The effect of grinding on micas. I. Muscovite.

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It has long been realized that grinding increases the cation-exchange capacity of minerals and that it damages their crystal structures. However, while a considerable amount of data has been accumulated with regard to the effect upon various minerals, and clay minerals in particular, very little is known about how micas behave and such results as are available are somewhat inconsistent (1, 2, 3). In view of this and of a fortuitous observation that short-period grinding in an agate mortar affected the nature of muscovite considerably, a more detailed study of this subject has been undertaken.

EXPERIMENTAL.

The muscovite used originated from Goshen, Massachusetts, and consisted of clear colourless sheets relatively free from inclusions. The optical data were α 1·566, β 1·577, γ 1·580, 2V fairly large, compared with α 1·552, β 1·582, γ 1·588, 2V 47° for pure muscovite (4). The chemical analysis in table I (B), as compared with the theoretical, calculated from the formula $KAl_2(AlSi_3)O_{10}(OH)_2$, indicates that the amount of

Table I. Chemical analyses of muscovite.

	A.	B.	C.
SiO_2	45·4	50·99	46·95
TiO_2	—	0·19	0·22
Al_2O_3	38·5	30·10	34·02
Fe_2O_3	—	2·54	2·63
MgO	—	0·61	0·30
CaO	—	0·07	2·23
Na_2O	—	0·54	0·33
K_2O	11·8	8·87	3·17
H_2O +105° C.	4·3	6·13	10·58
	100·0	100·04	100·43

A, Theoretical composition of muscovite, taken as $KAl_2(AlSi_3)O_{10}(OH)_2$.
B, Muscovite, Goshen, Massachusetts; filed, 200 mesh.
C, Muscovite, Goshen, Massachusetts; ground for 24 hours, 200 mesh.
Analysts: B. D. Mitchell and Miss E. S. Murdoch.

substitution in the tetrahedral layer is hardly so high as the theoretical (cf. SiO_2, Al_2O_3, and K_2O), and that this material has a small iron content.

Since filing is known to be very much less destructive than grinding, one part of the sample was filed to pass through a 200-mesh sieve to give a powder of unaltered material, while the other part was dry-ground in a mechanical agate mortar, samples being removed at various times up to 24 hours and sieved through 200-mesh. For the X-ray diffraction photographs Fe-$K\alpha$ radiation was used; intensities were measured visually and estimated by comparison with the strongest line in the photograph. Differential thermal analysis was performed according to standard procedure using 0·20 g. samples (5). Semi-micro methods were employed for determination of chemical composition, of cation-exchange capacities (6), and of dehydration curves, which were obtained by weighing the material after heating it for one hour at temperatures increasing by 50° C.

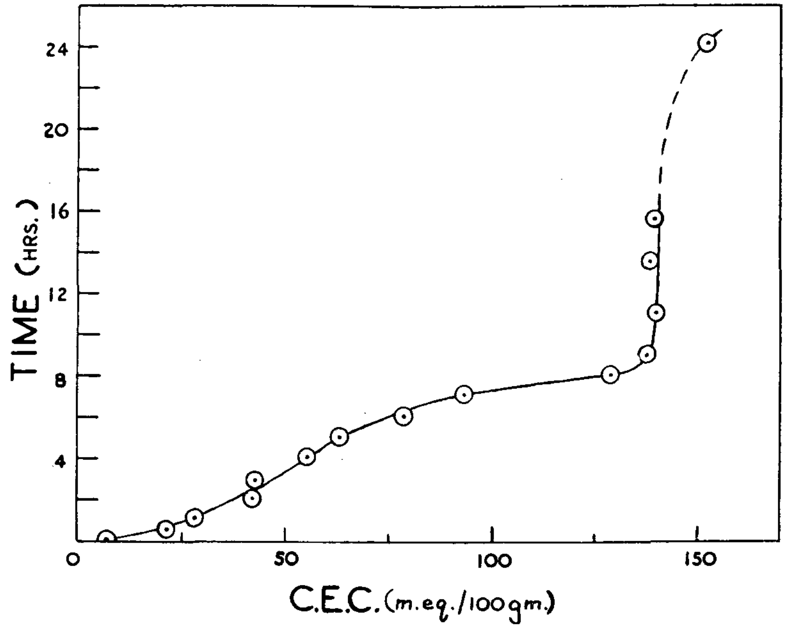

FIG. 1. Relationship between cation-exchange capacity and time of grinding for muscovite.

