'VERMICULITE' DETERMINATION ON WHOLE SOILS BY CATION EXCHANGE CAPACITY METHODS*

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Abstract—The proposed method is a modification of one by Alexiades and Jackson (1965). Calcium exchange capacity (CaEC) and potassium exchange capacity (KEC) are determined, after removal of organic matter and free iron oxides, by saturating the exchange complex with centrifuge washings of pH 7 acetate solutions of Ca or K, respectively. Excess salt in solutions remaining in contact with the soil after saturation is determined by measuring the weight and concentration of the excess solution. The exchangeable cations and excess salt are then replaced by centrifuge washings with 1 N acetate solutions of Mg (for CaEC) or NH$_4$ (for KEC), after overnight 110°C oven-drying to enhance K fixation for KEC. The replaced cations are determined and CaEC and KEC values are calculated. Per cent 'vermiculite' is based on the difference between CaEC and KEC (expressed in m-equiv/100 g) and an assumed 'vermiculite' interlayer exchange capacity of 154 m-equiv/100 g; percentage $Vr = (CaEC-KEC/154) \times 100$. The 'vermiculite' interlayer fraction (VIF) of the CaEC may also be calculated; $VIF = CaEC-KEC/CaEC$. The measured 'vermiculite' is shown in quotation marks since the method is open to criticism regarding exactly what is being measured, the assumptions made, etc. and to emphasize that the determination procedure is an operational one for the characterization of cation exchange complexes.

Removal of free iron oxides increased both CaEC and KEC values of several soils but percentage Vr was little affected. The amount of K fixation was affected by the drying treatment employed after K saturation (none vs air-drying vs oven-drying). Thoroughly crushing Montana and African vermiculites dramatically increased their CEC and measured 'vermiculite' values, but had little effect with two samples of saprolite from chloritic metabasalt.

INTRODUCTION

Procedures that determine the content of minerals on a whole soil basis are useful. Carbonate minerals (as CaCO$_3$ equivalent) and free iron oxides have commonly been determined in such a manner, but clay minerals have not. Whole soil analyses may give a more meaningful characterization in practical terms than a particle-size fractionation approach, especially if there are considerable amounts of the minerals of interest in coarse fractions and if the alternative approach would be to study only the mineralogy of the <2 µm clay. Whole soil methods may also, in some instances at least, eliminate the need to do particle-size fractionation and thus save much time.

The Alexiades and Jackson (1965) method for vermiculite determination by cation exchange capacity methods has no inherent assumptions that prevent its application to whole soils. The method is based on the assumption that all the interlayer cation exchange sites

of vermiculite (but not of any other minerals) are blocked by potassium fixation. Thus by measuring the CaEC (calcium exchange capacity; i.e. Ca saturation and Mg replacement) and the KEC (K saturation and NH$_4$ replacement), and by assuming an interlayer exchange capacity for vermiculite (154 m-equiv 100 mg), the vermiculite content may be calculated.

The objectives of this study were to develop, by modification of the Alexiades and Jackson (1965) procedure, a rapid method for the quantitative determination of 'vermiculite' on a whole soil basis and to illustrate the value of this method in characterizing soils and geologic materials. The mineral (minerals) measured by these procedures is (are) identified here as 'vermiculite'. This usage recognizes that what is measured may not coincide with ideal vermiculite (defined, for example, on the basis of layer type, interlayer material and layer charge in the AIPEA nomenclature committee report of *AIPEA Newsletter* No. 7).

MATERIALS AND METHODS

Of primary interest in this work were some vermiculitic soils developed in saprolite from chloritic metabasalt in the Middletown Valley of Maryland. A larger

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study (Coffman, 1972; Coffman and Fanning, 1974) to characterize the nature and the genesis of these soils, was being made and the 'vermiculite' method was developed especially for use in this characterization. The group included here belong to the Fauquier and Myersville soil series. The method was further tested with other materials (see Tables 1, 4 and 6).

In the standard method, approximately 0·5 g samples of air-dried soil, crushed to pass a 2 mm sieve, are quantitatively weighed into 15 ml centrifuge tubes. Four tubes of each soil are weighed in order to duplicate Ca and K saturation. The exchange complex is saturated with Na by adding approximately 10 ml of pH 5, 1 N NaOAc (sodium acetate) buffer (Jackson, 1956) to each tube. The tubes are placed in a water bath at 80°C for 30–60 min, then removed, centrifuged, and the supernatant discarded. The soils are centrifuge washed once more with NaOAc prior to organic matter removal. The NaOAc treatments assure a Na-saturated exchange complex and the somewhat acidic medium that is desirable prior to organic matter removal (Jackson, 1956).

Organic matter is removed from the soils by overnight heating (on a steam hot plate with the tubes in a water bath with 'Handiwrap' draped over the bath and secured with a rubber band to reduce evaporation) with 0·5 ml of 30 per cent H_2O_2 and 2–3 ml of the pH 5 1 N NaOAc. The soil is mixed with the H_2O_2 and NaOAc solution (e.g. with a Vortex mixer) prior to the overnight heating and is centrifuged down and the

out) and dividing by the density of the solution. Corrections to the volume of excess solution are normally not made for the quantity of organic matter or free iron oxides removed, but in cases of removal of large quantities of these substances (or carbonates, which could be removed by cooking in pH 5, 1 N NaOAc, Jackson, 1956) this should be done.

Before replacement of K, the tubes containing the K saturated samples are placed in a 110°C oven overnight. Calcium (potassium for K saturated samples) is replaced from each Ca (K) saturated soil using five centrifuge washings of approximately 10 ml each of 1·0 N MgOAc (NH_4OAc). The wash solutions are collected in a 100 ml volumetric flask, brought to volume with distilled water, and Ca (K) is determined. In the present study the elements were determined by flame photometry with a Technicon AutoAnalyzer. Standard solutions covering a concentration range of 0–60 $\mu g/ml$ are normally sufficient for the determinations. These are prepared in acetate solutions like the unknowns from concentration (500 $\mu g/ml$) standard solutions of Ca or K. The concentrated standard solutions are prepared in water from oven-dried $CaCO_3$, put into solution with a minimum of HCl, or from oven-dried KCl, respectively. From the data, CaEC and KEC values are calculated taking into consideration the exact weight of the soil and the amount of salts in the excess saturating solution.

