

## MINERALOGY AND CATION EXCHANGE PROPERTIES OF LIBBY VERMICULITE SEPARATES AS AFFECTED BY PARTICLE-SIZE REDUCTION\*

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**Abstract**—A vermiculite (Libby, Montana) sample obtained from the Zonolite company contained mostly coarse-grained separates with only 8.7 per cent clay. The 2–50  $\mu\text{m}$  fraction was used for particle-size reduction studies by wet and dry grinding, and size-fractionated into < 2, 2–5, 5–20 and 20–50  $\mu\text{m}$  sizes. About 18 per cent of the sample was attrited to clay after 64 hr of wet grinding, but as much as 59 per cent of the sample was attrited to clay after only 10 min of dry grinding. There was no evidence of damage to the crystal structure of derived clays or silts except for the 20–50  $\mu\text{m}$  fraction from dry grinding.

The observed CEC values of all the fractions decreased as grinding progressed, except for the 2–5  $\mu\text{m}$  fraction from wet grinding where the CEC increased. The decrease in CEC was attributed to an accumulation of biotite, either as a discrete mineral and/or a mixed-layer assemblage of biotite and vermiculite attrited to the clay fraction. In contrast, the fraction showing an increase in CEC was due to an increased concentration of higher charge-density (CEC) vermiculite. Biotite-free CEC data for vermiculite suggested that, in general, the coarser vermiculite separates had a higher CEC than the finer ones.

The susceptibility of minerals in the Libby vermiculite to cleavage by grinding was: vermiculite > hydrobiotite > biotite.

### INTRODUCTION

Specimen vermiculites employed in most studies are geologically derived from trioctahedral micas, phlogopite or biotite, by the geochemical replacement of interlayer K with Mg (or Ca). However, geologic deposits of vermiculite are seldom pure minerals; rather they contain, in addition to vermiculite, discrete or mixed-layer assemblages of the precursor mica with vermiculite. Regularly interstratified vermiculite–mica components were called hydrobiotite by Gruner (1934), but randomly interstratified assemblages of these components are too variable to justify a specific name.

Samples of vermiculite obtained from commercial suppliers, or collected by individual investigators, are usually coarse-grained particles or flakes. However, the samples employed in most ionic-equilibria studies are fine-grained, and are generally of clay size. Therefore, some kind of treatment is usually given to the coarse sample to obtain the desired particle-size separates. Exfoliation with  $\text{H}_2\text{O}_2$  to cleave the larger flakes, and wet grinding in the presence or absence of NaCl have most commonly been used (Alexiades and Jackson, 1965; Raman and Mortland, 1966; Rhodes, 1967; Sawhney, 1964; 1967; 1969). Also, some workers have

removed the interlayer K of vermiculite samples by treating them with NaCl before sample preparation (Carstea *et al.*, 1970; Ellis *et al.*, 1970; Rich, 1960). Various other chemical methods used to extract interlayer K from micas, e.g. neutral salt solution (Barshad, 1954), molten  $\text{LiNO}_3$  (White, 1956) and sodium tetraphenylboron (Reed and Scott, 1962) have not been employed on vermiculite as a pretreatment prior to particle-size reduction.

The literature on grinding reviewed by Grim (1968) indicated that grinding of minerals usually results in increased exchange capacity and may damage the crystal structure if the mineral is ground for long periods of time. Dry grinding is generally considered to be a severe treatment, but has been used for particle-size reduction of vermiculite (Malcolm and Kennedy, 1969; Wilding *et al.*, 1968).

The objectives of this investigation were to determine the effect of sample preparation methods on particle-size reduction, cation-exchange capacity (CEC) and consequent mineralogy of the resultant separates of Libby vermiculite. Emphasis will, however, be placed on the clay fraction. The silt fraction (2–50  $\mu\text{m}$ ) of the reference vermiculite was used for these studies because such separates are most likely to be reduced to finer grain-size separates upon attrition.

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### MATERIALS AND METHODS

A coarse-grained sample of Libby vermiculite was obtained through the courtesy of the Zonolite Company, Division of W. R. Grace & Co. This material is an alteration product of biotite and is believed to be of supergene origin (Bassett, 1959; Boettcher, 1966). Like most other vermiculites, it usually contains biotite as a discrete phase and/or mixed-layer assemblages of vermiculite–biotite; therefore, the mode of sample preparation was suspected of affecting the properties of the resultant separates. The sample was size-fractionated according to the methods of Rutledge *et al.* (1967) using 0.62 N  $\text{Na}_2\text{CO}_3$  as the dispersing agent and the automatic fractionator for clay ( $< 2 \mu\text{m}$ ) separation. Clay-size separates were removed by sedimentation and decanting, and the residual silt-size separates (2–50  $\mu\text{m}$ ) were oven-dried at  $100 \pm 2^\circ\text{C}$  and used for particle-size reduction studies by wet and dry grinding.

#### *Wet grinding*

Twenty-five g of the silt-size sample were weighed into a Waring Blendor cup containing 25 ml of 0.62 N  $\text{Na}_2\text{CO}_3$  and 250 ml of distilled water. The samples were ground for 0.5, 1, 2, 4, 8, 16, 32 and 64 hr. After grinding for specified time intervals, the suspensions were diluted to 1000 ml with distilled water. Aliquots consisting of 45 ml were transferred to centrifuge tubes, and centrifuged at 15,000 rpm (27,000 *g*) to remove the suspended particles. The sediment was returned to the original ground sample while the supernatant liquid was analyzed for K by atomic absorption (Perkin–Elmer 303).

