A Study of Some Chemical and Physical Properties of the Clay Minerals Nontronite, Attapulgite and Saponite

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Part I.

INTRODUCTION

This investigation is primarily concerned with those physical and chemical properties of nontronite, attapulgite and saponite clays which are of interest in soil research.

The clays, as a group, consist of several isomorphous mineral series in each of which the properties change with variation in the chemical composition. One may therefore anticipate that starting from a knowledge of a few well distributed members, the behavior of others may reasonably be predicted. In the beidellite-nontronite series the physical chemistry of the iron end member, nontronite, has been but little studied. Attapulgite, until recently considered as belonging to the montmorillonite series, is now known to be a member of a new series structurally related to the amphiboles. Very little is known of its physical chemistry, nor of its mode of origin. Saponite or magnesium bentonite is the magnesium end member of the montmorillonite series and it therefore has the same importance as nontronite, since various intermediate members of the montmorillonite-saponite-beidellite-nontronite group are of frequent occurrence in soils.

LITERATURE REVIEW

The information in relation to these three minerals will be outlined under separate headings, namely nontronite, attapulgite and saponite or magnesium bentonite.

Nontronite Clay

This mineral, first described by Berthier (5) in 1827, after its discovery near Saint Pardoux in the district of Nontron, France, was listed by Dana (15) as a hydrous iron silicate. Geilmann, Klemm and Meisel (21) stated that nontronite is a ferro-iron free ferric silicate, but analyses given by Larsen and Steiger (41), Dana (14) and others as outlined in table 1, indicate that nontronite and related mineral varieties are ferric iron silicates containing some ferrous iron and aluminium.

The first attempt to group nontronite and related minerals was made in 1876. Collins (12) considered chloropal, nontronite, gramenite, keffekilite, and bole as members of the chloropal group differing only in the relative proportion of aluminium and iron. In later years mineralogists came to the conclusion that nontronite, chloropal, pinguite, fettbol and

TABLE 1. CHEMICAL ANALYSIS OF NONTRONITE VARIETIES

Oxides	Nontronite Paulusbronn (44)		Stilpnochloran Gobitschau, Moravia (20)	Faratsihite Faratsiho Madagascar (19)	Beidellite (Iron rich) Spokane Wash. (50)	Nontronite Nontron France (1)	Nontronite Behenjy Madagascar (19)	Theoretical Composition	Nontronite Sandy Ridge N. Carolina (48)
SiO_2	40.02	40.42	36.45	41.60	46.06	44.00	44.30	41.86	41.36
Al_2O_3	10.55	10.42	6.03	22.68	12.22	3.60	5.37	-----	9.84
Fe_2O_3	26.16	25.31	34.24	15.22	18.54	29.00	29.47	37.21	27.47
FeO	1.37	0.45	-----	0.54	0.28	-----	0.56	-----	tr.
TiO_2	-----	-----	0.02	0.13	0.84	-----	0.18	-----	-----
P_2O_5	-----	-----	0.31	0.21	-----	-----	-----	-----	-----
MgO	-----	0.13	0.97	0.11	1.62	2.10	1.74	-----	tr.
CaO	-----	0.38	1.91	0.60	1.66	-----	1.70	-----	tr.
MnO	-----	-----	0.04	-----	-----	-----	-----	-----	-----
Na_2O	-----	-----	-----	0.16	-----	-----	-----	-----	tr.
K_2O	-----	-----	0.35	0.22	-----	-----	-----	-----	tr.
H_2O (-)	21.83	21.80	9.20	5.71	17.26	18.70	7.99	20.93	9.25
(+)	-----	-----	11.01	13.02	-----	-----	8.52	-----	12.10
Clay	-----	-----	-----	-----	-----	1.20	-----	-----	-----

gramenite were varieties of the same mineral. To this list Larsen and Steiger (41), in 1928, added mullerite or zamboninite, morencite and hoeferite; all minerals differing only in mineral composition, with the SiO_2/Fe_2O_3 ratio ranging around three. These authors also concluded that nontronite with an approximate formula, $Fe_2O_3 \cdot 3SiO_2 \cdot nH_2O$, was the ferric end member in an isomorphous series with beidellite.

Marshall (52) from calculations made on the chemical analyses of five silicates as given by Larsen and Steiger (41) found that nontronite and related mineral varieties had either the 2:1 or 3:2 type of lattice. He concluded that montmorillonite, beidellite and nontronite are structurally similar and that beidellite is isomorphous with nontronite. This was the first contribution in the determination of the structural relationship of nontronite to other clay minerals; although Weinschenk (72), in 1897, wrongly classified nontronite as the ferric equivalent of the kaolin clays.

Further information on this subject was contributed by Gruner (27) who, through X-ray examination, concluded that nontronite, morencite, pinguite, faratsihite, chloropal and stilpnochloran were structurally similar and almost identical with the montmorillonite structure. He believed that montmorillonite, beidellite and nontronite form an isomorphous, completely miscible series with the structural formula of nontronite as

$$(OH)_8 \ (Al \ Fe)_1 \ Si_{\frac{8+n}{3}} \ (Al \ Fe)_{16-n} \ O_n \ m \ H_{40} \ O_2$$
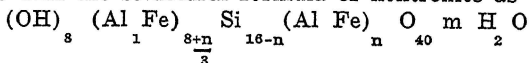
with n rarely below two or as high as four, while m may vary between eight and twenty-two.

The smaller unit cell of montmorillonite was explained as a probable consequence of the replacement of aluminium for iron in the lattice.

Further X-ray work by Nagelschmidt (59) confirmed Gruner's conclusions that montmorillonite, beidellite, nontronite and also magnesium bentonite or saponite were structurally similar.

Little is known about the quantity of nontronite in the earth's surface. However, Ross and Kerr (67) state that pure nontronites are widely distributed, but local in occurrence. It probably does not form sedimentary beds, although infrequent mention has been made of this clay as a weathering product in soil formation.

A considerable accumulation of information on the physical properties of nontronite and related mineral varieties is given in table 2.

The color of this mineral group varies from yellow through green to brown. Ross and Kerr (67) intimate that this color change is a function of the iron content since the color of the minerals in the beidellite-nontronite series varied from colorless through yellow to greenish-yellow. Berthier (5) considered the light color of nontronite to be a consequence of the presence of water of crystallization.

The specific gravity of the nontronite minerals varies from 2.0 to 2.7; a wide variation which Gruner (27) suggests may be unreliable because moisture conditions influence the layer spacings. These figures may be compared with those given by Marshall (51) who found the specific gravity of a middle member of the beidellite-nontronite series to be 2.45, while that of beidellite was 2.30. Thus the specific gravity of moist nontronite probably ranges from 2.45 to 2.70.

The luster of nontronite has been described as silky, earthy or pearly.

The crystal habit has usually been called fibrous, with a tendency to platiness. The platy form is apparently more evident in the more beidellite-like clays which, according to Marshall (51), usually have a blade or plate crystal habit.

The optical character of nontronite clay is negative with alpha, 1.560 to 1.630 and gamma, 1.585 to 1.660. The birefringence varies from .015 to .042. These values may be compared with those of other clays of this beidellite-nontronite series. Ross and Shannon (69) found that a clay containing only a small quantity of iron gave alpha, 1.488 and gamma, 1.527. Another clay with a Fe_2O_3/Al_2O_3 ratio of 0.66 gave alpha, 1.523 and gamma, 1.572. Thus it is evident from the available data that the refractive indices increase with the iron content.

TABLE 2. PHYSICAL PROPERTIES OF NONTRONITE VARIETIES

	Nontronite Woody, California (41)		Nontronite (41)		Morencite Morenci Arizona (72)	Stilpnochloran Gobitschau Moravia (31)	Nontronite (15)	Nontronite (25)	Nontronite (56)	Nontronite (51)	Gramenite mallacombe England (12)	Nontronite Nontron France (5)
Color	Dark olive green to dark olive buff when dry	Citron green to light yellow green	Yellow-green		Brownish yellow	"erbgelb" to ochre yellow	Straw Yellow to canary yellow, shades of green		Green, yellow olive green, orange		Dull green to yellowish green	Pale yellow-greenish yellow
Hardness	2+		1 - 2			2 - 3	2.5 - 4.5		1.0		1.0	2.0
Density	2.50		1.727? - 2.727			2.5	1.727?-2.105		2.5		1.89	
Luster	Silky						Earthy		Pearly		Greasy	Greasy
Crystal Habit	Coarse fibers and lathes	Platy to fibrous	Meta colloidal to very fine lamellae or fibers		Fibrous	Fan shaped and radial flakes			Prismatic fibrous	Blades and fibers		
Elongation	Z parallel to elongation											
Optical character	(-)	(-)	Lacroix (-)	Bergeat (+)	(-)		(-)		(-)			
Alpha	1.560 1.580 1.610		1.625	1.595	1.630	1.540 (minimum)	1.560 (minimum)	1.560	1.585			
Beta	1.585 1.590			1.610	1.645				1.593			
Gamma	1.585 1.600 1.625		1.655	1.620	1.660	1.600 (maximum)	1.650 (maximum)	1.610	1.608			
Birefringence	.029 .020 .015 .042		.030	.025	.030			.030 to .035	.023			

Attapulgite Clay

Large deposits of this clay, quarried for use as Fuller's Earth, occur at Attapulgus, Georgia, and Quincy, Florida. Although used industrially for some time, little information on its chemical properties and structure was available until 1933 when Grim (24) concluded that this clay consisted of 95 per cent montmorillonite.

In 1935, however, de Lapparent (16) decided, from data including chemical analysis, X-ray pattern and dehydration curves, that this clay from Attapulgus, Georgia, and a similar one from Moimoiron, France, were not montmorillonite clays but were related to the mineral sepiolite. Thermal curves also, as given by de Lapparent (18) indicate a similarity between attapulgite clay and the sepiolites and also some high magnesium-bearing minerals, described and named palygorskite minerals by A. Fersman (19).

Further work by Longchambon and Migeon (49), Longchambon (46) and deLapparent (18) on the structure and the chemical composition of attapulgite, sepiolite and the palygorskites indicated that these minerals are members of an isomorphous series.

The structure of the sepiolite minerals, including attapulgite, was considered by Longchambon and Migeon (49) and Longchambon (47) to be similar to that of the amphiboles; while Longchambon (44) concluded that the structure of sepiolite consisted of regular Si-O amphibole chains uninterrupted along the direction of the fibers and bound laterally by magnesium, oxygen and hydroxide ions. The general formula for these chains is $Mg_{2.58} Si_4O_{11}H_{0.84} 1H_2O$ (48).

However, Kerr (35), writing in 1937, disagreed with the viewpoint that attapulgite, sepiolite and palygorskite belong to an isomorphous series of minerals with an amphibole-like structure. He maintained that the optical properties of attapulgite were similar to montmorillonite and the difference in chemical composition did not warrant a distinct category. de Lapparent (17), (18) immediately challenged Kerr's deductions and, although maintaining that attapulgite clay had a micaceous structure, he was emphatic in pronouncing it different from montmorillonite. His conclusions were a result of X-ray, thermal curve and dehydration curve studies.

In 1938 Nagelschmidt (58) called attention again to the probability that the clay minerals known as the palygorskites, including both sepiolite and attapulgite, may have a structure similar to the pyroxenes and amphiboles. He suggested that this mineral may retain water between the $Si_4 O_{11}$ rings rather than between layers as do montmorillonitic clays. Later in the same year, this author (59) noted that the X-ray pattern and the lattice shrinkage of attapulgite clay differed from those of montmorillonite.

More recently Bradley (8) thoroughly investigated by X-ray methods the crystal structure of attapulgite. He concluded that this clay is structurally similar to the amphibole minerals except that the double silicate chains are joined through a single oxygen atom rather than through two oxygen and one calcium atoms, and that water molecules form part of the lattice. The chemical composition of an unit of this mineral is.

$$(OH_2)_4(OH)_2 Mg_5 Si_8 O_{20} 4H_2O$$
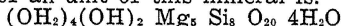
The four water molecules are held in the interstices between the molecular chains of the amphibole-like structure.

The structure of attapulgite clay as presented by Bradley is demonstrated by the accompanying photograph of a model (Fig 1) and by a modified diagram (Fig. 2) of the fundamental structure of the layers. Figure 2 gives the arrangement of the silica sheet and one-half of the "brucite" sheet. The amphibole-like chain is completed, normal to the "a" axis, by placing above the magnesium atoms the same sequence of atomic layers as outlined in the figure.

This study of Bradley's and the chemical analyses given in table 3 and by Dana (14) suggest that attapulgite is the intermediate member of an isomorphous clay mineral series which includes sepiolite and called, because of priority, the palygorskite group. The occurrence of an aluminium end member is doubted by Bradley (8) since the substitution of two aluminium atoms for three magnesium atoms would weaken the structural chains. de Lapparent (16) has suggested that if the divalent atoms number more
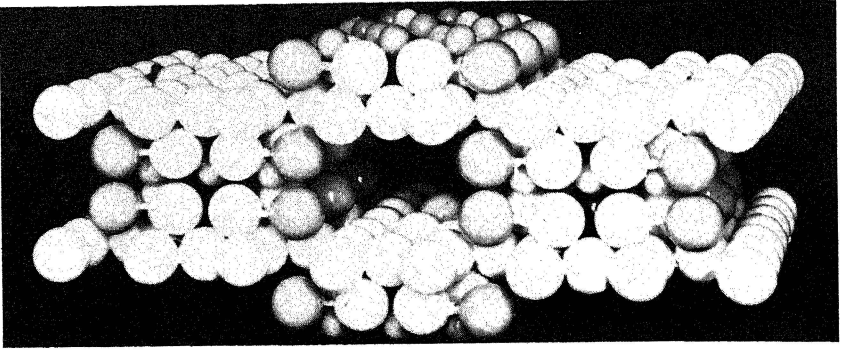
Fig. 1.—A sectional model of Attapulgite clay.   (View along amphibole-like chains parallel to the "c" axis.   (a) axis vertical.)
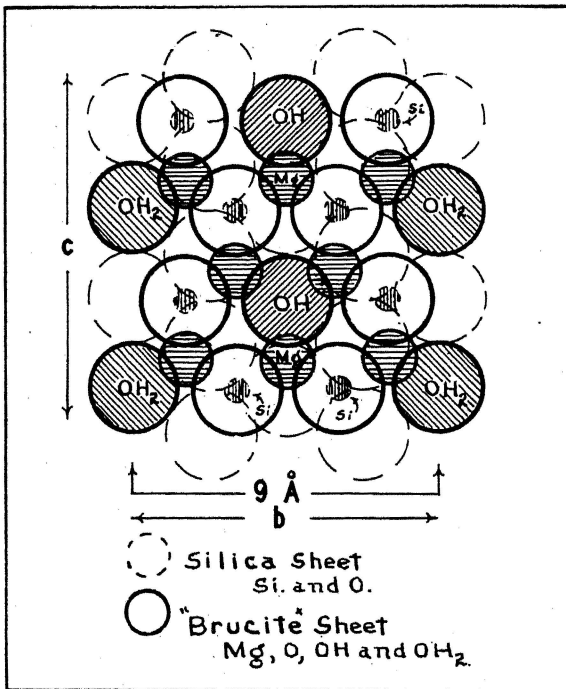
Fig. 2.—Idealized structure of attapulgite projected on to 100.   (Modified from Bradley)

than three times the trivalent atoms the mineral is sepiolite, if less, attapulgite.

The limited information available on the physical properties of attapulgite and sepiolite is summarized in table 4.

The color ranges from greenish-gray to white, the sepiolites apparently are white in color.   The flaky to fibrous shaped particles have a specific gravity ranging from 2.0 to 2.15 and a hardness of 2.0 to 3.0.

