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**Geochemistry of podzolized tills and the implications for aluminium mobility near industrial sites:  
a study in Kuopio, eastern Finland**

by Marja Liisa Räisänen



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**GEOCHEMISTRY OF PODZOLIZED TILLS AND THE IMPLICATIONS  
FOR ALUMINIUM MOBILITY NEAR INDUSTRIAL SITES: A STUDY  
IN KUOPIO, EASTERN FINLAND**

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Marja Liisa Räsänen

with 16 figures and 7 tables

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Geochemistry and clay mineralogy of podzolized tills were studied in the Kuopio-Siilinjärvi region of eastern Finland. The concentrations of the major elements in the podzolic layers and the parent till materials were determined by total dissolution and hot aqua regia extraction methods followed by AAS. Concentrations of Al and Fe in the mobile and immobile fractions were measured by selective weak extraction methods and AAS. Characteristics of clay minerals in the <(40 - 50) µm fraction within the profile were examined by XRD methods.

Chemical and XRD analyses demonstrated that the weathering of trioctahedral micas and chloritic clay minerals was the predominant process during podzolization, in both thick and shallow tills. However, the rate of weathering, as well as the rate and maturity of podzolization, were more dependent on the composition of the till and hydrological conditions in the soil profile than on the age of podzolization. Throughout the profile, the predominant clay minerals were vermiculitic mixed-layer clays. The natural acidification resulted in the formation of smectite-like clays in the eluvial layer, but interlayers filled with hydroxy-Al polycations were more characteristic of vermiculite in the illuvial layer.

In contrast to the podzols in thick tills, most of the shallow tills in rocky terrains near the chemical pulp mill at Kuopio were totally tinted red-brown. Examination suggested that the increase in acidity had caused the tinting by mobilizing Fe from the sulphide-bearing bedrock surface and from precipitates in the illuvial layer overlying the bedrock. Simultaneously, the increased mobility of Al led to the chloritization of vermiculite in the top soil layers. Since the Al and Fe contents of the secondary fractions tended to be lower in red-brown soils than in the visible podzolic layers, the acidification must have caused their partial outflow from the thin soil cover.

Key words (GeoRef Thesaurus, AGI): Podzols, till, geochemistry, aluminum, iron, mobility, mineralogy, clay minerals, acidification, weathering, Holocene, Kuopio, Siilinjärvi, Finland

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## INTRODUCTION

The most common surficial sediment in forested areas in Finland is till, unsorted drift loosened from bedrock and transported by the continental ice sheet. Soil-forming processes due to the successive development of plant cover started immediately after the retreat of the ice, about ten thousand years ago. A humid and cool climate, in which precipitation exceeds evaporation, promotes the podzolization in northern taiga regions (Fitzpatrick 1980). The characteristic podzolic horizons are a light-coloured leached (eluvial, E) layer a few centimetres thick and an underlying enriched (illuvial, B) layer reddish or rusty brown in colour. The illuvial layer grades into a less altered parent material (C layer). The transition zone between the B and C layers is called the BC layer.

Because areas in Finland were deglaciated and emerged from water as a result of uplift at different times, there is considerable variation in the age of podzolization and therefore in the maturity of podzols (Hyypä et al. 1992). According to Jauhiainen (1969), podzolic layers are more distinct in old than in young soil. In sandy soils, moreover, the degree of podzolization, viz. the chemical differentiation of the E and B layers, increases with age (Jauhiainen 1973). Koutaniemi et al. (1988) add to this that the variation of many parameters within the profile arises from the postglacial vegetation and climate history rather than podzolization. Aaltonen (1939 and 1941) and Jauhiainen (1969) have emphasized that the differentiation of the podzolic horizons largely depends on the permeability of the soil material.

A distinctive feature of Finnish podzols is

the slow rate at which biogenic material deposited on mineral soil decomposes (Jauhiainen 1969). Biogenic matter overlying mineral soil in forests mostly consists of slightly decomposed humus, organic debris and moss and is called moor humus (Hyypä et al. 1992). According to Räsänen (1989), the pH of the humus and underlying eluvial layer measured in dilute salt extracts is mostly between four and five, and increases downwards. Podzols in old spruce forests that are poorly drained often have a raw humus layer with pH even lower than four (Räsänen 1989).

Of primary interest in all pedological studies are the mineral alterations that occur and particularly the clay minerals transformed during podzolization. Distinguishing the weathering products formed before and after the deposition of tills may prove difficult. In general, the till deposits in Finland are thought to consist largely of material derived from the mechanical breakdown of unweathered rocks during the last glaciation (Koljonen 1992). Haldorsen (1983) and Lintinen (1995) nevertheless point out that geochemical and mineralogical variations in till beds and, in particular, in the fine fraction (<0.06 mm) of tills, depend heavily on glacial comminution and dewatering and not solely on bedrock variation. The dewatering is attributed to sorting caused by waters liberated during the deposition of till (Muller 1983). Lintinen (1995) suggests that the fine fraction of tills in Finland contains fines eroded from both preglacial weathered bedrock and interglacial sediments, and that it has been recycled several times. He reports that, in some



cases, the surficial part of tills is enriched in previously weathered material, while in others the redeposition of old fines weathered during an interglacial stage may explain the occurrence of vermiculite in the deep part of tills. This confuses and complicates any evaluation of the rate of postglacial weathering in the overlying pedon.

Given the shortness of the postglacial period, and the subarctic to arctic climate, one would expect chemical weathering to be largely limited to surficial tills, and in particular to podzolic layers, and to affect deeper tills only in restricted degree. Despite the difficulties involved in interpreting the origin of clay minerals in till beds, Lintinen (1995) has demonstrated the incipient weathering of biotite and chlorite in a few Finnish till profiles. In these profiles, biotite and chlorite in the top-most till under the pedon have been altered to mixed-layer clays containing vermiculite, which is lacking in the deeper part of the till (Lintinen 1995). More rapid postglacial alteration in the surficial part of tills is indicated by the occurrence of polymeric Al hydroxides in interlayers of vermiculite (interlayering) (Räsänen et al. 1992b, Lintinen 1995). Lintinen (1995) concluded that a gradual degradation of biotite and chlorite characterizes clay-rich tills more than tills poor in clay because acidic gravitational water has had more time to leach micas. He also mentioned that, in tills rich in sand and poor in clay, alterations in the surficial till below the pedon are weak.

Several Norwegian and Swedish researchers have reported that the gradual decomposition of biotite and chlorite is a major weathering process in the podzolic layers of tills (Gjems 1967, Wiklander & Aleksandrović 1969, Kapoor 1972, Melkerud 1983 and 1985). Kapoor (1972) concluded that the early stages of weathering in the B and C layers involve expansion of biotite to a mixed-layer mineral with concurrent formation of some vermiculite. More intense weathering in the eluvial layer leads to a progressive build-up

of mixed-layer mineral with a regular alteration of biotite and vermiculite units (hydrobiotite), and subsequently to the formation of vermiculite and smectite. This occurs as follows: biotite → mixed-layer mineral and vermiculite (C and B layers) → hydrobiotite (E layer) → vermiculite (E layer) → smectite (E layer) (Kapoor 1972).

Gjems (1967) inferred that recognizable amounts of expanding minerals are developed even after a few hundred years of soil formation. Wiklander and Aleksandrović (1969) and more recently Melkerud (1983 and 1985) did not include the intermediate stage of hydrobiotite before the formation of vermiculitic and smectitic clays in the eluvial layer but concluded that smectite is directly developed from degradation products of chlorite and vermiculite. Olsson and Melkerud (1989) were not as convinced of the source of smectite as the above researchers.

Wiklander and Aleksandrović (1969) and Melkerud (1983) added that Al-hydroxy interlayers characterize vermiculites, in particular in the illuvial layer of podzols. A similar finding was reported by Olsson and Melkerud (1989) and Hallbäck (1992). Gjems (1967) used the term acid weathering for the process leading to the chloritization of vermiculite (or smectite) with the deposition of Al-hydroxide complexes in the interlayer position. Also Righi et al. (1988) and Robert and Tessier (1992) emphasize the importance of the Al interlayer accumulation in acidification processes. In contrast to Wiklander and Aleksandrović (1969) and Melkerud (1983), Righi et al. (1988) link the interlayering of vermiculite and smectite to the formation of acid brown earths. According to them, podzols are characterized by the formation of smectite in the eluvial layer and the removal of Al and Fe as organomineral complexes downwards in the profile.

It is generally assumed that postglacial pedogenesis has altered the mineral composition of the Finnish podzol very little, so that the

pedon and parent material have the same main minerals, i.e. quartz and feldspars (Hyypä et al. 1992). According to Hyypä et al. (1992), in the podzolic layers of Finnish soils biotite and chlorite have either partly altered to mixed-layer minerals or disintegrated altogether. Räsänen and Jylänki (1990) report that vermiculitic interstratifications characterize both the eluvial and illuvial layers in podzolized tills in southern Finland. Vermiculites in the E and B layers in these soils are

characterized by hydroxy-interlayering (Räsänen & Jylänki 1990).

Though studies from other Nordic countries are available, no study from Finland describes a weathering sequence of micas and chlorites in any detail. It can nevertheless be assumed that also Finnish podzols are characterized, in variable extent, by a weathering sequence from mica and chlorite to vermiculite via intermediate stages of the mixed-layer minerals. Smectitic mixed-layer clays have been identi-

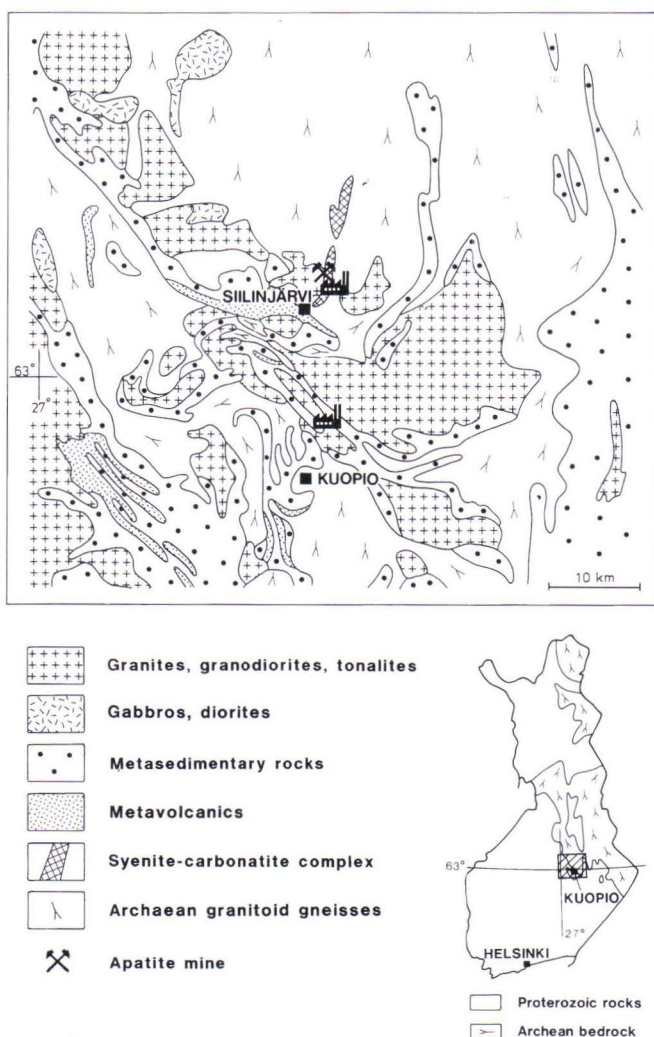


Fig. 1. Bedrock map of the study area modified from Lukkarinen (1991).



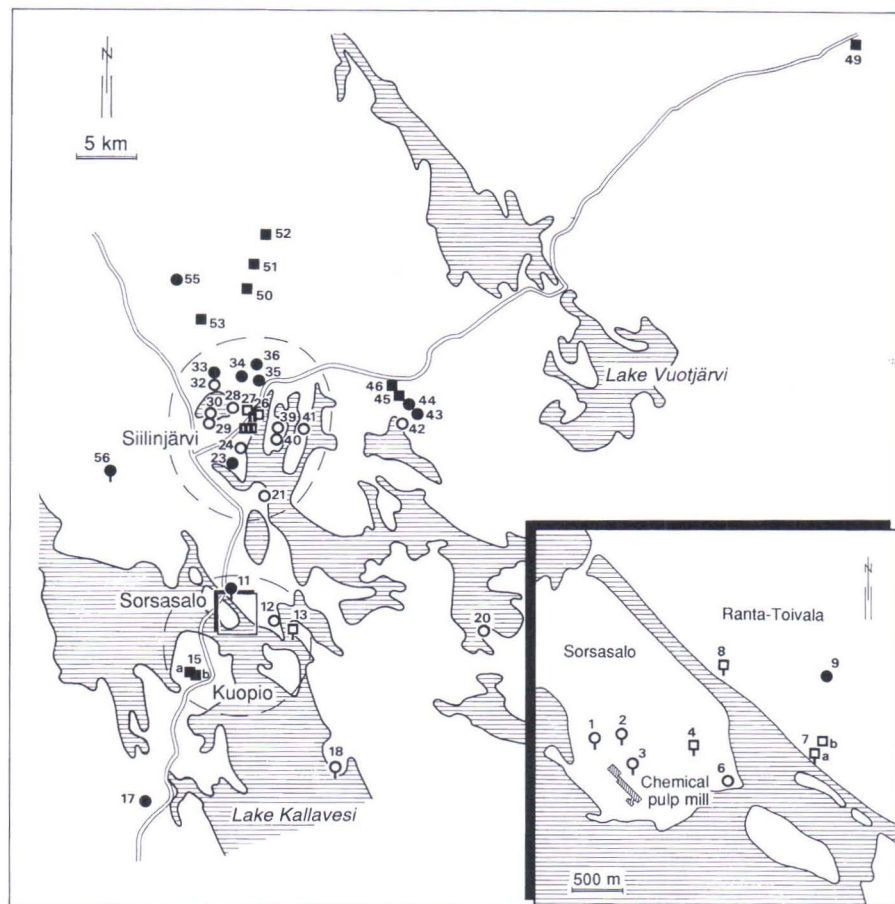


Fig. 2. Location of sampling sites in the Kuopio and Siilinjärvi (inside the circles) and background (outside the circles) study areas. The age of podzolization of sites located higher than 140 metres a.s.l. is ca. 9000 years or somewhat older (■), between >110 and 140 metres a.s.l. 7000 - 9000 years (●), between 105 metres a.s.l. and 110 metres a.s.l. 5000 - 7000 years (□) and below 105 metres a.s.l. ca. 5000 years or somewhat younger (○). Sampling sites in shallow till are marked with a small vertical line under the symbol.

fied in Quaternary clays (Sippola 1974) and weathered bedrock in Finland (Uusinoka 1975, Hyppä 1983, Räsänen et al. 1992b).

The work described here was carried out in the podzolized tills of the Kuopio - Siilinjärvi region in eastern Finland (Figs. 1 and 2) as a continuation of the earlier work of Räsänen (1989) and Jaloniemi and Räsänen (1991). In the earlier studies, the focus was the state of soil acidification relative to the appearance of the podzol, the permeability of the parent soil,

topography, vegetation and atmospheric acid load.

Reporting on this earlier work, Räsänen (1989) notes that the increase in acidification manifests itself in elevated Al-solubility values in the eluvial layer, or in the illuvial layer if this is close to the surface as in rocky terrains, gravel and sand-predominant soils. Comparable findings have been reported by Räsänen and Jylänki (1990), and Räsänen and Pulkkinen (1991). Jaloniemi and Räsänen

sänen (1991) found concentrations of exchangeable, organically and inorganically bound Al to be elevated in podzols of rocky terrains in the vicinity of the chemical pulp mill at Kuopio relative to podzols in the thick-layered overburden near the mill and the background area. They concluded that the abnormal mobility of Al and Fe in the top soil layers, causing the soils in rocky terrains to be tinted red-brown, is a sign of anthropogenic soil acidification. Their study did not, however, identify the source of the mobile Al and Fe, nor the solid phase of the red-brown coloured material.

The objectives of the research described here were to study silicate weathering and the clay minerals transformed during podzolization and, relevant to this, to determine whether the weathering processes in podzols might change as a result of acid deposition. Dissolution of Al in acid soils is one of the most pronounced soil chemical effects of acidic deposition. The study emphasizes metastable weathering products, as these constitute reservoirs of readily remobilizable Al, which can be taken up by plants from soil solution and by animals from stream, river and lake waters (Wilson 1986). Farmer et al. (1988) and Hallbäck (1992) suggest that Al-hydroxy interlayers in vermiculites are one source of readily mobilizable Al.

In the study of weathering, attention is paid to the vertical distribution of the major elements between resistant and easily weatherable silicates in podzolic layers and parent tills, and to the rate of silicate weathering (leaching) relative to the age of the podzol. It is here assumed that the increase in total concentrations of the earth alkali and alkali metals downwards in the profile indicates the

weathering of the main minerals, feldspars and ferromagnesian minerals, during the podzolization (Melkerud 1983). Further, it is assumed that the distribution of the major elements soluble in hot aqua regia describes the weathering of the mica and clay mineral fraction (Räisänen et al. 1994).

The transformation of clay minerals in soils subjected to acidification is examined only for sites in the vicinity of the pulp mill with a high acid deposition and for a few background sites with a less acid load (Fig. 2). The relation of the mobility of Al to podzolic weathering, and the possible increase in the mobility due to atmospheric acid load, are discussed. Also, the mobility of Fe relative to that of Al is examined. The distribution of Al and Fe in stable inorganic precipitates, labile complexes and easily leachable fractions, and the pH variations in podzols of shallow and thick-layered tills, were examined with the aid of several weak extraction methods, and the response of the interlayering of clay minerals to the mobility of Al was investigated by applying an acidified salt extraction method ( $AS_{pH2.3-2.4}$ ) (Räisänen 1989, Räisänen et al. 1994).

Contrary to the practice in traditional clay mineral studies, mixtures of the clay and silt (<(40 - 50)  $\mu\text{m}$ ) fractions were used as specimens for X-ray diffraction (XRD) analysis. Farmer et al. (1988) have suggested that Al-hydroxy interlayered vermiculitic clays are a sink and source of reactive Al in podzols, not only in the clay fraction but also in the silt fraction. It was also of interest to find out whether the mixture of the silt and clay fractions could be used in clay mineral identification.

#### PREVIOUS FINNISH STUDIES ON PODZOLIZATION AND ACIDIFICATION

The basic studies on Finnish podzols are those of Frosterus (1913), Aarnio (1915),

Aarnio and Stremme (1924), and Aaltonen (1935, 1939, 1941 and 1952). Frosterus



(1913) described visible differences in podzols, which he attributed to the deep washing and enrichment in gravelly and sandy soils compared with the only weak washing of soils rich in silt and clay. Aarnio (1915) examined the precipitation of Fe and Al oxides in podzols and in a further study with Stremme (1924) he grouped podzols into iron and humus podzols and brown and grey forest soils. However, the first pedological soil classification in Finland was published by Aaltonen in 1952. His soil classification, based on humidity, soil age and forest site type, distinguishes iron and humus podzols as the two principal types. Iron podzol occurs in dry and slightly moist gravel and sandy ground, and humus podzol in damp and wet ground (Aaltonen 1935, 1939, 1941 and 1952). Aaltonen (1935, 1939 and 1941) reported that Fe, Al and Si were accumulated deeper in younger than older podzols. He also showed that the ratio between Fe and Al in the soils' gel complex was higher in younger than older profiles and that Fe was deposited higher up in the profile than Al. These features, he said, characterize profiles in both glaciofluvial sands and sandy tills.

Later studies on soils have been conducted largely on sand soils, with interest in the age of pedogenesis and the forest vegetation. Factors studied are the grain size distribution; the variation of inorganic colloid complexes ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ), exchangeable cations ( $\text{Ca}^{2+}$ ,  $\text{K}^+$ ) and easily soluble phosphorus; and the abundance of organic matter within podzol profiles. However, podzolization in Finnish tills has been little investigated since Aaltonen's work in the fifties.

Jauhiainen (1969) noted that the concentrations of organic matter and colloidal Si, Al and Fe hydroxides in the illuvial layer of the podzol are higher in old than young soil. In further research along the northwestern coast he concluded that in sand soils a chemically apparent podzol profile forms within 200 to 300 years and a visually apparent profile

within 400 - 500 years (Jauhiainen 1973). Starr (1991) argued that podzolization is not recognizable in sand soils in the western coast area until after ca 1000 years. According to Starr, podzolization was rapid during the first 2500 years, but thereafter there has been little further development. Petäjä-Ronkainen et al. (1992) concluded that it takes more than 300 years but less than 1200 years for a recognizable podzol profile to form in sand soils.

Urvas and Erviö (1974) studied the relationship between the abundance of bioavailable nutrients and forest types. According to them, fine-grained soils are more fertile than coarse-grained soils. Moreover, the organic layer is the richest in bioavailable nutrients in every forest and soil type, while the content of many nutrients in the mineral soil layers increases with the abundance of the fine fraction independently of the forest type. They considered that the differences in nutrients between the mineral soil layers in a profile are small within the same forest type.

In an investigation of the role of quaternary processes in determining the properties of forest soils and vegetation on sorted soil materials, Sepponen (1985) concluded that present differences in the nutrient status arise during the development of the vegetation site types. This development is influenced by the physical properties of the soil, and these in turn by geological processes. Koutaniemi et al. (1988) reported that some features typical of podzolization in sand soils, such as the leaching of Fe and Al from the eluvial layer, are time-dependent, while some others arise from the geological factors and vegetational characteristics of the areas.

More recent investigations of Finnish podzols deal with soil acidification. Nuotio et al. (1990) suggest that the chemical properties of the topmost soil layers (humus, eluvial) are affected by vegetation, the thickness of the humus layer, the evolutionary stage of podzolization and the quality and quantity of atmospheric impurities. According to them, in

mineral soil below the depth of 0.5 m the buffering properties are controlled by the lithologies of the bedrock and the grain size and mineral composition of the soil. Tamminen and Starr (1990) emphasize the importance of the soil organic matter and clay contents and their distributions within the profile to the acidification and the acid neutralization capacity of soils. In addition to that, Räsänen (1989) and Petäjä-Ronkainen et al. (1992) report that the buffering capacity of the soil depends on the age of podzols. Old podzols (>7000 years) can more readily resist acid input than young ones.

Nuotio et al. (1990) report that low base saturation values and high  $H^+$  concentrations in the surface layers in southern, southeastern and northern Finland are caused by the high acid deposition in these areas. A similar interpretation is made by Starr and Tamminen (1992). However, they argue that present levels of soil acidification do not pose a threat to forest health.

Buffering properties of the soil and the level of soil acidification are commonly examined through the variation in pH, the ratio Ca/Al, cation exchange capacity (CEC), acid neutralizing capacity (ANC) and the base saturation (BS) index. Soil pH is usually measured in deionized water or else in dilute salt extracts. In contrast, there is wide variation in the extraction methods for the quantification of exchangeable base cations and exchange acidity. Elemental concentrations of base cations have been measured in 1 M ammonium acetate buffered at pH 4.65 and/or pH 7.0 by AAS or ICP (Vuorinen & Mäkitie 1955, Halonen et al. 1983, Tamminen & Starr 1990). Alternatively, exchangeability of cations has been measured in unbuffered 0.1 M barium chloride (Tamminen & Starr 1990) and in unbuffered 1 M ammonium chloride (Nissinen & Ilvesniemi 1990). The exchange acidity, representing the quantity of acid cations,  $Al^{3+}$  and  $H^+$ , is generally determined by the KCl titration method of Halonen et al. (1983).

Total and exchangeable acidities have been determined in acetate and barium chloride, respectively, by titration with sodium hydroxide to the endpoint of pH 7 (Tamminen & Starr 1990). In this case  $Fe^{3+}$  and  $Mn^{2+}$  are included in the group of acid cations.

Cation exchange capacity is generally calculated as the sum of base cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$ ) and acid cations ( $Al^{3+}$ ,  $H^+$ ) and the base saturation index is calculated as the percentage of base cations from the cation exchange capacity (Nuotio et al. 1990, Nissinen & Ilvesniemi 1990). Tamminen and Starr (1990) determined separately the effective cation exchange capacity ( $Ca^{2+}+Mg^{2+}+K^++Na^++Al^{3+}+Fe^{3+}+Mn^{2+}+H^+$ ) by the unbuffered barium chloride method and the potential cation exchange capacity (the above-mentioned sum) by the buffered ammonium acetate pH 7.0 method.

In the acid neutralizing capacity (ANC) extraction method, separate portions of the same soil sample are acidified to varying degree and allowed to equilibrate for 24 hours (Wyatt 1984, Räsänen 1989). The stage of acidification and the sensitivity of the soil to acidification are estimated from the change in pH (ANC value) and the leachability of base cations and Al during the acidified salt extractions (Räsänen 1989).

The models of acidification in Finnish soils are based on calculations of input and output budgets of easily leachable and exchangeable ions (Kenttämies 1991). The rate of acidification is estimated on the basis of ion balances: the amounts of ions entering a catchment area via deposition and those removed in water flow are determined (Kenttämies 1991, Pohjonen 1992) and the difference between the amounts, plus losses through biological fixation, corresponds to weathering (Kenttämies 1991).

Cation exchange theory as applied in ion balance studies assumes that an increase in proton ( $H^+$ ) input to the soil solution, e.g. through increased  $H^+$  deposition, leads to cat-



ion exchange between solution  $H^+$  and soil exchangeable base cations (Kenttämies 1991). This process continues until the proportions of base cations and  $H^+$  on the exchange sites in the soil correspond to those in equilibrium solution (Nissinen & Ilvesniemi 1990). According to Nissinen and Ilvesniemi (1990), in the humus and eluvial layers the most important reaction regulated by the  $H^+$  concentration in the soil solution is cation exchange. In the illuvial layer it is the dissolution of Al compounds, which occurs simultaneously with cation exchange. Kenttämies (1991) has proposed that acidification results in a gradual depletion of the soil's reserves of base cations. With the increase in soil acidity, aluminium is converted into a more soluble form (Kenttämies 1991).

In assessing the buffering of hydrogen ions under field conditions, Derome (1991) emphasized the role of the other cationic components of precipitation. In his view, an input consisting only of hydrogen ions would grad-

ually strip all the base cations from the surface soil, whereas a mixed input of hydrogen and base cations would not reduce the base saturation below a certain level. He argues that the prediction of long-term changes in base saturation and acid neutralizing capacity on the basis of existing soil models is seriously flawed by the oversimplifications made about cation inputs and cation exchange reactions. One example of the oversimplifications Derome mentions is studies of ion budgets, which treat soils more or less as a black box, ignoring the formation of decomposition products and translocation of substances within the box (Robert & Tessier 1992). Thus, the stability of amorphous Al compounds during acidification has been underestimated in Finnish studies, even though their precipitation is very pH-dependent (Farmer & Fraser 1982, Gustafsson et al. 1995). Moreover, the role of clay minerals in soil acidification has not been well studied in Finnish podzols (Räsänen & Jylänki 1990).

