

THE MINERALOGY OF ILLITES AND MIXED-LAYER ILLITE/MONTMORILLONITES

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ABSTRACT

Twenty-one samples of illite and mixed-layer illite/montmorillonite have been separated and analyzed after removal of organic material and free iron oxide. In addition, some illites were fractionated into several particle size ranges or further treated chemically before analysis. Some features of the group are: 1. All (including illites) examined are of the 1Md polymorph in the particle size range that excludes such detrital components as quartz. 2. They are close to ideally dioctahedral, with the sum of octahedral cations averaging 2.02 ± 0.02 (average deviation). 3. All have excess H_2O+ ; calculation of structural formulas by attributing excess H_2O+ to interlayer hydronium ion does not appear satisfactory; calculation in the normal manner results in structural charges considerably less than those of true micas. 4. The C.E.C. is proportional to the per cent expandable layers. 5. All have low tetrahedral charges with Al_n (tetrahedral) ranging from 0.13–0.50 in illite/montmorillonites and 0.26–0.59 in illites. 6. The relationship between K_n and per cent mica layers is excellent, but terminates at a potassium content significantly less than that of a true mica.

The excellent relationship between structure and composition in the group when excluding the possibility of H_2O+ (interlayer) leads to the conclusion that the non-expandable layers are of lower charge than true micas and contain lenses of trapped water. Some indication of this appears to be present in diffraction patterns of illites. It is suggested that illites represent one mineralogical end member of the montmorillonite-mixed-layer—illite group and remain distinct from true micas until the beginning of metamorphism.

INTRODUCTION

A crucial matter in the problem of the origin of illite is the ability to distinguish dioctahedral mica (or illite) that may form at low temperatures from those dioctahedral micas known to form at high temperatures. That is, to distinguish between possible diagenetic “illite” and “illite” that occurs as detritus derived from the weathering of igneous and metamorphic rocks.

One possible method of distinction is based on the temperature dependence of the stable polymorphs of ideal muscovite. Yoder and Eugster (1955) found that the 1Md polymorph formed metastably at all temperatures and was succeeded by $2M_1$ at high temperatures (> 200 – 350° C.) and 1M at low temperatures. Velde (1965) has re-examined the system and found that $2M_1$ is the stable polymorph at temperatures as low as 125° C. at 4.5 kb and has concluded that 1M is also metastable at the muscovite composition. However, the 1M polymorph appears to be a stable polymorph in dioctahedral micas containing considerable amounts of octahedral Mg and Fe such as glauconite and celadonite (Burst, 1958; Hower, 1961; Wise and Eugster, 1964).

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Weaver (1958) has examined illites from many ancient sediments and concluded that most materials called illite have the $2M_1$ polymorph and, on the basis of Yoder and Eugster's data, are thus detrital high temperature micas. In contrast to Weaver's conclusions, Velde and Hower (1963) found that although $2M_1$ dioctahedral mica is present in most Paleozoic shales, $1Md$ is by far the most abundant polymorph in the $<1 \mu$ fraction, thus reopening the consideration of illite as a diagenetic product. Independently of how these two sets of data can be reconciled, it does appear that the $2M_1$ polymorph can form at diagenetic temperatures and is thus not a certain criterion of origin.

Argillaceous sediments certainly contain detrital high temperature dioctahedral micas. The detrital nature of coarse mica flakes is obvious from thin section examination and from radioactive dating of these materials (*e.g.*, Evered *et al.* 1961; Hower *et al.* 1963). It is the nature of the more abundant, fine-grained 10 \AA material in argillaceous sediments that is in question.

Another possible method of attacking the problem is on the basis of the structural and compositional relationships of illite and mixed-layer illite/montmorillonite as related to high temperature micas. This paper is devoted to the mineralogical aspects of the montmorillonite—mixed-layer illite/montmorillonite series and its relationship to the trisilicic-tetrasilic dioctahedral mica series of Foster (1956). The writers hope that these structural and compositional relationships form the beginning of a framework on which the petrological aspects of the group can be examined in the near future.

ACKNOWLEDGMENTS

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SAMPLES AND ANALYTICAL TECHNIQUES

Samples. The samples used in this study are all from argillaceous sediments and include illites and mixed-layer illite/montmorillonites (some of which are K-beatonites) ranging up to 60+ % expandable layers. Table 1 lists the occurrence and original (untreated) mineralogy of the size fraction used for chemical analysis. The samples analyzed and reported here were selected from a larger group. Samples which showed heterogeneity

TABLE 1. OCCURRENCE OF SAMPLES AND ORIGINAL MINERALOGY OF SIZE CUT USED FOR CHEMICAL ANALYSIS

Sample (Formation)	Age	Original Mineralogy of Analyzed Cut
Interlake, well core, 9580-9590', Williston Basin, Montana	Silurian	Illite
Silver Hill, Jefferson Canyon, Montana	Cambrian	Illite
Clinton, New York	Silurian	Illite
Eau Claire, Illinois Basin	Cambrian	Illite
New Albany, Indiana	U. Devonian	Illite
Sylvan, Oklahoma	U. Ordovician	Illite and chlorite
Lowville, Fort Plain, New York	Ordovician	Illite
Gros Ventre, Wind River Canyon, Wyoming	U. Cambrian	Mixed-layer mica/mont.
Salona, Bellefonte, Pa.	Ordovician	Mixed-layer mica/mont. (K-bentonite)
Martinsburg, Tazewell, Va.	Ordovician	Mixed-layer mica/mont. (K-bentonite)
Onondaga, Cherry Valley, N. Y.	M. Devonian	Mixed-layer mica/mont. (K-bentonite)
Kalkberg, Cherry Valley New York	L. Devonian	Mixed-layer mica/mont. (K-bentonite)
High Bridge, Kentucky	Ordovician	Mixed-layer mica/mont. (K-bentonite)
Kinneulle, Sweden Chasmops Fm.	Ordovician	Mixed-layer mica/mont. (K-bentonite)
Two Medicine, Bowman's Corners, Montana	U. Cretaceous	Mixed-layer mica/mont.+septe (?) chlorite
Wilcox No. 1, Burst (1959) Well No. 10, 12,500', La.	Eocene	Mixed-layer mica/mont.+Kaolinite and chlorite
Colorado, Bozeman Pass, Montana	U. Cretaceous	Mixed-layer mica/mont.+septe (?) chlorite
Wilcox No. 2, Burst (1959) Well No. 5, 500', La.	Eocene	Mixed-layer mica/mont.+Kaolinite and chlorite

in amount of interlayering, quartz not removed by size fractionation, and large amounts of kaolinite were eliminated.

Analytical Techniques. All samples were disaggregated by ultrasonics and size-fractionated by centrifugal sedimentation. Diffraction patterns of the various size fractions were run on specimens oriented by the method of Kinter and Diamond (1956). Diffraction patterns were run on randomly oriented specimens at a scanning rate of $1^\circ 2\theta/\text{min.}$; the (060) spacing was determined by scans at $\frac{1}{4}^\circ 2\theta/\text{min.}$ with 4° divergence and scatter slits. All samples were treated for the removal of organic material and free iron oxide (Jackson, 1956). Samples which contained only illite or illite/montmorillonite were not generally treated further. Several specimens contained chlorite which was removed by heating in 1N HCl at 80°C. for one hour followed by boiling in a 3% Na_2CO_3 solution. Two

specimens contained kaolinite which was removed by the method of Hashimoto and Jackson (1960). Two illites (Interlake and Silver Hill) were further size-fractionated and aliquots of three illites (Interlake, Silver Hill, and Eau Claire) were boiled for thirty minutes in a 3% Na_2CO_3 solution in order to observe the effects of these treatments on structure and composition. All samples were analyzed for SiO_2 , TiO_2 , Al_2O_3 , Fe as Fe_2O_3 , MgO , CaO , and K_2O by *x*-ray spectrographic techniques on the undiluted sample (Hower *et al.* 1964). Sodium was determined by flame photometry and ferrous iron by the method of Reichen and Fahey (1962). $\text{H}_2\text{O}-$ was determined by weight loss at 110°C . and $\text{H}_2\text{O}+$ by further weight loss on ignition. Cation exchange capacities were determined by Sr-saturation and *x*-ray spectrographic analysis. Two samples (Interlake and Colorado) were soaked in a 1N KCl solution for 24 hours and reanalyzed for K_2O after washing.

