DISCUSSION OF THE OCCURRENCE AND ORIGIN OF SEDIMENTARY PALYGORSKITE–SEPIOLITE DEPOSITS

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Abstract—Marine and non-marine palygorskite–sepiolite deposits are found throughout the world and occur interbedded with chert, dolomite, limestone, phosphates and other non-detrital sedimentary rocks. The origin of these high-magnesium clays has long been attributed to either alteration of volcanic ash or the structural transformation of smectite clays. More recently, others have argued origin by direct crystallization (neo-formation). Recent laboratory studies support this latter concept, particularly in environments where the concentration of alumina is low, the silica concentration high, and the pH alkaline. Such an origin is proposed for the Georgia–Florida deposits in southeastern United States, since major obstacles exist against formation by alteration of volcanic ash or by transformation of smectites. Lateritic weathering during the Miocene would have favored direct precipitation of these clays in the shallow, marginal seas. The basinward increase in the $MgO : Al_2O_3$ ratio is further support.

Deep weathering of crystalline rocks in northern British Honduras and Guatemala would have produced similar high silica, low alumina conditions on the adjacent submerged Yucatan Platform during the late Tertiary. The seaward increase in the $MgO : Al_2O_3$ ratio, the lack of associated detrital constituents, and the absence of associated smectites strongly indicate a similar origin by direct crystallization of these Yucatan palygorskite–sepiolite clays.

Some occurrences of palygorskite and sepiolite may well be related to the alteration of smectite clays or volcanic ash. However, many of the large sedimentary deposits are more probably the result of direct crystallization adjacent to areas undergoing tropical or subtropical weathering.

INTRODUCTION

THE GENESIS of palygorskite and sepiolite has been the subject of much discussion. Mineable deposits of these minerals have been found throughout the world (India, Mexico, United States, the Soviet rocks, etc.), typically associated with non-clastic sedimentary rocks, such as limestone, dolomite, magnesite, opal, chert, and phosphates. Though both clays are found in the sedimentary environment, sepiolite has also been described in mafic igneous and metamorphic rocks, both as an alteration product of serpentine and as a hydrothermal mineral. The reader may consult Caillere (1936); Caillere and Henin (1948); Serdyuchenko (1949); Yusupova (1955); Midgley (1959) etc., for a discussion of sepiolite in crystalline rocks.

Though similar in many of their physical properties to sheet-silicate clays, palygorskite and sepiolite differ in that they are both made up of double chains of tetrahedra and are thus, structurally, more like amphiboles. Both are hydrous magnesium silicates; however, palygorskite also contains alumina as an essential constituent. Teodorovitch (1961) gives the following structural formulas

for the two: palygorskite, $MgAl_2(Si_4O_{10})$ $(OH)_2 \cdot 4H_2O$; sepiolite, $Mg_3(Si_4O_{11})H_2O \cdot 11H_2O$.

STRUCTURE AND CHEMISTRY

Structure

Palygorskite (also called attapulgite, pilolite, lassalite, mountain leather, etc.) was first recognized, many believe, as a distinct mineral species by de Lapparent (1935) who determined its chemical composition from samples obtained from the Georgia–Florida deposits and those at Mormoiron, France. Ovcharenko *et al.* (1964) report that Fersman (1913) was actually the first to describe in detail both palygorskite and sepiolite, and did so for samples obtained from the Palygorsk Range on the Popova River (U.S.S.R.) where the mineral palygorskite has been known since 1861. They further state that recent single crystal and electron microscope reflection analyses confirmed Bradley's (1940) proposal that the palygorskite structure is based chains an amphibole chain consisting of two pyroxene chains arranged to form regular hexagonal rings in a plane. Sepiolite (see Fig. 1) is similar

