Clays and Clay Minerals, 1968, Vol. 16, pp. 73–81. Pergamon Press. Printed in Great Britain

STRUCTURAL CHARGE SITE INFLUENCE ON THE INTERLAYER HYDRATION OF EXPANDABLE THREE-SHEET CLAY MINERALS

RAYMOND L. KERNS, JR.
Utah State University, Logan, Utah; formerly of the
Oklahoma Geological Survey, Norman, Oklahoma

and

CHARLES J. MANKIN
Director, School of Geology and Geophysics and Oklahoma
Geological Survey, University of Oklahoma, Norman, Oklahoma

(*Received* 30 *August* 1967)

Abstract—Previous investigations have demonstrated the influences of interlayer cation composition, relative humidity, temperature, and magnitude of interlayer surface charge on the interlayer hydration of montmorillonites and vermiculites. It has been suggested that the sites of layer charge deficiencies may also have an influence upon the amount of hydration that can take place in the interlayers of expandable clay minerals. If the interlayer cation-to-layer bonds are considered as ideally electrostatic, the magnitude of the forces resisting expansion may be expressed as a form of Coulomb's law. If this effect is significant, expandable structures in which the charge-deficiency sites are predominantly in the tetrahedral sheet should have less pronounced swelling properties than should structures possessing charge deficiencies located primarily in the octahedral sheet.

Three samples that differed in location of layer charge sites were selected for study. An important selection criterion was a non-correlation between tetrahedral charge sites and high surface-charge density, and between octahedral charge sites and low surface-charge density.

The effects of differences in interlayer cation composition were eliminated by saturating portions of each sample with the same cations. Equilibrium (001) *d* values at controlled constant humidities were used as a measure of the relative degree of interlayer hydration.

Although no correlation could be made between the degree of interlayer hydration and total surface-charge density, the investigation does not eliminate total surface-charge density as being significant to the swelling properties of three-sheet clay-mineral structures. The results do indicate a correlation between more intense expandability and predominance of charge deficiencies in the octahedral sheet. Conversely, less intense swelling behavior is associated with predominantly tetrahedral charge deficiencies.

INTRODUCTION

One of the most significant properties of montmorillonites and vermiculites is their ability to absorb and retain water between individual three-sheet layers at low temperatures over a wide range of relative humidity. This phenomenon is directly responsible for the somewhat variable *c*-axis dimensions of these minerals (particularly montmorillonite) and may be observed through X-ray-diffraction measurements of the interlayer spacings of the (001) planes.

Many previous investigations have considered the properties of expansion and the mechanism of interlayer water absorption in expandable clay minerals (Nagelschmidt, 1936; Hofmann and Bilke, 1936; Bradley, Grim, and Clark, 1937; Hendricks and Jefferson, 1938; Mering, 1946; Barshad, 1948; Mooney, Keenan, and Wood, 1952; Rowland, Weiss, and Bradley, 1956; Hofmann *et al.*, 1956; Walker, 1956). Hydration and dehydration studies have yielded strong evidence of cation-water molecule interactions in the interlayer region. The general consensus is that, at least for low to intermediate states of hydration, the interlayer region of expandable clays is occupied by water-cation complexes rather than simple monomolecular water layers. The initial state of hydration involves the separation of the three-sheet layers and development of a hydrated complex with the interlayer cations. The initial hydration energy, which is a function of the ionic potential of the cation and the partial pressure of water vapor in the system, must be strong enough to overcome the bond between the crystal structure and the interlayer cation. A factor contributing to the expandability of three-sheet clay minerals is the small magnitude of the forces with which adjacent layers are held together.

A property that contributes to the resistance to expansion is the surface-charge density, which is an expression of the number of equivalent layer-to-interlayer cation bonds per unit area, commonly given as equivalents of negative charge per unit cell. The implication is that there should be an inverse relationship between the magnitude of the surface-charge density and the tendency for expansion by absorption of interlayer water. Hofmann *et al.* (1956) indicated that a surface-charge density of less than 0.55 equivalents of charge per unit formula results in a crystal structure that is readily susceptible to interlayer water absorption. Clay minerals with layer charge deficiencies in excess of 0·65 equivalents per unit cell, when saturated with potassium, have a 10·3 Å basal spacing under both wet and dry conditions.

Another factor that has been considered, but not demonstrated, is the possible influence that the sites of the lattice charge deficiencies may have on bond strength (McAtee, 1958, p. 283) and, hence, on swelling properties. Marshall (1964) suggested that the strength of the bond between the cation and the layer may be a considerable factor in determining the extent and ease with which water absorption takes place. If the bonding energies are considered ideally electrostatic, the force resisting separation of adjacent three-sheet units may be expressed as a Coulomb's law relationship:

$$F \propto \frac{C^+ C^-}{r^2} \qquad (1)$$

where C^+ and C^- represent the charges (or valences) entering into the bond formation and r is their distance of separation. This would indicate that the distance of separation of a given interlayer cation from an equivalent charge deficiency is a critical factor in determining the magnitude of the bond strength involved, and would necessarily imply that a charge deficiency in the tetrahedral sheet would form a stronger layer-cation bond than would one in the octahedral sheet. The result of such differences, if significant, should be observable as differences in swelling behavior between mica-type materials having predominantly tetrahedral-sheet charge deficiencies and those having octahedral-sheet deficiencies.

