THE NATURE OF KENYA VERMICULITE AND ITS ALUMINUM HYDROXIDE COMPLEXES*

J. E. BRYDON and R. C. TURNER

Soil Research Institute, Canada Department of Agriculture, Ottawa, Ontario, Canada

Abstract – A specimen of Kenya vermiculite contained no mica or chlorite layers either as separate phases or as components of an interstratified structure. Dehydroxylation occurred in two stages, at 550° and 850°C, with approximately equal amounts of hydroxyl liberated in each stage. Al-saturated Kenya vermiculite showed low temperature dehydration characteristics similar to those of the natural Mg-saturated specimen, but the DTA, TGA and oscillating-heating X-ray diffraction patterns showed that the three stage dehydration process was not as clear-cut with the Al-saturated specimen.

As with montmorillonite, when small amounts of aluminum were precipitated by the addition of $Ca(OH)_2$ in the presence of vermiculite, the $Al(OH)_x$ was taken up and held indefinitely by the clay, the ion product $(Al)(OH)^3$ in solution was maintained at $10^{-33.0}$ and no gibbsite was formed with time. With large amounts, 800 and 1600 me $Al(OH)_x$ per 100g vermiculite, the hydroxide was held initially in the interlayer space, but gibbsite was eventually formed as $(Al)(OH)^3$ approached the solubility product of gibbsite. Unlike montmorillonite, the vermiculite specimens retained an appreciable amount of the interlayer hydroxide and did not regain the original C.E.C. values as gibbsite was formed.

Al-vermiculite which was repeatedly suspended in $AlCl_3$ with $(Al)(OH)^3$ maintained at a value less than $10^{-33.6}$ liberated 435 me Mg, took up 208 me Al as an interlayer hydroxide and caused a reduction in C.E.C. from 130 to 28 me per 100g clay. With vermiculite an appreciable amount of the interlayer $Al(OH)_x$ was stable with respect to gibbsite whereas with montmorillonite it was not.

INTRODUCTION

WHEN Al was precipitated from a suspension of montmorillonite in $AlCl_3$ by the addition of a base, one of two situations resulted; (a) with amounts of precipitated Al less than 900 me per 100 g clay, the precipitate was held in the interlayer spaces of the clay, the C.E.C. of the clay was reduced and the ion activity product $(Al)(OH)^3$ in solution was near $10^{-33.0}$ (Turner and Brydon, 1965, 1966); (b) with amounts of precipitated Al greater than 900 me per 100g clay or if the systems were seeded with gibbsite, the interlayer precipitate existed in the early stages of the reactions but eventually disappeared, the original C.E.C. of the clay was regained and $(Al)(OH)^3$ in solution approached the solubility product of gibbsite (Turner, 1967; Turner and Brydon, 1965, 1966). It was also shown (Turner, 1965; Hsu, 1968) that the OH/Al mole ratio of the interlayer material was near 2·7 regardless of the amount of base added to a montmorillonite–$AlCl_3$ suspension up to a base/Al equivalent ratio of about 0·9.

There are a number of publications (Hsu and Bates, 1964; Rich, 1960, 1968; Sawhney, 1968; Schwertmann and Jackson, 1964) indicating that hydroxy aluminum material reacts differently with vermiculite than it does with montmorillonite. For instance, the amount of interlayer hydroxyaluminum is generally smaller in vermiculite (Rich, 1960, 1968), and with vermiculite, the OH/Al mole ratio of the interlayer hydroxy–aluminum was found to be strongly affected by the ratio of base to Al used (Hsu and Bates, 1964). In these investigations, however, the base was added to the $AlCl_3$ solution before introducing the clay to the systems or the Al–salt and the base were added simultaneously to clay suspensions whereas the results reported above with montmorillonite (Turner, 1967; Turner and Brydon, 1965) the base was added to the clay-$AlCl_3$ suspension. It has been shown that there is a difference in the hydroxyaluminum material taken up by the clay if the clay is added to the $AlCl_3$ plus base from that obtained when the base is added to the clay-$AlCl_3$ suspension (Turner, 1967). Because of the difference in procedures used and because there are no reports on the magnitude of $(Al)(OH)^3$ in solution with vermiculite, work of a similar nature to that done with montmorillonite was done with vermiculite.

The object of the work reported here was to determine the effect of the amount of Al precipitated per unit weight of vermiculite, and the effect of the length of time of reaction on the interlayer

---

1

hydroxyaluminum, on the C.E.C. of the clay, on the formation of gibbsite and on the magnitude of $(Al)(OH)^3$ in solution when sufficient $Ca(OH)_2$ was added to a clay–$AlCl_3$ suspension to give an OH/Al mole ratio of about 2·5. The removal of Al from solution by vermiculite when no base was added to a suspension of vermiculite in $AlCl_3$ solutions was also investigated.

Vermiculite from Kipiponi, Kenya, was chosen for this investigation because of the absence of mica layers (Mathieson and Walker, 1954). In the interpretation of these experiments, establishing the presence or absence of hydroxyaluminum interlayers is important. Because the natural Kenya specimen showed a DTA endothermic peak at 560°C which might have been attributed to a chlorite component (Walker and Cole, 1957) the natural specimen was re-examined and the results are reported here.

MATERIALS AND METHODS

A sample of the vermiculite from Kipiponi, Kenya was obtained through the courtesy of the Chief Geologist, Ministry of Natural Resources, Kenya.

Analyses of the vermiculite

The naturally occurring large flakes were filed to give a powder and then separated into the various particle size ranges < 5, 5–20 and 20–500μ by sieving and gravity sedimentation without treatment. A portion of the $< 5\mu$ sample was saturated with Al^{3+} ions by suspending it twice in N $AlCl_3$, centrifuging and washing with 0·001N HCl to prevent hydrolysis of the Al^{3+}. The course fractions were dried in air but the $< 5\mu$ sample was freeze-dried to avoid aggregation. Part of the $< 5\mu$ sample was boiled in 30% H_2O_2 washed with water and then saturated with Al^{3+} as above or with Ca^{2+} by treating it twice with M $CaCl_2$ and washing out the excess salt with H_2O. In one experiment after boiling dry-ground vermiculite with 30% H_2O_2, a $< 2\mu$ fraction was separated by gravity sedimentation and saturated with Al^{3+} as above. X-ray diffraction, X-ray spectrochemical analyses, DTA and TGA were done by methods outlined previously (Brydon and Kodama, 1966). To prepare oriented specimens, aliquots of suspensions containing 20 mg of solids were centrifuged, the solids were washed once with H_2O and centrifuged again after which they were resuspended in 1 ml of H_2O and sedimented directly on half microscope slides. X-ray patterns were obtained using Fe-filtered Co radiation under controlled relative humidity, solvation with glycerol and after heating for $\frac{1}{2}$ hr at various temperatures. DTA patterns were obtained with an R. L. Stone Co. instrument with