SEPIOLITE

Projected onto 001

After Nagy and Bradley, 1955

- ⊛ HYDROXYL
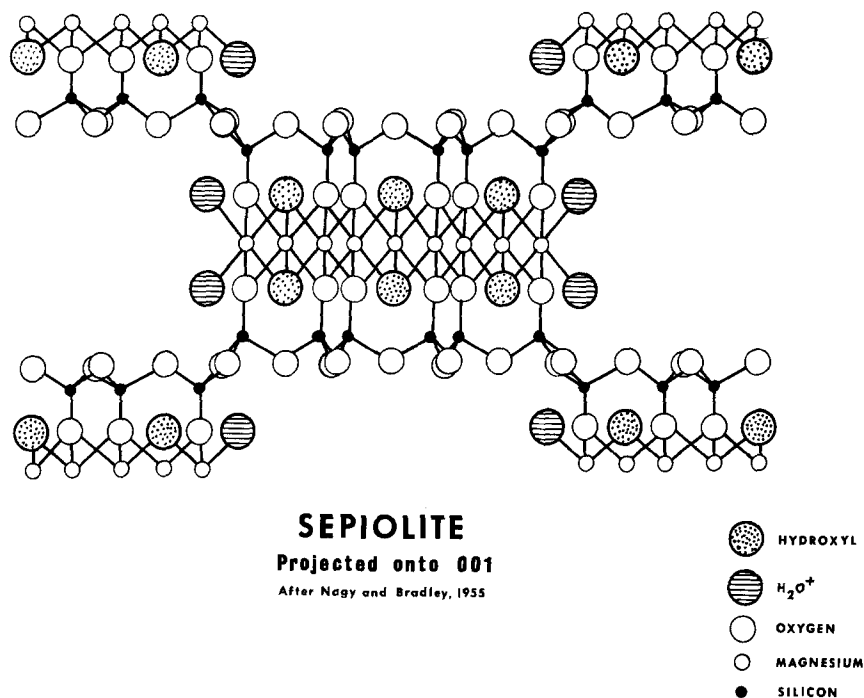- ⊜ H_2O^+
- ○ OXYGEN
- ○ MAGNESIUM
- ● SILICON

Fig. 1. Proposed structure of sepiolite projected onto 001 (modified after Nagy and Bradley, 1955).

but is composed of three pyroxene chains, rather than two. For this reason, Nagy and Bradley (1955) have said that sepiolite is not amphibole-like in character but actually represents a new type of silicate structure. Descriptions of the structural chemistry of both minerals can be found in Bradley (1940); Caillere (1951); Nagy and Bradley (1955); Brindley (1959); de Lapparent (1936) and Zayagin (1969).

Chemistry

Fersman (1913) believed that palygorskite and sepiolite were part of a complete isomorphous series that extended from a pure magnesium silicate to an aluminum end member. Kerr (1937) argued that no conclusive evidence was present to warrant calling palygorskite a new mineral species and believed that it might simply be a variety of montmorillonite. Bradley (1940) was able to show that palygorskite was indeed a new mineral and proposed that its ideal chemical composition was $(OH_2)_4(OH)_2Mg_5Si_8O_{20} \cdot 4H_2O$. He doubted that a complete substitution series existed betweeen the two minerals because extensive replacement of magnesium by iron or aluminum would weaken the structure. Caillere and Henin (1948) concluded that sepiolite was distinctly different than palygorskite but believed that palygorskite and attapulgite were similar, if not the same mineral. The lack of a

gradation in alumina content between palygorskite and the theoretical composition of sepiolite (Brauner and Presinger, 1956) suggests that little solid solution exists between the two. Table 1 lists analyses for samples from numerous locations.

Recent work has shown that palygorskite is probably more resistant than sepiolite to attack by chemical weathering. Acid dissolution studies by Abdul-Latif and Weaver (1969) indicated that the reaction rate constant for magnesium in sepiolite was about 240 times that for magnesium in palygorskite.

Synthesis

The occurrence of sepiolite as both a sedimentary and hydrothermal mineral suggested that laboratory synthesis should not be difficult to accomplish. Hast (1956) first synthesized sepiolite. However, Mumpton and Roy (1958) were unable to produce the mineral in a similar system to which Al_2O_3 had been added. More recently, Siffert (1962) and Siffert and Wey (1962) demonstrated room temperature synthesis by treating saturated solutions of amorphous silica with various concentrations of $MgCl_2$ to which NaOH had been added. Siffert and Wey noted that the formation of sepiolite occurred when the initial pH was ≥ 10 and fol-

Table 1. Chemical composition of selected palygorskite sepiolite clays

	Palygorskite							Sepiolite		
	1	2	3	4	5	6	7	8	9	10
SiO_2	55·03	52·6	53·92	53·0	55·64	61·60	55·65	52·97	52·50	45·8
Al_2O_3	10·24	12·6	10·60	15·3	8·76	6·82		0·86	0·06	0·35
TiO_2			0·27	0·55	0·60					
Fe_2O_3	3·53	3·8	7·33		3·36			0·70	2·90	0·16
				5·72		0·87				
FeO		0·8			0·23				0·70	0·04
CaO		2·2	0·47	0·45	2·02	0·67			0·47	0·28
MgO	10·49	8·4	6·73	4·40	9·05	14·22	24·89	22·50	21·31	19·8
H_2O^+	10·13		6·90	5·4	10·89		8·34	9·90	9·21	5·2
		19·6				14·16				
H_2O^-	9·12		10·00	9·4	9·73		11·12	8·80	12·06	25·6
MnO			0·1	0·20	0·03			3·14		
K_2O	0·47				2·6	0·75				0·09
			1·27							
Na_2O					1·25	0·83				0·92
Total	99·01	100·0	97·59		101·89	98·34	100·00	99·74	99·75	98·24

1 Attapulgus, Georgia (U.S.A.): Bradley (1940).
2 Tafraout, Morocco: Caillère (1951).
3 Cherkassy Region, U.S.S.R.: Ovcharenko et al. (1964).
4 Barracuda Escarpment, Atlantic Ocean: Bonatti and Joensuu (1968).
5 France: De Lapparent (1935).
6 Dornboom, South Africa: Heystek and Schmidt (1953).
7 Theoretical composition: Brauner and Preisinger (1956).
8 Little Cottonwood, Utah: Nagy and Bradley (1955).
9 Madagascar: Caillère (1936).
10 Mid Atlantic Ridge: Hathaway and Sachs (1965).

lowed initial rapid precipitation of brucite, some of which then reacted with silica to form sepiolite.

