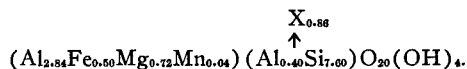


# EFFECT OF EXCHANGEABLE CATION ON X-RAY DIFFRACTION PATTERNS AND THERMAL BEHAVIOR OF A MONTMORILLONITE CLAY

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## ABSTRACT

A stratum of bentonite in the North Park (?) formation near Granby, Colorado, is composed largely of a dioctahedral Ca-montmorillonite whose formula is calculated to be



Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>++</sup>, and Mg<sup>++</sup> modifications were stored at 52 percent relative humidity and at 105° C-110° C. Results of X-ray diffraction, differential thermal, and thermal balance analysis depend upon the exchangeable cation and prior treatment. As with many montmorillonoids,  $d(001) = 22.7-30.1$  Å under room conditions;  $a_0 = 5.20$  Å and  $b_0 = 9.00$  Å. The (001) interference indicates that the unit cell typically includes two packets, or possibly more, which may be derived geometrically from each other by a glide of 1.73 Å along (110) and 180° rotation. Weight loss above 190° C-367° C exceeds that indicated by the Hofmann structure but conforms reasonably with loss indicated by a structure after that proposed by Edelman. Inverted Si-O tetrahedra are presumed to equal the number of univalent cations

It is suggested that the exchangeable cations form hydroxides during thermal analysis by reaction with (OH)<sup>-</sup> at the apex of inverted Si-O tetrahedra. The resulting H<sub>2</sub>O and NH<sub>4</sub>OH are lost during thermal analysis, thus explaining excessive weight loss. Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> so produced release one mole of H<sub>2</sub>O during thermal analysis. KOH, NaOH, and LiOH are not decomposed below 1,000° C.

Thermal products vary with exchangeable cation and crystallinity increases with prior drying. The Li<sup>+</sup> and Ca<sup>++</sup> modifications produce beta-quartz and alpha-cristobalite with spinel and glass, whereas the other modifications produce only spinel and glass.

## INTRODUCTION

The following report summarizes our initial studies to establish by X-ray diffraction and thermal studies the mineralogic nature of a bentonite encountered in the foundation of the Willow Creek pumping plant near Granby, Colorado. The foundation is a part of a sedimentary sequence tentatively correlated with the North Park formation of Miocene age. In this locality, the North Park (?) formation mainly is composed of alternating strata of sandstone and siltstone; beds of claystone and conglomerate are sparse.

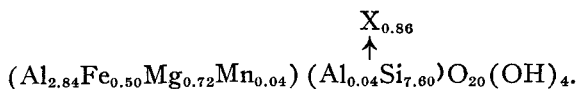
\* Deceased.

DESCRIPTION OF THE BENTONITE

The bentonite stratum from which the sample was taken occurs at a depth of 31 feet and is 6 to 9 inches thick. The bentonite is compact, waxy to soapy to the touch, and ranges from light brown to pinkish brown. Under the microscope, it is found to be composed primarily of a montmorillonite-type mineral. Small proportions of oligoclase-andesine, quartz, acidic volcanic glass, and very small proportions of biotite, diopside, and apatite also are present. The bentonite was developed by alteration of a dacite tuff. Granular particles greater than 2 microns constitute 2.3 percent of the sample. Quartz constitutes 2.5 percent of the fraction finer than 2 microns.

A representative portion of the sample was analyzed chemically (Table I) and the cation exchange capacity was determined (Table II). A portion of the sample was ground lightly and treated with an aqueous solution of NaCl to replace the original exchangeable cations and then was purified by repeated settling and centrifuging to remove particles larger than about 2 microns. The purified fraction then was analyzed chemically (Table I).

Using the method of Ross and Hendricks (1945, pp. 41-42) the chemical formula was calculated to be



This formula corresponds to that of a dioctahedral montmorillonoid,  $\Sigma$  being 4.10 per unit cell. The molecular weight ranges from 737.14 to 769.90, depending upon the exchangeable cation.

TABLE I.—CHEMICAL ANALYSIS

(Montmorillonite, North Park (?) Formation; Middle Park, Near Granby, Colorado—F. H. Geier, Analyst)

Component	Natural bentonite	Purified montmorillonite, Na treated <sup>1</sup>
SiO <sub>2</sub>	51.23	57.68
Al <sub>2</sub> O <sub>3</sub>	18.98	19.72
Fe <sub>2</sub> O <sub>3</sub>	3.83	4.71
TiO <sub>2</sub>	0.57	0.76
MnO	Tr.	0.41
MgO	3.86	3.48
CaO	3.76	Tr.
Na <sub>2</sub> O	0.93	n.d.
K <sub>2</sub> O	0.54	n.d.
H <sub>2</sub> O (+105° C)	6.21	7.05
H <sub>2</sub> O (−105° C)	9.17	4.14
P <sub>2</sub> O <sub>5</sub>	0.00	0.00
Total	99.08	97.95

<sup>1</sup> Includes 2.5 percent of quartz.

TABLE II. — SOLUBLE AND EXCHANGEABLE CATIONS<sup>1</sup>  
 (Montmorillonite, North Park (?) Formation; Middle Park,  
 Near Granby, Colorado)

Component or property	Milliequivalents per 100 g. of sample
Cation exchange capacity	95.0
Extractable sodium	2.15
Water soluble sodium	0.13
Exchangeable sodium	2.02
Extractable potassium	0.70
Water soluble potassium	0.05
Exchangeable potassium	0.65
Extractable calcium	111.2
Water soluble calcium	3.2
Exchangeable calcium	108.0
Extractable magnesium	13.6
Water soluble magnesium	1.0
Exchangeable magnesium	12.6
Exchangeable calcium and magnesium, by difference	92.33 <sup>2</sup>
Exchangeable calcium and magnesium, by extraction	120.6 <sup>2</sup>

<sup>1</sup> Determined by Methods 18 and 19 of the U.S. Salinity Laboratory (Richards, 1954, pp. 100-101).

<sup>2</sup> The discrepancy in these two values indicates the presence of compounds of calcium and magnesium which are soluble in neutral ammonium acetate solution but insoluble in distilled water.

A representative sample of the bentonite contains approximately 6.0 percent by weight of nonclay impurities. This value is used to correct the results of the thermal balance analyses where indicated below.

### CATION EXCHANGE TREATMENT

Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>++</sup>, and Mg<sup>++</sup> modifications of the montmorillonite were produced by treatment of representative portions of the bentonite. A 5.0 gm. sample of lightly ground bentonite was shaken vigorously for 5 minutes with 40 ml. of 1 N solution of the chloride of the cation to be introduced. The mixture was centrifuged and clear supernatant solution was decanted. This process was repeated three additional times, care being taken to avoid loss of granular constituents. The excess salt was flushed out by three 160 ml. charges of 95 percent ethanol. A total of 20 gm. of each ionic modification was prepared in this way.

A portion of each ionic modification was placed in an oven maintained at 105° C-110° C and dried to constant weight. A second portion of each sample was placed for a minimum of one week in a vessel in which the relative humidity was maintained at 52 percent over a saturated aqueous solution of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. In the humidification chamber small samples were spread in a thin layer on a watch glass.

Subsequently, the samples were subjected to differential thermal, thermal balance, and X-ray diffraction analysis. Our equipment and techniques of thermal analysis were described previously (Mielenz, Schieltz, and King, 1954, p. 285).

### DIFFERENTIAL THERMAL ANALYSIS

The samples previously humidified at 52 percent relative humidity show marked endothermic reactions between room temperature and 200° C or 300° C (Fig. 1). The differential thermal curve for the  $\text{NH}_4^+$  modification demonstrates an unusual endotherm which attains a maximum at 460° C and is correlated with loss of the exchangeable cation (compare the results obtained by Barshad (1950, p. 229)). A small exotherm occurs in the curves for the  $\text{NH}_4^+$  and  $\text{H}^+$  modifications at 530° C. The configuration of the curves above 600° C varies considerably with the exchangeable cation.

Drying of the samples prior to differential thermal analysis reduces the area of most of the low temperature endotherms (Fig. 2). Exceptions are the single endotherm produced by the  $\text{NH}_4^+$  modification at about 180° C and that produced by the  $\text{Mg}^{++}$  modification at 300° C. Comparison of these curves with those produced after humidification at 52 percent relative humidity indicates that not only the surface water but also a part of the water of hydration of the  $\text{H}^+$ ,  $\text{Li}^+$ , and  $\text{Ca}^{++}$  was lost during drying to constant weight of 105° C. On the contrary, the  $\text{Mg}^{++}$  remains hydrated at that temperature.

Decomposition and recrystallization of the modifications during thermal analysis produces mixtures of spinel and glass when the exchangeable cation is  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{H}^+$ ,  $\text{NH}_4^+$ , or  $\text{Mg}^{++}$ . The  $\text{Mg}^{++}$  modification produces a very small proportion of beta-quartz. The  $\text{Li}^+$  and  $\text{Ca}^{++}$  modifications develop a mixture of beta-quartz, spinel, alpha-cristobalite, and glass; a previously oven-dried  $\text{Ca}^{++}$  modification produces enstatite also. The development of differing crystalline products does not correlate simply with the configuration of the differential thermal curve above 800° C. The oven-dried modifications containing  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{H}^+$ , and  $\text{Ca}^{++}$  produce better crystallized thermal products than do the humidified modifications.

