

GEOLOGY, OCCURRENCE, AND GENESIS OF ESKİŞEHİR SEPIOLITES, TURKEY

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Abstract—The occurrences of sepiolite beds and nodules in alkaline and saline Miocene Eskişehir lake deposits provide unique examples of ancient lacustrine environments. Stockwork-type magnesite deposits, which were formed very close to the Miocene lake, served as parent rocks for sepiolite nodules (meerschau). The Miocene succession consists of calcareous clay, clayey carbonate, dolomite, a gypsum-bearing calcareous clay series, siliceous tuffs, sepiolite beds, sepiolite-bearing dolomite, and basal conglomerates of ultramafic rocks. Sepiolite beds were deposited by direct precipitation from Si-supersaturated lake water under alkaline and saline conditions. They are underlain by a gypsum series. Organic matter-rich sepiolites suggest the presence of water stratification with anoxic bottom waters, which developed due to high sulphate input at the base from the ascending hydrothermal solutions along the fracture systems with extensive fresh water input near to the surface. Sepiolite nodules resulted from diagenetic replacement of magnesite pebbles at shallow burial under alkaline conditions in the vicinity of paleo-shorelines. Sepiolite beds were deposited in three ways: 1) black (up to 2.8 wt. % TOC) sepiolite beds rich in organic matter accumulated in an anaerobic paleoenvironment; 2) brown (about 0.5 wt. % TOC) sepiolite beds poor in organic matter, containing minor amounts of white, 2–6 mm long, discontinuous, and very soft dolomite laminae formed in a dysaerobic paleoenvironment; and 3) white dolomitic sepiolite beds in which dolomite content is about 20–40% in an aerobic paleoenvironment.

Cyclic dolomite and gypsum series indicate hypersaline-evaporative paleoenvironments with rapid changes in lake water chemistry. These cyclic evaporative conditions are also related to cyclic changes in water depth. Based on X-ray powder diffraction data, except degree of crystallinity, no mineralogic difference was found between sepiolite in beds and nodules. SEM studies revealed fibers about 0.2 μm wide and up to 30 μm long in sepiolite beds; crystals less than 5 μm long with bent tips; and a more compacted appearance in sepiolite nodules.

Key Words—Environment, Lacustrine, Magnesite, Sepiolite, Turkey.

INTRODUCTION

Sepiolite nodules, known as “lületaşı” in Turkey (meaning pipestone in Turkish = meerschau = cuttlefish), have been exploited in the Eskişehir province since the time of the Roman Empire. Sepiolite occurs in both medium- to thick-bedded, black or white sedimentary-type layers and in snow-white nodular concretions. Sepiolite beds have also been reported from playa lake deposits in Nevada and California (Post, 1978; Hewett, 1956), Saudi Arabia (Shadfan *et al.*, 1985), and Spain (Galan and Ferrero, 1982). Sepiolite and palygorskite beds are common in lacustrine Spanish Tertiary basins, and some deposits have great economic importance. There are however, no reports of sepiolite nodules in Spain. Turkish sepiolite nodules are unique with regard to some physical properties, such as purity, softness, whiteness, etc. They are especially suitable for handcrafted souvenirs, such as tobacco pipes, chess pieces, necklaces, etc., and for use in the cosmetics industry.

Preliminary studies on two types of Eskişehir sepiolite deposits were reported by Akinci (1967). Initial mineralogical studies on sepiolite nodules from the Türkmentokat-Sarisu area in the Eskişehir basin were done using XRD, DTA, TG, DTG, and IR techniques

by Otsuka *et al.* (1973). They reported that the single fibers are often 0.5 μm in length and have a diameter of 0.05 μm . Also, mineralogical assemblages and occurrences of Miocene Yunak sepiolite nodules that are similar to Eskişehir sepiolites were reported from the Konya region by Yenişol and Öztunalı (1985). The aim of this study is to document the stratigraphic setting and mineralogic properties of two different types of sepiolite deposits and to analyze their relationship to the depositional paleoenvironments of the Middle to Upper Miocene sediments of the Eskişehir lacustrine basin.

GEOLOGIC SETTING AND STRATIGRAPHY

The study area covers two different types of sepiolite occurrences in the following areas: A) Nemli-Akçayır, B) Sepetçi-Margi-Taycılar, C) Sarisu-Türkmentokat, D) south of Sivrihisar (Gülçayır-Kurtşeyh-Ahiler-Tartarlar-Ilyaspaşa-Çakmak), and E) Kayakent (Figure 1). All are surrounded by hills consisting of Upper Cretaceous ultramafic rocks, partially surrounded by Upper Paleozoic dolomitic limestones, and covered by an alkaline and sulphate-bearing lake about 200 km long and 100 km wide from the Middle Miocene to Pliocene. This lake developed in a rift-related graben that

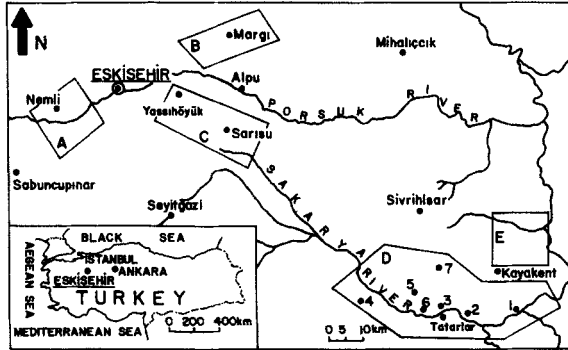


Figure 1. Index map of the study area. Sepiolite nodules were studied in areas A, B, and C and sepiolite beds in areas D and E. Numbers designate the following villages: 1) Çakmaklı, 2) Ilyaspaşa, 3) Ahiler, 4) Gülçayır, 5) İnüstü Tepe, 6) Kurtşeyh, and 7) Ertuğrul.

was formed at the Oligocene/Miocene boundary by the westward motion of the Anatolian block due to the northward push of the Arabian Platform and its consequent extension into the Aegean region. Field studies revealed that syntectonic sedimentation continued while grabens were forming.

A Cretaceous ophiolite complex, consisting largely of peridotites and serpentinites, lies tectonically over the Upper Paleozoic metamorphic rocks and is non-conformably overlain by the Miocene sepiolite-bearing lacustrine sedimentary succession of clayey limestone, calcareous clay, dolomite, gypsum-bearing clayey dolomitic series, and tuffs. The stratigraphic succession in the central part of the lake is not known in detail. For this study, the stratigraphy of the basin was established using the examination of exposures, as shown in a generalized stratigraphic section of the Ilyaspaşa area, south of Sivrihisar, in Figure 2.

