FACTORS AFFECTING POTASSIUM FIXATION AND CATION EXCHANGE CAPACITIES OF SOIL VERMICULITE CLAYS

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Abstract – Soil vermiculite clays of varying tetrahedral and octahedral composition and cation exchange capacity (CEC) were examined for their ability to *fix* K^+ in both the *wet* and *dry* states. Fixation capacity, expressed as per cent of the CEC, in the wet state was fairly high for most samples but it was enhanced greatly upon drying the K saturated samples. This enhancement indicated that each sample contained a number of vermiculite species with different CECs.

The vermiculite clays, as a group, exhibited a much higher *fixation capacity* at a much lower CEC than those of the coarse grained vermiculites. This enhanced fixation is believed due to the dioctahedral nature of the coarse grained vermiculites. In samples of nearly equal CECs only those containing Al^{3+} in tetrahedral positions exhibited an enhanced *fixation* capacity in the dry state but not in the wet state.

In was remarkable to find that the state of oxidation of crystal structure iron strongly affected the *fixation* and the CEC. Reduction of Fe^{3+} to Fe^{2+} caused a *decrease* in *fixation* even though the CEC increased as a result of this change. Conversely these reactions and their effects were found to be reversible.

The variation in the orientation of the dipole of the hydroxyl ion in the octahedral layer with respect to the cleavage plane of the crystal is believed to be responsible for some of the noted differences.

INTRODUCTION

THE RECENT finding by Barshad and Kishk (1969) that large variations exist in the chemical and physical properties among several species of soil vermiculite clays offered us an opportunity to reassess some of the factors which have been shown to or have been thought to affect the fixation of K^+ or NH_4^+ as defined by Barshad (1951/54), namely, the amount of adsorbed K^+ which is not replaceable by NH_4^+ or the amount of adsorbed NH_4^+ not replaceable by K^+ by repeated extraction of a K or an NH_4 saturated sample with an NH_4 or a K salt solution.

As seen in Table 1 the samples studied represent two species of vermiculites: those with and those without Al^{3+} in tetrahedra, species with Al^{3+} in octahedra but with small amounts of Fe^{3+} and Mg^{3+} or species with very little Al^{3+} in octahedra but with high amounts of Fe^{3+} and Mg^{3+}. Most samples tend to be more dioctahedral than trioctahedral and most of them had a lower cation exchange capacity (CEC) than coarse grained vermiculites. It varies from 150 to 250 me/100g. Furthermore it was found that octahedral Fe^{3+} can

be reduced to Fe^{2+} by sodium dithionite ($Na_2S_2O_4$) and that this Fe^{2+} can be reoxidized by sodium hypochlorite (NaOCl). The reduction of Fe^{3+} to Fe^{2+} caused a gain in the cation exchange capacity but the reoxidation eliminated this grain.

In light of these variations in the samples, the factors considered to affect fixations were: (1) drying, i.e. K^+ or NH_4^+ fixation by samples which were either wet or dried at 110°C immediately after being saturated with K^+ or NH_4^+. (2) magnitude of the layer charge or the cation exchange capacity (CEC). (3) isomorphous substituion of Al^{3+} for Si^{4+} in tetrahedral positions. (4) variation in chemical composition of the octahedral layer in terms of dioctahedral versus trioctahedral species, in terms of the presence of Al^{3+} vs. Fe^{3+} and Mg^{2+}, and in terms of the state of oxidation of octahedral iron, i.e. Fe^{3+} vs. Fe^{2+}.

MATERIALS

The vermiculite clays previously described (Kishk and Barshad, 1969; and Barshad and Kishk, 1969) were used in the present study. The suspensions of the clays after they were obtained from dispersed Na saturated and organic matter free soils were used and termed here "wet" stock in contrast to "dry" stock used previously (Barshad

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127

Table 1. Tetrahedral and dominant octahedral cations, and interlayer exchangeable Na^+ in soil vermiculite clays when their octahedral Fe was either in the natural occurring Fe^{3+} state, or in an artificially induced Fe^{2+} state, or in an artificially induced Fe^{3+} state after being in the Fe^{2+} state

Sample No.*	Moles per 10 oxygens and 2 hydroxyls											
	Tetrahedral		Octahedral				Interlayer Na^+					
	Si	Al	Al	Fe^{3+}	Mg	Σ	Natural Fe^{3+} state		Artificial Fe^{2+} state		Artificial Fe^{3+} state	
1	2·9	1·1	1·44	0·16	0·27	2·36	0·61	166†	0·60	160†	0·60	160†
2	2·9	1·1	1·47	0·21	0·25	2·40	0·64	173	0·66	178	0·66	178
3	3·2	0·8	1·24	0·20	0·35	2·24	0·64	166	0·70	182	0·67	173
4	2·9	1·1	0·93	0·44	0·46	2·40	0·67	182	0·60	164	0·60	163
6	3·8	0·2	0·20	0·55	1·11	2·28	0·82	185	1·00	226	0·83	188
7	3·2	0·8	0·77	0·55	1·87	3·38	0·59	152	0·71	180	0·61	156
8	4		0·33	0·49	1·26	2·22	0·68	168	0·78	193	0·62	154
9	4			0·47	1·91	2·44	0·82	207	0·92	233	0·78	196
10	4		0·88	0·42	0·66	2·06	0·63	161	0·77	196	0·59	150
11	4			0·90	1·22	2·17	0·81	204	1·00	256	0·69	174

*1 Taiwan; 2 Josephine; 3 Melbourne; 4 Shover; 6 Neuns; 7 Yorkville; 8 Aiken; 9 Sweeney; 10 Auburne; 11 Boomer (Barshad and Kishk, 1969).

