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Mineralogy of the rhizosphere in forest soils of the eastern United States

Mineralogic studies of the rhizosphere

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Abstract. Chemical and mineralogical studies of forest soils from six sites in the northeastern and southeastern United States indicate that soil in the immediate vicinity of roots and fine root masses may show marked differences in physical characteristics, mineralogy and weathering compared to the bulk of the forest soil. Examination of rhizosphere and rhizoplane soils revealed that mineral grains within these zones are affected mechanically, chemically and mineralogically by the invading root bodies. In SEM/EDS analyses, phyllosilicate grains adjacent to roots commonly aligned with their long axis tangential to the root surface. Numerous mineral grains were also observed for which the edge abutting a root surface was significantly more fractured than the rest of the grain. Both the alignment and fracturing of mineral grains by growing roots may influence pedogenic processes within the rhizosphere by exposing more mineral surface to weathering in the root-zone microenvironment. Chemical interactions between roots and rhizosphere minerals included precipitation of amorphous aluminium oxides, opaline and amorphous silica, and calcium oxalate within the cells of mature roots and possible preferential dissolution of mineral grains adjacent to root bodies. Mineralogical analyses using X-ray diffraction (XRD) techniques indicated that kaolin minerals in some rhizosphere samples had a higher thermal stability than kaolin in the surrounding bulk forest soil. In addition, XRD analyses of clay minerals from one of the southeastern sites showed abundant muscovite in rhizoplane soil adhering to root surfaces whereas both muscovite and degraded mica were present in the immediately surrounding rhizosphere soil. This difference in mineral assemblages may be due to either K-enrichment in rhizoplane soil solutions or the preferential dissolution of biotite at the root-soil interface.

Introduction

The rhizosphere is defined as the narrow zone of soil subject to the influence of living roots. Metabolic processes performed by the root create a physicochemical environment within the rhizosphere very different from that of the bulk soil (Curl & Truelove 1986; Rovira et al. 1983). Chief among these root functions is the uptake of nutrients and water. Other special processes occurring within the root zone include: exudation of various liquids and gases by the root, the sloughing of dead root cells, the habitation of root surfaces and rhizosphere soils by microorganisms, and the mechanical pressures exerted by roots on the surrounding soil.

Although the bulk of forest soil lies outside of the rhizosphere, soil in the root-zone interacts most directly with forest plants and is, therefore, a significant subcomponent of the forest nutrient cycle. In the light of recent reports of forest decline — 'Waldsterben' — in Europe and North America (Klein & Perkins 1988), it becomes critical to understand better the biogeochemical processes that occur within the rhizosphere of forest soils. The deficiency of essential cations such as calcium and magnesium, the increased mobility of competing ions such as aluminum, and the presence of heavy metals in soils have all been linked to the forest decline phenomenon. Because soils are a major source of these elements, and because few studies have addressed mineral-root dynamics in natural soils (e.g., Spyridakis et al. 1967; Barshad 1964; Mortland et al. 1956), we initiated a study to examine the reciprocal effects resulting from the interaction of plant roots and minerals in the rhizosphere. The intent of the investigation was twofold: first, to examine and compare the mineralogical differences that exist between rhizosphere soils and bulk forest soils; and second, to observe the effects (both mechanical and chemical) of the interactions between roots and mineral grains in the rhizosphere. The purpose of this paper is to present some of our initial results and observations on the nature of the rhizosphere.

Sampling and analytical techniques

Localities and sample collection

Sampling locations, selected on the basis of soil type, climate, elevation, forest type and geology, included two Adirondack watersheds in New York State (Huntington Forest and Whiteface Mountain) and four forest stands in the southern Appalachian Mountains of North Carolina (two sites at the Coweeta Hydrologic Laboratory and two sites in the Great Smoky Mountains National Park) (Fig. 1). These six sites were chosen to provide examples of high elevation/low elevation, deciduous/coniferous, and glaciated/nonglaciated forest ecosystems (a summary of site characteristics is given in Table 1). The sites were chosen from among the twenty currently operating monitoring sites of the Integrated Forest Study (IFS) — a five-year multidisciplinary research effort (of which this study is a part) to determine whether anthropogenic influences play a significant role in forest decline.

