5-3		+++++			ac			ac	ac		
A5-4		++	+		++		ac	ac			
A5-5		++	+	+	+		ac	ac			
A6-1		+++	+		ac		+	ac	ac		
A7-1	++	++					+	ac			
AA-8			++++					ac	+		
AA-10		+	++++					ac	ac		
AA-11		ac	++++					ac	+		
AA-12		+	+		+++			ac	ac		
AA-14	+++	++									
AA-15		+	++++					ac	ac		
AA-16			++++					ac	+		
AA-17		+++		+	+			ac			
AA-18		++	+	+	+			ac			
AA-19		++	+		++	ac		ac	ac		
AA-20		+++	+	+				ac	ac		ac
AA-21		++	++		+			ac	ac		
AA-22		+	++	ac	+			ac	+		
AA-23		++	+++		ac		ac	ac	ac		
AA-24		+	++		ac	ac		ac	ac	ac	
AA-25		+++	+		+		ac	ac	ac		
YK1-5			++		++				+		
YK1-8			++		+++				ac		
YK1-12			++		+++				ac		
YK1-29		++	+		++						
YK1-33		+	+++		+			ac	ac		
YK1-35		+	++		++			ac	ac		
YK1-36		+	+++		+			ac	ac		
YK1-37		+	++		++			ac	ac		
YK1-39		+	++		++			ac	ac		
YK2-22		++++			+				ac		
YK1-42		+	+++		ac	ac			+		
YK1-46		++			++			ac	+		
YK1-47		+	+++		+			ac	ac		
YK1-48			+++		+				+		
YK1-50		+	+		++			+	ac		

Sep: sepiolite, Pal: palygorskite, Sap: saponite, Chl: chlorite, Dol: dolomite, Cal: calcite, Fel: feldspar, Qz: quartz, Srp: serpentine, Amp: amphibole, Il: illite, +: relative abundance of mineral, ac: accessory

mineral in only a few samples. In addition, scarce serpentine, quartz and amphibole were detected in most of the samples. Serpentine increases slightly in saponite-dominated samples. Scarce chlorite was also observed in association with saponite in a few samples.

Sepiolite and palygorskite show basal reflections at 12.2 Å and 10.5 Å, respectively, and were not affected by treatment with ethylene glycol. Sepiolite collapsed to 11 and 10.3 Å and palygorskite to 9.3 and 9 Å after heating to 350 and 550ºC, respectively, for 2 h. The saponite has basal reflections varying between 14.5 and 15.8 Å which expand to 16.7 and 17.5 Å with ethylene glycol treatment and collapse to 9.6 Å and 9.7 Å after heating to 350 and 550ºC, respectively, for 2 h. The d_{060} value of smectite is ~1.52–1.53 Å, suggesting a tri-octahedral character (Brown and Brindley, 1980). Serpentine is distinguished by its basal reflections at 7.3 and 3.67 Å.

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SEM-EDX determinations

Representative sepiolite-, palygorskite- and saponite-dominated samples were selected for SEM-EDX analyses. Both sepiolite and palygorskite have a fibrous character (Figures 5a,b,c; 6a,b,c). Sepiolite occurs either as fibers grown out of, and on, dolomite (Figure 5a), or as dense fiber masses that are connected to each other by bridges of fiber bundles and sheafs in pure sepiolite beds where dolomite is absent (Figure 5b,c). Similar growth patterns have been described by Allison and Riggs (1994), Ece and Çoban (1994) and Yalçın and Bozkaya (1995). The free ends of some of the fiber bundles and sheafs are often narrow and sharp.

The palygorskite is characterized by fibrous networks growing out of dolomite into dissolution voids and cracks (Figure 6a,b,c). Sub-oriented fibers and fiber bundles forming platy, fan-like shapes, grew locally from dolomite surfaces (Figure 6c). Also, these fibers contain relicts of carbonate grains. Sepiolite and palygorskite fibers are ~6 µm long and <0.05 µm wide. The orientation of long fibers in platy and bundle-like forms may indicate that precipitation occurred under a condition of supersaturation, similar to that described by Gehring *et al*. (1995).