†m-equiv./100 g.

and Kishk, 1969). Removal of the clays from suspension and drying were avoided prior to saturation with K^+ or $NH_4{}^+$.

METHODS

Preparation of Na saturated clay samples with either reduced (Fe^{2+}) or oxidized (Fe^{3+}) crystal structure iron

To insure that adsorbed acidity would not interfere in the cation exchange capacity (CEC) and fixation measurements (Barshad, 1954a; Barshad and Kishk, 1969), the following procedure was used in preparing clay samples with either completely reduced or completely oxidized crystal lattice iron and free of adsorbed fixed aluminum.

To a portion of each of the "wet" stock suspensions enough sodium citrate was added so that the suspension became 1N with respect to sodium citrate. The pH was then raised to pH 7·5 with a solution of 2% $NaHCO_3$ and heated to 70°C. Powdered sodium dithionite was added to the suspension in small increments until the color of the clay ceased to change. The suspensions were centrifuged and re-extracted three times with 0·2 N NaCl to replace nearly all of the Na citrate–Na dithionite solution. The clays were then taken up with a solution having a concentration of 0·5 N with respect to NaCl and 0·2 N with respect to NaOH and heated to 70°C for 3 hr. The clay suspensions were centrifuged, and after the supernatant liquid was removed they were washed by using centrifugation with a solution of NaOH at

pH 9 for at least 2 times or until they could be resuspended without flocculation. These suspensions were divided into two aliquots. To one aliquot a solution of 5% sodium hypochlorite at pH 9·5 was added and left standing on a steam bath for 24 hr. During these 24 hr additional amounts of the sodium hypochlorite solution was added to the suspensions to insure that all of the Fe^{2+} was reoxidized to Fe^{3+}.

The two aliquots were centrifuged and after extracting them once with 0·2 N NaCl they were washed, using centrifugation, with a solution of NaOH at pH 9·0, until free of Cl^- ions. Each aliquot was resuspended into a stable suspension and the concentration of clay determined by drying a known aliquot at 110°C and weighing.

The state of oxidation of the crystal structure iron was verified to exist in the intended state by chemical means.

Measurement of the cation exchange capacity. Aliquots of the suspensions containing 0·2–0·5 g samples were extracted three times by means of centrifugation and redispersion over a period of 48 hr with a neutral N solution of either NH_4OAc or $MgCl_2$ and the Na^+ was determined in the extracts by flame photometers. Nearly identical results were obtained in the two solutions.

Measurement of K^+ and $NH_4{}^+$ fixation. After the concentrations of the Na^+ saturated clay suspensions were determined, the fixation studies were carried out on the clays with the reduced iron and on those in which the iron was first reduced and then reoxidized.

To determine the "fixation" the following measurements were made: (1) Proper duplicated aliquots of each suspension (15–25 ml or about 0·2 g of clay) were placed in centrifuge tubes to which was added either neutral N ($NH_4OAc + NH_4Cl$) or N ($KOAc + KCl$) to saturate the clays either with NH_4^+ or K^+. The suspensions were centrifuged and then the clays were extracted repeatedly (3 times) with these solutions over a period of 48 hr. All the extracts were collected in a 100 ml volumetric flask and the Na^+ was determined in them by flame photometry. (2) Immediately after the last extraction with the NH_4^+ or K^+ salt solution, the samples were thoroughly washed with neutral methanol until freed of soluble salts (as indicated by the absence of Cl^- using $AgNO_3$ as indicator). (3) One of the sets of the K or NH_4 saturated samples was dried at 110°C for 24 hr but the other set, while still wet with the alcohol, was extracted either with neutral 1N NH_4Ac or with neutral 1N KAc, depending on whether the samples were K saturated or NH_4 saturated. (Thus the K saturated samples were extracted with the NH_4 salt solution and NH_4^+ saturated samples were extracted with K salt solution). Three extractions, each with 25 ml of solution, were made over a period of 48 hr. The same procedure was carried out on the samples which were dried in the oven. The NH_4^+ was determined in the extracts of the K salt solution by distillation in a Kjeldahl apparatus, and K^+ was determined in the extracts of the NH_4 salt solution by flame photometry. (4) The amount of NH_4^+ or K^+ "fixed" by the samples was determined by subtracting from the CEC, as measured by the exchangeable Na^+ replaced by Mg^{2+} or NH_4^+, the amount of NH_4^+ replaced by K^+ or the amount of K^+ replaced by NH_4^+ (Barshad, 1951). This method for determining fixation may in fact be more reliable than a direct measurement of the amount of K^+ and NH_4^+ retained as determined by total chemical analysis particularly if the "fixed" K^+ or NH_4^+ had induced "trapping" of Na^+ (Barshad, 1954a). For the sake of brevity the results of K^+ fixation only will be reported herein (Table 3) since those of NH_4^+ fixation were nearly identical.