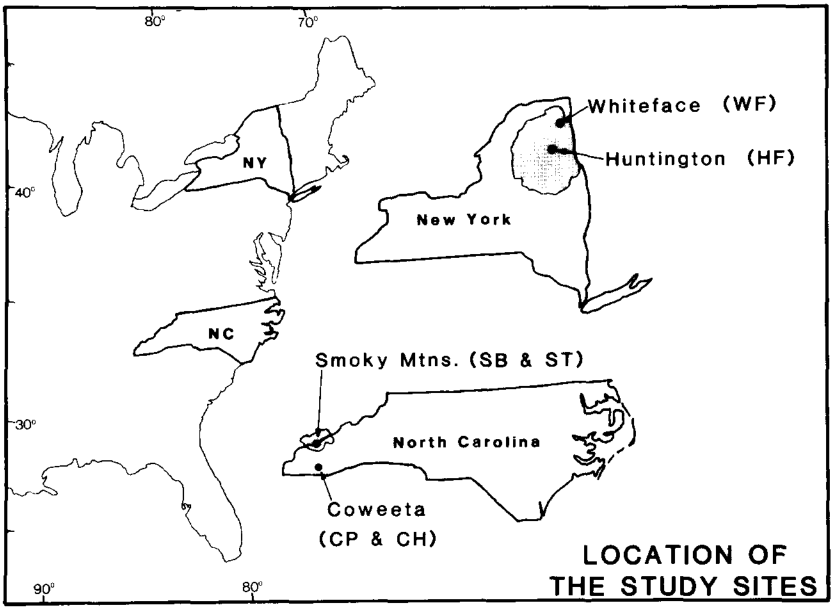

Fig. 1. Location of the study sites.

Three types of samples were collected at each site including bulk soil samples, cores and root specimens. Bulk samples were collected at vertical intervals within hand-dug sampling pits (~1 m deep) according to soil horizon or depth (depending upon how well soil horizons could be distinguished). Where roots were abundant, attempts were made to collect both 'rhizosphere' soil taken within 1–2 cm of root surfaces, and 'bulk forest' soil situated away from roots, so that the rhizosphere soil might be compared to soil from outside the root-zone. Core samples consisted of roots with the surrounding soil intact around them. At each site, cores were taken at increasing distances from one or two 'target trees' that represented the dominant tree species of the area. Core sampling was restricted laterally to the radius of the canopy cover and penetration of the core into the soil generally did not exceed 20 cm, as the majority of feeder roots for most tree species occur within this region of the forest floor (Raven et al. 1986). An average of five small cores (5 cm I.D.) and two large cores (10 cm I.D.) were collected at each site. Core samples were kept upright and refrigerated until processing, which began within 48 hours of core extraction. Two sets of root specimens were collected: fine (< 2 mm diameter) to medium (2 mm–20 mm diameter) roots cut from the root systems of adult trees, and entire root masses taken from several sizes of representative saplings. Care was taken to preserve, intact, as much of the soil surrounding these roots as was

Table 1. Summary of site characteristics.

Site	Location	Glaciation	Elevation	Slope	Aspect	Forest Type	Bedrock	Soil Type	Soil Characteristics
Huntington Forest (HF)	Adirondack Park, Newcomb, NY 43°59′N, 74°14′W	~ 14,000 ybp	Low ~ 530 m	10–15°	West	Deciduous (American Beech, Sugar Maple)	Hornblende - granitic gneisses with minor Metasediments	Typic Haplorthod Bouldery, sandy loam (Spodosol)	* pH: 3.9–5.5 **% clay: 3.84
Whiteface Mountain (WF)	Adirondack Park, Wilmington, NY 44°N, 73°W	~ 14,000 ybp	High ~ 1035 m	~ 30°	North	Coniferous (Red spruce, Balsam Fir, White Birch)	Anorthosite	Typic Cryohumod Loam (Spodosol)	pH: 3.6–5.3 % clay: 0.80
Coweeta Watershed #1 (CP)	Asheville, NC 35°03′N, 83°27′W	-	Low ~ 720 m	20–25°	Southeast	Coniferous (White Pine)	Precambrian Metamorphics (Biotite paragneisses, Biotite schists)	Typic Hapludult Micaceous, fine loam	pH: 5.2–5.9 % clay: 17.96
Coweeta Watershed #2 (CH)	Asheville, NC 35°03′N, 83°27′W	-	Low ~ 720 m	20–25°	Southeast	Deciduous (Oaks, Sourweed, Red Maple)	Precambrian Metamorphics (Biotite paragneisses, Biotite schists)	Typic Hapludult Micaceous, fine loam	pH: 5.2–5.8 % clay: 19.61
Smoky Mountain Beech Site (SB)	Smoky Mountains National Park, Indian Gap, NC 35°30′N, 83°22′W	-	High ~ 1600 m	~ 30°	South	Deciduous (American Beech, Buckeye, Red Spruce)	Metasediments (Slates, Phyllites, Schists)	Umbric Dystrochrept Sandy loam	pH: 3.8–4.8 % clay: 5.47
Smoky Mountain Tower Site (ST)	Smoky Mountains National Park, Nolan Divide, NC 35°30′N, 83°22′W	-	High ~ 1740 m	~ 15°	South	Coniferous (Red Spruce, Yellow Birch)	Sandstone	Umbric Dystrochrept Sandy loam	pH: 3.3–5.0 % clay: 10.09

* from Johnson, 1987

**From R. Newton, pers. comm. 1988

possible. Although these root samples were disturbed, many retained either soil masses or soil peds intact around the root bodies. As with the core samples, root specimens were refrigerated immediately after extraction.

Sample preparation and analytical techniques

Methods used to characterize the mineralogy and chemistry of forest soils, rhizosphere soils (taken in pits within 2 cm of root bodies and shaken from root masses), and rhizoplane soils (soil particles directly contacting the root surface) included X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis and scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS).