Per cent 'vermiculite' may then be calculated, equation (1).

$$\% \, Vr = \frac{[\text{CaEC(m-equiv/100 g)} - \text{KEC(m-equiv/100 g)}] \, 100}{154 \, (\text{m-equiv/100 g})} \tag{1}$$

solution discarded the following day. Free iron oxides are then removed following the procedure of Fanning et al. (1970) except that proportionately smaller quantities of solution and dithionite are employed to conform with the smaller sample size.

The tubes are then separated into two groups, one for Ca and the other for K saturation. CaOAc and KOAc solutions, adjusted to pH 7 with acetic acid, are used. The soils are centrifuge washed once with 10 ml of 0·5 N CaOAc or 0·5 N KOAc, then 5 times with 10 ml of 0·1 N CaOAc or 0·1 N KOAc. The concentration of these latter solutions may not be exactly 0·1 N, but the exact concentration is measured at the time the exchanged cations are measured. The supernatant solutions are discarded. After the last 0·1 N wash, the volume of excess solution remaining in the tubes is determined, before any evaporation takes place, by weighing the tubes and subtracting the weight of the tube and soil (recorded when the samples are weighed

Calculations may also be made, equation (2) for the fraction of the total CaEC attributable to 'vermiculite' interlayers (potassium fixing exchange sites). This fraction may be referred to as the 'vermiculite' interlayer fraction, abbreviated as VIF.

$$Vr \text{ interlayer fraction of CaEC} = VIF = \frac{\text{CaEC–KEC}}{\text{CaEC}}. \tag{2}$$

The standard exchange capacity 'vermiculite' method was also applied to particle-size fractions (Tables 2 and 3) obtained by fractionation essentially by the method of Kittrick and Hope (1963). The fractions of fine silt and finer were Ca saturated using $CaCl_2$ and dried from benzene for dry storage. However, all fractions were resuspended and satured with Ca, using Ca acetate, for CaEC determination, or with K, using K acetate, for KEC.

A study was made with certain samples (Table 4) to determine the effect on the exchange properties of removing as opposed to not removing the free iron oxides. The procedures were standard in each case except that the free iron oxide removal treatment was not given to one series of samples.

Studies were also made with samples of a Fauquier soil to compare wet and air-dried K fixation with the standard oven-drying procedure. For the wet K fixation treatment, 1.0 N NH_4OAc was used to replace exchangeable K immediately after K saturation of the soil and weighing for determination of salts in the excess saturating solution. For the air-dried K fixation, the soils were K saturated, excess saturating solution was determined, and then the samples were placed in a desiccator. When the surface of the samples appeared dry, K was replaced.

The effect of agate mortar crushing on measured 'vermiculite' contents was studied with certain vermiculite-rich samples derived from chloritic metabasalt and from biotite (Montana and African vermiculite obtained from Ward's Scientific Establishment) (Table 6). One sample of each material tested was given a standard crushing treatment (so as to pass a 2 mm sieve), and another sample was more finely crushed using an agate mortar and pestle on a motor driven
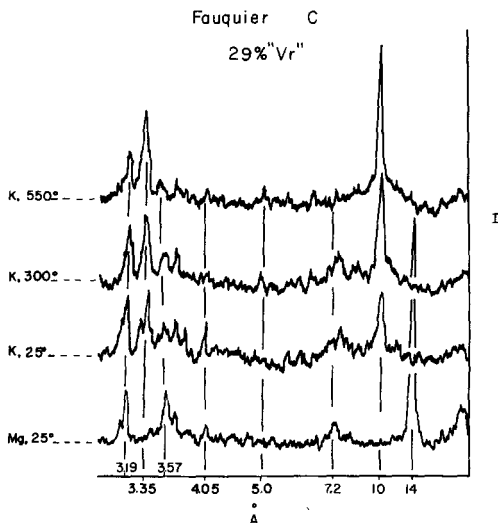

Fig. 1. X-ray diffraction pattern for a vermiculite-rich soil horizon (a Fauquier C horizon, whole-soil crushed for 15 min in an agate mortar on a motor driven turntable prior to Mg or K saturation) which contained 29 per cent 'vermiculite' by the cation-exchange capacity method. Diffraction specimens at 25°C were glycerol solvated. The patterns indicate the presence of vermiculite, feldspars and a trace of kaolinite. A higher estimate of the vermiculite content would probably have been made based on X-ray diffraction patterns alone.
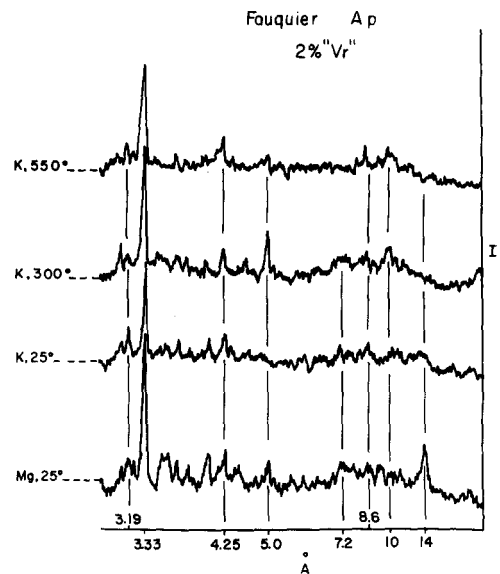

Fig. 2. X-ray diffraction patterns for a soil horizon that contained 2 per cent 'vermiculite' by the cation exchange capacity method (Fauquier Ap horizon, whole soil crushed for 15 min in an agate mortar on a motor driven turntable prior to Mg or K saturation). Diffraction specimens at 25°C were glycerol solvated. The patterns indicate the presence of vermiculite—with some interlayer material preventing complete collapse to 10 Å with K saturation and heat, quartz, feldspars, a trace of kaolinite, and amphibole (peaks at about 8·6 and 3·12 Å). The vermiculite content would probably have been overestimated based on X-ray diffraction patterns alone and may be underestimated by the exchange capacity method if hydroxy interlayers are preventing K fixation by zones of vermiculite between hydroxy-interlayer 'islands'.

turntable with rotation for 30 min. The standard crushing, to reduce the particle size to <2 mm, was done with a machine with rubber rollers in the University of Maryland Soil Testing Laboratory. In the crushing study, 0.3 g samples were employed for exchange capacity determinations, and with the Montana and African vermiculites only three drops rather than the standard 0.5 ml of H_2O_2 was employed.