## BEHAVIOUR OF ALUMINIUM DURING PODZOLIZATION AND CLAY MINERAL FORMATION

Both organic and inorganic acids are responsible for the natural dissolution of aluminosilicates and other minerals and the leaching of constituents in acidic soils such as podzols (Anderson et al. 1982, Rieger 1983, Buurman & Reeuwijk 1984). High concentrations of  $CO_2$  in soil solutions are responsible for weakly acidic conditions (pH 6 to 5), whereas more dissociated acids are required for pH values lower than about 5 (Bache 1985, Robert & Tessier 1992). Robert and Tessier (1992) underline that the formation of inorganic acids in soil is mainly due to oxidation mechanisms. In this context they note the oxidation of sulphur compounds present in the rock itself or in acid rain, nitrification ( $NH_4^+$  oxidation by bacteria giving rise to both nitrate and  $H^+$ ) and oxidation of iron in octahe-

dral sheets of phyllosilicates. The main sources of acidity in podzol are nevertheless organic acids, coming either from the decomposition of organic matter or the secretions of living organism (Rieger 1983, Chesworth 1992). An additional source of organic acids is the leaching of leaves, needles and tree bark with rainwater (Rieger 1983).

Podzols are formed in glaciogenic superficial deposits of subarctic and arctic forest regions and in well-drained soils of tropical and subtropical latitudes (Fitzpatrick 1980, Weaver 1989). The main processes of podzolization are the transfer of hydrous sesquioxides (Al-Fe-Si) and organic associations from the eluvial to the illuvial layer.

Farmer (1986) has summarized the occurrence of Al in podzolic soils as follows: Al

migrating from the surface soil layer can be precipitated (a) as insoluble Al humates and fulvates, (b) as hydrated aluminosilicate and a related amorphous form, or (c) as a polymeric hydroxyaluminium species in the underlying illuvial layer. Mobilized iron precipitates in the illuvial layer as iron humates and fulvates, and as a very poorly crystallized hydrated iron oxide (Farmer 1986, Buurman & Reeuwijk 1984).

Farmer et al. (1980) have proposed that aluminium released from primary minerals by non-complexing organic and inorganic acids in the eluvial layer is immediately converted to proto-imogolite, a soluble Al silicate complex (see also Anderson et al. 1982). Proto-imogolite is the predominant mobile form in which Al is transported to the illuvial layer (Farmer 1984). In the illuvial layer it precipitates as imogolite-type components, well-ordered imogolite and poorly ordered proto-imogolite allophane (Farmer & Fraser 1982). Materials of imogolite type are commonly referred to as short-range ordered aluminosilicates. Popular terms for this mineral group are non-crystalline or amorphous or inorganic Al precipitates.

Buurman and Reeuwijk (1984) have criticized the above theory, arguing instead that the mobilization, translocation and precipitation of sesquioxides are caused by complexing organic compounds. They explain the presence of imogolite in the illuvial layer by neoformation from silica in percolating soil solutions and Al species liberated from their organic compounds through the activity of micro-organisms. This suggestion is supported by the new research of Gustafsson et al. (1995) in northern Scandinavia. They conclude that short-range ordered minerals are mostly formed through congruent dissolution of Fe and Al from primary minerals followed by the downward migration of organometallic complexes to the B layer. The higher pH (i.e. higher than in the E layer), together with the microbial degradation of organic substances,

cause Fe and Al to precipitate in the B layer as proto-imogolite allophane, imogolite, ferrihydrite and goethite (Lundström 1994, Gustafsson et al. 1995). Gustafsson et al. (1995) add that a small amount of the organometallic precipitates in podzols of northern Europe have originated from the warmer postglacial period rather than the present.

In the evolution of clay minerals from forms typical of acid brown earths to forms typical of ferric podzols, the intensive weathering of chloritized clays results in the formation of expanding smectite-like clay minerals (Righi et al. 1988). In the more acidic and more organic soil environment of the podzol the formation of expanding smectite comes about through the gradual and continuous removal of Al from the eluvial layer (Herbauts 1982, Righi et al. 1988). Simultaneously the Al is fixed in interlayer spaces of vermiculite in the illuvial layer (Herbauts 1982, April et al. 1986). This clay is variously described as an Al-hydroxy interlayered vermiculite or simply an intergrade (MacEvan & Wilson 1980, Barnhisel 1977), or as a chloritized vermiculite, secondary chlorite or 'soil chlorite' (Barnhisel 1977, Herbauts 1982, De Coninck et al. 1987). Decomposition of organic complexes, release of Al and increase of pH are proposed to promote the interlayering of clays in the illuvial layer (Herbauts 1982, Huang 1991). Depending on these factors, the degree of filling of the interlayer spaces in vermiculite varies widely from podzol to podzol (Gjems 1967, Kodama & Brydon 1968, Kapoor 1972, April et al. 1986, Teveldal et al. 1990, Hallbäcken 1992).

The occurrence of Al-hydroxy interlayered minerals in podzolic soils has been widely debated. Righi et al. (1988) argue that Al-hydroxy interlayered vermiculites are characteristic not of podzols but of acid brown earths. In podzols, mobile Al is removed from the eluvial layer, and complexed by organic matter in solution (Herbauts 1982, Righi et al. 1988). Alternatively, under oxidizing and fre-



quent wetting and drying conditions, interlayering may also occur in the acidic surface layer (Olson 1988, Barnhisel & Bertsch 1989). According to Robert and Tessier (1992),  $\text{Fe}^{2+}$  ions can migrate to exchangeable positions on clays and, upon oxidation and  $\text{Fe}^{3+}$  hydroxylation, release protons that trigger a corresponding release of Al and the formation of intergrade minerals. Barnhisel and Bertch (1989) point out that the interlayer component in the surface layer interjects a metastability to the vermiculite minerals.

Rich (1968) concluded that Al-hydroxy interlayered clay minerals are formed under conditions of weakly acidic pH (pH~5), low organic matter content, and frequent wetting and drying of the soil. Because these factors

in many cases characterize the illuvial layers of podzols, as April et al. (1986), Bain et al. (1990) and Hallbäck (1992) have noted, hydroxy interlayered materials occur predominantly in these layers. Bain et al. (1990) and Hallbäck (1992) add that the degree of interlayering and removal of hydroxy-Al from interlayers are strongly dependent on pH. As the pH of a layer decreases, aluminium from the interlayer space will be mobilized and may find its way into percolating soil water (Olson 1988, Bain et al. 1990). According to Farmer et al. (1988), Al-hydroxy minerals occur in silt as well as in clay fractions (cf. Hallbäck 1992). They point out that, in both fractions, the clays may become sources of reactive Al if the acidity of podzols increases.

## DESCRIPTION OF THE STUDY REGION

### General geology

The bedrock in the northern and northeastern parts of the Kuopio - Siilinjärvi region is dominated by Archaean granitoid gneisses (Fig. 1) (Lukkarinen 1991). Proterozoic meta-sedimentary rocks in the region include greywackes, mica schists, arkosites, quartzites, and carbonaceous rocks (Luukkonen & Lukkarinen 1986). Metavolcanics of mainly mafic composition overlie the quartzites and carbonaceous rocks, and are in turn overlain

by greywackes and mica schists (Aumo 1983, Kousa 1986). The major plutonic rocks are granites and granodiorites, which dominate to the east, southeast and northwest of Siilinjärvi (Fig. 1). A syenite-carbonatite complex lies near the centre of Siilinjärvi and the Kemira fertilizer plant (Puustinen 1971). Apatite ore is being mined in the southwestern part of the formation, close to the fertilizer plant (Fig. 1).

### Quaternary geology and deposits

Quaternary deposits in the forested areas of Kuopio and Siilinjärvi and in the background area are mainly sandy till (Brander 1930, Rainio 1980). The topography rises gradually towards the north and northeast from Siilinjärvi. Two longitudinal eskers from the northwest and west join to form a massive esker formation in the centre of Siilinjärvi, which then continues as a flat formation to the southeast (Brander 1930). Smaller discontinuous,

longitudinal eskers occur in the city of Kuopio (Rainio 1980).

Tills in the lake valleys of Siilinjärvi and Kuopio are rich in silt, whereas tills in the hills are predominantly sandy (Brander 1930). Silty tills in cultivated areas at altitudes below ca. 100 metres a.s.l. are, at many sites, covered by lacustrine sediments deposited during the Suursaimaa transgression stage, ca. 6000 - 5500 years ago (Brander 1930, Eronen

1992).

According to Lintinen (1993 and 1995), a high clay content (20 - 30%) in till fines characterizes the topmost tills in Siilinjärvi and Riistavesi, to the east of Kuopio (see site No. 20 in Fig. 2). A zone with clay-rich till in the surficial part of the overburden extends from Siilinjärvi and Riistavesi to Bothnian Bay (Lintinen 1995). The topmost tills at Kuopio and to the south have low clay content but are rich in fines, while tills far away to the east and northeast (see site No. 49 in Fig. 2) mostly have low clay content (Lintinen 1995).

### Ancient shorelines and the age of podzolization

According to Sauramo (1928) and Saarnisto (1970), the ice margin retreated in the Kuopio district 9700 years ago. At that time the highest shoreline of the Yoldia Sea was approximately 140 metres above the present sea level (Saarnisto 1970, Eronen 1992). Even though soil processes began immediately after the retreat of the ice, it can be assumed that podzolization processes did not predominate before coniferous stands were well established. Saarnisto (1970) has dated the arrival of *Pinus* in the Kuopio district at ca. 9000 years B.P.

During the Ancyclus transgression, about 9000 years ago, the water level in the Kuopio and Siilinjärvi region varied between 110 and 125 metres above the present sea level (Donner 1957, Saarnisto 1970). At about 8000 B.P., *Pinus* contributed from 40% of the pollen rain in the southern part to 80% in the northern part of the study area (Birks & Saarnisto 1975). Later on, the water surface dropped to altitudes ranging from 80 to 90 metres a.s.l. (Okko 1965, Saarnisto 1970). This regression was dated to  $7610 \pm 115$  (Saarnisto 1970).

About 5500 years ago, the water level rose again, reaching altitudes from 100 to 105 metres a.s.l. in the Kuopio and Siilinjärvi region (Okko 1965, Saarnisto 1970). This

According to field observations by Räisänen (1989), the upper parts of surficial tills at some sites in the Siilinjärvi study area (see below) are covered by or mixed with lacustrine sediments due to re-sedimentation of the parent material during the Suursaimaa stage. At some sites, surficial till layers were outwashed, resulting in soil material rich in pebbles and stones. This kind of soil material was less common at the Kuopio sampling sites and at the background sites lying outside industrial and densely populated areas (outside the circles in Fig. 2) (Räisänen 1989).

youngest shoreline is called the Suursaimaa transgression stage. At that time *Picea* spread into eastern Finland (Donner 1957, Saarnisto 1970). At about 4000 B.P., the estimated contribution of *Picea* to isopollens was 10 - 20% in areas above the highest shoreline (Birks & Saarnisto 1975).

Since differentiation into podzolic layers takes from 500 to 1000 years in Finland, as suggested by Aaltonen (1952), Jauhiainen (1973) and Petäjä-Ronkainen et al. (1992), the duration of soil development can be estimated by subtracting 500 years from the dating of the highest shoreline. The age of the oldest podzols located above 140 metres in the present study is 9000 years or a few hundred years older. Even though the podzolization probably began less than 9000 years ago, pedons above the oldest shoreline are grouped separately from those in subaquatic areas (transgression stages of the Ancyclus and Suursaimaa Lakes). Podzols located between 110 and 140 metres a.s.l. vary from 7000 to 9000 years old, while those at altitudes from 105 to 110 metres are from 5000 to 7000 years old. The youngest podzols, located below 105 metres a.s.l., are ca. 5000 years old or a few hundred years younger. The water level in Lake Kallavesi is now 82 metres a.s.l.



## Anthropogenic emission sources and acid deposition

Municipal environmental authorities began close monitoring of air quality in the mid-1980's in Kuopio and a few years later at Siilinjärvi. Even though the quality of the measurements of atmospheric pollutants was not completely comparable during the years 1986 - 1988, Räsänen (1989) concluded that sulphur deposition was high in the Kuopio study area and, because of the prevailing wind direction to north and northeast, this also affected the Siilinjärvi area. In contrast, in the same years nitrogen load was somewhat higher in the Siilinjärvi than the Kuopio area.

The major emission source in Kuopio is a chemical pulp mill, which in 1986 - 1989 emitted 9000 - 10 000 tonnes of SO<sub>2</sub> and 400 tonnes of NO<sub>x</sub> annually (Emission survey of the Kuopio urban area 1987, Nerg & Holopainen 1991). In 1986 the calculated annual sulphur deposition in the Sorsasalo - Ranta-Toivala district of Kuopio (Fig. 2) varied from 3.2 g/m<sup>2</sup> in the vicinity of the mill to 0.7 g/m<sup>2</sup> in the eastern part (Air Quality in Kuopio 1988). In 1989, annual S deposition in the same area was 0.8 - 1.6 g/m<sup>2</sup> and 0.6 g/m<sup>2</sup> (Air

Quality in Kuopio 1990). Today, sulphur emissions of the mill are decreasing rapidly. The chemical pulp mill at Sorsasalo has been in operation about 30 years.

The phosphorus and nitrogen fertilizer plant is the main local source of SO<sub>2</sub> and NO<sub>x</sub> emissions in the centre of Siilinjärvi (Fig. 1). The plant has been in operation about 20 years. The open pit mine is situated northwest of the plant. In 1986 - 1987 annual emissions of the plant were 4400 - 5000 tonnes of SO<sub>2</sub> and 800 - 900 tonnes of NO<sub>x</sub> (Emission declaration of Kemira Oy 1988, Wulff et al. 1990). The annual S deposition in the Siilinjärvi area was not measured during the sampling year 1986. In 1987, in the centre of Siilinjärvi, the annual SO<sub>2</sub> concentration in air averaged 4 µg/m<sup>3</sup>, whereas in the same year in the vicinity of the chemical pulp mill in the Sorsasalo - Ranta-Toivala area the annual SO<sub>2</sub> concentration in air was 18 µg/m<sup>3</sup> (Emission declaration of Kemira Oy 1988, Air Quality in Kuopio 1988). The emissions of the fertilizer plant have decreased since the early 1990's.

## MATERIALS AND METHODS

### Study sites and soil materials

The study was carried out in the industrial and densely populated parts of Kuopio and Siilinjärvi (circled areas) and in the rural area 5 - 7 kilometres away from the emission sources (Fig. 2). The sites in the rural area, which were background sites with less acid deposition, were selected on the basis of the prevailing wind direction and were mostly located to the north and northeast of the plant sites (see Räsänen 1989). Study sites were selected from those of Räsänen (1989) and Jaloniemi and Räsänen (1991).

In areas of thick till overburden (thickness

of the overburden more than one metre), the study site was a circle of 15 metres diameter, in which the ground vegetation, tree cover and pedon appeared more or less uniform (Räsänen 1989). A greater area of 50x50 m<sup>2</sup> was chosen in rocky terrain because of the mottled appearance of the shallow till on the bedrock surface. In this case, patches of the till with similar ground vegetation were selected for sampling.

Soil materials were selected on the basis of the parent soil material and the appearance of the podzol. Samples were collected in 1986 -

Table 1a. Distribution of till types in sampling sites. Till types were determined according to the GEO classification (Haavisto 1983). n = number of profiles.

Till types	n	Kuopio	Siilinjärvi	Background
Sandy till, stony sandy till	25	6, 7b, 9, 12, 15a, 15b	24, 26, 27, 34, 35, 36, 39, 41	17, 18, 20, 43, 44, 45, 46, 49, 52, 53, 56
Gravelly sandy till	5	-	21, 23, 33	42, 51
Silty sandy till / sandy tills mixed with silt sediments	7	-	28, 29, 40 / 30, 32	50, 55
Sandy tills in rocky terrain	11	1-4, 7a, 8, 10, 11, 13	-	18, 56

Table 1b. Methods of chemical analysis and samples studied. n = number of samples.

Chemical methods	n	Kuopio (site No.)	Siilinjärvi (site No.)	Background (site No.)
Total dissolution	102	1, 4, 7a-b, 8, 9, 12, 13, 15a	21, 23, 24, 29, 30, 33, 35, 41	17, 18, 20, 42, 45, 46, 49, 51, 53, 55, 56
Hot aqua regia	147	all sites, except 3, 10 and 11	all sites	all sites
Speciation of Al, Fe	41	1-13	none	18, 56
XRD studies	55	1, 4, 7a, 11-12, 15 a and b	29, 30, 35	17, 18, 43, 46, 49, 53, 55, 56

1988. At sites with thick overburden, the sampling was targeted at podzol profiles representative of sand-rich and silt-rich tills (Table 1a). Podzols were haplic podzols according to the FAO Soil Taxonomy (FAO-Unesco 1988) or typic haplocryods according to the USDA Taxonomy (Soil Survey Staff 1992, see also Mount et al. 1995). The determination of the till and podzol types was based on field observations.

In shallow overburden in rocky terrain, samples were taken from profiles totally tinted red-brown (2.5 YR 2.5/3 or 2.5/4, Munsell Soil Color Chart 1990) and, where possible, adjacent to profiles with distinguishable podzolic layers (Fig. 3). The parent soil material sampled in rocky terrain was sandy till, a layer 10 - 50 centimetres thick on the bedrock surface (Räisänen 1989, Jaloniemi & Räisänen 1991).

Besides parent soil material and podzol appearance, another criterion in selecting sampling sites was that samples should represent

podzols of all possible ages occurring in the study areas.

On the basis of Jaloniemi and Räisänen's (1991) report that visible podzolic layers in shallow tills in many ways chemically resemble those in nearby thick sandy tills, it was here assumed that profiles with distinguishable podzolic layers represent the undisturbed podzolization and red-brown soil profiles disturbed podzolization. For that reason, in addition to the profiles of shallow tills of interest for the speciation of Al and Fe, a few profiles were selected from the thick sandy tills in the Sorsasalo and Ranta-Toivala district (Fig. 2 and Table 1). Shallow till sites in the background area possessed distinguishable podzolic layers (Räisänen 1989). As reported earlier by Räisänen (1989), the thin shore sands occurring sporadically on the surface of bedrock at background site 18 were totally tinted red-brown. These sands were excluded from the present study, however.





a)



b)

Fig. 3. Appearance of the profiles in shallow till near the chemical pulp mill in Kuopio. (a) profile with distinguishable podzolic layers (yellowish grey eluvial layer underlaid by a brown illuvial layer), (b) red-brown soil profile.



## Sampling

A grey eluvial (E), brown or reddish brown illuvial (B) and yellowish grey transition zone (BC) layer, and in most cases also a less altered (C) layer of till, were sampled from spade-dug pits at the sites of thick overburden (Räisänen 1989). Only in a few cases was the 2- to 3-centimetre-thick transition zone (EB) between the E and B layers separately sampled. If the BC layer was not sharply distinguished from either the darker B layer or the parent till, as was the case at many sites of silt and gravel-rich tills, a composite sample about 15 - 20 cm thick was taken from under the B layer. In addition, if the C layer differed genetically from the overlying layers because of sorting and washing of the upper soil layers during the deglaciation and water transgressions, the BC layer was selected as a representative sample for the parent soil material. In view of the chemical similarity, samples so grouped are signified by the index BC/C. Samples of the BC and C layers were grouped in much of the data processing.

In the thick tills, usually one profile per study site was sampled. Duplicate profiles were sampled only at a few study sites (Nos.

15, 23 and 26 in Fig. 2). The depth of the pit varied from 30 to 60 centimetres depending on the thickness of the E and B layers.

Depending on how homogeneous the profile appeared, one to five profiles were sampled at each sampling site of shallow tills in rocky terrains. Altogether 17 pedons of red-brown soil were sampled. In most cases the sample was taken as a composite sample of the shallow overburden on the bedrock surface. At four sites the top and underlying parts of the red-brown soil profile were separated as reference samples for visible podzolic layers. In this case the sampling thickness of the layer depended on the thickness of the corresponding podzolic layer in the neighbouring profile (Jaloniemi & Räisänen 1991). In addition to these, patches of the grey eluvial layer which occurred in three pits of the red-brown soil were separately sampled. The distinguishable eluvial and illuvial layers were separately sampled in six pits, and the eluvial layer alone was sampled in four pits where the illuvial layer on the bedrock surface was too thin to sample. A less altered BC layer could be sampled only at a few sites in rock terrains.

## Chemical analyses

### Total dissolution

Total concentrations of Si, Al, Fe, Ca, Mg, K and Na were determined in extracts prepared by the HCl-HNO<sub>3</sub>-HF-H<sub>3</sub>BO<sub>3</sub> dissolution method as modified by the Chemical Laboratory of the Geological Survey of Finland (GSF) in Kuopio. Altogether 102 air-dried samples of the eluvial (E), illuvial (B) and less altered till layers (BC/C) of profiles in Siilinjärvi, Kuopio and the background area were selected for analysis (Table 1b). The fraction size of the sieved samples used in this digestion, as well as in the other extractions

of the present study, was <0.5 mm. Differing from the other extractions, sieved samples for the total digestion were ground with a swing mill.

The procedure began with the mixing of conc. HCl and HNO<sub>3</sub> acids in the following way: a subsample of 0.1 g was mixed with 0.5 ml conc. HCl and 0.5 ml conc. HNO<sub>3</sub>; the mixture was shaken for a few minutes and then left overnight at room temperature. Next morning, 3 ml of HF acid was added, and the mixture was shaken gently and left to stand overnight. In the morning 50 ml saturated H<sub>3</sub>BO<sub>3</sub> with CsCl ionization buffer was mixed



into the solution and the mixture was left to equilibrate for one hour at room temperature. Before determinations, 46 ml de-ionized water was added, and the final mixture was shaken and left for several hours. The concentrations of dissolved elements were measured by atomic absorption spectrophotometry (AAS) using a nitrous oxide/acetylene flame for Al, Ca, Mg and an air/acetylene flame for Fe, K, Na.

### Partial dissolution with hot aqua regia

Digestion with hot (90°C) aqua regia [ $\text{HCl-HNO}_3$  (3+1)] is selectively used to determine the easily leachable components of micas, clay minerals and precipitates (Räsänen et al. 1992b). Altogether 147 air-dried samples of the <0.5 mm fraction were analysed by the hot aqua regia method (Table 1b). The procedure is described in Räsänen et al. (1992a). Abundances of Al, Fe, Ca, Mg, K, Na in leaches were determined by inductively coupled plasma spectrometry (ICP-AES) at the Chemical Laboratory of the GSF in Rovaniemi. Concentrations of silicon in leaches were very low because of the reprecipitation and are not interpreted in this study (see also Räsänen et al. 1992b).

The dissolving power of the hot aqua regia for silicates was examined by X-ray diffraction (XRD) for eight samples of the E, B and BC and C layers. The oriented aggregates were prepared from the untreated and leached samples. The diffractograms were run with a Philips diffractometer using Ni filtered  $\text{CuK}\alpha$  radiation at the Mineralogical Laboratory of the GSF in Kuopio. Results of this test are described in the section reporting on aqua regia soluble elements.

### Geochemical fractionation of aluminium and iron

Speciation analysis of an element in a sample involves the determination of the concentrations of the individual physico-chemical

forms of the element, which together constitute its total concentration (Van Loon & Barefoot 1992). A complex scheme of selective or sequential extractions progressing from weak extractant to strong chemical is employed to separate the various element species (Van Loon & Barefoot 1992). Badri and Aston (1983) use the term geochemical fractionation for selective leachings with appropriate reagents and name the identified species geochemical fractions. This terminology is adopted in the present study.

Geochemical fractions of Al and Fe were separately determined with the following extractions (non-sequential) and calculations: dilute  $\text{NH}_4\text{NO}_3$  extraction for the easily leachable and water-soluble fraction, KCl extraction for the exchangeable fraction, the remainder after subtracting the concentrations in  $\text{NH}_4\text{Ac}+\text{EDTA}$  and KCl extracts for the chelated fraction, and the remainder after subtracting the concentrations in  $\text{NH}_4$  oxalate and  $\text{NH}_4\text{Ac}+\text{EDTA}$  extracts for the precipitated fraction. The extractability of Al and Fe in acidic medium was determined with the acidified  $\text{NH}_4\text{NO}_3$  ( $\text{AS}_{\text{pH}2.3-2.4}$ ) extraction.

Forty-one samples were analysed by six weak extraction methods (Table 1b). Most of the samples were soils collected on rocky terrains of the Kuopio study area. The grain size of <0.5 mm was the same as in the strong acid leaches. The extraction procedures as modified by the author are described in the sections to follow. Concentrations were determined by atomic absorption spectrophotometry (AAS) using the nitrous oxide/acetylene flame for Al and the air/acetylene flame for Fe at the Chemical Laboratory of the GSF in Kuopio.

### Easily leachable and water-soluble aluminium and iron

Easily leachable and water-soluble Al and Fe were defined with the dilute  $\text{NH}_4\text{NO}_3$  extraction method modified by Räsänen (1989).

Subsamples of 2.5 g were mixed with 25 ml of 0.025 M  $\text{NH}_4\text{NO}_3$  solution in polypropylene tubes. The mixtures were gently agitated for 24 hours at room temperature, avoiding mechanical abrasion, and then centrifuged. The pH of the liquid portion was measured immediately after the centrifugation. Aluminium was measured in the filtered supernatant by flame AAS. The extracted Fe was mostly under the detection limit.

#### Exchangeable aluminium and iron

Exchangeable Al and Fe was defined with the KCl extraction method, modified after the method of Blakemore et al. (1981). A 2.0 g portion of subsample was mixed with 20 ml of 1 M KCl in a polypropylene tube. The mixture was allowed to stand overnight (about 18 h) at room temperature and the next morning it was agitated for one hour and centrifuged. pH was measured in the supernatant before filtering. The solid residue was washed with 9 ml de-ionized water, and 1 ml conc.  $\text{HNO}_3$  was added to the filtrate to avoid reprecipitation of Al and Fe during measurement by flame AAS. Supernatants with high concentrations were diluted with de-ionized water before determinations.

#### Leachability of aluminium and iron in acidic medium

The dilute ammonium nitrate solution acidified to pH 2.3 - 2.4 with dilute sulphuric acid was used for determining the extractability of Al and Fe in the acidic medium (Räisänen 1989). The extractant is here abbreviated  $\text{AS}_{\text{pH}2.3-2.4}$  (acidified salt) instead of ANC (acid neutralizing capacity) as earlier used by Räisänen (1989) and Räisänen and Pulkkinen (1991).