### THERMAL BALANCE ANALYSIS

The thermal balance curves produced by the several cationic modifications humidified at 52 percent relative humidity are roughly similar in that all show marked weight loss from 30° C-50° C to a temperature in the range from 190° C-367° C (Fig. 3 and Tables III and IV). The beginning of rapid evolution of water of cation hydration is indicated by a slight or marked shoulder in the curve at about 190° C to 225° C.

In the range from 190° C-367° C to 380° C-505° C, the precise temperature depending upon the exchangeable cation, weight loss occurs at a low rate. The total weight loss in this range varies from 0.25 to 2.92 percent

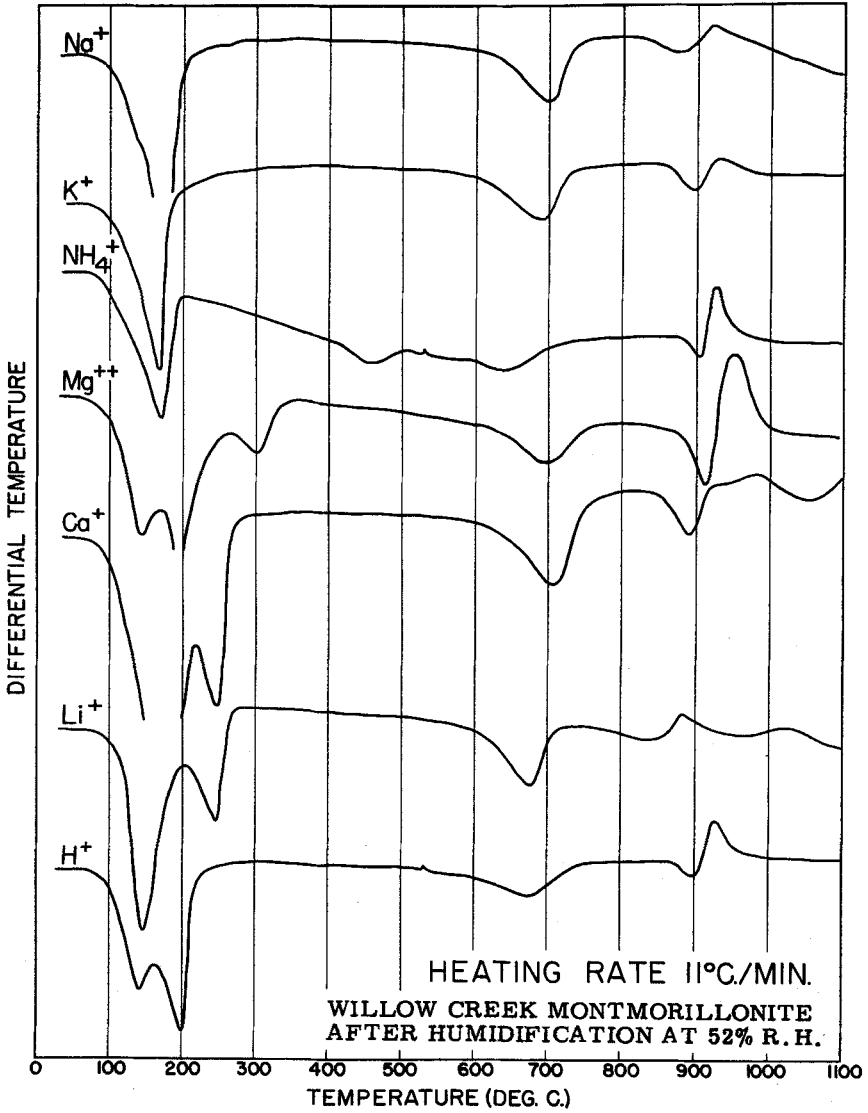


FIGURE 1.— Differential thermal curves for cationic modifications after humidification at 52 percent relative humidity.

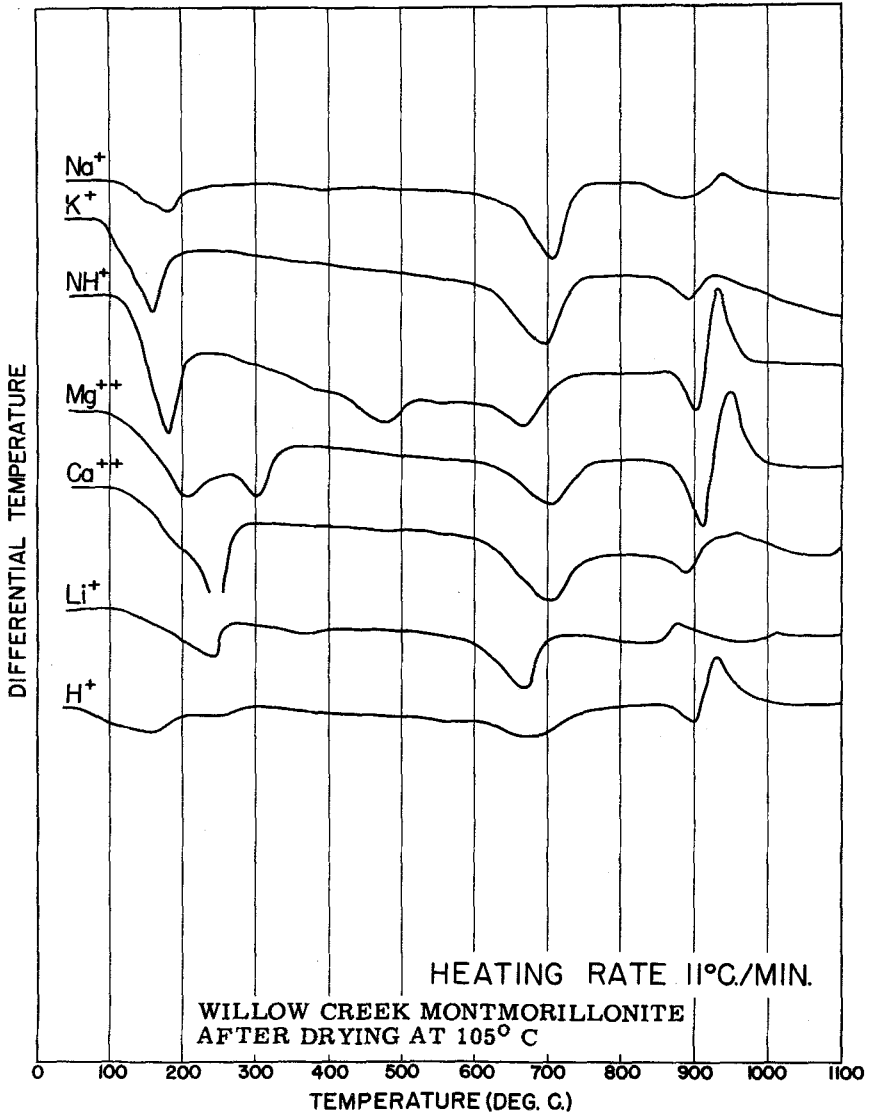


FIGURE 2. — Differential thermal curves for cationic modifications after drying at 105° C-110° C.

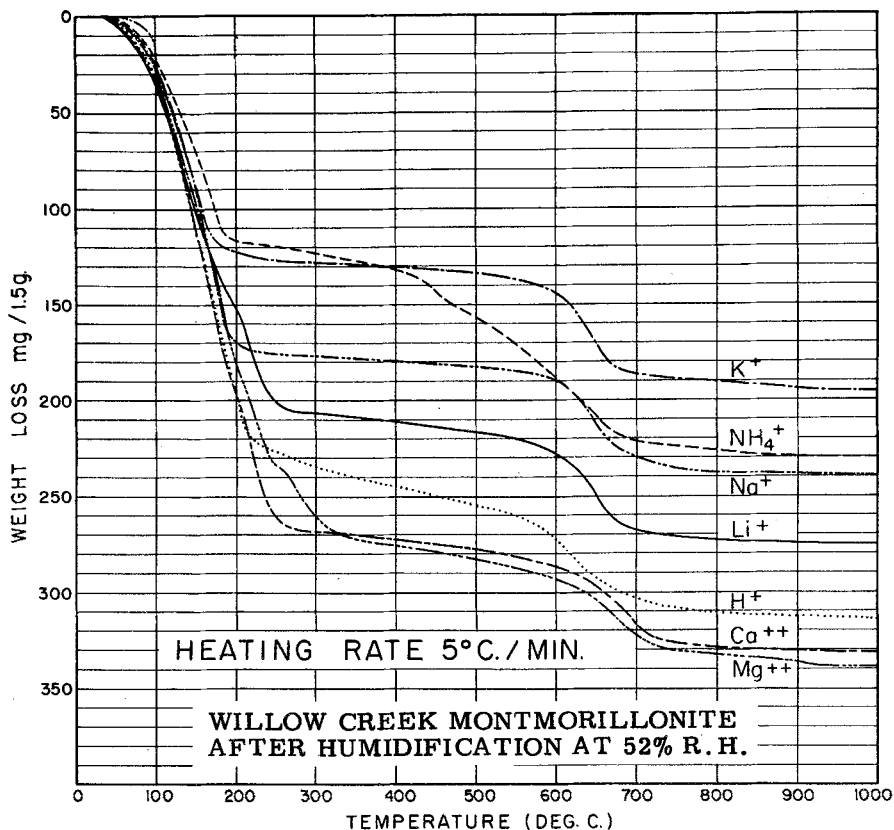


FIGURE 3.— Thermal balance curves for cationic modifications after humidification at 52 percent relative humidity.

of the base weight, that is, the weight of the sample following volatilization of all adsorbed water (Table IV).