X-ray diffraction patterns of agate mortar-crushed whole soil samples of the 'vermiculite' rich soils developed from metabasalt were prepared to verify their vermiculite content (Coffman, 1972 and Figs. 1 and 2).

RESULTS AND DISCUSSION

'Vermiculite' content of a variety of soil and geologic materials

For comparison purposes and to test the whole-soil 'vermiculite' method, analyses were done on a variety of soil and geologic materials (Table 1). The results

Table 1. CaEC, KEC, per cent 'vermiculite' and VIF (vermiculite interlayer fraction of CaEC) values for some soil and geologic materials. All CaEC and KEC values are the average of duplicate determinations

| | Vermiculitic soils* | | | | | Other soils* | | | | | Geologic materials | | |
| Soil series* Sampling site (state) Parent material | Fauquier Md. chloritic | | Myersville Md. saprolite | | Sharkey La. alluvium | Nellis N.Y. calc. gl. till | Manor Md. mica schist saprolite | | Elkton Md. coastal plain sediments | | Bentonite Wy. | Kaolin Ga. | Chloritic Rock Md. |
Soil Horizon, etc.	Ap	C	$Ap1$	$B2$	B	$B2$	Ap	$B2$	Ap	$B2$	$AP1\ H\text{-}25$		
CaEC (m-equiv/100 g)	11·5	50·7	16·3	42·2	47·5	6·4	7·3	8·0	6·9	15·4	102·1	5·1	3·4
KEC (m-equiv/100 g)	8·9	6·5	9·6	11·1	33·5	2·7	4·4	3·9	3·7	6·6	101·1	2·1	1·6
'Vr' (%)	1·7	28·7	4·4	20·0	9·0	2·4	1·9	2·7	2·1	5·7	0·6	1·9	1·2
CaEC–KEC/CaEC (or VIF)	0·23	0·87	0·41	0·74	0·29	0·57	0·40	0·54	0·46	0·57	0·01	0·59	0·53

*Or geologic material. The family placement of the soil series in the U.S. Soil Taxonomic System (Soil Survey Staff, 1972 and 1974) is as follows: Fauquier–Ultic Hapludalfs, fine, mixed, mesic; Myersville–Ultic Hapludalfs, fine loamy, mixed, mesic; Sharkey–Vertic Haplaquepts, very fine, montmorillonitic, nonacid, thermic; Nellis–Typic Eutrochrepts, coarse loamy, mixed, mesic; Manor–Typic Dystrochrepts, coarse loamy, micaceous, mesic; Elkton–Typic Ochraquults, clayey, mixed, mesic.

obtained were reasonable in terms of what was known about the samples.

Subsoil samples from the Middletown Valley of Maryland, that from X-ray diffraction patterns were rich in vermiculite (e.g. Fig. 1), gave the highest values for 'vermiculite' of any of the materials tested (Table 1). Values for the vermiculite interlayer fraction (VIF) of the CaEC were also high for these samples, Table 1.

X-ray diffraction patterns (Figs. 1 and 2) gave a qualitative indication that some samples might contain even more vermiculite than indicated by the exchange capacity method. This interpretation is based on the seemingly low content of minerals other than vermiculite shown by X-ray diffraction patterns with only 29 per cent (Fig. 1) or 2 per cent (Fig. 2) 'vermiculite' present in the samples by the exchange capacity method. In addition to vermiculite, the X-ray diffraction patterns indicated the presence of feldspars and kaolinite (Fig. 1), and quartz, feldspars, amphiboles and kaolinite (Fig. 2). It is difficult, however, to interpret these other minerals as representing as much as 60 per cent (Fig. 1) or 98 per cent (Fig. 2) of the samples. This discrepancy may mean that the CEC assumed for the 'vermiculite' interlayers (154 m-equiv/100 g) is too high for these materials, thus giving low values for 'vermiculite'. Another possible way that low values could develop would be if CaEC values were lower than theoretical because of inability of saturating cations to penetrate large particles. On the other hand, the 'vermiculite' values determined for a given material by the exchange capacity method were more reproducible than vermiculite peak intensities in X-ray diffraction patterns from two separately made diffraction specimens.

'Vermiculite' contents of samples taken from near soil surfaces (Ap horizons) were less than the values for corresponding subsoils (Table 1 and Fig. 2 vs Fig. 1), in line with the higher content of reactive minerals usually found in subsoil horizons. VIF values were also less in the A horizons, perhaps indicative of greater blocking of interlayers by hydroxy aluminum compounds. Rich (1968) has noted that hydroxy interlayers are usually best developed in A horizons, particularly if the A horizons are low in organic matter, as were the Ap horizons given in Table 1 and Fig. 2. The X-ray diffraction pattern of the Ap horizon of the Fauquier soil (Fig. 2) tended to confirm this reasoning by showing poorer collapse to 10 Å with K saturation and heat than was observed with the C horizon of the same soil (Fig. 1).

The other soils of Table 1 that were not considered to be vermiculitic gave lower 'vermiculite' values. From previous studies employing X-ray diffraction, it was known for most of these soils that their clay fractions did contain some vermiculite—either discrete or interstratified with other minerals. It is interesting to note that even though these soils had quite low 'vermiculite' contents, most of them still had relatively high VIF values. The montmorillonitic Sharkey B horizon (Table 1) was an exception. It contains about 30 per cent montmorillonite if its KEC value is attributed entirely to montmorillonite with a CEC of about 100 m-equiv/100 g. The montmorillonitic character is also reflected in the relatively low VIF value (0·29) even though this soil contained more Vr than many of the soils with higher VIF values.

