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SEPIOLITE-PALYGORSKITE FROM THE HEKIMHAN REGION (TURKEY)

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Abstract—Upper Cretaceous-Tertiary marine clayey-calcareous rocks of the Hekimhan basin contain fibrous clay minerals in significant amounts. Ophiolitic rocks in the provenance area have contributed the elements to form the clay minerals. XRD, SEM, major, trace and REE analyses were applied to samples taken from several stratigraphic sections. Diagenetic minerals such as smectite, dolomite, calcite, gypsum, celestite and quartz/chalcedony are associated with sepiolite-palygorskite group clays. Trace and rare earth elements (REE) are more abundant in palygorskite than sepiolite. REE abundances in the sepiolite-palygorskite are characterized by negative Eu and positive Nd anomalies when normalized with respect to chondrite and shale. Sepiolites with sharp XRD peaks are formed by diagenetic replacement of dolomite and diagenetic transformation of palygorskite, or by direct crystallization from solution. The average structural formula of the sepiolite is:

$$(Mg_{7.15}Al_{0.13}Fe_{0.31}Cr_{0.06}Ni_{0.04})(Si_{11.98}Al_{0.02})O_{30}(OH)_4(OH_2)_4Ca_{0.03}Na_{0.02}K_{0.02}.8H_2O$$

Palygorskite appears to be authigenic by direct precipitation from solution. It exists in both monoclinic and orthorhombic forms with the mean structural formula given below:

$$(Mg_{2.22}Al_{1.00}Ti_{0.04}Fe_{0.77}Cr_{0.01}Ni_{0.02})(Si_{7.68}Al_{0.32})O_{20}(OH)_2(OH_2)_4Ca_{0.07}Na_{0.05}K_{0.10}.4H_2O$$

Key Words—Geochemistry, Hekimhan, Mineralogy, Palygorskite, Rare Earth Elements, SEM, Sepiolite, Smectite, XRD.

INTRODUCTION

Sepiolite-palygorskite clay minerals are commonly associated with phosphatic sediments, salt deposits, sulphates, carbonates, zeolites, and siliceous rocks (Millot 1970; Velde 1985; Jones and Galan 1988). When the chronological and geographical distributions of these minerals are taken into consideration, it appears that their concentrations increase in Upper Cretaceous and especially Tertiary age sediments, with the zones from 30–40° N and S latitudes (Callen 1984). Sepiolite-palygorskite group minerals occur extensively in shallow-coastal lagoons (Weaver and Beck 1977; Callen 1977; Estéoule-Choux 1984), pedogenic (Singer 1984), and lacustrine (Millot 1970; Jones 1986) environments. Palygorskite is unique to deep-sea sediments (Couture 1977; Church and Velde 1979; Toyoda *et al* 1990).

Marine chain-structure clays were first identified in the Upper Cretaceous-Tertiary units situated in the eastern and southern parts of the Hekimhan region (Figure 1), northwestern Malatya, eastern Anatolia (Bozkaya and Yalçin 1991). These sepiolite and palygorskite deposits are similar to those situated within the Mediterranean belt in terms of chronostratigraphic distribution and lithologic assemblages.

The occurrence and the geological setting of sepiolite deposits and associated palygorskite in the Eskişehir region, Turkey, are well known (Brindley 1959; Ece and Çoban 1994). Miocene lacustrine sepiolite in the Eskişehir deposit occurs in stratiform and nodular masses (Ece and Çoban 1994). The authors asserted that bedded sepiolite interstratified with dolomite, dolomitic marl, calcareous clay, clayey limestone and gypsum, precipated directly from lake water. Sepiolite nodules are the products of diagenetic replacement of magnesite pebbles. The Konya-Yunak deposits display similarities with the Eskişehir "meerschaum" type sepiolite. They were formed by the in-situ replacement of pre-existing magnesite (Yeniyol 1986). They are considerably different from the Hekimhan region deposits with regard to many characteristics such as age, environment, occurrence and chemical composition.

The aim of this study is to clarify the occurrences and origins of fibrous clay minerals by means of their mineralogical and chemical properties, and to emphasize the new contributions to the geochemical composition of these minerals.

GEOLOGICAL SETTING

A conformable sequence of Upper Cretaceous-Lower Miocene sediments is found in the Hekimhan district (Bozkaya and Yalçin 1991), located in northwest Malatya (Figure 1). They are separated by an unconformity from the Upper Jurassic-Lower Cretaceous carbonate and ophiolitic series (serpentinized peridotite, pyroxenite, gabbro, basalt and radiolarite) below.

Boyalikdere formation begins with proximal turbidites that grade laterally into reefal limestones (Güzelyurt formation). They are overlain by volcano-clastic distal turbidites in the flysch facies intercalated with tuff containing clinoptilolite and analcime (Kösehasan formation), which is laterally transitional to volcanic lavas. Zorbehan formation is represented by clayey

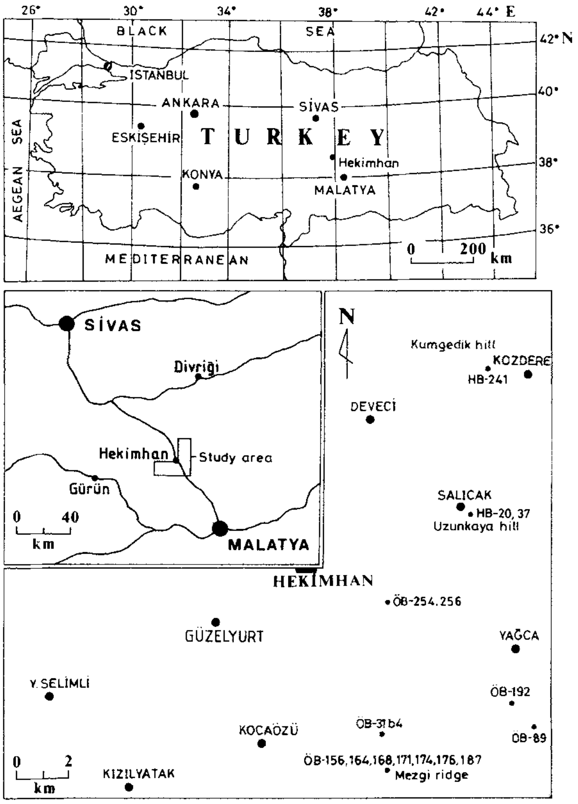

Figure 1. Index map of the Hekimhan area. (The numbers with symbols refer to locations of SEM and the analyzed samples.)

limestone with palygorskite and it also includes economic iron oxide and carbonate mineralization at the lower parts.

Yağca formation, where fibrous clay minerals are most abundant, consists of evaporitive lithologies containing gypsum, dolomite, dolomitic marl/claystone, limestone, cherty dolomite or limestone and minor celestite deposited in a shallow marine-coastal lagoon environment. Pure sepiolite levels in this unit are only found at the Mezgi ridge, Kocaözü village, in the south of the basin (Figure 1). Sepiolite occurs in three zones 15 to 20 cm thick, intercalated with siliceous dolomite units reaching up to 40–50 cm thickness. Pure palygorskite clay fractions were observed in two locations in the Yağca formation. One is to the south of the basin that rests on 5 m of sepiolite level within the dolomitic marls (30 cm) intercalated with dolomites (1 m) at the Mezgi ridge. A second is seen within an outcrop in the northern part, Uzunkaya hill, Salicak village (Figure 1). It is associated with the pinkish-orange colored dolomitic marls intercalated with cherty dolomite.