RESULTS

Diffraction Patterns. Figures 1 through 5 are diffraction patterns of representative samples ranging from undetectable ($<10\%$) to $60+\%$ expandable layers. Three (Interlake, Gros Ventre and Two Medicine) were separated from shales and three (Kalkberg, A-2, and B) from K-bentonites. The Gros Ventre and Two Medicine samples contain chlorite; Figure 3 shows diffraction patterns of these samples after chlorite removal. For samples containing twenty or more per cent expandable layers—*i.e.*, those showing resolution between the $001_{17}/001_{10}$ and $001_{10}/002_{17}$ on glycolation—the per cent expandable layers was generally determined by averaging individual results from the spacings of the $001_{10}/001_{12.4}$ on K-saturated samples and the $001_{17}/001_{10}$, $001_{10}/002_{17}$, and $002_{10}/003_{17}$ after glycolation as derived from MacEwan, Ruiz Amil, and Brown's (1961) and Weaver's (1956, p. 401) curves calculated using Hendricks and Teller's (1942) curves for infinite crystallites. For all samples but two the resulting per cent expandable layers for determinations from individual spacings had an average deviation of $\pm 3\%$. The two which did not give consistent results by this method are the Colorado and Kinnekulle B samples, both of which have large amounts of montmorillonite layers. In particular, both the samples have $001_{17}/001_{10}$ spacings of $17+\text{\AA}$ on glycolation and are thus better interpreted with MacEwan's (1958) curves calculated for 3- and 5-layer crystallites. For these two samples the reported per cent expandable layers is derived from an average of the $001_{10}/002_{17}$ and $001_{10}/001_{12.4}$ spacings. It is of interest to note that although the diffraction pattern of K-saturated Kinnekulle-B (which contains a small amount of kaolinite) confirms mixed-layering, the patterns of untreated and glycol solvated samples are quite similar to a

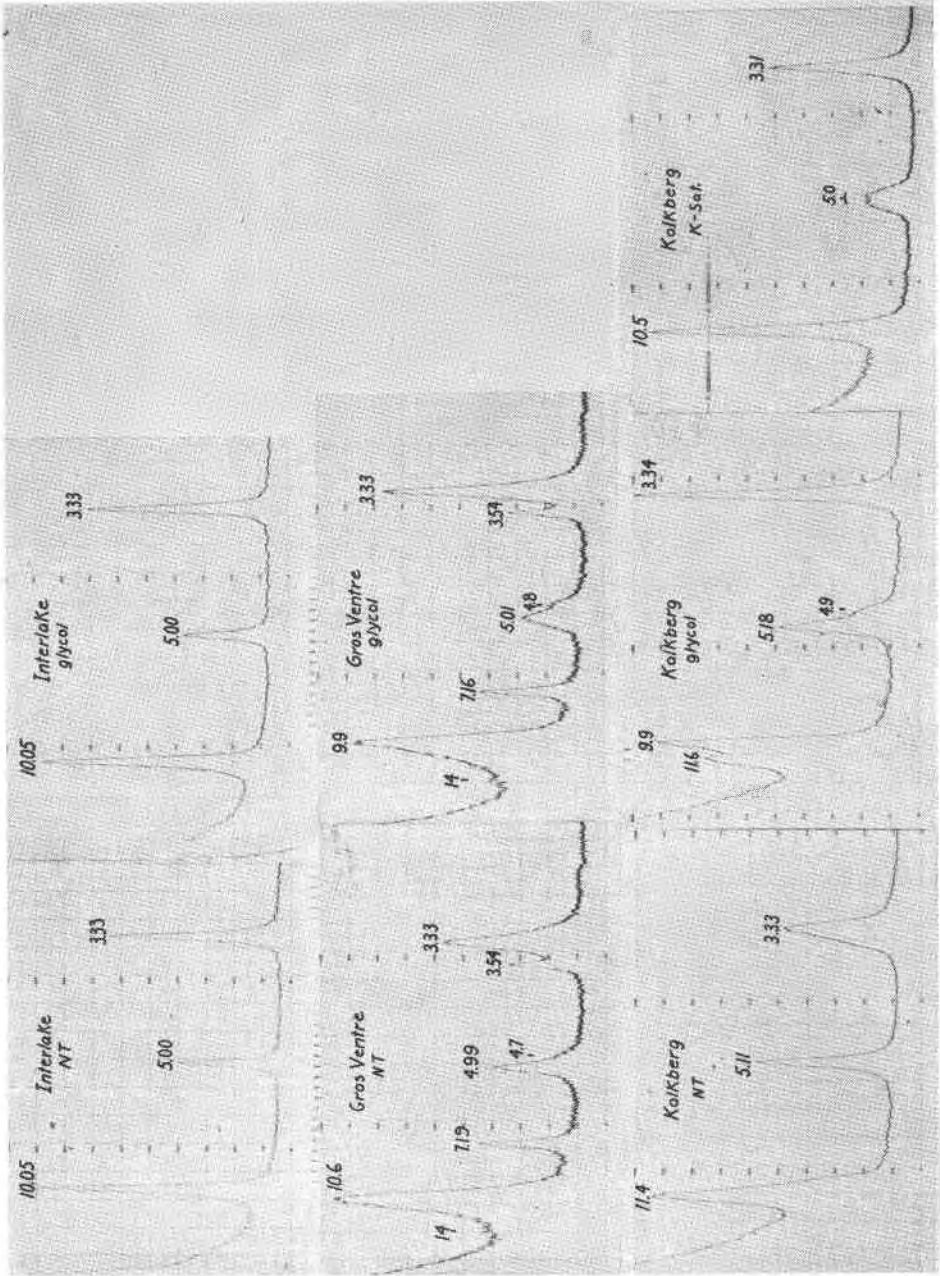


FIG. 1. Diffraction patterns of oriented specimens of untreated (NT), glycolated, and K-saturated Interlake Fm (<10% exp.), Gros Ventre Fm. (15% exp.) and Kalkberg Fm (24% exp.).

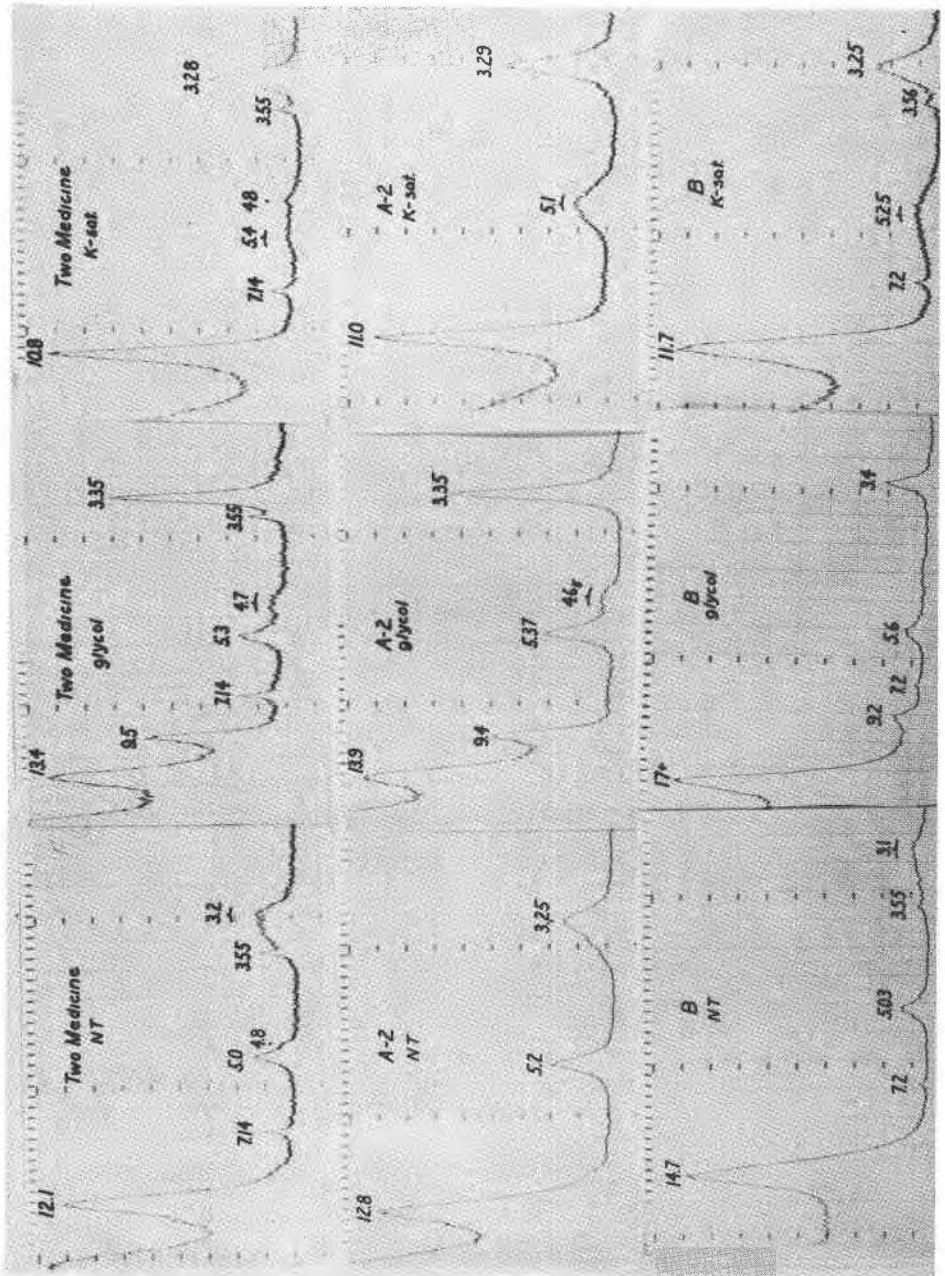


Fig. 2. Diffraction patterns of oriented specimens of untreated (NT), glycoled, and K-saturated Two Medicine Fm. (33% exp.), Kinnekulle Fm A-2 39% exp.), and Kinnekulle Fm. -B (63% exp.)

