

# INTRACRYSTALLINE SWELLING, CATION EXCHANGE, AND ANION EXCHANGE OF MINERALS OF THE MONTMORILLONITE GROUP AND OF KAOLINITE

*By*

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## ABSTRACT

The structural formulas were determined of very pure specimens of montmorillonite, beidellite, saponite, nontronite, hectorite, wolchonskoite, vermiculite, and batavite. The lattice perfection of these minerals and the nature and variation of their crystalline swelling depend significantly on the surface density of the exchangeable cations between the silicate sheets.

In a neutral solution of  $\text{NH}_4\text{F}$ , OH ions were replaced by F ions. The exchange capacity is smaller the greater the diameter of the silicate layers of the various montmorillonite minerals. Since the anion-exchange capacity of nontronite can be increased through oxidation of  $\text{Fe}^{2+}$  it is probable that the exchangeable OH ions are located on the boundaries of the octahedral layers.

With kaolinite, the cation-exchange capacity decreases with increasing thickness of the crystal plates. The OH ions of the basal surface can be exchanged with F ions, which leads to the destruction of the lattice.

A one-dimensional Fourier synthesis of K-batavite, like the investigations of Walker on vermiculite and of Brown and also Méring on montmorillonite, provides confirmation of the structure and enables the lattice positions of the K ions to be determined.

Especially pure, hand-picked specimens of various minerals of the montmorillonite group, including montmorillonite, beidellite, saponite, hectorite, nontronite, and wolchonskoite, were analyzed. The structural formulas were calculated from the chemical analyses. The calculations were based on the montmorillonite structure of Hofmann, Endell, and Wilm (1933) and on the assumptions of Marshall (1935) and Noll (1936) that the exchangeable cations are bound to the clay because of replacement in the tetrahedral or octahedral layers. The calculation was made in the following way:

1. The independently determined exchangeable cations were separated from the formula as cations.

2. The tetrahedral positions were completely filled with Si and Al. With these assumptions two calculations were made taking

- a) Complete filling of all O and OH positions; and

- b) Complete filling of the octahedral positions with two or three cations per unit formula.

The difference between the results from these two calculations lay near the analytical error. Therefore, an average value was taken.

The result shows the characteristic differences between the montmorillonite and beidellite types, already shown by the studies of Ross and Hendricks (1941; 1945) and others. In our studies, too, the minerals tested could be distinctly related to the dioctahedral or the trioctahedral type (Table 1).

TABLE 1.—STRUCTURAL FORMULAS OF VARIOUS MONTMORILLONITE MINERALS

Name and source	Mineral type and no. of octahedral cations	Structural formulas according to the chemical analyses			Exchangeable cations
		Octahedral layer	Tetrahedral layer		
Montmorillonite, Geisenheim	Mont. 2.03	diact. 2.03	$\left\{ \begin{array}{l} -0.28 \\ (\text{Mg}_{0.37}\text{Al}_{1.49}\text{Fe}_{0.17}^{3+})(\text{OH})_2 \end{array} \right\}$	$\left\{ \begin{array}{l} -0.06 \\ [\text{Si}_{3.86}\text{Al}_{0.14}\text{O}_9.96] \end{array} \right\}$	+0.34 Me <sup>+</sup> + x H <sub>2</sub> O
Montmorillonite, Cypren	Mont. 2.03	diact. 2.03	$\left\{ \begin{array}{l} -0.36 \\ (\text{Mg}_{0.46}\text{Al}_{1.46}\text{Fe}_{0.12}^{3+})(\text{OH})_2 \end{array} \right\}$	$\left\{ \begin{array}{l} -0.04 \\ [\text{Si}_{3.80}\text{Al}_{0.10}\text{O}_9.97] \end{array} \right\}$	+0.40 Me <sup>+</sup> + x H <sub>2</sub> O
Beidellite I, Unterrupsroth	Beid. 2.02	diact. 2.02	$\left\{ \begin{array}{l} -0.13 \\ (\text{Mg}_{0.19}\text{Al}_{1.82}\text{Fe}_{0.07}^{3+})(\text{OH})_2 \end{array} \right\}$	$\left\{ \begin{array}{l} -0.45 \\ [\text{Si}_{3.55}\text{Al}_{0.45}\text{O}_{10}] \end{array} \right\}$	+0.58 Me <sup>+</sup> + x H <sub>2</sub> O
Beidellite II, Unterrupsroth	Beid. 2.04	diact. 2.04	$\left\{ \begin{array}{l} -0.15 \\ (\text{Mg}_{0.37}\text{Al}_{1.76}\text{Fe}_{0.07}^{3+})(\text{OH})_2 \end{array} \right\}$	$\left\{ \begin{array}{l} -0.28 \\ [\text{Si}_{3.56}\text{Al}_{0.44}\text{O}_9.92] \end{array} \right\}$	+0.42 Me <sup>+</sup> + x H <sub>2</sub> O
Saponite, Groschlattengrün	Beid. 3.00	trioct. 3.00	$\left\{ \begin{array}{l} -0.05 \\ (\text{Mg}_{2.95}\text{Al}_{0.38}\text{Fe}_{0.02}^{3+})(\text{OH})_2 \end{array} \right\}$	$\left\{ \begin{array}{l} -0.62 \\ [\text{Si}_{3.38}\text{Al}_{0.62}\text{O}_{10}] \end{array} \right\}$	+0.57 Me <sup>+</sup> + x H <sub>2</sub> O
Hectorite, Hector, Calif.	Mont. 2.93	trioct. 2.93	$\left\{ \begin{array}{l} -0.15 \\ (\text{Mg}_{2.64}\text{Li}_{0.18}\text{Na}_{0.10}\text{Fe}_{0.07}^{3+})(\text{OH})_{0.99}\text{F}_{0.75} \end{array} \right\}$	$\left\{ \begin{array}{l} -0.08 \\ [\text{Si}_{3.92}\text{Al}_{0.08}\text{O}_{10}] \end{array} \right\}$	+0.24 Me <sup>+</sup> + x H <sub>2</sub> O
Nontronite, Untergriesbach	Beid. 2.02	diact. 2.02	$\left\{ \begin{array}{l} -0.05 \\ (\text{Mg}_{0.11}\text{Al}_{0.33}\text{Fe}_{1.76}^{3+})(\text{OH})_2 \end{array} \right\}$	$\left\{ \begin{array}{l} -0.48 \\ [\text{Si}_{3.50}\text{Al}_{0.50}\text{O}_9.99] \end{array} \right\}$	+0.52 Me <sup>+</sup> + x H <sub>2</sub> O
Wolchonskoite, Groschlattengrün	Mont. 2.15	diact. 2.15	$\left\{ \begin{array}{l} -0.37 \\ (\text{Mg}_{0.82}\text{Al}_{0.40}\text{Fe}_{0.38}\text{Cr}_{0.35})(\text{OH})_2 \end{array} \right\}$	$\left\{ \begin{array}{l} -0.18 \\ [\text{Si}_{3.92}\text{Al}_{0.18}\text{O}_{10}] \end{array} \right\}$	+0.54 Me <sup>+</sup> + x H <sub>2</sub> O
Pyrophyllite	.....	diact. ....	(Al <sub>3</sub> )(OH) <sub>2</sub>	[Si <sub>4</sub> O <sub>10</sub> ]	..
Talc	.....	trioct. ....	(Mg <sub>3</sub> )(OH) <sub>2</sub>	[Si <sub>4</sub> O <sub>10</sub> ]	..