The younger units that contain palygorskite are composed of limestone-dolomitic limestone-cherty dolmite (Kizilyatak formation), clayey limestone-limestone (Kocaözü formation), and sandstone-conglomerate-dolomitic limestone-marl (Uğurlu formation). Pure palygorskite clay fractions were obtained from zones within the greyish-green, laminated dolomitic marl of these units south of the Yağca village and Kumgedik hill, Kozdere village, respectively (Figure 1).

SAMPLING AND ANALYTIC METHODS

Stratigraphic sections representing different facies of the basin were measured for the units that included sepiolite and/or palygorskite. About 500 samples collected from an area of 520 km^2 were examined using optical microscopy and X-ray powder diffraction (XRD). Subsequently, scanning electron microscopy (SEM) investigations and chemical analyses were made on selected samples.

XRD studies were undertaken in the Department of Geological Engineering at Cumhuriyet University (Sivas) with a Rigaku DMAX IIIC model X-ray diffractometer with Ni-filtered CuKα radiation. Carbonate and sulphates in the pulverized rocks were removed by acid treatment. Clay fractions (<2 μm) were extracted by sedimentation in distilled water. XRD analysis of clay minerals was performed on oriented samples after air-drying, saturation with ethylene glycol for 12h and heating at 490°C for 4h. Unoriented powders of pure clay fractions were used to distinguish structural differences for palygorskite and to determine the b dimension d(060) for di- or trioctahedral smectite (Caillere *et al* 1982; Brindley 1980a). Semiquantitative weight percentages of both clay fraction and rock-forming minerals were calculated by an external standard method (Brindley 1980b).

SEM observations were undertaken on four representative specimens of the Yağca formation to emphasize the morphological features of the fibrous clay minerals and their textural relations to other minerals. The analyses were performed at Louis Pasteur University-CNRS (JEOL JSM-840 model), Strasbourg (France) and in the Department of Geology at Keele University (England). Minerals were also identified with an Energy Dispersion Spectrometer (EDS) on the SEM.

Analyses of major Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P (g/100 g) and trace (mg/kg) V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, Pb and Li elements were carried out on monomineralic phases of fibrous clay minerals in the Department of Geological Engineering at Cumhuriyet University, Sivas. The concentrations of these elements were measured by various spectrometers (Carl Zeiss Jena Spekol 11 model ultraviolet visible spectrophotometer-UV-VIS for P, Perkin Elmer 2380 model atomic absorption spectrometer-AAS for Li and Rigaku 3270 model X-ray fluorescence spectrometer-XRF for the other elements). USGS (Flanagan 1976) and CRPG rock standards (Govindaraju 1989) were used for calibration. The loss on ignition

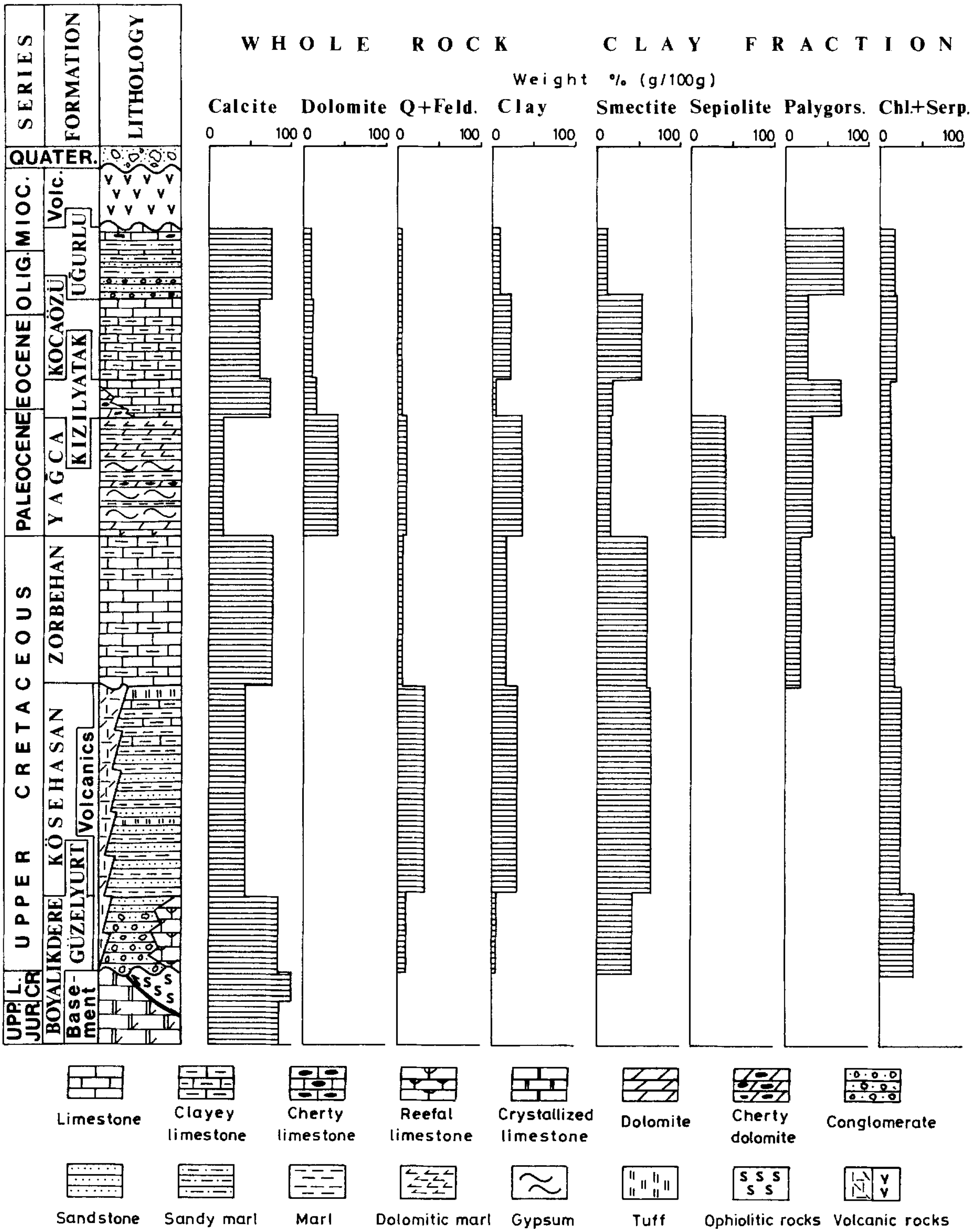

Figure 2. Except for sulphates, rock-forming and clay mineral abundances to formations in the Hekimhan region.

Table 1. Carbonate and clay paragenesis from the Hekimhan region.

Formations	Paragenesis
Uğurlu	Calcite + dolomite + palygorskite
	Calcite + dolomite + palygorskite + smectite ± chlorite ± serpentine
Kocaözü	Calcite ± dolomite + smectite + palygorskite ± chlorite ± serpentine
Kizilyatak	Calcite ± dolomite + palygorskite
	Calcite ± dolomite + palygorskite + smectite ± chlorite ± serpentine
Yağca	Dolomite + palygorskite
	Dolomite + palygorskite + smectite ± chlorite ± serpentine ± illite
	Sepiolite + palygorskite + smectite
	Sepiolite + palygorskite
	Sepiolite
	Dolomite + sepiolite + palygorskite
	Dolomite + sepiolite + palygorskite + smectite ± chlorite ± serpentine
	Dolomite + palygorskite + smectite
	Dolomite + calcite + palygorskite + smectite
Zorbehan	Calcite + palygorskite + smectite ± chlorite ± serpentine ± illite
Kösehasan	Calcite + smectite ± chlorite ± serpentine ± illite

at 1000°C was expressed as a percentage of sample weight dried in the oven at 110°C for 12 h, with an analytical reproducibility of ±2%. Analyses of some trace and REE such as Sc, Co, Zn, Ga, As, Be, Br, Mo, Ag, Cd, Sb, Cs, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Au, Hg, Th, U were carried out using an instrumental neutron activation analyses (INAA) method on two selected samples (palygorskite and sepiolite) at Krakow Physics and Nuclear Technics Institute in Poland. Details of experimental procedures were given by Janczyszyn *et al* (1989) and Wyszomirski and Janczyszyn (1991).

