

PALYGORSKITE SEPARATION FROM DODECYLAMMONIUM-TREATED CLAYS

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Abstract—Three methods were investigated to separate palygorskite from mixtures of clay minerals in soils and sediments. The methods were based on the hydrophobic properties of a dodecylammonium-smectite complex and used the $<0.2\text{-}\mu\text{m}$ fractions of reference palygorskites that contained smectite and sepiolite impurities. Palygorskite was separated from dodecylammonium-clay complexes by: (1) selective dispersion of palygorskite in H_2O ; (2) selective extraction of palygorskite by a water:decanol phase separation; and (3) selective extraction of palygorskite by a water:nitrobenzene phase separation. Whereas all three methods resulted in palygorskite separation, selective dispersion was the simplest and employed the more desirable reagents. Small amounts of relatively pure palygorskite in the $<0.2\text{-}\mu\text{m}$ fractions were concentrated from palygorskite-containing clays from Texas, Saudi Arabia, and Libya as shown by X-ray powder diffraction and transmission electron microscopy data. A sepiolite impurity in the Georgia palygorskite was concentrated with the palygorskite. Hydrolysis of the dodecylammonium-smectite complex was suggested by the decrease in d-spacing of some samples after the extensive washing necessary for dispersion. An appreciable amount of the fibrous mineral was intimately associated with layer silicates and could not be separated.

Key Words—Dodecylammonium smectite, Hydrophobic properties, Mineral separation, Palygorskite, Sepiolite, Smectite.

INTRODUCTION

Palygorskite is commonly associated with smectite and sepiolite in soils and sediments (Zelazny and Calhoun, 1977; Galan and Ferrero, 1982). Its characterization would be greatly improved, however, if it could be separated from such polymineralic assemblages. Inasmuch as many organic cations are capable of displacing inorganic interlayer cations in smectites (Greenland, 1965; Mortland, 1970; Mackintosh *et al.*, 1971; Theng, 1974), thereby producing complexes that flocculate in water and swell in certain organic solvents (Grim, 1967), it is reasonable that palygorskite can be separated from smectite by treating a mixture of the two minerals with a suitable organic cation followed by a differential flocculation in water of the organic-interlayered smectite and the fibrous clay. The present paper describes such a separation procedure based on the differential flocculation of smectite and by a phase separation between an organic liquid (nitrobenzene or decanol) and water. Because maximum swelling in organic solvents occurs when smectite is saturated with a material having an alkyl chain length of 12 (Jordan,

1949a, 1949b), a dodecylammonium cation was used to treat the clay.

MATERIALS AND METHODS

Sodium-saturated $<0.2\text{-}\mu\text{m}$ fractions of Florida and Georgia palygorskite were prepared by saturating bulk samples with 1 N NaCl and then washing them to remove excess salts. The $<2\text{-}\mu\text{m}$ clay fractions of a Harad soil from Saudi Arabia, the Cca horizon of the Miles soil series from northwest Texas, and the C horizon of the Zuwaylah soil series from Libya were prepared in the same manner. The soil samples had been previously freed of carbonates with pH 5, 1 N NaOAc dialysis (Grossman and Millet, 1961). All soil clays contained appreciable amounts of palygorskite, smectite, and kaolinite. The $<0.2\text{-}\mu\text{m}$ fractions of the soil clays were also separated and Mg-saturated as control specimens for X-ray powder diffraction (XRD) analysis.