TABLE 2.—STRUCTURAL FORMULAS OF BATAYITE AND VERMICULITE

Name and source	Mineral type and no. of octahedral cations	Octahedral layer	Tetrahedral layer	Exchangeable cations
Batavite Kropfmühl	Beid. trioct. 2.97	+0.33 { (Mg <sub>2.64</sub> Al <sub>0.33</sub> )(OH) <sub>1.94</sub> }	-1.01 [Si <sub>1.98</sub> Al <sub>1.01</sub> O <sub>10</sub> ]	+0.68 Me <sup>+</sup> + x H <sub>2</sub> O
Vermiculite (foliated), Kropfmühl	Beid. trioct. 3.00	+0.39 { (Mg <sub>2.61</sub> Al <sub>0.39</sub> F <sub>0.10</sub> <sup>6+</sup> )(OH) <sub>2</sub> }	-1.05 [Si <sub>1.98</sub> Al <sub>1.05</sub> O <sub>10</sub> ]	+0.65 Me <sup>+</sup> + x H <sub>2</sub> O

TABLE 3.—LATTICE PERFECTION AND COURSE OF INTRACRYSTALLINE SWELLING

Mineral and source	Cations between the silicate layers in equivalents per unit formula	X-ray pattern <i>hkl</i> or <i>hkl</i> reflections in addition to 00 <i>l</i> reflections,	Basal spacing in angstroms in the case of exchangeable Alkaline earths (Mg <sup>2+</sup> ) Dry				K <sup>+</sup> ions in H <sub>2</sub> O		Na <sup>+</sup> ions in H <sub>2</sub> O	
			0.00	<i>hkl</i>	constant, 9.2	Dry	Dry	Dry	Dry	Dry
Pyrophyllite, talc	0.00	<i>hkl</i>								
Hectorite,										
Hector, Calif.	0.24	<i>hk</i>	11.1	20.8	10.1	∞	9.8	∞	∞	∞
Montmorillonite,										
Geisenheim	0.34	<i>hk</i>	10.7	19.8	10.0	∞	9.9	∞	∞	∞
Montmorillonite,										
Cypem	0.40	<i>hk</i>	11.8	19.4	10.2	∞	9.9	∞	∞	∞
Beidellite II,										
Unterrupsroth	0.42	<i>hk</i>	11.8	18.8	10.3	∞	10.4	∞	∞	∞
Nontronite,										
Untergriesbach	0.52	<i>hk</i>	11.8	19.4	10.0	∞	10.3	∞	∞	∞
Saponite,										
Groschlattengrün	0.57	<i>hkl</i>	11.7	15.1	10.3	14.3	10.6	15.5	15.5	15.5
Beidellite I,										
Unterrupsroth	0.58	<i>hkl</i>	—	—	10.3	14.4	10.4	15.8	15.8	15.8
Vermiculite,										
Kropfmühl	0.65	<i>hkl</i>	11.6	14.5	10.2	10.4	9.8	14.9	14.9	14.9
Batavite,										
Kropfmühl	0.68	<i>hkl</i>	11.8	14.5	10.2	10.3	9.8	14.9	14.9	14.9
Illite,										
Sarospatak	0.705	<i>hkl</i>	—	—	10.1	10.1	—	—	—	—
Muscovite, biotite	0.8-1.0	<i>hkl</i>	—	—	10.0	10.0	—	—	—	—