X-ray measurement. To ascertain whether K^+

Table 2. X-ray $d(001)$ spacings (Å) for the vermiculite and montmorillonite fractions of the $<2\ \mu$ soil clays

Soil No.	Fe in Fe^{3+} state		Fe in Fe^{2+} state		
	Wet Na^+ Form*	Wet K^+ Form*	Wet K^+ Form*	Dry K^+ Form (250°C)	Rewetted K^+ Form†
1	14·45 (VS)	14·06 (VS)	14·06 (VS)		
	12·34 (S)	12·06 (W)	12·06 (S)		
		10·60 (W)	10·60 (W)	10·32 (S)	10·32 (S)
2	14·39 (VS)	13·94 (VS)	13·94 (S)		
		10·15 (W)	10·15 (W)	10·05 (VS)	10·12 (S)
3	14·66 (VS)	14·13 (VS)	13·94 (VS)		
		10·25 (W)	10·25 (W)	10·12 (VS)	10·12 (S)
4	14·26 (VS)	13·75 (VS)	14·06 (S)		
		10·60 (W)	10·60 (W)	10·60 (VS)	10·60 (S)
6	14·45 (VS)	14·19 (VS)	13·63 (VS)	12·85 (S)	12·64 (M)
		10·12 (S)	10·12 (S)	9·99 (S)	9·99 (S)
7	14·26 (VS)	13·94 (VS)	13·94 (VS)	12·90 (S)	13·29 (M)
		10·28 (S)	10·02 (S)	10·05 (S)	10·05 (S)
8	14·32 (VS)	14·32 (VS)	14·32 (S)		12·13 (VVW)
		10·22 (S)	10·22 (S)	10·02 (VS)	10·02 (VS)
9	18·27 (S)				
	14·66 (S)	14·32 (VS)	14·20 (VS)		13·57 (M)
		10·35 (W)	10·35 (W)	10·18 (VS)	10·18 (S)
10	18·49 (M)				
	14·45 (VS)	14·06 (VS)	14·13 (VS)		13·69 (M)
		10·22 (W)	10·22 (W)	10·05 (VS)	10·09 (S)
11	18·40 (VVW)				
	14·66 (VS)	14·06 (VS)	14·06 (VS)		
		10·22 (S)	10·22 (S)	10·18 (VS)	10·18 (S)

VS = Very strong; S = Strong; M = Medium; W = Weak; VW = Very weak.
*Glycerated salted pastes (Barshad, 1960).
†Rewetted with glycerol after drying at 110°C.

Table 3. Fixation of potassium by whole sample as measured by the loss in cation exchange capacity (CEC) upon K^+ saturation†

Sample No.	Fe in Fe^{3+} state			Fe in Fe^{2+} state		
	CEC ‡	K^+ fixation		CEC ‡	K^+ fixation	
		Wet state	Oven dry state		Wet state	Oven dry state
	m-equiv.*	m-equiv.*	m-equiv.*	m-equiv.*	m-equiv.*	m-equiv.*
1	62	7	36	62	7	36
2	91	22	59	91	22	59
3	93	26	63	97	20	51
4	74	31	46	81	21	33
6	78	35	52	101	23	55
7	70	32	50	81	28	52
8	82	34	57	100	42	58
9	109	34	69	129	23	73
10	85	27	48	109	32	58
11	97	39	61	135	43	74

*Per 100 g on the ignited basis without free oxides.

†As determined by leaching with neutral normal NH_4OAc of Na saturated and K saturated samples.

‡As determined by the amount of Na replaced by neutral normal NH_4OAc or $MgCl_2$ from the Na saturated samples in their suspended state.

"fixation" was accompanied by changes in the crystal lattice, X-ray analyses by Barshad's procedure (1960) were made of the glycerol saturated K^+ samples immediately after saturation while still wet with alcohol and also after drying. The results are reported in Table 2.

RESULTS

Calculation of fixation in relation to vermiculite content. To relate the amount of "fixed" K^+ to the vermiculite, it was necessary to calculate the "fixation" in relation to the content of vermiculite and its cation exchange capacity. This was done by the following steps: (1) The cation exchange capacity (CEC) of the clays, as determined by replaceable Na^+ with Mg^{2+}, was converted to the ignition basis. This was made possible by the measurements reported previously (Barshad and Kishk, 1969). (2) The mineralogical composition as previously determined on the samples as a whole were recalculated on the *oxide free* basis. (3) To calculate the contribution of exchangeable cations of the vermiculite fraction to the whole clay sample with the Fe^{3+}, the contribution of *the other* minerals present in the sample was first calculated by multiplying the CEC of these minerals (as given by Barshad, 1965) by their percentages in the samples, and then subtracting these amounts from the total CEC. The remainder was then assigned to the vermiculite fraction. By dividing

this amount by the vermiculite content the CEC of the vermiculite was obtained. For the samples in which montmorillonite was also present, an "average" CEC for the montmorillonite + vermiculite was also calculated by dividing their combined contribution of exchangeable ion to their *sum* in the sample. This calculation was necessary for proper interpretation of the "fixation" data, as will be discussed later. (4) To express "fixation" as a "capacity", assuming that vermiculite alone or that both vermiculite and motmorillonite cause fixation, the amounts of "fixed" K^+ were first divided either by the exchangeable cations contributed only by vermiculite or by the exchangeable cations contributed by both vermiculite and montmorillonite and then multiplied by 100. When this product is multiplied by the cation exchange capacity of the vermiculite or by the "average" CEC of the sum of vermiculite + montmorillonite, one obtains in m-equiv./100 g the amounts of K^+ fixed by vermiculite or by vermiculite + montmorillonite. The results of these calculations are summarized in Table 4.