Saturation with dodecylammonium ions

Na-saturated samples were saturated with dodecylammonium ions as follows: 20 ml of 0.2 N dodecylammonium hydrochloride was added to duplicate 500-mg samples of clay. The mixtures were heated for 24 hr at 65°C , and the supernatant was decanted. The procedure was repeated twice. The samples were then

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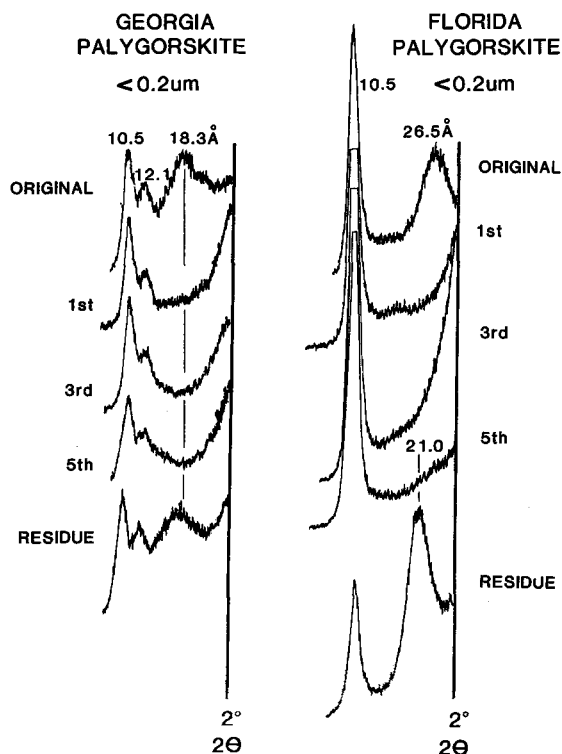


Figure 1. X-ray powder diffractograms of original, water-dispersed, and residual samples of dodecylammonium-saturated reference palygorskites.

freed of interstitial dodecylammonium hydrochloride solution by washing them 5 times with 10 ml of ethanol, and 4 times with 50% ethanol in water. The samples were air dried at room temperature.

Selective dispersion of clay in water

Thirty milliliters of deionized water was mixed with each sample, and the mixture was centrifuged for 27 min at 2500 rpm except as noted. The centrifuge time was selected to throw down all particles $>0.2\text{-}\mu\text{m}$ equivalent spherical diameter. The washing procedure was repeated 5–7 times until the supernatant was clear. The dispersed phase that remained in suspension after centrifugation was collected on $0.2\text{-}\mu\text{m}$ Millipore filters for XRD analysis after air drying. Separate samples of the dispersed phase were treated with 1 N MgCl_2 at 65°C and air dried for XRD after removal of the excess salts. The residue left after collection of the dispersed phase also was collected for XRD.

A Norelco X-ray diffractometer with a proportional counter detector, $\text{CuK}\alpha$ radiation, and a graphite monochromator was used. Subsamples of the dispersed and residual phases were air dried overnight on Formvar and carbon-coated, 300-mesh grids and examined with a Hitachi HU-11E transmission electron microscope (TEM) at an accelerating voltage of 75 kV.

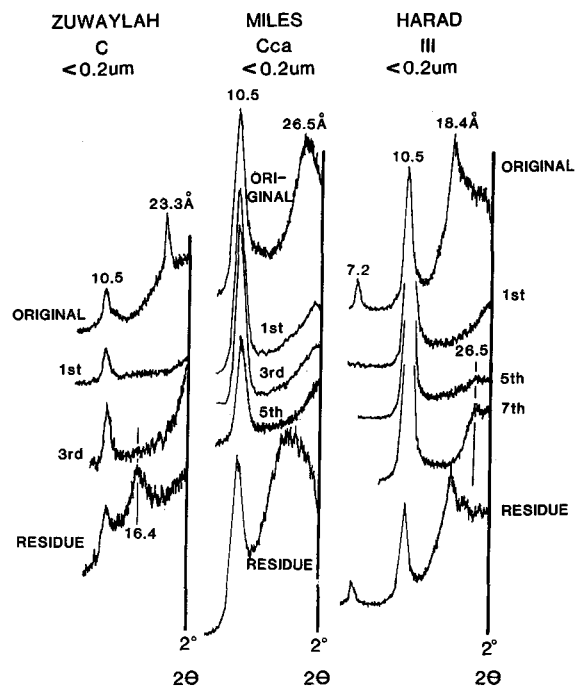


Figure 2. X-ray powder diffractograms of the original, water-dispersed, and residual soil clays saturated with dodecylammonium ions. Dispersed phases were collected after 27 min at 2500 rpm, except for the seventh dispersion of the Harad soil clay which was collected after 10 min centrifugation.