The refractive indices of attapulgite clay are somewhat similar to those of montmorillonite (Kerr (35)); alpha, 1.506 to 1.522 and gamma, 1.530 to 1.540.   The birefingence varies from .021 to .032.   The crystal system is monoclinic and the optical character is negative.

TABLE 3. CHEMICAL ANALYSIS OF ATTAPULGITE AND SEPOLITE CLAYS

	Attapulgite Attapulgus Georgia (8)	Attapulgite Attapulgus Georgia (16)	Attapulgite Attapulgus Georgia (69)	Attapulgite Moimoiron France (16)	Attapulgite Attapulgus Georgia (35)	Sepiolite (49)	Sepiolite (49)	Sepiolite (49)
SiO_2	55.03	53.7	51.28	53.6	53.42	53.85	53.24	52.90
Al_2O_3	10.24	9.0	10.56	10.6	10.06	.62	.19	.46
Fe_2O_3	3.53	3.6	6.76	6.5	3.40	.16	1.95	.74
FeO		.2		.3	.18			
$Ti\,O_2$					.52			
P_2O_5					.12			
MgO	10.49	9.6	10.40	4.6	9.16	24.68	22.87	23.20
CaO		1.2	1.44	2.1	1.29	.33	.46	.24
MnO					.02			.69
Na_2O		.9		.8	.02	.26	.27	.22
K_2O	.47	.5		.5	.64	.04	.15	.07
H_2O (-)	9.73	9.7	{ 20.28	11.6	11.83	{ 20.00	{ 20.39	{ 21.23
H_2O (+)	10.13	11.6		9.4	9.42			
Cl					.02			
CO_2					.10			

TABLE 4. PHYSICAL PROPERTIES OF ATTAPULGITE AND SEPIOLITE CLAYS

	Attapulgite Attapulgus, Georgia (35)	Attapulgite Attapulgus, Georgia (16)	Attapulgite Attapulgus, Georgia (8)	Sepiolite (48)	Sepiolite (15)
Color	Greenish-gray, when moist light gray, white when dry				Grayish white, white
Specific gravity				2.15	2.0
Hardness					2 - 2.5
Crystal Habit	Flakes		Fibrous	Fibrous	Fibrous
Crystal System			Monoclinic	Monoclinic pseudo ortho-rhombic	
Alpha	Cameron 1.511 Kerr 1.510	1.522	1.508		
Beta					1.506
Gamma	1.532 1.533	1.534	1.540		
Birefringence	.021 .023	.022	.032		
Optical character		(-)	(-)		(-)
General				Sample completely decomposed by cold 10% HCl in 10-48 hrs.	Decomposed by HCl

Saponite or Magnesium Bentonite Clay

Foshag and Woodford (20), in 1936, reported on a bentonitic clay at Hector, California; two samples of which were high in magnesium and had the chemical formula, $7MgO$, $10 SiO_2$. $5H_2O$ and $2 MgO$, $3SiO_2$. $3 H_2O$, respectively. These workers, and in addition Kerr (36) and Grim (25), consider this clay as closely related to saponite. This name will be adopted here.

Dana (14) states that saponite was first described in 1758. Much later, in 1840, a high magnesium clay discovered at Svardsjo, Sweden, and described by Svanberg is listed by Kerr (36) under the heading saponite minerals. Clark (11), in 1914, gave the saponite formula as $H_4Mg(OH)_2$ Si_2O_7 with aluminium present as an impurity.

Graham (23) described and named a mineral, from the physical properties portrayed containing 3.32 per cent Al_2O_3 and 25.91 per cent MgO, as saponite. This author differing with Clark considered alumina as a necessary constituent of saponite and significantly commented that saponites show changes in chemical composition in the ratio of $3MgO$ to one sesquioxide group. Palache and Vassar (65) reported a mineral from the copper deposits in Michigan, with the composition Al_2O_3, $9 MgO$, $10 SiO_2$, 15 or 16 H_2O, as saponite.

The structural data on these clays are a further aid in classifying them. Kerr (36) refers to the structural similarity between saponite and montmorillonite, while an X-ray study by Nagelschmidt (59) indicated that the clay from Hector, California, which he called magnesium beidellite, has the same structure as montmorillonite. Kerr and Cameron (37) also report a clay from Tchachapi, California, with montmorillonite structure and saponite properties.

Hence it is indicated that the clay from Hector, California, is a magnesium aluminium silicate (see table 5 and analyses by Dana (14)) and a member

TABLE 5. THE CHEMICAL ANALYSIS OF SAPONITE MINERALS

	Magnesium bentonite California (20)		Saponite Montreal (23)	Saponite Michigan (65)		Saponite Svardsjo Sweden (36)	Montmorillonite Saponite California (37)	Magnesium bentonite California (66)
SiO_2	53.68	51.26	46.45	42.78	42.99	50.89	53.88	55.86
Al_2O_3	0.60	0.36	3.32	6.44	6.26	9.40	11.66	0.13
Fe_2O_3	-----	0.09	.42	1.27	1.83	2.06	4.60	0.03
Feo	-----	0.06	.72	-----	2.57	0.00	-----	0.00
TiO_2	-----	-----	-----	-----	-----	-----	0.44	-----
P_2O_5	-----	-----	-----	-----	-----	-----	0.16	-----
CaO	0.52	2.60	-----	2.35	2.03	0.78	1.56	tr.
MgO	25.34	23.25	25.91	24.78	22.96	26.52	8.61	25.03
MnO	-----	-----	-----	0.12	0.11	-----	0.18	-----
Na_2O	3.00	3.47	-----	0.75	1.04	-----	0.15	2.68
K_2O	0.07	0.10	-----	-----	-----	-----	0.39	0.10
Li_2O	1.12	0.60	-----	-----	-----	-----	-----	1.05
H_2O (-)	7.28	11.56	14.48	13.96	13.60	11.06	8.21	9.90
H_2O (+)	8.24	5.14	8.13	7.90	6.85	-----	9.98	2.24
Cl	0.31	-----	-----	-----	-----	-----	-----	-----
F	-----	-----	-----	-----	-----	-----	-----	5.96

of an isomorphous series of clays in which montmorillonite is the known aluminium end member, while the magnesium end member is, according to Clark's' definition (11), saponite.

The physical properties of saponite clays, as given in the literature, are summarized in table 6.

Saponite is a white clay mineral, soft and plastic when wet, brittle when dry. It may or may not swell, a property probably depending on the adsorbed cation; and when pure, it is translucent around the edges of the mass and transparent in thin section (Foshag and Woodford (20) and Graham (23)).

The luster is earthy to greasy and the platy crystals have a specific gravity to 2.24 to 2.30.

The refractive indices are alpha, 1.470 to 1.479 and gamma, 1.490 to 1.527. The birefringence ranges from .020 to .037 and the optical character is negative. It is probably monoclinic, although Palache and Vassar (65) have suggested orthorhombic structure.

Dana (14) and Graham (23) have mentioned that saponite clay turned black upon heating, while Graham found that it became white again at higher temperatures.

Nutting (63) states that the Hector clay forms a permanent hydrogel in water. It breaks down in a weaker concentration of hot hydrochloric acid than does montmorillonite and when treated in concentrations between 0.1 per cent and 0.4 per cent the constant pH of the filtrate indicates a neutralization reaction with this quantity of acid.

TABLE 6. THE PHYSICAL PROPERTIES OF SAPONITE MINERALS

	Magnesium Bentonite	Saponite	Saponite	Saponite	Montmorillo-nite-saponite
	Hector, California (20)	(15)	Michigan (65)	Montreal (23)	California (37)
Color	White-cream	White, yellowish, bluish, reddish	White - light buff colored		White - light grayish white
Consistency		Soft when wet, brittle when dry	Somewhat plastic	Soft and plastic	
Hardness			1	Soft, with soapy feel (dry)	
Specific Gravity		2.24 - 2.30			
Luster	Earthy-'semi-waxy	Greasy			
Crystal System			Monoclinic perhaps orthorhombic		
Crystal Habit	Plates				
Alpha	1.470 - 1.500		Larsen 1.479	Larsen 1.490	
Beta			1.510	1.525	1.486
Gamma	1.490 - 1.520 ±.005		1.511	1.527	1.506
Birefringence	.020 - .005		.033	.037	.020
Optical Character			(-)	(-)	

GENERAL PHYSICAL PROPERTIES*

Nontronite Clay.—The sample of nontronite clay used in these investigations came from Sandy Ridge, North Carolina, and was received from Dr. C. S. Ross of the United States Geological Survey.

The aggregates were greenish-yellow in color and covered with a reddish-brown coating. The purified clay sample, when placed in a reducing atmosphere, changed to a dark green color which reverted to the original color when exposed to the air. The luster was dull and earthy, while the broken surface of the fragments had a granular appearance. The hardness was approximately 2.0.

The fibrous clay particles were combined in radial aggregates which were very difficult to disintegrate in consequence of the iron oxide coating.

Attapulgite Clay.—The sample studied was from a clay deposit, described by Kerr (35), at Attapulgus, Georgia. It was kindly furnished to us by the Attapulgus Clay Company.

The aggregates of this clay sample were light-gray in color while the suspension appeared white, while the fragments were minutely laminated and the individual particles appeared fibrous in crystal habit. The luster was earthy and the hardness was approximately 2.0.

The general physical properties of this clay are distinctly different from those of montmorillonite or saponite clays. Attapulgite is more sensitive to flocculation and is much more easily dispersed following coagulation. It does not form gels at such low concentrations as montmorillonite clay although at higher concentrations it will form a relatively stable gel in both distilled and salt water.

Saponite Clay.—The sample of saponite clay used in this investigation was received from Dr. W. F. Foshag, of the Smithsonian Institute, and was collected on the properties of the California Talc Company in the Mojave Desert near Hector, California. The description and the geology of this volcanic deposit is given by Foshag and Woodford (20).

This clay is white in color, has earthy to greasy luster and a hardness of about 1.0+. The brittle fragments broke with a conchoidal fracture. The aggregates rapidly swell in water to a relatively large fluffy mass which readily disintegrate to form a colloidal suspension which sets to a gel at a relatively low concentration.

This clay at higher temperatures changed from white to dark gray in color, a property previously described by Dana (14) and Graham (23).

The general physical properties of this saponite clay strongly resembled those of montmorillonite.

DISPERSION AND MECHANICAL ANALYSIS

The dispersion of the attapulgite and saponite clay material was attempted with sodium oxalate, sodium citrate, sodium carbonate, lithium carbonate, and, for comparative purposes, sodium silicate. The clay material was shaken, boiled and then made up to a 0.2 per cent suspension with an electrolyte concentration of 0.001N.

TABLE 7. THE EFFICIENCY OF DISPERSING AGENTS IN STABILIZING SUSPENSIONS OF ATTAPULGITE AND SAPONITE CLAYS.

Electrolyte	Condition of suspension after 24 hours	
	Attapulgite clay	Saponite clay
Water	Flocculated	Stable suspension
Sodium oxalate	Flocculated	Stable suspension
Sodium silicate	Stable suspension	Stable suspension
Sodium citrate	Stable suspension	Stable suspension
Sodium carbonate	Almost completely flocculated	Stable suspension
Lithium carbonate	Partially flocculated	Stable suspension

The results tabulated in table 7 show that saponite clay was stable in all suspensions, whereas only sodium citrate and sodium silicate maintained the dispersion of attapulgite clay. When the concentration of the suspensions were increased to 0.5 per cent the saponite suspensions remained stable but the attapulgite suspensions coagulated. The separation of attapulgite clay thus is effected only in dilute 0.2 per cent suspensions using sodium citrate as the dispersing agent, whereas saponite clay separation could be accomplished at higher concentrations, at least 0.5 per cent with or without electrolytes.

The nontronite clay fraction, which was only partially dispersed, even by extreme treatment, remained most stable using ammonium hydroxide and only slightly less stable when lithium carbonate or hydroxide were used in 0.002N concentration.

A mechanical analysis of these clay materials was made, using sodium citrate for the attapulgite and saponite clays and lithium carbonate for the nontronite clay, after a severe physical treatment which included shaking and highspeed mechanical stirring. Table 8 gives the results of the analyses as carried out by the sieve and pipette method (64).

The analysis of the saponite clay gives a relatively true picture of the mechanical composition of the material but the data obtained for the other two clays probably reflect the relative degree of cementation in place of an accurate picture of the ultimate particle size dis-

TABLE 8. THE MECHANICAL ANALYSIS OF ATTAPULGITE, NONTRONITE
AND SAPONITE CLAY MATERIALS. (0.2% suspensions).

Size Class	Saponite	Attapulgite	Nontronite Normal pretreatment	Nontronite Truog pretreatment
Sand >0.05 mm	4.96%	0.80%	0.20%	0.15
Silt 0.05-0.02 mm	2.01	10.96	25.25	17.31
0.02-0.01 mm	4.23	9.65	16.42	12.21
0.01-0.005 mm	2.23	11.40	14.20	5.77
0.005-0.002 mm	5.80	10.09	11.98	3.33
Clay <0.002 mm	81.11	56.58	31.07	15.31
Solution Loss				45.92

tribution. The data also show that the Truog pretreatment (71), used in an attempt to remove the cementing compound from the nontronite clay, was unsuccessful. It effected as great a solution of the clay as it did of the iron oxide cement.

For use in further work larger quantities of these clays, $< 2\,\mu$ particle size, were separated by sedimentation and dialyzed in collodion sacs. These partially sodium saturated suspensions were then separated quantitatively into several size fractions, namely $2\,\mu - 1\,\mu$, $1\,\mu - 0.5\,\mu$, $0.5\,\mu - 0.2\,\mu$, $0.2\,\mu - 0.05\,\mu$ and $< 0.05\,\mu$ effective diameter.

The separations at $1\,\mu$, $0.5\,\mu$ and $0.2\,\mu$ were made in a tube centrifuge using the double layer method developed by Marshall (36); while the separation at $0.05\,\mu$ was effected in the Sharples supercentrifuge by a double layer method outlined by Whiteside and Marshall (73). It was found necessary to slightly modify this method by substituting a 10:3 glycerol-water mixture for the original 10:1 mixture, because in this experiment the more viscous liquid pushed the clay from the lower part of the bowl.

The dialyzed saponite clay suspension before fractionation was diluted to 0.36 per cent to eliminate the mutual interference of the particles, while the separation of the attapulgite clay was made immediately after the dispersion of the 0.50 per cent alkaline suspension. However, it was found to be impossible to separate by centrifuge the $2\,\mu - 1\,\mu$ fraction of the attapulgite clay. The clay coagulated at the junction of the suspensions and the glycerol-water mixture unless the latter were diluted to 1:4 and made alkaline with sodium hydroxide. Consequently, since separation of the $2\,\mu - 1\,\mu$ size fraction required a 2:1 mixture, separation by the centrifuge was impossible.

The nontronite clay was effectively separated into size fractions by keeping the 0.60 per cent suspensions alkaline with sodium hydroxide.

When the tube centrifuge was used the mechanical analysis results were obtained by determining the clay deposited, on an ignited weight basis in terms of the total used. When the Sharples super-centrifuge was employed the clay remaining in suspension was determined in terms of the total.