Clay mineralogy

For clay mineral analysis, initial steps of sample processing differed for bulk, rhizosphere and rhizoplane soil samples. Bulk and rhizosphere soil treatments began by spooning a ten to fifteen gram (dry weight) aliquot of soil into a 250 ml polypropylene container that was then filled to the shoulder with distilled water, capped and shaken. By contrast, rhizoplane soils were collected for clay analysis by ultrasonically agitating root specimens submerged in a beaker of distilled water. Prior to immersion, roots were gently shaken to remove any loosely bound soil particles. After these initial steps, subsequent treatments were identical for all sets of samples.

The clay (< 2-μm) fraction was isolated by wet sieving and centrifugation. Samples were first ultrasonically disaggregated and washed through a 230-mesh sieve to remove particles sand-sized and larger. The clay fraction was then separated from the suspension by centrifugal sedimentation.

Characterization of clay minerals required that a variety of treatments be performed on each < 2-μm specimen. Eight diffractograms were routinely acquired for oriented mounts of each sample, including:

1. air dried,
2. ethylene glycol solvated,
3. potassium-saturated ('K-sat'),
4, 5, 6. progressive heat treatments of the K-saturated sample (200°C, 350°C & 530°C),
7. magnesium-saturated ('Mg-sat'), and
8. Mg-saturated, glycerol solvated.

In addition, selected samples from each site were boiled in 1N hydrochloric acid for two hours to test for the presence of kaolinite (Brown & Brindly 1980).

XRD analyses were carried out on a Diano XRD-8565 diffractometer, using Ni-filtered, CuKα radiation. A 45 KV X-ray tube voltage was used for all analyses. Scanning parameters and X-ray tube current were adjusted to maximize peak resolution. Oriented specimens were scanned at 2° 2θ/min over the interval $2\theta = 32°$ to 2°, using a 1° beam slit, medium resolution soller slit and a 0.1° receiving slit.

Epoxy impregnation

Core and root specimens were stabilized and preserved within 48 hours of sampling by impregnation with a low viscosity epoxy, EPO-TEK 301-2. This technique essentially 'froze' samples in their field state, locking components in situ and impeding decay processes that would alter root and soil chemistry. In addition, impregnation solidified these samples, preserving their texture and fabric, and enabling them to be sectioned and polished for SEM/EDS and petrographic microscope analyses.

Scanning electron microscopy

Specimens for SEM analyses were mounted as chips or thin sections. All samples were cut with a diamond tipped saw, and ground and polished with diamond pastes instead of alumina compounds to decrease the possibility of sample contamination. After polishing, samples were cleaned by ultrasonic agitation in distilled water, rinsed with methanol, and allowed to dry thoroughly before being coated with a thin film of carbon or gold. Epoxy-impregnated core and root-specimens were examined with a Cambridge SEM-5200 Scanning Electron Microscope utilizing both secondary electron (SE) and Z-contrast, back-scattered electron (BSE) imaging and energy dispersive spectroscopy. Standard thin sections were also prepared for petrographic microscope analyses.

Results and discussion

Rhizosphere soils displayed several qualities that were distinct from those of bulk forest soils. Interaction between roots and rhizosphere minerals was suggested by several physical, chemical and mineralogical properties that characterized these root zone soils.

Physical properties

Physical attributes of rhizosphere minerals that suggested mechanical alteration by adjacent roots included the realignment and bending of phyllosilicates, along with the fracturing of mineral grains. Reorientation of phyl-