Dilute (0.025 M)  $\text{NH}_4\text{NO}_3$  solution was acidified with a small amount of standardized 0.1 N  $\text{H}_2\text{SO}_4$  solution to decrease the pH of the salt extractant to 2.3 - 2.4. The soil:solution ratio and extraction time were the same as in

the dilute  $\text{NH}_4\text{NO}_3$  extraction without the acid input (Räisänen 1989). The pH of the liquid portion was measured immediately after the centrifugation. The extractability of Al and Fe was measured in filtrates by flame AAS. As in the dilute salt extraction, the leachability of Fe in the  $\text{AS}_{\text{pH}2.3-2.4}$  solution was insignificant, and results were disregarded.

#### Chelated aluminium and iron

The ammonium acetate and ethyldiamine-tetraacetic acid (EDTA) at pH 3.5 method was used here to determine Al and Fe concentrations in the less stable organic and inorganic complexes (Lakanen & Erviö 1971, Jaloniemi & Räisänen 1991). Since the mixture of  $\text{NH}_4\text{Ac}$  and EDTA extracts elements chelated in soil organic matter as well as exchangeable and readily soluble elements, concentrations in the chelated fraction are here calculated by subtracting the concentrations in  $\text{NH}_4\text{Ac}$  + EDTA and KCl extracts.

The procedure for  $\text{NH}_4\text{Ac}$ +EDTA was modified after the method of Lakanen and Erviö (1971). A subsample of 2 g was mixed with 20 ml of buffered 1 M  $\text{NH}_4$  acetate with the added 0.02 M EDTA agent. The pH of the extractant was adjusted with acetate acid to pH 3.5. The mixture was agitated gently for three hours at room temperature. After centrifuging and filtering, the residue was washed with 9 ml de-ionized water. One millilitre of conc.  $\text{HNO}_3$  was added to the filtrate before the measurements of Al and Fe by flame AAS. Supernatants with high concentrations were diluted with de-ionized water before determinations.

#### Precipitated aluminium and iron

Ammonium oxalate at pH 3.0 was used as a selective extractant for the short-range ordered aluminosilicates and iron hydrous oxides (McKeague & Day 1966, Parfitt & Henmi 1982, Evans & Wilson 1985). In the present study, contents of Al and Fe in the precipitated fraction were calculated by deducting con-



centrations of  $\text{NH}_4\text{Ac}+\text{EDTA}$  extractable Al and Fe from concentrations of oxalate extractable Al and Fe. It is assumed here that this fraction mostly includes Al and Fe tightly bound in inorganic precipitates.

The method used here is modified after that of Evans and Wilson (1985). 700 ml of 0.2 M  $\text{NH}_4$ -oxalate was mixed with 535 ml of 0.2 M oxalic acid, forming an oxalate extractant of

pH 3.0. A subsample of 1 g was extracted with 20 ml of the acid oxalate solution. The suspension was agitated for three hours in normal inside lighting at room temperature. After centrifuging and filtering, Al and Fe in the supernatant were determined by flame AAS. High concentrations were diluted before determination.

### X-ray diffraction (XRD) analysis

X-ray diffractometry was applied for the identification of silicate minerals and to characterize clay minerals. The main interest, however, was the characterizing of clay minerals. In this connection, comparative extraction methods and heatings were employed.

On the basis of the chemical analysis data, 55 samples were selected for XRD analysis (Table 1b). It was assumed that samples containing abnormal amounts of Al in the various chemical fractions were acidified (Jaloniemi & Räsänen 1991). Approximately half of the samples were taken in the area of the shallow till, where Räsänen (1989) and Jaloniemi and Räsänen (1991) observed unusual levels of soil acidification. The rest of the samples for XRD analysis were from areas with moderate to background levels of acid deposition (Räsänen 1989).

### Sample preparation

A 3-g portion of the dry-sieved <0.5 mm sample was weighed for the extractions listed below. Otherwise, the sample-to-solution ratio and procedures were the same as those for the chemical analyses. The oriented subsample was made by pipetting the desired fraction in water suspension onto a glass slide. Subsamples of the <(40 - 50)  $\mu\text{m}$  fraction were prepared from all studied samples and, in addition, subsamples of the <(10 - 20)  $\mu\text{m}$  fraction were prepared from samples rich in silt and clay. The settling time to obtain the

<(40 - 50)  $\mu\text{m}$  fraction was about 40 seconds, and to obtain the <(10 - 20)  $\mu\text{m}$  fraction 3 - 4 minutes. The subsample was pipetted from 1 - 2 cm below the surface of the suspension.

The treatments of the subsamples were as follows: (1) air-drying, (2)  $\text{AS}_{\text{pH}2.3-2.4}$  extraction, (3)  $\text{AS}_{\text{pH}2.3-2.4}$  extraction and treatment with ethylene glycol, (4)  $\text{AS}_{\text{pH}2.3-2.4}$  extraction and heating at 200 °C for 30 minutes, and (5)  $\text{AS}_{\text{pH}2.3-2.4}$  extraction and heating at 550 °C for 10 minutes. Ethylene glycol was added by pipetting a drop on the air-dried subsample and leaving it over night at room temperature. For comparison, most of the subsamples were extracted with KCl (K-saturation) and then heated at 200 °C and 550 °C. The samples rich in Fe precipitates were extracted with acid oxalate and heated at 200 °C and 550 °C. The precision of the preparation and XRD procedure was examined with the aid of duplicate subsamples for about one quarter of the samples.

Extractions and the preparation of oriented slides were carried out by the author at the Chemical Lab of the GSF, and most XRD analyses of the slides were made at the Mineralogical Laboratory of the GSF in either Kuopio or Rovaniemi, or in a few cases at the Geoanalytical Laboratory (GAL) of the Outokumpu Mining Services. Most of the subsamples analysed at GAL were, however, reanalysed at the GSF in Kuopio. In all labs, XRD-patterns were run at a scanning rate of 1° per minute using a Phillips X-ray diffractometer

with Ni-filtered  $\text{CuK}\alpha$  radiation. Even though the peak intensities of the XRD traces varied from lab to lab, the characteristic XRD traces recorded after extractions and heatings were comparable. Diffractograms were interpreted with the help of the handbooks of Thorez (1975), Dixon and Weed (1977 and 1989), and Brindley and Brown (1980).

## Mineral identification

### Main silicates

Quartz (Q) is easily identified from its 3.34 Å (101) and 4.26 Å (100) reflections. Plagioclase (Pl) was mostly recognized by the reflection at 3.19 Å, which is attributed to plagioclase rich in Na, and potassium feldspar (Mi = microcline) at 3.22 - 3.25 Å. Other stronger peaks occur at 4.04 - 4.02 Å and 3.70 - 3.83 Å for plagioclase and at 3.48 - 3.49 Å for K feldspar. Hornblende (H) is recognized by reflections at 8.3 Å or 8.4 Å and 3.12 Å (see Brown & Brindley 1980).

### Micas

Fine-grained mica is normally called illite. According to Šrodoň and Eberl (1984), an ideal illite is nonexpanding and dioctahedral, and the grain size is  $<4\ \mu\text{m}$ . In contrast to this, Wilson (1987) characterized 10 Å clays as illite if they contained 10% or more expandible layers. Since the grain-size of micas was not determined and the reflection at 10 Å was unaffected by ethylene glycol, all micas of the present study are referred to as illitic micas. The broad 10 Å reflection gently sloping on the low angle side indicates the partial degradation of the mica.

Dioctahedral mica was distinguished from trioctahedral mica on the basis of the ratio of the intensities of the peaks at 5 Å and 10 Å (Fanning & Keramidas 1977). If the 5 Å reflection is one third or more of the intensity of the 10 Å reflection (Wilson 1987) and if the reflection at 4.48 Å appears (Thorez

1975), the mica is considered to be dioctahedral. If a mica is trioctahedral, the 5 Å (002) reflection is very much weaker than the 10 Å (001) reflection.

If a mica diffractogram has a marked tail or plateau on the low angle side, it is attributed to mixed-layer minerals with variable water content, e.g. mica-vermiculite. The exchange of K in the mica causes broadening of the 10 Å peak, and the appearance of wide bands from 10 Å to 14 Å. On heating to 550 °C the 10 Å reflection becomes more symmetrical with increased peak height (Gjems 1967).

### Chlorite group minerals

Chlorites are identified by a series of basal reflections at approximately 14, 7, 4.7 and 3.6 Å. The (001) reflection at 14 Å is not affected by K saturation or solvation with ethylene glycol. After heating of the chlorite at 550 °C, however, the peak intensity of the 14 Å reflection usually increases two to five times (Barnhisel & Bertsch 1989). Differentiation of primary chlorite from Al-hydroxy interlayered vermiculite is discussed in the next section.

Identifying chlorite in a mixture with kaolinite is difficult because the (002) and (004) chlorite reflections (7 Å and 3.6 Å) overlap the (001) and (002) reflections of kaolinite. On heating at 550 °C, however, chlorite maintains a 14 Å reflection, whereas kaolinite decomposes (Barnhisel & Bertsch 1989). Another way to identify the chlorite is to treat the subsample with hydrochloric acid, which decomposes the chlorite minerals without seriously attacking the kaolinite (Barnhisel 1977). The heated XRD patterns showed kaolinite to occur only infrequently in samples of the present study, and it was not included in the list of minerals.

### Vermiculite group

The basal reflection (001) of vermiculite is at 14 - 15 Å when Mg or Ca is saturated and at 12.6 Å when Na is saturated (Wilson 1987).



Upon K saturation the lattice contracts to about 10 Å and takes on the character of biotite. In the present study, vermiculitic clays were differentiated from smectitic clays by ethylene glycol treatment. According to MacEvan and Wilson (1980) vermiculites give an expanded spacing of ~16 Å and smectites 16.9 - 17.1 Å upon ethylene glycol solvation. Vermiculite and chlorite are distinguished through K saturation at room temperature and upon heating.

The dehydration of vermiculite by heating varies with the interlayer cation. If the interlayer spaces of vermiculite are blocked by non-exchangeable material, the contraction of the lattice by heating or saturation with K is reduced. If the interlayer material contains Al-hydroxy polymers (e.g. gibbsite), the clay is commonly described as an Al-hydroxy interlayered vermiculite. The greater the degree of polymerization of the Al hydroxide incorporated in the interlayers, the higher is the temperature needed to obtain the collapse of the 14 Å peak to 10 Å (Barnhisel & Bertsch 1989). At high polymerization, properties of the clay approach those of chlorite and it is accordingly also called an "intergrade", "intergradient", soil chlorite, "aluminous" chlorite or secondary chlorite (Barnhisel 1977, MacEvan & Wilson 1980, Wilson 1987).

#### Mixed-layer clay minerals

The group of mixed-layer or interstratified clay minerals is of highly variable composition since the individual minerals are built up of two or more types of elementary layers. Micaceous are often present in soils as components of mixed-layer clays that have been partially transformed to expansible 2:1 minerals, i.e. mica is interstratified with the other minerals.

Mica is transformed to vermiculite, for instance, through replacement of its "nonexchangeable" interlayer cations by exchangeable cations, and through the exchange of Al for Si in the tetrahedral sheet (Fanning et al. 1989). In the layer weathering model, some interlayers are opened up all the way through a mica flake, while others remain essentially or entirely closed. The layer weathering leads to interstratified mica-vermiculite or mica-smectite.

Interstratification of layers may be regular or random. In regular interstratification, the stacking of the component layers follows a periodic succession, whereas in random interstratification the distribution of the layers lacks periodicity and is controlled only by the proportions of the various layers. The dominant component is listed first in describing the mixed-layers (Sawhney 1989). Higher integral peaks between 24 Å and 28 Å characterize regularly interstratified clays, whereas their absence indicates a random interstratification of layer silicates (Sawhney 1989).

Most of the mixed-layer clays of the present study exhibited random interstratification of layers, recognized by the reflections between 10 and 14 Å without higher integral peaks. Mixed-layer minerals containing vermiculite are identified by reflections between 12 and 14 Å, which totally shift to 10 Å upon K saturation at room temperature or upon heating at 550°C (Sawhney 1989). Smectitic components are recognized by their expanded reflections in glycol-treated samples. Interstratified chlorites, such as vermiculite-chlorite, are identified by a 10 - 14 Å diffraction effect after heating of the sample to 550 °C (Gjems 1967): the intensity of the 001 peak of the chlorite component decreases but remains close to 14 Å, while the vermiculite component collapses towards 10 Å (Sawhney 1989).

#### Statistical treatment of data

For the data processing, the sample profiles were classified areally depending on the

method into either two or three groups, comprising the Kuopio and/or Siilinjärvi industrial areas and the background area. Chemical differences between the study areas are mostly presented graphically with use of either the

MICROSOFT-CHART or HARWARD GRAPHICS 3.0 PC programs. Statistical analysis of the chemical composition was carried out with the SPSS 5.0 program for Windows.

## RESULTS

### Differentiation of the podzolic layers in thick tills

In earlier work in the study area (Räisänen 1989), the eluvial and illuvial layers were found to be most clearly distinguished in sand-rich tills. In contrast, podzolic layers were only weakly differentiated in tills rich in silt or gravel, as also reported by Aaltonen (1939). In sandy soils the flux of gravitational water downwards in the profile is greater than the uplift of pore water, which promotes the podzolization (Petersen 1976). In tills rich in gravel a rapid flux of water hinders the formation of distinct illuvial layer, whereas in soils rich in fines the periodical uplift of pore water restricts leaching (Räisänen 1989). Because of this, boundaries between the eluvial, illuvial and parent soil layers of tills rich in gravel as well as in soils rich in fines were gradual and often undetectable.

Further it was concluded (Räisänen 1989) that the poor permeability prevents layer differentiation in soils rich in fines. Thin brownish zones and patches in the pedon of silty tills indicate that the groundwater table has periodically risen to the surficial soil layers, creating reducing conditions and promoting the leaching of Fe to the groundwater, from which it partially reprecipitates, in patches, when the water table drops. This seasonal variation of the water table restricts the formation of a clear-cut illuvial horizon.

It should be added here that, although the

appearance of the podzols in this earlier study differed, all profiles were classified as haplic podzols (FAO-Unesco 1988) or typic haplocryod (Soil Survey Staff 1992, see also Mount et al. 1995). This suggests that the criteria for the podzol groups of the international soil classifications do not separate precisely enough the kind of podzolized tills described above. Weakly differentiated podzols might be classified as gleyic-like podzolic soils, but they lack the actual gleyic properties, that commonly characterize soils in tundra and in some cases in wetlands (Fitzpatrick 1980).

In the present study, except for two profiles in the background area, all the silty tills and tills mixed with silt sediments occurred in the lake valleys of the Siilinjärvi area. Here the age of podzolization was estimated at about 5000 years, as compared with over 7000 years for the two silty tills in the background area. In all cases the podzolic layers were weakly differentiated. In the gravelly tills, which were also only weakly differentiated, the age varied between 5000 and 9000 years. Since the differentiation of podzolic layers in the same till group did not significantly vary with the age, it is suggested that the grain size distribution of parent soils, as well as the hydrological conditions in top soils, have an important influence on the layer differentiation in thick tills.

### Differentiation of the podzolic layers in shallow tills

In contrast to the podzols in thick tills, two different profile types occurred side by side in



the shallow sandy tills in the vicinity of the chemical pulp mill in Kuopio: a profile with a distinguishable boundary between the eluvial and illuvial layers (Fig. 3a) and a profile totally tinted red-brown (Fig. 3b) (Räsänen 1989, Jaloniemi & Räsänen 1991). Exceptionally, in a few pits of the red-brown soil, grey patches occurred under the humus layer. The appearance of the profiles with distinguishable podzolic layers in rocky terrains was similar to that of thick sandy tills.

A return to the field in 1991 and 1992 showed that in the rocky terrain near the mill at Sorsasalo and in the rocky terrain at Ranta-Toivala (see Fig. 2), profiles with visible podzolic layers were in fact rare compared with red-brown soil profiles. Unexpectedly,

the occurrence of the red-brown profiles showed no correlation with ground vegetation, microtopography or altitude, nor with the thickness of the till on the bedrock surface. As reported earlier (Räsänen 1989), they occurred as often in till cover of 50 centimetres as in that of 10 or 15 centimetres.

Pits dug in shallow tills in rocky terrain showed that the surface of the granite gneiss bedrock was rusty at sites with red-brown soil. The bedrock was locally migmatized gneiss with veins rich in mica. Close study of the bedrock surface revealed that Fe-sulphides as well as mica flakes were weathered and tinted brown. Weathering, rather than the coloured soil, was thus responsible for the tinting of the bedrock surface.

### Geochemical properties of podzols in the Kuopio and Siilinjärvi region

It is here assumed that the main chemical processes of podzolization can be distinguished regardless of variations in the composition of parent materials, topography and vegetation (Fitzpatrick 1980, De Coninck 1980, Herbauts 1982). These factors, and the time and postglacial changes in climate, control the rate and intensity of weathering within the podzol profile (Fitzpatrick 1980). De Coninck (1980) described the main features of silicate weathering as follows: the acidity and especially the complexing tendency of the organic substances extract the alkali and alkali-earth elements and Fe and Al from silicates.

In the present study, geochemical properties of the industrial and background areas were compared and examined relative to the age of podzolization. The results of the strong acid leaches are relevant to this part of the investigation. The influence of the parent till on the rate of silicate weathering is discussed in only general terms because the number of pedons of the same age in each till group was too few to allow statistical examination (see Table 1a).

### Total concentrations of major elements in profiles of thick tills

#### Silicon

Total concentrations of  $\text{SiO}_2$  in podzolic layers and parent tills varied widely from 40 to 80% (Table 2). The difference between the layers within the profile was from 1 to 5%, with a few profiles showing variation of 10 to 15%. The variation in silica contents between profiles is evidently largely due to compositional differences in the parent tills, whereas the variation within profiles is caused either by the primary layering of the mineral material or the leaching during podzolization. Here the primary layering is associated with the sorting and impoverishment of clay material in the topmost till during deglaciation. On the other hand, low concentrations of  $\text{SiO}_2$  in some samples may be due to the undissolved silica residue (see Koljonen 1992). The recent research of the author shows that the X-ray fluorescence method gives better accuracy for total  $\text{SiO}_2$  than the total digestion method due to irregular dissolution of silica (see Räsänen

Table 2. Mean (x) and median (M) values and the range of total concentrations of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, K<sub>2</sub>O and Na<sub>2</sub>O. The grain size in the total dissolution was <0.5 mm (see also the text). The number of profiles is shown in brackets.

	Background (10)			Industrial (12)			Shallow till (6)			Red-brown soils (17)		
	x	M	range	x	M	range	x	M	range	x	M	range
SiO <sub>2</sub> c(w-%)												
E	61.7	64.6	42.1-73.4	63.7	67.2	46.2-79.1	70.0	74.7	57.8-81.3			
B	56.9	58.0	52.2-62.0	62.7	62.7	52.6-75.5	63.3	63.3	56.5-76.4	52.0	54.1	25.4-71.0
BC/C	58.9	57.5	49.0-71.9	62.7	66.3	52.6-75.1	-	-	-			
Al <sub>2</sub> O <sub>3</sub> c(w-%)												
E	9.2	9.1	6.6-12.1	9.9	9.6	7.6-13.4	9.6	9.5	8.9-10.8			
B	10.2	9.6	7.7-14.6	10.4	10.2	7.6-14.4	11.4	11.7	9.6-13.0	12.2	12.5	7.6-16.3
BC/C	10.6	10.8	8.5-14.2	10.6	10.4	7.9-13.6	-	-	-			
Fe <sub>2</sub> O <sub>3</sub> c(w-%)												
E	3.0	2.4	1.1-6.0	2.7	2.9	0.9-5.2	1.7	1.6	1.0-3.5			
B	4.5	4.7	1.7-6.3	3.9	4.2	2.7-5.0	4.3	4.7	2.3-6.2	8.5	8.5	1.6-15.2
BC/C	3.9	4.2	2.3-6.9	3.6	3.4	2.6-4.9	-	-	-			
MgO c(w-%)												
E	1.1	1.0	0.4-2.5	1.0	1.0	0.4-1.7	0.8	0.8	0.4-0.8			
B	1.2	1.2	0.7-2.1	1.3	1.2	0.8-2.2	1.1	1.1	0.6-1.1	1.5	1.0	0.3-4.8
BC/C	1.3	1.2	0.9-2.2	1.3	1.3	0.9-1.7	-	-	-			
CaO c(w-%)												
E	2.0	2.2	1.0-2.9	2.2	2.1	1.5-3.1	2.2	2.2	1.4-3.6			
B	1.9	2.0	1.0-2.7	2.3	2.1	1.5-3.6	2.1	2.1	0.6-3.5	2.0	1.8	0.5-4.4
BC/C	2.1	2.2	1.5-3.0	2.2	2.2	1.5-2.8	-	-	-			
K <sub>2</sub> O c(w-%)												
E	2.2	2.2	1.5-2.6	2.1	2.1	1.3-2.6	1.7	1.9	1.2-2.0			
B	2.2	2.2	1.4-3.0	2.1	2.1	1.2-2.8	1.6	1.7	1.4-1.7	1.6	1.8	0.5-3.0
BC/C	2.3	2.4	1.8-2.9	2.3	2.4	1.7-2.6	-	-	-			
Na <sub>2</sub> O c(w-%)												
E	2.8	3.0	2.2-3.3	3.0	3.1	2.5-3.5	2.6	2.6	2.3-3.2			
B	2.7	2.7	2.2-3.2	2.8	2.9	2.3-3.3	2.4	2.5	2.2-2.8	2.5	2.5	0.7-4.2
BC/C	2.9	2.9	2.5-3.3	2.9	2.9	2.5-3.2	-	-	-			

et al. 1995).

Silica appears mainly as crystalline quartz, which is resistant against leaching (Rieger 1983). Rieger (1983) has suggested that high SiO<sub>2</sub> in the eluvial (E) layer indicates leaching and the maturity of a podzol. As seen in Table 2, the mean and median values of total concentrations of SiO<sub>2</sub> were slightly higher in the eluvial (E) layer than in the illuvial (B)

and less altered (BC/C) till layers. Figure 4a shows the relationship between the concentration of silica in the eluvial layer and the age of podzolization. Values in this scatter diagram were calculated by subtracting the total SiO<sub>2</sub> concentration of the illuvial layer from that of the eluvial layer. The trend of the silica accumulation is expressed with a simple linear regression line, but the gentle slope of the



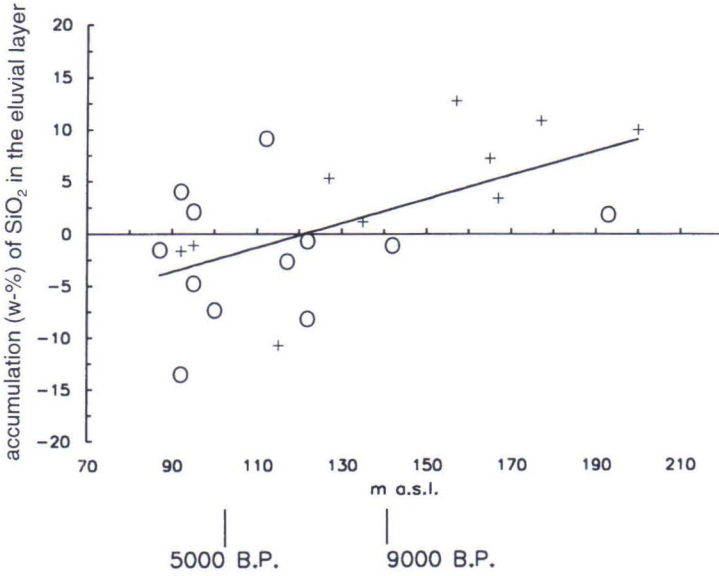


Fig. 4a. Accumulation of SiO<sub>2</sub> in the eluvial layer of podzols in thick tills plotted against altitude of the sampling site (ageing). Samples marked with an open circle (o) were taken from the industrial areas of Kuopio and Siilinjärvi and those with a cross (+) from the background area (see also the text).

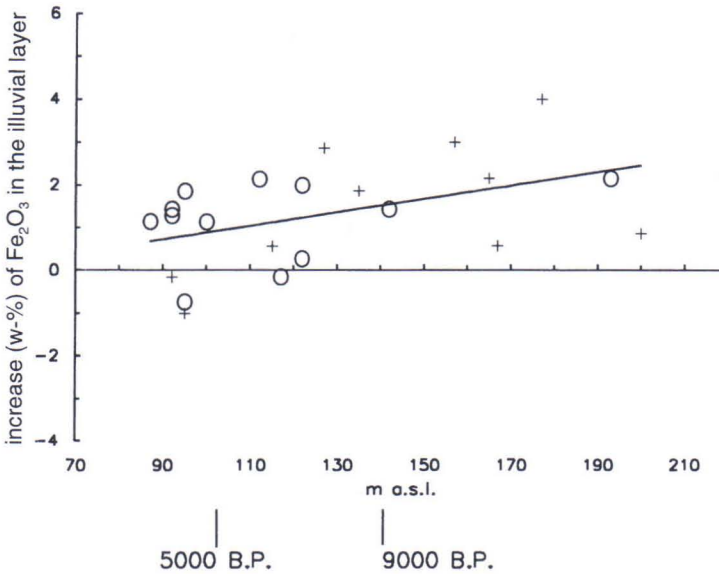


Fig. 4b. Total enrichment of Fe<sub>2</sub>O<sub>3</sub> in the illuvial layer of podzols in thick tills plotted against altitude of the sampling site (ageing). Samples marked with an open circle (o) were taken from the industrial areas of Kuopio and Siilinjärvi and those with a cross (+) from the background area (see also the text).

line shows that the intensity of leaching, and the rate of maturing, increased only slowly with the age of the podzol (Fig. 4a).

The dispersion in Figure 4a shows that the concentration of silica in the eluvial layer varied widely in both the younger and older podzols. As also seen in Figure 4a, a few of the younger profiles in the industrial area of Siilinjärvi displayed as great an accumulation of  $\text{SiO}_2$  in the eluvial layer as did the older podzols in the background area. Negative values in Figure 4a refer to profiles in which the podzolic layers were weakly distinguished and the parent till was rich in either silt or coarse sand and gravel. However, in the case of tills rich in silt, the variation in total concentrations of  $\text{SiO}_2$  within the profile could not be clearly linked to the primary layering.

Despite of the potential inaccuracy in the total  $\text{SiO}_2$  concentrations, it is concluded that accumulation of  $\text{SiO}_2$  in the eluvial layer of podzols was minimal in the industrial areas, and in particular in Siilinjärvi, relative to the accumulation in podzols of the background area. Podzols in the background area, where the parent till at study sites was predominantly sandy, showed a slow accumulation of silica in the eluvial layer with the age (Fig. 4a).