NATURE OF THE INVESTIGATION

The purpose of this study was to investigate the contribution of layer charge sites to the swelling properties of expandable three-sheet clay minerals and required the selection of samples that were significantly different in the tetrahedral and octahedral contributions to the total surface-charge density. The selection was made by detailed chemical and structural analyses to ensure that an absolute correlation between high surface-charge density and predominance of tetrahedral charge deficiencies was not possible. Any differences in the swelling behavior of the various materials could then be correlated to total surface-charge density or structural charge site. The effects due to differences in the interlayer cation composition were eliminated by base exchanging portions of each sample to produce mono-ionic interlayers. These samples were then subjected to various reproducible conditions of relative humidity, and the interlayer water absorption of samples containing identical interlayer cations were compared by X-ray-diffractometry measurement of the (001) interlayer spacings. Under these conditions differences in the swelling behavior of identically cation-saturated minerals could be attributed to properties of the mineral structure itself.

Selection and Characterization of Samples

Three samples were selected for study in which the magnitudes and sites of layer charge deficiencies were significantly different. Data concerning the characterization of these samples are listed in Table 1. A vermiculite sample designated as C_1 has a layer charge deficiency, on the half-unit formula basis, of minus 0·66. Sample C_2 is an iron-rich montmorillonite. The charge deficiency is −0·42/half-unit formula, with a charge distribution of 1 : 1 between the tetrahedral and octahedral sheets. The sample designated as C_3 is a montmorillonite with a layer charge deficiency of −0·53, of which −0·48 is in the octahedral sheet.

If the samples are arranged in order of the dedecreasing contribution of the tetrahedral-sheet charge deficiency to the total surface-charge density in each sample, the order is: $C_1 > C_2 > C_3$. Arranging the same samples on the basis of equivalents of interlayer cation charge, or total surface charge from highest to lowest values: $C_1 > C_3 > C_2$.

Preparation of cation-exchanged samples

Three grams of C_3-montmorillonite was converted to the hydrogen–ion form with hydrogen resin. This material was then split into seven equal portions and each was washed with a 0·1 N chloride

Table 1. Structural chemical data for selected samples

	CEC		Charge deficiency per half-unit cell			Number of octahedral
Sample	Measured	Calc.	Tetra.	Octa.	Total	cations
C_1	150 ± 10	151	−0·65	−0·01	−0·66	2·70
C_2	90 ± 10	90*	−0·21	−0·21	−0·42	2·12
C_3	121 ± 5	134	−0·05	−0·48	−0·53	2·00

*Not calculated; allocated on basis of measured CEC.

$$C_1\ (\mathrm{Si}_{3\cdot35}\mathrm{Al}_{0\cdot65})(\mathrm{Mg}_{2\cdot11}\mathrm{Fe}_{0\cdot47}\mathrm{Al}_{0\cdot12})\mathrm{O}_{10}(\mathrm{OH})_2\ \begin{array}{ll}\mathrm{Mg} & 0\cdot28\\ \mathrm{Ca} & 0\cdot04\\ \mathrm{K} & 0\cdot02\end{array}$$

$$C_2\ (\mathrm{Si}_{3\cdot79}\mathrm{Al}_{0\cdot21})(\mathrm{Fe}_{0\cdot99}\mathrm{Mg}_{0\cdot57}\mathrm{Al}_{0\cdot56})\mathrm{O}_{10}(\mathrm{OH})_2\ \begin{array}{ll}\mathrm{Mg} & 0\cdot13\\ \mathrm{Ca} & 0\cdot05\\ \mathrm{K} & 0\cdot05\end{array}$$

$$C_3\ (\mathrm{Si}_{3\cdot95}\mathrm{Al}_{0\cdot05})(\mathrm{Al}_{1\cdot49}\mathrm{Mg}_{0\cdot48}\mathrm{Fe}_{0\cdot03})\mathrm{O}_{10}(\mathrm{OH})_2\ \begin{array}{ll}\mathrm{Ca} & 0\cdot21\\ \mathrm{Na} & 0\cdot06\\ \mathrm{K} & 0\cdot04\end{array}$$

salt solution of either lithium, sodium, potassium, magnesium, calcium, strontium, or barium. Samples of the C_1-vermiculite and the C_2-montmorillonite were similarly treated. After conversion to the hydrogen form, these samples were split into four equal portions and washed with 0·1 N chloride salt solutions of sodium, potassium, magnesium, and calcium.

