

PALYGORSKITE FROM TERTIARY FORMATIONS OF EASTERN SAUDI ARABIA

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Abstract—The occurrence of palygorskite in some Tertiary sediments in eastern Saudi Arabia was studied. Mineralogical and chemical analyses were made of samples from two sections several meters thick from the Umm er Radhuma and Dammam Formations of Paleocene and Eocene periods, respectively. Layers of shales were observed within the sections of the dolomitic-calclitic limestone of the Umm er Radhuma Formation and of the dolomitic limestone of the Dammam Formation. After treatment for carbonate removal the shales consisted of more than 95% clay-size particles, most of which were <0.2- μ m in size. Palygorskite was the main constituent of some of the shales, with minor amounts of gypsum, soluble salts, and carbonates. The association of gypsum and other salts with palygorskite in the shale suggests that palygorskite formed in closed-basin environments. The presence of palygorskite and the absence of other minerals in the clay fraction of the limestones also suggests that the palygorskite formed under marine conditions.

Key Words—Fiber, Limestone, Palygorskite, Saudi Arabia, Shale.

INTRODUCTION

Natural occurrences of palygorskite in sediments and soils of arid regions have been widely reported (see reviews by Wiersma, 1970; Shadfan and Dixon, 1984). Tertiary sediments appear to be the main host of palygorskite in the Middle East (Yaalon, 1955; Wiersma, 1970; Millot, 1970; Shadfan and Dixon, 1984), and Shadfan and Mashhady (1985) described shales of Tertiary age in eastern Saudi Arabia that consisted mainly of palygorskite. Elprince *et al.* (1979) and Mashhady *et al.* (1980) indicated also the pedogenic formation of palygorskite in some soils of Saudi Arabia.

Inasmuch as palygorskite had been found in diverse genetic environments, namely marine (Millot, 1970), bay, lagoon, lake (Weaver and Beck, 1977), or soil environments, its mode of formation is not completely understood. Studying palygorskite-rich sediments is therefore helpful to understand the environmental conditions of formation of these fibrous clay minerals in soils and sediments.

The objectives of the present study were (1) to characterize the palygorskite and the associated sediments in eastern Saudi Arabia; and (2) to ascertain the genesis of the palygorskite in these sediments.

GENERAL GEOLOGY

The Arabian Peninsula can be divided into two structural provinces. The western province, known as the Arabian Shield, consists of igneous and metamor-

phic rocks forming a highland in the western part of the country. The eastern province, known as the Arabian Shelf, lies to the east of the shield. The rocks in the eastern province are a sequence of continental and shallow water marine sediments ranging in age from Cambrian to Pliocene (Figure 1). Paleozoic, Mesozoic, and lower Tertiary strata are exposed in the center of Saudi Arabia forming a great curved belt bordering the shield. East of the belt to the Arabian Gulf is a broad expanse of relatively low-relief terrain in which Tertiary and younger deposits effectively mask older units. Upper Cretaceous and Eocene rocks consist mainly of limestone and dolomite. The stratigraphic sequences above the Eocene consist of Miocene and Pliocene sandstone, sandy marl, and sandy limestone which are mostly of nonmarine origin. Above these rocks are unconsolidated Quaternary deposits which comprise great sand deserts and gravel sheets (Powers *et al.*, 1966; Al-Sayari and Zötl, 1978).

The Umm er Radhuma Formation of Paleocene and lower Eocene age forms a wide belt extending ~1200 km from south to north with a width of 60–120 km (Figure 1). The middle part of the belt is covered with eolian sand. The exposures of the Umm er Radhuma Formation form a gently undulating but rough surface with low isolated hills and benches. The formation consists of a repetitious series of calcitic and dolomitic limestone (Powers *et al.*, 1966).