Fixation on the "wet" vs. the dry state. To assess the effect of the CEC on the extent of fixation in the wet state vs. the dry state of the clays, it was assumed that the fixation which occurred while the sample remained in the wet state took place only in a fraction of the sample which possessed a cation exchange capacity of either 250 m-equiv/

Table 4. Calculated cation exchange capacities and potassium fixation capacities of soil vermiculite clays

Sample No.	Fe in Fe³⁺ state				Fe in Fe²⁺ state			
	CEC (m-equiv.*)	K⁺ fixation capacity (%)†		Increase in fixation by oven drying (%)	CEC (m-equiv.*)	K⁺ fixation capacity (%)		Increase in fixation by oven drying (%)
		wet state	oven dry state			wet state	oven dry state	
1	160	15	80	65	160	15	80	65
2	178	28	76	48	178	28	76	48
3	173	32	79	47	182	23	61	38
4	163	42	65	23	164	31	49	18
6	188	53	79	26	226	26	63	37
7	156	64	99	35	180	49	89	40
8	154	48	80	32	193	47	66	19
9	196	49	100	51	233	28	89	61
10	150	51	91	40	196	46	83	37
11	173	48	67	19	256	40	63	23
	When both vermiculite and montmorillonite fix K⁺							
9	169	32	66	34	201	19	50	31
10	145	36	63	27	190	32	58	26
11	169	48	76	28	250	36	62	26

*m-equiv./100 g.
†per cent of CEC.

100 g or 220 m-equiv/100 g. At these values, tri-octahedral vermiculites alter to micas upon adsorption of K⁺ in the wet state. These values amount to 1·0 equivalent and 0·8 equivalent of K⁺ per structural formula (of 10 O⁼ and 2 (OH)⁻). The amount of this fraction in a sample was assumed to be equal to the percentage fixation in the wet state. Consequently, the increase in fixation which occurred upon drying was attributed to the rest of the sample. By multiplying the per cent of "wet" fixation by 250 or 220 one obtains the contribution of exchangeable cations of the fraction which causes "wet fixation". Upon subtracting this amount from the CEC of the vermiculite in the sample, or from the average for the vermiculite + montmorillonite, one obtains the amount of exchangeable cations attributable to the fraction which fixes only upon drying. Dividing this amount by the per cent "wet replaceable" cations and multiplying by 100 one obtains the CEC of this fraction. To calculate the per cent fixation upon drying for this fraction of the sample, one divides the increase in the amount of fixed cations by the calculated CEC of the sample and multiplies by 100. The results of these calculations for the samples when wet fixation was assumed to occur at a CEC of 220 me/100 g, are given in Table 6. The results when wet fixation was assumed

to occur at a CEC of 250 me/100 g are not given here for a reason which will be discussed later.

Effect of Fe³⁺ vs. Fe²⁺ on fixation. To assess the effect on fixation of crystal structure ferric (Fe³⁺) vs. ferrous (Fe²⁺), it is necessary to calculate the changes in fixation in relation to the changes in the CEC of the vermiculite. This can be done by assuming either that fixation in the wet state occurs in the sample as a whole, and then calculate the changes in fixation for both the wet and the dry states in comparison with the change in the CEC, or that fixation in the wet state occurs at 220 m-equiv./100 g and then calculate the change in fixation in the material which fixes only upon drying. The results of these calculations are given in Tables 5 and 6, respectively.

DISCUSSION OF RESULTS

Effect of drying and magnitude of layer charge on fixation. It is quite evident from the results of Tables 3 and 4 that drying the K saturated samples prior to replacement causes a large increase in fixation in all samples. Previous studies of fixation in trioctahedral coarse grain vermiculite (Barshad, 1960, 1965), indicated that fixation in the wet state occurred only in species with a high CEC equal to about 250 m-equiv./100 g ignition basis. Therefore the cation exchange capacities

Table 5. Change in K^+ fixation due to reduction of crystal structure
Fe^{3+} to Fe^{2+}

Sample No.	Change in CEC (m-equiv.*)	Change in fixation in the wet state (%)	Change in fixation in the dry state (%)
1	0	0	0
2	0	0	0
3	9	−9	−18
4	1	−10	−16
6	56	−15	−10
7	24	−27	−16
8	39	−1	−14
9	37	−21	−11
10	46	−5	−8
11	83	−8	−4

Calculations made assuming that both vermiculite and montmorillonite
"fix" K^+

9	32	−13	−16
10	45	−4	−5
11	81	−12	−14

*m-equiv./100 g ignited basis.

of the vermiculite clays as calculated herein must be assumed to represent an average for species with different CECs. As was indicated previously, to estimate the CEC of the species which *fix* only upon drying, an assumption was made that the samples which *fix* K^+ in the wet state may have had an exchange capacity of either 250 or 220 m-equiv./100 g. Consequently, the CEC for the samples which causes "fixation" only upon drying, assuming that fixation in the wet state, was caused by a species having a CEC of 220 m-equiv./100 g, were given in Table 6. It is seen that the CEC's thus obtained, particularly for the samples with iron in the Fe^{3+} state, are very much lower than those of coarse grained trioctahedral vermiculites (Barshad, 1954b, 1960) in which fixation also occurs only after drying.