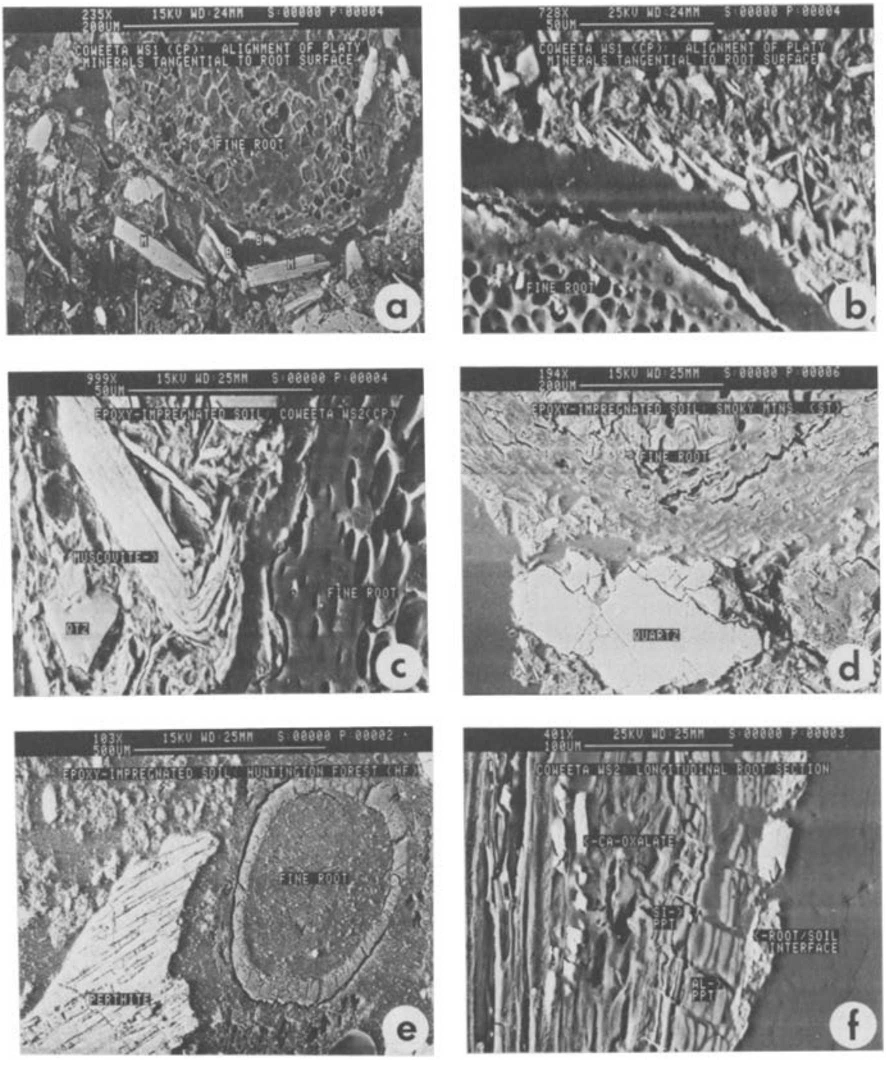

Plate I. SEM photographs. (*a*) Root cross-section showing tangential alignment of several silt- and sand-sized muscovite (M) and biotite (B) grains to the root surface. (*b*) Finer scale image of a root cross-section with tangentially aligned phyllosilicates. (*c*) Cross-section of a fine root next to which a silt-sized muscovite grain appears to have been bent by the growing root. (*d*) Cross-section of a fine root with an adjacent quartz grain showing better developed fractures at the edge abutting the root body. (*e*) The shape of the adjacent edge of a perthite grain replicates the root form suggesting possible preferential dissolution of the grain boundary nearest to the root. (*f*) Longitudinal cross-section of a fine root containing three cell-filling materials—aluminum precipitate, silica precipitate, and calcium oxalate—within discrete regions of differentiated root cells.

losilicate grains by the mechanical forces exerted by growing roots was suggested by the alignment of the long axis of these grains tangential to the root surface. This tangential arrangement was frequently observed in SEM analyses of both longitudinal and transverse cross-sections of root bodies and the surrounding soil (Plate 1a, b). Phyllosilicates, apparently bent by adjacent roots, were observed less often (Plate 1c). Finally, SEM analyses revealed, in numerous cases, that the edges of mineral grains oriented toward root surfaces were fragmented to a greater degree than the sides that faced away from the root (Plate 1d). Previous studies (Curl & Truelove 1986; Nye & Tinker 1977) noted compaction of rhizosphere minerals around the root but mentioned little regarding physical effects. Cockcroft et al. (1969) and Lund (1965) found that mineral grains in the rhizosphere were only slightly oriented by root growth.

Breakage and alignment of mineral grains are important because they effectively increase the amount of mineral surface area exposed to the weathering regime surrounding the root. Fracturing increases the surface/volume ratio, thereby subjecting more fresh mineral material to the rhizosphere soil conditions. In addition, the tangential alignment of phyllosilicates orients more of the grain surface toward the root where root-induced chemical gradients may accelerate mineral degradation.

Chemical interactions

Two types of chemical interactions between roots and minerals in the rhizosphere were noted in SEM analyses. Mineral grains displaying an edge that replicated the form of a contiguous root body were interpreted as evidence of preferential mineral dissolution by the root (Plate 1e). Such grains were uncommon (in fact, few grains large enough to permit observation of dissolution were found at root surfaces); therefore, although dissolution processes were suggested by this feature, they were not well documented. In addition to the preferential dissolution of mineral grains, precipitation of mineral material within root cells was commonly observed.

Aluminum, silica and calcium were identified by SEM/EDS analyses as constituents of the three compounds commonly observed within root cells (Plate 1f). Each compound was distinguished by the presence of either Al, Si, or Ca. Other elements in each compound were not resolved by SEM/EDS techniques suggesting that they were lighter than neon, as the EDS system does not detect elements with an atomic number less than 10. Although previous workers have noted the precipitation of aluminum in plant cells, they did not characterize the nature of the mineral species (Shortle & Smith 1988; Cronan et al. 1987; Tepper & Schaedle 1987; Huttermann & Ulrich

1984). The aluminum compounds found within these root cells had no discernible crystal structure and are likely amorphous oxides and hydroxides. Silica gel and opaline silica have been reported as precipitates within plant cells (Arnott 1982; Wilding et al. 1977) and, therefore, are probably the silica-phases present in these root cells. Calcium is precipitated most frequently as calcium oxalate on or in plant material (Cronan et al. 1987; Arnott 1982; Graustein et al. 1977). The morphology of the calcium compound found in the roots of this study corresponds well with documented Ca-oxalate habits (Graustein et al. 1977).

