

PALYGORSKITE AND SEPIOLITE – THE ENIGMATIC CLAY MINERALS

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Introduction

Perhaps because they very rarely occur in the intensively cultivated soils of the temperate or warm subhumid or humid zones of the world, the presence of palygorskite and sepiolite minerals has been largely overlooked until fairly recently. Only with the expansion of agriculture to the more marginal soils of semiarid and arid areas has the study of these clay minerals been intensified. In addition, the presence of the fibrous clay minerals in many of these soils may have been ignored for a long time because they rarely are dominant in the soil clay fraction.

Both palygorskite and sepiolite have relatively large specific surface areas, with various types of active sorption centers. The sorption of nonpolar organic compounds has been demonstrated repeatedly for monomineralic materials and is a particularly important feature. It is not known whether this capacity translates into specific soil properties. Thus, there is a lack of information on interactions of toxic soil pollutants (e.g., pesticides and herbicides) with fibrous clay in soils.

From studies on monomineralic materials, concentrated clay suspensions of palygorskite and sepiolite are known to be very stable. The stability of these clay suspensions even in relatively saline environments is particularly significant, and sets them apart from those of the more common smectite clay. If this stability is maintained in the soil environment as well, it might significantly affect rheological properties, such as hydraulic conductivity, which are so important in irrigated soil management practices.

Only scant new information has been added in the course of the past decade on the basic structure and morphology of the fibrous clay minerals. Much detail and refinement have been obtained, however, through the use of infrared spectroscopy, electron microscopy, and Mössbauer spectroscopy. Significant progress also has been made with regard to understanding the surface properties of these minerals. The state of the various types of H₂O associated with the minerals has been elaborated on, as well as the characteristics of the adsorption sites. These aspects are very important for the development of industrial uses for palygorskite-sepiolite in its pure form, as well as for an appreciation of the role these clay minerals play in agrochemistry and ecology when they occur as components of the clay fraction of soils.

Structure and morphology

The structures of both sepiolite and palygorskite contain continuous planes of tetrahedral basal O atoms - 0.65 nm apart. The apical oxygens point alternately up and down relative to the planes of basal oxygens in a pattern such that the tetrahedra pointing in the same direction form ribbons that extend in the direction of the *a*-axis. The ribbons have an average width along the *b*-axis of three linked tetrahedral chains in sepiolite and two linked chains in palygorskite. Ribbons with apices pointing up are linked vertically to ribbons with apices pointing down by forming octahedral coordination groups around Mg and Al. Two-to-one layers that are continuous along *a* but of limited lateral extent along *b* are thus formed (Bailey, 1980). The morphological expression of these structures projected into space are fibers that represent continuations of these basic units along the *a*-axis, which parallels the fiber axis.

In accordance with the differing width of the 2:1 ribbons, the number of octahedral-cation positions per formula unit differs from five in palygorskite to eight in sepiolite. Apparently, not all available positions are occupied. In many palygorskites, the occupancy is between four and five, while some palygorskites have been shown to be completely dioctahedral - that is, only four of the five available positions are occupied. In sepiolite, dioctahedral varieties appear to be very rare.

A small number of exchangeable Ca^{2+} and Mg^{2+} cations and variable amounts of zeolitic H_2O are contained in the rectangular channels that lie between the backs of opposing 2:1 ribbons and extend parallel to the fiber direction. In addition to zeolitic H_2O , four bound-water molecules (OH_2) per formula unit lie at the edges of the ribbons and are held more tightly because they participate in the coordination of the octahedral Mg and Al (Bailey, 1980).

Both palygorskite and sepiolite display lath-like or fibrous forms, representing crystals elongated along the *a*-axis. The length of palygorskite fibers varies greatly, from $<1 \mu\text{m}$ up to nearly $20 \mu\text{m}$. Average lengths vary between 1 to $2 \mu\text{m}$. The individual fibers have diameters varying from 0.1 to $0.5 \mu\text{m}$ and often are arranged in bundles or sheaths. Transverse cross-sections of palygorskite fibers were reported to appear cylindrical, polygonal, or six-sided (Martin Vivaldi & Robertson, 1971). Scanning-electron microscope (SEM) observations have shown fibers growing out from calcite, dolomite or gypsum crystals, and then branching out or intertwining. Other SEM observations show cleavages of fibers into two parallel subunits. The fibers apparently consist of aggregates or bundles of fine laths, in parallel orientation, of a width varying from 10 to 35 nm, and a thickness of 5 to 10 nm (Singer, 1981).