Outcrops of the Dammam Formation of lower and middle Eocene age are limited to a number of small but widely scattered patches in the Arabian Gulf coastal region especially in the vicinity of Dammam (Figure 1). The Dammam Formation is divisible into five

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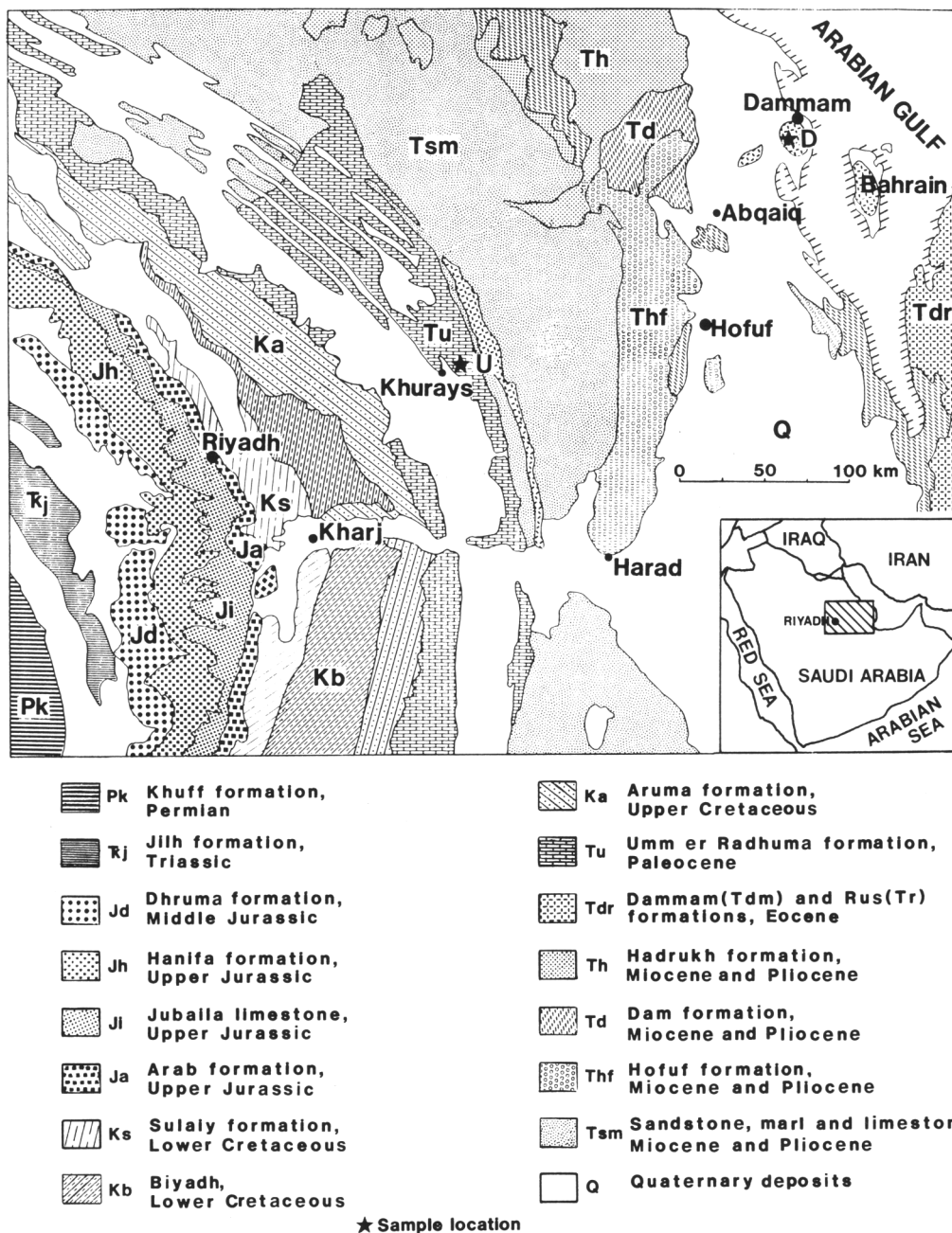


Figure 1. Geological map of area studied showing the sampling sites (modified from U.S. Geological Survey and the Arabian American Oil Company, 1963).

members from oldest to youngest: (1) Midra shale, (2) Sailsa shale, (3) Alveolina limestone, (4) Khobar dolomite and marl, and (5) Alat limestone and marl (Powers *et al.*, 1966).