These Al-, Si- and Ca-compounds reside in discrete regions within the cells of mature, differentiated roots (see Plate 1f). Aluminous compounds were found in the outermost portion, within the peridermal root cells. This occurrence is consistent with the findings of Cronan et al. (1987) and Tepper & Schaedle (1987) who found aluminum to be restricted largely to cells outside the endodermal zone of root cells. Silica compounds were found precipitated within the phellodermal cells, just inward of the aluminous material. The innermost precipitates noted in these roots were calcium oxalate crystals in cortical parenchymal cells.

Mineralogical effects

In general, rhizosphere and bulk forest soils contained similar mineral suites; however, two apparent distinctions were noted. For several samples from the Smoky Mountains and Coweeta, the thermal stability of kaolin minerals from the rhizosphere and bulk soils were different. In other samples from the Smoky Mountains (tower site; ST), XRD results indicated that rhizoplane soils contained abundant, well crystallized muscovite and vermiculite, whereas muscovite and degraded biotite were present in rhizosphere soils form the same root masses. The differences in clay mineralogy may be related to variations in the intensity of weathering, ionic activities and the abundance of organic ligands in the rhizoplane, rhizosphere, and bulk forest soil environments.

Thermal stability and crystallinity of kaolin minerals

Differences in the thermal stability of kaolin minerals were noted between rhizosphere and bulk soil samples from both Smoky Mountain and Coweeta soils. In XRD patterns, the (001) 7 Å kaolin peak was largely destroyed upon heating the < 2-μm fraction of the bulk soil samples to 530°C (Fig. 2a). By contrast, the (001) kaolin peak of the rhizosphere soils from the same sampling pit and soil horizon as the above samples survived the 530°C heat treatment (Fig. 2b). Extent of thermal dehydroxylation is known to be

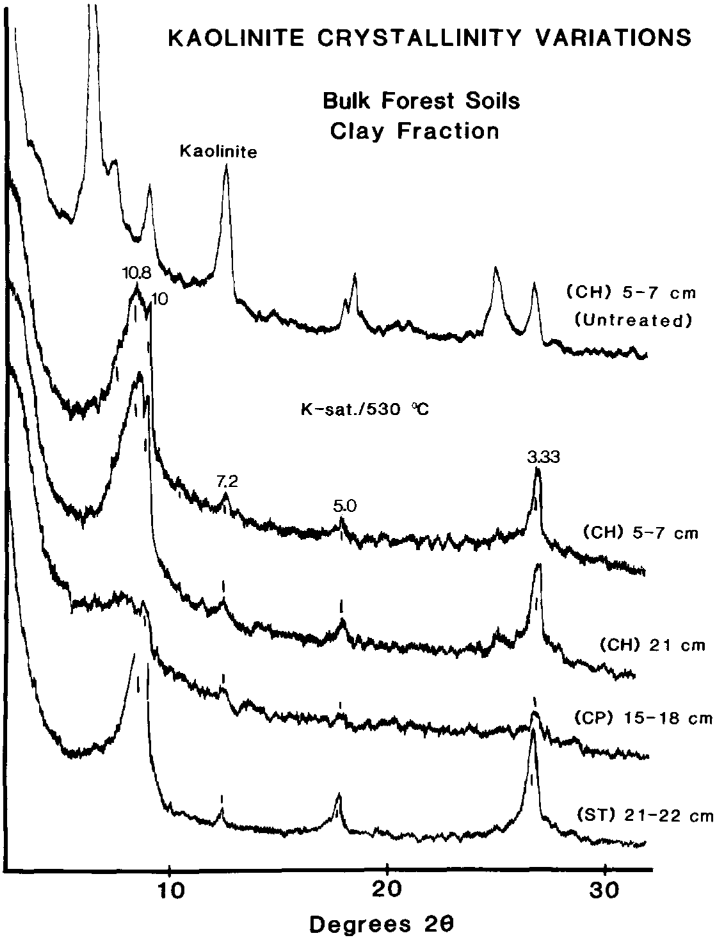

Fig. 2a. X-ray diffractograms of the < 2-μm fraction of *bulk forest soils* from different depths at Coweeta and the Smoky Mountains (tower site). Comparison of diffractograms for untreated, air-dried samples (top pattern) against samples heated to 530°C (lower patterns) shows a marked decrease in the (001) 7 Å kaolin peak in the latter, suggesting destruction of this clay mineral due to low thermal stability.

correlated with kaolin mineral crystallinity (Storr & Murray 1986; Wada & Kakuto 1983; Keller & Haenni 1978), although the inability to see well-crystallized kaolinite in SEM analyses makes it difficult to confirm the presence of this mineral in the present study. However, as enhanced crystallinity is indicated by the high thermal stability of kaolin in the rhizosphere, two theories which may account for this observation are suggested.

