THE NATURE OF VERMICULITE IN ADIRONDACK SOILS AND TILL

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Abstract—The clay and bulk mineralogy of soil and till from 26 Adirondack watersheds was studied. The materials consist typically of quartz, K-feldspar, plagioclase, mica, vermiculite, and kaolinite. Talc, smectite, halloysite, and hornblende are present in some samples. The clay fraction of the soils is composed predominantly of vermiculite, likely derived from the transformation of a mica precursor, and kaolinite. The soil vermiculite commonly contains hydroxy-Al interlayers which are especially prevalent in the B-horizon samples. Despite significant variation in the type of bedrock and the composition of heavy mineral assemblages in these watersheds, the clay mineralogy is remarkably uniform. This finding supports earlier suggestions that the occurrence of vermiculite in soils is more dependent on climate than on the nature of the parent material.

Key Words—Adirondacks, Hydroxy-Al, Soil, Till, Vermiculite, Weathering.

INTRODUCTION

During the past five years the authors have been involved in watershed studies in the Adirondack Park of New York State to investigate the effects of acid deposition on lake acidification (April and Newton, 1985). As part of this project, the mineralogy of soil and till has been determined in 26 watersheds widely distributed across the Adirondacks and underlain by a variety of bedrock types. Although quartz, K-feld-spar, and plagioclase are dominant in the unconsolidated material contained within these watersheds, the heavy mineral assemblages vary substantially and, for any given watershed, appear to reflect the heavy mineral abundances in the local bedrock. The heavy mineral content of some soils and tills may reach 20%. Because many of these minerals are relatively unstable under weathering conditions (e.g., hornblende, hypersthene, enstatite, augite, and garnet), we initially thought that the clay mineral assemblages would vary among watersheds and reflect these differences in parent mineralogy. This hypothesis proved incorrect, however, when clay mineralogical studies showed that vermiculite was ubiquitous and by far the predominant clay mineral in all 26 watersheds. This finding supports the suggestion of Barshad (1966) that for a given region the occurrence of vermiculite in soils is more dependent on climatic factors (i.e., mean annual precipitation) than on the nature of the parent material.

The purpose of this paper is to discuss the nature of the vermiculite in Adirondack soils and till and to present a hypothesis for its origin. Barshad and Kishk (1969) suggested that vermiculite in soils may form by either the transformation of a mica precursor giving rise to an aluminous vermiculite, or by synthesis from primary oxides released by weathering giving rise to a siliceous vermiculite. As will be shown, the former process better characterizes vermiculite formation in Adirondack soils and till.

GEOLOGIC SETTING

The Adirondack Mountains of New York State comprise a dome of multiply deformed Precambrian rocks that were subjected to large-scale regional metamorphism during the Grenvillian orogeny, about 1 billion years ago. Rock types in the Adirondack massif range from charnockitic quartzofeldspathic gneisses interlayered with quartzites, marbles, and calc-silicate rocks to metaigneous rocks of the anorthosite-charnockite suite which include cross-cutting pegmatites, granitic rocks, and olivine metagabbros (Fisher *et al.*, 1970).

Continental glaciers overrode the Adirondack region during the Pleistocene and last retreated from the area about 12,000 to 14,000 years ago. Unsorted, unstratified till was deposited over large areas during glacial retreat, and some sand and gravel was deposited by meltwater streams flowing from the glacier. During
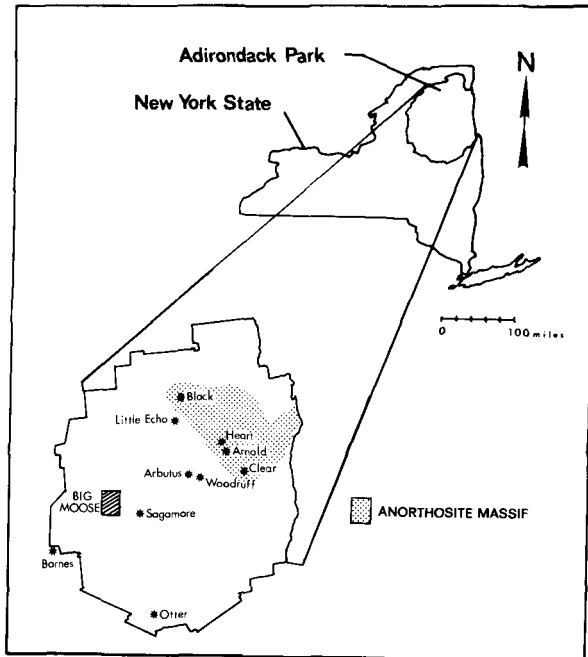
Figure 1. Location of Regional Integrated Lake-Watershed Acidification Study (RILWAS) sites in the Adirondack Park of New York State. (Big Moose system contains 16 catchments.)