The cation exchange capacities of these species are even lower when the assumption is made that the CEC of the species in which fixation occurs in the wet state is 250 m-equiv./100 g.

As compared with *fixation* for montmorillonites (Weir, 1965) many of the samples should not have exhibited any *fixation* in the dry state. But since fixation did occur one must conclude that fixation even in the wet state must have occurred in the clay vermiculite samples, particularly in those with the Fe^{3+} iron, at a *much* lower CEC than *220 m-equiv.* This is also true for several of the samples with the Fe^{2+} iron and containing tetrahedral Al^{3+}.

These results, therefore, lead to an important conclusion that in soil vermiculite clays K^+ fixation occurs at a much lower CEC than in trioctahedral coarse grained vermiculites.

Effect of the cation exchange capacity and Al^{3+} substitution in tetrahedral layer on fixation. To compare *fixation* among different samples which may have different ratios of external vs. internal surfaces and without knowing this ratio may lead to erroneous conclusions since *fixation* itself depends on this ratio. Nevertheless it is of interest to compare the *fixation* among the samples with the assumption that this ratio is more or less the same for all the samples since the particle size of these samples is in the colloidal range.

Fixation in the wet state. If we assume that fixation occurs only in the vermiculite fraction of the sample and that it is not confined to a fraction with a CEC of 220 m-equiv./100 g or higher, then a comparison does *not* show a direct proportionality between fixation of K^+ and CEC. There is a considerable variation in CEC for a given value of fixation. Similarly for fixation in the wet state there appears to be no correlation between fixation and presence or absence of tetrahedral Al^{3+}.

Fixation in the dry state. If we assume that fixation occurs not only in the vermiculite fraction but also in the montmorillonite fraction, then there appears to be an effect of tetrahedral Al^{3+} on fixation particularly for the samples with iron in

Table 6. Calculated cation exchange capacities and potassium fixation capacities for the fraction of the samples that fixes only upon drying. (Assuming that wet fixation occurs at 220 m.e./100 g)

Sample No.	Fe in Fe^{3+} state		Fe in Fe^{2+} state		Change in % fixation due to reduction of Fe^{3+} to Fe^{2+}
	CEC (m-equiv.*)	K^+ fixation capacity (%)†	CEC (m-equiv.*)	K^+ fixation capacity (%)	
1	110	74	110	74	0
2	162	52	162	52	0
3	152	53	170	41	−12
4	123	31	122	25	−6
6	151	32	265	34	+2
7	105	38	152	67	+29
8	92	54	170	21	−33
9	173	57	238	60	3
10	78	76	176	41	−35
11	131	24	330	22	−2
Calculations made assuming that both vermiculite and montmorillonite "fix" K^+					
9	133	42	196	34	−8
10	103	39	154	32	−7
11	121	40	230	28	−12

*m-equiv./100 g ignited basis.
†Per cent of the CEC.

the Fe^{2+} state. This is even more noticeable when a comparison is made assuming fixation in the wet state occurred at a constant high CEC and that both vermiculites and montmorillonites cause fixation as seen in Table 6. This effect may be summarized by stating that for a given CEC *fixation* of K^+ is higher for those samples with tetrahedral Al^{3+} than for those without tetrahedral Al^{3+} or that fixation is equal for samples with tetrahedral Al^{3+} to those without tetrahedral Al^{3+} even though their CECs are lower. This conclusion is in agreement with that of Wear and White, 1951.

The effect on the CEC and on fixation of reduction of crystal structure iron from Fe^{3+} *to* Fe^{2+}. A comparison of the CEC of the sample in the "natural" state, the "reduced" state, and the "reoxidized" state (Table 1) clearly indicates that the "reducing" action of sodium dithionite caused an increase in the CEC, whereas the oxidizing action of sodium hypochlorite eliminated this increase. In several samples the CEC of these treated samples was even lower than in their "natural" state, particularly in those samples which appeared to contain Fe^{2+} iron in the natural state, as indicated by their bluish green color in that state. From the change in color in the samples during these treatments, it is believed that the effects of these treatments resulted from their effect on the crystal structure iron. The sodium

dithionite treatment reduced the Fe^{3+} to Fe^{2+}, whereas the sodium hypochlorite oxidized it back to Fe^{3+}. This was confirmed by another study on biotites (Barshad and Kishk, 1968).

It can be concluded from these findings that it is practically impossible to determine the CEC of a clay mineral in its "natural" state as it occurs in a soil since a soil must always be treated in some way in order to "extract" the clay from it and to prepare it for the measurement.

It may be seen in Tables 5 and 6 that even though the CEC increased markedly upon reduction of Fe^{3+} to Fe^{2+}, the *fixation* for most samples decreased for both the *wet* and the *dry* state and whether or not one assumed that fixation in the wet state occurred at a constant level of CEC.