Water:organic phase separation

After saturation with dodecylammonium ions, samples were transferred to 250-ml Erlenmeyer flasks with 50 ml of nitrobenzene or decanol, 100 ml of deionized H_2O was added, and the mixture was stirred with a magnetic stirrer for 4 hr. The samples were then transferred to 250-ml separatory funnels and allowed to stand for one-half hour. The organic and water phases were collected in separate flasks, and the clays were washed with ethanol for XRD. The aqueous phase formed the lower layer in the decanol-water mixture and the upper layer in the nitrobenzene-water mixture. The material concentrated in the decanol layer was washed with ethanol, suspended in H_2O , mixed for 3 min with an ultrasonic probe (Heat Systems-Ultrasonics, Inc., Model 350) with an output of 5 on a duty cycle of 40% and re-treated with dodecylammonium ions. The dry residue was subjected again to a water-decanol separation as above, to separate more of the palygorskite.

RESULTS AND DISCUSSION

Palygorskite dispersion in water

Relatively pure palygorskite was obtained from the two dodecylammonium-treated reference samples (Figure 1). Palygorskite was concentrated in the dis-

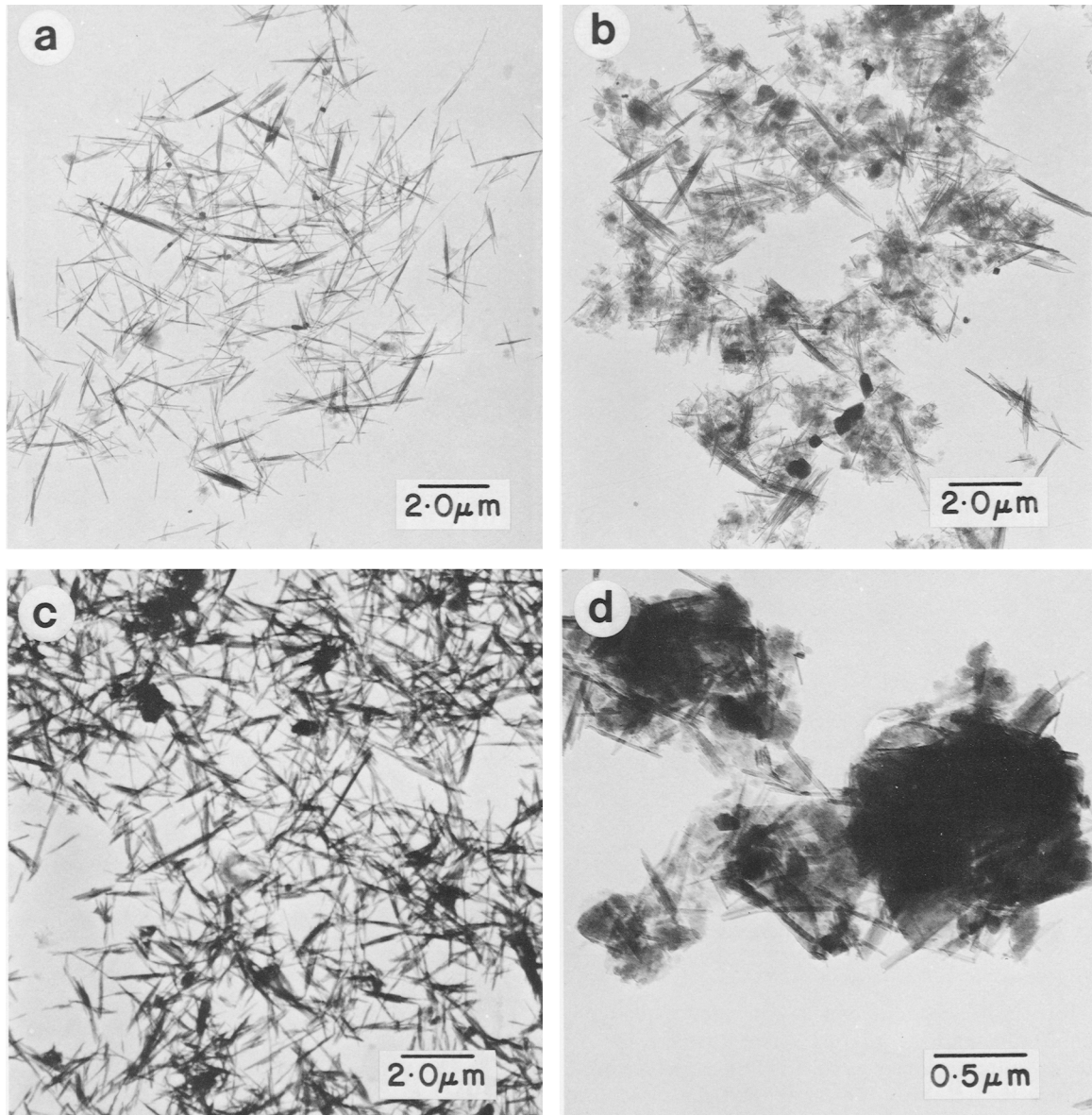