winter months when discharge was reduced, stream deposits were the sources of windblown (aeolian) silt that mantles some of the till in the region. Since deglaciation, Spodosols have developed on the surficial geologic materials, reflecting the cool, humid climate of the Adirondacks. Mean annual precipitation in the Adirondacks ranges from 100 to 140 cm/yr, depending on location.

SAMPLING AND ANALYTICAL TECHNIQUES

During the summers of 1982 through 1984, 401 samples of soil and glacial debris were collected from 97 sites in 26 forested, Adirondack watersheds (Figure 1). Sites were chosen, after detailed geologic mapping, to provide representative soil profiles from watersheds underlain by a variety of bedrock types. Soil augers were used in soil pits to obtain deeper samples, and glacial till was collected at recent natural exposures.

Samples were split and prepared for mineralogical, chemical, and textural analysis generally following the procedures suggested by Jackson (1974). The bulk mineralogy of the <4-mm fraction of each sample was determined using standard X-ray random-powder diffraction (XRD) techniques supplemented by optical microscopy. Heavy mineral assemblages (d > 2.96 g/cm^3) were determined separately by gravity settling of the fine-sand fraction in tetrabromoethane and point counting 300 grains using the standard Fleet method (Carver, 1971; Milner, 1962). The <63-μm clay-silt

fraction of each sample was obtained by washing the material through a 230-mesh stainless steel sieve. The clay and silt were mechanically disaggregated by sonification, reacted routinely with 30% H_2O_2 to remove organic matter, and then treated with sodium citrate-bicarbonate-dithionite (CBD method) to remove free Fe and Al oxides/hydroxides that interfere with XRD analysis (Jackson, 1974). The <2-μm fraction was collected using high-speed centrifugation and routinely prepared for XRD analysis by gravity-settling on glass slides. For more detailed work on selected samples, oriented mounts were prepared following the porous ceramic tile method of Kinter and Diamond (1956). Six XRD patterns were obtained of the <2-μm fraction of each sample treated as follows: (1) air-dried, (2) ethylene glycol-solvated, (3) K-saturated, (4) heated to 200°C, (5) heated to 350°C, and (6) heated to 530°C. If necessary, 1-N-HCl-treated and Mg-saturated, glycerol-solvated specimens were prepared to aid in the identification of kaolinite and swelling clays (e.g., vermiculite and smectite). XRD patterns were obtained on both a Diano XRD-8000 (Colgate University) and a Siemens D-500 (Dartmouth College) diffractometer using CuKα radiation. Patterns were normally run at a scanning rate of 1° or 2°2θ/min. X-ray tube voltage and amperage were adjusted accordingly for maximum intensity.

Chemical analyses of the clay-size material were obtained with a Diano XRF-8560 vacuum-path X-ray spectrometer. Samples were prepared using a modified version of Norrish and Hutton's (1969) method, which involves fusion of sample powder with lithium tetraborate to produce a silicate glass disc. Matrix corrections were applied to raw data using an iterative computer correction routine.

Grain sizes were analyzed using standard sieve and hydrometer methods, and statistics were calculated using the methods of Folk (1974).

RESULTS

General description

The Spodosols present in the 26 watersheds consist mainly of Haplorthods and Fragiorthods developed on till and locally on outwash or stratified sand. Typically, the humus layer is underlain by a bleached, eluvial (E) horizon and a spodic horizon containing a mixture of accumulated Al and Fe oxides and hydroxides. The naturally acidic soils, having pHs that range from about 6 in C horizons to 3 in organic layers, are generally less than 1 m deep and gradually grade into the underlying parent till. On the steeper slopes of most watersheds, shallow soils resting on bedrock have developed, and the entire thickness of the profile may be less than 50 cm.