Saponite occurs in irregular flakes which formed authigenically from Mg-rich solutions in dissolution voids of the red mudstone (Figure 7a) that enclose small volcanic-glass particles (Figure 7c), and no transitional form has been observed between saponite and palygorskite. Also, the growth of platy palygorskite fibers from smectite is not possible, as described by Trauth (1977) and Estéoule-Choux (1984).

Semi-quantitative EDX analysis has shown that the sepiolite (KA-38) is composed mainly of Si and Mg and smaller amounts of Fe and Al, while the palygorskite (YK2-22) is composed of Si, Mg and Fe and smaller

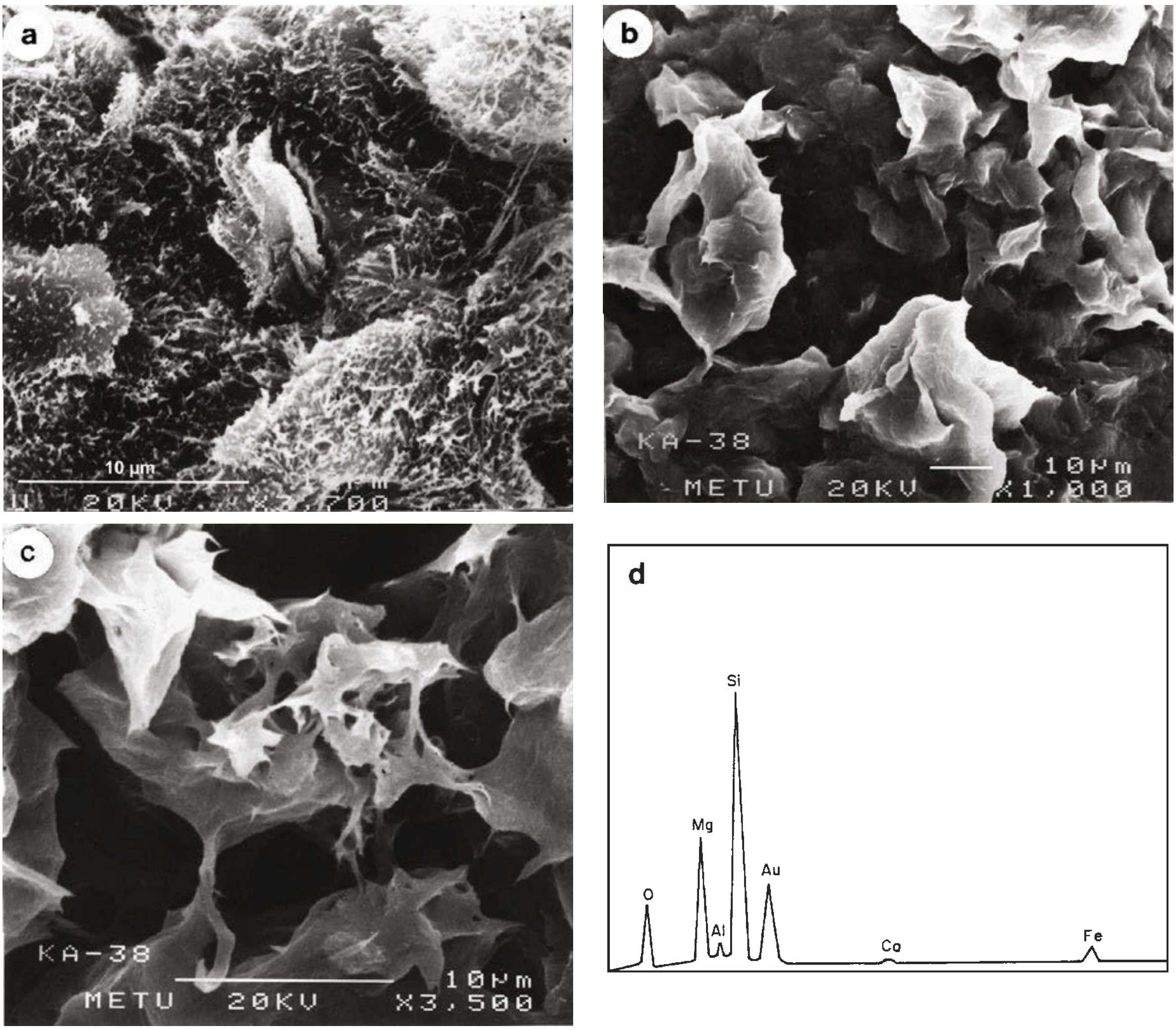

Figure 5. (a,b,c) SEM images of sepiolite fiber masses connected to each other by bridges of fiber bundles. (d) Semi-quantitative analysis of sepiolite fibers.

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amounts of Al and Ca (Figures 5d, 6d). Both sepiolite- and palygorskite-dominated sample AA-14 and palygorskite- and saponite-rich sample AA-21 which contain small amounts of volcanic-glass particles. Analysis by EDX of both saponite and enclosed particles shows the dominance of Si, Mg and Fe followed by small amounts of Al and Ca (Figure 7b,d). This indicates that volcanic glasses in the Kocapınar section were an important source of Fe and