Figure 3. Transmission electron micrographs of clays dispersed in water from clay-dodecylammonium complexes: (a) $<0.2\text{-}\mu\text{m}$ Georgia palygorskite; (b) nondispersed residue of the Georgia palygorskite; (c) dispersed $<0.2\text{-}\mu\text{m}$ Harad soil clay; and (d) aggregated palygorskite and smectite residue of the Harad soil clay.

persed phases for the seven washes that were made. After the seventh wash, further washing did not produce additional dispersion. The depth of the trough on the high-angle side of the $10.5\text{-}\text{\AA}$ XRD palygorskite peak was greater for the latter washings, suggesting a purer palygorskite or palygorskite + sepiolite (12.1 \AA) fraction. The first and second (not shown) washes of the Florida and Georgia samples had a low-intensity peak near 18 \AA suggesting the presence of a small amount of smectite. Sepiolite in the Georgia sample was concentrated along with the palygorskite. Much of

the palygorskite remained in the residue with the smectite. The Georgia palygorskite was not as completely separated from the smectite as was the Florida material, suggesting that palygorskite associated with lower charged smectite is more difficult to separate. The Mg-saturated samples of the dispersed phases revealed the same trends in fibrous mineral to smectite XRD peak intensities (not shown) as those displayed in Figure 1.

Smectite impurities associated with the reference palygorskites had different layer-charge distributions as indicated by their XRD spacings. The $18\text{-}\text{\AA}$ spacing

