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ORIGIN OF SEPIOLITE AND LOUGHLINITE IN A NEOGENE VOLCANO-SEDIMENTARY LACUSTRINE ENVIRONMENT, MİHALIÇÇIK–ESKİŞEHİR, TURKEY

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Abstract

The Middle to Upper Miocene volcano-sedimentary units in the Mihalıççık–Eskişehir area of Turkey consist mainly of altered tuff and claystone, with thin layers of dolomite and silica nodules and horizons. Ripple marks and desiccation cracks are common in the siliceous tuff and dolomite units. Green to yellowish green claystone exhibits either hard layered or friable features. Sepiolite and loughlinite are dominant in the claystone of the study area. These minerals are generally associated with opal-CT, analcime, feldspar, dolomite and calcite. At Mihalıççık, loughlinite and sepiolite are identified by *d*(110) reflections at 12.9 and 12.3 Å, respectively. Loughlinite and sepiolite occur as fibers in dissolution voids and along the sides of dissolved volcanic glass particles and casts of silicic nodules. The area is represented by a lacustrine environment of variable depth and salinity, controlled by synsedimentary step-faulting in arid and semi-arid climatic conditions. Under these conditions, volcanic glass as well as dolomite release Si and Mg, which are used for the formation of sepiolite. Increasing evaporation causes the dominance of Mg with Na and K in the depression zone in the Killik area, favoring the formation of loughlinite under alkaline conditions. Field observations and mineralogical determinations indicate that sepiolite and loughlinite are both formed authigenically and independently in different physicochemical environments rather than being the product of a transformation of one to the other.

Keywords: sepiolite, loughlinite, origin, Neogene, lacustrine, Eskişehir, Turkey.

Sommaire

Les unités volcano-sédimentaires d'âge miocène moyen ou supérieur de la région de Mihalıççık–Eskişehir, en Turquie, contiennent surtout des tufs et des argillites altérées, avec des intercalations de dolomite et de nodules de silice. Des rides de fond et des craquelures de dessication sont répandues dans les tufs siliceux et les horizons dolomitiques. Les argillites, de couleur verte ou vert jaunâtre, sont soit endurcies ou bien friables. La sépiolite et la loughlinite prédominent dans les argillites de ce secteur. Ces minéraux sont généralement associés à opale-CT, analcime, feldspath, dolomite et calcite. On peut distinguer la loughlinite et la sépiolite par leurs réflexions (110), à une valeur de *d* de 12.9 et 12.3 Å, respectivement. La loughlinite et la sépiolite se présentent sous forme de fibres dans des cavités dues à la dissolution, par exemple le long de particules de verre volcanique en voie de dissolution ou dans des endroits occupés antérieurement par des nodules de silice. La région présentait un milieu lacustre de profondeur et de salinité variables, régies par la formation synsédimentaire de failles en escaliers dans des conditions climatiques arides et semi-arides. Ainsi, le verre volcanique et la dolomite dégagent Si et Mg, qui ont servi à la formation de la sépiolite. Avec l'évaporation, il s'est développé une augmentation de Mg, Na et K dans la dépression de la zone de Killik, ce qui favorisa la formation de la loughlinite en milieu plutôt alcalin. Les observations de terrain et les déterminations minéralogiques montrent que sépiolite et loughlinite sont des phases authigènes, formées indépendemment dans des milieux géochimiquement distincts, et ne seraient donc pas les produits d'une transformation d'un à l'autre.

(Traduit par la Rédaction)

Mots-clés: sépiolite, loughlinite, origine, Néogène, milieu lacustre, Eskişehir, Turquie.

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INTRODUCTION

Sepiolite and palygorskite commonly form in saline and alkaline lakes all over the world (Singer & Galán 1984, Jones & Galán 1988, Singer 1989). Experimental investigations at atmospheric conditions by Wollast *et al.* (1968) indicate that the formation of sepiolite is favored in hypersaline environments. The experimental formation of a sepiolite-like substance from loughlinite in altered pyroclastic sediments of Eocene age in the Green River Formation in Wyoming is due to removal of Na and Si from loughlinite by prolonged leaching, as shown by Fahey *et al.* (1960). Echle (1967, 1974, 1978) also studied the transformation of sepiolite to loughlinite in the Miocene–Pliocene volcano-sedimentary units of Mihalıççık, Turkey. In these studies, he compared laboratory results with mineralogical data compiled from the field dealing with some unanswered questions, such as whether this reaction is invariably a "re-sepiolitization", and which of these minerals formed first. The aim of the present study is to determine and discuss the origin of sepiolite and loughlinite in view of their lateral and vertical distributions in the field. Also, these results are compared with those obtained by Echle (1967, 1974, 1978).

GEOLOGY

The basement rocks of the area (Fig. 1) consist of Paleozoic metamorphic and Mesozoic ophiolitic rocks (Çoğulu 1967, Kulaksız 1981). These rocks are unconformably overlain by the middle to upper Miocene lacustrine volcano-sedimentary units. These units are generally composed of clastic, clayey, dolomitic, tuffaceous, evaporitic, and silicified sediments. The yellowish green or darker green altered tuff and claystone units are dominated by sepiolite and loughlinite, and are known as the Akpınar Formation (Figs. 2A, B). Sepiolitic claystone is generally widespread, and characterized as pale yellowish green, hard, friable, and occasionally plastic. Loughlinite appears as greenish, massive, "soapy" lenses and layers within the sepiolitic claystone in the Killik area. The contact between sepiolite- and loughlinite-dominated claystones is sharp. The Akpınar Formation is intercalated with several horizons of silicified tuff units 10–40 cm thick, as well as with horizons of silica nodules influenced by volcanic activity. In places, ripple marks and desiccation cracks also are observed. These features indicate that evaporation and drying occasionally affected the basin. These units are overlain by the Pliocene Kırmızıtepe Forma-