Al, as well as Si, as reported by Karakaş and Kadir (2000) and Kadir and Karakaş (2002). The Ca, Fe and some of the Mg may well represent contamination from trace dolomite and volcanic glass. Therefore, EDX analyses of palygorskite and saponite possibly show overlap in the appearance of peak intensities for palygorskite or saponite and dolomite and/or volcanic glass, although the structures of sepiolite, palygorskite and saponite contain Fe.

Chemical analyses

Chemical analyses were conducted on sepiolite-, palygorskite- and saponite-dominated samples collected from both the Kuyucak and Kocapınar sections (Table 2). These units are mainly composed of SiO_2, MgO, Fe_2O_3, Al_2O_3 and CaO. The amount of SiO_2 and MgO decreases in YK1 samples in section IX (Figure 3) and CaO, Fe_2O_3 and Al_2O_3 contents are generally higher in some "A" samples, collected partially from the red argillaceous dolomitic sediments that contain small amounts of detritus in sections V and VI (Figure 3).

The chemical differences reflect the mineralogy and crystal chemistry of the clays and associated detrital minerals. SiO_2 and MgO are abundant in those Kuyucak and Kocapınar samples corresponding to an abundance of sepiolite, saponite and palygorskite. Therefore, MgO, SiO_2 and loss on ignition are relatively high basin-ward;