Wollast, Mackenzie and Bricker (1968) investigated the stability relationship of sepiolite in natural waters and also synthesized the mineral. They did so by treating natural sea water with sodium metasilicate, with the pH of the solution controlled to approximately 8·0 by the addition of hydrochloric acid. Their experiments indicated that the sepiolite–sea water equilibrium was definitely pH related and that the more rapid precipitation of sepiolite at higher pH was dependent on the OH^- concentration. They also showed that silica–sea water mixtures maintained at a pH < 7 will become saturated with silica, but no sepiolite will precipitate. On evaporation, the pH increases, which results in precipitation of the mineral by the following reaction:

$$2Mg^{+2} + 3SiO_{2aq} + (n+2)H_2O = Mg_2Si_3O_8(H_2O)_n + H^+.$$
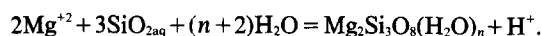
The free energy of formation for this reaction was determined as −4,407·0 kcal/mole. Thus, formation of sepiolite would be favored in environments of hyper-salinity, especially those in which the waters were silica-rich.

Another of their observations was that in the presence of alumina, magnesium was taken up into aluminosilicate structures and neither sepiolite nor palygorskite precipitated. The lack of palygorskite as an intermediate product suggests that it may be a secondary mineral formed by the transformation of other alumino–silicates (e.g., smectite clays) in a magnesium-rich environment. Though Kerr (1937) and Heystak and Schmidt (1953) believed such transformations were likely, Mumpton and Roy (1958) were unable to synthesize palygorskite from smectites. Since sepiolite and palygorskite are often mutually associated in sedimentary deposits throughout the world, it is probable that both are products of similar formational processes. The presence of high ratios of alumina to silica in a depositional basin should favor the formation of chlorite-like minerals whereas low alumina to silica concentrations might favor palygorskite. Like sepiolite, the formation of palygorskite is probably sensitive to pH, silica concentration and Mg^{2+} activity.

ORIGIN AND OCCURRENCE

Discussion

Sedimentary deposits containing either, or both, palygorskite and sepiolite have been described for a number of depositional environments. Both have been reported as forming in normal marine waters, marine and non-marine hyper-saline waters, and in fresh water lakes. Origins involving transformation of either volcanic ash, basalt or montmorillonite clay have been popular since Longchambon (1935) first reported that palygorskite was formed by alteration of amphiboles and pyroxenes. Since that time, Ovcharenko *et al.* (1964) have described palygorskite with relict amphibole cleavage from the Cherkassy deposits of the Ukrainian S.S.R. Authors who have called upon transformation mechanisms to explain various other deposits include: Kerr (1937) for the Georgia–Florida deposits; Heystek and Schmidt (1953) for the Transvaal deposits; Loughnan (1960) for those in Queensland, Australia; and Parry and Reeves (1968) for lacustrine clays in West Texas. In addition, Hathaway and Sachs (1965) have described sepiolite from dredge hauls obtained at a depth of 3,600–4,200 near Saint Paul's Rocks on the Mid-Atlantic Ridge. This latter occurrence was atrributed to magnesium, in solution, reacting with devitrified volcanic ash, with clinoptilolite, quartz, and montmorillonite as residual products. Similarly, Bonatti and Joensuu (1968) reported palygorskite in deep sea muds collected as a depth of 5,015 from the Barracuda Escarpment. Here the mineral was thought to have formed by transformation of montmorillinite clays acted on by magnesium-rich waters of hydrothermal origin.

A more recent hypothesis for the origin of some palygorskite–sepiolite deposits involves the mechanism of direct precipitation (neo-formation). Millot argued this hypothesis convincingly in his treatment of the deposits of former French West Africa and those in the French Tertiary basins (see Millot 1962, 1957 and Millot, Radier and Bonifas, 1957). Rogers, Martin and Norrish (1954) also explained by this mechanism the Queensland, Australia deposits, as did Demangeon and Salvayre (1961) the palygorskite from the Mont-Perdu Massif, in Spain.

Because of recent laboratory work on the SiO_2–Al_2O_3–MgO–H_2O system and work on the synthesis of magnesium silicates, it was decided to examine two of the major deposits of palygorskite–sepiolite clays to see if any modification of earlier genesis theories was warranted. Those investigated were: (1) the Georgia–Florida

deposits, and (2) the newly discovered deposits of the Yucatan Penunsula.

Georgia–Florida deposits

Sepiolite, palygorskite, and smectite clays are widespread in sediments of early and middle Miocene age in Florida and Georgia and can be traced northeastward into South Carolina. These non-plastic and highly sorptive clays are known locally as "Fuller's Earth" and, since their discovery in 1893, have been mined continuously and are the largest commercially worked deposits in the world. Yearly production averages over 500,000 tons and is valued in excess of $15,000,000. Principal uses include: drilling muds, cleaning compounds, insecticides, fillers, and absorbents for oil purification.