At least two glacial till units appear to be present in the Adirondack region; a sandy, upper-till in nearly all

Table 1. Percentage of heavy minerals in soils of selected watersheds of the Adirondacks.

	Lake Arnold	Little Echo Pond	Heart Lake	Clear Pond	Barnes Lake	Otter Lake
Hypersthene	40.2	10.6	21.3	14.8	2.2	13.2
Hornblende	2.5	20.1	14.9	3.8	10.1	3.3
Garnet	19.5	5.6	22.2	40.8	6.0	46.2
Opaques	11.0	46.3	17.2	10.1	45.2	16.3
Tourmaline	0.8	6.1	4.2	0.2	15.4	3.1
Zircon	0.2	2.3	2.0	0.2	2.3	0.7
Staurolite	0.0	2.3	1.3	0.4	0.4	0.3
Rock fragments	0.3	0.3	0.0	0.1	0.9	1.8
Unknown	1.1	3.8	1.4	1.4	2.1	0.7
Enstatite	23.6	0.0	11.9	2.2	1.2	6.5
Hematite	1.2	0.0	0.1	0.0	0.0	0.0
Epidote	0.0	0.0	3.5	8.6	6.0	1.8
Apatite	0.0	0.0	0.0	0.1	0.3	0.2
Augite	0.0	0.0	0.0	17.4	6.8	5.4
Others	0.0	2.6	0.0	0.0	1.1	0.5
Total heavy mineral content of soil	17.7	12.8	17.5	16.2	9.1	12.4
Bedrock in and around watershed	Anorthositic gabbro	Granitic gneiss and anorthosite	Anorthosite	Meta-anorthosite and anorthositic gneiss	Granitic gneiss	Garnetiferous granitic gneiss

of the watersheds sampled, and a more compact, clay-rich, lower-till that crops out only rarely. (The two different tills were first identified in Sagamore Lake watershed (April, 1983) and later in Woodruff Pond watershed, this study.) The tills were probably deposited separately and are differentiated primarily on the basis of texture. The upper-till, deposited during the last glaciation, is generally sandy although quite variable in texture, averaging 70% sand, 26% silt, and 4% clay. The lower-till, deposited possibly during an earlier glacial episode, is more uniform in texture, averaging 63% sand, 22% silt, and 15% clay. Mineralogically, the upper- and lower-tills are similar except that the lower-till appears to contain more low layer-charge vermiculite.

The upper-till may be subdivided into (1) an ablation phase which is very sandy (as much as 90% sand) and which contains lenses of stratified material, and (2) a lodgement phase which is more massive and less sandy than the ablation phase.

Soil mineralogy and texture

The bulk mineralogy of samples collected from the watersheds was determined by XRD, optical microscopy, and gravimetric analysis. Quartz, K-feldspar, and plagioclase feldspar constitute about 70–90% of the mineral matter in each watershed. The remaining 10–30% consists of clay minerals and accessory heavy and light minerals. Mean plagioclase compositions vary from about An_{17} in watersheds underlain by granitic gneisses or charnockites to An_{30-40} in watersheds on or

near the anorthosite massif. Heavy mineral abundances range from about 9 to 21% of the total sand-size fraction, with hornblende, hypersthene, garnet, opaque minerals (i.e., ilmenite and magnetite), enstatite, and augite being most common (Table 1). Other accessory minerals identified include tourmaline, zircon, staurolite, epidote, apatite, and hematite. The relative proportion of minerals comprising the light and heavy assemblages varies considerably among watersheds, reflecting the heterogeneity of bedrock types in the region and the strong influence of local bedrock petrology on the mineralogy of glacially derived sediment.

Grain-size analyses show that soils developed on glacial till are siltier and more clay-rich than soils developed on outwash or deltaic sands; however, the average amount of the clay-size fraction of Adirondack soils is still less than 5%. Average sand content of soils ranges from 54 to 96%; average silt content ranges from 11 to 43%.

