

AN EXAMPLE TO SEPIOLITE FORMATION IN VOLCANIC BELTS BY HYDROTHERMAL ALTERATION: KIBRISCIK (BOLU) SEPIOLITE OCCURRENCE

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ABSTRACT— Geological, mineralogical and chemical properties of a sepiolite occurrence, located in the south of Kibriscik township of Bolu Province, northcentral Turkey, have been investigated in detail, and new mineralogical data have been obtained. Differing from the sedimentary sepiolite deposits, mostly associated with the carbonate/evaporite sequences, Kibriscik sepiolite occurs in the Köroğlu (Gallatian) Volcanic Belt, and has formed by the hydrothermal alteration of the vitric tuff unit of Middle Miocene aged Deveören Volcanites. The mineral, which shows a similar XRD pattern to sepiolite, gives DTA and IR patterns with close resemblance to those of palygorskite, in addition to its chemical composition with rather high alumina content. There are indications of monoclinical symmetry, determined by XRD, and it is thought to be possible that the material represents a new mineral phase.

INTRODUCTION

Kibriscik sepiolite occurrence is located at the Uşakgöl yaylası (plain) district, about 25 km south of the Kibriscik town, 70 km southeast of Bolu Province. The mineralization is included within the Bolu H27 b3 topographic map sheet.

The investigated area is located within the Köroğlu Volcanic Belt, formerly recognized as the "Gallatian Massif", on the treshold between Central Anatolia and Western Black Sea regions. Elevation of the area ranges around 1000-1900 m. Kibriscik-Beypazarı road crosses the investigated area approximately in the north-south direction (Fig. 1).

Geological investigations carried out around the study area may be stated in chronological order as; Leonhard (1903), Milch (1903), Chaput (1931), Stchepinsky (1942), Blumenthal (1948), Erol (-1-952, 1954), Rondot (1956) and, more recently Türkecan et. al. (1991). In the study of Türkecan et. al. (1991), stratigraphy of a wide area, bordered by Seben-Gerede (Bolu Province), Güdül-Beypazarı (Ankara province) and Çerkeş-Orta-Kurşunlu (Çankırı province) has been outlined, and geological mapping in 1:25 000 scale has been realized.

The occurrence was discovered during the ceramic raw materials exploration program of MTA in 1988, and reported by İrkeç and Kırkoğlu (1989). In later years, 1:25 000 and 1:5 000 scale geologi

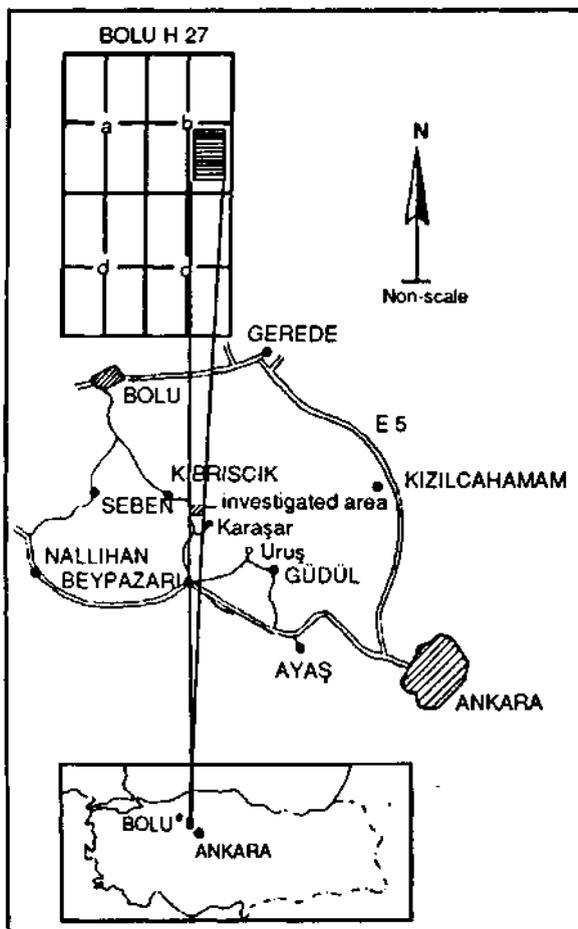


Fig. 1- Location map of the investigated area.

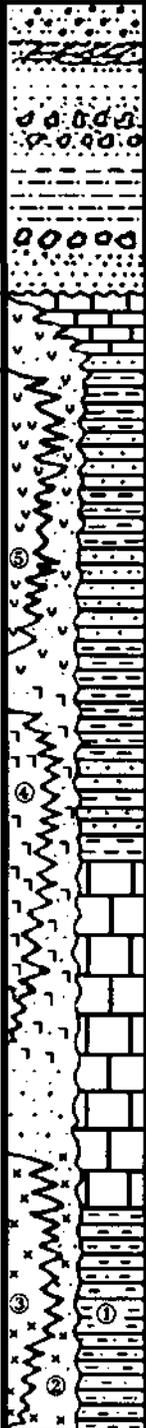
Erathem	System	Series	Stage	Group	Formanitor Member	Symbol	Thickness (m)	Lithology	Lithological Explanation	FOSSIL CONTENT					
C A I N O Z O I C	Quaternary	PLIOCENE			İlgaz Fm.	Qal	25		Alluvium						
						Tpi	~ 200 m		İLGAZ FM. (Tpi): Thick bedded, gray colored conglomerate, sandstone, siltstone, occasional tuff and claystone	Mimamys sp. Micromys sp.					
	T E R T I A R Y	M I O C E N E	Upper		K Ö R Ö Ğ L Ü G R O U P	Hüyükköy Fm.	Tmkhü		HÜYÜKKÖY FM. (Tmkhü): Tuff, tuffite, limestone, conglomerate, sandstone, siltstone, marl	Planorbarius sp.					
						İlçadere Volcanites	Tmkd	~ 700 m	İLÇADERE VOL. (Tmki): Gray-black-brown colored, massive basaltic and andesitic lava, agglomerate						
											Deveören Volcanites	Tmkd	DEVEÖREN VOL. (Tmkd): Gray-green black colored basaltic and andesitic lava, white tuff	Eumyanion sp. Mirabella sp. Sayimys sp. Desmanodan sp.	
						Bakacaktepe Volcanites	Tmkb		BAKACAKTEPE VOL. (Tmkb): Gray belge-black colored andesite-dacite, lava, tuff, agglomerate						
											İlçadere Volcanites	Tmki	İLÇADERE VOL. (Tmki): Sandstone, claystone, shale, tuffite. Silica bands and coal seams. Occasional trona deposits with economic significance		
						Lower									

Fig. 2- Generalized stratigraphic columnar section of the investigated area (simplified after Türkecan et. al., 1991).

minations. To figure out the crystallographic features and mineral paragenesis of Kibriscık sepiolite, 93 clay and altered rock samples were investigated by X-ray diffraction method. X-ray diffractograms of oriented, ethylene glycole treated and fired KIB-6C sample were obtained, and "step-scanning" applied in a trial to calculate the unit cell parameters. JEOL JDX-8P and RIGAKU-Geigerflex diffractometers were used.

Differential thermal analysis (DTA) and thermal gravimetric (TG) methods were applied on 9 sepiolite and altered tuff specimens to investigate the thermal behaviour, dehydroxilation steps, phase transformations and weight loss of the clay material. RIGAKU-DPS/8151 (Ver. 2.00) instrument was used.

Infrared spectroscopy studies were carried on 6 clay samples by JASCO Super 200 IR instrument, to determine the absorption bands due to the vibration and stretching of chemical bonds.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies were conducted in GIRIN Laboratories, to investigate the microstructural and micromorphological features. Seven sepiolite, one tuff and diatomite specimen each were investigated by HITACHI S 530 S and JEOL JEM-4000 FX scanning and transmission electron microscopes, respectively.

