

FORMATION OF DIOCTAHEDRAL VERMICULITE IN VIRGINIA SOILS¹

by

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ABSTRACT

The weathering of micas to form the dioctahedral analogue of vermiculite is a common process in acid soils. Laboratory weathering of the micaceous 5–2 μ fraction of parent materials of certain Virginia soils resulted in a product similar in character (whether mixtures of vermiculite and regularly and randomly interstratified mica-vermiculite, or vermiculite only) to those formed by natural weathering processes. The formation of vermiculite rather than (or, in addition to) kaolinite is attributed to substitution of Na and other ions for K, other structural imperfections, and the small size of the original mica flakes.

The low cation exchange capacity and stability, in contraction and expansion, of the 14 Å product is attributed partly to retention of hydroxy-Al and Fe groups in the interlayer spaces. The removal of these interlayers by natural or laboratory processes results in a product that contracts easily but may or may not expand to 18 Å on glycerol solvation. This may be associated with the original charge of the mica as evidenced by its K and Na content.

INTRODUCTION

The soils of southeastern United States commonly contain a mineral that appears to be the dioctahedral analogue of vermiculite. Previous studies in Virginia (Rich, 1958) suggest that the mineral is a weathering product of muscovite-like minerals and that the mechanism is largely one of exchange of potassium by hydrated cations accompanied by expansion of the mica. Such a mechanism is similar to that proposed by Barshad (1948) for the alteration of biotite to vermiculite.

The present study is concerned mainly with laboratory weathering of the fine silt (5–2 μ) fraction of the C horizons of soils that contain a considerable amount of fine-grained, dioctahedral, potassium mica in which sodium originally proxies for some of the potassium.

The 5–2 μ fraction was chosen for the weathering studies because the most likely initial source of clay is the fine silt fraction. Moreover, this fraction normally contains less quartz than coarser fractions and less kaolinite than

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finer fractions. The C horizon samples were chosen because they were the least weathered of the samples obtained.

A comparison is made of the natural weathering sequence exhibited by the soil with the artificial weathering sequence exhibited by the 5-2 μ fraction. It is assumed that the extent of natural weathering increases as the soil surface is approached and also increases as the particle size is reduced.

MATERIALS

The soils studied are located in Culpeper, Fluvanna, Fauquier, Louisa, and Orange Counties of Virginia. These residual soils belong to the Nason and Tatum series and are derived from the Wissahickon schist, which contains a considerable amount of fine-grained potassium mica, usually identified as sericite. The chemical and mineralogical properties of the soils are described elsewhere (Rich and Obenshain, 1955). Because the sericite weathering also has been described (Rich, 1958), only sufficient information on natural weathering is given here to provide a comparison with the laboratory weathering studies reported in this paper.

The samples of Ontario, Canada, muscovite and Libby, Montana, vermiculite-biotite were obtained from Ward's Natural Science Establishment, Rochester, New York.

PROCEDURE

Pretreatment of Samples

After separation of the size fractions of soil (Jackson, 1956), free iron oxides were removed by the method of Mehra and Jackson (1960). Unless otherwise indicated, the soil clay (2-0.2 μ) samples also were treated for 12 hr with sodium citrate according to the method of Tamura (1958) to remove interlayer aluminum. This 12-hr treatment did not remove all the interlayer material from some samples, as indicated by contraction of the clay on K saturation of the sample. Another method was used to remove the interlayers from a sample that contained well-developed or stable interlayers. This consisted of digesting a 0.1 g sample in 15 ml of a mixed solution (N NH₄Cl, 0.2 N NH₄F, 0.1 N HCl) for 1 hr at 70° C. The digestion was carried out in 50-ml polypropylene centrifuge tubes. After centrifuging the suspension and discarding the solution phase, the sample was washed 5 times in N NaCl. (A wash was made by mixing the sample with 10 ml of the solution and centrifuging out the solid phase.)

The samples were calcium or potassium saturated by washing 5 times with appropriate normal chloride salt solutions. After washing out excess salts, the samples were air-dried.