Anomalies. Some of the variations in *fixation* among the samples appear to be contrary to the factors which have been shown to affect fixation. These are as follows: (1) K fixation for sample No. 7 with Fe^{3+} iron in relation to its CEC is much higher than for most other samples. It is suggested that this may be a result of a higher ratio of internal to external surfaces in this sample than in any of the other samples. On the other hand sample No. 11 even though it has one of the highest CEC has one of the lowest fixation values. This possibly could be attributed to a low ratio of internal to external surface areas. (2) A comparison of fixation

among the samples without tetrahedral aluminum (Nos. 8, 9, 10, and 11) shows that sample No. 10 even though it has the lowest CEC has as much or higher fixation of K^+ than samples with a much higher CEC.

Changes in interlayer expansion upon K^+ saturation. The following observations were made regarding the effect of K^+ saturation on the $d(001)$ diffraction peaks which represent the extent of the interlayer expansion: (1) Extensive interstratification of 10 Å and 14 Å layers of either the Na or K saturated samples were nearly absent (No. 1 is the only exception). (2) The wet K saturated samples still retained the 14·5 Å spacing while exhibiting in addition the 10 Å which represents a contracted $d(001)$ spacing. (3) All the expanded $d(001)$ spacings of the K saturated samples disappeared upon heating to 250°C except for those of Nos. 6 and 7 (Yorkville and Neuns) — the two samples which contain chlorite. The 12·90 Å and 12·85 Å spacing, which these samples exhibit, represent interlayering of 10 Å and 14·5 Å materials. (4) All of the heated K saturated samples, except for those containing montmorillonite (Nos. 8, 9 and 10), did not exhibit expanded $d(001)$ spacing even after rewetting them with glycerol. The expanded $d(001)$ spacing of the samples containing montmorillonite represented interlayering of 10 Å and 14·5 Å materials.

Presence of montmorillonites with higher CEC than previously reported. The reduction of the Fe^{3+} to Fe^{2+} in the three samples which contain montmorillonite causes a large increase in CEC of the sample as a whole, and unless one assigns some of this increase to montmorillonite, the CEC of the vermiculites, which is obtained by calculation, is too high. It exceeds *one* equivalent per structural formula. When the increase in CEC is distributed to both vermiculite and montmorillonite, as explained previously, it is possible to calculate the CEC of the montmorillonites in their Fe^{2+} state. These values for sample Nos. 9, 10 and 11 were 154, 172 and 162 me/100 g, respectively. From a point of view of classification, (Walker, 1957, 1958) these minerals should be considered vermiculites rather than montmorillonites. In their X-ray patterns, however, the Na saturated form of No. 9 and No. 10 still possessed an 18·4 Å spacing but with a considerably weaker intensity than that of the samples with Fe^{3+} iron. In sample No. 11, however, the 18·4 Å spacing completely disappeared from the reduced form.

CONCLUSIONS

Two interesting conclusions emerge from the results as a whole which shed new light on the factors which appear to affect fixation: (1) the vermiculite clays as a group tend to fix K^+ at a much lower level of CEC than the coarse grained vermiculites even though they are much smaller in particle size, and (2) in the same sample a reduction of crystal structure iron from Fe^{3+} to Fe^{2+} causes a decrease in fixation even though there is an increase in CEC, or vise versa, oxidation of Fe^{2+} to Fe^{3+} causes an increase in fixation even though the CEC decreases. Both conclusions are therefore contrary to previous findings (Barshad, 1954b), namely, that fixations of NH_4^+ and K^+ is directly proportional to the CEC.

Dioctahedral nature of vermiculite clays. An explanation for the first conclusion is believed to emerge from the finding that in their composition vermiculite clays tend to be more dioctahedral than trioctahedral.

That this difference could affect fixation was suggested by Bassett (1960) on the basis of the difference in the orientation of the dipole of the hydroxyl ions in the octahedral layer of trioctahedral vs. dioctahedral micas. In trioctahedral micas the hydroxyl ions are oriented with their dipoles perpendicular to the cleavage plane whereas in dioctahedral micas the hydroxyl ions are oriented with their dipoles inclined to the cleavage plane. This difference in inclination of the O—H dipole places K^+ in the *contracted* crystal lattice in a more negative environment in a dioctahedral structure than in a trioctahedral structure. Consequently the K^+ is held much more tightly in the dioctahedral than in the trioctahedral micas of K saturated vermiculites and conversely this difference could bring about fixation of K^+ at a much lower interlayer charge in the former than in the latter vermiculite types. This is particularly true upon dehydration when the K^+ ions are forced into the hexagonal cavities of the oxygen interlayer surfaces. The noted anomaly of sample No. 10, the one sample with the lowest CEC among those without tetrahedral Al^{3+} but with the highest K^+ fixation capacity, could be advanced as evidence that the dioctahedral nature of a mineral favors or enhances fixation since this sample is the only one of this group that is entirely dioctahedral.

Although there is little direct data in the literature in support of the conclusion of the present study that dioctahedral vermiculites tend to fix K^+ at a lower charge than trioctahedral vermiculites, there is considerable data which indirectly supports this conclusion. A part of this data deals with the ease of replacement of "native" K^+ from various forms of micas, and a part deals with the K_2O content of weathered micas and illites.