1 (Me<sub>2</sub><sup>3+</sup>, Me<sub>3</sub><sup>2+</sup>) (OH)<sub>2</sub> [Si, Al]<sub>4</sub> O<sub>10</sub>

Disintegration of crystals into single silicate layers

TABLE 4.—LOSS OF INTRACRYSTALLINE SWELLING CAPACITY IN MONTMORILLONITE FROM GEISENHEIM (ORIGINALLY 0.34 EQUIVALENT EXCHANGEABLE CATIONS PER UNIT FORMULA)

Exchangeable cation	Temperature range (°C) in which intracrystalline swelling is lost.	Exchangeable cations before loss of intracrystalline swelling, in equivalents per unit formula.
H	200 to 300	0.20
Li	105 to 125	0.19
Na	300 to 390	0.27
Ca	300 to 390	0.16

The structural formulas of a sample of batavite and another of vermiculite were similarly calculated (Table 2). Both proved to be of the beidellite type and were trioctahedral.

There is a distinct connection between the quantity of exchangeable cations (in equivalents per unit formula) and the appearance as well as the variation of the intracrystalline swelling and the lattice perfection (Weiss, Koch, and Hofmann, 1955). This relation is shown in Table 3. Below 0.55 equivalent cations per unit formula a very intensive intracrystalline expansion in water is effected by exchangeable Na and K ions. Above 0.57 equivalents, even with alkali ions the intracrystalline swelling in water attains a limit of 14 to 16 Å for the layer spacing. Above 0.65 equivalents in the presence of K ions the basal spacing in water remains at 10.3 Å—the same value as in the dry state.

The micas, which display no intracrystalline swelling, contain more than 0.7 equivalents of K ions between the silicate layers. The disorder of the layer sequence in the lattice diminishes in the same order, as can be seen from the appearance of the *hkl* reflections. If there are no cations between the silicate layers the minerals display no intracrystalline swelling, and the lattice perfection is high, as in pyrophyllite and talc. Also, when intracrystalline swelling is lost by heating, the quantity of exchangeable cations falls below 0.25 equivalents per

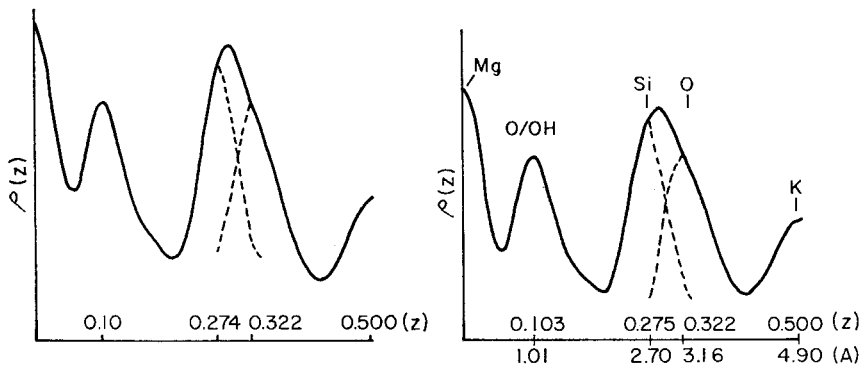


FIGURE 1.—One-dimensional Fourier projection of K-batavite (350° C) normal to the layers. Left curve: absorption taken into consideration.  $P$  = relative magnitude of the Fourier summation.

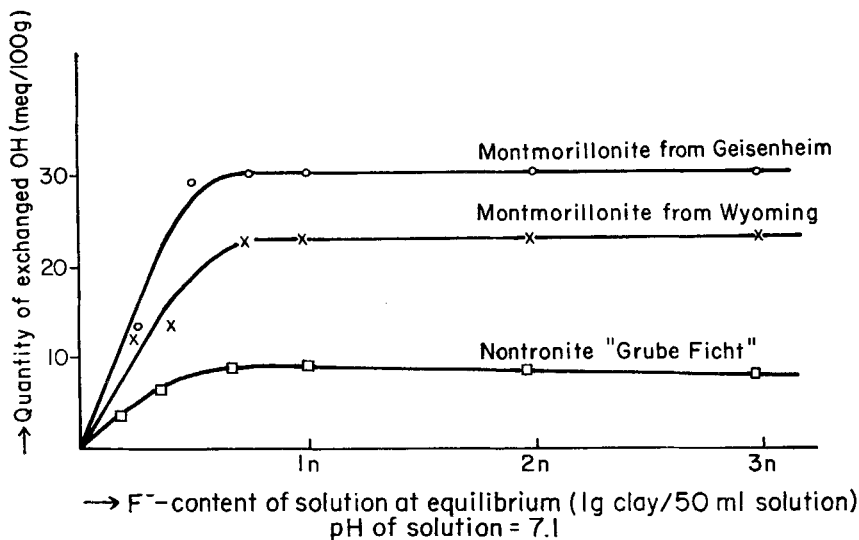


FIGURE 2. — Dependence of exchange of  $\text{OH}^-$  by  $\text{F}^-$  ions on the supply of  $\text{F}^-$  in the exchange solution.

unit formula (Hofmann and Endell, 1939; Hofmann and Klemen, 1950). The effect of heating on swelling is shown in Table 4.