Wyoming bentonite showed a very low 'vermiculite' content and by far the lowest VIF value (0·01) obtained for any of the materials examined (Table 1). Kaolin, which was nearly pure kaolinite by X-ray diffraction, appeared to contain a trace of 'vermiculite'. The VIF value for the kaolin indicated that this trace may account for 60 per cent of the entire CaEC of this material.

The chloritic rock, or greenstone, which is considered to be representative of the parent rock of the vermiculitic Myersville and Fauquier soils and associated saprolite, showed a low 'vermiculite' content (Table 1). This sample was crushed in an agate mortar prior to analysis and probably developed CEC during grinding.

The method was tested on standard Montana and African vermiculites only after the other studies reported in this paper had been completed. The results (Table 6) indicated that for these biotite derived vermiculites to show a significant 'vermiculite' content, it was necessary to crush them more than is recommended in the standard procedure. This effect of crushing is discussed further in a later section.

'Vermiculite' rich sand and silt fractions

The high 'vermiculite' content of sand and silt fractions of saprolite and of soil developed from chloritic metabasalt (Tables 2 and 3) illustrates the need for and value of methods that measure vermiculite on a whole soil basis.

In the saprolite (Table 2) the sand and silt fractions were richer in 'Vr' than were the clay fractions. Sand (weight percentage of 53 per cent) and silt (39 per cent) also composed more of this material than did the clay (8 per cent). Thus, when both the reactivity and the weight percentage of the fractions composing the saprolite are considered (Table 2, section on fractional contribution to whole soil properties), it is seen that 69 per cent of the Vr in the saprolite is sand-size, 32 per cent is silt-size, and only 3 per cent is clay-size. Some of the finer particles may have been produced by size reduction during particle-size fractionation so there is

Table 2. Some properties of particle-size fractions (organic matter and free iron oxides removed) of saprolite developed from chloritic metabasalt (in Middletown Valley, Md.) and the contribution of the fractions to the cation exchange properties and 'vermiculite' content of the whole soil. All CaEC and KEC values are the average of duplicate determinations

	Sand				Silt				Clay		Whole soil	
	vc	c	m	f	vf	c	m	f	c	f	Sum of fractions	Separate Detn.
Fraction properties												
Particle size†	2–1 mm	1–0.5 mm	0.5–0.25 mm	0.25–0.1 mm	0.1–0.05 mm	50–20 μm	20–5 μm	5–2 μm	2–0.2 μm	<0.2 μm	<2 mm	<2 mm
CaEC (m-equiv/100 g)	58.2	—	50.3	57.2	81.2	38.8	44.4	61.8	28.9	52.1	52.8	45.8
KEC (m-equiv/100 g)	0.9	—	1.7	2.5	5.6	2.6	1.6	17.2	16.8	30.4	4.0	5.0
Vr (%)	37.2	—	31.6	35.5	49.1	23.6	27.8	29.0	7.8	14.1	30.9	26.6
CaEC–KEC/CaEC or VIF	0.99	—	0.97	0.96	0.93	0.93	0.96	0.72	0.42	0.42	0.92	0.89
Properties expressed on whole soil basis												
Weight (%)	10.8	0.0	13.2 (53.0)	16.7	12.3	19.5	17.3 (38.9)	2.1	7.1 (8.1)	1.1	100.1	
CaEC (m-equiv/100 g)	6.3	0.0	7.6	9.6	10.0	7.6	7.7	1.3	2.1	0.6	52.8	
KEC (m-equiv/100 g)	0.1	0.0	0.2	0.4	0.7	0.4	0.3	0.4	1.2	0.3	4.0	
Vr (%)	4.0	0.0	4.2	5.9	7.0	4.6	4.8	0.6	0.6	0.2	30.9	
Fraction contribution to whole soil properties												
to CaEC (%)	11.9	0.0	14.4 (63.4)	18.2	18.9	14.4	14.6 (31.5)	2.5	3.9 (5.0)	1.1	99.9	
to KEC (%)	2.5	0.0	5.0 (35.0)	10.0	17.5	10.0	7.5 (27.5)	10.0	30.0 (37.5)	7.5	100.0	
to Vr (%)	12.9	0.0	13.6 (69.0)	19.1	19.4	14.9	15.5 (32.4)	2.0	2.0 (2.6)	0.6	100.0	

* Abbreviations: vc—very coarse; c—coarse; m—medium; f—fine; vf—very fine.
† Equivalent spherical dia.
Totals in parenthesis.

Table 3. Some properties of particle size fractions (organic matter and free iron oxides removed) of an *Ap* horizon (plow layer) of a Myersville silt loam, developed from chloritic metabasalt in the Middletown Valley, Md. and the contribution of the fractions of cation exchange properties and the 'vermiculite' content of the whole soil horizon material. All CaEC and KEC values are the average of duplicate determinations

| | Fraction* | | | | | | | | | | Whole soil | |
	Sand					Silt			Clay		Sum of fractions	Separate Detn.
Fraction properties Particle size†	vc 2– 1 mm	c 1– 0·5 mm	m 0·5– 0·25 mm	f 0·25– 0·1 mm	vf 0·1– 0·05 mm	c 50– 20 μm	m 20– 5 μm	f 5– 2 μm	c 2– 0·2 μm	f <0·2 μm	<2 mm	<2 mm
CaEC (m-equiv/100 g)	13·1	13·1	9·5	9·7	6·6	7·2	17·5	31·7	33·3	60·4	20·3	15·9
KEC (m-equiv/100 g)	0·0	3·1	2·3	4·1	0·3	1·4	4·7	13·2	12·0	35·2	7·3	8·1
'Vermiculite' (%)	8·5	6·5	4·7	3·6	4·1	3·8	8·3	12·0	13·8	16·4	8·4	5·1
CaEC–KEC/CaEC or *VIF*	1·00	0·76	0·76	0·58	0·96	0·81	0·73	0·58	0·64	0·42	0·64	0·49
Properties expressed on whole soil basis Weight (%)	1·1	3·1	4·3 (17·9)	4·7	4·7	21·6	30·8 (58·0)	5·6	17·8 (24·3)	6·5	100·2	100
CaEC (m-equiv/100 g)	0·14	0·41	0·41	0·46	0·31	1·56	5·39	1·78	5·93	3·93	20·32	15·9
KEC (m-equiv/100 g)	0·00	0·10	0·10	0·19	0·01	0·30	1·45	0·74	2·14	2·29	7·32	8·1
'Vermiculite' (%)	0·1	0·2	0·2	0·2	0·2	0·8	2·6	0·7	2·5	1·1	8·6	5·1
Fraction contribution to whole soil properties to CaEC (%)	0·7	2·0	2·0 (8·5)	2·3	1·5	7·7	26·5 (43·0)	8·8	29·2 (48·5)	19·3	100·0	100·0
to KEC (%)	0·0	1·3	1·4 (5·5)	2·6	0·1	4·1	19·8 (34·0)	10·1	29·2 (60·5)	31·3	100·0	100·0
to 'Vermiculite' (%)	1·8	2·3	2·3 (11·0)	2·3	2·3	9·3	30·2 (47·6)	8·1	29·1 (41·9)	12·8	100·0	100·0