Chemical analysis performed consist of rock, sepiolite and spring water analysis. Chemical analysis of 20 rock and sepiolite samples for geochemical interpretations were realized in the laboratories of MTA by titration and optic emission spectroscopy. In addition, 25 sepiolite samples were analysed in both GIRIN and MTA Laboratories, by titration, X-ray fluorescence (XRF), energy dispersive X-ray (EDX) and atomic absorption spectrometry (AAS) methods; and 3 present-day spring water specimen by EDTA, flame-photometry, spectrophotometry, AAS, titration and gravimetric methods.

Various technological tests were conducted to determine the specific surface area by BET method, water and oil absorption rates, bleaching capacity, cation exchange capacity, brightness, specific gravity and firing state for ceramic applications, in both GIRIN and MTA Laboratories (İrkeç, 1992).

GEOLOGICAL SETTING

Lithological units, distinguished in the investigated area and its close vicinity consist of the volcanic and sedimentary rocks of the "Köroğlu group"; Pliocene Ilgaz formation and Quaternary alluvium (Türkecan et. al., 1991). The Köroğlu Group, which is exposed in a wide area comprise,

Uruş formation,

Hüyükköy formation,

Bakacaktepe volcanites,

Deveören volcanites,

İlıcadere volcanites,

Kirazdağı volcanites,

Karasivri volcanites,

Uludere pyroclastites, and

Hirka formation, in geochronological order.

Sedimentary and volcanic units except for the Uruş formation, Kirazdağı and Karasivri volcanites are observed in the investigated area. Generalized stratigraphic columnar section of the area is given in Figure 2.

Kibriscık sepiolite occurrence crops out within the Deveören volcanites, which cover the northern half of the study area (Fig. 3), and is named after the Deveören village, around where it is exposed best (Bolu H27 b2 map sheet) (Türkecan et. al., 1991).

Deveören volcanites are composed of basalt, andesite and dacitic lava, tuff and agglomerate. Lavas are gray, black, green and brown in color, and the most typical property is the platy flow structure they show. They generally exhibit cryptocrystalline texture with very fine and random phenocrysts. Tuffs are white to pinkish, and agglomerates reddish in color.

In thin section studies, mineralogical composition of Deveören volcanites range on the boundary between andesite and basalt, and may occasionally be difficult to identify. Andesites (Va) are

generally in hyalopylitic texture, with relicts of plagioclase and opaque mafic mineral phenocrystals. The matrix consists of volcanic glass, plagioclase microliths and crystallites. Basaltic lava (Vb) exhibit fluidal structure and are composed of pyroxene and plagioclase microphenocrysts. These occur in a matrix of parallel aligned microliths and granules of opaque minerals filling the interspaces. Together with the basaltic lava, silica flows (Vs), sometimes reaching a thickness of over 1 m are common. These siliceous rocks may exhibit very different colors (red, white, blue etc.) and texture, and may occur as massive bodies, or oolitic and/or brecciated occurrences of silica replacement. In addition, silica precipitation around hot springs, forming chalcedony, are common (İrkeç,, 1992).

Tuffs of the Deveören volcanites bear significance, considered the occurrence of sepiolite within them. Tuffs are exposed in the Öküzçayırı stream and the mild slopes in northwest. Volcanic breccia crop out at the steep flanks, surrounding the Uşakgöl plain. Thickness of the unit ranges around 40-80 m.

Tuffs show a sequence of crystalline tuff, crystalline+vitric tuff, vitric tuff and resedimented tuff/tuffite transported by small braided streams, in ascending order. Crystalline tuff is dominant at the Uşakgöl plain, while vitric tuff and ash predominate at the northwestern flanks of the Öküzçayırı stream.

Vitric tuff, ash and pumiceous tuff generally exhibit aphanitic texture. They are slightly compacted, and show yellow, dirty white and whitish colors. Argillization is common, and they occasionally carry manganese dendrites and stainings in millirhetric scale along fractures. Zeolitization, recognized by its pale green color is also common. Pumice fragments, less than 1 cm in diameter, and irregular shaped, white silica nodules of variable size, which are thought to have generated from silica-rich intraformational water are occasionally identified. Besides, dark gray-greenish colored, silicified clay veinlets may also be distinguished. Borders of these veinlets with the tuff itself are gradational. These have been interpreted as extremely argillized volcanic intrusions in acidic composition, emplaced as veins or veinlets, cutting the tuffs. Angular chert fragments, which may occasionally reach

coarse block size have been interpreted as intraclasts within the tuff, which was displaced after deposition, probably due to the tectonic activities and the collapse of the crater, during which the fragments of the late-stage silica flows were trapped within them.

Sepiolite occurrences are observed within the vitric tuff. They are irregularly distributed showing gradation into tuff, mostly discontinuous and occasionally silicified, with variable dimensions. Manganese dendrites and staining are also observed within the sepiolite occurrences.

Small scale channel deposits, 1-5 m wide, are found within the tuffs, in the northwestern flanks surrounding the Öküzçayırı stream. These deposits have formed by the alternation of three zones. The system starts with well rounded and spherical volcanic pebbles (mostly augite-andesite), 1-12 cm in diameter, which lie over the tuffs on an erosional surface (Zone A). Pebbles are supported and the imbricate structure is well developed. Groups of pebbles are supported by a matrix in silt and sand size, whose components are again pyroclastic and volcanic originated material. Over Zone A lies a volcanogenic Zone B, comprising clay-silt and sand size material, without any pebbles and internal structure. The uppermost Zone C composes of fine and laminated volcanogenic material which make trough cross-bedding. Paleo-flow direction is thought to extend from north to south and southeast, according to sedimentological findings (İrkeç, 1992).

Volcanic breccia occurs in two varying characters. The first one comprises volcanic rock fragments, supported by yellow-grayish colored, semi-compacted tuff and pumice. Volcanic fragments, which are angular, having variable dimensions (1-40 cm) are distributed irregularly within the tuff and pumice. They are exposed at the steep flanks in the southeast and east of the Uşakgöl, plain, underlying the basal crystalline tuff, and also exhibiting a complex lateral gradation into the latter. Grains are not supported. Sorting has not developed. In the second type of volcanic breccia, volcanic rock fragments are more abundant, and rather supported, with a well-compacted, red colored, ferrous and welded matrix.

The basement of the tuff and breccia is not observable at the area, due to the overburden. The unit is overlain by basalts in general, and rarely by andesites. It is frequently observed at the same elevations with the andesites.

Fossil content is very poor. Some white colored, porous diatomaceous zones have been distinguished in the upper vitric tuffs. In the marginal zones and close to the channel deposits, locally abundant root-casts and carbonatized root remnants have been identified. Diameters of the root-casts are generally a few mm, and penetrate vertically. Thus, they are thought to be the casts of rushes in a limited swamp.

Structural Units

Very effective volcanic activity, lava flows and pyroclastic material deposition, generally makes the identification of structural units impossible. Generally, NE-SW and NW-SE trending normal faults are recognizable.

The Köroğlu volcanic belt has undergone the influence of NNW-SSE trending compressional regimes, until Late Miocene. Synclines, anticlines and recumbent folds have formed in the Upper Jurassic-Lower Cretaceous formations. Compressional forces, which prevailed until Late Miocene has given rise to the formation of intermountain type basins. North Anatolian Fault has become active in Late Miocene-Early Pliocene. Related tensional stresses have formed normal faults (Türkecan et al., 1991).

Asymmetrical anticlines and synclines may be observed in the Hirka formation in particular, to the south of Bolu H27 b3 map sheet, covering the investigated area. These are discontinuous and small scale tectonic structures.

Direct relation of the investigated sepiolite occurrence with regional tectonism may not be forwarded. It has developed by the effect of small-scale convective systems around the vein-like intrusions close to rhyolite in chemical composition, which filled the local fracture systems formed during volcanic activity.

MINERALOGICAL PROPERTIES

X-Ray Diffraction Results

Sepiolite and palygorskite are clay minerals belonging to in the phyllosiicate group. According to the determination of Brindley and Pedro (1972), they contain two dimensional continuous tetrahedral sheets in T_2O_5 (T=Si, Al, Be...) composition, and discontinuous octahedral sheets, which is the most prominent difference from other clay minerals. Such a feature gives rise to the formation of a channel structure, in rectangular cross section.