The chloride salt washing process was repeated with 500 ml of solution. After adding the solution, the samples were ultrasonically dispersed and the suspension allowed to stand undisturbed for 12 hrs, in which time all samples settled out completely by flocculation. The clear liquid was decanted and the process repeated for a total of ten washings.

Excess salt solution was removed by repeatedly flushing the samples with distilled water until the samples showed no flocculation during a 12-hr period. The exchanged samples were then centrifuged, dried at 60°C, ground to less than 80-mesh powders and stored in glass vials.

Differential thermal analysis

Dried powders of the cation-exchanged montmorillonite and vermiculite samples were humidified for 8 hrs at about 50 per cent relative humidity and subjected to differential thermal analysis. All thermograms were run with the same Robert L. Stone DTA unit (model 13-M) with an inconel sample holder. The dynamic gas was nitrogen and the unit was calibrated at 1·0 with a microvolt setting of 80. The heating rate was 10°C/min.

Figure 1 shows the DTA curves for the untreated and cation-exchanged C_3-montmorillonite. It is evident that the interlayer cation composition has a direct influence on the shapes and positions of the low-temperature dewatering endotherms. Significant differences are also in the high-temperature exotherms of samples saturated with different cations. The midrange endothermic reactions at 600–700°C are only slightly modified.

The high-temperature phases formed on firing of each of these samples were not considered essential to this study. However, the shapes and positions of the low-temperature dewatering endotherms are considered of primary importance. The temperature at which the sample is totally dehydrated, as indicated by the return of the endothermic curve to the baseline, is a direct function of the retention of interlayer water by the clay mineral. The shape of the endothermic loop is an expression of the dehydration mechanism in each case. Samples saturated with divalent cations are characterized by having more than one node on the low-temperature endotherm. The magnesium-saturated sample has two nodes of about equal intensity at slightly less and slightly more than 100°C. A smaller third node occurs at about 210°C. The endotherms for the strontium- and calcium-saturated samples are nearly identical. These show two partially resolved peaks at 100–200°C; the lower temperature node is more intense than the higher one. Both endotherms of the calcium-saturated sample occur at a slightly higher temperature range than those observed for the Sr-montmorillonite sample. The barium-saturated sample exhibits four poorly resolved nodes on a broad endotherm that is displaced toward a lower temperature than observed for any of the other

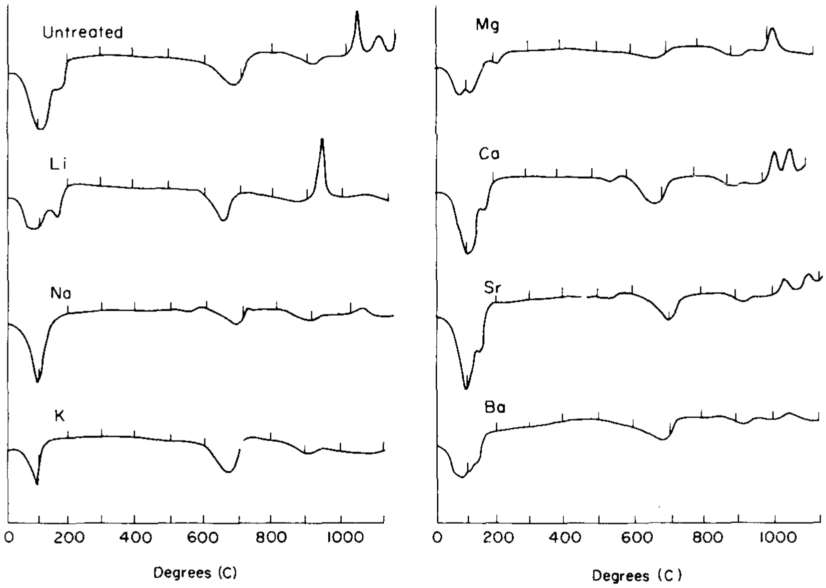

Fig. 1. Differential thermal analysis patterns of cation-exchanged C_3-montmorillonite.

divalent cation-saturated samples. The lithium-saturated sample displays an endothermic doublet similar to those of the divalent cation-exchanged samples. In the thermogram of this sample a broad hump reaches maximum intensity at less than 100°C, whereas a sharper well-resolved node occurs at about 170°C. The sodium- and potassium-saturated samples have single dewatering endotherms, but with sodium this occurs at a slightly higher temperature (100°C) than that of the potassium-saturated sample (about 90°C). The thermograms for the untreated and calcium-exchanged samples are similar, as should be expected on the basis of the chemical analysis obtained for this material.

Thermograms of the C_1 and C_2 samples are shown in Fig. 2. The untreated and magnesium-saturated samples have low-temperature dewatering endotherms similar to those observed for the magnesium-exchanged montmorillonite sample. The calcium-saturated samples again display an endothermic doublet similar to the magnesium samples, but displaced toward a lower temperature. The endotherm for the potassium-exchanged C_1-vermiculite is small and indicates little water loss during the dehydration process. The endotherms for the sodium- and potassium-exchanged C_2-montmorillonite samples are similar to, although somewhat broader than, the C_3-montmorillonite counterparts in Fig. 1.

