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MINERAL COMPOSITION AND ITS RELATION TO TEXTURE AND TO SOME CHEMICAL PROPERTIES IN FINNISH SUBSOILS

Selostus: Pohjamaanäytteiden mineraalikoostumuksesta ja sen suhteesta lajitekoostumukseen sekä eräisiin kemiallisiin ominaisuuksiin

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CONTENTS

MINERAL COMPOSITION AND ITS RELATION TO TEXTURE AND TO SOME CHEMICAL PROPERTIES IN FINNISH SUBSOILS

SIPPOLA, J. **Mineral composition and its relation to texture and to some chemical properties in Finnish subsoils.** Ann. Agric. Fenn. 13: 169—234.

The qualitative mineral composition of fractions separated from 56 subsoil samples mostly from Southern Finland was studied by differential thermal and X-ray diffraction analysis.

Mica, chlorite, vermiculite and smectite were identified in fine clay (< 0.2 μm). In coarse clay (0.2—2 μm) there were in addition indications of potash and plagioclase feldspars along with quartz, but not of smectite. In coarser fractions, the same minerals were present as in coarse clay, together with small amounts of amphibole and pyroxene minerals.

Contents of major minerals identified were estimated by chemical methods. The fine clay consisted on average of 31 % "mica", 21 % "chlorite", 19 % "smectite", 10 % "vermiculite" and 22 % "amorphous material". In coarse clay the proportion of "feldspars" and "quartz" together was almost 50 %, rising still further in coarser fractions.

The mineral composition of soil samples was assessed using weighted averages of conversion factors and the results of chemical analyses on unfractionated samples.

Multiple regression analyses indicated that "mica", "chlorite" and "vermiculite" were the mineral components which influenced most strongly the total major and trace element contents of samples.

INTRODUCTION

Texture is a decisive factor determining soil properties. In Finland the contents of several total soil elements are closely dependent on the clay content of the soil (SALMINEN 1933, 1935, KAILA 1973). Also the total contents of many trace elements in Finnish soils are significantly affected by soil texture (VUORINEN 1958, SILLANPÄÄ 1962). Readily extractable amounts of soil potassium and magnesium are closely correlated with the percentage of clay (SCHACHTSCHABEL 1961, KAILA 1967, 1973, HENRIKSEN 1971). The fixation of potassium by soils is correlated with the clay content although the dependence is not very close (SCHACHTSCHABEL and KÖSTER 1960, KAILA 1965). The percentage of clay affects the cation exchange capacity and also the contents and proportions of exchangeable cations (AARNIO 1942).

SALMINEN (1933) observed when studying the chemical composition of Finnish clays that differences in elemental composition between samples varying in texture did not depend on the age or depth but on mineral composition. He assumed that differences in hardness of minerals have resulted in their breaking down to characteristic particle size fractions when the soil parent material has been ground by glacial action.

Also in other than Finnish soils it has been found that in a given fraction certain minerals are abundant (SCHWERTMANN 1961, KHADER 1966, STOCH and SIKORA 1968). Thus in various particle size fractions different minerals predominate and the major minerals determine the soil properties.

According to the results of X-ray mineral analyses of Finnish clays (SOVERI 1956) and of fine fractions of Finnish Glacial tills (SOVERI and HYYPPÄ 1966), differences in the mineral composition of various particle size fractions are clear. Mica or trioctahedral illite types of minerals predominate in clay and the amount of feldspars and quartz increases in coarser fractions. The same type of distribution of minerals among particle size fractions is also found when chemical methods are used to determine the mineral composition of Finnish soils (SIPPOLA 1972). These determinations have shown that the contents of mica, vermiculite, chlorite and amorphous material in size fractions diminish with increasing particle size while the contents of feldspars and quartz increase.

The relationship between soil chemical properties, mineralogy and texture could be closer in Finnish soils than in soils of warmer climates. This is suggested by the formation of soils from rock material ground by continental ice sheets during glaciation. Also the relatively short period during which the soils have undergone the weathering action of a temperate climate suggests likewise.

The purpose of the present study is to investigate the mineral composition of various Finnish soils and their particle size fractions. The relationship between soil texture and mineral composition and the feasibility of determining the mineral composition using the results of mechanical analyses was studied. The dependence of some soil chemical properties on mineral composition was also examined.

1. Research material

The material consists of soil samples collected mostly from Southern Finland (Fig. 1). Many of the soils were sampled in connection with the soil survey carried out by the Institute of Soil Science of the Agricultural Research Centre. This explains why a large number of samples was taken in the Kouvola district. Seven samples were selected for each of the eight soil textural classes, which were set up according to AALTONEN et al. (1949) and VUORINEN (1961), (Table 1, Fig. 2). The basis for differentiating finer and coarser silt soil classes was the predominance of the 2—6 μm and 6—20 μm fractions respectively.

To avoid the difficulties which organic matter and its removal entail in mineral analyses, samples were taken from below the surface layer. Most of the fine textured samples are from subsoils of cultivated fields from depths of 20—40, 40—60 and 60—80 cm, but also samples from corresponding depths of virgin areas are included. The finesand and sand samples are from clearly podsolized soils representing A_2, B and C horizons. Some of the finesand and sand samples contain much fine material (Table 1). These samples do not, however, represent glacial till material. According to the regional distribution, the material could be divided into six groups (Fig. 1).

The pH, determined in a 0.01 M $CaCl_2$ suspension with a soil:liquid volume ratio of 1:2.5, ranges on average from 4.5 to 5.9 for the various soil textural classes (Table 2).

The content of organic carbon, estimated by a dichromate wet combustion method (WALKLEY and BLACK 1934), is low because samples were taken from subsoil. Sandy clays of the present material are richer than other clay soils in organic carbon. The variation within the finesand class is large because samples from podzol horizons rich in organic matter are included.

The particle size distribution was determined

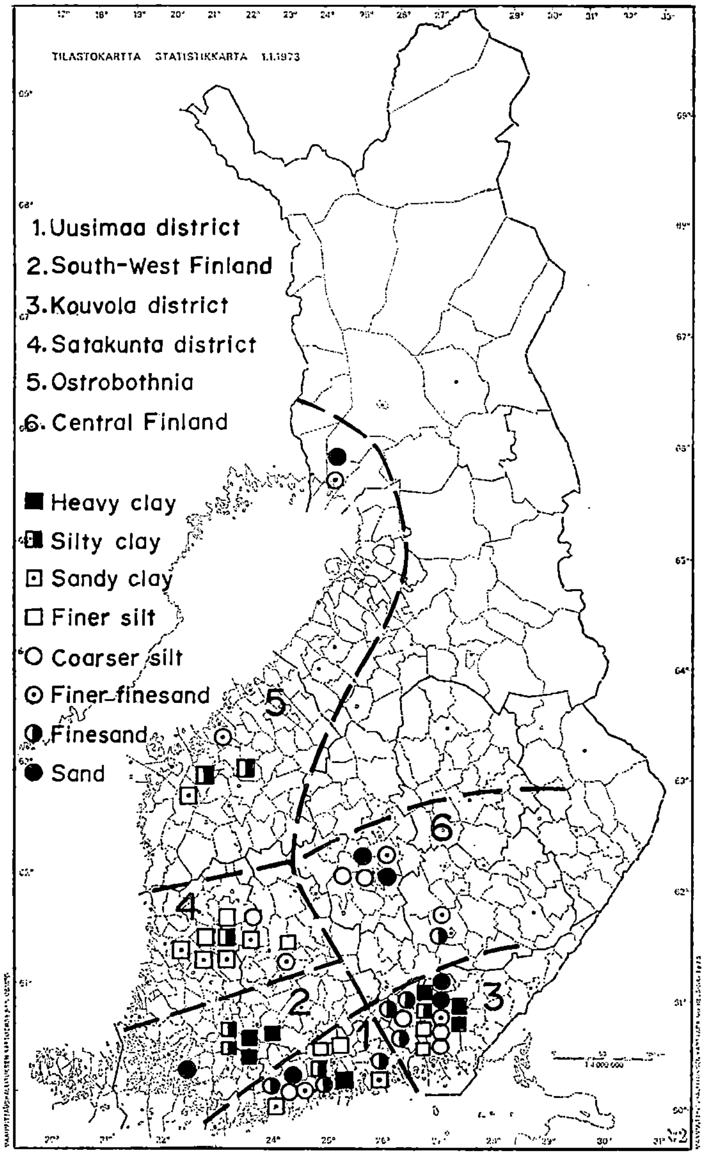

Fig. 1. Regional distribution of the samples. The localities marked show the approximate sampling sites. The broken lines serve only to distinguish the various regional groups.

by the pipette method (Elonen 1971). The fine clay fraction ($< 0.2\ \mu m$) was determined by centrifugal sedimentation. The grouping of samples into classes was based on the results of mechanical analyses. The heavy clay samples differ relatively little from each other in their textural composition (Fig. 2), whereas the other soil groups are more variable.

Table 1. Soil samples.

Sample No.	Locality	Soi use	Textural class	Horizon	Depth cm	$\text{pH}_{\text{CaCl}_2}$	Org. C %	Particle size (μm) distribution %						
								< 0.2	0.2—2	< 2	2—20	20—60	60—200	200—2000
1	Vantaa	Cultiv.	Heavy clay	C	60—90	5.4	0.8	39	49	88	9	2	1	0
2	Valkeala	,,		C	60—80	5.5	0.4	36	46	82	15	3	0	0
3	Sippola	,,	,,	C	60—80	6.2	0.4	33	52	85	11	3	1	0
4	Iitti	,,	,,	C	60—80	6.2	0.5	42	48	90	5	4	1	0
5	Pertteli	,,	,,	C	60—80	5.7	0.5	31	50	81	13	4	2	0
6	Somero	,,	,,	C	60—80	6.2	0.5	29	48	77	18	4	1	0
7	Tammela	,,	,,	C	60—80	6.1	0.4	48	46	94	4	2	0	0
8	Ikaalinen	Cultiv.	Silty clay	C	50—70	5.1	0.4	15	31	46	46	6	1	1
9	Iitti	,,		C	60—80	5.9	0.4	20	35	55	28	10	4	3
10	Isokyrö	,,	,,	C	60—80	5.7	0.9	18	35	53	41	5	1	0
11	Kauhava	,,	,,	C	60—80	6.3	0.5	11	40	51	46	3	0	0
12	Koski Tl. 1	Virgin	,,	C	60—80	6.2	0.5	17	38	55	30	10	4	1
13	Koski Tl. 2	Cultiv.	,,	C	60—80	6.2	0.4	14	44	58	32	8	1	1
14	Nurmijärvi	,,	,,	C	50—60	5.7	0.5	22	25	47	45	8	0	0
15	Ikaalinen	Cultiv.	Sandy clay	C	30—50	5.1	0.4	17	29	46	34	8	8	4
16	Laihia	,,		C	60—80	3.7	1.2	19	19	38	39	18	2	3
17	Karkku	,,	,,	C	40—60	4.6	1.1	8	27	35	41	11	7	6
18	Kiikoinen	,,	,,	B	20—40	5.4	0.8	12	23	35	37	6	12	10
19	Pernaja	,,	,,	B	20—40	5.0	1.0	16	24	40	17	31	11	1
20	Nakkila	,,	,,	C	40—60	4.0	1.5	9	31	40	39	17	3	1
21	Siuntio	,,	,,	B	20—40	5.1	1.4	12	39	51	24	10	11	4
22	Lavia	Cultiv.	Finer silt	C	40—60	4.7	1.1	10	26	36	50	1	4	9
23	Kuusankoski	,,		B	20—40	5.3	1.7	6	19	25	56	14	4	1
24	Iitti	,,	,,	C	40—60	5.9	0.3	6	19	25	67	6	1	1
25	Kangasala	Virgin	,,	B	20—35	4.2	1.4	1	25	26	67	3	1	3
26	Mouhijärvi	Cultiv.	,,	C	40—50	5.0	0.7	4	35	39	58	0	1	2
27	Hyvinkää 1	,,	,,	B	35—45	5.4	0.7	6	26	32	51	11	4	2
28	Hyvinkää 2	,,	,,	B	20—40	5.1	0.8	5.	25	30	59	5	3	3
29	Jyväskylä	Cultiv.	Coarser silt	C	40—60	4.8	0.9	1	23	24	60	15	1	0
30	Valkeala	,,		C	40—60	5.4	0.9	6	23	29	59	3	3	6
31	Ikaalinen	,,	,,	B	15—30	4.6	0.4	7	15	22	41	13	18	6
32	Iitti 1	,,	,,	C	40—60	5.5	0.3	9	18	27	58	13	1	1
33	Säynätsalo	,,	,,	C	40—60	5.2	0.4	2	15	17	50	25	4	4
34	Iitti 2	Virgin	,,	C	40—60	5.3	0.3	2	27	29	42	21	4	4
35	Siuntio	Cultiv.	,,	B	20—40	5.3	0.3	8	13	21	55	22	1	1
36	Kemin mlk	Cultiv.	Finer finesand	C	40—60	4.7	0.4	—	—	3	10	56	22	9
37	Mikkeli	,,		C	40—60	4.6	0.3	—	—	2	14	60	22	2
38	Laukaa	,,	,,	B	20—40	5.0	0.7	—	—	4	36	47	12	1
39	Valkeala	,,	,,	C	40—60	5.6	0.3	2	6	8	29	53	10	0
40	Pälkäne	,,	,,	C	40—60	5.1	0.5	4	9	13	31	39	16	1
41	Munsala	Virgin	,,	C	40—60	4.2	0.3	—	—	—	6	57	35	2
42	Kirkkonummi	Cultiv.	,,	C	40—60	6.0	0.2	4	10	14	28	33	18	7
43	Mikkeli	Cultiv.	Finesand	B	20—40	4.4	0.5	—	—	2	10	23	47	18
44	Iitti	,,	,,	C	40—60	5.3	0.4	—	—	4	4	10	66	16
45	Kaarina	,,	,,	B	20—40	4.8	1.0	7	13	20	10	7	41	22
46	Elimäki	Virgin	,,	B	15—25	4.1	2.8	—	—	—	—	8	59	33
47	Vantaa	,,	,,	C	50—70	4.3	0.6	—	—	3	1	5	51	40
48	Porvoo	Cultiv.	,,	C	40—60	4.6	0.4	—	—	4	2	11	73	10
49	Siuntio	,,	,,	C	40—60	4.4	0.4	3	7	10	7	11	54	18
50	Kemi	Virgin	Sand	C	50—70	4.6	0.1	—	—	—	—	—	2	98
51	Toivakka	,,	,,	B	10—40	5.0	0.7	—	—	—	—	2	6	92
52	Laukaa	,,	,,	B	10—20	4.5	0.2	—	—	—	—	1	4	95
53	Iitti 1	,,	,,	B	20—40	4.7	0.5	—	—	1	6	11	22	60
54	Iitti 2	,,	,,	A_2	5—15	4.1	1.2	—	—	2	8	15	18	57
55	Parainen	,,	,,	C	40—60	4.6	0.0	—	—	—	—	1	14	85
56	Lohja	,,	,,	C	40—50	5.0	0.2	—	—	—	—	—	3	97

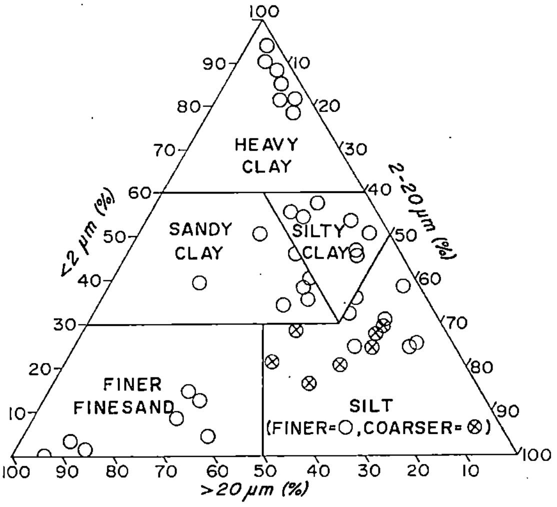

Fig. 2. The soil samples fitted into the textural triangle proposed by VUORINEN (1961). The finesand and sand samples are not shown but they would be concentrated in the left corner of the triangle.

Table 2. The pH, contents of organic C and dithionite extractable Fe, and particle size distribution of soil textural classes. Mean values with confidence limits at the 95 % level.

	Heavy clay	Silty clay	Sandy clay	Finer silt	Coarser silt	Finer finesand	Fine-sand	Sand
pH_{CaCl_2}	5.9 ± 0.3	5.8 ± 0.4	4.7 ± 0.6	5.1 ± 0.5	5.2 ± 0.3	5.0 ± 0.6	4.5 ± 0.4	4.6 ± 0.3
Org. C %	0.5 ± 0.1	0.5 ± 0.1	1.0 ± 0.1	0.8 ± 0.2	0.5 ± 0.1	0.4 ± 0.1	0.9 ± 0.4	0.5 ± 0.2
$Fe_{Extr.}$ %	1.5 ± 0.6	1.0 ± 0.6	1.7 ± 1.0	0.8 ± 0.3	0.8 ± 0.4	0.8 ± 1.4	0.3 ± 0.3	0.2 ± 0.2
Fraction:								
< 0.2 µm	37 ± 6	17 ± 4	13 ± 4	5 ± 3	5 ± 3	2 ± 2	1 ± 3	0 ± 0
0.2—2 µm	49 ± 2	35 ± 6	28 ± 6	25 ± 5	19 ± 5	4 ± 4	3 ± 5	0 ± 0
< 2 µm	86 ± 5	52 ± 4	41 ± 5	30 ± 5	24 ± 4	6 ± 3	6 ± 6	0 ± 1
2—20 µm	10 ± 5	38 ± 7	33 ± 8	58 ± 6	52 ± 7	22 ± 11	5 ± 4	2 ± 3
20—60 µm	3 ± 1	7 ± 3	14 ± 8	6 ± 5	16 ± 7	49 ± 9	11 ± 6	5 ± 6
60—200 µm	1 ± 0	2 ± 1	8 ± 3	3 ± 1	5 ± 6	19 ± 8	57 ± 10	10 ± 8
200—2 000 µm	0 ± 0	1 ± 1	4 ± 3	3 ± 2	3 ± 2	3 ± 3	23 ± 10	83 ± 16

2. Analytical methods

2.1 *Separation of particle size fractions*

To separate particle size fractions, 30 to 100 g of soil, depending on the texture of the sample, was treated with hydrogen peroxide and dithionite-citrate solution to remove organic matter and remove free iron oxides (MEHRA and JACKSON 1960). Two dithionite-citrate extractions were made followed by a mild hydrogen peroxide treatment to complete the extraction. After dispersion in 0.01 *M* sodium pyrophosphate the soil samples were fractionated by centrifugation, gravity sedimentation and sieving into the following six particle size fractions: < 0.2 µm, 0.2—2 µm, 2—20 µm, 20—60 µm, 60—200 µm and 200—2 000 µm (WHITTING 1965, DAY 1965).

The centrifugation time for separating the fine clay fraction (< 0.2 µm) was calculated using the integrated form of Stokes' law, which is given in the following form by WHITTING (1965):

$$\text{time in seconds} = \frac{n \log (R/S)}{3.81\, N^2 r^2 (\Delta S)}$$

where r is the particle radius (cm) and ΔS the difference in specific gravities of the particles and their suspension medium, which are 2.65 and 1.00, respectively. R is the radius of rotation (cm) of the top of the sediment in the tube. R was 22 cm in the MSE centrifuge used. S is the radius of rotation (cm) of the surface of the suspension. S was 10 cm in the separations made. When the height of sediment in the tube varied slightly during the separation, the height of the suspension was adjusted to keep the value of the expression log (R/S) constant. The viscosity n (in poises) is closely dependent on the temperature. Because the centrifuge warmed up during the separation, the suspensions were brought to the 30° C equilibrium temperature reached during the 46 minutes' centrifuging time before the centrifuging was started. The speed used was $N = 40$ revolutions per second.

After the centrifugation the supernatant liquid was decanted and the separation was repeated 5 to 6 times, or until the supernatant was almost clear. Coarse clay and silt were separated by gravity sedimentation and finer finesand, finesand and sand fractions by sieving.

For the various chemical, differential thermal and X-ray diffraction analyses, NH_4-, K- and Mg-saturated samples were prepared from the separated fractions (Whitting 1965). Normal chloride solutions were used for ion displacement in the centrifuge tubes. After three treatments the excess salts were first removed with water and finally with methanol. Fractions amounting to less than 5 % of the sample were separated, but only exceptionally were they prepared and analyzed further. Samples were dried at 50° C in an oven, ground fine in an agate mortar and stored in plastic vials.

2.2 *Differential thermal analysis*

Differential thermal analysis (DTA) was carried out with a Gerätebau Netsch apparatus. Samples for analysis were equilibrated over saturated $Mg(NO_3)_2$ solution, after which 700 mg was weighed for DTA without dilution (Mackenzie and Mitchell 1957). Ground potash feldspar was used as the inert reference substance. The rate of heating was 10° C per minute. Soil samples were first studied by DTA without any pretreatment. Separated particle size fractions were submitted to DTA as Mg-saturated samples.

DTA was also used to determine the amount of quartz in soil samples. The estimations were based on the area of the quartz peak occurring at 573° C (Grimshaw 1953). The area was calculated from the height and the half-height width of the peak. Particle size fractions of ground quartz diluted with powdered potash feldspar were used as standards for samples of respective soil textural classes.

2.3 *X-ray diffraction analysis*

X-ray diffractograms were obtained with a Philips diffractometer with Cu radiation filtered through Ni. Orientated slides of K- and Mg-saturated samples were prepared by drying the sample suspended in water at room temperature. To test for minerals with an expanding lattice, Mg-saturated samples on the slide were sprayed with dilute glycerol and dried at 50° C before the second X-ray examination. The K-saturated samples were heated at 500° C for one hour after the first X-raying to collapse the easily dehydrating interlayers. The contraction allows an assessment of the types of chlorites in the samples (Whitting 1965). The interpretation of the X-ray diffractograms was based mainly on the diffraction spacings of variously treated minerals (Table 3).

2.4 *Heavy mineral separations*

Heavy minerals were separated from some finesand and sand fractions. A mixture of density 2.68 was prepared from di-iodomethane and bromonaphthalene. Separation was carried out in a separating funnel. The heavy, non-floating minerals were run into a funnel in which a filter paper had been placed. The minerals and filter paper were washed with methanol and dried before weighing.

2.5 *Estimation of mineral components in particle size fractions*

The estimation of mineral components in particle size fractions was made with methods

Table 3. The principal X-ray diffraction spacings of layer silicates as related to the sample treatment (WHITTING 1965).

Diffraction spacing Å	Mineral indicated
	Mg-saturated, air-dried
14—15	Montmorillonite, vermiculite, chlorite
9.9—10.1	Mica
7.15	Kaolinite, chlorite
	Mg-saturated, glycerol solvated
17.7—18.0	Montmorillonite
14—15	Vermiculite, chlorite
9.9—10.1	Mica
7.15	Kaolinite, chlorite
	K-saturated, air-dried
14—15	Chlorite
12.4—12.8	Montmorillonite
9.9—10.1	Mica, vermiculite
7.15	Kaolinite, chlorite
	K-saturated, heated (500° C)
14	Chlorite
9.9—10.1	Mica, vermiculite, montmorillonite
7.15	Chlorite

proposed by ALEXIADES and JACKSON (1966). These methods are based on the chemical properties of minerals. The determination of vermiculite was based on that part of the cation-exchange capacity which is blocked by K fixation. Smectite was estimated on the basis of exchange capacity determined by K-saturation and subsequent displacement by NH_4. That part of this exchange capacity not allocated to other mineral components determined is assumed to represent smectite. The determination of chlorite was based on the relatively high hydroxyl water content, characteristic of chlorite (ALEXIADES and JACKSON 1967). The weight loss between 300 and 950° C is determined on the samples, and an average correction for the weight loss of other mineral components is made. The content of amorphous material was determined as the amount of alumina and silica which dissolves in alkali. The determination of mica and K feldspar was based on the K contents of these minerals (KIELY and JACKSON 1965). Total potassium was determined on the samples and the allocation of K to the two minerals was made by assuming that the K in the residue after pyrosulphate fusion to destroy sheet silicates represents K feldspar. Also Ca and Na feldspars were estimated on the bases of the Ca and Na contents in the fusion residue. A correction for dissolution of feldspars during the fusion was made. Quartz was determined as the difference between the fusion residue and the sum of feldspars estimated.

The chemical methods estimate the mineral composition of samples as endmember equivalent amounts (ALEXIADES and JACKSON 1966). Thus the estimates obtained for a given mineral include also amounts occurring as inclusions or mixed layers within crystals of other mineral species. The occurence in soils of such mineral mixtures is very common. To make a difference between minerals occuring as well crystalline material to which the names used refer and soil minerals which were estimated and are more variable in their properties, the names of minerals estimated are put in inverted commas. The determinations made were as follows:

"Feldspars" and "quartz". A 200 mg sample was weighed for determination of the amount of residue remaining after fusion with $Na_2S_2O_7$. Analysis for K, Na and Ca in the residue was carried out according to the HF-$HClO_4$ method (PRATT 1965).