RESULTS AND DISCUSSION

Distribution of clay minerals

Palygorskite appears to be concentrated in the uppermost parts of the Upper Cretaceous Zorbehan formation (Figure 2). Smectite, chlorite, serpentine and illite together with calcite and feldspar were mainly observed in the Kösehasan and Boyalikdere formations (Bozkaya and Yalçin 1991).

Variable proportions of carbonate (dolomite, calcite), sulphate (gypsum, celestite), clay (sepiolite, palygorskite, smectite, minor amounts of serpentine and chlorite) and silica (quartz/chalcedony) minerals, as well as plagioclase and Fe-oxide minerals of detrital origin were determined in the evaporitic series of the Yağca formation. Dolomite was abundant, and was commonly associated with sepiolite, palygorskite and smectite. Samples with only palygorskites in their clay fractions included dolomite in the Uzunkaya hill, whereas it was not detected in the samples with pure sepiolites in the Mezgi ridge.

Clay fractions from the Kizilyatak formation contained palygorskite with a minor smectite, chlorite and serpentine component. In addition, it was observed that pure palygorskite phases were mainly associated with calcite.

Calcite was the dominant carbonate mineral in the Kocaözü formation. The clay fraction was commonly represented by smectite, and partly by palygorskite, chlorite, and serpentine. Abundances of both dolomite and palygorskite were lower than those recognized in the Kizilyatak and Yağca formations, whereas that of smectite was higher.

The Uğurlu formation had mainly calcite, less do-

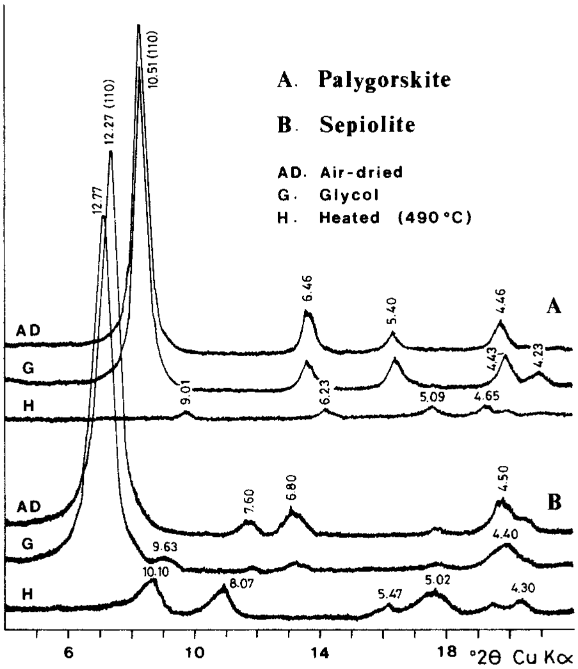

Figure 3. X-ray diffractograms of oriented sepiolite and palygorskite samples from the Hekimhan district.

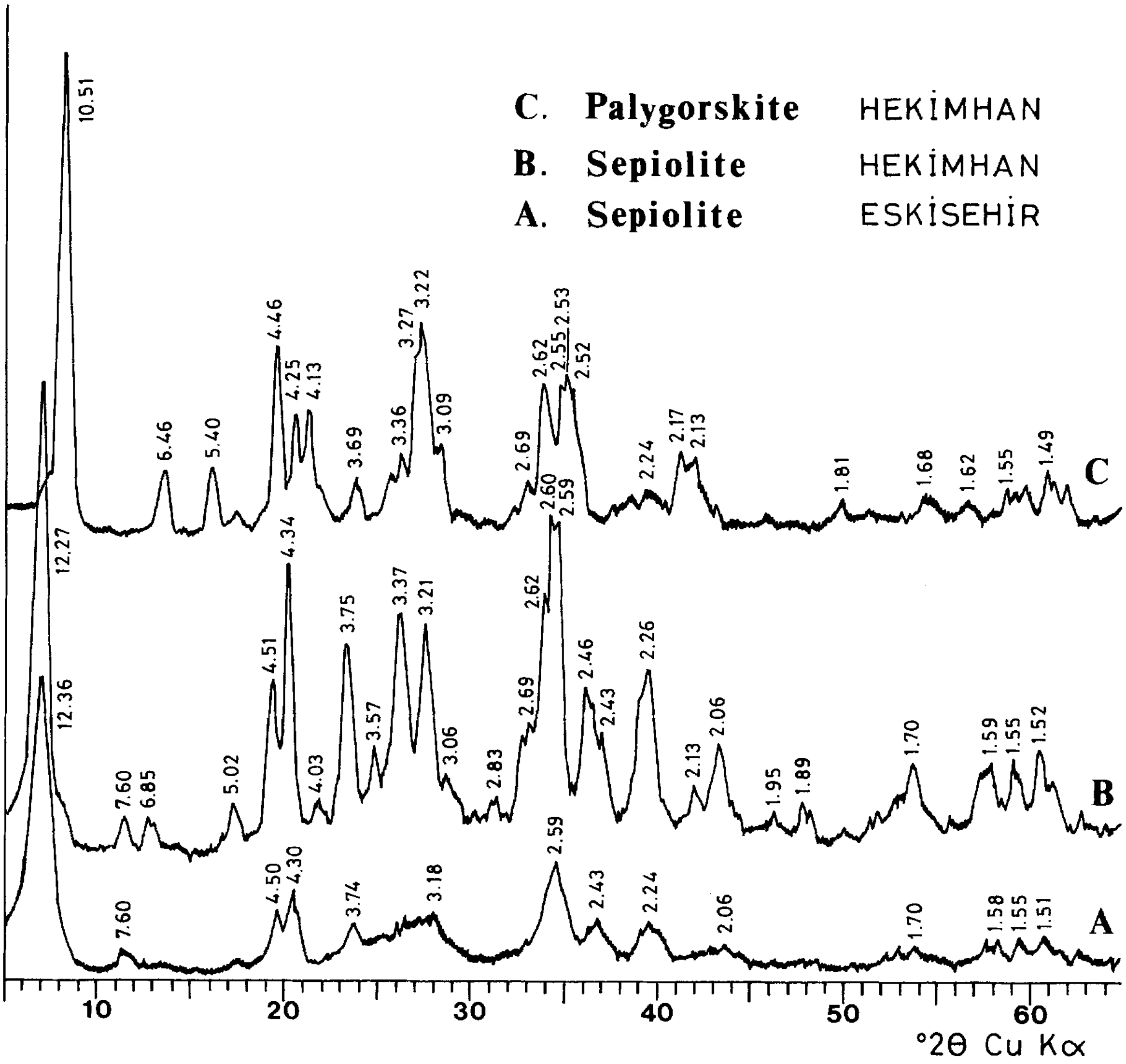

Figure 4. Non-oriented XRD patterns of sepiolite and palygorskite from the Hekimhan deposit.

lomite and clay minerals. Only palygorskite as well as palygorskite, smectite, chlorite and serpentine associations were contained in the clay fraction in the Kumgedik hill.