Controlled-humidity diffractometry

A small plastic chamber with thin polyethylene plastic windows was designed and fitted over the sample holder of the Siemens X-ray diffractometer. Drying conditions were produced by pumping air through magnesium perchlorate desiccant. Relative humidities of 15, 31, and 88 per cent at 24·5°C were also generated and the air flow was directed into the chamber so that it struck the center of the sample mount.

The powdered samples of cation-exchanged montmorillonites and vermiculite were prepared as (001) orientations by sedimenting the dispersed materials on glass slides and drying at 60°C. Each slide was placed in the diffractometer chamber and successively subjected to dry-air treatment and to 15, 31, and 88 per cent relative-humidity environments. A minimum of 8 hr was allowed for the attainment of equilibrium conditions in each case. A diffractometer scan at 1 degree two-theta per minute was made from 2 to 48 degrees two-theta, after which the scan was repeated over the first principal peak to ensure that no change had occurred during the time of measurement.

Zero relative humidity was not attained with the dry-air environment. The relative humidity in this case was reproducible, however, and was certainly much less than 15 per cent. The other reported values of relative humidity are thought to be fairly accurate and the deviations, due mainly to tempera-

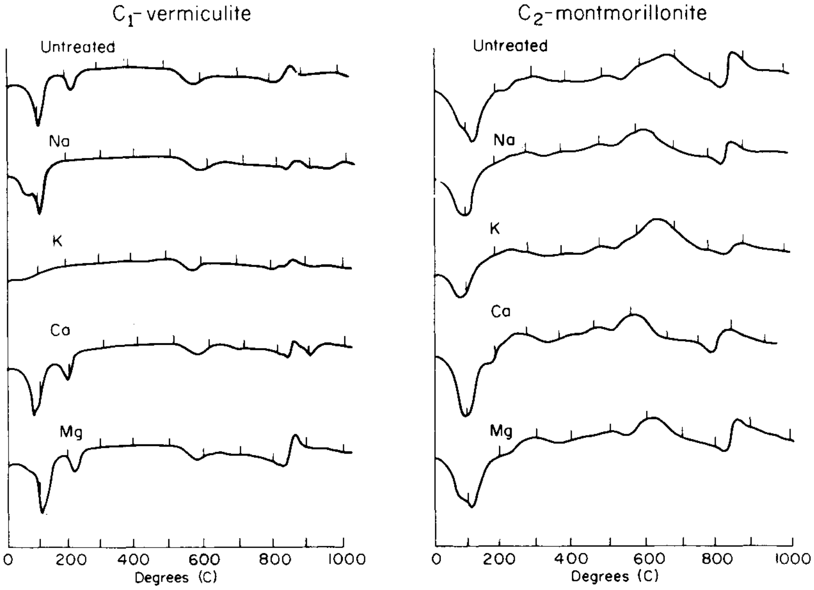

Fig. 2. Differential thermal analysis patterns of cation-exchanged samples of C_1-vermiculite and C_2-montmorillonite.

ture changes, were less than ±2 per cent. The main objective of this phase of the investigation was to submit the cation-exchanged montmorillonites and vermiculite to the same wide range of reproducible relative-humidity conditions and to observe the differences in relative amounts and rates of interlayer water absorption as a function of the increase in the (001) *d* values.

Tables 2, 3, and 4 list the equilibrium *d* values for the (001)-oriented samples subjected to different conditions of relative humidity. The first principal peaks of the C_1-vermiculite sample are reported as (001) although technically they are the (002) diffraction peaks. This was done in order to maintain a notation consistent with the montmorillonite samples.

In order to compare the expandable properties of the montmorillonite and vermiculite samples, data from Tables 2, 3, and 4 are plotted in Fig. 3. This illustration depicts the equilibrium (001) *d* values for the magnesium- and potassium- exchanged samples. These data were chosen because they represent the extremes of swelling behavior for each of the three substances studied.

The K-vermiculite sample (C_1) retained a 10·4 Å collapsed *d* value over the entire range of relative humidities up to 88 per cent. The potassium-saturated C_2- and C_3-montmorillonite samples responded similarly and expanded from dry 10·65 Å and 10·5 Å states to 12·4 Å and 12·32 Å states, respectively, at 88 per cent relative humidity. The magnesium-interlayered C_1-vermiculite and C_2-montmorillonite expanded identically from partially collapsed 11·5 Å states to about 14·5 Å at 88 per cent relative humidity. Under dry-air conditions the magnesium-exchanged C_3-montmorillonite collapsed to only 13 Å, revealing its higher retentive capacity for interlayer water. At 88 per cent relative humidity the (001) *d* values of the montmorillonite increased to 16·39 Å.