Clay mineralogy

Results from more than 1000 XRD traces of the <2-μm and <1-μm clay-size fractions show that the dominant clay mineral assemblage in Adirondack soils is vermiculite + kaolinite (Figure 2). For some samples, diffractograms show the presence of small amounts of mica (muscovite and/or biotite), mixed-layer mica/vermiculite, and traces of talc. Typically, vermiculite is the most abundant clay mineral constituting the bulk of the <2-μm fraction. As discussed by April and New-
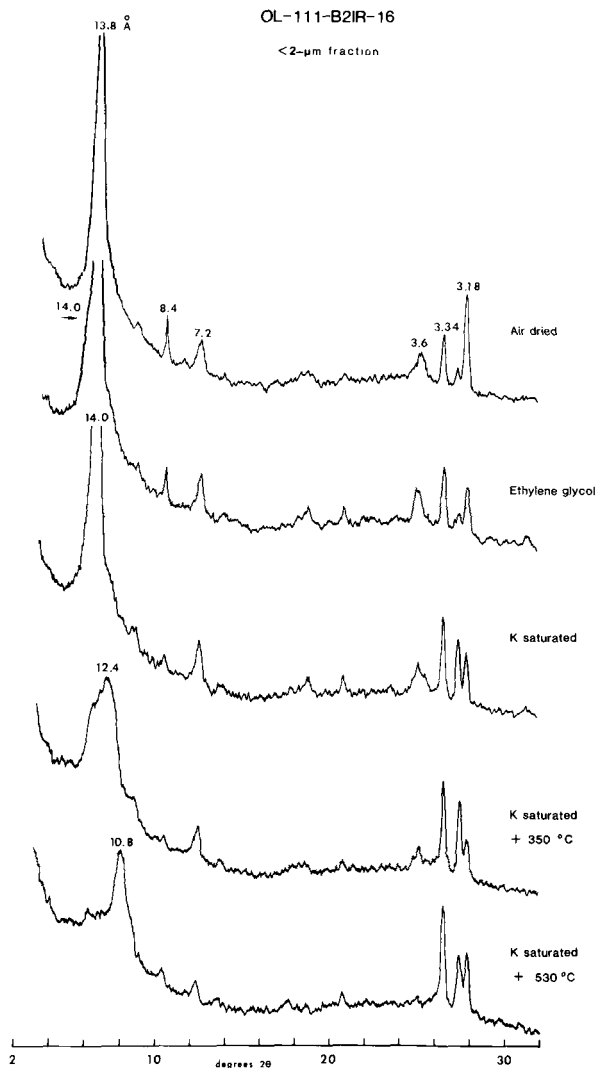
Figure 2. X-ray powder diffraction patterns of the <2-μm fraction from soil profile OL-111 in Otter Lake watershed showing a typical assemblage of vermiculite and kaolinite. Some quartz, feldspar, and hornblende are also present. Peak positions are given in Å. CuKα radiation.

ton (1983), vermiculite in the soil profiles commonly contains hydroxy-Al interlayers which prevent collapse of the 14-Å structure to 10 Å upon K-saturation. Sequential heat treatments from 200° to 530°C of the K-saturated sample resulted in either partial or complete collapse of the mineral as inferred from d(001) reflections ranging from slightly less than 14 Å to about 10 Å (see Figure 2). Such a collapse was also found for K-saturated specimens prepared from samples pretreated for as long as 8 hr with hot sodium citrate, indicating that the hydroxy-Al interlayers were strongly bound in these sites.

The clay mineral assemblage in the till differs from that in the soils by the presence of vermiculite con-

taining little to no hydroxy-Al interlayers and more 10-Å clays. At least a portion of the vermiculite in the till appears to be a low-layer-charge variety because it expands to 16–17 Å with ethylene glycol solvation, but remains at about 14 Å upon Mg-saturation and glycerol solvation (Figure 3). The remainder of the 14-Å clay material shows reflections that are more typical of vermiculite. Kaolinite and mixed-layer mica/vermiculite (or hydrobiotite) are also present in many till samples (Figure 3). Broad 7-Å reflections may indicate disorder in the stacking sequence of the kaolinite (Brindley, 1980) or the presence of discrete or randomly interstratified halloysite. (Attempts to identify halloysite with a scanning electron microscope were not successful.) Hornblende, quartz, K-feldspar, and plagioclase are present in most <2-μm fraction separates of the till, reflecting the presence of fine glacial flour.