During the Late Miocene-Early Pliocene period, volcanism provided mainly tuffs and minor amounts of volcanic breccia, agglomerate, and lava flows of dacite, trachyte, trachyandesite, and rhyodacite compositions in different episodes of explosions (Kulaksiz, 1981). The Sivrihisar igneous complex is located further to the north of the ancient lake. Tuffs were deposited about 20–60 km south of Sivrihisar, and they filled the paleolake during the closing stage.

The major nonconformity between the serpentinites and the conglomerates was better exposed only south of Kayakent. The cyclic sedimentation of green and Fe-oxide rich illitic clay zones with large gypsum (2–10 cm) crystals is exposed alternately and the base shows cyclicity of gypsum crystals with dolomite bands; whereas, thinly calcareous interbeds are randomly distributed, and these rocks are overlain by sepiolite-bearing dolomitic strata (Figure 2). Sepiolite occurrences are examined in two groups.

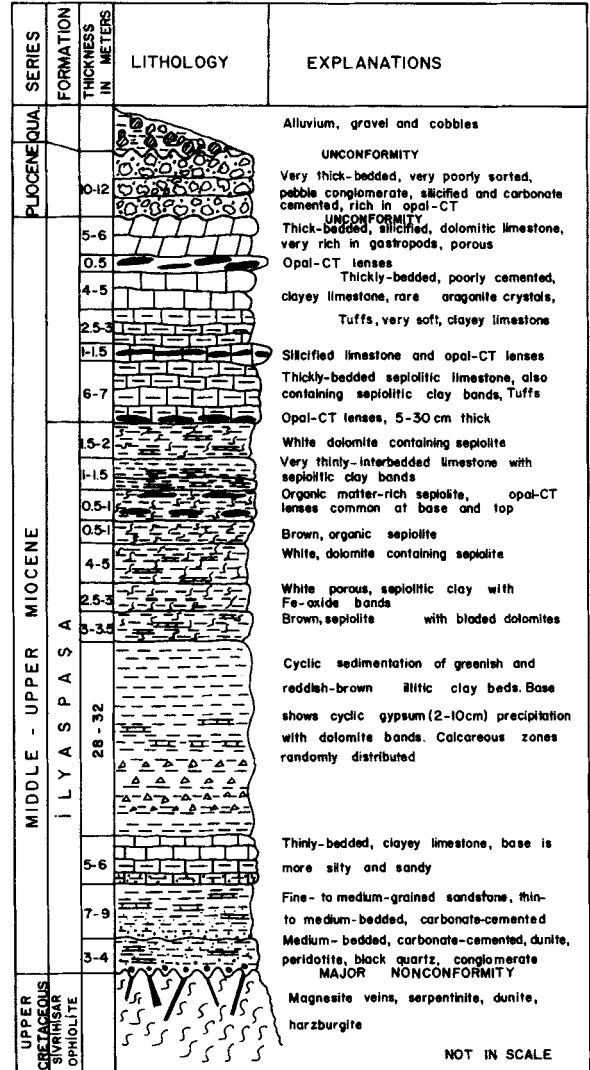


Figure 2. Stratigraphic section in the vicinity of Ilyaspaşa village. Area D in Figure 1.

Sepiolite beds

Three different types of sepiolite beds are recognized in central parts of the basin:

- 1) Organic matter-rich black sepiolite (up to 2.75% TOC).
- 2) Organic matter-poor brown sepiolite, which contains about 5% dolomite.
- 3) White, cream, pale yellow, and dolomitic (~20–40%) sepiolites.

The thickness of sepiolite beds varies throughout the Eskişehir basin; black sepiolites were deposited in the deeper part and are relatively thinner (0.5–2.0 m) than the other types. Black, organic matter-rich sepiolite beds are overlain by brown, discontinuous dolomite

laminae (about 5%) containing sepiolite beds. White sepiolite beds are rarely associated with gypsum crystals, but commonly associated with dolomites that range from 20% to 40%, and opal lenses range from 2 cm to 20 cm in size (Figures 2 and 3). These three different sepiolite occurrences can be examined in different strata of the same exposures (Figures 2 and 3).

An increase in opal-CT beds (5–20 cm thick), which are distributed irregularly and discontinuously in and overlying the sepiolitic clay beds, indicates that siliceous gel precipitated from supersaturated solution during and after sepiolite precipitation (Figure 3), then diagenetically converted to opal-CT (siliceous gel \Rightarrow Opal-A \Rightarrow Opal-CT). The Yassihöyük area (NE of Eskişehir) exhibits a unique feature of alteration of sequences of thinly bedded, clayey dolomitic limestone and organic matter containing medium bedded opal-CT in the upper part of the succession.

Sepiolite nodules

The shallow buried (<50 m) sepiolite nodule containing strata, about 50–100 cm thick, are located in the A) Nemli, B) Margi-Sepetçi, and C) Sarisu areas (Figure 1). The nodules are found in poorly sorted conglomerate beds that are composed of gravels and small blocks of ultramafics, and matrix is made of brown and strongly altered ultramafic rocks. The conglomerates do not exhibit any sedimentary structure, and they are products of landslides and large-scale erosion in different episodes in the vicinity of paleoshorelines of the Miocene lake. These conglomerate beds are directly underlain by ophiolite complex, and this contact exhibits E–W trending fault zone in the Margi and Nemli areas. The particle sizes of conglomeratic materials became relatively larger, as did those of magnesite pebbles and cobbles toward proximal facies. Magnesite cobbles were deposited a short distance from the fault contact and transferred to sepiolite nodule under the groundwater table. Field studies revealed that the rims of magnesite cobbles are sepiolite and the cores are still magnesite, which indicates diagenetic replacement and diffusion processes have not been completed. Generally, only 5% of total volume of materials that were exploited from underground operations are purely sepiolite nodules; the rest are a mixture of sepiolite and magnesite in different percentages, and only those pure sepiolites are suitable to use as souvenir materials.