Because the unit formula in all these minerals requires nearly the same surface in the plane of the silicate layer, and because the majority of the exchangeable cations lie between the silicate layers, this result, if confirmed in further studies, would mean that the density of the negative charge of the silicate layer measured per unit surface, or the density of exchangeable cations in equivalents per unit surface, is an important factor in the variations of lattice perfection and

TABLE 5. — DEMONSTRATION OF THE REVERSIBILITY OF THE EXCHANGES BETWEEN  $\text{OH}^-$  AND  $\text{F}^-$  IONS. (pH OF EXCHANGE SOLUTION, 7.1; CONCENTRATION OF  $\text{F}^-$ : 5,000 meq/100 g CLAY; 50 ml SOLUTION; SHAKING TIME 24 HOURS)

Sample	Test 1		Test 2		Test 3	
	Exchanged $\text{OH}^-$ ions meq/100 g	Added $\text{F}^-$ ions meq/100 g	Exchanged $\text{OH}^-$ ions meq/100 g	Added $\text{F}^-$ ions meq/100 g	Exchanged $\text{OH}^-$ ions meq/100 g	Added $\text{F}^-$ ions meq/100 g
Montmorillonite, Geisenheim (exchange- able Ca and Mg ions)	31.2	142	30.2	31.7	30.7	32.9
Same, with exchangeable Na ions	30.0	37.4	31.2	32.2	30.6	33.1
Montmorillonite, Cypern (Mg and Ca ions)	23.2	98	22.6	22.9	—	—
Nontronite, Ficht Mine (Mg ions)	9.8	95	9.6	11.1		

intracrystalline swelling and even for the existence of intracrystalline swelling (see Marshall, 1949; Hofmann and Klemen, 1950). The limits indicated here for the cation equivalents may be somewhat different in their final determination, if other factors exercise any influence on these characteristics.

Batavite with exchangeable K ions gives, especially when heated to 350° C, such a good x-ray pattern that a Fourier analysis could be performed along the layer normal, in a way similar to those described by Brown (1950) and Pézerat and Méring (1954) for montmorillonite, and by Mathieson and Walker (1954) for vermiculite. This Fourier analysis confirms the micallike structure of the silicate layer. The electron-density curve shows clearly the K ion between the silicate layers (Fig. 1). The space requirement demands that they be surrounded by 12 oxygen ions, just as in the micas.

As numerous studies have shown, the clay minerals have the property of anion exchange as well as cation exchange. The excellent résumé by Grim (1953) and the report of Romo and Roy (1955) should be mentioned here. For analytical reasons (Weiss, Mehler, Koch, and Hofmann, in press) we chose, for the studies of anion exchange in montmorillonite, the exchange of hydroxyl ions by fluorine ions. The clay was shaken, in plastic containers, with a solution of  $\text{NH}_4\text{F}$  for 24 hours. We found that the anion exchange can be measured only in a neutral solution. At lower pH Al may be dissolved from the lattice. At higher pH the

TABLE 6. — EXCHANGE CAPACITY OF OH FOR F IONS OF VARIOUS MINERALS OF THE MONTMORILLONITE GROUP

Test	Cation exchange capacity meq/100 g	Anion exchange capacity meq/100 g	Average particle diameter in angstroms computed from anion exchange capacity
DIOCTAHEDRAL			
Wolchonskoite from Groschlattengrün	125	36 <sup>1</sup>	280
Montmorillonite from Geisenheim	91	31	326
Montmorillonite from Wyoming (+12 percent quartz)	99	23	380
Montmorillonite from Cypern	108	23	438
Beidellite from Unterrupsroth	111	21	470
Nontronite from Ficht mine, Untergriesbach, Ndb.	88	20 <sup>1</sup>	508
Nontronite from the Rabenleite PfreimdtaI, Opf.	96	12 <sup>1</sup>	870
TRIOCTAHEDRAL			
Saponite from Groschlattengrün	142	21	—
Vermiculite from South Africa, coarsely laminated	142	4	—

<sup>1</sup> Based on oxidized samples.