Overall, the clay mineral assemblages in soils and till in the 26 watersheds are remarkably similar. With the exception of minor variations in the relative proportions of clays, no significant differences or trends due to areal distribution or local bedrock geology were observed. This finding supports Barshad's (1966) suggestion that the occurrence of vermiculite in soils is strongly influenced by climatic factors, i.e., mean annual precipitation, regardless of the nature of the parent material. One notable exception is the occurrence of smectite in a poorly drained soil on level ground close to the shore of Lake Rondaxe (Big Moose System, Figure 4). Smectite is common in poorly drained soils of low-lying areas (Borchardt, 1977).

DISCUSSION

Nature of the vermiculite

X-ray powder diffraction mineralogy. Vermiculite is an abundant and ubiquitous clay mineral in Adirondack soils and tills. Its characteristics, however, vary within soil profiles and between soil and parent glacial material. Within soil profiles, the relative degree of Al-fixation in interlayer sites is greatest in the B and possibly the upper-C horizon. Vermiculite from these horizons does not expand beyond about 14 Å upon ethylene glycol solvation or Mg-saturation and glycerol solvation, nor does it collapse upon K-saturation. Only upon successive heat treatments to 530°C does the 14-Å reflection migrate toward (but usually never reach) a spacing of 10 Å. The occurrence of broad reflections between 14 and 10 Å produced by this sequential heating suggests the presence of vermiculite layers in various degrees of collapse ranging in d-values from 14 to 10 Å.

In the bleached, eluvial (E) horizon, however, the vermiculite displays a different set of properties: (1) Al-fixation is low to absent as indicated by the nearly complete collapse of the mineral to 10 Å upon K-saturation (Figure 5). This small amount of Al-fixation
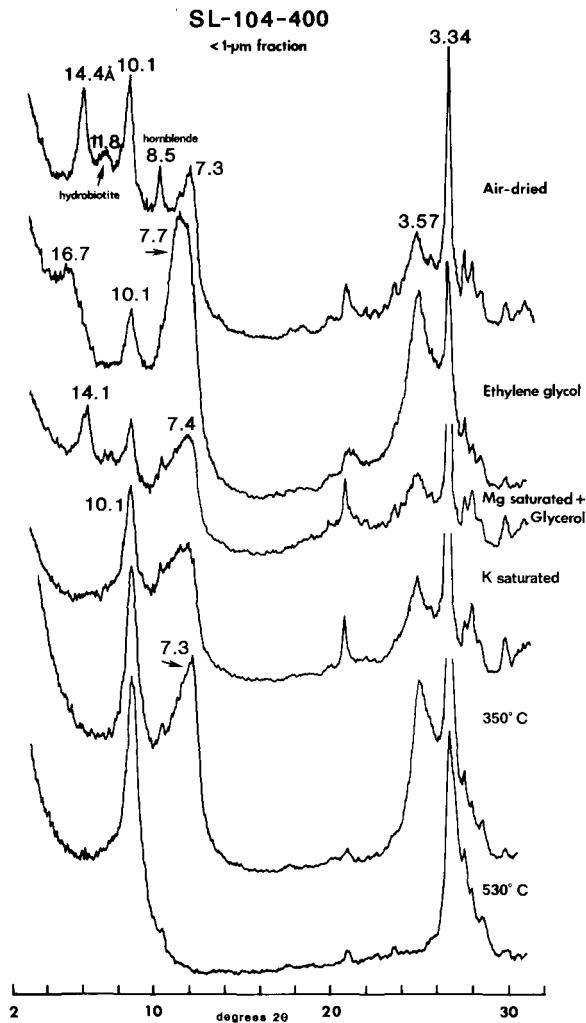
Figure 3.   X-ray powder diffraction patterns of the <1-μm fraction of a till sample collected at 400 cm depth in Sagamore Lake watershed. Clay mineral assemblage consists of vermiculite + biotite + kaolinite (interstratified with halloysite?). Peak positions are labeled in Å. CuKα radiation.

