

MORPHOLOGY OF VERMICULITE CLAY PARTICLES AS AFFECTED BY THEIR GENESIS

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ABSTRACT

Electron-microscopy established that the mode of formation of soil vermiculite clay affects the shape of its particles. When clay vermiculite forms by the alteration of biotite, muscovite, or chlorite the shape of some of its particles resembles that of the parent mineral and appears as large, translucent, irregular polygonal sheets with some of the edges frayed; but a large proportion of its particles appear as thin pseudo-hexagonal flakes or fragments. When vermiculite forms by synthesis from silica and alumina gels, its particles are mostly small hexagonally-shaped sheets resembling kaolinite. Many of the synthetic particles are also fragmented and have frayed edges and others aggregate into larger hexagonal sheets.

Since soil vermiculite clay is frequently associated with kaolinite, the present finding indicates that electron-microscopic analysis for the purpose of verifying purity of clay samples based on shape alone may not be reliable.

INTRODUCTION

A review of the literature on electron microscopy of clay minerals discloses that few studies have been done on vermiculite clays. Studies were done on ground, coarse-grained samples (Beutelspacher and van der Marel, 1968), Mukherjee (1963), Raman and Jackson (1964). These studies disclosed that the sheet morphology of the coarse-grained vermiculite was retained upon grinding. Irregular polygonal particles produced by grinding have a few edges that intersect at 120° , indicating occasional fracture along 010 and 110. Raman and Jackson (1964) reported that, unlike the smooth surfaces of micas, the vermiculite surfaces show small humps, prominent crystallographic steps on the basal cleavage planes, marginal rolling of the layers, and buckling of the layer. But upon potassium saturation these surfaces become similar to those of mica.

From the amount of vermiculite relative to the other clay minerals, as influenced by the mean annual precipitation, Barshad (1966) concluded that the vermiculite in soils derived from acid igneous rocks is a product of mica alteration, whereas vermiculite in soils derived from basic igneous rocks is a product of synthesis. Chemical and X-ray analyses of the clay fraction from eleven soils containing large amounts of vermiculite confirmed this conclusion. Vermiculite in soils from the acid igneous rocks is high in Al_2O_3 : Al^{3+} substitutes for Si^{4+} in tetrahedral positions in the same order of magnitude as in micas, and Al^{3+} is the dominant octahedral ion. Vermiculite in soils derived from basic igneous rocks is high in SiO_2 : only Si^{4+} occupies the tetrahedral positions, and Fe^{3+} and Mg^{2+} are the dom-

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TABLE 1. SOILS FROM WHICH VERMICULITE CLAYS WERE OBTAINED

Soil series	Great soil group	Location	Parent rock	Mode of formation of vermiculite
Taiwan	Lateritic red earth	Eastern Taiwan	Fine grain Schist	Alteration of mica
Josephine	Gray-brown podzolic	Humboldt Co., California	Sandstone and shale	Alteration of mica
Milbourne	Brown podzolic	Humboldt Co., California	Sandstone and shale	Alteration of mica
Shaver	Podzolic	Fresno, Sierra, California	Quartz diorite	Alteration of mica
Masterson	Podzolic	Tehama Co., California	Mica schist	Alteration of mica
Yorkville	Prairie	Humboldt Co., California	Chloritic greenstone	Alteration and synthesis
Neuns	Podzolic	Tehama Co., California	Greenstone	Alteration and synthesis
Aiken	Red podzolic	Lyttonville, California	Greenstone	Synthesis
Sweeney	Prairie	San Mateo Co., California	Augite-olivine barsalt	Synthesis
Auburne	Noncalcic brown	Knights Ferry, Merced, California	Greenstone	Synthesis
Boomer	Brown forest	Tehama Co., California	Basalt	Synthesis

inant octahedral ions. X-ray analysis indicated that the former vermiculite is often interlayered with mica whereas the latter never is. The detailed results of this study will be published elsewhere.

An electron-microscopy study of these vermiculite clays was undertaken to ascertain whether the variations in mode of formation and in chemical composition affected the shape of the particles.

MATERIALS

The sources of the materials used and the believed mode of formation of the vermiculite are given in Table 1.

Preliminary electron microscopy of several soil vermiculite clays disclosed that the shape of their particles appear to be hexagonal or pseudo-hexagonal similar to that of kaolinite. Since in this study the whole clay fraction was examined, it was necessary to select soil clays with a high content of vermiculite and with little or no kaolinite. As seen in Table 2

most of these clays met this criteria. The mineralogical composition of the clays was determined by methods devised by Barshad (1965) and Alexiades and Jackson (1966).