After prior drying of the samples at 105° C-110° C to constant weight, all of the cationic modifications except those containing K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> regain water during heating until the furnace temperature approaches 100° C (Fig. 4). In the range from room temperature to 190° C-225° C the samples lose 0.50 to 6.96 percent in weight, the maximum being from the Mg<sup>++</sup> modification (Table IV). Only for the Mg<sup>++</sup> modification does the shoulder beginning at 225° C persist as an indication that water of cation hydration is being released. It is interesting to note that the dehydration endotherm produced by the NH<sub>4</sub><sup>+</sup> modification during differential thermal analysis does not change in size with oven drying even though the weight loss in this temperature range is reduced by a factor of more than 10.

In the temperature range between 380° C and 505° C all of the cationic

TABLE III.—SUMMARY OF THERMOGRAVIMETRIC DATA  
(Weight Losses Based upon Original Weight of Sample (1.5000 g.)—Montmorillonite, North Park (?) Formation; Middle Park,  
Near Granby, Colorado)

Exchangeable cation	Condition of the sample	Weight loss, %						Total weight loss, %
		Dehydration		Intermediate range		Dehydroxylation		
		Temperature	Loss	Temperature	Loss	Temperature	Loss	
Na <sup>+</sup>	Oven dry (105° C)	R.T.-190	0.50	190-450	0.50	450-1,000	4.37	5.37
	52% R.H.	R.T.-267	11.71	267-490	0.44	490-1,000	3.82	15.97
K <sup>+</sup>	Oven dry (105° C)	R.T.-200	0.94	200-457	0.49	457-1,000	4.66	6.09
	52% R.H.	R.T.-254	8.46	254-420	0.23	420-1,000	4.34	13.03
Li <sup>+</sup>	Oven dry (105° C)	R.T.-264	2.33	264-409	0.50	409-1,000	4.88	7.71
	52% R.H.	R.T.-280	13.73	280-380	0.28	380-1,000	4.34	18.35
H <sup>+</sup>	Oven dry (105° C)	R.T.-204	0.60	204-420	1.38	420-1,000	5.34	7.32
	52% R.H.	R.T.-330	15.88	330-400	0.48	400-1,000	4.60	20.96
NH <sub>4</sub> <sup>+</sup>	Oven dry (105° C)	R.T.-200	0.85	200-250	0.17 <sup>1</sup>	490-1,000	5.55	9.12
	52% R.H.	R.T.-234	8.00	234-307	0.07 <sup>2</sup>	505-1,000	4.77	15.37
Ca <sup>++</sup>	Oven dry (105° C)	R.T.-263	2.73	263-481	0.72	481-1,000	4.34	7.84
	52% R.H.	R.T.-361	18.03	361-478	0.31	478-1,000	3.71	22.05
Mg <sup>++</sup>	Oven dry (105° C)	R.T.-363	6.45	363-490	0.75	490-1,000	4.35	11.55
	52% R.H.	R.T.-367	18.18	367-485	0.60	485-1,000	3.75	22.53

<sup>1</sup> Does not include loss of 2.55 percent between 250° C and 490° C.

<sup>2</sup> Does not include loss of 2.53 percent between 307° C and 505° C.



TABLE IV.—SUMMARY OF THERMOGRAVIMETRIC DATA  
 (Weight Losses Based upon Weight of Sample After Loss of Adsorbed Water — Montmorillonite, North Park (?) Formation;  
 Middle Park, Near Granby, Colorado)

Exchangeable cation	Condition of the sample	Weight loss, %						Total weight loss, %
		Dehydration		Intermediate range		Dehydroxylation		
		Temperature	Loss	Temperature	Loss	Temperature	Loss	
Na <sup>+</sup>	Oven dry (105° C)	R.T.-190	0.50	190-450	0.51	450-1,000	4.41	5.42
	52% R.H.	R.T.-267	13.33	267-490	0.50	490-1,000	4.35	18.18
K <sup>+</sup>	Oven dry (105° C)	R.T.-200	0.95	200-457	0.49	457-1,000	4.72	6.16
	52% R.H.	R.T.-254	9.26	254-420	0.25	420-1,000	4.75	14.26
Li <sup>+</sup>	Oven dry (105° C)	R.T.-264	2.40	264-409	0.51	409-1,000	5.02	7.93
	52% R.H.	R.T.-280	15.97	280-380	0.32	380-1,000	5.05	21.34
H <sup>+</sup>	Oven dry (105° C)	R.T.-204	0.61	204-420	1.40	420-1,000	5.45	7.46
	52% R.H.	R.T.-330	18.99	330-400	0.58	400-1,000	5.50	25.07
NH <sub>4</sub> <sup>+</sup>	Oven dry (105° C)	R.T.-200	0.88	200-250	0.18 <sup>1</sup>	490-1,000	5.75	9.46
	52% R.H.	R.T.-234	8.97	234-307	0.08 <sup>2</sup>	505-1,000	5.34	17.22
Ca <sup>++</sup>	Oven dry (105° C)	R.T.-263	2.82	263-481	0.74	481-1,000	4.56	8.12
	52% R.H.	R.T.-361	22.09	361-478	0.39	478-1,000	4.54	27.02
Mg <sup>++</sup>	Oven dry (105° C)	R.T.-363	6.96	363-490	0.81	490-1,000	4.69	12.46
	52% R.H.	R.T.-367	22.39	367-485	0.74	485-1,000	4.62	27.75

<sup>1</sup> Does not include loss of 2.65 percent between 250° C and 490° C.

<sup>2</sup> Does not include loss of 2.83 percent between 307° C and 505° C.

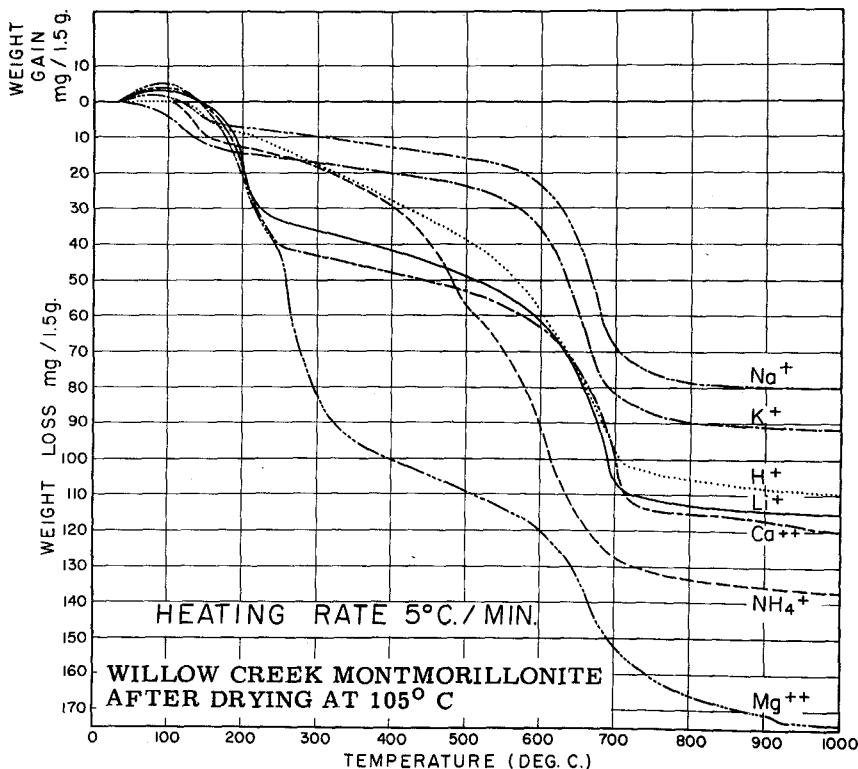


FIGURE 4.— Thermal balance curves for cationic modifications after drying at 105° C-110° C.

modifications begin to lose additional weight at a rapid rate, presumably as the result of dehydroxylation of the crystal structure. The temperature at which this reaction begins is taken as the base temperature for each modification. The thermal curves are smooth, though not always symmetrical, above the base temperature, giving no suggestion that hydroxyl groups are being lost from more than one structural environment.