The Georgia–Florida clays occur as discontinuous beds and lenses, interbedded with dolomites, limestones and phosphatic sands, and have been attributed to: (1) alteration of volcanic detritus, (2) the diagenetic alteration of montmorillonite, and (3) direct crystallization.

Grim (1933), the first to propose that the clays were the result of alteration of volcanic debris, based this proposal on the presence of interbedded montmorillonite and isotropic fragments that may have been either volcanic glass shards or organic remains. Kerr (1937), in a study of similar clays in the Florida panhandle, stated that he could find no evidence of volcanic source materials. Mansfield (1940) cited investigations of Bay and Nutting which were interpreted as supporting origin by alteration of volcanic material. Gremillion (1965) believed the clays were derived from ash produced by volcanic eruptions, possibly in south Texas. He proposed that ocean and wind currents transported the ash eastward to the Florida platform and offered as evidence the presence of over 500 ft of Miocene pyroclastics in southern Texas and (p. 88) "...considerable volcanic ash in the Catahoula Formation of Louisiana". As further evidence, he noted the presence of abundant diatoms and widespread quartz–opal and cristobalite that are also present in the clays. The opal and cristobalite he believed to be a product of the original ash fall, with the quartz resulting from subsequent alteration of some of the cristobalite. Heron and Johnson (1966) also favored alteration of volcanic ash for the contemporaneous palygorskite–sepiolite clays of the Hawthorn Formation of South Carolina. They did note, however, that some of the ions used in the formation of these clays may have been derived from lateritic weathering of older source rocks in

the Piedmont. They observed a significant basin-ward increase in the $MgO:Al_2O_3$ ratio, compatible with such a source for the ions. A similar phenomenon was observed by Slansky, Camez and Millot (1959) in the deposits of former French West Africa. One of the major lines of evidence supporting an origin by alteration of volcanics, according to Heron and Johnson, was the presence of small quantities of clinoptilolite.

Recent studies in the Gulf Coast have cast doubt on the validity of a "western source" for volcanic ash because both wind and longshore current directions are presently opposite to those required for eastward distribution of the material. The present coastal morphology clearly indicates that the longshore current flows in a *westerly* direction in the central Gulf Coast. In addition, completely different heavy and clay mineral suites are found in western, central and eastern Gulf Coast Miocene sediments, indicating that sediments in these regions were derived from several different source areas (see Isphording, 1970, 1971). Contemporaneous formations in western Florida and Alabama contain no palygorskite clays nor do they contain bentonitic montmorillonite. If the central Florida–southern Georgia Fuller's Earth clays resulted from alteration of volcanic detritus brought in from the west (i.e. Texas), then similar clays should be present throughout the central Gulf Coast. Also, the Miocene sediments of Alabama and Florida do not contain the glass shards that occcur in Miocene volcanic deposits of Texas and the Great Plains (see Swineford, Frye and Leonard, 1955; McBride, Lindemann and Freeman, 1968). Though shards were reported in the Georgia–Florida clays by Grim (1933), the writer has seen none in numerous samples examined. Espenshade and Spencer (1963) and McClellan (1964) were also unable to confirm the presence of shards in these deposits. Heron and Johnson (1966) believe the presence or absence of shards to be inconclusive since shards would probably have been destroyed by subsequent weathering or diagenetic alteration.

Recent work on synthesis of clinoptilolite and opal–cristobalite indicates that the presence of these minerals is not necessarily indicative of volcanic source materials. Authigenic zeolites (clinoptilolite) and cristobalite have been reported as constituents of deep sea Oligocene chalks in the South Atlantic and in Eocene chalks from the Caribbean by Wise, Buie and Weaver (1972). The cristobalite present has been interpreted as an intermediate step in the reaction: biogenic opal→ cristobalite→quartz-rich chert. Henderson *et al.* (1971) also supported the formation of opal-cristobalite by secondary processes and stated that it can be differentiated from that formed during igneous activity on the basis of the σ^{18} oxygen isotope abundance. Foster and Feicht (1946) had shown that sodium zeolites could be synthesized from aluminous clays (kaolinite) by treatment with sodium hydroxide. Loughnan (1966) obtained similar results by treating mixed-layer clays with sodium hydroxide and sodium silicate. Reynolds (1970) stated that the formation of clinoptilolite, in a marine environment, was favored where silica concentrations were high. Such conditions are realized: (1) in areas proximal to volcanic activity; (2) in restricted basins where volcanic ash or montmorillonite clays are undergoing diagenetic alteration; and (3) equally important, in shallow marine waters adjacent to areas undergoing lateritic weathering.

