PALYGORSKITE-SEPIOLITE CLAYS OF LEBRIJA, SOUTHERN SPAIN

E. Galan[1] and A. Ferrero[2]

Abstract—The Upper Pliocene sediments near Lebrija in southern Spain contain commercial deposits of palygorskite and sepiolite. These sediments of continental origin consist chiefly of carbonate, marl, and clay resting on marine Pliocene quartzose sand. The lowest unit, the "Marly-Calcareous Bed," consists of sepiolite-rich marl associated with concretions and irregular layers of chert, <0.5 m thick, and local diatomite layers, as well as limestone, sandy limestone, marl, and clayey sandstones. This unit has a maximum thickness of 30 m and contains three clay-mineral suites as follows: (1) bottom—sepiolite ± palygorskite; (2) center—sepiolite and palygorskite ± illite; (3) top—palygorskite and illite, ± sepiolite and smectite. Sepiolite decreases and palygorskite and illite increase toward the top, reflecting the composition of detrital material supplied to the basin. Beds 0.5–1 m thick locally and containing 50 to 60% sepiolite have been called "Tierra del Vino" (wine earth) because the material formerly was used to clarify and purify wine. The sepiolite-rich beds are as much as 15 m thick in the eastern part of the area. The upper unit is called the "Palygorskite Bed" because certain layers, 0.3 to 3 m thick, contain 35 to 75% palygorskite. The palygorskite-rich layers are interbedded with limestone and marl, and the entire unit is 15 m thick. The total resource of palygorskite is estimated at about 9 million tonnes.

The sediments are believed to have been deposited in a brackish, lacustrine environment. Originally, tectonic stability and an arid climate favored the formation of sepiolite at about pH 8. Later, after significant weathering of the source rocks, detrital illite was transformed to palygorskite in the Mg- and Si-rich waters. Here, palygorskite was also precipitated directly.

Key Words—Genesis, Palygorskite, Sedimentation, Sepiolite, Spain.

INTRODUCTION

Lebrija clay materials are well known in Spain and have been mined since ancient times for the clarification of wine ("Tierra del Vino" or "wine earth"). Calderon (1901) was the first to report analytical data on these materials; he described them as clays composed of Al and Mg silicates with accompanying carbonates and iron oxides. Gabala y Laborde (1916) described Lebrija Earth as a white or brown clay which was used for the clarification of wine because of its small particle size. Later, Gabala y Laborde (1959) studied the lacustrine materials of Lebrija, Cerro San Benito, Mesa del Cuervo, and other localities of this area and noted the occurrence of "Tierra del Vino," chert, and silicified limestone, assigning them a Pliocene age.

The first mineralogical study of the Lebrija continental clays was carried out at El Cuervo by Gonzalez Garcia and Peiró (1958). These authors distinguished two types of Lebrija continental clays at El Cuervo, one a white clay composed of equal proportions of palygorskite and illite, accompanied by carbonate, quartz, montmorillonite, and locally, kaolinite, at a depth of 8–10 m, and the second a thinner, darker clay (Tierra del Vino), higher in the series, and composed of illite and montmorillonite, the latter mineral having formed from illite. Huertas *et al.* (1974) studied the same profile described by Gonzalez Garcia and Peiró and found two layers of Tierra del Vino separated by a chert layer. The mineralogical composition given by these authors agrees with that of Gonzalez Garcia and Peiró, save for their finding sepiolite in the Tierra del Vino and in interbedded limestones. They also pointed out the close relationship between the Tierra del Vino and opaline chert layers. Peris Mora (1973) studied a deposit of diatomite in the lacustrine Pliocene of Cerro San Benito (Lebrija). Sepiolite is a common constituent of these deposits, together with quartz, noncrystalline silica, and cristobalite.

These economically important palygorskite-sepiolite clays have been ignored on the Spanish Industrial Mineral Map (I.G.M.E., 1974) and other relevant geological reports of the Lebrija area. Nevertheless, known resources of Lebrija palygorskite-sepiolite clays total about 9 million tonnes, and exploration continues to find other deposits in the lacustrine Pliocene terrains and in the Tertiary parimarine facies of this region. Palygorskite clays of Lebrija are selectively mined for their attractive adsorption properties. Materials suitable for carriers of pesticides, insecticides, and herbicides; animal litter; absorbents of industrial oils and grease; catalyst carriers; and mineral bleaching agents are produced by appropriate crushing, drying, firing, and grinding techniques.