#### Aluminium and iron

Several studies have suggested that the total enrichment of Fe and Al oxides in the illuvial (B) and transitional zone (BC) layers reveals the maturity and rate of podzolization (Aaltonen 1935, 1939 and 1941, Petersen 1976, Rieger 1983). In the present study, the increase of  $\text{Fe}_2\text{O}_3$  in the illuvial layer relative to the eluvial layer was determined by subtracting the total concentrations of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in the E layer from those in the B layer. Similarly to the concentrations of silica in the eluvial layer shown in Figure 4a, the trend of the Fe enrichment in Figure 4b is expressed with a simple linear regression line. As can be seen, the total enrichment of  $\text{Fe}_2\text{O}_3$  tended to

be slightly greater in the illuvial layer of the oldest podzols than in that of the youngest. This trend was more pronounced in profiles of sandy tills than other till types. Since the regression line slopes only gently, it is concluded that the accumulation of  $\text{Fe}_2\text{O}_3$  in the illuvial layer has increased very slowly with ageing.

The mean difference between the total concentrations of  $\text{Al}_2\text{O}_3$  in the eluvial and illuvial layers was smaller than the mean difference between the total concentrations of  $\text{Fe}_2\text{O}_3$  (Table 2). The concentration of  $\text{Al}_2\text{O}_3$  was maximum in the BC layer, whereas concentration of  $\text{Fe}_2\text{O}_3$  obtained a maximum in the B layer (Table 2). Just as for Fe in the B layer (Fig. 4b), the enrichment of Al in the BC layer was slightly greater in the older than the younger podzols. Also similarly to Fe, the change with age was more detectable in sandy tills than in tills rich in silt or coarse sand and gravel.

#### Alkali and earth alkali metals

As seen in Table 2, mean and median values of total concentrations of MgO, CaO,  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  did not vary much vertically within the profile in either the industrial or background areas. On the other hand, the total concentrations varied from profile to profile indicating compositional differences in the parent tills of the study sites. Differences were greatest in the concentrations of Mg and Ca (Table 2).

It is appropriate to point out that the total concentrations of alkali and earth alkali metals are linked to the main minerals, feldspars and ferromagnesian minerals. Therefore, minimal differences in the mean total concentrations within the profile, from podzolic layers to the parent till, also indicate a minimal difference in the composition of the main minerals within the profile (Table 2) (Melkerud 1983). The element variation between profiles, on the other hand, implies local differences in the proportions of the main minerals. However, this



variation did not follow the compositional change of the bedrock (Fig.1).

The distribution of individual elements within the profile (see mean and median values of Table 2) pointed to weak silicate weathering. The variation in total CaO and Na<sub>2</sub>O within the profile was minimal, indicating the resistance of Ca- and Na-bearing silicates and therefore only a weak leaching of Ca and Na from the eluvial layer downwards in the profile during podzolization. Lower total contents of MgO and K<sub>2</sub>O in the eluvial layer and slowly increasing values downwards in the profile suggest a partial weathering of Mg- and K-bearing minerals from the eluvial layer during podzolization (Table 2).

### Total concentrations of major elements in profiles of shallow tills

#### Silicon

On average, total concentrations of SiO<sub>2</sub> in the eluvial layer were greater in shallow than in thick tills (Table 2). This could indicate that the shallow till is more susceptible to leaching than the thick till (Räsänen & Jylänki 1990). However, the thinness of the eluvial layer in shallow tills did not support this interpretation. On the other hand, the number of shallow tills sampled was much smaller than the number of thick tills.

Alternatively, shallow tills in rocky terrain might have been outwashed by water during the transgressions of the Ancylus and Suursaimaa lakes, with resultant re-sedimentation of quartz-rich sand in the topmost part of the till. According to the field observations, most holes in the bedrock at an altitude less than 100 metres and sporadically also at higher altitudes were filled with shore sand or gravel. Careful search nevertheless failed to reveal primary layering in the profiles of the shallow tills.

It can reasonably be assumed, of course, that the physical and chemical changes taking

place during podzolization would mask any signs of the re-sedimentation. And soil processes would have effected more marked changes in the profiles in shallow tills, and especially in red-brown profiles, than in thick tills.

Neither did the distribution of total silica in red-brown profiles reveal anything about a possible re-sedimentation in shallow tills. As can be seen from Table 2, total concentrations of SiO<sub>2</sub> were low in samples from red-brown profiles. The low values were due to the difficulty of dissolving these Fe-rich samples in strong acids. Part of the dissolved silica re-precipitated during digestion, and the same thing happened in duplicate leaches. In explanation of this, Niskavaara (1980) has noted that exceptionally high contents of Fe and Al in a sample may promote the re-precipitation of silica during acid digestion. The silica concentrations measured in the red-brown soil samples (Table 2) were thus not comparable with those of the profiles with distinguishable podzolic layers.

#### Aluminium and iron

As seen in Table 2, the distribution of total Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> concentrations into eluvial and illuvial layers of the shallow till was generally similar to that in analogous layers of the thick till. A greater difference in the mean and median values of total Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> between the eluvial and illuvial layers of shallow than of thick tills would have indicated a more intensive leaching in the shallow tills. However, the results can be considered indicative only, owing to the smaller number of profiles sampled in shallow tills and the factors discussed in the preceding section.

It is further seen from Table 2 that the mean concentration of total Al<sub>2</sub>O<sub>3</sub> was slightly higher in red-brown soil samples than in the distinguishable eluvial and illuvial layers of shallow tills. The difference in total Fe<sub>2</sub>O<sub>3</sub> concentrations was more marked (Table 2).

Table 3 shows the variation between neighbouring profiles. Even though the light-coloured top layer typical of leaching could not be visibly distinguished in the red-brown soils, chemical analysis showed that Fe and Al had been leached from the top layer and enriched into the underlying layer. The difference between the top and lower soil layers of the red-brown soil profile was, however, distinctly less than the difference between distinguishable podzolic layers (Table 3, cf. Table 2).

Exceptionally, the red-brown profile at site No. 4 in Table 3 displayed a minimal variation in total contents of Fe and Al oxides within the profile. In this case the total concentration of Fe<sub>2</sub>O<sub>3</sub> was somewhat higher in the top than the underlying layer.

### Alkali and earth alkali metals

Compared with podzolic layers of the thick tills, those in shallow tills tended to exhibit lower concentrations of K<sub>2</sub>O, Na<sub>2</sub>O and MgO (Table 2). In particular, the red-brown soils were characterized by lower concentrations of alkali and earth alkali metals, as seen in the mean and median values in Table 2.

As the composition of the few neighbouring profiles in Table 3 demonstrates, the distribution of alkali and earth alkali metals within the profile varies widely in rocky terrains. For example, the total concentration of Na<sub>2</sub>O in the red-brown soil profile at site 7b was abnormally high in the upper layer compared with the lower layers (Table 3). Concentrations of CaO showed the same trend. The dif-

Table 3. Total concentrations (weight-%) of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, K<sub>2</sub>O, CaO and Na<sub>2</sub>O (total), and concentrations (weight-%) of the same oxides in the hot aqua regia leach (aq.) in selected shallow till profiles in the Kuopio area. Mineral soil samples were separately taken from profiles with grey eluvial (E) and brown illuvial (B) layers and from neighbouring profiles tinted with a red-brown colour. Samples from site No. 1 were taken from the same trench, where the colour of the upper mineral soil layer varied within a short distance from brownish grey to red-brown. The grain size in the aqua regia leach was <0.5 mm.

Site/ Layer	Al <sub>2</sub> O <sub>3</sub> total	Al <sub>2</sub> O <sub>3</sub> aq.	Fe <sub>2</sub> O <sub>3</sub> total	Fe <sub>2</sub> O <sub>3</sub> aq.	MgO total	MgO aq.	K <sub>2</sub> O total	K <sub>2</sub> O aq.	CaO total	CaO aq.	Na <sub>2</sub> O total	Na <sub>2</sub> O aq.
Site No.1												
grey E	10.2	0.36	1.9	0.40	0.8	0.04	1.9	0.04	2.7	0.10	3.2	0.04
upper red-b.	10.4	0.92	3.2	1.49	1.0	0.12	1.9	0.04	2.9	0.14	3.0	0.04
brown B	13.0	6.54	5.3	5.18	1.1	0.56	1.5	0.11	2.1	0.13	2.5	0.04
Site No. 4												
grey E	8.9	0.22	1.0	0.15	0.4	0.01	2.0	0	1.6	0.03	2.6	0.07
brown B	9.6	1.86	3.7	2.37	0.7	0.13	1.7	0.06	2.0	0.06	2.3	0.08
upper red-b.	12.3	2.57	12.9	11.29	0.7	0.42	2.1	0.15	1.1	0.04	1.9	0.08
lower red-b.	13.0	4.55	11.2	9.47	1.0	0.71	2.0	0.17	1.1	0.03	1.6	0.07
Site No. 8												
grey E	9.1	0.21	1.6	0.39	0.8	0.04	1.4	0.01	2.2	0.08	2.4	0.07
brown B	11.2	2.43	3.3	2.38	0.8	0.15	1.4	0.02	1.9	0.06	2.2	0.06
upper red-b.	12.7	0.90	1.6	1.26	0.3	0.18	0.6	0.06	2.4	0.06	3.9	0.07
lower red-b.	13.0	1.71	4.7	3.71	0.8	0.36	1.0	0.11	2.6	0.06	3.6	0.08
Site No. 7b												
upper red-b.	12.1	1.23	3.3	2.83	1.0	0.54	0.5	0.09	2.5	0.07	4.2	0.05
lower red-b.	12.7	4.27	8.6	8.29	1.6	1.39	0.9	0.31	1.9	0.06	3.4	0.04
lowest red-b.	14.7	10.46	11.0	8.96	3.3	3.12	1.8	1.07	1.0	0.09	1.6	0.06



ference in  $\text{Na}_2\text{O}$  and  $\text{CaO}$  concentrations between the top and lower layers was less at the other sites, but concentration levels varied considerably between the neighbouring profiles (see Table 3). It is, therefore, concluded that none of the profiles mentioned in Table 3 showed a distinct weathering of Ca- and Na-bearing minerals.

In contrast to Ca and Na, total concentrations of  $\text{MgO}$ , and to a lesser extent those of  $\text{K}_2\text{O}$ , were slightly lower in the top than the underlying layers of shallow tills irrespective of the profile type (Table 3). In a few cases the difference between the top and lower layers was marked, however, indicating a wide variation in the weathering rates of Mg- and K-bearing minerals.

### Distribution of aqua regia soluble elements in profiles of thick and shallow tills

Dissolving power of hot aqua regia for silicates

Räsänen et al. (1992b) have reported that hot aqua regia totally dissolves trioctahedral micas, Mg-bearing clay minerals and precipitates (see also Doležal et al. 1968). To verify this, in the present study a few test samples were examined by XRD before and after the hot aqua regia digestion. As seen in Figure 5, basal reflections of clay minerals at 12 Å and 14 Å disappeared, indicating their breakdown

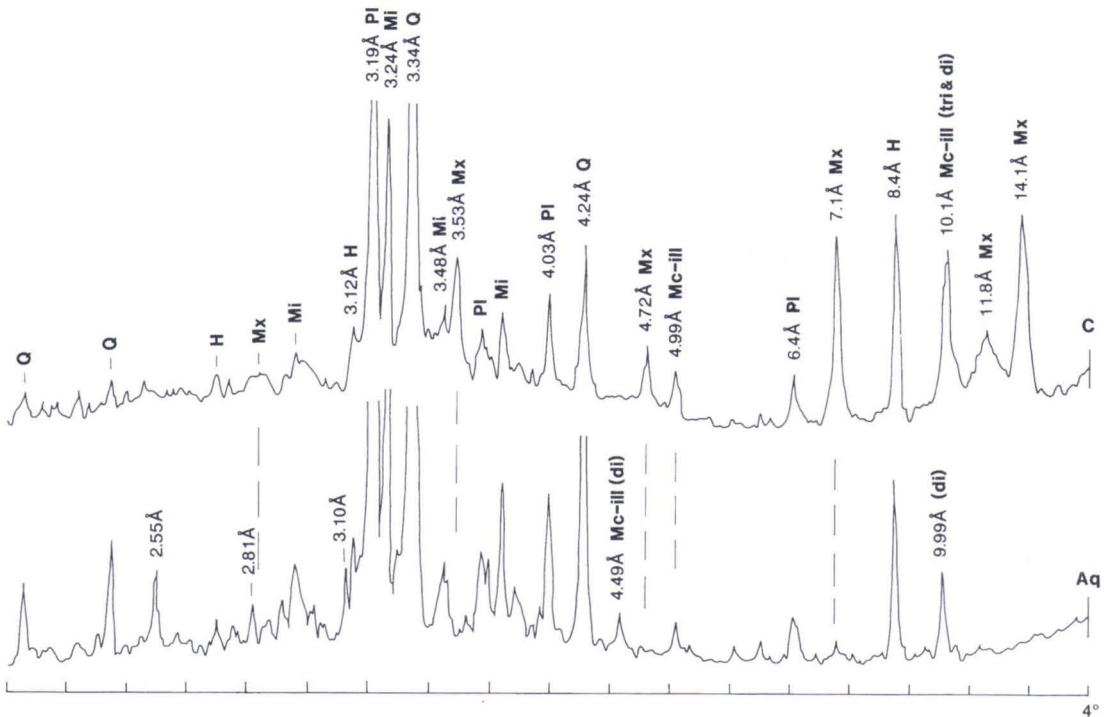


Fig. 5. XRD patterns recorded from the air-dried subsample (c) and the subsample leached with hot aqua regia (Aq) from the eluvial layer at site No. 30, Siilinjärvi. The grain size of the subsamples was  $<(40 - 50) \mu\text{m}$ . Keys to the XRD traces: Mx = mixed-layer clay, Mc-ill = illitic mica, di = dioctahedral and tri = trioctahedral, H = hornblende, Pl = plagioclase, Q = quartz, Mi = microcline (K-feldspar).

during digestion. Furthermore, the intensity of the 10 Å peak and the ratio of the intensities of the 5 Å and 10 Å peaks were decreased in the leached sample (Fig. 5). This indicates the decomposition of trioctahedral micas (mainly biotite). The residual peak at 10 Å and the increased intensity of the 5 Å peak after leaching are attributed to dioctahedral micas that remain undissolved, as also suggested earlier (Räisänen et al. 1992b).

Besides dioctahedral micas, the hot aqua regia failed to dissolve crystals of quartz, feldspars and amphiboles in any of the podzolized or parent till samples (see also Räisänen et al. 1992b). XRD traces attributed to quartz, feldspars and hornblende remained sharp after the digestion (Fig. 5). Räisänen et al. (1992b) have nevertheless inferred that minor amounts of elements, for example Ca, are dissolved from the surfaces of amphiboles and feldspars, in particular from partially weathered grains (cf. Foster 1973). Since the hot aqua regia selectively decomposed trioctahedral micas, clay minerals and precipitates, that fraction is here called the mica and clay mineral fraction. Furthermore, the chemical variation of the aqua regia soluble elements within the profile is assumed to indicate the weathering of trioctahedral micas and clay minerals and the accumulation of weathering products during the podzolization.

#### Areal variations in profiles with distinguishable podzolic layers

Profiles selected for the statistical examination of the aqua regia soluble elements were classified into three groups according to location: profiles of the Kuopio area, profiles of the Siilinjärvi area and profiles of the background area (Table 4). It should be noted that one in three of the profiles sampled in the Siilinjärvi area represented till rich in silt. The rest of the profiles were located in sandy tills or, occasionally, gravelly sandy till. Sandy till was the predominant parent soil in

profiles of the Kuopio and background areas. Furthermore, in view of the analogous distribution of the elements, samples from shallow tills with visible podzolic layers were grouped with those from thick tills of the Kuopio and background areas.

As seen in Table 4, the variation in the concentrations of aqua regia soluble Mg, Ca and K was wider in the Siilinjärvi area than in the Kuopio and background areas. Evidently the difference is due to the heterogeneity of tills in Siilinjärvi. Mean and median concentrations of Mg, Ca and K in podzolic layers and parent tills were nevertheless higher in the Siilinjärvi area than in Kuopio and the background area. This reflects the predominance of silt-rich tills in Siilinjärvi and of sandy tills in the other areas (Räisänen et al. 1992b).

The difference in the mean and median values of Mg between the eluvial and underlying layers was smaller in the Siilinjärvi area than in the Kuopio and background areas (Table 4). The distributions of K and Ca in profiles, however, revealed smaller differences in mean and median values between the top and lower layers in all three study areas.

Moreover, the mean and median values of Fe and Al concentrations in Table 4 indicate a weaker leaching of these elements from the eluvial layer into the illuvial and underlying layers in the Siilinjärvi study area than in the Kuopio and background areas. The variation in the distribution of Fe and Al concentrations within the profile was least in the silt-rich tills in the Siilinjärvi area. In all three study areas, the Fe and Al concentrations tended to be at maximum in the illuvial layer and to decrease slightly downwards in the profile. As can be seen from the mean and median values of Fe and Al concentrations in Table 4, the difference between the B and BC/C layers was greater in profiles of the Kuopio study area than in the Siilinjärvi and background areas.

In all three study areas, mean and median values of Al, Fe, Mg and K were lowest in the eluvial layer and increased downwards in the



Table 4. Mean (x), median (M) and range of concentrations of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, K<sub>2</sub>O and Na<sub>2</sub>O in hot aqua regia leaches (see also the text). The grain size in the aqua regia leach was <0.5 mm. The number of profiles is shown in brackets.

Background (13)			Kuopio (13)			Siilinjärvi (17)			Red-brown soils (20)			
x	M	range	x	M	range	x	M	range	x	M	range	
Al <sub>2</sub> O <sub>3</sub> w-%												
E	0.73	0.68	0.19-1.80	0.50	0.40	0.21-1.37	1.38	1.28	0.20-3.42			
B	2.40	2.25	0.94-4.97	2.84	2.90	1.77-4.17	1.89	1.90	0.47-3.65	3.17	1.96	0.40-10.46
BC/C	2.45	2.25	1.65-4.27	3.05	2.51	1.72-6.38	1.81	1.62	0.59-3.40			
Fe <sub>2</sub> O <sub>3</sub> w-%												
E	0.70	0.68	0.12-1.66	0.61	0.62	0.15-1.27	1.53	1.17	0.16-3.46			
B	2.20	2.05	0.32-3.45	3.03	2.93	2.17-4.12	2.08	1.91	0.37-4.53	4.86	4.44	0.59-11.80
BC/C	1.86	1.90	0.62-2.68	2.23	2.10	1.50-3.53	2.02	1.82	0.61-4.42			
MgO w-%												
E	0.16	0.13	0.02-0.58	0.11	0.09	0.01-0.38	0.50	0.39	0.03-1.37			
B	0.37	0.37	0.10-0.70	0.48	0.52	0.13-1.02	0.69	0.60	0.09-1.72	0.83	0.45	0.07-3.12
BC/C	0.46	0.46	0.21-0.74	0.53	0.49	0.12-0.91	0.68	0.57	0.23-1.74			
CaO w-%												
E	0.09	0.07	0.05-0.19	0.11	0.10	0.03-0.18	0.26	0.19	0.03-0.70			
B	0.15	0.16	0.06-0.30	0.18	0.16	0.06-0.33	0.34	0.29	0.05-0.84	0.09	0.06	0.03-0.28
BC/C	0.20	0.17	0.12-0.42	0.20	0.20	0.06-0.34	0.38	0.32	0.11-0.81			
K <sub>2</sub> O w-%												
E	0.03	0.03	0.01-0.07	0.04	0.03	0.00-0.11	0.11	0.07	0.02-0.40			
B	0.06	0.05	0.01-0.13	0.09	0.07	0.02-0.21	0.16	0.11	0.03-0.55	0.23	0.12	0.02-1.07
BC/C	0.09	0.06	0.03-0.24	0.13	0.12	0.02-0.23	0.18	0.14	0.04-0.58			
Na <sub>2</sub> O												
E	0.07	0.07	0.06-0.09	0.06	0.07	0.04-0.08	0.08	0.07	0.06-0.10			
B	0.07	0.07	0.06-0.09	0.07	0.07	0.04-0.08	0.08	0.07	0.06-0.12	0.06	0.07	0.04-0.08
BC/C	0.07	0.07	0.06-0.09	0.06	0.07	0.05-0.07	0.08	0.07	0.06-0.14			

profile, indicating the weathering of trioctahedral K-mica and Mg-bearing clay minerals, i.e. mainly biotite and chlorite (Räsänen & Jylänki 1990, Räsänen et al. 1994). Differences between the areas suggest a more intense weathering of micas and clay minerals in the Kuopio and background areas than in the Siilinjärvi area. Since concentrations of Na were similar throughout the profile, it can be presumed that the source of the aqua regia soluble Ca is partially weathered Ca-rich plagioclase and/or other Ca-bearing minerals, such as carbonates and apatite. According to Räsänen et al. (1992b) and Doležal et al.

(1968), these minerals decompose in hot aqua regia. Relevant to this, partially weathered plagioclase has been reported to exhibit slight alterations at grain edges and along cleavage zones (Meunier & Velde 1976). Epidote is another possible source for aqua regia soluble Ca, though its solubility in hot aqua regia is unknown (cf. Sverdrup 1990).

As the range of concentrations in Table 4 indicates, the distribution of the aqua regia soluble elements within the profile varied widely from sampling site to sampling site. The main reason for this is the difference in composition of the parent tills. Moreover, re-

sults of the aqua regia analysis better show the intensity of podzolic processes, viz. the intensity of leaching in the eluvial layer and precipitation of Fe and Al into the B and BC layers within the profile, than do results of the total dissolution analysis (cf. Tables 2, 3 and 4).

Comparisons of red-brown soil profiles and profiles with distinguishable podzolic layers

Element concentrations of the composite samples in Table 4 reveal a few distinct features of the red-brown profiles. Mean and median values of Fe were very much higher and those of Ca were lower in red-brown soils than in visible podzolic layers and parent tills. Moreover, the variation of Al was greater in red-brown soils than in visible podzolic layers. As seen in Table 4, however, mean concentrations of Al, Mg and K, and in particular the mean concentration of Na in red-brown soils were similar to those in visible podzolic layers and parent tills.

Table 3 shows a wide variation in element concentrations between neighbouring profiles of the shallow till. In spite of this variation, contents of Fe, Al, Mg and K were lower in the top layer of the red-brown soil profiles and increased downwards, resembling the element distribution within profiles with visible eluvial and illuvial layers (cf. Tables 3 and 4). It can be concluded that, as in the visible eluvial layer, the weathering of K-micas and Mg-bearing clays (chlorite) was the predominant weathering process in the top layer of the red-brown soil. Similarly to the illuvial layer, the lower layers of red-brown soils are characterized by the enrichment of Al and Fe.

In contrast to the other samples reported in Table 3, red-brown soil samples from sites 4 and 7b exhibited closely similar concentrations of Fe and Mg in the aqua regia leach and the total dissolution. In addition, the lowest sample from site 7b exhibited similar concentrations of aqua regia soluble and total Al and

K. Evidently the samples from sites 4 and 7b were exceptionally rich in Mg-bearing clays. The sample from the lowest layer of the red-brown soil at site 7b also contained abundantly K micas. In this case the simultaneous decrease of K and Mg from top to lower layers indicates an intensive weathering of K-micas in the top layer. However, the abnormally high concentrations of total Ca and Na in the top layer suggest, rather, a primary layering of the shallow till at this site.

As seen in Table 3, contents of Ca and Na, both in the aqua regia leach and in total dissolution, varied within the profile less at the other sites than at site 7b. Nevertheless, these examples demonstrate the variability of mineralogy and podzolic processes in profiles of shallow tills. In some cases the element distribution indicates the weathering of mica and clay minerals during soil formation, and in some cases compositional differences seem to be caused by the primary mineral layering.

Correlations between the aqua regia soluble elements

In view of the wide variation in element concentrations, correlation coefficients were calculated by Spearman's rank correlation method rather than by Pearson's correlation analysis method, which is more sensitive to anomalous concentrations (Rock 1988). Correlation coefficients were separately determined for the eluvial, illuvial and BC/C layers and red-brown soils (Table 5). Samples of the eluvial and illuvial layers of shallow tills were grouped together with the corresponding samples of thick tills.

As can be seen in Table 5a, Fe, Al, K, Mg, and Ca were correlated significantly and positively in the eluvial layer, whereas concentrations of Na showed no dependence on the concentrations of these elements. In the illuvial layer, Fe correlated significantly only with Al. In addition, Mg, Ca and K correlated with each other, but not with Al and Fe as they did in the eluvial



Table 5. Spearman's rank correlation coefficients for Al, Fe, Mg, K, Ca and Na extractable in hot aqua regia, in the (a) eluvial layer (43 samples), (b) illuvial layer (43 samples), (c) BC and C layers (42 samples) of thick and shallow tills and (d) red-brown soils (20 samples). See also the text.

a)							b)						
	Al	Fe	Mg	K	Ca	Na		Al	Fe	Mg	K	Ca	Na
Al	1.00						Al	1.00					
Fe	0.88	1.00					Fe	0.85	1.00				
Mg	0.94	0.92	1.00				Mg	0.24	0.39	1.00			
K	0.78	0.78	0.86	1.00			K	0.03	0.21	0.83	1.00		
Ca	0.82	0.84	0.87	0.77	1.00		Ca	0.12	0.18	0.80	0.82	1.00	
Na	0.40	0.41	0.34	0.04	0.38	1.00	Na	-0.03	-0.02	0.32	0.22	0.35	1.00

c)							d)						
	Al	Fe	Mg	K	Ca	Na		Al	Fe	Mg	K	Ca	Na
Al	1.00						Al	1.00					
Fe	0.73	1.00					Fe	0.88	1.00				
Mg	0.29	0.62	1.00				Mg	0.86	0.69	1.00			
K	0.03	0.45	0.89	1.00			K	0.81	0.84	0.80	1.00		
Ca	-0.20	0.29	0.73	0.88	1.00		Ca	-0.01	-0.29	0.20	-0.22	1.00	
Na	-0.13	0.23	0.42	0.45	0.46	1.00	Na	0.17	0.18	-0.10	-0.08	-0.17	1.00

layer (Table 5b). These findings support the special character of the B layer in being enriched in Al and Fe. As seen in Table 5c, a similar enrichment of Al and Fe characterized the sample group of the BC and C layers. In contrast to the illuvial layer, however, Mg correlated significantly with Fe in the BC and C layers. In red-brown soils, Fe, Al, Mg and K correlated significantly with each other, whereas concentrations of Ca and Na showed no dependence on any other element (Table 5d).

Räsänen et al. (1992b) have suggested that significant correlations between concentrations of Al, Fe, Mg and K indicate the total dissolution of mica and clay minerals in the aqua regia leach. Significant correlations were found in samples of the eluvial layer and red-brown soils but not in those of illuvial

layers. Possibly the abundance of sesquioxides in the illuvial and underlying layers has concealed the relationship between aqua regia soluble Fe, Al, Mg and K and so the fate of the micas and clay minerals.

Failing to find a correlation between the concentrations of Ca and those of K, Mg, Fe and Al in parent till samples, Räsänen et al. (1992b) concluded that a predominant source for aqua regia soluble Ca is partially weathered Ca-rich feldspar. By contrast, in the present study there was a significant correlation between Ca and K and Mg in all other samples except those from red-brown soil. This seems to indicate that the occurrence of Ca is associated in some degree with the abundance of mica and clay minerals in podzolic layers but not in the red-brown soils.