The morphology of sepiolite is similar to that of palygorskite, and variation within the mineral species is greater than that between the species. Sepiolite bundles appear to differ from those of palygorskite by being flatter and more frayed at the ends.

Chemical composition and physicochemical properties

Palygorskite and sepiolite are among the most Si-rich clay minerals stable at earth-surface conditions.

The composition of palygorskite is rather variable and comparable to that of smectite. The ideal structure corresponds to the chemical formula $\text{Si}_8\text{Mg}_5\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$. Because of isomorphous substitutions, however, this chemical formula rarely applies. Isomorphous substitution of Al for Si in the tetrahedra is very limited in both minerals. Tetrahedral occupancy for palygorskite ranges from $(\text{Si}_{7.88}\text{Al}_{0.12})$ to $(\text{Si}_{7.34}\text{Al}_{0.66})$. The sum of octahedral cations lies between 3.76 and 4.64, with a mean value of 4.00, indicating that the mineral

should be classed as dioctahedral (Newman & Brown, 1987). Al and Fe replace Mg in the octahedral sites. Fe and, to a less extent, Mg tend to occupy edge positions in palygorskite (Singer, 1977), whereas the interior positions are occupied predominantly by the smaller Al ion. Octahedral Mg is two to four times more abundant than in montmorillonite. Al fills 28 to 59 % of the occupied octahedral sites.

The ideal structural formula of sepiolite is $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$. Substitution of tetrahedral Si by Al or Fe is minor. Mg content ranges from 210 to 250 g kg^{-1} , and it fills 90 to 100 % of the octahedral positions. All octahedral sites are occupied; thus, sepiolites are truly trioctahedral minerals.

Both palygorskite and sepiolite usually contain small but variable amounts of Ca^{2+} , K^+ and Mn. K very probably is due to illite impurities. By carrying out chemical analyses on individual clay-sized palygorskite particles, Paquet et al. (1987), using an energy-dispersive spectrometer, were able to avoid contamination by smectite. The composition of a large number of particles suggests that the octahedral composition fields of smectite and the fibrous clays partly overlap. While Mg is the most common octahedral ion in sepiolites, other elements have been reported to be accommodated there (e.g., Fe, Ni, Mn, Na). For example, xylotile is a Fe-rich sepiolite that can have up to 9 % of the tetrahedral sites and 39 % of the occupied octahedral sites filled with Fe^{3+} (Newman & Brown, 1987). The composition of soil palygorskites apparently differs somewhat from that reported for palygorskite deposits. Since soil clays composed monominerally of either palygorskite or sepiolite are rare, this observation is difficult to confirm. Cation-exchange capacities of relatively pure palygorskite samples range from 5 to $30 \text{ cmol}_c \text{ kg}^{-1}$ and are primarily due to charge deficits in the tetrahedra. Higher values reported in the literature must be attributed to impurities, most commonly smectite. Reported exchange capacities for sepiolites range from 20 to $45 \text{ cmol}_c \text{ kg}^{-1}$ (Weaver & Pollard, 1973).

The total surface area of palygorskite and sepiolite computed from structural models is about 8 to $9 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$, including the surfaces of the channels (Serna & Van Scoyoc, 1979). The theoretical values far exceed experimental determinations because of the presence of wedge-shaped capillaries and tunnels that are not available for adsorption. The available surface area depends strongly on the nature (size, shape, and polarity) of the molecules used as sorbate. Nitrogen sorption reaches equilibrium rapidly, suggesting that N_2 molecules do not penetrate significantly into the intracrystalline tunnels. Particle size and surface topographic characteristics determine the extent of N_2 adsorption, and thus, values of the surface area measured by this method reflect the above characteristics (Serratos, 1979).

Nitrogen surface areas calculated by the Brunauer-Emmett-Teller (BET) adsorption isotherm method first increase as adsorbed H_2O and zeolitic H_2O are eliminated by outgassing, and then decrease at the temperature at which half the coordination H_2O is eliminated and crystal folding occurs. Beyond this point, the surface area remains constant. Prior to folding, N_2 surface areas of palygorskites range from 1.4 to $1.9 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$, whereas those of sepiolite vary from 2.3 to $3.8 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$ (Serratos, 1979). In palygorskite, coordination H_2O is more easily lost, and consequently, folding occurs at lower temperatures. Maximum and minimum surface areas and transition temperatures vary widely among different samples, probably as a result of differences in particle size distribution and crystal imperfections (Serratos, 1979).