Figure 4.   X-ray powder diffraction patterns of the <1-μm fraction from soil profile BMRO-103 collected in Rondaxe Lake watershed. The clay assemblage includes vermiculite + smectite + kaolinite. Peak positions are labeled in Å. CuKα radiation.

in vermiculite in the upper mineral soil horizons immediately below the litter layer may reflect the inability of these hyroxy-Al interlayers to form in the presence of organic acids (see e.g., Huang and Keller, 1971; Violante and Violante, 1980), or may result from dissolution of pre-existing hydroxy-Al interlayers and the subsequent mobilization of Al out of these soil horizons by a new, more aggressive weathering regime. (2) If the clay was pretreated using the Na-citrate-bicarbonate-dithionite method or Na-oxalate, the air-dried diffractogram showed a d(001) reflection at about 12.5 Å (Figure 5). This value is expected for a Na-saturated vermiculite in the air-dried state (Brown and Brindley, 1980). (3) Upon ethylene glycol solvation, a portion of the 14-Å mineral expanded to about 17 Å, indicating
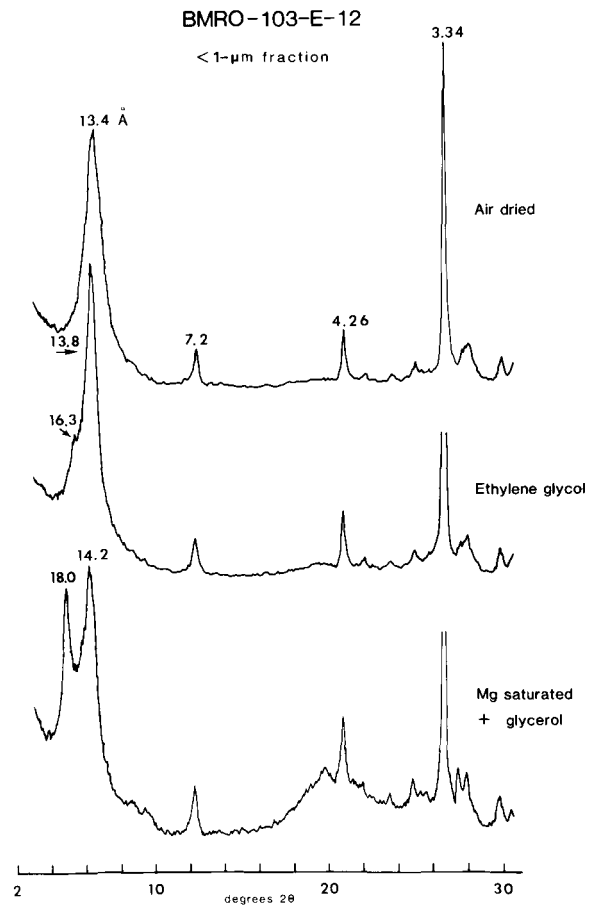
the presence of either a smectite or a low-layer-charge vermiculite. The fact that the mineral remains at 14 Å with Mg-saturation and glycerol solvation (Figure 5) suggests the latter (Walker, 1961). (5) The magnitude of the d(002) 5-Å reflection after K-saturation and collapse of the structure to 10 Å indicates the dioctahedral nature of the clay (Brown and Brindley, 1980, p. 336).

