

VERMICULITE SURFACE MORPHOLOGY

by

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ABSTRACT

A study of the surface morphology of vermiculites from several different sources by the electron microscope has indicated that, unlike the smooth surfaces of micas, the vermiculite surfaces show micromorphological structural variations such as small humps, prominent crystallographic steps on the basal cleavage planes, marginal rolling of the layers and layer buckling. The production of layer buckling may result from the inhomogeneity of interlayer population caused by the introduction of hydrated cations replacing potassium during weathering. The (110) steps on the surface of the cleavage can be observed and these are visualized as nuclei for weathering in addition to the particle edges.

The surface morphology of vermiculites is closely related to the nature of the interlayer cation. When treated with potassium or ammonium salts, the surfaces assume smooth morphology, the K and NH_4 ions occupying interlayer sites and collapsing the mineral. When treated with Na or Li salts, the complex surface morphology persists, and in some cases is enhanced, possibly by the slow exchange of residual potassium from the interlayer. On this basis, the presence of unweathered mica cores have been identified in natural vermiculites which show varying amounts of residual K_2O content. It is possible to offer an explanation from structural considerations for the complex morphology of the vermiculite surfaces including the curling of the layers on depletion of potassium. The morphological features of vermiculites have been produced on biotite mica by leaching with salt solutions.

INTRODUCTION

VERMICULITE occurs as an intermediate alteration product of mica in its transformation to montmorillonite, represented by the mineralogical equation: $\text{Mica} \rightleftharpoons \text{Illite} \rightleftharpoons \text{Vermiculite} \rightleftharpoons \text{Montmorillonite}$ of Jackson *et al.* (1952). The changes taking place by this transformation were summarized as follows: decrease in intensity and broadened angle of basal diffraction, with basal spacings intermediate between 10 and 18Å; increase in internal surface; lowered K content; higher H_2O or OH; lowered layer charge; and existence of "slow" exchange (Barshad, 1948) with other salt solutions. The position of vermiculite in the above equation is rather important, as the weathering of mica to vermiculite releases potassium while the presence of vermiculite in soils causes "fixation" of added potassium, making it difficultly available.

Vermiculite occurrences can be classified into two major categories, those consisting of macroscopic crystalline flakes or those consisting of microscopic silt or clay size vermiculite (Bassett, 1963). The present study will deal with the surface morphological features of the macroscopic vermiculites and other occurrences. The distribution and development of these in the coarser fractions of soils are probably as important as the clay size minerals.

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MATERIALS AND METHODS

Vermiculites from several different sources (Colorado, Texas, Montana, Pennsylvania, and S. Africa) and, for comparison, a biotite (Spruce Pine, N.C.) were used for this study. A preliminary X-ray diffraction study of the crystals showed that the minerals were relatively pure. A fresh cleavage of the surface for examination of the (001) plane was obtained by carefully splitting apart single crystals of the mineral with a razor. A self-shadowed carbon replica of the surface for electron microscopic examination was prepared *in vacuo* by evaporating carbon over the specimen at an angle of approximately 40 degrees. Earlier studies indicated that a self-shadowed replica is as efficient as the replica prepared after preshadowing with platinum (Bradley, 1954, 1961). The specimen flake was dissolved from the replica by floating it over several changes of HF and HCl. (Failure to use HCl in the first few washes sometimes resulted in the formation of magnesium fluoride which precipitates on the replica surface and once formed is very difficult to remove.) The resulting carbon film was washed in distilled water, picked onto a 200-mesh per inch grid and examined with a Siemens Elmiskop I instrument. At least three separate crystalline specimens were similarly prepared for every mineral source and several fields of each were examined under the microscope. Only those surface features which were present in each of the triplicate specimens were taken as representative. In experiments involving the study of the effect of cations on surface morphology, fresh cleavage surfaces of the specimens (in triplicate) were treated with the appropriate 1 N salt solutions overnight, washed gently by passing distilled water from one side of the specimen to the other to

remove the excess salts, and the surfaces were then examined as described above. In leaching experiments with magnesium chloride, flakes of biotite were immersed in 1 N solution, placed on a steam plate (75°C) for one hour, then removed and washed with distilled water to remove excess salts, and examined in the usual way.