[1] Departamento Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Zaragoza, Zaragoza, Spain.
[2] Tolsa, S.A., Madrid, Spain. Present address: Carbones de Berga, S.A., Serchs, Barcelona, Spain.
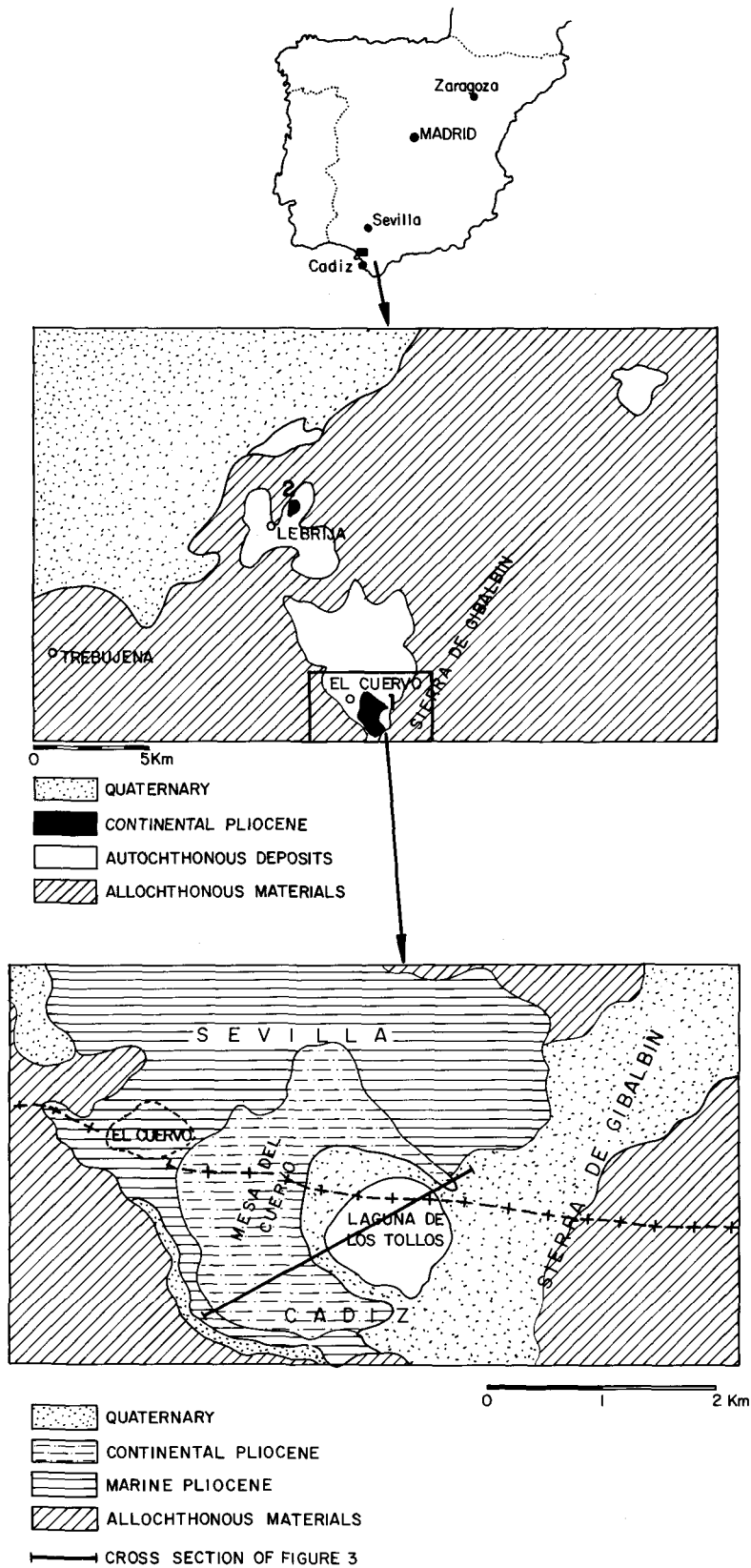
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Figure 1.   Maps showing location of the area studied. 1. Mesa del Cuervo. 2. Cerro San Benito.

REGIONAL SETTING AND PLIOCENE STRATIGRAPHY

The study area is located at the boundaries of the Sevilla and Cadiz Provinces (Figure 1) and includes part of the Guadalquivir Basin, a large structural unit filled mainly with Tertiary and Quarternary marine sediments. The most important highland is the Mesa del Cuervo, which extends from the town of El Cuervo to the Sierra de Gibalbin. The Sierra consists of allochthonous materials which range from Upper Cretaceous to Upper Miocene in age with a Triassic decollement bed. The rocks consist chiefly of white and gray sandy marls (Neogene), sandstones and sandy limestone (Paleogene), sandy limestone and red marls (Upper Cretaceous), and variegated marls, clays, dolomite rocks, limestones, and dolerites (Triassic) (I.G.M.E., 1977).

Autochthonous materials, from Tortonian (Upper Miocene) to Pliocene in age, lie discordantly above allochthonous material and can be divided into three formations: (1) bluish-gray marly clay, (2) sand (both marine facies), and (3) limestone, marl, and clay of continental character, listed from the bottom to the top. The last two formations are Pliocene in age. The continental Pliocene lies unconformably above the marine Pliocene and is mostly covered by Quaternary sediments and soils. The marine Pliocene sediments were concordantly deposited on Upper Miocene sediments and discordantly above the older rocks. Later tectonic adjustment occurred during Pliocene and Quaternary time producing slight folding. At the Mesa del Cuervo, continental Pliocene beds dip 5° towards the Laguna de los Tollos, a small intermittent lake in the lowest part of the area. Prior to the tectonic movements, this "mesa" was really a basin of which the Laguna de los Tollos is now a remnant.