RESULTS AND DISCUSSION.

The graph for variation in cation-exchange capacity (c.e.c.) with time of grinding (fig. 1) shows that although the c.e.c. of the filed material is very low (about 6 milliequivalents/100 g.), that of the material ground for one hour is already almost 30 m.e./100 g. It would appear, therefore, that figures of this order quoted in the literature (7) probably arise from a somewhat similar period of grinding and are not necessarily equivalent to the value for the unaltered material. The c.e.c. increases steadily with time of grinding until about 7 hours and between 7 and 8 hours it increases more rapidly. Thereafter, up to about 18 hours, it remains fairly constant, but between 18 and 24 hours again increases slightly. The value obtained after 24 hours fits in with the value of 208 m.e./100 g. obtained by Jackson and Truog (2) after 72 hours grinding, but is considerably higher than the other published values, viz. 76 m.e./100 g. (Kelley and Jenny, 1), and about 100 m.e./100 g. (Parkert et al., 3). The reason for this is not clear as these three investigations were all performed using ball-mills—where the conditions are probably less drastic than in an agate mortar.

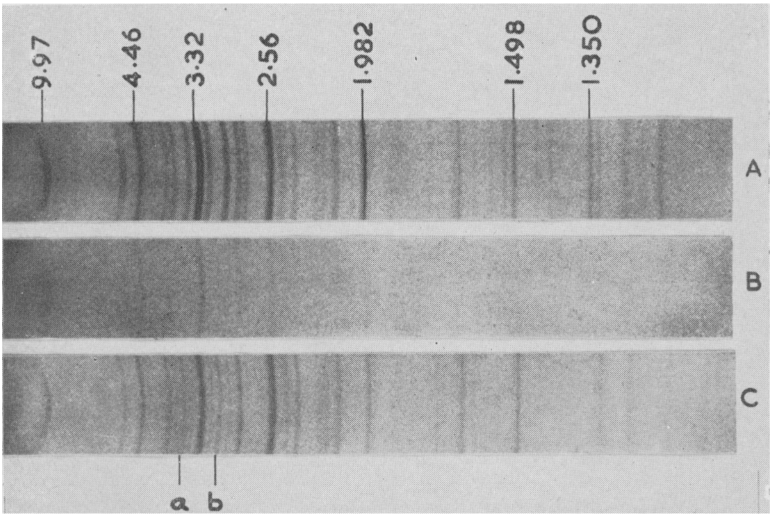

FIG. 2. X-ray diffraction patterns for muscovite samples:

A. Muscovite, Goshen, Massachusetts; filed, -200 mesh.
B. „ „ „ ground 8 hours, -200 mesh.
C. „ „ „ ground 24 hours, -200 mesh.

Fe-$K\alpha$ radiation; doubling of lines in A due to use of thick specimen with consequent specimen absorption: for details of *a* and *b* in C see text. (Spacings in Ångström units.)

The sharp reflections observed on X-ray photographs of the filed material (fig. 2 A) gradually weaken in intensity and become more diffuse on grinding until, after 8 hours, no sharp reflections remain (fig. 2 B). After a further period a diffraction pattern reappears, but this is different from the original in that the lines have different intensities and there become visible two new lines which are not present in the muscovite pattern but which are given by many hydrous micas (8, 9, 10) viz. those at 3·59 and 3·09 Å. (*a* and *b*, fig. 2 C). The diffraction pattern does not alter with further grinding up to 24 hours. The X-ray patterns of unground and ground muscovite together with those for hydromuscovite (9) and for Ballater illite (10) are listed and indexed in table II, and those lines which show considerable change on grinding are indicated. It will be observed that, generally, (*hkl*) reflections are enhanced while reflections of the type (0*kl*) with $k = 2n$ decrease in intensity. The former effect might be expected, but the disappearance of the (0*kl*) lines remains to be explained. Glycerol treatment of the ground material did not alter the basal spacing.