Evidence from replacement studies of native K^+ which indicates that K^+ in dioctahedral micas or in trioctahedral micas with a large substitution of

F^- for OH^- (which places K^+ in the same type of environment as in the dioctahedral micas) is more difficult to replace by artificial weathering than from trioctahedral micas, can be found in papers by Bassett (1960), Rausell-Colom, *et al.* (1965), Scott and Smith (1966) and Raman and Jackson (1965). Scott and Smith's data indicate that K^+ is not only more difficult to replace from muscovite than from biotite at an equal interlayer charge but that it is more difficult to replace the K^+ even at a very much reduced charge – as that of an illite with a charge of 160 m-equiv./100 g as compared with that of a biotite with a charge of about 200 m-equiv./100 g even though the illite has clay size particles and biotite has coarse grain particles. That K^+ is difficultly replaceable from dioctahedral illites even though their K_2O content ranges from 150 to 170 m-equiv./100 g was also found by Raman and Jackson (1966). An intensive period of treatment with 0·2 N sodium tetraphenylboron in 1 N NaCl for over 81 days (which is effective in replacing all the interlayer K^+ in trioctahedral micas – according to Scott and Smith, 1966) enabled them to replace only a small fraction of the total K^+ of the sample. De Mumbrum (1959) was one of the first to recognize that the "dioctahedral" nature of muscovite attributes to it a stronger fixing property for K^+ than trioctahedral mica. He states on page 194 "below 7·5% K_2O the mineral (muscovite) gained moist K-fixing capacity a property not typical of the trioctahedral micas at comparable total K values".

The experimental work of White (1956) and Cook and Rich (1962) using molten $LiNO_3$ to replace interlayer K^+ from muscovite indicated that upon reducing the interlayer charge to about 160 m-equiv./100 g brought about a drastic reduction in the ability of the $LiNO_3$ to replace K^+. At this level the "expanded" muscovite tended to "fix" any K^+ that was replaced by the Li^+ from the K^+ still left in the muscovite. This is in contrast to the finding of Barshad (1954b) that trioctahedral vermiculite hardly "fixed" any NH_4^+ or K^+ at 160 m-equiv./100 g exchange capacity.

The mere findings that most mica clays (illites) which accumulate in soils or in clay deposits are dioctahedral and are able to retain their structure even though their K_2O content is much lower than in pure muscovite and ranging from about 6 to 8 per cent [Gaudette *et al.* (1966), Weaver, 1958, 1965], or from about 0·6 to 0·75 equivalents of K^+ per structural formula [$O_{10}^{2-}(OH)_2^-$, is good evidence supporting the finding of this study that the *dioctahedral* nature of the vermiculite clays imparts to them the ability to *fix* K^+ or NH_4^+ at a much lower interlayer charge than *trioctahedral vermiculites*.

In view of the finding of the present study, it may

be concluded that the K^+ "fixing" clay named by Van der Marel (1954) "ammersooite" is simply a dioctahedral vermiculite and the "unusual" properties found by Van der Marel can be explained by its dioctahedral nature.

Effect of the state of oxidation of crystal lattice iron. The increase in "fixation" of K^+ upon oxidation of Fe^{2+} to Fe^{3+}, in spite of a concurrent decrease in interlayer charge, is believed to be due to a change in the orientation of the dipole of the hydroxyl ions in the octahedral layer from a perpendicular to a more inclined position to the cleavage plane. Recently this change was confirmed by Farmer, Russel, and Ahlriches (1968) and by Juo and White (1969). K^+ ions, therefore, upon adsorption find themselves in a more negative environment when the Fe is in the Fe^{3+} state than when the Fe is in Fe^{2+} state and hence they are more tightly held and more difficult to replace.

There is some evidence in the literature which tends to correlate the replaceability of native K^+ in mica with the state of oxidation of crystal lattice iron. Scott and Smith (1966) found that the rate of replaceability of K^+ from biotite was lower than from phlogopite even though both minerals had nearly equal interlayer charge before replacement and that the interlayer charge of the biotite was decreasing during the replacement. We suggest that this difference was caused by the oxidation of some of the Fe^{2+}, which is present in biotite and not in phlogopite, by the treatment which the minerals received during replacement of K^+.

An observation suggesting that the replaceability of K^+ in micas may be affected by the valency of the octahedral cations was made by Rausell-Colom (1965) at the International Clay Conference 1963, Vol. 2, p. 266. He indicated that an increasing amount of trivalent cations "seems to slow the the rate of replacement" of K^+ from micas. He also suggested that "this is probably due to the ability of trivalent ions of displacing the direction of the O—H bond of structural OH from right angles to the silicate sheet, which, in turn, should increase the strength of the K—OH bond".

That the state of oxidation of octahedral iron strongly affects the ease of replaceability of K^+ from biotite was recently demonstrated by Barshad and Kishk (1968).

Presence of species with different CEC. The occurrence of K^+ fixation in wet state and a very large increase in fixation upon drying, associated with the expected changes in interlayer expansion, suggests strongly that within each sample there exist a continuum of species having different cation exchange capacities.