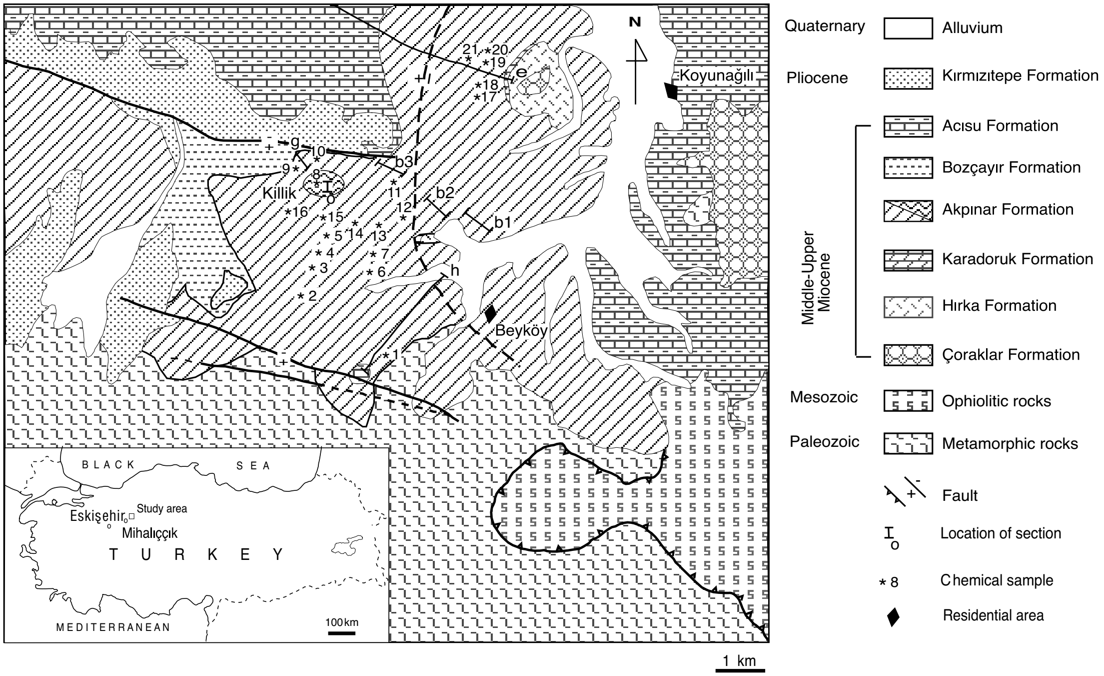

FIG. 1. Geological map of the Mihalıççık area (revised from Siyako 1982, 1983).

tion, which is composed of red conglomerate, sandstone and mudstone, followed by Quaternary alluvium. The basin around Killik was depressed by synsedimentary NW–SE step-faults (Fig. 1). The area is part of the central Anatolian Neogene basin, which is affected by N–S-trending tensional faults (Şengör 1979, Yağmurlu *et al.* 1987, İnci 1991).

METHODS

Field work was carried out on the basis of the geological maps of the Mihalıççık region (Siyako 1982, 1983). Sepiolite- and loughlinite-dominated facies were mapped separately. In order to identify the lateral and vertical distribution of sepiolite and loughlinite, five stratigraphic sections in the tuffaceous and lacustrine sediments of the study area were constructed (Fig. 1).

Eighty-four samples, representing the two facies, were analyzed for their mineralogical characteristics by X-ray powder diffraction (XRD) (Rigaku Geigerflex), and scanning electron microscopy (SEM–EDX) (Topcon Abt–60, JEOL JSM 84A–EDX). For petrographic studies, 80 thin sections were prepared from the samples. XRD analyses were performed using Cu$K\alpha$ radiation and a scanning speed of 1° 2θ/min. Unoriented mounts of powdered whole-rock samples were scanned to determine the mineralogy of the bulk sample. Samples for clay analysis (<2 μm) were prepared by separation of the clay fraction by sedimentation, followed by centrifugation of the suspension, after overnight dispersion in distilled water. The clay particles were dispersed by ultrasonic vibration for about 15 minutes. Four oriented specimens of the <2 μm fraction were prepared of each sample: air dried, ethylene-glycol-solvated at 60°C for 2 hours, and thermally treated at 350° and 550°C for 2 hours, respectively. Semiquantitative analyses were made by multiplying the intensities of the principal basal reflections of each mineral by suitable factors according to an external method developed by Gündoğdu (1982) following the method of Brindley (1980). The relative error of this method is less than 15%. Representative clay-dominated bulk samples were prepared for SEM–EDX analysis by glueing the fresh, broken surface of the sample onto an aluminum sample holder that had been covered with double-sided tape and coated with a thin film (~350 Å) of gold, using a Giko ion coater.

Chemical data were obtained for twenty-one representative samples of claystone and tuffaceous rocks by XRF (Rigaku X-ray spectrometer RIX 3000). Chemical analyses were performed using the rock standards supplied by MBH Reference Materials and Breitländer companies. The accuracy for elements is ±2%. Loss on ignition (LOI) of each sample was also determined by drying the samples at 105°C overnight, followed by calculation of their content of H_2O and other volatiles at 1050°C. Mineral compositions were determined on <2 μm fractions of sepiolite and loughlinite obtained by