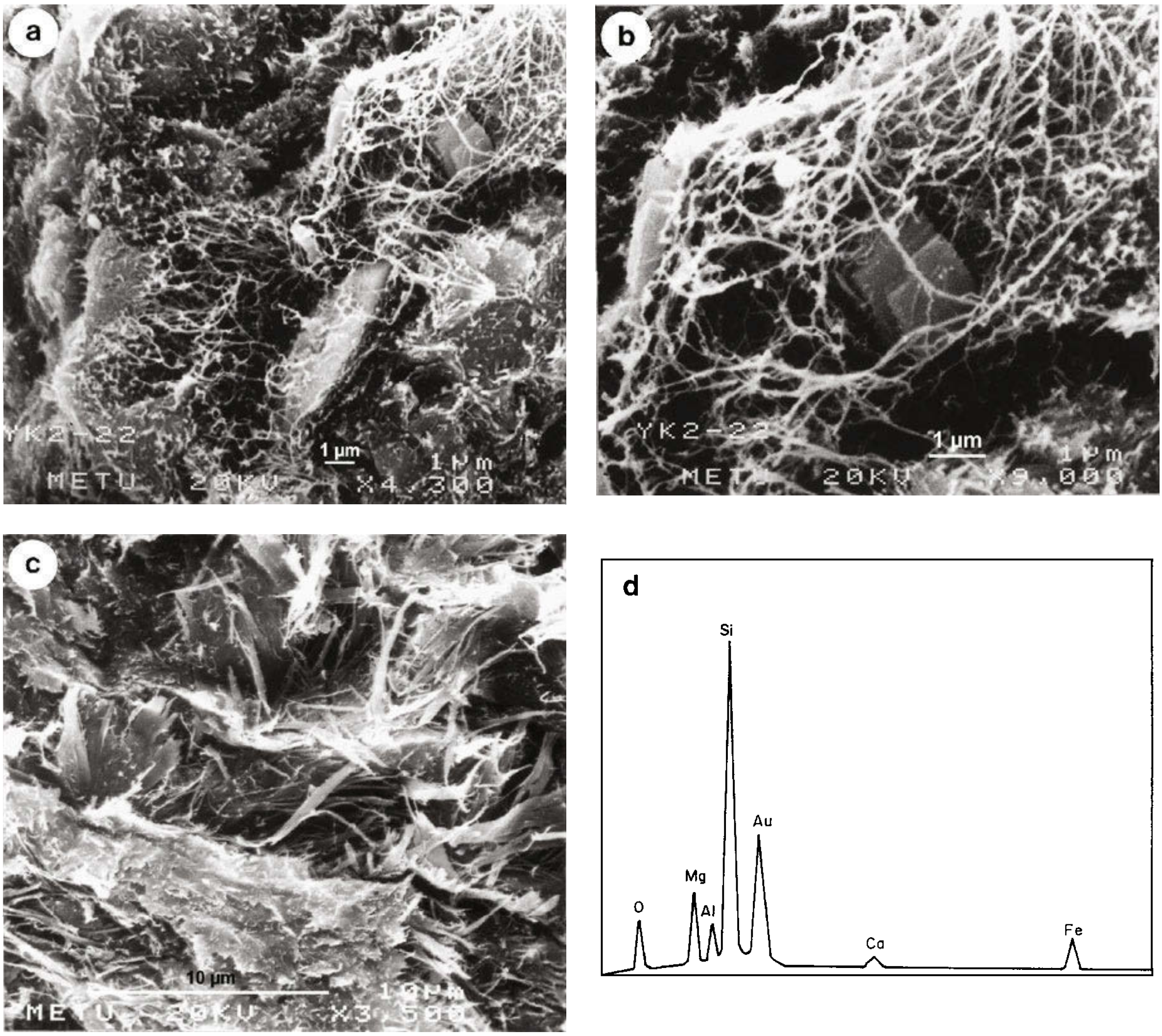

Figure 6. (a,b,c) SEM image of fibrous palygorskite networks in dissolution voids and cracks, developed from and enclosing relicts of dolomite. (d) Semi-quantitative analysis of palygorskite fibers.

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thus, carbonate and sepiolite are dominant and the detrital component is almost non-existent. This situation was also found in the Kocapınar section due to the predominance of saponite as well as of palygorskite. The CaO value is reflected in the presence of dolomite associated with clayey material. Therefore, there is a positive relationship between CaO and dolomite in an MgO-rich environment. Most of the Fe and Al occur in the marginal facies, dominated by saponite and palygorskite clay fractions, which are associated with volcanic material and small amounts of detritus.

The structural formulae of sepiolite, palygorskite and saponite were calculated from chemical analyses of the clay fractions of samples KA-38, A5-3 and A2-2, respectively (Table 3). Fe^{3+} plays an important role within the octahedral sites, and Al^{3+} in both the octahedral and tetrahedral sites of these minerals.

