

THE OCCURRENCE OF SEPIOLITE AND ATTAPULGITE IN THE CALCAREOUS ZONE OF A SOIL NEAR LAS CRUCES, NEW MEXICO

by

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ABSTRACT

SEPIOLITE and attapulgite were identified by X-ray diffraction, elemental, and thermal analyses in the calcareous zone of a soil formed on a relict basin-fill plain in Dona Ana County, New Mexico. Sepiolite occurs in the lower part of the zone of calcium carbonate accumulation; attapulgite occurs above, in, and below the sepiolite zone.

The sepiolite was observed as whitish aggregates remaining after the carbonate was dissolved with sodium acetate buffer (pH 5). Extended treatment with this buffer dissolved a significant amount of the sepiolite but did not appear to dissolve much attapulgite. Sepiolite was concentrated for analysis without significant solution by separating the <100 mesh material from the crushed soil, treating it with pH 5 buffer for a short time and separating the carbonate-free clay. The sepiolite is relatively high in aluminum compared to most sepiolites.

The sequence of dominant clay mineral with depth in the profile is montmorillonite, attapulgite, sepiolite, attapulgite, montmorillonite. No sepiolite or attapulgite was found above the calcareous zone; a little attapulgite was found at the base of the profile, which was not totally free of carbonates. Thin sections showed sepiolite and attapulgite occurring as aggregates, as coatings on mineral grains and as small fibers. The distribution of these minerals in the profile and the arrangement of the small fibers in the calcrete suggest that these minerals crystallized during the period of caliche formation.

As will be seen (Table 5) the sepiolite is present mainly in the nodular calcareous zone; the attapulgite, mainly in the blocky calcareous zone and in the transition zone below the calcareous zone (C6).

INTRODUCTION

THE SOIL profile under investigation (Soil Survey No. S61N.Mex-7-7) is one of many selected for a study of soils and landscapes in Dona Ana County, New Mexico, to be reported elsewhere. The soil is located on a relict basin-fill plain and has been described and illustrated (Soil No. 3, Gile, Peterson and Grossman, 1964, which is only two feet SE of "Profile No. 1", Gile, 1961. Although only one profile has been analyzed, soils with similar morphology occur extensively on the oldest geomorphic surface in the area. The landscape morphology of the area is described by Ruhe (1964).

A brief description of the soil is as follows:

The upper part of the solum is, for the most part, a reddish-brown loamy fine sand (noncalcareous). The calcareous zone begins at 19 in. and extends to a depth of 93 in. This zone is divided into five horizons (C1cam to C5ca), the calcium carbonate equivalent ranging from 89 per cent at the top to 41 per cent at the base. The carbonate at the top inch or less occurs in cemented laminar form. This layer is cemented to a massive or blocky layer underneath, which grades into a nodular layer. At the base of the calcareous zone, the cemented nodules occupy about 50 per cent of the volume of the soil. The calcareous zone grades into nearly noncalcareous sand (C7) at a depth of 107 in.

This profile was brought to the author's attention because of the persistence of an abundance of whitish aggregates in samples from the C4ca and C5ca horizons after the carbonate was all dissolved by several weeks treatment with pH 5.0 sodium acetate buffer using the method of Grossman and Millet (1961). This treatment is used routinely by the Soil Survey Laboratories as a preliminary step in the characterization of the noncalcareous components of calcareous soil samples.

The aggregates contain fine-grained, weakly birefringent crystalline material having refractive indices of about 1.52. Because the aggregates were suspected of being cemented with amorphous silica, they were referred to as "silica" aggregates. However, they did not disintegrate in sodium hydroxide unless a hot, concentrated solution was used.

X-ray spectrographic and diffraction analyses on ground samples of the untreated and buffer-treated whole soil were run. The high aggregate zone contained significantly more magnesium than the horizons both above and below this zone (Table 1) and magnesium remained significantly high in the buffer-treated residues to provide an indication of the presence of a magnesium component.

X-ray diffraction analyses of the untreated samples from the aggregate zone revealed the presence of a mineral having a diffraction maximum approximating 12.3 Å, which did not change with glycerol or with heat treatments up to 350°C. The X-ray diffraction traces of the buffer-treated samples in this zone gave a broadened 12.3 Å peak with a shoulder at about 10.8 Å, indicating some alteration of the sample by the buffer treatment. For this reason, only the untreated samples were used for the isolation of the mineral giving the 12 Å reflection.

X-ray diffraction analysis of the <325 mesh material from the buffer-treated samples showed that the mineral with the 12.3 Å spacing was more abundant in the finer material than in the coarser material. Some of the clay from crushed, untreated (calcareous) samples was dispersed for examination by repeatedly washing the crushed sample with water and agitating it in a centrifuge tube with a rubber plunger. Sufficient clay was dispersed by this treatment for X-ray spectrographic, diffraction, and thermal analyses.