1. Recrystallization from a metastable kaolin phase. Kaolin is found in

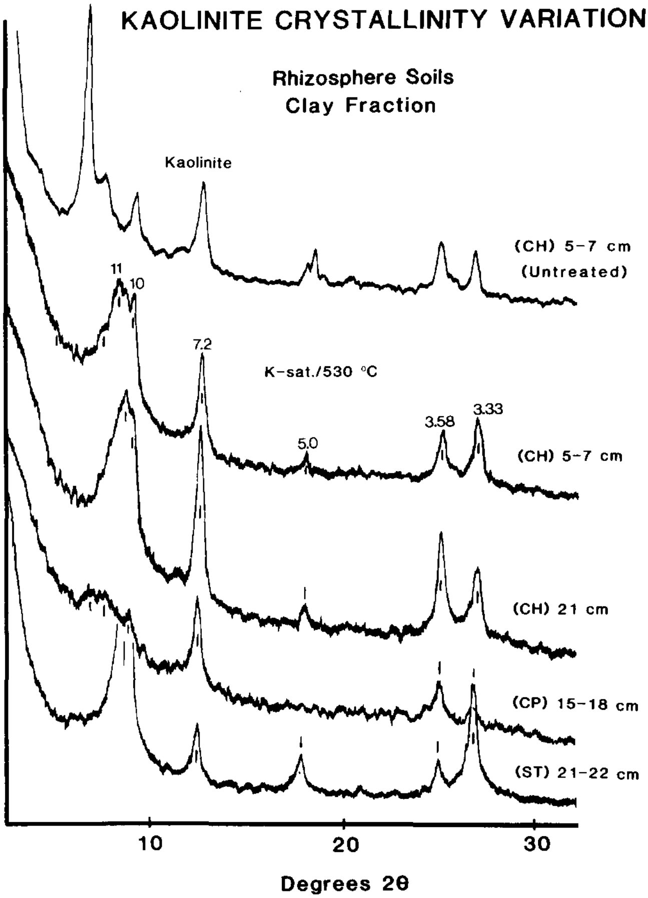

Fig. 2b. X-ray diffractograms of the < 2-μm fraction of *rhizosphere soils* from the same depths as seen in 2a. Comparison of diffractograms shows little diminishment of the (001) 7 Å kaolin peaks, suggesting greater thermal stability for this clay.

several morphologies which display various degrees of crystallinity. For example, Keller (1978, 1982) noted an elongated, halloysite-type kaolin in association with with a better-crystallized, platy, book-type kaolinite. He contended that the elongate mineral was a metastable precursor to the platy kaolinite because the former was more prevalent in less weathered soils, whereas the latter was typical of highly weathered soils. Wada & Kakuto (1983) discovered two forms of kaolin in soils containing a vermiculite/kaolin intergrade. The kaolin mineral associated with the integrade decomposed at temperatures that were similar to the temperatures at which the ('chloritized') vermiculite collapsed, around 375°C. By contrast, the discrete kaolin mineral required heating to approximately 500°C before decomposition took place. Furthermore, it has been observed that soils containing a mixture of two kaolin minerals with different crystallinities will produce XRD peaks with apparent crystallinity characteristics that fall somewhere between those of the individual components (Keller & Haenni 1978).

2. Interference of organic ligands. Enhancement of kaolinite crystallinity by the presence of certain organic species has been noted in various studies (Dixon 1977; Schnitzer & Kodama 1977). In particular, aluminum complexing by fulvic acid decreases the polymerization rate of hydrous-aluminum species, leaving more aluminum available for the kinetically-slower kaolinite-formation reaction. Another theory suggests that organic-aluminum complexes provide aluminum as Al-O, which facilitates its combination with silica to form kaolinite (Schnitzer & Kodama 1977).

We suggest, therefore, that the difference in decomposition temperatures of rhizosphere and bulk forest soil indicates the presence of two forms of this mineral. Rhizosphere kaolin (kaolinite) decomposes at higher temperatures and, by inference, is generally better crystallized than bulk forest soil kaolin. This may result from the existence of a more intensive weathering regime, as Keller (1978, 1982) suggested for his platy kaolinites, or from the presence of complexing organic species in the root zone. Accelerated weathering, associated with increased acidity due to the exudation of hydrogen ion, carbon dioxide or organic acids by roots, has been noted within the rhizosphere (Spyridakis et al. 1967). In addition, such conditions are suggested by the preferential dissolution of mineral grains noted in the previous discussion on chemical interactions between roots and minerals. Organic compounds are also commonly exuded by the apical portions of roots (Curl & Truelove 1986; Rovira et al. 1983) and are, therefore, another plausible cause of increased kaolin crystallinity in the rhizosphere. Because of its lower decomposition temperatures, the kaolin mineral found within bulk forest soils, in contrast to rhizosphere kaolinite, apparently consists either entirely or partially of a kaolin characterized by poorly-defined crystal morphology. The abundance of vermiculite in these soils as well as the decomposition of the kaolin mineral at temperatures comparable to those for vermiculite collapse suggest that this mineral may be similar to the kaolin present in the intergrade clay described by Wada & Kakuto (1983).