Two units can be distinguished in the continental Pliocene: a "marly-calcareous bed" and an upper "palygorskite bed." The base of the lower unit is usually a silicified limestone or a limestone with chert (white or gray), resting on a probable paleosol (Gonzalez Garcia and Peiró, 1958) with similar characteristics as those of the Tierra del Vino (vide infra), but, in certain places (e.g., Cerro Benito), diatomite forms the base of the Pliocene. The lower unit consists of limestone, marly and sandy limestone, marl and clayey marl, with interbedded thin beds (as much as 1 m thick) of dark brown, light brown, and pinkish white marly clay named "Tierra del Vino." Generally irregular layers of brown chert, ≤50 cm thick, occur immediately above and below the Tierra del Vino, and also change laterally to this material. Locally, the Tierra del Vino bed is 15 m thick. The "marly-calcareous bed" is 25–30 m thick (Figure 2).

The upper unit (≤15 m thick) is named the "palygorskite bed" because of its high content of palygorskite, which is presently being mined. The palygorskite layers range from 30 cm to 3 m in thickness, with the

layers decreasing in thickness upward. Limestone and marly limestone layers <0.5 m thick are interbedded in this unit. The top layer is a nodular limestone, 4–5 m thick.

The stratigraphy of the continental Pliocene has been described from cores of several drill holes made in the Mesa del Cuervo area[3] (Figures 2 and 3). Regional dip of the Pliocene materials is a consequence of (1) original basin morphology, (2) contemporary sinking with sedimentation, and (3) differential compaction. A great abundance of microfauna was noted in the marly and calcareous Pliocene (ostracods, gastropods, oogonia of Characeae, etc.), which are characteristic of a brackish facies or swamp of Upper Pliocene or Quaternary age (J. L. Saavedra, Centro de Estudios Hidrograficos, Madrid, 1979, private communication).

MATERIALS AND METHODS

Sixty samples were taken from drill holes and from pits where clays are being mined. Thirty-four representative samples of the different beds from 8 drill holes were used to construct a typical stratigraphic column for this area (Figure 2).

Samples were examined by X-ray powder diffractometry (XRD) including the use of oriented aggregates to attempt quantitative estimations of mineral constituents according to methods of Schultz (1964), Huertas (1969), and Dorronsoro (1978). Tierra del Vino (sepiolite-rich clay) and palygorskite-rich commercial clay were analyzed chemically by atomic absorption and also examined by transmission electron microscopy (TEM), using a Philips EM-300 apparatus.

RESULTS

The lower unit of the continental Pliocene, the "marly-calcareous bed," has a relatively high calcite content (40–80%) and contains about 10% quartz and minor sepiolite and palygorskite (Table 1, Figure 2). The "Tierra del Vino" and similar materials are typically 50% calcite and 50% sepiolite, with minor smectite, palygorskite, and quartz. This rock may be defined as a sepiolite marl. The chemical analysis (Table 2) of "Tierra del Vino" (LT-29) shows low Al_2O_3 and high MgO and CaO percentages corresponding to the above mineralogical composition. A "paleosol" located at the base of the continental Pliocene (LT-34) has more palygorskite and iron oxides and fewer carbonate minerals. Chert layers, associated with the "Tierra del Vino," are composed of quartz and cristobalite with minor sepiolite (LT-31), and in places contain significant amounts of calcite (whitish chert). Diatomite contains noncrystalline silica, quartz, and small quantities of carbonate and sepiolite. The SiO_2 content of cherty

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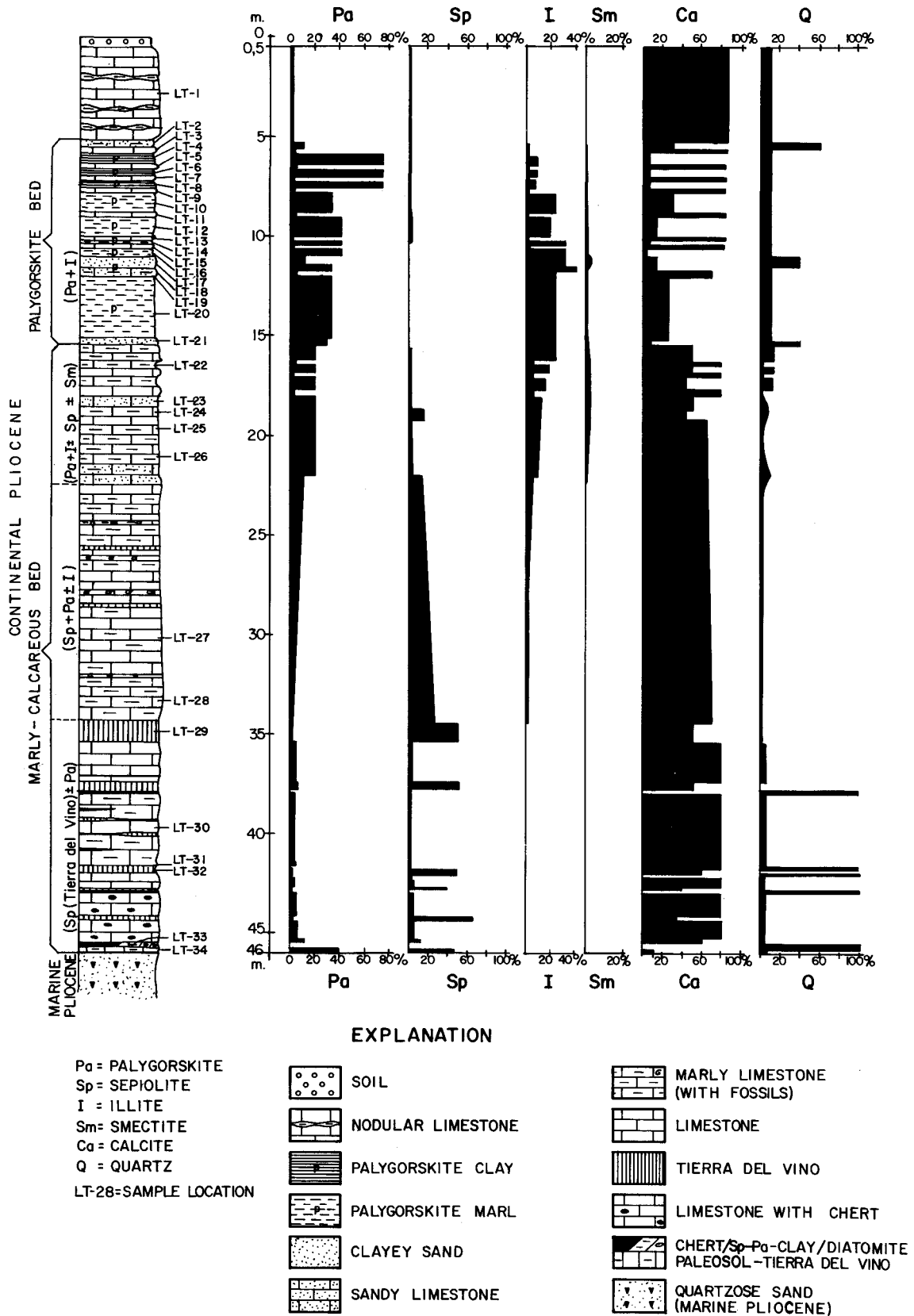[3] This exploration was carried out by Tolsa, S.A. Enterprise, which mines these deposits.