In the sepiolite-rich sample (KA-38), Fe^{3+} substitutes for Mg cations in the octahedral sheet, Al substitutes mainly for Si in the tetrahedral sheet, and a minor amount of Al substitutes for Mg in the octahedral sheet. This mineral has a composition similar to that of Al sepiolite from Tintinara in South Australia (Rogers *et al.*, 1956), except that it contains less Al and more Mg and Fe (Newman and Brown, 1987). Therefore, it can be defined as an FeAl sepiolite.

In the palygorskite-rich sample (A5-3), Al substitutes for Si in the tetrahedral sheet, and Fe^{3+} substitutes for some of the Al in the octahedral sheet. It has a composition similar to that of the palygorskite from Mt. Flinders, Queensland in Australia (Rogers *et al.*, 1954), but contains more Fe^{3+} and less Mg (Newman and Brown, 1987). Therefore, this palygorskite can be termed an Fe palygorskite.

In the smectite-rich sample (A2-2), some Fe^{3+} substitutes for Mg, which is dominant in the octahedral sheet, but still contains much Mg compared to Fe-rich montmorillonite and nontronite, while it contains less

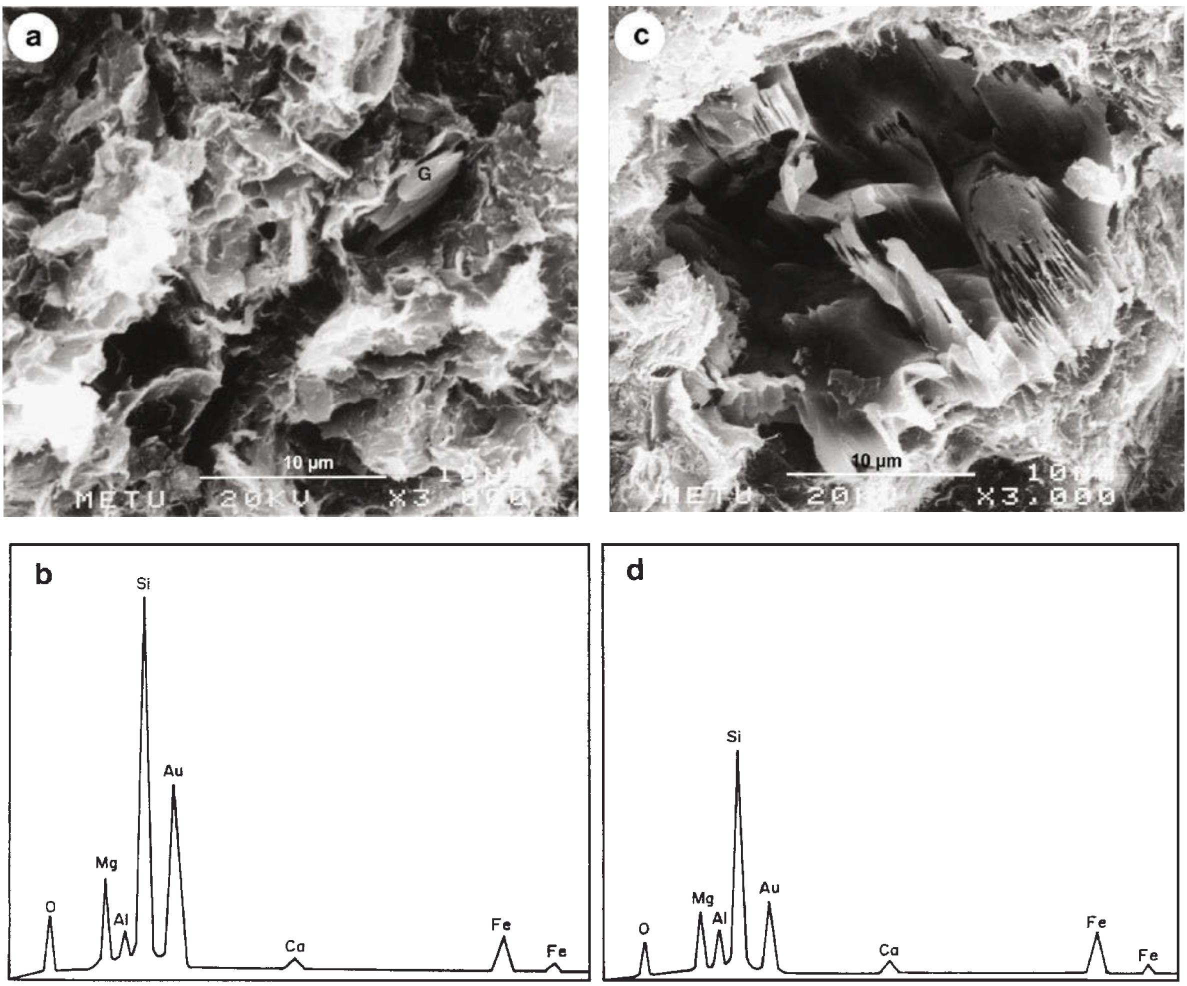

Figure 7. (a) SEM image of irregular flakes of saponite in dissolution voids, enclosing relics of volcanic glasses (G). (b) Semi-quantitative analysis of saponite flakes. (c) SEM image of volcanic glass, locally showing comb texture, due to partial devitrification. (d) Semi-quantitative analysis of volcanic glass.

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Mg but more Fe and Al than stevensite (Newman and Brown, 1987). Therefore, it is termed saponite.

The presence of trace Al, Fe, Ca, Mg and Si in the structure of the sepiolite, palygorskite and saponite may also be due to minor impurities (volcanic glass, dolomite, serpentine, *etc.*) which were not removed and not detected by XRD, as suggested by Galán and Carretero (1999).

DISCUSSION

The Çameli formation contains Fe-rich sepiolite, palygorskite, and saponite, which are dominant in dolomite and dolomitic limestone as well as in claystone horizons. Sepiolite predominates in the Kuyucak section – intercalated with saponite-dominated levels – whereas saponite accompanies palygorskite in the Kocapınar section where basaltic volcanism has occurred.

