

THE MINERALOGY OF SOME COMMERCIAL VERMICULITES

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ABSTRACT

A number of different commercial vermiculites have been examined and it has been found that the exfoliable minerals can be divided into three main groups; those which give a 26 Å spacing on an X-ray diffraction pattern, those which give a 14 Å spacing, and those which give various spacings and are partially dehydrated. All are mixed-layer minerals of one type or another, but all have some vermiculite layers in their constitution. The expansibility of these minerals is not linked with their structural types, but there is an indication that the largest expansion is associated with the occurrence of hydrobiotite and the lowest expansion with the occurrence of true vermiculite.

INTRODUCTION

'Vermiculites' are used extensively in the building industry for insulating material and as a lightweight aggregate for concrete. The material may be imported in the unexfoliated state and exfoliated near where it is needed. This is a considerable assistance in transport, which constitutes a major part of the cost of a building material.

A number of samples of commercial vermiculite have from time to time been submitted to the Building Research Station for examination, and the opportunity has been taken of making a mineralogical examination.

EXPERIMENTAL

Differential thermal analysis, X-ray flake and powder diffraction analysis, and expansibility measurements have been carried out on the samples.

Differential thermal analysis was performed in ceramic crucibles with chromel-alumel thermocouples, the temperature being measured in the sample; the heating rate was $10 \pm 1^\circ\text{C}/\text{min.}$ and between 0.7 g and 1.0 g of sample was used.

The X-ray diffraction patterns were recorded on films, using cylindrical cameras of 10 cm diameter; the radiations used were filtered $\text{CuK}\alpha$ and $\text{CoK}\alpha$. The samples used in the cameras were either flakes or powder. The flakes were cut from the mineral and

gave strongly oriented photographs, only the basal spacing being recorded. For the powder samples, the mineral was ground to pass a 100-mesh B.S. sieve and then introduced into a 0.2 mm cellulose acetate capillary; these gave non-oriented photographs, the basal reflections being supplemented by general reflections.

The expansibility was measured by the change in the apparent density. A known volume was weighed, exfoliated by heating in an electric muffle furnace at 750°C for about ten minutes, and the apparent volume again measured by tipping the loose fragments into a measuring cylinder without compaction. In some instances the volume was also measured by the volume of sand it displaced.

CLASSIFICATION

It was found convenient to divide the commercial vermiculites on the basis of the X-ray flake diagram into three groups—the 26 Å, the 14 Å, and the mixed. In the 26 Å group the flake X-ray diagram, but not always the powder diagram, showed a strong reflection at about 26 Å; the second group gave a strong 14 Å reflection but none at 26 Å, the mixed group showed various reflections and some indications of being partially dehydrated.

26 Å Group. Five samples, for which complete X-ray data are given in Table 1, fall into this class. As there are some differences between the samples it was possible to subdivide the group into two—namely, samples C and F, and samples O, E and N. Samples C and F showed in the flake photograph that there was ordering of the basal reflections, the d values being reasonably integral and all the reflections being present. The effect of heating a flake of C to 520°C is shown in Table 2; a similar result was obtained with Sample F.

This result is indicative of a mixture of a mica-type layer structure and a dehydrated or partially dehydrated vermiculite. It is therefore suggested that samples C and F are regular 1:1 mixed-layer vermiculite-mica minerals, equivalent to the hydrobiotite of Gruner (1934).

The other three samples of the 26 Å group, O, N and E, gave data similar to those quoted in Table 3 for sample O. From this Table it can be seen that the flake pattern is very similar to that of sample C, but in contrast to C the powder data for sample O are different from those given by a flake, showing a strong reflection at 15 Å as well as at 12.5 Å; the former expands to 24 Å on glycerol treatment. This is typical of a true vermiculite, and it is suggested that

TABLE 1—X-ray flake diffraction data for the 26 Å group.

C*		O*		F*		E*		N*		Indices
$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I	
25.5	vs	26.2	vw	24.3	w	24.1	vw	23.8	w	001
12.4	vs	12.1	ms	12.9	vs	12.3	vs	12.5	ms	002
8.2	w			8.1	ms	8.05	vw	7.9	vw	003
6.15	vw							6.5	vw	004
4.92	ms	4.88	s	4.86	s	4.88	vs	4.84	vs	005
4.11	vw									006
3.53	vs	3.47	vs	3.49	vs	3.50	vs	3.51	vs	007
3.09	vs	3.07	m	3.01	m	3.02	ms	3.03	w	008
		2.71	m	2.73	m	2.74	ms	2.74	w	009

*Sample designation.

TABLE 2—X-ray diffraction data for sample C.