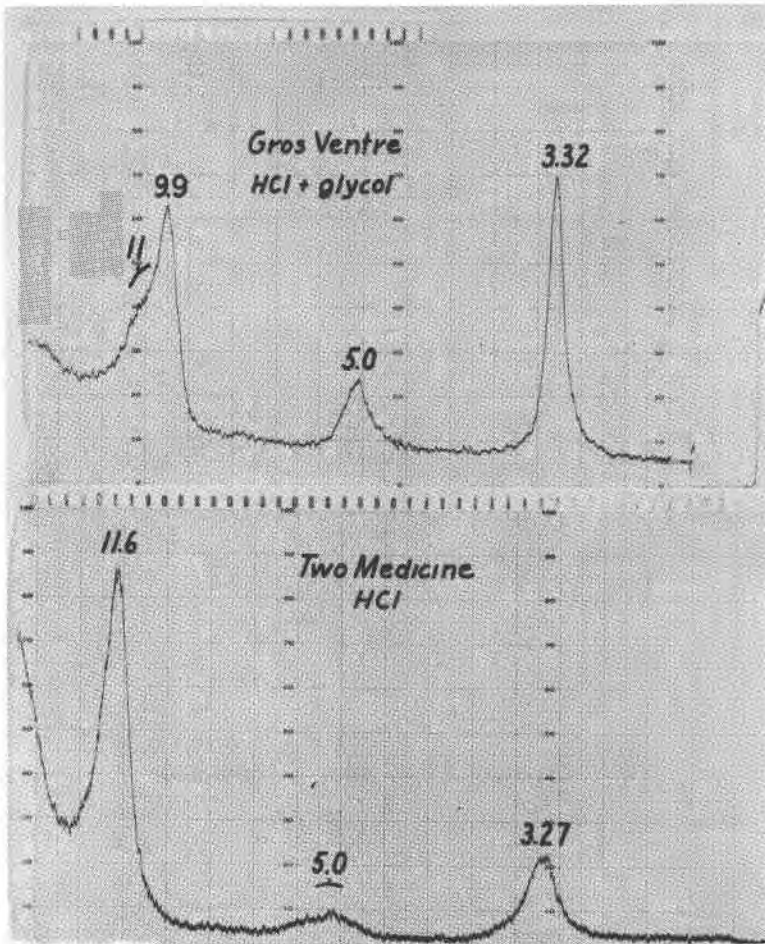


FIG. 3. Diffraction patterns of Gros Ventre and Two Medicine after chlorite removal.

non-mixed layer montmorillonite and might be mistakenly identified as such, if it were not for: 1. Irrational (001) sequences, 2. Relative intensities of the basal reflections somewhat different from those of montmorillonite, and 3. High scattering intensity at low angles—a phenomenon predicted for mixed-layer structures by calculation (MacEwan *et al.* 1961, p. 411). This last feature may be of the most use in detecting small amounts of interlayering at either extreme of a sequence.

At less than about 20 per cent expandable layers the $001_{10}/001_{17}$ is not resolved from the $001_{10}/002_{17}$ and peak displacements become small, so that a determination of amount of interlayering becomes less sure. The

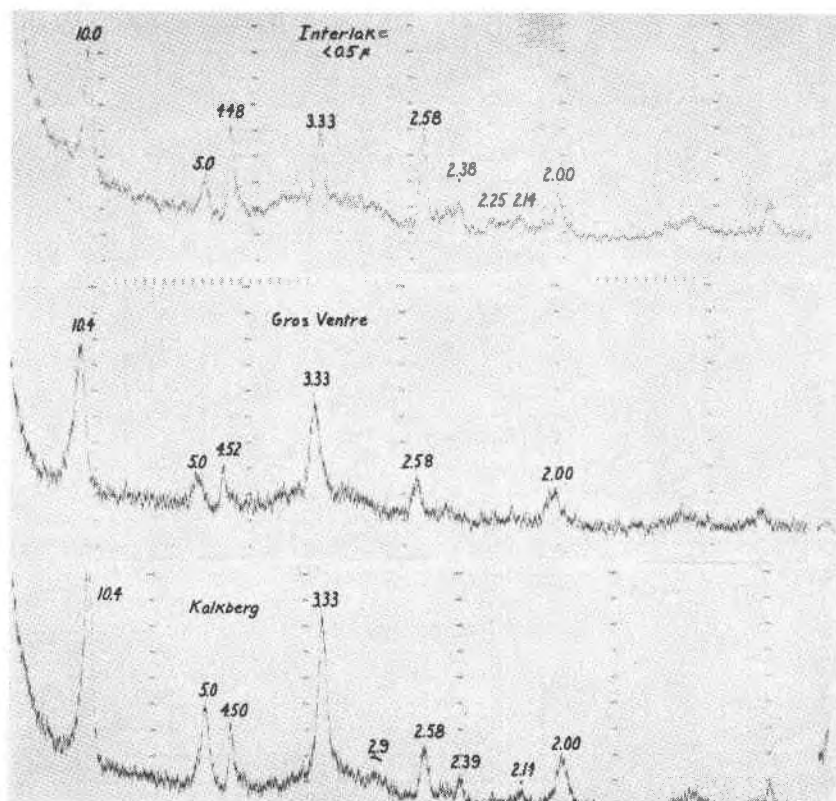


FIG. 4. Diffraction patterns of randomly oriented specimens of Interlake, Gros Ventre, and Kalkberg.

following criteria were used for determinations of <20 per cent expandable layers:

1. Development of a low angle bulge (at $11 \text{ \AA} \pm$) and shift to 9.9 \AA at the "10 \AA " peak on glycolation—these are presumably the unresolved $001_{10}/001_{17}$ and $001_{10}/002_{17}$ —and shift to $10.2 \text{ \AA} \pm$ on K-saturation \equiv 15 per cent expandable.
2. No appreciable shift of the "10 \AA " peak on glycolation, but intensification and sharpening of the "(003)"—actually the $003_{10}/005_{17}$ —at 3.33 \AA on glycolation \equiv 10 per cent expandable (cf. Weaver, 1956, p. 207).
3. No apparent peak shifts or changes in relative intensity of the basal reflections after any treatment \equiv 5 per cent expandable.

Figures 4 and 5 are diffraction patterns of randomly oriented specimens of the same samples. None show the ordering reflections of either the 1M or 2M polymorphs although the (200)—or (20)—reflection at 2.58 \AA which also exists in the 1Md polymorph is quite intense. On this basis, it was concluded that all samples (including illites) are close to 100% of the 1Md polymorph.

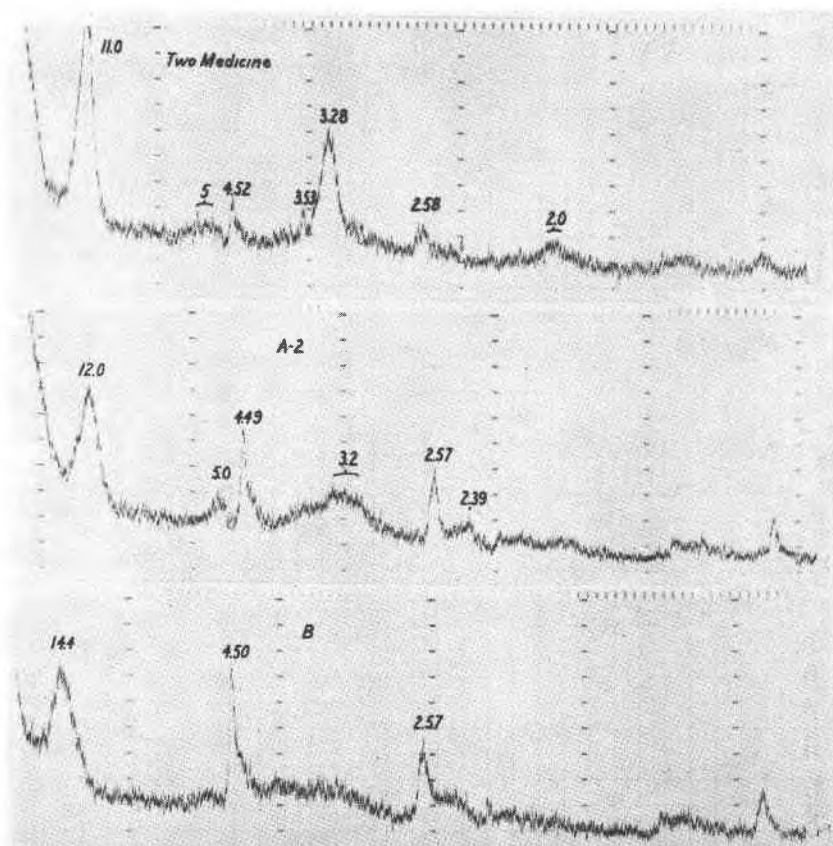


FIG. 5. Diffraction patterns of randomly oriented specimens of Two Medicine, Kinnekulle-A-2 and Kinnekulle-B.