METHODS

Preparation of the clay suspensions. To insure that the shape of the clay particles, as it occurs in the soil, remains unchanged in the course of preparing the sample for study, the least destructive methods were used. To disperse the soil, a 0.1N NaOH solution was added in amounts sufficient to raise the pH of the soil slurry to 9.5. These slurries were shaken gently for two hours, then transferred to 1000 ml sedimentary cylinders with a dilute NaOH solution having a pH of 9.5, and the $<2\mu\text{m}$ clay was extracted at the proper depth and after the proper sedimentation time, using a 25 ml pipette.

TABLE 2. MINERALOGICAL COMPOSITION OF THE CLAY FRACTION

Sample	Ve	Mi	Mo	Ch	Ha	Ka	Gi	Qu	Fe
Taiwan	36	30	—	—	—	29	—	5	—
Josephine	44	13	—	—	31	—	6	6	—
Melbourne	46	16	—	—	23	—	7	8	—
Shaver	41	10	—	—	32	—	7	5	5
Masterson	44	21	—	—	—	24	—	4	7
Yorkville	32	26	—	31	—	—	—	5	6
Neuns	35	14	—	14	—	12	—	—	25
Aiken	46	7	—	—	28	—	—	—	19
Sweeney	35	—	27	—	—	—	—	—	38
Auburn	35	3	17	—	34	—	—	6	5
Boomer	43	—	5	—	38	—	—	—	14

Ve=Vermiculite, Mi=Mica, Mo=Montmorillonite, Ch=Chlorite, Ha=Halloysite, Ko=Kaolinite, Gi=Gibbsite, Qu=Quartz, Fe=Feldspar.

The organic matter which occurs in natural soil clays was removed from the clay suspension by oxidation with a 5 percent solution of sodium hypochlorite adjusted with 6N HCl to a pH of 9.5, as suggested by Anderson (1963). The conventional hydrogen peroxide solution was not used because it exfoliates vermiculite. Uncombined Fe_2O_3 was removed from a part of this suspension by the sodium dithionite-sodium citrate method of Mehra and Jackson (1960) and then washed free of salt. A part of this Fe_2O_3 -free suspension was treated with KCl solution to obtain a state of K^+ saturation, washed free of salts with distilled H_2O , and resuspended.

Placement of the clay particles on the electron microscope grids. By one method the grids were sprayed with a dilute clay suspension, and by another the Formvar-coated grids were placed (with their films facing the water) on a clay film prepared by spreading a drop of clay suspension on the surface of a water-filled trough (Lucite, $1\times 4\times \frac{1}{2}$ in.). The grids were lifted out of the water, excess water drained off, and shadowed with uranium and carbon by standard electron-micrograph procedures. They were examined under an RCA Model EMU-3 Electron Microscope.

RESULTS

Effect of method of preparation of clay and placement on grids. Before describing the morphology of the vermiculite particles as depicted in Figures 1 to 9, the findings regarding the methods of preparation of the clay suspension and of depositing the clay particles on the grids may be summarized as follows: (1) The preparation of the clay in a state of sodium saturation and Fe_2O_3 -free yielded a clay suspension most suitable for electron microscopic examination of single particles. (2) Potassium saturation caused the clay particles to aggregate, preventing the observation of single particles. (3) When uncombined Fe_2O_3 was not removed, the clay particles, although sodium saturated, tended to aggregate and small

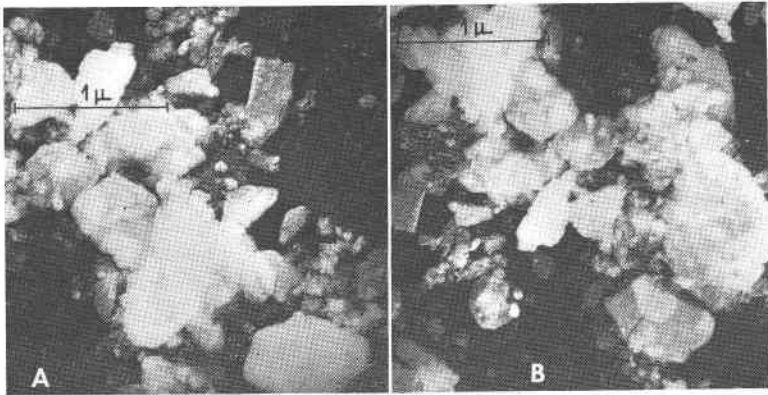


FIG. 1 (A and B) Taiwan; vermiculite, illite, and kaolinite by alteration of muscovite and biotite.

particles lodged on top of large ones, as seen in Figures 1A and 1B. (4) Depositing the clay on the grids by spraying represented the mineralogical composition of the clay more truly than by flotation. However, the flotation method deposited a large number of single particles that were more suitable for electron-microscopic examination. This method also favors deposition of flat sheet-like clay particles in preference to the tubular halloysite particles; the reason for this is not clearly understood.