The estimation of "Ca, K and Na feldspars" as endmember equivalent amounts in each fraction was as follows (KIELY and JACKSON 1965):

$$\%\ \text{"feldspar"} = \frac{\%\ \text{Ca, K or Na in residue}}{\text{(original sample basis)}} \times \begin{array}{c}\text{respective}\\ \text{conversion}\\ \text{factor}\end{array}$$

When calculating the amount of "Na feldspar" a special correction factor as proposed by KIELY and JACKSON (1965) for sodium absorption by potash feldspar during sodium pyrosulphate fusion was not used.

The percentage of "quartz" was calculated in each fraction by subtracting the sum of the estimated fusion residue of each "feldspar" from the percent fusion residue of the sample and correcting the result for dissolution of quartz as follows (KIELY and JACKSON 1965):

$$\%\ \text{"quartz"} = \frac{100}{\%\ \text{fusion residue of quartz}} \times \left(\%\ \text{fusion residue of the sample} - \sum \frac{\%\ \text{fusion residue of feldspar} \times \%\ \text{"feldspar"}}{100} \right)$$

The conversion factors and fusion residue percentages used (Table 4) were determined according to Kiely and Jackson (1965) using two sodium rich plagioclase feldspars, two K feldspars, three quartz samples and five sand fractions of soils. The feldspar samples and one quartz sample were provided by Mr. Ossi Näykki (Phil. Lic.), Department of Geology and Mineralogy, University of Helsinki. The two other quartz samples were quartz stones collected from South-West and Southern Finland. The sand fractions were separated from samples of sand soils collected from Southern Finland. Layer lattice minerals were removed from these sand fractions by pyrosulphate fusion before grinding in an agate mortar. The feldspar and quartz samples were similarly ground to obtain the needed size fractions by sedimentation and sieving.

Because feldspars went over to the fine fractions during the grinding of sand samples, it was not possible to determine the rate of dissolution of Ca, Na and K during separation. Therefore in calculating the conversion factors it was assumed that the component feldspars in fractions separated from sand soils dissolved at the same rate as the ground feldspars. The conversion factors used to estimate amounts as endmember equivalent feldspars were calculated according to Kiely and Jackson (1965).

"Mica". The percentage of "mica" was estimated from the amount of potassium alloted to "mica". The amount of "mica potassium" was obtained by subtracting "feldspar K" from the total K content of NH_4 saturated samples. The amount of potassium in feldspar was determined by the pyrosulphate fusion method (Kiely and Jackson 1965). The 7.5 per cent K content proposed as an average for trioctahedral mica by Alexiades and Jackson (1965) was used as the basis of the calculations as follows:

$$\%\ \text{"mica"} = \frac{\text{total K} - \text{"K feldspar" K}}{7.5} \times 100$$

"Amorphous material". "Amorphous material" was estimated as the sum of the

Table 4. Factors for converting the fusion residue K, Na and Ca to the respective endmember equivalent feldspars, and fusion residue percentages.

		Fraction µm				
		0.2—2	2—20	20—60	60—200	200—2 000
Conversion factors:						
K to K feldspar K	mean	1.75	1.20	1.12	1.08	1.05
	range	1.63 — 1.95	1.11 — 1.32	1.04 — 1.21	1.03 — 1.14	0.95 — 1.11
K to K feldspar	mean	13.0	8.63	8.04	7.67	7.47
	range	12.0 — 14.6	7.99 — 9.53	7.42 — 8.79	7.29 — 8.07	6.75 — 7.88
Na to Na feldspar	mean	15.1	12.2	11.8	11.6	11.6
	range	14.4 — 15.8	11.6 — 13.0	11.5 — 12.4	11.5 — 12.1	11.5 — 11.8
Ca to Ca feldspar	mean	14.7	9.31	8.14	7.47	7.24
	range	12.0 — 16.1	7.68 — 10.50	7.20 — 9.22	6.87 — 8.70	6.92 — 7.55
Fusion residue percentage of:						
K feldspar	mean	65.1	91.8	94.3	96.2	97.5
	range	61.3 — 68.8	91.5 — 92.2	93.9 — 94.6	96.1 — 96.2	96.3 — 98.7
Ca and Na feldspars	mean	56.2	88.4	92.6	95.9	96.5
	range	55.6 — 56.9	86.2 — 90.5	90.3 — 94.9	94.5 — 97.3	95.7 — 97.2
Quartz	mean	84.2	90.8	95.2	96.5	98.5
	range	82.0 — 86.3	89.4 — 92.7	94.6 — 96.7	95.9 — 96.9	97.3 — 99.6

amounts of Al_2O_3 and SiO_2 extracted by 0.5 $\mathcal{N}$ NaOH from K-saturated samples (HASHIMOTO and JACKSON 1960). Samples ranging from 100 mg to 1 g, depending on the texture, were boiled in 50 ml of 0.5 $\mathcal{N}$ NaOH for 2.5 minutes. The alumina and silica in centrifuged extracts were determined by atomic absorption spectroscopy. "Amorphous material" was assumed to contain 10 % water (ALEXIADES and JACKSON 1966).

"Vermiculite". "Vermiculite" was estimated from a difference between cation-exchange capacities determined in two ways. Firstly, exchange capacity was determined by saturating samples with calcium and using magnesium as the displacing ion. In the second determination, the same samples were saturated with potassium, washed free of excess salts, dried at 110° C overnight and then exchangeable potassium was displaced by ammonium. Neutral 1 $\mathcal{N}$ chloride solutions were used for displacements in leaching tubes. The exchanged calcium and potassium were determined by atomic absorption spectroscopy. The calculation of "vermiculite" was based on an average interlayer exchange capacity of 154 me/100 g for so called standard vermiculites studied by ALEXIADES and JACKSON (1965) as follows:

$$\% \text{ "vermiculite"} = \frac{CEC_{Ca}\text{-}CEC_K}{154} \times 100$$

where CEC_{Ca} is the exchange capacity in me/100 g determined by calcium saturation and CEC_K is the exchange capacity determined by potassium saturation (ALEXIADES and JACKSON 1965).

"Smectite". "Smectite" was estimated from the CEC_K values from which 5 me/100 g for external surface exchange capacity and 105 me/100 g for the component determined as "amorphous material" had been subtracted. The calculation was as follows (ALEXIADES and JACKSON 1965):

$$\% \text{ "smectite"} = \frac{CEC_K - (5 + 1.05 \times \% \text{ "amorphous material"})}{1.05}$$

"Chlorite". "Chlorite" was estimated from the weight loss due to ignition of K-saturated samples between 300 to 950° C (ALEXIADES and JACKSON 1967). The water loss in this temperature range due to other components was subtracted from the measured water loss of the sample to obtain the "chlorite" water loss. The water loss of other components was calculated by using the following average water contents: "mica" 4 %, "vermiculite" 4.5 % and "amorphous material" 8 %. A water loss of 14 per cent was used as the water loss of "chlorite". The weight gain caused by the oxidation of ferrous iron was directly converted to percent "chlorite". The calculation was as follows:

$$\% \text{ "chlorite"} = \frac{A\text{-}B}{14} \times 100 + (\% \text{ FeO}) \times 0.79$$

where A is the per cent ignition loss of the sample. B is the ignition loss caused by components other than "chlorite". FeO is the ferrous oxide percentage of each sample.

The variation coefficient of the chemical determinations used ranged from 2—4 % depending on the type of determination. The mean of duplicate determinations was calculated before estimating minerals. Therefore no estimates for variation in the actual mineral determinations were obtained. It is clear, however, that the various transformations made to calculate the contents of minerals cause an increase in the relative size of the error in the mineral estimates. Nevertheless, variation in the chemical properties used for the estimation of minerals is likely to be a more important source of error in the results.

2.6 *Estimation of mineral composition in the soil samples*

Method A. In method A, all chemical determinations for mineral analysis according to the method of ALEXIADES and JACKSON (1966) were made on unfractionated soil samples. The samples were saturated with the cation required by each analysis. "Mica", "chlorite", "vermiculite", "smectite" and "amorphous material" were calculated from the results of chemical analyses in the same way as for fractions using conversion factors based on the average properties of each component. The conversion factors and fusion residue percentages needed for calculating "feldspar" contents, the amount of potassium in "K feldspar" and the content of "quartz", were calculated for each sample as weighted averages of factors and residue percentages of particle size fractions according to the following formula:

$$a = \frac{\sum_{cc}^{s} bp}{\sum_{cc}^{s} p}$$

where
a is the conversion factor or fusion residue percentage of a soil sample for calculating "Ca-, Na-, K feldspar", "K feldspar" K or "quartz"
p is the percentage of a particle size fraction in the sample
b is the conversion factor or residue percentage for the respective particle size fraction
cc is coarse clay fraction
s is sand fraction

Method B. In method B, mineral contents of the various particle size fractions of each sample and the mechanical composition of the sample were used to calculate the mineral composition as follows:

$$B = \frac{\sum_{fc}^{s} mp}{100}$$

where
B is the percentage of a mineral in the soil sample
m is the percentage of the mineral in a particle size fraction
p is the percentage of the respective particle size fraction in the sample
fc is fine clay fraction
s is sand fraction

Method C. According to method C, the mineral composition of a given soil sample was calculated from the weighted average mineral composition of size fractions and from the particle size distribution of the sample. The weighted average mineral composition of a given fraction was obtained by using the percentage of the fraction in the sample as the weight in the following way:

$$w = \frac{\sum_{1}^{n} mp}{\sum_{1}^{n} p}$$

where
w is the weighted average percentage of the mineral in a particle size fraction
m is the percentage of the mineral in the respective particle size fraction of a sample
p is the percentage of the respective particle size fraction
n is number of samples analyzed

The calculation of the percentage amounts of minerals in samples was as follows:

$$C = \frac{\sum_{fc}^{s} wp}{100}$$

where
C is the percentage of a mineral in the soil sample
w is the weighted average mineral percentage of a fraction
p is the percentage of the fraction
fc is fine clay fraction
s is sand fraction

2.7 *Determination of some chemical properties of soils*

Air dried soil samples ground to pass through a 2 mm sieve were used for the determinations. Total analyses of K, Na, Ca, Mg and Fe were made using finely powdered NH_4-saturated 0.1 or 0.2 g samples. The HF-$HClO_4$ digestion was performed in teflon beakers and the residue was taken up in 6 *N* HCl. The solutions contained 0.5 % La to prevent interference in the atomic absorption spectroscopic determinations (Pratt 1965).

Total amounts of Cr, Co, Cu, Mn, Mo, Ni, Pb, Sr, V and Zn were determined using a 2 m ARL grating spectrograph. Silver and palladium were used as internal standards (Lappi and Mäkitie 1955). The excitation was made with 9 and 12 A currents for volatile and non-volatile elements respectively. The matrix of the standards was a gyttja clay.

Wet fixation of added potassium was determined according to Schachtschabel and Köster (1960). Ten grams of soil were shaken for one hour with 25 ml of 0.01 *N* KCl solution and 1 *N* ammonium acetate was used to displace the potassium. The estimates for potassium fixation on drying the sample were obtained in connection with the determination of "vermiculite".

Nonexchangeable acid-extractable potassium and magnesium were estimated by heating 5 g samples of soil in centrifuge tubes with 50 ml of 1 *N* HCl solution at 50° C in an oven for 24 hours (SCHACHTSCHABEL 1961). Stoppered centrifuge tubes containing the samples were shaken five times during the extraction period. Potassium and magnesium were determined by atomic absorption spectroscopy. Exchangeable cations were not removed before the extraction but the amounts of exchangeable potassium and magnesium determined by ammonium acetate extraction were substracted from the values obtained.

Basic exchangeable cations were extracted with 1 *N* neutral ammonium acetate. Titratable acidity was determined at pH 7 by the method of BROWN (1943). Exchange capacity (CEC_{Ac}) was estimated as the sum of basic exchangeable cations and titratable acidity. Values for cation exchange capacities (CEC_{Ca} and CEC_{K}) were also obtained in connection with the determination of "vermiculite".

Free iron was extracted by a dithionite-citrate solution and was determined by atomic absorption spectroscopy (HOLMGREN 1967). Ferrous iron was determined by titration with ammonium ferrous sulphate after decomposition of the sample with HF in presence of ammonium vanadate (WILSON 1960).

3. Minerals in the soil samples

Untreated soil samples were first studied by differential thermal analysis (DTA) to get a general idea of the types of minerals occuring in the samples. Because of great similarity of DTA curves obtained for samples in each soil textural class, only three curves of each class are shown in Fig. 3. Although there are minerals which cannot be detected in soils by DTA, the curves obtained indicate many of the minerals present in the samples studied.

In curves for the heavy clay soils, the relatively large first endothermic peak (maximum at 120—140° C) indicates the fineness of texture and large surface area in the material of these samples. In addition to smectites, or minerals of the montmorillonite-saponite group (BRINDLEY 1966), amorphous material and allophane produce a large endothermic reaction with a maximum at 120—140° C (GRIM and ROWLAND 1942, MITCHELL and FARMER 1962, BRACEWELL et al. 1970).

The peak with a maximum at 220—240° C indicates that there are minerals with crystal properties characteristic of vermiculite in these samples (e.g. BARSHAD 1948).

The temperature and intensity of the second endothermic maximum at 540—560° C is characteristic of illite-type minerals (GRIM and ROWLAND 1942, SOVERI 1950). The reactions at temperatures above 800° C caused by destruction of the structure of the layer lattice minerals are weak when compared to those of the normal illites (GRIM and ROWLAND 1942).

In silty and sandy clay samples, quartz is identifiable by the peak at 573° C in the DTA curves. Some of the sandy clay samples contain considerable amounts of organic matter (Table 1). This is indicated by a large exothermic reaction at the temperature range from 280—350° C in curves 18, 20 and 21. The endothermic reaction at 220—240° C which is noticeable in the curves of heavy and silty clays do not appear in the curves of sandy clays.

The DTA curves for finer finesand, finesand and sand soil samples (Fig. 3) show only a small primary endothermic peak, or it is totally absent. There are, however, indications of vermiculite, as shown by a shoulder at a little over 200° C in some of the curves. The size of the illite peak with the maximum between 500 and 600° C diminishes and there is no evidence of clay minerals in the curves for samples 50, 55 and 56 which belong to the sand soils. Instead the amount of quartz clearly increases when the particle size of samples increases.

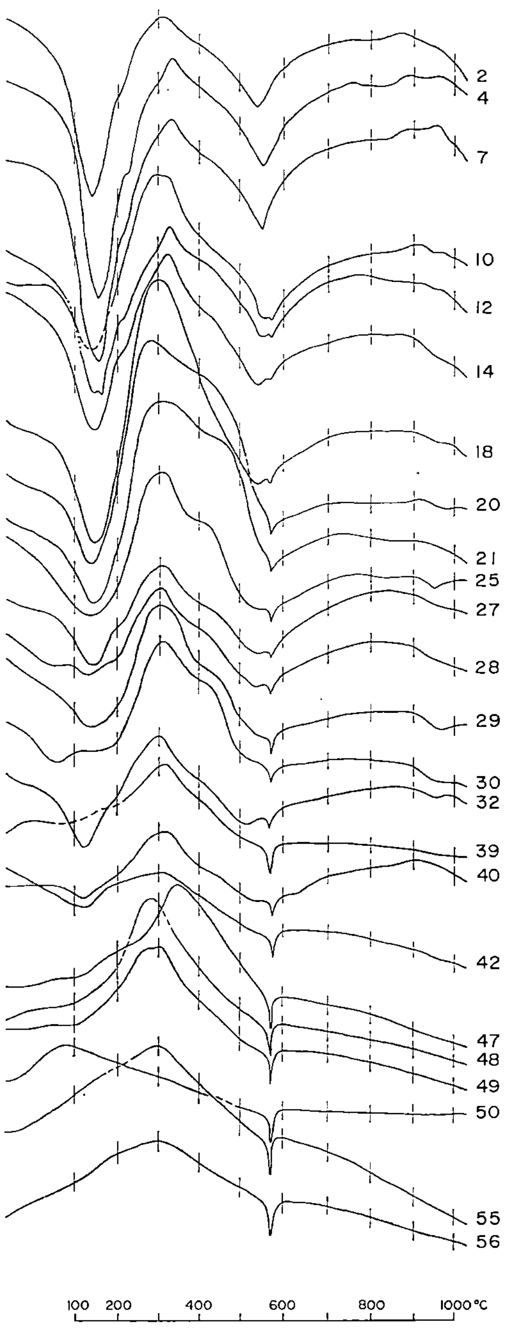

Fig. 3. DTA curves for heavy clay (2, 4, 7), silty clay (10, 12, 14), sandy clay (18, 20, 21), finer silt (25, 27, 28), coarser silt (29, 30, 32), finer finesand (39, 40, 42), finesand (47, 48, 49) and sand (50, 55, 56) soil samples. Numbers of the samples are as in Table 1.

3.1 *Mineral composition of particle size fractions*

Although it is possible to identify some minerals using the DTA method on untreated and non-fractionated samples, it is clear that fractionation will lead to a concentration of minerals into certain separates. Thus the identification of component minerals will be improved. Also the saturation of separated fractions with various ions, a method used extensively in the X-ray analysis of clay minerals, will help in identification with DTA. However, the treatments used to achieve particle size fractionation may cause some unwanted changes in the least stable minerals (BEUTELSPACHER and FIEDLER 1963, DOUGLAS 1967, EDWARDS and BREMNER 1967). Therefore intensive treatments should be avoided in the preparation of samples, and care should be used when the results are interpreted.

3.1.1 Qualitative mineral analyses of fine clay fraction

To determine which minerals are present in the fine clay fraction separated from various soils, differential thermal and X-ray analyses were carried out. The results are shown in Figs. 4 and 5. Because of the great similarity of DTA curves within each soil textural class of seven samples, only three curves are shown for each class. Of the three samples analysed with X-ray in each textural class, only one variously treated sample is shown in diffractogram form. Only three fractions of each textural class were studied by X-ray diffraction, since the DTA curves show that the mineral composition in each soil class was very similar. For X-ray investigations the most differentiating samples were selected.

DT-analyses. The DTA curves of fine clay did not indicate great dissimilarities between fractions separated from different soil textural classes. The height of the first endothermic reaction with the maximum at 140—160° C was of the same order for all classes and its size indicates a large amount of adsorbed water held by virtue of the fineness and large surface area of the material. The peak was broad, extending beyond 240°C, where the endothermic maximum, characteristic of vermiculite, occurs (Barshad 1948). The double peak as in curve 9 and less clearly in curve 26 indicates, however, the presence of vermiculite in this fraction. Also the broadening of the first endothermic peak at just above 200° C, as in curves 6, 13 and 22, shows that crystal lattices with the properties of vermiculite do occur in the fine clay (Kerns and Mankin 1967).

The second endothermic peak, the so-called clay mineral peak, with a maximum at 540 to 560° C was usually sharp, and resembled the peaks obtained with unfractionated heavy clay samples. The temperature of the peak maximum varied very little. Generally the peak temperature of clay soil separates was between 550 and 560° C whereas the peak temperature of silt soil separates was between 540 and 550° C. The size of the clay mineral peak was smallest with an average height of 47 ± 5 mm (mean with confidence limits at the 95 % level) measured on the original curves, in the curves for heavy clay separates. The height of the clay mineral peak increased with increasing particle size of samples from which the fine clay was separated. The average height of the corresponding peak in the curves for the fine clay fraction of coarse silt soils was 76 ± 10 mm. The second endothermic peak of the DTA curves does not indicate any differences in the mineral composition of fine clay fractions separated from various soils but does suggest that there are differences in the proportions of component minerals.

The temperature of the clay mineral peak suggests that it is caused by dehydroxylation of micaceous minerals or illites (Grim and Rowland 1942, Soveri 1950). The name illite was originally proposed as a general name for micaceous minerals occurring in sediments (Grim et al. 1937). This name has often proved useful for distinguishing clay micas from the well crystallized micas found in rocks.

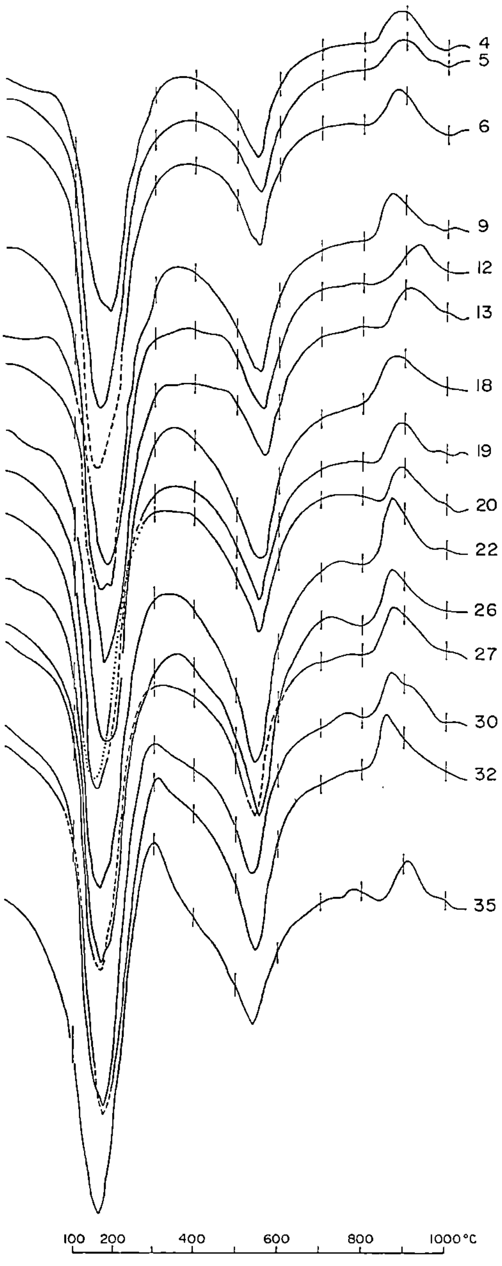

Fig. 4. DTA curves for fine clay fractions of heavy clay (4, 5, 6), silty clay (9, 12, 13), sandy clay (18, 19, 20), finer silt (22, 26, 27) and coarser silt (30, 32, 35) soils.

Many of the clay materials called illites, however, are better characterized as mixed layer minerals formed by interstratification of montmorillonite or vermiculite layers in a mica lattice (Gaudette et al. 1965). In particular, trioctahedral illites have been identified as interstratified mica-vermiculites or hydrobiotites (Farmer and Wilson 1970). However, also nonswelling trioctahedral illites have been identified (Weiss et al. 1956).

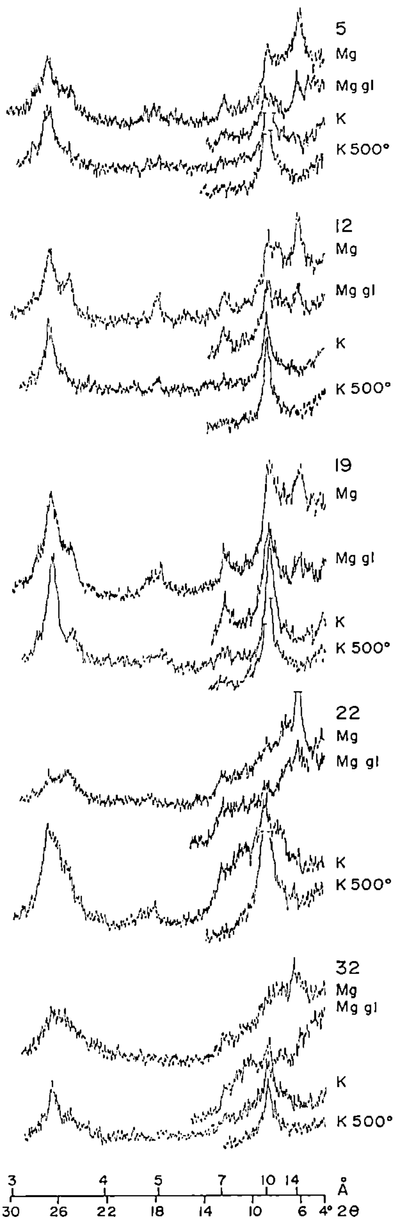

Fig. 5. X-ray diffractograms for fine clay fractions of heavy clay (5), silty clay (12), sandy clay (19), finer silt (22), and coarser silt (32) soils. The sample treatments are indicated as follows: Mg = magnesium saturated, Mg gl = magnesium saturated and treated with glycerol, K = potassium saturated, K 500° = potassium saturated and heated at 500° C for one hour.

Aluminium and iron rich chlorites release their crystal lattice water within the temperature range in which the maximum of the second endothermic reaction occurs in DTA curves for fine clay fraction separated from the present material (Phillips 1963, Alexiades and Jackson 1967). Soil montmorillonites also dehydroxylate below 600° C and may thus interfere (Schwertmann 1962). Thus the peak of dehydroxylation in curves for fine clay may be caused by several minerals and its use in identification is of doubtful value (Schwertmann 1961, Jørgensen 1965).