TABLE 9. THE MECHANICAL ANALYSIS OF SAPONITE, ATTAPULGITE AND NONTRONITE CLAY. (.002 mm)

Particle "Effective" diameter	Clay fraction in per cent of total		
	Nontronite	Attapulgite	Saponite
2 μ - 1 μ	58.36		17.13
		18.86	
1 μ - 0.5 μ	16.52		12.45
0.5 μ - 0.2 μ	12.13	51.42	16.40
0.2 μ - 0.05 μ	11.97	26.26	45.75
< 0.05 u	1.02	3.46	8.27

A survey of the results listed in table 9 shows a distinct modal group in each distribution. The nontronite clay had more than 50 per cent of its weight made up of particles between 2 μ — 1 μ effective diameter. This is probably indicative of the cementation of this clay, a feature confirmed by microscopic examination. The attapulgite clay had more than half its weight comprised of particles between 0.5 μ to 0.2 μ effective diameter; while almost 50 per cent of the saponite clay consisted of particles 0.2 μ to 0.05 μ in size. A common feature of these distributions is the small quantity of material less than 0.05 μ.

ELECTRODIALYSIS

An investigation of many clay properties may be facilitated if a hydrogen clay system can be produced. This can be brought about most quickly and satisfactorily by electrodialysis, a procedure first studied by Cameron and Bell (10), by König, Hasenbaumer and Hassler (39) and by König, Hasenbaumer and Krupp (40). Mattson (53), (54), Humfeld and Alben (32), Bradfield (7) and Crowther and Basu (13) later discovered that electrodialysis would remove completely the ex-change cations of a soil and usually in the following order (calcium, potassium, sodium), magnesium, aluminium, (iron and manganese). Mattson also noted the presence of silica in the cathode chamber, and concluded that it transferred as a constituent of a positively charged complex molecule.

In this investigation the stability of attapulgite, saponite and non-tronite clays in an electric field and the production of the hydrogen systems was ascertained by electrodialyzing one gram samples in a

three compartment Bradfield cell, with parchment paper membranes, for 968 hours. The degree of stability was determined by draining the cathode and anode chambers at frequent intervals and analyzing the dialysates. A flushing liquid of 0.02N hydrochloric acid was satisfactorily employed to remove precipitated material until the lengthening sampling periods made quick dissolution impossible.

The results are presented in table 10 to 12. The bases extracted at the cathode in the later periods of extraction, when an unremovable precipitate was forming, are listed as a total, while the final precipitate retained in the chamber is given as a unit.

It is evident from the data presented that the saponite clay decomposed under the treatment, whereas attapulgite and nontronite were only slightly affected. The electrodialysis of the saponite clay extracted silica to 15.6 per cent of the sample. The magnesium, 25.08 per cent, was completely removed and gives confirmation to Nutting's statement (63) that electrodialysis removed all the magnesium from this clay. It is evident that hydrogen attapulgite and nontronite clays but not hydrogen saponite clay can be produced by electrodialysis.

One of the most striking features of this study was the large quantity of silica that passed to the cathode chamber. This was particularly emphasized in the treatment of the unstable clay, saponite, from which relatively huge quantities of silica combined with magnesium were removed, as well as calcium, lithium and sodium, apparently as Mattson has suggested, in the form of complex molecules. These molecules apparently are fragments of the lattice broken from the clay under the influence of an electric field and positively charged through the cation constituents.

The maximum extraction rate of the cations was reached in the following order.

Saponite clay
$$Ca > Na > Li > Mg > (Al, Fe)$$
Attapulgite clay
$$Mg > Ca > (Al, Fe)$$
Nontronite clay
$$Li > Na > Ca > Mg > (Al, Fe)$$

The anode, rather than the cathode, dialysate analyses probably better indicated the relative stability of attapulgite and nontronite clays. A very small amount of silica was extracted from the nontronite, a little more from the attapulgite and, of course, a large quantity from saponite clay. It is interesting to note that less silica was present in the anode than in the cathode chamber, while some calcium and magnesium, particularly magnesium from the saponite clay, had been transferred to the anode chamber. This confirms the investigation of Bradfield (7) and Löddesol (43) in which cations were found in the anode chamber of electrodiolysis cells, and it again points out the probability of the migration of charged complex molecules, fragments broken from the clay lattice.

TABLE 10. MATERIALS REMOVED FROM NONTRONITE CLAY BY ELECTRODIALYSIS

CATHODE CHAMBER
Milliequivalents per 100 gms. (Ignited basis)

Time period	Hours	Calcium Amount	Rate per hour	Magnesium Amount	Rate per hour	Sodium Amount	Rate per hour	Lithium Amount	Rate per hour	Silicon Amount	Rate per hour	Aluminium and iron as (Fe) Amount	Rate per hour
1 hrs.	1	0.38	0.38	----	----	2.52	2.52	4.80	4.80	2.50	2.50	0.39	0.39
1 -4 "	3	1.72	0.57	2.39	0.80	4.09	1.36	12.53	4.18	3.92	1.31	0.23	0.23
4 -5 "	1	0.23	0.23	0.49	0.49	----	----	1.12	1.12	0.86	0.86	0.99	0.99
5 -9 "	4	1.92	0.48	1.72	0.43	----	----	0.92	0.23	2.35	0.59	1.80	0.45
9-15 "	6	1.79	0.30	0.77	0.13	----	----	0.38	0.06	1.08	0.18	0.83	0.14
15-51 "	36	2.14	0.06	2.52	0.07	----	----	0.50	0.01	4.78	0.13	3.05	0.08
Total	51	8.18		7.89		6.61		20.25		15.49		7.29	
Total Precipitated material	51 to 968	4.69		4.04		0.52		0.51		85.19		12.70	
		19.94		7.05		1.13		0.33		32.22		20.51	
Total	968	32.81		18.98		8.26		21.09		132.90		40.50	

ANODE CHAMBER

Time period	Hours	Calcium Amount	Rate per hour	Magnesium Amount	Rate per hour	Sulfate Amount	Rate per hour	Chloride Amount	Rate per hour	Silicon Amount	Rate per hour
0-147	147	0.32	.002	0.34	.002	2.20	.015	3.55	.024	8.08	.055
147-968	821	1.03	.001	0.67	.001	7.85	.010	5.19	.006	----	----
Total	968	1.35		1.01		10.05		8.74		8.08	

TABLE 11. MATERIALS REMOVED FROM ATTAPULGITE CLAY BY ELECTRODIALYSIS

CATHODE CHAMBER
Milliequivalents per 100 gms. (Ignited basis)

Time period	Hours	Calcium Amount	Rate per hour	Magnesium Amount	Rate per hour	Sodium Amount	Rate per hour	Lithium Amount	Rate per hour	Silicon Amount	Rate per hour	Aluminium and iron as (Fe) Amount	Rate per hour
1 hrs.	1	2.99	2.99	0.83	0.83					----	----	0.93	0.93
1 - 2 "	1	3.25	3.25	0.46	0.46			0.71	0.71	2.55	2.55	1.17	1.17
2 - 5 "	3	8.01	2.67	1.97	0.66					3.70	1.23	2.26	0.75
5 - 6 "	1	2.49	2.49	0.68	0.68					1.06	1.06	1.95	1.95
6 -11 "	5	6.36	1.27	2.20	0.44	0.80	0.16			6.87	1.37	3.27	0.65
11-27 "	16	5.50	0.44	2.27	0.14	0.68	0.04			4.58	0.29	4.83	0.30
27-99 "	72	7.10	0.10	3.64	0.05	0.61	0.01	1.32	0.02	12.60	0.18	4.83	0.07
Total	99	35.70		12.05		2.09		2.03		31.36		19.24	
Total	99 to 968	12.75		15.23		0.33		0.14		39.65		14.56	
Precipitated material		20.10		26.07		0.41		0.11		17.88		6.77	
Total	968	68.55		53.35		2.83		2.28		88.89		40.57	

ANODE CHAMBER

Time period	Hours	Calcium Amount	Rate per hour	Magnesium Amount	Rate per hour	Sulfate Amount	Rate per hour	Chloride Amount	Rate per hour	Silicon Amount	Rate per hour
0-147	147	1.78	.012	1.57	.0111	1.60	.011	3.72	.025	8.64	0.059
147-968	821	0.84	.001	0.43	.0005	6.05	.007	4.46	.005	22.13	0.027
Total	968	2.62		2.00		7.65		8.18		30.77	

TABLE 12. MATERIALS REMOVED FROM SAPONITE CLAY BY ELECTRODIALYSIS

CATHODE CHAMBER
Milliequivalents per 100 gms. (Ignited Basis)

Time period	Hours	Calcium Amount	Rate per hour	Magnesium Amount	Rate per hour	Sodium Amount	Rate per hour	Lithium Amount	Rate per hour	Silicon Amount	Rate per hour	Aluminium and iron as (Fe) Amount	Rate per hour
1 hrs.	1	12.79	12.79	3.06	3.06	1.09	1.09	0.24	0.24	----	----	----	----
1 - 3 "	2	22.51	11.26	10.46	5.23			1.91	0.96	2.39	1.20	----	----
3 - 5 "	2	7.57	3.78	18.86	9.43			2.55	1.28	2.39	1.20	----	----
5 - 7 "	2	1.46	0.73	27.69	13.84			1.96	0.98	2.90	1.45	----	----
7 -11 "	4	0.56	0.14	26.76	6.69			2.88	0.72	5.70	1.45	1.02	0.26
11 -15 "	4	0.25	0.06	17.94	4.48			1.77	0.44	2.39	0.60	1.82	0.46
15 -27 "	12	1.72	0.14	61.42	5.12	1.05	0.09	7.64	0.64	17.53	1.25	3.95	0.33
27 -39 "	12	0.63	0.05	50.89	4.24			4.84	0.40	16.63	1.66	4.02	0.33
39 -48 "	9	0.70	0.08	75.59	8.40			3.88	0.43	19.77	2.20	2.27	0.25
48 -61 "	13	0.65	0.05	86.76	6.67	0.42	0.03	5.03	0.39	31.93	2.46	1.90	0.15
61 -93 "	32	0.96	0.03	52.81	1.65	3.74	0.12	3.80	0.12	12.41	0.39	6.80	0.21
Total	93	49.80		432.24		6.30		36.50		114.04		21.78	
Total Precipitated	93 to 968	19.88		219.71		2.42		10.30		543.11		12.95	
material Diffusion for 2 hrs. at end of ninth hr.		23.07		584.70		1.09		0.49		309.08		12.87	
		0.16		7.26				----		8.44		----	
Total	968	92.91		1243.91		9.81		47.29		974.69		47.60	

ANODE CHAMBER

Time period	Hours	Calcium Amount	Rate per hour	Magnesium Amount	Rate per hour	Sulfate Amount	Rate per hour	Chloride Amount	Rate per hour	Silicon Amount	Rate per hour
0 -9	9	0.29	.032	0.88	.098	0.50	.056	2.38	.264	44.44	4.937
9 -48	39	----	----	6.12	.157	9.40	.241	4.02	.103	144.93	3.716
48 -93	45	0.45	.010	0.30	.006	0.40	.009	5.25	.117	121.88	2.708
93 -579	486	0.45	.001	0.42	.001	2.45	.005	7.19	.015	57.56	0.118
579 -771	192	0.23	.001	0.42	.002	0.50	.003	2.97	.015	82.12	0.428
771 -968	197	0.14	.001	1.00	.005	1.65	.008	3.15	.016	50.38	0.256
Total	968	1.56		9.14		14.90		24.96		501.31	

Hydrogen saponite and attapulgite clays are rather unstable, with magnesium from the lattice probably replacing some of the inactive hydrogen. This is indicated by the change in the hydrogen ion concentration of an attapulgite clay suspension which stood for 197 days, from a pH of 3.90 to 4.76 and of the partially decomposed saponite clay from 3.95 to 4.44.

It was concluded from an experiment in which attapulgite and saponite suspensions were stirred for variable periods of time up to at least two hours without a change occurring in the pH or hydration, that vigorous stirring does not break the clay particles, with a consequent change in reaction. Thus this clay dispersion method is satisfactory for the preparation of suspensions used in titration curve studies.

SUMMARY AND CONCLUSIONS

A perusal of the literature relating to the properties of these three clays indicates that nontronite clay is the iron member of the beidellite-nontronite isomorphous series of clay minerals. Attapulgite clay with an amphibole-like structure is the first clay mineral found to have other than a micaceous structure. The clay from Hector, California, which has been called magnesium bentonite or magnesium beidellite is now considered to be a saponite mineral.

The physical properties of the clay samples examined resemble those listed in the tabulated data from the literature. Some properties of saponite, such as relative ease of dispersion, the stability of suspensions, the formation of viscous gels at low concentrations and swelling phenomena, resemble those of montmorillonite. Attapulgite, however, has distinctly different properties. Stable suspensions are produced only with difficulty and are maintained, and that only for a short time, by alkali hydroxides. The coagulum is easily redispersed, while gels are formed only at relatively higher concentrations of clay. Nontronite clay properties resemble those of beidellite but a stable suspension is dependent on the maintenance of an alkaline reaction.

Dilute solutions of untreated saponite can be dispersed in water, whereas untreated attapulgite required the use of sodium citrate or sodium silicate.

Nontronite and attapulgite clays can be electrodialyzed and a hydrogen clay produced. Saponite clay on the other hand is rapidly decomposed. Much of the silica removed from these clays is transported to the cathode, a feature particularly pronounced in the treatment of saponite clay. It seems that the silica is transported as a constituent of a positively charged, base containing complex molecule which is probably a fragmental part of the clay lattice.

Part II.

CHEMICAL ANALYSES

The importance of the information derived from the chemical analysis of the different size fractions of clay minerals in a study of their properties, has been pointed out by Marshall (52) and Holzner (31). From such investigations the homogeneity of the clay can be inferred, the lattice type determined and the atomic replacement and the charge distribution in the clay lattice calculated.

In this investigation the clay fractions, separated as previously described (Part I of this series of papers), and following their use in the determination of the base exchange capacity, were analyzed for their chemical constituents.

The samples were prepared by drying the clay suspensions and powdering the dried flakes in an agate mortar. The analytical methods· were, in general, those outlined by Hillebrand and Lundell (30) and Kolthoff and Sandell (38), but it may be of interest to mention the manner in which some of the more infrequently ascertained constituents were determined. The titanium content was given by the colorimteric H_2O_2 method, while the manganese was determined colorimetrically as the permanganate. The alkalies were brought into solution by hydrofluoric and perchloric acids, and after separation of the other metals, sodium and potassium were estimated by determining sodium as the uranyl zinc acetate salt. In solutions containing lithium, the alkalies were determined spectrographically by Dr. V. Ells of the Agricultural Chemistry Department. A modified form of the Cooke method (30) was used for the ferrous iron determination, and Mervin's modification of Steiger's method (30) was employed in ascertaining the fluorine content of the saponite clay.

The maximum weight of a sample used in any series of determinations was 0.47 gram and the minimum 0.15 gram.

The analysis of the nontronite fractions as given in table 13 show that this clay contains only a surprisingly small content of other constituents apart from the usual silica, alumina and iron oxides. A considerable variation is noted in the composition of the fractions with the silica content decreasing with particle size, while the Al_2O_3/Fe_2O_3 ratio is very irregular. In the two larger size fractions this ratio was 1.2 and 2.0, respectively, whereas in the smaller size fractions it was less than unity.