The sepiolite and palygorskite contain accessory silt, sand and serpentinite pebbles originating from nearby ultrabasic rock units. Neither clay mineral is detrital but formed by direct precipitation from lake water. Similar precipitation has also been reported from a number of evaporitic basins in central Anatolia (Yeniyol, 1992; Gençoǵlu *et al.*, 1993; Ece and Çoban, 1994), differentiated from the Acıpayam-Serinhisar basin by the presence of gypsum. The silica and Mg in the sepiolite were derived from surrounding ultrabasic and detrital rocks, and partly from devitrification of volcanic glass (Figure 7d) produced by basinal basaltic volcanism (exclusively in the Kocapınar section), and partly by dissolution of dolomite. The Al and Fe ions in solution were supplied mainly by the dissolution of volcanic glass (Figure 7d), similar to that described by Millot (1970), Kawano *et al.* (1997) and Kadir and Karakaş (2002), although some of the Fe may have been derived from the basement rocks.

Micromorphological images reveal that both sepiolite and/or palygorskite grew as interwoven fibers or fiber bundles and masses in pure sepiolite beds where dolomite is absent (Figure 5a,b,c). On the other hand, sepiolite and palygorskite in dolomitic sepiolite and/or dolomitic palygorskite formed authigenically from interstitial pore-water (between dolomite rhombs) having high pH and high Si and Mg, along with small amounts of Al for palygorskite formation and lower Al activities for sepiolite, as reported by Singer and Norrish (1974), Singer (1979), Singer and Galán (1984), Singer (1989), Jones and Galán (1988), Inglès and Anadón (1991), Ece and Çoban (1994), Hillier (1995), Singer *et al.* (1998), Kadir and Akbulut (2001) and Kadir *et al.* (2002). The evidence for such authigenic formation is that both sepiolite and palygorskite fibers grow out of and upon the corroded surfaces of dolomite crystals and enclose relicts of dolomite (Figure 6a,b,c). Precipitation was controlled by evaporation, and by rain and fresh-water flows that temporarily changed the pH in some parts of the closed basin. However, in the Kocapınar and