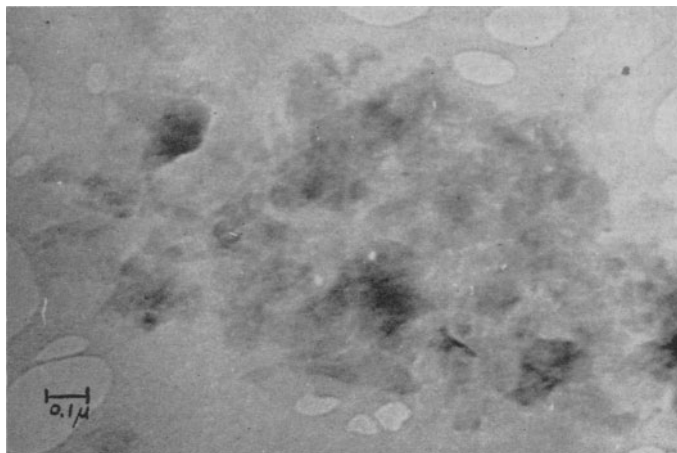


FIGURE 3.— Electron micrograph of montmorillonite from Geisenheim.

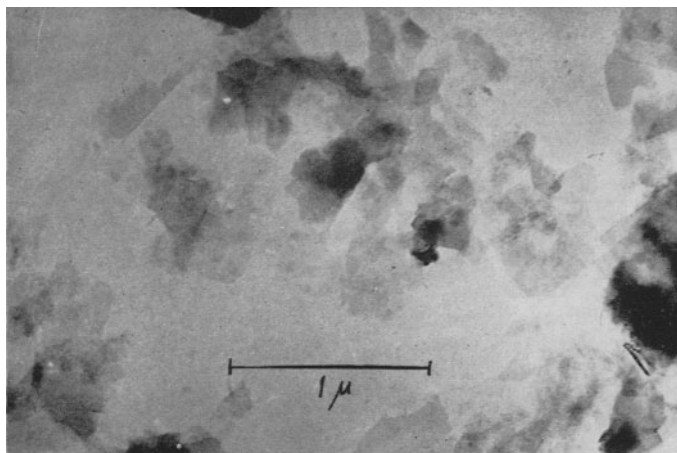


FIGURE 4.— Electron micrograph of montmorillonite from Wyoming.

fluorine ions are exchanged for the OH ions of the solution. In a neutral solution of  $\text{NH}_4\text{F}$ , the exchange isotherms showed a constant final value if the concentration of the solution was greater than 1 *N* (Fig. 2).

In the first treatment of a montmorillonite with the  $\text{NH}_4\text{F}$  solution many more F ions disappear from the solution than OH ions pass into the solution, if the montmorillonite sets free such cations as, for example, Ca ions, which form difficultly soluble fluorides (Table 5). For a similar reason such impurities as iron hydroxide, aluminum hydroxide, and calcium carbonate cause difficulty. Furthermore, the exchange is reversible if one again exchanges the F ions for OH ions in a 0.02 *N* hydrous  $\text{NH}_3$  solution.



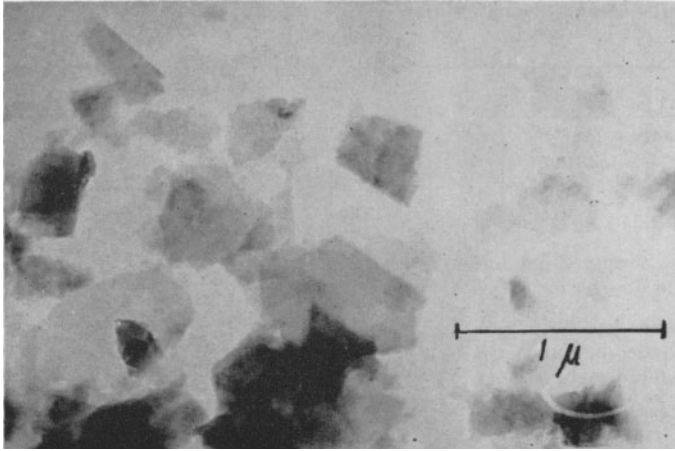


FIGURE 5 — Electron micrograph of beidellite from Unterrupstoth.

The quantity of exchangeable cations in the various montmorillonite specimens was rather constant. But the quantity of exchangeable OH ions for different montmorillonites varied inversely with the diameter of the crystal lamellae as seen in the electron microscope (Table 6). Figures 3, 4, and 5 give ex-

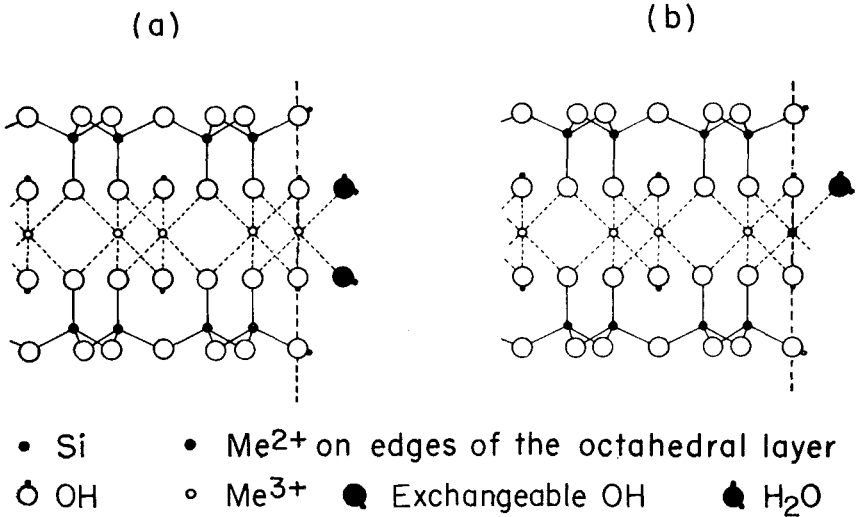


FIGURE 6. — Schematic presentation of the edge of the octahedral layer of a dioctahedral montmorillonite. (a) Me<sup>3+</sup> on edges. Charge equalization and completion of the six-fold coordination through one OH<sup>-</sup> and one H<sub>2</sub>O. (b) Me<sup>2+</sup> on edges. Charge equalization and completion of the six-fold coordination through two H<sub>2</sub>O.