The temperature effects of reactions connected with the destruction of the crystal lattice at temperatures above 800° C are clear compared with effects in curves for unfractionated soil samples (Fig. 3). Differences in the intensity of this reaction were not large but the peak temperature seemed to vary. Most commonly the peak occured at below 900° C but curves 12 and 13 show that the reaction may also occur above 900° C, and in curve 30 both types seem to appear. A high temperature exothermic reaction without preceding endotherm is characteristic of alteration products of biotite (Soveri 1950). In some of the curves (numbers 20, 22, 26, 30 and 35 in Fig. 4) there is, however, a weak preceding endotherm which suggests that there may be a small amount of dioctahedral or normal illite in fine clay also (Jørgensen 1965). The specificity of this endotherm is, however, rather poor since also some chlorites show such a reaction at this temperature (Phillips 1963).

X-ray analyses. In X-ray diffractograms for fine clay (Fig. 5) fractions of clay soils the 10 Å peak characteristic of mica minerals is clear (cf. Table 3). The intensity of the 10 Å peak was, however, weaker in diffractograms of fine clay fractions of silt soils than in those of clay soils. The reflections of fine clay fractions of silt soils were also much broader than those of fractions of clay soils (Fig. 5, curves 22 Mg and 32 Mg). The 5 Å peak of mica was weak or totally absent, indicating that the mica in fine clay is trioctahedral rather than dioctahedral (Bradley and Grim 1961).

Vermiculite was identified very clearly in fine clay fractions of all investigated samples by the 14 Å peak, which was eliminated almost completely by potassium saturation of the samples (cf. Table 3). In most cases the 14 Å peak was higher than the 10 Å peak. No differences in the relative heights of the 10 and the 14 Å peaks were found between different soil textural classes.

The reflections appearing between 10 and 14 Å show that there are mixed layer minerals in the samples (WHITTING 1965). The weak maximum at about 12 Å (Fig. 5, diffractogram 19) is an indication of a regularly interlayered type (SAWHNEY 1967). The reflections between 10 and 14 Å without any clear maximum (Fig. 5, diffractogram 12) indicate random interlayering (BROWN and MACEWAN 1950).

The glycerol treatment of Mg-saturated samples (Mg gl) seemed to reduce the intensity of the 14 Å reflection. Also the reflections between 10 and 14 Å were weakened while those above 14 Å appeared in some of the samples to increase in intensity (diffractograms 5, 22, 32). Most of the fine clay fractions analysed with X-rays behaved like samples 12 and 19. They do not show any noticeable effect due to glycerol treatment other than weakening of the 14 Å reflection. A reduction in the intensity of reflections between 10 to 14 Å indicates the presence of expandable crystal spacings as mixed layers with mica (WHITTING 1965). The diffuseness of the reflections above 14 Å indicates that the material reacting to glycerol treatment does not have any well defined crystalline structure. The poorly crystalline structure may be caused by fineness of the material (FIELDES and FURKERT 1966). The greater expansion of small particle size fractions compared with that of larger sized material has been observed with fractions prepared by grinding and also with material separated from soil vermiculite (JONAS and ROBERSON 1960, KERNS and MANKIN 1967). It is thus possible that fine grained vermiculite causes the changes observed in diffractograms of fine clay fractions treated with glycerol (SOVERI 1956, 1957, van der MAREL 1959). However, also smectites originating from soils have a poorly defined crystal structure and they resemble vermiculites in many respects (SCHWERTMANN 1962). Therefore the changes observed in diffractograms after treatment with glycerol may be taken as indicative of smectitic interlayers.

The remaining reflections in X-ray diffractograms from potassium saturated crystal lattices larger than 10 Å did not have a clear maximum. Most of the intensity appeared as a broadening of the 10 Å peak indicating the presence of chlorite components in the mica crystal (RAMAN and JACKSON 1966). This broadening is very clear in curve 22 K.

In some of the diffractograms of potassium saturated samples the 7 Å peak was still present although it was weaker than in the diffractograms of magnesium saturated samples. Heat treatment of potassium saturated samples sharpened the 10 Å peak considerably and reflections between 10 and 14 Å and at 7 Å weakened or disappeared. This is an indication of the presence of aluminium hydroxy interlayers forming secondary chlorite (van der MAREL 1964).

The relatively intense background reflections and broad peaks in X-ray diffractograms of fine clay indicate that the material has a poorly defined crystal structure. Particularly the diffractograms for fine clay fractions of silt soils resemble somewhat diffractograms of allophane which is amorphous to X-rays (BEUTELSPACHER and van der MAREL 1961).

3.1.2. Mineral composition of fine clay fraction

The results of mineral determinations in fine clay are shown in Table 5. Since the coarse textured soils contain very little fine clay material, only fine clay fractions of clay and silt soils were analysed. Readily identifiable minerals — mica, chlorite, smectite and vermiculite — were estimated. In addition extractions with boiling 0.5 N NaOH were made to characterize the poorly defined mineral material.

The highest "mica" content, 50 %, was determined in a fine clay fraction of a heavy clay soil containing 89 % clay and 39 % fine clay. The average "mica" percentage in the fine clay fractions of all three clay soil groups is of the same order. The proportion of "mica" in the fine clay fraction of silt soils tends to be lower

Table 5. Mineral composition (%) of fine clay fraction (< 0.2 µm) of various soil textural classes (the number of samples in parentheses). Mean values with confidence limits at the 95 % level.

Mineral	Heavy clay (7)	Silty clay (7)	Sandy clay (7)	Finer silt (7)	Coarser silt (7)
"Mica"	37 ± 7	36 ± 6	36 ± 9	25 ± 4	23 ± 8
"Chlorite"	11 ± 6	13 ± 4	20 ± 6	34 ± 5	27 ± 7
"Vermiculite"	14 ± 5	14 ± 3	11 ± 5	5 ± 2	8 ± 4
"Smectite"	24 ± 3	23 ± 5	22 ± 5	12 ± 9	13 ± 5
"Amorphous material"	16 ± 1	18 ± 3	20 ± 4	29 ± 3	26 ± 3
Total	102 ± 4	104 ± 5	109 ± 9	105 ± 3	97 ± 4

than in that of clay soils. The lowest amount of "mica" determined in the group of coarse silt soils was 18 % and the highest 29 %.

The percentages of "chlorite", in contrast to those of "mica", tend to increase with increasing coarseness of the texture of the soils from which the fractions were separated. The fine clay fractions of heavy and silty clay soils contain on average almost identical amounts of "chlorite". In the present material the average "chlorite" percentage of the fine clay fractions of fine silt soils is higher than the mean "chlorite" content of the fine clay fractions of clay soils.

The average amount of "vermiculite" in the fine clay fractions of all clay and silt soils is 10 %. High contents of "vermiculite" were found in clay soil fractions and contents tended to be low in silt soil fractions. Especially in the finer silt soil fractions the content of "vermiculite" was low, the values were ranging from 1 to 8 %. The maximum amount, 22 % of "vermiculite", was found in the fine clay fraction of a heavy clay soil.

The content of "smectite" in fine clay tends to decrease with increasing coarseness of the texture of the soil from which the fine clay was separated. In fine clay fractions of all three clay soil groups the average content of "smectite" is very similar. The average "smectite" content of the two silt soil groups is relatively low. Because of the large variation within textural classes only the average for the coarser silt soil group is significantly lower than the average for the heavy clay group.

The values in Table 5 show that a considerable amount of "amorphous material" dissolves when fine clay is extracted with 0.5 N NaOH according to the method proposed by HASHIMOTO and JACKSON (1960) for estimating amorphous material in soils. The average amounts of "amorphous material" tend to increase with increasing coarseness of texture of the soils from which the fine clay fraction was separated. Low amounts of "amorphous material" were extracted from the fine clay fraction of heavy clay soils, indicating a better crystallinity in this fraction than in the fine clay fraction of coarser textured soils. Also in fractions separated from heavy clay soils the variation in the amount extracted is small. High amounts of "amorphous material" were extracted from the fine clay fractions of silt soils. The maximum amount, 34 %, was extracted from a fine silt soil fraction.

3.1.3 Comparison of results of chemical and physical analyses

Because of overlapping of peaks, it is not permissible to draw conclusions from a comparison of peak heights in diffractograms or DTA curves with mineral amounts estimated by chemical methods. However, an examination of some relationships is interesting (Figs. 4 and 5). The diminution in intensity of the 10 Å mica reflection with increasing coarseness of the soil from which the fraction was separated, is in accordance with the diminution of the respective

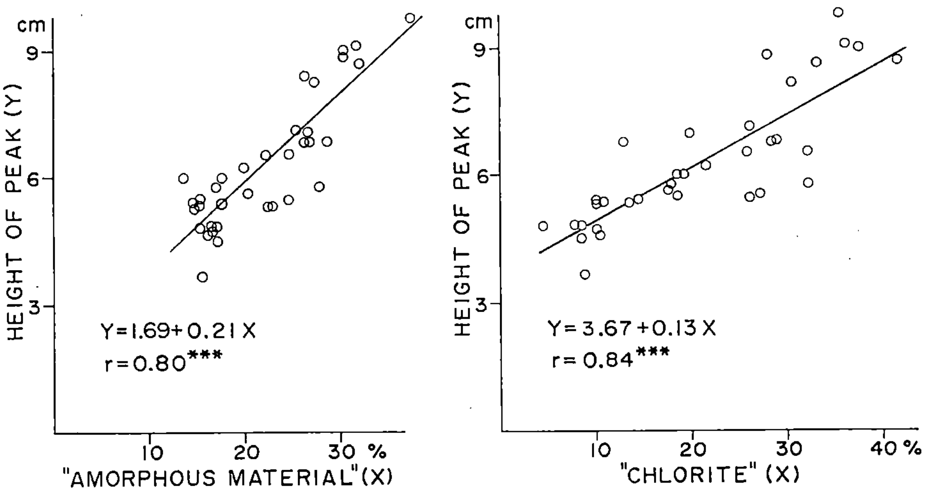

Fig. 6. Relationship between the height of the maximum of the clay mineral peak occurring in DTA curves at 540—560° C and the contents of "amorphous material" and "chlorite" in fine clay fractions.

"mica" values (Table 5). The height of the clay mineral peak in the DTA curves showed a negative correlation with the percentages of "mica" ($r = -0.68^{***}$) and "smectite" ($r = -0.65^{***}$). The height of the clay mineral peak was reasonably well correlated with the contents of "chlorite" ($r = 0.84^{***}$) and "amorphous material" ($r = 0.80^{***}$, Fig. 6).

Together the contents of "chlorite" (X_2) and "amorphous material" (X_3) explained 77 % of the variation in the height of the clay mineral peak (X_1, cm) according to the following regression equation (Ezekiel and Fox 1959):

$$X_1 = 2.39 + 0.081\ X_2 + 0.102\ X_3$$

$$R = 0.87^{***} \qquad \beta X_2 = 0.54$$

$$S = 0.77 \qquad \beta X_3 = 0.39$$

The effect of "amorphous material" in explaining the height of the clay mineral peak, as indicated by the regression analysis, suggests that the NaOH extractable material in Finnish soils is not related to allophane, the amorphous material characteristic of volcanic deposits. The DTA curve for allophane shows only a large, low temperature endotherm caused by the release of absorbed water and an exothermic reaction at about 900° C (Mitchell and Farmer 1962, Campbell et al. 1968).

The correlation of the height of the clay mineral peak with the "chlorite" content indicates that the chlorite in fine clay is of an aluminium or iron rich type rather than of a magnesium rich type which dehydroxylates above 600° C (Phillips 1963).

Although the X-ray diffractograms indicate only weakly the presence of chlorite in fine clay, chemical estimations reveal that "chlorite" is an important component of fine clay. In individual comparisons of X-ray diffractograms and chemical determinations, it was usually found that in cases where the amount of "chlorite" was high, the reflections between 10 and 14 Å remained high after potassium saturation (Fig. 5). This suggests that in fine clay a large part of the chlorite occurs as a mixed layer mineral.

Generally the peaks in the diffractograms for the fine clay fraction of silt soils were not so sharp as the peaks for the corresponding fraction of clay soils. The broadness of peaks suggests poor crystallinity and is in accordance with the high contents of "amorphous material" in fine clay fraction of silt soils.

3.1.4 Mineral composition of the coarse clay fraction

Physical analyses. In the DTA curves for coarse clay (Fig. 7) reactions typical of

Table 6. Mineral composition (%) of the coarse clay fraction (0.2 — 2 µm) of various soil textural classes (the number of samples in parentheses). Mean values with confidence limits at the 95 % level.

	Heavy clay (7)	Silty clay (7)	Sandy clay (7)	Finer silt (7)	Coarser silt (7)	Finer finesand (3)
"Mica"	33 ± 5	26 ± 4	30 ± 6	30 ± 5	23 ± 7	37 ± 18
"Chlorite"	9 ± 2	14 ± 3	17 ± 4	15 ± 4	15 ± 3	14 ± 16
"Vermiculite"	8 ± 1	7 ± 2	7 ± 2	6 ± 2	6 ± 4	4 ± 7
"Amorphous material"	3 ± 1	3 ± 1	6 ± 2	6 ± 2	5 ± 1	5 ± 7
"K feldspar"	12 ± 2	13 ± 2	10 ± 3	11 ± 3	14 ± 3	11 ± 9
"Na feldspar"	20 ± 1	18 ± 1	14 ± 2	16 ± 4	17 ± 3	15 ± 11
"Ca feldspar"	5 ± 1	5 ± 1	4 ± 1	4 ± 1	5 ± 1	4 ± 4
"Quartz"	14 ± 2	16 ± 4	13 ± 1	14 ± 3	15 ± 3	13 ± 9
Total	104 ± 2	102 ± 3	101 ± 4	102 ± 2	100 ± 3	103 ± 3

vermiculite at temperatures of 140 and 240° C were very clear in most of the curves. In the curves for samples 35 and 39 which were separated from silt and finer finesand soils, respectively, these peaks did not occur but there was a maximum at 200° C. Because the peaks at 140 and 240° C are formed by the stepwise removal of the water of hydration of magnesium in vermiculite (Walker and Cole 1957), the change in dehydration suggests that the environment of the sorbed magnesium differs in these samples from that in normal vermiculite. Curve 40 indicates that little vermiculite is present in this sample. At higher temperatures, there is a quartz peak at 573° C as well as the large endothermic reaction with the peak at 540 to 560° C. The reactions at higher temperatures seem to be strong in those curves in which the peak caused by quartz is absent, as in curves 18, 35 and 40.

In X-ray diffractograms for coarse clay fractions (Fig. 8), sharper peaks than those for fine clay fractions (Fig. 5) indicate that the minerals in coarse clay have a better crystal order than those in fine clay. In addition to peaks for the minerals found in fine clay peaks for quartz (4.21 Å), K feldspar (4.17 and 3.25 Å) and plagioclase feldspar (3.18 Å) appeared (van der Marel 1961). The peak with a maximum at 7.1 Å caused by chlorite is also very clear. Heat treatment at 500° C for one hour decreased the intensity of this peak but the peak did not disappear completely. Thus also primary chlorite is present in the coarse clay fraction. In some of the diffractograms, especially those of fractions prepared from sandy clay soils, reflections at about 8.5 Å caused by minerals of the amphibole group appeared (Soveri 1956). The position of the maximum of this peak varied, probably due to differences in amounts of the various constituent minerals in the amphibole. The amphiboles were ignored when determinations of minerals were made by chemical methods.

Chemical analyses. The variation in the contents of different minerals between various soil classes is smaller for coarse clay than for fine clay (Tables 5 and 6). In the coarse clay fraction, "mica" is on average more abundant than any other mineral. The "mica" content of individual fractions ranged from 11 % in a fraction separated from a coarser silt soil to 45 % in a coarse clay fraction of a finer finesand soil. There are no significant differences in the average "mica" contents between textural classes.

Low contents of "chlorite", from 6 to 12 %, were found in heavy clay soils. The content of "chlorite" in other soil classes ranged from 9 to 24 %.

The mean content of "vermiculite" in the coarse clay fraction tends to be lower in coarse- than in fine-textured soils but no statistically significant differences between soil groups were found. In many diffractograms the height of the 14 Å peak caused mainly by vermiculite is

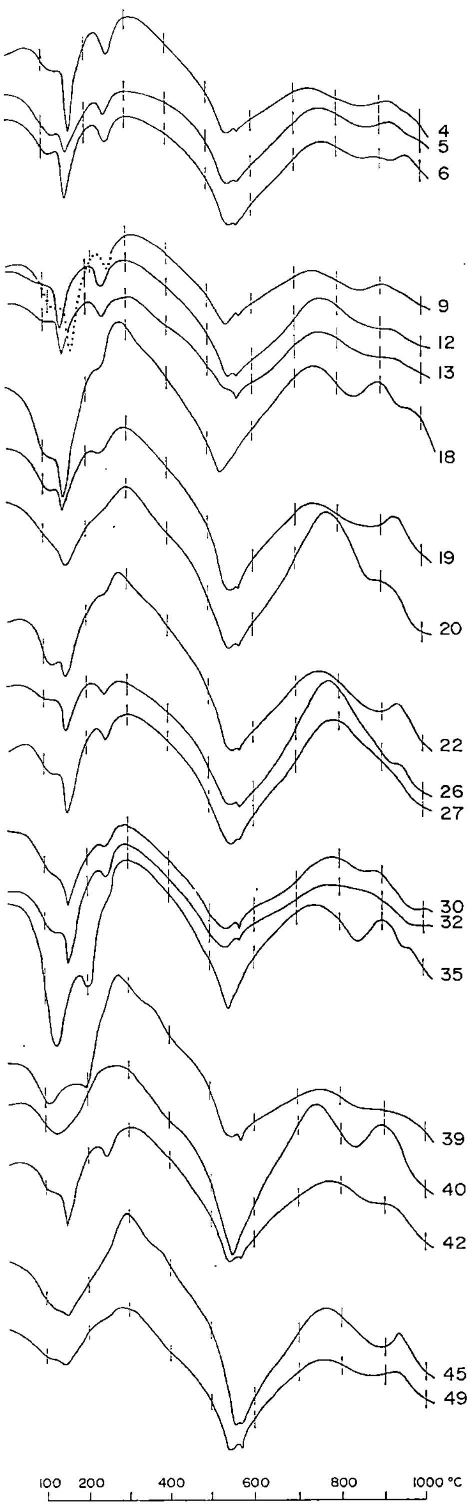

Fig. 7. DTA curves for coarse clay fractions of heavy clay (4, 5, 6), silty clay (9, 12, 13), sandy clay (18, 19, 20), finer silt (22, 26, 27), coarser silt (30, 32, 35), finer finesand (39, 40, 42) and finesand (45, 49) soils.

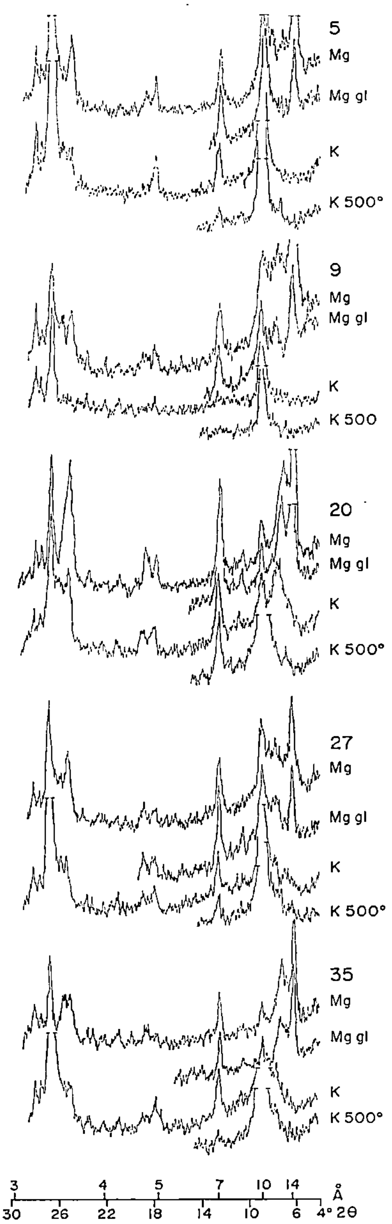

Fig. 8. X-ray diffractograms for coarse clay fractions of heavy clay (5), silty clay (9), sandy clay (20), finer silt (27) and coarser silt soils (35). The treatments are indicated in Fig. 5.

higher than the 10 Å mica peak. No clear agreement between the relative heights of these peaks and the results of chemical analyses was, however, found in the comparisons made. The effect of chlorite on the 14 Å peak may, indeed, make such a comparison impossible.

In the coarse clay fraction of heavy and silty clay soils the content of "amorphous material" is only about one half of the content of "amorphous material" in the coarse clay of sandy clay, finer and coarser silt and finer finesand soils. The widest range of determined values, extending from 4 to 11 %, was found in fractions separated from the finer silt soil group.

The three "feldspar" components form an important part of the minerals in coarse clay. The variation in the content of "K feldspar" between soil textural classes is small. The highest and lowest means of "Na feldspar" contents were found in fractions separated from heavy and sandy clay soils, respectively. The mean contents of "Ca feldspar" in the coarse clay fraction of all soil textural classes were very similar, ranging from 4 to 5 %. The widest range of the "Ca feldspar" content was found among fractions separated from heavy clay soil, and extended from 3 to 7 %.

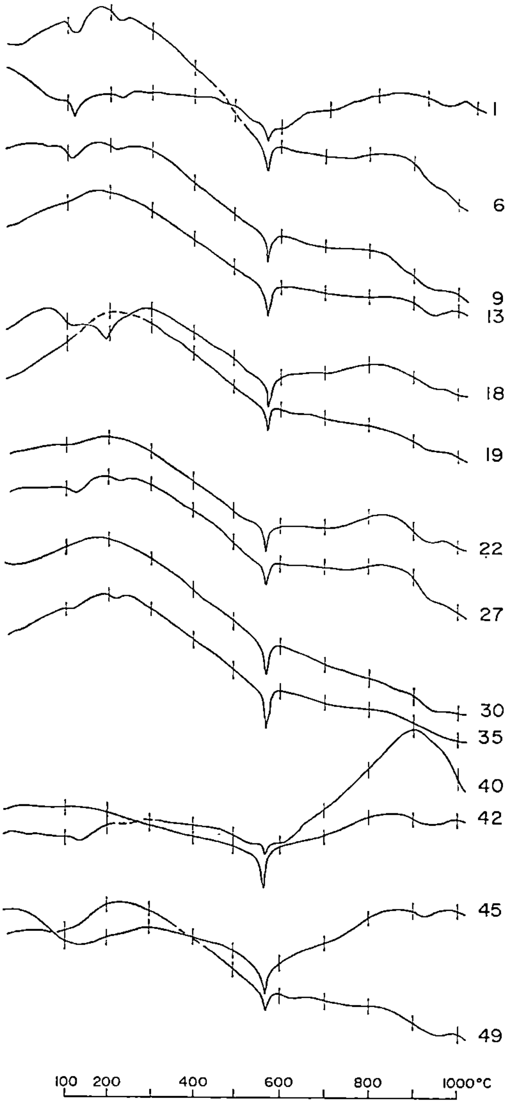

Fig. 9. DTA curves for silt fractions of heavy clay (1, 6), silty clay (9, 13), sandy clay (18, 19), finer silt (22, 27), coarser silt (30, 35), finer finesand (40, 42) and finesand (45, 49) soils.

The textural class averages for "quartz" contents vary relatively little. The difference between the lowest and highest mean is three per cent and the variation within textural classes is large, so that the "quartz" contents of coarse clay in soil classes under study do not deviate from each other. The lowest amount of "quartz" was 9 % in a coarse silt soil fraction and the highest 24 % in a silty clay soil fraction.

3.1.5 Mineral composition of the silt and coarser fractions

Physical analyses. In most of the DTA curves for silt fractions the clearest thermal reaction was the quartz peak at 573° C (Fig. 9). In some of the curves it was possible to identify traces of vermiculite. The DTA curves for finer finesand, finesand and sand fractions were similar to the curves obtained for the unfractionated soil samples of the respective particle size (curves 39—56 in Fig. 3). Curves for these fractions showed an increase in the content of quartz with increasing particle size of fractions, and there were no indications of other minerals.