Based on the preceding discussion, the writer strongly favors an origin by direct precipitation for the Georgia–Florida palygorskite–sepiolite deposits. Conditions on the Gulf Coast during the Miocene were probably ideal for direct precipitation on the shallow nearshore shelf and in basins and lagoons of elevated salinity. Faunal and floral studies (see Dorf, 1960; Berry, 1916a, 1937) indicate that tropical and sub-tropical climates existed throughout eastern and southeastern United States during this time. The accompanying lateritic weathering would have made the nearshore waters rich in colloidal and dissolved silica. Evidence for the exisence of such conditions in eastern United States can be found as far north as New Jersey where several hundred feet of diatomaceous, clastic sediments are present in the downdip portion of the Miocene-age Kirkwood Formation (see Isphording, 1970). The combination of ideal conditions, the occurrence of the palygorskite–sepiolite clays with largely non-clastic sediments (limestones, dolomites, phosphates, etc.), and the basinward increase observed in the $MgO:Al_2O_3$ ratios, supports an origin by direct precipitation.

Though the writer has strong reservations about any direct alteration of either ash or montmorillonite to palygorskite or sepiolite, he does believe that both weathering and diagenesis of these can play an important role. The post-depositional destruction of ash and montmorillonite could supply the silica needed in the formation of both of the minerals. Shabayeva (1962) attributed the palygorskite clays of Turkmenia to a reaction of silica released from the decomposition of volcanic glass,

and McLean, Allen and Craig (1972) explained the origin of palygorskite and sepiolite in the southern High Plains of the United States in this way. To a limited extent, this process may have yielded some of the minerals in the Georgia–Florida deposits.

Yucatan Peninsula

The palygorskite–sepiolite clays of the Yucatan Peninsula, which also occur interbedded with limestones and dolomites, differ from the Georgia–Florida clays in that little montmorillonite is associated with them, nor are clastics or phosphatic sediments present. Arnold (1967, 1971), in his studies of Maya ceramic-ware, was the first to report the presence of palygorskite on the Peninsula but made no mention of associated sepiolite clays. Analyses by the writer have shown that, although palygorskite was usually the most abundant constituent, sepiolite was ubiquitous and, locally, may be the dominant mineral present (see Fig. 2). The Yucatan clays are found as white to tan, structureless lenses and beds that range in thickness from a few millimeters to over three meters. The clays are typically blocky and massive but near the ancient Maya ruins of Edzna were found in a 10 cm thick lens made up of paper thin layers. X-ray diffraction analyses indicated that sepiolite was the major and palygorskite the minor constituent in the sample. Occurrence in extremely thin layers has been reported before and is attributed to a pronounced preferred orientation of the minerals.

Shepard (in Brainerd, 1958) believed the origin of certain Yucatan clays to be the result of the post depositional alteration of volcanic ash, but left unclear whether she referred specifically to the deposits of *Sac lu'um* (Maya for "white earth"), since identified as palygorskite. Arnold (1971) refers to a probable volcanic origin but also offers no supporting evidence. The writer, after numerous insoluble residue analyses on thoroughly dispersed palygorskite–sepiolite samples from the northern peninsula, has found no evidence that would suggest a volcanic related origin. Quartz, zircon, feldspar, garnet, and other minerals found in fresh or altered ash are completely lacking, as are glass shards and associated smectites. The -2 and $+2\,\mu m$ fractions both consist of palygorskite–sepiolite, carbonates (dolomite and Mg-poor calcite), and minor amounts of chlorite and talc. Schultz *et al.* (1971), in a study of mixed-layer montmorillonite–kaolinite clays that occur as lenses and beds in the same rock units that contain the palygorskite–sepiolite clays, concluded that the mixed-layer clays originated by weathering of vol-
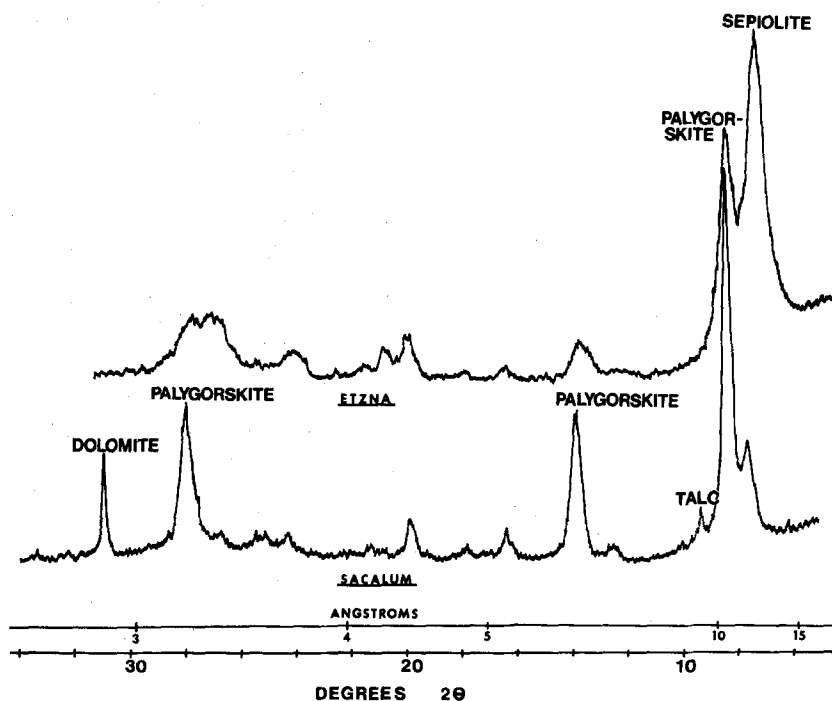