Analysis of N_2 sorption data permit calculation of the fraction of specific surface area that corresponds to micropores (width of 1.6 to 2.0 nm or less) and that corresponds to pores of radius $>1.5 \text{ nm}$. Prior to folding, as much as 60 to 70% of the surface area in both palygorskite

and sepiolite corresponds to micropores. Most of the micropores disappear at the temperature at which folding is completed (i.e., 300-450°C). The BET surface area of sepiolite from Amboseli, Tanzania, was found to be $3.16 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$ using N_2 adsorption (at -197°C) and $2.12 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$ with ethanol vapor adsorption (at 25°C, assuming a molecular cross-sectional area of 2.5 nm), indicating a possible greater penetration of pores and channels by N_2 than by ethanol vapor under these conditions. The pore-size distribution revealed that approximately 55 % of the surface area measured by N_2 adsorption was contributed by micropores.

Cation exchange capacities of relatively pure palygorskite samples range from 5 to 30 $\text{cmol}_c \text{ kg}^{-1}$ and are primarily due to charge deficits in the tetrahedra. Higher values reported in the literature must be attributed to impurities, most commonly smectite. Reported exchange capacities for sepiolites range from 20 to 45 $\text{cmol}_c \text{ kg}^{-1}$ (Weaver & Pollard, 1973).

Occurrence, distribution and formation

A. Abundance and distribution

Palygorskite- and sepiolite-containing soils occur almost exclusively in soils with xeric, ustic and aridic moisture regimes in climates where potential evapotranspiration greatly exceeds precipitation. While most of these soils have ustic to xeric moisture regimes, some are more moist, the extra moisture being associated with shallow ground water or surface bodies of water such as in marshes. In these latter cases, the water is saline in varying degrees. Both palygorskite and sepiolite occur not only in soils *senso stricto* but also in surface features that are at least partly attributed to pedogenic processes, such as calcretes. Also, some paleosols contain palygorskite. Palygorskite in modern soils is particularly common in Northern Africa and the Near and Middle East. Some occurrences have been reported from South Africa. Palygorskite seems to be quite common in Australia also. Many occurrences have been reported from the U.S.A. Southwest, and some from Central America. Palygorskite is rare in Europe, the Far East and South America. Sepiolite in soils has been reported from only a few localities. Both clay minerals occur in sedimentary rocks and deposits.

B. Formation

1. Equilibrium constants

The equilibrium constant of a Mg-rich Australian palygorskite has been determined by a dissolution method, and the standard free energy of formation (ΔG_f°) was calculated to be -9482 kJ mol^{-1} , or -9466.38 kJ mol^{-1} if a correction of 14.7 kJ mol^{-1} is made for the ΔG_f° of Al-containing species (Singer & Norrish, 1974). According to the diagram constructed by Weaver & Beck (1977), palygorskite is stable only at relatively high Si and Mg activities and alkaline pH. Using acid-dissolution data, the free energy of formation for an Al-rich Australian palygorskite was estimated at -9584.2 kJ mol^{-1} (Singer, 1977). Acid-dissolution data for the two Australian palygorskites indicate that both Fe and Mg are preferentially dissolved over Al, suggesting that the small Al ion is concentrated in the more interior positions, while the large Mg and Fe ions are situated in edge positions (Singer, 1977). Consequently, Mg- and Fe-rich palygorskites can be expected to have a lower stability compared to Al-rich varieties.

On the basis of a diagram constructed by Elprince (1979) and using soil saturation extracts data, Ducloux et al. (1995) showed that both smectite and palygorskite may be currently forming in an Aridisol from northern Mexico.

Wollast et al. (1968) calculated a $\Delta G_f^\circ = -7569.6 \pm 4.20 \text{ kJ mol}^{-1}$ for a dehydrated sepiolite precipitate in equilibrium with experimentally obtained sea water, and a $\Delta G_f^\circ = -9232.66 \text{ kJ mol}^{-1}$ for an ideal sepiolite of the theoretical composition $8\text{H}_2\text{O Mg}_8(\text{H}_2\text{O})_4(\text{OH})_4\text{Si}_{12}\text{O}_{30}$. The activity diagram constructed by these authors suggests that, while surface sea waters and most fresh waters are undersaturated with respect to sepiolite, some solutions from saline and alkaline lake environments would be favorable for sepiolite formation. Stoessell (1988) obtained $\Delta G_f^\circ = -9248.68 \text{ kJ mol}^{-1}$ for a sepiolite from Amboseli, Kenya.

2. Synthesis

No reproducible synthesis of palygorskite has yet been reported in the literature. By dissolution of forsterite in solutions of Al and Si at pH 6.1 to 9.05, La Iglesia (1977) obtained crystalline precipitates that were identified by XRD and transmission electron microscopy (TEM) as palygorskite. In contrast to palygorskite, sepiolite has been obtained repeatedly by synthesis. An extensive discussion on the synthesis and stability of both palygorskite and sepiolite is given by Jones and Galan (1988).