The first study on the structural model of sepiolite was carried out by Nagy and Bradley (1955), who suggested the possibility of both orthorhombic and monoclinic symmetries, yet favored the C2/m space group. Later, Brauner and Preisinger (1956) and Preisinger (1959) proposed a new model in the Pnan space group of the orthorhombic system. The main difference between the two models lies in the description of the inversion of tetrahedral sheets, in the centre or edge of the Si-O-Si zig-zag chains.

Number of the octahedral cation positions per unit formula is 8 for sepiolite and 5 for palygorskite. However, all positions need not be occupied. Octahedral vacancy/cation ratio may be tolerated up to 4/1 for palygorskite, and 7/2 for sepiolite. In sepiolite, tetrahedral silicium may be substituted by Al^{3+} and Fe^{3+} in a ratio of 0.2-1.3 per 12 positions. Total octahedral cation number is between 7.0 and 8.0. Octahedral cations are generally Mg^{2+} , however, Al^{3+} , Fe^{3+} , Fe^{2+} , Mn^{2+} and Ni^{2+} substitutions may be possible. By the distribution of occupied octahedral cation positions within the 2:1 chain structure, instead of a regular alternation between the adjacent chains, A2/a (C2/c) space group of monoclinic structure is also theoretically possible.

The Brauner and Preisinger model, thus the Pnan space group of orthorhombic symmetry has been emphasized in numerous studies (Brindley, 1959; Zvyagin, 1967; Gard and Follet, 1968; Rautureau et al., 1972; Rautureau, 1974; Rautureau and Tchoubar, 1974; Yücel et al., 1981). On the other hand, one of the few findings indicating monoclinic

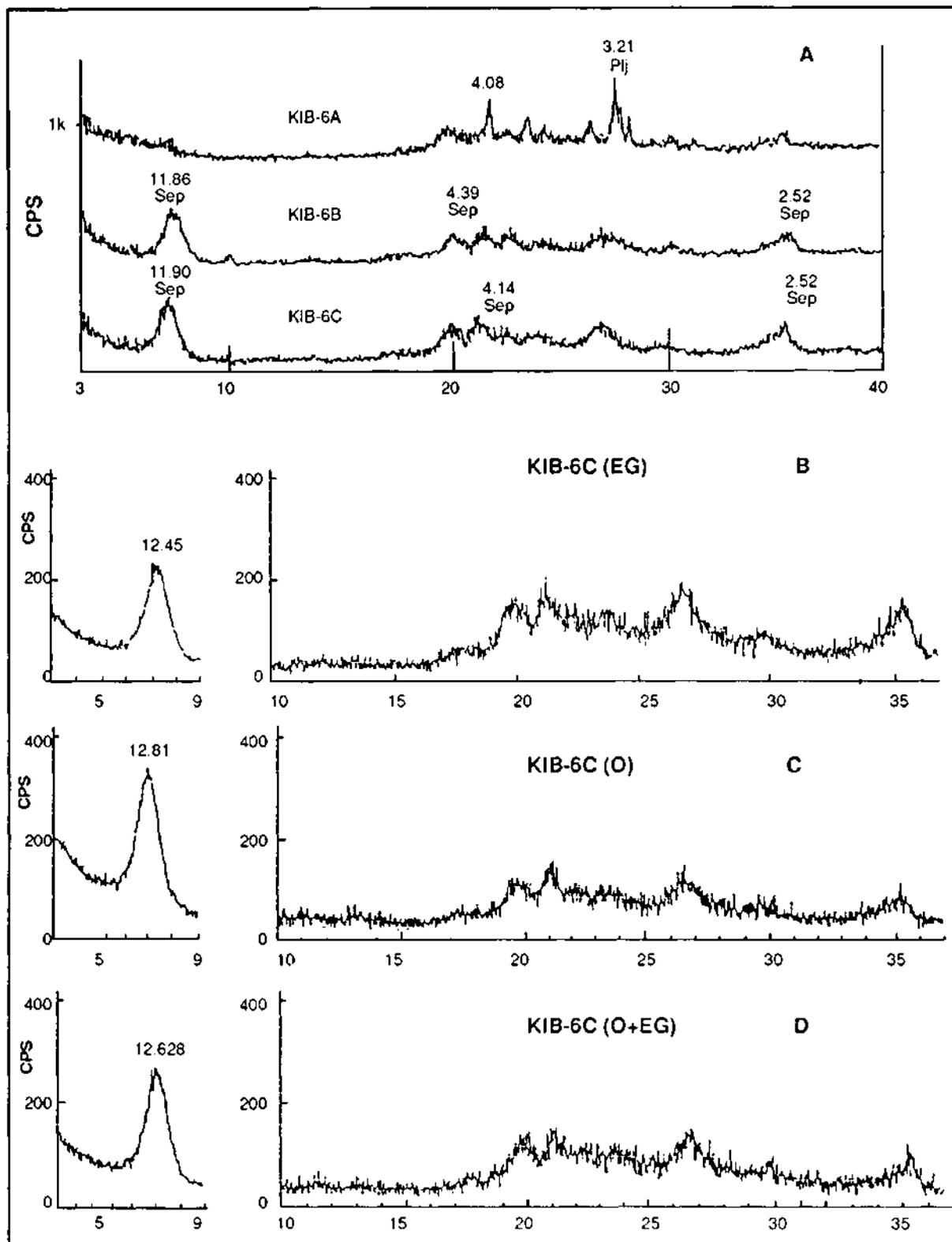


Fig. 4- Original XRD patterns of KIB-6 A, B and C samples (A), ethylene glycolated (B), oriented (C) and EG+O (D) X-ray diffractograms of KIB-6C sample.

Table 1- X-ray diffraction data for the Kıbrısçık sepiolite samples, collected from the trenches in the south of the Uşakgöl plain

Trench No.	Sample No.	Mineral Content									
		Sep	Qtz	CrS	Zeo	Amr	Mnt	Cl	Mcl	Plg	K-Fld
UY-3	UYX-3					●					
	KIB-21	X	○		X	△-○	X			X?	
UY-4	UYX-4	●									
	KIB-20	○		X		○					
	UY-4	●					X				
UY-5	UYX-5					●					
	BX-7a	X		X		●		△ 100° 110° 120°			X
	BX-7b		<X			●		△ 100° 110° 120°			X
	BX-7c		<X			○	○-○		<X		X-△
	KIB-19	X _B [?]	<X	X		○-○	△ _B				<X
UY-6	UYX-6	●									
	KIB-6a	X	△	○						○	
	KIB-6b	○									
	KIB-6c	●									
	UY-6	●									
UY-7	BX-8a	X		<X		○		△ 100° 110° 120°			X
	BX-8b	△	<X	X		○					
	BX-8c	△ _B		X		○-○	X				X
	KIB-16					●					
UY-8	KIB-17	△ _B		X		○				○	
UY-9	BX-9	X _B [?]		△		△	△-○			△-○	
	KIB-18			○		○-○				△	
UY-10	BX-10a			X		○-○			X	○	
	BX-10b	X _B [?]				●		X _B [?]			
	UY-10			X		○	X _B [?]	X _B [?]		X	X
UY-13	BX-11a	△		X		△-○		X _B [?]		○	
	BX-11b	○				△					△
	BX-11c	●	X							X	
	UY-13	○	△							X	
UY-14	BX-12a	X _B [?]				●					
	BX-12b	△	<X			○				X	
	UY-14	△ [?]				●					
	UY-14a			<X		●					
	UY-14b	△ [?]				●					
UY-15	BX-3	△				○-○	○-○				
	BX-13a	○			X					<X	
	BX-13b	○-○			△					○-○	
	BX-13c	△		△		△ [?]					X-△
UY-16	BX-14		<X	△		△		○		△	
UY-17	BX-15	○	<X	X		△					<X
	UY-17	○	△			○					
UY-20	BX-16		<X	X		○	△-○			X	