INTERPRETATIONS

The influence of the interlayer cation composition on the hydration and dehydration properties of montmorillonite and vermiculite is evident from the DTA and constant-humidity X-ray-diffraction data. The endothermic doublets associated with the samples containing the divalent cations of magnesium, barium, and strontium are directly correlated to the occurrence of 14–15 Å equilibrium (001) *d* values at moderate relative humidities. The first node on the endotherm reflects the shift from an octahedrally coordinated, or two monomolecular water-layer configurations, to a single monomolecular water-layer state. The second node is due to the removal of the single water layer and a total collapse of the (001) interlayer spacing to about 10 Å. The single dewatering endotherm of the sodium- and potassium-saturated samples reflects the collapse of the (001) interlayer spacing to 10 Å from a single water-layer 12·4 Å state. The double endotherm of lithium montmorillonite is

Table 2. Constant-humidity X-ray data for cation-exchanged C_3-montmorillonite

Interlayer cation		Relative humidity (per cent at 24·5°C)			
		Dry	15	1	88
		d(Å)	d(Å)	d(Å)	d(Å)
Ba	(001)	10·78	12·28	16·4	16·83
	(002)	5·13	—	—	—
	(003)	3·31	—	5·34	5·37
	(004)	—	3·18	—	—
	(005)	—	—	3·20	3·23
Sr	(001)	11·95	12·63	15·78	16·22
	(002)	5·91	6·19	—	—
	(003)	3·08	—	5·28	5·34
	(004)	—	3·13	—	—
	(005)	—	—	3·14	3·16
Ca	(001)	12·2	13·28	15·64	16·1
	(002)	5·87	6·56	—	—
	(003)	—	—	5·22	5·31
	(004)	—	3·29	—	—
	(005)	—	—	3·12	3·15
Mg	(001)	13·0	14·14	16·08	16·39
	(002)	6·15	—	—	—
	(003)	—	4·87	5·31	5·40
	(004)	—	3·51	—	—
	(005)	—	—	3·18	3·21
K	(001)	10·5	12·11	12·28	12·32
	(002)	5·05	—	—	—
	(003)	3·35	—	—	—
	(004)	—	3·24	3·24	3·23
Na	(001)	10·04	12·63	15·64	16·4
	(002)	4·90	—	—	—
	(003)	3·23	—	5·22	5·28
	(004)	—	3·16	—	—
	(005)	—	—	3·12	3·13
Li	(001)	12·11	12·54	15·73	16·1
	(002)	5·99	6·15	—	—
	(003)	—	—	5·31	5·34
	(004)	3·03	3·12	—	—
	(005)	—	—	3·12	3·19

Table 3. Constant-humidity X-ray data for cation-exchanged C_2-montmorillonite

Interlayer cation		Relative humidity (per cent at 24·5°C)			
		Dry	15	31	88
		d(Å)	d(Å)	d(Å)	d(Å)
K	(001)	10·65	12·11	12·3	12·4
	(002)	—	—	—	—
	(003)	3·43	—	—	—
	(004)	—	3·43	3·10	3·11
Na	(001)	10·4	13·02	14·62	14·62
	(002)	—	—	7·38	7·38
	(003)	3·38	—	4·80	4·90
	(004)	—	—	3·58	3·60
Ca	(001)	11·86	13·39	15·01	15·01
	(002)	—	—	7·44	7·44
	(003)	—	—	4·98	4·98
	(004)	2·93	—	—	—
	(005)	—	—	3·00	3·00
Mg	(001)	11·50	14·20	14·21	14·53
	(002)	—	7·31	7·25	7·25
	(003)	—	4·80	4·82	4·81
	(004)	2·88	3·59	3·60	3·60
	(005)	—	2·87	2·89	2·89

probably due to a shift from a 12·4 Å single water-layer state to the 11·5 Å imperfect octahedrally coordinated configuration (actually a special case of the single water-layer state) to a final totally collapsed state. The temperatures at which dehydration is completed and the relative ease of hydration of the various cation-exchanged samples of montmorillonite are in close agreement. From interpretations of the DTA data and the (001) d values given in Tables 2, 3, and 4, an arrangement of the samples from highest to lowest water-absorption capacity, based on interlayer cation composition, is:

Mg, Ca, Sr, Li, Ba, Na, K.

A direct correlation can be made between this property and the radius (r) and the charge (c) of the interlayer cation. The two values may be combined as the ionic potential (c/r) and these data are provided in Table 5. Listing of the interlayer cations in the order of highest to lowest value of ionic potential results in:

Mg, Ca, Sr, Li, Ba, Na, K.