### MOBILITY OF ALUMINIUM AND IRON, AND SOIL ACIDITY NEAR THE CHEMICAL PULP MILL IN THE KUOPIO AREA

Räsänen (1989) and Jaloniemi and Räsänen (1991) have suggested that the activity

of Al in the soil significantly affects the buffering rate during acidification. Thus the main interest here is the distribution of Al into mobile and immobile fractions and the influence of Fe and pH on the behaviour of Al. It is assumed that the concentrations of Al and Fe in easily leachable, exchangeable and chelated fractions reflect the mobility of these elements in the short-term, whereas their precipitation in the inorganic phase is a long-

term soil process (Berrow & Mitchell 1980, Räsänen et al. 1992a, Gustafsson et al. 1995). In the interpretation of the data, profiles with distinguishable eluvial and illuvial layers, both from shallow and from thick tills, were assumed to represent natural, undisturbed podzolization. As suggested by Jaloniemi and Räsänen (1991), the profiles tinted red-brown represented disturbed podzolic soils in the rocky terrain.

### Variation of acidity (pH) in distinguishable podzolic layers and in red-brown soils

In all three extracts ( $\text{NH}_4\text{NO}_3$ ,  $\text{AS}_{\text{pH}2.3-2.4}$ , KCl) of samples from the Kuopio area the lowest values of pH were obtained for samples of the eluvial layer and the highest ones for samples of the illuvial layer (Table 6). As can be seen, the pH of the red-brown soils (Table 6c) lies between the pH values of the eluvial (Table 6a) and illuvial (Table 6b) layers.

The pH values were 0.1 - 0.4 higher in the ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) than the potassium chloride (KCl), owing to the weaker ionic strength of the  $\text{NH}_4\text{NO}_3$  solution (Bache 1985). The difference in pH between the non-acidified and acidified ( $\text{AS}_{\text{pH}2.3-2.4}$ ) salt extracts was 0.3 - 1.3. The difference was distinctly greater for samples of the eluvial layer than those of the illuvial layer and red-brown soils.

### Distribution of aluminium and iron in geochemical fractions

#### Effectiveness of extractants

Easily leachable and water-soluble Al and Fe were determined by the dilute  $\text{NH}_4\text{NO}_3$  extraction method, and exchangeable Al ( $\text{Al}_{\text{ex}}$ ) and Fe ( $\text{Fe}_{\text{ex}}$ ) by the KCl extraction method (stronger ionic strength). The extractability of Al and Fe in the acidified salt solution ( $\text{AS}_{\text{pH}2.3-2.4}$ ) was assumed to indicate their potential mobility in

a strongly acidic environment (Räsänen 1989). As expected, the leachability of Al was much lower in the dilute  $\text{NH}_4\text{NO}_3$  than in the  $\text{AS}_{\text{pH}2.3-2.4}$  and KCl extracts, but the difference between the  $\text{AS}_{\text{pH}2.3-2.4}$  and KCl extracts was surprisingly small, except for red-brown soils (Table 6). Compared with Al, the extractability of Fe in nonacidified and acidified  $\text{NH}_4\text{NO}_3$  was mostly under the detection limit (10 ppm), and therefore not discussed here.

Trace elements available for plants are commonly determined by extraction with a mixture of ammonium acetate and the chelating agent EDTA, buffered at pH 3.5 (Lakanen & Erviö 1971). According to Lakanen and Erviö (1971), this mixture extracts elements that are chelated with the soil organic matter as well as exchangeable and readily soluble elements. Berrow and Mitchell (1980) and Farmer et al. (1983) report that chelating agents such as EDTA selectively extract chelated ions from organic and organomineral complexes, whereas acid oxalate mainly removes ions co-precipitated with or adsorbed and occluded by inorganic oxides or other amorphous compounds.

Parfitt and Henmi (1982), Farmer et al. (1983) and Gustafsson et al. (1995) report that acid oxalate dissolves imogolite, proto-imogolite allophane and poorly ordered hydrated iron oxides. However, Carlson (1982) and Wada (1989) note that it also extracts organ-



Table 6. pH in  $\text{NH}_4\text{NO}_3$ ,  $\text{AS}_{\text{pH}2.3-2.4}$  and KCl extracts, and mean (x), median (M) and range values of Al and Fe species in samples of (a) the eluvial layer (16 samples), (b) the illuvial layer (9 samples) and (c) the red-brown soil profile (18 samples) from profiles in the Kuopio study area. The grain size in the weak leaches was <0.5 mm (see also the text).

(a)				(b)			
	x	M	range		x	M	range
pH( $\text{NH}_4\text{NO}_3$ )	3.70	3.70	3.30-4.20	pH ( $\text{NH}_4\text{NO}_3$ )	4.30	4.40	3.45-4.85
pH( $\text{AS}_{\text{pH}2.3-2.4}$ )	2.70	2.70	2.55-3.20	pH ( $\text{AS}_{\text{pH}2.3-2.4}$ )	3.65	3.70	2.90-4.00
pH(KCl)	3.50	3.50	3.10-4.10	pH (KCl)	4.20	4.35	3.30-4.60
speciation of aluminium	c(ppm)	c(ppm)	c(ppm)	speciation of aluminium	c(ppm)	c(ppm)	c(ppm)
easily leachable Al ( $\text{NH}_4\text{NO}_3$ )	30	30	10-70	easily leachable Al ( $\text{NH}_4\text{NO}_3$ )	50	35	10-120
Al in acidic medium ( $\text{AS}_{\text{pH}2.3-2.4}$ )	180	160	110-380	Al in acidic medium ( $\text{AS}_{\text{pH}2.3-2.4}$ )	290	290	220-370
exchangeable Al (KCl)	230	190	100-410	exchangeable Al (KCl)	230	210	0-520
chelated Al [( $\text{NH}_4\text{Ac}+\text{EDTA}$ )-KCl]	390	240	20-1730	chelated Al [( $\text{NH}_4\text{Ac}+\text{EDTA}$ )-KCl]	1490	1290	310-2600
precipitated Al [ $\text{NH}_4\text{Ox}-(\text{NH}_4\text{Ac}+\text{EDTA})$ ]	240	220	0-890	precipitated Al [ $\text{NH}_4\text{Ox}-(\text{NH}_4\text{Ac}+\text{EDTA})$ ]	6690	6600	1070-14270
sum ( $\text{Al}_{\text{ex}}+\text{Al}_{\text{ch}}+\text{Al}_{\text{pr}}$ )	860	650	-	sum ( $\text{Al}_{\text{ex}}+\text{Al}_{\text{ch}}+\text{Al}_{\text{pr}}$ )	8410	8100	-
speciation of iron	c(ppm)	c(ppm)	c(ppm)	speciation of iron	c(ppm)	c(ppm)	c(ppm)
exchangeable Fe (KCl)	80	60	10-390	exchangeable Fe (KCl)	40	40	10-110
chelated Fe [( $\text{NH}_4\text{Ac}+\text{EDTA}$ )-KCl]	730	550	130-1600	chelated Fe [( $\text{NH}_4\text{Ac}+\text{EDTA}$ )-KCl]	1160	710	340-3720
precipitated Fe [ $\text{NH}_4\text{Ox}-(\text{NH}_4\text{Ac}+\text{EDTA})$ ]	490	250	0-1270	precipitated Fe [ $\text{NH}_4\text{Ox}-(\text{NH}_4\text{Ac}+\text{EDTA})$ ]	6540	5710	4220-13890
sum ( $\text{Fe}_{\text{ex}}+\text{Fe}_{\text{ch}}+\text{Fe}_{\text{pr}}$ )	1300	860	-	sum ( $\text{Fe}_{\text{ex}}+\text{Fe}_{\text{ch}}+\text{Fe}_{\text{pr}}$ )	7740	6460	-

ically complexed Fe and Al.

As reported by Jaloniemi and Räsänen (1991), the leaching power of  $\text{NH}_4\text{Ac}$  at pH 3.5 with added chelating EDTA agent is close to or slightly less than that of Na-pyrophosphate at pH 10, but much weaker than that of  $\text{NH}_4$  oxalate buffered at pH 3.0 (see also Räsänen et al. 1992a). Sodium pyrophosphate extractant is conventionally used for the total quantification of organically bound Al and Fe

(Blakemore et al. 1981, Parfitt & Henmi 1982, Farmer et al. 1983).

Here it is proposed that Al and Fe extractable in acidic  $\text{NH}_4\text{Ac}+\text{EDTA}$  are less firmly bound in organic and inorganic complexes than are oxalate extractable Al and Fe (see Farmer et al. 1980). Since acid  $\text{NH}_4\text{Ac}+\text{EDTA}$  extracts both the chelated and exchangeable Al and Fe, concentrations of Al ( $\text{Al}_{\text{ch}}$ ) and Fe ( $\text{Fe}_{\text{ch}}$ ) in the chelated fraction were calculated

Table 6. cont.

c)	x	M	range
pH(NH <sub>4</sub> NO <sub>3</sub> )	3.80	3.80	3.40-4.50
pH(AS <sub>pH2.3-2.4</sub> )	3.20	3.10	2.40-4.10
pH(KCl)	3.70	3.65	3.10-4.40
speciation of aluminium	c(ppm)	c(ppm)	c(ppm)
easily leachable Al (NH <sub>4</sub> NO <sub>3</sub> )	80	70	40-230
Al in acidic medium (AS <sub>pH2.3-2.4</sub> )	320	320	180-540
exchangeable Al (KCl)	500	460	210-1050
chelated Al [(NH <sub>4</sub> Ac+EDTA)-KCl]	1600	730	0-6510
precipitated Al [NH <sub>4</sub> Ox-(NH <sub>4</sub> Ac+EDTA)]	2940	1900	90-12560
sum (Al <sub>ex</sub> +Al <sub>ch</sub> +Al <sub>pr</sub> )	5040	3090	-
speciation of iron	c(ppm)	c(ppm)	c(ppm)
exchangeable Fe (KCl)	90	90	10-210
chelated Fe [(NH <sub>4</sub> Ac+EDTA)-KCl]	1730	1710	660-3560
precipitated Fe [NH <sub>4</sub> Ox-(NH <sub>4</sub> Ac+EDTA)]	4560	3650	0-9870
sum (Fe <sub>ex</sub> +Fe <sub>ch</sub> +Fe <sub>pr</sub> )	6380	5450	-

by subtracting the concentrations in KCl extracts from the concentrations in NH<sub>4</sub>Ac+EDTA extracts (Table 6). Similarly, the concentrations (Al<sub>pr</sub> and Fe<sub>pr</sub>) in the precipitated fraction were calculated by subtracting the concentrations in NH<sub>4</sub>Ac+EDTA extracts from the concentrations in NH<sub>4</sub> oxalate extracts. It is suggested that the Al and Fe in this fraction are mostly bound in inorganic compounds. In the absence of the IR analyses, the

type of short-range ordered minerals in which they exist in samples of the present study cannot be discussed (see Gustafsson et al. 1995).

In summary, the leachability of Al in both podzolic layers and red-brown soils increased in the order of the extractants dilute NH<sub>4</sub>NO<sub>3</sub> < acidified NH<sub>4</sub>NO<sub>3</sub>(AS<sub>pH2.3-2.4</sub>) ≤ KCl < NH<sub>4</sub>Ac+EDTA pH 3.5 < NH<sub>4</sub> oxalate pH 3.0. The leachability of Fe increased in the order KCl < NH<sub>4</sub>Ac+EDTA pH 3.5 < NH<sub>4</sub> oxalate pH 3.0. Exceptionally, in a few samples concentrations of Al and Fe were the same in NH<sub>4</sub>Ac+EDTA and acid oxalate extracts within the limits of the precision (zero in Table 6).

#### Comparisons between distinguishable podzolic layers and red-brown soils

As seen in Tables 6a and b, the mean and median concentrations of easily leachable and exchangeable Al, as well as the concentration of Al in acidic medium, were lowest in the eluvial layer and slightly higher in the illuvial layer. In both layers, the mean concentration of Al in acidic medium was surprisingly close to the concentration of exchangeable Al. Compared with the podzolic layers, mean and median concentrations of Al were noticeably increased in the easily leachable fraction and even more so in the exchangeable fraction of red-brown soils (Table 6c). Even though the concentrations of Al in the acidic medium were about the same in red-brown soils as in the illuvial layer, the concentrations of exchangeable Al exceeded the concentrations of Al in acidic medium in many of the red-brown soils.

In contrast to Al, the mean concentrations of the exchangeable Fe were rather low (Table 6). As seen in Tables 6a, b and c, the difference in the mean and median values was small between the podzolic layers and red-brown soils. However, the wide range in the concentrations indicated that single samples from the



Table 7. Spearman's rank correlation coefficients for pH values and species of Al and Fe (a) in samples (25) of the eluvial and illuvial layer in shallow and thick tills and (b) in samples (18) of the red-brown soil profile in the Kuopio study area. Keys: pH = pH of the  $\text{NH}_4\text{NO}_3$  extract,  $\text{pH}_2$  = pH of the  $\text{AS}_{\text{pH}2.3-2.4}$  extract,  $\text{pH}_k$  = pH of the KCl extract, Al = Al species in the  $\text{NH}_4\text{NO}_3$  extraction,  $\text{Al}_2$  = Al species in the  $\text{AS}_{\text{pH}2.3-2.4}$  extraction,  $\text{Al}_{\text{ex}}$  and  $\text{Fe}_{\text{ex}}$  = Al and Fe species in the KCl extraction,  $\text{Al}_{\text{ch}}$  and  $\text{Fe}_{\text{ch}}$  = calculated chelated Al and Fe species,  $\text{Al}_{\text{pr}}$  and  $\text{Fe}_{\text{pr}}$  = calculated precipitated Al and Fe species.

a)

	pH	$\text{pH}_2$	$\text{pH}_k$	Al	$\text{Al}_2$	$\text{Al}_{\text{ex}}$	$\text{Al}_{\text{ch}}$	$\text{Al}_{\text{pr}}$	$\text{Fe}_{\text{ex}}$	$\text{Fe}_{\text{ch}}$	$\text{Fe}_{\text{pr}}$
pH	1.00										
$\text{pH}_2$	0.81	1.00									
$\text{pH}_k$	0.97	0.80	1.00								
Al	-0.21	0.25	-0.12	1.00							
$\text{Al}_2$	0.47	0.73	0.56	0.56	1.00						
$\text{Al}_{\text{ex}}$	-0.29	0.12	-0.30	0.63	0.41	1.00					
$\text{Al}_{\text{ch}}$	0.49	0.75	0.48	0.36	0.54	0.28	1.00				
$\text{Al}_{\text{pr}}$	0.72	0.89	0.75	0.30	0.86	0.14	0.62	1.00			
$\text{Fe}_{\text{ex}}$	-0.59	-0.26	-0.55	0.51	0.19	0.47	-0.01	-0.12	1.00		
$\text{Fe}_{\text{ch}}$	-0.01	0.27	-0.16	0.23	0.08	0.54	0.49	0.13	0.16	1.00	
$\text{Fe}_{\text{pr}}$	0.77	0.84	0.73	0.14	0.70	0.17	0.64	0.86	-0.19	0.32	1.00

b)

	pH	$\text{pH}_2$	$\text{pH}_k$	Al	$\text{Al}_2$	$\text{Al}_{\text{ex}}$	$\text{Al}_{\text{ch}}$	$\text{Al}_{\text{pr}}$	$\text{Fe}_{\text{ex}}$	$\text{Fe}_{\text{ch}}$	$\text{Fe}_{\text{pr}}$
pH	1.00										
$\text{pH}_2$	0.90	1.00									
$\text{pH}_k$	0.97	0.87	1.00								
Al	0.18	0.40	0.24	1.00							
$\text{Al}_2$	0.32	0.44	0.41	0.74	1.00						
$\text{Al}_{\text{ex}}$	0.12	0.38	0.09	0.65	0.44	1.00					
$\text{Al}_{\text{ch}}$	0.65	0.80	0.62	0.16	0.29	0.24	1.00				
$\text{Al}_{\text{pr}}$	0.79	0.94	0.77	0.43	0.36	0.52	0.69	1.00			
$\text{Fe}_{\text{ex}}$	-0.20	-0.14	-0.32	0.12	-0.07	0.46	-0.19	0.02	1.00		
$\text{Fe}_{\text{ch}}$	0.22	0.42	0.11	0.23	0.16	0.62	0.60	0.49	0.56	1.00	
$\text{Fe}_{\text{pr}}$	0.51	0.65	0.53	0.63	0.64	0.72	0.32	0.73	0.30	0.44	1.00

eluvial layer and also from red-brown soils contained surprisingly high concentrations of exchangeable Fe compared with the illuvial layer.

As seen in Tables 6a and 6b, mean and median values of both the chelated and precipitated Al were lowest in the eluvial layer and very much higher in the illuvial layer. The distribution of Fe in these fractions showed the same trend. Comparison of the results for the red-brown soils with those for the podzol-

ic layers shows the mean concentration of chelated Fe and to a lesser extent that of chelated Al to be higher in red-brown soils than in the illuvial layer, whereas the mean concentrations of precipitated Al and Fe were distinctly lower in red-brown soils than in the illuvial layer (cf. Tables 6a, b and c).

To summarize, in the eluvial layer Al and Fe were predominantly bound in the mobile fractions, whereas in the illuvial layer most was in the immobile fraction, i.e. precipitated

as short-range ordered minerals. This finding is in agreement with our general understanding of the chemical differentiation of podzolic layers (see e.g. De Coninck 1980, Farmer 1986). In contrast to profiles with distinguishable podzolic layers, the red-brown soils contained abnormally high concentrations of both Al and Fe in the mobile fractions. In particular, the high concentrations of exchangeable and chelated Al and chelated Fe characterized a few individual red-brown soil profiles, as seen from the range of concentrations in Table 6c (cf. Table 6a and b). As in the illuvial layer, most of the Al and Fe in red-brown soils occurred in the precipitated fraction, although in lower concentrations. The sum of the concentrations of exchangeable, chelated and precipitated Al and Fe was, however, distinctly lower in red-brown soil profiles than in profiles with distinguishable podzolic layers (Table 6).

As the range in concentrations of Al and Fe in Table 6 indicates, the quantity of Al and Fe in different geochemical fractions varied widely from profile to profile. The above-described differences between soil types based on mean and median values must therefore be considered only as indicating a trend.

#### Correlations between pH and geochemical fractions

Correlation coefficients for pH and geochemical fractions were calculated by Spearman's rank correlation method, since the Al and Fe concentrations in the geochemical fractions varied widely within the profile types. In the processing of the data, samples of the eluvial and illuvial layers of shallow and thick tills were grouped together. Samples from the red-brown soil profiles formed the comparative group, which consisted of both the composite samples from the whole profile and separate samples from the top and underlying layers. Results for profiles with distinguishable podzolic layers are presented in

Table 7a, and those for red-brown soil profiles in Table 7b.

As seen in the tables, correlations between the pH values in the three extracts were significant both in the profiles with distinguishable podzolic layers and in the red-brown soil profiles. In none of the soil types, however, did pH influence the concentrations of easily leachable and exchangeable Al in the sample. Only in podzolic layers did the leachability of Al in acidic medium display a positive and significant correlation with pH in the extracts. This correlation might indicate slight hydrolysis of Al during buffering reactions. As reported by Yuan (1963), the pH measured in a salt extract with or without protons added does not unambiguously express the activity or acidity of the Al and Fe ions themselves.

Tables 7a and 7b also show the positive and significant correlation coefficients between pH and precipitated Al and Fe, both in podzolic layers and in red-brown soils. This indicates that the increase in pH has promoted the precipitation of Al and Fe, as is characteristic of podzolization (Farmer 1986, Gustafsson et al. 1995). In contrast to precipitation of Al and Fe, the relationship between pH and chelated Al and Fe differed in red-brown soils and in profiles with distinguishable podzolic layers. In the red-brown soils the concentration of chelated Al correlated positively and significantly with all three pH values, whereas the concentration of chelated Fe seemed to vary independently of the pH (Table 7b). Also in podzolic layers, the correlation between chelated Fe and pH was insignificant, while the correlation between chelated Al and pH was significant in acidified salt extracts but not in nonacidified salt extracts (Table 7a). Nevertheless, the positive correlation in both profile types between the chelated and precipitated Al and pH in the acidified extract indicates that the chelation and complexation of Al is a strong buffering process which by binding protons prevents the decrease of pH.

As the correlation coefficients between Al



and Fe fractions in Tables 7a and 7b demonstrate, the behaviour of Al and Fe was to some extent analogous in the two profile types. Concentrations of precipitated Al and Fe were positively and significantly correlated (Table 7). In addition, in both profile types the concentration of Al in the easily leachable fraction correlated significantly with that in the exchangeable fraction, and the concentration of chelated Al with the concentration of pre-

cipitated Al. In contrast, the concentrations of easily leachable and exchangeable Al were more dependent on the rate of Fe precipitation in red-brown soil profiles than in profiles with distinguishable podzolic layers. This trend is rather confusing. In general, podzolic processes are characterized by the precipitation of Fe, which does not promote the mobility of Al (cf. Farmer et al. 1980, Huang 1991).

## Mineralogy of podzols in the Kuopio and Siilinjärvi region

### Profiles with distinguishable podzolic layers

#### Main minerals

Proportions of the main silicates were roughly estimated on the basis of intensity ratios of their strongest reflections. As Figures 6, 7 and 8 demonstrate, the fine fraction (<40 or <50  $\mu\text{m}$ ) of the podzolic layers and parent tills was dominated by quartz, plagioclase and K-feldspars. The mineral groups next in importance were with some variation amphiboles (hornblende), illitic micas and mixed-layer clay minerals.

In contrast to micas and clay minerals, it was difficult to estimate differences in the abundances of quartz, feldspars and hornblende within the profile (weathering rate) and between the three study areas. Very possibly the variation of hornblende within the profile (Figs. 6 and 8), as well as the variation of feldspars and quartz, is primarily due to the inhomogeneity of subsamples and the preparation method. The preferred orientation of phyllosilicates and in some cases the abundance of Fe precipitates, as discussed below, distort the proportions of the minerals (Wilson 1987).

#### Illitic micas

Figures 6, 7 and 8 illustrate the typical

behaviour of di- and trioctahedral illitic micas within the profile. The diffractograms in Figure 6 show an absence of micas in the eluvial, transition zone (EB) and illuvial layers and a minor occurrence of trioctahedral mica in the BC and C layers. Here there has been a total weathering of trioctahedral mica in the podzolic layers. In Figures 7 and 8 dioctahedral illitic mica is seen to dominate the eluvial (E) layer, while in Figure 8 the content of trioctahedral mica increases noticeably from the illuvial (B) to the BC layer. A decrease in the ratio of the intensities of the peaks at 5 Å and 10 Å in going from the eluvial layer to lower layers indicates the weathering of trioctahedral mica (Wiklander & Aleksandrović 1969). In the same way, the decrease in the intensity of the peak at 5 Å downwards in the profile could indicate a pedogenic origin for dioctahedral mica, i.e. dioctahedral mica is formed from trioctahedral mica in the eluvial layer during podzolization. Although the intensities of both the 5 Å and 10 Å peaks in Figures 7 and 8 decreased downwards in the profile, the fact that their ratio did not abruptly change suggests that the dioctahedral mica occurs in minor amount also in the B and BC/C layers. As Wilson (1987) and Fanning et al. (1989) have pointed out, a weak peak at 5 Å could indicate a trioctahedral mica and/or a minor presence of dioctahedral mica (see also Fig. 5).

The abundance of both illitic micas within the profile varied widely from one sampling

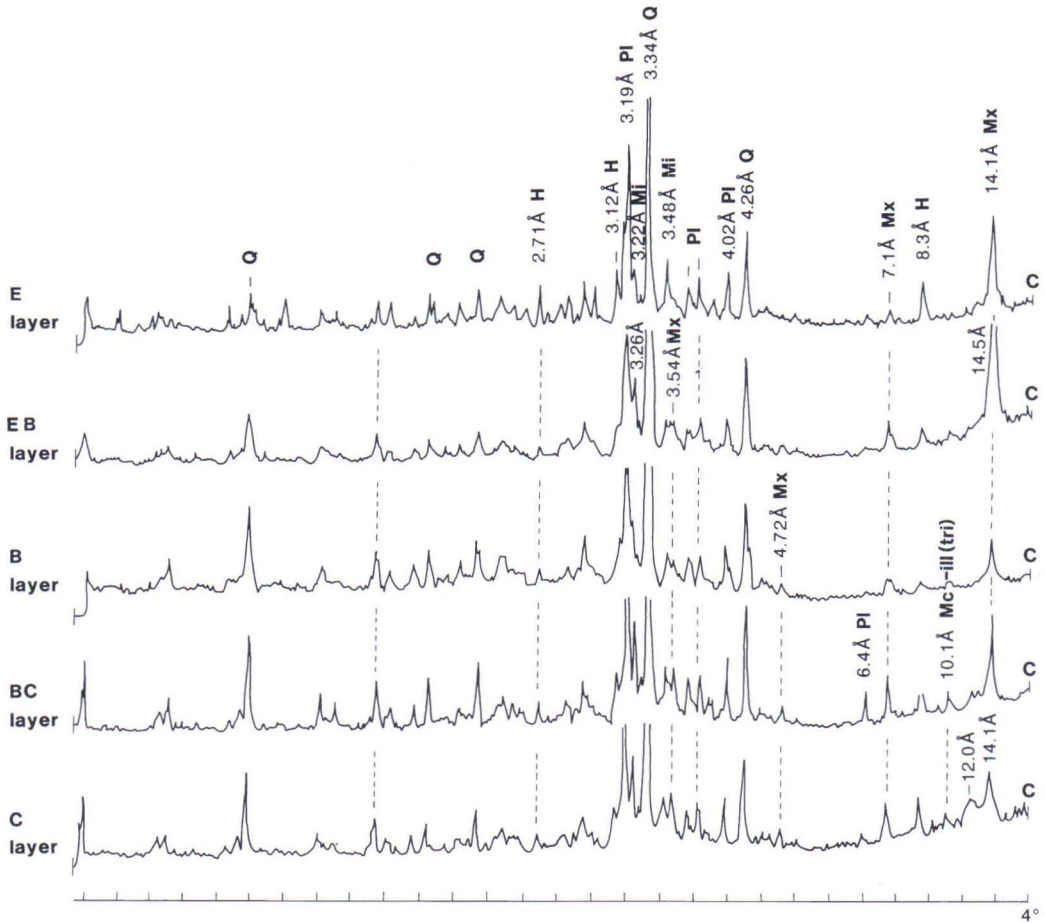


Fig. 6. XRD patterns of air-dried subsamples from the 9000-year-old podzol in the thick till at site No. 15b, Kuopio. The grain size of the subsamples was <math>(40 - 50) \mu\text{m}</math>. For keys see Fig. 5.

site to the next in all three study areas. Some differences can nevertheless be suggested. Both di- and trioctahedral illitic micas occurred throughout the profile only in the Sii-  
 linjärvi area. There were two types of mica occurrences in the Kuopio and background areas. In one, trioctahedral mica was lacking in the eluvial layer, but was the predominant mica in the less altered layers. At the same time dioctahedral mica was totally lacking. In the other type, dioctahedral illitic mica dominated the eluvial layer and decreased in abundance downwards in the profile. Trioctahedral

mica, in turn, was the predominant mica in the lower layers.