* Abbreviations: *vc*—very coarse; *c*—coarse; *m*—medium; *f*—fine; *vf*—very fine.
† Equivalent spherical dia.
Totals in parenthesis.

probably a bias toward overestimating the contribution of the finer particles in this analysis compared to the actual situation in the field.

The VIF values were also greater for the sand and silt fractions than for the clay. This situation may indicate some true differences in the mineralogy and exchange properties of the clay as opposed to the sand and silt. If so, this information could not have been determined by the whole soil 'vermiculite' method. The lower VIF values of the clay are reflected in the higher contribution of the clay to the KEC of the whole material (38 per cent) than to the CaEC (5 per cent) or to the 'Vr' content (3 per cent) (Table 2).

CaEC and 'Vr' content values for the sand and silt fractions for the Ap horizon of a Myersville soil (Table 3) sampled a few meters from the site of the underlying saprolite (Table 2), were considerably lower than for the corresponding fractions of the saprolite. In the Ap horizon, the coarse fractions still were reactive enough, however, to contribute significantly to the cation exchange characteristics and 'vermiculite' content of the soil. The silt contributed more to the 'vermiculite' content of the Ap material (48 per cent) than did the clay (42 per cent) although the reverse was true with respect to the CaEC and KEC values. As with the saprolite, the clay contributed most to the KEC (61 per cent) and least to the 'Vr' content (42 per cent) with an intermediate contribution to the CaEC (48·5 per cent).

Although VIF values for the Ap fractions (Table 3) generally tended to decrease with decreasing particle size, as in the saprolite (Table 2), the values were more erratic. Since CaEC is the denominator in the VIF equation (CaEC–KEC/CaEC), VIF values change more for a given change in CaEC or KEC with small CaEC values. CaEC values were generally much less for a given fraction in the Ap than in the saprolite (Tables 2 and 3), except for the clay fractions.

Fractions of the $B2$ and C horizons of the Myersville soil were also studied (Coffman, 1972; Coffman and Fanning, 1972). Fraction properties and contributions to whole soil behavior were generally between those of the saprolite and Ap horizons reported here.

Values for CaEC, KEC, and Vr content obtained for the whole soil by summation of the values for the various fractions, weighted for the amount of each fraction in the soil, were generally similar to the values obtained by separate whole-soil measurements (Tables 2 and 3). Although the CaEC and percentage Vr were somewhat less by direct measurement, the differences appear within what might be expected from experimental error. There is a higher probability of experimental error with the fractionation approach because of the larger number of measurements involved. Also,

fractionation may tend to produce more fine particles, and reduction in particle size may increase exchange capacity values and Vr contents of some materials (Table 6).

In connection with these particle-size studies it should be noted that we have also found (unpublished data) exchange capacity, Vr content and VIF relationships between particle-size fractions of Montana and African vermiculites similar to those found with the saprolite from metabasalt. Similar relationships have also been observed by Alexiades *et al.* (1973) with particle-size fractions of a soil from Greece developed from granite and containing vermiculite apparently derived from mica. Most notably, in all of these studies VIF values decreased with decreasing particle size. Part of this change may be related to true differences in the mineralogy of the different particle-size fractions. For example, Alexiades *et al.* (1973) report kaolinite and considerable pedogenic chlorite in the clay fraction of their soil and no kaolinite and less chlorite in coarser fractions. On the other hand, different particle sizes of a given vermiculite may differ in their cation exchange behavior (Ross and Rich, 1973).

Effect of removing free iron oxides

The effect of removing free iron oxides was studied with 3 B horizon samples of Fauquier soil that varied in free iron oxide content and with B horizon samples of some acid Coastal Plain soils (Beltsville, Matapeake, and Elkton). With all the soils studied (Table 4), removal of the free iron oxides increased both CaEC and KEC values. However, the measured 'vermiculite' content was relatively unaffected or increased only slightly. VIF values generally decreased slightly. Thus it appears that free iron removal by the citrate–dithionite method tends to preferentially open up exchange sites that do not fix potassium—presumably edge sites rather than 'vermiculite' interlayer sites.

The B horizons of the Fauquier soils are considered to have vermiculite that is trioctahedral and relatively free of aluminum interlayers. However, no additional opening of 'vermiculite' interlayer sites by the free iron removal treatment was observed with the other soils of Table 4, which are considered to contain dioctahedral vermiculite with hydroxy aluminum interlayers.

There was some tendency (Table 4) for increase in the CaEC and KEC values to be associated with the amount of free iron removed; however, the relationship was not consistent. The differences caused by taking the amount of free iron extracted into consideration in making the CaEC and KEC calculations were small (Table 4, compared values not in parentheses with those in parentheses in the 'Free Fe removed' column).