### DISCUSSION OF THE THERMAL DATA

According to the Hofmann-Endell-Wilm structure (1933, 1934), weight losses during dehydration may fall into any one of four categories, namely (1) water adsorbed on the surface of the clay structure, including both broken edges and corners as well as the (001) interlayer surface, (2) water of hydration of the exchangeable cations, (3) evolution of exchangeable cations themselves or portions thereof, especially  $\text{NH}_4^+$  and (4) water produced as the result of release from the crystal structure of hydroxyl groups, including both those in the octahedral layer and those which might be pres-

ent in the tetrahedral layer as  $(\text{OH})_4$  groups substituting for Si-O tetrahedra in accordance with ideas developed by McConnell (1950, 1951). For the Hofmann-Endell-Wilm structure, water of dehydroxylation from the octahedral layer theoretically ranges from 4.68 to 4.89 percent for the montmorillonite under investigation, depending upon the equivalent weight of the exchangeable action.

Classification of weight losses into the four categories cannot be accomplished accurately now. However, an approximation can be made (Tables V and VI).\*

Except for the  $\text{Na}^+$  modification, the corrected weight loss above the base temperature exceeds the theoretical water of dehydroxylation of the Hofmann-Endell-Wilm structure. The loss in the intermediate temperature interval also varies from modification to modification, being least for the alkali modifications, intermediate for the alkali-earth modifications, and greatest for the  $\text{H}^+$  and  $\text{NH}_4^+$  modifications. The excessive weight loss from the  $\text{NH}_4^+$  and  $\text{H}^+$  modifications in the intermediate temperature range is approximately consistent with the Hofmann-Endell-Wilm structure only if the  $\text{NH}_4^+$  and  $\text{H}^+$  are assumed to be hydrated even after drying at  $105^\circ\text{C}$ . Furthermore, it must be assumed that the water of cation hydration is released only after heating in the range from  $200^\circ\text{C}$  to over  $400^\circ\text{C}$ . If these ions are hydrated and if the  $\text{NH}_4^+$  hydrate is lost according to the reaction  $\text{NH}_4^+ \cdot \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{H}_2\text{O} + \text{H}^+$ , with the  $\text{H}^+$  being retained by the clay, the weight loss from the  $\text{NH}_4^+$  and  $\text{H}^+$  modifications would be 3.89 and 2.10 percent, respectively.

Since water of hydration of exchangeable  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ , and  $\text{Li}^+$  is indicated by differential thermal and thermal balance analysis to be lost below  $200^\circ\text{C}$ – $367^\circ\text{C}$ , the weight loss in the intermediate range must be relegated to water of dehydroxylation, according to the Hofmann-Endell-Wilm structure. The excess of weight loss in the high temperature range over the theoretical amount of water of dehydroxylation varies from 0.44 to 1.38 percent of the base weight, and is 2.5 to 7.6 times the amount postulated by McConnell (1951, p. 182) to be present in the tetrahedral layer as  $(\text{OH})_4$  groups.

In this treatment (Tables V and VI) no attempt has been made to assign specific quantities to water of surface hydration.

As is indicated above, this development requires assumption of two circumstances which are inconsistent with the differential thermal data, namely that the  $\text{NH}_4^+$  ion is hydrated and that the  $\text{H}^+$  ion is able to retain its water of hydration during long-continued drying at  $105^\circ\text{C}$ . Consequently, the Hofmann-Endell-Wilm structure should be reexamined to determine if these apparent discrepancies can be reconciled.

The Edelman-Favajee (1940) structure has been discussed repeatedly

\* The values in Tables V and VI are corrected for nonclay impurities constituting 6.0 percent of the original sample or 6.85 percent of the sample after loss of adsorbed water. The data in Table IV are multiplied by 100.00/93.15 to derive those in Tables V and VI.

TABLE V.—POSSIBLE DISTRIBUTION OF WATER OF DEHYDRATION ACCORDING TO THE HOFMANN-ENDELL-WILM STRUCTURE<sup>1</sup>  
(Montmorillonite, North Park (?) Formation; Middle Park, Near Granby, Colorado—Humidified at 52% R.H.)

Exchangeable cation	Surface dehydration		Cation dehydration		Dehydroxylation			
	Temperature range (° C)	%	Temperature range (° C)	%	Octahedral		Tetrahedral (?)	
					Temperature range (° C)	%	Temperature range (° C)	%
H <sup>+</sup> .....	{R.T.-330	18.91	R.T.-330	1.48	400-1,000	4.89	400-1,000	1.01
	{330-400		330-400	0.62				
	{R.T.-234	8.90	R.T.-234	0.73				
NH <sub>4</sub> <sup>+</sup> .....	{234-307		234-307	0.09	505-1,000	4.79	505-1,000	0.94
	{307-505		307-505	3.07	367- 485	0.90		
Mg <sup>++</sup> .....	{R.T.-367	17.82	R.T.-367	6.22	485-1,000	3.93	485-1,000	1.03
	{R.T.-263	17.54	R.T.-263	6.17	263- 478	0.42	478-1,000	0.51
Ca <sup>++</sup> .....	{R.T.-280	11.06	R.T.-280	6.08	280- 380	0.34	380-1,000	0.91
Li <sup>++</sup> .....	{R.T.-254	9.94			254- 420	0.27	420-1,000	0.69
K <sup>+</sup> .....	{R.T.-267	14.31			267- 490	0.54	490-1,000	0.44
Na <sup>+</sup> .....					490-1,000	4.23		

<sup>1</sup> Weight losses corrected for 6.0 percent of nonclay impurities, in the original sample.

TABLE VI. — POSSIBLE DISTRIBUTION OF WATER OF DEHYDRATION ACCORDING TO THE HOFMANN-ENDELL-WILM STRUCTURE<sup>1</sup>  
 (Montmorillonite, North Park (?) Formation; Middle Park, Near Granby, Colorado — Oven-dried at 105° C)

Exchangeable cation	Surface dehydration		Cation dehydration		Dehydroxylation			
	Temperature range (° C)	%	Temperature range (° C)	%	Octahedral		Tetrahedral (?)	
					Temperature range (° C)	%	Temperature range (° C)	%
H <sup>+</sup> .....	{ R.T.-204	0.05	{ R.T.-204	0.60	420-1,000	4.89	420-1,000	0.96
	{ R.T.-200	0.07	{ 204-420	1.50				
NH <sub>4</sub> <sup>+</sup> .....	{ R.T.-200		{ R.T.-200	0.87	490-1,000	4.79	490-1,000	1.38
	{ R.T.-363	1.25	{ 200-250	0.19	363- 490	0.87		
Mg <sup>++</sup> .....	{ R.T.-363		{ 250-490	2.83	490-1,000	3.96	490-1,000	1.07
			{ R.T.-363	6.22				
Ca <sup>++</sup> .....			{ R.T.-263	3.03	263- 481	0.79	481-1,000	0.91
Li <sup>+</sup> .....			{ R.T.-264	2.58	264- 409	0.55	409-1,000	1.09
					409-1,000	4.30		
K <sup>+</sup> .....	{ R.T.-200	1.02			200- 457	0.53	409-1,000	0.92
					457-1,000	4.15	457-1,000	
Na <sup>+</sup> .....	{ R.T.-267	0.54			267- 400	0.55	400-1,000	0.51
					400-1,000	4.22		

<sup>1</sup> Weight losses corrected for 6.0 percent of nonclay impurities, in the original sample.

and usually has been rejected because the suggested structure requires excessive water loss during dehydroxylation inasmuch as each inverted Si-O tetrahedron requires addition of a hydroxyl group to the octahedral layer as well as one at the apex of the inverted tetrahedron. In a later paper (1947, p. 4), Edelman accepted the possibility that the number of inverted tetrahedra might be less than was proposed originally.

If it is assumed that the inversion of the Si-O tetrahedra is related electrostatically and numerically to the cation exchange capacity, a reasonable explanation of the thermal data can be developed. Assuming that one Si-O tetrahedron is inverted for each exchangeable cation, the Hofmann-Endell-Wilm structure becomes as follows:

Content of Unit Cell	Charge
X <sub>0.43</sub> .....	0.43
(OH) <sub>0.43</sub> .....	- 0.43
Si <sub>0.43</sub> .....	1.72
O <sub>8.00</sub> .....	-12.00
Si <sub>3.37</sub> Al <sub>0.20</sub> .....	14.08
(OH) <sub>2.43</sub> O <sub>3.37</sub> .....	- 9.57
Al <sub>2.44</sub> Fe <sub>0.50</sub> Mg <sub>0.72</sub> Mn <sub>0.04</sub> .....	11.54
(OH) <sub>2.43</sub> O <sub>3.37</sub> .....	- 9.57
Si <sub>3.37</sub> Al <sub>0.20</sub> .....	14.08
O <sub>8.00</sub> .....	-12.00
Si <sub>0.43</sub> .....	1.72
(OH) <sub>0.43</sub> .....	- 0.43
X <sub>0.43</sub> .....	0.43
Net charge .....	0.00

According to this arrangement 0.43 of each four Si-O tetrahedra are inverted, or approximately 1 in 11. This structure is really a compromise between the Hofmann-Endell-Wilm structure and the Edelman-Favajee structure inasmuch as only 6 of 7 unit cells, on the average, will differ at all from the Hofmann-Endell-Wilm structure. The possible hydroxyl water in the proposed structure (including both that derived from the (OH) groups in the interlayer space and that from those in the octahedral layer) ranges from 6.56 to 6.85 percent, depending upon the atomic weight and valence of the exchangeable cation. If the exchange capacity is reduced by a factor of 7 to 12 percent to compensate for cation exchange at broken edges and corners of the lattice (Cornet, 1943, p. 226), the excess hydroxyl water will be decreased proportionately. Water of dehydroxylation from the octahedral layer theoretically ranges from 5.57 to 5.82 percent. As will be indicated below, all of the potential hydroxyl water may not be released during the thermal analysis due to formation in the (001) interlayer space of hydroxides which are not decomposed below 1,000° C.