RESULTS

Mica surface.—The surfaces of untreated mica have comparatively smooth morphology (Plate 1), with occasional folds of one or several individual flexible layers of unit cell thickness. These folds, in many cases at 120° angles, appear to give rise to observed fracture edges seen on the faces after weathering. Flexibility of the structural layers would afford easy accommodation of hydrated cations and other interlayer material introduced by weathering.

Surfaces of natural vermiculites.—An indication that the surfaces of vermiculites may not possess the smooth morphological features of the micas from which they are derived, is provided by the fact that transmission micrographs of vermiculites show striations and other morphological features not usually observed on micas (Plate 2). A surface study of these mineral faces brings out the complexities and micromorphological structural variations of the vermiculite surface (Plate 3) suggested by the striations of the transmission photograph (Plate 2). The surfaces are no longer even, but show discontinuity of layers, and marginal curling, with undulations and humps of varying size, much in contrast to the smoothness of biotite (Plate 1). While most of the well-weathered vermiculite surfaces show this complex morphology, some of the areas are smoother than others (Plate 4). As discussed below, and as has been reported elsewhere (Raman and Jackson, 1963), such smooth morphological features are associated with the presence of K in the interlayer. On this basis, the smooth areas in the micrograph (Plate 4) are identified as unweathered mica cores (Jackson, 1963). Reports on chemical composition of vermiculites compiled by Foster (1963) show varying K₂O content. The clay fraction from the sample of Colorado vermiculite (Plate 4) contains 1.5 per cent K₂O and has a 10Å shoulder on the 14Å diffraction peak.

Other natural vermiculites from several different localities have been examined and in general they show the general morphological characteristics discussed above. Representation of this is illustrated by the electron micrographs of vermiculite samples from Chester, Pennsylvania (jefferisite, Plate 5), Libby, Montana (Plate 6) and Llano, Texas (Plate 7).

In addition to the general complex morphology of the surface, the steps of the dislocation planes in the crystal faces can also be observed in the samples from Montana and Texas (Plates 6 and 7). In his studies with blende crystals, Verma (1956) observed that in the intensive substructure

of some crystal faces, one can occasionally see step lines running along certain crystallographic directions and cutting across the growth steps. The step lines in the micrographs (indicated by arrows) intersect at very near 60° or 120° , the prism angles of micas, $110 \wedge \bar{1}\bar{1}0$ and also $110 \wedge 010$ (Winchell and Winchell, 1951, p.365).

Concomitant with the above features, the vermiculite from Texas also shows a characteristic layer buckling (Plate 7). This phenomenon of buckling on crystal surfaces has been studied by several workers in relation to crystal growth. According to Frank (1949), in the growth of crystals, the initial crystal plate formed by the nucleation process gets self-stressed through inhomogeneous distribution of the impurities. When this stress reaches the yield stress, the plate buckles and shears, raising terminated steps which are not of constant height all along. As one of the major changes in the transformation of mica to vermiculite is the replacement of interlayer K by hydrated cations and the resulting lattice expansion, heterogeneity of interlayer population can be expected at any stage of weathering. This could cause a strain in the crystal and buckling of structural layers may result. Such buckling of surface layers has been observed to take place in micas on depletion of potassium (Raman and Jackson, 1963).

Vermiculite possesses a lower surface charge and usually a slightly higher content of Al than is expected theoretically. Most natural vermiculites do not collapse to 10\AA on K saturation at room temperature and give greatly broadened peaks. Cook and Rich (1963) observed that when dioctahedral vermiculites are treated with solutions that remove interlayer material, the negative charge of the mineral increases, reaching approximately that of true micas. These facts would suggest that vermiculites are partially interlayered with hydroxy sesquioxides. The general puckered appearance of the surface with little humps of varying diameter would suggest a heterogeneous interlayer population, as homogeneous interlayering would give smooth surface features. It may be observed that while some of the bumps may be on the surface layer, several of them originate from the lower layers and are silhouetted through overlying layers. The discontinuity of the layers is visualized as arising from the shrinkage of the layers in the *b*-direction when K is lost from the interlayers of mica (Burns and White, 1963), which may cause the layers to break at intervals of a few microns.