Normal flake		Heated to 520°C	
$d(\text{Å})$	I	$d(\text{Å})$	I
25.5	vs	13.5	w
12.4	vs	12.15	w
8.2	w	9.85	vs
6.15	vvw		
4.92	ms	4.88	vw
4.11	vw	4.54	vvw
3.53	vs	4.06	vw
3.09	vs	3.27	m

the second sub-group is a mixture of hydrobiotite and vermiculite. The mixture occurs within each individual flake but there is no ordered repeating of the layers. Such minerals could represent stages in the interlayer hydration of the basic mica layer structure.

The differential thermal curves of the 26 Å group of commercial vermiculites are reproduced in Fig. 1; they do not show so clearly the division into the two sub-groups. All the curves show large endothermic peaks at about 157°C together with smaller ones at about 270°C, and all show peaks of varying height at about 550°C and 600°C. There is some difference between samples C and F (hydrobiotites) and samples O, N and E (hydrobiotite-vermiculite mixtures), in that the hydrobiotites have the smaller peaks at 820°C. However, the size of this peak is probably influenced by the type of exchangeable ion present and is not characteristic of the structural type (Barshad, 1948; Ernst, Havens and Wilson, 1958). It has been shown by Ernst, Havens and Wilson (1958) that the smallest peak in this region is obtained when K^+ is the exchangeable ion. The samples in the first sub-group contain more mica layers than those in

TABLE 3—X-ray diffraction data for sample O.

Flake		Powder		Glycerol-treated		Heated to 520°C	
$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I
26.2	vw	15	vs	24	s b		
12.1	m	12.5	s	12.5	s	10.15	vs
4.88	s	4.5	ms	4.9	s	4.96	mw
3.47	vs	3.4	m	3.5	s	3.37	m
3.07	mw	2.75	w	3.02	w		
2.71	mw	2.6	m				

TABLE 4—X-ray flake diffraction data for the 14 Å group.

Indices	AB*	M*	AA*	R*	P409*	P136*
	$d(\text{Å})$ I	$d(\text{Å})$ I	$d(\text{Å})$ I	$d(\text{Å})$ I	$d(\text{Å})$ I	$d(\text{Å})$ I
002	14.3 vs	14.4 vs	14.4 vs	14.2 s	14.4 vs	14.3 s
004	7.1 mw	7.2 mw	7.13 mw	7.15 w	7.15 mw	7.15 mw
006	4.74 s	4.78 ms	4.78 m	4.78 s	4.79 s	4.80 s
008	3.56 vs	3.58 s	3.58 vs	3.59 vs	3.59 vs	3.58 vs
00,10	2.85 vs	2.87 s	2.875 vs	2.87 vs	2.88 vs	2.87 s
00,12	2.38 vw	2.39 vw	2.40 vw	2.38 w	2.40 vw	
00,14	2.04 m	2.05 vw	2.05 vw		2.06 vw	

*Sample designation.

the second, which is quite consistent with this interpretation since they will have a greater proportion of interlayer K^+ .

14 Å Group. The samples in the 14 Å group all give similar X-ray flake diffraction photographs (Table 4), and all except M, are of a similar nature. They will be discussed as one group with reference to sample AB, for which X-ray diffraction data on treatment with glycerol and on heating to 520°C are given in Table 5.

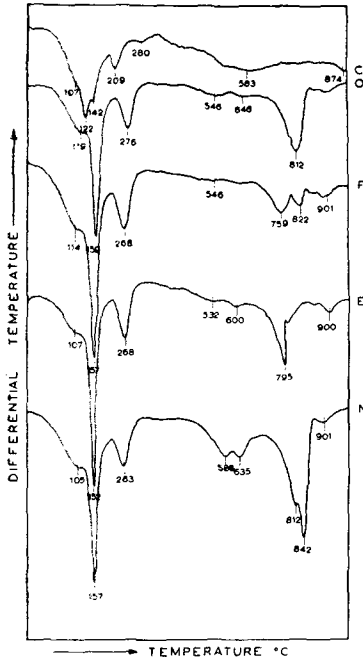


FIG. 1—Differential thermal curves for commercial vermiculites of the 26 Å group.

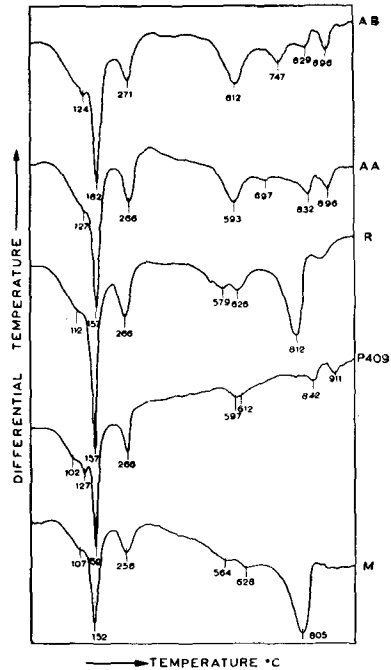


FIG. 2—Differential thermal curves for commercial vermiculites of the 14 Å group.