In the X-ray diffractograms of silt fractions, mica and vermiculite were evident with peaks at 10 and 14 Å, respectively (Fig. 10). The reflections caused by these sheet silicates were weak in diffractograms of fractions coarser than silt. Indications of mica were still, however, present even in diffractograms of sand fractions. In some of the diffractograms of silt fractions, vermiculite reflections were very strong as in sample 22 (Fig. 10), whereas in others these reflections were very weak as in sample 32

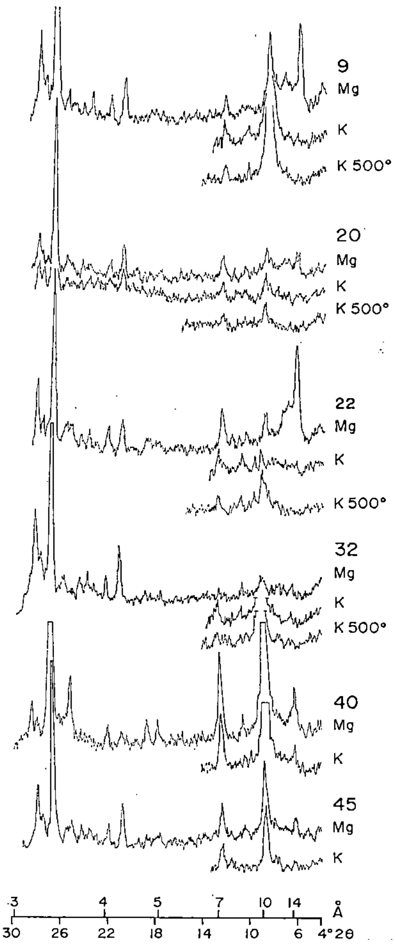

Fig. 10. X-ray diffractograms for silt fractions of silty clay (9), sandy clay (20), finer silt (22), coarser silt (32), finer finesand (40) and finesand (45) soils. The treatments are indicated in Fig. 5.

(Fig. 10). Vermiculite collapsed easily on potassium saturation, and heat treatment did not destroy the 7 Å peak indicating normal chlorite (van der Marel 1964). In sand fractions only minor amounts of vermiculite and chlorite were indicated by the peaks in the diffractograms.

In the diffractograms of silt fractions, reflections of potassium and plagioclase feldspars as well as the quartz peak were strong, indicating higher amounts of these minerals in silt than in finer textured fractions. In the X-ray diffractograms of finer finesand, finesand and sand fractions, the strength of the reflection caused by quartz was even more intense (Fig. 11).

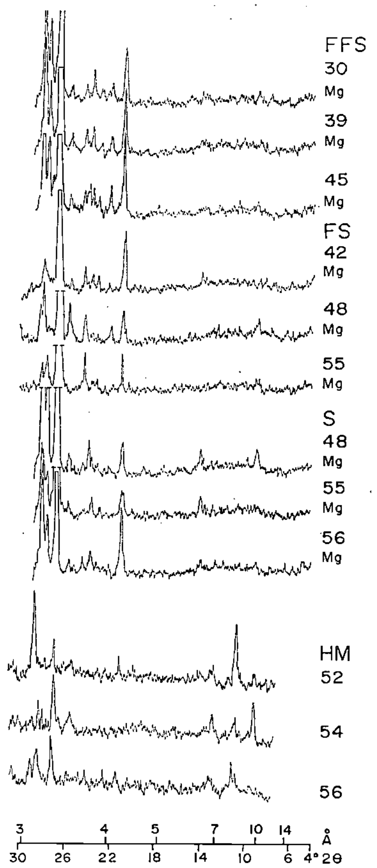

Fig. 11. X-ray diffractograms for some finer finesand (FFS 30, 39, 45), finesand (FS 42, 48, 55), sand (S 48, 55, 56) and heavy mineral (HM 52, 54, 56) fractions. Mg refers to magnesium saturation.

In most of the diffractograms of silt and coarser fractions, reflections of amphibole minerals were also observed. To allow more certain identification of these minerals, separations with a liquid of specific gravity 2.68 were made. The contents of heavy minerals in seven finesand and sand fractions separated varied from 2 to 17 % with an average of 7 %. As shown by the X-ray diffractograms (Fig. 11, HM diffractograms) the heavy mineral fraction contained minerals of the amphibole and pyroxene groups as well as mica, chlorite and calcium rich plagioclase. The strongest reflections of amphibole minerals were at about 8.5 and 3.13 Å. The pyroxene reflections were most evident at 3.36, 3.20 and 2.88 Å.

Table 7. Mineral composition (%) of the silt fraction (2 — 20 µm) of various soil textural classes (the number of samples in parentheses).
Mean values with confidence limits at the 95 % level.

	Heavy clay (6)	Silty clay (7)	Sandy clay (7)	Finer silt (7)	Coarser silt (7)	Finer finesand (7)	Fine-sand (3)
"Mica"	11 ± 4	11 ± 2	9 ± 3	11 ± 8	7 ± 3	12 ± 10	11 ± 4
"Chlorite"	10 ± 2	5 ± 2	8 ± 2	4 ± 2	4 ± 2	9 ± 7	8 ± 2
"Vermiculite"	3 ± 1	2 ± 1	2 ± 1	1 ± 1	1 ± 1	1 ± 1	1 ± 1
"Amorphous material"	1 ± 0	1 ± 0	3 ± 2	1 ± 0	1 ± 0	2 ± 2	3 ± 5
"K feldspar"	16 ± 3	14 ± 2	15 ± 2	18 ± 3	18 ± 3	14 ± 4	13 ± 2
"Na feldspar"	25 ± 3	23 ± 3	24 ± 3	27 ± 3	27 ± 2	23 ± 5	21 ± 5
"Ca feldspar"	8 ± 1	6 ± 1	7 ± 1	8 ± 2	8 ± 1	8 ± 2	7 ± 5
"Quartz"	30 ± 3	33 ± 4	32 ± 3	29 ± 4	33 ± 3	29 ± 10	32 ± 4
Total	104 ± 2	95 ± 4	100 ± 2	99 ± 2	99 ± 3	98 ± 4	96 ± 7

Chemical analyses. Chemical determinations indicate that the silt fraction separated from various soil textural classes is more homogeneous in mineral composition than coarse clay fraction (Tables 6 and 7).

"Mica" constitutes on average 10 % of the silt fraction (Table 7). The highest content of "mica" in individual samples was 33 % in the silt fraction of a finer finesand soil. In finer finesand, finesand and sand fractions the textural class averages for "mica" ranged from 1 to 6 % (Tables 8, 9 and 10). The variations within soil textural classes were relatively large so that no differences between textural classes are evident. The "mica" content in 20 to 2 000 µm fractions varied from 0 to 13 % in finer finesand, from 0 to 20 % in finesand and from 1 to 9 % in sand soils. The exceptionally high "mica" content, 20 % in a finesand fraction, was found in a finer finesand soil from Pälkäne, Central Finland. Also other size fractions of this soil contained high amounts of "mica".

The variation in the content of "chlorite" in the silt fraction (Table 7) was relatively large. The amounts ranged from 0 to 23 % in individual samples. Due to this large variation, no statistically significant differences were found in the average "chlorite" contents between textural classes. For the finer finesand fraction the average "chlorite" contents of the textural classes analyzed range from 1 to 4 % (Table 8). The corresponding ranges for finesand and sand fractions were 1 to 6 % and 3 to 5 %, respectively (Tables 9 and 10).

The proportion of "vermiculite" in the silt fraction is generally low and the average amount tends to decrease with increasing coarseness of the soil textural class from which the frac-

Table 8. Mineral composition (%) of the finer finesand fraction (20 — 60 µm) of various soil textural classes (the number of samples in parentheses).
Mean values with confidence limits at the 95 % level.

	Silty clay (6)	Sandy clay (7)	Finer silt (3)	Coarser silt (6)	Finer finesand (7)	Fine-sand (7)
"Mica"	4 ± 4	2 ± 2	2 ± 1	3 ± 2	4 ± 4	4 ± 2
"Chlorite"	2 ± 2	4 ± 2	3 ± 1	1 ± 1	2 ± 2	3 ± 2
"Vermiculite"	1 ± 0	1 ± 1	1 ± 0	0 ± 0	1 ± 0	0 ± 0
"Amorphous material"	1 ± 1	1 ± 0	0 ± 0	0 ± 0	0 ± 0	1 ± 1
"K feldspar"	15 ± 3	15 ± 1	19 ± 7	17 ± 3	15 ± 2	13 ± 2
"Na feldspar"	23 ± 5	25 ± 3	26 ± 2	25 ± 2	26 ± 2	23 ± 2
"Ca feldspar"	8 ± 2	9 ± 1	9 ± 3	9 ± 1	10 ± 1	11 ± 2
"Quartz"	44 ± 4	44 ± 6	37 ± 8	41 ± 3	40 ± 5	42 ± 3
Total	98 ± 4	101 ± 2	97 ± 8	96 ± 3	98 ± 2	97 ± 3

Table 9. Mineral composition (%) of the finesand fraction (60—200 µm) of various soil textural classes (the number of samples in parentheses).
Mean values with confidence limits at the 95 % level.

	Sandy clay (5)	Finer finesand (7)	Fine-sand (7)	Sand (4)
"Mica"	3 ± 6	6 ± 6	3 ± 2	3 ± 4
"Chlorite"	1 ± 2	5 ± 5	3 ± 1	6 ± 9
"Vermiculite"	0 ± 0	1 ± 1	0 ± 0	0 ± 0
"Amorphous material"	0 ± 0	0 ± 0	0 ± 0	3 ± 6
"K feldspar"	13 ± 4	15 ± 4	15 ± 4	17 ± 8
"Na feldspar"	22 ± 2	24 ± 2	23 ± 1	22 ± 3
"Ca feldspar"	8 ± 2	7 ± 1	8 ± 2	8 ± 2
"Quartz"	54 ± 3	45 ± 5	50 ± 3	45 ± 12
Total	101 ± 4	103 ± 2	102 ± 3	104 ± 1

tion was separated. In finer finesand and finesand fractions the proportion of "vermiculite" is small and none could be found in the sand fraction (Tables 8, 9 and 10).

The amount of "amorphous material" in the silt fraction is quite small. The averages for all textural classes range from 1 to 3 % (Table 7). However, in some fractions separated contents up to 6 % were found. In finer finesand, finesand and sand fractions, the amount of "amorphous material" is small, but occasionally also relatively high contents appeared, as in the finesand fraction of sand soils.

The average content of "K feldspar" ranges from 13 to 18 % in the silt fractions of various textural classes (Table 7). The corresponding range is from 13 to 19 % in finer finesand and 13 to 17 % in finesand soils (Tables 8 and 9). The content of "K feldspar" in the sand fraction is on average 20 % in the two textural classes from which this fraction was analyzed (Table 10). The variation within textural classes is large and therefore no differences between textural classes are evident. The lowest "K feldspar" content in the silt fraction was 8 %, and was found in a finer finesand soil. The highest value was 23 % in the silt fraction of a coarse silt soil.

"Na feldspar" constitutes roughly one quarter of the silt fraction (Table 7) and also in the coarser fractions its proportion is similar (Tables 8—10).

In the silt fraction the content of "Ca feldspar" varied little between the textural classes. The finer finesand fraction of finesand soils are rich in "Ca feldspar". The content of "Ca feldspar" was very similar in the finesand and sand fractions of all textural classes.

"Quartz" is the most abundant mineral in the silt fraction, amounting on average to almost one third of the total fraction. The silt fraction of finer finesand soils varied most in its "quartz" content. In this fraction the values ranged from 13 % to 41 %. Due to large variations within soil groups the differences between textural classes are not significant. In the finer finesand fraction the "quartz" content of individual soil samples ranged from 32 to 56 %. In the finesand and sand fraction the respective ranges of variation were from 35 to 58 % and from 40 to 53 %, respectively.

Table 10. Mineral composition (%) of the sand fraction (200—2 000 µm) of various soil textural classes (the number of samples in parentheses).
Mean values with confidence limits at the 95 % level.

	Finesand (7)	Sand (7)
"Mica"	4 ± 3	1 ± 2
"Chlorite"	3 ± 1	5 ± 1
"Vermiculite"	0 ± 0	0 ± 0
"Amorphous material"	0 ± 0	1 ± 1
"K feldspar"	20 ± 4	20 ± 5
"Na feldspar"	24 ± 2	22 ± 2
"Ca feldspar"	6 ± 2	6 ± 2
"Quartz"	46 ± 3	49 ± 4
Total	103 ± 2	104 ± 2

3.1.6 Accuracy of the mineral estimations

The chemical methods estimate the main mineral groups as endmember equivalent amounts. Actually each mineral group in the analysis scheme used includes many types differing in their properties. For example three micas, muscovite, biotite and phlogopite are common in soils (Soveri 1956, Foster 1962, Jackson 1965, Raman and Jackson 1966, Wilson 1966). Each of these minerals varies in content of potassium (Deer et al. 1962) which property was used for the estimation of mica in this study. The fine grained soil micas, the illites, are still more variable in composition (Weaver 1965). Therefore estimation of the illite content, based on the total potassium content, has been considered worthless (van der Marel 1966).

However, at least some of the illites are mixed layer minerals with interlayers of mica with vermiculite, smectite or chlorite (Gaudette et al. 1965, Raman and Jackson 1966). Even though all the associate minerals in illites are taken into account, the mica component is likely to contain less potassium than the large particle sized micas in rocks because of the loss of potassium from cleavage and edge surfaces. This loss is considerable when the particle size becomes very small (Ståhlberg 1960 a, Raman and Jackson 1966). The 7.5 % potassium content of mica used in the calculations allows for some reduction in the content of total potassium when the particle size decreases, compared with the theoretical potassium content of trioctahedral mica. The potassium content of the mica in fine clay may, however, be still lower. Therefore for comparison "mica" values are calculated assuming that the total potassium content of mica in fine clay is 7.0 or 6.5 % (Table 11).

A one per cent unit decrease in the potassium content of mica has a lower effect on the sum of all minerals than on the "mica" values because of the decrease in "chlorite" values. The occurence of small amounts of minerals not clearly identified in fine clay with X-ray and differential thermal analysis must be taken into account. The detection of small amounts of kaolinite in samples which contain also chlorite is difficult due to overlapping of their 7 Å peaks (von Engelhardt 1961). Thus small amounts of kaolinite originating from Preglacial weathered rocks (Frosterus 1928) may occur in fine clay. This is confirmed by the results of the infrared analysis of a Finnish Glacial clay carried out by van der Marel (1966). In fine clay low contents of feldspars and quartz may also occur (Sippola 1972).

Also a potassium content lower than 7.5 % may not be very suitable for estimating the mica content, because a part of the mica in the sam-

Table 11. "Mica" contents (%) of fine clay fractions calculated assuming the content of potassium in "mica" to be 7.5, 7.0 and 6.5 % K and the effects of variations in "mica" content on the content of "chlorite" and total minerals.

	Heavy clay	Silty clay	Sandy clay	Finer silt	Coarser silt
"Mica", calculation based on:					
7.5 % K	37	36	36	25	23
7.0 % K	39	39	38	27	25
6.5 % K	42	42	41	29	26
"Chlorite"	11	13	20	34	27
	10	12	19	33	26
	9	11	18	32	26
"Vermiculite" + "Smectite" + "Amorphous material"	54	55	53	45	47
Total	102	104	109	104	97
	103	106	110	105	98
	105	108	112	106	99

ples studied may be of dioctahedral type whose potassium content is higher than that of trioctahedral mica. Indications of the presence of dioctahedral mica were obtained with differential thermal and X-ray analyses.

Soils contain several types of chlorite which differ from each other in their chemical composition and dehydroxylation properties (van der MAREL 1964). Primary or normal chlorite originates from rocks and contains magnesium or iron fixed as hydroxide sheets in their interlayers. Secondary chlorite formed through weathering has aluminium as the major cation forming the interlayer hydroxide sheet. The amount of hydroxyl water, on which the estimation of "chlorite" was based, is variable and may range from 9.1 to 15.0 % (DEER et al. 1962). The 14 % hydroxyl water content used for chlorite estimation in the present study is an experimentally deduced value yielding close to 100 % recoveries with tested samples representing standard minerals and soil clays (ALEXIADES and JACKSON 1967). The 14 % water loss is high when compared with values reported in the literature (DEER et al. 1962). It may, however, take in account also some of the effects of organic matter which is usually present even in subsoils and which is difficult to destroy completely with H_2O_2.

The accuracy of "chlorite" estimations is affected also by the fact that feldspars and quartz may contain water which is lost only at a higher temperature than 300° C (KELLEY et al. 1935). Also the correction made for "amorphous material" may be a source of error due to variability of the composition of the poorly defined material extracted by NaOH. Variable contents of crystal lattice water in micas and vermiculites may add to the uncertainty of "chlorite" estimates (DEER et al. 1962).

The interlayer exchange capacity, 154 me/100 g, used to estimate vermiculite is an average for standard vermiculites studied by ALEXIADES and JACKSON (1965). For newly formed vermiculite, interlayer exchange capacities ranging from 177 to 198 me/100 g have been found (RAMAN and JACKSON 1966). A vermiculite isolated from soil had an exchange capacity of only 95 me/100 g (LE ROUX et al. 1963).

The variation in the hydration and dehydration properties of vermiculite in Finnish soils observed by SOVERI (1956) may possibly affect potassium fixation, which was used to estimate the amount of vermiculite.

The reflections from 10 to 13 Å in the diffractograms are also indicative of various intermediate stages of weathering, and show the diffuse limit between the various mineral categories. The content of "vermiculite" obtained by chemical estimations is a value for total fixation capacity where all materials capable of fixing potassium are included. The smectite formed in soil has properties similar to those of the minerals from which it has been weathered (SCHWERTMANN 1962). Therefore in the method used potassium fixing smectite is included in the estimate for vermiculite.

Smectite was not clearly identifiable by X-ray analysis. Its most likely mode of occurence in fine clay is therefore as a mixed layer component in the crystals of other sheet silicates. The 105 me/100 g interlayer exchange capacity used to estimate smectite is a mean value proposed by ALEXIADES and JACKSON (1965). The exchange capacities of twelve smectites studied by HARWARD et al. (1969) ranged from 95 to 138 me/100 g with an average of 118 me/100 g. Thus also the exchange capacity of smectite like that of vermiculite is variable and is a source of error in estimations.

The so-called standard smectites occur as particles even larger than 2 μm. Soil smectites, however, occur mostly as particles smaller than 0.2 μm (SCHWERTMANN 1962). The fact that no indications of smectite were found in coarse clay shows that the smectite in Finnish soils is of the type characteristic of soils.

It is generally agreed that amorphous or poorly defined mineral material exists in soils. In contrast to the allophane of volcanic origin so-called soil allophane has a highly variable composition (MITCHELL et al. 1964). Generally it is assumed that soil allophane occurs as surface coatings of soil particles. The difficulties involved in characterizing soil allophane are obvious and there is no generally approved method for its determination. NaOH solution is considered to be quite an effective extractant but its specificity is probably rather poor. For example it has been used for extracting the interlayer aluminium of soil clays (Scheffer et al. 1961 b, Wilson 1966). Also fine crystalline material is attacked by NaOH to some degree (Wada and Greenland 1970). Potassium saturation of the samples before the extraction treatment, however, obviously reduces the dissolution of material from the interlayers and also of crystalline minerals.

The variability in the chemical composition and crystal structure causes errors also in chemical estimations of feldspars and quartz. This is indicated in the present study by the differences in conversion factors and fusion residue percentages obtained with minerals of various origin. The largest variation was in the Ca feldspar conversion factor for coarse clay which ranged from 12.0 to 16.1 (Table 4). In accordance with the results of Kiely and Jackson (1965) a coarse clay fraction, prepared from a plagioclase with 60 % equivalent Ca feldspar content, yielded a fusion residue of only 8 %. It is obvious that the estimation of fine particle sized plagioclase feldspars rich in Ca is highly uncertain.

Kiely and Jackson (1965) proposed different factors for samples of various types of plagioclase feldspars classified according to the Na_2O/CaO ratio. The five sand preparates from various parts of Finland, used for determination of the conversion factors, ranged from 9 to 18 % in their Ca feldspar equivalents. The total analysis showed that there were no samples very rich in Ca in the material studied. Therefore only one conversion factor was used to transform the Ca in fusion residue to "Ca feldspar".

The Na feldspar conversion factors, determined using fractions prepared from sand soil samples and used for Na feldspar determination of coarse clay fractions, appeared to vary relatively little, ranging from 14.7 to 15.8. However, the two plagioclase feldspars yielded much larger conversion factors, 20.0 and 22.0. Since it is likely that sodium is absorbed differently during fusion by a sample containing K feldspar and quartz in addition to plagioclase as compared with plagioclase alone, the high factors were ignored when an average conversion factor was calculated for the estimation of Na feldspar in coarse clay. For coarser fractions the conversion factors obtained from plagioclase fractions were in the range of those determined using fractions ground from sand soils.

The relatively low variation of the conversion factor for Na feldspar may have been caused by a substantial adsorption of sodium by the sample. A special factor suggested by Kiely and Jackson (1965) for correcting for this adsorption was not used, because the adsorption was not found to be correlated with the content of K feldspar and because the increase in Na content is taken into account in calculating the conversion factor.

The K feldspars studied dissolved during the fusion treatment to a similar degree to the samples of Kiely and Jackson (1965). Also the conversion factors obtained for fractions ground from sand soils were of the same order as the factors obtained by Kiely and Jackson (1965).

The estimated amounts of feldspars are also affected by Ca, K and Na in other minerals resisting dissolution during fusion and remaining in the residue. Clay sized pyroxenes have a fusion residue of 58—86 %. They are thus relatively stable and increase the Ca feldspar values (Chapman et al. 1969). Amphiboles seem to be more easily destroyed, the respective fusion residue ranging from 21 to 32 %.

The three quartz samples studied dissolved to a somewhat greater extent than the rock crystal specimen studied by Kiely and Jackson (1965). Thus even quartz samples of various origin appear to differ in their resistance to dissolution during the $Na_2S_2O_7$ fusion.

It is thus evident that the results obtained are only estimates, and a higher degree of accuracy is not obtainable with methods using average conversion factors. Generally the quantitative determination of minerals is a difficult problem (van der Marel 1966). For instance, determinations of kaolinite in a sample by nine laboratories led to estimates ranging from 60 to 95 % and mica contents analyzed in the same sample varied from 2 to 30 % (KONTA 1963). Also the present results show that no great accuracy is achieved in mineral analyses with the present methods, although McNEAL (1968) claimed that with chemical methods the accuracy of the estimates may be better than ± 5 %.

3.1.7 Comparison of results with those of previous studies

Relatively few mineral analyses have been made on Finnish soils. The results published are made partly on different particle size fractions from the results of the present study. SALMINEN (1935) has estimated the mineral composition of some clay sediments and clay fractions based on chemical analysis. He estimated the mica as muscovite, and contents were 38 and 41 % in two clay fractions which values are in the range of "mica" contents found in coarse and fine clay fractions in the present study (Tables 5 and 6). KERÄNEN (1946) estimated that the sum of mica and K feldspar in Finnish clay fractions is about 70 % which is in agreement with the results obtained here. In Sweden, estimates for illite contents of clay fractions range from 50 to 90 % (WIKLANDER and LOTSE 1966). These values are high when compared with the "mica" contents obtained in the present study. If illite is considered to be a mixed layer mineral of mica and chlorite the values obtained here are of similar order to the values of WIKLANDER and LOTSE (1966). In Norway illite contents ranging from 25 to more than 40 % in clay fractions have been found (JØRGENSEN 1965). The mica contents of a few so-called standard illites have been found to range from 58 to 65 % (RAMAN and JACKSON 1966) indicating that contents of micaceous minerals are lower in clay fractions of Finnish soils than in the specimen illites.

In accordance with results obtained by SOVERI (1956) both primary and secondary chlorite are present in the fractions studied. Although chlorite has been identified in Finnish soils, its content has not been determined. In clay fractions of Norwegian origin chlorite contents of up to 40 % have been estimated (JØRGENSEN 1965). These estimates are high when compared with the "chlorite" contents of clay fractions in the present study. Chlorite is second in abundance to mica in dioctahedral illite specimens (RAMAN and JACKSON 1966). The results obtained show a similar importance of chlorite in the clay fractions of Finnish soils.

The relatively high content of "chlorite" in the fine clay fraction of coarse textured soils is an indication of more intense weathering in these soils than in the fine textured soils (SCHEFFER et al. 1961 b).

In accordance with the results of SOVERI (1956), the results of the present study show that "vermiculite" is a common mineral in Finnish soils although its content is not so high as that of "mica" and "chlorite". The contents range from 1 to 22 % in fine and coarse clay fractions and are of a similar order to contents in clay fractions of Swedish cultivated soils (WIKLANDER and LOTSE 1966). In Norwegian clay fractions the content of vermiculite can be as high as 25 % (JØRGENSEN 1965).

There are no earlier estimates of the content of "smectite" in Finnish soils. The values obtained for the fine clay fraction seem high when compared with the values found by ALEXIADES and JACKSON (1966) for fine clay separates of Dutch and Greek soils.

The content of "amorphous material" in the fine clay of samples studied is high compared with the results of ALEXIADES and JACKSON (1966) but they analyzed relatively few samples of clay fractions from soils of various origin.

The higher amount of "amorphous material" in the fine clay fraction of silt soils than in that of heavy and silty clay soils reflects the differences in mineral composition of these soils and suggests that changes caused by weathering have occured in silt soil more than in clay soils. Since silt soils contain much feldspar and quartz, it follows that the fine fractions of silt soils are likely to contain more of these minerals than the fine fractions of clay soils. An experiment carried out by Tamm (1929) has shown that feldspars with a particle size of less than 0.2 µm are very unstable. Therefore small particles of feldspars and the weathered surface layers of feldspars may dissolve in alkali extractant to a greater extent than the layer lattice minerals, which are stable as fine material.