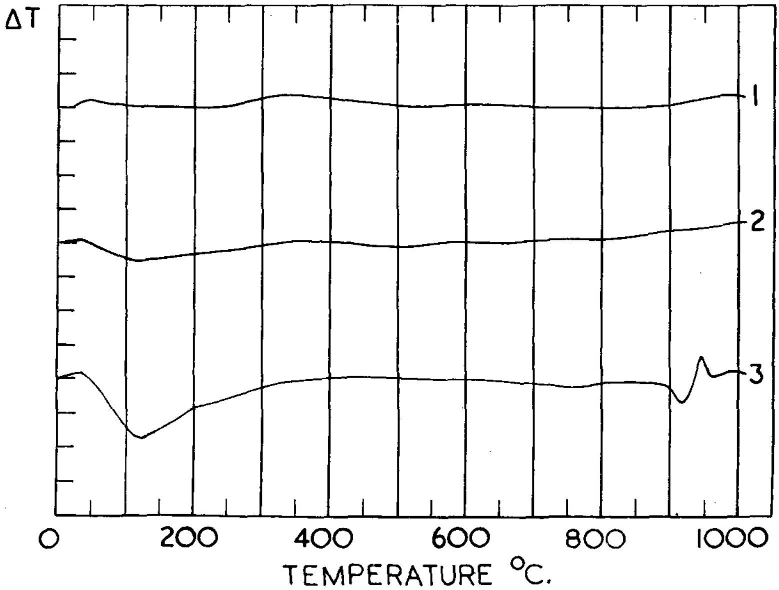

Fig. 3. Thermograms for muscovite: 1. Filed; 2. Ground for 2 hours; 3. Ground for 24 hours.

The thermogram for filed muscovite (fig. 3) shows virtually no thermal

TABLE II. X-ray data.

Indices	Muscovite Goshen, Mass. *d.*	Int.	Hydromuscovite, Ogofau, Wales (9). *d.*	Int.	Muscovite Ground 24 hours. *d.*	Int.	Illite Ballater (10). *d.*	Int.
002	9·97	s	9·98	s	9·85	s	9·9	s
004	4·99	w	5·02	s	4·94	mw	4·9	m
110†	4·46	m	4·51	m	4·43	s	4·45	vs
111	—	—	—	—	—	—	4·28	w
022*	4·11	vw	—	—	—	—	4·10	w
11$\bar{3}$†	3·87	w	—	—	3·85	mw	3·87	m
023*	3·72	mw	3·62	s	—	—	3·64	mw
113†	—	—	—	—	3·59	mw	—	—
11$\bar{4}$	3·48	w	—	—	3·47	vw	—	—
006	3·32	vs	3·34	vs b	3·32	vs	3·35	vs
114	3·18	w	—	—	3·18	vw	—	—
11$\bar{5}$†	—	—	3·09	s	3·09	m	3·09	mw d
025*	2·98	mw	—	—	2·97	vw	—	—
115†	2·85	w	2·89	s	2·85	ms	2·85	md
11$\bar{6}$	2·78	w	—	—	2·78	vw	—	—
13$\bar{1}$, 200		—	—	—	2·59	vw	—	—
131, 20$\bar{2}$	2·56	ms	2·59	vs	2·55	s	2·56	vs
008, 13$\bar{3}$, 202	2·46	vw d	2·47	m	2·44	w	2·45	mw
20$\bar{4}$, 133†	2·37	w	2·39	s	2·37	m	2·39	m
22$\bar{1}$	—	—	2·27	w	2·248	—	—	—
041*	2·24	vw	—		—	vw	2·235	mw
221, 22$\bar{3}$	2·19	vw	2·18		2·187	vw	—	—
20$\bar{6}$, 043, 135	2·123	mw	2·135	s	2·126	m	2·14	m
044*	2·045	vw	—	—	—	—	—	—
0010*	1·982	s	1·994	vs	1·978	m	1·988	m
206†	—	—	—	—	1·953	vw	1·940	w
208†	1·722	vw	1·715	vw	1·712	vw	—	—
20$\overline{10}$, 312	1·638	w	1·648	s	1·640	mw	1·647	m d
313	1·597	vw	—	—	1·612	vw	—	—
	—	—	—	—	1·575	vw	—	—
314	1·552	vw	—	—	1·546	vw	—	—
1310*	1·518	vw	—	—	—	—	—	—
060, 33$\bar{1}$	1·498	w	1·505	s	1·498	ms	1·497	s
331	1·451	vw	—	—	—	—	—	—
0014*	1·410	vw	1·416	vw	—	—	—	—
33$\bar{7}$	1·390	vw	1·380	vw	—	—	—	—
335	1·350	w	1·350	m	1·338	vw	1·342	mw d
	1·333	w	1·336					
260	1·320	vw	—	—	—	—	—	—
40$\bar{2}$, 400	1·294	vw	1·297	m	1·293	vw	1·294	m
402	1·267	vw	—	—	—	—	1·266	w
0016, 264	1·243	vw	1·245	w	1·239	vw	1·243	mw