From a petrological point of view it is of interest to note that the Kalkberg (along with Salona and Onondaga) represent the minimum amount of expandable layers (20+%) of all monomineralic K-bentonites examined. In contrast, for example, the "illite" phase of the "Catawba" K-bentonite from the Ordovician Moccasin Fm. contains about 10 per cent expandable layers but coexists with another layer silicate which appears to be an "expanding chlorite." It was not possible to remove the chlorite by mild chemical treatment and the sample was therefore not analyzed.

Chemical Analyses. Table 2 is a listing of the chemical analyses of the samples studied along with other pertinent data. The sequence of samples is of increasing per cent expandable layers followed by the size frac-

TABLE 2. CHEMICAL COMPOSITION, SIZE FRACTION, d_{060} , CATION EXCHANGE CAPACITY, AND PER CENT EXPANDABLE LAYERS OF ILLITES AND MIXED-LAYER MICA/MONTMORILLONITES INVESTIGATED

Oxide	Interlake	Silver Hill	Clinton	Eau Claire	New Albany	Sylvan (Coarse)	Lowville	Gros Ventre	Sylvan (Fine)	Salona KB	Martins-Onondaga burg KB	KB
SiO ₂	51.5	55.1	49.3	53.6	52.1	54.4	55.5	51.5	54.1	54.3	54.4	53.9
TiO ₂	0.77	0.63	0.20	0.82	0.42	0.54	1.11	0.75	0.19	0.11	0.35	0.61
Al ₂ O ₃	28.5	22.0	23.4	21.7	22.3	21.1	20.4	22.8	20.2	25.1	24.1	27.7
Fe ₂ O ₃	0.61	5.28	2.70	2.81	2.69	3.54	3.19	3.89	4.23	0.34	2.43	0.89
FeO	0.91	1.34	0.96	1.24	0.43	0.80	0.26	2.07	0.85	—	—	0.20
MgO	3.0	2.8	2.4	3.4	2.8	2.9	3.7	2.0	3.1	3.7	4.3	1.8
CaO	0.05	0.02	0.01	0.03	0.03	0.02	0.08	0.02	0.01	Tr	0.02	0.05
Na ₂ O	0.10	0.08	0.11	0.08	0.08	0.25	0.10	0.11	0.36	n.d.	n.d.	n.d.
K ₂ O	9.07	8.04	6.94	7.08	6.38	6.47	6.58	7.33	6.01	6.64	6.88	6.34
H ₂ O—	0.7	1.0	3.8	2.2	1.6	2.1	1.9	2.5	2.9	0.9	1.2	0.5
H ₂ O+	5.5	6.4	7.6	7.7	9.5	7.4	8.2	6.0	7.0	7.7	8.0	8.0
Total	100.71	102.69	97.36	100.66	98.33	99.52	101.02	98.97	98.95	98.79	101.68	99.99
Size Fraction	<0.5	<0.5	<0.13	<0.5	<0.25	<0.5	<1	<1	—	<0.5	<0.5	<0.5
d_{060} (Å)	1.502 ₀	1.509 ₀	1.504 ₀	1.505 ₆	1.503 ₃	1.505 ₇	—	1.505 ₀	1.505 ₇	—	1.503 ₃	1.501 ₆
CEC (meg/100 gm)	12	15	21	20	24	13	25	24	16	23	25	34
% Expandable Layers	<10	<10	10	10	15	15	15	15	20	22	23	23

TABLE 2—(Continued)

Oxide	Kalkberg KB	High Bridge	Two Medicine	Kinnekulle KB-A-1	Kinnekulle KB-A-2	Wilcox No. 1	Colorado	Wilcox No. 2	Kinnekulle KB-B
SiO ₂	56.0	56.9	49.0	56.2	55.7	55.6	54.9	54.4	53.7
TiO ₂	0.28	0.13	1.45	0.17	0.22	1.10	0.81	1.16	0.07
Al ₂ O ₃	24.4	20.0	22.2	23.2	21.8	23.6	18.1	20.5	19.0
Fe ₂ O ₃	1.04	1.13	6.10	1.89	2.19	1.20	7.30	2.20	3.04
FeO	—	—	0.72	—	—	0.93	1.19	1.42	—
MgO	4.1	5.5	1.3	4.1	4.1	2.6	2.7	2.8	3.9
CaO	0.16	0.08	0.05	0.18	0.52	0.03	0.05	0.04	0.78
Na ₂ O	Tr	Tr	—	n.d.	Tr	n.d.	0.04	n.d.	—
K ₂ O	6.47	5.41	5.16	5.10	4.64	4.81	4.41	2.50	2.30
H ₂ O—	1.7	4.2	3.8	4.5	4.3	3.6	2.9	6.3	3.3
H ₂ O+	7.0	8.0	10.4	7.7	7.6	7.4	6.5	9.3	14.7
Total	101.15	101.35	100.18	103.04	101.07	100.87	98.90	100.62	100.79
Size Fraction	<0.5	<0.5	<0.5	<1	<1	<0.2	<0.25	<0.2	<0.5
d ₉₀₀	1.503 ₅	1.503 ₃	1.504 ₄	—	1.502 ₄	1.503 ₁	1.507 ₉	1.503 ₅	1.502 ₉
CEC (meg/100 gm)	31	31	37	33	42	35	50	45	61
% Expandable Layers	24	33	33	37	38	40	45	55	63

TABLE 3. CHEMICAL COMPOSITIONS OF WELL CHARACTERIZED ILLITES AND MIXED-LAYER MICA/MONTMORILLONITES FROM OTHER SOURCES

Oxide	Morrison ¹	Burnt Bluff ²	Steamboat Springs ³	Nealmont ⁴	Kinneulle No. 8 ⁵	Kinneulle No. 15 ⁵
SiO ₂	49.03	52.87	51.0	52.44	52.86	58.87
TiO ₂	1.06	1.02	0.27	0.44	0.36	0.18
Al ₂ O ₃	17.93	24.90	28.7	26.38	22.97	22.34
Fe ₂ O ₃	13.11	0.78	0.59	0.31	1.64	2.53
FeO	1.31	1.19	0.39	—	0.55	0.36
MgO	2.79	3.60	2.31	3.57	3.11	4.23
CaO	0.39	0.69	0.30	0.66	1.40	0.12
Na ₂ O	0.10	0.22	0.15	0.16	—	0.16
K ₂ O	7.84	7.98	7.78	7.39	4.83	2.75
H ₂ O—	—	2.56	1.99	3.07	5.79	0.77
H ₂ O+	6.00	6.73	5.96	4.78	6.76	7.75
Total	99.93	99.61	99.44	99.57	100.27	99.29
Size Fraction	<2	<2	<2	<1	<2	<0.5
CEC (meg/100 gm)	—	21	—	n.d.	38	66
% Expandable Layers	<10	<10	10	~20	~40	~60

¹ Keller, 1958.² Gaudette, 1965.³ Schoen, 1964, pers. comm.⁴ Weaver, 1953.⁵ Bystrom, 1956.

tionated samples or those samples which were boiled in a 3% Na₂CO₃ solution (designated Na₂CO₃). The concentrations of the interlayer cations K, Ca, and Na reported in Table 2 are for fixed cations only; those removable by cation exchange are included in the cation exchange capacity. Table 3 is a similar listing of data obtained from well-characterized samples from other sources.

The most useful way of examining the chemical analysis of a mineral is, of course, to calculate first a structural formula. This, however, assumes that one knows the structure completely and the proper distribution of ions within the various lattice sites. This is not known for the illite (or mixed-layer illite/montmorillonite) structure. There are two particular problems: 1. All illites and mixed-layer illite/montmorillonites contain H₂O+ in excess of the "normal" 4.5% ± of aluminum dioctahedral

TABLE 4. CALCULATION OF CATIONS PER 11 OXYGENS, OCTAHEDRAL OCCUPANCY, AND LATTICE CHARGE

Position	Ion	Number of Cations/11 Oxygens										
		Interlake <0.5	Interlake Na ₂ CO ₃	Interlake .3-.5	Interlake .1-.3	Interlake <.1	Silver Hill <0.5	Silver Hill Na ₂ CO ₃	Silver Hill .1-.3	Silver Hill <.1	Silver Hill <.1	Morrison
Tetrahedral	Si	3.43	3.44	3.41	3.45	3.44	3.66	3.69	3.64	3.62	3.48	
	Al	0.57	0.56	0.59	0.55	0.56	0.34	0.31	0.36	0.38	0.52	
	Charge	-0.57	-0.56	-0.59	-0.55	-0.56	-0.34	-0.31	-0.36	-0.38	-0.52	
Octahedral	Al	1.66	1.68	1.67	1.66	1.67	1.38	1.36	1.35	1.38	0.98	
	Fe ³⁺	0.03	0.03	0.04	0.03	0.04	0.26	0.25	0.27	0.25	0.70	
	Fe ²⁺	0.05	0.05	0.05	0.04	0.03	0.07	0.09	0.08	0.09	0.08	
	Mg	0.30	0.27	0.27	0.31	0.30	0.28	0.30	0.31	0.31	0.29	
	Sum	2.04	2.03	2.03	2.04	2.04	1.99	2.00	2.01	2.03	2.05	
Charge	-0.23	-0.23	-0.23	-0.23	-0.21	-0.38	-0.39	-0.36	-0.31	-0.22		
Total												
Lattice		-0.80	-0.79	-0.82	-0.78	-0.77	-0.72	-0.70	-0.72	-0.69	-0.74	
Charge												
Interlayer	K	0.77	0.76	0.79	0.76	0.76	0.68	0.69	0.69	0.68	0.71	
	Na	0.01	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.01	
	X ¹⁺	0.02	0.01	—	—	0.01	0.03	0.02	0.03	0.02	0.03	
	Interlayer											
Charge	+0.80	+0.79	+0.81	+0.78	+0.79	+0.72	+0.72	+0.73	+0.72	+0.75		