Environment of occurrence

From the activity diagrams and equilibrium conditions outlined above, it is evident that both palygorskite and sepiolite require alkaline conditions and high activities of Si and Mg in solution for stability. Palygorskite also requires an appropriate input of Al (and Fe). Even at $\text{pSi} = 2.6$ - the saturation solubility of amorphous Si-palygorskite will not form below a pH of 5.9, and even then a pMg of 2 would be required to keep it stable. At a pSi of 3.6, which is close to the range encountered in normal soils, palygorskite would not be stable under a pH of 7.7 at high Mg concentrations ($\text{pMg} = 2$) or under 9 at low Mg concentrations ($\text{pMg} = 4$) (Singer & Norrish, 1974). For sepiolite stability, Mg activities have to be even higher. These requirements control palygorskite and sepiolite distributions in space and time. Palygorskite occurs in marine, lacustrine, and soil environments. Limited occurrences also are associated with hydrothermal activity, in both marine and continental environments. Sepiolite occurs under similar conditions, but is extremely rare in the soil.

1. Marine environment

Palygorskite and sepiolite occurrences in the marine environment have been reviewed by Singer (1979) and Kastner (1981), and more recently by Weaver (1984). In marine sediments, those palygorskite and sepiolite deposits that are not detrital have formed either by precipitation from solution or by transformation of precursor minerals. Ideally, sea water should have a lower-than-normal salinity (schizohalynic) and a higher-than-normal temperature for palygorskite-sepiolite formation. Ionic strength affects Si solubility, and the higher temperature is expected to increase pH (due to increased photosynthesis) and silica solubility. Thus, favored sites for palygorskite or sepiolite formation are peri-marine, shallow-water environments adjacent to land masses undergoing intensive desiccation by weathering (Weaver, 1984). A climate favorable to intensive evaporation and tectonic calm, thereby

preventing the arrival of large masses of detrital material, is a necessary supporting condition. The principal sources of soluble Si are siliceous sediments bearing porcellanite, opal-cristobalite-tridymite, volcanic ash, and clay minerals such as smectite. Organisms such as diatoms and radiolaria also may supply the required silica. Magnesium-rich smectite, basic volcanic glass, and interstitial H₂O have been suggested as sources of Mg. With the limitations noted above, the chemical composition of sea water is reported to satisfy the conditions for palygorskite-sepiolite genesis.

Palygorskite contains, in addition to Si and Mg, significant amounts of Al. The activity of Al in normal sea water is very low, on the order of 10⁻⁶ to 10⁻⁷ mol L⁻¹, and should limit palygorskite formation. Thus, a smectite-to-palygorskite transformation, whereby the required Al is supplied by smectite, is thought by some to be the principal formation process for marine palygorskite (Weaver & Beck, 1977; Weaver, 1984; Tazaki et al., 1987). Palygorskite should form from smectite at a pSi of 4.29, which is close to that of normal sea water at pSi = 4.7. A short-range dissolution and precipitation process is proposed.

An exclusive peri-marine environment of formation for palygorskite and sepiolite is disputed by some researchers who claim that these minerals also can form in deep sea water of normal salinity. In particular, it is proposed that the solution chemistry requirements for formation can be satisfied in the interstitial H₂O of marine sediments at normal temperatures (Couture, 1977). Interstitial solutions in contact with altering basement rocks may actually be oversaturated with respect to both palygorskite and sepiolite, particularly when some hydrothermal activity is involved.

Palygorskite and sepiolite authigenesis by precipitation from hydrothermally affected solutions has been suggested by Bonatti and Joensuu (1968) for occurrences in the Atlantic Ocean. Evidence of hydrothermal activity was obtained only a few kilometers from the sampling site.

Detrital palygorskite and sepiolite are widespread in Late Tertiary sediments of the northwestern Indian Ocean, Gulf of Aden, Red Sea, Gulf of Persia and Mediterranean Sea (Callen, 1984). Many deep-sea occurrences in the western and eastern Atlantic Ocean also are probably detrital. For other reported occurrences, such as in the Central and Western Pacific, and in the Indian Ocean, the detrital origin is not certain, and these may represent authigenic formations. Both palygorskite and sepiolite are rare in recent marine sediments, present in younger than Eocene sediments, and more common in Eocene and older sediments.