Influence of size and charge of exchangeable cations on surface morphology of vermiculites.—On treatment with KCl, to replace the exchangeable magnesium and calcium, the complex morphology of Colorado vermiculite surface (Plates 3 and 4) largely disappears and a relatively smooth surface with tiny humps is obtained (Plate 8). In many areas, the plastered down edges of the discontinuous layers (arrows) give the appearance of having been unrolled (the edges having been rolled up in the natural materials, Plates 3 and 4). This would indicate that the high K preference exhibited

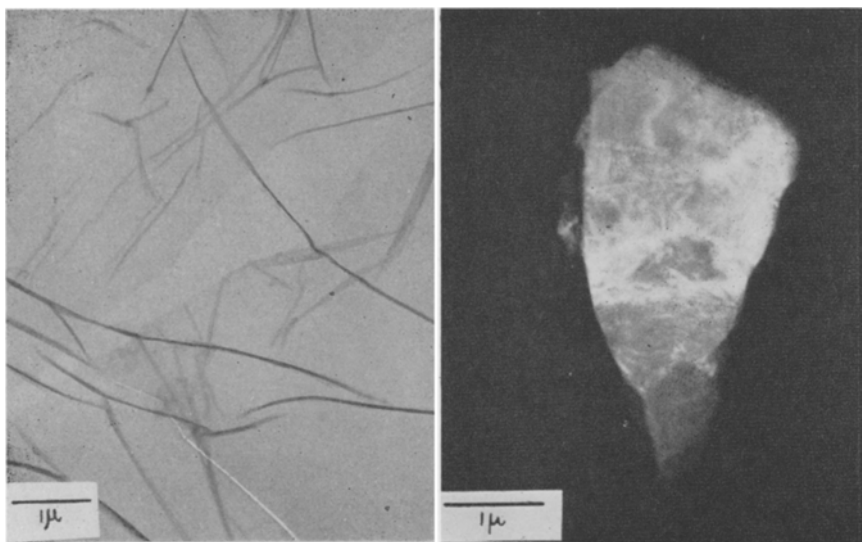


PLATE 1.—Surface of a fresh cleavage of biotite showing smooth surfaces without pits or falls.

PLATE 2.—Transmission electron micrograph of a single crystal of vermiculite from Colorado showing striations indicative of a rough surface structure.

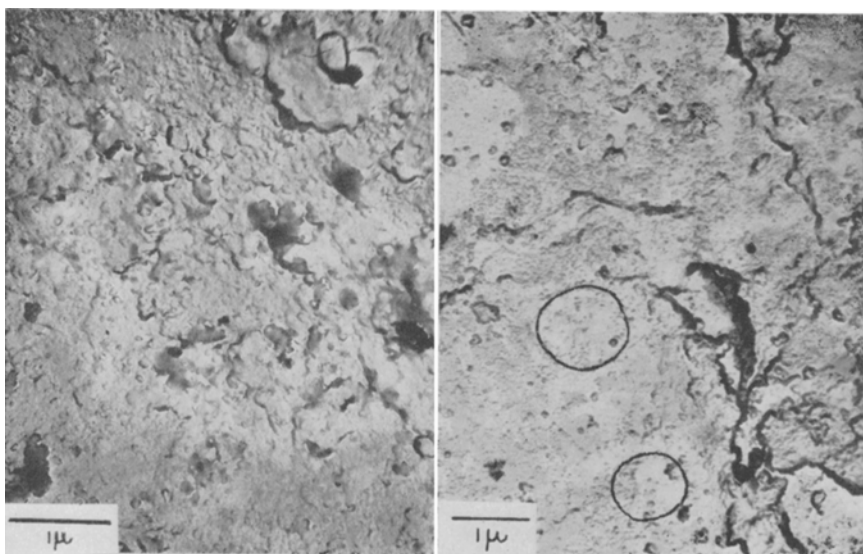


PLATE 3.—Fresh cleavage surface of Colorado vermiculite. The surfaces show humps, marginal rolling and discontinuity of the layers.