TABLE 4—(Continued)

Position	Ion	Burnt Bluff	Steamboat Springs	Clinton	Eau Claire	Eau Claire Na ₂ CO ₃	New Albany	Sylvan (Coarse)	Lowville	Gros Ventre
Tetrahedral	Si	3.58	3.45	3.56	3.69	3.67	3.68	3.75	3.79	3.60
	Al	0.42	0.55	0.44	0.31	0.33	0.32	0.25	0.21	0.40
	Charge	-0.42	-0.55	-0.44	-0.31	-0.33	-0.32	-0.25	-0.21	-0.40
Octahedral	Al	1.56	1.74	1.55	1.45	1.43	1.53	1.46	1.43	1.47
	Fe ³⁺	0.04	0.03	0.15	0.16	0.15	0.14	0.18	0.16	0.20
	Fe ²⁺	0.07	0.02	0.05	0.07	0.07	0.03	0.05	0.02	0.12
	Mg	0.36	0.23	0.26	0.34	0.37	0.30	0.30	0.37	0.21
	Sum	2.03	2.02	2.01	2.02	2.02	2.00	1.99	1.98	2.00
Charge	-0.34	-0.19	-0.28	-0.35	-0.38	-0.33	-0.38	-0.38	-0.45	-0.33
Total Lattice Charge		-0.76	-0.74	-0.72	-0.66	-0.71	-0.65	-0.63	-0.66	-0.73
Interlayer	K	0.69	0.67	0.64	0.62	0.64	0.58	0.57	0.57	0.65
	Na	0.03	0.02	0.02	0.01	0.01	0.01	0.03	0.01	0.01
	X ¹⁺	0.05	0.03	0.06	0.05	0.05	0.07	0.02	0.07	0.07
	Interlayer Charge	+0.77	+0.72	+0.72	+0.68	+0.70	+0.66	+0.61	+0.61	+0.65

TABLE 4—(Continued)

Position	Ion	Sylvan (Fine)	Nealmont	Salona	Martins- burg	Onondaga	Kalkberg	High Bridge	Kinneulle A-1	Kinneulle A-2	Two Medicine	Kinneulle No. 8
Tetrahedral	Si	3.76	3.55	3.65	3.62	3.58	3.69	3.84	3.73	3.77	3.58	3.69
	Al	0.24	0.45	0.35	0.38	0.42	0.31	0.16	0.27	0.23	0.42	0.31
	Charge	-0.24	-0.45	-0.35	-0.38	-0.42	-0.31	-0.16	-0.27	-0.23	-0.23	-0.42
Octahedral	Al	1.41	1.66	1.64	1.51	1.75	1.58	1.43	1.55	1.51	1.49	1.58
	Fe ³⁺	0.22	0.02	0.02	0.12	0.04	0.05	0.06	0.09	0.11	0.33	0.09
	Fe ²⁺	0.05	—	—	—	0.01	—	—	—	—	0.04	0.03
	Mg	0.32	0.36	0.37	0.43	0.18	0.40	0.55	0.41	0.41	0.14	0.32
	Sum	2.00	2.04	2.03	2.06	1.98	2.03	2.04	2.05	2.03	2.00	2.02
Charge	-0.37	-0.24	-0.28	-0.25	-0.25	-0.31	-0.43	-0.26	-0.32	-0.32	-0.18	-0.29
Total Lattice Charge		-0.61	-0.69	-0.63	-0.63	-0.67	-0.62	-0.59	-0.53	-0.55	-0.60	-0.60
Interlayer	K	0.53	0.64	0.57	0.58	0.54	0.54	0.47	0.43	0.40	0.48	0.43
	Na	0.05	0.02	—	—	—	—	—	—	—	—	—
	X ¹⁺	0.03	0.05	0.06	0.07	0.10	0.09	0.09	0.10	0.14	0.13	0.16
	Interlayer Charge	+0.61	+0.71	+0.63	+0.65	+0.64	+0.63	+0.56	+0.53	+0.54	+0.61	+0.59

TABLE 4—(Continued)

Position	Ion	Wilcox No. 1	Colorado	Wilcox No. 2	Kinnekulle No. 15	Kinnekulle B
Tetrahedral	Si	3.76	3.80	3.84	3.80	3.88
	Al	0.24	0.20	0.16	0.20	0.12
	Charge	-0.24	-0.20	-0.16	-0.20	-0.12
Octahedral	Al	1.65	1.27	1.55	1.50	1.44
	Fe ³⁺	0.05	0.38	0.12	0.12	0.17
	Fe ²⁺	0.04	0.07	0.08	0.02	—
	Mg	0.26	0.27	0.24	0.41	0.43
	Sum	2.00	1.99	2.04	2.05	2.04
Charge	-0.30	-0.37	-0.25	-0.28	-0.31	
Total Lattice Charge		-0.54	-0.57	-0.41	-0.48	-0.43
Interlayer	K	0.41	0.39	0.22	0.22	0.22
	Na	—	—	—	0.02	—
	X ¹⁺	0.11	0.17	0.16	0.22	0.23
	Interlayer Charge	+0.52	+0.56	+0.38	+0.46	+0.45

potassium micas (Foster, 1964, p. F3) which is attributable to structural hydroxyl in the ideal single layer unit of $O_{10}(OH)_2$, and 2. There is, *per se*, not one structural formula that can be written for a mixed-layer structure. A mixed-layer structure is obviously not compositionally homogeneous.

Excess H_2O+ . The excess H_2O+ in mixed-layer illite/montmorillonites can, perhaps, be attributed to the trapping of interlayer water molecules on dehydration during the determination of H_2O . In fact, the whole procedure of how and at what temperature to determine H_2O- is open to question (Warshaw, 1957; Foster, 1964, p. F3). It follows, however, that if this explanation is generally applicable, illites which contain no detectable expandable layers should not contain excess H_2O+ . But they do. Under these circumstances, it may be possible to attribute excess H_2O+ to an abnormally high (OH) content or to the presence of the interlayer cation H_3O+ proxying for $K+$. Brown and Norrish (1952) examined these possibilities and opted for H_3O+ because calculation of the structural formula of two of Grim *et al.*'s (1937) type illites in this manner yielded structural charges equal to micas and reduced the octahedral cation population to close to the ideal 2.00 per $O_{10}(OH)_2$. Table 5 lists the structural formulas for the best characterized illites available—i.e., those with apparently no expandable layers, which are monomineralic, and have chemical analyses. Two (Interlake <0.5 and Morrison) turn out quite nicely; however, most yield octahedral cation populations considerably less than 2.00 and some very high and unbalanced charges. This may result from poor H_2O+ determinations and should be further examined, but the writers consider at this time that there are fairly good reasons for excluding the possibility of H_3O+ and explaining excess H_2O+ in another manner (as will be explained later).

Other possibilities exist that can explain chemical analyses that yield structural formulas of lower than true mica charges for illites. The samples may actually be compositionally (and structurally) heterogeneous with respect to particle size. This possibility has been treated by Jonas (1960) and Jonas and Roberson (1960) who give logical explanations to explain such changes based on increased surface area with decreasing particle size. In the present study, the two best illites were fractionated (Interlake and Silver Hill) into three size ranges—0.3–0.5 μ , 0.1–0.3 μ , and <0.1 μ —and each fraction was analyzed. As can be seen from Table 2, the compositions do not vary much over this range of particle size, except for TiO_2 which decreases rapidly with decreasing particle size; it is considered to be a separate phase and is excluded from structural formula calculations. There is a slight indication of decreasing potassium with decreasing particle size as predicted by Jonas and by Jonas and Rober-

TABLE 5. CALCULATION OF CATIONS PER 11 OXYGENS BY THE METHOD OF BROWN AND NORRISH
 (EXCESS $H_2O = H_3O^+$ INTERLAYER) FOR ILLITES

