PROPERTIES OF VERMICULITES AND SMECTITES: EXPANSION AND COLLAPSE*

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Abstract – Samples of smectites and vermiculites were evaluated to (1) determine the effects of source and amount of charge, (2) determine if a continuum of properties exists, and (3) improve the basis for differentiating criteria for identification.

The montmorillonites expanded to the equivalent two-layer complex upon solvation by condensation of ethylene glycol or glycerol vapor. Beidellite exhibited the one-layer complex with glycerol vapor and the two-layer complex with ethylene glycol. The vermiculite samples did not yield regular two-layer complexes regardless of saturating cation, prior moisture or solvating agent. A number of different complexes of vermiculite were obtained depending on conditions of solvation. These corresponded to spacings of approx 13·6, 14·0, 14·3, 15·0, and 15·3 Å. Two or more of the complexes may be present in the same sample.

Potassium-saturated vermiculites and smectites both exhibited collapsed layers in a dry atmosphere. Hydration of smectites occurred at humidities above 20 per cent and resulted in poorly ordered diffraction maxima of 11–12 Å. The K-saturated vermiculites tended to retain the collapsed lattice and exhibited diffraction maxima of 10–10·6 Å with integral higher orders. Some hydration occurred as evidenced by peak asymmetry or the appearance of a small 14·3 Å line at higher humidities, although the collapsed spacing predominated. The tendency of vermiculite to hydrate decreased as the exchange capacity increased.

Differences in properties can be related to both source and amount of charge. Nevertheless, a continuum in the properties of expansion and collapse between the smectites and vermiculites was not observed. The data indicate two discrete populations. These properties may be used as differentiating criteria for identification.

INTRODUCTION

PHYSICO-CHEMICAL properties in relation to crystal structures of phyllosilicates are of interest. The behavior of vermiculites and smectites to different cation saturations and adsorption of polar compounds has received particular attention. It is clear, however, that a number of questions still exist. In his review of the ethylene glycol and glycerol complexes of smectites and vermiculites, Brindley (1966) concluded "that it is still not possible to give adequate answers to many of the more fundamental questions which can be asked concerning their nature. It is established that ... vermiculites tend to form single layers and smectites double layers. Beyond this, it is difficult or impossible to state the relations between the magnitude and source of the layer charge, the nature of the interlayer cations, and the number and organization of the organic molecules."

Difficulties in clearly establishing relationships of structure to properties for these groups occur since three structural variables are involved — source of charge, charge density, and particle size. Walker (1957, 1958) studied expansive properties upon solvation of five vermiculites and obtained differences which were related to surface charge, interlayer cation, initial hydration, and solvating agent. He did not include smectites but pointed out that if the groups grade into one another with respect to layer charge, the question of where the dividing line occurs becomes essentially one of terminology and criteria selected. Since none of his Mg-saturated samples expanded beyond 14·5 Å when solvated with glycerol, he recommended this as a criterion. However, he

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stated that the universal validity of the test cannot be regarded as established until a wider range of vermiculites and smectites has been examined. Harward and Brindley (1965) found that the amount of isomorphous substitution in synthetic smectites fell within a relatively narrow range. They did not have a variable of charge density and they did not have members of the vermiculite group. It was shown, however, that beidellite, in comparison with montmorillonite, exhibited differences in expansion upon solvation consistent with stronger ionic attractions for tetrahedral than for octahedral charge sites. Similar results have been obtained with natural samples (Sayegh, 1964). Differences in methods and techniques are reflected in the observed phenomena. It is therefore necessary to evaluate both groups simultaneously under the same conditions. Other characteristics in addition to expansion on solvation need to be evaluated. Walker (1957) recognized the possible use of lattice contraction upon treatment with K^+ or NH_4^+ (Barshad, 1948, 1950; Walker, 1949; Weaver, 1956, 1958). This was not included in his studies because of possible effects of interlayer contaminants.

The study reported here was initiated with these factors in mind. Specifically we wished to (1) evaluate the effects of source of charge and charge density, (2) determine if a continuum exists and (3) improve the methods and criteria for identification.

EXPERIMENTAL

Materials and methods

Samples reported to be smectite or vermiculite were collected and treated to obtain mono-mineralic systems. They were treated for removal of organic matter, dispersed by boiling in 2% Na_2CO_3, and size fractions were separated by centrifugation (Jackson, 1956). The vermiculite samples, as received, contained some mica components. They were digested, therefore, at 80°C for 7 days in 5 N NaCl to remove interlayer K (Rich, 1960; Carstea, 1967); solutions were changed daily. Treatment for removal of interlayer K (conversion of mica to vermiculite) was quite successful although small amounts of K ($<$ 0·3 per cent on final dry weight basis) remained in some samples. Cation exchange capacities were adjusted on the basis of K (mica) content (Table 2). Both the vermiculites following NaCl digestion and the smectites were treated for removal of "free iron", hydroxy-interlayers and amorphous constituents (Jackson, 1956; Hashimoto and Jackson, 1958; Cook and Rich, 1963). Samples were then selected which were essentially monomineralic as indicated by X-ray diffraction. Samples representing eleven

montmorillonites, one beidellite, and twelve vermiculites (Tables 1 and 2) were analyzed for properties of expansion and collapse. It is not claimed that the samples were entirely pure and minor amounts of other constituents could still have been present after the "clean-up" procedures. Pure vermiculite samples were the most difficult to obtain. In a few cases, very small peaks in the range 15·4–16·4 Å upon Ca- or Mg-saturation and equilibration at 54% r.h. were observed. These spacings decreased or disappeared on solvation. Two of the vermiculites (Nos. 3 and 13) occasionally exhibited small peaks at 8·37–8·39, 4·91, 3·40 or 3·12–3·18 Å which may have been due to small amounts of amphiboles. The peaks, small in comparison with those of the main components, were not included in tabulations of subsequent data. It is recognized that in these cases the cation exchange capacities may be under-estimated.