specimens diluted 1:1 with calcined alumina at a heating rate of 10° per min. In most cases the atmosphere was uncontrolled but in certain cases reduced pressure (0·5 mm Hg) was used. TGA curves were obtained on 75-mg specimens at a heating rate of 5° per min. Oscillating X-ray diffraction analysis of the 001 reflection during heating at 10°C per min was very kindly done by Dr. K. Oinuma. A Rigaku Denki diffractometer with heating stage was used with the following conditions: Ni-filtered CuK_α radiation, 30 KV-15 mA power 1°–1°-0·4 mm slits, 2° per min scanning speed and 2° per sec time constant. The Al^{3+} and Ca^{2+} saturated and untreated clays were extracted with 2N NaCl and the Al, Ca and Mg concentrations in the extracts were determined. The C.E.C. in each case was calculated from the concentrations of these cations in the extracts.

Complexes between vermiculite and aluminum

Bulk samples of the vermiculite were dry-ground with mortar and pestle and then boiled in 30% H_2O_2. The $< 2\mu$ fraction was separated by gravity sedimentation. For *Procedure A* below the clay was saturated with Ca^{2+} by treating it twice with 1M $CaCl_2$ at pH 2·6 and washing out the excess salt with H_2O.

Procedure A. Precipitation of Al by addition of $Ca(OH)_2$: The $< 2\mu$ vermiculite was suspended in 0·034N $AlCl_3$ and 0·044N $Ca(OH)_2$ added dropwise with vigorous stirring to an OH/Al ratio of 2·5. The amount of Al precipitated per 100g clay was calculated from the difference between the total amount added as $AlCl_3$ and that recovered in solution and in the exchangeable form. In the three experiments the amounts of Al precipitated were 650, 800 and 1600 me per 100g clay. The suspensions were stirred by bubbling $NaOH–H_2SO_4$ $–H_2O$ washed air through them in a water bath at 25°C. The pH of each suspension was followed over many months and aliquots were extracted periodically for the determination of Al concentrations in solution and for X-ray examination of the solid phase. At the end of the experiments the exchangeable bases were extracted from the clay with 2N NaCl.

Procedure B. No base added to the systems. One g of untreated $< 2\mu$ vermiculite was suspended in 200 ml of 0·01N $AlCl_3$ and the pH was adjusted immediately to 3·3 by the addition of HCl. The suspensions were then shaken until (Al)-$(OH)^3$ in solution had increased to $10^{-34·0}$ when it was centrifuged. The solids were resuspended and treated exactly as before. After the second centrifugation, the clay was resuspended eight times in 0·001N $AlCl_3$ at pH 3·3 and the suspensions were shaken each time until $(Al)(OH)^3$ in solution had

increased to slightly less than $10^{-34\cdot0}$ when they were centrifuged. After these 10 treatments, which will be referred to as the first stage, half of the clay was extracted with 2N NaCl for exchangeable cations. The other half was resuspended in 0·001N $AlCl_3$, shaken for 1 month and centrifuged. This was repeated three times and then a final time in which the reaction time was 6 months. During this second stage, $(Al)(OH)^3$ in solution increased beyond $10^{-34\cdot0}$ but the highest value was less than $10^{-33\cdot6}$. The exchangeable cations were extracted with 2N NaCl at the end of the experiment. The amount of Al fixed and Mg released was calculated from the differences in solution concentrations before and after contact with the clay.

In all experiments the Ca and Mg concentrations in the supernates and NaCl extracts were determined by the EDTA titration method. The Al in the supernates was determined by the aluminon method and in the NaCl extracts by the aluminon method and by titrating aliquots with standardized NaOH as outlined previously (Turner, 1967). X-ray diffraction, X-ray spectrochemical analyses, DTA and TGA were done, by methods described above, on the solids at the end of each experiment.

RESULTS

In the total analysis of the vermiculite specimen, potassium could not be detected (Table 1) and the lack of a 10 Å reflection indicated the absence of mica as a separate phase. The rational series of

Table 1. Chemical analysis and calculated formula for two samples of Kenya vermiculite

	As % of ignited wt	
	Mathieson and Walker	Present sample
SiO_2	42·55	43·71
TiO_2		1·01
MnO_2		0·05
Al_2O_3	19·21	16·74
Fe_2O_3	10·01	8·48
FeO		1·48
MgO	28·22	30·04
CaO	0·00	0·28
Na_2O	0·00	
K_2O	0·00	0·00
C.E.C. me per 100g air-dry weight	130	130

Mathieson and Walker (1954)
$(Mg_{2\cdot36}Fe_{0\cdot48}Al_{0\cdot16})(Si_{2\cdot72}Al_{1\cdot28})O_{10}(OH)_2[Mg_{0\cdot32}]^{+0\cdot64}$
Present sample
$(Mg_{2\cdot54}Fe^{2+}_{0\cdot08}Fe^{3+}_{0\cdot40}Ti_{0\cdot50})(Si_{2\cdot76}Al_{1\cdot24})O_{0\cdot0}(OH)_2[Ca_{0\cdot02}-Mg_{0\cdot28}]^{+0\cdot60}$

vermiculite basal spacings under a variety of conditions (Table 2) indicated the absence of interstratified mica layers in the vermiculite. The cation exchange capacity value of 130 me/100g was identical with that of Mathieson and Walker (1954) and yielded a unit half-cell charge of 0·60 which is well within the range cited by Hoffman et al. (1956) for the vermiculite group.

The C.E.C. values calculated as the sum of the exchangeable cations did not vary appreciably with particle size, with peroxidation or with cationic species (Table 2). The values when Ca- and Al-saturated tended to be lower than the untreated specimen (Mg-saturated) and probably reflects a dissolution of Mg from the edges. The decomposition of the vermiculite in the Al-saturated condition was 3 me/100g clay in the $< 5\mu$ samples and was zero in the H_2O_2 treated $< 2\mu$ sample. Hydrogen peroxide had no obvious effect upon the basal spacings; the rationality was retained and the layers in all of the specimens collapsed on heating at 700°C to give a basal spacing below 10 Å.