TABLE 7.—ANION EXCHANGE CAPACITY OF NONTRONITE IN NATURAL, OXIDIZED, AND REDUCED CONDITION

	meq/100 g	At surface of octahedral layers
Anion exchange capacity		
of natural nontronite	9.2	Fe <sup>2+</sup> and Fe <sup>3+</sup>
of oxidized nontronite	19.6	Fe <sup>3+</sup>
Increase by oxidation	10.4	
On oxidation of natural nontronite with Br <sub>2</sub> in CS <sub>2</sub> , forming bromide	10.6	
Anion exchange capacity		
of oxidized nontronite	19.6	Fe <sup>3+</sup>
of reduced nontronite	2.5	Fe <sup>2+</sup>
Loss by reduction	17.1	
On oxidation of reduced nontronite with Br <sub>2</sub> in CS <sub>2</sub> , forming bromide	18.0	

amples. This seems to prove that the exchange of anions is effected chiefly at the edges of the silicate layers.

According to the studies of Fricke, the surface of aluminum hydroxide exchanges mainly OH ions. These observations suggest the likelihood that the OH ions situated at the edges of the octahedral layers are exchanged for the F ions (Fig. 6).

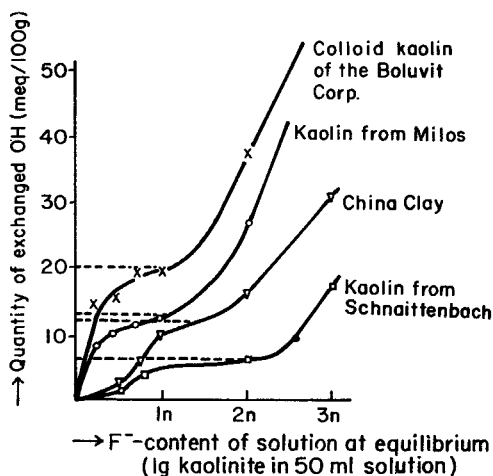


FIGURE 7.—Exchange isotherms of kaolinite from various deposits (pH of the exchange solution 7.1; supply of F<sup>-</sup>, 5,000 meq/100 g clay; 50 ml solution/1 g clay; shaking time 24 hours).

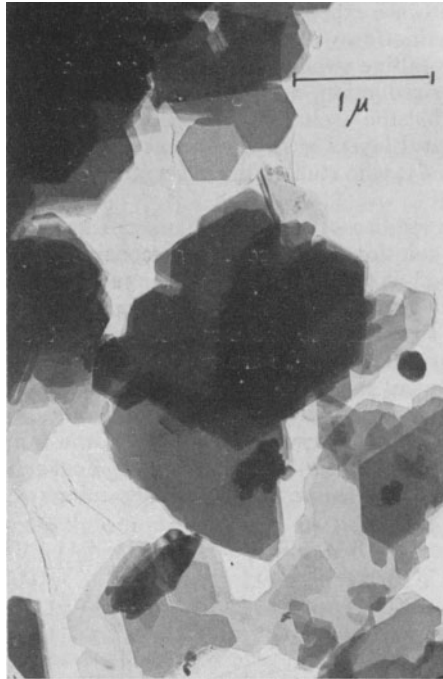


FIGURE 8.— Electron micrograph of Schnaittenbach kaolin.

This assumption was confirmed by further studies of nontronite. When the  $\text{Fe}^{2+}$  ions situated at the edges of the octahedral layers were oxidized to  $\text{Fe}^{3+}$  ions by bromine in carbon disulfide, the consumption of bromine was equivalent to the increase of the anion exchange resulting from oxidation by air or hydrogen peroxide in 0.05 *N*  $\text{NH}_3$  solution (Table 7). When the  $\text{Fe}^{3+}$  ions were reduced again with a sodium hydrogen sulfite solution of pH 4.8, the anion exchange decreased equivalently. It is likely that in this reduction and oxidation only those

TABLE 8.— COMPARISON OF THE CATION- AND ANION-EXCHANGE CAPACITY OF SOME KAOLINS

Kaolin	Cation-exchange capacity meq/100 g	Anion-exchange capacity meq/100 g	Thickness of crystal platelets (in angstroms) computed from	
			Anion-exchange capacity	$\text{N}_2$ -adsorption by B E T
Colloid kaolin from Boluvit Corp.	10.5	20.2	416	410-430
Kaolin from Milos	7.2	13.3	634	—
China clay	4.2	12.2	690	—
Kaolin from Schnaittenbach	2.6	6.6	1,270	1,200-1,500

iron ions reacted that were exposed at the edges of the octahedral layers. This is especially true for oxidation with bromine in carbon disulfide, because in this medium no intracrystalline swelling occurs. By oxidation nontronite becomes brown to yellow; by reduction, deep green.