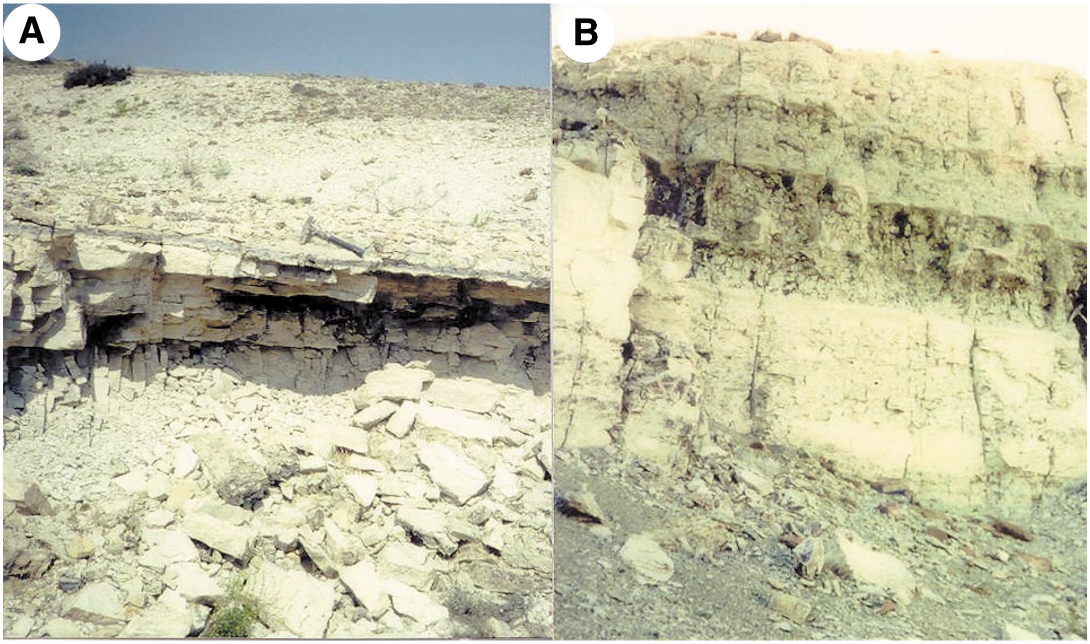

FIG. 2. View of sepiolite-dominant (A) and loughlinite-dominant (B) claystones in Akpınar Formation in the area of Mihalıççık.

sedimentation of samples B–15 and O–3, with the highest sepiolite and loughlinite content, respectively, followed by centrifugation of the suspension up to 15000 rps for 10 minutes, after soaking in distilled water overnight. The structural formulae of sepiolite and loughlinite were calculated on the basis of 32 atoms of oxygen per formula unit (Newman & Brown 1987).

RESULTS

Petrography

The Akpınar Formation is composed of dolomite and tuff. The dolomite is very fine-grained, displaying a dolomicritic texture. Brecciated black intraclasts are very widespread in the dolomicritic matrix (Fig. 3A). Also, polygonal desiccation cracks, root casts and microvugs are abundant. Desiccation cracks and dissolution voids are lined with dogtooth-type sparitic cement (Fig. 3B). Some of the geopetal type of cavities in the dolomite may have been produced by root-cast activities similar to what has been reported by Freytet & Plaziat (1982) and Platt (1989). Some of the cavities were partly filled with vadose silt and meniscus cement, probably derived from the inner walls of the cavities by influx of fresh water in a very shallow environment following development of the fractures and desiccation cracks in a period of drought. Tuffs are composed of quartz, biotite, altered feldspar and accessory epidote and opaque minerals in a volcanic glass groundmass. Chalcedony with a spherulitic texture, calcite, quartz and iron oxide minerals occur within the cracks (Fig. 3C).

XRD determination

To determine the genetic relationship between sepiolite and loughlinite, an X-ray analysis was carried out on closely spaced samples collected from lenses and layers of loughlinite-dominated claystone and sepiolite-bearing claystone in contact with each other in the Killik area (Figs. 1, 4, Table 1). Sepiolite and loughlinite are dominant at different levels of the Akpınar Formation. A thin horizon of sepiolite occurs in the upper part of the loughlinite-dominant levels. Loughlinite is observed in the lower part of the sepiolite-dominant levels around Killik. Sepiolite, associated with dolomite, opal-CT and analcime, is the dominant clay mineral in the Akpınar Formation. The decrease in sepiolite content at any level leads to the predominance of dolomite. On the other hand, loughlinite is mainly associated with calcite, opal-CT, analcime, feldspar and palygorskite. Loughlinite from the Mihalıççık area is identified by the 110 reflection at 12.9 Å (Fig. 5A). Sepiolite in the same area shows a basal reflection at 12.3 Å (Fig. 5B). There are no intermediate peaks detected between 12.9 and 12.3 Å in any sample, as would be expected if there is a transformation from one into the other, as claimed by Echle (1978) (Figs. 5A, B, C). Slight increases in the XRD background in some of loughlinite- and sepiolite-bearing samples may well indicate the presence of amorphous materials (Jones & Segnit 1971).

SEM–EDX determinations

SEM observations indicate that loughlinite and sepiolite occur as fibers approximately 5 μm long and exhibit distinct morphological shapes and associations. Fibers of loughlinite display a complex meshwork morphology developed in the dissolution voids and along the edge of glass shards and also enclose relics of volcanic glass (Figs. 6A, B). Loughlinite shows a concentric morphology around casts formed by removal of mineral grains, most probably rounded to subrounded silicic nodules (Fig. 6C). On the other hand, sepiolite is observed either as bridges of fibers between partly abraded dolomite aggregates, or growing out of dolomite crystallites either as individual fibers or masses of fibers, such as described by Aqrawi (1993), Karakaş & Kadir (1998) and Kadir & Akbulut (2001) (Fig. 6D). The semiquantitative EDX analyses of the loughlinite fibers show strong peaks of Si, Mg, and minor amounts of Na, Al, Fe and K (Fig. 6E). Sepiolite fibers have a composition similar to loughlinite fibers, except Na was not detected (Fig. 6F).

CHEMICAL COMPOSITIONS OF THE WHOLE ROCKS AND CLAY MINERALS

The chemical composition of the whole rocks is presented in Table 2. Na_2O and K_2O contents of the loughlinite-dominant part (central part of the basin) in the Killik area are 0.48–7.00% and 2.04–5.70%, respectively. Na_2O and K_2O contents decrease significantly toward the north and south, where sepiolite is the dominant clay mineral and loughlinite is absent. The Fe_2O_3 content of the tuffaceous rocks in Killik area is in the range 3.9–9.0%, and relatively lower in the northern and southern parts, probably owing to the substitution of Fe^{3+} for Al^{3+} in the layers of octahedra of loughlinite, sepiolite and smectite, in which Fe^{3+} is relatively greater in the lowest elevation of the study area around Killik. The MgO values are high in the sepiolite-dominant samples and lower in the loughlinite-rich samples.