MATERIALS AND METHODS

Samples were taken from two sections of Tertiary sediments in the Umm er Radhuma and Dammam

Formations near Khurays and Dammam, respectively, eastern Saudi Arabia (Figure 1). Descriptions of the two sections are presented in Figure 2. The samples were ground, sieved wet with a 50- μ m sieve, and treated with 1 N Na-acetate solution (pH = 5) for carbonate removal (Jackson, 1969). Treated samples were dispersed with Calgon, and the <2- μ m clay fraction was separated by centrifuge and analyzed with a Philips

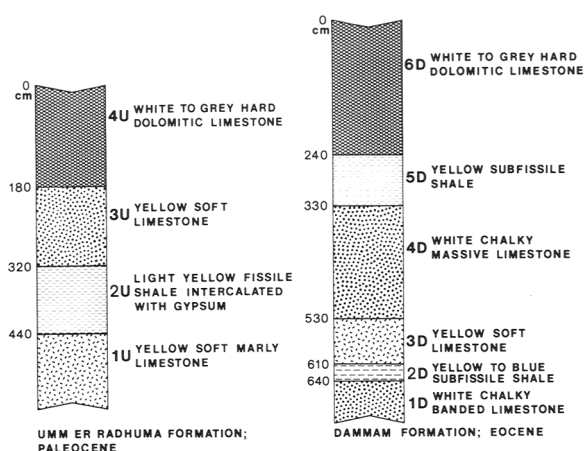


Figure 2. Composite section of the Umm er Radhuma (U) and Dammam (D) Formations.

X-ray diffractometer with a graphite monochromator and Cu-target X-ray tube operated at 35 kV and 15 mA. Untreated powdered samples were also analyzed by X-ray diffraction (XRD). Transmission electron microscopy was used to identify the fibrous minerals in the clay fractions. Untreated bulk samples were examined by scanning electron microscopy. Carbonates were determined for the untreated samples using the calcimeter method (Black, 1965).

Samples from the Umm er Radhuma shale (2U) and the Dammam shale (5D) in both sections (Figure 2) were analyzed for electrical conductivity (1:5 sample to water extract), cation-exchange capacity (Na-acetate method), and particle-size distribution (pipet method and the centrifuge for the clay fraction) as described by Black (1965). Gypsum was determined using the precipitation method with acetone described in U.S.D.A. Agricultural Handbook 60 (Richards, 1954). Infrared (IR) absorption spectra for the clay fraction were obtained using KBr disks with 1-mg samples and a Perkin Elmer Spectrophotometer (No. 283). Total chemical analyses by HF dissolution (Jackson, 1969) and elemental determination by atomic absorption using acetylene and nitrous oxide gasses were carried out on the clay fraction.

Table 1. Total carbonate in samples from the Umm er Radhuma (U) and Dammam (D) Formations.

Sample	Carbonate equivalent (%)	Sample	Carbonate equivalent (%)
4U	95.2	6D	97.1
3U	85.4	5D	2.4
2U	4.1	4D	96.9
1U	79.2	3D	90.2
		2D	7.4
		1D	95.2