Figure 2.   Stratigraphic column with diagrams showing mineral composition of beds at Laguna de los Tollos.
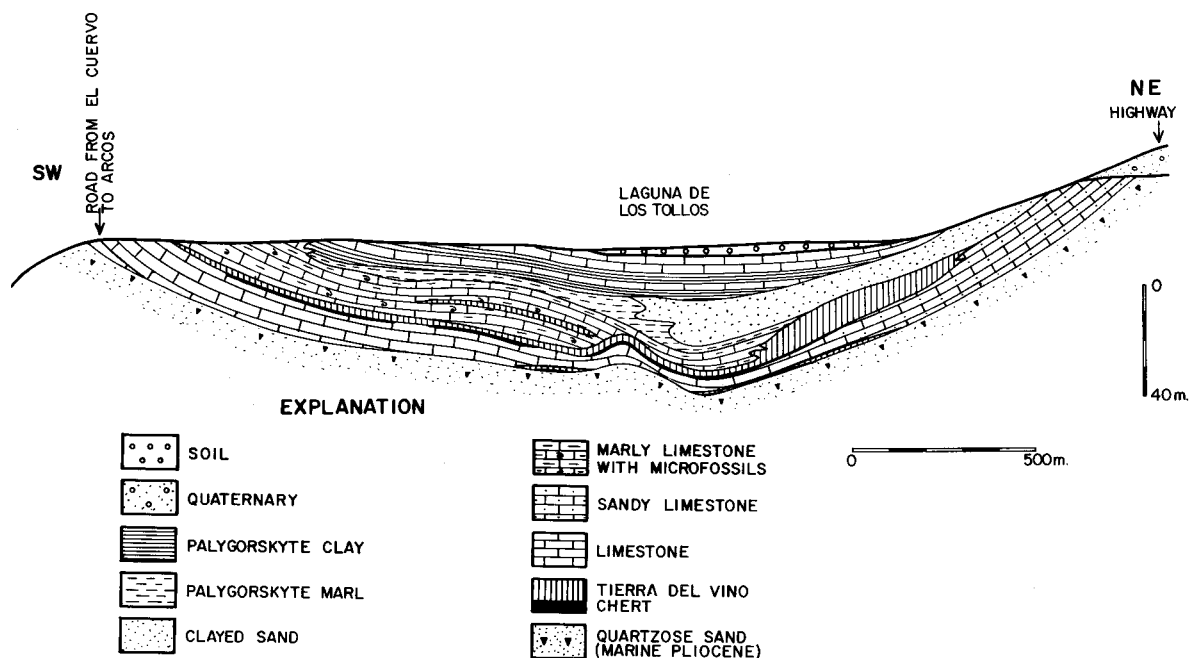
Figure 3.   Cross section SW–NE across the Mesa del Cuervo and Laguna de los Tollos.

layers ranges between 80 and 90%. The sepiolite content decreases and the palygorskite content increases upward. About 5 to 20% illite, <5% smectite, and traces of chlorite, kaolinite, mixed-layer clay minerals, and gypsum are also present in the upper part of this lower unit. Three clay-mineral suites exist in this lower unit; sepiolite ± palygorskite in the bottom; sepiolite + palygorskite ± illite in the center; and palygorskite + illite ± sepiolite ± smectite in the upper part.