Our assumption that the exchange of F ions for OH ions takes place at the edges of the octahedral layers is in agreement with the results of Goldshtaub, Hénin and Wey (1954), who studied the adsorption of phosphate ions by montmorillonite.

In our analogous studies of anion exchange in kaolinite we found that in ammonium-fluoride solutions of concentration considerably greater than 1 *N* the kaolinite is almost completely destroyed and ammonium cryolite  $(\text{NH}_4)_3 \text{AlF}_6$  and amorphous silicic acid are produced. The electron microscope showed that the crystal plates of the kaolinite had disappeared. In their place small grains were visible; these are judged to be amorphous silicic acid (Figs. 8 and 9).

With concentrations of the solution in the neighborhood of 1 *N* the exchange isotherms showed a flattening (Fig. 7). When the values for the still reversible anion exchange were taken under these conditions, the various kaolins showed significant relationship between the anion-exchange capacity and the thickness of the crystal plates as determined from electron micrographs. (Table 8 and

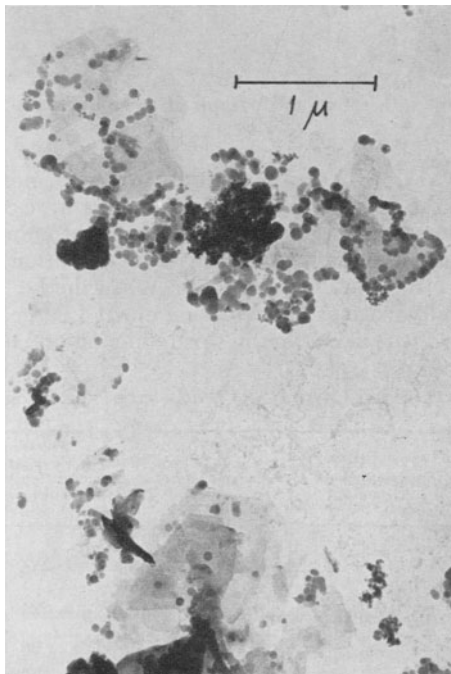


FIGURE 9. — Electron micrograph of Schnaittenbach kaolin, treated repeatedly with 3*N*  $\text{NH}_4\text{F}$  solution.

Fig. 10.) The thicker the crystal plates, the smaller was the anion exchange capacity. It is, therefore, supposed that with the exchange of anions, as far as it occurs reversibly, not only the OH ions situated at the edges of the octahedral layers but also the many more OH ions on the basal surface of the kaolinite crystal are exchanged for F ions (Fig. 11).

Thus one can calculate from the flat sections of the isotherms the thickness of the crystal plates. Also from the total surface (which we found by aid of nitrogen adsorption according to B E T) the thickness of the crystal plates can be calculated, neglecting the prism faces. The two calculations led to similar values for two kaolins (Table 8). But the *very* good agreement may be only accidental and I think that our explanation of the anion exchange of kaolinite is only plausible rather than proved.

The cation exchange of the same kaolins showed rather smaller values than the anion exchange. There appeared, however, the same decrease with increasing thickness of the crystal plates. If this identical behavior should be confirmed by further measurements, this should mean that the basal surfaces also play a part in the exchangeability of cations in kaolinite. This would agree well with the results of Robertson, Brindley and Mackenzie (1954) who attribute the cation exchange of the kaolinite to replacement in the tetrahedral and octahedral layers.

In the investigation of the anion exchange of halloysite, i.e., the fully hydrated halloysite from Djebel Debar, it was shown that the lattice of halloysite was attacked by neutral  $\text{NH}_4\text{F}$  solution more easily than that of kaolinite. Probably the  $\text{NH}_4\text{F}$  was enabled to enter the water layers of the halloysite.

From a bend in the exchange isotherm taken with 0.6 *N* solution, a value of 80 meq OH ions per 100 g could be extrapolated. If this value is taken as a measure of the anion-exchange capacity of the undecomposed halloysite, then one obtains for the basal surface of halloysite in which the OH ions lie, a value of 38  $\text{m}^2/\text{g}$ .

According to Bates, Hildebrand, and Swineford (1950) crystals of halloysite have the form of tubes. The OH ions of a basal surface lie in the interior wall

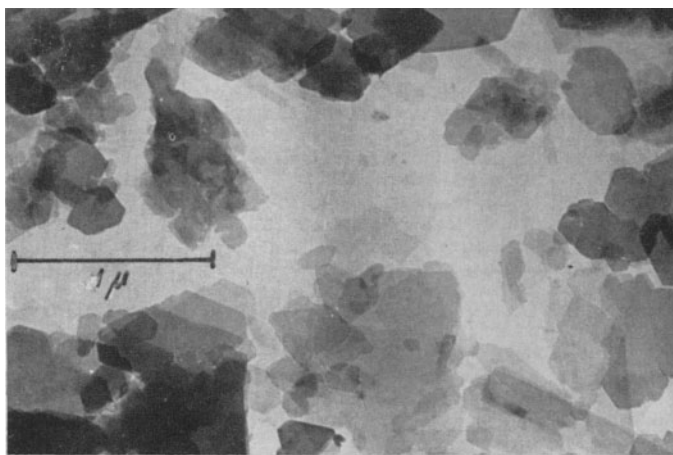


FIGURE 10. — Electron micrograph of colloidal kaolin of the Boluvit Corp.