Mica weathering in rhizoplane and rhizosphere soils

Abundant muscovite was noted in several of the rhizoplane soils from the Smoky Mountain tower site (ST) by the presence of a sharp (001) 10 Å peak in XRD patterns that was not significantly enhanced by potassium-satura-

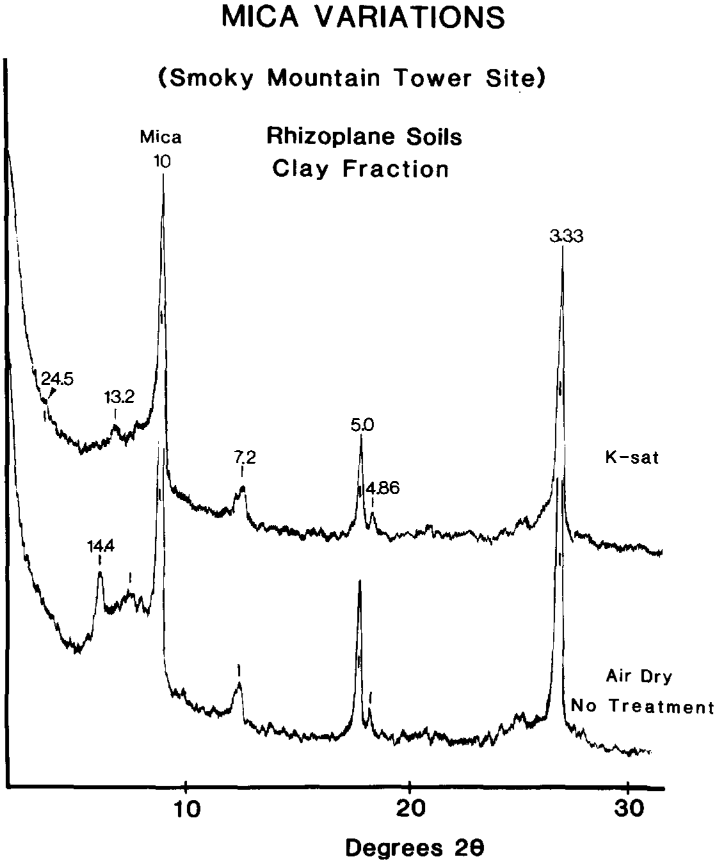

Fig. 3a. X-ray diffractograms of the < 2-μm fraction of *rhizoplane soils* (washed from root surfaces) from the Smoky Mountains tower site. The (001) 10 Å mica peak in the diffractogram for the untreated clay (lower pattern) is similar to the mica peak in the artificially potassium-saturated aliquot of the same sample (upper pattern). Most vermiculite has collapsed from 14 Å to 10 Å upon K-saturation.

tion of the sample with 1 N KC l (Fig. 3a). By contrast, weathered mica (randomly interstratified mica/vermiculite), displaying an obvious peak shift to 10 Å following potassium-saturation, dominated the clay fraction of rhizosphere soils contained within the same root masses (Fig. 3b).

Although this finding is somewhat surprising, it seems reasonable in light of previous work. For example, it is well documented that mica weathering (i.e., K-release) is strongly influenced by the activity of potassium in the surrounding soil solution (Scott & Smith 1966; Fanning & Keramidas 1977). When the activity of potassium falls below some critical level (highly dependent on the variety of mica involved), interlayer K is replaced by other

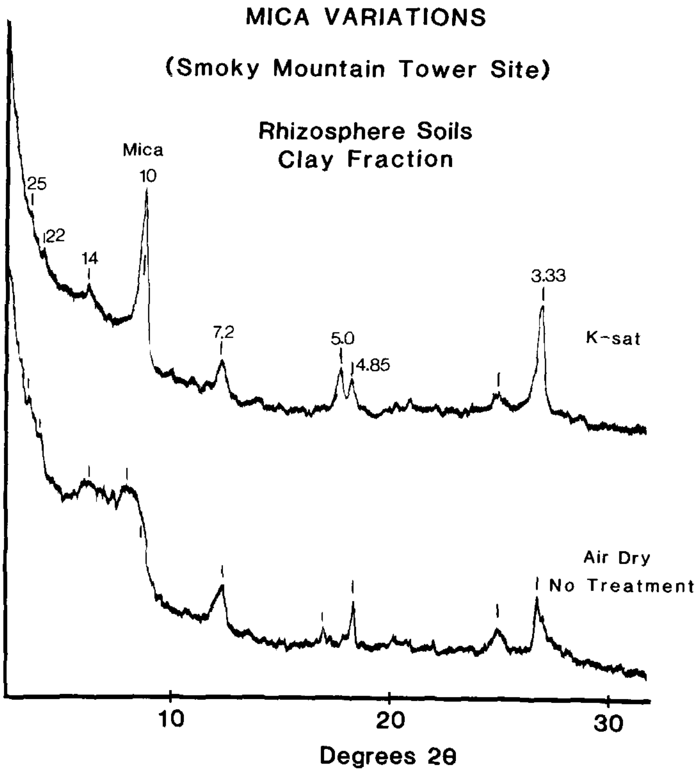

Fig. 3b. X-ray diffractograms of the < 2-μm fraction of *rhizosphere soils* shaken off the same root sample as in 3a. The diffractogram for the untreated clay (lower pattern) shows a diffuse band of peaks between 10 and 14 Å, in contrast to the defined 10 Å peak in the artificially potassium-saturated aliquot of the same sample (upper pattern). The clay assemblage comprises degraded mica (muscovite and biotite), randomly interstratified mica/vermiculite and gibbsite.