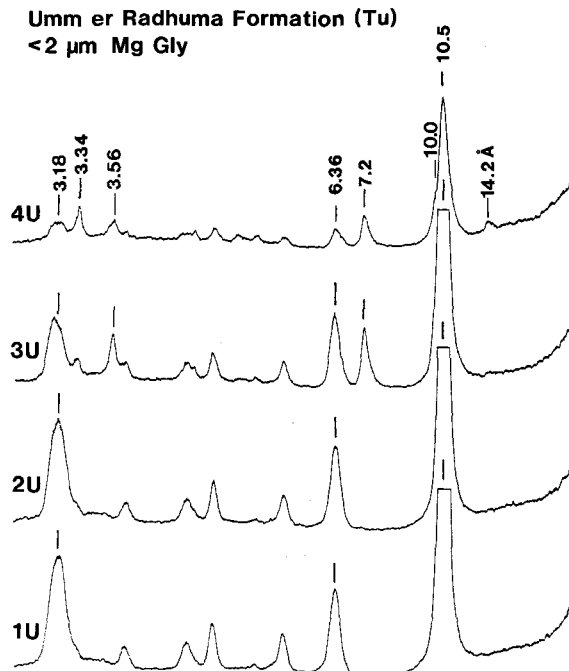


Figure 3. X-ray diffraction patterns for <2- μ m fraction of the Umm er Radhuma (U) section. (Full scale = 2500 counts/sec.)

RESULTS AND DISCUSSION

The sampled section of the Umm er Radhuma Formation consisted of different layers of limestones and a light-yellow fissile shale. The limestone varied from hard dolomitic with more than 95% carbonate (Table 1) on the top to marly limestone below the shale with 79% carbonate. The least amount of carbonate was found in a 120-cm thick shale layer (sample 2U) which contained only about 4% carbonate.

The section of Dammam Formation sampled is believed to be from the Khober Member and consisted of alternating limestone and shale layers. The top layer in the section (6D) was composed of hard dolomitic limestone with 97% carbonate (Table 1). A similar carbonate content was found in the chalky massive limestone (samples 1D and 4D); the soft yellow limestone (sample 3D) contained 90% carbonate. The two subfissile shale layers, 30-cm (sample 2D) and 90-cm (sample 5D) thick, contained 7 and 2% carbonates, respectively.

The XRD patterns of powdered samples of the different layers in the Umm er Radhuma section showed that the surface layer sample (4U) consisted mainly of dolomite with minor amounts of calcite and quartz (data not shown). The soft yellow limestone (samples 3U and 1U), however, contained mainly calcite and very small amounts of dolomite and palygorskite. Palygorskite with smaller amounts of gypsum and halite

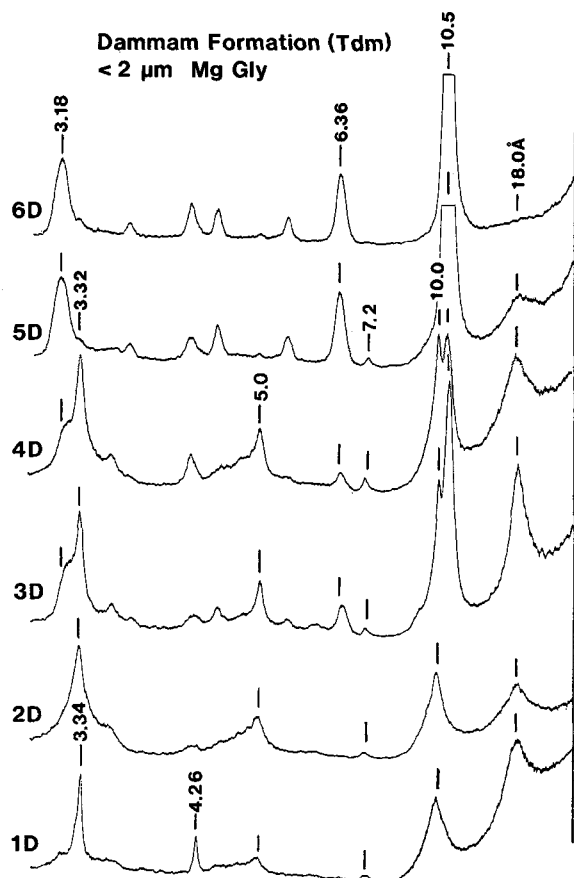


Figure 4. X-ray diffraction patterns for $<2\text{-}\mu\text{m}$ fraction of the Dammam (D) section. (Full scale = 2500 counts/sec.)