If the interlayer cation composition were the only factor determining the swelling behavior of montmorillonites and vermiculites, then all such minerals possessing the same interlayer cation composition should have the same equilibrium (001) d values under the same conditions of relative humidity. That this was not the case in this study is evidenced by the data plotted in Fig. 3. The water-absorption capacities of the montmorillonite and vermiculite samples are distinctly different. If these are arranged on the basis of relative degree of expandability over the range of relative humidities considered in this investigation, it is observed that:

Table 4. Constant-humidity X-ray data for cation-exchanged C_1-vermiculite

Interlayer cation		Relative humidity (per cent at 24·5°C)			
		Dry	15	31	88
		d(Å)	*d*(Å)	*d*(Å)	*d*(Å)
K	(001)	10·33	10·40	10·46	10·46
	(002)	4·93	4·93	4·93	4·93
	(003)	3·39	3·39	3·39	3·39
	(004)	2·53	2·53	2·53	2·53
	(005)	2·02	2·02	2·02	2·02
Na	(001)	10·04	12·20	14·77	14·80
	(002)	4·87	—	7·38	7·44
	(003)	3·39	—	4·96	4·96
	(004)	—	2·98	3·72	3·72
	(005)	1·96	—	2·99	2·99
	(006)	—	2·00	—	—
Ca	(001)	11·79	12·37	15·11	15·21
	(002)	5·91	—	7·50	7·56
	(003)	—	—	5·04	5·04
	(004)	2·94	3·00	3·77	3·77
	(005)	—	—	3·01	3·02
Mg	(001)	11·55	14·53	14·53	14·54
	(002)	5·79	7·31	7·31	7·25
	(003)	3·83	4·80	4·81	4·82
	(004)	2·88	3·60	3·60	3·63
	(005)	—	2·88	2·87	2·90

C_3-montmorillonite > C_2-montmorillonite > C_1-vermiculite. Because the contributions from the interlayer cations were held constant within the experimental system, some other factor or factors must partially account for the differences in the expanding properties of montmorillonite and vermiculite. The two possible alternatives are the effect of total surface-charge density and the sites of the charge deficiencies within the layer. A correlation with respect to total surface-charge density is not possible with the substances included in this investigation. If the three samples are arranged on the basis of increasing surface-charge density the results are: C_2-montmorillonite < C_3-montmorillonite < C_1-vermiculite. On this

Table 5. Ionic radii and potentials for selected cations (from Pauling, 1948)

Cation	Radius (*r*)	Ionic potential (*c*/*r*)
	Monovalent	
Li	0·60	1·67
Na	0·95	1·05
K	1·33	0·75
	Divalent	
Mg	0·65	3·08
Ca	0·99	2·02
Sr	1·13	1·77
Ba	1·35	1·48

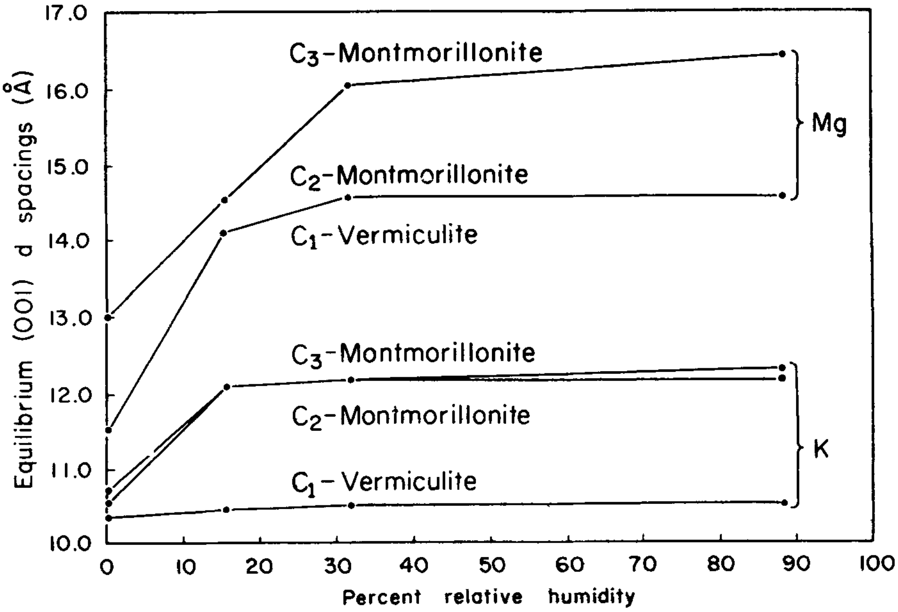

Fig. 3. Equilibrium (001) *d* values for Mg- and K-exchanged montmorillonites and vermiculite.

basis the C_2-montmorillonite should expand more readily than the C_3-montmorillonite sample under the same interlayer-cation and relative-humidity conditions. This was not observed. However, a correlation may be made with respect to the site of layer charge deficiencies and differences in the expandability of the three samples. If the samples are arranged on the basis of distance of separation of the structural charge sites from the interlayer cations, that is, decreasing octahedral vs. increasing tetrahedral charge deficiencies, the result is: C_3-montmorillonite > C_2-montmorillonite > C_1-vermiculite, which is the order of decreasing expandability, as shown in the following summary:

Increasing surface-charge density	Decreasing octa./tetra	Decreasing expand-ability
C_2 (−0·42)	C_3 (−0·48/−0·05)	C_3
C_3 (−0·53)	C_2 (−0·21/−0·21)	C_2
C_1 (−0·66)	C_1 (−0·01/−0·65)	C_1

Acknowledgments—The technical services section of the Oklahoma Geological Survey prepared the illustrations and edited the manuscript. In this connection, the services of Mrs. Marion Clark and Mr. David Deering, draftsmen, and Mr. Alex. Nicholson, Geologist-Editor, are gratefully acknowledged.