Position	Ion	Interlake <0.5	Interlake <0.1	Silver Hill <0.5	Silver Hill <0.1	Eau Claire	Burnt Bluff	Clinton	Steamboat Springs	Morrison
Tetrahedral	Si	3.40	3.37	3.60	3.56	3.61	3.53	3.48	3.42	3.44
	Al	0.60	0.63	0.40	0.44	0.39	0.47	0.52	0.58	0.56
	Charge	-0.60	-0.63	-0.40	-0.44	-0.39	-0.47	-0.52	-0.58	-0.56
Octahedral	Al	1.62	1.55	1.30	1.29	1.33	1.49	1.42	1.68	0.92
	Fe ³⁺	0.03	0.04	0.30	0.24	0.15	0.04	0.14	0.03	0.69
	Fe ²⁺	0.05	0.04	0.04	0.09	0.07	0.07	0.06	0.02	0.08
	Mg	0.30	0.29	0.27	0.31	0.34	0.28	0.26	0.23	0.29
	Sum	2.00	1.92	1.91	1.93	1.89	1.88	1.88	1.96	1.98
Charge	-0.35	-0.57	-0.58	-0.61	-0.74	-0.61	-0.61	-0.68	-0.37	-0.43
Total										
Lattice		-0.95	-1.20	-0.98	-1.05	-1.13	-1.08	-1.20	-0.95	-0.99
Charge										
Interlayer	K	0.76	0.74	0.67	0.67	0.61	0.68	0.62	0.66	0.69
	Na	0.01	0.02	0.01	0.02	0.01	0.03	0.02	0.02	0.01
	H ⁺	0.14	0.42	0.28	0.34	0.48	0.33	0.53	0.22	0.27
	X ⁺	0.02	0.01	0.03	0.02	0.14	0.05	0.08	0.04	0.03
	Interlayer									
Charge	+0.93	+1.19	+0.99	+1.05	+1.24	+1.09	+1.25	+1.25	+0.94	+1.00

son. This factor appears to be of little significance, especially when one considers that only 18% of Interlake <0.5 and 27% of Silver Hill <0.5 is in the <0.1 range. It is also possible that amorphous alumina and silica are present. This would not be detectable by diffraction but would contribute tetrahedral and octahedral and not interlayer ions to the structural formula calculation. An attempt was made to remove the possible amorphous alumina and silica by boiling three illites (Interlake <0.5 , Silver Hill <0.5 , and Eau Claire <1) in a 3% Na_2CO_3 solution. No weight loss occurred except a few per cent attributable to loss during transfer and, as can be seen from Table 2, the compositions are not significantly different from the untreated samples. It is concluded, therefore, that the samples are monomineralic and homogeneous.

Formulas for Mixed-layer Structures. As mentioned above, and as has been pointed out by Weaver (1965), a single structural formula will not suffice for a mixed-layer structure. Weaver has suggested that mixed-layer illite/montmorillonites be considered as having two compositional units: an "illite" unit with an 8–10 weight per cent K_2O composition and a charge of about 80% that of a mica and a montmorillonite unit with a charge of 35–40% that of a mica and no fixed potassium. This is certainly better than viewing a mixed-layer structure as homogeneous, but is most likely too simple a model. Some reasons for believing Weaver's model too simple are as follows:

1. It cannot explain the sequence of inter-layer charges in randomly interstratified illite/montmorillonites unless the structure can be centered on the interlayer lattice positions rather than the 2:1 unit. Although tetrahedral compositions and charges can be assigned easily with this model, a similar assignment in the octahedral layer becomes a dilemma; 2. It allows for no compositional gradation with a given lattice unit between montmorillonite and dioctahedral mica—a feature which seems unlikely from a petrological viewpoint.

It is tentatively suggested here that the "homogeneous" single structural formula represents the mean 2:1 unit composition and that some sort of distribution of composition lies about this mean. Until the nature of mixed-layering can be examined more carefully, it is considered sufficient to write a single "mean" structural formula with the realization that it represents no more than that.

STRUCTURAL AND COMPOSITIONAL RELATIONSHIPS

As explained above, it appears that the samples investigated are compositionally and structurally homogeneous and that structural formulas calculated from the chemical analyses should be meaningful. It also appears that the structural formulas should be calculated neglecting excess

H_2O+ . Table 4 is a listing of cations per 11 oxygens from which structural formulas can be written. The calculated interlayer charges vary from 0.81 equivalents per 11 oxygens (for the best illite, Interlake) to approximately 0.40 equivalents for mixed-layer illite/montmorillonites containing about 60% expandable layers. Figure 6 is a plot of fixed interlayer potassium against total charge. Included diagrammatically is a

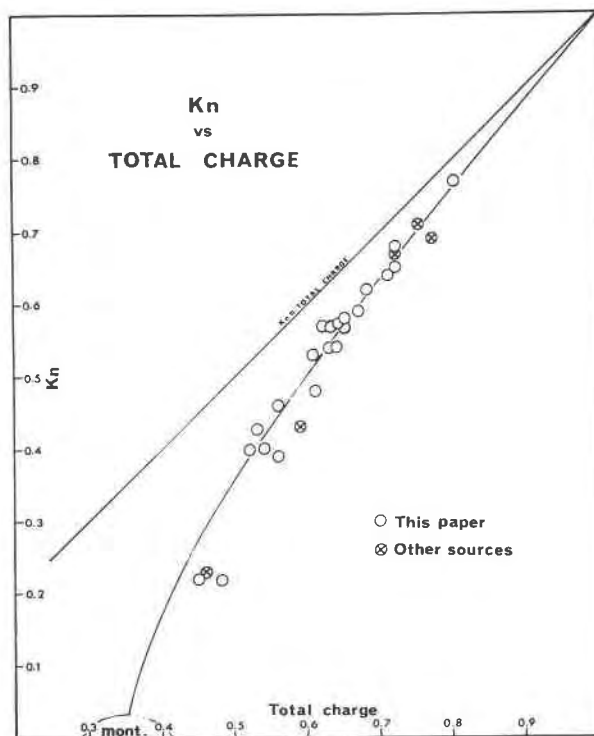


FIG. 6. The relationship between fixed interlayer potassium, K_n , and structural charge in illites and illite/montmorillonites.

field for montmorillonite, assuming a mean charge of 0.35 equivalents. Also included is a straight line which represents K_n total charge *i.e.*, the theoretical potassium content if all the interlayer charge were satisfied by fixed potassium. The deviation between the two curves is charge-satisfied by exchangeable cations. The curve extrapolates nicely to all fixed cations at the mica (1 equivalent) end to all exchangeable cations at the montmorillonite (0.35 equivalent) end.

Figure 7 is a plot of per cent expandable layers against the number of fixed interlayer cations per structural unit. The relationship is very satis-

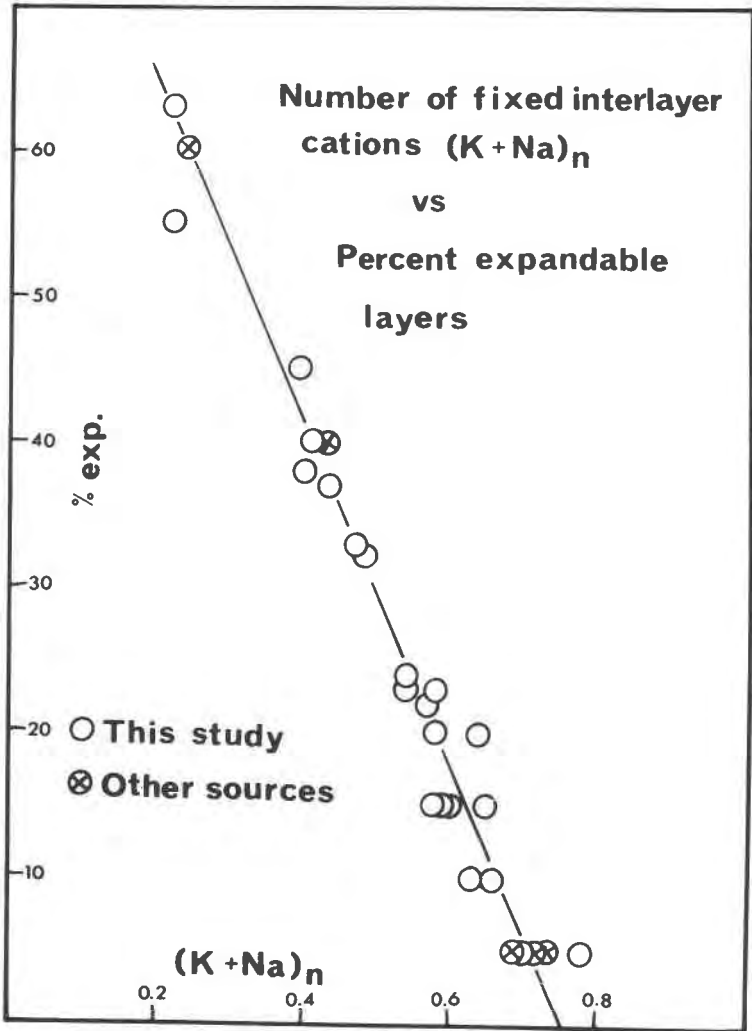


FIG. 7. The relationship between per cent expandable (montmorillonite) layers and fixed interlayer cations in illites and illite/montmorillonites.