The suspensions were then transferred with distilled water to settling containers of the automatic fractionator for separation of the clay fraction. Subsequently, 25 ml of 0.62 N  $\text{Na}_2\text{CO}_3$  were added to the 2–50  $\mu\text{m}$  residue sediment in the automatic fractionator and the 2–5  $\mu\text{m}$  silt fraction removed. The residual material (5–50  $\mu\text{m}$ ) was transferred to a sliding-base silt fractionator (Beavers and Jones, 1962) to separate the 5–20 and 20–50  $\mu\text{m}$  fractions. Excess NaCl (about 300 g) was added to the carboys containing clay ( $< 2 \mu\text{m}$ ) and fine silt (2–5  $\mu\text{m}$ ) separates to flocculate the suspensions. The supernatant was siphoned off, and the clay and the fine silt fractions were washed to remove the excess NaCl. The clay samples were air-dried, whereas other fractions were oven-dried for storage and subsequent analyses.

#### *Dry grinding*

Twenty-one grams of the 2–50  $\mu\text{m}$  silt sample were dry-ground in a disc-mill-type grinder, Siebtechnik Type T

100, for 2.5, 5.0 and 10.0 min. Twenty-five milliliters of 0.62 N  $\text{Na}_2\text{CO}_3$  were added to a 20 g aliquot and the resulting suspension shaken. Procedures for K assay and particle-size fractionation were similar to those of wet grinding.

#### *Cation-exchange capacity determination*

The CEC determination of vermiculite separates was made by saturating the exchange sites with a non-fixable cation, Ca (Sawhney *et al.*, 1959). Approximately 0.1 g of the sample was weighed accurately into a pre-weighed centrifuge tube, soaked overnight with about 20 ml of distilled water, and saturated with Ca by washing four times with 25 ml aliquots of 1 N  $\text{CaCl}_2$ . A Sorvall RC2-B, centrifuge was used to recover all of the sample after each washing. In order to avoid probable errors arising from hydrolysis and salt retention (Frink, 1964), the samples were then washed four times with 0.01 N  $\text{CaCl}_2$  solution. Immediately after the last washing, the centrifuge tubes were covered with parafilm and weighed. The adsorbed and occluded fractions of Ca were desorbed with four washings of 1 N  $\text{MgCl}_2$ . Total Ca in the  $\text{MgCl}_2$  displacing solution was determined using atomic absorption. Corrections for the occluded volume of 0.01 N  $\text{CaCl}_2$  were made before calculating the CEC.

#### *Total K determination*

Total K in the clay-, silt- and sand-size separates of the vermiculite was determined by X-ray spectrographic techniques using a sample: boric acid ratio of 7:3. Procedures and machine operating conditions followed were as outlined by Wilding *et al.* (1971).

#### *X-ray analysis*

X-ray diffractograms were obtained for all size separates collected as a function of grinding mode after selected time periods. These were compared with the reference fraction to determine the changes in component minerals of those fractions. In order to insure uniform thickness of clay, a 0.1 g (oven-dry basis) of the sample was used for each plate. The clays were Mg-saturated and plated on porous ceramic plates according to the methods used by Wilding *et al.* (1971). Only one plate was prepared for each treatment. Air-dried plates were scanned over the range of  $2\text{--}32^\circ 2\theta$ . The plates were then heated to  $400^\circ\text{C}$  and X-rayed again. For the 2–5, 5–20 and 20–50  $\mu\text{m}$  separates, the samples were suspended in acetone and plated on glass slides using a dropper technique. Random powder samples were also prepared in aluminum holders for the 2–50 and  $> 50 \mu\text{m}$  separates.

Table 1. Particle-size distribution, total K, calculated biotite content and cation-exchange capacities of different size-fractions of the reference vermiculite

Particle size	Particle size distribution* (%)	Total K (%)	Biotite content† (%)	CEC
				m-equiv. 100 g <sup>-1</sup>
Clay (< 2 μm)	8.7	1.80	21.7	132.5
Silt (2–50 μm)	54.9	5.52	66.5	74.6
Sand (> 50 μm)	36.4	6.00	72.3	nd‡

\* Based on 1175 g of the reference sample fractionated.

† Calculated on the basis of 8.3 per cent K in biotite (Boettcher, 1966).

‡ nd—not determined.

## RESULTS AND DISCUSSION

The particle-size distribution of the reference Libby vermiculite sample along with total K, calculated biotite content and cation-exchange capacities of different size-fractions are given in Table 1. According to the supplier, the reference sample as received from the Zonolite Company had already been ground to pass a 150-mesh sieve (about 100 μm). Particle-size distribution data indicated that most of the reference sample was composed mostly of silt, with a lesser proportion of sand and only 8.7 per cent clay. This particle-size distribution is typical of vermiculite samples obtained from the suppliers and explains why some workers who used finer fractions in their studies provided some means, usually grinding, for particle-size reduction (Alexiades and Jackson, 1965; Rhodes, 1967; Sawhney, 1967; Weed and Weber, 1969).