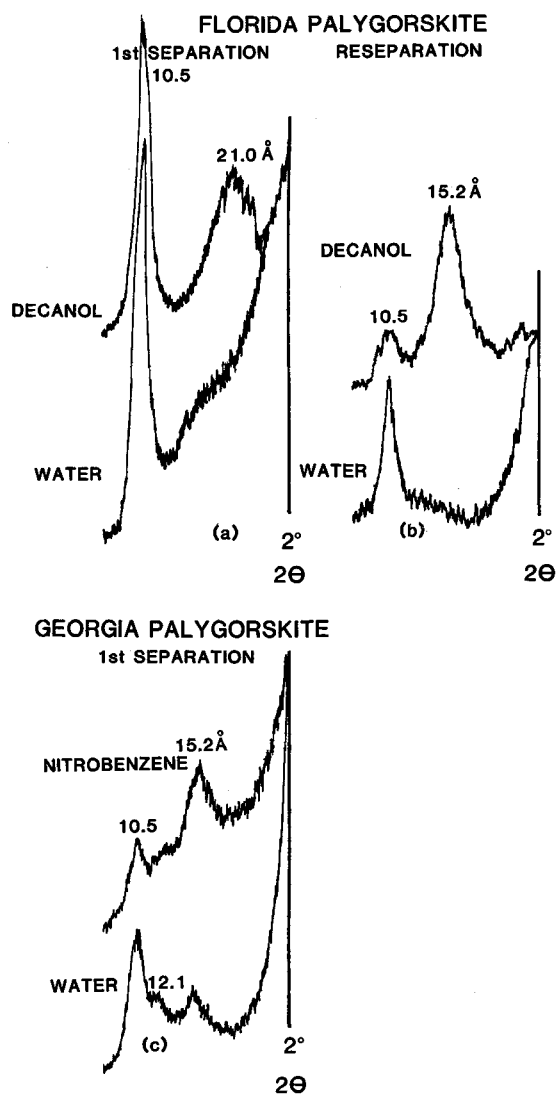


Figure 4. X-ray powder diffractograms of $<0.2\text{-}\mu\text{m}$ dodecylammonium-clay complex collected from organic and aqueous phases after extraction with decanol: water solutions.

of the dodecylammonium-saturated smectite from the Georgia sample indicates that it had a lower layer charge than the 23–26-Å smectite from the Florida sample (Lagaly and Weiss, 1969, 1975).

The first water-dispersion of the dodecylammonium-soil clay complexes contained relatively pure palygorskite from the Harad, Miles, and Zuwaylah soil clays (Figure 2). Whereas the first dispersion of the Harad clay was relatively pure, the fifth dispersion had a 26.5-Å XRD peak indicative of the presence of a high-charge smectite. The seventh dispersion of the Harad clay (centrifuged for only 10 min) contained more smectite than any of the other dispersions, probably because the centrifuge time was not long enough to throw down undispersed aggregates of smectite and

palygorskite. It is not known why the fifth and seventh dispersions of the Harad soil yielded 26.5-Å spacings indicative of a high-charge smectite unless some of the coarser particles were swept off the top of the centrifuge cake during decantation. The major portion of the smectite in the Harad sample had a low charge density (i.e., an 18-Å spacing).

The Harad soil clay contained the lowest and the Miles soil clay the highest charge smectite, as shown by the lower d-spacings of the dodecylammonium-clay complexes of the former (Figure 2). The three soil clays, thus, contained a low-, medium-, and high-charge smectite, according to the criteria of Lagaly and Weiss (1975). The higher charge smectite exhibited a shift to a lower 001 spacing after extensive washing (Figure 2). Shifting of 001 peaks was also reported by Weiss (1963) for pure alkylammonium-saturated smectites due to the hydrolysis and removal of alkylammonium cations. After about 5 washings white material was noted floating on the supernatant which may have been organic material resulting from the hydrolysis of the alkylammonium clay to alkylamine + H-clay. The white floating material contained no layer silicates as detected by XRD.

TEMs of the dispersed and residual material from the Georgia palygorskite and the cation-exchange capacity of the Harad soils clay show the relative purity of the dispersed palygorskite and the heterogeneity of the residue (Figure 3). The fibers in the dispersed material were well separated, whereas palygorskite in the residues commonly occurred in aggregates of fibers and layer silicates. Palygorskite from the Harad soil clay was composed of thin needles with relatively sharp ends. The Harad sample was almost free of platy contaminants. Cation-exchange capacities of 10 to 17 meq per 100 g suggest that palygorskite-smectite mixtures purified from the soil clays by the proposed selective flocculation method contained about 10% smectite and 90% palygorskite (Abudelgawad *et al.*, 1986).