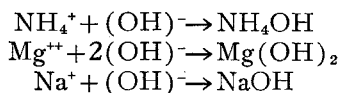
Inversion of a Si-O tetrahedron means that (1) the Si<sup>+++</sup> nests in the same three O<sup>-</sup> at the base of the tetrahedron but is shifted to the opposite side of the plane containing the centers of the oxygen ions, a distance of 1.04 Å approximately parallel to the "c" axis and (2) an (OH)<sup>-</sup> is affixed to this Si<sup>+++</sup> by virtue of the polarity of the Si-O tetrahedron resulting

from the asymmetrical position of the  $\text{Si}^{++++}$ . The exchangeable cation likewise is held weakly to the  $(\text{OH})^-$ , which, like an  $\text{H}_2\text{O}$  molecule, becomes strongly polar. In this structure, the electrostatic field of the  $\text{Si}^{++++}$  may be considered to replace one  $\text{H}^+$  of the  $\text{H}_2\text{O}$  molecule and the exchangeable cation to be bonded to the  $(\text{OH})^-$  at the polar area opposite the location of the  $\text{Si}^{++++}$  and  $\text{H}^+$ . Both the adsorbed cation and the  $(\text{OH})^-$  should be subject to exchange reactions.

The inverted position of the  $\text{Si}^{++++}$  may depend upon the substitution of an  $(\text{OH})^-$  group spacially in the octahedral layer. In turn, the replacement of  $\text{O}^{--}$  by  $(\text{OH})^-$  probably would take place most readily in a dioctahedral montmorillonoid when the octahedrally coordinated cation is divalent rather than trivalent. It will be noted that the additional  $(\text{OH})^-$  groups in the modified Edelman structure in the montmorillonite under investigation exceeds just slightly the number of octahedrally coordinated  $\text{Mg}^{++}$  and  $\text{Mn}^{++}$  per unit cell. The  $(\text{OH})^-$  group, being polar with the hydrogen atom oriented toward the tetrahedral layer, would inhibit deposition of the  $\text{Si}^{++++}$  in the adjacent space. Rather, the  $\text{Si}^{++++}$  would tend to be deposited in an equivalent position 1.04 Å away parallel to the "c" axis, nesting in the ring of three oxygen ions at the base of the tetrahedron, external to the silicate packet.

A distal position of the  $\text{Si}^{++++}$  also might result from accumulation of oxygen atoms in the outer portion of the tetrahedral layer at a rate exceeding the emplacement of  $\text{Si}^{++++}$ , such that the normal site for the  $\text{Si}^{++++}$  is closed before a cation is deposited there.

At some elevated temperature, it is expected that the external, adsorbed  $(\text{OH})^-$  group in the interlayer space will break away from the silica sheet either to produce water by the reaction  $2(\text{OH})^- \rightarrow \text{H}_2\text{O} + \text{O}^{--}$  or to combine with the exchangeable cation to produce a hydroxide by reactions such as



These reactions will maintain the electrostatic neutrality of the structure by removal of equal numbers of positive and negative ions.

If the hydroxide resulting from this reaction is volatile at temperatures attained during the thermal analysis, the hydroxide will escape into the atmosphere of the furnace.  $\text{H}^+$  and  $\text{NH}_4^+$  would be affected by this action. If the hydroxide is decomposed in the temperature range attained in the thermal analysis, one molecule of water for each two equivalents of exchange capacity will be released. Such dehydration would be expected of  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ , which in the crystalline form decompose at  $580^\circ\text{C}$  and  $350^\circ\text{C}$ , respectively. In contrast, the  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  will produce hydroxides which would not be expected to decompose below  $1,000^\circ\text{C}$ .

The experimentally determined weight losses can be distributed into vari-

ous categories on the basis of the modified Edelman structure as was done for the Hofmann-Endell-Wilm structure (Tables VII and VIII).† A reasonable correlation is established.

The hypothesis that hydroxides are formed is consistent with considerable data. As has been pointed out, the differential thermal analysis data indicate that water of cation hydration is lost during drying at 105° C from the H<sup>+</sup> modification. This is indicated also by the distribution of water according to the modified Edelman structure. The weight loss in the intermediate temperature range is correlated with the loss of water produced by the reaction of the H<sup>+</sup> and the OH<sup>-</sup> at the apex of the inverted Si-O tetrahedra.

According to the modified Edelman structure the NH<sub>4</sub><sup>+</sup> is anhydrous, as is indicated also by the differential thermal analysis. The weight loss during the intermediate temperature range is considered to represent volatilization of NH<sub>4</sub>OH. This release develops the small endotherm between 400° C and 500° C. The loss of NH<sub>4</sub>OH takes place predominantly in two intervals, one from room temperature to 200° C-234° C, and the second from 307° C to 505° C or from 250° C to 490° C. Two intervals of release of ammonia by NH<sub>4</sub><sup>+</sup> montmorillonite were reported also by Cornet (1943, pp. 225-226).

Decomposition of the secondary Mg(OH)<sub>2</sub> takes place below 490° C and evidently contributes to the persistent endotherm whose peak is at 300° C. A similar loss for the Ca<sup>++</sup> modification is indicated below 481° C, and largely below 263° C. This dehydration might be expected close to 580° C, because of the resistance of crystalline calcium hydroxide to decomposition. However, the thermal balance analysis indicates that if the decomposition occurs at all, it must take place below 481° C. The breakdown may combine with dehydration of the Ca<sup>++</sup> ion to produce the large endotherm whose peak is close to 250° C.

## X-RAY DIFFRACTION ANALYSIS

### *Procedure*

X-ray diffraction patterns were made in General Electric X-ray Corporation single-crystal, 10 cm. diameter cameras with the samples in the following conditions: (1) Oven-dried (3 to 10 days) at 105° C-110° C; exposure made while the specimens were sealed in Pyrex capillaries (Fig. 5); (2) air-dried, using Duco cement as a binder and rods rolled to 0.013-inch in diameter (relative humidity unknown); (3) air-dried, with samples unsealed in Pyrex capillaries (relative humidity of the atmosphere was measured but not controlled); (4) after humidification at 52 percent relative humidity for 8 to 14 days; exposure made with specimens in sealed Pyrex capillaries (Fig. 5); (5) oriented films or flakes of the cationic modifications produced by settling from water suspension (Fig. 6); the flakes were

† See discussion on pp. 155-156.



TABLE VII.—POSSIBLE DISTRIBUTION OF WATER OF DEHYDRATION ACCORDING TO THE MODIFIED EDELMAN STRUCTURE<sup>1</sup>  
(Montmorillonite, North Park (?) Formation; Middle Park, Near Granby, Colorado — Humidified at 52% R.H.)

Exchangeable cation	Surface dehydration		Cation dehydration		Hydroxide loss or dehydration		Dehydroxylation (octahedral)		Remarks
	Temperature range (° C)	%	Temperature range (° C)	%	Temperature range (° C)	%	Temperature range (° C)	%	
H <sup>+</sup> .....	{ R.T.-330	16.27	{ R.T.-330	2.06	{ R.T.- 330	1.36	{ 400-1,000	5.82	
	{ 330- 400				{ 330- 400	0.62			
	{ 400-1,000				{ 400-1,000	0.08			
NH <sub>4</sub> <sup>+</sup> .....	{ R.T.-234	8.88			{ R.T.- 234	0.75			
	{ 234- 307				{ 234- 307	0.09			
	{ 307- 505				{ 307- 505	3.07			
	{ 505-1,000				{ 505-1,000	0.02			
Mg <sup>++</sup> .....	{ R.T.-367	17.04	{ R.T.-367	6.10	{ R.T.- 367	0.90	{ 505-1,000	5.71	
	{ 367- 485				{ 367- 485	0.12	{ 367- 485	0.78	Deficient 0.40% in hydroxyl water
	{ R.T.-263	16.66	{ R.T.-263	6.04	{ R.T.- 263	1.01	{ 478-1,000	4.87	Deficient 0.02% in hydroxyl water
Ca <sup>++</sup> .....	{ R.T.-280	11.01	{ R.T.-280	6.13			{ 263- 478	0.42	Deficient 0.20% in hydroxyl water
	{ R.T.-254	9.94					{ 280- 380	0.34	Deficient 0.46% in hydroxyl water
Li <sup>+</sup> .....	{ R.T.-267	14.31					{ 380-1,000	5.42	
							{ 254- 420	0.27	
							{ 420-1,000	5.10	
							{ 267- 490	0.54	
							{ 490-1,000	4.67	

<sup>1</sup>Weight losses corrected for 6.0 percent of nonlayer impurities in the original sample.