were found in the yellow fissile shale (sample 2U). The mineral composition of the clay fractions showed a dominance of palygorskite in the layers of Umm er Radhuma strata (Figure 3). The clay fraction of the shale layer (sample 2U) consisted chiefly of palygorskite. In addition to palygorskite, some mica and kaolinite were found in the upper part of the strata (samples 3U and 4U). The presence of mica and kaolinite indicate their possible detrital origin in that part of the limestone.

The XRD patterns of powdered samples from the Dammam Formation showed that the limestones were dolomitic with variable amounts of silicate clays (data not shown). The shale of the lower part of the section (sample 2D) consisted of smectite, mica, quartz, and orthoclase. The presence of mica and orthoclase in this part of the section suggests a detrital origin for these materials, probably from the igneous and metamorphic rocks of the Arabian Shield. In the upper part of the section (samples 5D and 6D) palygorskite was found in addition to the dolomitic limestone. The shale (sample 5D) consisted mainly of palygorskite with minor amounts of halite. The clay fraction of samples from

Table 2. Chemical and physical properties of the shales in the Umm er Radhuma (U) and Dammam (D) Formations.

Electrical conductivity (mmho/cm)	Size fractions							
	Gyp-sum (%)	CO ₃ ²⁻ (%)	CEC ² (meq/100 g)	2 mm-50 μm (%)	50-2 μm (%)	2-0.2 μm (%)	<0.2 μm (%)	
2U	10	8	4 ¹	11	4	11	22	63
5D	17	0	2 ¹	13	1	2	19	78

¹ Expressed as % CaCO₃.

² CEC = cation-exchange capacity, Na by NH₄ (Black, 1965).

the Dammam Formation (Figure 4) showed some variation in the mineral composition within the section. No palygorskite was found in the lower layers of the section (sample 1D and 2D). The clay mineral composition of these layers consisted mainly of smectite, mica, and minor amounts of kaolinite. Quartz was also present in sample 1D. In the middle of the section (samples 3D and 4D) palygorskite was found in addition to smectite, mica, and kaolinite. The clay fraction of the surface layers (samples 5D and 6D) consisted mainly of palygorskite. In the shale layer (sample 5D) minor amounts of smectite and kaolinite were present in addition to palygorskite. In general, the palygorskite increased with a decrease in smectite and mica from the lower part of the section toward the surface.

The association of smectite with palygorskite in limestones has been widely reported (Millot, 1970). Because montmorillonite is more aluminous than palygorskite, as long as appreciable amounts of Al are present, the neoformation of montmorillonite is preferred. When Al decreases, montmorillonite is replaced by palygorskite, and when Mg occurs alone, sepiolite forms (Millot, 1970).

The presence of soluble salts in the shales was also obvious from the high electrical conductivity of the water extract (Table 2). In addition to sodium chloride, the Umm er Radhuma shale contained about 8% gypsum which was intercalated between the layers com-

Table 3. Chemical composition of the clay fraction ($<2\text{ }\mu\text{m}$) of shales from the Umm er Radhuma (U) and Dammam (D) Formations.