Vermiculite also predominates in the clay-size fraction of the till, and, in many respects, its properties seem similar to those of the vermiculite in the eluvial soil horizon (see Figure 3). Al-fixation is low to absent in most upper- and lower-till samples, and both high- and low-charge varieties of vermiculite are present. The mineral collapses to 10 Å with K-saturation, shows both 14- and 17-Å reflections after ethylene glycol solvation, and remains at 14 Å upon Mg-saturation and glycerol solvation. Only upper-till samples within 300 cm of the surface contain vermiculite with some hydroxy-Al interlayers, possibly marking the depth below
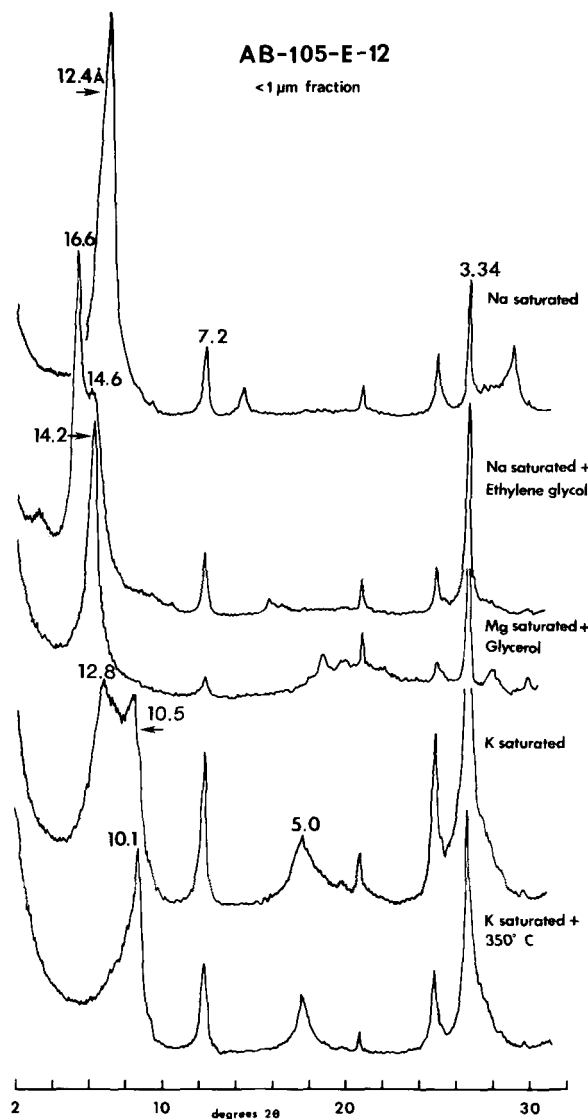
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<1 µm fraction

Figure 5.   X-ray powder diffraction patterns of the <1-µm fraction from the E horizon collected in Arbutus Lake watershed. The clay assemblage includes high- and low-charge vermiculite + kaolinite. Peak positions are labeled in Å. CuKα radiation.

Table 2.   Structural formulae for vermiculite.

	Sample 1[1]	Sample 2[1]
Octahedral		
Al	1.73	1.65
Fe³⁺	0.16	0.24
Mg	0.06	0.04
Ti	0.05	0.07
Σ	2.00	2.00
Tetrahedral		
Si	3.33	3.14
Al	0.67	0.86
Σ	4.00	4.00
Interlayer		
Al	0.11	0.22
Ca	0.04	0.01
K	0.15	0.12
Na	0.15	0.14
Layer charge		
Octahedral	−0.01	+0.03
Tetrahedral	−0.67	−0.86
Total	−0.68	−0.83

[1] Sample 1 = single sample; sample 2 = composite.

content. The material was then analyzed by XRD for mineralogy, and the least contaminated samples were chosen for XRF analysis. We were never able to obtain pure vermiculite; small amounts (estimated to be less than 5%) of quartz, kaolinite, and feldspar were present in all <1-µm fractions.

Table 2 shows the calculated structural formulae for vermiculite present in soil-B horizons. Sample 1 provided enough material (about 1 g) for a chemical analysis, whereas sample 2 represents a mixture of the <1-µm material of B horizons from three separate sites.

Even with the uncertainty caused by the presence of mineral contaminants, the following conclusions can be drawn from the chemical data: (1) the vermiculite is an aluminum-rich, dioctahedral variety, (2) excess Al is fixed in interlayer sites, (3) the base cation content is low, and (4) the high, net layer-charge is derived mainly from substitution of Al for Si in the tetrahedral sheet.

Origin of the vermiculite

In light of the data on hand, three hypotheses may be considered for the origin of vermiculite in Adirondack soils.

Detrital. As stated above, vermiculite is present in the till and is apparently relatively stable in the active weathering zone of soil profiles. Inasmuch as the properties of the vermiculite in the till and the eluvial soil horizon are similar, its presence can possibly be explained by detrital inheritance from a pre-glacial weathered landscape containing vermiculitic soils. During post-glacial pedogenesis, Al was mobilized and

which Al mobilization and fixation in interlayer clay sites becomes negligible.