Conversations and correspondence with Dr. E. C. Jonas, The University of Texas, provided much of the background for this investigation. His many helpful suggestions are sincerely appreciated.

The manuscript was critically reviewed by Mr. C. R. Nichols, and Mr. W. H. Bellis. Their many constructive suggestions contributed to a substantial improvement in the manuscript.

Finally, the authors gratefully acknowledge the time and effort of Dr. S. W. Bailey, Editor of *Clays and Clay Minerals*, for expediting the publication of this article.

REFERENCES

Barshad, Isaac (1948) Vermiculite and its relation to biotite as revealed by base exchange reactions, x-ray analyses, differential thermal curves, and water content: *Am. Mineralogist* **33**, 655–678.

Bradley, W. F., Grim, R. E., and Clark, G. L. (1937) A study of the behavior of montmorillonite upon wetting: *Z. Krist.* **97**, 216–222.

Hendricks, S. B., and Jefferson, M. E. (1938) Structures of kaolin and talc-pyrophyllite hydrates and their bearing on water absorption of the clays: *Am. Mineralogist* **23**, 863–875.

Hofmann, U., and Bilke, W. (1936) Über die innerkristalline quellung und das Basenaustsch-vermogen des montmorillonits: *Kolloid-Z.* **77**, 239–251.

Hofmann, U., Weiss, A., Koch, G., Mehler, A., and Scholz, A. (1956) Intracrystalline swelling, cation exchange, and anion exchange of minerals of the montmorillonite group and of kaolinite: *Clays and Clay Minerals* Natl. Acad. Sci.—Natl. Res. Council Publ. **4**, 273–287.

Marshall, C. E. (1964) *The Physical Chemistry and Mineralogy of Soils*, Wiley, New York, Vol. 1, 388 pp.

McAtee, J. L. (1958) Heterogeneity in montmorillonite: *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council Publ. **566**, 279–288.

Mering, J. (1946) On the hydration of montmorillonite: *Trans. Faraday Soc.* **42-B**, 205–219.

Mooney, R. W., Keenan, A. G., and Wood, L. A. (1952) Absorption of water vapor by montmorillonite: *J. Am. Chem. Soc.* **74**, 1367–1374.

Nagelschmidt, G. (1936) On the lattice shrinkage and structure of montmorillonite: *Z. Krist.* **93**, 481–487.

Pauling, L. (1948) *The Nature of the Chemical Bond*: Cornell University Press, Ithaca, New York.

Rowland, R. A., Weiss, E. J., and Bradley, W. F. (1956) Dehydration of monoionic montmorillonites: *Clays and Clay Minerals* Natl. Acad. Sci.—Natl. Research Council Pub. **4**, 85–95.

Walker, G. F., 1956, The mechanism of dehydration of Mg-vermiculite: *Clays and Clay Minerals* Natl. Acad. Sci.—Natl. Res. Council Publ. 101–115.

Résumé—Des recherches antérieures ont démontré l'influence de la composition des cations interstratifies, de l'humidité relative, de la température et de la grandeur de la charge de surface des feuillet sur l'hydratation de la couche intermédiaire de montmorillonites et de vermiculites. On a proposé que les zones de déficience de charge sur le feuillet pouvaient aussi influencer la quantité d'hydratation qui peut avoir lieu dans les couches intermédiaires des minéraux argileux dilatables. Si on considère, pour une situation idéale, que les liens retenant les cations au feuillet intermédiaire sont électrostatiques, on peut exprimer la grandure de l'expansion des forces de résistance comme une forme de la loi de Coulomb. Si cet effet est significatif, les structures dilatables pour lesquelles les zones de déficience en charge prédominent dans le feuillet tétraédrique devraient avoir des propriétés de dilatation moins prononcées que les structures possédant des déficiences en charge situées premièrement dans le feuillet octaédrique.

On a choisi pour l'étude trois échanitllons pour lesquels les zones de charge des feuillet sont localisées différemment. Un critère important de cette sélection, a été la non-corrélation entre les zones de charge tétraédriques et la haute densité de la charge en surface et entre les zones de charge octaédriques et une faible densité de la charge en surface.

Les effets des différences dans la composition en cations interstratifies ont été éliminées par des portions saturantes de chaque échanitllon avec les mêmes cations. Des valeurs d'équilibre (001) *d* à des humidités contrôlées constantes ont été utilisées en tant que mesure du degré relatif de hydratation entre les feuillets.