Fig. 2. X-ray diffraction patterns of samples from Yucatan. Sample labeled Etzna taken near Campeche; sample labeled Sacalum collected approximately 80 k south of Merida.

canic debris. They admit that a volcanic origin is "highly speculative" but called upon this mechanism because (p. 139) "... (1) volcanic ash or montmorillonite derived from it is the parent material of the mixed-layer kaolinite–montmorillonite in Florida and Japan; (2) many volcanic ashes and bentonites derived therefrom are very low in quartz, as are the Yucatecan clays; (3) much volcanic debris occurs in the Tertiary rocks in the Gulf of Mexico region; and (4) because an ash fall is one of the few reasonable mechanisms for introducing nearly pure alumino–silicate material into a sedimentary environment dominated by carbonate rocks". The writer would like to comment on these four reasons because they also relate to the origin of the palygorskite–sepiolite clays that are found in the same rock units.

With regard to (1), the writer knows of no mixed-layer clays in Florida with a proved volcanic origin. On the contrary, all recent evidence argues against transportation by wind or ocean currents of volcanic ash to the Florida Platform. Point (2), that of "low associated quartz content," could also be explained as resulting from a lack of clastic sedimentation, a common feature of limestone shelf areas. Recent sediments on the submerged portion of the Yucatan Platform, on both the northern and western sides, also contain negligible quartz, due to the distance to a suitable source of clastics. Samples collected farther to the south, in the Bay of Campeche, become increasingly richer in clastic components. The logical reason for this difference is that the nearby Usumacinta River serves as a source for clastics, whereas on the northern portion of the platform no rivers are present (see Fig. 3).

The abundance of volcanic debris in the Gulf of Mexico (point 3), is not disputed by the author but is must be shown how such debris could have accumulated on the Yucatan Platform. With present wind directions, the only possible Miocene sources would lie hundreds of miles to the east, in Jamaica, Hispaniola and the Antilles. Though such long distance transport of ash is certainly possible, in light of other evidence the writer considers it unlikely.

With regard to point (4), an ash fall is not the only "reasonable mechanism" for introducing pure alumino–silicate material into a sedimentary sequence of carbonate rocks. Jeans (1971) estimated that each year some 475×10^6 tons of alumina and silica are carried in solution and deposited in brackish and marine depositional environments. A disproportionately large amount is deposited adjacent to areas undergoing tropical weathering. Much of
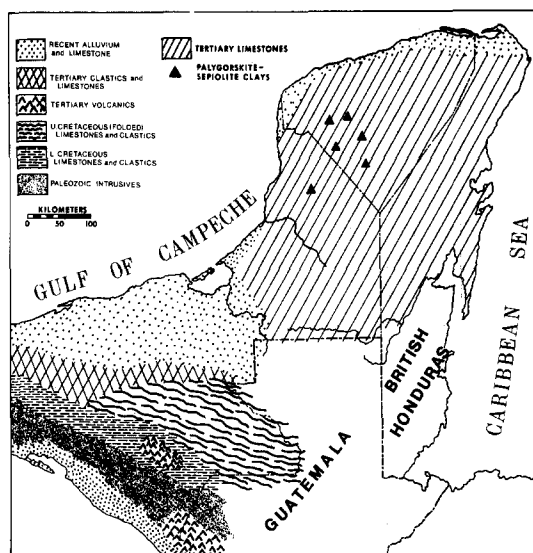

Fig. 3. Generalized geologic map of southern Mexico and Yucatan showing locations where palygorskite–sepiolite clays were found.

the alumina, silica and iron carried into the marginal seas is then precipitated, because of the alkaline pH, in the form of hydroxide gels. Subsequent pH and ion concentration will determine which of the various clay minerals will then crystallize.

Another point made by Schultz et al. (1971) was that the transformation of ash to montmorillonite probably took place under acidic conditions and, thus, not in the marine depositional site. They state that (p. 139) "Weathering more likely occurred in nearby land areas, and the weathered material was transported by streams so sluggish that they could carry little material coarser than the very fine grained mixed-layer clays". This statement is also a serious flaw in the argument because, in the entire 30,000 km^2 of the emerged portion of the Yucatan Platform, *there is not one surface stream*! North of the Champoton River, all drainage is subterranean and the only surface waters found are in aguadas, cenotes and lakes found in block-fault basins along the eastern part of the Peninsula, in Quintana Roo Territory. Deep wells drilled by Petroleos Mexicanos in the northern Peninsula indicated that the bedrock to a depth of well over 1,000 meters is similar to the exposed bedrock and is composed of limestones, dolomites and marls, ranging in age from Cretaceous to recent. Thus, even if ash did fall on the peninsula during the Tertiary, concentration of the weathered debris in marginal basins would have been difficult, if not impossible. If the ash fell in the nearshore waters, the lack of corrosion of the limestones underlying the clay units ar-

gues against the acidic conditions which they consider necessary to convert the parent material to kaolinite.