The "palygorskite bed" consists of alternating clays, marls, and limestones (Figure 2, Tables 1 and 2). The main clay-mineral suite is palygorskite + illite. Locally, sepiolite and smectite are present in minor amounts. Palygorskite varies from 35 to 75% in the clay and marl samples and is present in amounts up to 5% in the limestone. Illite is more abundant in clay beds (≤40%), but decreases towards the top. Quartz is relatively constant in the unit at about 10%. The sand beds found at the bottom and at the middle of this unit (LT-21 and LT-17) are very rich in calcite, quartz, palygorskite, and illite. The "palygorskite bed" is overlain by a thick limestone bed, whose composition is similar to other limestone beds in the continental Pliocene.

A transmission electron micrograph of "Tierra del Vino" (Sample LT-29) shows sepiolite (Figure 4), while that of the palygorskite clay (Sample LT-12, Figure 5) shows elongate crystals of palygorskite and platy illite. Figure 6 shows XRD patterns of these samples.

EVOLUTION OF THE BASIN AND GENESIS OF THE CLAY MINERALS

According to the regional geological data, Triassic masses and the overlying materials moved towards the northwest in the Lebrija area during Miocene time. These movements ended during the Late Miocene, and autochthonous materials, marly and sand sediments, were deposited in a shallow-sea environment above the allochthonous material. During the Pliocene, tilting of the basin produced a general marine regression, and sedimentation occurred in a brackish, lacustrine environment and continued into Quaternary times (Laguna de Los Tollos).

The sedimentation in the lacustrine Pliocene of Lebrija is similar to that described by Millot (1970, p. 76) as a negative sequence. At the beginning of the marine regression a lagunar environment (or perhaps a playa-lake type) existed, where carbonate minerals, clay, and silica were deposited and locally diatoms flourished. In such a setting the formation of a soil very rich in palygorskite and sepiolite from the marine Pliocene sand is unlikely. Rather, the "paleosol" considered above was probably the first Tierra del Vino layer formed. Later, in a true lacustrine environment, sedimentation of those materials continued, but diatoms were exterminated under a warmer climate and after a salinity change. Diatoms formed deposits of diatomaceous earth and, in part, dissolved.

Sepiolite was formed in significant amounts at the

Table 1. Mineralogical composition of drillhole and pit samples.[1]

Sample[2]	Qtz	Cal	Pal	Sep	Ill	Sme
LT-1	10	80–85	5	Tr	—	—
LT-2	60	30	10	Tr	Tr	Tr
LT-3	10–15	80–85	5	Tr	Tr	Tr
LT-4	10	5	75	Tr	10	Tr
LT-5	10	80–85	5	Tr	Tr	Tr
LT-6	10	5	75	Tr	10	Tr
LT-7	10	85	5	Tr	Tr	Tr
LT-8	10	5	75	Tr	10	Tr
LT-9	10	75	5	Tr	Tr	Tr
LT-10	<10	30	35	Tr	25	Tr
LT-11	10	85	5	Tr	Tr	Tr
LT-12	<10	15	40–45	5	20–25	Tr
LT-13	10	85	5	—	Tr	Tr
LT-14	<10	10	40–45	<5	30	<5
LT-15	10	80	5	Tr	Tr	Tr
LT-16	10	5	40–45	Tr	30	<5
LT-17	40	15	10	Tr	30	5
LT-18	10	<10	35	Tr	40	<5
LT-19	<10	70	<5	Tr	20–25	Tr
LT-20	10	25	35	—	20–25	Tr
LT-21	40	5	35	—	20–25	Tr
LT-22	<10	50	20	—	15	<5
LT-23	15	50	20	Tr	10–15	<5
LT-24	<10	40	20	10–15	10	<5
LT-25	5	65	20	5	5–10	Tr
LT-26	<10	65	20	5	5–10	Tr
LT-27	<5	65	10	25	<5	Tr
LT-28	Tr	70	5	25	<5	Tr
LT-29	Tr	50	Tr	50	—	Tr
LT-30	5	80	5	5	Tr	—
LT-31[3]	—	Tr	—	Tr	—	—
LT-32	—	35	Tr	65	—	—
LT-33	10	60	15	15	—	—
LT-34[4]	5	5	40	45	—	—

Qtz = quartz, Cal = calcite, Pal = palygorskite, Sep = sepiolite, Ill = illite, Sme = smectite, Tr = trace.

[1] See Figure 2 for graphical representation.

[2] See Figure 2 for location of samples and graphical representation of mineralogy. (LT = Laguna de los Tollos).

[3] Plus cristobalite.

[4] Plus iron oxides.

Table 2. Chemical analyses of representative clay materials from Lebrija, southern Spain.

	Palygorskite clays		Tierra del Vino	"Paleosol"
	LT-12	LT-18	LT-29	LT-34
SiO_2	51.00	54.90	28.2	64.00
Al_2O_3	14.12	15.72	1.28	5.66
Fe_2O_3	6.02	6.01	0.63	9.05
MgO	4.60	5.15	11.2	9.70
CaO	8.00	3.30	30.5	0.50
Na_2O	0.30	0.61	0.34	0.30
K_2O	3.00	3.90	0.14	0.90
Ign. loss	12.98	10.26	28.00	9.98
	100.02	99.85	100.31	100.09

For mineralogy, see Table 1.

icates and carbonates). Sepiolite crystallization should take place under conditions similar to those of the homogeneous precipitation,[4] noted for kaolinite, palygorskite, sepiolite, and other phyllosilicates by La Iglesia and Martin Vivaldi (1975), La Iglesia *et al.* (1976), and La Iglesia (1977, 1978). These conditions are more likely in natural environments than those proposed by other authors for the synthesis of these clay minerals at room temperature (e.g., Siffert, 1962; Wollast *et al.*, 1968).