TABLE VIII. — POSSIBLE DISTRIBUTION OF WATER OF DEHYDRATION ACCORDING TO THE MODIFIED EBELMAN STRUCTURE<sup>1</sup>  
(Montmorillonite, North Park (?) Formation; Middle Park, Near Granby, Colorado — Oven-dried at 105° C)

Exchange-able cation	Surface dehydration		Cation dehydration		Hydroxide loss or dehydration		Dehydroxylation (octahedral)		Remarks
	Temperature range (° C)	%	Temperature range (° C)	%	Temperature range (° C)	%	Temperature range (° C)	%	
H <sup>+</sup> .....	R.T.-204	0.12			R.T.- 204	0.53			Deficient 2.06% in water of cation hydration
					204- 420	1.50			
					420-1,000	0.03	420-1,000	5.82	
NH <sub>4</sub> <sup>+</sup> .....	R.T.-200	0.49			R.T.- 200	0.45			
					200- 250	0.19			
					250- 490	2.83			
					490-1,000	0.46	490-1,000	5.71	
Mg <sup>++</sup> .....	R.T.-363	0.51	R.T.-363	6.10	R.T.- 363	0.85			
					363- 490	0.16	363- 490	0.71	
					R.T.- 263	1.01	490-1,000	5.03	
Ca <sup>++</sup> .....	R.T.-263	0.51	R.T.-263	1.51			263- 481	0.79	Deficient 4.53% in water of cation hydration
							481-1,000	4.90	
							264- 409	0.39	
Li <sup>+</sup> .....	R.T.-264	0.50	R.T.-264	2.08			409-1,000	5.39	Deficient 3.89% in water of cation hydration
			264-409	0.16					
K <sup>+</sup> .....	R.T.-200	1.02					200- 457	0.50	Deficient 0.39% in hydroxyl water
	200-457	0.03					457-1,000	5.07	
							190- 450	0.55	
Na <sup>+</sup> .....	R.T.-190	0.54					450-1,000	4.73	

<sup>1</sup> Weight losses corrected for 6.0 percent of nonclay impurities in the original sample.

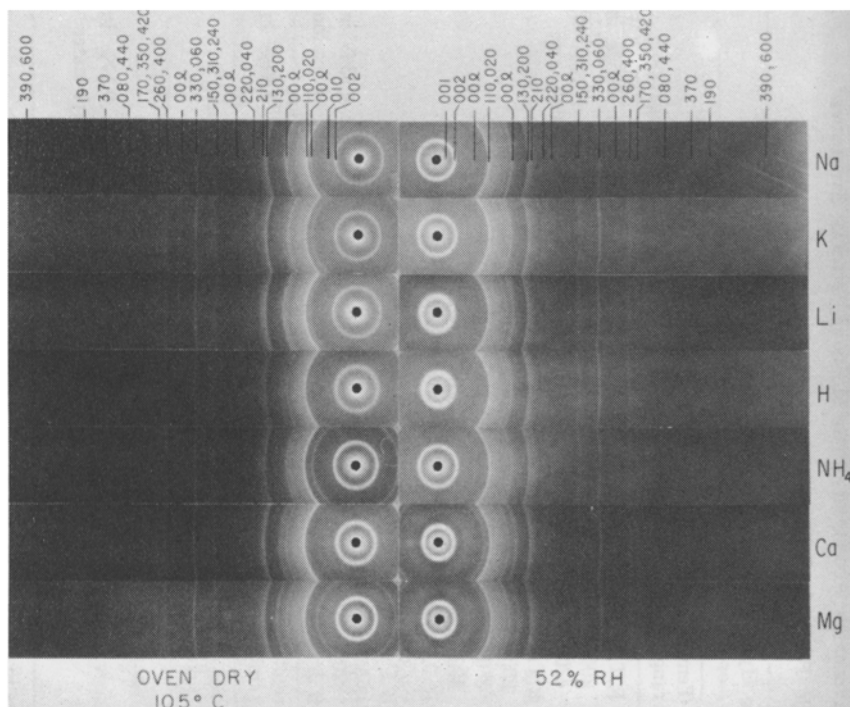


FIGURE 5.—X-ray diffraction powder patterns of cationic modifications sealed in Pyrex capillaries.

mounted at an angle of 30 degrees to the defined X-ray beam; ‡ and (6) reaction products of the thermal analyses.

### *The (001) Interference*

The (001) interference is recorded in the X-ray diffraction patterns as a line corresponding to  $d$  spacings ranging from about 19 to 30 Å. The  $d$  spacing and the intensity of the line depend upon the exchangeable cation and the water content of the specimen (Fig. 5). Oven drying of the sample causes this line practically to disappear from the patterns of the alkali modifications and to be appreciably weakened in the patterns of the  $H^+$ ,  $NH_4^+$ ,  $Ca^{++}$ , and  $Mg^{++}$  modifications. With readsorption of water, this line reappears or becomes much more intense. Consequently, this interference must be associated with the structure and position of the adsorbed water and, possibly indirectly, with the exchangeable cation.

‡ The flakes contained no binder. The specimens were cut into strips 0.3 to 0.5 mm. wide. The relative humidity was not measured or controlled. Preliminary studies demonstrated the 30 degrees position of the flake with respect to the beam to be the most satisfactory for investigation of the (001) and (hk0) interferences.

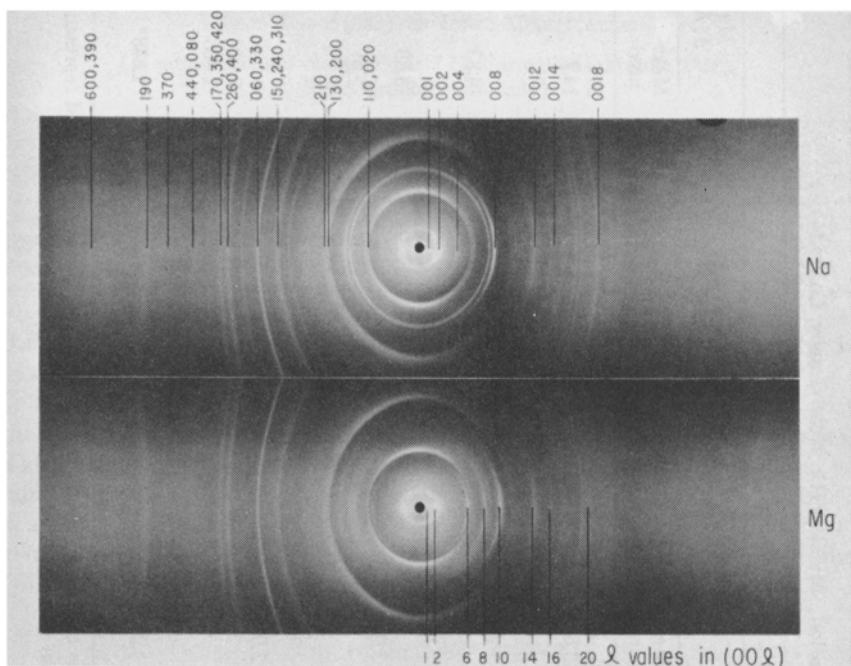


FIGURE 6.—X-ray diffraction patterns of oriented flakes of the Na- and Mg-modifications under room conditions (flakes set at 30° to beam).

This line is considered to represent the first order of the (001) group because (1) its dimension agrees with that calculated from the position of the line representing  $d$  spacings of 9.5 to about 15 Å, assuming that the latter represents  $d(002)$  (Table IX); (2) some of the higher orders of (001) require that this line be correlated with  $d(001)$ , or even with  $d(002)$  in the case of the  $K^+$ ,  $H^+$ , and  $NH_4^+$  modifications, in order that they may be indexed as integers; and (3) the line orients itself with the other orders of (001) in the patterns produced by the oriented films of clay and varies in position with water content of the sample.

### *The (002) Interference*

The diffraction line corresponding to the (002) interference assumes characteristic positions depending upon the exchangeable cation and the conditions of humidification or drying of the sample (Fig. 5). For the oven-dried modifications,  $d(002)$  ranges from 9.7 to 12.0 Å (Table X). For the  $Na^+$ ,  $K^+$ , and  $NH_4^+$  modifications the  $d(002)$  spacing does not vary greatly over even a wide range of humidity. On the other hand, considerable change occurs in  $d(002)$  for the  $Li^+$  and  $H^+$  modifications in the range of relative humidity commonly experienced under room conditions. For

TABLE IX. — (001) LINES OBSERVED IN X-RAY DIFFRACTION PATTERNS PRODUCED BY ORIENTED FILMS OF THE CATIONIC MODIFICATIONS (Montmorillonite, North Park (?) Formation; Middle Park, Near Granby, Colorado)