The chronostratigraphic distribution of the carbonate and clay minerals can be summarized in Table 1.

XRD patterns

X-ray diffraction patterns of sepiolite and palygorskite following various treatments are shown in Figure 3. The intensities of the (110) peaks of both palygorskite and sepiolite samples were strongly reduced after heat treatment. Following glycolation, there was no swelling in palygorskite, whereas the (110) peak of sepiolite slightly expanded to 12.77 Å. Similar properties were also observed in the Eskişehir (Ece and Çoban 1994) and Yunak sepiolites (Yeniyol 1986).

Sharper peaks in the powder diffractograms of unoriented samples (Figure 4) suggest that the crystallinity of the sepiolite from the Hekimhan area is better developed than in the Eskişehir (Brindley 1959; Caillere and Hénin 1963; Ece and Çoban 1994) and Yunak area (Yeniyol 1986). Three "diagnostic regions," 4.0–4.5 Å (2θ = 19–23°), 3.05–3.3 Å (2θ = 25–30°), and 2.5–2.6 Å (2θ = 33–36°), were proposed by Christ *et al* (1969) and Chisholm (1990, 1992) in order to distinguish between orthorhombic and monoclinic forms of palygorskite. The peaks of 4.25, 3.09, and 2.54 Å for orthorhombic and 4.33–4.37, 4.13, 3.27, 2.55, and 2.48 Å for monoclinic forms were distinctive. Observation of peaks both at 4.25 Å and at 4.13 Å of similar

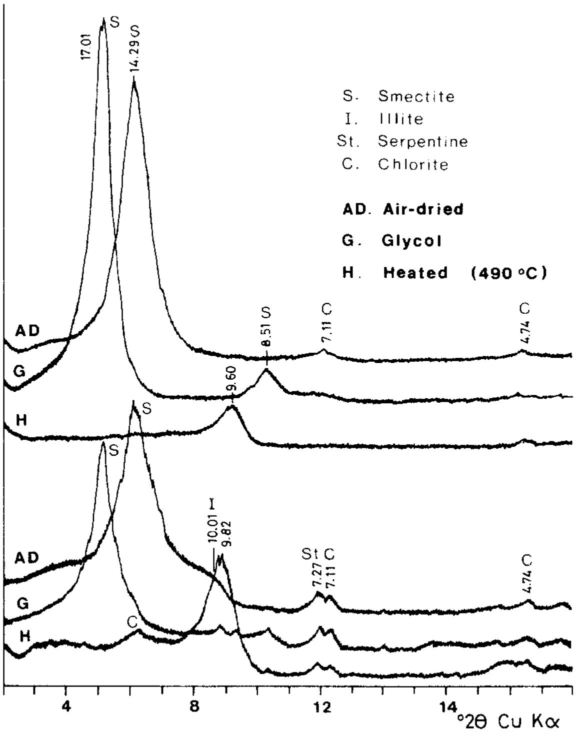

Figure 5. XRD patterns of oriented trioctahedral smectite-rich clays.

intensity in the Hekimhan palygorskite (Figure 4) indicates that the sample included both orthorhombic and monoclinic forms. Additional peaks at 3.69, 3.09, 2.69, and 2.53 Å for orthorhombic forms and at 3.27, 2.62, 2.55 and 2.52 Å for monoclinic forms support this conclusion. Palygorskite assemblages including both orthorhombic and monoclinic forms were also pointed out by Chisholm (1992).

Smectites are indicated by expansion of the (001) reflection to about 17 Å on ethylene glycol solvation and collapse to 9.28 Å on heating to 490°C (Figure 5). Smectites are always associated with chlorite and/or serpentine and sometimes illite. The percentage of these clay minerals in the smectite-rich clay fraction ranges from 5 to 20 weight %. The smectites have d(060) values in the trioctahedral range (1.532 to 1.537 Å) corresponding to saponite (Brindley 1980a; Caillere *et al* 1982).

SEM investigations

Sepiolite occurs as thin fibers completely coating dolomite crystals that can be realized by their trigonal crystal forms in the clayey dolomite (ÖB-156, Figure 6A). Sepiolite fibers form fan-like bundles and they have threadlike, bended morphology (Figure 6B). The bent sepiolite filaments have a length of 10–20 μm with a width and thickness of less than 1 μm.

In the claystone (ÖB-168) containing palygorskite plus sepiolite association without carbonate minerals of the Yağca formation, palygorskite particles have tabular shape with smooth edges and the acicular morphology was recognized at the tips of the plates (Figure 6C). The particles have a length of 10–15 μm, a width of 1–5 μm, and a thickness of 1–2 μm. Thread-like sepiolites in this photomicrograph may have grown on the palygorskites.

In the other sample (ÖB-164, Figure 6D), iron framboids without sulphur and hexahedric and octahedric pyrites of authigenic origin were observed in the micropores of dolomitic claystone of the Yağca formation. This sample contained smectite (70 wt %) and chain-structure clays (30 wt %). Fe-framboids are seen as spherical aggregates with sizes up to 10 μm. Smectites, which show very thin irregular lamellae, are partly curled on the upper side of the photomicrograph. Smectite aggregations of very small particles look fluffy. The chemical composition (%) of the cracked coatings surrounding the framboids on the left side of the photomicrograph using EDS method is determined as SiO_2 = 15.03–16.12, Al_2O_3 = 18.03–18.78, Fe_2O_3 = 16.16–16.38, Cr_2O_3 = 37.83–39.57 and MgO = 10.99–11.11. This composition is quite similar to the mixed chemistry of chromite inclusion-bearing mafic minerals. This data is evaluated in that there is a close relationship between sepiolite-palygorskite occurrences and dark-colored ferromagnesian minerals that are transported into the basin from the surrounding rocks (ophiolite complex) together with colloidal and dissolved constituents.

Chemical analyses

Major, trace and REE element analyses of three sepiolite samples (ÖB-171, ÖB-174, ÖB-176) and two palygorskite samples (ÖB-187, HB-37) collected from the Yağca formation, one palygorskite sample (ÖB-89) from the Kizilyatak formation, one palygorskite sample (HB-241) from the Uğurlu formation, four samples of trioctahedral smectites (ÖB-31b4, ÖB-192, ÖB-254, ÖB-256), which largely outcrop in the Zorbehan formation, and one from the Yağca formation (HB-20) are reported in Tables 2–4. Chemical analyses of the Eskişehir sepiolite (ES-1) are also reported for correlation. The structural formulas were calculated (Table 2) on the basis of 32 oxygen atoms for sepiolite, 21 for palygorskite and 11 for smectite (Weaver and Pollard 1973).