factory but extrapolates to about 0.8 equivalents of fixed interlayer cations for no expandable layers rather than 1 equivalent as in micas. This feature is puzzling and is the reason that Brown and Norrish (1952) considered including H_3O^+ as a fixed interlayer cation. An explanation should be given why the present writers ignore the possibility of H_3O^+ ; they are as follows:

1. Assuming the H_2O^+ determinations to be reasonably reliable, the formulas calculated by the method of Brown and Norrish do not give consistent—and sometimes not reasonable—results. In contrast to the considerably varying octahedral cation population (1.88–2.00) which averages 1.93 occupied positions when including H_3O^+ , normal formulas have octahedral populations ranging from 1.98 to 2.06 and average 2.02. This is close to ideally dioctahedral and the appeal is one of simplicity. 2. If H_3O^+ is present, one must consider that the H_3O^+/K^+ ratio in illites and illite/montmorillonites is quite constant, otherwise the good relationship shown in Figure 7 would not exist. Since the H_3O^+/K^+ ratio in the structure would undoubtedly reflect the H_3O^+/K^+ in the solutions which contributed

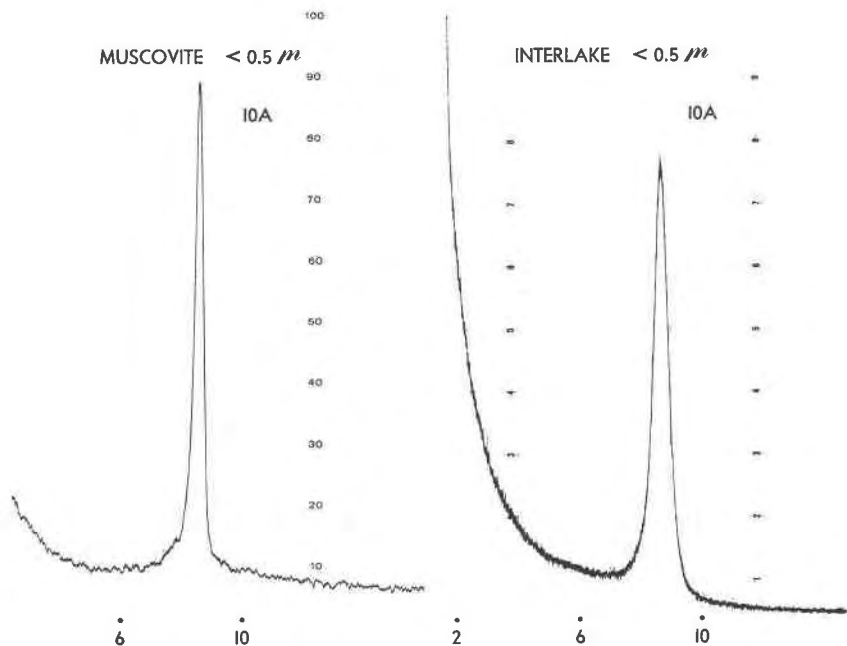


FIG. 8. A comparison of diffraction patterns of Interlake and a muscovite, both sized to $<0.5\mu$.

the interlayer cations this demands a very restricted acidity to potassium ion concentration in these solutions. This does not seem reasonable, especially when one considers the range of H^+/K^+ ratio over which Meyer and Hemley (1959) found muscovite stable. 3. Warsaw (1960) was able to synthesize a simplified "illite" quite readily with K^+ as the interlayer cation, but was unable to synthesize "illites" which included H_3O^+ . 4. The last point is positive rather than negative, and is an attempt to explain the minor differences between diffraction patterns of the best illites (*e.g.*, Interlake) and muscovite, when both are in the clay size range.

Figure 8 is a comparison of Interlake illite and a muscovite. Both have been sized to $<0.5\mu$. There are two main differences: 1. Interlake's basal reflections are considerably broader—a feature which cannot be attrib-

uted to peak broadening caused by smaller particle size, and, perhaps more significantly, 2. There is considerable scattering intensity at low angles in the Interlake pattern, but not the muscovite. As mentioned previously, high scattering intensity at low angles is an inherent feature of mixed-layer structures. Yet the 10 Å peak of Interlake is very close to ideal (10.05 Å) and there is no apparent shift or change of relative intensity of the basal reflections under any treatment. It is of interest to note that in a 40,000 ft. section of the Precambrian Belt sediments in Idaho, the dioctahedral 10 Å material in the $<1\mu$ fraction goes from a non-interlayered 1Md structure with significant scattering intensity at low angles (the same features as Interlake) at the top of the section gradually to a 2M structure with low scattering intensity at low angles (as in the muscovite pattern) at the bottom of the section where porphyroblasts of biotite make their appearance (greenschist facies) (Maxwell, 1964).

With some temerity it is now suggested that the excess $\text{H}_2\text{O}+$ in illites is present as neutral H_2O trapped in non-expandable layers. The H_2O molecules may be present either in the interlayer structural positions not occupied by K^+ and/or as lenses of water. This may cause the less regular basal repeat distance in illites (as shown by broader basal reflections) and also the higher scattering intensity at low angles. This appears to be a characteristic of illite until it is converted to a true mica of the beginning of metamorphism. It seems to the writers that it would be a remarkable coincidence if it took exactly 1 equivalent of interlayer K^+ (plus H_3O^+ Na^+ , etc.) to collapse a 2:1 structure to near 10 Å and there is no obvious reason why it could not happen at a somewhat lower charge. There are valid structural reasons for having 1 mole of K per $\text{O}_{10}(\text{OH})_2$ as a maximum—but not as a minimum. An elucidating further step not yet taken would be to extract the interlayer cations—and thus expand the layers—of an illite like Interlake with sodium tetraphenyl boron and determine the available charge with a cation of high hydration energy such as Mg^{2+} or Ca^{2+} (so that the layers will not prematurely collapse). If the available charge turns out to be near the 250 meg/100 gm \pm theoretical C.E.C. for muscovite, then the present concept is wrong, Brown and Norrish (1952) are probably right, and H_3O^+ is present. If, however, the charge is approximately 200 meg/100 gm, it would appear that the excess $\text{H}_2\text{O}+$ is either attributable to retention of $\text{H}_2\text{O}-$ water above 105–110° C. or is present as neutral H_2O in the non-expandable layers.

Figure 9 is a plot of cation exchange capacity against per cent expandable layers. The curve extrapolates to about 100 meg/100 gm at 100% expandable layers (a reasonable value for montmorillonite) and to something less than 10 meg/100 gm at 0% expandable layers (a reasonable

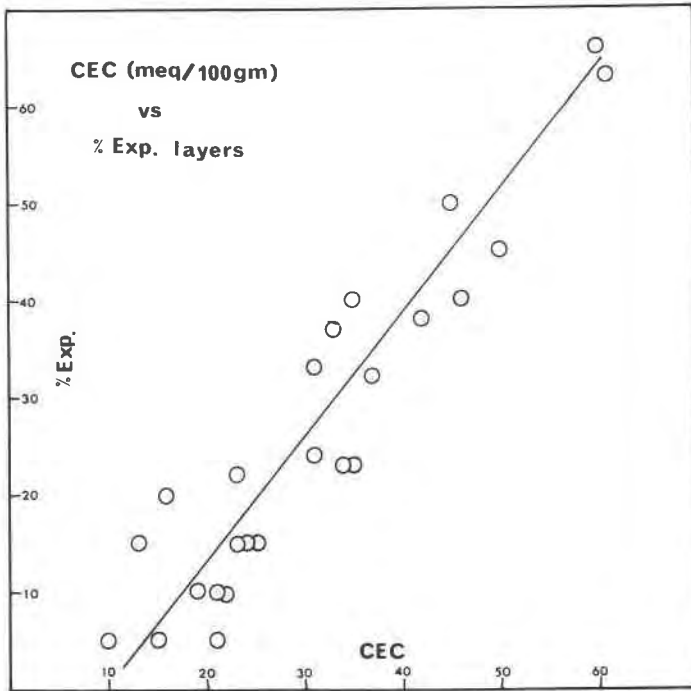
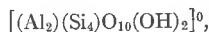


FIG. 9. The relationship between cation exchange capacity and per cent expandable layers in illites and illite/montmorillonites.

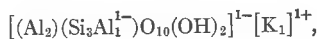
value for edge exchange). Although the relationship is quite good, the scatter of points is outside of the experimental error. There are some unexplained features which determine C.E.C.