With 650 me of Al precipitated per 100g clay (*Procedure A*) there was no change in either the Al concentration or the pH of the solution after the first month of reaction so that $(Al)(OH)^3$ in solution remained constant after the first month and equal to $10^{-33\cdot0}$ (Table 3). When the amount of Al precipitated was 800 me per 100g clay the pH of the solution remained constant after the first month of reaction but the Al concentration in solution decreased continually (Table 4). With 1600 me of precipitated Al (Table 5) there was very little change in the Al concentration after the first month but the pH of the solution decreased continually. In the latter two cases the value of $(Al)(OH)^3$ in

Table 2. Cation exchange capacity, exchangeable cations and X-ray basal spacings of Kenya vermiculite after various treatments

	$< 5\mu$			$< 2\mu$	
			H_2O_2		H_2O_2
	Mg	Al	Al	Ca	Al
C.E.C.	134	126	127	130	130
Ex. Al	0	123	124	0	130
Ex. Ca + Mg	134	3	3	130	0
Basal spacing					
45% R.H.	14·6/n	14·0/n	14·0/n	14·7/n	14·2/n
0% R.H.*	11·7	13·8/n	13·8/n	11·9	N.D.
heated†	9·33	9·50	9·38	9·42	9·7

*Equilibrated over P_2O_5.
†The (001) reflection after heating to 700°C.

Table 3. Conditions in solution after the precipitation of 650 me Al per 100g vermiculite. Initial OH/Al mole ratio in solution 2·4

Time days	pH	Al $M/L \times 10^4$	$-\log (Al)(OH)^3$
initially	5·00		
1	4·54		
3	4·55	2·4	32·55
30	4·49	2·0	32·81
44	4·41		
63	4·42	1·9	33·02
76	4·41		
112	4·42		
140	4·41		
163	4·42		
170	4·41	2·0	33·03

C.E.C. at the end of the experiment was 16 me per 100g clay.

Table 4. Conditions in solution after the precipitation of 800 me of Al per 100g vermiculite. Initial OH/Al mole ratio in solution 2·5

Time days	pH	Al $M/L \times 10^4$	$-\log (Al)(OH)^3$
Initially	5·00		
1	4·68		
4	4·58	6·0	32·06
9	4·48		
15	4·41		
22	4·36		
32	4·34		
54	4·30	2·6	33·32
79	4·29		
112	4·30	2·1	33·42
139	4·28	1·4	33·55
161	4·29		
198	4·30		
249	4·29	1·2	33·61
285	4·29	1·1	33·63

C.E.C. at the end of the experiment was 34 me per 100g clay.

solution decreased with time and was approaching the solubility product of gibbsite after 9½ months of reaction (Tables 4 and 5). Regardless of the amount of Al precipitated, however, the C.E.C.'s of the vermiculite at the end of the experiments were considerably less than the original value of 130 me per 100g clay.

In the experiment (*Procedure B*) in which no base was added to the vermiculite–AlCl$_3$ suspension but in which the solution was changed many times, never allowing (Al)(OH)^3 in solution to become greater than $10^{-34.0}$ during the first stage

Table 5. Conditions in solution after the precipitation 1600 me Al per 100g vermiculite. Initial OH/Al ratio in solution 2·6

Time days	pH	Al $M/L \times 10^4$	$-\log (Al)(OH)^3$
Initially	5·00		
1	4·75		
4	4·68	20·0	31·26
9	4·48		
15	4·36		
22	4·27		
32	4·25		
54	4·16	4·6	33·39
79	4·13		
112	4·13	4·5	33·49
139	4·11	3·8	33·62
161	4·10		
198	4·10		
249	4·07	4·1	33·70
285	4·07	4·1	33·70

C.E.C. at the end of the experiment was 28 me per 100g clay.

and never greater than $10^{-33.6}$ during the second stage of the experiment, a total of 208 me Al was taken up (Table 6). This corresponds to about one-eighth of a complete interlayer gibbsite-like sheet. At the same time, 435 me Mg (approximately ¼ of the octahedral sheet) was released, and the C.E.C. was reduced from 130 me to 28 me per 100g of vermiculite.

X-ray diffraction patterns of the vermiculite specimens showed significant changes after the precipitation of Al by the addition of Ca(OH)$_2$. For example, the d-spacings of the first five (00l) reflections (Fig. 1, curve A) were shifted slightly and the third and fifth (00l) reflections were split into doublets (curve C). The non-rationality of the

Table 6. Removal of Al from dilute solutions of AlCl$_3$ and release of Mg by vermiculite and the effect on the C.E.C. of the clay

No. of* treatments	(Al)(OH)^3† in solution	Al taken up, me per 100g vermiculite	Mg released, me per 100g vermiculite	C.E.C.‡ me per 100g vermiculite
10	$10^{-34.0}$	136	336	59
15	$10^{-33.6}$	72	99	28

*Number of times the solution was changed.
†The suspensions were centrifuged and fresh AlCl$_3$ added to the solids before (Al)(OH)^3 reached values greater than these.
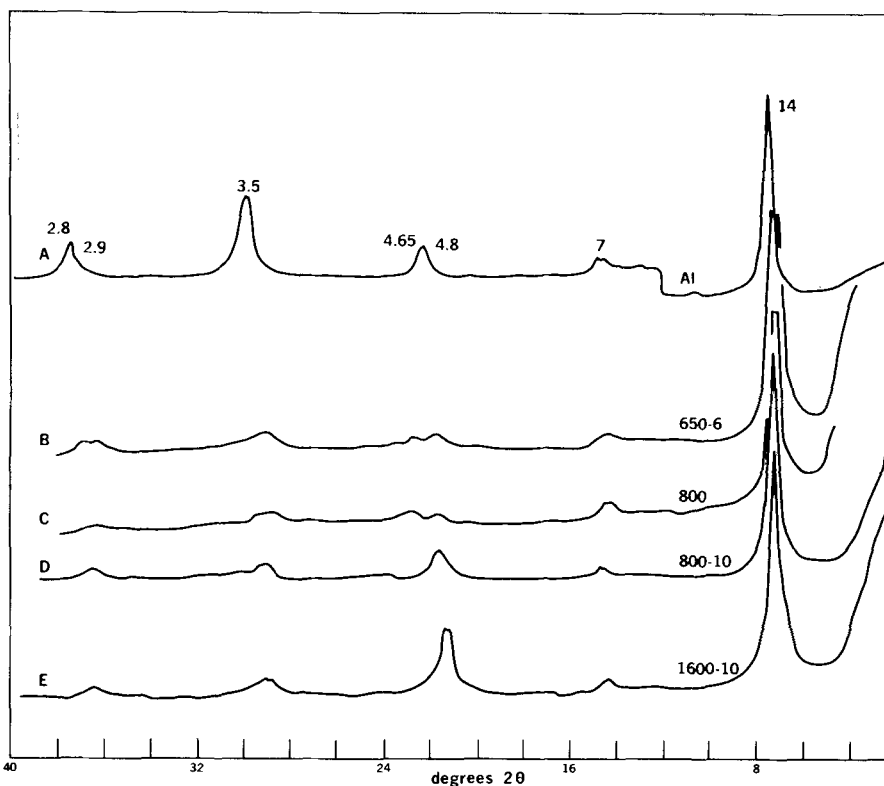‡The C.E.C. at the completion of these treatments.