The content of ”amorphous material” in finesand and sand fractions is relatively large because the samples originate from the B horizons of podzol soils. The Al and Si removed from coarse textured soils may be quite different in nature from that extracted from clay soils.

Soveri (1956), using X-ray analysis, estimated that the content of K and plagioclase feldspars averages 11 % in the 1 to 2 µm fraction. This value is much lower than the contents estimated by the chemical methods used in the present study. In the silt fraction the content of feldspars was found by Soveri (1956) to be 21 %.

The quartz contents in the 1 to 2 µm and 2 to 20 µm fractions analyzed by Soveri (1956) were 11 and 24 %, respectively. These values are close to the contents obtained with the chemical methods in the present study. Keränen (1946) found the quartz contents of a few clay fractions of Finnish soils to be 16 to 27 % and Salminen (1935) found the quartz contents of two clay fractions to be 18 and 19 %. These values are within the range of contents determined in the present study.

3.1.8 Distribution of minerals among particle size fractions

In Fig. 12 mean contents of minerals in different particle size fractions are compared except for ”smectite”, which was found only in fine clay. In spite of the large variation in the content of each mineral within particle size fractions, many differences between fractions are evident.

The mean content of ”mica” in fine clay is similar to its content in coarse clay. The percentage of ”mica” diminishes in silt to one third of that in the two clay fractions. In finer finesand the ”mica” percentage is at the same level as in coarser fractions.

The largest differences in the content of ”chlorite” are between the two clay separates and silt fraction. In the finer finesand, finesand and sand fractions the ”chlorite” content is of the same order.

The content of ”vermiculite” diminishes from fine clay to finer finesand and remains in this

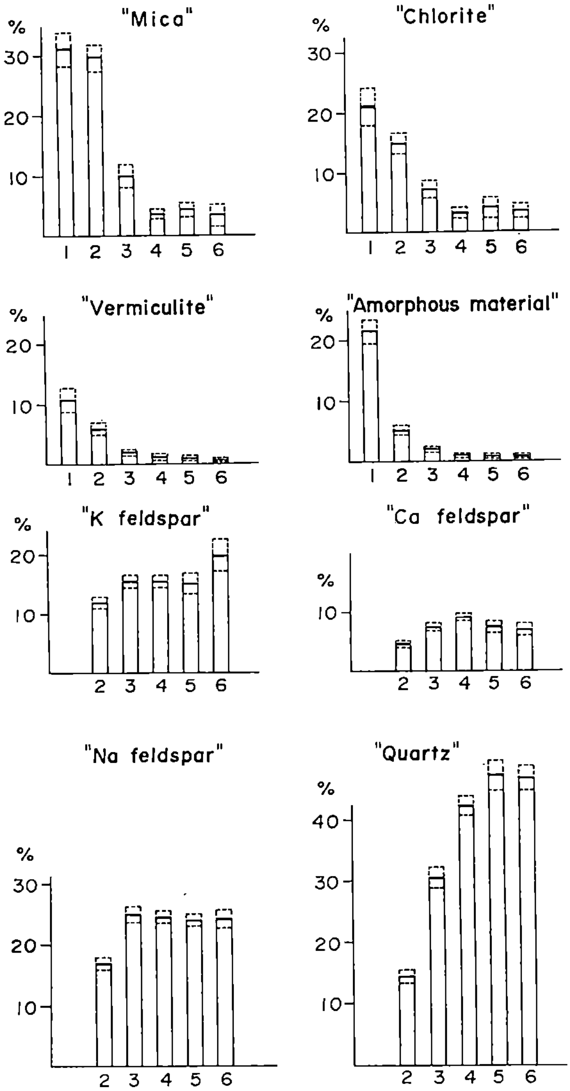

Fig. 12. The distribution of mineral components, except ”smectite”, among particle size fractions. The fractions are marked as follows: 1 = < 0.2 µm, 2 = 0.2—2 µm, 3 = 2—20 µm, 4 = 20—60 µm, 5 = 60—200 µm, 6 = 200—2 000 µm. The broken lines indicate confidence limits at the 95 % level.

Table 12. Weighted average mineral composition (%) of fractions

	Fraction, µm					
	< 0.2	0.2—2	2—20	20—60	60—200	200—2 000
"Mica"	34.8	29.5	9.6	3.3	3.4	2.1
"Chlorite"	15.4	13.1	5.7	2.4	3.4	4.0
"Vermiculite"	12.6	6.8	1.5	0.5	0.5	0.1
"Smectite"	22.1	—	—	—	—	—
"Amorphous material"	18.4	4.5	1.3	0.5	0.5	0.6
"K feldspar"	—	11.8	16.1	15.2	14.9	19.8
"Na feldspar"	—	17.3	25.2	24.8	22.9	22.5
"Ca feldspar"	—	4.4	7.4	9.5	7.7	6.3
"Quartz"	—	14.3	31.3	41.2	48.7	48.4
Total	103.3	101.7	98.1	97.4	102.0	103.8

and the coarser fractions at the same level. Very striking is the difference between fine and coarse clay in the content of "amorphous material". The mean content of "amorphous material" in coarse clay is only about a quarter of that in fine clay and the content diminishes by almost the same ratio between the coarse clay and silt fractions. In fractions coarser than silt the proportion of "amorphous material" is small and the variation in content of samples is relatively large.

In contrast to "mica" and other minerals, characteristic of clay, the content of "quartz" is on average twice as high in the silt fraction as in the coarse clay fraction. Also the difference in "quartz" contents between silt and finer finesand is large. The content of "feldspars" increases with increasing particle size of the fraction from coarse clay to silt but is constant in coarser fractions, with the exception of "potassium feldspar", the content of which in the sand fraction is higher than in the other fractions. The mean content of "K feldspar" in the sand fraction is high because two samples exceptionally rich in this mineral from the rapakivi rock area in the Kouvola district were included. These samples also lowered the mean content of "quartz" in the sand fraction. The content of "Ca feldspar" reaches a maximum in the finer finesand fraction.

Differences in the contents of "quartz", "amorphous material", "chlorite", "vermiculite" and also "mica" between particle size fractions are large. The close dependence of mineral composition on particle size suggests that it is feasible to estimate the mineral composition of Finnish soils from their particle size distribution and average mineral composition of particle size fractions.

3.2 *Mineral composition of soil samples*

The mineral composition of unfractionated samples was determined in three ways. Method A involved the use of a soil sample without any other preparation of fractionation than the extraction of exchangeable cations and their replacement with those needed for various analyses. To estimate feldspars and quartz in coarse clay and coarser fractions the conversion factors needed were determined for each sample as means weighted for amounts of particle size fractions.

In method B the estimation of minerals was based on the mechanical composition of samples and the mineral composition of separated fractions. Since fractions comprising less than 5 % of a sample were not analyzed, the values do not include the minerals which these fractions contain.

Method C was planned to enable the estimation of the mineral composition when the particle size distribution of a sample is known. Weighted average mineral compositions of fractions were used. The weighted averages obtained from the material analyzed are shown in Table 12. These weighted means of particle size fractions deviate most from the means of those textural classes whose relative proportion is small.

Table 13. Comparison of soil mineral composition (% in dry matter) determined by three methods. Means of soil textural classes with confidence limits at the 95 % level.

Mineral	Method	Heavy clay	Silty clay	Sandy clay	Finer silt	Coarser silt	Finer finesand	Finesand	Sand
"Mica"	A	27 ± 5	18 ± 5	16 ± 3	13 ± 7	9 ± 4	8 ± 7	5 ± 3	2 ± 1
	B	30 ± 1	20 ± 2	16 ± 3	15 ± 6	10 ± 2	7 ± 7	4 ± 2	2 ± 2
	C	28 ± 1	20 ± 1	17 ± 1	15 ± 1	13 ± 1	6 ± 2	5 ± 2	2 ± 0
"Chlorite"	A	12 ± 2	12 ± 2	13 ± 2	12 ± 2	9 ± 1	6 ± 3	6 ± 2	4 ± 1
	B	10 ± 3	9 ± 2	10 ± 1	8 ± 2	6 ± 1	4 ± 3	3 ± 1	4 ± 1
	C	13 ± 1	10 ± 0	8 ± 1	8 ± 0	7 ± 1	4 ± 1	4 ± 1	4 ± 0
"Vermiculite"	A	9 ± 2	6 ± 1	2 ± 1	2 ± 1	2 ± 1	0 ± 0	0 ± 0	0 ± 0
	B	9 ± 2	6 ± 1	4 ± 1	2 ± 1	2 ± 1	2 ± 2	0 ± 0	0 ± 0
	C	8 ± 1	5 ± 0	4 ± 0	3 ± 0	3 ± 0	1 ± 0	1 ± 1	0 ± 0
"Smectite"	A	5 ± 1	1 ± 1	1 ± 2	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0
	B	9 ± 2	4 ± 1	3 ± 1	1 ± 1	1 ± 0	0 ± 0	0 ± 0	0 ± 0
	C	8 ± 1	4 ± 1	3 ± 1	1 ± 1	1 ± 1	0 ± 0	0 ± 1	0 ± 0
"Amorphous material"	A	8 ± 2	6 ± 2	5 ± 2	3 ± 1	4 ± 1	2 ± 1	2 ± 1	1 ± 1
	B	7 ± 1	4 ± 1	5 ± 1	4 ± 1	3 ± 1	1 ± 0	1 ± 0	1 ± 1
	C	9 ± 1	5 ± 0	4 ± 1	3 ± 0	3 ± 0	1 ± 1	1 ± 1	1 ± 0
"K feldspar"	A	10 ± 2	13 ± 2	12 ± 1	16 ± 3	16 ± 3	14 ± 3	16 ± 5	20 ± 5
	B	7 ± 1	11 ± 1	11 ± 1	14 ± 3	15 ± 2	14 ± 3	15 ± 3	18 ± 3
	C	8 ± 1	12 ± 0	13 ± 1	14 ± 0	14 ± 0	15 ± 0	16 ± 1	19 ± 1
"Na feldspar"	A	16 ± 1	19 ± 2	18 ± 2	21 ± 3	22 ± 3	23 ± 2	22 ± 1	23 ± 3
	B	12 ± 2	17 ± 2	17 ± 1	21 ± 4	22 ± 2	23 ± 3	22 ± 2	21 ± 2
	C	12 ± 1	18 ± 1	19 ± 1	22 ± 1	22 ± 1	21 ± 1	22 ± 1	23 ± 0
"Ca feldspar"	A	4 ± 1	6 ± 1	6 ± 1	7 ± 0	7 ± 1	8 ± 1	7 ± 2	6 ± 2
	B	3 ± 1	5 ± 0	5 ± 1	6 ± 1	7 ± 1	8 ± 1	7 ± 2	6 ± 2
	C	3 ± 0	5 ± 0	6 ± 0	6 ± 0	7 ± 0	8 ± 0	7 ± 0	7 ± 0
"Quartz"	A	12 ± 1	22 ± 2	28 ± 3	27 ± 3	35 ± 5	40 ± 4	45 ± 7	46 ± 4
	B	10 ± 3	21 ± 3	24 ± 2	22 ± 4	28 ± 2	36 ± 7	44 ± 3	47 ± 4
	C	12 ± 2	21 ± 1	26 ± 2	27 ± 1	29 ± 2	39 ± 2	45 ± 3	47 ± 1
Totals	A	103 ± 3	103 ± 3	101 ± 2	101 ± 2	104 ± 2	101 ± 3	103 ± 4	102 ± 3
	B	97 ± 2	97 ± 2	95 ± 3	93 ± 5	94 ± 4	95 ± 4	96 ± 3	99 ± 4
	C	101 ± 0	100 ± 0	100 ± 0	99 ± 0	99 ± 0	96 ± 2	101 ± 2	103 ± 1

3.2.1 Comparison of methods for determining the mineral composition of soil samples

The results of the three methods for determining the mineral composition of soil samples are shown as means of soil textural classes (Table 13). Similar mean values were obtained for all three methods but significant differences were found, too.

"Mica". Method A tends to give low values for "mica", but owing to the large variation within textural classes no significant differences were found. There were, however, very large differences in the contents of "mica" obtained for individual samples by different methods. For example, the "mica" content of a heavy clay sample was estimated to be 20 % using method A whereas methods B and C resulted in "mica" contents of 32 and 30 % respectively. In a silty clay sample, the "mica" content was 10 % according to method A and almost 20 % with methods B and C. The correlation coefficient between the results of methods A and B was $r = 0.91$***, between the results of method B and C, $r = 0.94$ ***and between A and C, $r = 0.85$***.

The reason for the relatively large differences between the "mica" values of individual samples determined by different methods may be that in method A the determinations were made using samples without such pretreatments as the removal of organic matter or free oxides. Although the results obtained with method A have been corrected for moisture and free iron content, they have not been adjusted for organic matter or other material which might have dissolved in the purification treatments made in method B before fractionation. Thus the total potassium contents of samples have been underestimated leading to lower "mica" values than would have been the case had samples been purified before analysis. The fact that the content of potassium in "mica" is expressed as the difference between total potassium and "K feldspar" potassium increases the relative size of the error of determination in the "mica" estimates.

"Chlorite". Method A tends to result in higher "chlorite" estimates than methods B or C. However, the differences between methods are significant only in the sandy clay and coarser silt classes.

The "chlorite" estimates are based on the weight loss occurring on ignition of samples. The untreated samples used for determinations by method A contained low amounts of organic matter. The oxidation of organic matter may have caused a positive error in the determination of "chlorite". According to some estimates made, on average 80 % of the organic matter was oxidized during the 16 hour heating period made to establish the 300° C weight bases needed for weight loss determination in "chlorite" analyses. The 20 % remaining in the samples will oxidize at higher temperatures, and will be included in the weight loss from which the percentage of "chlorite" is calculated. The samples analyzed contained on average 1—2 % of organic matter. Therefore the error due to organic matter is generally small.

The sandy clay group contained the highest average content of organic matter, and in this group method A does give a higher average "chlorite" content than method C. However, the mean obtained with method A is not larger than that obtained with method B.

It is evident that in "chlorite" determinations a correction for organic matter must be made if samples high in organic matter are analyzed without peroxide treatment, which omission may on some counts be desirable.

The percentage of "chlorite" in fine clay ranges on average from 20 % in heavy clay soils to 38 % in finer silt soils, and the weighted mean used in calculations in method C is 23 %. Thus the values for soils high in clay may be overestimated and those for soils low in clay may be underestimated. The results obtained with method C do show such a tendency but the differences between other methods are not usually significant. The correlation coefficient between values determined with methods A and B was $r = 0.79^{***}$ compared with $r = 0.77^{***}$ between values obtained with methods A and C.

"Vermiculite". All three methods gave similar average "vermiculite" contents for the soil textural classes. The correlation coefficient between methods A and B was $r = 0.91^{***}$ compared with $r = 0.90^{***}$ between methods A and C.

The estimation of the "vermiculite" content with methods B and C is based on the "vermiculite" content of fractions cleaned with hydrogen peroxide and dithionite, which reagents effectively remove organic matter and free iron. Adsorbed on the surfaces of clay, these materials will reduce potassium fixation, which property was used to estimate the content of vermiculite. Used to excess, the treatments mentioned have also been found to modify the crystal structure of mica, allowing the layers to expand and thus to fix potassium when "vermiculite" is determined (Douglas 1967). The factors mentioned may explain to some degree the differences in estimates from different methods, determined on individual samples.

"Smectite". Except for sandy clay soils the "smectite" estimates obtained with methods B and C are higher than the estimates from method A, which were based on the analytical results of unpurified soil samples. The purification increases the cation exchange capacity used to determine "smectite". This may be the reason for the high estimates obtained with methods B and C. The correlation coefficient between the results of methods A and B was r = 0.86*** and between those of methods A and C, r = 0.85***.

"Amorphous material". Variable results were obtained for the estimates of "amorphous material" in individual samples. For example a heavy clay sample contained 5 % "amorphous material" according to method A but almost 10 % according to methods B and C. In a finer finesand soil method A gave the "amorphous material" content as 4 % whereas methods B and C gave it as 1 %. However, no differences between textural class means obtained with the different methods were found. The tendency for method A to give higher results may be due to dissolution of some easily extractable amorphous constituents when samples where prepared for the determinations needed in methods B and C. The correlation coefficient between methods A and B was r = 0.86*** and between methods A and C, r = 0.88***.

"K feldspar". Method A tends to overestimate K feldspar although differences between textural class means are not significant. One reason for the comparatively low "K feldspar" estimates with methods B and C is that the amount of "K feldspar" was not determined on the fine clay fraction because of its low amount and uncertainty of estimation (Sippola 1972).

"Na feldspar". Similar mean values were obtained also for "Na feldspar" with the three methods. The high mean for method A in the heavy clay class may be due to the fact that the fine clay contains "Na feldspar" which has not been taken in account in methods B and C. The correlation coefficients between methods A and B was r = 0.83*** and between A and C, r = 0.68***.

"Ca feldspar". Method A gives higher estimates for the content of "Ca feldspar" in finer silt soils than method C. For other textural classes the values obtained with method A are in the same range as the results of methods B and C.

"Quartz". In general good agreement between different methods for estimating "quartz" was obtained. This is indicated by the correlation coefficients which were r = 0.93*** between methods A and B and r = 0.94*** between methods B and C.

The amount of quartz was also determined quantitatively by the DTA method. The results obtained are compared with those obtained with method A (Fig. 13). The DTA method tended to give lower values than the pyrosulphate fusion method with heavy clay, finesand and sand soils. With the other soils the results were well within the range of values obtained with method A. The correlation coefficient between quartz percentages determined with DTA and method A was r = 0.98***. With the DTA method the estimation of quartz in heavy clay soils was quite uncertain because of the small amount of quartz in these soils, and also because the thermal effect of fine-grained quartz is smaller than that of coarser fractions (Grimshaw 1953). For example a heavy clay soil containing 94 % of clay contained only 4 % quartz according to a DTA determination, compared with 9 % "quartz" obtained with method A.

Total minerals. The sums of minerals determined with method A do not deviate significantly from 100 % except for coarser silt textural class (Table 13). The sums of individual samples deviated more, the range being from 97 to 107 %. Except for the sand soil class, the averages of sums of minerals determined with method B are lower than 100 %. This result was expected, as fractions comprising less than 5 % were not analyzed. The sums of minerals for method C are close to 100 %. The amounts of those minerals which were not estimated would increase the sums to some extent. This would lead to sums by far exceeding 100 % of the results obtained with method A.

3.2.2 Mineral compositions of different soil textural classes

The results obtained with method A (Fig. 14) enable a comparison of mineral compositions

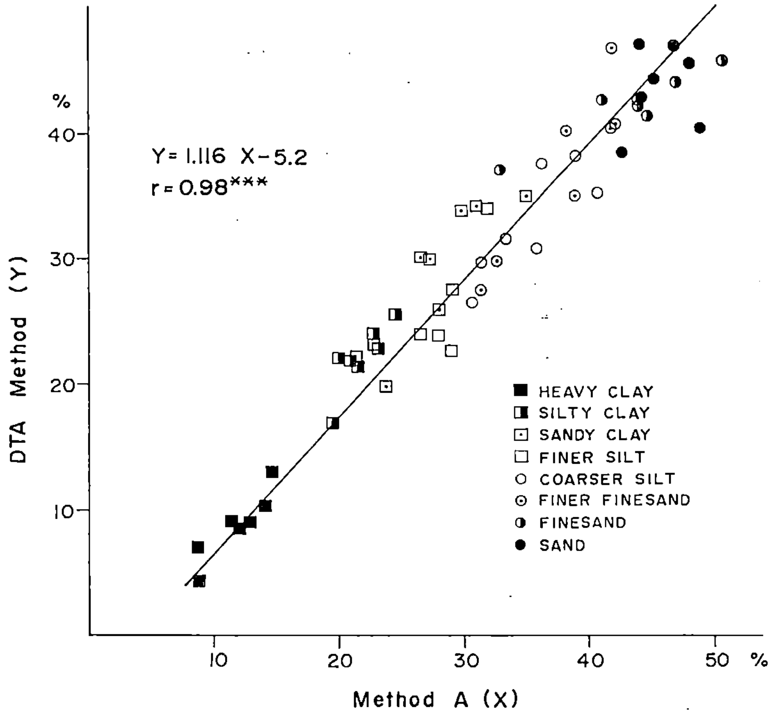

Fig. 13. A comparison of soil quartz estimates obtained with the pyrosulphate fusion method (Method A) with contents obtained by the differential thermal analysis method (DTA method).

of different soil textural classes. "Mica" is the predominant mineral in heavy clay soils, comprising 19 to 33 % in the material studied and on average 27 % for all heavy clay samples. Second in abundance to "mica" in heavy clay soils is "Na feldspar" but the content of "chlorite" is of a similar order. The contents of "vermiculite", "smectite" and "amorphous material" are relatively high in heavy clay soils, but these components are least abundant of any components except "Ca feldspar".

In heavy clay soils the sum of contents of

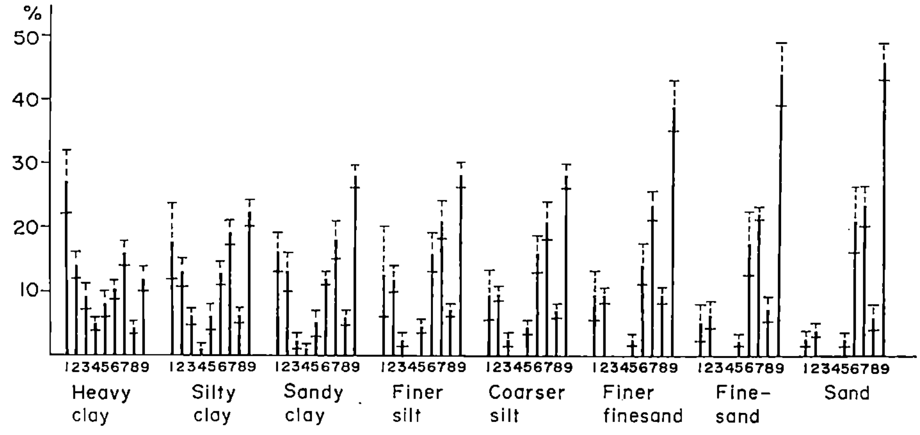

Fig. 14. Comparison of the mineral composition of various textural classes. The numbers refer to the following components: 1 = "mica", 2 = "chlorite", 3 = "vermiculite", 4 = "smectite", 5 = "amorphous material", 6 = "K feldspar", 7 = "Na feldspar", 8 = "Ca feldspar", 9 = "quartz".

"mica", "chlorite", "smectite", "vermiculite" and "amorphous material" makes up more than half of the sample, whereas in other soils "feldspars" and "quartz" form the major portion. In all clay and in finer silt textural classes the average content of "chlorite" is nearly constant, ranging from 12 to 14 %. The content of "chlorite" diminishes more slowly with increasing coarseness of samples than the contents of other clay minerals. Thus "chlorite" is the most abundant layer lattice mineral in finesand and sand soils, comprising on averages 6 ± 2 and 4 ± 1 % of the respective soil textural classes. Typical of sandy clays is the lower content of "vermiculite" and higher content of "quartz" relative to silty and heavy clay soils. With regard to other minerals silty and sandy clays are very similar.

The finer silt soils have on average a lower "quartz" content than the coarser silt soils. Particularly as regards to the contents of "feldspars" the silt soil groups are very similar. Compared with the silty clay soils, the finer silt soil group has a higher content of "quartz" and a lower content of "vermiculite". The "mica" content of finer finesand soils is very variable, ranging from 0 to 22 %. Despite the high "mica" content of some samples the "vermiculite" content is low; on average less than 0.5 %. Also in finesand and sand soils there was generally no "vermiculite".

In finer finesand soils the "Ca feldspar" content is on average 9 ± 1 %. Sand and finesand soils consist almost entirely of "feldspars" and "quartz". In sand soils the content of "quartz" ranged from 43 to 49 %. Although high contents of "amorphous material" are characteristic of clay soils, even sand soils contain some "amorphous material".

3.3 *Regional differences in mineral composition*

The soils of Finland are relatively young. The material from which soils are formed was deposited during or after the Quaternary. The soil material originates from Precambrian igneous and metamorphic rocks and possibly to a small extent from Preglacial soils (Soveri 1956). The rock material has been crushed, pulverized and mixed by a continental ice sheet. The coarser material has been transported only a relatively short distance by meltwaters. The finer material has been carried further away from its origin. Clay material may even have been deposited in several cycles.

The clays of the present coastal areas were sedimented in deep water and their texture is fine. Especially the clays in South-West Finland are very heavy. The sorted material in higher areas of Central Finland was deposited in shallow water and its texture is coarser, or generally of silt size.

Since the mineral composition of soils appears to be closely connected with the texture, regional differences are to a large extent related to textural differences of the samples from various regions (Fig. 1). The effect of texture could possibly be reduced by comparing the composition of similar size fractions from different regions. Therefore in the following the mineral contents of fractions are presented, calculated as averages for certain regions.