cations. However, when the activity of potassium rises above this critical level (for muscovite, this value is extremely small; see Scott & Smith 1966), not only does mica cease to weather, but previously degraded mica may reincorporate K from solution into interlayer sites. Whereas ionic depletion, especially of potassium, is commonly expected around roots (Brewster & Tinker 1970), various factors have been cited as affecting potassium concentrations in the root-zone. For instance, rapid transpiration causes the accumulation of any cations for which influx rates are slower than rates of transpirational efflux (Marschner 1983). Perhaps more significantly, polyvalent cations within the soil solution, particularly aluminum, have been found to alter the uptake of potassium by plant roots. Roy et al. (1988) and Cumming et al. (1985) have shown that aluminum can both stimulate and inhibit potassium uptake. Stimulated uptake is common when levels of aluminum in (artificial) soil solutions are low (e.g., 1–4 mg/L for red spruce) (Cumming et al. 1985). At higher aluminum concentrations, a net accumulation of potassium near root surfaces may result when plasmalemma permeability within root cells is reduced by significant incorporation of aluminum (or similar cations) into the cell structure.

An accumulation of potassium within the immediate vicinity of the root surface due to the antagonistic effects of polyvalent cations (especially aluminum) would cause retardation of mica weathering and, perhaps, the reconstitution of some degraded micas by potassium fixation, and could account for the disparity in mica abundance between rhizoplane and rhizosphere soils from the tower site. As previously discussed, the accumulation of aluminum within the peridermal root cells is observed in SEM analyses of the core samples from this site (see the section on chemical interactions). Although high transpiration rates are not likely at the Smoky Mountain tower site, as this is a high elevation site characterized by relatively cool average temperatures and humid atmospheric conditions (Oak Ridge National Laboratory, 1986), this mechanism cannot be ruled out as possibly contributing to K-enrichment in rhizoplane soil solutions.

Alternatively, the clay mineral suites in the rhizoplane and rhizosphere may reflect differences in the intensity of weathering in the two soil environments. XRD and SEM/EDS data confirm the presence of both muscovite and biotite in the Smoky Mountain soil samples. Upon weathering, biotite easily loses interlayer K, transforming to vermiculite often via mixed-layer biotite/vermiculite (Banfield & Eggleton 1988; Douglas 1977). Muscovite, however, retains interlayer K except under very low solution concentrations of potassium and, consequently, is relatively resistant to weathering, even under moderate to extreme soil acidities (Walker 1975). In the rhizoplane where enhanced weathering occurs (as suggested earlier in this paper), biotite is depleted leaving muscovite as the dominant mica, as evidenced by the intense, narrow 10 and 5 Å peaks in diffractograms (Fig. 3a). The distinct 14 Å vermiculite peak in the untreated rhizoplane sample supports the biotite-depletion hypothesis in that vermiculite is a common product of biotite weathering. In contrast, biotite is not so weathered or depleted by weathering in the rhizosphere and the presence of both muscovite and biotite gives rise to the broad 10 Å peak and the high 10 Å/5 Å peak ratio displayed in diffractograms (Fig. 3b). Less K-depletion (weathering) of biotite in the rhizosphere has produced randomly interstratified biotite/vermiculite, but no pure vermiculite phase, as suggested by the diffuse band of XRD peaks between 10 and 14 Å and the absence of a well-defined 14 Å peak.

Conclusions

A study of the mineralogy and chemistry of bulk forest soils and rhizosphere soils from six sites in the eastern United States has led to the following observations:

- Root-soil interactions can change the character of the mineralogy (especially clay mineralogy) in the rhizosphere, suggesting that the pedogenic processes in the root zone differ from those operating in the bulk forest soil.
- Mechanical effects of the root on adjacent mineral grains thought to expose greater amounts of fresh, mineral material to the weathering regime of the rhizosphere include:
  - fracturing in areas of the grain that abutted root bodies, and
  - tangential alignment and bending of phyllosilicate minerals.
- Preferential dissolution of a few mineral grains was suggested by replication of the shape of the root surface on adjacent grain edges.
- Precipitation of amorphous aluminum oxides/hydroxides, opaline and amorphous silica, and calcium oxalate was common in the cells of mature root bodies.
- Greater thermal stability of rhizosphere kaolinite compared to bulk soil kaolin indicates that the former was better crystallized. Mechanisms suggested for this enhanced crystallinity include:
  - recrystallization due to a more intensive weathering environment within the rhizosphere, and
  - interference by organic ligands causing more aluminum to remain in a form that is available for kaolinite formation.
- Muscovite is abundant within rhizoplane soils sampled in the Smoky Mountains, whereas degraded micas and mixed-layered clays predominate within rhizosphere soils further from root surfaces. Interferences by polyvalent cations, especially aluminum, may cause K-enrichment in rhizoplane soil solutions resulting in less mica weathering at the root surface. Alternatively, biotite may weather preferentially in the root-zone microenvironment leaving muscovite as the predominant mica mineral in rhizoplane soils. The presence of vermiculite in the rhizoplane seems to support the biotite-depletion hypothesis.

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