Characterization treatments

Saturation with Ca, Mg, or K was accomplished using four washings with the appropriate 1 N chloride salt solutions followed by two washings with distilled H_2O and in the case of Ca and Mg, two additional washes with methanol. Cation exchange capacities were determined as previously

Table 1. Smectite samples used in experimental work

No.	Sample and source	CEC me/g
1	Vol clay, Aberdeen*	1·23
2	Vol clay, SPV*	0·97
5	Montmorillonite-21, Polkville, Miss.†	1·14
6	Montmorillonite-24, Otay, Calif.†	1·28
8	Montmorillonite S34-6, Colo.‡	1·25
9	Montmorillonite S34-1, Colo.‡	1·38
17	Montmorillonite-30a, Baynard, N. M.†	1·33
19	Montmorillonite-23, Chambers, Ariz.†	1·27
20	Montmorillonite-26, Clay Spur, Wyo.†	0·99
21	Montmorillonite-20, Husband Mine, Polkville, Miss.†	1·16
22	Montmorillonite-27, Belle Fourche, So. D.†	0·95
32	Beidellite-R4762, Black Jack Mine, Idaho§	1·18
	Av.	1·18

*Obtained through courtesy of American Colloid Company, Skokie, Illinois.
†Wards Natural Science Establishment, Rochester, New York.
‡Obtained through courtesy of R. D. Dirmeyer and W. R. Schmehl, Colorado State University.
§Obtained through courtesy of U.S. National Museum.

Table 2. Vermiculite samples used in experimental work

			After separation and purification		
No.	Sample and source	Prior CEC (me/g)	CEC (me/g)	mica* (%)	Adjusted† CEC (me/g)
1	V33-Kipiponi, Nairobi‡	1·42	1·42	0	1·42
2	Zonolite, high grade ore, coarse and fine§	1·03	1·73	1·3	1·75
3	Waldrep Mine, So. Carolina§	0·45	1·75	0·5	1·76
4	Lincoln County, Montana‖	0·75	1·83	3·3	1·89
5	Northern Transvaal, Africa‖	1·01	1·78	0·1	1·78
6	African vermiculite¶	0·88	1·71	0·1	1·71
7	Kipiponi, Kenya M5700/86; EAA 481b**	1·38	1·38	0·2	1·38
8	Zonolite, low grade ore, coarse and fine§	0·69	1·70	0·1	1·70
9	Zonolite, high grade ore, type A§	0·35	1·66	0·4	1·67
10	M5700/145, B17650**	1·33	1·47	0	1·47
12	V32-Kalanga Hill‡	0·11	1·37	9·8	1·52
13	Allen type ore, Moore-Williams Mine§	1·24	1·35	0·1	1·35
					Av. 1·62

*% mica = % K × 1·208 × 10. (Jackson, 1956).
†Adjusted for mica impurities: Adj. CEC = CEC/(1-% mica/100).
‡Obtained through courtesy of Mines and Geological Department, Nairobi, Kenya.
§Obtained through courtesy of Zonalite Company, Travelers Rest, South Carolina.
‖Obtained from Wards Natural Science Establishment, Rochester, New York.
¶Obtained through courtesy of Perlite Company, Portland, Oregon.
**Obtained through courtesy of E. R. Varley, Mineral Resources Division, England.

described (Harward and Brindley, 1965). Oriented specimens were prepared on glass slides using the paste method (Theisen and Harward, 1962). Solvation was accomplished by condensation of ethylene glycol vapor (Kunze, 1955), glycerol vapor (Brown and Farrow, 1956), and by adding the liquids with a dropping tube until the slides were visibly moist. The specimens were allowed to equilibrate overnight after addition of solvate. The moisture status of unsolvated slides prior to and during diffraction analyses and prior to solvation was controlled as indicated in the text. Diffraction analyses were made with CuKα, over a range of 2–31° 2θ. This permitted measurement of the first five orders of d(001) which was sufficient to determine whether the spacings were ordered and integral. The basal spacings were determined from the centers of the peaks at half-peak height and by averaging the orders of 001, unless otherwise specified in the text.

RESULTS AND DISCUSSION

Particle size

It was most convenient to use the silt (50–2 μ) fraction for vermiculites and the clay (< 2μ) fraction for smectites. Based on data obtained by Walker (1957, 1958), we anticipated that particle size would affect only the rate of reaction and not the final equilibrium. Separation and comparison of different size fractions obtained from natural bulk samples are subject to the criticism that the system may contain more than one component with different particle sizes. This ambiguity was avoided by measuring expansion and collapse of 50–2 μ fractions of several vermiculite samples. Sub-samples of the same material were then suspended and sheared in a blender. The < 2 μ particles were separated and their properties compared with the properties of the silt-size material from which they were derived. The results (Table 3) verify the findings of Walker (1957, 1958). Differences between samples of smectite and vermiculite may be ascribed to charge characteristics and not to particle size.