METHODS OF THE STUDY

Two hundred representative outcrop samples were collected from various exposures around the lacustrine basin. Fifty thin sections of the samples were prepared for petrographic study. Hand-broken, dried clay chips, with fresh surfaces turned upward, were adhered onto the sample holders for scanning electron microscope (SEM) studies. SEM studies were conducted on 200 Å

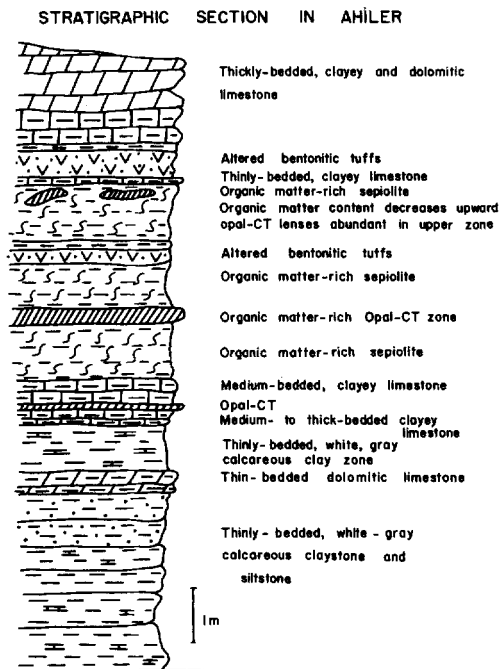


Figure 3. Stratigraphic section in the north of Sakarya river, west of Ahiler. Area D in Figure 1.

thick Au-Pd film-coated sample chips, using an Anatech Hummer VII model sputter coater. The mineralogical composition of the samples was examined using a Philips 1140 X-ray powder diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation and a scanning speed of $1^\circ 2\theta/\text{min}$. Air-dried, ethylene-glycol-solvated, thermally treated samples were used to aid identification.

For clay mineral analysis, the samples were ground in a porcelain mortar and dispersed in 600 ml of deionized water using a heavy-duty soil mixer. For marl and carbonate-rich samples, carbonates were decomposed in warm sodium acetate solution buffered at $\text{pH} = 5$ (Jackson, 1975). The clay fractions of the samples were washed three times with deionized water by centrifuging the slurry in order to get rid of excess cations, which cause flocculation. The $<2 \mu\text{m}$ clay fractions were obtained based on Stoke's law, and the excess water was removed by centrifuging. Smear glass samples were prepared from the remaining clay fractions (Gibbs, 1965, 1968), and their X-ray diffraction patterns were taken for comparison purpose from the following samples: a) air-dried, b) ethylene-glycol-treated, and c) heated up to 500° , 600° , 700° , and 800°C . Sepiolite and palygorskite identifications were based on X-ray data presented by Jones and Galan (1988).

CLAY MINERALOGY

Clay mineral assemblages of the studied sections of Tatarlar, Ilyaspaşa, and İnüstü Tepe consist mainly of sepiolite, and more rarely of minor amounts of smec-

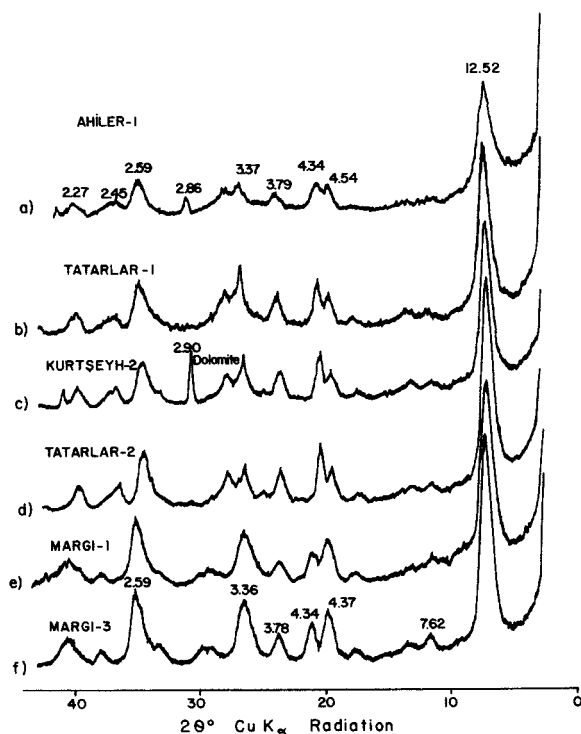


Figure 4. Whole rock X-ray diffraction patterns of sepiolite nodules and beds. The upper two samples belong to organic matter-rich black sepiolite beds; the middle two samples to brown sepiolite beds containing minor amounts of dolomite; and the bottom two samples are from sepiolite nodules. Samples were collected from near Tatarlar, Kurtseyh, Ahiler, and Margi villages. Numbers indicate d-values of peaks in Å.

tite and illite. Illite never coexists with sepiolite. However, rare associations of smectite and sepiolite were found in organic matter-rich sepiolite beds in the Yasıhöyük area. Illite occurs as a result of low-temperature alteration of smectite in K-rich lake waters (A. Singer, personal communication) and is deposited in light green cyclic zones (0.5–1.5 m) in the upper part (Ertuğrul-Ahiler area in Figure 1) and in the lower part (Ilyaspaşa area in Figure 1) of the stratigraphic succession. These illitic zones sometimes contain gypsum crystals.

Table 1. XRD data of Eskisehir sepiolites.

hkl	Bedded	Nodular
110	12.52 Å	12.52 Å
130	7.72	7.84
200		
040	6.75	6.80
150	5.04	5.09
060	4.52	4.57
260	3.74	3.79
080	3.35	3.38
0,10,0	2.69	2.69

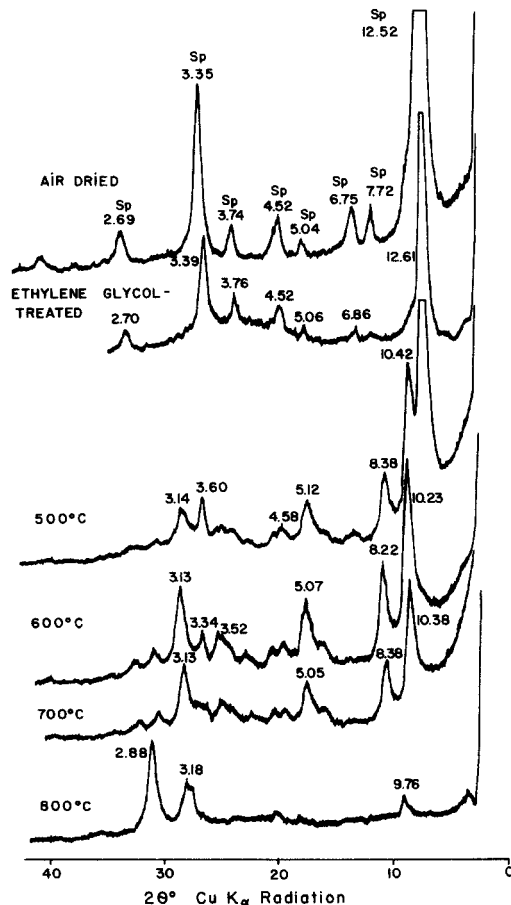


Figure 5. X-ray diffraction patterns of oriented <2 μm clay fractions of bedded sepiolite from Kurtseyh village. Numbers indicate d-values of peaks in Å.