From the structural formulas of sepiolite, it can be seen that there is very little tetrahedral Al for Si substitution (0.01–0.07). Mg is the dominant cation in the octahedral site, accompanied by minor amounts of Fe, Al, Cr, Ni, and rarely Ti. Interlayer cations are Ca, Na, and K. Octahedral composition of the Eskişehir sepiolite differs significantly from Hekimhan sepiolite, as seen in Table 2. Octahedral Mg is higher than for the

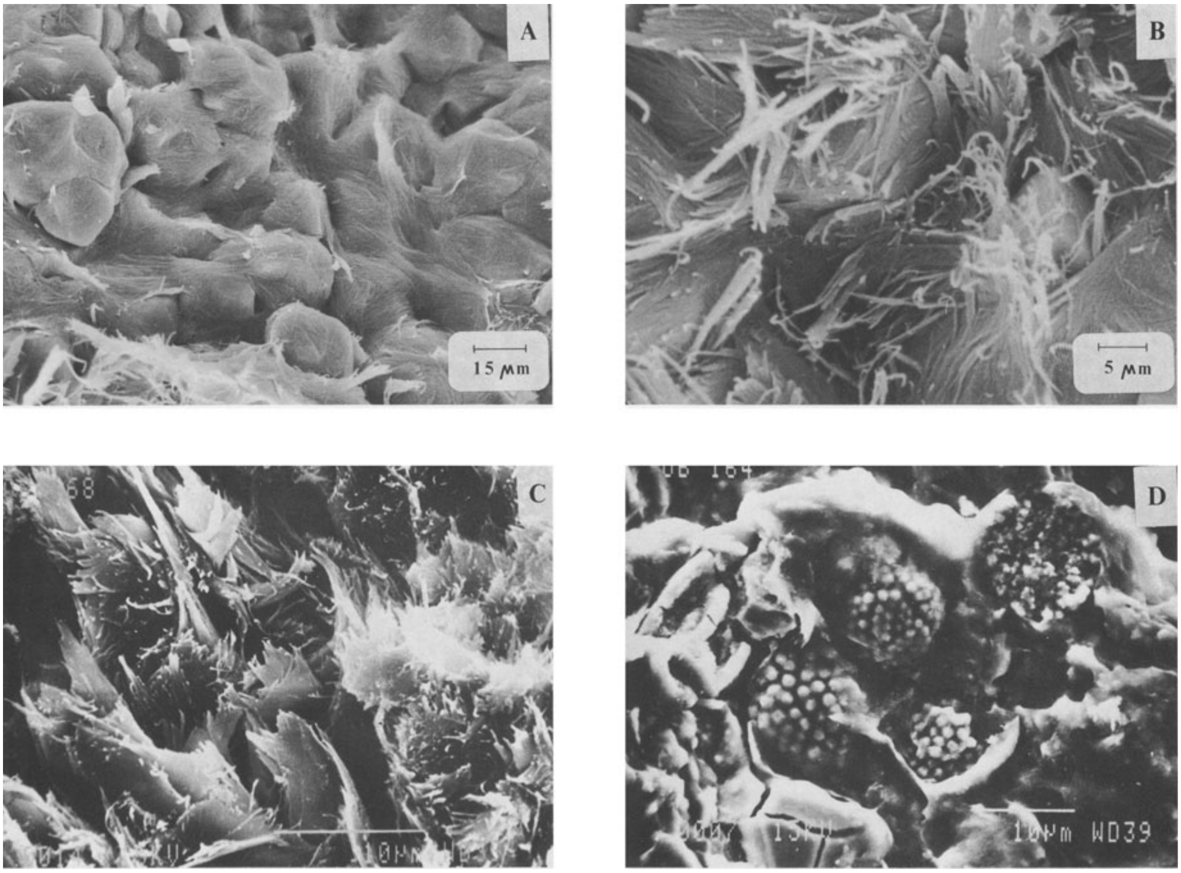

Figure 6. Scanning electron photomicrographs: A) The thin meshworks of sepiolite coating dolomite grains. B) Fan-like forms of fibrous-threadlike sepiolites. C) Acicular-tabular palygorskites. D) Iron framboids surrounded with smectites.

Hekimhan sepiolites, whereas Fe, Al, Cr, and Ni concentrations are lower. The layer charge of the Eskişehir sepiolite is similar to Yunak sepiolite because its chemical composition (Yeniyol 1986) is also very low, while loss on ignition is nearly twice that of the Hekimhan sepiolite. This difference is due to their degree of crystallinity, as pointed out at the studies of XRD powder diffraction. It can be concluded that the Hekimhan sepiolite contains less Al but more Fe than the other reported sepiolites (Imai *et al* 1969; Stoessel and Hay 1978; Weaver and Pollard 1973; Jones and Galan 1988; Torres-Ruiz *et al* 1994).

Palygorskite contains a larger quantity of tetrahedral substituted Al than sepiolite. This results in an increase of the layer charge. Mg, Al, and Fe are the dominant octahedral cations accompanied by lower amounts of Ti, Ni, and Cr. In order of abundances the interlayer cations are Ca, K, and Na. The Hekimhan palygorskite is similar to some palygorskite samples from various countries (Attapulgus, Georgia-U.S.A.: Bradley 1940, Kuzuu-Japan: Imai *et al* 1969, Jbel Ghassoul-Morocco: Chahi *et al* 1993, Atikokan-Ontario: Kamineni *et al* 1993, Spain: Torres-Ruiz *et al* 1994), particularly with regard to their mean major elements. However, tetrahedral Al substitution is higher, octahedral Al is lower, but Fe is higher for the Hekimhan palygorskite.

Smectites from Mg-bearing clay minerals may be called Al-Fe saponite (Weaver and Pollard 1973), although pure phases were not obtained from clay fractions, and their tetrahedral substitutions are high (0.35–0.58). Amounts of Cr and Ni with smectites are lower than sepiolites. Their H_2O^+ content is lower, while layer charges are higher compared to the chain-structure clays. Cr, Ni and Sr concentrations of one saponite sample (HB-20) from the Yağca formation are higher than in the other four samples of the Zorbehan formation. The high content of K in the smectites is related to illite in minor amounts as observed from clay X-ray patterns. In addition, Li is preferentially concentrated in the Mg-smectite phase as against that of sepiolite-palygorskite as pointed out by Tardy *et al* (1972).

Chemical compositions of sepiolite, palygorskite, and Al-Fe saponite are shown in Figure 7. On the tetra-

Table 2. Major element compositions and structural formulas of clay minerals.