The iron oxide content of the clay fractions was much less, and the alumina content considerably higher, than the analyses of nontronite and varieties given by Larsen and Steiger (41) or listed in table 1, or that of a sample taken from the same deposit as the material used in this investigation (66). In fact, the Fe_2O_3/Al_2O_3 ratio of the two smaller clay fractions was smaller than the ratio for an iron-rich beidellite (68). It is evident that this clay, when freed from the adhering iron oxide coating around the aggregates, is not a high iron

TABLE 13. ANALYSES OF THE FRACTIONS OF ATTAPULGITE NONTRONITE AND SAPONITE CLAY. (110° BASIS)

Oxide content in per cent	Nontronite				Attapulgite			Saponite				
	2 μ-1 μ	1 μ-0.5 μ	0.5 μ-0.2 μ	0.2 μ-0.05 μ	2 μ-0.5 μ	0.5 μ-0.2 μ	0.2 μ-0.05 μ	2 μ-1 μ	1 μ-0.5 μ	0.5 μ-0.2 μ	0.2 μ-0.05 μ	0.05 μ
SiO_2	45.56	43.80	42.36	41.51	57.14	55.19	54.81	55.02	56.71	56.80	56.69	54.85
Al_2O_3	16.69	12.22	21.06	20.33	12.72	13.07	15.21	2.50	2.07	1.57	3.19	2.15
Fe_2O_3	20.35	24.71	18.20	19.39	3.62	1.57	1.90	0.47	0.29	0.47	0.54	1.20
FeO	1.25	1.15	1.15	0.61	1.10	0.95	1.14	0.00	0.00	0.00	0.00	0.00
TiO_2	0.00	0.00	0.00	0.00	0.06	00.05	0.04	0.00	0.00	0.00	0.00	0.00
P_2O_5	0.08	0.15	0.21	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GaO	0.31	0.07	0.14	0.15	0.47	0.45	0.43	0.46	0.11	0.11	0.38	0.09
MgO	0.03	0.00	0.00	0.00	7.79	10.14	9.06	24.55	24.46	24.35	25.25	24.25
MnO	0.00	0.00	0.00	0.00	0.02	0.02	0.02	0.00	0.00	0.00	0.00	0.00
Na_2O	0.00	0.00	0.00	0.00	0.07	0.03	0.04	0.00	0.00	0.00	0.00	0.00
K_2O	0.00	0.03	0.07	0.10	1.13	0.22	0.24	0.00	0.00	0.00	0.00	0.00
Li_2O	-----	-----	-----	-----	-----	-----	-----	0.80	0.65	0.88	0.81	0.62
H_2O (Ignition)	12.78	14.38	15.53	16.58	15.46	16.73	15.55	13.95	13.22	13.25	11.20	13.70
Adsorbed NH_4	0.89	0.88	0.91	0.80	0.26	0.27	0.32	1.00	1.11	1.18	1.28	1.18
F	-----	-----	-----	-----	-----	-----	-----	0.51	0.51	0.51	0.52	0.51
(O) equivalent of (F)	-----	-----	-----	-----	-----	-----	-----	0.21	0.21	0.21	0.22	0.21
Total	97.95	97.39	99.63	99.67	99.84	98.69	98.76	99.05	98.92	98.91	99.64	98.34

clay, but an intermediate member of the beidellite-nontronite series. It is impossible, judging from the chemical analysis, to state whether the larger fractions were impure or whether there was a variation in the composition of the different fractions. However, it would seem that the latter condition is the more probable because, although recently acquired electron microscope pictures show these fractions to be aggregated, possibly by cementation, the optical properties indicate a pure clay.

The analyses show that attapulgite clay is an aluminium magnesium silicate, and indicate that in all probability, the two smaller size fractions consisted of pure mineral, whereas the larger fractions may have contained some impurities, a conclusion indicated by the presence in the latter of larger quantities of potassium and silica and a relatively lower content of magnesium.

The analyses of the saponite fractions indicate that this clay is a magnesium silicate containing small additional quantities of alumina, lithium and fluorine. These results were similar to the analysis of other samples from Hector, California (see table 5), although in these latter the alumina content was lower and fluorine was unreported, with the exception of samples investigated by Ross and Hendricks (66). It may be concluded that this clay sample is pure, since there is only slight variation in composition between the samples and that all fractions may be used in the subsequent lattice study.

CALCULATION OF LATTICE TYPE AND LATTICE REPLACEMENTS

Marshall (52) showed that there are several types of micaceous structures possible within the expanding clay group and that nontronite and its varieties belonged principally in the 2:1 or 3:2 lattice types. The same author has also indicated how the base exchange properties of a clay are developed by the isomorphous replacement of atoms by those of lower valency.

Nagelschmidt (59) found that nontronite clay and also the saponite clay from Hector, California, had a 2:1 lattice structure, while Ross and Hendricks (66) and Hendricks (28) list the saponite clay and nontronite clay from Sandy Ridge, North Carolina, as members of the 2:1 lattice type group.

Little is known regarding the lattice structure and atomic replacement of attapulgite, although from X-ray data, Bradley (8) has concluded that it has an amphibole-like structure with type formula $Mg_5Si_8O_{21}$.

Nagelschmidt (59) states that the charge development in the nontronite clay is a consequence of the substitution of aluminium for silicon and the replacement of some trivalent ions by magnesium and ferrous iron. Ross and Hendricks (66) and Hendricks (28) indicate that the charge on nontronite is a result of replacement of silicon by aluminium, while the charge on the saponite from Hector, California,

is produced by the substitution of lithium for magnesium, although Nagelschmidt (59) also includes in the lattice the substitution of aluminium for silicon.

The calculated lattice replacements of attapulgite, and saponite and nontronite are given in tables 14, 15, and 16, in which is outlined, in tabular form, the chemical composition of each sheet in the clay with the consequent charge developed by atomic replacement. The base exchange capacity figures are those given by adsorption of cations from neutral calcium acetate and referred to the clay dried at 110° C. The calculations, based on the chemical analysis of attapulgite clay, support Bradley's' conclusions that this clay has an amphibole-like structural with dehydrated formula $Mg_5Si_8O_{21}$. The negative charge is developed by the substitution of aluminium for silicon and is partially balanced by the positive charge that is provided by the presence of trivalent ions in the modified brucite sheets of the amphibole structure. The base exchange capacity, it is to be noted, agrees closely with the calculated negative charge, indicating that the analysis fits the structure well and that Marshall's theory (52) of exchange capacity as a consequent result of atomic replacement in the lattice of micaceous clays can be extended to amphibole-like clays.

TABLE 14. MOLECULAR COMPOSITION AND CHARGE DISTRIBUTION OF THE
FRACTIONS OF ATTAPULGITE CLAY

Size Fraction (microns)	Theoretical Dehydrated Formula	Type	Sheet	Composition	Charge
2 μ-0.5 μ	$Mg_5Si_8O_{21}$	Amphibole	Silica	Si Al 7.726 .274	(−) .274
			Modified Brucite	Al Fe^{3*} Fe^{2**} Ti Mg Ca Mn K Na 1.751 .368 .125 .012 1.569 .060 .002 .195 .018	(+) .130
				Total	(−) .144
				Exchange capacity	(+) .156
0.5 μ-0.2 μ	$Mg_5Si_8O_{21}$	Amphibole	Silica	Si Al 7.603 .397	(−) .397
			Modified Brucite	Al Fe^3 Fe^2 Ti Mg Ca Mn K Na 1.726 .163 .109 .005 2.082 .066 .003 .038 .008	(+) .253
				Total	(−) .144
				Exchange capacity	(+) .146
0.2 μ-0.05 μ	$Mg_5Si_8O_{21}$	Amphibole	Silica	Si Al 7.453 .547	(−) .547
			Modified Brucite	Al Fe^3 Fe^2 Ti Mg Ca Mn K Na 1.889 .194 .127 .004 1.833 .063 .002 .042 .011	(+) .368
				Total	(−) .179
				Exchange capacity	(+) .161

$*Fe^3$-Ferric $**Fe^2$-Ferrous

The saponite clay as indicated from the calculations has a 2:1 lattice structure and its negative charge is produced by substitution of aluminium for silicon in the silica sheet and by replacement of magnesium by lithium in the incompletely filled brucite sheet. It is interesting to note the variation in the distribution of the charge

TABLE 15. MOLECULAR COMPOSITION AND CHARGE DISTRIBUTION OF THE
FRACTIONS OF SAPONITE CLAY.

Size Fraction (Microns)	Theoretical Dehydrated Formula	Type	Sheet	Composition	Charge
2 μ-1 μ	$(Al_4)Si_8O_{22}$ Mg_6	2:1	Silica	Si Al 7.736 .264	(-) .264
			Brucite	Al Fe^{3*} Mg Ca Li F .149 .050 5.144 .069 .449 .226 Total Exchange capacity	(-) .302 ---------- (-) .566 (+) .532
1 μ-0.5 μ	$(Al_4)Si_8O_{22}$ Mg_6	2:1	Silica	Si Al 7.892 .108	(-) .108
			Brucite	Al Fe^3 Mg Ca Li F .233 .030 5.070 .014 .360 .224 Total Exchange capacity	(-) .459 ---------- (-) .567 (+) .533
0.5 μ-0.2 μ	$(Al_4)Si_8O_{22}$ Mg_6	2:1	Silica	Si Al 7.920 .080	(-) .080
			Brucite	Al Fe^3 Mg Ca Li F .178 .049 5.058 .017 .495 .224 Total Exchange capacity	(-) .450 ---------- (-) .530 (+) .539
0.2 μ-0.05 μ	$(Al_4)Si_8O_{22}$ Mg_6	2:1	Silica	Si Al 7.693 .307	(-) .307
			Brucite	Al Fe^3 Mg Ca Li F .204 .055 5.103 .055 .448 .223 Total Exchange capacity	(-) .236 ---------- (-) .533 (+) .565
Less than 0.5 μ	$(Al_4)Si_8O_{22}$ Mg_6	2:1	Silica	Si Al 7.767 .233	(-) .233
			Brucite	Al Fe^3 Mg Ca Li F .127 .128 5.118 .013 .355 .223 Total Exchange capacity	(-) .390 ---------- (-) .623 (+) .617

*Fe^3-Ferric

between the size fractions. The fractions 1 μ to 0.5 μ and 0.5 μ to 0.2 μ have less than one-fourth of the negative charge on the silica sheet whereas in the other fractions it is more evenly divided. The charge, principally developed on the brucite sheets, has a similar distribution to that of the montmorillonite clay (52). The negative charge on saponite clay was closely balanced by the exchangeable cations.

The nontronite clay belongs to the 2:1 lattice type clays; and the negative-charge is entirely developed by replacement of silicon by aluminium and balanced partially by an excess of trivalent ions in the gibbsite sheet and partially by the exchangeable cations. This charge distribution is in distinct contrast to that found in the montmorillonite and saponite clays.

The nontronite and beidellite clays have been considered as 2:1 and 3:2 lattice type clays. However, it seems evident that if it is conceded that the gibbsite layer can contain atoms in excess of the theoretical values, then it may be deduced that the 2:1 lattice is the fundamental structural type of all expanding clays.

It is interesting to discuss the possibility of other fundamental structural types, as for example, a 2:1 lattice type with the composition of a 3:2 lattice. Such a fundamental uncharged structure, would

TABLE 16. MOLECULAR COMPOSITION AND CHARGE DISTRIBUTION
OF THE SIZE FRACTIONS OF NONTRONITE CLAY.

Size Fraction (Microns)	Theoretical Dehydrated Formula	Type	Sheet	Composition	Charge
2 μ-1 μ	$(Al_4)Si_8O_{22}$ Fe_4	2:1	Silica	Si P Al 6.830 .012 1.158	(-) 1.146
			Gibbsite	Al Fe^{3*} Fe^{2**} Ca Mg 1.789 2.294 .157 .050 .006	(+) .675
				Total	(-) .471
				Exchange capacity	(+) .484
1 μ-0.5 μ	$(Al_4)Si_8O_{22}$ Fe_4	2:1	Silica	Si P Al 6.879 .021 1.100	(-) 1.079
			Gibbsite	Al Fe^3 Fe^2 Ca K 1.163 2.919 .150 .011 .006	(+) .574
				Total	(-) .505
				Exchange capacity	(+) .509
0.5 μ-0.2 μ	$(Al_4)Si_8O_{22}$ Fe_4	2:1	Silica	Si P Al 6.391 .026 1.583	(-) 1.557
			Gibbsite	Al Fe^3 Fe^2 Ca K 2.160 2.067 .144 .023 .013	(+) 1.028
				Total	(-) .529
				Exchange capacity	(+) .517
0.2 μ-0.05 μ	$(Al_4)Si_8O_{22}$ Fe_4	2:1	Silica	Si P Al 6.348 .027 1.625	(-) 1.598
			Gibbsite	Al Fe^3 Fe^2 Ca K 2.037 2.231 .077 .025 .018	(+) 1.016
				Total	(-) .582
				Exchange capacity	(+) .543

$*Fe^3$-Ferric $**Fe^2$-Ferrous

have the highly hydrated formula $O_{12}(Si_6Al_2)OH_{12}Al_4OH_2(Si_6Al_2)O_{12}$ which makes it doubtful that such a structure could exist save under exceptional circumstances. Thus the 3:2 ratios in clay probably can best be accounted for by assuming the possibility of an excess of trivalent atoms in the gibbsite sheet as well as a large substitution of aluminium for silicon in silica sheet.

Now Ross and Hendricks (66) would call the nontronite clay examined in this investigation an iron-rich beidellite by reason of its having excess trivalent ions in the gibbsite sheet. However, such a division, in which this clay is classified separately from nontronite, is rather arbitrary and confusing and consequently it seems more logical to consider it as an aluminous nontronite, a member of the beidellite-nontronite isomorphous series.

An outstanding point resulting from the calculation of the charge distribution on the lattice of these clays is the great difference between the montmorillonite-saponite clays and the nontronite-beidellite clays, a difference which offers a suggestion as to how these clay minerals may be classified in a practical and systematic manner.

The first division is based on the structural classification of silicates and separates the clays belonging to the SiO_3 structural group, such as attapulgite clay, from the remainder of the clays which are included in the Si_2O_5 structural group or micaceous silicates. The next division, limited within the latter group, is based on the lattice type, and segregates these clays into the 2:1 lattice group and the 1:1 kaolin lattice group.
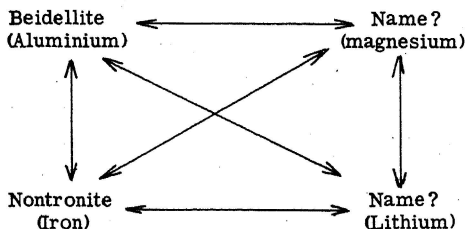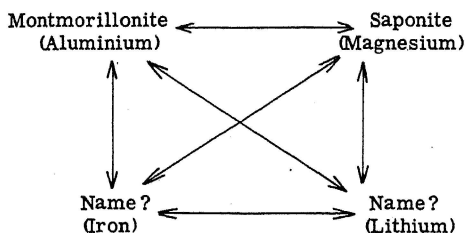
The 2:1 lattice group may be classified into several categories. The first and at present unsatisfactorily defined and classified division is that which includes those clays, such as illites, which appear to be transition types between micas and true clays. The remaining 2:1 clays, all with an expanding lattice, may be classified as those in which the negative charge is predominately located on the silica sheets, such as beidellite, and those in which the charge is chiefly on the brucite or gibbsite sheets, as in montmorillonite. This latter grouping is in accord with the differences in several physical properties of clay which are to be expected as a consequence of variation in the distribution of the charge. Further separation in all the categories is principally based on the chemical composition of the central sheet of the clay lattice. These ideas with respect to clay classification are graphically outlined as follows:

CLASSIFICATION OF THE CLAYS

Silicate basis of structure

SiO_3
Fibrous clays
Amphibole-like structure
(Attapulgite, Sepiolite)

Si_2O_5

Complete sheets

2:1 lattice type

1:1 lattice type

Transition group
between micas
and clays
(Illite - Bravaisite)
(Vermiculites)
(Micaceous halloysite)

Expanding lattice
Clays

Hydrated
(Halloysite)

Dehydrated
(Metahalloysite)
(Kaolinite)
(Nacrite)
(Dickite)

Net charge is chiefly
due to replacement in
center gibbsite sheet
(Montmorillonite-Saponite)

Net charge is chiefly
due to replacement in
silica sheets.
(Beidellite-Nontronite)

In the beidellite-nontronite isomorphous series it is possible to have clays in which iron, magnesium or even lithium, to a greater or less extent, has replaced aluminium; while clays in the montmorillonite-saponite series may have aluminium replaced by magnesium, iron or lithium. Thus either of these series may be expanded by the discovery and naming of these end members.