Sep: Sepiolite, Qtz: Quartz, Crs: α -cristobalite, Zeo: zeolite minerals (mostly heulandite, clinoptilolite and mordenite), Amr: amorphous silica (volcanic glass, opal-CT), Mnt: montmorillonite, Cl: undetermined clay mineral, Mcl: micaceous clay minerals, Plg: plagioclase, K-feld: potassium feldspar

- Dominant mineral
- Abundant mineral
- Medium abundance
- △ Little amount
- X Very little amount
- ↑ Uncertain reflection
- B Broad reflection

sepiolite structure is a sepiolite occurrence in a volcanic sequence, exposed around the Karaşar village of Beypazarı town, Ankara Province. Analytical data from XRD, IR and DTA-TG studies yielded significant variations from those of the sedimentary sepiolite. The most outstanding difference in the

Mineral paragenesis of 42 specimens collected from the trenches marked in Figure 3, determined by XRD analysis, are given in Table 1. Amorphous material predominating in most of the specimens may be vitric tuff, volcanic glass or diatomite originated. Amorphous silica from tuffaceous

Table 2- Comparison of the basal reflections of Kıbrısçık sepiolite with others

<i>hkl</i>	<i>d calc</i>	<i>1</i>	<i>I/Io</i>	<i>2</i>	<i>I/Io</i>	<i>3</i>	<i>I/Io</i>	<i>4</i>	<i>I/Io</i>
110	12.07	11.90	100	12.03	100	12.20	100	12.10	100
130	7.482	-	-	7.493	8	7.40	10	7.50	7
060	4.495	4.453	80	4.498	19	4.52	80	4.49	25
131	4.301	4.145	90	4.303	30	4.31	60	4.29	35
260	3.741	3.714	69	3.735	20	3.76	20	3.74	25
080	3.370	3.306	81	3.341	24	3.34	20	3.34	45
331	3.195	-	-	3.188	18	3.16	20	3.18	15B
370	2.928	-	-	-	-	-	-	2.95	5
0.10.0	2.697	-	-	-	-	-	-	2.66	8NR
441	2.618	-	-	2.609	20	2.58	70	2.59	45NR
281	2.617	-	-	2.588	23	-	-	-	-
371	2.557	2.521	71	2.557	26	-	-	-	-
550	2.414	-	-	2.436	14	2.44	30	-	-
222	2.409	-	-	-	-	-	-	2.39	20NR
321	2.261	-	-	2.253	15	2.25	30	2.26	20
082	2.072	-	-	-	-	-	-	2.06	10

hkl: reflection surface I/Io: intensity NR: not resolved B: broad

1. Kıbrısçık sepiolite; Irkeç, 1991, 1992; 2. Eskişehir-Sivrihisar-Ahiler sepiolite (VN-3); Irkeç., 1991, 1992; 3. Tintinara (South Australia) Al-sepiolite; Rogers et. al., 1956; 4. Vallecas (Spain) sepiolite; Brindley, 1959

comparison of the XRD patterns is the splitting of 131 and 331 reflections. 3 angle was determined to be 96,80, suggesting the monoclinical symmetry (Irkeç, 1992).

material and volcanic glass dominates in UY-3,5.7 and 10 trenches, while tuff+diatomite dominate in UY-14 trench. Tuff originated amorphous material is generally accompanied by feldspar, quartz and cris-

tobalite. Occurrence of clay minerals such as sepiolite and montmorillonite have been identified locally in certain trenches and horizons. These are generally accompanied by zeolite minerals.

UY-6 trench is the one where sepiolite formation is most intensive. The uppermost 30 cm section of the 1,5 m deep profile consists of weakly altered, medium to fine particled, abundant feldspar bearing crystalline tuff. In the XRD pattern of the KIB-6A specimen characterizing this section (Fig 4A), reflections of feldspar [plagioclase (An:38 %)] have been determined (3.211 Å, 4080Å, 3.766Å, 2.527Å). (110) reflection of sepiolite at 12.21 Å and (060) reflection at 4.479Å reflect a weak alteration. (421) reflection of heulandite at 3.931 Å is typical. The rising up of the background starting from $2\theta = 18^\circ$ shows the inclusion of amorphous material.

Down the tuff horizon, alteration becomes more effective. KIB-6B specimen has been taken from this horizon, which is fine grained, light brown to beige colored when wet with a dotted texture. The most prominent feature in the XRD pattern is the increase in the distinction and intensities of the sepiolite reflections (Fig. 4A). 8.84 Å and 3.93 Å zeolite reflections (possibly heulandite) are determined.

At the basement of the second tuff horizon, 80 cm deep, massive sepiolite horizon lies, from which the KIB-6C sample has been taken (Fig. 4A). The sample is beige colored and has a soapy appearance when wet. It has a very low density ($\sim 0.66 \text{ gr/cm}^3$). XRD recording of ethylene glycolated, oriented and EG+oriented sample has been taken. Step-scanning XRD has been conducted on the centrifugated sample, in a trial to calculate the unit cell parameters. Basal reflections determined and comparison with other sepiolites are presented in Table 2.

No significant shift has been determined in the positions of the reflections, for the EG treated sample (Fig. 4B), as sepiolite and palygorskite do not have the property of swelling by the absorption of organic compounds into their channels. Only some slight shifts in the positions of the reflections with the c-parameter may occur by 0.2-0.3 Å. In the KIB-6C sample, 11.904 Å peak has shifted to 12.45 Å position after glycolation. As the absorption cen-

teris are mostly structural channels and there occur no exchangable cations (CEC=5-40 meq/100 g) in the interlayer space, swelling does not occur.

On the other hand, the intensity of (110) reflection increases considerably and shifts to 12.81 Å position in oriented samples. (Fig. 4C). By the glycolation of oriented sample, (110) reflection shifts to 12.628 Å position (Fig. 4D).

Heating at 200°C causes no significant change in the position of the (110) reflection. At 400°C, this reflection shifts to lower 2θ angle (6-7 Å) position.

Data obtained by step-scanning XRD have been refined by computer program, to calculate the unit cell parameters. These are, $a=13.73 \text{ Å}$, $b=26.52 \text{ Å}$, $c=5.00 \text{ Å}$, and $B=90^\circ$ (orthorhombic).

Aluminum is an element that can make substitution in the tetrahedral and octahedral sheets of the sepiolite crystal lattice. High alumina content of the Kibriscik sepiolite is comparable to the Tintinara Al-sepiolite in southern Australia (Table 2). Tintinara sepiolite is a pedogenic occurrence and consists of montmorillonite, illite, kaolinite and fine grained dolomite, as a mixture with sepiolite (Rogers et. al., 1956). Basal reflections determined from the XRD pattern of the acid treated clay fraction of the Tintinara sepiolite yielded the values given in Table 2, which accord well with those of several others. Tintinara sepiolite contains 52.43 % SiO_2 , 7.05 Al_2O_3 , and 15.08 MgO . Chemical composition of Kibriscik sepiolite resembles that of palygorskite, however, XRD data do not support it.