2. Lacustrine environment

Both sepiolite and palygorskite are known to occur in lacustrine environments of semiarid to arid regions. These occurrences are associated with aquatic conditions characterized by alkaline solutions with high activities of Si and Mg. Such environments may be created by various combinations of factors.

The most common environmental setting for lacustrine palygorskite and sepiolite authigenesis are playa deposits, ancient lacustrine terraces, or closed-basin deposits of other types. The high Mg and Si activities in these closed catchments are attributed to the concentration of groundwater solutions by evaporation close to the surface, or to cyclic inundations and subsequent concentration of solutions by evaporation. The fibrous clay minerals, therefore always occur in close association with a large variety of evaporates such as carbonates (primarily dolomite), sulfates (mainly gypsum), halite, thenardite, and chert. Often there also is an association with Mg-rich layer silicates such as saponite, talc, kerolite and stevensite.

Both direct precipitation from solution and solid-state transformation of precursor minerals, such as saponite, have been proposed as formation mechanisms.

Volcanic ash is a most commonly cited source for Si and Mg in lacustrine waters. Silicon, Mg, and Al also may be derived in some cases by the weathering of basic rocks surrounding the depositional basin (Galan & Castillo, 1984; Hay & Stoessel, 1984). Availability of Al appears to be the controlling factor determining the formation of palygorskite or sepiolite.

3. Atmospheric environment

Palygorskite and sepiolite may form under continental-atmospheric conditions as meteoric alteration products of rock and as products of pedogenic processes in soils. Sometimes the former occurs under normal atmospheric conditions; frequently, however, some hydrothermal activity is involved.

a. Rock alteration environment. Palygorskite and sepiolite may form by pseudomorphic replacement of various primary minerals, mainly those exhibiting a chain structure. For example, Longchambon (1935) found palygorskite as an alteration product of amphiboles and pyroxenes. Likewise, the relict amphibole cleavage in a palygorskite from the Ukraine revealed its origin by replacement of primary minerals (Ovcharenko, 1964).

Sepiolite also has been reported as an alteration product of basic igneous rocks formed by the interaction of descending meteoric water along cracks and fissures. For example, Imai and Otsuka (1984) describe sepiolite and xylolite occurring as veinlets in altered rocks of the Japanese serpentine belt.

More common are occurrences where some hydrothermal activity is involved, though there is not always conclusive evidence for that activity.

b. Pedogenic environment. The presence of palygorskite and sepiolite in soils has in the past been attributed exclusively to inheritance from the parent materials. This reasoning was based on two considerations:

- Both palygorskite and sepiolite have been shown to be rather unstable in the pedogenic environment. According to Paquet & Millot (1973), palygorskite weathers into smectite when the mean annual rainfall exceeds 300 mm.
- The sedimentary parent materials of many palygorskite-containing soils contain this mineral as well. Tertiary calcareous rocks in particular are rich in palygorskite.

Recent evidence, however, indicates that palygorskite and sepiolite also may be forming pedogenically. Direct evidence has been obtained by petrographic and micromorphological studies of mineral weathering in soils and soil calcic horizons. For example, Millot et al. (1977) noted the in situ formation of fibrous clay minerals by the weathering of primary aluminosilicates in calcareous crusts (calcrete) of Morocco. In calcretes of Mediterranean and tropical areas with a marked dry season, palygorskite has been shown to be stable (Paquet, 1983). Singer & Norrish (1974) described cutans composed of palygorskite coating soil peds from which palygorskite was absent in Australian soils. Delicate palygorskite fibers radiating perpendicularly into pore spaces of a New Mexico Aridisol, as revealed by SEM, led Monger & Daugherty (1991) to the conclusion that the mineral formed authigenically. Applying

similar considerations, Chahi et al. (1993) decided that palygorskite in Moroccan sediments was of authigenic origin.

Indirect evidence for the pedogenic formation of palygorskite includes the compatibility of the chemical composition of water extracts from aridic soils with the stability fields of palygorskite (Singer & Norrish, 1974; Elprince et al., 1979; Ducloux et al., 1995). The feasibility of pedogenic palygorskite formation also is suggested by recent studies of evaporative processes active in arid zones. Fibrous clay minerals were obtained by the experimental evaporation of natural ground waters on the surfaces of soil materials and the feasibility of palygorskite neof ormation was demonstrated by the evaporative concentration of irrigation waters in a Saudi Arabian oasis (Elprince, 1985).