Table 3. Comparison of silt and clay reduced from silt size vermiculite (six samples)

	Basal spacings (Å)		
	Ca-satn. 54% r.h.	Ca-satn. Eth. gly.	K-satn. air dry
Silt			
Range	14·8–15·0	15·2–15·7	10·2–10·5
Mean	14·9	15·4	10·3
Clay			
Range	14·8–14·9	15·3–15·7	10·0–10·4
Mean	14·8	15·5	10·2

Expansion on solvation

There was no apparent effect of amount of charge on the solvation of smectites (Tables 1 and 4). The exchange capacities were within a relatively narrow range of 0·95–1·38 me/g. The montmorillonites generally expanded to the equivalent two-layer complex with either ethylene glycol or glycerol. Five integral orders of the solvation complex were usually evident and the average deviation of spacings for individual samples from the group mean were generally less than 0·1 Å. Incomplete solvation and the presence of mixed layer phases were observed on some samples with the glycerol vapor treatment. This occurred to a greater extent with Mg- than with Ca-saturation and more often on samples dried at 105°C prior to solvation. The effect of moisture status has been noted previously (Walker, 1957; Jackson, 1956).

The effect of source of charge is obtained from the comparison of beidellite with montmorillonite. Solvation with glycerol vapor resulted in the equivalent one-layer complex with beidellite and the two-layer complex with montmorillonite. The use of ethylene glycol or glycerol liquids gave the two-layer complex with both minerals. These data are consistent with previous work on synthetic samples and confirm the differences between beidellite and montmorillonite (Harward and Brindley,

1965). The interaction between minerals and solvating agents is interpreted to be due to the lower dipole moment of glycerol than glycol and the greater ionic attraction in beidellite than in montmorillonite. The reason why the one-layer glycerol complex is formed in beidellite by vapor condensation but a two-layer complex with excess liquid is not clear although it is assumed to be a mass action effect.

Regular basal spacings equivalent to the two-layer complex were not obtained on solvation of the vermiculites with conventional procedures. Additional treatments were imposed to try and induce the two-layer vermiculite-solvate complex. These consisted of increasing the oven temperature (and thereby the vapor pressure) prior to condensation of vapor and heating with free liquid on the sample (Table 5).

Samples equilibrated at 54% r.h. gave spacings about 0·5 Å greater for Ca- than for Mg-saturation. The greater electrostatic field strength of Mg (Brindley, 1966), therefore, must be manifested in attraction between the charged surfaces that is greater than attraction for H_2O dipoles. This difference due to cation was not observed with montmorillonite (Table 4) but did occur with beidellite. The data thus substantiate stronger ionic attractions with tetrahedral than with octahedral charge.

Table 4. Basal spacings (Å) of smectites upon solvation (means of orders and samples)

Prior equil.	Solvation method	Montmorillonite (11 samples)		Beidellite (1 sample)	
		$\bar{d}$	$(d-\bar{d})/N$*	$\bar{d}$	$(d-\bar{d})/N$*
Ca-Satn.					
54% r.h.	—	15·3	0·07	15·2	0·07
54% r.h.	Glycerol vapor	17·3	0·19	14·6	0·28
54% r.h.	Eth. Glycol vapor	16·9	0·09	16·7	0·04
105°C	Glycerol vapor	$\begin{cases} 17·5 \\ 16·7(2)† \end{cases}$	0·07	14·5	0·12
105°C	Glycerol liquid	17·8	0·09	—	—
105°C	Eth. Glycol vapor	16·8	0·04	16·7	0·02
Mg-Satn.					
54% r.h.	—	15·3	0·10	14·7	0·24
54% r.h.	Glycerol vapor	$\begin{cases} 17·4 \\ 16·1(5)† \end{cases}$	0·22	14·4	0·19
54% r.h.	Eth. Glycol vapor	16·9	0·07	16·8	0·06
105°C	Glycerol vapor	$\begin{cases} 17·7 \\ 16·6(9)† \end{cases}$	0·05	14·3	0·10
105°C	Glycerol liquid	17·9	0·12	—	—
105°C	Eth. Glycol vapor	16·9	0·08	16·8	0·06

*$(d-\bar{d})/N$ = average deviation of individual samples from group mean.
$(d-\bar{d})/n$ = average deviation of individual orders from sample mean.
$\bar{d}$ = mean of orders and samples.
†1st order peak for mixed layer systems. (x) is number of samples which contained mixed layer phase.