(001) index	Exchangeable cation													
	Na <sup>+</sup> d(Å)		K <sup>+</sup> d(Å)		Li <sup>+</sup> d(Å)		H <sup>+</sup> d(Å)		NH <sub>4</sub> <sup>+</sup> d(Å)		Ca <sup>++</sup> d(Å)		Mg <sup>++</sup> d(Å)	
	Meas-ured	Calcu-lated	Meas-ured	Calcu-lated	Meas-ured	Calcu-lated	Meas-ured	Calcu-lated	Meas-ured	Calcu-lated	Meas-ured	Calcu-lated	Meas-ured	Calcu-lated
001	24.1	24.82	— <sup>1</sup>	22.67	23.7	24.55	— <sup>2</sup>	27.48	24.1	23.59	30.2	30.14	29.2	28.96
002	12.2	12.41	11.4	11.33	12.6	12.28	13.6	13.74	11.9	11.79	15.1	15.07	14.7	14.48
004	6.18	6.20			6.13	6.14			5.99	5.90				
004½			4.99	5.04			6.23	6.11						
005½							4.96	4.99						
006											5.09	5.02	4.83	4.83
007			3.215	3.24										
007½					3.066	3.068			3.138	3.145				
008	3.114	3.103									3.729	3.768	3.58	3.62
009							3.078	3.053			3.007	3.014	2.91	2.90
0010														
0011			2.051	2.060										
0011½									2.051 <sup>2</sup>	2.051				
0012	2.056	2.069			2.046	2.045								
0013							2.082	2.112						
0014	1.790	1.773			1.753 <sup>2</sup>	1.753			1.701	1.685	2.142	2.152	2.067	2.068
0016			1.417 <sup>2</sup>	1.417					1.374	1.387	1.885	1.885	1.808	1.810
0017			1.343	1.334										
0018	1.379 <sup>2</sup>	1.379					1.374 <sup>2</sup>	1.374						
0020											1.370 <sup>2</sup>	1.370	1.448 <sup>2</sup>	1.448
0021														

<sup>1</sup>The (001) interference is recorded, but the line is too broad for unique measurement. The line is so broad that it could represent several interferences ranging from about  $d=20$  Å to  $d=50$  Å, the maximum  $d$  spacing which can be indicated by our camera.

<sup>2</sup>Higher orders used to calculate (001) values.

TABLE X.— $d(002)$  OF IONIC MODIFICATIONS  
(Montmorillonite, North Park (?) Formation; Middle Park,  
Near Granby, Colorado)

Condition	$d(002)$ in Angstrom units						
	Na <sup>+</sup>	K <sup>+</sup>	Li <sup>+</sup>	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Mg <sup>++</sup>	Ca <sup>++</sup>
Oven dry (105° C)	9.7	10.4	9.9	11.0	10.8	11.8	12.0
52% R.H.	12.6	12.4	14.7	15.3	11.9	15.0	15.3
Room dry	12.6	12.5	13.1	12.4	12.4	15.0	15.0

the Ca<sup>++</sup> and Mg<sup>++</sup> modification, the change with relative humidity is moderate.

The value of  $d(002)$  for the various cationic modifications is such that the group to which the exchangeable cation belongs, such as the alkalis, alkali earths, etc., usually can be identified from it, if the condition of humidification or drying is known. For the alkali modifications,  $d(002)$  is about 12.5 Å under ordinary conditions, whereas it is about 15 Å for the alkali-earth modifications. As with the (001) line, the intensity of the (002) line decreases with drying and increases with rewetting.

#### *The (004) Interference*

The  $d(004)$  spacing ranges from 4.80 to 6.13 Å for the Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and Mg<sup>++</sup> modifications after oven drying and from 6.10 to 6.28 Å for the Na<sup>+</sup>, K<sup>+</sup>, and NH<sub>4</sub><sup>+</sup> modifications conditioned at 52 percent relative humidity. The line is virtually absent from patterns of the oven-dried Ca<sup>++</sup> and H<sup>+</sup> modifications. It is also absent or is extremely weak in patterns produced by the Li<sup>+</sup>, H<sup>+</sup>, Ca<sup>++</sup>, and Mg<sup>++</sup> modifications after humidification at 52 percent relative humidity. After humidification at 52 percent relative humidity, the Ca<sup>++</sup> and Mg<sup>++</sup> modifications produce a similar diffraction line in the general vicinity of the position of the (004) line in patterns of the oven-dried Na<sup>+</sup> and K<sup>+</sup> modifications, but it must be indexed as (006).

#### *Higher Orders of the (001) Interferences*

All interferences representing higher orders of (001) vary considerably in  $d$  spacing from one cationic modification to another and with content of adsorbed water (Fig. 6). On the other hand, some lines of the (001) group having approximately, or exactly, the same  $d$  spacing in patterns of two or more cationic modifications must be indexed differently. Similar variations occur as the result of changed water content in patterns produced by the same cationic modification.

For some cationic modifications, the higher order (001) interferences can be indexed readily and show good agreement with the  $d$  spacings calculated from one of the higher order interferences, whereas for other cationic

modifications the agreement is very poor. For example, for the  $K^+$  modification, the 4.99 Å spacing must be indexed as  $(004\frac{1}{2})$ . Again, for the  $H^+$  modification, the (001) interference corresponding to  $d=6.23$  Å must be indexed as  $(004\frac{1}{2})$  and the 4.96 Å interference as  $(005\frac{1}{2})$ . For the  $K^+$ ,  $H^+$ , and  $NH_4^+$  modifications, the indexing is irregular, requiring mixed odd- and even-numbered orders, whereas the remaining modifications produce a sequence of (001) interferences in which values of  $l$  are always even.

The sequence of (001) interferences of higher order varies with exchangeable cation (Table IX) and condition of humidification or drying.

Some of the interferences corresponding to higher orders of (001), especially an interference in the general vicinity of  $d=3.18$  Å, are of considerable interest. The interference at  $d=3.18$  Å is rather intense and its position is related to the ionic radius and valence of the exchangeable cation (Table XI). In general, the interference moves to smaller diffraction angles with an increase in ionic radius and to larger angles with a decrease in ionic radius of the exchangeable cation. Increase in valence has the same effect as a decrease in ionic radius. The shift in the position of this line with swelling apparently is contrary to that expected and observed for other (001) lines. Water sorption by the montmorillonite has little effect on the intensity of the line in the pattern. Patterns of the oriented films produced by sedimentation prove that this line belongs to the (001) group. Consequently, this line appears to be associated with the position of the

TABLE XI. — RELATION OF  $d$  SPACING OF (001) LINE AT  $d=2.86-3.55$  Å TO EXCHANGEABLE CATION AND HUMIDITY

(Montmorillonite, North Park (?) Formation; Middle Park, Near Granby, Colorado)

Exchangeable cation	Ionic radius (Å) <sup>1</sup>	Oven dried	52% R.H.	Room conditions		Room conditions (Humidity unknown) <sup>2</sup>
				$d$ (Å)	R.H. (%)	
Na <sup>+</sup>	0.95	3.20	3.12	3.11	17.1	3.17
K <sup>+</sup>	1.33	3.37	3.18	3.18	17.1	3.25
Li <sup>+</sup>	0.60	3.21 <sup>a</sup>	3.07	3.10	27.5	3.20
H <sup>+</sup> <sup>4</sup>	1.3	3.19 <sup>b</sup>	3.18	3.06	27.5	3.36 <sup>o</sup>
NH <sub>4</sub> <sup>+</sup>	1.48	3.55	3.16	3.13	28.0	3.22
Ca <sup>++7</sup>	0.99	3.07 <sup>a</sup>	3.01	3.01	32.0	3.01
Mg <sup>++7</sup>	0.65	2.97 <sup>a</sup>	2.94	2.94	32.0	2.86

<sup>1</sup> Glasstone, 1946, p. 383; and Lipson and Cochran, p. 315.

<sup>2</sup> Duco cement used as binder.

<sup>a</sup> Still hydrated.

<sup>4</sup> The  $d$  spacings for the  $H^+$  modification do not conform to the trend established by the other modifications.

<sup>b</sup> Very weak double line, the second being at  $d=3.05$  Å.

<sup>o</sup> Line is abnormally strong.

<sup>7</sup> Ca<sup>++</sup> and Mg<sup>++</sup> modifications produce an additional line at  $d=3.76-3.78$  Å and 3.55-3.67 Å, respectively, with absorption of water.

exchangeable cation rather than with the amount and structure of the adsorbed water.

The position of this line is useful in identifying the adsorbed cation present if one cation greatly predominates. However, with differing conditions of hydration, the position of the line might be approximately the same for several cationic modifications.

#### *(hk0) Interferences*

The (hk0) interferences are identified readily and the equivalent  $d$  spacings are essentially constant with change of exchangeable cation and content of adsorbed water. The  $d$  spacings for given (hk0) planes agree closely with those compiled for montmorillonite by MacEwan (1951, Table IV, 1) from several sources. Variations in the spacings are random and nearly always within the experimental error. From  $d(600) = 0.866 \text{ \AA}$  and  $d(060) = 1.50 \text{ \AA}$ ,  $a_0$  and  $b_0$  are calculated to be  $5.20 \text{ \AA}$  and  $9.00 \text{ \AA}$ , respectively.

#### *(hkl) Interferences*

Detailed study of X-ray diffraction patterns reveals no (hkl) interferences. Those interferences identified by Winkler (1943) as (hkl) interferences of  $\text{Na}^+$  montmorillonite are apparent in patterns of the montmorillonite under investigation, but they are either (00l) interferences, interferences arising from  $K\beta$  radiation, interferences developed by granular constituents of the bentonite, such as quartz, or combinations of these.