FIG. 3. Photomicrographs of dolomite and altered tuffs. A. Development of brecciation as a result of polygonal desiccation cracks and fractures. B. Dogtooth-type sparitic cement occurs on the inner wall of the geopetal cavities, filled with fine sediments. C. Chalcedony with spherulitic texture in altered tuff.

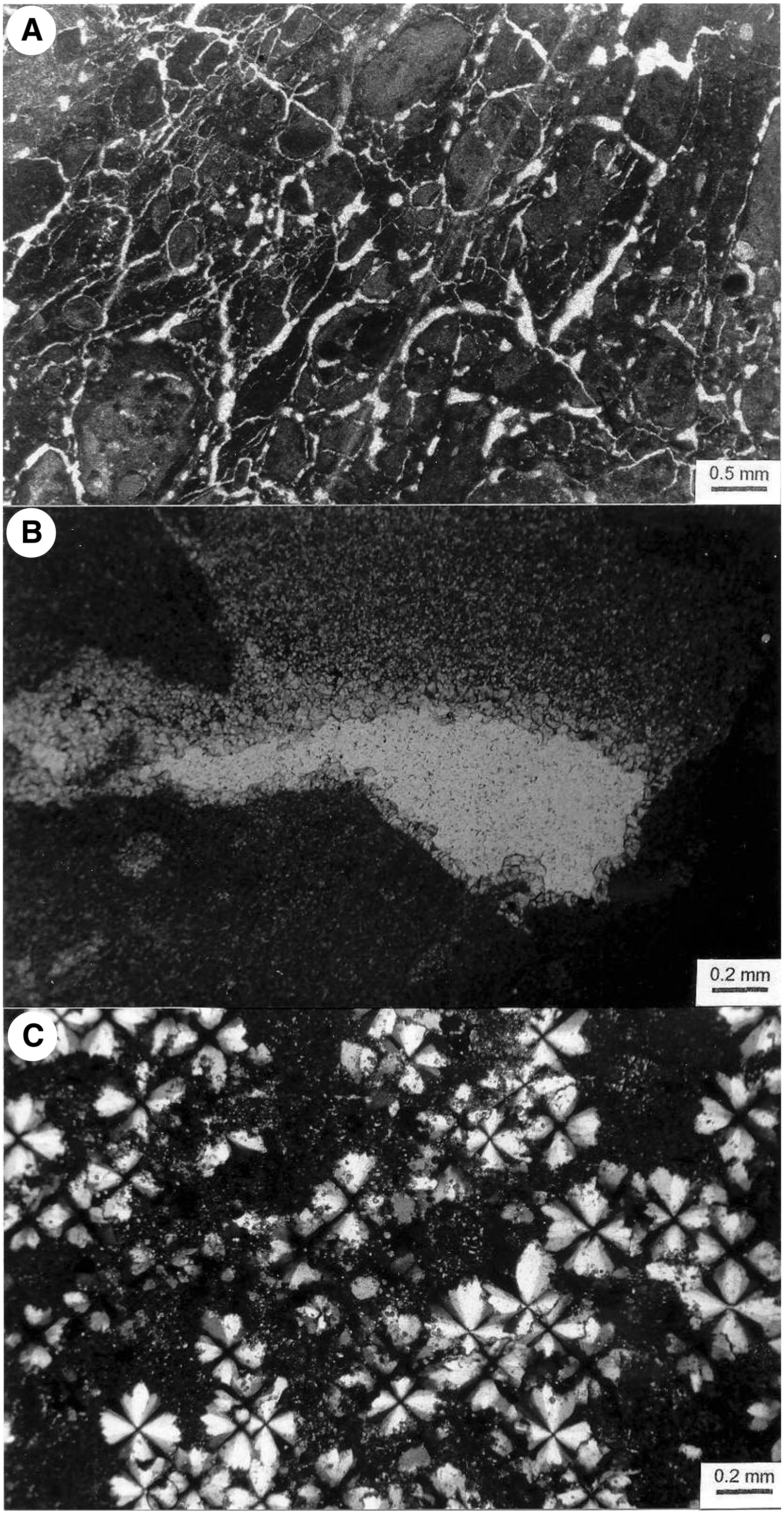
A
0.5 mm
B
0.2 mm
C
0.2 mm

TABLE 1. MINERALOGICAL VARIATION ALONG STRATIGRAPHICAL SECTIONS OF THE MIHALIÇÇIK AREA, TURKEY

	Sep	Lou	Pal	Sm	Anl	Dol	Cal	Mgs	Fel	Ill	Qtz	Op	Amp	Tlc
O-1		+++		ac	+		+		ac					
O-2		++++			+		ac		ac					
O-3		+++			+		+		ac					
O-4		++++			+				ac					
O-5		++++			+				ac					
O-6					+		++++							
O-7		+++	+		+									
O-8		++++			+	ac			ac					
O-9		+++		ac	+	ac	+		ac					
O-10		++++			+		ac		ac					
O-11		++++	ac		+				ac					
O-12		++	+		++				ac					
O-13		+++		ac	+		+		ac	ac				
O-14		+++			+		+		ac					
O-15		+++			+	+	ac		ac	ac				
O-16		+++			+		+		ac					
O-17	+++			+	++				ac					
O-18		++++		ac	+				ac					
O-19		++++			+				ac					
O-20		++++			+				ac	ac				
G-1	+++				+		+		ac	ac				
G-2		++++	ac		+		ac		ac					
G-3	+++		ac		++				ac					
G-4	+++				+		+		ac					
G-5	++			+	+	+			ac	ac				
G-6	+++			+	+		ac		ac					
G-7	+++		ac		++		ac		ac				ac	
G-8	+++				+		ac		ac	ac				
G-9			+				+		+++		ac			
B-1				+	++				+		+			
B-2				++	+	+				++	ac		ac	
B-3				++		++				+				ac
B-5						++++					+			
B-6A								+++				++		
B-6B									+	+++		+	ac	
B-7				+	+	+				+++	ac		ac	
B-8	+								+++		+			
B-9		++++			+		ac		ac					
B-10				+++	+				ac					
B-11									+++	+	+			
B-12									+++	+	+			
B-13	+++				+		+		ac					
B-14	++++				+		ac		ac					
B-15	+++				++		ac		ac					
B-16		++++			+		ac		ac	ac				
B-17	+++				+				ac	ac				
B-18	+++				+		+		ac					
B-19		++		+	+		+		ac					
H-11				+		++		++		ac				
H-13						+		++++						
H-15B						+++					++			
H-16	ac				+	+++			+	ac	ac	ac		
H-17	+				+	+++			ac					
H-18	++				+	+			ac			+		
H-19	+				+	+++			ac	ac			ac	
H-21	++				+	+			ac	ac		+		
H-22						ac			+	ac	+	+++		
H-23						+++			+	+			ac	
H-24B						++++	ac				+			
E-1				+	+	+	+		ac	+				
E-2				ac	+	+	+		ac	+	ac			
E-3				+	+	++				+	ac		ac	
E-4				+	+	++			ac	+	ac			
E-5						++++			ac		+			
E-6						++++			ac		+			
E-7	+++				ac	++			ac		ac			
E-9						++			++		+			
E-10	++				+	++								
E-11	+++				+	+			ac		ac			
E-12	++			+					+		+			
E-13						ac			++	++	+			
E-14	+++				+		+		ac					
E-15	+++				+	ac	ac		ac	+				
E-16	++			+	+	+	ac		ac	ac				
E-17				++	++	ac	+		ac	ac				
E-18	+			+	++	+			+	ac				
E-19	+			++	+	ac	+		ac	ac				
E-20							+++++							
E-21							+++			+	+			
E-22	+++				+	+			ac	ac	ac			
E-23						+++	++							
E-24				+++	+		+		ac	ac				
E-25							+++++							
E-26						+++	++							