X-ray diffraction traces of the clay (both oriented films and powder) extracted from the C4ca and C5ca horizons, the zone of heaviest aggregate

TABLE 1.—ELEMENTAL ANALYSIS OF THE WHOLE GROUND SOIL FROM PROFILE S61 N.MEX. 7-7 BY X-RAY SPECTROGRAPHY* AND IGNITION LOSS DETERMINATIONS (IN PER CENT, OVEN-DRY BASIS)

Oxide	Sample number and horizon						
	14979c A	14980c B21t	14981c B21t	14982c B22t	14983c B23tca	14984c C1cam (Whole)	14991c C1cam (Laminar)
SiO ₂	79.9	78.7	78.2	77.2	65.7	16.9	8.06
Al ₂ O ₃	8.84	9.35	9.82	9.82	9.10	2.13	1.34
Fe ₂ O ₃	2.81	2.97	2.98	3.05	2.60	0.65	0.56
TiO ₂	0.49	0.51	0.48	0.49	0.39	0.09	0.07
CaO	0.92	0.97	0.97	1.39	7.89	44.2	49.5
K ₂ O	2.59	2.62	2.63	2.64	2.11	0.48	0.25
MgO	0.44	0.38	0.48	0.49	0.76	0.64	0.32
Ign. loss	2.10	2.02	2.27	2.83	8.58	35.60	39.73
Total	98.1	97.5	97.8	97.9	97.1	100.7	99.8

Oxide	Sample number and horizon						
	14992c C1cam (Nonlaminar)	14985c C2cam	14986c C3cam	14987c C4ca	14988c C5ca	14989c C6	14990c C7
SiO ₂	19.1	29.6	36.4	41.9	46.4	74.9	81.0
Al ₂ O ₃	2.20	2.84	3.01	3.47	3.85	6.99	7.56
Fe ₂ O ₃	0.67	0.67	0.68	0.79	0.85	1.47	1.59
TiO ₂	0.08	0.11	0.11	0.13	0.13	0.27	0.28
CaO	42.1	34.9	28.7	25.3	21.9	6.22	2.51
K ₂ O	0.48	0.72	0.73	0.86	0.93	1.95	2.22
MgO	0.73	1.37	3.95	4.29	5.41	1.20	0.85
Ign loss	34.63	29.60	25.93	22.69	20.56	5.99	2.56
Total	100.0	99.8	99.5	99.3	99.9	99.0	98.6

* Samples were fused in LiBO₂ (1:5) and glass disks prepared for X-ray analysis. Matrix corrections were made (Vanden Heuvel, 1965).

accumulation, gave a sufficient number of reflections to identify sepiolite as the major constituent in addition to calcite. The identification was made by comparing the diffraction patterns with those of clay extracted in like manner from sepiolite from Vallecas, Spain, obtained from Ward's Natural Science Establishment and from data in the literature (Brown, 1961, ch. 8).

For the elemental analyses, CO₂ and thermal analyses were carried out in addition to X-ray spectrographic analyses, so that a carbonate and water of composition allocation could be made. From these data, it was calculated that the number of moles of CO₂ in each sample is practically equal to the number of moles of CaO in each sample. This confirms the X-ray evidence

that calcite is the only carbonate mineral present. When CaCO_3 was subtracted from the elemental analyses, the compositions of the remainder of the clay fractions from C4ca and C5ca were nearly identical even though the calcite contents are variable (Table 2). The compositions of the clays calculated on a noncalcareous basis (Table 2) are similar to that of an aluminous sepiolite found in an Australian soil by Rogers, Quirk, and Norrish (1956; also *in* Brown, 1961, p. 333).

TABLE 2.—ELEMENTAL ANALYSIS OF NA-SATURATED CLAY EXTRACTED FROM CRUSHED WHOLE SAMPLES AND CALCULATION OF THE NONCALCAREOUS COMPONENT (IN PER CENT AIR-DRY BASIS)

Oxide	14987c <2 μ (C4ca)				14988c <2 μ (C5ca)			
	Calculated				Calculated			
	Elem. Anal.	Carb. Subt.	Remain-der	Carb.-free com-position	Elem. Anal.	Carb. Subt.	Remain-der	Carb.-free com-position
SiO ₂	29.4		29.4	54.0	34.9		34.9	54.2
Al ₂ O ₃	3.05		3.05	5.61	3.98		3.98	6.18
Fe ₂ O ₃	1.10		1.10	2.02	1.58		1.58	2.45
TiO ₂	0.11		0.11	0.20	0.14		0.14	0.22
CaO	25.3	25.3	0.0	0.0	19.2	19.2	0.0	0.0
K ₂ O	0.20		0.20	0.37	0.38		0.38	0.59
MgO	9.5	0.2	9.3	17.1	10.6	0.6	10.0	15.5
CO ₂	20.1*	19.9† 0.2†	0.0	0.0	15.8*	15.1† 0.7†	0.0	0.0
H ₂ O—	3.79		3.79	6.97	4.76		4.76	7.39
H ₂ O+	5.80		5.80	10.66	6.71		6.71	10.42
Total (1)	98.4	45.6	52.8	96.9	98.1	35.6	62.5	97.0
Others‡	1.6		1.6	2.9	1.9		1.9	3.0
Total (2)	100.0		54.4	99.8	100.0		64.4	100.0

* CO₂ was collected in NaOH solution in an absorption train after addition of acid to the sample. The NaOH solution and blank were then titrated with standard acid solution and the CO₂ absorption calculated.