The K content of different size fractions indicated that the silt and sand fractions contained about three times as much K as the clays (Table 1). Based on the reported 8.3 per cent K (10.0 per cent K<sub>2</sub>O) content

for biotite in the Libby vermiculite sample from the same location as of Boettcher (1966), it would appear that the biotite content of these fractions was approximately 22, 66 and 72 per cent in the clay, silt and sand fractions, respectively. X-ray diffractograms (Fig. 1) showed that in the clay fraction, biotite was present only as a regularly or randomly interstratified component with vermiculite as evidenced by broad peak in the region of 25 Å. In silts, biotite appears to be present both as a discrete mineral (10 Å peak) and as a regularly interstratified component (25 and 12.5 Å peaks). However, in the sand fraction, biotite was primarily present as a discrete mineral with lesser proportions as perhaps randomly and regularly interstratified components with vermiculite (11 and diffuse 25 Å peaks). In this fraction, the lack of an observable vermiculite peak (14.5 Å) indicates that the vermiculite present was only in mixed-layer association with biotite but not as a discrete mineral. Since the reference sample had been previously ground by the supplier, it is probable that the concentration of vermiculite in the clay and silt fractions is an indication that the

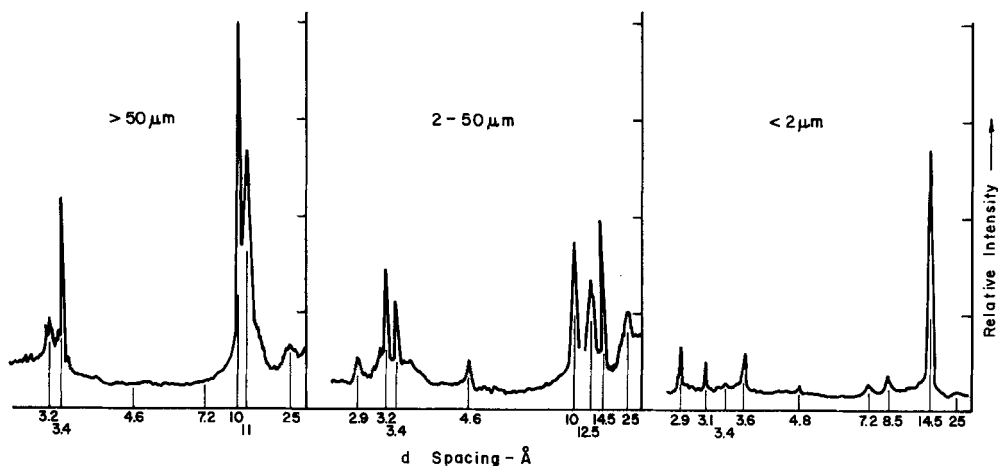


Fig. 1. X-ray diffractograms of different particle-size fractions separated from reference vermiculite sample (air-dry treatment).

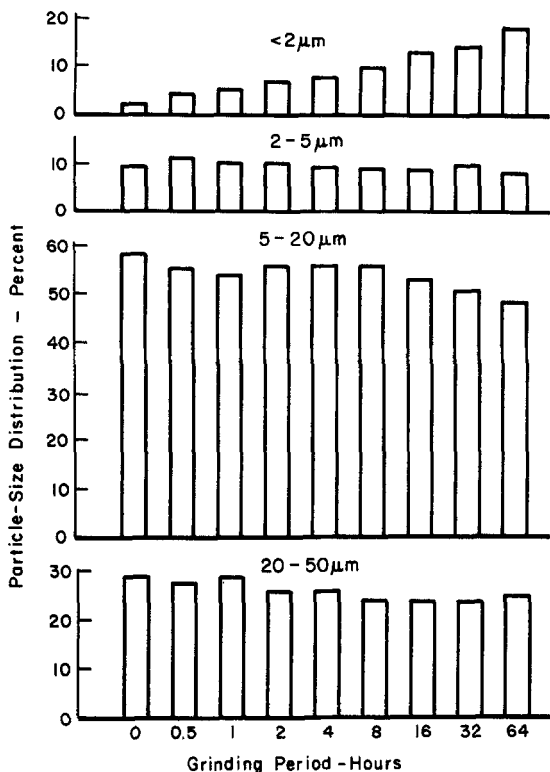


Fig. 2. Particle-size distribution of the 2-50  $\mu\text{m}$  reference vermiculite as affected by wet grinding.

biotite is more resistant to grinding than the vermiculite. This may be attributed to the weaker Mg-double-water-layer bonding between the planar sheets of vermiculite compared to the stronger K bonding in the case of biotite.