At the basal part of the UY-6 trench, fractures and fissures cutting the massive sepiolite occurrence from bottom to top contain a black colored mineral, stuccoed and impregnated. XRD pattern of the black colored material yielded 2.401 Å, 2.186 Å, 3.47 Å and 1.423 Å reflections, which are characteristic to manganese oxide minerals. These reflections possibly characterize manjiroite $[(\text{NaK})(\text{Mn}^{2+}\text{Mn}^{4+})_2\text{O}_{16}\cdot 2\text{H}_2\text{O}]$ and hollandite $[\text{BaK}_2(\text{Mn}^{4+}\text{Mn}^{2+})_2\text{O}_{16}\cdot 2\text{H}_2\text{O}]$. These veinlets and disseminations of manganese oxide minerals show that the hydrothermal activities in the region continued after the hydrothermal stage that produced the sepiolite-

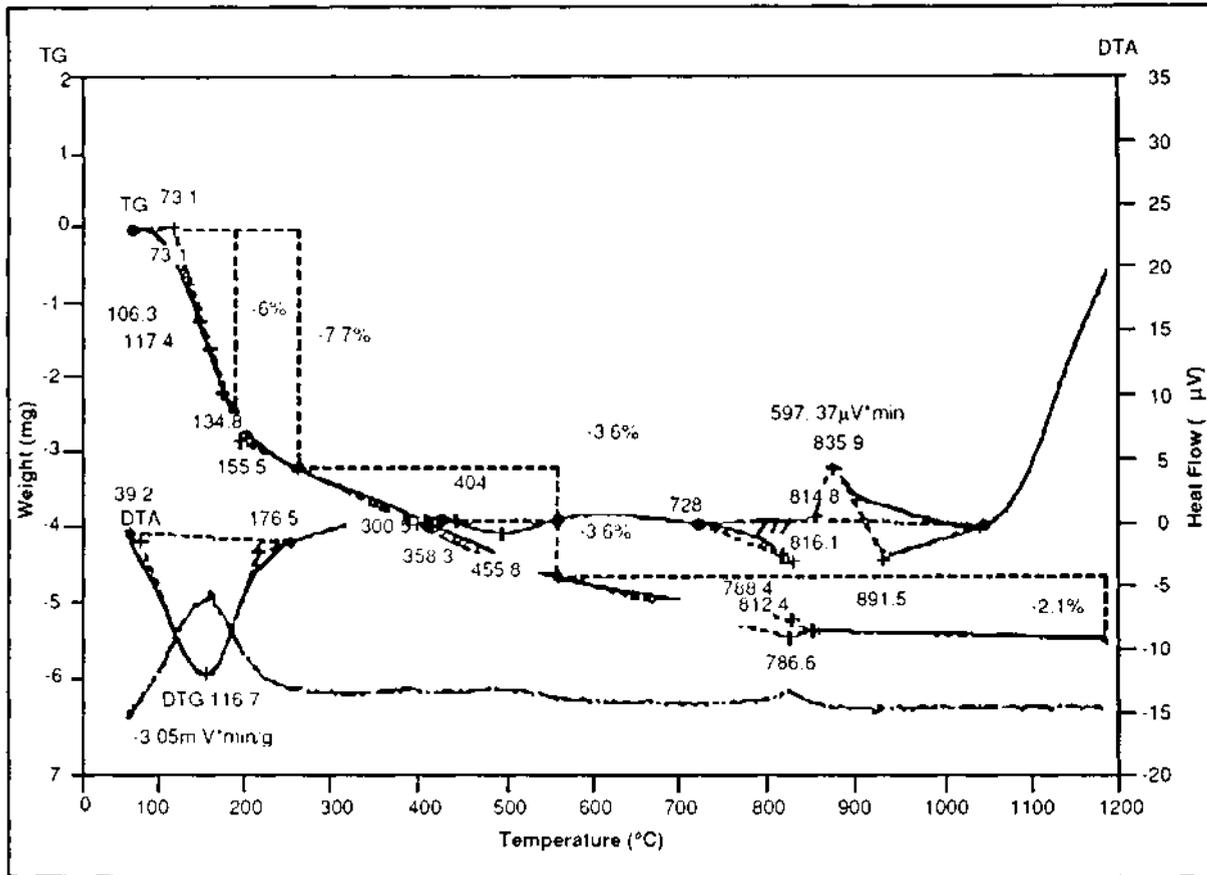


Fig. 5. DTA and TG pattern of KIB-6C sample.

zation. Temperature of the solutions should be less than 100°C, considered the paragenetic relationship. Sepiolite and manganese oxide occurrences are overlain by andesitic and basaltic lava flows around the hill with 1666 m. elevation.

At the UY-14 trench, located about 50 m. SSW of the UY-6 trench, some important features have been determined. Crystalline tuff that proceed into vitric tuff toward the upper portion dominate at the basal parts. Nodular chalcedony occurrences, 5-7 cm. in diameter, are common together with angular silica blocks. Vitric tuff contains diatomite mats, and siliceous and altered volcanic veins. In this trench, gradation from vitric tuff into sepiolite may be observed by barren eye. A completely altered, pinkish-beige colored volcanic structure yielded a chemical composition close to. rhyolite (Table 3). A sample from the west wall of the trench, on the vitric tuff-sepiolite gradation has

yielded sepiolite reflections with low intensity, in addition to opal-CT. Splitting of the (131) reflection reminds monoclin symmetry. Lithological and paragenetic relations in this trench point to a hydrothermal effect.

Mineral paragenesis for the Kibriscik sepiolite may be summarized as follows:

sepiolite + feldspar (mostly plagioclase);

sepiolite + plagioclase + quartz + a-cristobalite;

sepiolite + zeolite (heulandite, clinoptilolite) + feldspar,

montmorillonite + sepiolite + heulandite + plagioclase + quartz;

montmorillonite+ plagioclase+ quartz (+ a-cristobalite) + mica;

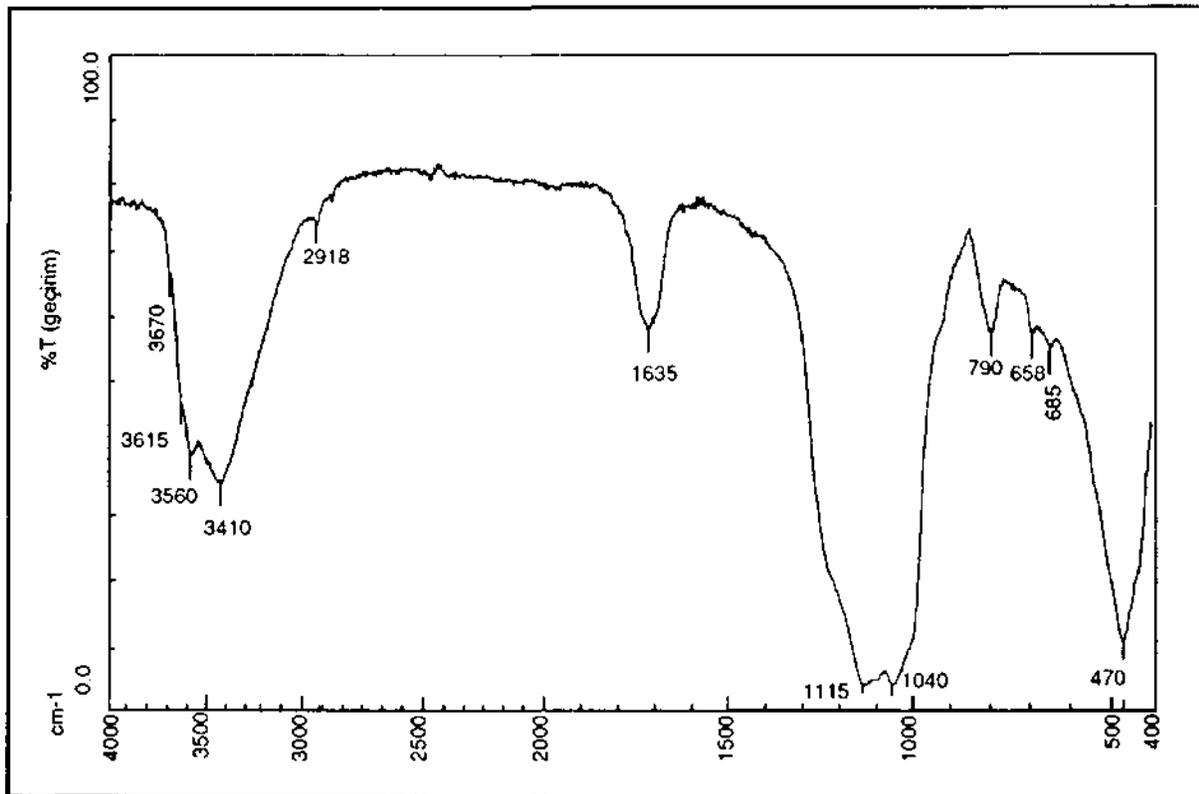


Fig. 6- IR spectrum of KIB-6C sample.

opal-CT + quartz+ α -cristobalite.