Table 2. Chemical analyses (wt.%) of different lithologies dominated by sepiolite, palygorskite and saponite in the study area (see Table 1 for the mineralogical compositions of the samples).

Sample	SiO_2	Al_2O_3	FeO	tFe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	TiO_2	P_2O_5	LOI	Total
KA-35	54.9	3.8	0.2	3.7	23	2	0.1	0.2		0.3	0.1	11.81	99.91
G53-3	26.5	2.1	0.30	2.5	18.8	17.4	0.1	0.1	0.1	0.1	0.1	31.35	99.05
G53-4	53.5	3.5	0.25	4.9	22	1.8	0.1	0.1	0.1	0.2	0.1	13.15	99.45
G53-5	37.5	2.5	0.20	3.5	19.5	12	0.1	0.1	0.1	0.1	0.1	23.65	99.15
KA-11	41	5		8.5	21.5	1	0.1	0.2	0.1	0.4	0.1	22	99.9
KY1-6	42	3.1	0.10	3.5	21.5	8.9	0.1	0.2	0.1	0.2	0.1	19.25	98.95
KY1-9	39.1	1.9	0.10	1.8	21.8	11.3	0.1	0.1	0.1	0.1	1.8	21.92	100.02
KY1-16	47.5	3.7	0.10	4.5	21.5	5.4	0.1	0.2	0.1	0.2	0.1	16	99.3
A1-1	35.5	2.6		4.5	19	12.5	0.1	0.2	0.1	0.2	0.1	24.35	99.15
A1-2	50.8	6.4		11.5	15.2	1.2	0.1	0.6	0.1	0.4	0.1	13.6	100
A1-3	50.1	4.9		11.7	20.1	1.1	0.1	0.5	0.1	0.4	0.1	10.7	99.8
A1-4	52.9	6.1		11.4	14.8	1.1	0.1	0.6	0.1	0.4	0.1	12.43	100.03
A1-5	50.4	5.4		11.4	19.8	1.3	0.1	0.5	0.1	0.4	0.1	10.62	100.12
A2-1	38	3		5.5	24	8	0.1	0.3	0.1	0.2	0.1	20.75	100.05
A3	49.8	5.4	0.76	7	21.4	2	0.1	0.6	0.1	0.3	0.1	13.2	100
A5-1	37	5.5	0.62	8.5	15	11	0.1	0.8	0.1	0.3	0.1	21.25	99.65
A5-2	32.5	4.5	0.58	7.5	17	13	0.1	0.7	0.2	0.3	0.1	23.6	99.5
A5-4	37	6	0.27	9	14	10.9	0.1	1	0.1	0.4	0.1	20.85	99.45
A5-5	45.6	8.7	0.58	10.2	11.1	6.4	0.1	1.5	0.2	0.6	0.1	15.5	100
A6-1	55.7	5.5	0.32	10.9	14.3	0.8	0.1	0.3	0.1	0.4	0.1	11.8	100
A7-1	56.1	3.7	0.24	10.9	16.4	0.6	0.1	0.3	0.1	0.3	0.1	11.4	100
AA-11	40	4.9		12.5	19	4.5	0.1	0.2	0.1	0.4	0.1	18	99.8
YK1-29	25.2	3	0.10	4.6	15.7	18.2	0.1	0.1	0.1	0.2	0.1	32.25	99.55
YK2-22	41.5	4.5	0.2	8	13	10	0.1	0.2	0.1	0.2	0.1	21.7	99.4

tFe_2O_3: total iron oxides; LOI: loss on ignition at 1050ºC

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Table 3. Chemical analyses (wt.%) of and structural formulae for sepiolite (KA-38), palygorskite (A5-3), and saponite (A2-2).