Based on the field evidence and the laboratory investigations cited earlier in this writing, the writer proposes that the Yucatan clays formed by direct crystallization in lagoons of elevated salinity and on the shallow sea floor of the Yucatan Platform. The source of the necessary ions were streams originating far to the south in the recently uplifted rocks of the Chiapas Laramide regions of northern British Honduras and the Peten area of Guatemala. These areas were, during the Miocene, undergoing rigorous tropical weathering and would have provided an ample source of silica, alumina, iron, magnesium, etc. Marine currents subsequently transported these materials northward onto the partially submerged limestone platform where crystallization occurred. Polymerization of hydroxide gels and their reaction with other ions in solution resulted in the formation of smectites and kaolinite near the river mouths and in the nearshore, brackish environment. Further from shore, and northward along the partially submerged platform, where pH was higher and the concentrations of alumina lower, palygorskite and sepiolite formed. Support for this is obtained from experimental evidence of Wollast, Mackenzie and Bricker (1968), who concluded that magnesium silicates are the only non-aluminous, cation-bearing silicates that can precipitate from normal sea water. Slansky, Camez and Millot (1959) proposed a clay sequence grading seaward that includes: kaolinite, montmorillonite, attapulgite (palygorskite), and sepiolite. This gradation would correspond to an increase in the $MgO:Al_2O_3$ ratio with distance from shoreline. Though the Miocene shoreline probably varied a great deal in position, the principal clays associated with the Miocene limestones in the southern part of the peninsula are kaolinites and montmorillonites, with lesser amounts of chlorite. The palygorskite–sepiolite clays are found only in the northwestern portion of the peninsula, a location which would represent the greatest distance from any clastic source (and therefore should be an invironment of higher $MgO:Al_2O_3$ ratio). Some of the deposits may also have formed in small lagoons, following local emergence of portions of the platform, by the mechanism already proposed for the Georgia–Florida occurrences. The proposed origin would also explain the lack of associated clastics and why these clays are found as lenses within shallow water limestones and dolomites.

SUMMARY AND CONCLUSIONS

Deposits of palygorskite–sepiolite clays are widespread throughout the world in marine, transitional marine, and lacustrine depositional environments. Their origin has been attributed to direct crystallization, alteration of volcanic ash, and to transformation of smectite clays. Recent experimental work on the stability relationships of sepiolite indicate that, in environments where the concentration of alumina is low and the pH is alkaline, sepiolite is the most likely clay mineral to form. Such environments exist on limestone platforms in tropical regions and in marginal waters of elevated salinity. Similar conditions also exist in lakes and in certain landlocked basins.

Strong evidence for direct precipitation of palygorskite and sepiolite can be demonstrated for the deposits found in Yucatan. These clays are generally devoid of inter-mixed smectite clays and are wholly lacking in clastic components. They occur interbedded with limestones and dolomites and evidence indicates they were formed far from any source of clastic influx.

The deposits in the Georgia–Florida area of the United States differ from those in Yucatan in that they also contain montmorillonite and a limited amount of clastic components. A marked seaward increase is present in the $MgO:Al_2O_3$ ratio, however, and recent evidence argues against their being products of alteration of ash or the transformation of montmorillonite clays.

A review of the literature on palygorskite and sepiolite deposits indicates no sedimentary deposits unequivocally originating by direct alteration of ash or transformation of smectites. Evidence for the necessary release of silica by the destruction of ash and montmorillonite and subsequent reconstitution to palygorskite and/or sepiolite has been reported at several locations. Many of the large sedimentary deposits, however, are most probably the product of neo-formational processes, especially when formed adjacent to areas that have undergone lateritic weathering.

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Résumé — Les dépôts marins et non marins de palygorskite–sépiolite existent partout dans le monde et se présentent en mélange avec des chailles, de la dolomite, du calcaire, des phosphates et d'autres roches sédimendaires non détritiques. L'origine de ces argiles à haute teneur en magnésium a long-temps été attribuée soit à l'altération de cendres volcaniques, soit à la transformation structurale de smectites. Plus récemment d'autres auteurs ont défendu l'hypothèse d'une origine par cristallisation directe (néoformation). Des travaux de laboratoire récents confirment ce dernier concept, notamment dans le cas des environnements à concentration en alumine basse, à concentration en silice élevée et à pH alcalin. Une telle origine est proposée pour les dépôts de Georgie et Floride dans le sud-est des Etats-Unis, puisque des obstacles majeurs s'y opposent à l'altération d'une cendre volcanique ou à la transformation de smectites. Une altération latéritique pendant le miocène aurait favorisé la pré-cipitation de ces argiles dans des mers marginales peu profondes. L'augmentation du rapport MgO : Al$_2$O$_3$ en allant vers la cuvette est un argument supplémentaire.