† The upper and lower figures are the amounts of CO₂ allotted to CaO and MgO, respectively.

‡ Includes cumulative experimental error.

The effect of the pH 5 buffer on the noncalcareous components of the samples was checked by comparing total elemental analyses before and after buffer treatment and calculating what was dissolved differentially. The calculations showed that more magnesium was dissolved from the samples from horizons C3cam, C4ca, and C5ca by the buffer treatment than could be allocated to carbonate. From the proportion of total magnesium dissolved and the lower than expected X-ray intensities of the 12.3 Å reflection ob-

tained from whole soils after the buffer treatment, it was estimated that this treatment had dissolved about 80 per cent of the sepiolite from the C3cam sample and about 60 per cent of the sepiolite from the C4ca and C5ca samples.

To concentrate the sepiolite for more detailed X-ray diffraction analysis, a method of dissolving the carbonate without dissolving the sepiolite was needed. As was shown above, buffer treatment of the whole soil long enough to dissolve all of the carbonates also dissolved some of the sepiolite. If the buffer treatment were given to the clay extracted from the whole soil, however, the fine-grained carbonate dissolved very rapidly, leaving the sepiolite intact. Thus, an excellent sepiolite X-ray diffraction pattern, free of calcite lines, was obtained when the clay extracted from the whole soil of horizon C3cam was treated with pH 5 buffer for only 1 hr.

This method was then used to remove carbonate from clays extracted from other whole samples in the profile. X-ray diffraction patterns of oriented clay films from samples from horizons C2cam and C6 then showed sharp 10.8 Å reflections that were unaffected by glycerol treatment. This indicated the presence of attapulgite (palygorskite), which is often associated with sepiolite. There was no indication of sepiolite in these horizons, however.

For the most detailed study of the attapulgite and sepiolite, additional clay was extracted from the C2cam, C3cam, C4ca, and C5ca horizons. To increase the clay yield, the buffer treatment was given to <100 mesh material separated from the whole crushed soil. Then clay was separated from the carbonate-free samples in larger quantities. The time required for the buffer treatment was still relatively short (about 5 hr). Because of limited amounts of sample from horizons C2cam and C3cam, this treatment was given in these cases to <100 mesh material from which calcareous clay had already been extracted for the previous study.

Photographs of X-ray diffraction patterns of clays concentrated in the above manner, compared with patterns of clay extracted from mineralogical specimens of sepiolite (from Vallecas, Spain) and attapulgite (from Attapulgus, Georgia), are shown in Figs. 1, 2, and 3. The patterns of the clay from the C2cam and C4ca horizons match very well the patterns of standard attapulgite and sepiolite respectively, while the patterns for the clay from horizon C3cam indicate that both sepiolite and attapulgite are present. A slight "shoulder" on the 12 Å peak of the C4ca pattern indicates that a small amount of attapulgite is also present in this sample. The sepiolite powder patterns also match those shown by Brindley (1959; also *in* Brown, 1961).

The X-ray diffraction patterns of the oriented clay films are illustrated here (Figs. 2 and 3) to show the effects of standard pretreatments used for the analysis of soil clays on sepiolite and attapulgite. The glycerol was added to the water suspension of the clay before transferring some of the suspension to a glass slide (Jackson, 1956, para. 4-35). Although glycerol has little effect on the spacing of the major diffraction maximum of sepiolite (12.3 Å), the remainder of the X-ray pattern is markedly different from the one without