Paragenetic relations reflect a hydrothermal origin. No carbonate sequence has been determined around the hill with 1666 m. elevation. The presence of heulandite, which is a Ca-zeolite, show a silica saturated or oversaturated environment. This mineral is not stable over 400°C, and is synthesized at 200-360°C, under 15.000-37.000 psi pressure.

Sepiolitization is concentrated around the fissures and fractures, which have served as conduits for the uprisal of the hydrothermal fluids. Probably the same fluids, which have produced the alteration into sepiolite, has continued to be effective after the formation, and given rise to the occurrence of manganese oxide veinlets. Some of these fissures have later been filled by silica forming veins.

DTA and TG investigations

Palygorskite and sepiolite generally exhibit

similar thermal behaviour (Caillere and Henin, 1957; Hayashi et. al., 1969; Imai et. al., 1969; Martin Vivaldi and Fenoll, 1970; Nagata et. al., 1974; Serna et. al., 1975; Mifsud et. al., 1978). DTA patterns of these minerals may be examined in three temperature ranges: (1) low temperature region (<300°C), (2) central region (300-600°C), and (3) high temperature region (>600°C).

Due to the extraordinary chemical composition with rather low magnesia and high alumina content, which is related to the mode of occurrence by hydrothermal alteration, DTA pattern of Kibriscik sepiolite varies significantly from that of a sedimentary one (Fig. 5). The endothermic peak related to the loss of absorbed and zeolitic water below 300°C appears around 110-120°C, being broader and lower in intensity. In the central region, instead of two characteristic endothermic peaks at 350°C and 500-550°C in sedimentary sepiolite, due to the loss of coordination water, Kibriscik sepiolite generally yields a single and weak endotherm at 460-

480°C, reflecting the pattern of palygorskite. In the high temperature region over 600°C, the sharp endothermic peak at 800°C due to the complete dehydroxylation of the structure is not observed for the Kibriscik sample; and enstatite formation is more gradual. Some weak endotherms at around 780-820°C, which may be due to the feldspar content, are observable, a-cristobalite conversion probably starts at around 1000°C for the investigated sample, which should normally be expected around 1200°C.

Infrared (IR) investigations

IR pattern of the Kibriscik sepiolite shows different peculiarities from the other sepiolites (Fig. 6). In the IR pattern of KIB-6C sample, 3685-3625 cm⁻¹ bands due to the Mg-OH vibration (Otsuka et. al., 1968) have not developed well. Instead of a single band at 1200 cm⁻¹ due to Si-O-Si p bonding, a broad band appears combined to the 1100-1000 cm⁻¹ bands. Intensity of the 470 cm⁻¹ band is increased probably due to a chemical composition rich in silica. Possible substitution of Al³⁺ in the tetrahedral layer for Si⁴⁺, and that of Al³⁺ and Fe³⁺ for Mg²⁺ in the octahedral layer have affected the IR spectrum considerably. The absence of the 3685 cm⁻¹ and 1200 cm⁻¹ bands resembles the IR spectrum of palygorskite.

SEM and TEM investigations

Three sepiolite, one tuff and one diatomite specimen from the Uşakgöl area have been investigated under SEM. Instead of the characteristic fibrous structure (fibres generally being longer than 5 m) observed under SEM for sedimentary sepiolite, Kibriscik sepiolite composes of laths, whose length ranges in nanometer scale. In the SEM micrograph of KIB-6B specimen (Plate 1, Photo 1), glass-shard structure is seen to be preserved, while alteration becomes more effective and total crystallization trend increases locally (Plate 1, Photo 2).

In the TEM micrograph of KIB-6C specimen (Plate 1, Photo 3), sepiolite laths growing on the margins of volcanic glass particles are typical. Length of these laths, which have not obtained a fibrous form yet, ranges around 50-200 nm.

GEOCHEMICAL INVESTIGATIONS

Chemical analysis of rock samples

To make an approach to the mode of occurrence of Kibriscik sepiolite by geochemical methods, 20 rock and clay samples have been collected and analysed under 8 groups (Table 3). Results of the rock chemistry studies are summarized below:

1- Almost similar elemental composition determined in all the samples shows that the sepiolite-bearing area has continuously been effected by hydrothermal alteration, which produced homogenization among the elements.

2- The oldest hydrothermal alteration stage that could be determined in the field is the spilitization of basic rocks, and points to an aqueous environment, which is thought to compose of shallow and intermittent lakes.

3- The next hydrothermal alteration stage is that caused by the intrusion of veins, in rhyolitic composition, around which hydrothermal convective cells with meteoric and occasionally magmatic water interference have produced local alterations in the host rocks. Sepiolite formation is possibly in close connection with this system.

4- Aluminum source for the Kibriscik sepiolite, which is a Mg-Al silicate, is the vitric tuff itself. Values given in Table 3 clearly reveal it. On the other hand, these tuffs are almost sterile, considered Mg. Thus, an external source of Mg needs to be looked for. This source is thought to be essentially basalts, and to a minor extent, the andesites.

5- Occurrence of sepiolite at the contacts between the tuff and the veins in rhyolitic composition and the high SiO₂ and MgO contents versus other components in these veins, are results arising from the effective role of these veins in the leaching of the neighbouring rocks. As supported by field evidence, local temperature changes produced by these veins and the percolating solutions have dissolved Mg from the basalts and andesites, and migrated into tuffs, where Al was also supplied, thus producing the unusual Mg-Al silicate mineral.

6- Final ring of this effective hydrothermal al-

Table 4- Chemical analysis results of several sepiolite samples from the Kibriscik area

Oxides	KIB-6C (UY-6)	KIB-6B (UY-6)	KIB-6A (UY-6)	BK-13A (UY-15)	BK-13B (UY-15)	BK-16 (UY-17)
SiO ₂	71.26	68.80	70.20	57.00	60.50	71.00
Al ₂ O ₃	4.40	10.75	6.20	8.50	8.00	8.60
MgO	11.10	7.18	9.60	10.10	9.70	7.07
Fe ₂ O ₃	3.01	2.60	2.40	2.50	2.00	3.00
FeO	-	0.10	0.20	-	-	0.20
MnO	0.05	<0.10	-	0.20	0.30	<0.10
TiO ₂	0.25	0.50	-	0.30	0.30	0.30
CaO	0.44	0.45	0.55	2.00	2.50	0.39
Na ₂ O	trace	0.01	0.20	3.70	3.90	0.11
K ₂ O	0.74	1.00	0.95	1.20	0.70	1.00
P ₂ O ₅	0.04	0.10	-	0.30	0.20	0.10
L.O.I	8.72	7.25	8.65	13.35	10.60	6.80
TOTAL	100.01	98.79	98.95	99.15	98.70	98.62

(-) not analysed; DL: % 0.01

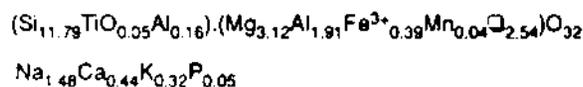
teration chain is represented probably by the veinlet systems, rich in Mn and Ba, cutting all the former products, Mg content of these veinlets are again considerably high, in accordance with its mobile character. This geochemical cycle has been tried to be schematised in Figure 7.

7- Assuming that the final weathering process had effected all the samples under the same conditions, final alteration effects have not been taken into account.

Chemical composition of the sepiolite

One of the most prominent properties of Kibriscik sepiolite is the unusual chemical composition of the material. It resembles that of palygorskite, and is thought to be in close connection with the composition of the host rock and mode of formation. Chemical analysis results of sepiolite samples collected around the Uşakgöl Plain are given in Table 4.

An approach has been made to calculate the structural formula of the BK-13A sample, whose XRD pattern contains only the reflections specific to sepiolite. Assumed that there is no other crystalline phase intercalated in the sample, the structural formula has been calculated as;



and the mineral described as Al-Fe Sepiolite.