The stability and formation of large, well-formed crystals of sepiolite are favored by pH ~8, according to the experimental data of the above-mentioned authors. Above pH 9, smectites and talc were formed in Siffert's experiments and brucite in Wollast's synthesis. On the other hand, calcite precipitation requires a pH of about 8 (Garrels and Christ, 1965). Thus, the precipitation of sepiolite and calcite, without brucite or talc, occurred at a pH of 8, and silica precipitated when its saturation was reached (Tierra del Vino-chert-carbonate). The formation of calcite and not dolomite in the presence of Mg is compatible with a log $pCO_2 < -5.0$ (Lippmann, 1979), but other factors, such as the ion activity and saturation index (the activity product of a mineral divided by its solubility constant) of the carbonate and silicate minerals as the alkalinity increases, must also be taken into account.

Sedimentation occurred in a closed continental basin of the alkaline type. Tectonic stability and a dry climate favored sepiolite formation. After the last major deposit of Tierra del Vino (bed 29), the climate became wetter because of a slight subsidence of the basin, and weath-

base of the continental formation where silica was available from the source area and from the diatom colonies. Relationships between chert beds, diatomites, and the Tierra del Vino (richest in sepiolite) are obvious: the Tierra del Vino is very close to the chert, which also contains sepiolite as an impurity. This relationship between sepiolite and diatoms was also reported by Fleischer (1972) in the Santa Cruz Basin of California. Also, Patterson (1974) suggested that much of the silica in the palygorskite of the Attapulgus, Georgia, "fuller's earth" comes from the dissolution of diatoms.

The Mg was supplied from the surrounding dolomites and dolerites. The environment must have been slightly alkaline in which silica and Mg were supplied slowly (by dissolution of diatoms and by the weathering of sil-

[4] Precipitation from homogeneous solutions, or kinetically controlled precipitation, is an effective technique for regulating pH and for the *in situ* generation of ions, usually by the temperature-dependent hydrolysis or by slow decomposition of suitable materials. Selective precipitation occurs slowly because oversaturation remains very low in any part of the solution.
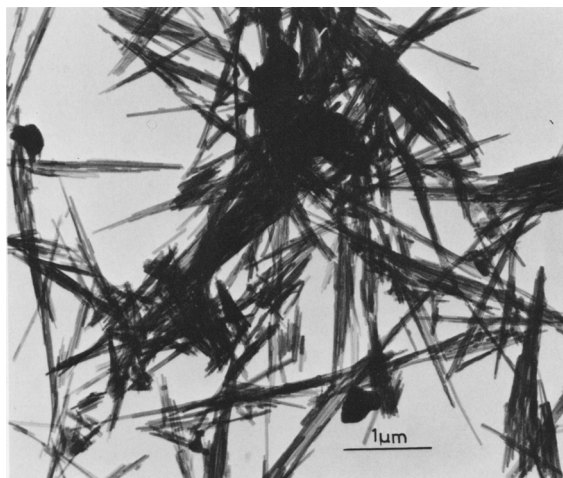
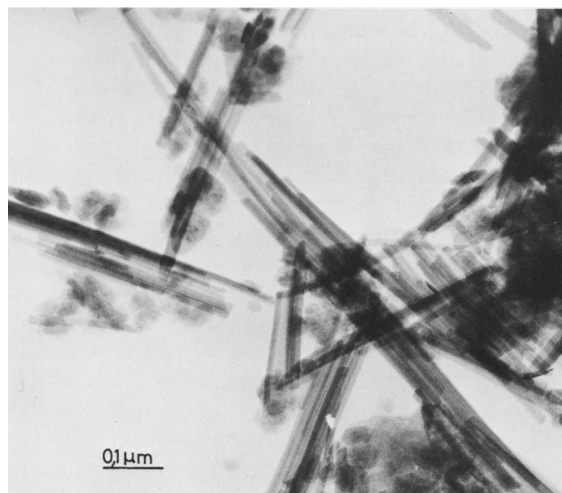Figure 4. Transmission electron micrograph of sepiolite crystals (Tierra del Vino).

Figure 5. Transmission electron micrograph of palygorskite and illite crystals in palygorskite clay.

ering of the source rocks increased, supplying to the basin a greater amount of magnesium, iron, silica, etc., as ions or gels, and detrital minerals (quartz, mica, chlorite). Under these conditions, palygorskite formed rather than sepiolite. Additionally, detrital minerals (especially micas) transformed to palygorskite in the brackish environment. The twofold origin of palygorskite (neoformation and transformation) increased the percentage to about 70%. Occasionally, climatic or tectonic changes produced abundant detrital materials that interfingered into the series (e.g., bed 21).

The neoformation of palygorskite required aluminum in a medium where alumina has a very low solubility and in which silica and magnesium are soluble. Under such conditions, palygorskite more likely formed as a result of an equilibrium between the unstable detrital phyllosilicates, mainly illite, and the solution that caused layer silicates to transform to palygorskite. Nevertheless, Al_2O_3 may have entered the basin as an organic complex or from other unstable clay minerals, such as chlorite or kaolinite (Velde, 1977, pp. 150–151), which can also liberate aluminum. In addition, palygorskite neoformation cannot be excluded. The physical-chemical conditions for the precipitation of palygorskite are closely similar to those of the precipitation of sepiolite (La Iglesia, 1977).