The effects of wet and dry grinding on particle-size distribution are shown in Figs. 2 and 3. A small amount of clay, 2.4 per cent, was formed with no grinding treatment; this is probably a consequence of slaking at the edges of the oven-dried reference sample upon suspension, sedimentation and decantation during the 8-10 cycles of the automatic fractionator. Alternatively, incomplete clay separation of the reference sample may have yielded a portion of this clay. From the histograms, it is apparent that the clay formed increased with increasing periods of both wet and dry grinding. A maximum of about 18 per cent of the sample was converted into clay after 64 hr of wet grinding whereas up to 59 per cent of the sample was converted into clay after only 10 min of dry grinding. For wet grinding, the 2-5  $\mu\text{m}$  fraction remained almost constant over the entire range of grinding periods while the tendency for the 5-20 and 20-50  $\mu\text{m}$  fractions was to decrease with the increase in grinding time (Fig. 2). This implies that there was a balance between the

coarser separates attrited to 2-5  $\mu\text{m}$  and the 2-5  $\mu\text{m}$  fraction attrited to < 2  $\mu\text{m}$ . However, in the case of dry grinding, the 2-5  $\mu\text{m}$  fraction first increased with time reaching a maximum of about 27 per cent after 5 min of grinding, after which the proportion dropped to about 19 per cent (Fig. 3). Both 5-20 and 20-50  $\mu\text{m}$  fractions decreased with increasing grinding times as was observed in the case of wet grinding (Figs. 2 and 3).

X-ray diffractograms of the Mg-saturated clays derived from wet grinding indicated that the relative peak intensities (14.5  $\text{\AA}$ ) of the air-dried samples increased in the clays derived from longer periods of wet grinding (Fig. 4). Progressive enhancement of this peak was consistent over the entire range of wet grinding periods; i.e. 0-64 hr. The increase in peak intensities may be due to an increase in particle size and/or an increase in crystallinity of the clays contributed after longer grinding periods. When the samples were heated to 400°C (diffractograms not shown), the same trends were observable upon collapse of the 14.5  $\text{\AA}$  peak to 10  $\text{\AA}$  which may partially reflect increased hydrobiotite with grinding time. In contrast, there was no significant difference in the peak intensities of clay samples in the case of dry grinding (Fig. 5). However, when the samples were heated, the 10  $\text{\AA}$  peak intensity

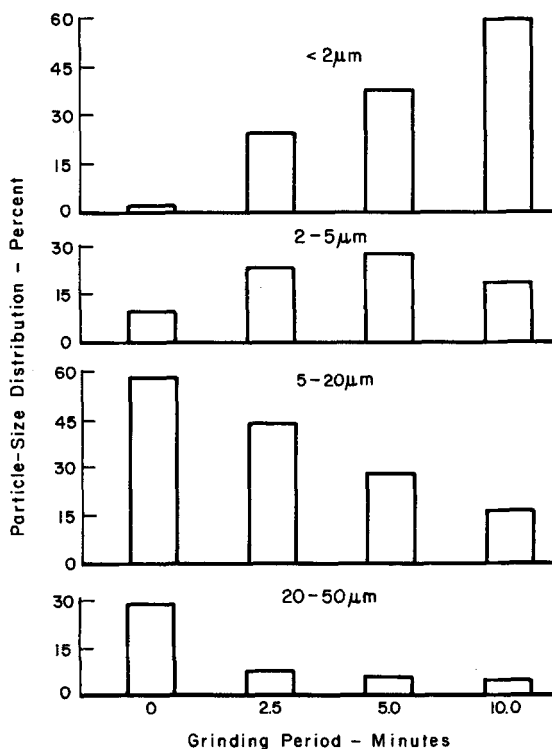


Fig. 3. Particle-size distribution of the 2-50  $\mu\text{m}$  reference vermiculite as affected by dry grinding.

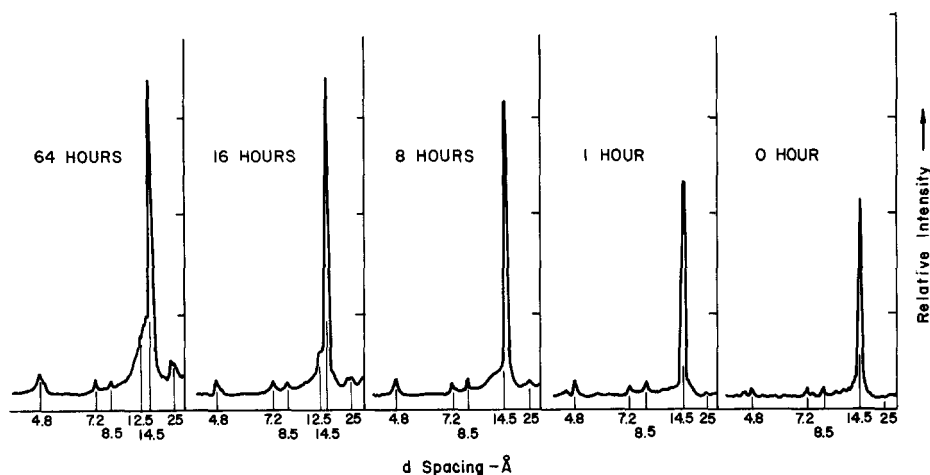


Fig. 4. X-ray diffractograms of Mg-saturated clay-size separates obtained by wet grinding of the 2–50  $\mu\text{m}$  reference vermiculite (air-dry treatment).

of the sample ground for 10 min was greater than the sample ground for only 2.5 min (diffractograms not shown). This increase in 10 Å peak intensities with grinding time may also be attributed to the interstratified component which collapsed on heating and was additive to the collapsed 10 Å vermiculite peak.