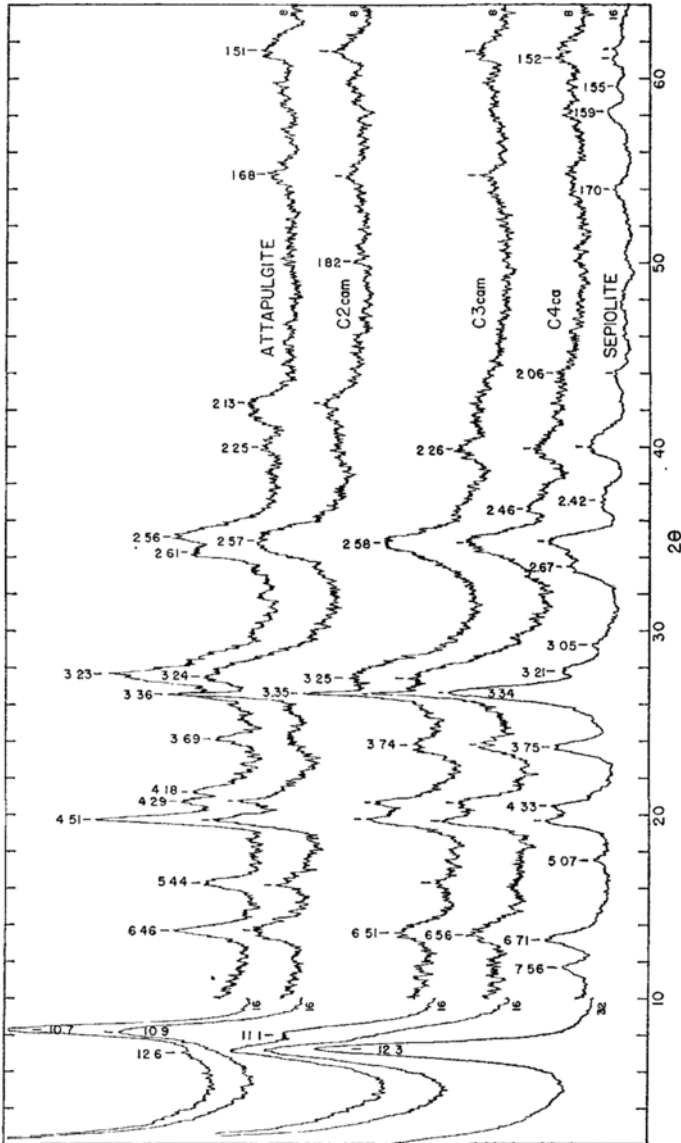


FIG. 1. Photograph of X-ray diffraction patterns of randomly oriented soil clay powders ($<2\mu$ extracted after short buffer treatment of <100 mesh samples) compared with those of reference clays (all Na-saturated). Cu radiation. Spacings in Å. 2θ in degrees. Time constant = 4 sec. Scale factor given next to pattern segment.

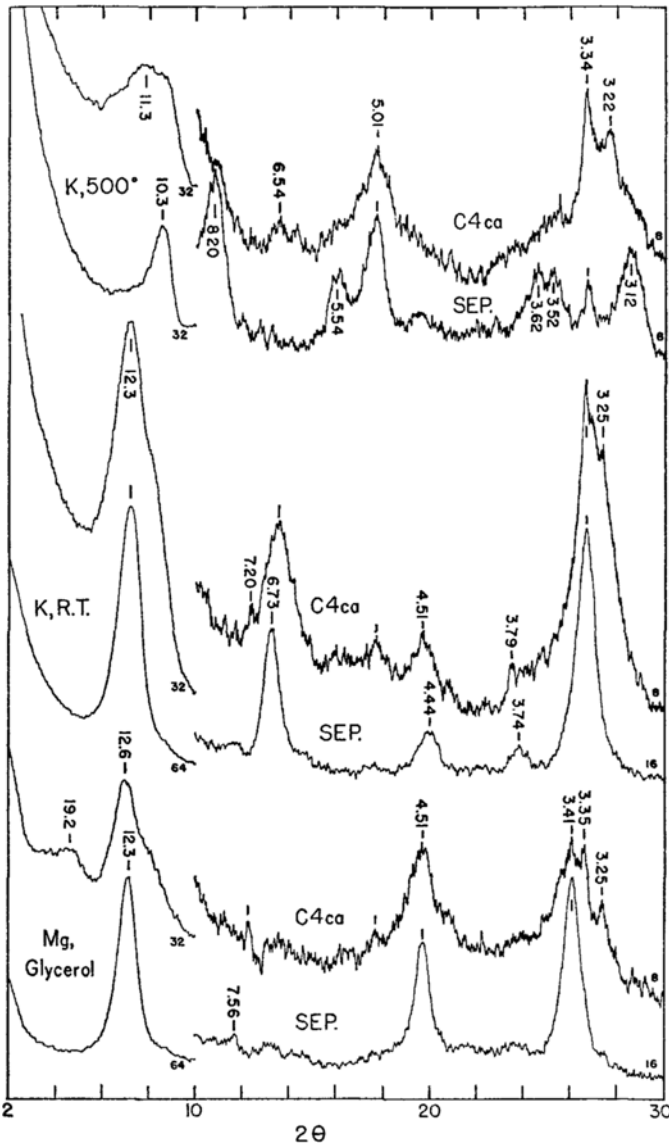


FIG. 2. Photograph of X-ray diffraction patterns of preferentially oriented clay films of soil and reference sepiolite after indicated pretreatment. Samples, X-ray conditions, and units are the same as for FIG. 1.

glycerol (Fig. 2). The same is true for attapulgite (Fig. 3) but to a lesser degree. These results indicate that glycerol displaces the zeolitic water in the internal channels of both the sepiolite and attapulgite structures, which is not unexpected (Caillère and Hénin, *in* Brown, 1961). Montmorillonite, kaolinite, and quartz peaks are present in some of the patterns, although it is difficult to know how much of the 3.34–3.36 peak is due to quartz and how much to sepiolite and attapulgite. Upon heating to 500°C, both the sepiolite and attapulgite X-ray patterns are modified, indicating structural changes (Preisinger, 1959; Caillère and Hénin, *in* Brown, 1961). For some unknown reason, the pattern of the sepiolite from the soil after heat treatment (Fig. 2) bears a greater resemblance to the pattern of the attapulgite from the soil after the same treatment (Fig. 3) than to the Vallecas sepiolite after heating.