Fig. 1. X-ray diffraction patterns of oriented specimens of $< 2\mu$ Kenya vermiculite in air-dry condition (90% relative humidity). (A) Al–saturated (C.E.C. 127 me per 100g); 0–12°, 2θ–300,000 counts, full scale; 12–40°, 2θ–30,000 counts full scale; (B) Al–vermiculite + 650 me Al(OH)$_x$ per 100g, aged 6 months (C.E.C. 16 me per 100g); 40,000 counts, full scale; (C) Al–vermiculite + 800 me Al(OH)$_x$ per 100g, aged 4 days; 20,000 counts, full scale; (D) Same as C, aged 10 months (C.E.C. 34 me per 100g); 100,000 counts, full scale. (E) Al–vermiculite + 1600 me Al(OH)$_x$ per 100g, aged 10 months; 40,000 counts, full scale.

reflections indicated that the precipitated Al(OH)$_x$ had induced a complex interstratified assemblage. There was approximately a ten-fold decrease in the relative intensity of the (001) reflection and the relative intensities of the first few (00l) reflections from each specimen correspond to less than half of a complete interlayer (Brindley and Gillery, 1956; Brydon and Kodama, 1966; Rich, 1968). After 10 month reaction time, when the ion product (Al)(OH)^3 approached the solubility product of gibbsite, gibbsite was identified in the specimens containing 800 and 1600 me Al(OH)$_x$ per 100g in several ways. Since the strongest gibbsite diffraction peak has the same d-spacing as the vermiculite (003) reflection, the increase in the relative intensity of the 4·8Å peak (curve D and E) provides the first indication. At zero relative humidity the vermiculite (00l) series shifted to 11 Å/n from 14 Å/n (not shown) thereby isolating the gibbsite 4·8 Å peak. After heating the specimen at 260°C the gibb-

site structure was decomposed, and rehydration at 90% relative humidity returned the relative intensity of the 4·8Å peak to that of the vermiculite (003) reflection. Gibbsite could not be detected in the aged sample containing 650 me Al(OH)$_x$ per 100g nor in the specimens from the vermiculite–AlCl$_3$ experiment after repeated changes of the AlCl$_3$ solution.

Further evidence of the presence of gibbsite in the aged samples containing 800 and 1600 me Al(OH)$_x$ per 100g was provided by DTA. Curves E and F, Fig. 2, show the sharp gibbsite dehydroxylation at about 300°C. The samples containing Al(OH)$_x$ and the specimen from the vermiculite–AlCl$_3$ experiment showed a broad endothermic peak at 390°C which in montmorillonite systems is associated with interlayer hydroxide (Barnhisel and Rich, 1963; Brydon and Kodama, 1966). Weak, broad peaks at 105° and 255°C were more similar to the patterns of the montmorillonite–
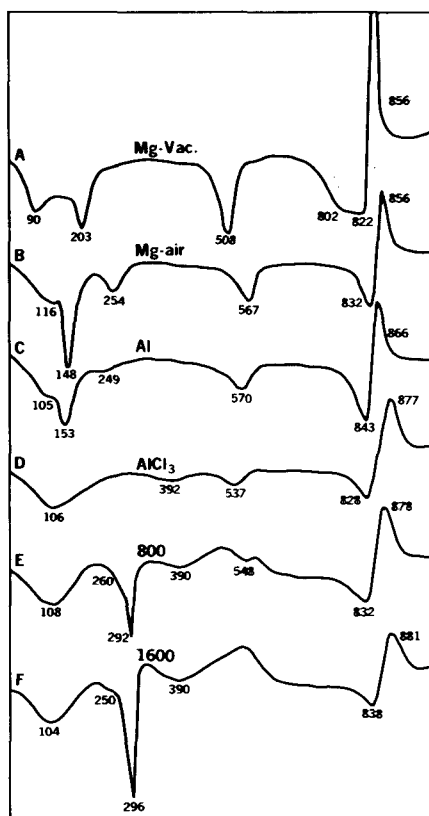
Fig. 2. Differential thermal analysis curves of various specimens of Kenya vermiculite. (A) $< 5\mu$ specimen at 0·5 mm Hg pressure; (B) $< 5\mu$ specimen at normal atmospheric pressure; (C) $< 5\mu$ specimen, Al–saturated; (D) $< 2\mu$ specimen after repeated saturation and aging in $AlCl_3$; (E) $< 2\mu$ specimen containing 800 me $Al(OH)_x$ per 100g after 10 months aging; (F) $< 2\mu$ specimen containing 1600 me $Al(OH)_x$ per 100g after 10 months aging.

$Al(OH)_x$ complex than to that of Al–vermiculite (curve C). Both Mg– and Al–vermiculite (curves B and C) showed the usual three dehydration peaks in the low temperature region and a high temperature dehydroxylation endotherm at 830–840°C which were altered and shifted by using a reduced pressure of 0·5 mm Hg. In addition, the two samples show a prominent endotherm at 570° which is shifted to 508°C at reduced pressure. Other size fractions 5–20μ, 20–500μ, showed virtually identical DTA patterns with prominent endotherms at 570° and 830°C. Small endotherms near 500°–600°C have been reported in other vermiculite samples but they have been attributed to chlorite or mica impurities (Walker and Cole, 1957).

Although chlorite as a separate phase was not

identified in Kenya vermiculite, the absence of interstratified chlorite or random interlayer hydroxides is more difficult to establish. The various fractions of untreated Mg–saturated specimens showed collapsed basal spacings which decreased with increasing particle size, i.e. 9·7Å ($< 2\mu$), 9·4Å ($< 5\mu$), 9·3Å (20–5μ) and 9·2Å (200–20μ). The peaks were symmetrical and prolonged heating at 700° or 750°C did not alter the values. Walker (1961) also reported size-dependent values, i.e. 9·02Å for macroscopic vermiculite and 9·5Å for the $< 2\mu$ fraction when both were heated at 750°C.