The following diagrams illustrate this point.

```
Montmorillonite  ⟵⟶  Saponite
(Aluminium)            (Magnesium)
      ↕          ✕          ↕
   Name?        ⟵⟶      Name?
   (Iron)               (Lithium)
```

```
Beidellite  ⟵⟶  Name?
(Aluminium)       (magnesium)
      ↕      ✕        ↕
  Nontronite ⟵⟶   Name?
  (Iron)          (Lithium)
```

Minerals in an isomorphous series such as we are here dealing with may be named in accordance with the predominant replacements. No general agreement has yet been arrived at in the case of this group of the clays and it seems that the important thing at present is to keep the series open so as to fit in new analyses of homogeneous samples.

Hendrick's attempt to introduce new names based on minor changes seems likely to cause great confusion. The four names which are well established are nontronite, beidellite, montmorillonite, and saponite, and these seem sufficient at present, until new end members are discovered, for approximate orientation as to composition. The detailed description of minerals within these two series requires only exact figures for replacements rather than innumerable new names.

BASE EXCHANGE CAPACITY

The capacity of nontronite clay has been given by Jackson and Truog (33) as 108 M. E. while Hendricks and Alexander (29) describe a sample with a capacity of 92 M. E. These values are high in comparison with those of the beidellites given by Gieseking and Jenny (22) as 60 M. E. and by Marshall (52) as 63.5 M. E.

The only figures available on the exchange capacity of attagulgite clay has been given by Bradley (8) who found that 21 M. E. of ammonia were absorbed by the 0.1 μ to 0.05 μ size fraction.

The exchange capacity has been given for saponite as 21.8 M. E. (59), a very low and doubtful value for this clay.

In this investigation the exchange capacity of the fractions of attapulgite, saponite and nontronite was determined by the adsorption of ammonia from a neutral 0.1N ammonium acetate solution and of calcium from 0.1N calcium acetate solutions with pH values of 5.0, 7.0, and 9.0. These four determinations were made on the same sample of each size fraction. The weight of the sample used varied from 0.21 to 0.76 gram. The determination was conducted by repeated decantation and centrifuging, while the cations were determined in the supernatant liquid.

The results of this study are given in table 17, and are expressed on the basis of ignited clay.

TABLE 17. BASE EXCHANGE CAPACITY OF FRACTIONATED NONTRONITE, ATTAPULGITE AND SAPONITE CLAYS.

Clay	Fraction Size	Milliequivalents per 100 gms. (Ignited basis)			
		Ammonium pH 7.0	Calcium pH 5.0	Calcium pH 7.0	Calcium pH 9.0
Nontronite	2 μ - 1 μ	60.8	57.7	62.3	63.9
	1 μ - 0.5 μ	61.0	58.2	62.8	66.0
	0.5 μ - 0.2 μ	64.3	60.8	68.4	66.3
	0.2 μ - 0.05 μ	57.0	64.9	71.5	70.6
Attapulgite	2 μ - 1 μ	18.0	21.4	22.8	24.2
	1 μ - 0.5 μ	19.0	19.2	21.2	21.2
	0.5 μ - 0.2 μ	22.2	22.7	23.5	25.3
Saponite	2 μ - 1 μ	69.3	68.1	74.0	70.6
	1 μ - 0.5 μ	76.0	75.8	74.3	75.8
	0.5 μ - 0.2 μ	81.5	76.0	75.3	74.6
	0.2 μ - 0.05 μ	86.3	76.8	79.2	75.3
	<0.05 μ	81.4	81.6	85.2	79.3

The exchange capacity of the nontronite clay fractions ranged between 57 and 71 M. E., values considerably lower than those given in the literature (33), (66). There was a small increase in capacity with decreasing size, but the influence of the exchangeable cation or the variation in the alkalinity of the solutions gave values too irregular to show significant differences.

The fractions of attapulgite clay had exchange capacities ranging from 18.0 to 25.3 M. E.   The ammonia absorbed was less than that of calcium; while it is evident that more calcium was adsorbed from the more alkaline solutions.

The exchange capacity of the saponite size fractions ranged from 68.1 to 86.3 M. E. which is much higher than the figure determined by Schofield (59).   In general, there was an increase in the exchange capacity with decreasing particle size, but the base adsorption from the different solutions was too irregular to permit any conclusions as to their relative effect.

In summary these data on the three clays indicate first, there was a slight increase in exchange capacity with decreasing particle size; second, there was a greater quantity of calcium adsorbed from the neutral than from the alkaline solution; and third, there was little difference in the quantity of calcium and ammonia adsorbed by the clay.

TITRATION CURVES

Hydrogen.—Since Bradfield (6) developed the theory that clays were weak colloidal acids, many investigators have tried to use titration curves as a means to define clays and soils.   Anderson and Byers (2) determined the curves for halloysite and montmorillonite clay minerals and for some soil colloids; while Baver (3) and Bradfield (6), among others, have studied the acid properties of the Putnam colloid, a beidellite clay.

There is no information available concerning the titration curves of nontronite and attapulgite clays, consequently, an experiment was set up to obtain data on this point using the electrodialyzed $< 2\,\mu$ fraction in dilute suspensions of .353 per cent and .452 per cent, respectively.

In the case of nontronite clay, sodium potassium, calcium and barium curves were determined, while with attapulgite clay the magnesium curve was also included.

The results of this study, which were obtained with the use of a glass electrode on samples which stood two days, are given in figures 3 and 4.   The base equivalents were calculated on the ignited clay basis, and each point on the curves corresponds to a separate suspension sample.

In general form the titration curves of nontronite and attapulgite clays resemble those of montmorillonite and beidellite. It should be noted how the curves of the different cations group together at pH 7.0, and although the upper section does not permit any conclusions regarding the influence of the cation on the relative position of the curves, the curves below a pH of 7.0 do show the influence of the valency and the hydration of the cations upon their adsorptions by the clay.   The monovalent cations, in consequence of their weaker adsorption, gave higher pH values per unit of added base, than did the more

strongly adsorbed divalent cations, and thus indicated the variable strength of a colloidal acid depending upon the degree and type of saturation of the colloid, (Mitra (57), Baver (3)).
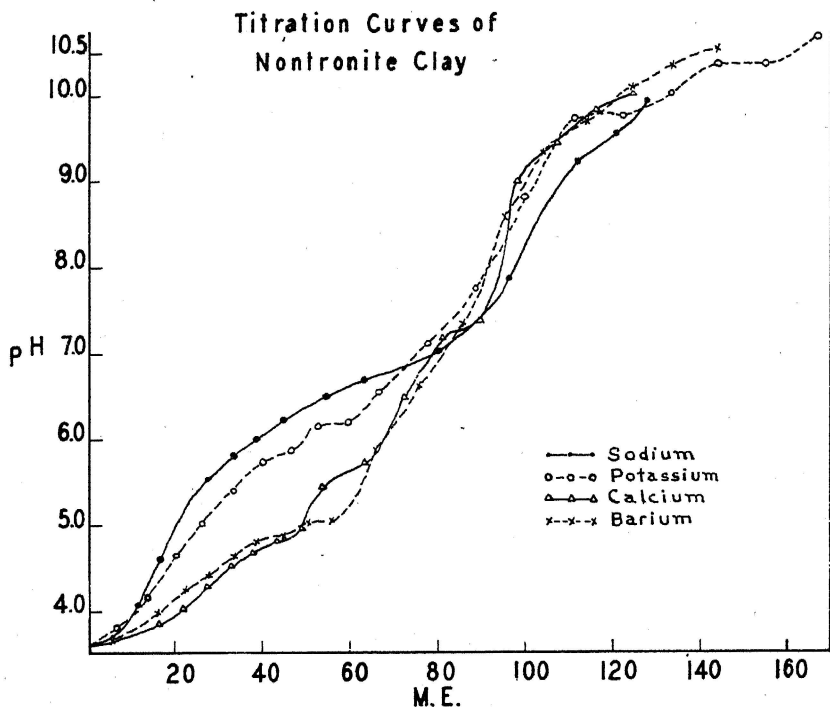
Fig. 3.—Titration curves of nontronite clay.

The base requirement of the 0.353 per cent suspensions, dependent on the cation used ranged from 76 to 82 M. E. to give a neutral reaction and from 90 to 100 M. E. to bring a curve inflexion. These values are higher than the exchange capacity of the clay, 64.3 and 60.8 M. E., as determined by neutral calcium and ammonium acetate, respectively.

The titration curves show that attapulgite clay has a greater degree of variation between the quantity of different cations required for a pH of 7.0 than has nontronite clay. In the acid range of the curves the greater hydrogen replacing power of calcium and barium over sodium and potassium was repeated; and in addition, the relationship of the complete sodium and potassium curves were indicative of the greater replacing power of potassium.

The magnesium curve, near the origin, indicated that magnesium, like the other divalent cations, had a strong replacing potential. But the remainder of the curve was irregular and, surprisingly, reached

a constant value at a pH of 8.25, although the original oxide suspension, diluted, had a pH value of 10.1.
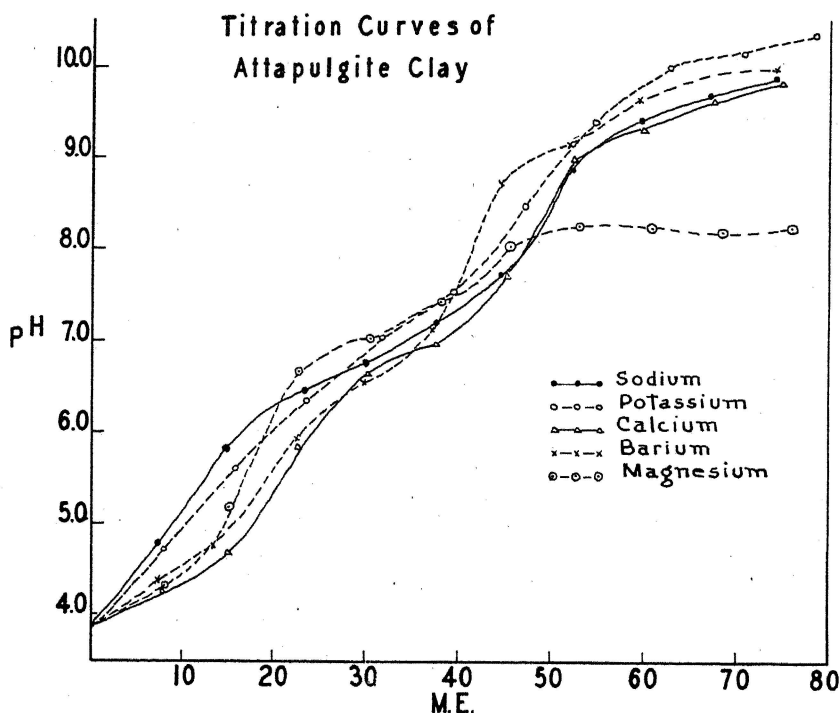
Fig. 4.—Titration curves of attapulgite clay.

The base requirement at pH 7.0 varied from 28.0 to 37.5 M. E. with the cations in the following order—

$$Ca > Ba > Na > K > Mg$$
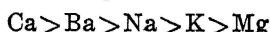
At the inflection point on the curves, the requirement reached the higher value of about 45.0 M. E. These values were much higher than the exchange capacity of 19.8 and 22.2 M. E. as determined by the use of neutral ammonium acetate and calcium acetate, respectively.

A striking feature of the data presented is the fact that the base equivalent of attapulgite and nontronite clays as estimated by leaching with neutral electrolytes, is given by the hydroxides at pH values below 7.0, and even as low as 5.80 and 6.00. It may be suggested that this difference is produced by the more complete ionization in the hydroxide solution of the hydrogen more closely adsorbed in the clay, and also, as suggested by Schofield (70), by the ionization of the OH groups in the more alkaline medium, present for a time following the addition of the hydroxide. Thus, the base exchange capacity

of a clay is a value much dependent upon environment, and apparently quite sensitive to a variable alkaline reaction.

Further information on the reaction of the hydroxides and clay, confined probably to the OH groups of the clay lattice, was revealed by an experiment in which the reaction of a series of attapulgite and nontronite clay samples was determined after they stood for variable periods of time. The reaction of nontronite clay determined after periods of two, eleven and twenty-one days, showed a marked decline from original pH values above 6.0 to 6.5, the amount depending on the cation used, while only a little decline occurred in the lower section of the curves. It may be of more than passing interest to note that this hinge on the titration curve corresponded approximately to the pH value equivalent to the exchange capacity of the clay as determined by the absorption of electrolytes.

The reaction of the titrated attapulgite suspensions as it changed with time, was also determined. In similar manner to the nontronite clay, little change occurred in the more acid suspensions, but in suspensions above an original pH value varying between 6.8 and 7.2, a very abrupt decline in reaction took place. However, this extreme fall in values occurred in suspensions in which the original pH values were below 9.0 whereas in suspensions above this value the decline was even less than in the equivalent nontronite suspensions. The most rapid fall in pH values developed in those suspensions in which the original reaction was just below 9.0.

Apparently this result, a fall in pH above equilibrium values of approximately 6.0 and below 9.0, is a consequence of the reaction between the added hydroxide and the hydrogen ionizing from the OH group of the clay lattice.

In the case of the attapulgite clay it seems apparent, that in suspensions with an original pH value above 9.0, the easily ionizable or accessible OH groups had all reacted with the hydroxide and little change took place. The reaction above a pH of 9.0 is probably one in which dissolution of the clay occurs. Such reactions indicate that there is no clear demarcation, as determined by bonding energy, between hydrogen in the so-called exchangeable form and hydrogen as part of the OH group of the lattice. This, supports the previous conclusion that the exchange capacity of a clay is a property markedly modified by the conditions of the experiment. It also may be concluded that base exchange capacity of a clay is primarily determined by the atomic replacements in the fundamental lattice structure and is modified by the degree of ionization of the (OH) lattice groups in that structure.

Potassium.—The potassium ion activity in nontronite and attapulgite clays was also determined in dilute suspensions of .353 per cent and .452 per cent concentration, respectively, by W. E. Bergman, after the method developed by Marshall and Bergman (53).

The data obtained are presented in table 18 and figures 5 and 6.

TABLE 18.   POTASSIUM ION ACTIVITY IN NONTRONITE AND ATTAUPLGITE CLAYS.