A similar mechanism for the transformation of montmorillonite to palygorskite was suggested by Weaver and Beck (1977) in a perimarine environment in southeastern United States. In the Lebrija area the close relationship between illite and palygorskite, as well as in the example shown in Figure 6 (Sample LT-17), seem to support this hypothesis. This sample is composed of illite, quartz, calcite, and a mineral with principal XRD peaks at 10.27 Å (nonexpanding) and 3.24 Å and an elongate shape similar to palygorskite. The latter min-

eral may be a random interstratification of illite and palygorskite.

The smectite in these rocks could be detrital (dioctahedral smectites), or it could have formed by the trans-
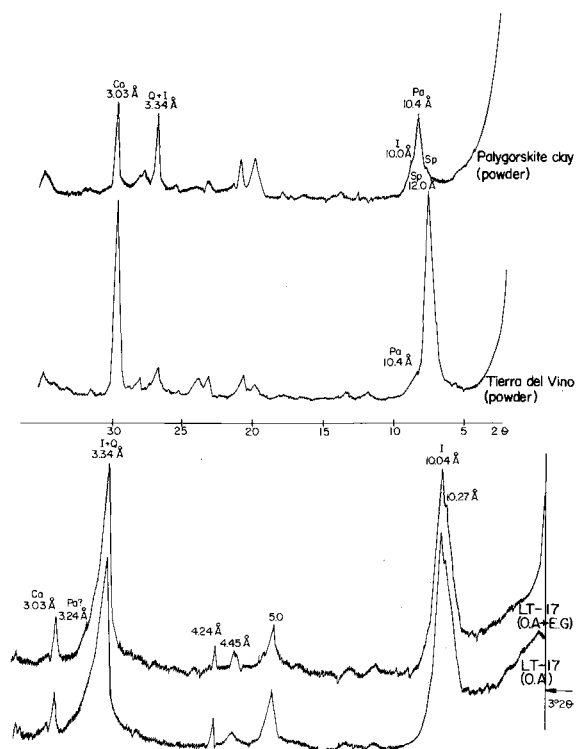

Figure 6. X-ray powder diffraction patterns (CuKα radiation) of palygorskite clay, Tierra del Vino and sample LT-17 (oriented aggregate with and without ethylene glycol). Ca = calcite, Q = quartz, I = illite, P = palygorskite, Sp = sepiolite.

formation of chlorite, illite, or palygorskite (di- and trioctahedral smectites) or by neoformation (trioctahedral smectites). The small amount of smectite precludes serious speculation on its genesis. The alternation of marly and clayey layers in the "palygorskite bed" was possibly a result of periodic climatic changes. Wet periods with materials supplied to the basin favored the formation of palygorskite from degraded illite. During drier periods, evaporitic carbonate sedimentation took place, with little sepiolite or smectite formation and a lack of detrital minerals. This cycle was repeated eight times at least, forming the commercially important clays and the interbedded carbonates. The upward decreasing thickness of the palygorskite beds indicates a basin evolution toward stable tectonic conditions and perhaps a climate with shorter and drier periods and milder weathering.

The genetic sequence of the principal clay minerals of Lebrija from the base to the top is:

(1) Dominant neoformation (sepiolite + palygorskite) (beds 29 to 34)
(2) Neoformation decreasing upward (sepiolite + palygorskite) and increasing transformation (palygorskite + sepiolite?). Important detrital clay minerals (e.g., illite) (beds 26 to 28)
(3) Dominant transformation (palygorskite) and detrital clays (illite). Occasional neoformation (sepiolite) (beds 1 to 26)

ACKNOWLEDGMENTS

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Резюме—Осадки верхнего плиоцена в поблизости Лебрия в южной Испании содержат коммерческие залежи палигорскита и сепиолита. Эти осадки континентадьного происхождения состоят главным образом из карбоната, мергеля и глины, расположенных на морском плиоценовом кварцевои песке. Наинижей расположенная система, ''мергелоизвестковая залежь,'' состоит из мергеля, богатого в сепиолит, связанного с конкрециями и нерегулярными слоями черта толщиной <0,5 м и местными слоями диатомита, а также известняком, песковым известняком, мергелем и глиновыми песчаниками. Эта система имеет максимольную толщину 30 м и содержит следующие три типа глинистых минералов: (1) на дне—сепиолит с либо без палигорскита, (2) в середине—сепиолит с либо без иллита, и (3) наверху—полигорскит и иллит с либо без сепиолита и смектита. Содержание сепиолита уменьшается, а полигорскита и иллита увеличивается по направлению вверх, отображая состав детритого материала, питающего бассейн. Слои с местной толщиной 0,5–1 м, содержащие от 50 до 60% сепиолита, были названы ''Терра дель Вино'' (земля и вино), так как материал использовался прежде для получения прозрачного и очищенного вина. Толщина залежей, богатых в сепиолит, доходит до 15 м в восточной части области. Верхняя система называется ''полигорскитовой залежью,'' так как определенные слои толщиной от 0,3 до 3 м содержат от 35 до 75% полигорскита. Слои, богатые в палигорскит, перемежаны с известняком и мергелем, и целая система имеет толщину 15 м. Полный ресурс палигорскита оценивается на 9 миллионов тонн.