By plotting of (Al+Fe)^{vi} and Mg^{vi} values, calculated according to 6+charge in octahedral layer, on the Weaver and Pollard (1973) and Foster (1960) diagrams, Kibriscik sepiolite is located at the compositional gap region, and seems to be close to palygorskite; but trivalent cation number is lower.

These data suggest that the Kibriscik sepiolite may be a new clay mineral with its own characteristics, but detailed crystallographic investigations still remain to be carried out.

Chemical analysis of some present-day spring water were carried out, and the activity coefficients calculated according to the Debye-Hückel equation were plotted on the MgO-SiO₂-H₂O activity diagram of Wollast et. al. (1968). It was seen that the values plotted lie on the border between the sepiolite precipitation and amorphous silica saturation areas. pH of the water specimens range around 9-9.5 and concentration of silica is very high. Thus, it was decided that direct chemical precipitation of sepiolite from present-day spring water is not possible.

MODE OF OCCURRENCE

Contrary to the sedimentary type sepiolite occurrences, which are generally associated with the carbonate/evaporite sequences, Kibriscik sepiolite has formed in a volcanic sequence, by the alteration of pyroclastic material. The source rock proved to be vitric tuff, according to field observations and mineralogical evidence.

Alteration and recrystallization processes of natural glasses under hydrothermal conditions have been investigated by many researchers (White, 1983; Crovisier et. al., 1983; Thomassin, 1983; Touray and Thomassin, 1984; Thomassin et. al., 1989). Wirsching (1976), Holler and Wirsching (1978), and Barth-Wirsching and Holler (1989) have simulated the formation of natural zeolites using various glasses in open and closed systems. Different zeolites have been synthesized depending on the chemical composition of the starting material, pH and concentration of the solution, temperature and pressure conditions.

One of the most recent and detailed investigation on the alteration of natural glasses under various physicochemical conditions is that of Larsen et. al. (1991). Basalt wool, diabase wool, glass wool and glass fiber have been used as the starting materials. Samples that were ground to 100 mm. were treated with deionized water at 100°, 125°, 150° and 200°C under autogenous pressure and at 200°C under 2000 bar pressure, without stirring the solution. The tests were carried out under closed system conditions and in 2-30 days period. Glass wool has produced analcime and sepiolite, at 125°C and 30 days of reaction period. Formation of analcime accords well with the findings of Abe and Aoki (1976), for closed systems. According to these researchers, analcime easily forms around 100°C and at pH values over 10. According to the published data of Bowen and Tuttle (1962), Echle (1974) and Hast (1956), sepiolite starts to form at 125°C and pH>10, and the process continues up to 200°C.

Under experimental conditions, hydrothermal alteration is controlled by the solubility of the glass,

and formation of the amorphous and crystalline reaction products. Glass solubility is controlled by the removal of modifying ions from the crystal structure producing a hydrated glass tayer, followed by the dissolution of the components of structure (Holland, 1966; Scholze, 1988). This process also prevails for the hydrothermal alteration. High content of Na and K in the starting material increases the reactivity of the material and alteration proceeds faster.

Experimental conditions and findings seem to suit well with those of the natural associations. Mineral paragenesis of Kibriscik sepiolite is considerably different from the Sivrihisar sedimentary sepiolites, with zeolites (mainly heulandite and clinoptilolite, to a lesser extent phillipsite and mordenite) mostly accompanying sepiolite, in addition to feldspar, quartz and montmorillonite. High Na and K content of the Kibriscik sepiolite is another important criterion indicating the different mode of occurrence. Observations and findings indicating the hydrothermal alteration for the formation of Kibriscik sepiolite may be summarized as follows:

1- Kibriscik sepiolite occurrence is completely located in a volcanic sequence of the Koroğlu volcanic belt, without any neighbouring carbonate or evaporite sequence.

2- As revealed clearly in UY-14 trench, alteration increases gradually from the vitric tuff towards the veins in rhyolitic composition, and sepiolite formation is accelerated. Silica veins and nodules in the same trench also show the hydrothermal activity.

3- Manganese oxide minerals determined within sepiolite in UY-6 trench (manjiroite and hollandite) contain high amount of alkalis. Especially the high content of Ba in hollandite reveal the effect of hydrothermal activity. In the KTU-20 sample given in Table 3, Ba content as high as 3000 ppm has been determined.

4- As stated in Coombs et. al. (1959), heulandite is a zeolite mineral characterizing the environments saturated or oversaturated by silica. Formation by the hydrothermal alteration of acidic

volcanic rocks or volcanic glass is very common. It forms at a temperature range of 200-360°C, and the structure is deformed over 400°C. Thus, temperature of the hydrothermal solutions may be estimated to be between 125°C and 360°C.

5- X-ray diffraction data reveal a sepiolite structure; however, other mineralogical analysis, such as DTA, IR and the chemical analysis results yield data more closer to those characteristic for palygorskite. It seems quite possible that the material described as Al-Fe sepiolite in this study may be a new mineral species, with an intermediary composition between sepiolite and palygorskite.

6- Microtextural interpretations, especially the "mineral growth with total crystallization trend" accompanying "solution breccia" like structures, specified by SEM and TEM studies, point to a stat-

ic-inhomogenous environment.

7- Sr content of Kibriscik sepiolite is lower than Sivrihisar sedimentary sepiolite, while it is characterized by higher contents of Cu, Mn, Ti, V, Zr and Ba (Irkeç, 1992). These elements have a genetic meaning in the identification of hydrothermal activities, and their relationship with each other yield important hint points in the establishment of genetic models.

8- As mentioned earlier, source of Mg^{2+} ions is thought to be the neighbouring widespread basic volcanic rocks, from which it is mobilized by percolating hydrothermal solutions. Due to the very limited extension of the veins in rhyolitic composition, which realized heat transfer to the convection, alteration and mass transfer in the host rocks were limited. Possibly a weakly developed connection be-

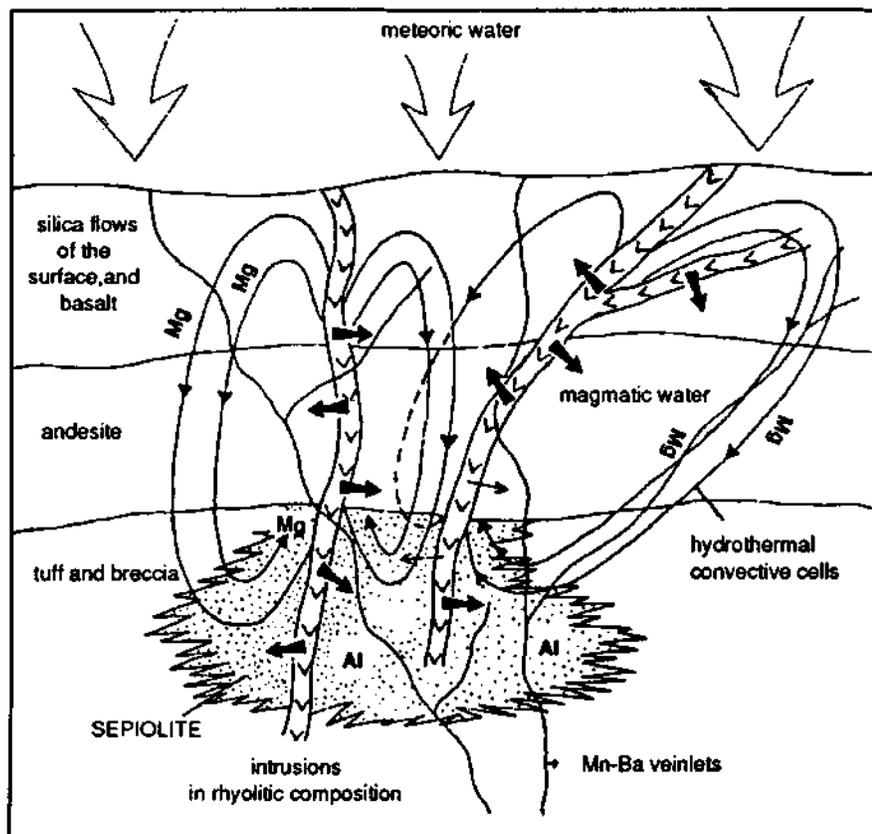


Fig. 7- Schematized mode of occurrence of Kibriscik sepiolite.

tween the fissures that served as the conduits for hydrothermal fluids, and free discharge to the surface limited the system as small convective cell, and did not permit the formation of a widespread mineralization.