Additional evidence that the shoulders on the 12 Å peaks of the C3cam and C4ca X-ray patterns are due to attapulgite was found by examining the clays that had been subjected to a long buffer treatment, in which sepiolite appears to dissolve more rapidly than attapulgite. Thus, the clay removed from the C3cam buffer-treated sample gave only an attapulgite pattern; there was no evidence of sepiolite. The sepiolite in the lower horizons appears to be more stable to buffer treatment, however. While the shoulder at 10.8 Å becomes more pronounced with long buffer treatment, the 12 Å peak remains dominant in the C4ca and C5ca patterns. This was also true with clay from the C5ca that was first separated after a short buffer treatment and then given a six-week buffer treatment.

The sepiolite : attapulgite ratio in the clay extracted from the C3cam sample varied with the ease of clay extraction. The noncalcareous clay, concentrated by a short buffer treatment (2 hr) after calcareous clay was extracted from the <100 mesh soil, had a higher sepiolite : attapulgite ratio than the additional noncalcareous clay extracted from the same <100-mesh material after it was given a short buffer treatment (5 hr). This indicates greater immobilization of the attapulgite than of the sepiolite by the calcite aggregates.

Elemental and thermal analyses of the same samples used for X-ray diffraction analyses in Figs. 1, 2, and 3, are given in Tables 3 and 4. The composition of the noncalcareous clay from the sample 14987 was essentially the same as its calculated composition when the analysis was performed on the calcareous sample (Table 2). This indicates that the short buffer treatment did not cause a significant amount of sepiolite to dissolve. Although the content of the soil sepiolite is high for a sepiolite, it is not so high as it is in alumina attapulgite. The near equality of the summations of the alumina and magnesia contents of each sample shows the complementary relationship between these two oxides in the two minerals.

Anhydrous structural formulae have been calculated, in the manner of Caillère and Hénin (*in* Brown, 1961), from the elemental analyses in Table 3 that are most representative of pure soil attapulgite and pure soil

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TABLE 3.—ELEMENTAL ANALYSIS AND DERIVED ANHYDROUS STRUCTURE FORMULAE OF THE NA-SATURATED SOIL AND REFERENCE CLAYS USED FOR FIG. 1. (IN PER CENT, AIR-DRY BASIS)

Oxide	Sample and source				
	Attapulgite (Georgia)	14985 (C2cam)	14986 (C3cam)	14987 (C4ca)	Sepiolite (Spain)
SiO ₂	53.5	53.9	53.4	54.6	55.7
Al ₂ O ₃	10.7	10.7	6.18	5.80	0.78
Fe ₂ O ₃	4.50	3.60	2.56	2.40	0.49
TiO ₂	0.45	0.34	0.24	0.22	0.03
CaO	0.86	0.07	0.07	0.06	0.02
K ₂ O	0.59	1.03	0.69	0.75	0.19
MgO	8.65	9.44	14.9	15.6	22.8
H ₂ O—	8.43	9.80	10.12	10.78	10.10
H ₂ O+	10.75	11.17	10.76	9.71	10.16
Total	98.4	100.1	98.9	99.9	100.3

Sepiolite (Spain) : (Si_{12.09} Mg_{7.40} Al_{0.20} Fe_{0.08}) O₃₂
 Sepiolite (C4ca) : (Si_{11.99} Al_{0.01}) (Mg_{5.11} Al_{1.50} Fe_{0.40} Ti_{0.04}) O₃₂
 Attapulgite (Georgia) : (Si_{7.77} Al_{0.23}) (Mg_{1.87} Al_{1.61} Fe_{0.49} Ti_{0.05}) O₂₁
 Attapulgite (C2cam) : (Si_{7.78} Al_{0.22}) (Mg_{2.04} Al_{1.61} Fe_{0.39} Ti_{0.04}) O₂₁

TABLE 4.—WEIGHT LOSS OF NA-SATURATED SOIL AND REFERENCE CLAYS USED FOR FIG. 1 BETWEEN GIVEN TEMPERATURES OF HEATING (IN PER CENT, AIR-DRY BASIS)