Предполагается, что осадки были сложены в соленой озерной окружающей среде. Первоначально, тектоническая стабильность и сухой климат благоприятствовали образованию сепиолита о рН равном 8. Позднее, после значительного подвержения атмосферным влияниям исходных горных пород, детритовый иллит был преобразован в палигорскит в водах, богатых в Mg и Si. При этом палигорскит также был непосредственно осажден. [E.C.]

Resümee—Die oberpliozänen Sedimente in der Nähe von Lebrija in Südspanien enthalten abbauwürdige Lagerstätten von Palygorskit und Sepiolith. Diese Sedimente sind kontinentaler Entstehung, bestehen hauptsächlich aus Karbonat, Mergel, und Ton und liegen auf einem marinen pliozänen Quarzsand. Die unterste Schicht, das ''Marly-Calcareous Bed,'' besteht aus Sepiolith-reichem Mergel mit Konkretionen und unregelmäßigen Lagen aus Kieselschiefer, die eine Mächtigkeit unter 0,5 m haben. Außerdem weist diese Schicht stellenweise Diatomitlagen sowie Kalkstein, sandigen Kalkstein, Mergel, und tonige Sandsteine auf. Diese Schicht hat eine maximale Mächtigkeit von 30 m und enthält folgende Abfolge von Tonmineralen: (1) Unten Sepiolith mit oder ohne Palygorskit; (2) in der Mitte Sepiolith mit oder ohne Illit und (3) oben Palygorskit und Illit mit oder ohne Sepiolith und Smektit. Nach oben zu nimmt Sepiolith ab, während Palygorskit und Illit zunehmen. Dies spiegel die Zusammensetzung des detritischen Materials im Liegenden wieder. Lagen von stellenweise 0,5–1 m Mächtigkeit, die 50–60% Sepiolith enthalten, wurden ''Tierra del vino'' (Weinerde) gennant, da dieses Material früher verwendet wurde, um Wein zu klären und zu reinigen. Die Sepiolith-reichen Lagen sind im östlichen Teil des Gebietes bis zu 15 m mächtig. Die obere Schicht wird ''Palygorskite Bed'' genannt, da manche Lagen, 0,3 bis 3 m mächtig, 35–75% Palygorskit enthalten. Die Palygorskit-reichen Lagen wechsellagern mit Kalkstein und Mergel. Die gesamte Schicht ist 15 m mächtig. Der gesamte Vorrat an Palygorskit wird auf etwa 9 Millionen Tonnen geschätzt.

Es wird angenommen, daß die Sedimente in einem brackischen, lakustrischen Milieu abgelagert wurden. Ursprünglich förderten die tektonische Stabilität und ein arides Klima die Bildung von Sepiolith bei einem pH von etwa 8. Später, nach einer beträchtlichen Verwitterung der Ausgangsgesteine, wurde detritischer Illit in Mg- und Si-reichen Wässern in Palygorskit umgewandelt. Außerdem wurde Palygorskit auch direkt ausgefällt. [U.W.]

Résumé—Les sédiments du haut Pliocène près de Lebrija en Espagne du sud contiennent des depôts commerciaux de palygorskite et de sépiolite. Ces sédiments d'origine continentale consistent principalement de carbonates, de marles, et d'argile reposant sur du sable marin quartzose d'age Pliocène. L'unité la plus basse, la ''Marly-Calcareous Bed'' consiste de marle riche en sépiolite associée avec des concrétions et des couches irrégulières de chert <0,5 m d'épaisseur et de couches locales de diatomites, ainsi que de pierre à chaux, de pierre à chaux sablonneuse, de marle, et de grès argileux. Cette unité a une épaisseur maximum de 30 m et contient 3 suites de minéraux argileux: (1) sépiolite de base avec ou sans palygorskite; (2) sépiolite centrale avec ou sans illite; et (3) palygorskite et illite du dessus avec ou sans sépiolite et smectite. La sépiolite décroit et la palygorskite et l'illite accroissent vers le haut, réflectant la composition de matière détritale fournie au basin. Des lits de 0,5–1 m d'épaisseur localement et contenant 50 à 60% de sépiolite ont été nommés ''Tierra del Vino'' (terre de vin) parceque la matière était autrefois utilisée pour clarifier et purifier le vin. Les lits riches en sépiolite atteignent une épaisseur de 15 m dans la partie ouest de la région. L'unité du haut est appellée ''Palygorskite Bed'' parceque certaines couches de 0,3 à 3 m d'épaisseur contiennent de 35 à 75% de palygorskite. Les couches riches en palygorskite sont séparées par des pierres à chaux et des marles, et l'unité entière a 15 m d'épaisseur. La ressource totale de palygorskite est estimée à a peu près 9 million de tonnes.

On croit que les sédiments ont été deposés dans un environment saumure lacustrin. Originalement, la stabilité tectonique et un climat aride ont favorisé la formation de sépiolite à un pH d'à peu près 8. Plus tard, après altération significative des roches sources, l'illite détritale a été transformée en palygorskite dans les eaux riches en Mg et Si. Ici, la palygorskite a aussi été precipitée directement. [D.J.]