Based on XRD studies, no difference was found in the mineralogy of the sepiolites between white pure nodules, organic matter-poor brown beds, and organic matter-rich black beds (Figure 4). Identifications of sepiolite bedded and nodular were done according to d-values listed in Table 1.

Typical XRD patterns of sepiolite beds and nodules in the <2 μm fractions are shown in Figures 5 and 6, and sepiolite beds commonly occur as fibers bridging between rhombic dolomite crystals (Figure 7D). Sepiolite also occurs as branch-like fibers about 0.2 μm wide and up to 30 μm long (Figures 7A and 7B). Consequently, there is more distance between crystal fibers due to lack of overburden pressure. In contrast, sepiolite crystals in sepiolite nodules consist of fibers less than 5 μm long that form bundles and have tips that are slightly bent (Figure 8). Original magnesite crystals as a parent rock have compact and crypto-crystalline texture; that is the reason for the existence of the appearance of “bundles of fibers” in sepiolite nodules. No palygorskite was identified in nodules and beds by

XRD, yet palygorskite occurs, as rare examples, in the matrix of conglomerates (Figure 8C) that also contain antigorite, dolomite, calcite, amorphous iron oxides, and altered ultramafic materials. In Figure 7D, the sepiolite fibers on the well-crystallized rhombs indicate that dolomitization took place just before sepiolite precipitation. SEM studies also revealed that some dolomite rhombohedrons have subhedral-anhedral morphology due to partial dissolution. In this case, secondary sepiolite fibers were formed as infiltration product on the subhedral dolomites, and they are relatively shorter (Figure 7D). By contrast, primary sepiolite fibers are much longer (Figures 7A and 7B). Moreover, honeycomb-like texture indicates partial dissolution of dolomites, and the cavity in each honeycomb is about 1 μm wide. However, these SEM studies were made on the specifically selected samples from the bed top underlying thick dolomitic limestones for detailed investigations. Therefore, this early dolomitization prior to sepiolite precipitation is not applicable for all white dolomitic sepiolite beds in the basin because these are the products of late-stage diagenetic sepiolite precipitation between the micropores of dolomite crystals at the top of beds due to infiltration of Mg- and Si-rich solutions from the overlying layers.

Heating studies (Figures 5 and 6) showed that nodules are more stable at 500°C than beds. But beginning at 600°C and higher, sepiolite beds became more stable based on peak heights. Samples from both beds and nodules show a new secondary mineral phase forming at 800°C. This study revealed that directly precipitated sepiolite crystals are more stable at high temperature than diagenetically formed counterparts. The reason for this feature is related to the crystal size and morphology.

The bulk chemical composition of the organic matter-rich sepiolite bed is similar to that of sepiolite nodules (Table 2). Only those sepiolite bed samples that contain certain amounts of dolomite are not close to the theoretical composition of sepiolite. We attribute the high Al_2O_3 contents of samples (S_3 , S_6 and S_7 in Table 2), which were collected from the Çakmaklı village area along the Sakarya river, to the presence of illite. These organic matter-poor brown samples also contain high amounts of Fe_2O_3 . This indicates that there is no significant difference in terms of chemical composition between the two different types of sepiolite occurrences. Also, whole rock chemical results were contaminated by impurities.

DISCUSSION

Sepiolite beds

The presence of thinly to medium-bedded clayey dolomite; limestone; marl and laminated clay zones; and rhythmic, grading, and even horizontal structures in the examined sections indicated deposition from

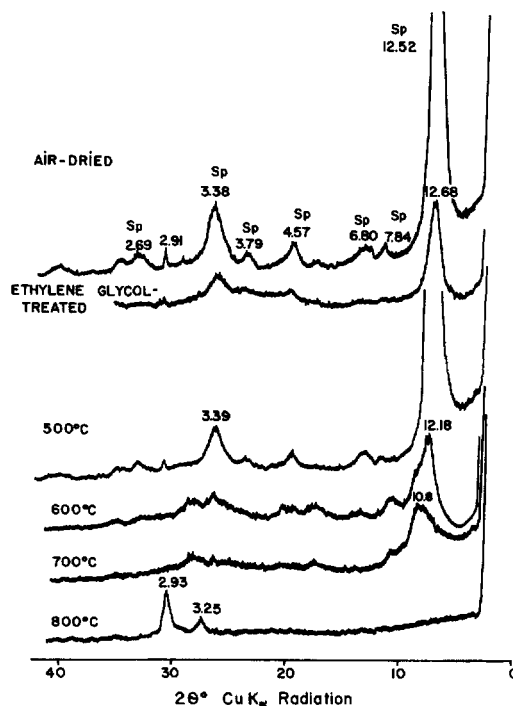


Figure 6. X-ray diffraction patterns of oriented $< 2 \mu\text{m}$ clay fractions of sepiolite nodule sample from Margi village. Sepiolite nodules have lower crystallinity than sepiolite beds. Numbers indicate d-values of peaks in \AA .

shallow lake waters. Gypsum occurs at several horizons in almost all exposures, suggesting that hypersaline-evaporitic conditions frequently existed both before and after major sepiolite precipitation. But this feature was much stronger and longer lasting after sepiolite precipitation.

Organic matter-rich sepiolite beds suggest the existence of water stratification—pycnocline—with bottom water anoxia in the deepest part of the Miocene Eskişehir Lake. Black sepiolite beds that contain close to 98% sepiolite and 2% organic matter are overlain and underlain by brown sepiolite beds, which contain thin irregular lenses of fine dolomite (about 5% of whole rock). These relations suggest the presence of dysaerobic conditions before and after the anoxia maximum, which prevented vertical circulation of lake water. We attribute the anaerobic conditions to pycnoclines formed by high sulphate concentrations that sulphate input came from the hydrothermal activities in the vicinity of the paleolake. The stratigraphic succession suggests the water depth increased progressively during basin subsidence due to extension of the graben. Based on field studies, it is obvious that sepiolite directly precipitated from lake water during anaerobic and dysaerobic episodes to form 1 m to 4 m thick sepiolite beds throughout the whole basin. Moreover, white dolomitic (20–60% of whole rock) sepiolite beds that overlie black and brown sepiolite horizons indicate