Analytical Methods

The cation-exchange capacity was determined by analysis of the exchangeable calcium content of a 20 mg calcium-saturated sample (Rich, 1961). The

same sample, Mg saturated in the process of the C.E.C. determination, was glycerol solvated. This sample was transferred to a glass slide and air-dried. X-ray diffraction patterns were obtained as in a previous study (Rich, 1958). Intensities were recorded logarithmically.

Total potassium and sodium were determined by the method of Corey and Jackson (1953).

Laboratory Weathering Methods

Samples (25–100 mg) of the 5–2 μ fraction were first sodium-saturated and then boiled in normal sodium citrate for various periods of time. Unless otherwise indicated, the sodium citrate solution was replaced daily.

The method of Hashimoto and Jackson (1960) was employed to remove kaolinite and aluminum oxides. A preheating temperature of 550°C, rather than 500, was used, however, because it was found that the higher temperature was required to destroy kaolinite in the silt-size (5–2 μ) samples studied. Following the heat treatment, the samples were boiled for 2.5 min in 0.5 N NaOH to remove the dehydroxylated kaolinite and aluminum oxides.

RESULTS AND DISCUSSION

A Comparison of Natural and Laboratory Weathering

X-ray diffraction patterns (Fig. 1) provide a comparison of the natural weathering sequence of the 5–2 μ and 2–0.2 μ fractions of the soils with the sequence of weathering indicated by the laboratory treatment of the 5–2 μ fraction. The natural weathering sequence of the mica is indicated by the increase of the vermiculite (14 Å) component in the surface soil (A horizon) compared with parent material (C horizon) and the increase of the vermiculite component of the 2–0.2 μ fraction as compared with the 5–2 μ fraction in the same horizon.

The particle size function (Jackson *et al.*, 1948) in weathering of these soils was more apparent than the horizon depth function (Rich, 1958). There were greater differences between the 5–2 μ and 2–0.2 μ fractions in the C horizon than between the 2–0.2 μ fractions in the A and C horizons (Fig. 1).

In the Nason soils from Louisa and Fluvanna Counties, there appears to be more mica (10 Å component) in the 2–0.2 μ fraction of the A horizon than in the same fraction of the C horizon. Translocation of clay from the A horizon, accumulation of resistant portions of the mica at the surface, and uptake by plants of potassium from the subsoil and subsequent return to the soil surface are possible confounding factors in considering the depth function of weathering. There is less confounding of chemical weathering in the C horizon compared to the A horizon.

The laboratory weathering of the 5–2 μ fraction is demonstrated by a comparison of the X-ray diffraction patterns of untreated samples with those boiled in sodium citrate. Very small (25 mg) samples were boiled in 100 ml of normal sodium citrate for 4 days. In one series the samples were separated by centrifuging and the solution was changed daily; in another series the

study was made of the effect of prior cation saturation on expansion. The results are presented in Fig. 2.

Prior saturation with K^+ caused an irreversible collapse of the expanded mica, whereas H^+ and Al^{3+} saturation caused an increase in the intensity of the 14.5 Å reflection. A peak at 16.3 Å also appeared. Prior Li^+ and Ca^{2+} saturation had little effect, except that Li^+ saturation resulted in sharper peaks and a greater C.E.C. than did Ca^{2+} saturation.

The increase in C.E.C. is attributed partly to concentration of the 2:1 layer silicates as kaolinite was removed. The lack of irreversible collapse on Li^+ and Al^{3+} saturation and heating is attributed to the influence of tetrahedral charge of these minerals (Mathers, Weed and Coleman, 1955).

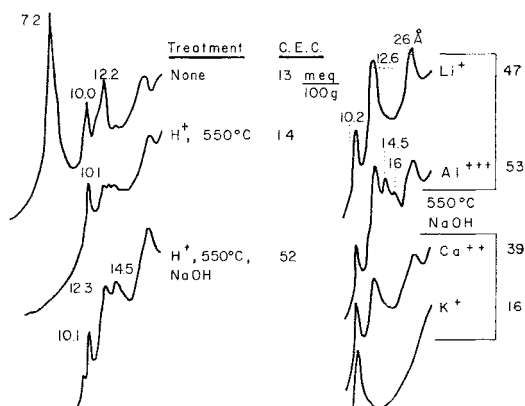


FIGURE 2.—X-ray diffraction traces showing the effect of saturating cation prior to heating at 550°C on the subsequent expansion of a 5-2 μ fraction of Louisa Nason soil after treatment with NaOH. All samples were magnesium saturated and glycerol solvated.