Table 4. The effect of free Fe removal on the CaEC, KEC, per cent 'vermiculite' and VIF ('vermiculite' interlayer fraction of CaEC) values of the B horizons of three Fauquier soils (developed from chloritic metabasalt) and of three acid Coastal Plain soils. All values are based on duplicate CaEC and KEC determinations

	Free Fe removed*	Free Fe not removed*
	Fauquier 10-4 $B2$ (2·02% free Fe)	
CaEC (m-equiv/100 g)	42·0 (42·2)	40·2
KEC (m-equiv/100 g)	10·8 (11·1)	8·4
% Vr	20·3 (20·0)	20·1
VIF	0·74 (0·74)	0·79
	Fauquier 10-1 $B2t$ (2·96% free Fe)	
CaEC (m-equiv/100 g)	36·1 (36·6)	33·2
KEC (m-equiv/100 g)	6·4 (7·0)	5·2
% Vr	19·3 (19·2)	18·2
VIF	0·82 (0·79)	0·84
	Fauquier 10-6 $B22t$ (5·73% free Fe)	
CaEC (m-equiv/100 g)	34·8 (35·7)	28·2
KEC (m-equiv/100 g)	16·3 (17·3)	12·2
% Vr	12·0 (11·9)	10·4
VIF	0·53 (0·49)	0·57
	Beltsville $B22tx$ (1·32% free Fe)	
CaEC (m-equiv/100 g)	10·9 (11·1)	8·1
KEC (m-equiv/100 g)	5·5 (5·8)	3·6
% Vr	3·5 (3·4)	2·9
VIF	0·49 (0·48)	0·56
	Matapeake $B2t$ (1·31% free Fe)	
CaEC (m-equiv/100 g)	10·9 (11·1)	8·9
KEC (m-equiv/100 g)	9·1 (9·3)	5·2
% Vr	1·2 (1·2)	2·4
VIF	0·17 (0·16)	0·41
	Elkton $B2tg$ (0·55% free Fe)	
CaEC (m-equiv/100 g)	13·7 (13·8)	10·8
KEC (m-equiv/100 g)	7·9 (7·9)	6·1
% Vr	3·9 (3·8)	3·1
VIF	0·43 (0·43)	0·44

* All values are based on the original sample weight (air-dried soil, free Fe unremoved). Values not in parentheses under the Free Fe removed column were corrected for the extra excess salts that should have been present because of the removal of free iron (all free iron assumed to have been present as goethite, $FeOOH$) whereas values in parentheses were not corrected.

The standard Vr determination method includes the removal of free iron oxides. Such a procedure does allow for measurement of free iron oxides on the same samples. The data given in this section indicate, however, that similar values of Vr content may be obtained without such removal. Omission of this step from the 'Vr' determination would speed up the procedure, and should give exchange capacity data that would be more representative of field conditions. Perhaps the H_2O_2 removal of organic matter could also be left out of the Vr procedure. This possibility was not tested since it was thought that the CEC data would be difficult to interpret when organic matter was present.

Effect of different drying treatments for K fixation with a Fauquier soil

The effect of different drying treatments for potassium fixation were studied with samples from the Ap, $B2t$ and underlying saprolite of a Fauquier soil (Table

5). In this table the values for the individual determinations of CaEC and KEC are given, in addition to the average of the duplicates, to indicate the precision obtained in the exchange capacity determinations.

The data show very little wet fixation of K in the Ap horizon, whereas air-drying and oven-drying gave about equal amounts of fixation, about four times that of wet fixation. In the $B2t$ horizon, on the other hand, there was about as much fixation when the soil was wet as when it was air-dried. However, oven-drying gave an additional increment of K fixation. In the saprolite, there were about equal amounts of fixation under all three treatments. It is speculated that the vermiculite of A and B horizons may contain hydroxy–aluminum or other interlayer materials from pedogenesis that block the interlayers to some extent and cause the drying treatments to give increased fixation.

Although these data (Table 5) do not represent a complete study of the effect of different drying treat-

Table 5. Effect of different drying treatments for K fixation on KEC and 'vermiculite' values for samples from a Fauquier soil and underlying saprolite sampled near Middletown, Md.

		CaEC (m-equiv/ 100 g)	KEC (wet) (m-equiv/ 100 g)	KEC (air dry) (m-equiv/ 100 g)	KEC (oven dry) (m-equiv/ 100 g)	Vr (wet) (%)	Vr (air dry) (%)	Vr (oven dry) (%)
Fauquier Ap	1	16·4	14·8	8·6	9·7	1·0	5·0	4·4
(0–22 cm)	2	15·6	14·4	10·2	10·0	0·8	3·5	3·6
	av.	16·0	14·6	9·4	9·9	0·9	4·3	4·0
Fauquier $B2t$	1	31·0	17·9	17·4	12·1	8·5	8·8	12·3
(35–56 cm)	2	31·4	17·6	16·5	12·8	9·0	9·7	12·1
	av.	31·2	17·8	17·0	12·5	8·7	9·3	12·2
Fauquier	1	15·3	5·6	4·3	4·1	6·3	7·1	7·3
Saprolite	2	12·8	5·9	4·9	3·5	4·5	5·1	6·0
(235–245 cm)	av.	14·1	5·8	4·6	3·8	5·4	6·1	6·7

ments upon K fixation, they do indicate that different quantities of 'vermiculite' will be reported depending upon how 'vermiculite' is defined. A definition based on K fixation (exchange capacity reduction) during overnight oven-drying at 110°C was suggested by Alexiades and Jackson (1965) and has been followed in our standard method. However, a definition based on fixation under wet or air-dried conditions would probably be more meaningful in terms of predicting the field behavior of soils.

Effect of coarse vs fine crushing of chlorite and mica derived vermiculites

Finely crushing the saprolites from chloritic metabasalt had little or no effect upon their CaEC, KEC, percentage Vr and VIF values (Table 6). On the other hand, with the biotite-derived African and Montana vermiculites, CaEC, KEC, and percentage Vr values increased dramatically upon fine crushing and VIF values decreased (Table 6). These results cast doubt on the ability of whole-soil cation exchange capacity methods to adequately measure mineralogical vermiculite when it occurs in large mica derived flakes—probably with mica cores. On the other hand, exchange capacity data from crushed micaceous samples may not be applicable to the material as it occurs in the field if it occurs as large flakes.