	Sepiolite				Palygorskite				Smectite				
% Oxide	ÖB-171	ÖB-174	ÖB-176	ES-1	ÖB-187	HB-37	ÖB-89	HB-241	ÖB-254	ÖB-31b4	ÖB-192	ÖB-256	HB-20
SiO_2	60.30	60.16	60.24	54.13	56.73	57.72	58.85	58.50	52.09	52.32	48.55	49.09	50.06
TiO_2	0.01	0.10	0.04	0.02	0.44	0.36	0.52	0.55	0.80	0.09	1.03	0.63	0.54
Al_2O_3	0.67	0.67	0.81	0.25	8.72	6.72	8.57	10.07	13.10	12.16	11.63	11.09	11.33
ΣFe_2O_3	2.14	2.38	1.64	0.13	7.81	10.41	5.78	7.02	10.49	9.53	10.93	9.85	10.65
MnO	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.04	0.03	0.05
Cr_2O_3	0.38	0.43	0.38	0.01	0.07	0.08	0.10	0.06	0.07	0.06	0.06	0.10	0.07
NiO	0.25	0.25	0.23	0.17	0.24	0.11	0.25	0.16	0.09	0.07	0.10	0.13	0.26
MgO	24.32	23.50	24.67	23.75	12.16	9.78	12.60	10.52	9.07	11.78	14.27	15.35	14.45
CaO	0.13	0.13	0.20	0.01	0.56	0.55	0.45	0.41	1.76	1.24	1.45	1.46	0.80
Na_2O	0.04	0.04	0.05	0.03	0.13	0.25	0.12	0.19	0.15	0.25	0.26	0.17	0.37
K_2O	0.06	0.07	0.06	0.02	1.07	0.42	0.40	0.42	2.53	2.24	1.97	1.71	2.49
P_2O_5	0.06	0.06	0.06	0.02	0.07	0.11	0.04	0.07	0.68	0.75	0.59	0.49	0.23
L.I.	11.07	10.86	10.92	20.33	11.69	12.89	10.84	11.60	8.15	7.80	7.33	8.88	9.14
TOTAL	99.44	98.66	99.31	98.89	99.71	99.44	98.54	99.59	99.01	98.32	98.21	98.98	100.44
Tetrahedral													
Si	11.96	12.00	11.93	11.99	7.53	7.80	7.71	7.66	3.63	3.65	3.42	3.47	3.49
Al	0.04	—	0.07	0.01	0.47	0.20	0.29	0.34	0.37	0.35	0.58	0.53	0.51
T.C.	—	—	0.07	0.01	0.47	0.20	0.29	0.34	0.37	0.35	0.58	0.53	0.51
Octahedral													
Al	0.12	0.16	0.12	0.06	0.89	0.87	1.03	1.21	0.71	0.65	0.39	0.36	0.42
Ti	—	0.02	0.01	—	0.04	0.04	0.05	0.05	0.04	—	0.05	0.03	0.03
Fe	0.32	0.36	0.24	0.02	0.78	1.06	0.57	0.69	0.55	0.50	0.58	0.52	0.56
Cr	0.06	0.07	0.06	—	0.01	0.01	0.01	—	—	—	—	0.01	—
Ni	0.04	0.04	0.04	0.03	0.03	0.01	0.02	0.01	0.01	—	0.01	0.01	0.01
Mg	7.19	6.99	7.28	7.84	2.41	1.97	2.46	2.05	0.94	1.22	1.43	1.55	1.46
O.C.	0.04	0.09	0.06	0.02	—	0.06	0.01	—	0.20	0.11	0.01	0.01	—
T.O.C	7.73	7.64	7.75	7.95	4.16	3.96	4.14	4.01	2.25	2.37	2.46	2.51	2.48
Interlayer													
Mg	—	—	—	—	—	—	—	—	—	—	0.07	0.07	0.04
Ca	0.03	0.03	0.04	—	0.08	0.08	0.06	0.06	0.13	0.09	0.11	0.11	0.06
Na	0.02	0.02	0.02	0.01	0.02	0.08	0.03	0.05	0.02	0.03	0.04	0.02	0.05
K	0.02	0.02	0.01	0.01	0.18	0.07	0.07	0.07	0.23	0.20	0.18	0.15	0.22
I.L.C.	0.10	0.10	0.11	0.02	0.36	0.31	0.22	0.24	0.51	0.41	0.58	0.53	0.47
T.L.C	0.08	0.09	0.13	0.03	0.47	0.26	0.30	0.34	0.57	0.46	0.59	0.54	0.51

ΣFe_2O_3 = Total Iron, K.I. = Loss on Ignition, T.C. = Tetrahedral Charge, O.C. = Octahedral Charge, T.O.C. = Total Octahedral Cation, I.L.C. = Interlayer Charge, T.L.C. = Total Layer Charge.

hedral+octahedral Si-Mg-Al+Fe^{+3} diagram, smectites are distributed in or near the region plotted by Eberl *et al* (1982) for saponite and Jones (1983) for smectite. Sepiolite and palygorskite are distributed in the zones defined by Weaver and Pollard (1973). On the octahedral Mg-Al-Fe^{+3} diagram, sepiolite values are close to those values given by Weaver and Pollard (1973). Palygorskite and smectite values are distributed outside the regions plotted by the above authors. This is a result of the higher Fe-contents of palygorskite and smectite from the Hekimhan district.

Trace and REE data for pure sepiolite and palygorskite are rare in the literature, which made the comparison difficult. However, the compositions of the Hekimhan sepiolite-palygorskite are compared with some published values. The contents of trace elements arranged according to their similar geochemical behaviour are comparatively given in Figure 8 comprising representative sepiolite (ÖB-171) and palygorskite (ÖB-187) samples. Amounts of these elements in palygorskite are higher than in sepiolite, except Cr and Br. This indicates that palygorskite can accomodate most elements possibly due to their crystal structure, which is very convenient for the substitution of these elements. Palygorskite bearing trace amounts of montmorillonite is formed of alteration of serpentine minerals from Iraq (Dhannoun and Al-Dabbagh 1988) that contains similar concentrations of Cr and Co, but low concentration of Ni compared with the Hekimhan palygorskite. These authors also noticed that unsoluble Cr, Ni, and Co were structurally associated with palygorskite. Concentrations of some transition series (V, Cr, Co, Ni, Cu, Zn) and low field strength elements (LFSE) such as Ba and Sr of the neoformed sepiolite from Spanish deposits (Torres-Ruiz *et al* 1994) are remarkably lower, while Li values are close to those of the present study. Sepiolite-palygorskite minerals with low Li contents are formed by chemical precipitation as proposed by the above writers.

The Hekimhan palygorskite shows a noticeable low

Table 3. Concentrations of selected trace elements in the clay minerals.

	Sepiolite						Palygorskite						Smectite						
	ÖB-171	ÖB-174	ÖB-176	Mean	S.D.	ES-1	ÖB-187	HB-37	ÖB-89	HB-241	Mean	S.D.	ÖB-254	ÖB-31b4	ÖB-192	ÖB-256	HB-20	Mean	S.D.
Cr	2613	2957	2618	2729	197.2	69	483	550	665	413	525	103.0	481	415	413	688	481	496	112.7
Ni	1969	1928	1796	1898	90.4	1333	1878	829	1955	1234	1474	538.0	739	540	775	1045	2054	1031	599.7
Co	63	67	44	58	12.3	45	55	44	34	68	50	14.6	45	22	68	46	45	45	16.3
V	31	32	32	32	0.6	24	84	68	139	104	99	30.6	n.a.	n.a.	n.a.	n.a.	n.a.	—	—
Cu	21	22	20	21	1.0	8	23	18	121	14	44	51.5	63	42	42	42	17	41	16.3
Pb	24	22	21	22	1.5	21	23	27	18	24	23	3.7	74	247	20	22	52	83	94.4
Zn	33	195	100	109	81.4	78	56	145	87	167	114	51.2	223	151	153	167	251	189	45.3
Rb	39	38	40	39	1.0	39	79	79	25	79	66	27.0	236	157	156	162	157	174	35.0
Ba	151	148	136	145	7.9	131	166	185	120	171	161	28.2	34	55	72	51	63	55	14.2
Sr	33	31	33	32	1.2	51	34	120	9	80	61	49.2	100	66	63	99	438	153	160.2
Li	51	52	40	48	6.7	10	49	39	42	45	44	4.3	140	70	41	90	78	84	36.2
Nb	16	17	17	17	0.6	17	22	20	10	25	19	6.5	16	16	13	9	13	13	2.9
Zr	<4	<5	<4	4	0.6	<5	50	32	46	84	53	22.1	115	116	107	66	150	111	30.0
Y	1	1	1	1	0.0	1	2	2	3	2	2	0.5	17	6	11	6	10	10	4.5

n.a. = Not Analyzed, S.D. = Standard Deviation.

Table 4. Some trace and REE contents of representative sepiolite and palygorskite using INNA method.