The "mica" content of the fine clay of coastal region samples (regions 1, 2 and 5) was 36 ± 4% (mean with confidence limits at the 95 % level) compared with 29 ± 4 % for the fine clay of samples from other areas, but due to the large variation the difference is not significant. The content of "vermiculite" was 16 ± 3 % in the fine clay of samples from South-West Finland, where heavy clay soils are very common. The percentage of "vermiculite" was 10 ± 2 % in the fine clays of the other regions. The content of "amorphous material" was lower in the fine clay of South-West Finland and Ostrobothnia (regions 2 and 5), 16 ± 1 % than in the fine clay of other regions, 24 ± 2 %.

The mineral composition of coarse clay from various regions was more homogeneous than the composition of fine clay. The content of "chlorite" in coarse clay from South-West Finland (region 2) was 9 ± 2 % compared with 14 ± 1 % for the other regions. The contents of "amorphous material" from corresponding regions were 3 ± 1 % and 5 ± 1 %, respectively

The silt and coarser fractions from different regions were very similar in their contents of various minerals, with the exception of ”K feldspar”, the content of which was higher in the Kouvola district than in similar fractions from the other areas. The content of ”K feldspar” in the silt fraction of the samples from the Kouvola district was 18 ± 2 % compared with 14 ± 1 % in the other areas, in the finer finesand fraction 18 ± 2 % and 14 ± 1 %, in the finesand fraction 20 ± 2 % and 13 ± 1 %, and in the sand fraction 25 ± 4 % and 17 ± 2 % for Kouvola and other areas respectively.

Soveri (1956) concluded that regional variations in the mineral composition of Finnish clays are not extensive. He could, however, trace the influence of the sedimentation environment and also that of bedrock on the composition of clays. In the present study the differences observed in the composition of the clay fractions of coastal and higher areas may be related to the differences in sedimentation environment. The effect of bedrock on the composition of the silt, finer finesand, finesand and sand fractions of samples taken from the rapakivi area of the Kouvola district was very clear.

4. Relation between mineral composition and some soil chemical properties

Total major and trace element contents, extractable nonexchangeable K and Mg, fixation of K, basic exchangeable cations and exchange capacity were determined on the 56 soil samples whose mineral composition was estimated. Stepwise multiple regression analysis with an automatic data processing system was used to study the relationships between determined chemical properties and mineral composition of samples (Ezekiel and Fox 1959). In some cases also chemical properties together with the percentage of clay were used as independent variables.

According to the calculations made ”quartz” proved to be in close negative correlation with the properties studied. Quartz apparently does not have any direct effect on these properties, but it acts rather as a diluent in the soil. Therefore ”quartz” was not included as an explanatory variable in the final calculations. This allowed more certain recognition of the order of importance of those minerals which had a positive effect.

Of the three methods used to estimate the minerals in soil samples, method A yielded values which explained better the variation in chemical properties than did methods B or C. Thus there are shown none of the results of regression analyses using results of methods B or C as independent variables.

4.1 *Total potassium, sodium, calcium, magnesium and iron*

Potassium. The average total content of potassium in soil textural classes ranges from 2.47 ± 0.35 to 3.20 ± 0.15 % K in the material under study (Table 14). The average potassium content of the sand soil group is high when compared with reported potassium contents of Finnish sand soils (Keränen 1946, Kaila 1973). The high potassium content obtained for the sand soils is due to two samples exceptionally rich in potassium feldspar from the Kouvola district, where rapakivi is a common bedrock material (Sederholm 1924). Excluding these two samples the average for the sand soil class was 2.64 ± 0.40 % K. Clearly, also the high average potassium content of finesand soils has been affected by three samples from the rapakivi area.

The total potassium content of samples was rather poorly correlated with the percentage of clay, r = 0.38**. In the three clay soil groups the correlation coefficient of total potassium with the percentage of clay was r = 0.62**. The correlation coefficient between total potassium and the percentage of coarse clay was r = 0.41**. No significant correlation was found to exist between the content of fine clay and that of total potassium.

Table 14. Total contents of some major elements (%) in soil samples. Means of soil textural classes with confidence limits at the 95 % level.

	Heavy clay	Silty clay	Sandy clay	Finer silt	Coarser silt	Finer finesand	Fine-sand	Sand
K	3.20 ± 0.15	3.07 ± 0.35	2.74 ± 0.17	3.05 ± 0.27	2.84 ± 0.32	2.47 ± 0.35	2.65 ± 0.51	3.03 ± 0.70
Na	1.41 ± 0.17	1.62 ± 0.23	1.51 ± 0.16	1.81 ± 0.17	1.88 ± 0.11	2.04 ± 0.24	1.68 ± 0.22	2.11 ± 0.30
Ca	0.93 ± 0.18	1.07 ± 0.23	0.97 ± 0.13	1.08 ± 0.11	1.14 ± 0.14	1.24 ± 0.11	0.97 ± 0.29	0.77 ± 0.13
Mg	2.03 ± 0.21	1.53 ± 0.08	1.24 ± 0.18	1.22 ± 0.39	0.93 ± 0.16	0.78 ± 0.42	0.47 ± 0.33	0.27 ± 0.11
Fe	7.1 ± 0.6	5.1 ± 0.5	5.1 ± 1.3	4.1 ± 0.8	3.5 ± 0.1	2.9 ± 2.1	1.4 ± 0.8	1.6 ± 0.8

The greater importance of coarse clay than fine clay in accounting for total soil potassium is also evident when the potassium contents of separated fractions are compared (Table 15). The mean total potassium content of fine clay of various textural classes ranged from 1.72 ± 0.23 to 2.78 ± 0.45 % K. Low contents were found in clay fractions separated from silt soils and high ones in those separated from heavy clay soils. The mean total potassium content of the coarse clay fractions of various textural classes ranged from 3.49 ± 0.24 to 4.06 ± 0.18 % K (Table 16). The highest contents were found in the coarse clay fractions separated from heavy clay soils and the lowest contents in the coarse clay from sandy clays whereas the coarse clay fractions of silt soils contained intermediate amounts of potassium.

Sodium. Contrary to the case with potassium, the lowest sodium contents occur in clay soils, and the amount increases with increasing particle size, with the exception of samples in the finesand group (Table 14). The negative correlation (r = —0.64***) of total sodium with the amount of the clay fraction, however, is rather poor.

The fine clay fraction contained considerably less sodium than the coarse clay fraction (Tables 15 and 16). The fine clay fractions separated from different groups of soils contained variable amounts of sodium. Fractions separated from finer silt soils had a low average content whereas high contents were found in fractions separated from heavy clay soils. Also the coarse clay fractions of heavy clay soils contained relatively large amounts of sodium. The silt fractions of various soil textural classes contained similar amounts of sodium except for finesand soils, in which relatively low contents were present (Table 17).

In the multiple regression analyses of the estimated mineral components, other than "quartz", "mica" and "Na feldspar" appeared to be significant in explaining the variation in the content of total sodium. The obtained regression coefficients (b) with the confidence limits at the 95 % level, and the coefficients of determination (d) were following:

	"Mica" b	"Na feldspar" b	d
Fractions			
Fine clay	0.017 ± 0.010		0.27
Coarse clay		0.074 ± 0.017	0.70
Silt		0.062 ± 0.021	0.52
Soil		0.063 ± 0.018	0.48

Table 15. Total contents of some major elements (%) in the fine clay fractions (< 0.2 μm) of various soil textural classes (the number of samples in parentheses). Mean values with confidence limits at the 95 % level.

	Heavy clay (7)	Silty clay (7)	Sandy clay (7)	Finer silt (7)	Coarser silt (7)
K	2.78 ± 0.45	2.70 ± 0.42	2.69 ± 0.64	1.88 ± 0.27	1.72 ± 0.23
Na	0.68 ± 0.17	0.56 ± 0.16	0.39 ± 0.26	0.22 ± 0.09	0.42 ± 0.36
Ca	0.29 ± 0.05	0.19 ± 0.06	0.15 ± 0.08	0.11 ± 0.03	0.12 ± 0.02
Mg	2.17 ± 0.27	1.98 ± 0.31	1.94 ± 0.28	1.65 ± 0.20	1.45 ± 0.23
Fe	7.76 ± 0.68	8.11 ± 0.55	7.95 ± 0.76	7.42 ± 0.69	7.44 ± 0.83

Table 16. Total contents of some major elements (%) in the coarse clay fractions (0.2 — 2 μm) of various soil textural classes (the number of samples in parentheses). Mean values with confidence limits at the 95 % level.

	Heavy clay (7)	Silty clay (7)	Sandy clay (7)	Finer silt (7)	Coarser silt (7)
K	4.06 ± 0.18	3.70 ± 0.32	3.49 ± 0.24	3.73 ± 0.10	3.71 ± 0.31
Na	1.97 ± 0.16	1.76 ± 0.19	1.44 ± 0.15	1.57 ± 0.30	1.60 ± 0.19
Ca	1.17 ± 0.12	1.05 ± 0.11	0.88 ± 0.18	0.84 ± 0.14	0.85 ± 0.18
Mg	2.34 ± 0.19	2.06 ± 0.51	2.26 ± 0.22	2.14 ± 0.43	2.10 ± 0.30
Fe	5.45 ± 0.54	4.97 ± 1.08	5.34 ± 0.58	5.44 ± 0.92	5.52 ± 0.44

Table 17. Total contents of some major elements (%) in the silt fractions (2—20 μm) of various soil textural classes (the number of samples in parentheses). Mean values with confidence limits at the 95 % level.

	Heavy clay (7)	Silty clay (7)	Sandy clay (7)	Finer silt (7)	Coarser silt (7)	Finer finesand (7)	Fine-sand (7)
K	3.08 ± 0.12	2.80 ± 0.20	2.69 ± 0.08	3.23 ± 0.23	3.05 ± 0.30	2.74 ± 0.50	2.53 ± 0.29
Na	2.22 ± 0.17	2.33 ± 0.25	2.01 ± 0.22	2.26 ± 0.29	2.37 ± 0.13	2.00 ± 0.42	1.77 ± 0.23
Ca	1.57 ± 0.16	1.44 ± 0.26	1.34 ± 0.17	1.49 ± 0.22	1.50 ± 0.26	1.52 ± 0.31	1.34 ± 0.21
Mg	1.06 ± 0.21	0.97 ± 0.26	0.94 ± 0.21	0.89 ± 0.37	0.71 ± 0.25	1.23 ± 0.88	1.03 ± 0.24
Fe	2.68 ± 0.43	2.30 ± 0.40	2.28 ± 0.41	2.47 ± 0.83	2.03 ± 0.52	3.52 ± 2.05	2.82 ± 0.57

The proportion of the variation in the content of total sodium explained by "Na feldspar" is relatively low. This suggests that "Na feldspar" is not the only mineral contributing to soil total sodium. According to data presented by DEER et al. (1962) micas contain considerable amounts of sodium. The sodium content of muscovite may vary up to 2.0 % and that of biotite up to 1.1 %. In the fine clay fractions in which Na feldspar was not estimated, "mica" was suggested to contribute significantly, to the total sodium content. Vermiculites and chlorites contain much lower amounts of sodium than do micas (DEER et al. 1962).

The low correlation of total sodium on "Na feldspar" may have been caused partly by inaccurate estimation of "Na feldspar". The narrow range of variation of the conversion factors used for "Na feldspar" (Table 4) suggests that sodium adsorption during fusion may mask some of the variation in the content of "Na feldspar". The plagioclase particles from soil may also behave differently during fusion than samples which have been ground in the laboratory. The increase in dissolution of plagioclase when the content of the anortite component increases adds also to the uncertainty of "Na feldspar" estimation.

Calcium. The total content of calcium varies among various groups of soils less than other elements determined (Table 14). The highest mean calcium content was found in the finer finesand class in the present material but differences between groups are not significant. Although the total amount of calcium tends to be lower in fine textured samples, no significant correlation was found between the content of clay and total calcium.

The content of calcium in fine clay was low, ranging from 0.11 ± 0.09 % in fine silt soil fractions to 0.29 ± 0.05 % in heavy clay soil fractions (Table 15). The calcium content of the coarse clay fraction ranged on average from 0.84 ± 0.14 % in finer silt soils to 1.17 ± 0.12 % in heavy clay soils (Table 16).

Multiple regression analyses showed that as well as "Ca feldspar" also "mica" and "smectite" were significant in explaining the total calcium content (Table 18). The relatively poor correlation of "Ca feldspar" with total calcium suggests that the samples contain also other calcium-bearing minerals. X-ray diffraction anal-

Table 18. Regression coefficients (b) with confidence limits at the 95 % level, β-coefficients and coefficients of determination (d) for the relationship between the total content of calcium and mineral components.

	"Mica"		"Smectite"		"Ca feldspar"		d
	b	β	b	β	b	β	
Fractions							
Fine clay	0.004 ± 0.003	0.40	0.004 ± 0.003	0.40	—	—	0.49
Coarse clay	—	—	—	—	0.101 ± 0.066	—	0.23
Silt	—	—	—	—	0.097 ± 0.056	—	0.28
Soil	0.008 ± 0.007	0.31	—	—	0.093 ± 0.034	0.71	0.36

ysis indicated the precence of minerals of the amphibole and pyroxene groups in the coarse clay and coarser fractions. These minerals were also identified in heavy mineral separates. Amphiboles and pyroxenes may contain up to 9 % calcium (Annersten and Ekström 1971). Since, according to the estimates, the content of calcium feldspar is low, even small contents of amphibole and pyroxene minerals may have an important effect on total soil calcium.

Various micas, chlorites, smectites and vermiculites may contain low amounts of calcium (Deer et al. 1962). For the present material this was also suggested by the regression analyses, which indicated that "smectite" and "mica" were significant in explaining the variation in total calcium content of fine clay, and "mica" together with "Ca feldspar" in explaining the variation in calcium content of unfractionated soil samples.

Magnesium. Differences in the total content of magnesium between soil textural classes are very clear (Table 14). Average Mg contents of textural classes range from 0.27 ± 0.11 % in sand soils to 2.03 ± 0.21 % of Mg in heavy clay soils. Total magnesium contents within the same range have been found previously in Finnish soils by Kaila (1973). The close dependence of total magnesium content on the clay content is indicated by the correlation coefficient, r = 0.89***.

The total analysis of separated fractions showed that the content of total magnesium is lower in fine clay than in coarse clay. The average total magnesium content in fine clay ranged from 2.17 ± 0.27 % in heavy clay soil fractions to 1.45 ± 0.23 % in fractions separated from coarser silt soils (Table 15). In coarse clay the total magnesium had a narrower range of variation from 2.34 ± 0.19 to 2.06 ± 0.51 % (Table 16).

According to multiple regression analyses, "mica" together with "chlorite", "vermiculite" or "Ca feldspar" was significant in explaining the variation in the content of total magnesium of fine clay, coarse clay and silt fractions and of the soil samples (Table 19). On the basis of the β-coefficients "mica" is suggested to have a larger effect on total magnesium than "chlorite" or "vermiculite". The importance of "mica" in explaining total magnesium indicates that a trioctahedral type of this mineral is present in Finnish soils.

According to the analyses of Lokka (1943) a biotite from Southern Finland contained 3.2 % Mg whereas a sample from Central Finland

Table 19. Regression coefficients (b) with confidence limits at the 95 % level, β-coefficients and coefficients of determination (d) for the relationship between the total content of magnesium and mineral components.

	"Mica"		"Chlorite"		"Vermiculite"		"Ca feldspar"		d
	b	β	b	β	b	β	b	β	
Fractions									
Fine clay	0.029 ± 0.011	—	—	—	—	—	—	—	0.45
Coarse clay	0.037 ± 0.025	0.64	0.057 ± 0.034	0.69	—	—	0.235 ± 0.159	0.60	0.32
Silt	0.039 ± 0.012	0.67	0.054 ± 0.019	0.55	—	—	—	—	0.72
Soil	0.031 ± 0.012	0.45	0.053 ± 0.021	0.33	0.054 ± 0.031	0.27	—	—	0.87

contained only 0.51 % Mg. The magnesium content of biotites generally ranges from less than 0.1 % to 8.1 % (DEER et al. 1962). According to the same reference, magnesium rich trioctahedral mica or phlogopite may contain from 8.9 to 17.2 % magnesium. The regression coefficients obtained for "mica" in the equations calculated are low, suggesting that the average mica in Finnish soils is biotite rather than phlogopite. However, it is more likely that various types of mica are present, including muscovite, and that the regression coefficient obtained is an estimate of the average effect of all these types.

Chlorites have variable magnesium contents as is suggested by the material to which DEER et al. (1962) refer, in which values range from 0.1 to 19.7 %. A chlorite from Central Finland reported by LOKKA (1943) contained 7.0 % magnesium and the chlorites studied by SEITSAARI (1954) 8.5 and 9.0 %. These values are higher than the regression coefficient of "chlorite" on its magnesium content. It should be noted, however, that "chlorite" includes also aluminous secondary chlorite and iron rich chlorite, whose magnesium contents are low.

Also vermiculite is rich in magnesium. In the present material "vermiculite", however, appeared to have a significant effect on the content of total magnesium only in material consisting of unfractionated samples. Reported magnesium contents of vermiculite range from 11 to 16 % (DEER et al. 1962, BOETTCHER 1966). The effect of soil vermiculite on Mg content, as estimated by the regression coefficient is much lower than the total content of large particle sized vermiculites would suggest. Also the evidence that vermiculites are weathering products of phlogopites rather than of biotites suggests that the effect of vermiculite on total magnesium would be large (FOSTER 1962).

It has been found, however, that the total magnesium content of vermiculite decreases whereas the total iron content increases with decreasing particle size. In the material analyzed by KERNS and MANKIN (1967) 0.25 — 0.5 μm vermiculite from soil contained 5.4 % magnesium compared with 14.5 % in coarse crystalline material of the same sample. Also the finding of BARSHAD and KISHK (1969), that soils contain in addition to the magnesium containing type also an aluminous type of vermiculite, suggest that soil vermiculite may not affect total magnesium to such a degree as the coarse grained vermiculites. BARSHAD and KISHK (1969) calculated that the aluminous types of soil vermiculites which they studied contained 1.6 to 4.7 % magnesium.

The fact that the regression analysis indicates that "Ca feldspar" contributes to the total magnesium content of coarse clay implies that some minerals, for example pyroxenes or amphiboles, containing both magnesium and calcium have affected the "Ca feldspar" estimates.

Iron. The content of total iron in soil samples decreases with increasing coarseness of texture (Table 14). The dependence of the content of total iron on the percentage of clay fraction is close, r = 0.83***.

There were no differences in the content of total iron between fine and coarse clay nor between silt fractions separated from various soil textural classes (Tables 15, 16 and 17). Contrary to the case for the other major elements analyzed the content of total iron was higher in fine clay than in coarse clay.

Multiple regression analyses indicated that "mica", "chlorite", "vermiculite", "smectite" and also "amorphous material" were important in explaining the variation in the content of total iron of clay and silt fractions. In the case of the unfractionated samples the proportion of dithionite extractable iron (Table 2) was subtracted from total iron to give an estimate of iron crystallized in silicate minerals. After this subtraction "mica", "chlorite", "vermiculite" and "smectite" explained 82 % of the variation in the iron values obtained (Table 20).

Of the variation of the total iron in the two clay fractions only a very low proportion is accounted for the estimated mineral components. The β-coefficients suggest that in silt fraction "mica" affects most to the total iron content. To the total iron in soil samples "chlo-

Table 20. Regression coefficients (b) with confidence limits at the 95 % level, β-coefficients and coefficients of determination (d) for the relationship between the total content of iron and mineral components.

	"Mica"		"Chlorite"		"Vermiculite"		"Smectite"		"Amorphous material"		d
	b	β	b	β	b	β	b	β	b	β	
Fractions											
Fine clay	—	—	—	—	0.072 ± 0.050	0.52	0.075 ± 0.044	0.80	0.092 ± 0.070	0.71	0.35
Coarse clay	—	—	0.065 ± 0.058	0.37	—	—	—	—	—	—	0.14
Silt	0.087 ± 0.024	0.73	0.086 ± 0.040	0.44	—	—	—	—	—	—	0.70
Soil	0.041 ± 0.035	0.23	0.141 ± 0.065	0.34	0.157 ± 0.104	0.31	0.159 ± 0.144	0.19	—	—	0.82

rite" and "vermiculite" are indicated to have a larger effect than "mica".

The iron content of biotite in rocks may range from 14 to more than 21 % (Lokka 1943, Eskola 1949) and in chlorite similar or higher contents have been found (Seitsaari 1954, Deer et al. 1962). The low value of the regression coefficient for "mica" compared with the iron contents of biotites indicated that the "mica" in the samples analyzed contain also types low in iron. Also the "chlorite" regression coefficient estimating the effect of the average chlorite in soil samples on the total iron is lower than the iron content of chlorites found in rocks. This is the case because among the various types of chlorites occuring in soil also types low in iron are included.

Large particle size vermiculites generally contain less than 7 % of iron (Foster 1962, Deer et al. 1962, Boettcher 1966). Even the highest contents reported are far below the contents found in biotites and chlorites. However, according to estimates of Barshad and Kishk (1969) the iron content of soil vermiculite can be as much as 12 %. This shows that fine grained soil vermiculite may contain more iron than coarser, well crystallized vermiculites of hydrothermal origin.

The significance of "amorphous material" in accounting for the total iron of fine clay fractions may indicate that as result of weathering iron is accumulating in that fraction of alumina and silica which is determined as "amorphous material". However, fine grained smectites or other fine minerals also dissolve in the treatment used to estimate amorphous material (Alexiades and Jackson 1966, Wada and Greenland 1970) which may explain the significance of "amorphous material" in accounting for total iron.

4.2 *Total trace elements*

Some of the trace elements in rocks are present in independent minerals, but many replace major structural elements in mineral crystals (Mitchell 1965). Thus the total trace element content of soils may depend mainly on the trace elements which the common soil forming minerals contain. Similarities in ionic size make

Table 21. Total contents of some trace elements (mg/kg) in soil samples. Means of soil textural classes with confidence limits at the 95 % level.

	Heavy clay	Silty clay	Sandy clay	Finer silt	Coarser silt	Finer finesand	Fine-sand	Sand
Cr	178 ± 10	138 ± 24	105 ± 17	98 ± 34	71 ± 6	53 ± 42	34 ± 13	—
Co	29.2 ± 2.1	25.8 ± 2.1	21.6 ± 6.4	17.6 ± 5.1	15.3 ± 1.9	9.6 ± 7.1	6.6 ± 4.0	—
Cu	98 ± 24	58 ± 8	35 ± 15	35 ± 13	22 ± 4	18 ± 16	—	—
Mn	1 023 ± 154	1 232 ± 363	1 457 ± 973	937 ± 326	781 ± 229	992 ± 1560	392 ± 201	342 ± 394
Mo	—	—	5.3 ± 0.9	5.2 ± 0.9	4.7 ± 0.4	3.7 ± 1.3	3.2 ± 0.9	3.5 ± 0.3
Ni	68 ± 7	53 ± 5	38 ± 6	38 ± 11	31 ± 14	22 ± 10	15 ± 14	15 ± 11
Pb	32 ± 4	31 ± 3	32 ± 3	34 ± 5	40 ± 9	29 ± 5	29 ± 5	29 ± 12
Sr	303 ± 38	333 ± 35	322 ± 25	377 ± 56	415 ± 50	360 ± 36	284 ± 27	261 ± 46
V	245 ± 15	179 ± 28	146 ± 28	133 ± 41	106 ± 13	69 ± 35	45 ± 15	35 ± 15
Zn	78 ± 10	59 ± 8	56 ± 15	54 ± 12	58 ± 10	37 ± 14	24 ± 10	20 ± 9

substitutions possible and particularly ferromagnesian silicates may be rich in various trace elements. The degree of replacement depends, however, on the conditions of crystallization. Therefore the trace element content even of the same mineral species may vary considerably depending on its origin. Although in the present study the main soil minerals were determined as broad groups it was considered that some knowledge about the distribution of trace elements in the soil minerals could be obtained with multiple regression analysis. Furthermore, the spectrographic method used for the determination of total amounts of trace elements is not considered to be very accurate. The coefficient of variation for parallel determination of various elements may range from 5 to 14 % (Mäkitie 1961). An error of similar order may be caused also because of the variation in the total composition of the samples compared with that of a gyttja clay sample which was used as the matrix for the standards (Mäkitie and Lappi 1958).

Chromium. The data in Table 21 shows that on average the total chromium contents of fine textured soil groups are much higher than those of coarse textured soils. The chromium contents of individual samples ranged from 190 ppm in a heavy clay soil to non-detectable contents in various sand soils. The chromium content of heavy clay soils in the present material seems to be slightly higher than that in the Southern Finnish subsoils reported by Erviö and Virri (1965). The means for coarser soils are similar to values reported previously for Finnish soils.

The close association of the contents of chromium and clay is illustrated by the high value for the correlation coefficient, r = 0.90***. Coarse clay was correlated with total chromium to same degree (Table 22) as the total clay fraction but judged by z-transformation test (Snedecor and Cochran 1972) the fine clay seemed to be less closely connected.