Most of the electron micrographs in Figures 1 to 9 were made from clay suspensions saturated with sodium after the removal of the uncombined Fe_2O_3 , using the flotation technique.

To relate the morphology of the vermiculite particles to their genesis, the electron micrographs of the clays are arranged as follows: Figures 1 to 5 represent mainly alteration products, and Figures 6 to 9 represent synthetic products.

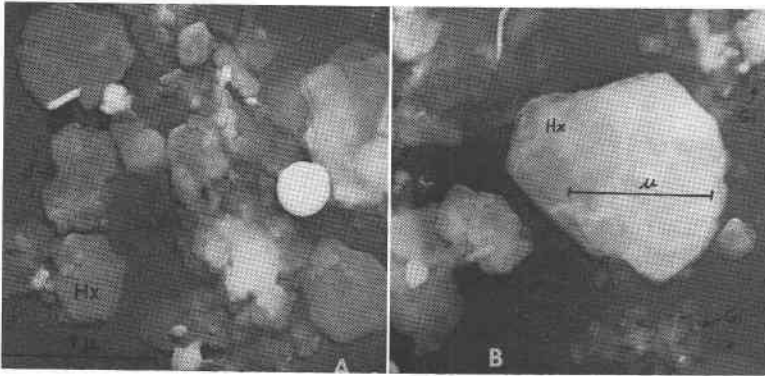


FIG. 2 (A and B) Josephine; vermiculite and illite by alteration of muscovite and biotite.

Morphology of vermiculite clays.

(1) The most common feature among all the soil clay particles is their appearance as pseudo-hexagonal plates or flakes. Examples are marked by (Hx) in Figures 1 to 9. Because of this thinness many of these particles are translucent to the electron beam and outlines of numerous smaller particles lodging beneath them can be seen.

(2) Many of the pseudo-hexagonal particles are fragmented but others appear to be jointed at one or more edges (marked by J).

(3) Surfaces of many particles are outlined by hexagonal fractures as seen in Figures 2A, 5B, 7B, 8B, 9A and 9B. Other particles have cracks that outline either a complete or a partial hexagon (Figure 8B).

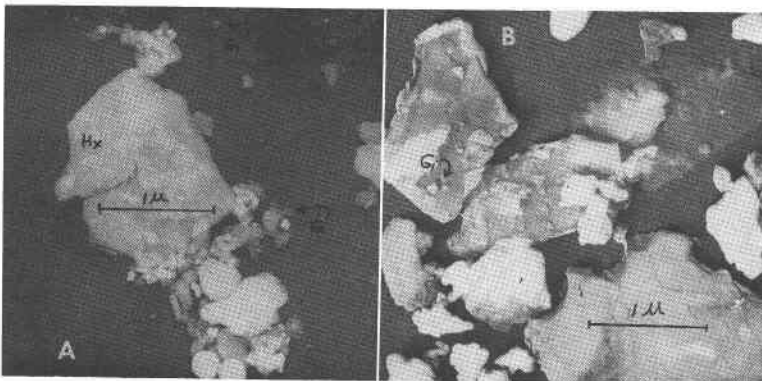


FIG. 3 (A-Melbourne, B-Shaver); vermiculite and illite by alteration of muscovite and biotite.