In the wet-ground clay samples, the first order 25 Å peak started to appear after 1-hr grinding treatment (Fig. 4). This peak can probably be ascribed to the random and/or regular interstratification of vermiculite and biotite. The second-order peak, 12.5 Å, of this interstratified component was not evident until after 16 hr of grinding. However, both of these peaks increased in intensity with time of grinding. In contrast, the first- and second-order peaks of the interstratified component were visible after the first 2.5 min of the dry-grinding treatment, and these peak intensities increased substantially when the sample had been ground for 5 and 10 min (Fig. 5).

There was a positive linear relationship between the clay formed and K released in both wet and dry grinding treatments (Fig. 6). Increasing amounts of K released with increased amounts of clay formed, both by wet and dry grinding, probably reflect the absolute amount of biotite as a discrete mineral, an interstratified component, or both, attrited to clay fraction. However, such information does not elucidate the type of cleavage (planar or vertical) involved.

In addition to vermiculite, X-ray diffractograms of the derived clay samples indicated that only the hydrobiotite of the reference sample was going into the clay fraction, and its relative proportions increased as the grinding progressed (Figs. 4 and 5). The absence of biotite (10 Å peak) in the derived clay samples, therefore, suggests that biotite present in the reference sample was more resistant to grinding than hydrobiotite.

Based on the mineralogical composition of the different fractions obtained by the grinding of 2–50  $\mu\text{m}$

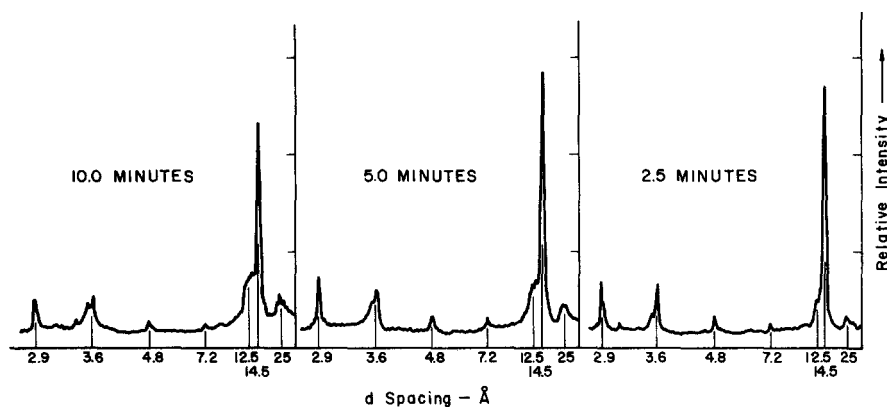


Fig. 5. X-ray diffractograms of Mg-saturated clay-size separates obtained by dry grinding of the 2–50  $\mu\text{m}$  reference vermiculite (air-dry treatment).

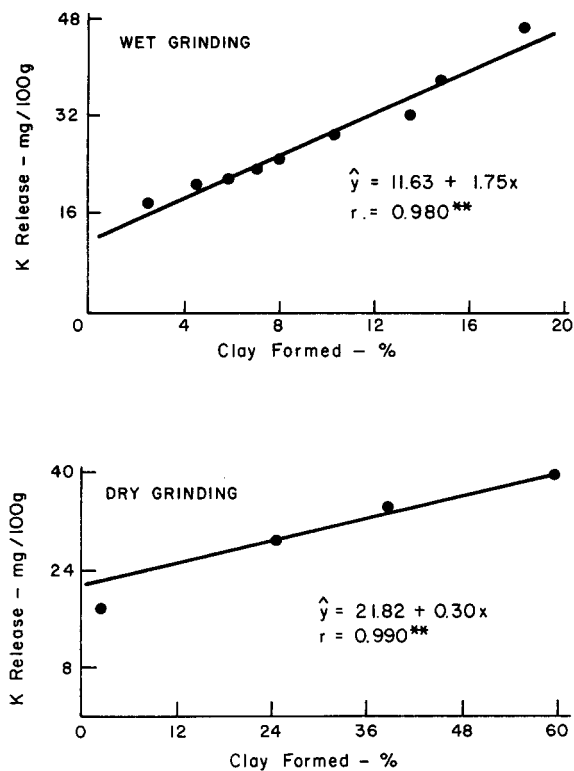


Fig. 6. Potassium release in relation to clay formed by wet and dry grinding of the 2–50  $\mu\text{m}$  reference vermiculite.

fraction and the original reference sample, it is, therefore, proposed that the order of susceptibility to cleavage of these minerals by grinding Libby vermiculite is:

Vermiculite > Hydrobiotite > Biotite.

The CEC values of all the size-fractions obtained by wet and dry grinding are shown in Figs. 7 and 8. The 20–50  $\mu\text{m}$  sample used for wet and dry grinding studies contained vermiculite, hydrobiotite and biotite (Fig. 1). The CEC values of similar minerals, but of soil origin, have been reported to be 111, 48 and 15 m-equiv 100  $\text{g}^{-1}$ , respectively (Coleman *et al.*, 1963).