Table 5. Basal spacings (Å) of twelve vermiculites upon solvation (Means of orders and number of samples — samples equilibrated at 54% r.h. prior to solvation)

Treatment	Parameter*	Ca satn. Complexes observed‡			Mg. satn. Complexes observed‡	
		1st	2nd	3rd	1st	2nd
54%, r.h.	$\bar{d}$	14·82			14·29	
	N	12			12	
	$(d-\bar{d})/N$	0·04			0·01	
Glycerol vap.	$\bar{d}$	13·62	14·25	15·09	14·11	13·81
	N	12	7	3	12	1
	$(d-\bar{d})/N$	0·07	0·07	0·03	0·02	
Glycerol liquid	$\bar{d}$	14·33	14·90	ML†	14·17	13·81
	N	12	1	1	12	1
	$(d-\bar{d})/N$	0·04			0·02	
Eth. Glycol vap.	$\bar{d}$	15·01	15·39	ML	14·22	ML
	N	11	8	1	12	1
	$(d-\bar{d})/N$	0·07	0·07		0·03	
Eth. Glycol liq.	$\bar{d}$	15·29	ML		14·25	ML
	N	12	1		12	1
	$(d-\bar{d})/N$	0·08			0·02	
Glycerol vap. 200°	$\bar{d}$	14·04	13·64	ML	—	
	N	12	4	7		
	$(d-\bar{d})/N$	0·06	0·02			
Glycerol liquid { 4 hr @ 200° 2 cycles	$\bar{d}$	14·07	14·2	ML	14·08	ML
	N	12	1	2	12	8
	$(d-\bar{d})/N$	0·05			0·03	
Eth. Glycol liq. { 4 hr @ 150° 2 cycles	$\bar{d}$	13·5-ML	14·08	15·95	14·05	ML
	N	10	5	6	10	7
	$(d-\bar{d})/N$		0·08	0·06	0·03	

*$\bar{d}$ = mean of orders and all samples exhibiting a given phase.
N = number of samples exhibiting a given phase.
$(d-\bar{d})/N$ = average deviation of individual samples from group mean.
†ML = mixed layer systems present.
‡1st, 2nd, and 3rd refer to frequency of occurrence of different complexes (spacings) for a given treatment.

There was no consistent evidence for the two-layer organic solvation complex with the vermiculite (Table 5). Spacings of 15·9–16·1 Å were obtained on six Ca-saturated samples undergoing repeated heating at 150° with excess liquid glycol. However, these samples also exhibited diffuse or asymmetric peaks in the range 12·5–13·8 Å and apparently contained mixed layer systems. The higher heat treatments do not appear to serve any useful purpose for differentiation.

A number of different one-layer equivalent spacings (13·6–15·4 Å) were obtained depending on experimental conditions. The statistical data are included to demonstrate the degree of