The results are what would be expected from a true vermiculite, but could also be produced from a vermiculite-chlorite mixed-layer mineral. Walker and Cole (1957) have shown that these two types can be distinguished by their differential thermal curves; the pure vermiculite does not have an endothermic peak at about 600°C, while chlorite-vermiculite mixtures do. From the curves in Fig. 2 it can be seen that samples AB, AA, R and P409 have a peak at about

TABLE 5—X-ray diffraction data for sample AB.

Flake		Glycerol-treated		Heated to 520°C	
$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I
14.3	vs	14.4	vs	9.15	s
7.1	w	7.1	m		
4.74	s	4.79	m	4.61	w
3.56	vs	3.59	vs		
2.85	vs	2.87	s	2.98	m
2.38	vw				
2.04	m				

600°C, sample R having the smallest and sample AA the largest; this indicates that sample R is the nearest to a pure vermiculite found in this investigation. No curve can be given for sample P136 as insufficient material was available.

The mineralogy of sample M is, however, more complicated than that of any of the samples so far discussed; X-ray diffraction data are given in Table 6.

From the flake data it would appear that the sample is similar to the vermiculite or chlorite-vermiculite minerals, but the powder data show an additional spacing at 12.5 Å, which when glycerol-treated expands to 30 Å and 15 Å, the 14 Å spacing remaining unaffected. When a sample is heated to 520°C spacings at 12.7 Å and 10.2 Å are produced in the diffraction pattern, and it is suggested that under these conditions the 14 Å spacing is reduced to 10 Å, while the 12 Å spacing is unaffected. From this it is concluded that the lattice that gives the 14 Å spacing, which is unaffected by glycerol and which is reduced to 10 Å on heating, is of the vermiculite type; while the lattice that gives a 12.5 Å spacing which

TABLE 6—X-ray diffraction data for sample M.

Flake		Powder	Glycerol-treated	Heated to 520°C
$d(\text{Å})$	I	$d(\text{Å})$	$d(\text{Å})$	$d(\text{Å})$
14.4	vs	14	30	12.7
7.2	mw	12.5	15	10.2
4.78	ms	7.5	14	
3.58	s	4.5	7.0	4.98
2.87	vs	3.55	4.7	
2.39	vwv	2.85	3.55	3.36
2.05			2.85	

TABLE 7—X-ray diffraction data for the mixed group.

A*		B*		AD*		AC*	
<i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I
9.875	s	15.4	w	25.5	vw	27	vw
4.98	mw	9.95	s	15.6	vw	10.5	mw
4.58	vw	4.98	mw	11.0	m	9.4	vw
4.12	vw	4.16	mw	9.2	mw	5.54	vs
3.31	vs	3.33	vs	4.96	mw	4.98	s
				4.15	w	4.11	w
				3.41	vs	3.41	s
				3.24	s	3.25	s

*Sample designation.

expands to 15 Å and 30 Å on glycerol treatment and which is not affected by heat, is thought to be a mixed-layer mineral of montmorillonite and mica.

This makes sample M a mixture of vermiculite and a mixed-layer montmorillonite-mica.

Mixed group. The X-ray diffraction data for the mixed group are given in Table 7. All have spacings at about 10 Å and it is therefore suggested that they are partially dehydrated. None of the specimens were exfoliated when received, but as neither their origin nor their previous history was known, no further discussion of their mineralogy is possible.

EXPANSIBILITY

All the commercial vermiculites reported in this paper expanded and exfoliated, and their volume expansion is given in Table 8.

These data indicate that the minerals with the highest expansibility are C, O, F, E, N, AC, AD and M; all of these except M contain a lattice which gives a 26 Å spacing and are probably hydrobiotites; M is a mixed-layer mineral. Those which gave the lowest expansion

TABLE 8—Volume expansion of some commercial vermiculites.

26 Å group		14 Å group		Mixed group	
Sample	Expansion	Sample	Expansion	Sample	Expansion
C	6.0	M	6.1	A	2.0
O	7.0	AA	3.5	B	2.0
F	6.9	AB	5.5	AC	9.0
E	6.0	R	5.8	AD	6.3
N	7.0	P409	3.4		

were the vermiculite-chlorite mixed-layer minerals and the two mixed group specimens A and B which had probably already been heated.

CONCLUSIONS

Of 16 commercial vermiculites examined, which show expansibility ranging from $\times 2$ to $\times 9$, none were true vermiculites; six were mixed-layer vermiculite-chlorite minerals, two were hydrobiotite (mixed-layer vermiculite-mica), three were mixed-layer vermiculite-hydrobiotite minerals, one a mixture of vermiculite and a mixed-layer montmorillonite-mica mineral; four showed signs of dehydration—of these two were probably hydrobiotite, one was a mixed-layer mineral, and one (A) was of unknown structure.

The greatest expansibility is found in those minerals with a hydrobiotite layer structure, the minerals with vermiculite-chlorite layers having the lowest expansion.

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