#### Clay minerals

##### *Eluvial layer*

Diffraction patterns recorded from the eluvial (E) layer of thick and shallow tills displayed a broad reflection with single or double maxima lying between 12 Å and 14 Å. This kind of trace indicates a variable composition of



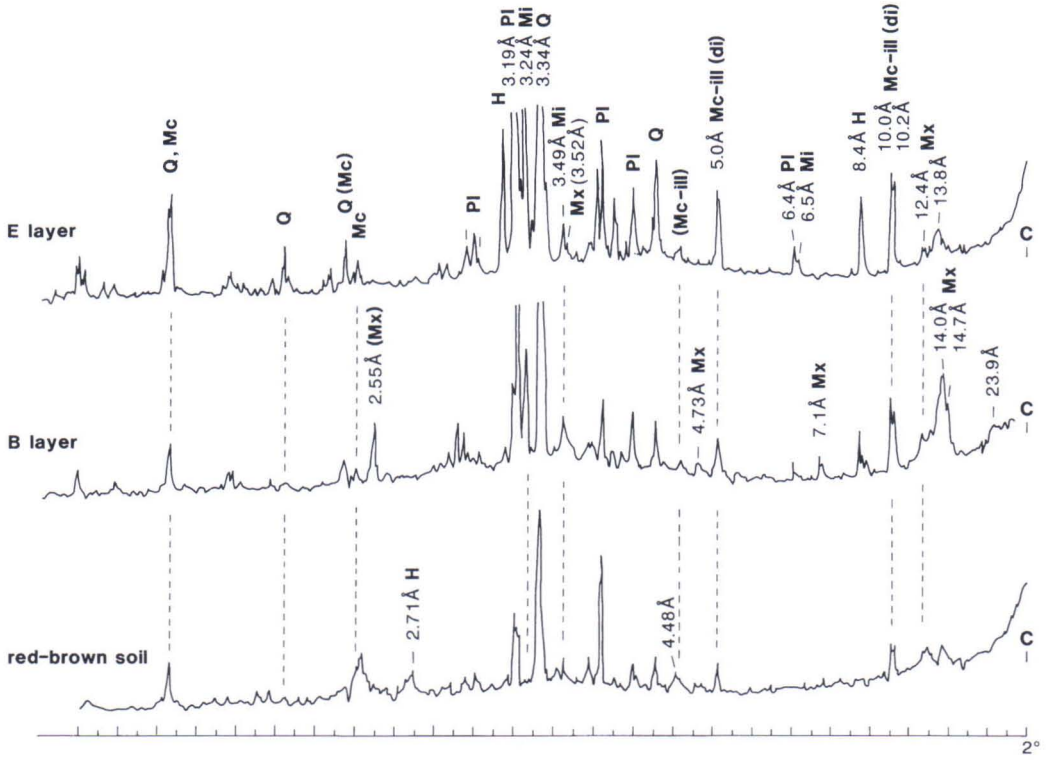


Fig. 7. XRD patterns of air-dried subsamples from the profile with distinguishable eluvial and illuvial layers and the red-brown soil profile in the shallow till at site No. 4, Kuopio. The grain size of the subsamples was  $<(40 - 50) \mu\text{m}$ . The age of the soil formation varied between 5000 and 7000 years. For keys see Fig. 5.

mixed-layer clay minerals (Figs. 9, 10 and 11a).

The XRD patterns in Figure 9a - 9c were recorded from the eluvial layer of samples of increasing age. Patterns in Figure 9a and b were attributed to a vermiculite-chlorite, and those in Figure 9c to vermiculite mixed with a minor amount of chlorite. In both cases the vermiculite contained Al-hydroxy interlayers. After the acidified salt extraction, vermiculite displayed an expanded peak of variable intensity at 15 Å. However, it did not show an expanding reflection upon ethylene glycol solvation. The occurrence of the residual 14 Å peak at 550°C (Figs. 9a - c) could, alternatively, indicate the discrete occurrence of chlorite. However, since the peak gradually shift-

ed towards 10 Å and at the same time decreased in intensity in samples of increasing age heated at 550°C, it is attributed to the presence of hydroxy interlayering in vermiculite rather than to the weathering of chlorite. Also, the increased intensity of the expanded peaks at 15 Å upon  $\text{AS}_{\text{pH}2.3-2.4}$  treatment shows a gradual vermiculization of chlorite with the age of the sample (Figs. 9a - 9c). Moreover, the 14 Å peak did not totally collapse upon K saturation, which indicates that vermiculite was present in the interstratified mixture (Sawhney 1989).

The hump reflection at 12.8 Å in Figure 9b is attributed to a minor presence of the interstratified mica-vermiculite (Sawhney 1989). Even though the behaviour of the peak at 12-

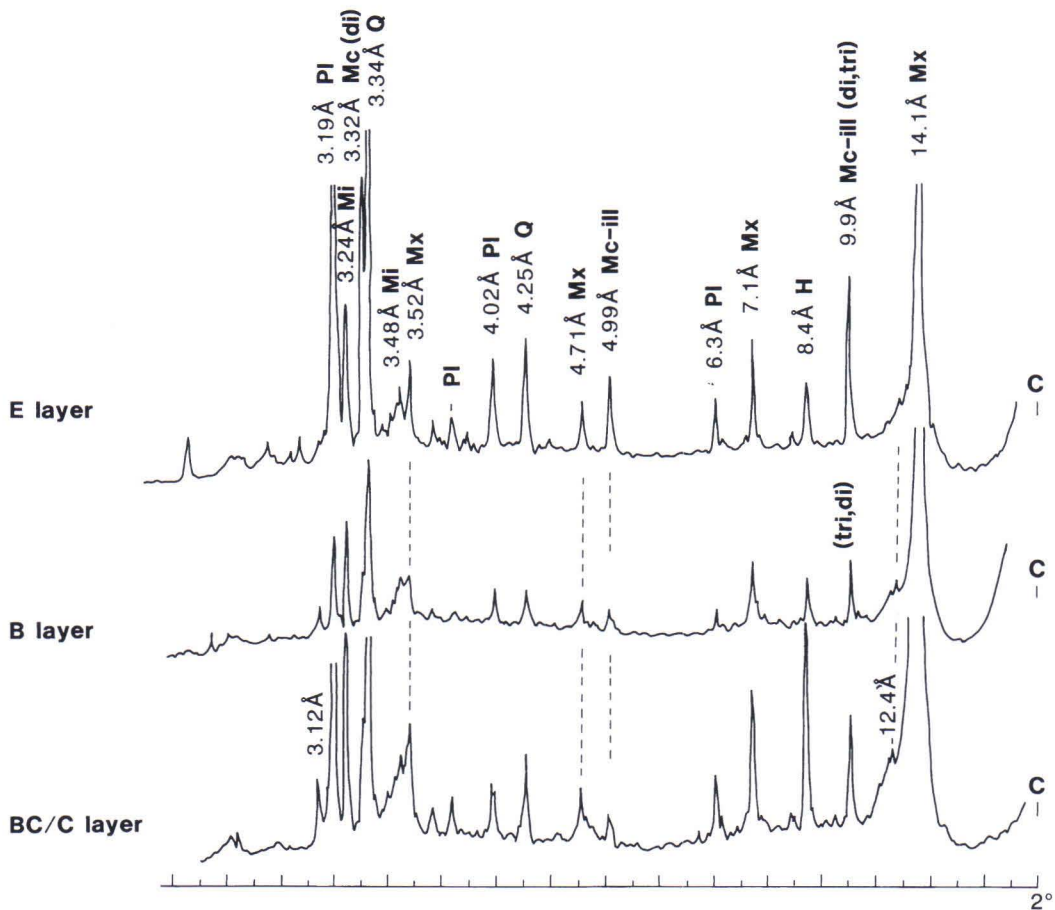


Fig. 8. XRD patterns of air-dried subsamples from the podzol in the thick till at site No. 35, Siilinjärvi. The grain size of the subsamples was <math><40 - 50\ \mu\text{m}</math>. The age of the podzolization is between 7000 and 9000 years. For keys see Fig. 5.

13 Å was obscured by the strong peak at 14 Å appearing with the various treatments, interlayers of vermiculite must also have been filled with hydroxy polymers (Fig. 9b). Vermiculite did not swell when solvated in ethylene glycol.

A weakly swelling mixed-layer clay which occurred in a few samples of the eluvial layer gave either a single peak at 12 - 13 Å (Fig. 10a, younger podzol) or diffuse traces between 11 and 14 Å (Figs. 10b and 11a, older

podzol). Even though the expanded peak at 17 Å diagnostic for smectite was not obtained upon ethylene glycol solvation (MacEwan & Wilson 1980), properties of this mixed-layer clay differed significantly from those of vermiculite-chlorite (shown in Figs. 9a - 9c). As seen in Figure 10a, the basal spacing of 12.8 Å expanded to 14.2 Å, broadening towards 16.5 - 17.2 Å upon ethylene glycol solvation. Figure 10b, in turn, shows a combination peak between 11 Å and 14 Å shifted towards 14 Å



with a weaker series of higher order reflections. The weak resistance against collapse on heating at 200°C indicates that interlayers of this clay possess a low degree of hydroxy interlayering. Unlike the sample of the younger podzol in Figure 10a, the sample in Figure 10b contained a minor amount of chlorite. The oxalate-treated sample depicted in Figure 11a

gave a weak peak at 14 Å on heating at 550°C and the clay was interpreted as an interstratification of vermiculite and mica with a minor content of chlorite.

As the XRD patterns in Figures 9 and 10 demonstrate, the properties of the mixed-layer clays after acidified salt extraction varied with the degree of interlayering and the pres-

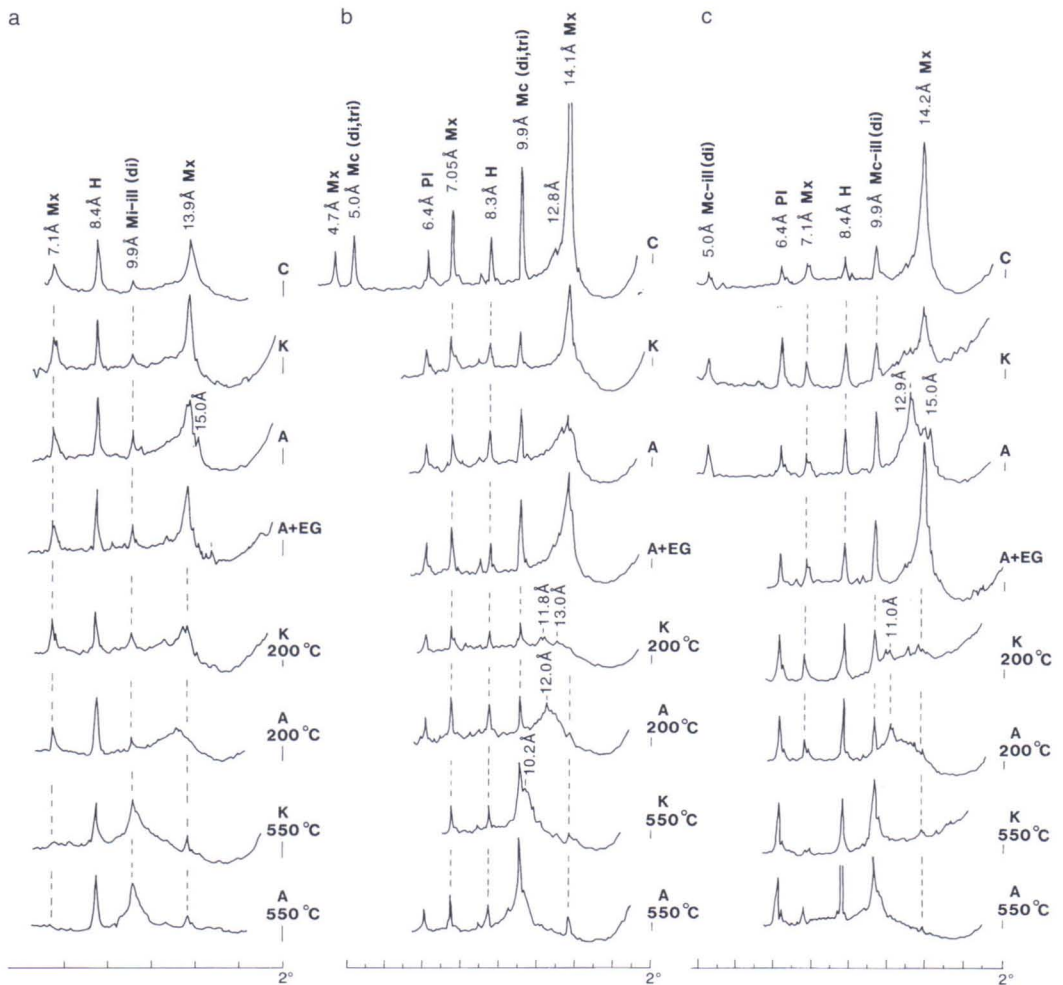


Fig. 9. XRD patterns of the eluvial layer from the podzols in thick till at sites (a) No. 29 (87 m a.s.l.) and (b) No. 35 (122 m a.s.l.) in Siliinjärvi and at site (c) No. 17 (135 m a.s.l.) in the background area. The grain size of the subsamples was <math>(40 - 50) \mu\text{m}</math>. The age of podzolization is ca. 5000 years at site No. 29 and 7000 - 9000 years at sites Nos. 35 and 27. Keys to treatments: C = air-dried, K = K saturation, A =  $\text{AS}_{\text{pH}2.3-2.4}$  extraction and EG = ethylene glycol solvation. See also keys for minerals in Fig. 5.

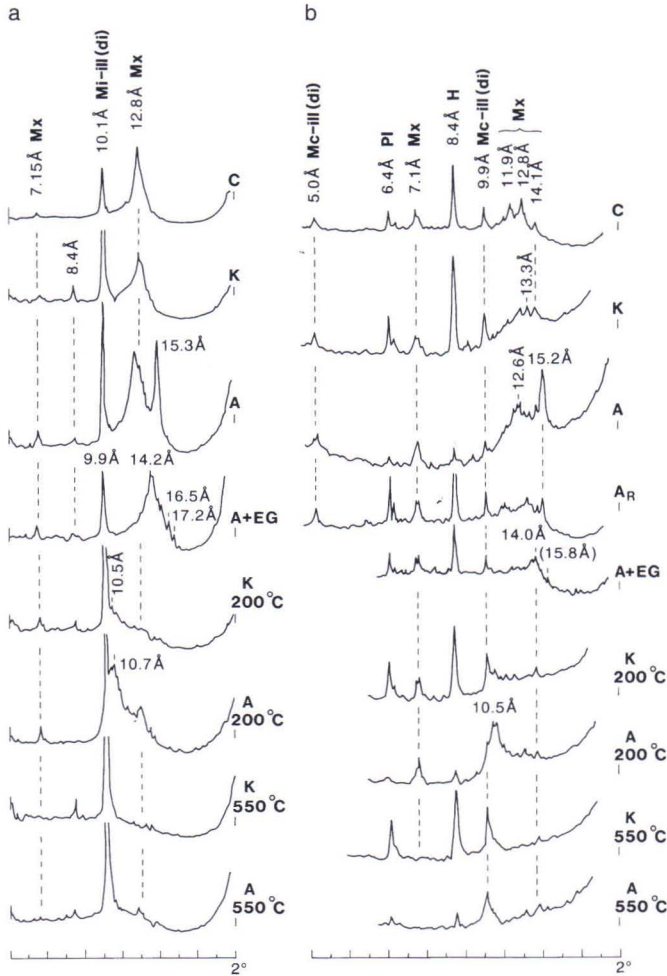


Fig. 10. XRD patterns of the eluvial layer from podzols (a) in the shallow till at site No. 4 (110 m a.s.l.) and (b) in the thick till at site No. 15a (190 m a.s.l.) in Kuopio. The grain size of the subsamples was <math><40 - 50\ \mu\text{m}</math>. The age of podzolization is 5000 - 7000 years at site No. 4 and ca. 9000 years at site No. 15a. For explanations see Figs. 5 and 9.

ence of chlorite. The mica-vermiculite without the chlorite component (Fig. 10a) showed a higher resistance against collapse after the acidified salt extraction and heating at 200°C than did the K-saturated mica-vermiculite. A similar kind of change was weakly seen in the sample of Figure 10b. In contrast to these clays, the heat-resistance of the vermiculite-chlorite and non-expanding mica-vermiculite in Figure 9 differed very little in the  $A_{S_{pH2.3-2.4}}$  and KCl treatments. Nevertheless, these examples demonstrate, in conformity with Räsänen et al. (1994), that the vermiculite in the eluvial layer can adsorb hydroxides in the interlayer

sites in a strong acidic medium.

Inspection of the XRD patterns allows a number of conclusions to be drawn on the occurrence of the mixed-layer clays relative to the age of podzols. Hydroxy-interlayered vermiculite with a minor content of chlorite and vermiculite-chlorite occurred in both young ( $\leq 5000$  B.P.) and old ( $> 5001$  B.P.) podzol profiles. In spite of this, the eluvial layer in most of the podzols older than 7000 years lacked chlorite. The weakly expanding mica-vermiculite occurred only in a few samples of the eluvial layer of shallow tills (5000 - 7000 years old) and the older podzols of thick tills



(>7000 years old). Non-expanding mica-vermiculite occurred rarely and it was not associated with any age group or till type.

*Illuvial layer and parent tills*

As seen from the examples in Figures 11b and c, 12 and 13, illuvial (B) and transitional zone (BC) layers and parent tills (C) were dominated by vermiculite-chlorite giving a basal spacing at 14.0 - 14.2 Å. This and other clays of the illuvial and less altered till layers (BC, C) were resistant against collapse on heating at 200 °C, indicating that the interlayers of the vermiculite were largely occupied by hydroxy polymers (Sawhney 1989). An asymmetrical reflection at about 10 Å and a weak residual peak at about 14 Å upon heating

at 550°C (Figs. 11a - b, 12 and 13) suggest the interstratification of vermiculite and chlorite (Gjems 1967, Sawhney 1989).

The broad reflection at 12 - 13 Å in Figure 13a-b was attributed to a minor content of mica-vermiculite interstratification. Even though, upon treatment, XRD traces of mica-vermiculite were partly obscured by reflections of vermiculite-chlorite, vermiculite in this interstratification also seemed to possess a high degree of interlayering (Fig. 13a - b).

In contrast to that in the eluvial layer, vermiculite-chlorite and mica-vermiculite in the B and BC layers and parent tills did not expand upon ethylene glycol solvation or after AS<sub>pH2.3 - 2.4</sub> extraction at room temperature (Figs. 12 and 13). Overall, the behaviour of vermiculite-chlorite of the lower soil layers

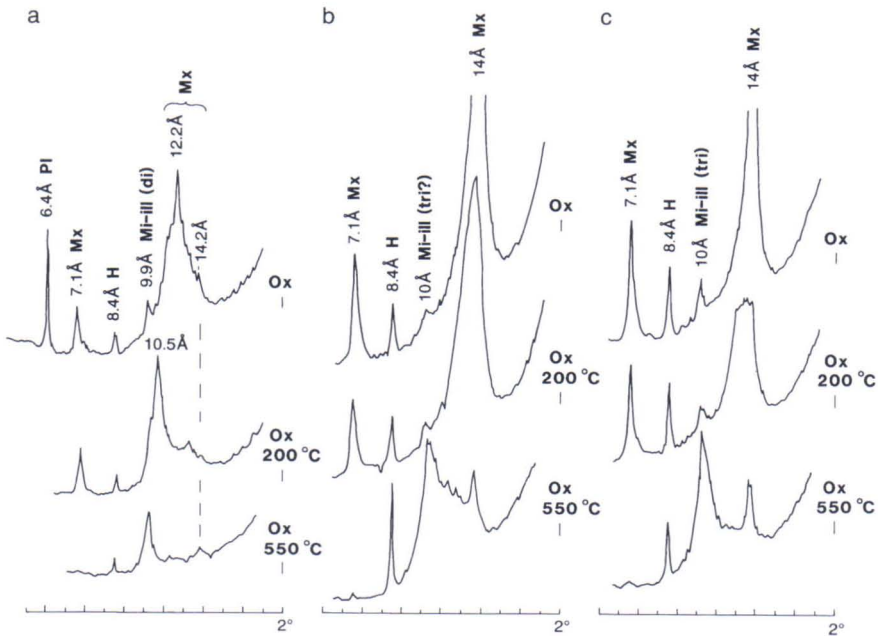


Fig. 11. XRD patterns of oxalate (Ox)-treated subsamples of the (a) eluvial, (b) illuvial and (c) BC layers of the 9000-year-old podzol at site No. 15a, Kuopio. The grain size of the subsamples was <10 µm. For explanations see Figs. 5 and 9.

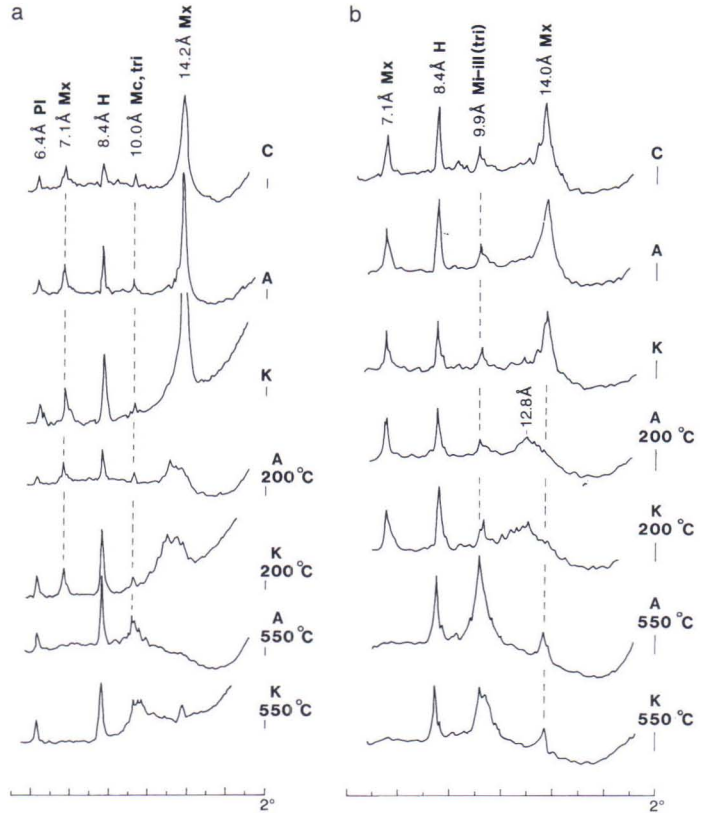


Fig. 12. XRD patterns of the (a) illuvial layer and (b) parent till from the 9000-year-old podzol at site No. 15a in Kuopio. The grain size of the subsamples was <math>(40 - 50) \mu\text{m}</math>. For explanations see Figs. 5 and 9.

upon K-saturation and heating did not differ much from the behaviour upon acidified salt extraction and heating. Comparable results were obtained for till samples earlier (Räisänen et al. 1992b).

The intensity of the  $14 \text{ \AA}$  peak upon heating at  $550 \text{ }^\circ\text{C}$  in most cases was greatest in the parent till and BC layer and increasingly smaller in the B layer (Figs 12 and 13). Likewise, as seen in Figure 11 for samples from site No. 15a, the increase in the  $10 \text{ \AA}$  reflection upon heating at  $550 \text{ }^\circ\text{C}$  was more marked in the BC than the B layer (see also Fig. 12). By contrast, the lattice of vermiculite in the eluvial layer collapsed even at  $200 \text{ }^\circ\text{C}$ . Broad traces between  $10 \text{ \AA}$  and  $14 \text{ \AA}$  for the sample of the illuvial layer (Fig. 11b) can be attributed to the more intense chloritization of ver-

miculite in the illuvial layer than in the eluvial or less altered layers (Olson 1988). It is therefore concluded that the abundance of chlorite and its vermiculization decrease gradually from the illuvial layer downwards to the parent till. Since clays of the illuvial layer of the 9000-year-old podzols were more resistant to collapse on heating than those of the younger podzols, it is suggested that the degree of interlayering of vermiculite increases with ageing.

However, leaving aside the above-mentioned exceptions, the properties of vermiculite-chlorite in the illuvial and less altered till layers differed little between the study areas and with the age of podzolization. Non-expanding mica-vermiculite occurred only rarely in the B and less altered layers.



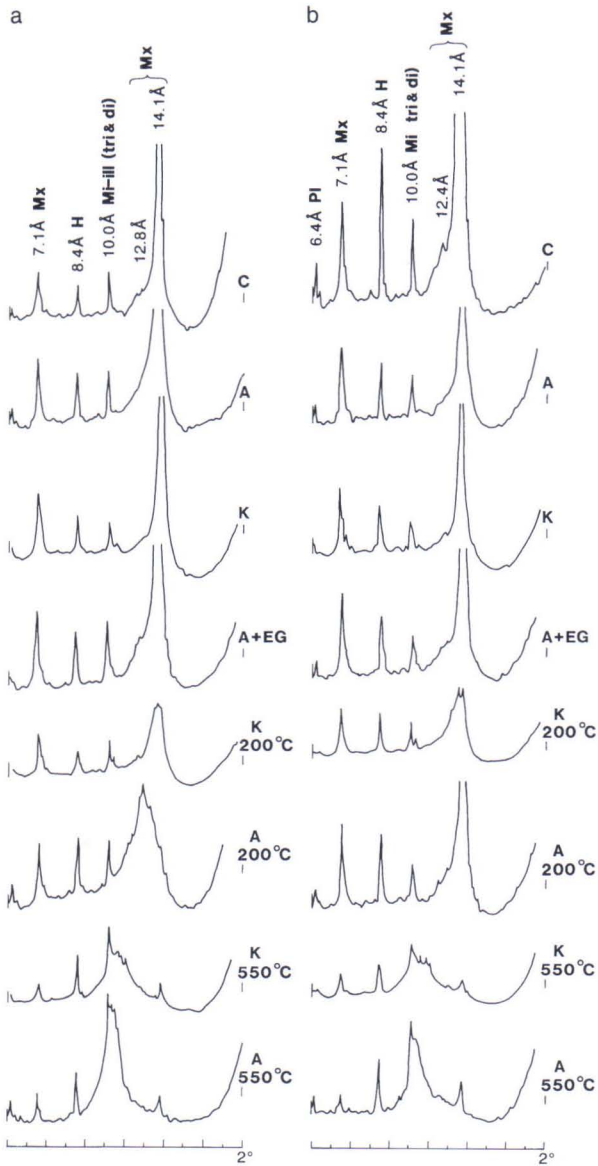


Fig. 13. XRD patterns of the (a) illuvial and (b) BC layers in the representative thick till at site No. 35 in Siilinjärvi. The grain size of the subsamples is  $<(40 - 50) \mu\text{m}$  and the age of podzolization 7000 - 9000 years. For explanations see Figs. 5 and 9.