	Sepiolite ÖB-171	Palygorskite ÖB-187
Sc	1.79 (±0.07)	17.9 (±0.07)
Cd	<8	<8
W	4.1 (±0.4)	7.7 (±0.6)
Mo	<8	<8
As	0.47 (±0.14)	1.15 (±0.16)
Se	<1.7	<2.3
Sb	<0.2	0.41 (±0.08)
Ag	<1.8	<1.8
Au	<0.010	<0.012
Hg	<0.9	<0.9
Cs	<0.29	13.4 (±0.8)
Ga	<8	12 (±4)
Ta	0.16 (±0.03)	0.56 (±0.06)
Hf	<0.19	1.22 (±0.11)
Th	<0.3	2.6 (±0.02)
U	1.3 (±0.3)	2.6 (±0.3)
La	0.19 (±0.05)	3.7 (±0.3)
Ce	<5	10.7 (±1.1)
Nd	<8	<7
Sm	<0.06	0.39 (±0.06)
Eu	<0.009	0.090 (±0.006)
Tb	<0.09	<0.11
Yb	<0.27	0.53 (±0.17)
Lu	<0.1	0.11 (±0.03)
Σ REE	<13.719	<22.63
Br	4.9 (±0.5)	<0.6

total REE content (<22.63 ppm) compared with those of different origin. For example, palygorskites from fracture zones in the Eye-Dashwa Lakes granitic pluton (Kamineni *et al* 1993) have high total REE concentrations (1984 ppm). Similarly, the REE amount of sepiolite from the Hekimhan region is lower than that of Spain sepiolite (Torres-Ruiz *et al* 1994).

Palygorskite shows a noticeable enrichment (Figure 9) in the light REE with regard to chondrites (Haskin *et al* 1968). Sepiolite is markedly enriched in Nd. Fibrous clay minerals have a small light rare earth element (LREE) variability (La 0.6-12x chondritic) and a narrower range in heavy rare earth element (HREE; Yb < 1.6–3× chondritic). LREEs of palygorskite are high, when compared with sepiolite. Concentrations of HREEs are partly similar in both, and Eu exhibits a large negative anomaly, whereas Nd has a positive anomaly. Chondrite-normalised REE abundances in harzburgites and dunites belonging to the ultramafics representing Oman ophiolites (Pallister and Knight 1981) are also shown in Figure 9. They have a pattern of relative abundance similar to that of the chain-structure clays. However, the concentrations are naturally lower which may indicate that there is elemental fractionation, and no significant amounts of detrital material can be re-incorporated particularly into sepiolite (Church and Velde 1979; Trauth 1977).

Total REE concentrations of chain-structure clays of marine origin from Hekimhan region were consider-

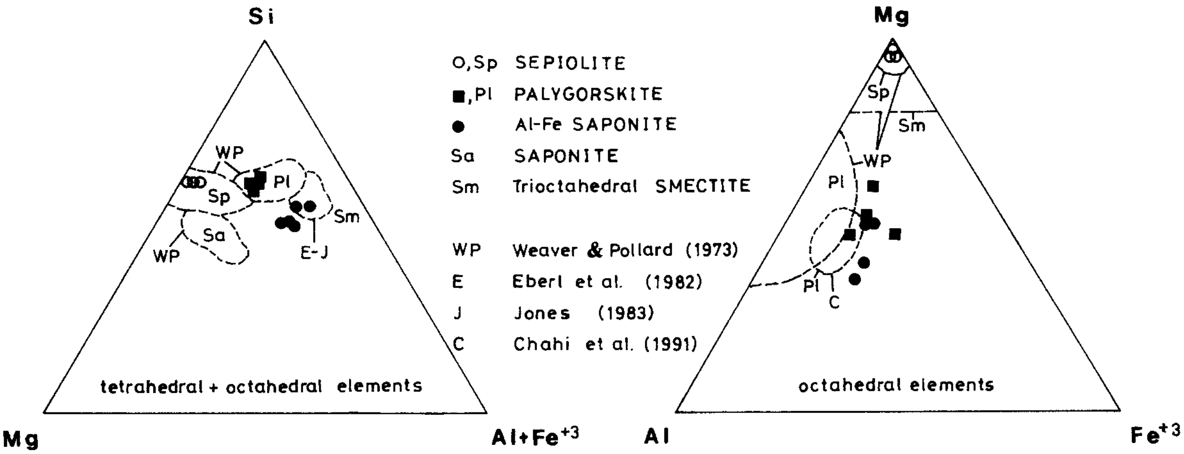

Figure 7. Tetrahedral+octahedral and octahedral compositions of clay minerals.

ably lower than those of the North American Shale Composite-NASC (Haskin *et al* 1968; Fleet 1984; Taylor and McLennan 1985; McLennan 1989), clay fractions of pelites (Caggianelli *et al* 1992) and Pacific pelagic sediments (Toyoda *et al* 1990). Consequently, no REE rich accessory phases were present in the studied clay samples, which have contents of transition metals and HFSE distinctly lower than the average values re-

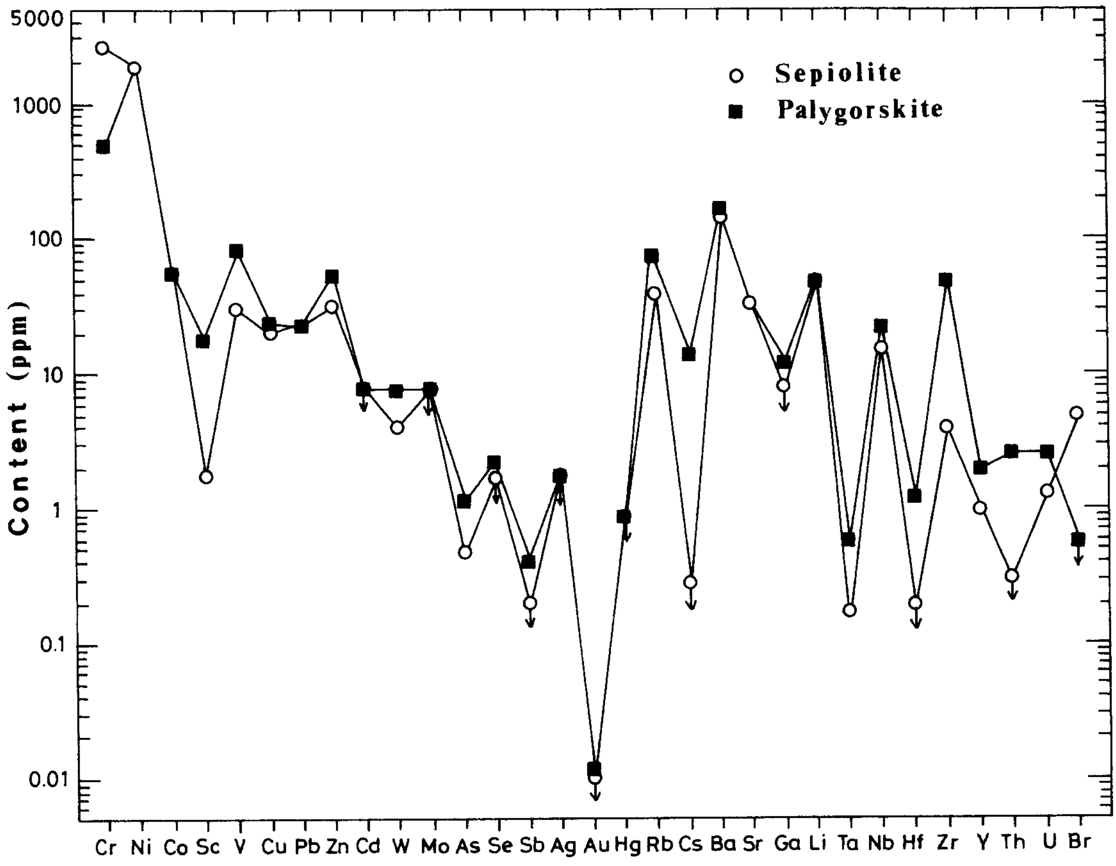

Figure 8. Trace element distribution in the representative sepiolite and palygorskite. Arrows indicate values below the determination limits.