PLATE 4.—Another area of Colorado vermiculite surface. The smoother areas (inside the circles) indicate unweathered mica cores.

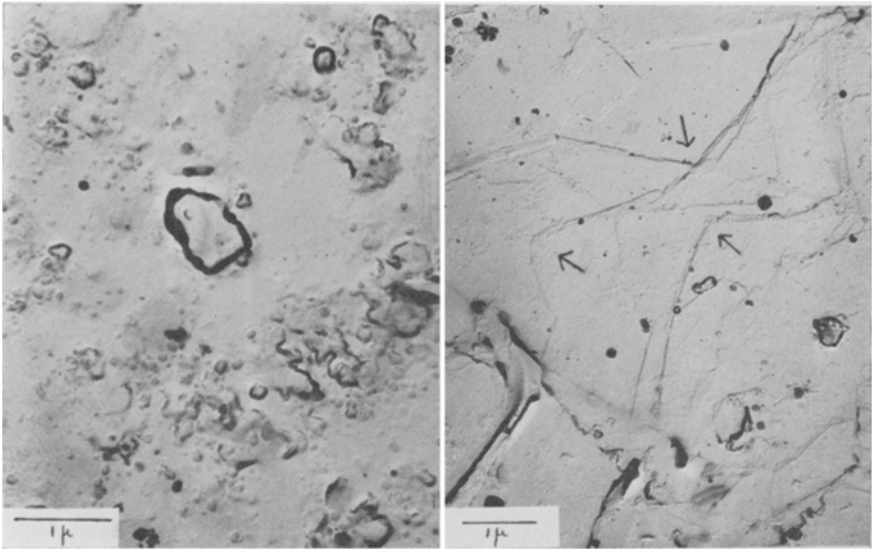


PLATE 5.—Surface of jefferisite from Chester, Pennsylvania. Large areas of unweathered mica cores can be seen in addition to general complex morphology of vermiculites.

PLATE 6.—Surface of vermiculite from Libby, Montana, showing steps (cleavage as possibly growth steps and dislocation planes) on the surface of the crystal (arrows) intersecting in (110) crystallographic directions.

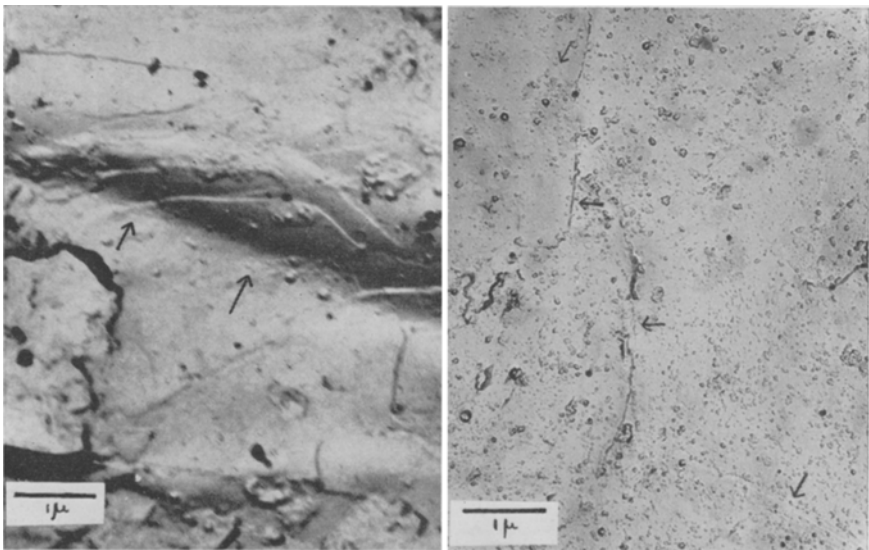


PLATE 7.—Surface of Texas vermiculite showing dislocations and layer buckling (arrows).

PLATE 8.—Surface of Colorado vermiculite treated with KCl. The layers become relatively smooth with only tiny humps on the surface. In certain areas, the edges of layers which have rolled back to place can be observed (arrows).