Of the minerals determined ”mica” was the best correlated with total chromium content of the samples, r = 0.90***. Multiple regression analyses revealed that the variation in total chromium content of the samples was not significantly explained by minerals other than ”mica”, ”vermiculite” and ”chlorite” (Table 23).

The three minerals together explained a very high proportion, 93 %, of the variation in the content of total chromium. On the basis of the β-coefficients ”mica” is more important than ”vermiculite” or ”chlorite” in determining the total chromium in studied samples.

Geochemically chromium resembles iron in many respects, and indeed chromium occurs in iron ores in high concentrations. Independent chromium minerals such as chromium mica or chromium chlorite are rare (Rankama and Sahama 1952). A more important mode of occurence is as a replacing ion in the structures of silicate minerals, in which Cr^{3+} replaces not only ferric iron but also, despite valence differences, ferrous iron and magnesium. The

Table 22. The correlation coefficients of the total contents of some trace elements with three clay fractions and dithionite extractable iron.

	Cr	Co	Cu	Mn	Mo	Ni	Pb	Sr	V	Zn
Clay fractions:										
< 2 μm	0.90***	0.83***	0.91***	0.27*	0.60***	0.93***	ns	ns	0.94***	0.82***
0.2—2 μm	0.90***	0.85***	0.83***	0.31*	0.69***	0.92***	ns	ns	0.84***	0.69***
< 0.2 μm	0.80***	0.72***	0.90***	ns	0.37*	0.85***	ns	ns	0.94***	0.86***
Dithionite extractable iron	0.43**	0.61***	ns	0.80***	0.61***	0.45***	ns	ns	0.54***	0.42**

ns = P>0.05, *= P<0.05, **= P<0.01, ***= P<0.001.

Table 23. Regression coefficients (b) with confidence limits at the 95 % level, β-coefficients and coefficients of multiple determination (d) for the relationship between the total contents of some trace elements and mineral components.

	"Mica"		"Chlorite"		"Vermiculite"		d
	b	β	b	β	b	β	
Cr	3.0 ± 0.8	0.49	4.1 ± 1.5	0.27	5.8 ± 2.0	0.37	0.93
Co	0.2 ± 0.2	0.22	1.2 ± 0.4	0.50	1.1 ± 0.5	0.37	0.86
Cu	1.1 ± 0.6	0.30	3.0 ± 2.4	0.19	5.6 ± 1.8	0.56	0.88
Ni	0.6 ± 0.3	0.29	1.5 ± 0.6	0.30	3.1 ± 0.8	0.51	0.91
V	3.8 ± 1.0	0.45	4.8 ± 1.9	0.25	9.3 ± 2.7	0.39	0.93
Zn	1.6 ± 0.5	0.62	1.6 ± 1.2	0.28	—	—	0.70

occurrence of chromium replacing the iron and magnesium in biotite explains the importance of "mica" in accounting for total soil chromium.

According to the partial regression coefficient the chromium content of the samples studied increases at a rate of about 3 mg/kg for a one per cent increase in "mica". This rate gives low values compared with the chromium contents of Canadian biotites and phlogopites which contents range from less than 340 mg/kg to 6 400 mg/kg (Rimsaite 1967). Lower contents, ranging from 4 to 700 ppm, have been found in biotites from granites (Lovering 1969). Obviously the content of chromium in biotites is variable and the relatively low effect of soil "mica" may be due to the fact that in the "mica" component estimated also types deficient in chromium may be present.

According to a few analyses found in the literature, the chromium content of vermiculite may range from 3 300 to 3 600 ppm (Foster 1962). Such values are much larger than the value implied by the regression coefficient.

In iron and magnesium rich forms of chlorite, chromium can replace these elements. Chromium contents of chlorite ranging from 0.78 to 5.39 % Cr have been found (Lapham 1958), but much lower contents are more common. Also the regression coefficient points to a chromium content lower by far than these values in the "chlorite" of the samples studied.

Cobalt. The average cobalt content of fine textured soil groups is higher than that of coarse textured soils (Table 21). The correlation between total cobalt and the percentage of clay is close, r =0.83*** (Table 22). The content of total cobalt seems to be more closely associated with the coarse clay (r = 0.85***) than with the content of fine clay (r = 0.72***). The correlation coefficient between dithionite extractable iron and cobalt was r = 0.61***.

According to the multiple regression analyses, "mica", "vermiculite" and "chlorite" were together significant in explaining the variation in the content of total cobalt in samples (Table 23).

A relatively high proportion of the variation, 86 %, is explained by these three mineral components. The β-coefficients indicate that "chlorite" may be more important than "mica" or

”vermiculite” in determining the amount of total cobalt in soils.

In igneous rocks, cobalt is not present as an independent mineral but it replaces ferrous iron and magnesium in ferromagnesian silicates (Rankama and Sahama 1952). In accordance with this principle, the results obtained suggest that the cobalt in soil is located in the magnesium and iron rich minerals ”mica”, ”chlorite” and ”vermiculite”.

As the results of the studies of Hodgson and Tiller (1962) indicate, cobalt added to the soil may be sorbed to some extent in the interlayers of vermiculite but in even greater measure it is situated in defects on the surfaces of mineral particles. The weakness of the correlation of total cobalt with the percentage of fine clay and free iron suggests that mechanical grinding and chemical weathering have not brought about much dislocation of cobalt in Finnish soils as has been found elsewhere (Le Riche and Weir 1963). Instead the results obtained suggest that the bulk of the cobalt in the soils studied occurs in the crystal lattices of ”mica”, ”chlorite” and ”vermiculite”.

Copper. The average total copper content of soil textural classes ranges from 98 ± 24 ppm in heavy clay soils to non-detectable amounts in finesand and sand soils (Table 21). The average total copper content of heavy clay soils is high when compared with total copper values reported earlier for Finnish soils (Vuorinen 1958). Erviö and Virri (1965) have, however, found values within the range from 80 to 120 ppm, so that the mean for heavy clays in the present material, although high, is not exceptional. The average copper content of silty clay soils is higher than the contents found by Erviö and Virri (1965) whereas averages for the sandy clay and the silt soils are closer to those found previously in Finnish soils.

The decrease in copper content with increasing particle size is very clear (Table 21) as has been found also in earlier investigations (Vuorinen 1958). The dependence of the total content of copper on the clay content is close, $r = 0.91^{***}$. Contrary to the case with most other trace elements, the total content of copper tends to be better correlated with the content of fine clay than with the content of coarse clay (Table 22).

None of the individual minerals estimated was correlated with total copper to a higher degree than the percentage of clay. ”Mica”, ”vermiculite” and ”smectite” appeared to be the only components which, according to the multiple regression analysis, were together significant in explaining variation in the total copper content of samples (Table 23).

The partial regression coefficient suggests that ”vermiculite” has a large effect on the copper content of samples. The effect of a one per cent unit of ”vermiculite” is about 5 times the effect of a one per cent unit of ”mica”. Also the β-coefficients suggest that ”vermiculite” is more important than ”mica” or ”smectite” in accounting for the total copper in soils.

According to Krauskopf (1972) a part of the copper in igneous rocks occurs as microscopic grains of sulphide between the silicate crystals and another part substitutes Mg and Fe in ferromagnesian minerals. Thus trioctahedral mica may contain copper, as well as many other trace elements. The copper content of biotites may range from 6 to 220 ppm (Rimsaite 1967, Annersten and Ekström 1971). On the basis of the regression coefficient the effect of a one per cent unit of ”mica” on the total copper content is in this range.

Manganese. The manganese content has a relatively large range of variation within soil textural classes of the sample material analyzed (Table 21). Similar values to those obtained for the present material have also been found earlier in Finnish soils (Erviö and Virri 1965). Only a very low correlation ($r = 0.27^{*}$) was found to exist between the percentage of clay and total manganese content (Table 22). Of the minerals estimated ”chlorite” was more closely correlated ($r = 0.47^{***}$) with the content of total manganese than the other components analysed. According to the multiple regression analyses, other minerals had no significant additional effects. A close correlation ($r = 0.80^{***}$) was found to exist between the percentage of dithionite extractable iron and total manganese.

According to RANKAMA and SAHAMA (1952) manganese occurs in rocks in such easily weathering minerals as olivine and hornblende but also in biotite. Manganese resembles iron in its occurence and properties. It is precipitated together with iron in conditions where a high redox potential prevails.

The association of large quantities of manganese with free oxides and hydroxides has been found when British soils have been treated with specific extractants (LE RICHE and WEIR 1963). The results obtained may suggest that an important part of soil total manganese exists also in Finnish soils in surface coatings of particles and in concretions formed by precipitation.

Molybdenum. Possibly due to differences in the matrix composition of heavy clay and silty clay samples compared with that of the standards used, the estimation of total molybdenum in these textural classes was highly uncertain. Therefore the results for these soil textural classes are not reported. In the other groups the content of total molybdenum tends to decrease when the particle size of samples increases (Table 21). The correlation of total molybdenum with the percentage of clay was not very close ($r = 0.60^{**}$). The percentage of coarse clay is better correlated ($r = 0.69^{**}$) than the content of fine clay with total molybdenum ($r = 0.37^{*}$).

The association of molydenum with oxalate extractable iron has been observed in several studies (LE RICHE and WEIR 1963, JAAKKOLA 1972). In the present data a significant correlation, $r = 0.61^{***}$, was found between dithionite extractable iron and total molybdenum. Of the minerals estimated ”chlorite” was more closely correlated than other minerals with the content of total molybdenum in the samples ($r = 0.66^{***}$).

In granites, molybdenum is usually present as the sulphide, molybdenite (RANKAMA and SAHAMA 1952). Molybdenum may also be incorporated in members of the so-called heavy mineral group (MITCHELL 1965). Concentrations of molybdenum ranging from 0 to 11 ppm have been reported in biotites of Swedish origin (ANNERSTEN and EKSTRÖM 1971), and also feldspar structures may contain considerable quantities of molybdenum (KRAUSKOPF 1972). The occurence of molybdenum in biotite and feldspar was not, however, indicated by the results obtained.

Nickel. The average content of nickel in the present material (Table 21) is of the same order as contents previously found in Finnish soils (ERVIÖ and VIRRI 1965). The association of nickel with clay is illustrated by a high correlation coefficient, $r = 0.93^{***}$, and total nickel may be in combination with coarse clay, $r = 0.92^{***}$, rather than with fine clay, $r = 0.85^{***}$ (Table 22). The correlation of total nickel with free iron was not close, $r = 0.45^{***}$. The closer correlation of total nickel with coarse clay than with fine clay and its low correlation with dithionite extractable iron indicates that the nickel in the soils studied is more likely located in the crystal lattices of minerals than in weathering products.

The correlation coefficients between the contents of total nickel and ”mica”, ”chlorite”, ”vermiculite”, ”smectite” and ”amorphous material” ranged from 0.69^{***} to 0.88^{***}. The multiple determination coefficient of the regression equation in which the percentages of ”mica”, ”chlorite” and ”vermiculite” together explain the variation in the content of total nickel was 0.91^{***} (Table 23).

According to the β-coefficients ”vermiculite” is more important than ”mica” or ”chlorite” in determining the content of nickel in soil. Also the value of the partial regression coefficient for ”vermiculite” is higher than the same coefficients for ”mica” and ”chlorite”.

According to RANKAMA and SAHAMA (1952) nickel occurs in large amounts in basic igneous rocks. In granitic rocks nickel replaces magnesium because of the similar ionic size of these elements. Nickel contents up to 1 200 ppm with a median content of about 50 ppm have been found in biotite from rocks (LOVERING 1969). In a number of biotites of Swedish origin nickel contents ranged from 12 to 89 pp, (Annersten and Ekström 1971). The nickel content of soil "mica", according to the regression coefficient, is of the same order as that of rock biotites.

In vermiculites, nickel contents ranging from 500 to 2 200 ppm have been found (Foster 1962). The regression coefficient for soil "vermiculite" is low compared with the nickel contents of coarse-grained vermiculites.

Since primary chlorites are rich in magnesium and iron, nickel can also occur in this mineral.

Lead. The average content of lead is very similar in all textural classes (Table 21). The lead contents in the present material are lower than values reported by Sillanpää (1962) but higher than those reported by Erviö and Virri (1965) for subsoils in Southern Finland. The regression analysis did not indicate any relationship between the contents of lead and the clay fraction. Nor was any correlation found between the contents of total lead and dithionite extractable iron in the present material, although in some British soils oxalate extracts a large proportion of total lead (Le Riche and Weir 1963).

No significant correlations were found between the contents of total lead and the minerals determined. Multiple regression analysis indicated, however, that "mica" and "K feldspar" together explained a small (23 %) but significant part of the variation in the content of total lead of the samples.

The radius of the Pb^{2+} ion is 1.32 Å compared with 1.33 Å for the K^+ ion. This similarity makes it possible for lead to replace potassium in feldspar structures (Rankama and Sahama 1952). Considerable quantities of lead occur in rocks in this form, especially in pegmatites. Contents of up to 160 ppm have been found in alkali feldspars of Norwegian origin, but on average contents of about 25 ppm are common (Heier and Taylor 1959). Lead has been detected also in biotite, contents ranging from 12 to 23 ppm in samples of Swedish origin (Annersten and Ekström 1971). The occurence of lead in feldspars and biotites may explain its even distribution in soils differing in texture although the occurence of lead in the minerals mentioned appears on the basis of the results obtained here to be of minor importance.

Strontium. The highest strontium content, 490 ppm, was found in a coarser silt sample. The lowest strontium contents were found in the finesand and sand soil groups (Table 21). In the present data the total strontium contents are about half of mean values obtained for a larger material of Finnish soils (Lakanen and Sillanpää 1967) but also values in the range of the present study have been obtained (Erviö and Virri 1965).

Total strontium was not correlated with any of the clay fractions determined (Table 22). Of the minerals analyzed "Na and Ca feldspars" were positively correlated with total strontium, but the correlation coefficients were low, $r = 0.29^*$ and $r = 0.34^{**}$, respectively.

Strontium resembles calcium closely in its chemical properties. Thus strontium occurs with calcium in rock minerals (Rankama and Sahama 1952). In plagioclase feldspar, strontium contents ranging from 1 000 to 5 000 ppm have been found by Wager and Mitchell (1951). Nagasawa (1971) reported much lower values, ranging from 66 to 590 ppm.

Because of similarity in ionic size, strontium may also replace potassium in many minerals. In biotites of Swedish origin strontium contents from 2 to 50 ppm have been found (Annersten and Ekström 1971). In K feldspars, values ranging from 50 to 216 ppm have been reported (Nagasawa 1971). Thus strontium occurs in various minerals replacing calcium and potassium, possibly also in minerals whose contents were not determined.

Vanadium. Fine textured soils appear to contain much more vanadium than soils of coarse texture (Table 21). The correlation coefficient between the contents of total vanadium and clay is high, $r = 0.94^{***}$ (Table 22). The content of vanadium tends to be more closely correlated with the content of fine clay ($r = 0.94^{***}$) than with that of coarse clay ($r = 0.84^{***}$). The vanadium contents in

Table 21 are of the same order as contents reported previously for Finnish soils (Vuorinen 1960).

A stepwise calculation of multiple regression equations revealed that "mica", "chlorite" and "vermiculite" were significant in explaining the variation in total soil vanadium (Table 23).

The β-coefficients suggest that "mica" is more important than "vermiculite" or "chlorite" in determining total vanadium in the soils studied.

In rocks, vanadium occurs in basic minerals, in whose crystal structure it replaces titanium and iron (Rankama and Sahama 1952). Vanadium may also replace aluminium, but not in feldspars. In igneous rocks vanadium replaces iron and possibly also titanium in biotites as well as in some members of the so-called heavy mineral group. Vanadium contents from 30 to 240 ppm have been found in biotites of Swedish origin (Annersten and Ekström 1971). In the material studied by Lovering (1969) the median vanadium content of biotites from granitic rocks was about 200 ppm. The vanadium content of soil "mica" estimated from the regression coefficient is higher than the usual contents in rock biotites. According to the partial regression coefficient the effects of a one per cent unit of "chlorite" and "vermiculite" are still higher.

Zinc. The average total zinc content of 78 ppm in the heavy clay group is almost four times as high than that of the sand soils (Table 21). Other fine textured soils also seem to be rich in zinc compared with the coarser textured soil groups. The correlation coefficient between the contents of total zinc and clay was $r = 0.82^{***}$ (Table 22). The zinc content was more closely correlated with the percentage of fine clay than with the percentage of coarse clay.

Of the determined mineral constituents "mica" was best correlated with total zinc. According to the multiple regression analysis, in addition to "mica", "chlorite" significantly explains the variation in the zinc content (Table 23).

The role of "mica" in contributing to soil total zinc is understandable, since biotite together with amphiboles and pyroxenes are the main zinc-containing minerals in igneous rocks (Rankama and Sahama 1952). Annersten and Ekström (1971) found zinc contents from 84 to 748 ppm in Swedish biotites. Although zinc may also replace magnesium as well as ferrous iron in silicate minerals, the zinc content of magnesium rich mica is lower than that of biotite (Erämetsä 1945). The low contribution of magnesium rich minerals to total zinc is confirmed also by the fact that in this study "vermiculite" has no significant effect on the zinc content. However, "chlorite" increases the zinc content at a similar rate to "mica".

4.3 *Potassium fixation*

The average amounts of fixed potassium, determined by adding 25 ml of 0.01 *N* KCl to 10 g soil (corresponding to 97.7 mg K/100 g soil), range from 2.5 — 61.9 mg/100 g soil among different textural classes (Table 24). According to the data, fixation increases with increasing fineness of samples. The sandy clay samples in the present material have a relatively low fixation capacity compared with heavy and silty clay soils. The silt soils have a relatively high fixation capacity, and also finer finesand soils fix potassium to a considerable degree.

The correlation coefficient between the amount of fixed potassium and the percentage of clay was $r = 0.78^{***}$. The respective correlation coefficients with fine and coarse clay fractions were $r = 0.70^{***}$ and $r = 0.77^{***}$.

The amount of potassium fixed with drying, determined in connection with the estimation of "vermiculite", was much higher than the amount of potassium fixed without drying (Table 24).

A relatively close positive correlation ($r = 0.82^{***}$) was found between the pH and fixation of potassium without drying. The correlation coefficient between the percentage of "vermiculite" and potassium fixation ($r = 0.85^{***}$) was of a similar order. As well as "vermiculite" (X_2) and pH (X_3), exchangeable potassium (X_4, me/100 g) and the percentage of clay (X_5) had a significant effect on the amount of fixed potassium (X_1, mg/100 g soil). The regression equation was as follows:

Table 24. Fixation of potassium, mg/100 g soil, without and with drying. Means of soil textural classes with confidence limits at the 95 % level.

	Heavy clay	Silty clay	Sandy clay	Finer silt	Coarser silt	Finer finesand	Fine-sand	Sand
Without drying:								
K fixed from an addition of 97.7 mg/100 g of soil	60.5 ± 16.0	61.9 ± 11.4	27.6 ± 15.5	33.2 ± 15.3	33.8 ± 16.3	15.4 ± 9.1	3.1 ± 1.6	2.5 ± 0.7
With drying:								
K fixed when saturated with K	524 ± 108	385 ± 78	144 ± 84	102 ± 72	108 ± 36	18 ± 12	—	—

$$X_1 = -56.1 + 4.0\,X_2 + 14.3\,X_3 - 39.6\,X_4 + 0.5\,X_5$$

$$R = 0.92^{***} \qquad \beta X_2 = 0.51 \quad \beta X_3 = 0.38$$

$$S = 9.9 \qquad \beta X_4 = 0.49 \quad \beta X_5 = 0.52$$

The clay percentage appears to be very important in determining potassium fixation. The significance of ”vermiculite” in the fixation of potassium is clear since ”vermiculite” was estimated from the amount of potassium fixed when samples were dried. The effects of pH and exchangeable potassium relative to the effects of ”vermiculite” appear to be high. The four variables together explained 85 % of the variation in potassium fixation. Elimination of the effect of clay percentage decreased the proportion of variation explained to 64 %. When the effects of other significant variables were eliminated ”vermiculite” alone explained only 21 % of the variation in potassium fixation.

Although amorphous forms of silica and alumina have been reported to fix potassium (van Reeuwijk and De Villiers 1968, Raman and Mortland 1969), the multiple regression analysis did not indicate that ”amorphous material” had a significant effect on K fixation.

The effect of ”vermiculite” on potassium fixation is obvious, but the effect of pH is not so readily understandable. The raising of soil pH by liming has been found to result in increased fixation of potassium (Wiklander and Koutler-Andersson 1959). On the other hand certain studies have indicated that absorption of aluminium or hydroxy-aluminium may decrease the sorption of cations and also influence the fixation of potassium by restricting collapse of the layers needed to effect fixation (Cook and Hutcheson 1960, Schwertmann and Politz 1964, Schwertmann 1966).

The sandy clay samples of the present material fix relatively little potassium compared with samples of other clay or silt soils. Characteristic of the sandy clay soils in the present material is a lower pH than in other clay soils. Also the contents of free iron and ”chlorite” are relatively high in the sandy clay samples.

High levels of exchangeable potassium in the soil indicate a good supply of potassium. In such a soil potassium fixation is not likely to occur.

Table 25. Nonexchangeable K and Mg extractable with 1 *N* HCl from soil samples. Means of soil textural classes with confidence limits at the 95 % level.

	Heavy clay	Silty clay	Sandy clay	Finer silt	Coarser silt	Finer finesand	Fine-sand	Sand
Potassium								
mg/100 g soil	459 ± 70	340 ± 36	253 ± 89	267 ± 100	207 ± 33	142 ± 135	78 ± 70	16 ± 9
% of soil total K	14 ± 2	11 ± 1	9 ± 3	9 ± 3	7 ± 1	5 ± 4	3 ± 3	1 ± 1
% of "mica" K	23 ± 5	27 ± 9	21 ± 8	38 ± 23	34 ± 12	23 ± 11	19 ± 14	20 ± 22
Magnesium								
mg/100 g soil	864 ± 85	619 ± 23	422 ± 85	440 ± 113	344 ± 38	196 ± 135	117 ± 77	44 ± 45
% of total Mg	43 ± 4	41 ± 4	34 ± 4	39 ± 11	38 ± 5	25 ± 13	29 ± 14	16 ± 12

4.4 *Acid extractable nonexchangeable potassium and magnesium*

Extractable nonexchangeable potassium. The data in Table 25 indicate that 1 *N* HCl extracts higher quantities of potassium from heavy clay soil samples than from samples of other textural classes. The silt soils are relatively rich in acid extractable nonexchangeable potassium whereas low quantities are extracted from sand soils. The mean values of extractable nonexchangeable potassium for the soil textural classes in Table 25 are lower than mean values for a larger material of subsoil samples of Finnish origin (Kaila 1967).

Extractable nonexchangeable potassium as a percentage of total potassium is on average 1 % in the sand soil group and 14 % in heavy clay soils, although the total potassium contents of these textural classes are almost identical in the material under study (Table 14).

Extractable nonexchangeable potassium calculated as the percentage of the amount of potassium in "mica" ranges on average from 19 to 38 % in the various soil groups (Table 25). Because of large internal variation no differences are, however, evident between various textural classes. No significant correlation was observed between extractable nonexchangeable K expressed as a percentage of "mica" K and percentage of clay, indicating that the potassium in "mica" differing in particle size may be extractable to the same degree.

The correlation between extractable nonexchangeable K and percentage of clay was close, $r = 0.87^{***}$. According to multiple regression analysis, as well as the percentage of clay (X_2), the percentage of "mica" (X_3) was significant in explaining the variation in the content of extractable nonexchangeable potassium (X_1, mg/100 g soil). The regression equation obtained was as follows:

$$X_1 = 34.8 + 2.5\,X_2 + 9.1\,X_3$$

$$R = 0.91^{***} \quad \beta\,X_2 = 0.44$$

$$S = 67.3 \quad \beta\,X_3 = 0.53$$

Elimination of the effect of clay in the above equation reduced the proportion of variation explained from 81 % to 27 %. After elimination of the effect of "mica" the clay percentage alone explained 23 % of the variation in the amount of extractable nonexchangeable potassium. The "K feldspar" did not account significantly for extractable nonexchangeable potassium. Experiments in which powdered minerals have been extracted with acid also indicate that K feldspar is of little importance in explaining extractable, nonexchangeable potassium. Ståhlberg (1960 a) extracted various minerals with boiling 1 *N* HCl for 10 minutes, and found that 14 % of the total K of a K feldspar of clay texture was released. Of the total K of clay sized biotite 99 % was brought into solution. Clay sized muscovite released 35 % of its total potassium in the same treatment and 46 % of the total K of a fine silt sized phlogopite was extracted.

The values for extractable nonexchangeable potassium, expressed as percentages of "mica" K (Table 25) are low when compared with amounts extracted from clay sized biotite by 1 *N* HCl (Ståhlberg 1960 a). The percentage amounts are even lower than those extracted from phlogopite and muscovite. The methods used are not, however, quite comparable.

Extractable nonexchangeable magnesium. As with potassium, high amounts of nonexchangeable magnesium are extracted from fine textured soils (Table 25). The correlation of the content of extractable nonexchangeable magnesium is closer, $r = 0.97^{***}$, than that of extractable potassium with the percentage of clay.