The muscovite samples were photographed with Fe-$K\alpha$ radiation in a 9-cm. camera. *d*-spacings in Ångström units and intensities estimated visually. vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; d, diffuse; b, broad.

* Lines which decrease in intensity on grinding.

† Lines which increase in intensity on grinding.

reaction, but after as little as 2 hours' grinding a slight development of a hygroscopic moisture peak is apparent. After 24 hours the hygroscopic moisture peak is quite pronounced, a very small peak has developed at about 750° C. (cf. Ballater illite (10)); and a very distinct endothermic–exothermic inversion, reminiscent of that appearing on illites, e.g. Fithian, Illinois (10), and montmorillonoids, but rather more pronounced, is noted at 900–950° C. The increase in moisture content with grinding is also clearly indicated by the dehydration curves (fig. 4). For the ground sample the greatest moisture loss is in the 100–400° C. region, the rate of loss thereafter being reasonably uniform up to about 700° C., above which there is very little change; there appears to be no 'step' corresponding to the 915° C. endothermic peak, although it must be noted that the dehydration curves are for Ca-saturated material, while the thermograms refer to the original unexchanged material.[1] For the

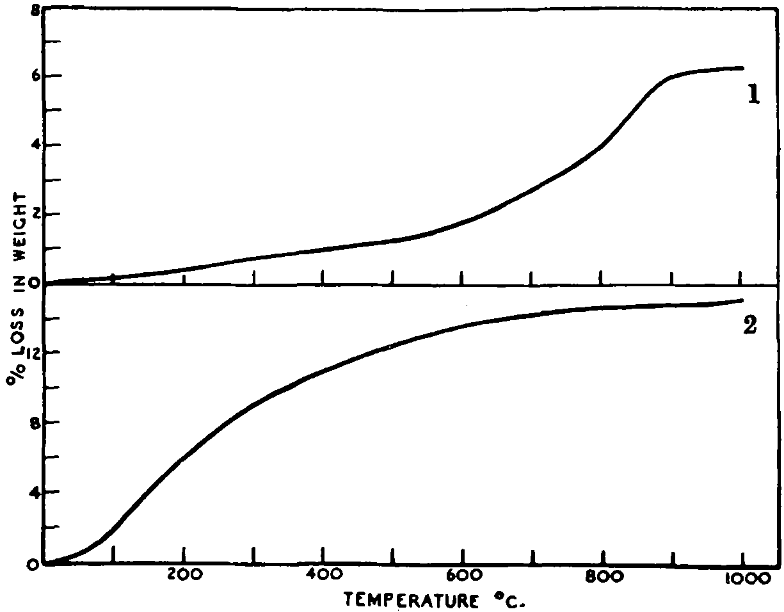

Fig. 4. Dehydration curves for muscovite: 1. Filed (Ca-saturated); 2. Ground for 24 hours (Ca-saturated).