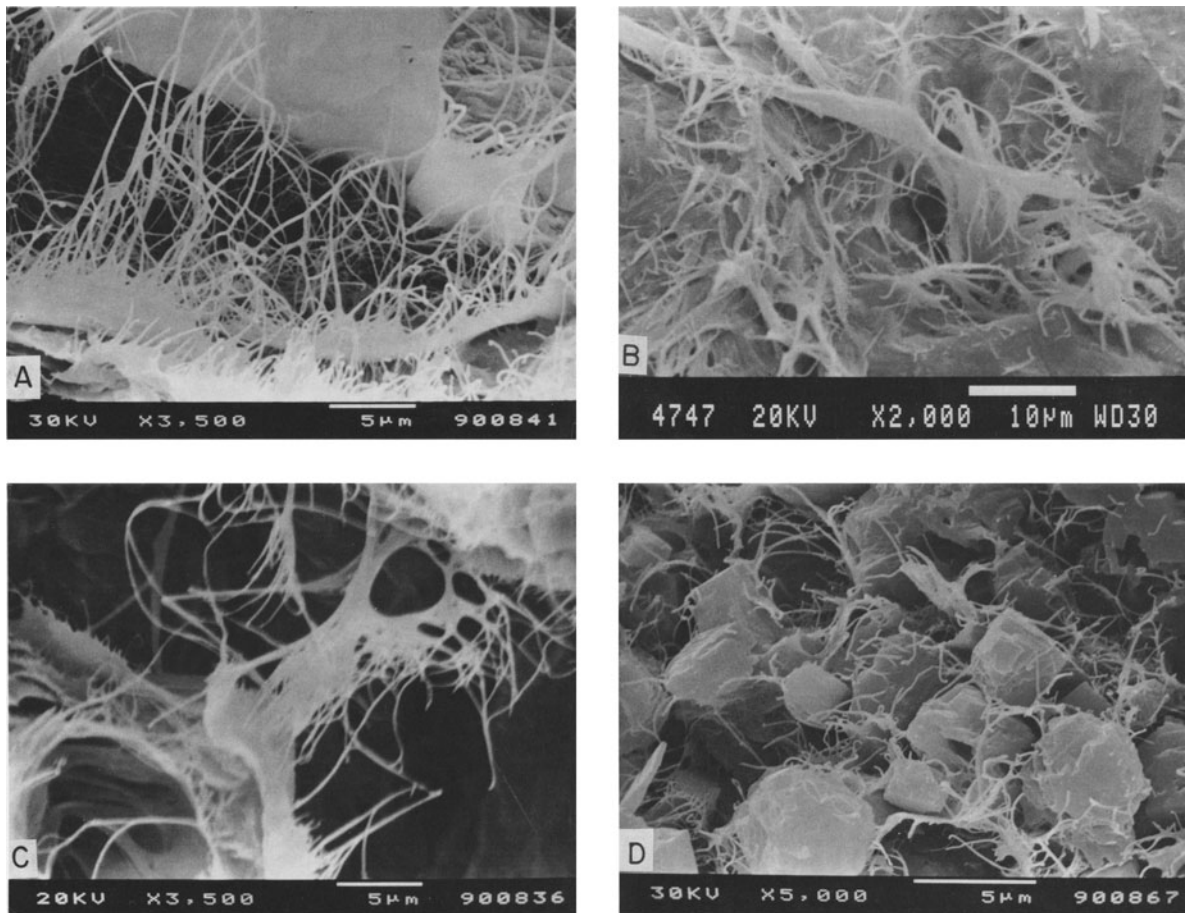


Figure 7. Scanning electron photomicrographs illustrate coexistence of sepiolite fibers and dolomite rhombs (D). A, B, and C show mats of interwoven fibers of sepiolite from beds. Sepiolite beds (A, B, and C) show fibers of sepiolite bridging and lining pores between detrital (?) grains under higher magnification.

that direct precipitation also took place during aerobic episodes as well (Figures 2 and 3).

The black organic matter-rich sepiolite beds were totally free of calcium carbonate. An environment was probably formed above the lake floor whereby calcite deposition in the black sepiolite beds was precluded. The oxidation of organic carbon in the photic zone represents an important source of total carbonate in deep waters. When oxidation of organic carbon is inhibited by oxygen-deficient waters, bottom water becomes undersaturated with respect to calcium carbonate, and the deep lake water becomes corrosive. The buffer capacity of lake water decreases with salinity, permitting lower pH due to phytoplankton and thus lowering saturation of calcium carbonate. The cause of anaerobic sediments lacking carbonate laminae in the Miocene Eskişehir Lake deposit was probably water stratification due to salinity and density differences.

Dolomitization is persistent at the upper layer of carbonate rock (Figures 2 and 3), and partial dolomi-

tization is more common in intermediate zones. In an early episode, the lake water was sulphate-rich, and water depth was very shallow; consequently, gypsum precipitated prior to sepiolite layers. Later, water depth increased due to extension of graben system and water stratification developed due to salinity differences; pycnocline, the large volume of fresh water input from ancient Sakarya river and high sulphate concentration in the lake water that resulted from silicic volcanism and sulphur-bearing hydrothermal activities in the vicinity of the paleolake; and sepiolite precipitated under favorable physicochemical conditions. The development of pycnocline was caused by deposition of almost 98% pure sepiolite beds. This purity suggests the existence of "starved basin" for a short episode in the central part of the ancient lake. Later, the basin grew more shallow due to uplift, and dolomitization became a major diagenetic process (Figure 9).

Abundance of large gypsum crystals (2–10 cm) in the lacustrine series suggests late dolomitization in a shal-