The oscillating diffractometer data during dynamic heating of the Mg– and Al–saturated $< 5\mu$ specimens (Fig. 3), show three-stage dehydrations. The Mg–vermiculite d–spacings correspond to those· found previously (Mathieson and Walker, 1954), but Al–vermiculite differed. Whereas Mg–vermiculite has a stable 1 H_2O layer configuration at a spacing of 11·8Å, the first stable d-spacing in the Al–saturated specimen 11·0Å is attributed to an interstratified structure. The 10·4Å spacing probably reflects the discontinuous lateral distribution of H_2O molecules in the Al–vermiculite as in the Mg specimens (Walker, 1961). The difference of 0·35Å between the (001) values at high temperature might be associated with the residues from the dehydration of $Al(OH)^{2+}$ or $Al(OH)_2^+$ in spite of the care used to prevent hydrolysis of Al^{3+} during the specimen preparation.

The TGA curves of Mg– and Al–saturated vermiculite (Fig. 4) show several rapid losses in weight superimposed upon a general loss in weight up to 900°C as found previously for montmorillonite and vermiculite (Brydon and Kodama, 1966;
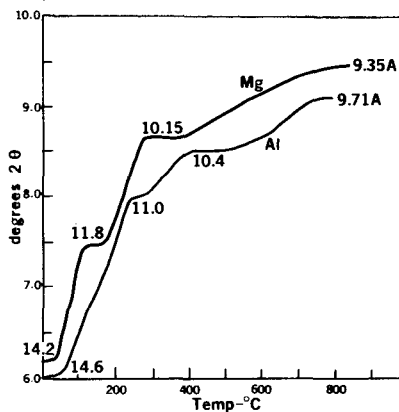

Fig. 3. Variation of $d(001)$ of Mg– and Al–saturated Kenya vermiculite when continuously heated using an oscillating diffractometer and heating stage. Ni–filtered Cu radiation; 1°–1°–0·4 mm slits; scanning speed 2°/min; oscillation period 4·5° 2θ; heating rate 10°C/min.
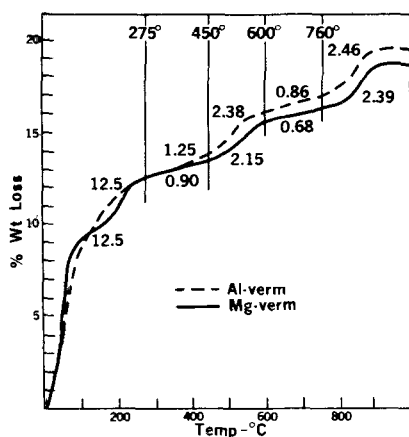
Fig. 4. Thermogravimetric Analysis curves of Mg– and Al–saturated Kenya vermiculite at a heating rate of 5°C per min. The weight loss is plotted as % of the "dry" weight at 275°C, and the increments are indicated for arbitrarily-chosen temperature ranges.
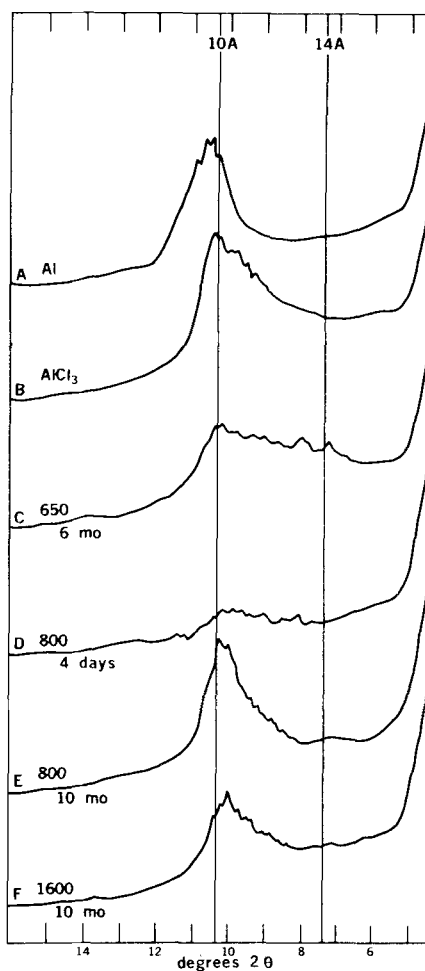

Fig. 5. X-ray diffraction patterns of oriented specimens of Kenya vermiculite after heating at 700°C. (A) Al–saturated; (B) After suspending repeatedly in $AlCl_3$ solutions; (C) Al–vermiculite plus 650 me $Al(OH)_x$ per 100g, after 10 months in suspension; (D) Al–vermiculite + 800 me $Al(OH)_x$ per 100g after four days in suspension; (E) Al–vermiculite + 800 me $Al(OH)_x$ per 100g after 10 months in suspension; (F) Al–vermiculite + 1600 me $Al(OH)_x$ per 100g after 10 months in suspension.

Fripiat, Chaussidon and Rouillaux, 1960; Neumann, 1963). The loss in weight at approximately 275°C was similar for both samples and was attributed to interlayer water. The loss above 275°C was tentatively ascribed to structural OH and adsorbed water and was greater for the Al–vermiculite. Using the chemical composition of Mg–vermiculite (Table 1), the theoretical OH calculated as emitted water is 4·49%. The total loss above 275°C for the Mg–vermiculite exceeds this amount but the increments from 450° to 600°C and from 760°C to 1000°C yield a value of 4·54%. Attribution of this weight loss increment in other ways does not give a close fit and provides evidence that the structural hydroxyl is liberated from this specimen of vermiculite in two stages at about 550° and 850°C in about equal amounts 2·15 and 2·39%. The calculated total amount of adsorbed water 14·08%, is less than the amount, 17·2%, required to satisfy the ideal configuration of 12 H_2O per exchangeable cation according to Walker (1956). The presence of traces of chlorite, i.e. layers or islands of $Mg(OH)_2$ cannot be disproved by the TGA results. With the Al–saturated specimen, the attribution of weight loss above 275°C was less successful and may reflect the presence of partially hydrolyzed species or the interactions of Al with the layer silicate (Brydon and Kodama, 1966).