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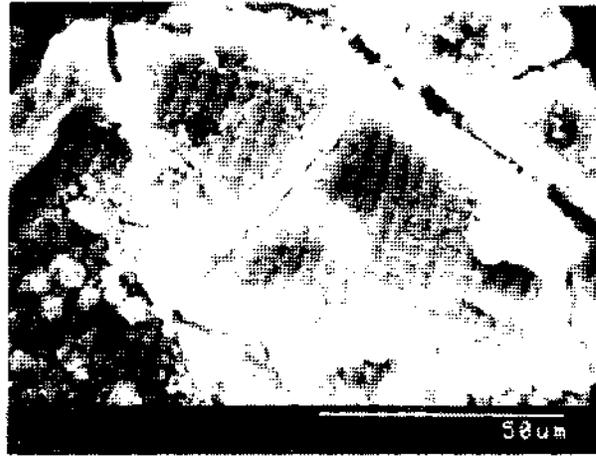
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PLATE

PLATE-I

- Photo 1- SEM micrograph of the KIB-6B sample (preserved glass-shard texture).
- Photo 2- SEM micrograph of the KIB-6B sample (effect of alteration and total crystallization trend).
- Photo 3- TEM micrograph of KIB-6C sample (sepiolite fibers and volcanic glass relicts).



1



2



3

ORIGIN AND PETROLOGY OF EKECİKDAĞ GRANITOID IN WESTERN CENTRAL ANATOLIAN CRYSTALLINE MASSIF

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ABSTRACT— A belt formed by a number of granitoid intrusions is situated at the western part of the Central Anatolian Crystalline Massif. One of the granitoid intrusion at the southwest of the belt crops out between Aksaray and Ortaköy and is called Ekecikdağ. Ekecikdağ granitoid, which is composed of monzogranites and granodiorites, intruded both the metamorphic and ophiolitic host rocks. Ekecikdağ granitoid is differentiated into following subunits with respect to their petrographical and chemical composition: Borucu granodiorite-monzogranite, Sinandı mikrogranite, Hisarkaya porphyritic granite, Kalebalta teucogranite and aplite granite. All these subunits are genetically related to each other. Borucu granodiorite-monzogranite represents the main magmatic phase whereas aplite granite the latest. Ekecikdağ granitoid has a calcalkaline character and show aluminofelitic trend. It has features which favour both I and S types of granite. Enclaves observed in granitoid is thought to be xenoliths derived from pre-existing gabbroic rocks during the emplacement of the granitic magma. The geochemical data suggest a post collisional tectonic setting and a continental crustal source for Ekecikdağ granitoid. In regard to regional data, during Upper Cretaceous, the existence of an ensimatic arc to the north of the Central Anatolian Crystalline Massif is suggested. It is also proposed that collision and obduction of this ensimatic arc on to the Central Anatolian continental crust caused crustal thickening and increase in the geothermal gradient in the region. This gave rise to the partial melting of the continental crust and to the formation of a granitic magma.

STRATIGRAPHY OF THE EASTERN SECTION OF THE PASINLER-HORASAN (ERZURUM) REGION

Cevdet BOZKUŞ***

ABSTRACT— In the eastern part of the Pasinler-Horasan Neogene basin, the lowermost section consists generally of tuffs, andesites and basalts. This association is nomenclated as "Karakurt volcanics". They are underlain by an ophiolitic melange of Lower Cretaceous age which is unconformably overlain by the Oligocene Çayarası formation consisting of clastic rocks. The basin is bounded by sinistral strike-slip faults controlling sedimentation of various continental detritic rocks. These are distinguished as Aras and Horasan formations, both Pliocene in age, representing respectively marls and claystones of deep lagoonal environment, conformably overlain by fine grained sediments. Terrace gravels, alluvial fans and colluvium represent the Quaternary sedimentation.

CLAY SEDIMENTOLOGY OF SEDIMENTARY SEQUENCE BELONG TO ÇAN (ÇANAKKALE). ORHANELİ AND KELEŞ (BURSA) LIGNITE OPEN PIT MINE

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ABSTRACT— In this study clay fraction belonging to the Miocene aged sedimentary coal bearing sequence from Çan, Orhaneli, Keleş districts have been separated and smectite, illite, kaolinite and chlorite paragenesis have been defined. Major element analysis have been made of monomineralic smectites. These are dioctahedral (beidellite) and trioctahedral (saponite) in character, and occurrences of these smectites have been examined. Smectites belonging to the tuffaceous series have been formed from the alteration of volcanic material whereas those from clayey carbonaceous series either as in situ neoformation of detrital materials or as the transformation of detrital smectites, kaolinite have been formed as a result of alteration of rocks with feldspar, while illite and chlorite have been derived from metamorphic rocks.

MAJOR-, MINOR-, AND TRACE-ELEMENT ANALYSES OF REFRACTORY SILICATES USING A SINGLE BORATE DISINTEGRATION METHOD

Bahattin AYRANCI*

ABSTRACT._ Fusion disintegration performed under non-oxidizing conditions using an induction oven is an alternative procedure for the decomposition of samples containing refractory components, so that the oxidation states of iron as well as major-, minor-, and trace-element analyses can be determined from a single sample disintegration.

A NEW TYPE SEDIMENTARY-DIAGENETIC SEPIOLITE IN SIVRIHİSAR (ESKİŞEHİR)

Mefail YENİYOL**

ABSTRACT._ This study describes a meerschaum sepiolite that differs from the conventional meerschaums of lump type with respect to its genesis, mode of occurrence, texture and composition. The present one is found together with layered sepiolite deposits in the upper section of Neogene dolomitic sequence in the south of Sivrihisar. It is layered, lens shaped and consists of dolomite and/or calcite minerals as detritic grains. Sepiolite had been formed during diagenesis, after deposition of reworked carbonate material, and occupied the intergranular space in varying proportions. The best ones are porous, lightweight, white and they can be easily carved when they are immersed in water.

A HUMIC ACID STUDY OF THE BEYPAZARI-ÇAYIRHAN LIGNITES USING IR-SPECTRAPHOTOMETER

Gültekin KAVUŞAN***

ABSTRACT.- Davutoğlan and Kuzey faults are two important tectonic features in Beypazarı-Çayırhan (Türkiye) basin. The basin has 3 seams of coal, one in the lower horizon with narrow extension and two in the upper horizon with an overall thickness of 3 m on the average. The samples were obtained by drilling several boreholes in the perpendicular direction to the faults and ground to 0.25-0.70 mm. Huminite macerals were separated with $ZnCl_2$ solution ($d= 1.44-1.50 \text{ gr/cm}^3$). Maceral-rich samples were then treated with KOH solution (5%) and the alkali-soluble fraction was then precipitated with concentrated HCl. The humic acids so purified were examined by IR-spectroscopy. The H/C ratios of coal seams display an increasing trend in van Krevelen diagrams due to the increasing burial depth and it has been seen that the H/C-O/C values of the seams taken from the drills close to Davutoğlan fault, lower than the average seam values. This behavior indicates that an increase in coalification rate is the consequence of the rise in temperature and tectonic pressure caused by Davutoğlan fault. The strong IR band at $1600-1620 \text{ cm}^{-1}$ indicates the presence of $>C=C<$ bands and remarkable aromatization in the structure. On the other hand, characteristic C-H stretching bands at $2800-3000 \text{ cm}^{-1}$ is an indication for the presence of $-CH_2$ and $-CH_3$ groups.

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