The small effect of finely crushing the chlorite-derived saprolites (Table 5) implies that the CaEC and KEC values of uncrushed chlorite-derived materials may more adequately measure their mineralogical vermiculite content than in the case of the mica-derived samples and shows that vermiculites derived from chlorite (see Ross *et al.*, 1974 and Fanning and Coffman, in manuscript, for recent evidence of this transformation) may sometimes behave differently than

Table 6. Effect of crushing treatments (standard, so as to pass 2 mm sieve, vs fine, that is crushed in agate mortar on motor driven turntable for 30 min) on CaEC, KEC, per cent 'vermiculite' and VIF ('vermiculite' interlayer fraction of CaEC) values for saprolites from chloritic metabasalt from the Middletown Valley of Maryland and for mica derived Montana and African (Transvaal) vermiculites

	Crushing treatment							
	Saprolites from chloritic metabasalt				Vermiculites			
	1		2		African		Montana	
	<2 mm	fine	<2 mm	fine	<2 mm	fine	<2 mm	fine
CaEC (m-equiv/100 g)*	43·7	44·1	37·3	38·4	19·5	87·1	18·4	95·4
KEC (m-equiv/100 g)*	8·3	8·8	7·7	8·6	0 (−0·2)†	8·4	0 (−2·2)†	13·1
Vr (%)	23·0	22·9	19·2	19·4	12·7	51·1	11·9	53·4
VIF	0·81	0·80	0·79	0·78	1·00	0·90	1·00	0·86

* Values for the chloritic metabasalt samples are averages of quadruplicate determinations, values for the vermiculites are averages of duplicate determinations.

† Negative values were found. These were taken to be zero for the calculation of percentage Vr and VIF. The negative values may be the result of trapping (against replacement) of saturating solution salts in large particles.

those derived from mica. Thus, one should know whether vermiculites to be studied were derived from micas or chlorities.

The full effects of the finer crushing are not known. All the materials were visually much finer after the agate mortar crushing, but particle-size distribution was not determined for either the coarse or the finely crushed samples. Some of the differences between the mica-derived and chlorite-derived materials may have been caused by the smaller amount of H_2O_2 used with the former samples (see Methods section). Unpublished data indicate that increasing the amount of H_2O_2 may increase the CEC values of the African and Montana vermiculites. This result is being further tested. In this study less H_2O_2 was used with the African and Montana vermiculites because, when the standard 0·5 ml of H_2O_2 was used, the large mica-derived particles tended to pop open and trap gases to the extent that the samples 'boiled' out of their tubes during H_2O_2 treatment. The chlorite-derived samples did not behave in this way upon H_2O_2 treatment. These samples seemed finer with only standard crushing than did the mica-derived vermiculites. On the other hand, it seems remarkable that the finer crushing had such a small effect with the chlorite-derived saprolites, since the different naturally-occurring particle-size fractions of similar material obviously had different CEC properties (Table 2).

Further criticisms of the method

The main faults of the method proposed in the present paper appear associated with the underlying assumptions. The main assumptions are (1) that vermiculite has an interlayer exchange capacity of 154 m-equiv/100 g, (2) that this capacity is entirely blocked by K fixation, (3) that vermiculite is the only potassium-fixing component of the material being analyzed, and (4) that the interlayer cation exchange sites of vermiculite are accessible to saturation by Ca and that such Ca is entirely replaced by Mg. All of these assumptions may be criticized.

The 154 m-equiv/100 g value was chosen by Alexiades and Jackson (1965) as an average, workable, value for the vermiculites that they examined. Vermiculites in soils, however, presumably range in interlayer exchange capacity from values less than this (which may be the case for the vermiculitic soils reported here in Tables 1–3) to values that approach the layer charge of true micas (Scott and Reed, 1965). Also, it may be that the potassium fixation in vermiculites is not associated with the total interlayer charge, but more with that part of the charge originating in the tetrahedral sheet (Mering and Pedro, 1969; Harward et al., 1969). However, this wouldn't matter if all the

vermiculite interlayer exchange sites were blocked by K fixation by some of them.

With regard to the second assumption it seems likely that vermiculite in some intergradient chlorite–vermiculites may not fix potassium if the layers are propped open by hydroxy islands (Jackson, 1964).

The third assumption would be wrong if other minerals in the mixture also fix potassium. A likely candidate here would be beidellite or beidellitic montmorillonite. Such minerals, also referred to as illite-derived montmorillonite, have been indicated to be potassium fixers under natural conditions by some workers (Niederbudde et al., 1969). Thus, 'vermiculite' as it is defined in this paper probably includes most true vermiculite along with some beidellite, and perhaps also some high charge or tetrahedral charge zones of montimorillonites, saponites, etc. At the same time, some 2:1 layers with vermiculite charge characteristics may not be measured if K fixation is prevented (e.g. by hydroxy interlayer islands) or if the exchange sites are not accessible to Ca saturation and Mg replacement [assumption (4) violated]. The experiment on effect of crushing (Table 6) indicates that assumption (4) may not hold for large flakes of mica-derived vermiculites.

In spite of these shortcomings, the 'vermiculite' and *VIF* concepts do allow at least a crude measure of the amounts, the kinds, and the contributions of certain reactive minerals in a material, at the same time that information about the cation exchange complex itself is being obtained. It is also pointed out that this can be done without particle-size fractionation and that the data so obtained may give a more meaningful characterization of the cation exchange complex of a soil material, particularly as it exists under field conditions, than data for its particle-size fractions.