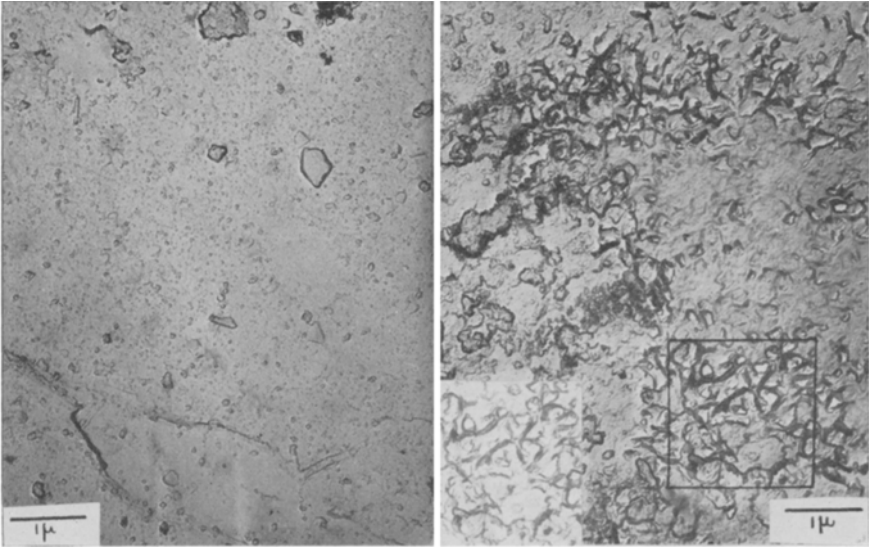


PLATE 9.—Surface of Colorado vermiculite treated with NH_4Cl . The surface is relatively smooth except for tiny humps.

PLATE 10.—Surface of Colorado vermiculite treated with lithium chloride. In many areas, the complex structural morphology is enhanced and there is increased rolling of the layers on the surface. Inset at left, a lighter print of the marked area, shows these features more clearly.

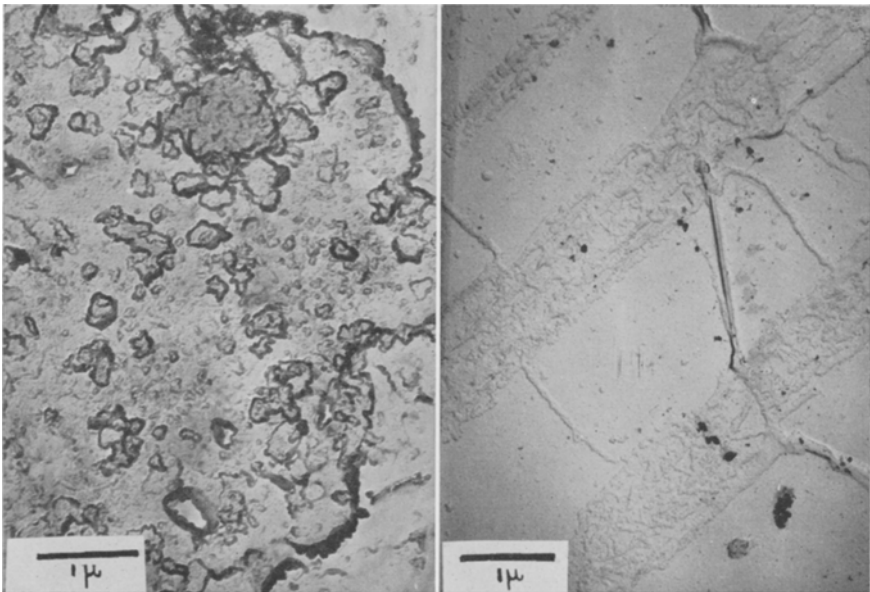


PLATE 11.—Surface of Colorado vermiculite treated with NaCl . The general morphology resembles closely that of lithium treated sample in Plate 10.