Temperature range, °C	Sample and source				
	Attapulgite (Georgia)	14985 (C2cam)	14986 (C3cam)	14987 (C4ca)	Sepiolite (Spain)
R.T.—110	8.43	9.80	10.12	10.78	10.10
110—200	2.28	3.25	2.31	1.79	0.90
200—300	2.18	1.93	2.18	1.87	2.42
300—400	2.42	2.31	2.01	1.87	1.88
400—500	1.83	1.63	1.54	1.22	1.28
500—600	0.74	0.73	0.73	0.68	0.58
600—700	0.21	0.26	0.38	0.47	0.46
700—800	0.76	1.03	1.32	1.17	1.98
800—900	0.33	0.04	0.30	0.65	0.66
Total	19.18	20.98	20.89	20.50	20.26

sepiolite and are compared with structural formulae calculated for reference materials. Since some of the samples contain quartz, kaolinite, montmorillonite and possibly mica or feldspar (deduced from the K₂O content), the calculated structural formulae for attapulgite and sepiolite are only approximate. It will be noted that after 12 ions have been assigned to the tetrahedral positions of the half-unit cell of sepiolite (Brauner-Preisinger structure, 1956;

also Preisinger, 1959) the remaining ions assigned to the octahedral positions occupy 7.68 and 7.05 positions of a theoretical 8. Likewise, after assigning 8 atoms to tetrahedral positions in the half-unit cell of attapulgite (Bradley structure, 1940), the octahedral ions occupy about 4 of a theoretical 5 positions. The difference from the theoretical number of octahedral positions in both sepiolite and attapulgite can be readily explained on the basis of the trivalent cations occupying only two-thirds of the positions that divalent cations would occupy. (The theoretical value is based on divalent cations.) Thus, if the number of positions occupied by Al and Fe are increased 50 per cent, the total number of octahedral positions becomes 7.82, 8.00, 5.07, and 5.08 respectively, in the structural formulae for the four samples in Table 3. The calcium content of the Georgia attapulgite was assumed to be associated with phosphate, as some phosphorus was found in the sample. Any exchangeable calcium had been replaced with sodium.

The weight-loss data in Table 4 show close similarity between the soil and reference attapulgite and sepiolite. It is difficult, from these data, to subdivide the weight losses that represent the three types of water associated with these minerals, i.e., zeolitic (absorbed within the channels of the fibrous structure), bound, and hydroxyl. Caillère and Hénin (*in* Brown, 1961) have used breaks in integral thermal analysis curves (*in* Mackenzie, 1957) to establish the temperature range in which each type of water is lost. For sepiolite the selected ranges are <250°, 250°–620°, and 620°–1000°C for zeolitic, bound, and hydroxyl water respectively. For attapulgite, the corresponding selected ranges are <200°, 250°–400°, and >400°C. Theoretically, using the Brauner-Preisinger structure for sepiolite, which has the half-unit cell $\text{Si}_{12}\text{Mg}_8\text{O}_{20}(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$, the amounts of water in the three categories in order of loss with heating are 11.1, 5.5, and 2.7 per cent, totalling 19.3 per cent. The data in Table 4 for the sepiolites conform quite well to these figures when approximating the above temperature ranges. The structural formula for attapulgite according to Bradley's structure is $\text{Si}_8\text{Mg}_5\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$, which contains 8.6, 8.6, and 2.2 per cent zeolitic, bound, and hydroxyl water respectively, totalling 19.4 per cent. In this case, as in the thermal data of other attapulgites reported by Caillère and Hénin (*in* Brown, 1961), there is less conformity with the theoretical when the specified temperature ranges for attapulgite are used. The presence of montmorillonite impurity may cause some of the discrepancy. Caillère and Hénin concluded from the data they have examined that more detailed structural studies of attapulgite are necessary to account for the thermal discrepancies.

Thin sections of the cemented portions of the profile were prepared in order to examine the microstructure, particularly the location and arrangement of the sepiolite and attapulgite. To dissolve the calcite so that these and other minerals could be seen some of the thin sections were immersed in pH 5 sodium acetate buffer in a petri dish until evolution of bubbles ceased (about 1 hr later) before the cover glass was placed on the section. All the photographs (*in* Plates 1 and 2) are of buffer-treated sections.

Sepiolite and attapulgite were identified in the thin sections by their optical properties and by comparisons with fine sand and coarse silt-size aggregates separated from both the buffer-treated soil and the mineralogical specimens. The observed refractive index of the sepiolite was about 1.52 and of the attapulgite, about 1.53. The birefringence of the sepiolite was greater than that of the attapulgite. Both sepiolite and attapulgite occur in several different forms. The most conspicuous are the sepiolite aggregates of coarse-silt or fine-sand size illustrated in Plate 1a. The edges are brighter (in polarized light) than the center because of the orientation of the individual particles near the surface of the aggregate. These aggregates, as well as coatings on mineral grains (Plate 1a, top), occur in what appear to be former solution channels in the calcrete (cemented caliche). These solution channels, most conspicuous in the C4ca horizon, are sharply separated from the calcrete matrix by a sepiolite lining on the channel wall. The channels are conspicuous in thin sections because they contain a concentration of large mineral grains (mostly quartz, some feldspar and rhyolite fragments). Also, unlike the calcrete matrix, the structure is open and loose; i.e. the grains and aggregates are not cemented solidly together by the carbonate. The channels do contain an abundant number of calcite grains, however, which occur as aggregates and coatings and penetrate the sepiolite aggregates. Before the buffer treatment was given to the thin section, the sepiolite aggregates could hardly be observed because of the interpenetrating calcite grains, some of which still remain after the buffer treatment (Plate 1a).