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Résumé—La méthode proposée est une modification de celle d'Alexiades et Jackson (1965). La capacité d'échange pour le calcium (CaEC) et la capacité d'échange pour le potassium (KEC) sont déterminées, après élimination de la matière organique et des oxydes de fer libres, en saturant le complexe d'échange par des lavages à la centrifugeuse avec des solutions à pH 7 d'acétate de Ca ou de K selon le cas. Le sel en excès dans les solutions restant en contact avec le sol après la saturation est dosé en mesurant le poids et la concentration de la solution en excès. Les cations échangeables et le sel en excès sont alors remplacés par des lavages à la centrifugeuse avec des solutions 1 N d'acétate de Mg (pour CaEC) ou de NH_4 (pour KEC), après un séchage à l'étuve à 110°C pendant une nuit pour augmenter la fixation de K pour KEC. Les cations remplacés sont dosés et CaEC et KEC sont calculées. Le pourcentage de 'vermiculite' est tiré de la différence entre CaEC et KEC (exprimée en m-equiv/100 g) et d'une capacité d'échange interfeuillet 'vermiculite' de 154 m-equiv/100 g; $Vr = (CaEC − KEC/154) × 100$. La fraction interfeuillet 'vermiculite' (VIF) de la CaEC peut également être calculée; $VIF = CaEC − KEC/CaEC$. La 'vermiculite' ainsi déterminée apparaît entre guillemets, car la méthode soulève certaines critiques concernant ce qui est exactement mesuré, les hypothèses faites, etc; on souligne aussi de la sorte que le protocole de détermination a, dans le cas de la caractérisation des complexes d'échange de cations, un caractère conventionnel.

L'élimination des oxydes de fer libres augmente à la fois les valeurs de CaEC et KEC, mais le pourcentage de 'Vr' est peu modifié. L'intensité de la fixation de K est affectée par le traitement de séchage utilisé après la saturation par K (pas de modification lors d'un séchage à l'air comparé à un séchage à l'étuve). Un broyage poussé de vermiculites du Montana et d'Afrique augmente considérablement leurs CEC et les valeurs mesurées pour la 'vermiculite', mais a peu d'effet avec deux échantillons de saprolite provenant d'un métabasalte chloritique.

Kurzreferat—Die vorgeschlagene Methode stellt eine Abwandlung des von Alexiades und Jackson (1965) eingeführten Verfahrens dar. Die Calciumaustauschkapazität (CaEC) und die Kaliumaustauschkapazität (KEC) werden bestimmt, indem nach Entfernung der organischen Substanz und der freien Eisenoxide der Austauschkomplex durch Auswaschen mit Acetatlösungen von Ca bzw. K bei pH 7 in der Zentrifuge abgesättigt wird. Der Überschuß an gelöstem Salz, der nach der Sättigung in Kontakt mit dem Boden verbleibt, wird durch Messung des Gewichtes und der Konzentration der überschüssigen Lösung bestimmt. Die austauschbaren Kationen und der Salzüberschuß werden dann durch Auswaschen in der Zentrifuge mit 1 N Acetatlösungen von Mg (für CaEC) oder NH_4 (für KEC) verdrängt, nachdem zur Förderung der K-Fixierung für KEC über Nacht Ofentrocknung bei 110°C erfolgte. Die verdrängten Kationen werden bestimmt und CaEC und KEC berechnet. Der Prozentgehalt an 'Vermiculit' ergibt sich aus der Differenz zwischen CaEC und KEC (ausgedrückt in m-equiv/100 g) und einer angenommenen Zwischenschichtaustauschkapazität für Vermiculit von 154 m-equiv/100 g; % 'Vr' = $(CaEC-KEC/154) × 100$. Der 'Vermiculit'-Zwischenschichtanteil (VIF) der CaEC kann ebenfalls berechnet werden; $VIF = CaEC-KEC/CaEC$. Der gemessene Vermiculit wird in Anführungszeichen widergegeben, da die Methode bezüglich der Frage der Kritik ausgesetzt ist, was eigentlich gemessen wird, welche Annahmen zugrunde liegen, usw., sowie um zu betonen, daß das Bestimmungsverfahren den Charakter einer Arbeitsmethode zur Kennzeichnung des Kationenaustauschkomplexes hat.

Die Entfernung der freien Eisenoxide erhöht sowohl die CaEC- als auch die KEC-Werte mehrerer Böden, jedoch wurde % '*Vr*' wenig beeinflußt. Die Höhe der K-Fixierung wurde durch das nach der K-Sättigung vorgenommene Trocknungsverfahren (ohne Trocknung verglichen mit Lufttrocknung verglichen mit Ofentrocknung) beeinflußt. Gründliches Vermahlen von Vermiculiten aus Montana und Afrika führte zu einer drastischen Erhöhung ihrer Austauschkapazitäten und der gemessenen 'Vermiculit'-Werte, hatte jedoch nur geringen Einfluß bei zwei Proben von Saprolit aus chloritischem Metabasalt.

Резюме — Предлагаемый метод является измененным методом, применявшимся Алексиадесом и Джаксоном (1965 г.). Обменная способность кальция (СаЕС) и обменная способность калия (КЕС) определяются после удаления органических веществ и свободных окисей железа, насыщением обменного комплекса Са или К при помощи центробежной промывки растворами ацетата с рН 7, соответственно. Избыточная соль в растворах, остающимися в контакте с землей после насыщения, определяется путем измерения веса и концентрации избыточного раствора. Затем обменные катионы и избыточная соль заменяются центробежной промывкой в 1N ацетатном растворе с добавлением Mg (для СаЕС) или NH_4 (для КЕС). После высушивания в печи при температуре 110°C в продолжение одной ночи с целью усиления фиксации К для КЕС, определяются замененные катионы и высчитываются СаЕС и КЕС. Процент «вермикулита» основан на разнице между СаЕС и КЕС (выраженной в мэкв/100 г) и на предполагаемой прослоечной обменной способности «вермикулита» 154 мэкв/100 г; % '*Vr*' = $\dfrac{CaEC - KEC}{154} \times 100$. Также можно высчитать прослоечную фракцию (*VIF*) «вермикулита» СаЕС: $VIF = \dfrac{CaEC - KEC}{CaEC}$. Измеряемый «вермикулит» приводится в этой работе в ковычках, так как при этом методе возникают вопросы: Что же в самом деле измеряется? Что за предположения? и т. д. Также можно возразить, что это определение операционная процедура для характеризации катионообменных комплексов.

Удаление свободных окисей железа повысило значения СаЕС и КЕС разных почв, но никакого влияния почти не оказало на процент '*Vr*'. На количество связанного К повлияла температура высушивания после насыщения К (визави воздушной сушки или высушивания в печи). Тщательное дробление монтанского и африканского вермикулитов значительно повысило их СЕС и измеренные величины «вермикулита», но очень мало повлияло на два образца сапролита из хлористого метабазальта.