Isotopic compositions of oxygen of palygorskites enriched in ^{18}O , and of oxygen and carbon of calcites associated with calcretes from Portugal and Morocco, show strong evidence that evaporation of meteoric water is an important process for the crystallization of these minerals. While in the uppermost calcrete sample oxygen isotopic equilibrium is roughly achieved between calcite and local meteoric waters (assuming a precipitation temperature between 25 and 35°C), for the other samples an enrichment in ^{18}O is to be noted, which suggests precipitation from evaporated solutions. In semiarid climates, palygorskite crystallizes when evaporation is maximum during the dry seasons, whereas calcite precipitates during more humid periods.

Pedogenic palygorskite has been proposed to form by precipitation from solution, or by alteration of precursor minerals such as smectite (Velde, 1985).

Certain threshold values of pH and Mg and Si concentration have been demonstrated where palygorskite was stable (Singer & Norrish, 1974). Suitable physical microenvironments relating to pore space also may be required. Under specific pedological or geomorphological circumstances, the required concentrations of Mg and Si apparently can be attained: (i) in soils affected by rising ground water and submitted to conditions of strong and continuous evaporation; or (ii) in soils or sediments with distinct and sharp textural transitions. Water moving in the soil, when passing from finer to coarser textured horizons, is likely to accumulate at the boundary in order to attain the high pressure needed to fill the larger pores. These boundary horizons therefore are likely to remain saturated longer, even under arid conditions. Possible pedogenic palygorskite accumulations are associated with these boundary layers.

Where palygorskite coexists with secondary dolomite, soluble Mg concentrations evidently have been adequate for palygorskite formation. In many other occurrences, the conversion of high-Mg calcite into low-Mg calcite during crust formation apparently mobilizes sufficient Mg into the pore water for palygorskite formation. In soils affected by rising ground water, such as in the saline sebkha soils described from eastern Saudi Arabia, concentrations in the soil solution may reach values as high as $p\text{Mg} = 0.69$ (Elprince et al., 1979). Precipitation of Ca in the form of gypsum also may be significant in raising the soluble Mg activity.

In specific pedogenic environments, such as calcretes and duricrusts, discrete secondary silica that occurs adjacent to authigenic palygorskite suggests that substantial soluble Si was available at some time. The soluble Si may have been released from silicate minerals or quartz by replacement with calcite.

4. Time of formation in soils

Little is known about the time required for palygorskite formation and accumulation in soils. The fact that palygorskite occurred in only two pedons out of about 20 analyzed for the desert project in southern New Mexico is attributed to the age factor (Monger & Daugherty, 1991). Palygorskite was found only in soils associated with the upper and lower La Mesa surfaces, which are some of the oldest in the Desert Project area, ranging from Early to Middle Pleistocene. Bachman & Machette (1977) found that palygorskite is progressively more abundant in older soils in the Albuquerque, NM area, so that palygorskite is the predominant clay mineral in soils older than 300,000 years. Monger and Daugherty (1991) suggest that this relationship may be related to the time required to accumulate Mg and indurate sediments to the extent that calcite begins replacing silicate grains and releasing Si and Al into the soil solution. Palygorskite was identified only in the petrocalcic horizons of mid-Pleistocene age of a soil formed on alluvium in a desert region of New Mexico. In carbonate soils on the Kyle Canyon Fan, Nevada, the greatest authigenic palygorskite accumulations were found in the oldest surface soils, dated at about 800,000 years, in amounts more than twice as much as in the youngest, late Pleistocene soils (Reheis et al., 1992). In appropriate environments, such as modern soils formed in flood plains, palygorskite formation may probably take place in less time (see below).

5. Landscapes of occurrence

From the activity diagrams and equilibrium conditions outlined above, it is evident that both palygorskite and sepiolite require alkaline conditions and high activities of Si and Mg in solution for stability. Palygorskite also requires an appropriate input of Al and Fe. For sepiolite stability, Mg activities have to be even higher.

While traces of palygorskite can be identified in a wide variety of soils, significant amounts of the pedogenically formed mineral commonly are associated with one of three situations:

- Modern soils that are or have been affected by fluctuating ground water
- Soil morphology that includes distinct and sharp textural transitions (this group includes many paleosols)
- Pedogenic features, not necessarily associated at present with soils, such as calcretes, crusts, and caliche.

The most common landscape associated with modern palygorskite-containing soils is that of flood plains or low terraces. Saline or alkaline ground water frequently is affecting soil formation, such as in the case of the sebkhas (flat, saline plains) of the most arid areas. Fine-textured calcareous, alluvial or aeolian sediments are common parent materials for these soils. Most of these soils are relatively young (Late Pleistocene-Holocene) soils, yet it seems that palygorskite formation becomes substantial only on somewhat older soils, such as those formed on low terraces. Palygorskite-containing soils invariably are calcareous throughout, mildly alkaline, and commonly highly saline. Soil pH values typically vary between 7.5 and 8. The most common clay minerals associated with pedogenic palygorskite are smectite, illite and interstratified illite-smectite.