The CEC values of the < 2, 5–20 and 20–50  $\mu\text{m}$  fractions derived by wet grinding decreased with time whereas those of the 2–5  $\mu\text{m}$  fraction increased (Fig. 7). X-ray diffractograms of the clay samples indicated that as the grinding progressed, more of the hydrobiotite along with vermiculite went to the clay fraction (Fig. 4, Table 2). Since this interstratified component has much lower CEC compared to vermiculite (Coleman *et al.*, 1963), the decrease in CEC of the clay samples derived from longer periods of grinding should be expected. In the 5–20 and 20–50  $\mu\text{m}$  fractions, the decrease in CEC may be attributed to a concentration of

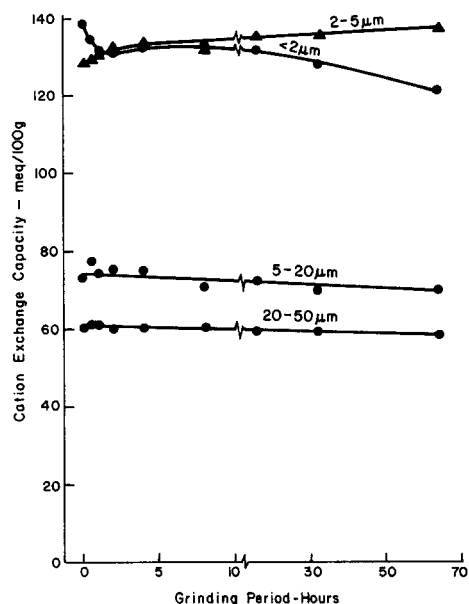


Fig. 7. Cation-exchange capacity of the various separates as affected by wet grinding of the 2–50  $\mu\text{m}$  reference vermiculite.

the residual hydrobiotite and biotite which have lower CEC (Table 2). The increase in CEC of the 2–5  $\mu\text{m}$  fraction with grinding time probably represents an accumulation of vermiculite with higher CEC in this fraction that was not subsequently attrited to the clay fraction. Note the higher CEC vermiculite in the 5–20

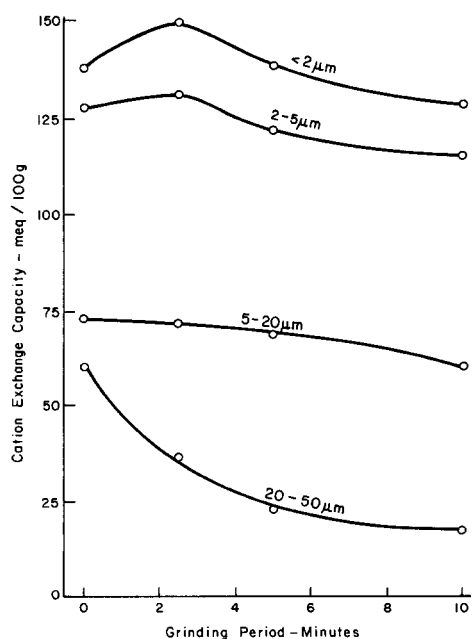


Fig. 8. Cation-exchange capacity of the various separates as affected by dry grinding of the 2–50  $\mu\text{m}$  reference vermiculite.

Table 2. Cation-exchange capacity, total K and calculated biotite content of the separates obtained by wet grinding of the 2–50  $\mu\text{m}$  reference vermiculite

Grinding period (hr)	CEC (m-equiv 100 g <sup>-1</sup> )		Total K (%)	Biotite content‡ (%)
	Observed	Biotite-free basis†		
< 2 $\mu\text{m}$				
Ref. sample				
0, 1 & 2	132.5	165.4	1.82	21.9
4 & 8	134.6*	155.5	1.24	14.8
8 & 16	133.0*	157.5	1.53	18.4
64	133.0*	163.2	1.70	20.4
	121.6	164.8	2.40	28.8
2–5 $\mu\text{m}$				
Ref. sample				
0	130.5	152.6	1.34	16.0
4	128.3	150.2	1.35	16.2
8 & 16	133.4	154.2	1.25	15.0
2, 16 & 32	132.2*	152.8	1.24	14.9
32	135.6*	154.2	1.11	13.3
64	135.8	157.8	1.28	15.4
	137.1	157.0	1.17	14.0
5–20 $\mu\text{m}$				
Ref. sample				
0	69.5	199.4	5.71	68.6
4	73.1	207.3	5.66	68.0
8	75.3	219.0	5.72	68.8
16	71.1	208.3	5.76	69.2
32	72.5	216.7	5.81	69.8
64	70.0	209.2	5.82	69.9
	70.2	211.2	5.83	70.1
20–50 $\mu\text{m}$				
Ref. sample				
0	61.6	166.4	5.58	67.0
4	60.2	161.9	5.57	66.9
8	60.3	167.2	5.66	68.0
16	60.2	168.8	5.69	68.4
32	59.7	167.1	5.69	68.4
64	59.7	167.7	5.70	68.5
	58.2	166.8	5.76	69.3

\* In some treatments, the sample was insufficient for total K determination, therefore, different treatment samples were mixed and a calculated CEC reported on the basis of the observed CEC and the proportions of each sample in the mixture.

† The CEC of biotite was assumed to be 15 m-equiv 100 g<sup>-1</sup> for the < 2 and 2–5  $\mu\text{m}$ , and 10 m-equiv 100 g<sup>-1</sup> for the 5–20 and 20–50  $\mu\text{m}$  separates.

$$\text{Biotite-free CEC} = \frac{\text{Observed CEC} - \text{CEC due to biotite}}{100 - (\% \text{ biotite})} \times 100$$

‡ Calculated on the basis of 8.3 per cent K in biotite (Boettcher, 1966).

and 20–50  $\mu\text{m}$  fraction when computed on biotite-free basis (Table 2).