## Red-brown soil profiles

### Main silicates

In contrast to the samples from visible podzolic layers, traces of the main minerals in red-brown soil samples were difficult to interpret

due to the abundance of Fe precipitates (Fig. 7). In most cases the peaks sharpened after the acid oxalate extraction. Like the visible podzolic layers, red-brown soils were dominated by quartz and feldspars. The abundance of amphiboles (hornblende) and illitic micas, however, varied more from profile to profile

than in profiles of the visible podzolic layers.

### Illitic micas

In general, micas occurred sporadically in the samples of red-brown soil profiles. Traces of micas, if present, were exclusively attributed to a dioctahedral type (Fig. 7), which could indicate that trioctahedral micas were either totally weathered from the fine fraction of the whole profile or that these soils did not originally contain any trioctahedral mica. Since concentrations of K in aqua regia leaches of the samples indicated the presence of biotite, it is assumed that trioctahedral micas occur at least in the coarser fraction of the red-brown soil, even though they may have been weathered totally from the fine fraction (see Tables 4 and 5).

### Clay minerals

Properties of the clay minerals in red-brown soils varied either from the top to lower layer or were unchanged through the profile. The XRD patterns in Figures 14a and b describe the representative red-brown profile at site No. 7a in which, upon treatment, the behaviour of the mixed-layer clay in the top layer differed from that in the lower soil layer. The XRD patterns in Figure 15 describe the same mixed-layer clay but now collected as a composite sample from the top and lower layers. The samples of Figures 14a, 14b and 15 were taken in the profiles within a distance of 7 metres.

Upon air-drying and K-saturation, the mixed-layer clay in the top layer (Fig. 14a) gave a broad reflection at 13 - 14 Å. After the acid oxalate extraction, the basal peak intensified markedly, and after heating to 200°C, the peak at 12 - 13 Å shifted to 10 Å and a hump appeared on the low angle side. Upon acid oxalate extraction and heating to 550°C a contraction was obtained at 10 Å, but the peak was weak and broad. Peaks were more diffuse after the KCl and  $AS_{pH2.3-2.4}$  treatments and heating than after the oxalate treatment. Despite these

changes the properties of this mixed-layer clay in the top red-brown soil layer are similar to those of the mica-vermiculite in the distinguishable eluvial layer (cf. Figs. 10b and 11a). Furthermore, the clay of Figure 14a displayed slightly expanded peaks at around 15 Å both after acidified salt extraction and upon ethylene glycol solvation. It is therefore interpreted as mica-vermiculite with a low degree of hydroxy interlayering.

Similarly to the diffractograms recorded from the sample of the top soil layer, traces for the clay from the lower soil layer (Fig. 14b) were stronger after the acid oxalate extraction than after K saturation or  $AS_{pH2.3-2.4}$  extraction. After all these extractions the basal peak was at about 14 Å. The effect of ethylene glycol on the basal peak was, however, less than for the clay of Figure 14a. The incomplete collapse towards 10 Å upon heating at 200°C and the diffuse traces between 10 Å and 14 Å after heating at 550°C suggest a higher degree of interlayering in the sample of Figure 14b. As Olson (1988) has noted, the plateau-like reflections on heating at 550°C result from a poorly crystalline mixed-layer clay. Nevertheless, the response of the clay described in Figure 14b to treatment was in many respects like that of vermiculite-chlorite in the visible illuvial layer (cf. Figs. 11b and 12a). The clay was therefore identified as a poorly crystalline vermiculite-chlorite.

Unlike the mixed-layer clays of Figure 14a-b, the clay described in Figure 15 displayed a sharp and strong reflection at 14 Å upon air-drying and K-saturation as well as after extractions with  $AS_{pH2.3-2.4}$  solution and acid oxalate. The peak did not expand upon ethylene glycol treatment (trace not shown). The incomplete contraction on heating at 200°C and also at 550°C indicated an almost complete degree of filling of the interlayer space. Furthermore, XRD patterns suggested that the mixed-layer clay of Figure 15 possessed more crystalline material than that of Figure 14b. As Sawhney (1989), April et al. (1986) and Farm-



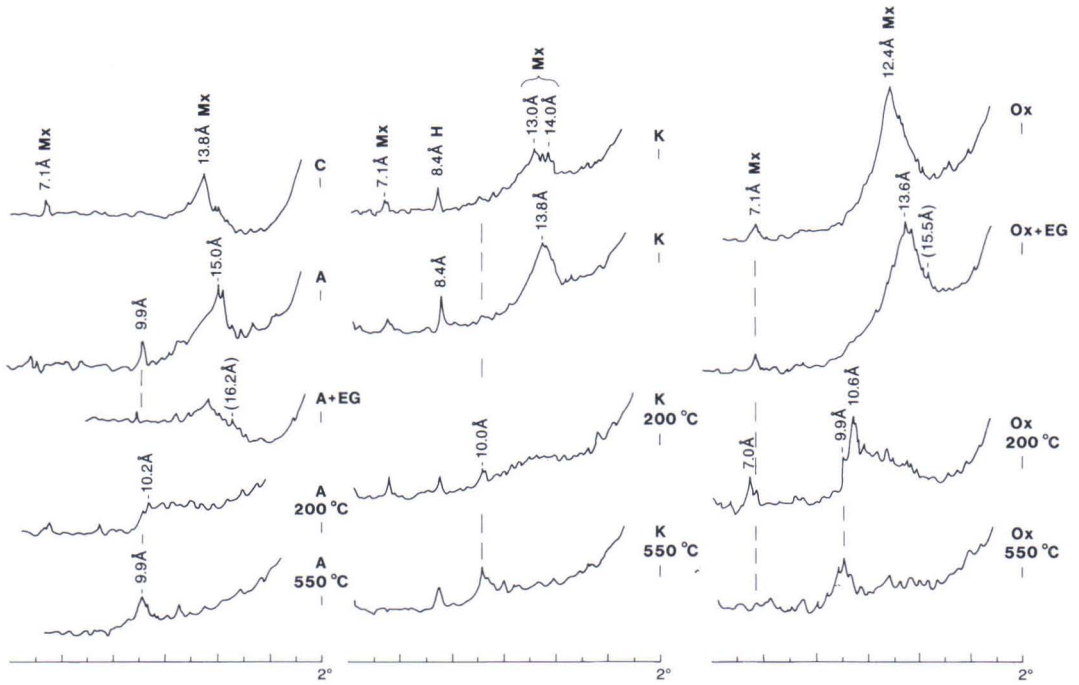


Fig. 14a. XRD patterns of the 3-cm-thick top layer under the humus layer, from the red-brown soil in the representative shallow till at site No. 7a. The age of the soil is 5000 - 7000 years and the grain size of the subsamples <(40 - 50) μm. For explanations see Figs. 5, 9 and 11.

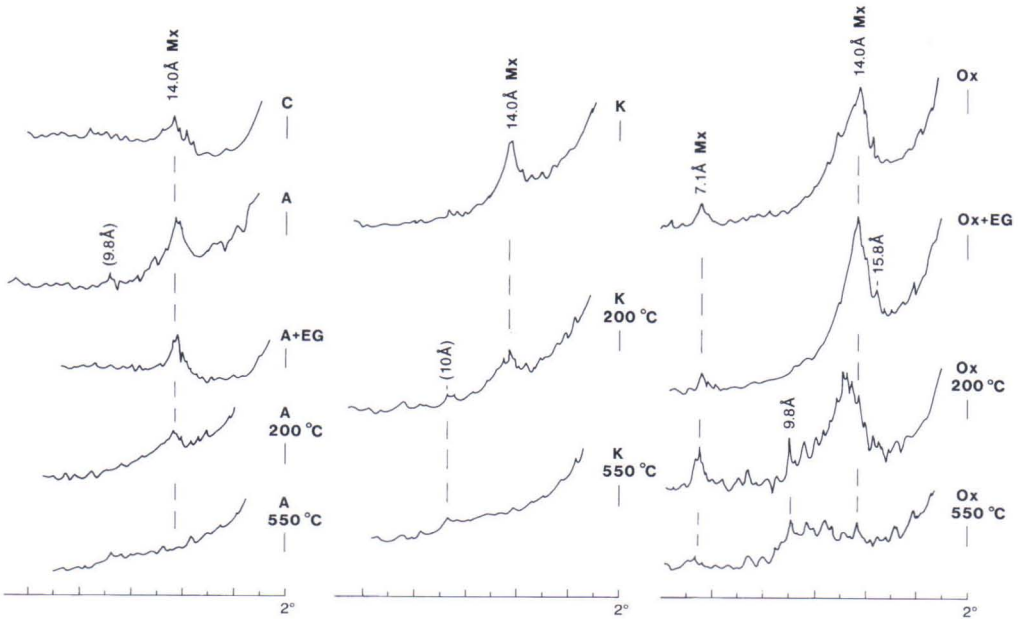


Fig. 14b. XRD patterns of the lower layer underlying the top layer of Fig. 14a, from the depth of 3 to 10 cm. The grain size of the subsamples was <(40 - 50) μm. For explanations see Figs. 5, 9 and 11.

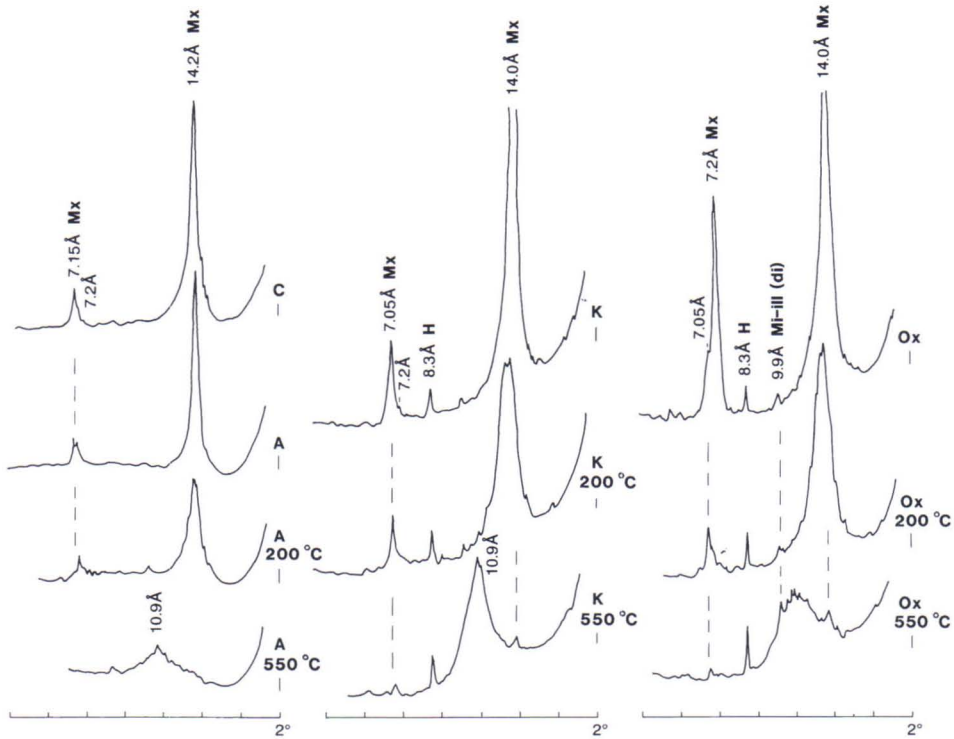


Fig. 15. XRD patterns of the red-brown soil sample taken as a composite sample from under the humus layer (of 6 cm thickness) down to a depth of 22 cm, in the representative shallow till at site No. 7a. The grain size of the subsamples was <math>(40 - 50) \mu\text{m}</math>. For explanations see Figs. 5, 9 and 11.

er et al. (1988) have pointed out, it is difficult to differentiate an intergrade with heat-resistant lattice from a primary chlorite. Therefore,

the mixed-layer clay in Figure 15 is interpreted to be a chloritized vermiculite or a secondary chlorite.

## DISCUSSION

### Maturity and rate of podzolization in thick tills

A small increase in total concentrations of  $\text{SiO}_2$  in the eluvial (E) layer and of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in the illuvial (B) and transitional zone (BC) layers with age indicated a slow weathering of podzols in thick tills in the industrial areas of Siilinjärvi and Kuopio and the background area. The total concentration of  $\text{Fe}_2\text{O}_3$  was maximum in the B layer and that of  $\text{Al}_2\text{O}_3$  in the underlying BC layer of the older podzols (>5001 years). In the younger

podzols (5000 years), total  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  were maximum in the B layer.

According to Aaltonen (1941), in an old podzol the maximum content of Al oxides occurs either together with the maximum of Fe oxides in the upper illuvial layer or else it occurs separately in lower layers; in a young podzol the total content of  $\text{Al}_2\text{O}_3$  in the upper illuvial layer exceeds that of  $\text{Fe}_2\text{O}_3$  in the same layer. The difference between the present find-



ings and those of Aaltonen might partly be due to the sampling and partly to the analytical method. In this study the podzolic layers were identified and sampled on the basis of colour, whereas Aaltonen (1935, 1939 and 1941) took samples of constant thickness five centimetres throughout the profile.

Even though the enrichment of Fe and Al oxides in the B and BC layers, in particular in those of sandy tills, seemed to increase with the age of the podzol, the chemical differentiation of the podzolic layers depended more on the grain size distribution of the parent soil and the hydrological conditions in the pedon. This is seen in the finding that total concentrations of Al and Fe oxides were only weakly differentiated within the profile in tills rich in silt or coarse sand and gravel regardless of the age of podzolization. Moreover, the enrichment of sesquioxides in the B and BC layers varied with the age, in some cases even within the same till type. This indicates that also mineralogical differences between the parent tills significantly affect the rate of the chemical differentiation during podzolization (Gjems 1967). It should be added, too, that the varying rate of decomposition of humus in the different study sites may have affected the behaviour of

Al and Fe during podzolization (De Coninck 1980).

Petäjä-Ronkainen et al. (1992) report that podzolic layers in glaciofluvial sand profiles more than 330 years but less than 1200 years old can be distinguished by the total content of  $\text{Fe}_2\text{O}_3$ . In addition, they observed that, in the same soil medium, a division into podzolic layers based on total contents of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  is achieved in about 6000 years. In the present study, the differentiation of Fe and Al oxides within sandy till profiles was as detectable in the younger as in the older podzols. The accumulation of  $\text{SiO}_2$  in the eluvial layer, in turn, was detectable only in 9000-year-old podzols of sandy tills. In contrast to sandy tills, podzolic layers in silty and gravelly tills of any age were weakly distinguished by total contents of Si, Al and Fe oxides. Overall, it can be concluded that the age does not directly and unambiguously explain the rate of podzolization in tills. In many cases, differences in the composition of the parent soil and the hydrological conditions in the surficial till seemed to account for the variable differentiation of sesquioxides within the profile (see also Räsänen & Jylänki 1990).

### **Maturity and rate of podzolization in shallow tills**

Results from profiles of shallow tills gave a confusing picture of the maturity and rate of podzolization. First, shallow tills visually exhibited two types of profiles: a profile with distinguishable podzolic layers and a profile totally tinted red-brown. Secondly, relative to podzols of thick tills, the variation of total  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  indicated in some cases of both profile types an intensive leaching, and in some cases of red-brown profiles a minimal leaching from the top soil layer

downwards in the profile. However, the intensity of podzolic processes in shallow tills seemed to depend more on the local variation of the parent till than on the topography, vegetation or age of the soil formation. Furthermore, later chemical processes have obscured the original differentiation of sesquioxides within the profile of red-brown soils, as suggested by Jaloniemi and Räsänen (1991). This will be discussed below in the section on the mobility of Al.

### **Weathering of main silicates in distinguishable podzolic layers and red-brown soils**

Results of the total dissolution and XRD analyses showed the <0.5 mm fraction of

podzolic layers and parent tills, and the same fraction of red-brown soils, to be dominated by quartz and feldspars. The silicate group next in size consisted variably of amphiboles, illitic micas and mixed-layer clay minerals. Comparable mineral proportions have been reported for the sand, silt and clay fractions of parent tills (Soveri & Hyypä 1966, Perttunen 1977, Räsänen et al. 1992b, Lintinen 1995).

The variation in total concentrations of alkali and earth alkali metals within the profile indicated a partial weathering of Mg- and K-bearing minerals and a minimal weathering of Ca- and Na-bearing minerals during podzolization of thick tills (Table 3). Since contents of aqua regia soluble Mg, K, Fe and Al were diminished in the eluvial layer and increased downwards in the profile (Table 5), it is concluded that the Mg- and K-bearing minerals that are weathered are solely trioctahedral K-mica (mainly biotite) and chloritic clay minerals. A similar difference in the aqua regia concentrations occurred between the top and lower layers of red-brown soils (Table 4). The differences in the concentrations of K and Mg between the illuvial and the underlying layers were less than those between the eluvial and illuvial layers, which indicates a minor weathering of biotite and chloritic clays in the illuvial layer (see Table 5). Räsänen and Jylänki (1990) concluded from aqua regia data that biotite and chloritic clays in podzols of the Inkoo area on the southern coast of Finland were similarly predominantly weathered only in the eluvial layer.

Melkerud (1983) has suggested that the decrease of total  $K_2O$  in the eluvial layer is due to the partial weathering of K feldspar during podzolization. In addition, he argues that amphiboles in podzolic layers have first weathered to chlorite and then to vermiculite. In the present study chemical data did not clearly confirm the partial decomposition of either K feldspar or hornblende in podzolic layers and red-brown soils. The depletion of total MgO and  $K_2O$  in the eluvial layer was comparable

to the depletion seen in the aqua regia data, which supports the weathering of trioctahedral K-mica and chloritic clay minerals rather than that of K feldspar.

In contrast to the total Ca content, the aqua regia soluble Ca was lower in the eluvial than the illuvial layer and the parent till, pointing to the weathering of Ca-bearing minerals (Table 5). Since concentrations of the aqua regia soluble Na were similar throughout the profile and did not correlate with Ca, it can be supposed that the source of the aqua regia soluble Ca was partially weathered Ca-rich plagioclase (anorthite) and/or other Ca-bearing minerals, such as carbonates, apatite and possibly epidote. The correlation matrix showed a significant correlation between K, Mg and Ca in distinguishable layers but not in red-brown soils, suggesting a different source for the aqua regia soluble Ca in the latter. In podzolic layers, aqua regia soluble Ca seemed to follow the abundance of micas and clay minerals, which would indicate that the source of Ca occurring as an exchangeable cation was a clay mineral. However, the concentration of aqua regia soluble Ca was three times the concentration of exchangeable Ca measured earlier by Räsänen (1989), and on this basis it is suggested that most of the aqua regia soluble Ca was derived from other Ca-bearing minerals, not clay minerals. Clearly, the abundance and also the weathering rate of the Ca-bearing minerals are related to the weathering of K micas and the formation of secondary clay minerals. Element correlations in red-brown soil samples, in turn, indicate a different weathering regime.

It needs to be added here that the rates of the mineral weathering in the profiles of thick and shallow tills are comparable only to some extent. In part this is due to the absence of the less altered till in rocky terrains, but also some features of the element distributions in profiles of shallow tills, and the presence of shore sands and gravels, indicate the heterogeneity of the parent material in rocky terrains, which



makes it harder to estimate the rate of weathering within the profile. Some samples from the top layer were rich in silica and some in total Na and Ca (plagioclase), or samples showed abundant K and Mg in the aqua regia leach indicating the predominance of biotite over the other main minerals (Tables 3 and 4). In spite of these features, results of the aqua regia data showed distinctly that the weathering of trioctahedral micas and chloritic clay minerals is the predominant weathering process in profiles of thick and shallow tills with distinguishable podzolic layers, just as in red-brown soils. This interpretation is supported by the XRD results. For further, discussion see the next section.

By contrast, the difference in the weathering rate of the other main minerals, such as feldspars, remains to be clarified. Results of the chemical analyses showed any distinct proof of the weathering of these minerals (except Ca-rich plagioclase) in the upper soil layers during podzolization.

#### **Weathering rate of micas and chloritic clays in different till types**

Results of the aqua regia leach showed differences in the weathering rate of the mica and clay mineral fraction between the till types and also between the study areas. In general, the depletion of Fe, Al, Mg and K in the eluvial layer, indicating the weathering of trioctahedral mica and chloritic clay, was more evident in sandy till than in tills rich in silt. The depletion of these elements in the eluvial layer of gravelly tills was somewhere between the depletions in the above-mentioned till types. However, the findings should be considered only as indicative owing to the small number of profiles in silt-rich and gravel-rich tills investigated.

Moreover, the difference in the element concentrations between the eluvial and underlying layers seemed to be greater in the older than younger podzols of sandy tills. A similar

difference was not observed in the older and younger podzols of silty tills. On average, the rate of weathering was nevertheless lowest in the profiles of the Siilinjärvi area, where one third of the sampled profiles were located in silty tills and where the studied podzols tended to be younger than those in Kuopio and the background area. It is, therefore, suggested that not only the age of the soil formation but also the composition of the parent till affects the podzolic weathering of thick tills.

Lintinen (1995) has concluded that the weathering of the surficial till during postglacial time is greatest in tills rich in fines. In his view, the rate of weathering depends mostly on the oxidation-reduction conditions in the till. As mentioned above, the rate of weathering in the mica and clay mineral fraction was lowest in tills rich in silt. These soils are mostly characterized by reducing conditions, due to the seasonal uplift of the groundwater table into the overlying soil. This, in turn, has hindered the intensive weathering of micas and chloritic clays in silty tills. According to Gjems (1967) and Weaver (1989), podzolic weathering, as in the decomposition of biotite, occurs under oxidizing conditions. Petersen (1976) concluded that soils rich in sand usually possess ideal conditions for podzolization. A similar trend was identified in the present study.

Results of the XRD analyses support the above interpretation of the aqua regia data. No discrete trioctahedral illitic mica was found in the fine fraction of the eluvial layer in thick and shallow tills of the Kuopio and background areas. Likewise none was found in the fine fraction of red-brown soils. However, it occurred in variable amount in the illuvial and less altered layers in the above-mentioned areas. Both the di- and trioctahedral micas occurred as separate minerals throughout the profile only in Siilinjärvi. It may be added here that, in both the eluvial and underlying layers of some profiles of both the thick and shallow tills, mica occurred as a layer compo-

ment of the non-expanding mixed-layer mineral. Nowhere, however, did mica occur in this way in red-brown soils. Whether it was di- or trioctahedral remained unresolved owing to the sample preparation techniques that were adopted.

In contrast to the trioctahedral mica, the weathering of dioctahedral illitic mica during podzolization could not be unambiguously interpreted from diffractograms. In Kuopio and the background area, dioctahedral mica sometimes occurred predominantly in the eluvial layer and in minor amount in the lower layers, and sometimes it was lacking in the whole profile. In Siilinjärvi it occurred throughout the profile, together with trioctahedral mica. Dioctahedral mica dominated in red-brown soils.

Where dioctahedral mica dominated in the eluvial layer and was absent in the lower layers, it may have been formed during podzolization. According to Weaver (1989), trioctahedral mica can convert to a dioctahedral illitic mica, and further to vermiculite or smectite. During the alteration, mobile  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  are removed from the octahedral layer and replaced by immobile  $\text{Al}^{3+}$ . Weaver

(1989) points out that dioctahedral mica is formed in weathering only if the concentrations of  $\text{K}^+$  and  $\text{Al}^{3+}$  are high enough, such as in the vicinity of weathered K-feldspars. However, no weathering of K feldspar was observed in podzols of the present study. It is, therefore, concluded that more dioctahedral than trioctahedral mica in the eluvial layer only reflects its resistance during podzol weathering (Gjems 1967).

According to XRD analysis, chlorite occurred in the interstratified mixture with vermiculite, both in the eluvial and illuvial layers and in parent tills. Since the heated XRD patterns did not support the occurrence of discrete chlorite in podzolic layers or in samples of the parent till, it is proposed that the chlorite has been weathered to the vermiculitic mixed-layer clay throughout the profile. Lintinen (1995) argues that the vermiculization of chlorite, and also micas, in the surficial till bed (viz. under the pedon) is a post-glacial weathering process. The XRD results of the present study likewise suggest that the weathering of chlorite is continuous from the podzolic layers downwards into the less altered till layers.

### Formation of clay minerals during podzolization

In most podzols, both younger ( $\leq 5000$  B.P.) and older ( $> 5001$  B.P.), a vermiculite-chlorite was present in the eluvial, illuvial and BC layers as well as in the parent tills. Unlike the vermiculite-chlorite in the B and BC layers and parent tills, the vermiculite of the mixed-layer clay in the eluvial layer exhibited a varying degree of hydroxy interlayering, and expanded slightly upon acidified salt extraction but not upon ethylene glycol solvation.

A more intense weathering regime was observed in a few samples of the eluvial layer in shallow and thick tills. There the eluvial layer was characterized by micaceous interstratification with a smectite-like vermiculite. Again in this case, vermiculite-chlorite dominated

the B and BC layers and parent tills.

The above-described features of the clay mineral sequence within the podzol indicate that vermiculization of chlorite and mica occurs during podzolization, is more intense in the eluvial layer and gradually decreases downwards to the parent till. Since the degree of the interlayering of vermiculite, measured as the heat-resistance of the lattice, gradually increased downwards in the profile and was greatest in the illuvial layer, most noticeably in 9000 year-old podzol, the interlayering must have increased during the podzolization. According to De Coninck et al. (1983), an accumulation of heat-resistant layer silicate in the illuvial layer is the result of a gradual



transformation of mica and chlorite into vermiculite layers.

The hydration of the clay during  $AS_{pH2.3-2.4}$  extraction indicated the presence of entirely open interlayers of vermiculitic clay in the eluvial layer (e.g. Fig. 10). Only in a few samples of the eluvial layer did the clay expand upon ethylene glycol solvation, indicating the presence of smectite-like clay and, therefore, a more intense weathering. Since the swelling properties of the clay in the eluvial layer did not unambiguously increase with age of the podzol, it is concluded that the composition of the parent till and, even more, local differences in oxidation-reduction conditions and acidity, have more effect on the weathering rate than does the ageing (Gjems 1967, Weaver 1989).

As mentioned above, vermiculite-chlorite in the B and BC layers and parent tills was not visibly affected by acidified salt extraction. In most samples of the lower layers, diffractograms recorded after acidified salt extraction and heating were similar to those recorded after K saturation and heating. A like similarity was found earlier for vermiculitic clays of parent tills (Räsänen et al. 1992b). Lintinen (1995) reports that hydroxy-interlayering of vermiculite is common in surficial tills in Finland. Its occurrence in lower till beds is clearly linked to the intensity of the podzolic processes in the topmost till and to the Al contents of gravitational waters percolating within the till bed, as suggested by Räsänen et al. (1992b).