Soils that contain sharp textural transitions sometimes contain pedogenic palygorskite. The palygorskite occurs adjacent to the textural transition, in the form of cutans (palygorskans) or

aggregates that fill voids. Occurrences of this type are typical for paleosols. Since they are paleosols, palygorskite formation does not necessarily reflect present climatic conditions. Most of these soils are non-saline or only slightly saline.

Pedogenic conditions leading to secondary carbonate accumulation and calcareous crust development also are frequently favorable for in situ palygorskite formation. A six-stage morphogenic scheme for the formation of calcretes containing palygorskite and sepiolite in the southwestern USA was proposed by Bachman & Machette (1977). According to Watts (1980), who has reviewed palygorskite occurrences in calcretes, the pedogenesis of this mineral, as well as that of sepiolite and dolomite in Kalahari calcretes, may be related to the release of Mg by high-Mg to low-Mg calcite transformations at high pH. An evaporitic origin for palygorskite identified in calcretes from the Negev, Israel was proposed by Verrecchia & Le Coustumer (1996). Both palygorskite and sepiolite were associated with the carbonates in B_K horizons of Aridisols formed on carbonate-free quartz sands in Namaqualand, South Africa (Singer et al., 1995). Petrocalcic horizons in some Aridisols of New Mexico contain palygorskite. Most of these soils are relatively old, Mid to Late Pleistocene in age.

Environmental Significance

A. Sorption properties and environmental implications of fibrous clay minerals

1. Active sorption centers

Three types of active sorption centers may be distinguished in palygorskite and sepiolite:

- Oxygen ions on the tetrahedral sheets of the ribbons behave as weak electron donors and display a weak interaction with sorbed species.
- Water molecules are coordinated to Mg ions at the edges of structural ribbons at the ratio of 2H₂O for each Mg²⁺.
- SiOH groups are associated in large numbers with terminal Si tetrahedra at the external surfaces; broken Si-O-Si bonds compensate their residual charge by accepting H⁺ or (OH)⁻ and become Si-OH groups.

2. Sorption properties

Zeolitic H₂O as well as H₂O adsorbed at the external surfaces of palygorskite and sepiolite are H-bonded to the H₂O coordinated to the edge Mg²⁺ ions, and also interact with the octahedral OH groups. Both zeolitic and coordinated H₂O molecules may be replaced by D₂O and NH₃, thus indicating that external and intracrystalline channels are accessible to small molecules of high polarity (Serna & Van Scoyoc, 1979). Short-chain primary alcohols (CH₃OH and C₂H₅OH) penetrate inside the channels and replace zeolitic H₂O. Initially the alcohols are H-bonded to coordinating H₂O molecules, but subsequently they replace part of the H₂O coordination by successive sorption and desorption. The sorption of alcohols of longer chain length and of acetone is confined to open channels at the external surface (Serna & Van Scoyoc, 1979). Soil-derived humic acid is mostly adsorbed on external surfaces of palygorskite and sepiolite, though some possibly also penetrates channels (Singer & Huang, 1989).

Sorption of nonpolar organic compounds is restricted to external surfaces and is strongly affected by the size and shape of the sorbate molecules. Sorption appears to be dependent on the degree of accommodation of the sorbate molecules into the channels of the external surface. Selectivity of sepiolite for nonpolar molecules differs from that of palygorskite, apparently as a consequence of differences in the tunnel width. In both minerals, selectivity is lost at outgassing temperatures above 200°C due to folding of the structure and collapse of the tunnels. Because of these properties, the fibrous clay minerals are being used in a wide range of industrial applications, that are partly environmentally related, such as oil and grease absorbents, pet litter, pesticides and fertilizers, drilling mud (Galan, 1996).

B. Environmental implications of sorption properties

Palygorskite and sepiolite exhibit large amounts of external Si-OH groups, and these may enter into covalent bonds with organic molecules forming organo-mineral derivatives. The organic molecules can be adsorbed either through the vapor phase or in solution with inert organic solvents. A variety of compounds can be obtained by grafting reactions on sepiolite through formation of Si-O-Si bonds when the mineral reacts with organo-chlorosilanes (Ruiz-Hitzky & Fripiat, 1976).