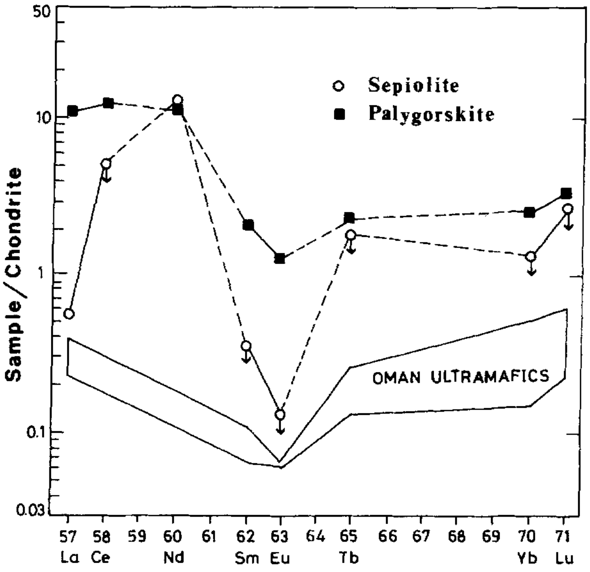

Figure 9. Chondrite-normalized REE abundances in sepiolite and palygorskite (Chondrite: Haskin *et al* 1968, Oman ultramafics: Pallister and Knight 1981). Arrows indicate values below the determination limits.

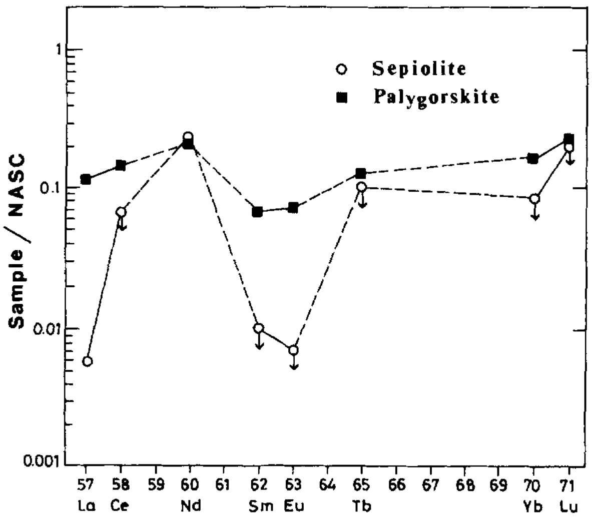

Figure 10. Shale-normalized REE pattern of fibrous clay minerals (NASC = North American Shale Composite from Haskin *et al* 1968). Arrows indicate values below the determination limits.

ported by Taylor and McLennan (1985) for typical shales. The shale-normalized REE pattern (Haskin *et al* 1968) is irregular, with a significant elemental fractionation and a negative anomaly in Eu (Figure 10). REE contents of sepiolite and paligorskite range from 3 to 163 and 4 to 14 times for the NASC values, respectively. Furthermore, in comparison with the NASC pattern, particularly sepiolite with a noticeable depletion in REE shows that these elements are not mainly supplied by detrital minerals. Both this difference and ΣREE contents suggest that palygorskite tends to be the principal REE carrier with respect to sepiolite.

OCCURRENCE

Sepiolite and palygorskite deposits from the Hekimhan district have different geological settings and geochemical properties. Sepiolites found with dolomites appear to have partially formed by displacement of dolomites, as seen in the SEM photomicrographs. Occurrences of fibrous clay minerals coating carbonate grains were also observed by Hassouba and Shaw (1980), Estéoule-Choux (1984) and many others, and were interpreted as suggesting an authigenic origin rather than detrital. Reactions of pore waters rich in silicic acid with dolomite suggests the type occurrences as below:

$$8CaMg(CO_3)_2 + 12H_4SiO_4 \rightarrow Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4.8H_2O + 2H_2O + 8Ca^{++} + 16\ HCO_3^-$$

Absence of dolomite in the sepiolitic claystone in the Hekimhan region shows that sepiolite may have been formed by direct crystallization, as many writers worked in several environments (Millot 1970; Singer 1979; Weaver 1984; Isphording 1984; Estéoule-Choux 1984; Singer 1984; Chahi *et al* 1993; Torres-Ruiz *et al* 1994), formulized in the reaction as follow (Jones 1986):

$$8Mg^{+2} + 12H_4SiO_4 + 16(OH^-) \rightarrow Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4.8H_2O + 18H_2O$$

SEM observations of the sepiolite+palygorskite sample without smectite or the other clay minerals, suggested that sepiolites may have been formed from palygorskites. This mechanism should have taken place as a diagenetic transformation:

$$Mg_2(Al,Fe^{+3})_2Si_8O_{20}(OH)_2(OH_2)_4.4H_2O + 6Mg^{+2} + 4H_4SiO_4 + 6(OH^-) \rightarrow Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4.8H_2O + 6H_2O + (Al,Fe^{+3})_2$$

Transformation of another clay, for example illite (Galan and Castillo 1984), smectite (Singer 1984), or detrital phyllosilicates (Torres-Ruiz *et al* 1994) to generate palygorskites are proposed. But there was no evidence on the SEM observations of palygorskites which was accompanied by calcite and/or dolomite. Authigenic or direct precipitation mechanisms were suggested for the palygorskites. The reaction is given below:

$$2Mg^{++} + (Al,Fe^{+3})_2 + 8H_4SiO_4 + 10(OH^-) \rightarrow Mg_2(Al,Fe^{+3})_2Si_8O_{20}(OH)_2(OH_2)_4.4H_2O + 12H_2O$$

It is suggested that occurrences of sepiolite, palygorskite, smectite, dolomite and calcite were controlled by pH, salinity and/or alkalinity, cation proportions (Si/Al + Fe, Ca/Mg and Mg/H), and concentration of H_4SiO_4 in the solution. Si, Mg, Al, and Fe may have been derived in solution from ophiolitic suite as a result of hydrolysis of mafic minerals in the basic environment. Ca is generally related to the carbonate rocks in the surrounding area. Occurrences of chert in the carbonate rocks indicate that the environment was saturated with silicic acid. Trace and especially REE concentrations indicate that no detrital clay phases of terrestrial sources provided the elements to form sepiolite-palygorskite.

The cyclical variations in the mineral distribution considerably in the Yağca formation are inconsistent with the homogenous mineral paragenesis in the other units. These can be explained only by changes of physicochemical conditions of the environment and/or controlling each other's occurrences of the diagenetic minerals such as clay and carbonate minerals. A possible role of clay minerals in the formation of dolomite were reported by Kahle (1965) and Ataman (1966), and the importance of magnesium in the formation of smectites by Harder (1972). In other words, Mg-clay (especially sepiolite) + dolomite assemblage may occur when the Mg/Ca ratio is too high; Mg-clay (palygorskite, smectite) and/or calcite appears if this ratio is lower. This was observed for the vertical distribution of clay-carbonate minerals from the Hekimhan region.

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