ILLITE AND ILLITE/MONTMORILLONITE COMPOSITIONS IN TERMS OF THE END MEMBERS PYROPHYLLITE- MUSCOVITE-CELADONITE

From a petrological point of view it is of interest to examine illite and illite/montmorillonite compositions in terms of the end members pyrophyllite,



muscovite



and celadonite,



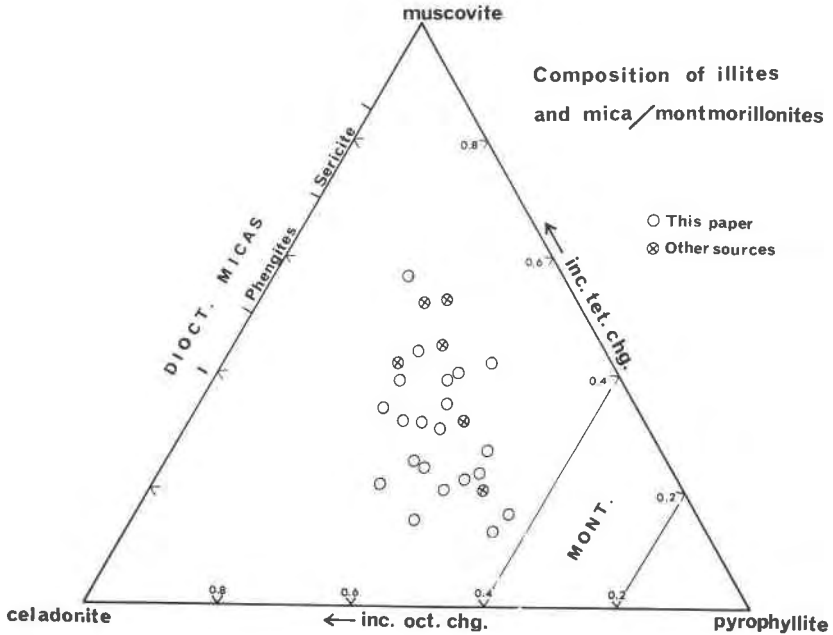
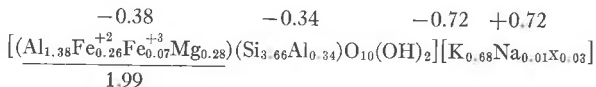


FIG. 10. The distribution of illite and illite/montmorillonite compositions within the composition triangle pyrophyllite-muscovite-celadonite.

Figure 10 is a composition triangle with these minerals at the vertices and is a slightly modified version of that of Yoder and Eugster (1955). The muscovite-celadonite side is the well-known trisilicic-tetrasilicic dioctahedral potassium mica series of Foster (1956). The pyrophyllite-muscovite and pyrophyllite-celadonite sides should logically represent a gradation from non-expandable pyrophyllite through mixed-layer pyrophyllite/montmorillonite structures, montmorillonite mixed-layer mica (or illite)/montmorillonites, to mica. Beidellite would lie on the pyrophyllite-muscovite side and "classical" montmorillonite on the pyrophyllite-celadonite side. A field for montmorillonite is outlined as lying between a lattice charge of 0.2 to 0.4 equivalents. The field may actually be smaller than this.

The compositions of all samples are plotted on this diagram according to the layer charge distribution obtained from structural formulas. To give an example, the illite from the Silver Hill Fm. ($<0.5\mu$) has the structural formula:



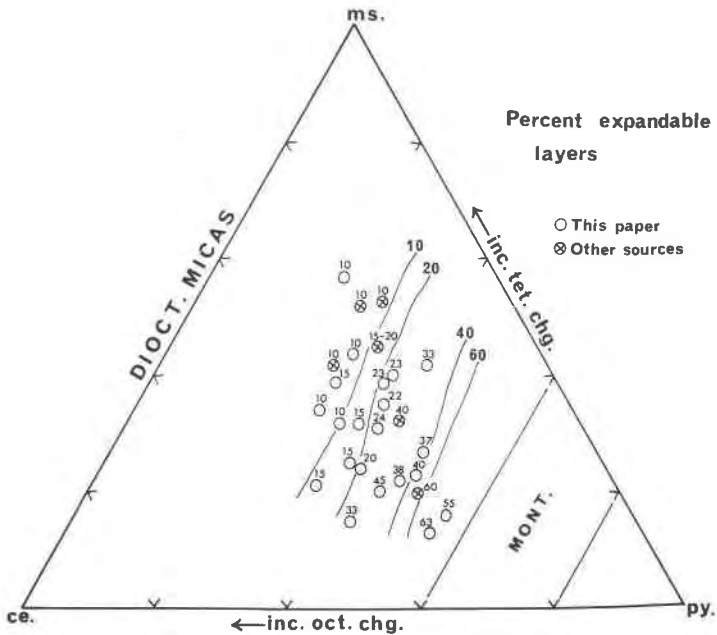


FIG. 11. The relationship between number of fixed interlayer cations and structural charge in illites and illite/montmorillonites.

On the basis of this structural formula, the Silver Hill illite is considered to consist (compositionally) of 38% celadonite, 34% muscovite, and 28% (the remainder) pyrophyllite.

Figures 11 and 12 are contoured plots of the same parameters (number of fixed interlayer cations and percent expandable layers) as was shown in a different manner in Figs. 6 and 7. The contours are, within the reliability of the data, parallel to the mica side. Therefore, it appears as if these features are not affected by tetrahedral-octahedral charge distribution as would logically be deduced from crystal chemistry (Weaver, 1958b).

All samples fall within the field of mixed-layer structures, which they are except for the illites with <10% expandable layers. The points nearest the montmorillonite field are Kinnekulle B, a K-bentonite, and Wilcox #2, a mixed-layer structure separated from the Eocene Wilcox Fm., both of which contain about 60% expandable (montmorillonite) layers. K-bentonites with about 20% expandable layers (such as Kalkberg, Onondaga, and Salona) plot far from the montmorillonite field, having structural charges (0.6+ equivalents) approaching illites. They are thus not merely montmorillonites with potassium as the interlayer cation.

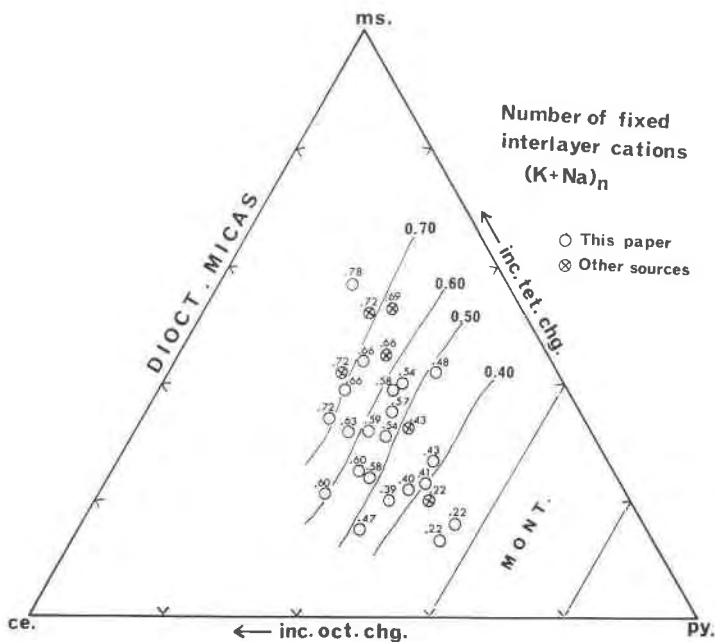


FIG. 12. The relationship between per cent expandable (montmorillonite) layers and structural charge in illites and illite/montmorillonites.

Therefore, the suggestion which persists in the literature—of which the latest example is that of Huff (1963)—that K-bentonites are merely K-exchanged montmorillonites is invalid. It is certainly possible that high charge montmorillonites formed originally in a potassium deficient environment (such as in acid hydrothermal alteration associated with ore deposition) would convert to highly expandable mixed-layer illite/montmorillonites when introduced into a K-rich environment (the ocean, for example). Weaver (1958) has already suggested a similar possibility. K-bentonites with 80% illite layers are another story. They cannot be explained simply by the shuffling of interlayer cations. Their origin involves either an original mechanism of formation different from normal bentonites (Bystrom, 1956) or a later alteration including compositional changes involving the 2:1 structure.

The relationships in Figs. 6, 7, 10, 11, and 12 also show that montmorillonite layers do not collapse to 10 Å unless the charge is available to fix sufficient potassium. Therefore, there appears to be no evidence for the collapse of montmorillonite layers with increasing depth of burial—unless burial depth involves not only increasing pressure, but compositional changes as well.

A further feature of interest is shown by the distribution of points in Fig. 10. There appears to be a limited field occupied by illites and illite/montmorillonites. None lie near the celadonite or muscovite vertex. Even the best illites do not approach sericites in terms of tetrahedral charge, and only a few are up in the phengite field. Therefore, unless something chemically drastic—such as alteration of the tetrahedral Al/Si ratio—happens during weathering, illites and illite/montmorillonites do not appear to be degraded high temperature dioctahedral micas derived from igneous and metamorphic rocks. Illite and illite/montmorillonite compositions deserve an attempt at a petrological interpretation in terms of the recent phase equilibria studies of pertinent systems (*e.g.*, Velde, 1964)—especially since it appears that some mixed-layer clays may be stable rather than metastable structures (Iiyama and Roy, 1963).

CONCLUSIONS

Montmorillonites, mixed-layer illite/montmorillonites, and illites form a continuous mineralogical sequence in which the composition and structure are quite nicely related. The illite end of the sequence appears to be distinct from true dioctahedral micas. The compositional range of this mineral group within the limits pyrophyllite-muscovite-celadonite indicates that the group deserves a petrological interpretation different from that of degraded high temperature dioctahedral micas.

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