	Attapulgite				Nontronite		
M.E. KOH added	pH	pK	Fraction K Active	M.E.KOH added	pK	pK	Fraction K Active
8.3	4.97	3.62	0.744	16.9	4.94	----	-------
16.5	5.92	3.56	0.470	33.7	5.98	4.03	0.101
24.8	6.32	3.40	0.451	50.6	6.34	3.56	0.197
33.1	6.92	3.28	0.445	67.4	6.60	3.34	0.242
41.4	7.33	3.06	-----	84.3	6.94	3.15	0.303
50.0	8.41	3.02	-----	101.1	7.20	2.97	0.384
57.9	9.46	2.97	0.521	118.0	7.48	2.88	0.405
66.2	9.37	2.84	-----	134.9	8.73	2.79	0.435
74.4	10.10	2.83	0.559	151.7	9.25	2.68	0.492
82.7	10.36	2.70	0.684	168.6	10.06	2.64	0.485
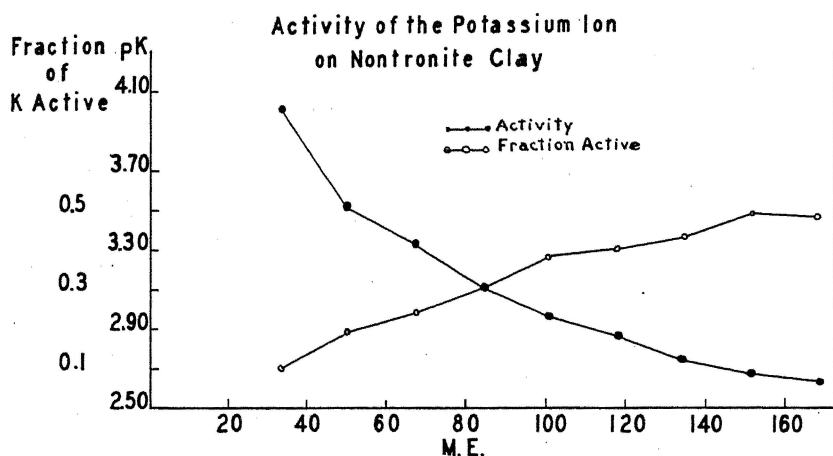
Fig. 5.—Activity of the potassium ion on nontronite clay.
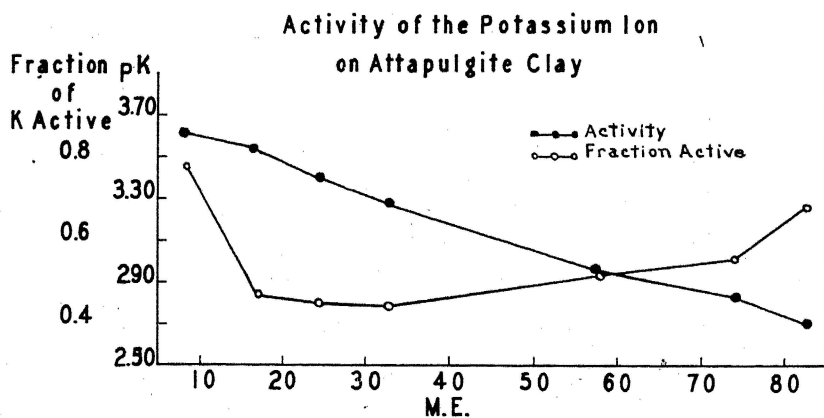
Fig. 6.—Activity of the potassium ion on attapulgite clay.

Nontronite clay had a pK value of 3.08 at a pH of 7.0, given by 87 M. E. of potassium with 0.32 as the fraction active. The first increment of potassium had only 0.101 fraction active, but this increased with further additions until a high value, 0.492, was reached with 151.7 M. E.

The pK of attapulgite clay was 3.25 at a pH of 7.0, given by 35 M. E. of potassium with a fractional activity of 0.45. The first increment of potassium gave a fractional activity of 0.744, a high value; while further additions produced a decrease followed by an increase to higher values, 0.684 with an increment of 82.7 M. E.

It is noted that this lowest fraction active value for attapulgite clay is only slightly below the highest value for nontronite, and indicates that the potassium salt of attapulgite is a very much stronger electrolyte than the corresponding nontronite salt.

It is evident that both nontronite and attapulgite potassium titration curves are distinctly different from the montmorillonite and beidellite curves, and that further detailed work is needed to evaluate the causes of these differences.

SUMMARY AND CONCLUSIONS

It is concluded from the recalculation of the chemical analyses that the nontronite clay from Sandy Ridge, North Carolina, and saponite from Hector, California, are micaceous clays with a 2:1 lattice structure. This nontronite clay is also seen to be a member of the beidellite-nontronite isomorphous series, whilst the saponite clay is a member of the montmorillonite-saponite series. The attapulgite clay from Attapulgus, Georgia, is a mineral with a amphibole-like structure with the fundamental structural dehydrated formula $Mg_5Si_8O_{21}$, a conclusion supporting Bradley's' experimental results.

The 2:1 lattice structure seems to be the structural form of all expanding clays with other composition ratios being produced only by replacement. A 3:2 uncharged lattice structure is possible but the OH group requirement is so large that its development is improbable.

The atomic replacements in the lattice of all the size fractions of the nontronite, attapulgite and saponite clays produced a negative charge equivalent to the exchange capacity. This supports the theory that atomic replacement in the lattice of micaceous clay is responsible for the exchange capacity, and also allows the extension of the theory to include those clays with amphibole-like structure, such as attapulgite.

The negative charge on the nontronite clay was all given by a large substitution of aluminum for silicon in the silica layer; while it was partially balanced by an excess of trivalent atoms in the gibbsite layer. The attapulgite clay had its negative charge produced by the substitution of silicon by aluminium in the silica sheet which was partially balanced by trivalent ions in the brucite sheet.

A substitution of aluminium for silicon in the silica sheet and a deficiency of metal atoms in the brucite sheet gave saponite a negative

charge. This charge was predominately developed in the brucite sheets, a distribution of charge quite different from that in the other two clays.

A classification of clays has been outlined in which the primary division is based on silicate structure and the second division is made on the basis of the lattice type. In the next category the distribution of the negative charge on the lattice is considered; while the final units are separated on the basis of the chemical composition of the gibbsite or brucite sheets of the clay lattice. It is also pointed out that each isomorphous clay series in the expanding clays may have four end, and innumerable intermediate, members. However, the occurrence of all four end members in any series is extremely doubtful. The chemical composition, a very variable feature of clays, rather than new names should be emphasized in further subdivisions.

The hydrogen titration curves of dilute nontronite and attapulgite clay suspensions gave higher exchange capacity values than cation adsorption from electrolytes in a medium at the same final pH value. For example the capacity determined in neutral electrolyte solution is given by the hydroxide titration at pH values below 7.0 and even as low as 5.8. Thus it is evident that the capacity given by hydroxides at a certain pH value is the capacity given by salts in more alkaline solutions and this indicates a reaction between the hydrogen ionizing from the OH groups of the lattice and the base. This reaction is further demonstrated by the decline in the pH values with time in titrated suspensions. Base exchange capacity, then, is primarily a consequence of atomic replacement in the clay structure and is modified from the normal value by the degree of ionization of the OH groups of the lattice.

The potassium titration curves of dilute nontronite and attapulgite suspensions indicate that potassium attapulgite is highly ionized whereas potassium nontronite is similar in its electrolyte properties to potassium beidellite and montmorillonite.

Part III.

DEHYDRATION STUDIES

Previous investigations on nontronite have been carried out by Collins (12), Katzer (34), Weinschenk (72), Lindgren and Hillebrand (42) and Norton (61). In summary, their results indicated considerable loss of water up to 100° C., a minimum rate of loss somewhere between 100° and 350° C., and a greater loss at some temperature above 350° C.

Attapulgite, like montmorillonite, is reported to lose considerable water at low temperatures, but at 600° C. it is already completely dehydrated (62, 17). The rate of loss reaches a maximum below 200° C. and again around 400° C. The closely related sepiolites show in addition a third zone of rapid loss of water around 750° C. (45).

Little exact information is available for saponite, which, according to Norton (61) loses the greater part of its water between 100° and 225° C. Nutting (63) states that one molecule of water is held up to 650° C. and it is only completely removed at 1000° C.

Montmorillonite, belonging to the same group as saponite shows a rapid loss of water up to 200° C. and a second region of rapid loss between 450° C. and 500° C.

The experimental method here used was determined by the very limited quantities of the various fractions available. The clay suspension in water (in the case of nontronite, sodium-lithium systems and in that of attapulgite and saponite calcium-magnesium-sodium systems were used) was slowly dried at room temperature in a porcelain crucible and when a gel had formed it was brought to equilibrium with an atmosphere of 42.5 per cent humidity at 30° C. The dried clay took the form of a thin film or flake covering the base and side of the crucible. Since the weight of clay did not exceed 0.15 gram, it was brought to equilibrium at eight temperatures up to 850° C. in this same form.

The data are presented in table 19 and graphically in figures 7, 8 and 9, all calculated on an ignited basis.

Two important features of these results are immediately apparent.

(a) A comparison of table 19 with figures taken from the literature shows that for all three clays the present determinations give high results, which in the case of saponite persist to the higher temperatures.

(b) There is no regular relationship between particle size and hydration.

These facts demand explanation. This would appear to lie in the preparation of the samples. Clay films prepared by slow evaporation possess a considerable degree of particle orientation caused by the anisotropic character of the particles themselves. In studying a clay film, therefore, we have, superimposed upon the moisture relationships
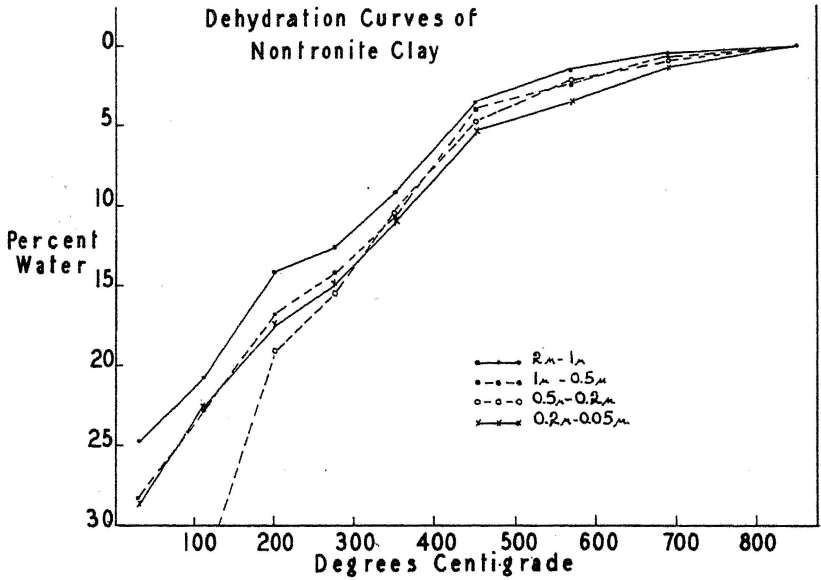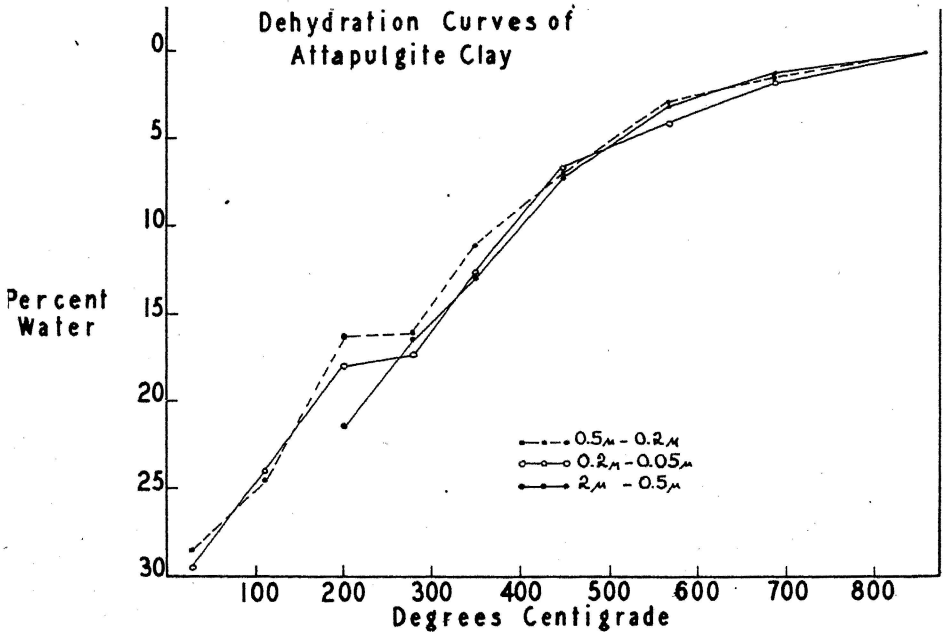
Fig. 7.—Dehydration curves of nontronite films.

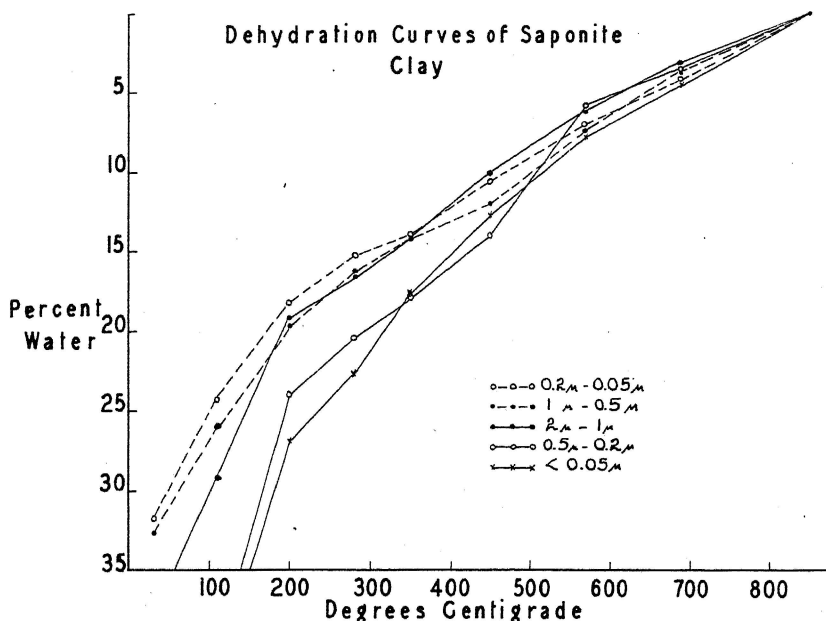Fig. 8.—Dehydration curves of attapulgite films.

Fig. 9.—Dehydration curves of saponite films.

of the individual clay particles, a new set of moisture relationships belonging to the structure built up. This structure is formed, in many instances, by the parallel orientation of plates or laths. When water has been sufficiently removed, these may approach each other as closely as do the individual lattice units in the "expanding lattice" clays. The dehydration curve of a clay film will, therefore, be enormously affected by the conditions which operate during its formation and which determine the extent and perfection of the orientation of the clay particles. Under such circumstances it is not surprising that there should be no relationship between particle size and hydration.

The correctness of this view may also be seen by a comparison of the 110° figures in table 19 with those for ground samples of the same fractions reported in table 13. For nontronite we have, ground fractions 15-20 per cent, films 21-23 per cent; for attapulgite, ground fractions 18-20 per cent, films 24 per cent; for saponite, ground fractions 13-16 per cent, films 24-29 per cent.

As a further check, a film was prepared from the whole clay fraction of nontronite $< 2 \mu$. At 110° it retained 21.35 per cent water. A similar film after being ground in a mortar at room temperature and being heated to 110° retained only 13.68 per cent water. The heating was continued long enough to make certain that equilibrium had been established in each case.

That the differences may remain large up to quite high temperatures is shown by saponite. We may, therefore, conclude that lattice

TABLE 19. THE DEHYDRATION OF FRACTIONS OF NONTRONITE,
ATTAPULGITE AND SAPONITE CLAYS. (Ignited Basis.)