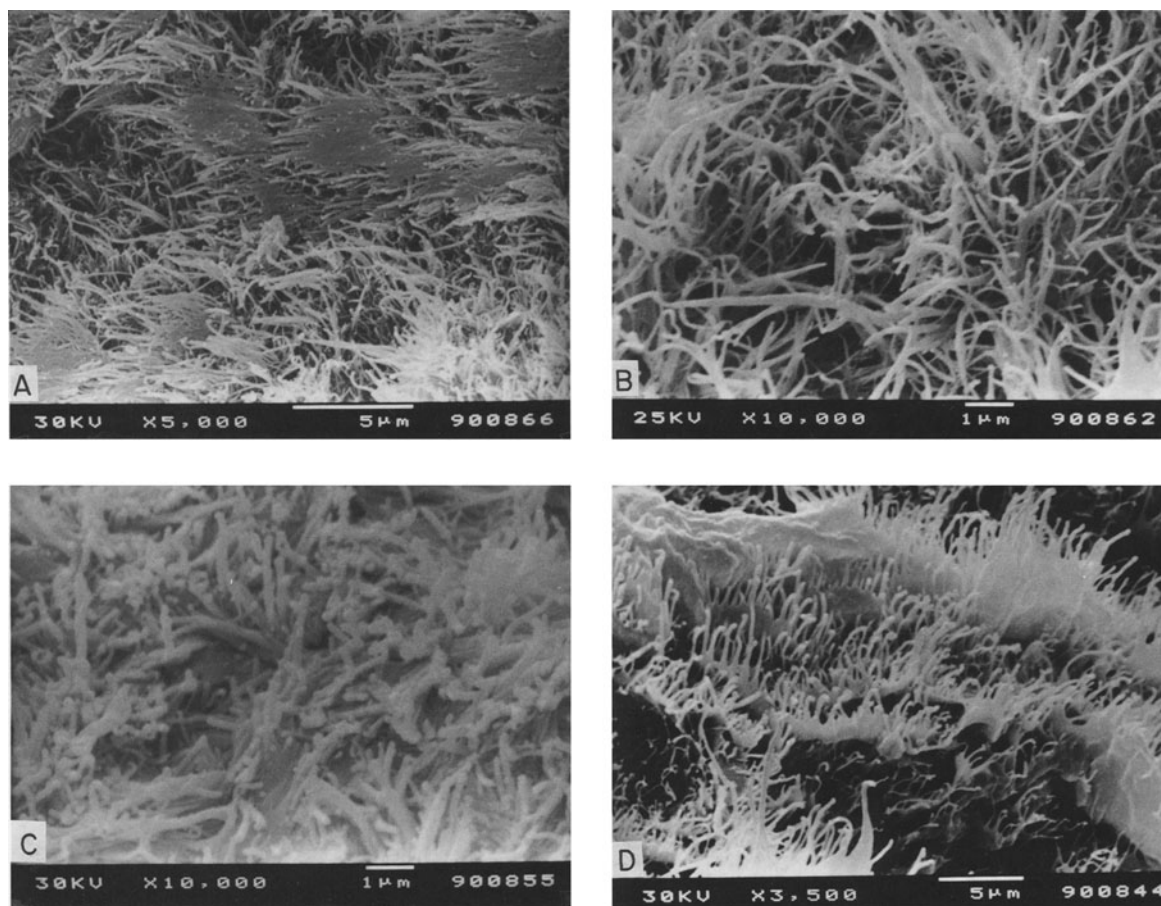


Figure 8. Scanning electron photomicrographs of sepiolite nodules show bundles of sepiolite, tightly interwoven fibers, and massive fiber morphology with bent tops. C shows a unique example of palygorskite occurrence from the matrix of conglomerates of ultramafic rocks where nodules existed.

low water environment, characterized by high evaporation and seasonally periodic flushing with fresh waters, resulting in rapid fluctuations of salinity between hypersaline and nearly fresh water conditions (Folk and Siedlecka, 1974; Folk and Land, 1975; Longman, 1980). The texture and morphology of gypsum crystals are depending on the porosity and permeability of the host sediments and on the seasonal fluctuation of the groundwater table—"evaporatic pumping"—in the sabhka environment. For instance, bigger and better crystallized gypsum crystals (up to 25 cm long) were found within the more coarsely grained sediments. In schizohaline environments, sulphate-rich lake water and excess Mg from the dissolution of serpentinites created solutions with Ca/Mg ratios and high salinities that are conducive to the formation of dolomite.

Based on SEM studies, sepiolite occurs as interwoven fibrous mats and as coating, pore-filling, and pore-bridging cements in dolomitic marl. This textural evidence also suggests a direct chemical precipitation of sepiolite from Mg-rich solutions post-dating dolomi-

tization under alkaline and saline conditions during diagenesis. High Mg and Si activity with some Al and a pH of about 8 are necessary geochemical conditions for sepiolite precipitation (Weaver and Beck, 1977; Velde, 1985). In addition, when sepiolite coexists with dolomite, the concentration of Mg in solution has been found to be adequate for sepiolite formation (Singer, 1984). Therefore, the Mg concentrations of Miocene lake waters were sufficiently high to cause dolomitization of limestones and subsequent precipitation of sepiolite. Also, sepiolite precipitation consumed total alkalinity of the lake water. Dry climates favor sepiolite precipitation in alkaline and saline lakes due to increases in saturation. We also observed more recent sepiolitization occasionally in the uppermost part (10–15 cm) of magnesite veins in open-pit magnesite deposits. A similar observation was reported from Konya province by Yeniyol (1986).

Morphological studies on the SEM revealed that well-crystallized dolomite rhombohedrons, as shown in Figure 7D, are the evidence of late dolomitization after

Table 2. Whole rock chemical analyses of sepiolite bed samples.

SAMPLE No	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	L.O.I.
A-1	51.95	2.14	0.41	0.08	2.77	23.35	0.22	0.36	0.52	18.46
A-2	53.95	0.91	0.51	0.10	0.29	26.41	0.23	0.25	-	17.35
S 3	58.03	13.89	5.33	0.73	1.69	7.93	0.89	2.34	0.26	8.91
S 6	42.16	10.55	6.23	0.78	10.09	10.34	1.02	1.88	0.16	16.65
S 7	43.11	12.62	7.51	0.70	7.31	10.08	0.80	2.33	1.08	15.25
T 1	69.49	0.35	0.70	0.10	0.16	25.34	0.10	0.20	-	3.56
T 2	54.55	5.76	1.30	0.10	0.35	23.58	0.10	0.50	-	13.76
T 3	48.35	0.80	0.60	0.15	6.80	25.26	0.18	0.33	-	17.53
T 4	56.95	1.05	0.93	0.15	2.45	23.35	0.11	0.41	-	14.60
T 5	49.40	0.40	1.35	0.30	3.00	22.85	0.94	0.25	-	21.51
T 6	55.85	4.78	0.80	0.10	0.22	23.90	0.09	0.35	-	13.91
T 7	55.70	5.45	1.45	0.10	0.48	22.45	0.17	0.70	-	13.95

direct precipitation of sepiolite. However, we interpret some honeycomb-like textures as products of late-stage diagenetic events. These features are distributed heterogeneously on a very small scale. We attribute them to late-stage dissolution of dolomites that released Mg and led to sepiolite precipitation when excess silica

from dissolution of diatomites in the upper dolomitic sepiolite beds became available.