Locations of the samples are given in Figures 1 and 4. Symbols used: Sep: sepiolite, Lou: loughlinite, Pal: palygorskite, Sm: smectite, Anl: analcime, Dol: dolomite, Cal: calcite, Mgs: magnesite, Fel: feldspar, Ill: illite, Qtz: quartz, Op: opal-CT, Amp: amphibole, Tlc: talc, +: relative abundance of mineral phase. ac: accessory.

Therefore, the presence of loughlinite is positively correlated, and that of sepiolite, negatively correlated with Na and K, and *vice versa* with respect to Mg content. The Na content reflects the presence of loughlinite, analcime and feldspar, whereas the K content reflects the presence of illite and K-feldspar. High SiO_2 values are observed in sepiolite and loughlinite as well as in volcanic glass, analcime, and quartz (Table 2, Fig. 4). Higher values of Al (3.6–10.6% Al_2O_3) are related to the presence of analcime, smectite, feldspar and illite, in addition to the sepiolite and loughlinite clay fractions, which contain little aluminum.

The structural formulae of sepiolite and loughlinite were calculated for B–15 and O–3 clay fractions, respectively (Table 3). The tetrahedrally coordinated sites of both minerals are filled mainly with Si, which is partly substituted by Al in sepiolite, and Al and Fe in loughlinite. Mg is the dominant octahedrally coordinated cation in both sepiolite and loughlinite, accompanied by 0.23 *apfu* Al (in the sepiolite), 0.41 and 0.23 *apfu* Fe, and 0.05 and 0.04 *apfu* Ti, respectively. The proportion of octahedrally coordinated Mg and Al is slightly higher, and that of interlayer Na is lower in sepiolite than in loughlinite. Also, the Al_2O_3 value in sepiolite and loughlinite of Mihalıççık is higher than that of other samples of sepiolite reported by Newman & Brown (1987). Moreover, the MgO content is higher and Na_2O content is lower in loughlinite of Mıhalıççık than in that of the type locality, Sweetwater County, Wyoming (Fahey *et al.* 1960, Table 3). The presence of some of the Al, Fe, Ca, Na, and K is probably due to minor impurities (analcime, feldspar, calcite, glass shards,