Clay	Equivalent diameters	Per cent "Water" Present							
		30°C	110°C	200°C	280°C	350°C	450°C	570°C	690°C
Nontronite	2 μ - 1 μ	24.65	20.79	14.17	12.66	9.17	3.67	1.67	0.56
	1 μ - 0.5 μ	28.27	22.73	16.83	14.28	10.67	3.99	2.32	0.78
	0.5 μ-0.2 μ			19.11	15.47	11.42	4.77	2.37	0.95
	0.2 μ-0.05 μ	28.52	22.54	17.37	14.83	10.90	5.16	3.58	1.34
Attapulgite	2 μ - 0.5 μ			22.61	16.42	12.92	7.24	3.05	1.26
	0.5 μ-0.2 μ	28.54	24.58	16.31	16.14	11.18	6.97	2.94	1.35
	0.2 μ-0.05 μ	29.56	23.98	18.00	17.59	12.62	6.90	4.21	1.76
Saponite	2 μ - 1 μ	37.60	29.31	19.37	16.67	14.19	10.10	6.24	3.22
	1 μ - 0.5 μ	32.77	26.00	19.70	16.49	14.68	12.16	7.50	3.66
	0.5 μ-0.2 μ			24.20	20.55	18.13	14.16	6.02	3.57
	0.2 μ-0.05 μ	31.90	24.45	18.33	15.41	14.12	10.70	7.18	4.22
	<0.05 μ			27.01	22.74	17.65	12.79	7.73	4.60
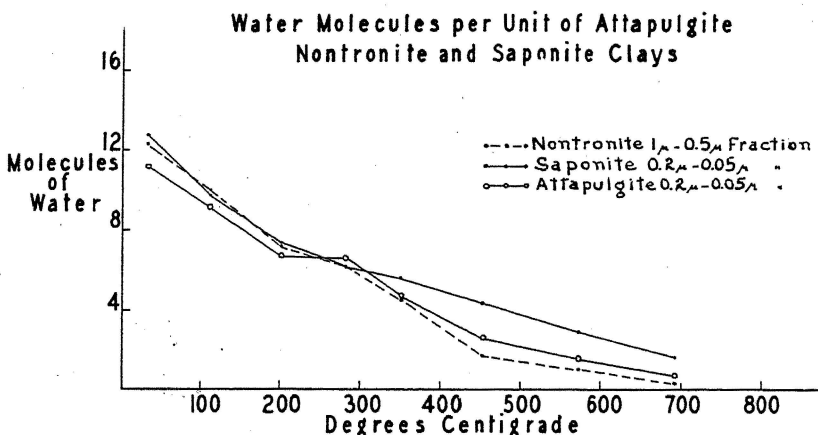
Fig. 10.—Water molecules per unit cell in relation to temperature.

water (OH groups perhaps excepted) and film structure water are
frequently indistinguishable, being held by a bonding energy of the
same order of magnitude.   The presence of film structure water might
well obliterate differences between fractions and even differences be-
tween minerals.

Bearing these limitations in mind it is, nevertheless, interesting to
compare the three minerals with one another.   In figure 10 typical
fractions only are given and the results are recalculated as water mole-
cules per unit cell of the clay lattice.   The most striking case is that
of attapulgite, for which the curve is practically horizontal between
200° and 270° C.   It would appear that six water molecules per unit
cell of ideal composition $Mg_5-Si_8O_{21}$ are held somewhat differently
from those lost at temperatures below 200° C.

In Bradley's suggested structure for attapulgite there are four water molecules incorporated as H_2O and one as 20H. The absence of any break above 300° C. would indicate another possibility, namely that five molecules of water might equally well be incorporated as 10 OH belonging to the lattice. This would give an idealized composition $O_6Si_4O_4(OH)_3Mg_5(OH)_7Si_4O_6$ having the advantage that the extra H_2O molecules present at lower temperatures would not be fixed to the lattice and that the break in the curve between 200° and 270° could be explained. This change involves simply a redistribution of the hydrogen, spreading it more evenly in the brucite layers. The magnesium atoms still find themselves in the usual octahedral positions. The extra molecule of water held at 300° C. (six are actually found instead of five as suggested above) might perhaps be regarded as due to film structure.

Density Determinations

The density of the various clay fractions was determined in potassium iodide solutions, using the mixture technique of Marshall (50). Care was taken to remove dissolved air, and sedimentation was hastened by the use of a tube centrifuge.

The results given in table 20 show a general decrease in density with decreasing particle size, in agreement with earlier data on other clays (51). The finest fractions of nontronite and attapulgite clays gave very distinctly lower values than the coarser fractions. Compared with the figures given in the literature, the nontronite values are distinctly low, no doubt due in part to the low iron content of this sample. The attapulgite values (except that of the finest fraction) are slightly higher than those previously given whilst those of saponite are slightly lower.

Considering clays of the reactive group, it is evident that the density will vary with the moisture content of the individual particles and therefore that it can only be uniquely determined for a given vapor pressure. Determinations made by drying clays at 110° C. cannot be expected to agree with determinations made in an aqueous solution of potassium mercuric iodide, and the latter will not be identical with the actual densities in pure water.

Stability and Coagulation

In setting up the electrometric titration series as reported in Part II, the opportunity was taken of observing the stability and coagulation behavior of the clays saturated with different monovalent and divalent cations. For nontronite the order of the cations in decreasing the stability of the suspensions was as follows: $Ba = Ca > H > K = Na$. This is in line with the behavior of beidellite (Putnam clay) (3). For attapulgite the order was $H = Mg > Ca > Ba > K = Na$. In both cases

potassium and sodium gave stable suspension over the range studied. Even at high dilutions the hydrogen attapulgite system coagulated.

TABLE 20. THE DENSITY OF THE FRACTIONS OF
NONTRONITE, ATTAPULGITE AND SAPONITE CLAYS.
MEASURED IN POTASSIUM MERCURIC IODIDE SOLUTIONS.

Equivalent diameter	Specific gravity of clay		
	Nontronite	Attapulgite	Saponite
2 μ - 1 μ	2.51	2.28	2.20
1 μ - 0.5 μ	2.49	2.32	2.23
0.5 μ - 0.2 μ	2.47	2.30	2.19
0.2 μ - 0.05 μ	2.46	2.28	2.16
<0.05 μ	2.12	2.06	2.10

Optical Studies

Refractive Indices of Suspensions and of Flakes.—Two techniques have been used in recent years for the determination of the refractive indices of fractionated clays, the potassium mercuric iodide method which employs a dark ground condenser and gives the mean refractive index (51), and the dried flake method which employs oils as immersion liquids and yields values both for n_2 and n_7 (9). In view of the effect of film formation on the hydration properties and in the light of Wiener's theory of the birefringence of regular colloidal structures, it seemed advisable to make a thorough investigation of these three clays using both techniques.

The precision of the refractive index determinations by both methods was 0.002 — 0.003; thus the values for birefringence obtained by the flake method may be in error by 0.005. The flakes were prepared by drying dilute suspensions in small beakers; with these clays the orientation so produced was as good as that given by the use of the centrifuge. Because of the ease of decomposition of the saponite, dialysis was used in the preparation of the suspensions and subsequently a little sodium hydroxide was added to insure stability.

Table 21 summarizes the results on the fractionated clays. In the preparation of the flakes at 110° C. evaporation from the beakers was relatively rapid and perfect orientation was probably not achieved. It will be noted that the mean refractive index determined by the flake method is higher in the case of nontronite and saponite than that given by the suspension method. This would naturally be expected, since the 110° fractions should be more compact than the more hydrous fractions in potassium mercuric iodide solution. For attapulgite, however, the converse is found. The explanation lies in its more rigid structure. When water is lost at low temperatures there is little or no shrinkage within the lattice; hence the space occupied by water molecules becomes a void and the refractive index falls. This property sharply distinguishes attapulgite from the swelling clays.

TABLE 21. THE REFRACTIVE INDICES OF THE FRACTIONS OF
NONTRONITE, ATTAPULGITE AND SAPONITE CLAYS.

Clay	Size of fraction (microns)	Suspension (Mean)	Flakes dried @ 110° C		
			Alpha	Gamma	Birefringence
Nontronite	2 μ - 1 μ	1.580	1.563	1.596	.033
	1 μ - 0.5 μ	1.558	1.553	1.588	.035
	0.5 μ - 0.2 μ	1.563	1.556	1.592	.036
	0.2 μ - 0.05 μ	1.568	1.554	1.595	.041
	<0.05 μ	1.570	1.551	1.598	.047
Attapulgite	2 μ - 0.5 μ	1.542	1.520	1.545	.025
	0.5 μ - 0.2 μ	1.550	1.518	1.535	.017
	0.2 μ - 0.05 μ	1.550	1.517	1.536	.019
	<0.05 μ	1.558	1.529	1.555	.026
Saponite	2 μ - 1 μ	1.487	1.488	1.524	.036
	1 μ - 0.5 μ	1.492	1.486	1.520	.034
	0.5 μ - 0.2 μ	1.492	1.486	1.528	.042
	0.2 μ - 0.05 μ	1.491	1.493	1.529	.036
	<0.05 μ	1.493	1.490	1.513	.023

The refractive indices for the various fractions are seen to be in
good agreement. The 2μ—1μ fraction of nontronite falls appreciably
out of line, probably due to cementing material of a higher index,
since aggregation could be observed under the microscope.

Since clay fractions reflect in some properties their previous history,
experiments were carried out on the influence of drying and rehydra-
tion upon the refractive indices. The whole clay fractions $< 2 \mu$ were
used for these experiments, summarized in table 22. Here a compari-
son is given of the mean refractive indices of the original suspensions
(measured in $KHgI_3$ solution), of flakes prepared at 30° and heated to
100° C. (measured in oils) and of suspensions prepared by grinding
the 110° flakes in water (measured in $KHgI_3$ solution).

As would be expected, the refractive indices of nontronite and
saponite are increased by heating to 110° and rehydration brings them
back to the original values. Attapulgite behaves differently. The
refractive index falls on heating to 110° and it does not return to
the original value. Here, then, is a second feature of diagnostic value.

Experiments on the influence of electrodialysis upon the refractive
index showed only minor and transient changes, except for saponite,
which decomposes.

TABLE 22. THE REFRACTIVE INDICES OF NONTRONITE
ATTAPULGITE, AND SAPONITE CLAY AS INFLUENCED BY
DRYING AND REHYDRATION.

Clay (< 2 μ)	Mean refractive indices		
	Original suspension	Flakes dried at 110°C	Suspension of rehydrated material
Nontronite	1.578	1.590	1.577
Attapulgite	1.552	1.539	1.539
Saponite	1.490	1.495	1.488

The Effect of Heat Treatment Upon Refractive Indices

Using the whole clay fractions $< 2\,\mu$, a series of experiments was undertaken to obtain the complete refractive index-temperature of pretreatment curves for the three clays. The flakes were prepared by very slow evaporation of the suspensions at 30° C. in an atmosphere of 42.5 per cent relative humidity. The "air dry" figures in table 23 refer to this condition. The flakes were heated to five higher temperatures up to 860°. In each case, after cooling in a desiccator, a portion of the flake was rapidly ground and covered with the immersion oil. The results are shown graphically in figures 11, 12, and 13.

The figures and the curves for nontronite seem to indicate a distinct change between 200 and 470° C., where the refractive indices and birefringence show a marked increase.
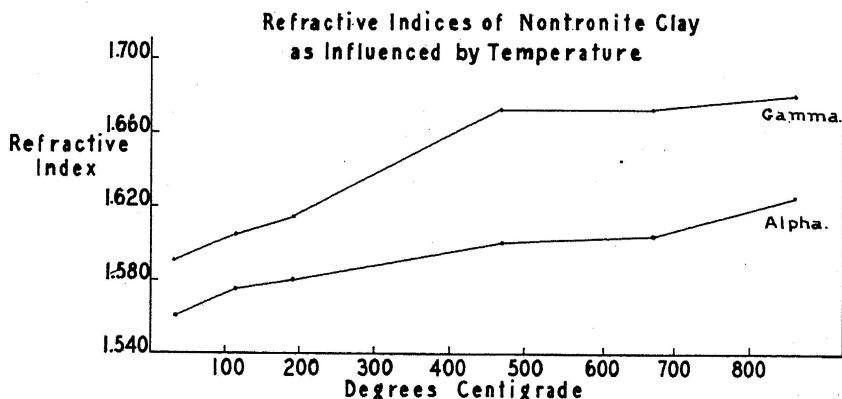
Fig. 11.—Refractive indices of nontronite flakes in relation to temperature of pretreatment.
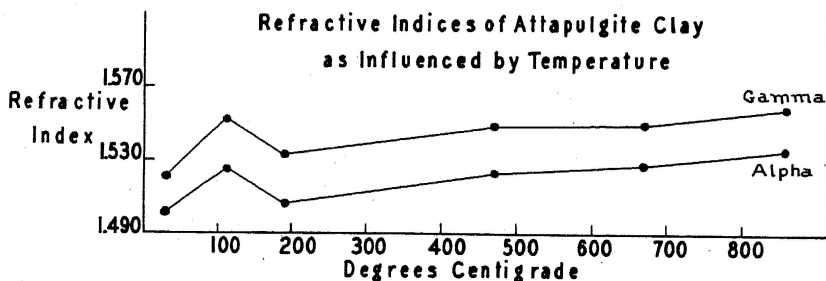
Fig. 12.—Refractive indices of attapulgite flakes in relation to temperature of pretreatment.
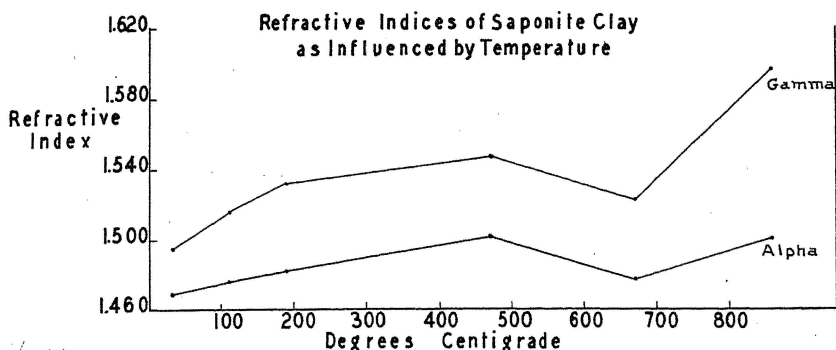
Fig. 13.—Refractive indices of saponite flages in relation to temperature of pretreatment.

The behavior of attapulgite is distinctive. At 30° C. both indices of the flakes are much lower than the mean index of the suspension as given in table 21. This may be due to the water enmeshed in the film structure as well as to loss of water from the lattice. At 110° part of the film structure water has been removed and the mean index has increased, but between 100 and 200° this effect is more than counterbalanced by loss of water from the rigid lattice of the clay particles themselves. Hence the refractive index falls. It should be noted that

TABLE 23. THE REFRACTIVE INDICES OF NONTRONITE, ATTAPULGITE AND SAPONITE CLAYS AS INFLUENCED BY TEMPERATURE.

Clay	Temperature	Index Values		Birefrigence
		Alpha	Gamma	
	Air dry	1.560	1.590	.030
	110°C	1.575	1.605	.030
	190°C	1.579	1.614	.035
Nontronite	470°C	1.600	1.671	.071
	670°C	1.603	1.671	.068
	860°C	1.624	1.679	.055
	Air dry	1.501	1.525	.024
	110°C	1.526	1.552	.026
	190°C	1.506	1.532	.026
Attapulgite	470°C	1.523	1.548	.025
	670°C	1.527	1.548	.021
	860°C	1.534	1.557	.018
	Air dry	1.469	1.495	.026
	110°C	1.476	1.515	.039
	190°C	1.482	1.531	.049
Saponite	470°C	1.501	1.546	.045
	670°C	1.477	1.521	.044
	860°C	1.500	1.595	.095

the mean index of the film at 110° is still below that of the suspension reported in table 21. At temperatures above 200° C. both indices rise slowly and there is no indication of sudden structural changes up to 870° C. Saponite shows a steady increase of refractive index with temperature up to 470° C., then a minimum at 670°, and a higher value at 870° associated with a much greater birefringence.