Chemistry. Attempts to determine the chemistry of the vermiculite were only partially successful, but the results nonetheless provide some useful information. The procedure consisted of first inspecting diffractograms of the <2-µm fraction of soil samples to determine which contained substantial amounts of the mineral and little else. Selected samples were then further size-fractionated by centrifugation to obtain the <1-µm fraction in the hope of reducing the quartz and feldspar

entered interlayer sites, and presently reaches maximum fixation in the B horizon.

Weathering and transformation of biotite. An important difference between parent till and soil clay-mineral assemblages is the relative abundance of 10-Å micas in the former and their paucity in the latter. The d-values of 060 reflections indicate that the 10-Å mica is predominantly trioctahedral and, therefore, likely biotite. Also, a number of diffractograms display a reflection near 12.5 Å, indicating the presence of mixed-layer biotite/vermiculite or hydrobiotite in the till (see Figure 3). Although the transformation of biotite to vermiculite is not fully understood, the occurrence of mica/vermiculite have often been cited as evidence that the process does indeed occur (see, e.g., Jackson, 1963; Barshad, 1949; Walker, 1949; and a review by Fanning and Keramidas, 1977).

The transformation of biotite to this particular vermiculite requires a change from a trioctahedral to a dioctahedral structure. This phenomenon has been observed in Fe-rich species by Farmer *et al.* (1971). Adirondack biotites, however, are commonly Ti-rich, containing as much as 5–9% Ti (Whitney and Mc-Lelland, 1983; Engel and Engel, 1960). The loss of these octahedral cations during weathering in an acidic soil environment may result in their replacement by Al, especially mobile at low pH (Garrels and Christ, 1965; May *et al.,* 1979), forming the aluminous, dioctahedral vermiculite seen in the soils. Finally, the chemistry of the Adirondack vermiculites (see Table 2) falls within, or reasonably near, the range of tetrahedral and octahedral occupancy given by Barshad and Kishk (1969) for mica-derived vermiculites.

Weathering of other primary aluminosilicates. The formation of vermiculite by the weathering of other primary aluminosilicates is perhaps the most speculative of the three hypotheses, but it cannot be discounted simply for lack of data. Heavy mineral trends in most Adirondack soil profiles show that the amphiboles (chiefly hornblende) and pyroxenes are largely depleted in upper soil horizons (April and Newton, 1983; this study). According to Huang (1977), chlorite is a typical weathering product of both minerals in soil environments. Furthermore, in an aggressive weathering regime (e.g., Adirondack Spodosols) chlorite can transform further to vermiculite, usually via an intermediate chlorite/vermiculite (Stephen, 1952; Ross and Kodoma, 1976). Likewise, feldspar weathering can lead to the formation of vermiculite through an intermediate mica phase. The absence of chlorite and the low abundance of micas and interstratified clays such as mica/vermiculite and chlorite/vermiculite in the soils, however, suggest that these reactions are not significant. On the other hand, the very absence or low abundance of intermediate weathering products indicates

that reactions proceed quickly to completion under extant conditions in Adirondack soils. Reactions may, for example, either bypass intermediate steps or form metastable minerals of short-lived duration.

Of the three hypotheses considered, our evidence suggests that most vermiculite in Adirondack soils forms from the weathering and transformation of a mica (biotite?) precursor. The possibility that more than one of the processes described above have occurred, or have operated during different stages in the development of these soils cannot be ruled out.

CONCLUSIONS

The results of our study on the mineralogy of Adirondack soils and till indicates the following:

1. Vermiculite is the dominant clay mineral in Adirondack soils and till. Kaolinite, mica, and mica/vermiculite are also present. Smectite and traces of talc have also been identified locally.

2. Mobilization of Al by organic complexation and low pH in the O and E soil horizons results in downward transport of Al in the soil profile. Fixation of hydroxy-Al interlayers in vermiculite occurs chiefly in the B soil horizon where (1) organic complexes decompose releasing the Al, and (2) pH increases causing the formation of hydroxy-Al precipitates.

3. The vermiculite in Adirondack soils is an aluminous, dioctahedral variety and is likely derived from the weathering and transformation of a mica (biotite?) precursor.

4. Barshad's (1966) suggestion that the occurrence of vermiculite in soils is more dependent on climatic factors than on the nature of the parent material apparently holds true for the Adirondack region.

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