Under basic conditions, silica is released by the dissolution of serpentinites underlying the lake and surrounding highlands and by dissolution of diatomites, which is the primary source of silica. Silica from diatomite is a potential source that is readily available due to the large surface area and high permeability of the diatomite. Based on SEM studies, sepiolite and diatomite association from the Ahiler area are shown in Figure 10. The major source of Mg is released from the dissociation of serpentinites. The writers propose that it is the necessity of supplying a supplement of silica to form sepiolite beds from the dissolution of serpentinites, as follows:

DIRECT PRECIPITATION MODEL

FOR SEPIOLITE BEDS

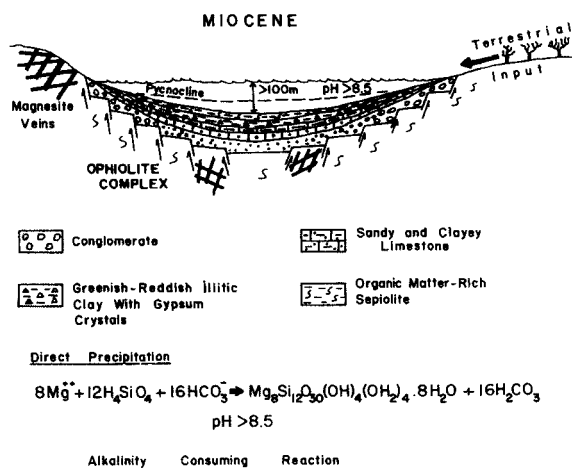
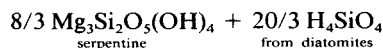
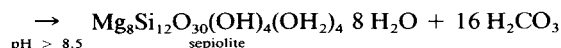
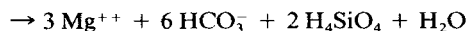
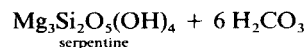


Figure 9. Proposed direct precipitation model for sepiolite beds from lake water, associated with dolomites, gypsum, and organic matter.



Under alkaline weathering conditions, the concentration of silicic acid is strongly affected by pH vari-

ations; it increases from 120 mg/liter at pH = 8.0 to 490 mg/liter at pH = 10.26 (Yariv and Cross, 1979). Under near neutral and acid weathering conditions, organic and humic substances have a direct impact on silica solubility. Under such conditions, the solubility of Si is less pH-dependent and ranges from 100 mg/liter at pH = 7.7 to 150 mg/liter at pH = 3.0 depending on the substances in solutions.

The effect of Mg ions on the solubility of Si differs at various pH levels. In the presence of Mg, the solubility of Si decreases rapidly in the narrow pH range between 10 and 12. For very high Mg concentrations, the solubility of silicic acid decreases rapidly at pH levels between 8 and 9. In the present system, the dissolved silica precipitated as Mg-silicate (Wey and Siefert, 1961).

Laboratory synthesis of sepiolite at 25°C and 1 atm. conditions using artificial lake water have not been reported, but Wollast *et al.* (1968) studied this problem by using artificial sea water. They concluded that sepiolite is the only non-aluminous cation-bearing silicate, which will precipitate directly from sea water as the dissolved silica concentration is increased. Depression of the pH of sea water prevents the precipitation of sepiolite and allows the concentration of silica to increase to saturation with respect to amorphous silica. Wollast *et al.* (1968) concluded that for the precipitation of sepiolite, the absence of aqueous aluminum species is very important, and activities of Mg^{++} , OH^- , and SiO_2 consistent with the equilibrium constant for sepiolite. They suggested that the stability of sepiolite probably increases at lower temperature, thus promoting sepiolite precipitation in cold, interstitial waters. In contrast, solubility of amorphous silica decreases from 115 ppm at 25°C to about 60 ppm at 0–5°C (Krauskopf, 1956). In marine sediments, the precipitation of sepiolite, which forms fibrous to membrane-like habit, association with Miocene diatomite in the Santa Cruz Basin, California, is caused by reaction of Mg-rich groundwaters or sea water with silica-rich connate water of the diatomite (Fleischer, 1972).

Williams and Crerar (1985) also reported based on experimental studies that the silica dissolution has been almost totally depressed by the presence of $Mg(OH)_2$ in solution at pH = 9.4. In contrast, the polymerization appears to be inhibited by the presence of $CaCO_3$, Al_2O_3 , kaolinite, Fe_2O_3 , and bentonite in artificial sea water during the same experiments. Colloidal silica particles carry high negative charge between pH 2–10.7, and they will flocculate in the presence of positively charged Mg hydroxides. Under natural conditions, $Mg(OH)_2$ should carry a positive surface charge, enabling it to flocculate silica sols and perhaps explaining polymerization of silica with multivalent cations to form insoluble Mg-hydro-silicates (Williams and Crerar, 1985).

Excess dissolved silica precipitated as irregular and discontinuous thin opal-CT beds within and above the

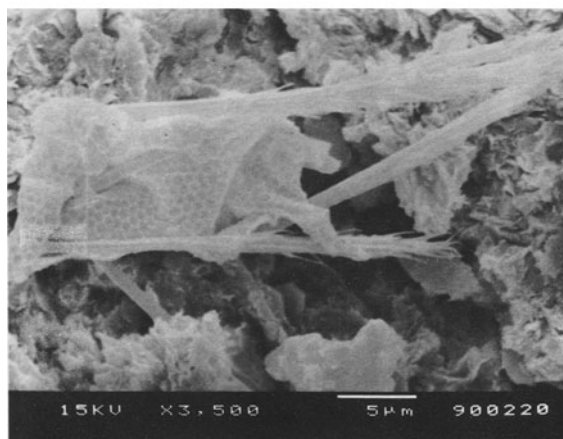
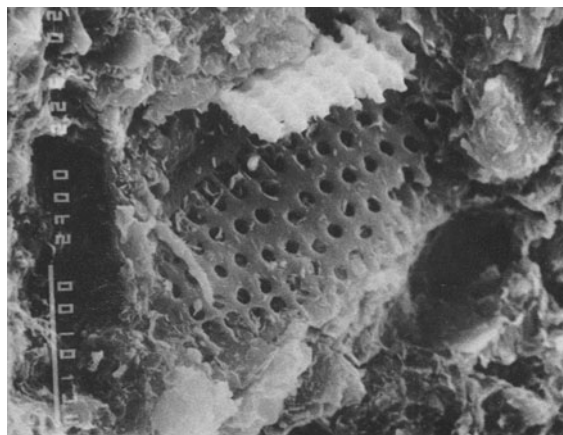


Figure 10. Scanning electron photomicrographs reveal coarsely fibrous sepiolite association with diatomite from the Ahiler area.

organic matter-rich sepiolite beds, which indicates that silica concentration was very high during and after sepiolite precipitation. The presence of major opal lenses a few hundred meters in diameter overlying sepiolite beds in the east of Yassihöyük area indicate extra local silica input, independent from diatoms, from underneath the Miocene lake by ascending basic hydrothermal solutions along the fracture systems that were developed during the extension of the graben. Similar observations about large opal lenses have not been done in any part of the Eskişehir basin.