The cause of the increase in expanded layers following H^+ or Al^{3+} saturation is not apparent. Further work is being undertaken to determine the changes in layer charge and the possibility of fixation of aluminum in the tetrahedral layer.

The soil micas studied here differ considerably from well crystallized muscovite in ease of weathering. Figure 3 shows that the Ontario muscovite was altered little by the 550°C heat-NaOH treatment or the sodium citrate digestion,¹ whereas mica from the Tatum (Louisa) was changed considerably.

For some samples there was an indication of low layer charge, which permitted the sorption of two layers of glycerol by some layers (Walker, 1957). As shown in Fig. 4, 32 Å and 16.0 Å peaks appeared when the sample was magnesium saturated and glycerol solvated. These reflections are attributed

¹ For experiments in which kaolinite was removed, 100-mg samples were boiled in 100 ml of normal sodium citrate for 14 days, with daily change of the solution.

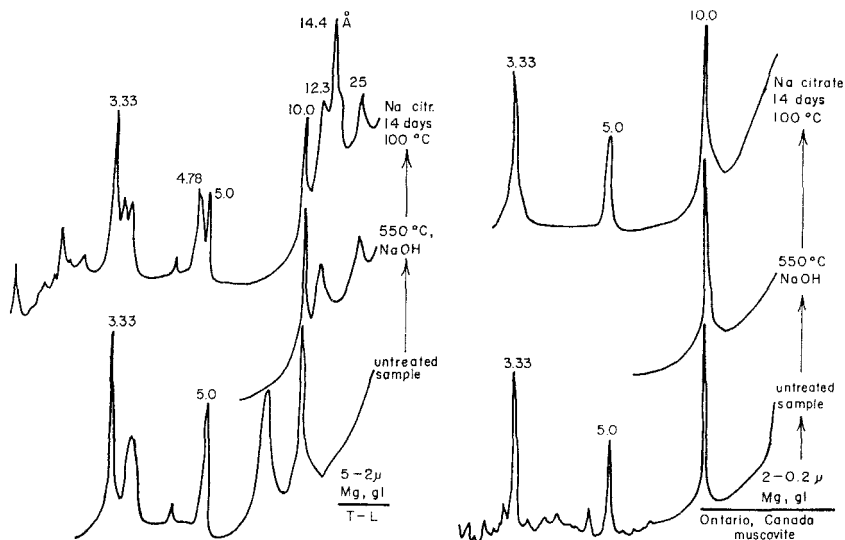


FIGURE 3.—A comparison, as indicated by X-ray diffraction traces, of laboratory weathering of the 5-2 μ fraction from a Louisa Tatum soil with the 2-0.2 μ fraction of Ontario, Canada, muscovite.

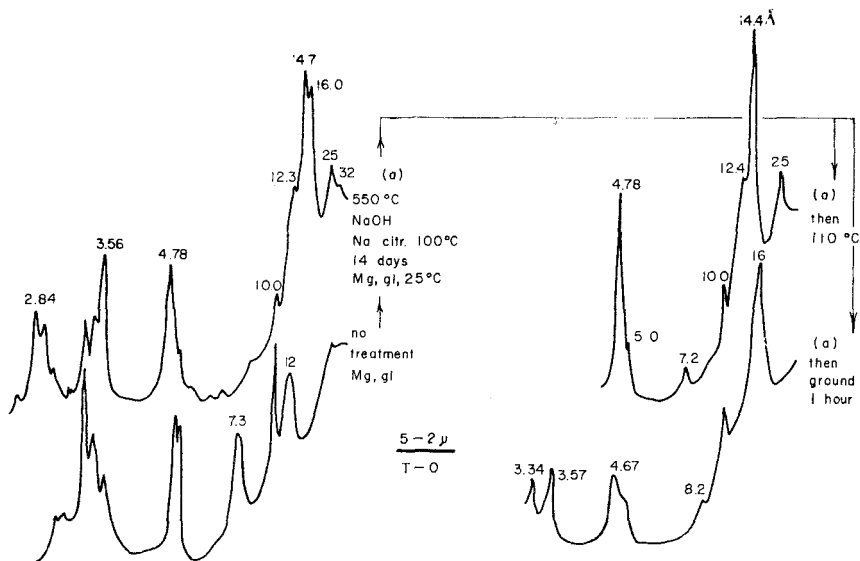


FIGURE 4.—Effect of laboratory weathering, followed by heating at 110° C, and grinding of a 5-2 μ fraction of the Orange Tatum soil, as indicated by X-ray diffraction traces.