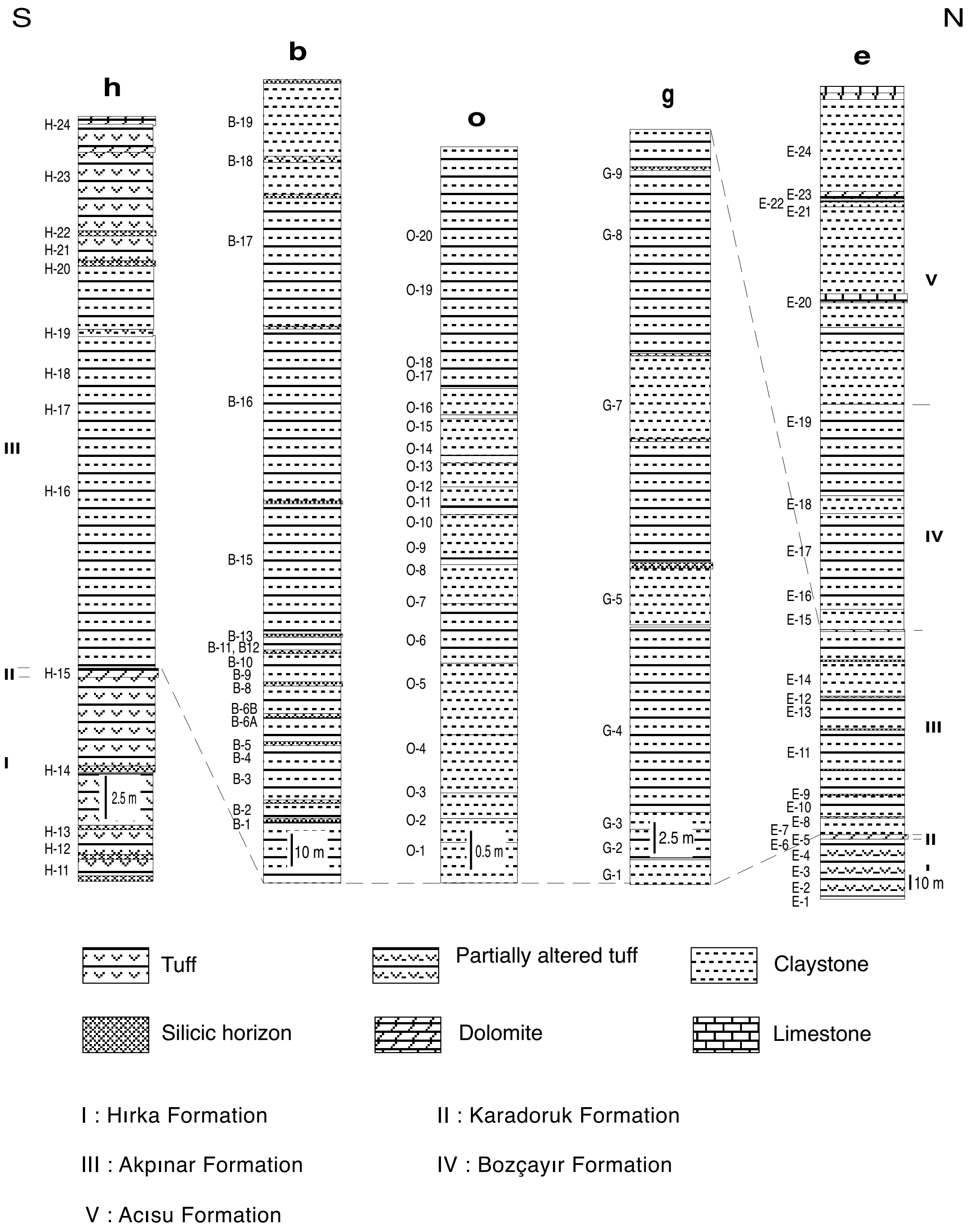

FIG. 4. Distribution of the principal lithologies of the Mihalıççık area.

TABLE 2. CHEMICAL COMPOSITION AND MINERALOGY OF SAMPLES COLLECTED FROM VARIOUS ROCK-TYPES FROM SOUTH TO NORTH IN THE STUDY AREA

Location	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Sample	H-23	KK-2	KK-3	KK-4	KK-5	AK-1	AK-2	O-5	OÇ-1	OÇ-2	OÇ-3	OÇ-4	OÇ-5	OÇ-6	OÇ-7	OÇ-8	E-7E	E-7D	E-7A	E-7B	E-11
SiO_2 wt%	20.14	55.20	56.75	56.10	55.30	49.71	50.54	53.30	52.30	50.60	52.00	42.50	56.00	54.30	52.40	56.71	34.34	15.81	35.86	55.24	39.56
Al_2O_3	5.66	6.80	6.95	7.55	5.25	6.95	10.38	4.65	5.70	5.70	5.30	4.10	4.50	3.60	7.90	10.55	7.35	2.27	4.44	6.75	5.68
Fe_2O_3	2.76	2.00	2.20	2.30	2.00	1.70	2.77	6.80	9.00	6.40	7.00	4.00	6.50	4.30	3.10	3.86	3.71	0.47	0.42	1.16	1.68
TiO_2	1.18	0.18	0.25	0.15	0.17	0.10	0.45	0.35	0.60	0.40	0.45	0.20	0.30	0.25	0.10	0.33	0.54	0.06	0.12	0.12	0.26
MgO	14.00	19.70	19.60	17.60	18.00	17.00	13.00	13.80	12.70	14.20	15.40	13.25	15.00	18.70	11.80	14.49	19.68	32.14	28.75	20.74	17.87
CaO	20.00	0.95	0.60	1.15	3.20	2.00	4.70	0.65	0.95	2.50	1.50	9.10	1.00	1.50	4.60	2.18	9.69	13.30	9.30	2.98	11.32
Na_2O	0.78	0.90	2.00	2.20	1.50	0.80	2.20	7.00	4.50	4.70	3.50	2.00	3.90	3.20	5.30	0.48	0.46	0.02	0.40	0.44	0.43
K_2O	2.20	1.30	1.00	1.60	0.85	1.38	1.70	4.00	5.70	4.60	4.50	2.70	3.20	2.30	4.10	2.04	2.37	0.08	0.13	1.90	1.30
LOI	32.94	12.70	10.45	10.70	12.90	20.17	13.90	9.50	8.30	10.70	10.15	21.80	9.70	11.80	10.60	9.38	20.36	36.84	20.57	10.51	21.89
Total	99.66	99.73	99.80	99.35	99.17	99.81	99.94	100.05	99.75	99.80	99.80	99.65	100.10	99.95	99.90	99.99	98.50	100.99	99.96	99.84	99.99
Sep		+	++	++	++	+++	++		++	++	+++	ac	ac	+++	++	++	++	+	++	+++	+++
Lou								++++													
Pal										ac											
Sm		++	+	+	+	+	++		+			+	+			++		ac		+	ac
Anl	ac		+	+	+	ac	+	+	++	++	++	+	+	+	++	ac	ac		ac	ac	ac
Dol	+++	+	+	+	+	+	ac					+	+		+	ac	++	+++	++		+
Cal					ac	ac			ac	+	ac	+		+						ac	
Mgs													+								
Fel	+	ac		ac			ac	ac	ac	ac	ac		ac		ac		ac	ac	ac		ac
Ill	+	+									ac	ac	+			ac					
Qtz			ac									ac					ac	ac	ac	ac	ac
Op												+		ac							
Amp	ac																				
Tlc		ac																			

LOI: Loss on ignition at 1050°C. Symbols used: Sep: sepiolite, Lou: loughlinite, Pal: palygorskite, Sm: smectite, Anl: analcime, Dol: dolomite, Cal: calcite, Mgs: magnesite, Fel: feldspar, Ill: illite, Qtz: quartz, Op: opal-CT, Amp: amphibole, Tlc: talc, +: relative abundance of mineral phase, ac: accessory. The location of the samples is given in Figure 1.

etc.), which were not removed and not detected by XRD analyses, as stated by Galán & Carretero (1999).