PLATE 12.—Surface of biotite mica leached with 1 N magnesium chloride solution at 75°C for one hour. Surface morphological changes such as tiny humps enlarging into larger ones and 120° angle breakages, occur.

by the mineral may be associated with surface morphological changes. The surfaces after K treatment are, however, not as smooth as the mica surfaces, as the mineral may be partially interlayered with hydroxy sesquioxides and may not permit free or complete exchange of K. The same features are observed on treatment of Colorado vermiculite with ammonium chloride solution (Plate 9), the creases resulting from considerable unrolling being prominent.

Treatment with Li or Na salt produces a contrastingly different effect (Plates 10 and 11) as compared to K or NH_4 . Not only do the surface complexities persist, but in certain areas are also enhanced, believed to be the result of the slow exchange of the residual potassium with Li or Na. Surface relief is shown by the prominent shadows. The inset at left in Plate 10, a lighter print of the marked area, shows clearly that the surface irregularities arise from much curling of the edges, mainly developed into prominent scrolls or rolls, the hollow nature of which is evidenced by the lighter streak in the center. This general morphology is the same as found in natural vermiculites, though the development of the scrolls is less.

The curling of the layers consequent on the removal of K from the interlayers of mica may result for a number of reasons. Radoslovich (1960), in his investigation of the structure of muscovite, showed that the silica tetrahedrons are slightly rotated relative to one another, making the cavity in the silica sheet ditrigonal, instead of being truly hexagonal. When K is removed, a structural rearrangement of the oxygens was indicated. Burns and White (1963) observed that removal of K from muscovite resulted in a decrease in the *b*-axis length. Coupled with this, there is also the strain on the layers as a result of the introduction of the larger sized hydrated cations which would exert a levering effect. Schofield and Samson (1954) regarded the attraction of the positive charges on the edges for the negative charges of the faces of the crystals as the cause of the flocculation of kaolinite which occurs in the absence of salt. A similar phenomenon can be visualized as taking place in the system under consideration, the positive layer edges rolling back to touch the negative faces. All the above effects acting at the same time may cause the curling of the surface layers depleted of potassium. The curling could cause trapping of water or H_2O_2 and account for the macroscopic exfoliation of vermiculite noted when gas is formed.

Vermiculite-like morphology by treatment of biotite.—Leaching of biotite mica with magnesium chloride solution for prolonged periods has been shown to produce vermiculite (Barshad, 1948; Bassett, 1959). A sample of biotite mica leached with magnesium chloride was therefore studied to determine whether or not the complex morphological features of natural vermiculites are produced during weathering. It is observed that the smooth surface of mica develops tiny humps all over the surface, the little ones in many areas merging together to form larger humps (Plate 12), similar to the ones found on natural vermiculites. Also cleavage along (110)

crystallographic directions, possibly along growth steps, takes place, as seen from the relative orientations of these features, which are at 120° or 60° angles, or tend to form regular hexagonal structures. Jackson (1963) proposed that mica weathering proceeds at the surface at dislocation edges as well as the particle edges. The humps developing all over the surface would indicate that weathering action may proceed on these planes at the surface. The presence of discontinuous layers and marginal rolling in vermiculites would support the contention, because these dislocation planes could easily give rise to such irregularities during weathering as borne out by more extensive mica weathering studies (Raman and Jackson, 1963).

SUMMARY AND CONCLUSIONS

The main points that arise from the data presented in this study are:

(1) Unlike the relatively smooth surface of micas, vermiculite surfaces show micromorphological structural variations such as small humps, prominent crystallographic steps, marginal rolling and discontinuity of layers.

(2) The characteristic buckled appearance of some vermiculite surfaces may result from heterogeneity in interlayer population.

(3) On treatment with potassium or ammonium salts to replace the exchangeable Mg and Ca, the rolled-up layers on the surface unroll to a large extent, giving a relatively smooth surface. On the other hand, treatment with Li or Na salts accentuated the surface irregularities consequent on numerous curling of edges progressing to scrolls, indicating that the surface morphology is closely associated with the nature of the interlayer cation.

(4) Structural considerations are used to explain the complex morphology of vermiculite surfaces including the curling of the layers on depletion of potassium and macroscopic exfoliation when gas is formed in the interlayer spaces.

(5) The morphological features observed on natural vermiculites have been produced by leaching biotite with magnesium chloride.

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