to a regular sequence of expanded mica layers with one and two layers of glycerol alternating between the mica layers. When the sample was heated for 2 hr at 110°C the two layers of glycerol reduced to one layer, as evidenced by the loss of the 32 Å and 16 Å reflections and the increase in intensity of the 14.4 Å reflection.

When ground for 1 hr in a mortar, the magnesium-saturated, glycerol-solvated sample indicated only a 16 Å reflection in this region. This may be caused by a random mixture of 14.7 Å and 18 Å components and suggests that some interlayers, two glycerol layers thick, were produced in the 14.7 Å component present in the unground sample.

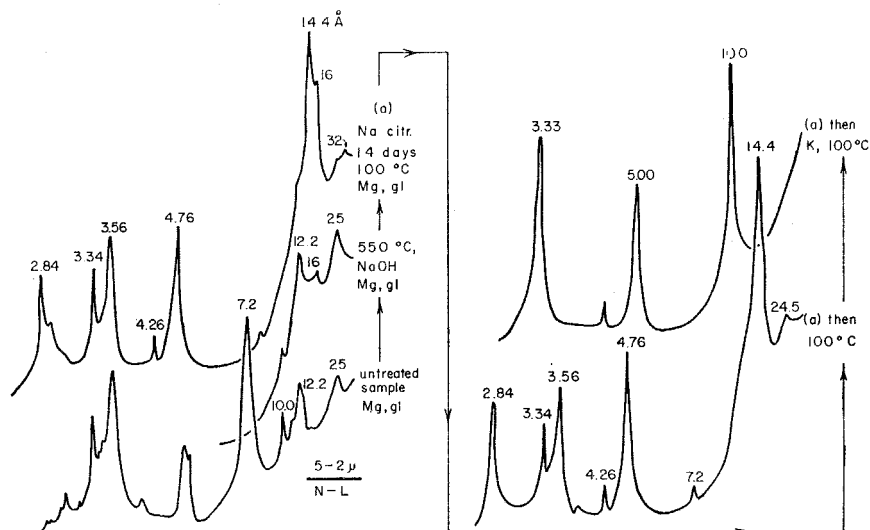


FIGURE 5.—Laboratory weathering of a 5-2 μ fraction of a Louisa Nason soil and alteration of the product by potassium saturation, as indicated by X-ray diffraction traces.

After laboratory "weathering", the expanded layers were collapsed easily to 10 Å on potassium saturation (Fig. 5).

When NaCl was substituted for sodium citrate, the rate of forming expanded layers increased but the product was not easily collapsed by potassium saturation. The salt treatments not only exchange Na⁺ for K⁺ but attack the octahedral layer, releasing Al³⁺ ions. The first reaction proceeds at the faster rate.

Aluminum ions, released by weathering, may become fixed as hydroxy groups in the interlayer space and inhibit collapse. Citrate complexes Al³⁺ and keeps it from becoming fixed, whereas a salt such as NaCl promotes hydrolysis of Al³⁺ ions. If the salt treatment is continued long enough the entire mica structure can be destroyed, as was done with the easily weathered Fluvanna Nason sample.