DISCUSSION

The Mihallıççık region represents part of a widespread Neogene lacustrine basin in central Anatolia. Sepiolite and loughlinite in the area were formed in the volcano-sedimentary basin. The formation of sepiolite and related minerals in Neogene volcano-sedimentary lake basins was reported by Sheppard & Gude (1968) and Starkey & Blackmon (1979, 1984). Sepiolite is accompanied by dolomite, and loughlinite by calcite, analcime and feldspar. This finding contrasts with that of Echle (1978), who reported an association of loughlinite with dolomite, because the Mg released during the conversion of sepiolite to loughlinite was consumed to form dolomite, contrary to the case of sepiolite accompaning calcite because Mg was consumed during conversion of loughlinite to sepiolite. Echle also reported that in loughlinite, the small amount of Mg in the sepiolite structure is replaced by 2Na, one of them placed with H_2O in the channels of the structure. Loughlinite is exposed as lenses and layers at the lower part of the strata, where it appears as a layer a few cm thick enriched in that species, extending laterally and alternating with sepiolite-dominant layers. The contact between sepiolite- and loughlinite-dominated claystones is sharp, and no association of sepiolite with loughlinite was detected in any sample from the area. Our field observations, XRD analyses and SEM images do not reveal the presence of a transitional phase between sepiolite and loughlinite. If there were any transitional phase between these minerals, there would be a gradational contact between sepiolite- and loughlinite-dominated claystone. Moreover, SEM images also indicate that loughlinite developed as a network of fibers on the inner surfaces

TABLE 3. CHEMICAL COMPOSITION AND STRUCTURAL FORMULAE PURE SAMPLES OF SEPIOLITE AND LOUGHLINITE

	Sepiolite	Loughlinite	
	B-15	O-3	Wyoming
SiO_2 wt%	55.00	53.00	50.80
Al_2O_3	3.48	2.60	0.66
TiO_2	0.30	0.27	0.02
Fe_2O_3	2.60	2.65	3.36
CaO	0.50	0.15	
MgO	22.50	22.00	16.01
Na_2O	0.60	4.75	8.16
K_2O	0.70	0.70	
LOI	14.32	13.88	20.50
Total	100.00	100.00	99.51

The structural formulae are calculated on the basis of 32 atoms per formula unit of oxygen. Data on Wyoming loughlinite: Fahey *et al.* (1960). Partial structural formulae: sample B-15: $(Si_{11.38}Al_{0.62})_{\Sigma 12}(Al_{0.23}Fe_{0.41}Ti_{0.05}Mg_{6.94})_{\Sigma 7.63}Ca_{0.11}Na_{0.24}K_{0.18}$; sample O-3: $(Si_{11.16}Al_{0.65}Fe_{0.19})_{\Sigma 12}(Fe_{0.23}Ti_{0.04}Mg_{6.90})_{\Sigma 7.17}Ca_{0.03}Na_{1.94}K_{0.19}$

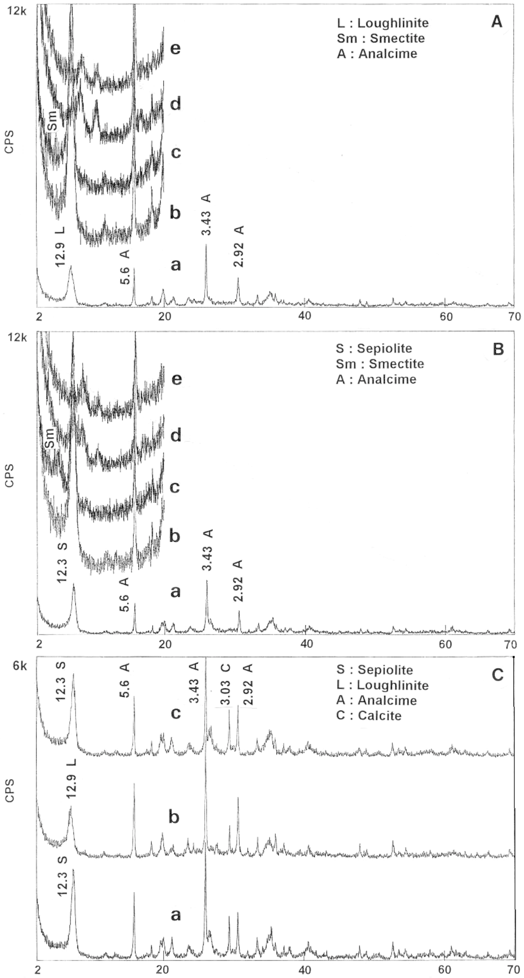

FIG. 5. X-ray diffraction pattern of A. Loughlinite (O–18) and B. Sepiolite (O–17), [a. air dried, b. oriented, c. ethylene glycolated, d. heated 350°C, e. heated 550°C]. C. Occurrence of loughlinite between sepiolite-dominant horizons, a. sepiolite (B–15), b. loughlinite (B–16) and c. sepiolite (B–18).

of dissolution voids in domains of volcanic glass, in contrast to sepiolite, which occurs as bridging fibers between crystallites of dolomite, indicating that these minerals are formed authigenically under different physicochemical environmental conditions rather than resulting from a transformation process from one to the other (Galán & Castillo 1984, Jones 1986, Jones & Galán 1988, Ece & Çoban 1994, Ece 1998, Singer *et al.* 1998). On the other hand, Wollast *et al.* (1968) observed the precipitation of sepiolite under laboratory conditions, but they did not explain the precipitation of loughlinite. McLean *et al.* (1972) also reported occurrence of sepiolite in a lake deposit that has a mineralogical composition similar to that at Mıhalıççık.