### DISCUSSION OF THE X-RAY DIFFRACTION DATA

The X-ray diffraction data indicate that  $a_0 = 5.20 \text{ \AA}$  and  $b_0 = 9.00 \text{ \AA}$ , with but small variation, and that  $c_0 = 19.4\text{--}30.6 \text{ \AA}$  or larger, depending upon the exchangeable cation and the conditions of drying or humidification. Since  $a_0$  corresponds to four oxygen radii, the effective ionic radius of  $\text{O}^{--}$  in the tetrahedral layer is indicated to be  $1.30 \text{ \AA}$ . The same result is obtained from  $b_0$  since the oxygen radius is equal to  $b/8\cos 30^\circ$ . The centers of the  $\text{O}^{--}$  at the apex of the Si-O tetrahedra are spaced  $3.00 \text{ \AA}$  apart, *i.e.*, the peripheries of adjacent  $\text{O}^{--}$  in the octahedral layer are  $0.40 \text{ \AA}$  apart. These results correspond to those illustrated by Grim, Bradley, and Brown (1951, p. 141, Figure V, 3).

The structure of the tetrahedral layer requires a radius of approximately  $0.30 \text{ \AA}$  for the  $\text{Si}^{++++}$ , in contrast to about  $0.40 \text{ \AA}$  as usually given (Glasstone, 1946, p. 383). This smaller radius corresponds to the Si-O distance of  $1.60 \text{ \AA}$  accepted by Smith (1954, p. 481) for silicate and silica minerals.

The values of  $d(\text{hk}0)$  vary at random with change of adsorbed cation or content of adsorbed water and the variations are within the limits of error of measurement of the patterns.

The values of  $d(00l)$  are affected to varying degree by exchangeable cation and water content (Table IX). Certain of these interferences are



influenced primarily by the structure and amount of adsorbed water whereas others apparently are influenced primarily by the exchangeable cation. Furthermore, for the  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$  modifications, the higher orders of the (001) interferences bear a simple relation to  $d(001)$  and appear as a simple sequence of even numbered orders. On the contrary, the  $\text{K}^+$ ,  $\text{H}^+$ , and  $\text{NH}_4^+$  modifications produce some interferences which must be indexed as half orders, *e.g.*,  $(001\frac{1}{2})$ , and the other (001) interferences are in an irregular sequence of even and odd numbered orders. Also, the (001) interference produced by the latter modifications is broad and appears to represent  $d$  spacings considerably larger than 30 Å. These observations indicate that a differing structural periodicity exists in the  $c$  direction for the modifications containing large exchangeable cations, such as  $\text{K}^+$ ,  $\text{H}^+$ , and  $\text{NH}_4^+$ , in contrast to modifications containing small cations in exchange positions.

The interference corresponding to  $d(001) = 19.4\text{--}30.6$  Å, or occasionally larger values, is produced by nearly all montmorillonoids for which we have obtained patterns. Development of this interference indicates that the unit cell typically contains two silicate packets. If the modified Edelman structure exists as previously described, the inverted Si-O tetrahedra must fit into the holes in apposing oxygen surfaces in order that  $d(001)$  spacings can be as small as 19.4 Å. The proper repetition of structural planes in correct orientation can be developed by a glide of the second packet a distance of 1.73 Å along the  $(1\bar{1}0)$  plane and a rotation of  $180^\circ$  about  $c$ . The (001) interference usually is less intense than that corresponding to  $d$  spacings of 9.7–15.3 Å (our  $d(002)$ ); however, some montmorillonoids produce an (001) interference which is distinctly more intense than the (002) interference.

The (001) interference disappears from patterns produced by the alkali modifications after prolonged drying at  $105^\circ\text{C}$ – $110^\circ\text{C}$ , but develops again with partial rehydration. This interference is apparent in patterns produced by the other modifications even after oven drying, but is strengthened by humidification or wetting. Evidently, the mutual relationship of successive packets, which is such as to give repetition in every other packet, is destroyed with prolonged drying of the alkali modifications at  $105^\circ\text{C}$ – $110^\circ\text{C}$ . This may occur because of shifting and distortion of the packets as required for inverted tetrahedra to find their place in holes in the apposing oxygen surface. This shifting and distortion is required, not because of lack of holes, but because the sparse inverted tetrahedra probably are not distributed in a consistent pattern, and consequently will not always appose a hole in the adjacent surface.

Apparently, the alkali modifications, which yield minimum values of  $d(001)$  and  $d(002)$  after oven drying, are affected by this distortion and reorientation sufficiently to destroy the two-layer unit cell. This process does not progress far with oven drying of the other modifications because the  $d(001)$  interference is weakened but not lost from the pattern.

With rehydration, the proper orientation of adjacent packets is resumed because the inverted Si-O tetrahedra are withdrawn from the holes in the apposing oxygen surfaces.

The  $d$  spacing ranging from 2.86 to 3.55 Å and indexed as (007) to (0010) (Tables IX and XI) corresponds to an interference produced by Wyoming bentonite (Na-montmorillonite) and indexed as  $d(002) = 3.18$  Å by Winkler (1943). The position of this interference in the pattern appears to be influenced primarily by the size and position of the exchangeable cation. However, the change in  $d$  from modification to modification is small compared with the difference in radii of the exchangeable cations. Furthermore, the change in  $2\theta$  is not related to the quantity of water adsorbed. In fact,  $2\theta$  increases slightly with water sorption and swelling. Consequently, we are inclined to agree with Winkler that this interference arises in a different way than do the other (001) interferences.

Winkler (1943) correlated with  $d(001)$  of Na-montmorillonite an interference corresponding to an interplanar distance of 6.4 Å, which he interpreted as originating within individual packets at the outer oxygen surfaces, since he concluded also that this interference does not shift significantly with hydration or drying. Hence, this interference should not shift with change of exchangeable cation or condition of hydration. Because he had investigated only Na-montmorillonites, Winkler apparently did not discover that this spacing changes with the exchangeable cation. Moreover, our observations indicate that this interference does in fact shift with change in condition of hydration.

These observations indicate that the interference corresponding to  $d = 3.18$  Å, or thereabouts, is not the second order of the interference corresponding to  $d =$  about 6.4 Å, as is proposed by Winkler. The interference identified as (001) by Winkler is a higher order of our (001) at  $d = 19.4$ - $30.6$  Å and responds as expected to swelling or shrinkage with change of adsorbed water content. Furthermore, this interference commonly is absent from the diffraction patterns, whereas that corresponding to  $d = 2.86$ - $3.55$  Å always is recorded.

## CONCLUSIONS

1. The montmorillonite occurring in the bentonite under investigation is a dioctahedral type whose  $\Sigma$  is 4.10.
2. Exchangeable  $\text{Li}^+$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$  are hydrated at the rate of three molecules of water per equivalent at 52 percent relative humidity, but about 63.4 and 75.0 percent of this water is lost from the  $\text{Li}^+$  and  $\text{Ca}^{++}$ , respectively, during prolonged heating at  $105^\circ\text{C}$ - $110^\circ\text{C}$ . The  $\text{Mg}^{++}$  remains completely hydrated at this temperature.
3. Weight loss above  $190^\circ\text{C}$ - $367^\circ\text{C}$  exceeds that which can be calculated from the Hofmann-Endell-Wilm structure (Hofmann, Endell, and Wilm, 1933 and 1934) but conforms reasonably well with a structure modified after those proposed by Edelman and Favajee (1940) and Edelman

(1947). In this structure the inverted Si-O tetrahedra are presumed to correlate numerically and spacially with the univalent exchangeable cations, the cation being bonded to the inverted tetrahedron through an  $(\text{OH})^-$  at the apex. The  $(\text{OH})^-$  at the apex of the inverted tetrahedron is believed to project into the holes in the apposing oxygen surface when the montmorillonite is dry. The thermal balance data do not indicate the presence of  $(\text{OH})_4$  groups in the tetrahedral layer.

4. The unit cell is indicated typically to include two silicate packets, or possibly more, the adjacent packets being derived geometrically from each other by a glide of 1.73 Å along the (110) plane and a rotation of 180 degrees.

5. The exchangeable cations are presumed to form hydroxide molecules along the (001) interlayer surface by interaction at elevated temperatures with the  $(\text{OH})^-$  at the apex of the Si-O tetrahedra. The resulting  $\text{H}_2\text{O}$  and  $\text{NH}_4\text{OH}$  are volatile and are lost completely during thermal analysis. The  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  formed by this interaction are thought to release one molecule of water per mole during the thermal analysis. The  $\text{LiOH}$ ,  $\text{NaOH}$ , and  $\text{KOH}$  are presumed to resist decomposition below  $1,000^\circ\text{C}$ .

6. The  $d(001)$  interference corresponds to a  $d$  spacing of 19.4 to 30.6 Å, the precise dimension depending upon the exchangeable cation and the content of adsorbed water. The number of orders of (001) recorded and their indices vary greatly from one cationic modification to another and with sorption of water by an individual modification. An (001) interference variously indexed from (007) to (0010) and corresponding to  $d=2.86$  to  $3.55$  Å apparently originates by diffraction within the silicate packet.

7. Additional work correlating thermal data, chemical composition, and X-ray diffraction data on montmorillonite and other clay and clay-like minerals is necessary to full understanding of their crystallographic structure and properties.

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