The CEC values of different fractions obtained by dry grinding followed the same general trends as wet grinding (Fig. 8). However, the disparity in CEC values between the < 2  $\mu\text{m}$  and the 20–50  $\mu\text{m}$  fractions was much larger, especially for the 10-min grinding period. Possible explanation for this phenomenon is that most

of the vermiculite attrited to the finer fractions, especially clay, and the residual coarser fractions, particularly 20–50  $\mu\text{m}$ , were mostly biotite which has much lower CEC (Table 3). In fact, from the CEC data one would argue that most of the vermiculite in the 2–50  $\mu\text{m}$  fraction attrited to < 2  $\mu\text{m}$  in 2.5 min of dry grinding with a minimum contamination of hydrobiotite components.

Table 3. Cation-exchange capacity, total K and calculated biotite content of the separates obtained by dry grinding of the 2–50  $\mu\text{m}$  reference vermiculite

Grinding period (min)	CEC (m-equiv 100 g <sup>-1</sup> )		Total K (%)	Biotite content† (%)
	Observed	Biotite-free basis†		
	< 2 $\mu\text{m}$			
Ref. sample				
2.5 & 5.0	132.5	165.4	1.82	21.9
5.0	143.8*	200.0	2.53	30.4
5.0	139.3	199.8	2.72	32.7
10.0	129.3	210.9	3.47	41.7
	2–5 $\mu\text{m}$			
Ref. sample				
2.5	130.5	152.6	1.34	16.0
5.0	131.4	164.9	1.86	22.3
5.0	122.6	159.6	2.13	25.6
10.0	115.8	153.0	2.24	27.0
	5–20 $\mu\text{m}$			
Ref. sample				
2.5	69.5	199.4	5.71	68.6
5.0	72.7	213.0	5.75	69.1
5.0	69.2	206.8	5.82	69.9
10.0	60.5	185.5	5.93	71.2
	20–50 $\mu\text{m}$			
Ref. sample				
2.5	61.6	166.4	5.58	67.0
5.0 & 10.0	36.7	126.6	6.42	77.1
5.0 & 10.0	20.9*	67.6	6.74	81.0

\* In some treatments, the sample was insufficient for total K determination, therefore, different treatment samples were mixed and a calculated CEC reported on the basis of the observed CEC and the proportions of each sample in the mixture.

† The CEC of biotite was assumed to be 15 m-equiv 100<sup>-1</sup> for the < 2 and 2–5  $\mu\text{m}$ , and 10 m-equiv 100 g<sup>-1</sup> for the 5–20 and 20–50  $\mu\text{m}$  separates.

$$\text{Biotite-free} = \frac{\text{Observed CEC} - \text{CEC due to biotite}}{100 - (\% \text{ biotite})} \times 100$$

‡ Calculated on the basis of 8.3 per cent K in biotite (Boettcher, 1966).

In summary, the decrease or increase in CEC of derived fractions from both grinding modes was associated with the proportion of biotite (or hydrobiotite) of lower CEC (Tables 2 and 3). Increase in biotite based on total K content is merely a manifestation of physical breakdown of lower K-components (vermiculite and hydrobiotite) to finer fractions upon grinding.

Calculated biotite-free CEC values for vermiculite are presented in Tables 2 and 3. In general, the data for wet grinding (Table 2) indicated that the CEC values of vermiculite in the finer fractions were lower compared to the coarser fractions, especially the 5–20  $\mu\text{m}$  separates. Similar results were obtained by Kerns and Mankin (1966) while working with Llano vermiculite. Their explanation, based on total chemical analyses of different separates, was that the coarser fractions primarily consisted of trioctahedral vermiculite whereas

smaller crystallites were dioctahedral. In the case of dry grinding (Table 3), vermiculite in the < 2 and 5–20  $\mu\text{m}$  fractions had almost the same CEC. Dry grinding is a more vigorous treatment than the wet grinding as supported by the greater amount of clay formed (Figs. 2 and 3), so it is possible that the higher CEC vermiculite in the coarser fractions was attrited to < 2  $\mu\text{m}$  during grinding. Very low CEC values of the 20–50  $\mu\text{m}$  vermiculite were probably due to crystal damage as suggested by diffuse X-ray diffraction patterns (diffractograms not shown).

## CONCLUSIONS

There was no evidence of damage to the crystal structure of derived clays or silts except for the 20–50  $\mu\text{m}$  fraction from dry grinding. However, the CEC of



clays formed by progressive wet and dry grinding decreased slightly with the exception of higher CEC values after 2.5 min dry grinding. The small decreases in CEC values with both wet and dry grinding were attributable to hydrobiotite attrited to the clay fraction. It is, therefore, suggested that either of the two modes of grinding can be used to obtain greater yields of the clay-size separates depending upon the availability of equipment and the clay yields desired. Optimum observed CEC values of about 150 m-equiv.  $100 \text{ g}^{-1}$  were obtained in the case of 2.5 min dry grinding with clay yields much greater than that after 64 hr wet grinding. Thus, short periods of dry grinding and perhaps longer periods of wet grinding could be used safely to obtain desired amounts of clay-size materials.