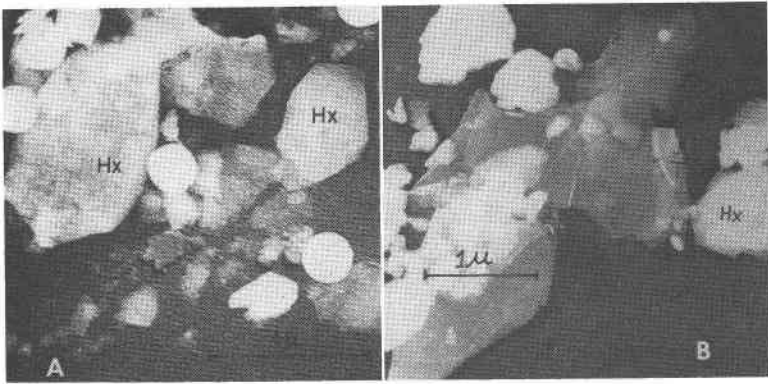


FIG. 4 (A and B) Masterson; vermiculite, illite and kaolinite by alteration of muscovite and biotite.

(4) Very large and thin sheets tend to be buckled or folded, as seen in Figure 6B.

(5) The differences between the pseudohexagonal vermiculite particles formed by alteration from mica or chlorite (Fig. 1 to 5) and those formed by synthesis (Fig. 6 to 9) are: (a) greater translucency to the electron beam of the former, (b) edges of many of the former particles are smooth whereas those of the latter are frayed, and (c) most of the former particles are larger than the latter.

(6) The hexagonal particles of the clay derived from basic igneous rocks are vermiculite and not kaolinite, as proved by X-ray and differential thermal analysis.

(7) The very small, dense, hexagonal particles marked by (Gi) in Fig-

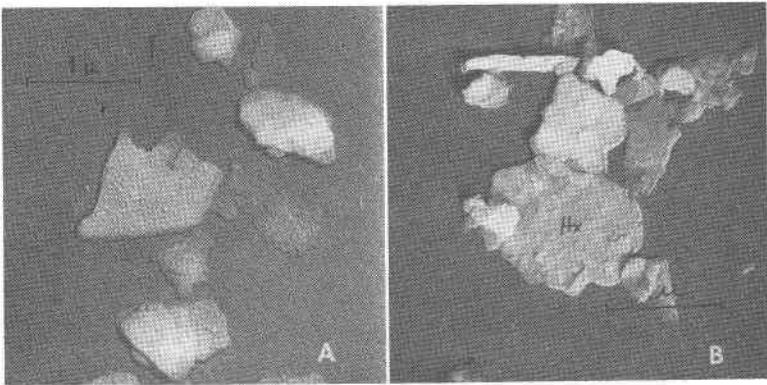


FIG. 5. (A-Yorkville, B-Neuns); vermiculite and illite by alteration of chlorite and biotite.

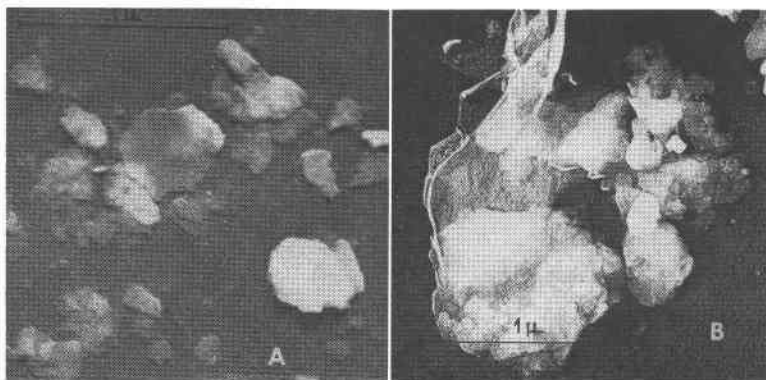


FIG. 6 (A, B) Sweeney; vermiculite and montmorillonite by synthesis.

ures 2 and 3 are believed to be the gibbsite determined in these clays by X-ray and differential thermal analyses.

(8) Many of the clay particles that are probably pseudomorphs after mica or chlorite appear as large ($>2\mu\text{m}$) irregular polygonal sheets, as seen in Figures 1 to 5. The surface of these particles have a highly fractured texture rather than a smooth one. Large irregular polygonal sheets are also present in the clays derived from the basic igneous rocks but are believed to represent a mosaic of jointed pseudo-hexagonal sheets as seen in Figures 7B, 8A, and 8B.