In addition to that occurring in the solution channels, which make up only about one-tenth or less of the volume of the calcrete nodules examined from the lower part of the calcareous zone, the sepiolite could be observed as a network of fiberlike particles (many of them clay-size) in the calcrete matrix after the calcite was dissolved by the buffer (Plate 1b). These fibers show low birefringence and are generally distributed throughout the matrix, although there is some tendency for them to concentrate around the edges of calcite aggregates (now dissolved except for some large calcite grains around the edges of these aggregates, Plate 1b).

The attapulgite also occurs as aggregates and as individual networks of fibers. The most conspicuous aggregates in the upper calcrete zone appear as bright rings with crossed nicols often arranged loosely around mineral grains (Plate 2a). As in the case of the sepiolite aggregates, the brighter interference colors at the edges are due to orientation effects. In addition to these more or less well-organized aggregates, there are smaller particles of attapulgite distributed throughout the calcrete matrix of the upper calcareous zone, some of which are concentrated into what appear to be very loose aggregates. In the C6 horizon, the attapulgite is organized into thick coatings on mineral grains in addition to tightly formed aggregates (Plate 2b). The somewhat higher birefringence of the coatings in certain places is probably due to montmorillonite mixed with the attapulgite.

To assist in interpreting the presence of the sepiolite and attapulgite in the

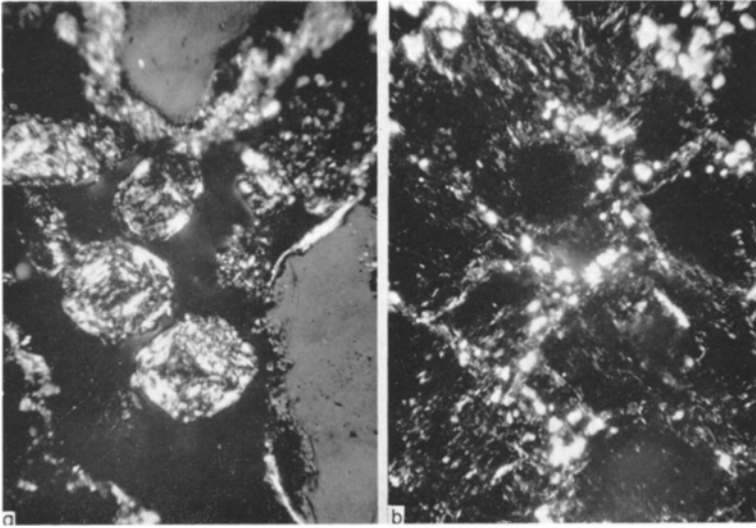


PLATE 1. A Sepiolite aggregates and coatings in solution channel (horizon C4ca, 320 \times). B Sepiolite fibers (low birefringent material, horizon C5ca, 320 \times) Sections buffer-treated and viewed with crossed polarized light.

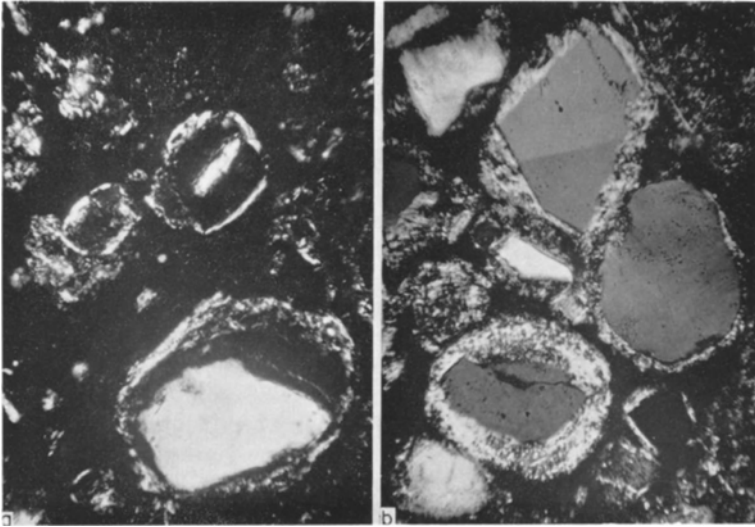


PLATE 2. A Attapulgite coatings and aggregates (horizon C2cam, 320 \times). B. Attapulgite and montmorillonite coatings (horizon C6, 145 \times). Sections buffer-treated and viewed with crossed polarized light.