Birefringence and the Wiener Theory

The quantitative theory of the birefringence of interstratified layers of materials of different refractive indices has been worked out by Wiener. The theory as originally developed considered alternate regular layers whose thickness was small compared with the wave length of light. These were supposed to be isotropic; however, measurements quoted by Ambronn-Frey (1) show that the Wiener effect can be superimposed on systems which are already birefringent. The sign of the Wiener birefringence for plate-shaped clay particles interstratified with any liquid would be the same as is actually found to occur, and the same as is found in the compact minerals pyrophyllite and talc. Thus the inherent birefringence of the silicate layers and the Wiener birefringence always reinforce one other in the expanding lattice group. A maximum is attained when the volume of interstratified liquid is equal to that of the silicate. The Wiener effect can arise in clay films in two ways—firstly, due to the water within the clay particles which separates the lattice units from each other, and secondly, by a less perfect interstratification of clay plates and water films in the clay mass. There seems no reason why the two Wiener effects should not be superimposed, giving rise to complex moisture content—birefringence curves. However, the present measurements would not show such complexities, since the region here covered deals only with clays having relatively low moisture contents. In this region, however, another effect may show itself. .f, at some point on the drying curve shrinkage should cease, then further removal of water would give rise to unoccupied spaces in the clay film. The refractive index would thereupon fall, but the birefringence would rise. This is the kind of thing observed in the case of attapulgite. Shrinkage can occur between particles with concomitant rise in the refractive index of the film, but loss of water from the lattice causes a decrease in refractive index and at the same time an increase in birefringence. It seems probable that a more detailed study of dehydration and refractive index curves would throw valuable light on the dehydration process itself, especially as a possible means of distinguishing lattice —OH groups from interstratified water molecules.

In the case of saponite the minimum in the refractive index curve occurs at the point above which the lattice loses four OH groups. A similar minimum was found by Grim and Bradley (26) for montmoril-

lonite. Attapulgite although different in structure, also shows a minimum above which there is no further break. Nontronite appears to be different in this respect but the evidence is not conclusive because of the wide temperature intervals used.

A further avenue partially opened up in this research would lead to the identification and even the estimation of clay minerals in mixtures such as are found in soils. By accurately determining refractive indices under three or four different conditions single clay minerals are very readily identified. Mixtures of two components can also be analysed with considerable certainty. However, this prospect is not yet completely fulfilled since not all clay minerals have been investigated with this in mind.

Conclusions

These dehydration and optical studies taken together show very clearly the intermingling of the two factors lattice structure and film structure. In the expanding lattice clays nontronite and saponite they cannot easily be separated. Attapulgite, because of its rigid lattice allows us to form a partial estimate of the influence of film structure.

Certain practical conclusions also follow. Film structure has the effect of increasing the moisture content of clays. Thus on grinding a clay film the moisture contents falls. However, with very fine grinding, as Kelley, Jenny and Brown showed, the moisture content again rises. What degree of grinding must we employ, therefore, in order to reach the minimum moisture content for a given sample? It is evident that some attention should be paid to this matter. It has long been known that consistency in moisture determinations on separated clays could only be secured by grinding and sieving. The reason is now evident—film structure must be broken up.

SUMMARY

1. The dehydration curves of nontronite, attapulgite and saponite were determined at temperatures up to 690° C. on clay fractions in the form of films. Such films give considerably higher figures for water retained than do ground samples. The differences are ascribed to water held in the film structure, which cannot easily be distinguished from crystal lattice water in dehydration studies.

2. In the case of attapulgite a distinct break in the dehydration curves at 200-270° C. and the absence of a break at high temperatures suggested that Bradley's structure might advantageously be modified by putting 10 OH groups in the brucite layers instead of 4 H_2O molecules and 2 OH groups.

3. Density determinations were carried out on all fractions by the potassium mercuric iodide method.

4. The ease of coagulation of the clay suspensions saturated with various cations followed the order: for nontronite $Ba = Ca > H > K = Na$; for attapulgite $H = Mg > Ca > Mg > K = Na$.

5. Refractive index determinations were made on all fractions both by the potassium mercuric iodide method on suspensions and by the dried flake method using oils. Attapulgite is sharply distinguished from the expanding lattice clays by the fall in refractive index on drying from suspension and by the irreversibility of this effect.

6. The effect of heat treatment was also followed by means of determinations of refractive indices and birefringence and the curves for the three minerals nontronite, attapulgite and saponite are given up to 870° C.

7. The Wiener theory of the birefringence of regular aggregates is briefly considered in the light of a possible film structure superimposed on the normal lattice structure. In the case of attapulgite the effect of film structure can clearly be seen.

8. The application of these results to the technique of moisture determinations and to the optical identification of clay minerals is briefly considered.

REFERENCES

(1) Ambronn, H., and Frey, A. 1926. Das Polarisationsmikroskop. Leipzig. Akademische Verlagsgesellschaft. M. B. H.
(2) Anderson, M. S., and Byers, H. G. 1936. Neutralization Curves of the Colloids of Soils Representative of the Great Soil Groups. U. S. D. A. Tech. Bul. 542.
(3) Baver, L. D. 1929. The Effect of the Amount and Nature of Exchangeable Cations on the Structure of Colloidal Clay. Missouri Agr. Exp. Station Research Bul. 129.
(4) Baver, L. D., and Horner, G. M. 1933. Water content of soil colloids as related to their chemical composition. Soil Science, 36:329.
(5) Berthier, P. 1827. Nontronite, nouveau mineral découvert dans le départment de la Dordogne. Annales de chimie et de physique. Series 2, 36:22.
(6) Bradfield, R. 1923. The nature of the chemical reactions of colloidal clay. Colloid Symposium Monograph, 1:369.
(7) Bradfield, R. 1928. The use of electrodialysis in physicochemical investigations of soil. Proc. First International Congress of Soil Science, Washington, 1927, 2:264.
(8) Bradley, W. F. 1940. The structural scheme of attapulgite. American Mineralogist, 25:405.
(9) Bray, R. H., Grim, R. E., and Kerr, P. F. 1935. Application of clay mineral technic to Illinois clay and shale. Bulletin of the Geological Society of America, 46:1909.
(10) Cameron, F. K., and Bell, J. M. 1905. The mineral constituents of the soil solution. U. S. Dept. Agr. Bureau of Soils Bul. 30.
(11) Clark, F. W. 1914. The constitution of the natural silicates. 1914. U. S. Geological Survey Bul., 588:109.
(12) Collins, J. H. 1877. Remarks on gramenite from Smallacombe and on the chloropal group of minerals. Mineralogical Magazine, 1:67.
(13) Crowther, E. M., and Basu, J. K. 1929. Note on the simple two-compartment electrodialysis cell for the determination of exchangeable bases. 1929 Transactions of Commission II, International Soil Science Society, Budapest, A:100.
(14) Dana, E. S. 1909. System of Mineralogy. Sixth Edition, New York: John Wiley and Sons.
(15) Dana, E. S. 1932. A Textbook of Mineralogy. Fourth Edition, New York: John Wiley and Sons.
(16) de Lapparent, J. 1935. Sur un constituent essential des terres à foulon. Comptes Rendus, 201:481.
(17) de Lapparent, J. 1937. A propos de l' attapulgite. Zeitschrift fur Kristallographie, 97:237.
(18) de Lapparent, J. 1938. Formules structurales et classification des argiles. Zeitschrift fur Kristallagraphie, 98:233.
(19) Fersman, A. 1908. Uber die Palygorskitegruppe. Bulletin of the Academy of Imperial Science of St. Petersburg, 2:255.
(20) Foshag, W. F., and Woodford, A. O. 1936. Bentonitic magnesium clay mineral from California. American Mineralogist, 21:238.
(21) Geilmann, W., Klemm, W., and Meisel, T. 1932. Das auftreten hochmagnetischer Zwischenstufen bei der thermischen Zersetzung des Nontronits. Die Naturwissenschaften, 20:639.
(22) Gieseking, J. E. and Jenny, Hans. 1936. Behavior of polyvalent ions in base exchange. Soil Sci., 42:273.
(23) Graham, R. P. D. 1918. On Ferrierite, a new zeolite from British Columbia; with notes on some other Canadian minerals. Transactions of the Royal Society of Canada, Series III, 12:185.
(24) Grim, R. E. 1933. Petrography of the Fuller's Earth Deposits, Olmstead, Illinois. Economic Geology, 28:344.
(25) Grim, R. E. 1939. Properties of clay. Recent marine deposits—a symposium. Tulsa, Oklahoma. American Association of Petroleum Geologists.
(26) Grim, R. E., and Bradley, W. F. 1940. Investigation of the effect of heat on the clay minerals illite and montmorillonite. American Ceramic Society, 23:242.

(27) Gruner, J. W. 1935. The structural relationship of nontronites and montmorillonites. American Mineralogist, 20:475.
(28) Hendricks, S. B. 1942. Lattice structure of clay minerals and some properties of clay. Journ. of Geologly, 50:276.
(29) Hendricks, S. B., and Alexander, L. T. 1940. Semiquantitative estimation of montmorillonite in clays. Proc. Soil Sci. Amer., 5:95.
(30) Hillebrand, W. F., and Lundell, G. E. F. 1929. Applied Inorganic Analysis. First Edition. New York: John Wiley and Sons.
(31) Holzner, J. 1934. Neue Daten uber den Stilpnochloran von Gobitschau (Mähren), zugleich Bericht uber ungewohnliche Umtausch-reactionen. Centralblatt fur Mineralogie A:250.
(32) Humfeld, H., and Alben, A. O. 1927. Electrodialysis of the soil I. A study of the method. Jour. Amer. Soc. Agron., 19:984.
(33) Jackson, M. L. and Truog, E. 1939. Influence of grinding soil minerals to near molecular size on their solubility and base exchange properties. Proc. Soil Sci. Soc. Amer., 4:136.
(34) Katzer, F., 1895. Mineralogische und petrographische mitteilungen, 14:514.
(35) Kerr, P. F. 1937. Attapulgus clay. American Mineralogist, 22:534.
(36) Kerr, P. F. 1938. A decade of research on the nature of clay. Jour. Amer. Ceramic Soc., 21:267.
(37) Kerr, P. F., and Cameron, E. N. 1936. Fuller's Earth of bentonitic origin from Tchachapi, California. American Mineralogist, 21:230.
(38) Kolthoff, I. M., and Sandell, E. B. 1938. Textbook of Quantitative Inorganic Analysis. New York: The Macmillan Company.
(39) König, J., Hasenbaumer, J. and Hassler, C. 1911. Bestimmung der Kolloide im Ackerboden. Landwirtschaftliche Versuchstationen, 75:377.
(40) König, J., Hasenbaumer, Jr., and Kuppe, C. 1923. Beziehung zwischen den im Boden Vorhandenen and den von Roggen and Futterreihen Aufgenommenen Leichtloslichen Nahrstoffen. Landwirtschaftliche Jahrbücher, 59:65.
(41) Larsen, E. S. and Steiger, G. 1928. Dehydration and optical studies for Alunogen, Nontronite and Griffithite. American Journal of Science, 215:1.
(42) Lindgren, W., and Hillebrand, W. F. 1904. Minerals from the Clifton-Morenci District, Arizona. American Journal of Science, 168:448.
(43) Löddesol, Aasulv. 1932. Investigations concerning separation of similarly charged ions from soils by electrodialysis. Soil Sci., 33:375.
(44) Longchambon, H. 1935. Sur le formule chimique et la constitution de la sépiolite d' Ampandrandana. Comptes Rendus, 200:1607.
(45) Longchambon, H. 1936. Sur des proprieties characteristiques des palygorskites. Comptes Rendus, 203:672.
(46) Longchambon, H. 1937. Sur des characteristiques des palygorskites. Comptes Rendus, 204:55.
(47) Longchambon, H. 1937. Sur certaines characteristiques de la sépiolite d' Ampandandrana; discussion sur la formule des sépiolites. Bulletin de la societé française de mineralogie, 60:233.
(48) Longchambon, H., and Migeon, G. 1935. Sur la definition des sépiolites. Comptes Rendus, 200:1946.
(49) Longchambon, H., and Migeon, G. 1936. Sur les sépiolites. Comptes Rendus, 203:431.
(50) Marshall, C. E. 1931. Studies in the dispersion of the clays. I. Notes on the technique and accuracy of mechanical analysis using the centrifuge. Jour. of Soc. of Chemical Industry, 50:444.T.
(51) Marshall, C. E. 1935. Mineralogical methods for the study of silts and clays. Zeitschrift fur Kristallographie, 90:8.
(52) Marshall, C. E. 1935. Layer lattices and the base exchange clays. Zeitschrift fur Kristallographie, 91:433.
(53) Mattson, S. 1928. The electrokinetic and chemical behaviour of the alumino-silicates. Soil Sci., 25:289.

(54) Mattson, S. 1933. The laws of soil colloidal behavior. XI. Electrodialysis in relation to soil processes. Soil Sci., 36:149.
(55) Mehmel, M. 1937. Beiträge zur Frage des Wassergehaltes der Minerale Kaolinit, Halloysit und Montmorillonit. Chemie de Erde, 11:1
(56) Milner, H. B. 1940. Sedimentary Petrography. Third Edition, London, Thomas Murby and Company.
(57) Mitra, R. P. 1940. One the nature of reactions responsible for soil acidity, VII. The electrochemical properties of colloidal solutions of hydrogen clay. Indian Journ. of Agri. Sci., 10:317.
(58) Nagelschmidt, G. 1938 Rod-shaped clay particles. Nature, 142:114.
(59) Nagelschmidt, G. 1938-40. On the arrangement and variability of the members of the montmorillonite group. Mineralogical Magazine, 25:140.
(60) Noll, W. 1930. Zur Kenntis des Nontronits. Chemie der Erde, 5:373.
(61) Norton, F. H. 1939. Critical study of the differential thermal method for the identification of the clay minerals. Journal of the American Ceramic Society, 22:54.
(62) Nutting, P. G. 1933. The Bleaching Clays. United States Geological Survey Circular No. 3.
(63) Nutting, P. G. 1940. A study of the association of magnesia with silica in a pure magnesium clay. Journal of Washington Academy of Sciences, 30:233.
(64) Olmstead, L. B., Alexander, L. T., and Middleton, H. E. 1930. A pipette method of mechanical analysis of soil, based on improved dispersion technic. U. S. D. A. Technical Bul. 170.
(64) Palache, C., and Vassar, H. E. Some minerals of the Keeweenawan copper deposits; Pumpellyite, a new mineral; Sericite, Saponite.
(66) Ross, C. S., and Hendricks, S. B. 1941. Clay minerals of the montmorillonite group, their mineral and chemical relationships and the factors controlling base exchange. Proceedings of the Soil Sci. Soc. Amer., 6:58.
(67) Ross, C. S., and Kerr, P. F. 1931. Clay minerals and their identity. Journal of Sedimentary Petrology, 1:55.
(68) Ross, C. S., and Shannon, E. V. 1925. The chemical composition and optical properties of beidellite. Journal of Washington Academy of Science, 15:467.
(69) Ross, C. S., and Shannon, E. V. 1926. The minerals of bentonite and related clays and their physical properties. Journal of American Ceramic Society, 9:77.
(70) Schofield, R. K. 1939. The electric charge on clay particles. Soil and Fertilizers, Imperial Bureau of Soil Science, 2:1.
(71) Truog, E., and et al. 1936. Procedure for special type of mechanical and mineralogical soil analysis. Proc. Soil Sci. Soc. Amer., 1:101.
(72) Weinschenk, E. 1897. Beitrage zur mineralogie Bayerns. Zeitschrift fur Kristallographie, 28:150.
(73) Whiteside, E. P., and Marshall, C. E. 1939. Studies in the degree of dispersion of the clays. III. The two layer method as applied to the Sharples centrifuge. Proc. Soil Sci. Soc. Amer., 4:100.