Sepiolite nodules

The sepiolite nodules have very close genetic relationship with Stockwork-type magnesite deposits that are located near the Miocene lake, serving as parent rocks. Sepiolite nodules are the product of the diagenetic replacement of finely crystalline $<40 \mu m$ cobbles and pebbles of magnesite by alkaline formation waters in the shallow subsurface near the paleoshorelines of the Miocene lake. Magnesite cobbles were transported

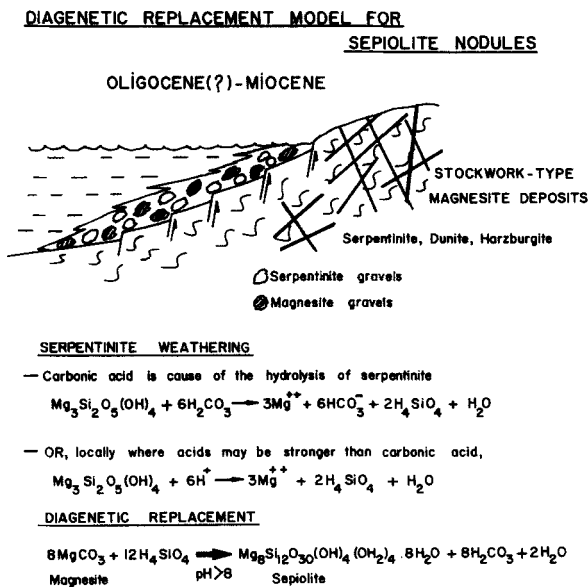
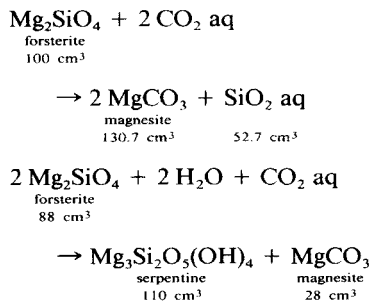


Figure 11. Proposed diagenetic replacement model for sepiolite nodules in the vicinity of the paleoshorelines.

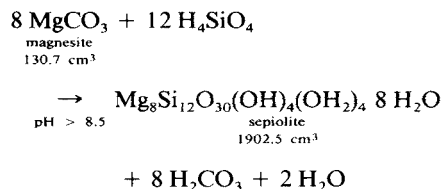
intermittently by landslides while the erosion of serpentinites was going on. Early diagenesis took place under the influence of pore water chemistry in shallow depths as a function of available Si and Al and pH of about 8 to 9 (Figure 11).

In terms of abundance, Mg and Fe are soluble under acidic conditions, and Si is more soluble under basic conditions. Because of the mobility of these elements when CO_2 -rich waters were rising under high temperature and pressure, Mg first dissociated from serpentinites—which is an essentially acid-consuming reaction—and later, when pH became neutral or slightly basic, magnesite began to precipitate. This results from the volume balance of the following carbonitization reaction:



Moreover, when the pH rose further, Si became mobile with hydrothermal solutions continuing to rise up along the fracture systems toward the surface, and secondary minerals precipitated from solutions when pressure dropped suddenly at the surface. For this reason, secondary Fe-silicate cap-rocks are very common in near-

ly all magnesite deposits. Erosion of the upper layers of these magnesite vein deposits were the source materials of the sepiolite nodules after diagenesis took place in the shallow lake environment under alkaline conditions, according to the following volume expansion reaction:



Palygorskite was only found in the cement of conglomerates, where sepiolite nodules are formed, and it requires Al in solution. In the vicinity of paleoshorelines, palygorskite formed as a result of an equilibrium between strongly altered detrital minerals and the pore-water chemistry that favored the transformation of smectite to palygorskite. In addition, the alteration of smectite into palygorskite under highly saline and alkaline conditions has been proposed in southern Iran soils (Abtahi, 1977). The amounts of smectite seen as the by-product of the alteration of ultramafic rocks is likely very small. $\text{Al}(\text{OH})_3$ more likely entered the basin by dissolution of serpentinites and periodotites, which can release Al in amounts that are very small but still sufficient for the diagenetic transformation of palygorskite as a cement in clay-size fractions. In these conglomerates, only magnesite pebbles and cobbles transformed to sepiolite. This observation clearly indicates that physicochemical conditions were adequate for the precipitation of sepiolite. Clay and silt-size magnesite materials reacted much faster to form palygorskite in the presence of very small amounts of Al in porewater than magnesite pebbles and cobbles; and almost all the Al was consumed during the reaction. It is likely, from the kinetics point of view, that very fine-grained magnesite can react faster with porewater than cobbles; consequently, clay-silt size fractions converted to palygorskite, Al in solution was almost totally consumed, and cobbles then converted to sepiolite in Al-deficient micro-environments.

CONCLUSIONS

Major sepiolite beds lie beneath the gypsum series in the Eskişehir basin. However, gypsum-bearing beds are rarely found beneath the black and brown sepiolite beds in some stratigraphic sections, such as the Ilyaspaşa area. There were two major sabhka environments where gypsum precipitated: the former in the clayey-silty units and the latter in the dolomitic marl and tuffs during the opening and closing stages of the rift-related basin. More gypsum crystals were precipitated in the second stage. Sepiolite beds were deposited in about 100 m water depth during the maximum opening stage

of the rift, which was necessary to develop the pycnocline and, consequently, the anoxic episode. The morphology of gypsum crystals depends on fluctuation of groundwater table—evaporatic pumping—and permeability and porosity of the sediments.

Sepiolite in the Middle-Upper Miocene lacustrine succession formed mainly in saline to alkaline environments under an arid to semiarid climate with possible humid intervals due to seasonal fluctuation in climate, which can be examined in the rock records. Changes in the salinity content of the lake water did not effect the precipitation of sepiolite because sepiolite beds are found closely associated with gypsum and dolomite series in which sepiolite contents are varied. Ninety-eight percent sepiolite containing organic matter-rich sepiolite beds was deposited in a “starved basin” by the result of high organic productivity and very low terrigenous input.

Sepiolite nodules were formed diagenetically from magnesite cobbles within the basal conglomerates and in the vicinity of paleoshorelines under alkaline and shallow buried conditions. In contrast, sepiolite beds were precipitated in the central part of the same paleolake under alkaline and saline conditions, and paleolake water was saturated with respect to silica. Soluble Mg and Si with minor amounts of Al were supplied by the dissolution of ultrabasic rocks under alkaline conditions. Mg primarily came from the ophiolite complex and secondarily from the dissolution of dolomites. In addition to the primary silica source of diatomites, basic hydrothermal solution from underneath the paleolake along the fracture systems was the second major source of excess silica, which precipitated as lense-shaped opal beds overlying the organic matter-rich sepiolite beds.

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