L'altération profonde de roches cristallines dans le nord du Honduras britannique et au Gautemala aurait produit des conditions similaires — richesse en silice et pauvtreé en alumine — sur la plateforme voisine submergée du Yucatan pendant la fin du tertiaire. L'augmentation du rapport MgO : Al$_2$O$_3$ en allant vers la mer, l'absence de constituants détritiques et de smectites associés indiquent avec force une origine comparable par cristallisation directe de ces palygorskites–sépiolites du Yucatan.

Certains gisements de palygorskite et de sépiolite sont sans doute reliés à l'altération de smectites ou de cendres volcaniques. Cependant, la plupart des grands dépôts sédimentaires est beaucoup plus probablement le résultat d'une cristallisation directe adjacente à des zones ayant subi une altération tropicale ou subtropicale.

Kurzreferat — Marine und nichtmarine Palygorskit–Sepiolit–Lagerstätten werden in der ganzen Welt gefunden und treten eingebettet in Quarzit, Dolomit, Kalkstein, Phosphate und andere nichtdetritische Sedimentgesteine auf. Die Entstehung dieser hochmagnesiumhaltigen Tone wurde lange entweder der Umbildung vulkanischer Aschen oder der Strukturumwandlung von Smectiten zugeschrieben. Neuerdings wurde von anderen Autoren eine Entstehung durch direkte Kristallisation (Neoformation) erörtert. Neuere Laboruntersuchungen stützen das letztgenannte Konzept besonders für Umwelt-bedingungen, in denen die Aluminiumkonzentration gering, die Kieselsäurekonzentration hoch ist und der pH-Wert im alkalischen Bereich liegt. Eine solche Entstehung wird für die Georgia–Florida–Lagerstätten in den südöstlichen Vereinigten Staaten vorgeschlagen, da hier einer Bildung durch Umsetzung vulkanischer Aschen oder durch Umwandlung von Smectiten größere Hin-dernisse entgegenstehen. Lateritische Verwitterung während des Miozäns würde in den flachen Rand-seen eine direkte Fällung dieser Tonminerale begünstigt haben. Der beckenwärts erfolgende Anstieg im MgO : Al$_2$O$_3$–Verhältnis ist eine weitere Stütze.

Tiefgründige Verwitterung kristalliner Gesteine im nördlichen Britisch–Honduras und Guatemala würden während des späten Tertiärs ähnliche kieselsäurereiche, aluminiumarme Bedingungen in der benachbarten überschwemmten Yucatan-Plattform hervorgerufen haben. Der seewärts erfolgende Anstieg im MgO : Al$_2$O$_3$–Verhältnis, das Fehlen von Beimengungen detritischer Bestandteile und die

Abwesenheit von Smectit deuten stark darauf hin, daß diese Yukatan-Palygorskit-Sepiolit Tone in ähnlicher Weise durch direkte Kristallisation entstanden sind.

Einige Vorkommen von Palygorskit und Sepiolit mögen wohl mit der Umwandlung von smectitischen und vulkanischen Aschen in Beziehung stehen, jedoch sind viele der großen sedimentären Lagerstätten mit großer Wahrscheinlichkeit das Ergebnis direkter Kristallisation in der Nachbarschaft von Gebieten, in denen tropische und subtropische Verwitterung ablief.

Резюме — Морские и неморские отложения палыгорскита-сепиолита находят по всему свету и они встречаются залегающими между пластами кремнистого сланца, доломита, известняка, фосфора и других необломочных осадочных горных пород. Происхождение этих глин с высоким содержанием магния давно уже предписывалось или изменениям вулканического пепла или структурной трансформации смектитных глин. Недавно выдвинули мнение, что происхождение это является непосредственной кристаллизацией (новонаслоением). Современные лабораторные исследования подтверждают последнюю консепцию, особенно, если в окружающих условиях концентрация глинозема низка, а концентрация кварца высока и при этом pH щелочный. Считают, что отложения в Джорджии-Флорида в Южных Соединенных Штатах такого происхождения, так как существуют важные возражения против изменения вулканического пепла или трансформации смектитов. Латеритовое выветривание в период миоцена повело бы к непосредственному осаждению этих глин в мелководных побережных морях. Увеличение отношения $MgO:Al_2O_3$ по направлению к бассейну является добавочным подтверждением.

Глубокое выветривание кристаллических горных пород в Британских Гондурас и Гватемала создали бы такие условия высокого содержания кварца и низкого содержания глинозема на смежной погруженной платформе Юкатана во воремя позднего третичного периода. Повышение отношения $MgO:Al_2O_3$ по направлению к морю, отсутствие ассоциированных наносных компонентов и отсутствие ассоциированных смектитов явно указывают на непосредственную кристаллизацию этих юкотанских палыгорских-сепиолитных глин.

Иногда происхождение палыгорскита и сепиолита может быть связано с изменениями смектитных глин или вулканического пепла. Однако многие крупные осадочные отложения являются, наверно, результатом непосредственной кристаллизации рядом с областями подвергающихся тропическому или субтропическому выветриванию.