The present results, confirm Barshad's (1960) and Walker's (1957) conclusion that there is a

continuum of clay minerals in the montmorillonite-vermiculite group which are differentiated by their CEC. Furthermore, that by oxidizing or reducing octahedral iron it is possible to transform one mineral into another, particularly those species with a CEC ranging between 150 to 160 m-equiv./100 g.

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Résumé — Des vermiculites de sol argileuses de différente composition tétraèdrique et octaèdrique, ainsi que de différente capacité d'échange de cations (CEC) ont été observées dans leur abilité à fixer K⁺ à l'état *sec* et *humide*. La capacité de fixation, exprimée en % de la CEC est relativement élevée à l'état humide pour la plupart des échantillons, mais elle augmente considérablement lorsque on sèche les échantillons saturés de K. Cette augmentation indique que chaque échantillon contient un certain nombre de vermiculites de CEC différents.

Les vermiculites argileuses, en tant que groupe, présentent une *capacité de fixation* beaucoup plus élevée, à une CEC beaucoup plus basse que celle des vermiculites en gros granulés. Cette fixation accrue est considérée comme étant due à la nature dioctaèdrique des vermiculites argileuses, par opposition à la nature trioctaèdrique des grains grossier. Parmi les échantillons de CEC sensiblement égale, seuls ceux contenant Al³⁺ en position tétraèdrique présentent une *fixation* accrue à l'état sec, mais pas à l'état humide.

Il est remarquable de constater que le degré d'oxydation du fer de structure cristalline affecte

fortement la *fixation* et la CEC. La réduction de Fe^{3+} en Fe^{2+} provoque en *affaiblissement* de la fixation alors même que cette réduction augmente la CEC. Il a également été observé que ces réactions et leurs effets sont réversibles.

La variation de l'orientation du dipôle de l'ion hydroxyle dans la couche octaèdrique, en conjonction avec le plan de clivage du cristal est considérée comme responsable pour une partie des variations observées.

Kurzreferat — Bodenvermiculittone verschiedenartiger tetraedrischer und oktaedrischer Zusammensetzung und Kationenaustauschkapazität (CEC) wurden im Hinblick auf ihre Fähigkeit zur *Fixierung* von K^+ im *feuchten* sowie im *trockenen* Zustand untersucht. Die Fixierungskapazität, ausgedrückt als Prozentsatz der CEC, war für die meisten Proben recht hoch im feuchten Zustand, wurde jedoch durch Trocknen der K-gesättigten Proben beträchtlich erhöht. Diese Erhöhung deutet darauf hin, dass jede Probe eine Anzahl Vermiculitarten mit verschiedenen CEC enthielt.

Die Vermiculittone als eine Gruppe zeigten eine bedeutend höhere *Fixierungskapazität* bei viel niedrigerer CEC als derjenigen der grobkörnigen Vermiculite. Es wird angenommen, dass diese erhöhte Fixierung eine Folge der dioktaedrischen Natur der Vermiculittone im Gegensatz zu der trioktaedrischen Natur der grobkörnigen Vermiculite ist. In Proben mit beinahe gleicher CEC zeigten nur die, welche Al^{3+} in tetraedrischen Stellungen enthalten eine erhöhte *Fixierungskapazität* im trockenen Zustand aber nicht im feuchten Zustand.

Es war interessant festzustellen, dass der Oxydationszustand des Kristallgefügeeisens die *Fixierung* und die CEC stark beeinflusste Eine Reduzierung des Fe^{3+} zu Fe^{2+} verursachte eine *Abnahme* der *Fixierung* obzwar die CEC als Ergebnis dieses Wechsels zunahm. Umgekehrt wurde gefunden, dass diese Reaktionen und ihre Wirkungen reversibel sind.

Es wird angenommen, dass die Veränderung in der Orientierung des Dipols des Hydroxylions in der oktaedrischen Schicht in Bezug auf die Spaltebene des Kristalls für manche der vorgefundenen Unterschiede verantwortlich ist.

Резюме — Была изучена способность почвенных вермикулитовых глин с различными октаэдрическими и тетраэдрическими ионами и с различной способностью к катионному обмену (СКО) фиксировать K^+ как во влажном, так и в сухом состоянии. Способность к такой фиксации, выраженная в процентах от СКО, у большинства глин во влажном состоянии была довольно высокой; после высушивания у образцов, носыщенных калием, она сильно увеличилась. Это указывает, что каждый образец содержал ряд вермикулитов с различными СКО. Глины вермикулитовой группы обнаружили более высокую способность фиксировать калий при значительно более низких значениях СКО, чем грубокристаллические вермикулиты. Предполагается, что усиления фиксация калия вызвана диоктаэдрической природой грубокристаллических вермикулитов. В образцах с почти равной СКО повышенную фиксацию в сухом (но не во влажном) состоянии обнаружили только те, которые содержат Al^{3+} в тетраэдрических позициях. Весьма интересно, что на фиксацию калия и на СКО сильно влияет степень окисления структурного железа. Восстановление Fe^{3+} до Fe^{2+} вызвало уменьшение фиксации калия несмотря на возрастание СКО в результате восстановления железа. Показано, что эти реакции и их результаты обратимы.

Некоторые из отмеченных различий рассматриваются как следствие вариаций в ориентировке диполей гидроксильных ионов в октаэдрических слоях по отношению к плоскостям спайности слоистого силиката.