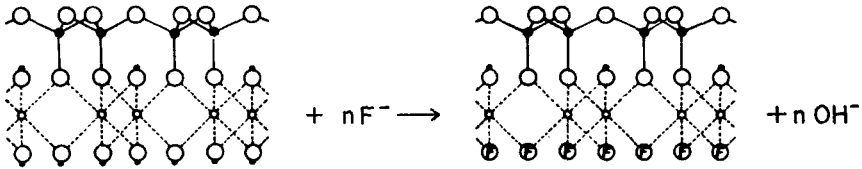


FIGURE 11.—Diagram of the anion exchanges of the basal surface of kaolinite. The OH ions of a basal surface of the crystal are exchanged by F ions.

of the tube. Our halloysite tubes had a diameter of about 1000 Å. If the wall thickness of the tubes is 100 Å, this gives for the interior surface of the tubes a value of 35 m<sup>2</sup>/g which is practically the same as that derived from the anion exchange isotherms.

If the exchange in a 1*N* solution is measured after various times, there is obtained in the first 24 hours a relatively rapid reaction in which again about 80 meq of OH ions per 100 g are exchanged. Thereafter the reaction proceeds very slowly, until after about 48 hours it is again faster until finally the halloysite crystals are extensively destroyed. If the anion exchange at first takes place effectively on the inner surface of the tubes, it is understandable that the silicic acid, which is formed by the commencement of lattice break-up after exchange of OH ions from the internal basal layers, blocks the tubes and thus slows down further reaction until the walls are so far broken down that the reaction can again proceed rapidly.

## REFERENCES

- Bates, T. F., Hildebrand, F. A., and Swineford, Ada, 1950, Morphology and structure of endellite and halloysite: *Amer. Min.*, v. 35, p. 463-484.
- Brown, George, 1950, A Fourier investigation of montmorillonite: *Clay Minerals Bull.*, v. 1, p. 109-111.
- Goldsztäub, S., Hémin, S., and Wey, R., 1954, Sur l'adsorption d'ions phosphoriques par les argiles: *Clay Minerals Bull.*, v. 2, p. 162-166.
- Grim, R. E., 1953, *Clay mineralogy*: McGraw-Hill Book Company, Inc., New York, 384 p.
- Hofmann, Ulrich, and Endell, J. 1939, Die Abhängigkeit des Kationenaustausches und der Quellung bei Montmorillonit von der Vorerhitzung (Auszug): *Z. Angewandte Chemie*, v. 52, p. 708.
- Hofmann, Ulrich, Endell, K., and Wilm, D., 1944, Kristallstruktur und Quellung von Montmorillonit: *Z. Krist.*, v. 86, p. 340-347.
- Hofmann, Ulrich, and Klemen, R., 1950, Verlust der Austauschfähigkeit von Lithiumionen an Bentonit durch Erhitzung: *Z. anorg. Chem.*, v. 262, p. 95-99.
- Marshall, C. E., 1935, Layer lattices and base-exchange clays: *Z. Krist.*, v. 91, p. 433-449.
- , 1949, *The colloid chemistry of the silicate minerals*: Academic Press, Inc., New York, 180 p.
- Mathieson, A. McL., and Walker, G. F., 1954, Crystal structure of vermiculite: *Amer. Min.*, v. 39, p. 231-255.
- Noll, W., 1936, Synthese von Montmorilloniten: *Chem. Erde*, v. 10, p. 129-154.
- Pézerat, H., and Méring, J., 1954, Influence des substitutions isomorphes sur les paramètres de structure des phyllites: *Clay Minerals Bull.*, v. 2, p. 156-162.
- Robertson, R. H. S., Brindley, G. W., and Mackenzie, R. C., 1954, Mineralogy of kaolin clays from Pugu, Tanganyika: *Amer. Min.*, v. 39, p. 118-138.
- Romo, L. A., and Roy Rustum, 1955, F-OH exchange in layer silicates (Abs.): in *Clays and clay minerals*, *Natl. Acad. Sci.—Natl. Res. Council Pub.* 395, p. 402.

- 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: *Soil Sci. Soc. Amer. Proc.*, v. 6, p. 58-62.
- , 1945, Minerals of the montmorillonite group: U. S. Geol. Survey Prof. Paper 205B, p. 23-79.
- Weiss, Armin, Koch G., and Hofmann, Ulrich, 1955: *Ber. Dtsch. Keram. Ges.*, v. 32, p. 12.
- Weiss, Armin, Mehler, A., Koch, G., and Hofmann, Ulrich, 1956, *Z. anorg. Chem.*, v. 284, p. 247.