Evidence of the nature of the added hydroxide is shown by the diffraction patterns in the low angle region of the various specimens after heating to 700°C (Fig. 5). The pattern for pure Al–vermiculite shows a symmetrical peak at 9·4Å (curve A). The samples containing 650, 800 and 1600 me Al per 100g each showed a broad hump similar to curve D after four days indicative of a complicated interstratified structure. After 10 months, the samples containing 800 and 1600 me Al per 100g show sharp peaks at 10·3Å with a low angle tail (curves E and F) whereas the sample with 650 me Al remained largely unchanged during the aging period (curve C). It is obvious that at least some of the

added hydroxide entered the interlamellar space of the vermiculite and caused a complicated interstratification. As the time of the reaction increased, the sample containing 650 me Al per 100g remained unchanged whereas, with the samples containing 800 and 1600 me per 100g, the nature of the interstratification changed as gibbsite formed. The sample which was suspended in $AlCl_3$ (curve B) showed impeded collapse after heating to 700°C indicating that $Al(OH)_x$ had been formed in the interlayer space.

DISCUSSION

The Kenya vermiculite specimen conformed to the characteristics outlined by Mathieson and Walker (1954) in most respects. It had a similar structural formula and charge per unit cell. There were no interstratified mica layers and the dehydration took place in the normal three-stages (Figs. 2 and 3). On the other hand, the specimen showed a two-stage dehydroxylation (Figs. 2 and 4) at 500°–550°C and 800°–850°C. Since the various size-fractions showed similar dehydroxylation features and since there was no evidence of interstratification, it can be concluded that the material was not a mixture of layer types. About half of the octahedral OH is liberated near 550°C and there is no conclusive evidence for either a continuous (alternating complete sheets) or discontinuous (portions of all octahedral sheets) mechanism of dehydroxylation.

Trioctahedral phyllosilicates are generally unstable in acidic solutions (Brydon and Ross, 1966). However, freshly made Al–saturated vermiculite yielded only 3 me Mg per 100g during the extraction procedure for the determination of C.E.C. There was some evidence that some of the exchangeable Al became hydrolyzed with time, even during dry storage. The $d(001)$ spacing of the Al-specimen shifted on heating to 9·5–9·7Å whereas that of the Mg-specimen was about 9·35Å. The high temperature loss in weight of the Al–specimen was about 0·8% greater than that of the Mg–specimen. In the experiment in which no base was added, about a quarter (435 me per 100g) of the octahedral Mg was brought into solution in 10 months, presumably by the H–Mg "interchange reaction" (Barshad and Foscolos, 1970). Structural Al was probably also released but it cannot be accounted for because there was a net uptake of 208 me Al per 100g. Part of the decline in C.E.C. from 130 to 28 me per 100g may be attributed to the interchange reaction. In spite of the substantial degradation, the remaining structure retained its crystallinity and showed strong, sharp X-ray diffraction peaks.

Chlorite as a separate phase was not detected by X-ray diffraction. While the (001) vermiculite peak after heating to 700°C was 9·35Å, it was slightly skewed toward low angles and a few chlorite-like layers may have been present. However, since the collapsed spacing decreased with increasing particle-size, it was considered more likely that the skewness was due to lattice distortion in the finer sizes. Therefore, the DTA endotherm at 550°C could not be attributed to chlorite or to mica. The TGA data showed that all of the weight loss was required to satisfy the $H_2O + OH$ of ideal vermiculite. It can be concluded therefore that Kenya vermiculite has a two stage dehydroxylation.

When $Ca(OH)_2$ was added to the $AlCl_3$ suspensions of vermiculite precipitated Al entered the interlamellar spaces of the vermiculite as shown by the reduction in C.E.C. and by the impeded collapse of the layers on heating. The broad diffraction band between 10 and 14Å after heating (curves C and D, Fig. 5), can be attributed to a non-uniform intercalcation of $Al(OH)_x$. Although the presence of well-ordered interlayers, islands or partially-filled layers cannot be identified specifically, some portion of the structure, perhaps the rim of the particles, must have had a complete interlayer population in order to yield a 14Å spacing after heat treatments as in curve C, Fig. 5. The low temperature H_2O endotherm and the broad endotherm at 390°C (curves D–F, Fig. 2) are similar to those shown by the montmorillonite–$Al(OH)_x$ complexes (Barnhisel and Rich, 1963; Brydon and Kodama, 1966).

When the amount of Al precipitated by the addition of $Ca(OH)_2$ in the presence of vermiculite was varied, the results were similar in some respects to those obtained with montmorillonite (Barnhisel and Rich, 1963; Turner and Brydon, 1965). Thus, with the smallest amount precipitated (650 me of Al per 100g of vermiculite), $Al(OH)_x$ was taken up by the clay and $(Al)(OH)^3$ in solution was maintained at $10^{-33·0}$ and no gibbsite was formed, whereas with the large amounts, 800 and 1600 me of Al per 100g of vermiculite, although $Al(OH)_x$ was taken up by the clay, gibbsite was eventually formed and $(Al)(OH)^3$ in solution approached the solubility product of gibbsite. Furthermore, the C.E.C. of the vermiculite was reduced to very low values by the interlayer hydroxide. There was a real difference between the results with vermiculite and those with montmorillonite. When gibbsite formed with montmorillonite the interlayer $Al(OH)_x$ disappeared with time and the clay mineral regained essentially all of its original C.E.C. (Turner and Brydon, 1965, 1966) whereas with vermiculite much of the interlayer hydroxide remained and the original C.E.C. was not regained with the formation of gibbsite. A

logical conclusion is that an appreciable amount of the interlayer $Al(OH)_x$ with vermiculite is stable relative to gibbsite whereas with montmorillonite it is not. This conclusion is supported by the results obtained when vermiculite was suspended in $AlCl_3$ solution without adding any base.