	KA-38	A5-3	A2-2
SiO_2	56.25	51	47
Al_2O_3	3.7	6	3.6
Fe_2O_3	5.3	9.3	7.5
MgO	22.1	10	19.5
CaO	0.5	1.1	1.1
Na_2O	0.1	0.1	0.1
K_2O	0.2	0.3	0.5
MnO	0.1	0.1	0.1
TiO_2	0.1	0.2	0.3
P_2O_5	0.2	0.1	0.1
LOI	11.45	21.55	19.45
Total	100	99.75	99.25
Tetrahedral			
Si	11.29	7.64	7.37
Al	0.71	0.36	0.63
Σ	12.00	8.00	8.00
Octahedral			
Al	0.17	0.7	0.04
Fe	0.8	1.05	0.89
Mg	6.61	2.23	4.56
Mn	0.01	0.02	0.02
Ti	0.02	0.02	0.04
Σ	7.61	4.02	5.55
Interlayer			
Ca	0.11	0.18	0.18
Na	0.04	0.03	0.03
K	0.05	0.06	0.1
P	0.04	0.02	0.01
Layer charge	0.49	0.55	0.54
Interlayer charge	0.51	0.55	0.54

The structural formulae are calculated on the basis of 32, 21 and 22 atoms per formula unit of oxygen for sepiolite, palygorskite and saponite, respectively. LOI: loss on ignition at 1050ºC

Kuyucak areas, semi-arid climatic conditions interrupted by humid intervals prevailed, and these did not allow the development of evaporitic facies except for dolomites and/or limestones. The filling of the basin with fine sediments and associated water-level changes caused the development of swampy and/or semi-swampy, alkaline lake environments during some periods in the basin. Sepiolite-palygorskite and dolomitic sepiolite or palygorskite were precipitated in these environments, respectively. Chemical analyses indicate that both reddish brown and white outcrops in the vicinity of Kocapınar village tend to have two to three times more Al and Fe than those of the Kuyucak section. This difference is due to synsedimentary basaltic volcanic activity in the Kocapınar area. Some Fe-rich sepiolite and palygorskite levels in lacustrine sediments that surround volcanic activity centers in the Kocapınar area are white to beige. In some periods, the environment was calm and lacked the circulation of oxygenated water, and was rich in carbonate and Fe but poor with respect to organic material. Conversely, some sepiolite, palygorskite and even some saponite levels are reddish brown due to enrichment in organic material, such as carbonized plant remnants, root imprints, *etc*.

Saponite occurs either in dolomite and dolomitic claystone, or among the detrital beds, although some saponite is encountered in green dolomitic claystone; it commonly predominates in the brown claystones. Synsedimentary basaltic volcanism supplied abundant silica, Fe and some Al to the basin which was already rich in Mg. Brown saponite formed locally by direct precipitation in a swampy and Fe-, plant-rich lake environment which was occasionally agitated and oxygenated by hot springs related to volcanic activity on the substrate. On the other hand, green saponite also formed by direct precipitation, affected by Fe-rich waters in a part of the lake rather far away from the periodically agitated lacustrine sections.

CONCLUSIONS

Although palygorskite and, rarely, sepiolite are associated with saponite, there are several saponite layers where palygorskite is absent which locally have more or less sharp contacts with the upper and lower palygorskite and/or sepiolite levels due to rapid changes in the physicochemical conditions of the environment. Moreover, micromorphologically, no transitional form is observed between saponite and palygorskite-sepiolite, suggesting that these minerals formed either by direct precipitation from lake water or authigenically from interstitial pore-water between dolomite rhombs, rather than by means of mutual transformation.

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