reliability of the measurements and to show that the different spacings represent ordered structures. In most cases, four or five orders which agreed closely were present in each pattern. The means for different samples also agreed very well. Many of the patterns contained orders of different complexes in the same sample. Examples are shown in Figs. 1 and 2 for vermiculite number 4. Spacings of 13·5–13·8 Å were usually obtained with Ca saturation and solvation with either glycerol or glycol (Table 5). Complexes with spacings of 14·0–14·1 and 14·2–14·3 Å were obtained with both cation saturations and both solvating agents. A 15 Å complex was obtained only with Ca satu-
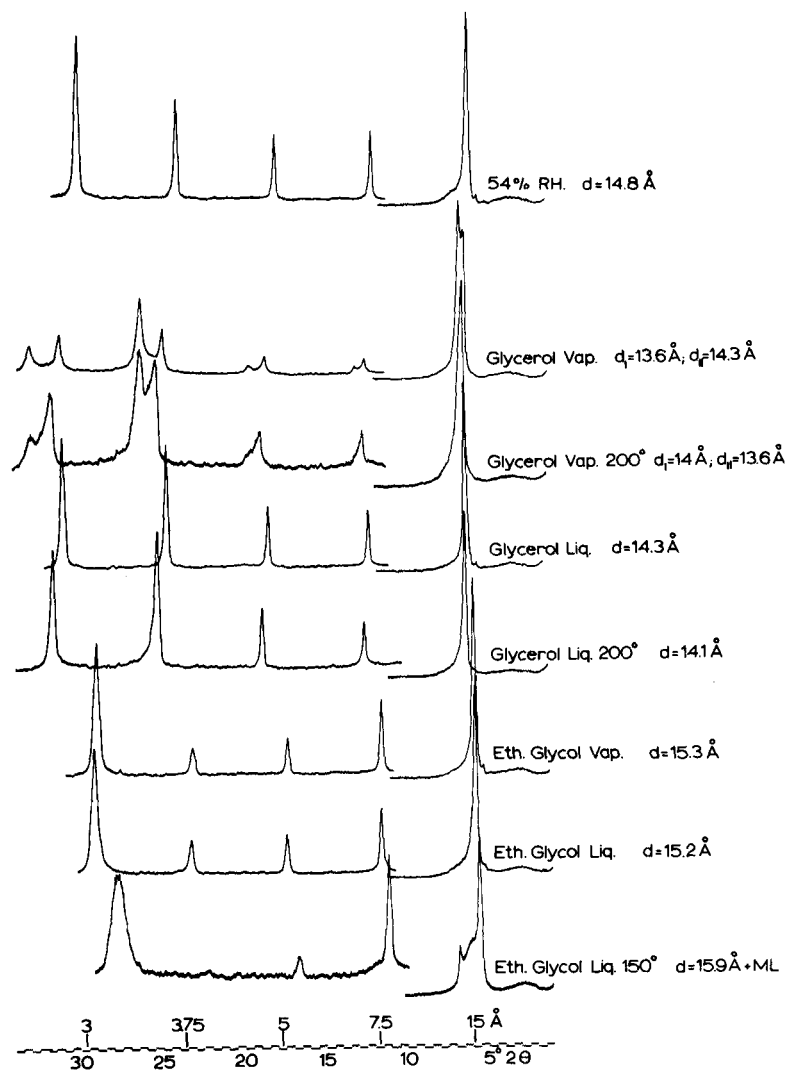
Fig. 1. Solvation complexes of Ca-saturated Montana vermiculite (sample # 4 of Table 2).
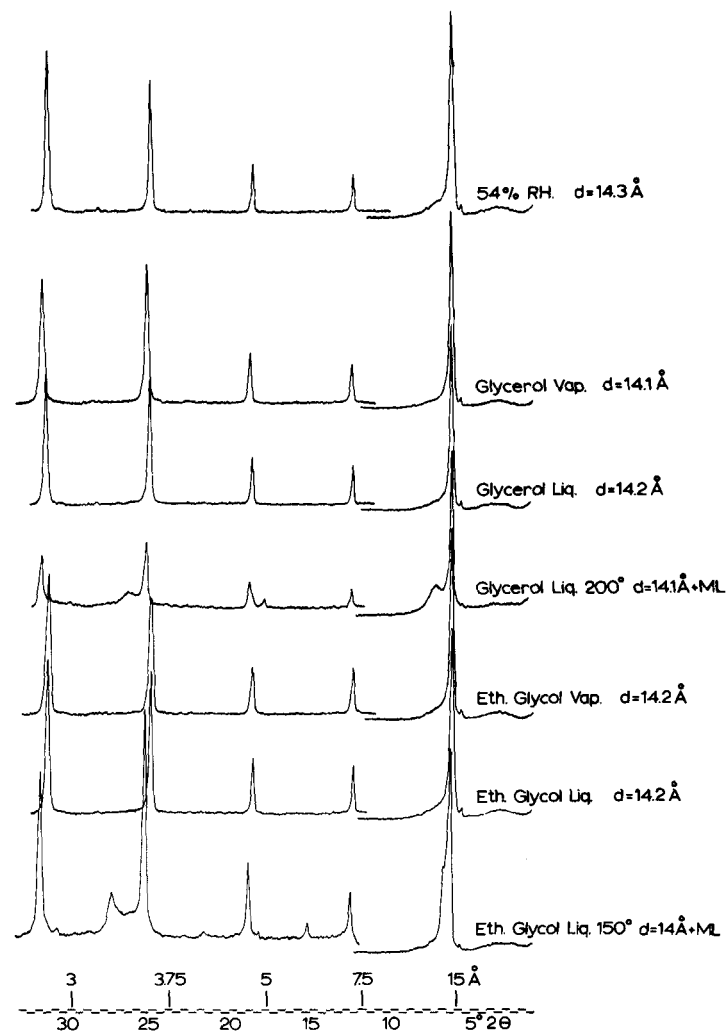
Fig. 2. Solvation complexes of Mg-saturated Montana vermiculite (sample # 4 of Table 2).

ration on solvation with glycerol or ethylene glycol. Spacings in excess of 15 Å were obtained only with Ca saturation and ethylene glycol.

After reviewing data by Barshad and Walker, Brindley (1966) stated that low charge vermiculites mainly have $d(001) = 16 \cdot 2$ Å and high charge vermiculites have $d(001)$ as small as $14 \cdot 3$ and $12 \cdot 9$ Å upon solvation with glycol; many glycol vermiculites appear to give irregular layer sequences with $d(001)$ of approx $15 \cdot 2 - 15 \cdot 6$ Å which probably represent random interlayerings of $14 \cdot 3$ and $16 \cdot 2$ Å spacings. On the basis of data presented here, the $15 \cdot 0 - 15 \cdot 3$ Å spacings are regular. Peaks in the range of $11 \cdot 8 - 12 \cdot 9$ Å were only observed in the presence of mixed-layer systems and no evidence for regular orders was found. As discussed previously, samples giving some orders of approximately 16 Å also contained mixed-layer systems. Thus, there is some question of whether the $12 \cdot 9$ and $16 \cdot 2$ Å spacings are regular. Mg-saturated samples were more consistent and gave spacings in the range of $14 \cdot 1 - 14 \cdot 3$ Å for both solvating agents. In this respect, the data are in agreement with Walker (1958) who also observed less variability with Mg-saturation although he did observe a difference between glycerol and ethylene glycol.

Higher spacings were observed here with glycerol than with ethylene glycol in both Ca- and Mg-montmorillonites. Larger spacings with ethylene glycol than with glycerol were obtained in Ca-vermiculites; there was little or no difference due to solvating agents for Mg-vermiculites. This must indicate the complex interactions between ions, dipoles, and strength of charge in the silicate structure. The possible effects of electrostatic field strength of ions and molecular structure of solvating agents has been discussed by Brindley (1966). It is believed that the variations in spacings observed here represent differences in molecular packing and orientation. The question arose as to whether the different spacings represent differences in orientation and packing of the organic molecules, of water, or both. Three of the vermiculites were dried at 105°C for 24 hr prior to solvation. Spacings similar to those reported in Table 5 were obtained. The data therefore suggest that the spacings are due to organization of the organic molecules. An analysis of these data using packing models similar to those presented by Barshad (1949) for H_2O, along with consideration of molecular structure and orientation would be informative.