The experiment in which no base was added showed that when $(Al)(OH)^3$ in solution was maintained below the solubility product of gibbsite $(10^{-34 \cdot 0})$ an interlayer hydroxide was formed and the C.E.C. was reduced to 59 me per 100g, in accordance with results in the literature (Schwertmann, 1966; Sawhney, 1968). Thus, an interlayer hydroxide was formed in vermiculite by an interchange reaction or "autotitration" under conditions where no interlayer hydroxide developed with montmorillonite. If it is assumed that the H required for the H–Mg interchange arose through hydrolysis of water and yielded an equal amount of OH, and that all of the OH reacted with this Al taken up to form interlayer $Al(OH)_x$, the OH/Al ratio becomes $2 \cdot 1$ as compared to the value of $2 \cdot 7$ found for montmorillonite–$Al(OH)_x$ complexes (Turner, 1965). When $(Al)(OH)^3$ in solution was allowed to increase to $10^{-33 \cdot 6}$, which was only slightly greater than it was after 10 months aging with the large amounts of precipitated Al, there was a further reduction of the C.E.C. to 28 me per 100g. At this stage the C.E.C., the X-ray diffraction and DTA patterns were similar to those of the aged specimens with large amounts of precipitated Al. The X-ray pattern of the heated specimens of the aged sample with 650 me of Al per 100g of vermiculite (curve C, Fig. 5), however, was different from these but resembled the unaged samples containing larger amounts of precipitated Al (curve D, Fig. 5). These results provide further evidence that some of the freshly precipitated hydroxide was concentrated at the rim of the vermiculite particles but that this portion was dissolved after the formation of gibbsite. The single broad peak (curve B, Fig. 5) can be attributed to the effects of a randomly distributed interlayer hydroxide whereas the broad band and 14Å spacing (curve C and D) point to a more heterogeneous distribution with an accumulation at the rim. Removal of the rim material as gibbsite is formed might be expected to yield a more random distribution of the remaining interlayer hydroxide and this interpretation is supported by the similarity of curves E, F and B (Fig. 5). On the basis of these results there does not seem to be any doubt that even though some of the interlayer hydroxide is removed from vermiculite when gibbsite is formed, there is a considerable amount of it that is less soluble than gibbsite. It would be expected therefore, in agreement with results reported by Barn-

hisel*, that with some soil clays gibbsite would dissolve with the formation of hydroxyl aluminum interlayers.

REFERENCES

Barnhisel, R. I. and Rich, C. I. (1963) Gibbsite formation from aluminum interlayers in montmorillonite: *Soil Sci. Soc. Am. Proc.* **27**, 632–635.

Barshad, I. and Foscolos, A. E. (1970) Factors affecting the rate of interchange reaction of adsorbed H on the 2 : 1 clay mineral: *Soil Sci.* **110**, 52–60.

Brindley, G. W. and Gillery, F. H. (1956) X-ray identification of the chlorite species: *Am. Mineralogist* **41**, 169–186.

Brydon, J. E. and Kodama, H. (1966) The nature of aluminum hydroxide–montmorillonite complexes: *Am. Mineralogist* **51**, 875–889.

Brydon, J. E. and Ross, G. J. (1966) Stability of chlorite in dilute acid solutions: *Soil Sci. Soc. Am. Proc.* **30**, 740–744.

Fripiat, J. J., Chaussidon, J. and Touillaux, R. (1960) Study of the dehydration of montmorillonite and vermiculite by i.r. spectroscopy: *J. Phys. Chem.* **64**, 1234–1241.

Hofmann, U., Weiss, A., Koch, G., Mehler, A. and Scholz, A. (1956) Intracrystalline swelling, cation exchange and anion exchange of minerals of the montmorillonite group and of kaoline: *Clays and Clay Minerals* **4**, 273–287.

Hsu, Pa Ho (1968) Heterogenity of montmorillonite surfaces and its effect on the nature of hydroxy-aluminum interlayers: *Clays and Clay Minerals* **16**, 303–311.

Hsu, Pa Ho and Bates, T. F. (1964) Fixation of hydroxy-aluminum polymers by vermiculite: *Soil Sci. Soc. Am. Proc.* **28**, 763–769.

Mathieson, A. M. and Walker, G. F. (1954) Crystal structure of Mg–vermiculite: *Am. Mineralogist* **39**, 231–255.

Neumann, Barbara S. (1963) The thermal stability of acid extracted montmorillonite: *Proc. Intern. Clay Conf., Stockholm* 1963, pp. 85–96.

Rich, C. I. (1960) Aluminum in interlayers of vermiculite: *Soil Sci. Soc. Am. Proc.* **24**, 26–32.

Rich, C. I. (1968) Hydroxy interlayers in expansible layer silicates: *Clays and Clay Minerals* **16**, 15–30.

Sawhney, B. L. (1968) Aluminum interlayers in layer silicates: *Clays and Clay Minerals* **16**, 157–163.

*Barnhisel, R. I. Stability of gibbsite in the presence of Al–interlayered soil clays. *Agronomy Abstracts* p. 169, 1970 Annual Meeting, American Society of Agronomy, Tucson, Arizona.

Schwertmann, U. (1966) Das Verhalten von Vermiculiten Gegenuber Kalium, Aluminum and Andern Kationen— II. Chemische Untersuchungen: *Z. Pflanzenernahr. Dung., Bodenkunde* **115**, 200–209.

Schwertmann, U. and Jackson, M. L. (1964) Influence of hydroxy aluminum ions on pH curves of hydroxy-aluminum clays: *Soil Sci. Soc. Am. Proc.* **28**, 179–183.

Turner, R. C. (1965) Some properties of aluminum hydroxide precipitated in the presence of clays: *Can. J. Soil Sci.* **45**, 331–336.

Turner, R. C. (1967) Aluminum removed from solution by Montmorillonite: *Can. J. Soil Sci.* **47**, 217–222.

Turner, R. C. and Brydon, J. E. (1965) Factors affecting the solubility of $Al(OH)_3$ precipitated in the presence of montmorillonite: *Soil Sci.* **100**, 176–181.

Turner, R. C. and Brydon, J. E. (1966) The effect of length of time of reaction on some properties of sus-pensions of Arizona bentonite, illite and kaolinite in which aluminum is precipitated: *Soil. Sci.* **103**, 111–117.

Turner, R. C. and Brydon, J. E. (1967) Removal of inter-layer aluminum hydroxide from montmorillonite by seeding the suspensions with gibbsite: *Soil Sci.* **104**, 332–335.

Walker, G. F. (1956) The mechanism of dehydration of Mg–vermiculite: *Clays and Clay Minerals*, **4**, 101–115.

Walker, G. F. (1961) Vermiculite minerals. *The X-ray Identification and Crystal Structures of Clay Minerals* (Edited by G. Brown), Chap. VII, The Mineralogical Society, London.

Walker, G. F. and Cole, W. F. (1957) Vermiculite miner-als. *The Differential Thermal Investigation of Clays* (Edited by R. C. MacKenzie), The Mineralogical Society, London.