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[1] The dehydration curves were determined in connexion with the chemical analyses, for which all samples were Ca-saturated in order to obtain some measure of the amount of K^+ exchanged.

filed material the main loss of water occurs at 600–900° C. corresponding to the very shallow trough on the thermogram.

After heating to 1000° C. it was noted that the material ground for 24 hours tends to cake, while the filed material remains free: X-ray photographs showed that the unground material still gave the muscovite pattern although the lines were rather more diffuse, while the material ground for 24 hours gave the distinctive pattern of leucite. From the X-ray results it would appear that the exothermic peak is explicable on the basis of recrystallization into leucite.

Correlation of the above data suggests that more or less complete breakdown of the muscovite structure is induced by about 8 to 9 hours' grinding, and that after this recrystallization takes place. In muscovite the alkali ions are in the positions normally occupied by exchangeable cations in comparable clay minerals, and if *primary* rupture occurs along the sheet surface (as would be expected, although fracture in other directions undoubtedly occurs), one would expect these ions to become exchangeable. The chemical analysis of the ground material, after three treatments with calcium acetate and removal of excess Ca^{+2} (table 1, C), shows that this has in fact happened—the decrease in alkali content corresponding reasonably with the increase in c.e.c. In addition to this change, however, and the expected changes in CaO and H_2O contents, the ground material appears to contain *more* Al_2O_3 and *less* SiO_2 than the filed sample. Calculation shows that the increase in CaO content is not sufficient to satisfy the c.e.c. entirely and some of the exchangeable positions may therefore be filled by aluminium; but, even if $Al(OH)_2^+$ were present, this is not sufficient to account for the increase in Al_2O_3 content, and consequently, it seems that some silica must have been freed by grinding and was not centrifuged out during the treatment with calcium acetate.

However this may be, a similarity is observable between the chemical analysis of the ground muscovite and those published for samples of illite and illidromica (8, 10, 11), supporting the observation made above of the similarity between the X-ray patterns of the two materials. The product of recrystallization after prolonged grinding appears, therefore, to be a form of illite, the main distinction being the high c.e.c. (about 150 m.e./100 g.) as compared to that of illite (20 to 40 m.e./100 g.). In muscovite, with a substitution of approximately one Al^{+3} for every three Si^{+4} ions, a very large charge density is produced along the sheet surface and such a large charge density is not normally found in illite, which presumably during its formation as a secondary mineral in nature does not attain such a high substitution state. The difference in c.e.c. is therefore reasonably understandable.

If one accepts the conclusion that primary breakdown during grinding occurs by cleavage perpendicular to the *c*-axis whereby the (SiO) surface becomes exposed and liable to alteration (cf. the decrease in SiO_2 of the ground material), then the hypothesis of McConnell for montmorillonite (12) might be applicable to the final endothermic peak, i.e. that it is due to evolution of water from tetrahedral (OH) groups. The absence of a corresponding step on the dehydration curve is, however, not in accord with this explanation and, although the dehydration curve was determined on Ca-saturated material, the product of calcination was still leucite.

The main conclusion from these experiments is the, at first sight, rather surprising sensitivity of muscovite to dry-grinding for very short periods, and the deep-seated nature of the changes occurring on further grinding. Consideration, however, suggests that these changes are not so extraordinary in view of the stresses set up during dry-grinding, and in this connexion it is worthy of note that preliminary experiments have indicated that vermiculite is rather more resistant to dry-grinding than muscovite, presumably because of the lubricative action of the water layers between the sheets.

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