A comparison was made between the trioctahedral vermiculite "weathered" with NaCl from a Libby, Montana, vermiculite-biotite sample and the dioctahedral vermiculite "weathered" with sodium citrate from a 5–2 μ fraction of the Culpeper Tatum soil (Fig. 6). One striking feature of the dioctahedral vermiculite is the low intensity of the second order reflection

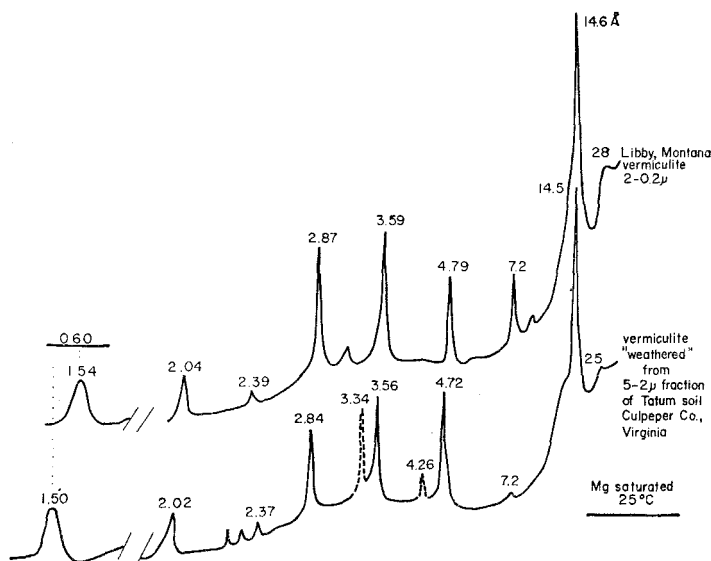


FIGURE 6.—X-ray diffraction traces of trioctahedral vermiculite "weathered" from vermiculite-biotite (Libby, Montana) and dioctahedral vermiculite weathered from sericite (Culpeper Co., Virginia).

(7.2 Å) but the fairly intense peaks for third (4.72), fourth (3.56), and fifth (2.84) orders (Fig. 6). The 060 reflections at 1.54 and 1.50 Å for the two minerals confirm their trioctahedral-dioctahedral relationship. The 4.26 and 3.34 Å peaks are quartz reflections.

Potassium and Sodium Content and Cation-Exchange Capacity

The cation-exchange capacity of the "weathered sample" increased, as would be expected, after removing kaolinite and exchanging out much of the potassium. The cation-exchange capacity of the Orange Tatum sample, after treatment, was 139.5 meq/100 g. The sample, however, also contained a total of 115.4 meq/100 g of potassium and sodium. The sum of C.E.C., Na⁺, and K⁺ is 254.9 meq/100 g, close to the theoretical potassium content of pure muscovite. The other samples indicate a charge deficiency but further corrections are needed for impurities such as quartz before this indication could be verified.

TABLE 1.—POTASSIUM AND SODIUM CONTENT AND CATION-EXCHANGE CAPACITY OF CALCIUM-SATURATED, 5–2 μ FRACTIONS OF THE C HORIZONS OF EIGHT VIRGINIA SOILS BEFORE AND AFTER A 550°C–NaOH AND SODIUM CITRATE TREATMENT (BASED ON WEIGHT AT 300°C)

Soil series	County	Before treatment				After treatment			
		K	Na	C.E.C.	Total	K	Na	C.E.C.	Total
		meq/100 g							
Nason	Fauquier	35.6	2.2	11.8	49.6	—	—	52.9	—
Nason	Fluvanna	58.2	18.2	21.0	97.4	—	—	5.3	—
Nason	Louisa	45.9	4.3	9.2	59.4	—	—	112.3	—
Nason	Orange	131.3	5.6	26.2	163.1	51.7	7.6	137.0	196.3
Tatum	Culpeper	51.5	7.8	4.2	63.5	75.4	29.8	122.1	227.3
Tatum	Fluvanna	202.6	23.5	4.0	230.1	127.0	17.9	94.3	239.2
Tatum	Louisa	92.8	8.7	6.8	108.3	—	—	103.9	—
Tatum	Orange	163.6	4.4	18.9	186.9	99.6	15.8	139.5	254.9

Because of the great affinity of weathered dioctahedral mica for potassium, it is capable of removing this element from solutions of “pure” NaCl, sodium citrate or other salts. Thus, in saturating such micas with a cation for the purposes of cation-exchange capacity measurements, or for other reasons, some potassium also may be added.

Nomenclature of Weathered Dioctahedral Mica

The products of dioctahedral mica weathering present difficult problems in nomenclature. Figure 7 illustrates some of these problems.