Résumé—On présente un échantillon de vermiculite du Kenya qui ne contient ni mica ni couches chloritiques, soit en phases séparées soit comme constituants d'une structure interstratifiée. La déshydroxylation comporte deux étapes, à 550° et 850°C; à chacune d'elles les hydroxyles sont libérés en quantités approximativement égales. La vermiculite du Kenya saturée par l'aluminium a des caractéristiques de déshydratation à basse température semblables à celles de l'échantillon saturé par le magnésium, mais les courbes d'ATD et d'ATG et les diagrammes de diffraction X obtenus par la technique de chauffage—oscillations montrent que le processus de déshydratation en trois étapes n'est pas aussi net dans le cas de l'échantillon saturé par l'aluminium.

Comme cela se passe avec la montmorillonite, si l'on précipite en présence de vermiculite de petites quantités d'aluminium par addition de $Ca(OH)_2$, le composé $Al(OH)_x$ se fixe sur l'argile qui le retient indéfiniment; le produit ionique $(Al)(OH)^3$ en solution est maintenu à $10^{-33,0}$, et il n'y a pas formation de gibbsite dans le temps. Avec de grandes quantités, 800 et 1600 me $Al(OH)_x$ pour 100 g de vermi-culite, l'hydroxyde est fixé initialement dans l'espace interfeuillet, mais la gibbsite peut se former lorsque le terme $(Al)(OH)^3$ devient voisin du produit de solubilité de ce minéral. Contrairement à ce qui se passe avec la montmorillonite, les échantillons de vermiculite retiennent une quantité appré-ciable d'hydroxyde interfeuillet et ne retrouvent pas la valeur de leur C.E.C. d'origine lorsqu'il y a formation de gibbsite.

Une vermiculite Al, traitée d'une façon répétée par mise en suspension dans $AlCl_3$ en maintenant le produit $(Al)(OH)^3$ à une valeur inférieure à $10^{-33,6}$ a libéré 435 me de Mg et fixé 208 me d'Al sous forme d'hydroxyde interfeuillet, ce qui a causé une réduction de la C.E.C. de 130 à 28 me pour 100 g d'argile. Avec la vermiculite, une quantité appréciable d'$Al(OH)_x$ interfeuillet est stable par rapport à la gibbsite, ce qui n'est pas le cas avec la montmorillonite.

Kurzreferat—Eine Probe von Kenya Vermiculit enthielt keine Glimmeroder Chloritschichten, weder als separate Phasen noch als Bestandteile eines zwischengeschichteten Gefüges. Dehydroxylierung erfolgte in zwei Stufen bei 550° und 850°C, wobei in jeder Stufe ungefähr gleiche Mengen von Hyd-roxyl freigemacht wurden. Al-gesättigter Kenya Vermiculit zeigte niedrige Temperature Dehydratisie-rungseigenschaften ähnlich denjenigen der natürlichen Mg-gesättigten Probe, doch zeigten die DTA, TGA und oszillierendheizenden Röntgenbeugungsbilder, dass der dreistufige Dehydratationsprozess bei der Al-gesättigten Probe nicht so deutlich war.

Wie bei Montmorillonit, wurde beim Niederschlag kleiner Mengen von Aluminium durch Zugabe von $Ca(OH)_2$ in der Gegenwart von Vermiculit, das $Al(OH)_x$ durch den Ton aufgenommen und un-begrenzt festgehalten, das Ionenprodukt $(Al)(OH)^3$ in Lösung blieb, weiter bei $10^{-33,0}$ und es bildete sich kein Gibbsit im Laufe der Zeit. Bei grossen Mengen, 800 und 1600 me $Al(OH)_x$ pro 100 g Vermiculit, wurde das Hydroxyd anfänglich im Zwischenschichtenraum festgehalten, doch wurde bei Annäherung des $(Al)(OH)^3$ and das Lösungsprodukt des Gibbsit schliesslich Gibbsit gebildet. Zum Unterschied von Montmorillonit heilten die Vermiculitproben eine beträchtliche Menge des Zwis-chenschichthydroxyds zurück und erreichten bei der Bildung des Gibbsit die ursprünglichen CEC Werte nicht.

Al-Vermiculit, wiederholt suspendiert in $AlCl_3$, mit $(Al)(OH)^3$ auf einem Wert unterhalb $10^{-33,6}$ festgehalten, setzte 435 Mg frei, nahm 208 me Al als Zwischenschichthydroxyd auf und rief eine Verminderung in C.E.C. von 130 auf 28 me pro 100 g Ton herbei. Bei Vermiculit war eine beträcht-liche Menge des Zwischenschicht $Al(OH)_x$ stabil in bezug auf Gibbsit während dies bei Montmoril-lonit nicht der Fall war.

Резюме — Вермикулит из Кении не содержал слюдяных и хлоритовых слоев, а также отдельных фаз или компонентов смешаннослойной структуры. Дегидратация проходила в две стадии — при 550° и 850°C с выделением приблизительно равных количеств гидроксилов. Насыщенный алюминием кенийский вермикулит обнаружил особенности низкотемпературной дегидратации, аналогичные характерным для природного образца, насыщенного магнием; однако кривые ДТА и ТГА, как и осциляционные рентгенограммы, полученные при нагревании образцов, показали, что трех-стадийная дегидратация не столь четко выражена у образца, насыщенного Al.

Как и в случае монтмориллонита, когда небольшие количества алюминия осаждались при добавлении $Ca(OH)_2$, в присутствии вермикулита $Al(OH)_x$ поглощался глиной и неограниченно удерживался ею; произведение растворимости $(Al)(OH)_3$ в растворе поддерживалось равным $10^{-33,0}$, образования гиббсита с течением времени не происходило. При больших количествах (800 и 1600 м — экв $Al(OH)_x$ на 100 г. вермикулита) гидроокись находилась первоначально в межслоевых промежутках, но в тех случаях, когда произведение растворимости $(Al)(OH)_3$ отвечало таковому гиббсита выделялся гиббсит. В отличие от монтмориллонита образцы вермикулита удерживали значительное количество межслоевой гидроокиси и не восстанавливали первоначальной способности к обмену катионов после образования гиббсита.

Al—вермикулит, который повторно переводился в суспензию $AlCl_3$, содержащую $(Al)(OH)_3$ при произведении растворимости менее $10^{-33,6}$, освобождал 435 м-экв Mg, поглощал 208 m экв Al в качестве межслоевой гидроокиси и вызывал уменьшение способности к обмену катионов с 130 до 28 м-экв на 100 г. глины. С вермикулитом заметное количество межслоевого $Al(OH)_x$ было устойчиво по отношению к гиббситу, тогда как в случае монтмориллонита это не имело места.