A few profiles contained another type of mica-vermiculite, which gave the same basal reflection at 12 - 13 Å as the expanding mica-vermiculite. In this case, the vermiculite was non-expanding and possessed a higher degree of interlayering. Since it occurred only sporadically in the eluvial and underlying layers, it was clearly not formed during the podzolization.

Nevertheless, the XRD results did not definitively show that the trioctahedral mica in

the eluvial layer had first weathered to chlorite and then to a vermiculitic mixed-layer. Vermiculite-chlorite was more often found in the eluvial layer than was the expanding mica-vermiculite with a minor content of chlorite or without chlorite. Where vermiculite-chlorite was present the eluvial layer contained both tri- and dioctahedral mica as discrete minerals, but where mica-vermiculite was present instead, discrete mica was predominantly dioctahedral. Nevertheless, in both cases the mixed-layer clay became more chloritic downwards in the profile. Gjems (1967) has argued that the transformation of mica-vermiculite to more swelling clays (vermiculite and smectite) is accompanied by the transformation of interstratified chlorite.

Finally, it may be noted that, in the present study, the properties of clay minerals were studied from a mixture of the silt and clay fractions. As seen from diffractograms, pure clay types such as smectite, which presumably were formed during the podzolization, could not be identified from the fraction mixed with silt and clay, though they have recently been identified in the clay-size fraction of the podzol samples from eastern Finland (Righi et al. 1996). Results of the XRD analysis nonetheless revealed several features typical of podzolic weathering and were compatible with the findings of chemical analysis.

### **Acid weathering in distinguishable podzolic layers**

Several researchers have reported that trioctahedral micas and chlorite have been decomposed completely in the eluvial layer and partially in the illuvial layer of podzols in glaciated regions (Kodama & Brydon 1968, Kodama 1979, Teveldal et al. 1990, April et al. 1986). The results of the present study point to a similar conclusion.

The removal of the interlayer  $K^+$  from micas during podzolic weathering leaves behind a vermiculite lattice, which can transform to a

smectite through a decrease of the layer charge (Brydon et al. 1968, De Coninck et al. 1987). A reduction in the layer charge can occur through oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  during or following the opening of the interlayer (removal of  $\text{K}^+$ ) (Newman & Brown 1966). This mechanism is usually associated with the transformation of micas to vermiculites (Fanning et al. 1989). Another mechanism for reducing the layer charge is the exchange of Si for Al in the tetrahedral sheet (Fanning et al. 1989). The chemical weathering of chlorite starts with the removal of the interlayer OH sheet and its substitution by hydrated cations (De Coninck et al. 1983, Barnhisel & Bertsch 1989).

The above processes are described by the term vermiculization. As long as the removal of  $\text{K}^+$  in micas or  $\text{OH}^-$  in chlorites is incomplete, the minerals have a partially vermiculite composition (De Coninck et al. 1987). The degradation produces vermiculitic interstratifications, e.g. mica-vermiculite or mica-smectite, and chlorite-vermiculite or chlorite-smectite. These intergrades are not stable on heating and the temperature of collapse lowers as the replacement of the OH sheet proceeds (De Coninck et al. 1983).

Alternatively, an intergrade with a structure comparable to that obtained in degradation may be formed by  $\text{Al}^{3+}$  entering from solution into the interlayer space of the vermiculite or smectite layers (Jackson 1960, Ragland & Coleman 1960, De Coninck et al. 1987, Hallbäck 1992). Through deprotonation and polymerization of  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  (aluminumhexahydronium ion), incomplete Al-hydroxy sheets (gibbsite layers) are formed within the interlayer space (Jackson 1963, Rich 1968). Since these Al-hydroxy sheets do not fully fill the interlayer space, it often is difficult to differentiate the Al-hydroxy interlayered vermiculite from the intergrade of degradation (De Coninck et al. 1987). The chloritization of vermiculite was long ago described as an acid weathering (Gjems

1967).

Given the lack of agreement about the source of Al hydroxides in the interlayer sites of vermiculite, some discussion is required. Righi et al. (1988) contend that hydroxy-interlayering of vermiculite characterizes acid brown earths and not podzols and conclude that the formation of smectite dominates in the eluvial layer of podzols. According to Farmer (1984), hydroxy interlayering in vermiculites may result from the decrease of pH and the increase of Al in the solution percolating in the illuvial layer of podzols (see also Hallbäck 1992). Also Laverdière et al. (1977), Kodama (1979), April et al. (1986) and Law et al. (1991) have reported that the illuvial layer of podzolized tills is characterized by fixation of hydroxy-Al interlayers in vermiculites. Extra Al ions in the illuvial layer are derived from weathering of feldspars in the eluvial layer (Law et al. 1991).

Vicente et al. (1977) have suggested that Al-hydroxy vermiculite can be formed internally from the vermiculite itself. In this case the formation of Al hydroxy clay does not require a solution especially rich in free Al. Medium acidity below pH 5 is sufficient to induce the transformation of micas. In the present work, the pH of the soil in salt extracts was below five for most samples of both the illuvial layer and the eluvial layer. Vicente et al. (1977) report that protons play the main role in mica opening, and in Al migration from octahedral or tetrahedral layers to interlayer spaces. This kind of process has been responsible for the hydroxy interlayering of vermiculites in podzols of the present study, since the weathering of feldspars was insignificant in both the eluvial and the illuvial layers. Moreover, a significant accumulation of Al from the eluvial layer in the interlayer sites of vermiculite in the illuvial layer (Law et al. 1991) probably can explain the difference in the degree of interlayering between these layers.

The polymerization of Al in the interlayer



space is controlled by the Al/OH ratio and pH (Jackson 1960, Rich 1968, Bloom et al. 1977, Hallbäck 1992). Hence, if the pH decreases to near pH 3, vermiculite will possess many 'exchangeable' Al<sup>3+</sup> ions (Vicente et al. 1977). According to Vicente et al. (1977), this kind of evolution in the presence of certain organic acids, e.g. products or precursors of fulvic acids, can result in a smectite-like interstratification. It is here suggested, therefore, that the mica-vermiculite with some smectite-like layers has resulted from a more intense weathering via the process described by Vicente et al. (1977). Furthermore, it can be inferred that the natural acidification results in the formation, in the eluvial layer, of smectite-like clays with a low degree of interlayering or none at all (cf. Hallbäck 1992). The new study of Righi et al. (1996) confirms that smectites are formed only in the eluvial layer and are the dominant clay mineral in the clay fraction (<2 µm) of podzols older than 6 000 years.

### Acid weathering in red-brown soils

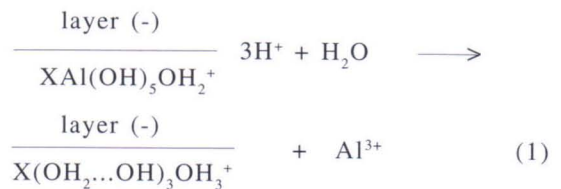
Two types of clay sequence occurred in the red-brown soil profiles: 1) profiles with mica-vermiculite with weak resistance against collapse on heating in the top layer and a poorly crystalline vermiculite-chlorite with increased heat-resistance in the lower layer, and 2) profiles with vermiculite-chlorite with heat-resistant layers in both the top and lower layers. Even though Fe-Al oxyhydroxide coatings caused weak and diffuse traces upon KCl and AS<sub>pH2.3-2.4</sub> treatment, in this way hindering identification, these mixed-layer clays turned out to share many properties with the mixed-layer clays in profiles with visible podzolic layers.

Unlike the clays in visible podzolic layers, some of those in red-brown soil profiles possessed a poor crystalline structure, and some a more chloritized structure. The differences point to divergent weathering regimes. As was shown in the XRD patterns, hydrated interlay-

ers displaying an expanded peak at 15 Å were formed during the acidified salt extraction of most samples of the eluvial layer and also a few samples of the top red-brown soil layer. In contrast, the mixed-layer clay with a sharp peak at 14 Å from some samples of the top layer of red-brown soil did not expand on AS<sub>pH2.3-2.4</sub> extraction. This clay displayed a high resistance against heating at 200°C, similarly to vermiculite in the illuvial layer of the oldest podzol. Evidently the abundance of mobile Al has promoted the formation of chloritized structure (Räsänen et al. 1994).

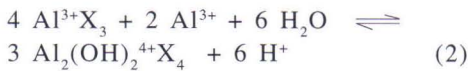
The greater chloritization in the red-brown soils can be interpreted on the basis of the experiment involving acidified salt extraction. In general, this extraction resulted in slight expansion of the interlayers of the clay in the eluvial layer and non-expansion of those in the illuvial layer.

Ragland and Coleman (1960) and Jackson (1963) have observed that leaching with dilute acid does not completely liberate Al hydroxides from the interlayer site. Jackson (1963) suggests the following reaction for the reactivation of interlayer Al with a dilute acid:



XAl(OH)<sub>5</sub>OH<sub>2</sub><sup>+</sup> represents the interlayer Al with net positive charge: Al is six-coordinated, OH<sub>2</sub> carries the extra proton that provides the net (+) charge (see below), and X represents various sizes of interlayer Al-hydroxy units. One mole of Al is released at the point of OH<sub>2</sub> substitution for OH. The OH<sub>3</sub><sup>+</sup> formed in the reaction is exchangeable in additional washing (Jackson 1963). The solubility of Al decreases with increase in the degree of crystallinity in the interspace (Carstea et al. 1970).

In the sample of the eluvial layer that contained mica-vermiculite with some smectite-like layers, the extraction with  $AS_{pH2.3-2.4}$  solution and heating at 200°C led to a partially heat-resistant layer silicate. This result explains why in some cases the solubility of Al in the  $AS_{pH2.3-2.4}$  extract did not markedly increase even though the pH dropped drastically (Räisänen 1989). Jackson (1963) describes the additional adsorption of Al from solution onto Al-exchangeable clay (X) with the following equation:



He explains that in aqueous solution each unit (+) charge of  $Al^{3+}$  and of the more complex Al ions is carried by two substituted hydronium ions,  $(-OH^{0.5+})_2$  (omitted here) for ease of collation with exchange sites,  $X^-$  (see also Jackson 1960).

The suggestion of this study that hydroxy interlayering can form in any strong acidic medium is in agreement with this reconstruction. The increase of Al in solution has promoted alumination of the clay in the red-brown soil profile. Räisänen et al. (1994) concluded earlier that chloritized vermiculites in the eluvial layer in dieback forests in the Kola Peninsula have been formed through the

increase of mobile Al and acidity.

### Mobility of aluminium and acid weathering

It is widely accepted that increased acidity in percolating soil water mobilizes Al (e.g. Bache 1986, Wilson 1986). In the present study, the leachability of Al with a strongly acidified salt was compared with the leachability in KCl. Barnhisel and Bertsch (1982) assume that potassium chloride extracts exchangeable, and mainly ionic Al. As seen in Figure 16, the protons added in the  $NH_4NO_3$  extractant displaced Al from exchange sites into solution only in limited quantity. The samples with higher content of exchangeable Al (KCl extracts) displayed the same concentration of Al in acidic medium as the samples with low content of exchangeable Al (Fig. 16). This indicates that extra exchangeable Al ions were sorbed back onto colloids or reprecipitated as hydroxy complexes during the acidified salt extraction, as the curve in Figure 16 demonstrates. This process was more characteristic of the samples of red-brown soils than the samples of distinguishable eluvial and illuvial layers.

Räisänen (1989) and Räisänen and Pulkkinen (1991) proposed that the addition of protons to the soil mobilized Al from the inter-

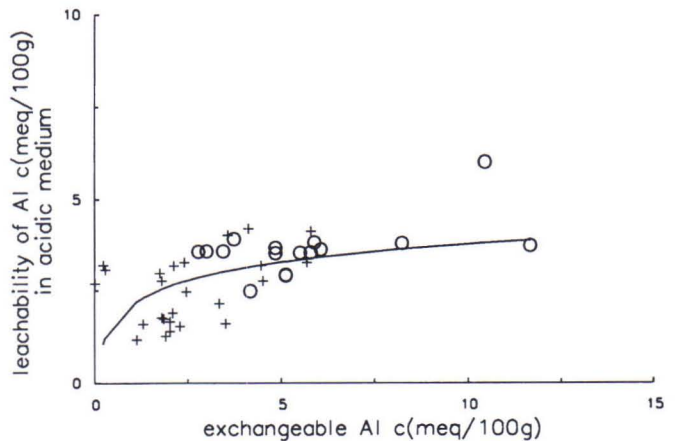


Fig. 16. The relationship between concentrations of Al in acidic medium ( $AS_{pH2.3-2.4}$  extraction) and the exchangeable fraction (KCl extraction) in samples from podzols with distinguishable podzolic layers (+) and in samples from red-brown soil profiles (o).



layer site of clays, and decreased the pH via the hydrolysis of Al. According to them, the increase of Al in the acidified salt extract depends on the buffering capacity of the podzolic layer and the stability of Al compounds. The polymerization rate of Al in hydroxy interlayers of the clay and the affinity of organic complexes for Al largely control the leachability of Al and the decrease in pH during acidification (Räsänen 1989, see also Hallbäcken 1992).

The results of the present study show that the relationship between the mobilization of Al and the decrease of pH in acidic medium is more complicated than earlier assumed (Räsänen 1989). Relative to the increase in Al leachability in the acidified salt extract, the pH dropped on average more in the eluvial layer samples than in samples of the underlying illuvial layer (Table 6). The relationship between leachability and pH in the red-brown soils was close to that in the illuvial layer. In some samples of red-brown soils the increase in Al leachability did not, however, lead to a drop in pH.

Contrary to the above findings, the clay in the eluvial layer and in the top layer of red-brown soils exhibited almost the same and only in a few cases lower degree of interlayering than the clay in the illuvial layer and the lower layer of red-brown soils. Except in some profiles of red-brown soils, where there was no apparent difference, only the expanding properties of the clays upon the  $AS_{pH2.3-2.4}$  treatment differed between the top and lower layers of podzols and red-brown soils.

In samples containing a heat-resistant clay, collected from the illuvial layer, the lower layers of red-brown soils and occasionally from the top layer of red-brown soils, the relationship between the leachability of Al and the pH can be explained in terms of reaction (1) (see the preceding section): the solubility of Al decreases with the increase in degree of polymerization in the interspace of vermiculite. In these samples the dissolution of Al in

acidic medium did not result in hydrolysis and a marked drop in pH as it did in the eluvial layer and in the top layer of some red-brown profiles. Alterations in the interlayer space of clay in the top layers during the acidified salt extraction are described in more detail below.

In contrast to the clay in the illuvial layer, the basal spacing of the clay in the grey eluvial layer and top layer of some red-brown soils expanded at 15 Å with varying intensity after the  $AS_{pH2.3-2.4}$  treatment. In addition, the smectitic clay in Figure 10a displayed a more heat-resistant lattice upon acidified salt treatment than upon K-saturation (Fig. 10a). These alterations indicate that the mixed-layer clay adsorbs extra hydroxide in acidic medium, giving it slightly hydrated interlayers. In illustration of this, the leachability of Al in acidic medium remained fairly constant, even for samples with high content of KCl-extractable Al (Fig. 16). The pH nevertheless decreased in some cases (Räsänen 1989). Evidently the Al displaced by protons in acidic medium was partially adsorbed back onto clay surfaces and the drop in pH was due to the hydrolysis of the adsorbed  $Al^{3+}$  (reaction 2, Jackson 1963). According to Bloom et al. (1977), Al adsorbed on the surface is hydrolysed to a greater degree than is solution Al. This implies that the addition of protons to the soil, as modelled in the  $AS_{pH2.3-2.4}$  extraction, causes reprecipitation of Al.

On the basis of the above findings, it is proposed that the highly chloritized mixed-layer clay in the top and lower layers of some red-brown soil profiles has been formed through the increase in acidity and the readorption of solution Al into the interlayer sites (reaction 2). A similar interpretation was offered earlier (Räsänen et al. 1994) for the acidification of soils in the dieback forest near Monchegorsk in the Kola Peninsula. This interpretation is strikingly opposed to the cation exchange theory, which assumes the outflowing of Al from the soil into waters during accelerated acidification (Nissinen &

Ilvesniemi 1990, Kenttämies 1991).

On the other hand, the difference in the sums of mobile and immobile Al and Fe between the red-brown soils and profiles with visible podzolic layers indicates that both Al and Fe have partly flowed out from the red-brown soils. This feature suggests that neo-chloritized clay, as well as Al chelates and complexes formed during the accelerated acidification, are not stable. The addition of protons via acid deposition and/or the hydrolysis of reabsorbed Al (reaction 2) evidently promotes some outflowing of Al. According to Farmer (1986), metastable precipitates, both inorganic and organic, are readily remobilized upon further acidification and may release Al into streams if the solutions are not neutralized in subsoils. In this context, the

results support the removal of Al during elevated acidification, as suggested by Nilsson and Bergkvist (1983) and Mulder et al. (1989).

To summarize, in red-brown soils, accelerated acidification leads to both the reprecipitation of and the gradual outflowing of Al. Which of these processes predominates will largely depend on the chemical balance between the chloritization of the clay and chelation and complexation of Al on the one hand and the quantity of acidity (proton addition) on the other. It needs to be added that the quality of soluble organic complexes and the activity of micro-organisms influence the mobility of Al during acidification (Oades 1988, Huang 1991). Their role in acidification and clay mineral weathering is not well understood, however.

### Formation of the red-brown soil

Räisänen (1989) and Jaloniemi and Räisänen (1991) suggested that acid deposition was responsible for the formation of the red-brown soils near the chemical pulp mill. Results of the present study, however, indicate an additional factor for the increased acidity in soil in rocky terrains.

Mica-rich patches in the exposed granite-gneiss were found to contain dispersed grains of weathered iron sulphides. Evidently the acid flush, which was incompletely neutralized in the overlying thin soil layer, activated the weathering of Fe-sulphides in the surface part of the bedrock. Solutions rich in iron and sulphate then contaminated the soil, causing accelerated acidification and the increase of Fe in the soil. In addition, soil water enriched in sulphate mobilized Fe and Al from precipitates in the illuvial layers bordering the bedrock surface. Such a process easily accounts for the unusual correlation between the contents of the easily leachable and exchangeable Al and precipitated Fe in red-brown soils. In profiles with distinguishable podzolic layers, the content of precipitated Fe correlated sig-

nificantly with the contents of both chelated and precipitated Al. It is, therefore, concluded that, by promoting the weathering of sulphides in the bedrock surface and so mobilizing Fe in the soil, the anthropogenic acid load has been responsible for the formation of the red-brown soils.

Jaloniemi and Räisänen (1991) have reported an increase of chelated Al and Fe not only in upper mineral soil layers but also in the humus layer in rocky terrains near the mill. In addition, in this study a few red-brown soil profiles were found to exhibit abnormally high contents of Al and Fe in the aqua regia leach (Tables 3 and 4). These findings support the interpretation that, at some sites, part of the mobile Al and Fe has risen into the surface layers. Abnormally high aqua regia soluble Al also characterized the eluvial layer in thick tills of the dieback forest in the Kola Peninsula (Räisänen et al. 1994). There the eluvial layer tended to be grey in colour and only a few profiles were red-brown up to the contact of the humus layer. Similarly, the deteriorated litter and humus layer of the dieback forest



contained abnormally high content of Al compared with areas with less acid load (unpublished data, M. L. Räsänen).

As proposed by Jaloniemi and Räsänen (1991), microbial or root activity might have activated the removal of Al and Fe throughout the shallow till upwards to the humus layer. In the present work, the thin soil layer above the bedrock surface in rocky areas was found to be saturated with water during the melting of snow in spring and after heavy rains in summer. This suggests that mobile Al and Fe species may also have uplifted to the surface layers through diffusion or capillary pressure when the soil was saturated with water. Alternatively, Fe may have partially dissolved when the mineral soil up to humus was saturated with the water (reducing conditions) and then reprecipitated as the water level subsided (Carlson et al. 1980).

The wide variation in chemical and physical

conditions in rocky terrains, as well as the heterogeneity of the parent soil material, have led to more variation in the podzolization and acidifying processes in shallow tills than in thick tills. Findings such as the leaching of elements from the top layer and the enrichment of Al and Fe in the lower layer, however, indicate that podzolization has been going on in red-brown soils. Readsorption of Al onto the vermiculitic clay in both the top and lower soil layers, and the depletion of Al and Fe in the immobile fraction (amorphous precipitates) at some sites, reveal later changes in soil processes due to acid deposition. Evidently anthropogenic acidification is a complex process. One clear feature of the increased acidification is, nevertheless, that Al-rich compounds at anthropogenically acidified sites are less stable than Al-rich compounds formed during long-term podzolization.

## CONCLUSIONS

The higher total concentrations of  $\text{SiO}_2$  in the eluvial (E) layer and of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in the illuvial (B) and transitional zone (BC) layers and the tendency for the differences to increase with age indicate a slow maturation of podzols in thick tills. The maturation was more pronounced in sandy than in silty and gravelly tills. Comparisons of individual profiles showed that the rate and maturity of podzolization depend more on the composition of the till and hydrological conditions in the pedon than on the duration of the podzolization process. Nevertheless, the differentiation of the sesquioxides during podzolization was weakest in the Siilinjärvi area, where the podzols were located predominantly in silty and gravelly tills and their age was, in most cases, less than 7000 years.

Visually there were two types of profiles in the shallow tills: a profile with distinguishable podzolic layers and a profile totally tinted

red-brown. The podzolic processes were more complex and variable in shallow than thick tills. Findings indicated that they depend more on the compositional variation of the parent till than the topography, vegetation or age of the soil formation. Furthermore, later chemical changes have obscured the original differentiation of the sesquioxides by tinting the whole profile red-brown.

From the results of the aqua regia and XRD analyses, the weathering of trioctahedral micas (mainly biotite) and chloritic clay minerals was taken to be the predominant process both in the visible eluvial layer of thick and shallow tills and in the top layer of red-brown soils. In contrast to chlorite, the trioctahedral illitic mica occurred as a discrete mineral in the eluvial layer in the Siilinjärvi study area and sporadically in the illuvial layer and more predominantly in the underlying layers in the Kuopio and background areas. Red-brown

soils lacked trioctahedral mica. In most profiles in all three study areas, chlorite occurred as a layer component in the vermiculitic interstratification throughout the profile. Exceptionally, a few podzols older than 5000 years totally lacked chlorite residue in the eluvial layer.

Moreover, neither the XRD or chemical data showed detectable weathering of dioctahedral mica, feldspars or hornblende in any profile during podzolization. The reduced aqua regia soluble Ca in the eluvial layer and the increasing values downwards in the profile nevertheless might indicate partial weathering of plagioclase rich in Ca. Other possible Ca-bearing minerals weathered during the podzolization are apatite and carbonates.

The depletion of K, Mg, Al and Fe in the eluvial layer, indicating the weathering of trioctahedral mica and chloritic clay, was more evident in sandy till than in tills rich in silt. The concentrations of these elements in the eluvial layer of gravelly tills were somewhere between the concentrations in the sandy and silt-rich till. Moreover, the differences in the element concentrations between the eluvial and underlying layers seemed to be greater in the older than younger podzols, though the trend was pronounced only in profiles of the sandy till. Differences between the types of till suggested, however, that not only the age of the podzol but the composition of the parent till and hydrological conditions in the surficial till affect the weathering rate of the mica and clay mineral fraction in thick tills.

Podzolic layers and parent tills in most cases were dominated by vermiculite-chlorite, the resistance of which against collapse on heating and the intensity of the residual peak for chlorite increased gradually downwards in the profile. The eluvial layer in some old (9000 years) podsols in thick tills and in some younger (5000 - 7000 years) podzols in shallow tills contained a weakly swelling mixed-layer clay with some smectite-like layers. In these cases also the illuvial layer was domi-

nated by hydroxy-interlayered vermiculite with a minor content of chlorite.

Mixed-layer clays in the podzols were formed via a gradual vermiculization of mica and chlorite during podzolization. The increasing acidity as podzolization progresses triggers a migration of Al from the octahedral or tetrahedral layers to the interlayer spaces of vermiculite. The possibility that interlayer Al was solely formed from solution Al was excluded since no intense weathering of feldspars was detected in the podzols. The occasional lower degree of interlayering in the vermiculite of the eluvial layer was due to the partial removal of hydroxides from the interlayer space by organic complexing substances. It is concluded that natural acidification in the podzol leads to the increasing formation of smectite-like clays with a low degree of interlayering.

Chemical and mineralogical properties of most of the red-brown soils were similar to those of the distinguishable podzolic layers in shallow and thick tills. These soils must therefore originally have possessed a grey eluvial and brown illuvial layer. Relative to those in the visible podzolic layers, however, the average contents of mobile Al and Fe were higher in both the top and underlying layers of the red-brown soils. In contrast to the eluvial layer, the top layer of some red-brown soils contained a poorly crystalline mixed-layer clay. In some other cases a more chloritized vermiculite was observed. It is suggested that the abundance of mobile Al and the increase of acidity led to the formation of a more chloritized structure of vermiculite. The source of Al was more likely the partial decomposition of precipitates in the illuvial layer than weathered feldspars in the eluvial layer.

The formation of red-brown soils was evidently due to a combination of acidic rain water and the weathering of Fe sulphides on the bedrock surface. Field observations showed weathered sulphides to occur in mica patches of granite gneiss and predominantly



under the sites of red-brown soils. The acidification at these sites induced a partial outflowing of Al, but also its reprecipitation in the soil. Similarly to Al, Fe was partially leached from the soil and partially reprecipitated within the profile, tinting the soil red-brown. Nevertheless, the results of the present study do not allow a conclusive explanation of how Al and Fe migrate upwards in the profile. One feasible mechanism is the uplifting of mobile Al and Fe via diffusion or capillary pressure when the soil is saturated with melt water in the spring and after heavy summer rains. Alternatively, Fe may partially dissolve when the mineral soil up to humus is saturated with the water (reducing condition) and then reprecipitate at the level where the water level starts to decrease. The role of microbial or root activity in the removal of Al and Fe cannot be excluded moreover, though the process is less researched in Finland.

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The weathering rate of podzols in weakly weathered glacial tills appears to be better defined by aqua regia analysis than by the total dissolution method. The process of the accelerated acidification should be examined not only by determining the exchange capacity, or acid neutralizing capacity, and pH of soils, but also by quantifying the mobility and immobility of Al. Moreover, small changes in weathering processes can be interpreted from the interlayering properties of clays. In this connection, the acidified salt extraction method will better clarify the changes in the interlayer sites occurring during accelerated acidification than will the K saturation method. However, the mixture of the silt and clay fractions that had to be used in the XRD analyses of the present study does not easily allow the determination of properties of the pure clay formed during the podzolization.

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