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**Résumé**—On a reçu de la Zonolite Company un échantillon de vermiculite (Libby, Montana) qui contenait principalement un matériau de granulométrie grossière avec seulement 8,7 pour cent d'argile. La fraction 2–50  $\mu\text{m}$  a été utilisée pour étudier la réduction de la taille des particules par broyage humide et sec; elle a été séparée en fractions <2, 2–5, 5–20 et 20–50  $\mu\text{m}$ . Environ 18 pour cent de l'échantillon a été réduit par broyage humide jusqu'à la dimension argile, en 64 hr; par contre, 10 min ont suffi, en broyage sec, pour amener 59 pour cent de l'échantillon à la dimension argile. Il n'y a pas eu de preuve de détérioration de la structure cristalline des argiles ou des limons obtenus, excepté pour la fraction 20–50  $\mu\text{m}$  provenant du broyage sec.

Les valeurs de la CEC de toutes les fractions ont diminué lors du broyage, sauf pour la fraction 2–5  $\mu\text{m}$  provenant du broyage humide où la CEC a augmenté. La diminution de la CEC a été attribuée à une accumulation de biotite, comme minéral individualisé et/ou comme assemblage interstratifié de biotite et de vermiculite réduit à la dimension argile. Inversement, l'apparition d'une fraction où la CEC a augmenté est due à la concentration de vermiculite à densité de charge (CEC) plus élevée. Les valeurs de la CEC de la vermiculite sans biotite suggèrent qu'en général les grains de vermiculite grossière ont une CEC plus élevée que les grains plus fins.

Les susceptibilités au clivage lors du broyage des minéraux de la vermiculite de Libby se classent dans l'ordre suivant: vermiculite > hydrobiotite > biotite.

**Kurzreferat**— Eine Vermiculitprobe (Libby, Montana), die von der Zonolit Company erhalten wurde, enthielt vorwiegend grobkörnige Anteile mit nur 8,7 Prozent Ton. Zu Untersuchungen über die Teilchengrößenverminderung durch feuchtes und trockenes Mahlen, wurde die 2–50  $\mu\text{m}$ -Fraktion herangezogen und in die Korngrößenfraktion en <2, 2–5, 5–20, 20–50  $\mu\text{m}$  unterteilt.

Nach 24 Stunden feuchten Mahlens waren etwa 18 Prozent der Probe zu Ton zerkleinert, während nach nur 10 min Trocken-mahlung 59 Prozent der Probe zu Ton umgewandelt worden war. Außer bei der Fraktion 20–50  $\mu\text{m}$  bei trockenem Mahlen ergaben sich keine Hinweise auf eine Zerstörung der Kristallstruktur bei den erhaltenen Tonen oder Schluffen.

Die beobachteten Austauschkapazitätswerte aller Fraktionen nahmen mit fortschreitendem Mahlen ab, außer bei der 2–5  $\mu\text{m}$ -Fraktion, die durch feuchtes Mahlen erhalten wurden. Hier stieg die Austauschkapazität an. Die Abnahme der Austauschkapazität wurde auf eine Anreicherung von Biotit zurückgeführt, der entweder als gesondertes Mineral und/oder als Wechsellagerung von Biotit und Vermiculit zu Ton zerkleinert wurde. Im Gegensatz hierzu war die Fraktion, die einen Anstieg der Austauschkapazität zeigte, das Produkt einer Konzentrationszunahme von Vermiculit hoher Ladungsdichte (Austauschkapazität) Austauschkapazitätswerte biotitfrier Vermiculite lassen vermuten, daß im allgemeinen gröbere Vermiculitfraktionen eine höhere Austauschkapazität als die feineren aufweisen.

Die Empfindlichkeit der im Libby-Vermiculit enthaltenen Minerale gegen eine durch Mahlen ausgelöste Aufspaltung war folgendermaßen abgestuft: Vermiculit > Hydrobiotit > Biotit.

**Резюме** — Образец вермикулита (Либби), полученный от фирмы Зонолит содержал большей частью отдельные осадения и только 8,7% глины. Фракция размером 2–50  $\mu\text{m}$  использовалась для изучения редуции размера частиц путем мокрого и сухого размалываний; частицы фракционировали до <2, 2–5, 5–20 и 20–50  $\mu\text{m}$ . После 64 часового мокрого размалывания только примерно 18% образца истерлось в глину, но после десяти минутного сухого размалывания такое большое количество как 59%. В полученных глинах или осадках не было замечено никакого повреждения структуры, исключая фракции 20–50  $\mu\text{m}$  после сухого размалывания.

Обратили внимание на то, что во время размалывания величины СЕС всех фракций понизились и только величина СЕС фракции 2–5  $\mu\text{m}$  увеличилась от мокрого размалывания. Уменьшение СЕС отнесли к скоплению биотита в виде разобщенного минерала и/или в виде смешанных слоев биотита/вермикулита притертых к фракциям глины. В то время как повышение СЕС во фракции отнесли к повышению концентрации вермикулита более высокого заряда. Данные о СЕС для вермикулита свободного от биотита наводят на мысль, что в общем СЕС грубозернистого вермикулита выше, чем мелкозернистого.

Способность минералов в вермикулите Либби раскалываться при размалывании следующая:

вермикулит > гидробиотит > биотит.