	Sample 2U (wt. %)	Sample 5D (wt. %)
SiO ₂	58.93	54.64
Al ₂ O ₃	10.33	11.34
Fe ₂ O ₃	4.12	6.48
MnO	0.52	0.55
MgO	10.35	9.46
CaO	0.30	0.30
Na ₂ O	1.26	0.90
K ₂ O	0.39	0.84
H ₂ O	14.50	14.40
Total	100.70	98.91

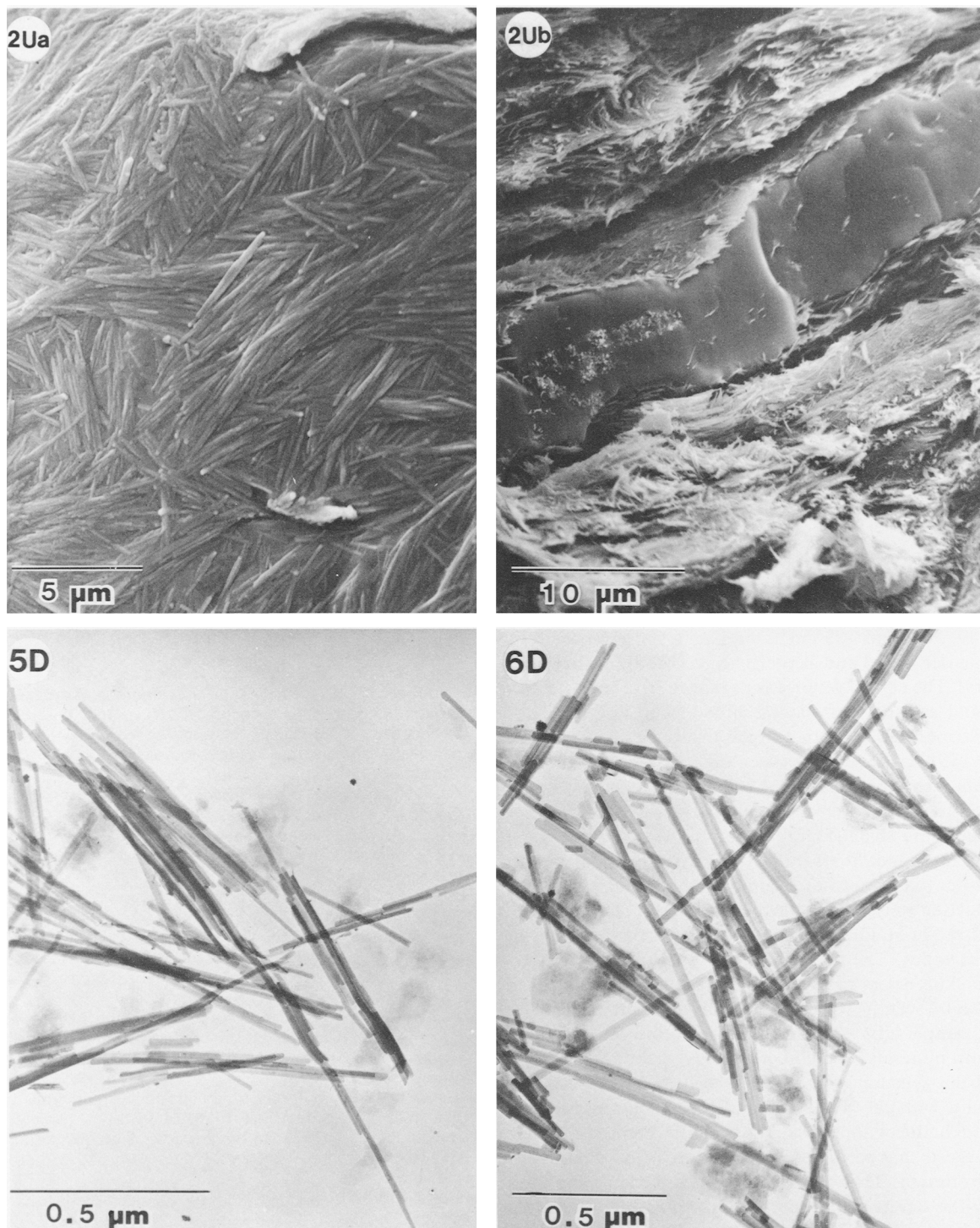


Figure 5. Scanning electron micrographs for samples 2Ua and 2Ub from the Umm er Radhuma Formation and transmission electronmicrographs for the clay fraction ($<2 \mu\text{m}$) of samples 5D and 6D from the Dammam Formation.