Climatic conditions, sources of Na, Mg and tectonism of the basin apparently control the mineralogical characteristics and distribution of sepiolite and loughlinite, which are formed independently. The mineralogical associations of sepiolite indicate that the lake environment is characterized by alkaline and saline conditions, similar to those reported by Surdam & Sheppard (1978). Ripple marks and desiccation cracks in claystone, tuff and intercalated siliceous tuff indicate arid climatic conditions. Decreases in input of fresh water and increasing evaporation caused the early precipitation of dolomite. The presence of very finely crystallized dolomite in dolomicrite reveals that the water body was very shallow, as a result of drought, causing the development of desiccation cracks, dissolution voids and brecciation. Regression of the lake water and enrichment of the volcano-sedimentary deposit with pore and connate waters caused the dissolution of volcanic glass and dolomite. Sepiolite precipitated as a result of the dominance of Mg and Si in the basin. XRD and SEM analyses indicate that sepiolite is associated with dolomite and opal-CT, and sepiolite fibers occur between dolomite grains in dissolution voids of volcanic glass, supporting the above hypothesis. The basin was later affected by synsedimentary faults, developed as a result of tectonic activity during the Miocene, as reported by Şengör (1979) and Yağmurlu *et al.* (1987). Thus, precipitation was controlled by both climatic conditions and the development of step faulting. Increasing evaporation caused the enrichment of soluble Mg as well as Na and K in the down-dropped blocks. Altaner & Grim (1990) also stated that evaporation in the lake environment would be expected to cause enrichment in the easily dissolved elements. In dominantly alkaline enviroments, Mg- and Na-rich solutions react with volcanic glass, resulting in the formation of loughlinite. Moreover, a gradational decrease in the values of Na + K from Killik outward supports this idea (Table 1). The association of K-feldspar with loughlinite, in contrast to sepiolite where K-feldspar is absent, indicates that loughlinite in the Killik area in the central part of the basin is the product last precipitated during the cycle of continuous evaporation. Formation of similar authigenic K-feldspar follows the precipitation of analcime in the central part of Pleistocene Lake Tecopa (Surdam & Sheppard 1978). Therefore, the transformation model between sepiolite and loughlinite proposed by Echle (1978) is not applicable in the area. The origin of both minerals is compatible with the same alkaline and saline lacustrine environment rich in volcano-sedimentary rocks. The availability of Na and the ratio Na/Mg will govern the precipitation of one or the other of the two minerals.

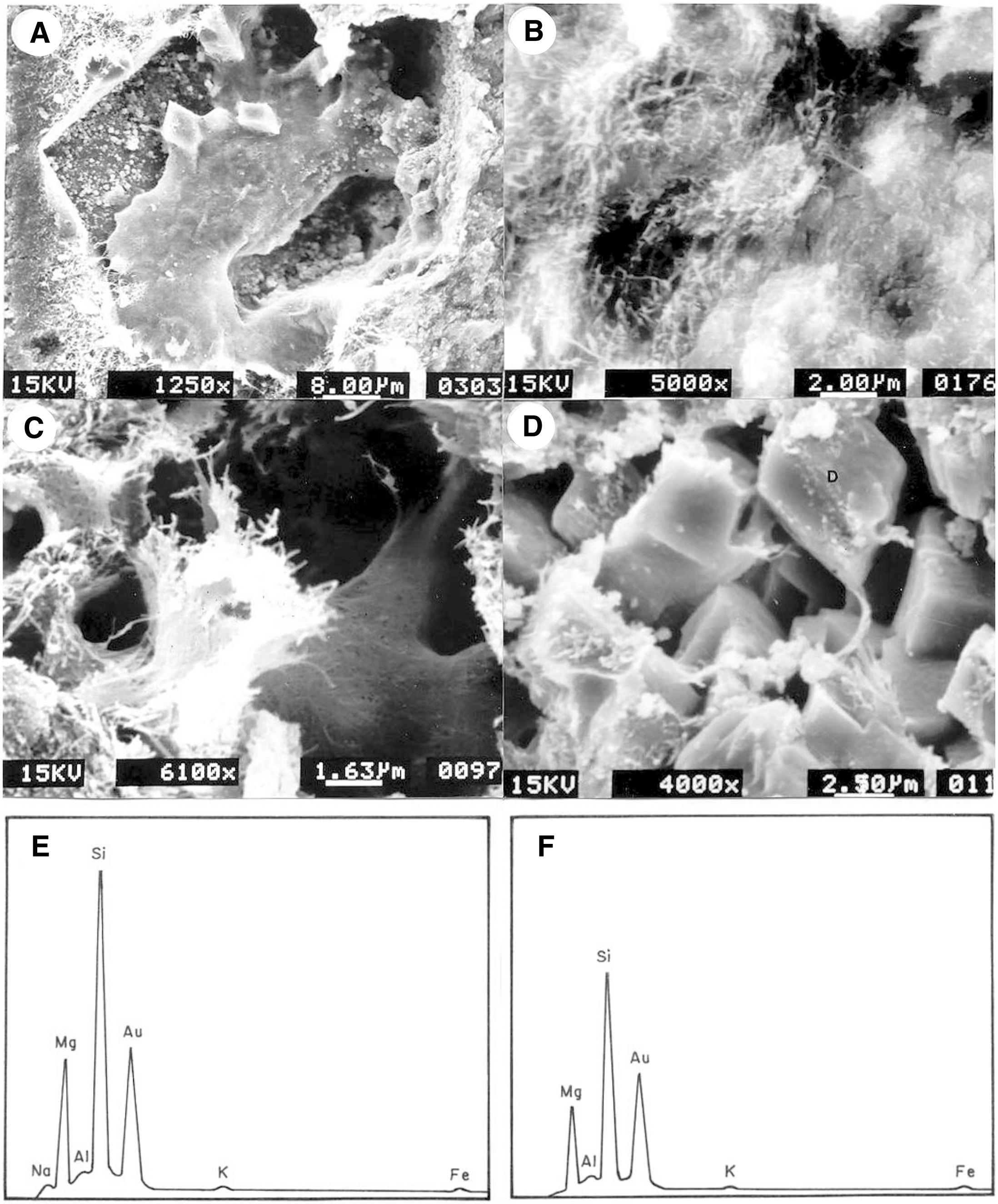

FIG. 6. Scanning electron microscope (SEM) photographs. A. Formation of loughlinite at the edge of dissolved volcanic glass. B. Loughlinite fibers enclose relict particles of volcanic glass. C. Concentric development of loughlinite around casts left by removal of silicic nodules. D. Formation of sepiolite fibers in close relation with dolomite (D). E. EDX analyses of loughlinite fibers. F. EDX analyses of sepiolite fibers.

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