No apparent relationship existed between cation exchange capacities of vermiculite (either before or after K-depletion) and the spacings of the solvation complexes. This is at variance with the data presented by Walker (1957). Some of our samples were from the same source as those used by Walker. Although there was some overlap in ranges, exchange capacities of the samples after separation and "clean-up" were generally higher than the systems studied by Walker. If anything, our exchange capacities may be underestimated as previously discussed. It is felt that vermiculites with exchange capacities of $1 \cdot 20 - 1 \cdot 40$ me/g should be suspect of containing some impurities. Walker's pretreatment of samples and methods of solvation were also different from ours and perhaps explanations of differences observed are to be found along those lines.

It is important to emphasize that although there were variations in the spacings observed for the vermiculites, there was no overlap of spacings with those for montmorillonites. The montmorillonites clearly yielded basal spacings of $16 \cdot 8 - 17 \cdot 9$ Å while vermiculites solvated by conventional procedures had spacings of $15 \cdot 4$ or less.

Collapse with K-saturation and rehydration

Both smectites and vermiculites collapse to approx. $10 \cdot 3$ Å upon K-saturation provided a dry atmosphere is maintained (Sayegh et al., 1965). Differences between the groups occur, however, upon rehydration (Table 6). The smectites expand to the equivalent thickness for one interlayer of water at a relative humidity of 20 per cent or more. The vermiculites tend to remain collapsed. Apparently this is due to the combined effects of source and amount of charge as indicated by expansion on hydration of montmorillonite > beidellite ≫ vermiculite.

It was thought initially that the broad peaks obtained in the range $11 \cdot 5 - 12 \cdot 5$ Å upon hydration of K-montmorillonites were due to random interstratification of 10 and 14 Å components. Closer inspection of the data, however, revealed weakly ordered systems (Fig. 3). This is indicated by shift of both 001 and 003 lines in response to hydration. The data thus suggest mono-interlayers of H_2O except for relative humidity of 100 per cent when spacings of $14 \cdot 2 - 15$ Å corresponding to the two-layer thickness are sometimes observed.

Slight hydration of some K-saturated vermiculites did occur but in a manner different from the smectites. As relative humidity was increased, some line broadening and slight shifts from mean values of $10 \cdot 3 - 10 \cdot 6$ Å occurred. Some samples exhibited smaller but definite peaks at approx $14 \cdot 3$ Å when exposed to relative humidities of 33 per cent*. The intensity of the $14 \cdot 3$ Å peak

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*The appearance of a 14 Å component upon hydration of K-saturated samples was first observed by A. H. Sayegh, unpublished data.

Table 6. Basal spacings (Å) upon hydration of K-saturated samples (means of 001 for all samples)

% r.h.	Montmorillonites (11 samples)		Beidellite (1 sample)	Vermiculites (12 samples)	
	$\bar{d}$	Range	$\bar{d}$	$\bar{d}$	Range
0	10·3	10·2–10·4	10·3	10·3	10·0–10·8
7	10·3	10·2–10·4	10·4	10·4	10·0–10·9
20	11·5	10·5–11·9	11·5	10·4	10·0–10·9
33	11·8	11·0–12·1	11·5	10·4	10·0–11·0†
45	12·1	11·8–12·3	11·6	10·4	10·0–10·9
54	12·1	11·9–12·3	11·6	10·4	10·0–11·0
63	12·2	11·9–12·4	11·6	10·4	10·0–11·0
79	12·3	12·2–12·6	11·5	10·5	10·0–11·0
88	12·3	12·2–12·6	11·5	10·5	10·0–11·1
100	⎰12·4* ⎱14·8*	⎰11·9–12·8 ⎱14·2–15·2	11·8	10·6	10·0–11·2

*Seven montmorillonite samples gave 12·4 and four gave 14·8 Å at 100% r.h.

†Five vermiculite samples exhibited small peaks at approx 14·3 Å after equilibration at or greater than 33% r.h.
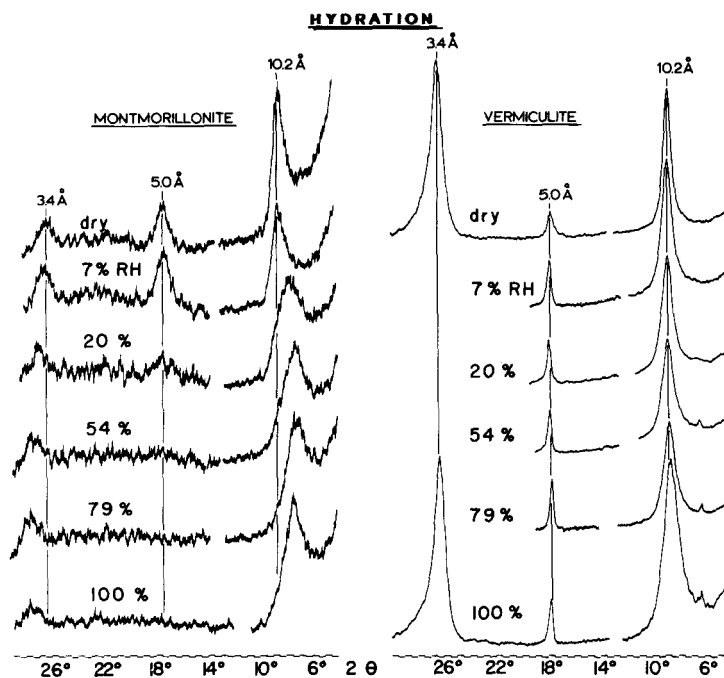