To produce similar compounds with palygorskite, the number of active Si-OH groups on the surface of the mineral usually is increased by pretreatments, including cohydrolysis. Organo-mineral derivatives of sepiolite and palygorskite are of great interest to industry, because they have the surface and reactive properties of the grafted organic molecules but preserve the mechanical properties of the mineral framework (Alvarez, 1984). The role of such compounds in soil environments is as yet unexplored.

Other organic molecules such as parathion can be adsorbed by palygorskite and sepiolite via H-bonds between the NO₂ group of the pesticide and the hydrogens in H₂O molecules of the hydration shell of adsorbed cations (Gerstl & Yaron, 1981). Bonding also can occur by direct interaction with the cation. Thermal pretreatment of the clay usually affects adsorption. Preheating to 105°C tends to increase adsorption by elimination of competing zeolitic H₂O. Preheating to 250°C results in structural changes that decrease parathion adsorption (Gerstl & Yaron, 1978).

For some applications, the adsorptive capacity of both palygorskite and sepiolite can be increased by acid activation, which preferentially attacks the octahedral layers. Materials with an increased microporosity are obtained (Gonzalez et al., 1989; Vicente Rodriguez et al., 1994). These can be used for bleaching and adsorption of oils and can be applied for the removal of oil spills on soils.

Pyridine sorption on palygorskite and sepiolite has been shown to take place in two well-defined steps: (i) first as monolayer adsorption on external surfaces, with the pyridine molecules lying with their planes parallel to the (001) plane of the clay crystals and (ii) then as a bilayer coverage. Pyridine molecules are associated by H-bonding to the external Si-OH groups and also to H₂O coordinating the terminal Mg²⁺ ions at the edges of the structure ribbons (Ruiz-Hitzky et al., 1985; Blanco et al., 1988). Even fatty acids, such as stearic acid, can be adsorbed by both palygorskite and sepiolite (Yariv & Heller-Kallai, 1984).

Both palygorskite and sepiolite were found to be useful in mercury elimination from gas streams (Daza et al., 1991).

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INTERPRETATION OF K-AR DATES OF ILLITES AIDED BY TECHNIQUES OF QUANTIFYING CLAYS AND THEIR PROPERTIES

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K-Ar dates of illitic clays from sedimentary rocks may be "mixed ages", i.e., may be ages that are intermediate between the ages of end-member components. Two phenomena that may cause mixed ages are: (1) long-lasting reaction during the burial illitization of smectite, and (2) physical mixing of detrital and diagenetic components.

The first type of the mixed age can be modelled using thermal history data and fractions of illite crystallized at different stages of the thermal history. The fractions of illite can be obtained by modelling of the illitization path with the use of the computer program GALOPER, which simulates the evolution of crystal size in the course of illite nucleation and growth. Results of such modelling indicate that if burial is long-lasting, the resulting mixed age strongly depends on the burial history. Distribution of K-Ar ages with respect to crystal thickness is indicative of the illitization mechanism and the duration of the reaction.

The challenge offered by the second type of mixed ages is in extracting pure end-member ages of the detrital and the diagenetic component. This is done by the extrapolation of K-Ar data of subsamples, containing the two components in different proportions (grain size fractions). Any type of extrapolation requires a possibly accurate measurement of the proportion of the two components. If the detrital component is exclusively $2M_1$, the polytype ratio can be applied. A feasible alternative, insensitive to polytypes, is a decomposition of illite crystal size distribution into detrital and diagenetic component. This can be attempted using data from MudMaster, a computer program measuring crystal size distributions of clay minerals by Bertaut-Warren-Averbach analysis of 001 XRD reflections.

Dating of artificial mixtures confirms a non-linear relation between mixed ages and the proportions of the components, which makes the extrapolation technique based on K-Ar dates much more difficult to apply. It is advantageous than to apply the extrapolation technique to K and radiogenic Ar separately, because these values offer a linear relation with the proportions of the components. Both ages can be calculated from the extrapolated K and Ar values. This technique can be applied, if all non-illitic components of the sample have been quantified.

A quantitative XRD technique has been designed, which applies an internal standard (ZnO), random preparations, and individual selected reflections, least sensitive to structural and chemical variations of minerals (060 reflections for clays). The technique has been automated recently using evolutionary programming. It keeps the main advantage of the original method: the use of "trusted" reflections, but avoids a disadvantage of operator-biased and time consuming manual decomposition of the overlapping peaks. A promising complementary FTIR technique uses KBr pellets and also applies evolutionary programming to cope with the problem of background, of the scaling of reference spectra, and of fitting the spectra of mixtures with the spectra of pure standards. The FTIR technique is particularly accurate in quantifying kaolinite and quartz admixtures.