TABLE 5.—CLAY MINERAL COMPOSITION OF EXTRACTED SOIL CLAYS (<math> < 2\mu </math>, CARBONATE-FREE) ESTIMATED FROM X-RAY DIFFRACTION PATTERNS OF ORIENTED FILMS

Sample No.	Horizon	Depth (in.)	Clay mineral				
			Mont.	Mica	Kaol.	Sep.	Att.
14979	A	0-2	xx	xx	x		
14980	B21t	2-7	xx	xx	x		
14982	B22t	10-14	xx	xx	x		
14983	B23tca	14-19	xx	xx	x		
14991	C1cam Laminar	19-29	xx	d?	x		xx
14992	C1cam Nonlaminar	19-29	xx		x		xxx
14985	C2cam	29-40	x		x		xxxx
14986	C3cam	40-59	x	d?	x	xxx	xx
14987	C4ca	59-73	x		d	xxxx	x
14988	C5ca	73-93	x		d	xxxx	x
14989	C6	93-107	xx		x		xx
14990	C7	107-139	xxx		xx		x

Key: xxxx = dominant, xxx = abundant, xx = moderate, x = small, d = detected.

soil under study, the clay-mineral distribution throughout the profile was determined by X-ray diffraction analysis (Table 5). It will be noted that the attapulgite distribution is greater than that of the sepiolite in the profile, even though it appears for the most part to be present in smaller amounts. Also, mica is present significantly only in the top (noncalcareous) part of the profile and attapulgite begins where mica leaves off. Whether there is any genetic significance to this mica-attapulgite sequence is not known. The presence of some potassium in the clay of the lower zone (Table 3) indicates that mica is not totally absent from the lower zone, although potassium feldspar may account for some of the potassium present.

Estimates of the total sepiolite or attapulgite present in some of the horizons can be made from the total magnesia contents of the samples given in Table 1, using some reasonable assumptions in regard to other magnesium-containing minerals present. From the analyses in Table 2, it is assumed that the amount of MgO present as the carbonate is on the order of 1 per cent of the CaO content if carbonates are present. Also, on the basis of the MgO content of the upper horizons, the MgO allocated to other magnesium minerals was about 0.5 per cent (noncalcareous basis). Assuming, then, that the MgO contents of the attapulgite and sepiolite are 10 and 18 per cent respectively (calculated on an oven-dry basis from Table 3), the attapulgite contents of horizons C2cam and C6 can be calculated to be about 10 and 5 per cent respectively and the sepiolite contents of horizons C4ca and C5ca, about 20 and 25 per cent respectively. These percentages are based on the whole soil; all but one would be substantially higher if calculated on a carbonate-free basis. Even though the above figures are very approximate, they do show the large quantities of sepiolite and attapulgite present in this soil.

Present knowledge is insufficient to establish whether the sepiolite and attapulgite were formed in the soil, were inherited from the parent material and subsequently weathered and re-worked, or were carried in from another source by the wind. There are no reported instances in the literature where sepiolite has been thought to form in place in soil. The sepiolite present in a South Australian soil (Rogers, Quirk, and Norrish, 1956) was inherited from the parent material. Sepiolite and attapulgite are usually formed in nature in sedimentation basins (Millot, *et al.*, 1960; Millot, 1962) or by hydrothermal action (Caillère and Hénin, *in* Brown, 1961), although attempts to synthesize these minerals hydrothermally have not been successful (Mumpton and Roy, 1958). Their occurrence in some calcareous soils may have been previously overlooked because treatments used to dissolve the carbonates may also have dissolved sepiolite and attapulgite, particularly the former.

The absence of sepiolite below the carbonate zone and its strict association with the calcite make it improbable that the sepiolite was inherited from the soil parent material. The microstructure of the calcrete (Plate 1b) also indicates that the sepiolite was not present in the soil before the formation of the calcrete. If it were, one would expect the predominance of well-formed sepiolite aggregates, similar to those found in the solution channels (Plate 1a) instead of many individual fibers distributed loosely in the calcrete.

The closest known deposit of sepiolite is near Silver City, New Mexico, (Dunham, 1935) about 100 miles northwest of the soil site. This is in another drainage basin and movement of significant amounts of sepiolite by wind over this distance is considered unlikely. No deposits of attapulgite have been reported in the adjacent area.

From the thin sections, it seems reasonable to conclude that the sepiolite and attapulgite crystallized in the soil during the period of caliche formation, the fibers being distributed as in Plate 1b. Then, during periods of higher rainfall when the caliche was partially dissolved along solution channels, the sepiolite, attapulgite, quartz, feldspar and other mineral grains were concentrated, the sepiolite and attapulgite forming aggregates and coatings as in Plates 1a and 2a and b. During subsequent drier periods, fresh calcite then crystallized in the solution channels, but, in some cases at least, only partially filled them.

The source of the calcium, magnesium and silicon forming the calcite, sepiolite and attapulgite and the probable environmental conditions for the formation of these minerals will be considered in relation to the other soils of the area. These studies will be reported elsewhere.

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