Palygorskite dispersion in water by decanol or nitrobenzene

The separation of smectite from palygorskite was based upon the swelling of dodecylammonium-smectite in polar organic liquids. The behavior of two dodecylammonium-saturated reference smectites (montmorillonite, Gonzales, Texas, cation-exchange capacity, 85 meq/100 g; bentonite, Camargo, Oklahoma, cation-exchange capacity, 140 meq/100 g) was observed in nitrobenzene:water and decanol:water systems. The smectites were completely separated into the polar organic phases. The Georgia and Florida palygorskites were subjected to the same treatments. The decanol layer contained a mixture of smectite and palygorskite, and the water layer contained predominantly palygorskite (Figure 4a). Clays from the water layers were also Mg-saturated for XRD (not shown); no smectite peaks

were detected. After the material in the decanol layer was resubjected to the decanol: water phase separation, the water layer contained primarily palygorskite and the decanol layer contained more smectite than palygorskite (Figure 4b). In the nitrobenzene: water separation of the Georgia palygorskite, a relative concentration of smectite occurred in the nitrobenzene layer, and sepiolite + palygorskite were concentrated in the water phase (Figure 4c). Because nitrobenzene is toxic and decanol is ill smelling, and because neither yields superior results to the water dispersion method, water dispersion is recommended to concentrate palygorskite from clays.

REFERENCES

- Abudelgawad, G., Ahlrichs, J. L., and Dixon, J. B. (1986) Palygorskite and sepiolite separated from soil clays by dodecylamine hydrochloride: *Soil Sci.* (in press).
- Galan, E. and Ferrero, A. (1982) Palygorskite-sepiolite clays of Lebrija, southern Spain: *Clays & Clay Minerals* **30**, 191–199.
- Greenland, D. J. (1965) Interaction between clays and organic compounds in soils. Part I. Mechanisms of interaction between clays and organic compounds: *Soils and Fertilizer* **28**, 415–425.
- Grim, R. E. (1967) *Clay Mineralogy*: 2nd ed., McGraw-Hill, New York, 596 pp.
- Grossman, R. B. and Millet, J. L. (1961) Carbonate removal from soils by a modification of the acetate buffered method: *Soil Sci. Soc. Amer. Proc.* **25**, 325–326.
- Jordan, J. W. (1949a) Alteration of the properties of bentonite by reaction with amines: *Mineral. Mag.* **29**, 598–605.
- Jordan, J. W. (1949b) Organophilic bentonite I. Swelling in organic liquids: *J. Phys. Colloid Chem.* **53**, 294–306.
- Lagaly, A. and Weiss, A. (1969) Determination of the layer charge in mica type layer silicates: in *Proc. Int. Clay Conf., Tokyo, 1969*, L. Heller, ed., Israel Univ. Press, Jerusalem, 61–80.
- Lagaly, A. and Weiss, A. (1975) The layer charge of smectite layer silicates: in *Proc. Int. Clay Conf., Mexico City, 1975*, S. W. Bailey, ed., Applied Publishing Ltd., Wilmette, Illinois, 157–172.
- Mackintosh, E. E., Lewis, D. A., and Greenland, D. J. (1971) Dodecylammonium-mica complexes. I. Factors affecting the exchange reactions: *Clays & Clay Minerals* **19**, 209–218.
- Mortland, M. M. (1970) Clay-organo complexes and interaction: *Advan. Agron.* **22**, 75–117.
- Theng, B. K. G. (1974) *The Chemistry of Clay-Organic Reaction*: Wiley, New York, 343 pp.
- Weiss, A. (1963) Organic derivative of mica-type layer silicates: *Angew. Chem.* **2**, 134–143.
- Zelazny, L. W. and Calhoun, F. G. (1977) Palygorskite, (attapulgitite), sepiolite, talc, pyrophyllite, and zeolites: in *Minerals in Soil Environments*, J. B. Dixon and S. B. Weed, eds., Soil Science Society of America, Madison, Wisconsin, 435–470.

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