Fig. 3. Effect of hydration on expansion of K-saturated montmorillonite and vermiculite.

increased as humidity was further increased (Fig. 3). An inverse relationship between the phenomenon and exchange capacity was observed (Fig. 4). The five samples with highest exchange capacities (1·71–1·86 me/g) did not exhibit 14 Å peaks. Of the other seven samples with exchange capacities of 1·7 me/g or less, five exhibited the 14 Å peaks at 33% r.h., one gave a small 14 Å peak after 64% r.h. and the other gave indications of a 14 Å line only at 88% r.h.

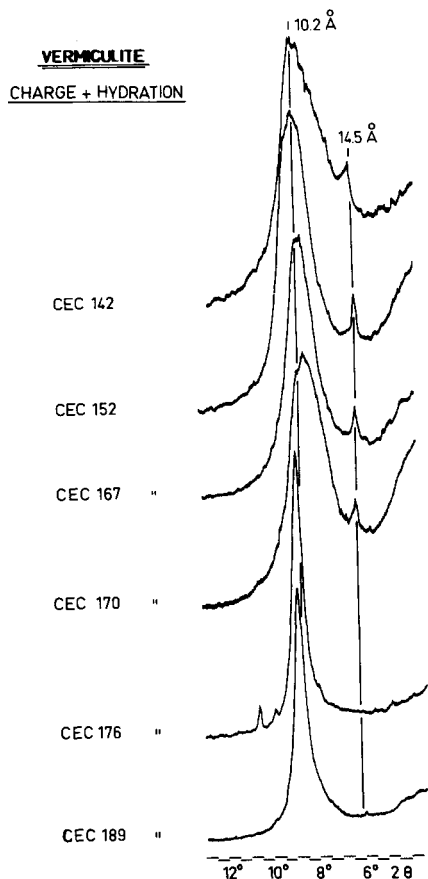The relationship involving the small 14 Å peak on hydration of K-vermiculites is not understood.

Fig. 4. Relationship of cation exchange capacity to expansion upon hydration (100% r.h.) of K-saturated vermiculite.

The data indicate two phases with the collapsed phase redominating. At this point, two speculative mechanisms can be offered. The first possibility is that it represents "zonality" with hydration of K around the edges of the vermiculite particles. This would not explain why the K at the edge of vermiculites hydrates to two layers but montmorillonite hydrates to one layer throughout. The 14 Å phase can be induced in some montmorillonites by heating treatments prior to hydration*. An alternative explanation involves the release of divalent cations such as Mg from the structure during heating with adsorption on exchange sites near the edges. Upon hydration, the Mg hydrates to the usual 14 Å spacing.

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*The appearance of a 14 Å component upon hydration of K-saturated samples was first observed by A. H. Sayegh, unpublished data.

CONCLUSIONS

Differences in properties of smectites and vermiculites can be related to both source and amount of charge. There was no evidence that a continuum exists; the data indicate discrete populations. The properties, therefore, may be properly used as differentiating criteria for identification. The proposed criteria are given in Table 7.

Table 7. Criteria for identification, $d(001)$

Treatment*	Mont- morillonite	Beidellite	Vermi- culite
Mg-sat'n, 54% r.h.	15·3	14·7	14·3
Mg-sat'n, Glycerol vapor	17·4	14·4	14·1
Mg-sat'n, Eth. Glycol vapor	16·9	16·8	14·2
K-sat'n, dry air	10·3	10·3	10·3
K-sat'n, 54% r.h.	12·1	11·6	10·4

*Mg-saturation gives more consistent results than Ca-saturation for solvation of vermiculites. The reverse is true for montmorillonites.

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Résumé—On a évalué des échantillons de smectite et de vermiculite afin de (1) déterminer les effets de la source et taux de charge (2) déterminer s'il existe un continuum de propriétés et (3) améliorer la base de différentiation des critères d'identification.

Les montmorillonites se sont dilatés vers le complexe équivalent à deux feuillets lors de la solvation par condensation de vapeur d'éthylène-glycol ou de glycérol. Le beidellite a montré le complexe à une seule feuillet avec la vapeur de glycérol et le complexe à deux feuillets avec l'éthylène-glycol. Les échantillons de vermiculite n'ont pas donné des complexes réguliers à deux feuillets sans tenir compte du cation de saturation, de l'humidité antérieure ou de l'agent de solvation. On a obtenu un nombre de complexes différents de vermiculite selon les conditions de solvation. Ceux-ci correspondaient à des intervalles d'environ 13,6, 14,0, 14,3, 15,0 et 15,3 Å. Deux ou encore plus des complexes peuvent être présents dans le même échantillon.