DISCUSSION AND CONCLUSION

The hexagonal shape of vermiculite clay particles is most convincingly demonstrated by the Sweeney clay since it does not contain any similarly shaped kaolinite particles. If we assume that the shape of halloysite

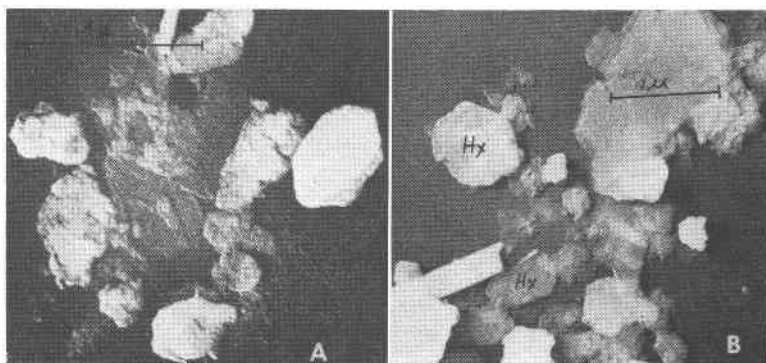


FIG. 7 (A and B) Aiken; vermiculite by synthesis.

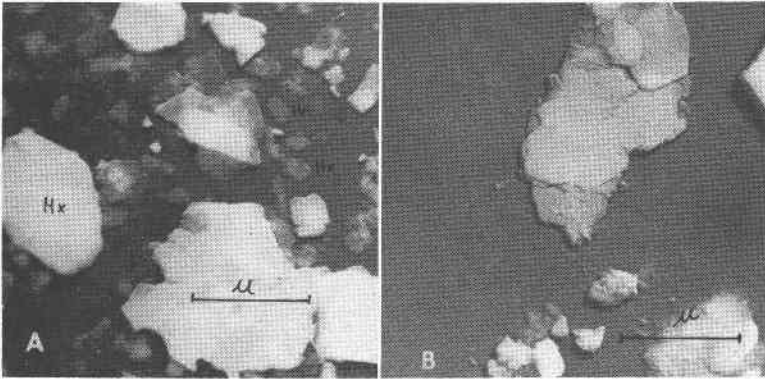


FIG. 8 (A and B) Auburn; vermiculite by synthesis.

particles is mostly tubular, then this conclusion is reinforced by several of the other clays, which contain halloysite but no kaolinite: Aiken, Auburn, Boomer, Josephine, Melbourne and Shaver.

The resemblance of some of the vermiculite particles—those with irregular polygonal sheets—to illite or chlorite particles from which they may have been derived and with which they may still be interleaved (as revealed by X-ray analysis) is to be expected. The appearance in these samples of vermiculite particles in the form of large pseudo-hexagonal sheets suggests that after the “vermiculitization” process of the mica sheets is completed, the mica particles either break up into hexagonal sheets or that a part of the particle in which vermiculitization is completed breaks off as a hexagonal flake.

Similar particles with hexagonal outline can be observed in the electron

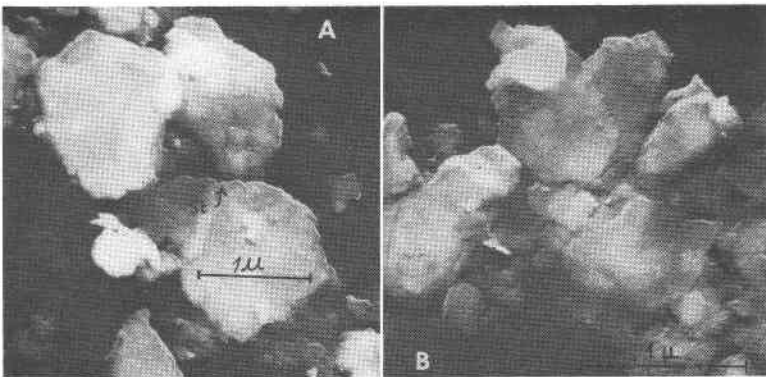


FIG. 9 (A and B) Boomer; vermiculite by synthesis.

micrographs published by White (1956) (in his study on the conversion of muscovite to montmorillonite with molten LiNO_3) and by Beutelspacher and van der Marel (1968) for "hydrous muscovite," "expanded illite" and "swelling illites." That these samples may either be entirely vermiculite or contain a large fraction of vermiculite follows from the definition of vermiculite—an expanded and hydrated mica.

Since illite alters to vermiculite, some of the particles reported as illite in the electron microscopy studies of illite (Grim 1953, 1968, and Bates 1955) may actually have been vermiculite.

Some of the clays which are associated with illite have X-ray diffraction spacing (determined by us) represent interleaving of mica and vermiculite, suggesting that the process of vermiculitization occurred not only at the perimeter of the particle (Barshad, 1954; and Jackson, 1964) but also at preferred planes throughout a single mica particle.

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