Bien qu'il n'ait pas été possible d'obtenir un accord entre le degré d'hydratation entre les feuillets et la densité totale de la charge en surface, la recherche n'élimine pas la densité totale de la charge en surface comme étant significative des propriétés de dilatation des structures minérales argileuses à trois feuillets. Les résultats indiquent une corrélation entre une dilatation plus intense et la prédominance des déficiences en charge dans le feuillet octaédrique. Réciproquement, un comportement avec dilatation moindre est associé aux déficiences en charge d'ordre surtout tétraédrique.

Kurzreferat—Frühere Untersuchungen haben die Wirkungen der Zusammensetzung der Kationenzwischenschicht, der relativen Feuchtigkeit, der Temperatur und der Grösse der Oberflächenladung der Zwischenschicht auf die Zwischenschicht-Hydratisierung von Montmorilloniten und Vermiculiten dargelegt. Es ist die Vermutung ausgesprochen worden, dass die Schichtladungsmangelstellen ebenfalls einen Effekt auf die in den Zwischenschichten von aufgeblähten Tongesteinen mögliche Hydratisierung haben könnten. Wenn man die Bindung des Zwischenschichtkations zur Schicht als ideal elektrostatisch betrachtet, so kann die Grösse der der Aufblähung entgegenwirkenden Kräfte in der Form des Coulombschen Gesetzes ausgedrückt werden. Wenn diese Wirkung bedeutungsvoll ist, so sollten aufgeblähte Gebilde, in welchen die Ladungsmangelstellen hauptsächlich in der tetrahedralen Schicht auftreten, weniger ausgesprochene Quelleigenschaften besitzen als diejenigen-Gebilde in welchen die Ladungslücken vorzugsweise in der oktahedralen Schicht liegen.

Es wurden drei Proben mit unterschiedlicher Lage der Schichtenladungs-stellen zur Untersuchung herangezogen. Ein wichtiges Kriterium für die Auswahl war die Abwesenheit einer Korrelation zwischen tetrahedralen Ladungsstellen und hoher Oberflächenladungsdichte, beziehungsweise zwischen oktahedralen Ladungs-stellen und niedriger Oberflächenladungsdichte.

Die durch den Unterschied in der Zusammensetzung der Zwischenschicht Kationen hervorgerufene Wirkung wurde durch Sättigung aller Proben mit den gleichen Kationen ausgeschaltet. Gleichgewichtswerte (001) d unter konstantgehaltenen Feuchtigkeitsverhältnissen wurden als Masse für den relativen Umfang der Zwischenschichtenhydratisierung herangezogen.

Obwohl sich keine Korrelation zwischen dem Umfang der Zwischenschichten-hydratisierung und der gesamten Oberflächenladungsdichte ergab, besagt die Untersuchung keineswegs, dass die gesamte Oberflächenladungsdichte unwesentlich hinsichtlich der Quelleneigenschaften von dreischichtigen Tonsetinbildungen ist. Die Ergebnisse deuten aber auf eine Korrelation zwischen intensiverer Aufblähbarkeit und Vorherrschen von Ladungslücken in der oktahedralen Schicht hin. Andererseits konnte das weniger intensive Quellverhalten mit vornehmlich tetrahedralen Ladungslücken in Zusammenhang gebracht werden.

Резюме—Предыдущие исследования показали влияние прослоенного катионного состава, относительной влажности, температуры и величины заряда прослоенной поверхности на прослоенную гидратацию монтмориллонитов и вермикулитов. Говорят, что места отсутствия зарядов могут также оказать влияние на размер гидратации, происходящей в прослойках расширяемых глинистых минералов. Если связи прослоечных катионов со слоями считают идеально электростатическими, то величина сопротивляющихся расширению усилий может быть выражена как вид закона Кулона. Если эффект этот является значительным, то расширяемые структуры, в которых места отсутствия заряда являются преобладающими, в четырехгранном листе должны обладать менее отчетливо выраженными свойствами набухания чем в структурах, обладающих отсутствием заряда, которые преимущественно находятся в восьмигранном листе.

Для изучения выбрали три образца, которые были разными касательно расположения мест заряда слоев. Важным критерием выбора являлось отсутствие корреляции между четырехгранными местами зарядов и большой поверхностной плотности зарядов, а также между восьмигранными местами зарядов и низкой поверхностной плотностью зарядов.

Вмляния разниц в прослоечном катионном составе устранялись насыщением порций каждого образца теми же катионами. Значения равновесия (001)$_p$ при регулируемых постоянных влажностях применяются для измерения относительной степени прослоечной гидратации.

Хотя нельзя было установить корреляцию между степенью прослоечной гидратации и общей поверхностной плотностью, исследование не исключает, что поверхностная плотность зарадов имеет значение для набухающих свойств трехлистовых глинистых минеральных структур. Результаты показывают корреляцию между более интенсивной расширяемостью и преобладанием недостатка зарядов в восьмигранном листе. Наоборот, менее интенсивное набухание связано с преимущественно четырехгранными отсутствиями зарядов.