Les vermiculites saturés de potassium ainsi que les smectites saturés du même élément ont tous les deux montré des feuillets effondrées en atmosphère sèche. L'hydratation des smectites a eu lieu à des humidités dépassant 20% et a eu pour résultat des maxima de diffraction sans ordre précis de 11–12 Å. Les vermiculites saturés de K ont eu tendance à retenir le réseau effondré et ont montré des maxima de diffraction de 10–10.6 Å avec des ordres supérieurs intégraux. Une certaine hydratation a eu lieu; cela est prouvé par l'asymétrie de pic ou par la présence d'une petite ligne de 14,3 Å aux humidités plus élevées malgré la dominance de l'intervalle d'effondrement. La tendance vers l'hydratation du vermiculite réduisait à mesure que la capacité d'échange augmentait.

Les différences dans les propriétés montrent une certaine relation avec la source et la quantité de la charge. Pourtant on n'a pas observé un continuum dans les propriétés d'expansion et d'effondrement entre les smectites et les vermiculites. Les données indiquent deux populations discontinues. Ces propriétés peuvent être utilisées comme critères de différentiation en vue de l'identification.

Kurzreferat—Es wurden Smectit- und Vermiculitproben verwendet, um (1) Wirkungen der Ladungsquelle und Ladungsmenge zu bestimmen, (2) um festzustellen, ob ein Kontinuum der Eigenschaften besteht, und (3) um die Basis für eine Differenzierung der Identifizierungskriterien zu verbessern.

Bei der Solvatation durch Kondensierung von Äthylenglykol- oder Glyzerindämpfen quollen die Montmorillonite zu den entsprechenden Zweischichtenkomplexen an. Beidellit ergab einen Einschichtenkomplex mit Glyzerindampf und einen Zweischichtenkomplex mit Äthylenglykol. Die Vermiculitproben ergaben unabhängig vom Sättigungskation, der Vorbefeuchtung oder dem Solvatationsmittel keine regulären Zweischichtenkomplexe. Je nach den Solvatationsbedingungen wurde eine Reihe verschiedener Vermiculitkomplexe erhalten, welche Abständen von etwa 13,6, 14,0, 14,3, 15,0 und 15,3 Å entsprechen. In der gleichen Probe können zwei oder mehrere der Komplexe anwesend sein.

Vermiculite und Smectite, die mit Kalium gesättigt waren, wiesen in einer trockenen Umgebung zusammengeklappte Schichten auf. Die Hydratation der Smectite trat bei Feuchtigkeiten von über 20% auf und ergab schlecht geordnete Beugungsmaxima von 11–12 Å. Die K-gesättigtem Vermiculite neigten dazu, die zusammengeklappten Gitter beizubehalten und wiesen Beugungsmaxima von 10–10.6 Å mit ganzzahligen, höheren Ordnungen auf. Wie aus der Spitzenasymmetrie oder dem Auftreten einer geringen 14,3 Å Linie hervorgeht, tritt bei höheren Feuchtigkeitsgehalten etwas Hydratation auf, jedoch herrschen die zusammengeklappten Abstände vor. Mit zunehmender Austauschkapazität nahm die Neigung des Vermiculits zur Hydratation ab.

Die Unterschiede in den Eigenschaften können sowohl mit der Ladungsquelle als auch mit der Ladungsmenge in Beziehung gebracht werden. Hingegen konnte eine Kontinuum in den Quell- und Zusammenklappeigenschaften der Smectite und Vermiculite nicht beobachtet werden. Die Daten

deuten auf zwei getrennte Systeme hin. Diese Eigenschaften können als differenzierende Kriterien für die Identifizierung herangezogen werden.

Резюме—Образцы сукновальных глин и вермикулитов изучались: (1) для определения эффекта источника и размера изменения; (2) для определения наличия непрерывности свойств, и (3) для усовершенствования базиса отличающих критериев, требуемых для отождествления.

Монтмориллониты вспучиваются до эквивалента двухслойного комплекса при сольватации конденсацией этиленгликоля или паров глицерина. Бейделлит показал однослойный комплекс с парами глицерина, а двухслойный комплекс с этиленогликолем. Образцы вермикулита не дали регулярных двухслойных комплексов независимо от пропитывающего катиона, предшествующей влаги или сольватирующего агента. Соответствуют они расстояниям прибл. 13, 6; 14, 0; 14, 3; 15, 0 и 15, 3 А. В одном и том же образце может присутствовать по два комплекса или более.

Как насыщенные калием вермикулиты, так и сукновальные глины показали в сухой атмосфере обрушенные слои. Гидратация сукновальных глин произошла при влажности свыше 20% и дала впоследствии плохо распределенные дифракционные максимуму 11-12 А. Насыщенные калием вермикулиты обычно сохраняют обрушенную решетку и показывают дифракционные максимумы 10-10,6 А при интегрально более высоком порядке. Некоторая гидратация произошла, как это доказывается пиковой ассиметрией или появлением небольшой линии 14,3 А при более высоких влажностях, хотя преимущественным были обрушенные расстояния. По мере увеличения обменной способности уменьшилась склонность вермикулита гидратироваться.

Разницу в свойствах можно сопоставить как с источником, так и с размером заряда. Несмотря на это, непрерывность свойств увеличения в объеме и обрушения между сукновальными глинами и вермикулитами не наблюдалась. Свойствами этими можно пользоваться как различающими критериями для отождествления.