posed primarily of palygorskite (Table 2; Figure 5, sample 2U). As indicated above, the carbonate mineral content was very small in the shale and was difficult to identify from XRD patterns, especially that of sample 5D. The cation-exchange capacity (CEC) of samples 2U and 5D (11 and 13 meq/100 g, respectively) fall within the range given by Weaver and Pollard (1973) for palygorskite. The higher CEC value of sample 5D was probably due to the presence of smectite in that shale. The predominance of the fine clay fraction ($<0.2 \mu\text{m}$) in both shales as shown by the particle size distribution of samples 2U and 2D (Table 2) indicates that palygorskite was usually concentrated in the fine clay as has also been reported by McLean *et al.* (1972) and Shadfan and Dixon (1984). The residues of the shales after the removal of carbonates, gypsum, and salts consisted of more than 95% clay. The total chemical analyses of both samples 2U and 5D also showed similar composition to palygorskite (Table 3). The MgO value was about 10%, similar to palygorskite from Florida (van Olphen and Fripiat, 1979). The high Al, Fe, and K content of sample 5D indicate the presence of smectite, as also shown in the XRD patterns.

The infrared (IR) spectra (data not shown) showed sharp bands for palygorskite at 3618, 3540, 3270, 1040, 989, 513, and 483 cm^{-1} , similar to those reported by van der Marel and Beutelspacher (1976) for that mineral. The crystal water was indicated by a fairly narrow band at 3618 cm^{-1} and a broad band at 3400 cm^{-1} (Farmer, 1974). Both samples exhibited an absorption at 1198 cm^{-1} which has been suggested for palygorskite (Mendelovici, 1973).

The scanning electron micrograph of the Umm er Radhuma shale (Figure 5, sample Ua) showed some orientation of fibers indicating possibly crystal growth rather than a detrital origin of the material, suggesting that the palygorskite formed in place. The fibers occurred in bundles of about 5 μm length and 0.5 μm or less width. The intercalation of gypsum among palygorskite layers in the Umm er Radhuma shale could also be seen in scanning electron micrographs (Figure 5, sample Ub) which suggests an authigenic origin for both minerals. Some fibers of palygorskite were found in the gypsum layer. The association of gypsum and halite with palygorskite in the Umm er Radhuma shale and halite with palygorskite in the Dammam shale suggests that palygorskite formed in a closed basin environment. This mode of origin is further supported by the report of Powers *et al.* (1966) which indicated widespread precipitation of evaporites in eastern Saudi Arabia during Early Eocene time.

Chamley (1979) indicated that physiography is an important factor for the formation of fibrous clay minerals. He reported that palygorskite and sepiolite in Early Eocene time are indicators of closed or semi-closed marginal basins in which fibrous minerals formed

under warm and confined conditions. Shallow water and higher than normal temperature might have increased the pH (due to photosynthesis) and consequently the silica solubility and supply that was necessary for palygorskite formation (Weaver and Beck, 1977). The presence of palygorskite in the Tertiary dolomitic limestone might also indicate a marine formation of palygorskite in that part of the section. This mode of origin is supported by the presence of uniform palygorskite fibers and the absence of other clays in the dolomitic limestone (sample 6D) in the transmission electron micrograph (Figure 5, sample 6D). Palygorskite in the limestones apparently was not of detrital origin because of the similarity of fibers in the shale (sample 5D) and the limestone (sample 6D) as shown in transmission electron micrographs (Figure 5, samples 5D and 6D).

ACKNOWLEDGMENTS

The authors gratefully acknowledge L. A. Kippenberger for X-ray diffraction and drafting assistance and F. A. Mumpton for his constructive comments on the manuscript.

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(Received 10 December 1984; accepted 20 February 1985; Ms. 1431)