In the process of natural weathering of these micas, hydroxy-aluminum and iron groups accumulate in the interlayer space. These groups occupy or block exchange sites and inhibit contraction of the mineral on K saturation or heating, or both, and restrict expansion by liquids. The process of interlayer filling can be reversed when natural chelating agents (organic matter) are abundant. The interlayers also can be removed in the laboratory with citrate, fluoride, or other complexing agents. The weathering product, containing interlayers, has been described as a chlorite-vermiculite intergrade (Jackson, 1959). This name, although descriptive, does not indicate the extent of filling of the interlayer space, nor does it indicate the composition of the interlayer material.

When interlayer material is absent or very small in amount, there is often a difference in expansion with glycerol depending on the cation with which the sample is saturated. When the 2–0.2 μ fraction of Louisa Nason was calcium saturated and glycerol solvated, there was expansion to 17.2 Å so one might conclude that montmorillonite is present (Tamura, 1958). On the other hand, if the sample is first magnesium saturated, the spacing remains

at about 14.5 Å. Such reactions are typical of low-charge vermiculites (Walker, 1957).

On the other hand, there were studied occasionally products of natural weathering of the dioctahedral micas that expand like montmorillonite even when magnesium saturated. Similar evidence was presented for the artificially weathered micas.

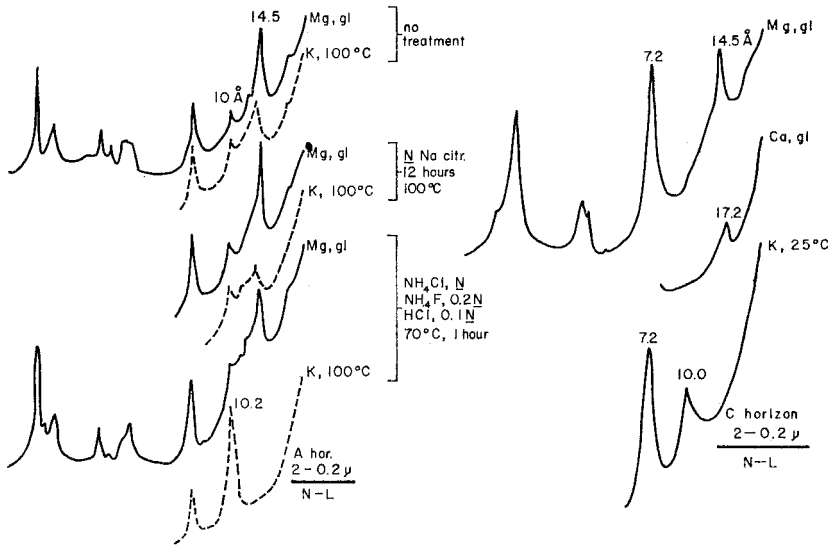


FIGURE 7.—Effect of cation saturation on expansion with glycerol solvation of the 2–0.2 μ fraction of the C horizon and effect of interlayer removal on collapse with potassium saturation of the 2–0.2 μ fraction of the A horizon of the Louisa Nason soil.

CONCLUSIONS

This study indicates that the alteration of muscovite-type micas in acid soils is affected by the mineral itself. Variations in the product of weathering depend on the structure, crystallinity, isomorphous substitution, layer charge, particle size, and probably many other properties of the mica. Dioctahedral micas in similar soils exhibited marked differences in degree of weathering. Silt fractions of some C horizons contained considerable amounts of expanded mica, particularly as interstratified mica-vermiculite. In contrast, mica in other soils persisted abundantly even in the clay-size fraction of the surface horizons.

Laboratory “weathering” experiments also demonstrated striking variations among dioctahedral potassium micas. Ontario muscovite, of 2–0.2 μ size, was altered little, whereas all the soil micas studied, even of coarser size (5–2 μ), were altered considerably.

Among the micas found in the C horizons of the soils studied, the extent of weathering by natural or artificial processes was greatest when the parent mica was interstratified with vermiculite. It is suggested that this is in part a continuation of a more rapid weathering rate already naturally exhibited by the parent mica as it weathered from the fresh schist to the soil parent material of the C horizon.

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