The extractable nonexchangeable magnesium expressed as a percentage of total magnesium is higher, ranging from 16 to 43 %, than the corresponding potassium percentage (Table 25). The extractable magnesium percentage is high compared even with nonexchangeable extractable potassium expressed as a percentage of "mica" potassium.

Multiple regression analyses showed that percentages of "mica" (X_3), "chlorite" (X_4) and "vermiculite" (X_5) as well as the percentage of clay (X_2) significantly explained the variation in the amount of extractable magnesium (X_1, mg/100 g soil). The equation was as follows:

$$X_1 = 9.6 + 4.2\,X_2 + 7.3\,X_3 + 11.3\,X_4 + 20.8\,X_5$$

$$\begin{array}{llll} R = 0.97^{***} & & \beta\,X_2 = 0.43 & \beta\,X_3 = 0.23 \\ S = 67.1 & & \beta\,X_4 = 0.16 & \beta\,X_5 = 0.23 \end{array}$$

Elimination of the effect of clay reduced the proportion of variation explained by the above equation from 94 % to 34 %. Also the β-coefficients indicate that the percentage of clay is an important factor determining the extractability of soil magnesium.

A possible explanation for the relatively large partial regression coefficient of "vermiculite" on acid extractable magnesium compared with that of "mica" is that the vermiculite in the samples studied has formed from magnesium rich types of trioctahedral mica, as has been found to be the case generally (Foster 1962), rather than from iron rich types.

The correlation of "mica" with acid extractable magnesium is easily understood, since trioctahedral types of mica contain magnesium and their crystal structure is relatively easily decomposed by acid. According to studies of Ståhlberg (1960 b), 13—45 mg Mg/g, depending on particle size, was extracted by 1 *N* HCl from one gram of biotite containing 4.8 % Mg during a 10 minute boiling. The same treatment extracted 28—87 mg Mg/g from a phlogopite with 15.7 % Mg. The regression coefficient indicates that magnesium is extracted from "mica" at a rate of 7.3 mg/g in the material analyzed. This rate is low compared with extraction rates from biotite and phlogopite. This result suggests that the "mica" component in the samples studied composed also of types which do not contain magnesium.

The effect of "chlorite" on acid extractable magnesium was expected, as the presence of primary chlorite was shown by X-ray analyses, and magnesium rich types of primary chlorite are common. An effect of "chlorite" on total magnesium was also revealed by the multiple regression analysis. Chlorite is readily destroyed by acid (Wiklander and Lotse 1966) and thus the elements in its crystal structures are released.

"Vermiculite", "mica" and "chlorite" were the mineral components estimated which together with the percentage of clay were significant in explaining the variation in acid extractable magnesium. The same minerals were also significant in explaining the variation in the content of total magnesium. However, according to the β-coefficients the order of importance was different so that the effect of ”vermiculite” on acid extractable magnesium was larger than that of ”chlorite”. This result suggests that ”vermiculite” is more completely destroyed by the extraction treatment than ”chlorite”. This is understandable, since vermiculite as an expanding lattice mineral has a larger surface area open to attack by acid than have mica and chlorite.

4.5 *Basic exchangeable cations*

Basic exchangeable cations were extracted by centrifuging with neutral 1 *N* ammonium acetate. Results of the determinations are given in Table 26. The mean content of exchangeable calcium ranges from 0.1 me/100 g in sand soils to 14.7 me/100 g in heavy clay soils of the present material. The content of exchangeable magnesium increases from sand to heavy clay soils at a rate similar to that of exchangeable calcium. Similarly high contents of exchangeable magnesium have been determined in the deeper layers of Finnish soils also previously (Aarnio 1942, Marttila 1965).

The correlation coefficients between the percentages of various clay fractions and the contents of exchangeable bases appear in the following:

Clay fraction	Correlation coefficients			
	Exch. Ca	Exch. Mg	Exch. Na	Exch. K
< 2 µm	0.93***	0.92***	0.91***	0.87***
$0.2 - 2$ µm	0.88***	0.84***	0.84***	0.82***
< 0.2 µm	0.89***	0.92***	0.92***	0.83***

Multiple regression analysis was used to study the association of mineral components analyzed with the variation in amounts of exchangeable cations. As well as the clay percentage (X_2), the ”vermiculite” percentage (X_3) was significant in explaining variation in the amount of exchangeable Ca and Mg. The regression equation for exchangeable Ca (X_1, me/100 g) was as follows:

$$X_1 = 0.53 + 0.10\,X_2 + 0.63\,X_3$$

$$R = 0.95^{***} \qquad \beta\,X_2 = 0.57$$
$$S = 1.58 \qquad \beta\,X_3 = 0.39$$

The percentages of clay and ”vermiculite” explained together 90 % of the variation in the content of exchangeable calcium. The β-coefficients indicate that the clay content appears to be more important than the content of ”vermiculite” in explaining the variation in exchangeable calcium.

The multiple regression equation between the content of exchangeable magnesium (X_1, me/100 g) and contents of clay (X_2) and ”vermiculite” (X_3) was as follows:

$$X_1 = -0.34 + 0.05\,X_2 + 1.27\,X_3$$

$$R = 0.96^{***} \qquad \beta\,X_2 = 0.27$$
$$S = 1.46 \qquad \beta\,X_3 = 0.71$$

In contrast to the case with exchangeable calcium, ”vermiculite” appears to be more important than clay in explaining the variation in the content of exchangeable magnesium. Together clay and ”vermiculite” explained 92 % of the variation in the content of exchangeable magnesium. After elimination of the effect of clay, ”vermiculite” alone explained 56 % of the variation.

The remarkably high correlation of ”vermiculite” with exchangeable magnesium may

Table 26. Basic exchangeable cations (me/100 g soil) in soil samples.
Means of soil textural classes with confidence limits at the 95 % level.

	Heavy clay	Silty clay	Sandy clay	Finer silt	Coarser silt	Finer finesand	Finesand	Sand
Ca	14.7 ± 2.7	8.8 ± 2.5	5.9 ± 2.4	5.5 ± 1.6	4.5 ± 1.6	1.8 ± 1.0	1.1 ± 1.1	0.1 ± 0.1
Mg	15.3 ± 3.3	10.3 ± 1.9	4.1 ± 2.5	3.3 ± 1.3	2.8 ± 1.4	1.0 ± 1.1	0.2 ± 0.2	—
K	0.97 ± 0.10	0.45 ± 0.10	0.39 ± 0.16	0.20 ± 0.03	0.17 ± 0.04	0.10 ± 0.06	0.18 ± 0.23	0.03 ± 0.01
Na	0.43 ± 0.07	0.37 ± 0.10	0.21 ± 0.11	0.16 ± 0.03	0.15 ± 0.04	0.08 ± 0.04	0.04 ± 0.03	0.02 ± 0.01

be related to the fact that vermiculite has been found to adsorb magnesium preferentially to calcium (Peterson et al. 1965). The selectivity of vermiculite of geological origin for magnesium has been found to be especially strong when the degree of Mg saturation exceeds about 30 to 40 %. In the present material the average Mg saturation percentage was 44 and 46 % of the cation-exchange capacity determined at pH 7 in heavy and silty clay soils, respectively. The selectivity of vermiculite for magnesium is explained by the stability of the Mg-H_2O interlayer compared with that of the Ca-H_2O interlayer (Peterson et al. 1965).

None of the mineral components analyzed was significant in explaining the variation in the content of exchangeable potassium (X_1, me/100 g) when the percentage of clay was also taken into account. When the percentage of clay was replaced by cation exchange capacity (X_2, me/100 g) then also the percentage of "mica" (X_3) proved to be of significance and the equation was as follows:

$$X_1 = -0.050 + 0.021\,X_2 + 0.010\,X_3$$

$$R = 0.89^{***} \qquad \beta\,X_2 = 0.65$$
$$S = 0.14 \qquad \beta\,X_3 = 0.28$$

The relationship of "mica" with soil exchangeable potassium implied by the equation above is readily explicable, as mica minerals contain a significant portion of the soil potassium in a form which is relatively easily released as exchangeable.

Of the mineral contents determined, those of "chlorite" (X_2) and "vermiculite" (X_3) were significant in explaining the variation in the content of exchangeable sodium (X_1, me/100 g) and the percentage of clay did not appear to have any additional effects:

$$X_1 = -0.005 + 0.009\,X_2 + 0.040\,X_3$$

$$R = 0.92^{***} \qquad \beta\,X_2 = 0.22$$
$$S = 0.061 \qquad \beta\,X_3 = 0.78$$

Possibly the high exchange capacity of "vermiculite" is important in determining the amount of exchangeable sodium in the samples studied. "Na feldspar" did not appear to have any significant effect on the content of exchangeable sodium.

4.6 *Cation-exchange capacity*

The cation-exchange capacities determined by the three methods used are shown in Table 27. The exchange capacity determined by ammonium acetate extraction (CEC_{Ac}) is the sum of Ca, Mg, K and Na exchangeable in 1 *N* neutral ammonium acetate and titratable acidity determined by Brown's (1943) method at pH 7. The exchange capacities determined by calcium (CEC_{Ca}) and potassium (CEC_K) saturation and subsequent displacement with magnesium and ammonium respectively, were obtained in connection with the determination of "vermiculite".

The results indicate that the exchange capacity depends closely on the texture of samples. In the group of heavy clay soils CEC_{Ac} ranged from 28.1 to 42.5 me/100 g. The exchange capacities of silty and sandy clays are considerably lower than those of heavy clays. The two silt soil groups do not differ in their exchange capacities. The finesand soil group contained one sample having a CEC_{Ac} value of 13.3 me/100 g, due to a high amount of titratable acidity. Also according to the other methods this sample had a relatively high exchange capacity.

The CEC_K values represent the exchange capacity of the outer surfaces of soil particles. This exchange capacity is only slightly over half of the CEC_{Ca} values in the clay soil groups. The difference between CEC_{Ca} and CEC_K diminishes in the coarser textured soils.

The dependence of exchange capacity values upon the percentage of clay is close. This is shown by the following correlation coefficients:

Clay fraction	Correlation coefficients		
	CEC_{Ac}	CEC_{Ca}	CEC_K
< 2 µm	0.96***	0.96***	0.93***
0.2 — 2 µm	0.90***	0.89***	0.87***
< 0.2 µm	0.94***	0.94***	0.91***

Of the mineral components analyzed "vermiculite" proved to be more closely correlated than the others with CEC_{Ac} and CEC_{Ca} values.

Table 27. Cation-exchange capacities (me/100 g) of soils determined by three methods. Means of soil textural classes with confidence limits at the 95 % level.

	Heavy clay	Silty clay	Sandy clay	Finer silt	Coarser silt	Finer finesand	Fine-sand	Sand
Ammonium acetate extraction (CEC_{Ac})	34.8 ± 4.8	22.6 ± 3.9	17.2 ± 2.6	13.2 ± 1.5	10.8 ± 2.5	5.4 ± 2.5	6.0 ± 3.6	2.6 ± 2.1
Ca saturation (CEC_{Ca})	31.2 ± 3.9	20.9 ± 3.8	13.2 ± 2.7	10.2 ± 2.1	9.2 ± 2.5	3.8 ± 1.6	4.9 ± 2.8	1.8 ± 1.8
K saturation (CEC_K)	18.4 ± 1.7	11.3 ± 2.2	9.7 ± 2.3	7.6 ± 1.5	6.4 ± 1.8	3.3 ± 1.5	4.4 ± 3.0	1.8 ± 1.8

The regression coefficients were $r = 0.93^{***}$ and $r = 0.96^{***}$, respectively. The CEC_K values were correlated closely with ”amorphous material”, $r = 0.89^{***}$.

According to multiple regression analysis the content of organic carbon had a significant contribution to the exchange capacity. The effects of the percentages of clay and organic carbon were eliminated when the effect of mineral components to the exchange capacities was studied by regression analysis with the soil sample material. In case of fractions of which organic matter was removed by oxidation with H_2O_2 such an elimination was not made.

The regression coefficients obtained for ”vermiculite”, ”smectite” and ”amorphous material” are evidently related to the exchange capacity values used in connection of their estimation (Table 28). Still, however, the proportion of variation accounted for in the soil sample material is relatively low.

Particle size appears to have a clear effect on the regression coefficients of ”amorphous material”. The value obtained with fine clay is close to that of ”smectite”, indicating a possible relationship of the components estimated as ”smectite” and ”amorphous material” as suggested by ALEXIADES and JACKSON (1966). RAMAN and MORTLAND (1969) have reported exchange capacities varying from 66—95 me/100 g for amorphous material of podzols. AOMINE and JACKSON (1959) have found more variable exchange capacities for allophanes of various origin, depending on the pretreatments.

The regression coefficients suggest that the effect of ”chlorite” on the exchange capacity of soils is much smaller than that of ”vermiculite”, ”smectite” or ”amorphous material”. Generally exchange capacity of chlorite ranges within rather wide limits from 10 to 40 me/100 g depending on the particle size (GRIM 1953). Also in the present material the effect of particle size on the exchange capacity of ”chlorite” is clear.

Table 28. Regression coefficients (b) with confidence limits at the 95 % level, β-coefficients and coefficients of determination (d) for the relationship between cation exchange capacity and mineral components.

	"Chlorite"		"Vermiculite"		"Smectite"		"Amorphous material"		d
	b	β	b	β	b	β	b	β	
CEC_{Ac}									
Soil	—	—	1.68 ± 0.48	0.63	0.92 ± 0.47	0.47	0.83 ± 0.50	0.31	0.64
CEC_{Ca}									
Fractions									
Fine clay	—	—	1.45 ± 0.10	0.92	0.96 ± 0.08	0.90	0.92 ± 0.13	0.63	0.98
Coarse clay	0.19 ± 0.16	0.18	1.55 ± 0.26	0.88	—	—	0.40 ± 0.34	0.18	0.85
Silt	0.08 ± 0.06	0.15	1.52 ± 0.21	0.87	—	—	—	—	0.93
Soil	—	—	1.96 ± 0.33	0.77	0.94 ± 0.33	0.24	0.63 ± 0.34	0.37	0.82
CEC_K									
Fractions									
Fine clay	—	—	—	—	0.95 ± 0.08	1.48	0.91 ± 0.11	1.02	0.89
Coarse clay	0.18 ± 0.15	0.37	—	—	—	—	0.40 ± 0.34	0.36	0.34
Silt	0.07 ± 0.05	—	—	—	—	—	—	—	0.19
Soil	—	—	0.42 ± 0.33	0.27	0.94 ± 0.33	0.59	0.63 ± 0.34	0.40	0.50

5. Discussion

Since weathering has altered the least stable soil minerals, the identification of mineral components is an important prerequisite to their estimation. This is especially the case when estimation is based on the results of chemical analyses. However, the variability in the properties of minerals formed in soil and even of minerals of primary origin makes their estimation difficult. The determination of very stable minerals such as quartz can be fairly accurate, as was indicated by the relatively high correlation coefficients between results obtained by various methods. On the other hand, although the relatively soft layer lattice minerals are stable as fine grained material, (JACKSON et al. 1952), they may still be very variable in their chemical composition.

In fine fractions the crystallinity of minerals is generally poorer than in coarse fractions (FIELDES and FURKERT 1966). Therefore in fine fractions the differences in properties of minerals are not sharp, but gradually change between different categories (ROBERSON and JONAS 1965). Thus, soil smectites have been found to resemble vermiculite in many respects (SCHWERTMANN 1962). They have a higher contractability on potassium treatment and higher surface charge density than so called standard smectites. In addition soil smectites are poorly crystallized, and occur as finer grained particles than specimen smectites. Also the temperature of dehydroxylation of soil smectites is much lower than that of smectites of hydrothermal origin.

SCHEFFER et al. (1961 a) discussed the swelling properties of expanding lattice minerals and they identified several stages by means of certain tests. In the present study the only test for expanding lattice minerals was glycerol solvation of magnesium saturated samples. This method is considered to be effective for distinquishing between vermiculite and smectites (HARWARD et al. 1969). However, since the properties of the vermiculite and smectite occurring in soils overlap, the differentiation between these two groups is difficult. Also the differences in expansion resulting from various pretreatments and from saturation of the interlayer space with different ions show that the methods of testing for smectites are subject to interference (BEUTELSPACHER and FIEDLER 1963, GJEMS 1963).

The pronounced tendency of some fine clay fractions in the present study to swell was taken to indicate the presence of smectite occurring as mixed layers. The estimation of "smectites", based on exchange capacity, led to contents ranging from 12 to 24 % in the fine clay fractions studied. Amounts of this order should be clearly identifiable in X-ray analyses assuming that the smectite occurs as well defined crystals.

Small occurences of montmorillonite have been found in Finnish rocks as weathering products in veins where different rock types adjoin (NIINI and UUSINOKA 1971). The amount of material in such deposits may, however, be small when compared with other rock material ground during the Glacial period. The inclusion of material from Preglacial sediments and weathering crusts in present-day clays has possibly a larger importance (COLLINI 1950, ROSENQVIST 1961).

Intense mixing with other minerals has, however, diminished the possibilities of identifying materials of Preglacial origin in present-day soils. Weathering processes may also have changed the character of the minerals, so that only after drastic treatments are the original properties evident, as is the case with montmorillonite in the B horizons of podzols (WIKLANDER and ALEKSANDROVIC 1969).

The weathering of mica to smectite may not occur under the present climatic conditions prevailing in Finland (ISMAIL 1970). In the very acid and intense leaching environment in the A_2 horizon of Scandinavian podzols, however, a swelling lattice mineral characterized as montmorillonite has been detected (GJEMS 1960, WIKLANDER and ALEKSANDROVIC 1969).

The possibility that even vermiculite, which has a high interlayer charge, expands when the particle size becomes very small has been suggested by JONAS and ROBERSON (1960). They concluded that the force binding the layers is a function of the charge density of interlayer surfaces and the surface area of the particles. When the particle size decreases then also the binding force decreases and the glycerol is able to penetrate the interlayer space and cause the layers of vermiculite to expand. A more thorough investigation is needed to throw light upon the nature of expanding lattices and to study the conditions under which expansion occurs.

Because of the diffuseness of limits between mineral categories, the NaOH used to estimate the content of "amorphous material" may have dissolved also fine grained smectitic minerals. The use of KOH instead of NaOH would keep the layers of expanding minerals collapsed and thus reduce the dissolution of the crystal lattice (BRINER and JACKSON 1969). The extraction of interlayer material, which are determined as "chlorite", would also be reduced.

The estimation of "vermiculite" was based on potassium fixed when the samples were dried. Also smectite is known to fix potassium when it is dried (WEAVER 1958). Therefore it may be possible that smectite has contributed to the "vermiculite" values.

The occurence of different types of micas with varying contents of potassium makes the estimation of mica somewhat arbitrary. In addition the various weathering products of mica increase the error of the determinations. According to RAMAN and JACKSON (1966), however, the non-expanded layers in mixed layer minerals have changed little. WEAVER (1965) estimated that the K content of the mica layers in illites is 7.5—8.3 %. Although the 7.5 % average potassium content used in the estimation of "mica" takes into account some lowering in the content of potassium in mica with decreasing particle size (RAMAN and JACKSON 1966), the use of a special conversion factor for each fraction would possibly be justified (STÅHLBERG 1960 a). However, the results obtained when estimations of the "mica" content in fine clay were based on potassium contents of 7.0 and 6.5 % were no better than when a 7.5 % content was used. Also the determination of a factor for each fraction may be difficult because soil micas may vary in their potassium content from sample to sample.

The presence of primary and secondary types of chlorite in the samples was indicated by DTA, the X-ray diffractograms and also by the multiple regression analyses used to study the relationship between minerals and the chemical properties of samples. The variable composition of these chlorites makes the estimation of this mineral group difficult. In addition, organic matter in the samples may increase the water loss upon which the analysis of "chlorite" is based. A correction would improve the "chlorite" estimates obtained for samples rich in organic matter.

The instability of fine grained feldspars (Tamm 1929) impairs the accuracy of their estimation. Considerable sorption of sodium by the sample during the $Na_2S_2O_7$ -fusion apparently causes large errors in the results. Therefore "Na feldspar" estimates for the 0.2—2 μm fraction are considered to be only approximate (Kiely and Jackson 1964). Better "Na feldspar" estimates could possibly be obtained by a fusion-dissolution treatment not involving sodium.

It is thus clear that the chemical methods used in this study to determine the mineral composition of soil samples are not very accurate. However, none of the methods generally used in soil mineral analysis are very satisfactory (Konta 1963, van der Marel 1966, Gjems 1967). The estimation of soil minerals in samples composed of several more or less weathered minerals is difficult.

The regression analyses indicate that "mica" influences many of the chemical properties of Finnish soils. The trioctahedral type rich in iron and magnesium is apparently more common than the dioctahedral type, as is the case also in Finnish rocks (Rankama and Sahama 1952). "Mica" appears to be the main mineral giving rise to the high content of total magnesium in the soils studied. Trioctahedral mica has been put forward also earlier as the source of the relatively high magnesium content of Finnish soils (Frosterus 1910, Aarnio 1942). The results of the present study indicate that "mica" contributes significantly to the total contents of those trace elements: chromium, cobalt, copper, nickel, vanadium and zinc, whose ions are of the same size as magnesium and ferrous ions.

Regression analyses indicated also that "mica" affects the contents of exchangeable potassium and nonexchangeable acid extractable potassium in soil. Acid extractable amounts of potassium expressed as percentages of "mica" potassium imply that potassium is not extracted from soil to the same extent as from freshly ground biotite (Ståhlberg 1960 a). This suggests the presence of dioctahedral mica or muscovite.

Multiple regression analyses indicated that "chlorite" may contribute to the total contents of magnesium and iron. In diffractograms of magnesium rich chlorites the ratio of intensities of the 7 and 14 Å peaks is about 1 to 1 compared with 3 to 1 in iron rich chlorites (Droste 1956). Since the 14 Å peak of the diffractograms was weak compared with the 7 Å peak, the chlorite in the samples studied is probably of the iron rich type. The temperature of dehydroxylation of iron rich chlorites is between 500 and 600° C whereas the magnesium rich types dehydroxylate above 600° C (Phillips 1963). The fact that the dehydroxylation peak of all the soil samples occured at below 600° C confirms the importance of the iron rich types. The relatively larger effect of "chlorite" upon total iron than upon total magnesium indicated by the regression analyses points in the same direction.

Regression analyses suggested that "chlorite" contributes to the total contents of chromium, cobalt, nickel, vanadium and zinc in soils. The implied contribution of "chlorite" to extractable nonexchangeable magnesium is consistent with the fact that chlorite is easily decomposed by acid treatment.

According to multiple regression analyses, "vermiculite" contains relatively high amounts not only of magnesium but also of iron, as has been found also elsewhere (Kerns and Mankin 1967, Barshad and Kishk 1969). The analyses indicated that "vermiculite" contributes especially to the total content of copper.

Characteristic of amorphous material is a large surface area, which causes a high chemical reactivity (van Olphen 1971). Thus although "amorphous material" occurs in Finnish soils in relatively low amounts, it may have an important effect upon soil properties. The "amorphous material" estimated did not appear to be involved in the potassium fixation although in some soils such a relationship has been found (van Reeuwijk and De Villiers 1968, Raman and Mortland 1969).

K feldspar is the main source of total potassium in coarse textured soils. Regression analyses did not, however, indicate that "K feldspar" has any effect upon the soil chemical properties studied.

6. Summary

The purpose of the present study was to investigate the mineral composition of Finnish soils and of specific particle size fractions. The dependence of some soil chemical properties on mineral composition was also examined. The sample material for the study was collected mostly from Southern Finland and it contains 56 subsoil samples mainly from cultivated areas and from depths varying between 5 and 80 cm.

Minerals in particle size fractions. To study the mineral composition of the fractions, samples were separated into fine clay (< 0.2 µm), coarse clay (0.2—2 µm), silt (2—20 µm), finer finesand (20—60 µm), finesand (60—200 µm) and sand (200—2 000 µm) fractions with centrifugal and gravity sedimentation and sieving. Qualitative mineral analyses of fractions were carried out using differential thermal analysis (DTA) and X-ray diffraction analysis. For X-ray diffraction, slides orientated for analysis were prepared from Mg and K saturated samples. Glycerol and heat treatments were used to facilitate mineral identification.

These methods enabled the identification of mica, chlorite, vermiculite and smectite in fine clay. X-ray diffractograms of the fine clay of clay soils showed sharper peaks than those of silty soil separates. DTA and X-ray analyses indicated that the mica in fine clay was trioctahedral rather than dioctahedral. Chlorite was of the easily dehydrating or clay chlorite type. Smectite occurred most probably as a mixed layer mineral.

As well as mica, chlorite and vermiculite, also potassium and plagioclase feldspars were identified along with quartz in the coarse clay fraction. No indication of the presence of smectite in coarse clay was found. In fractions coarser than clay the same minerals were present, and in addition small amounts of amphibole and pyroxene minerals were detected.

The contents of mineral components in fractions were estimated by chemical methods. The conversion factors needed for calculating the contents of "feldspars" and "quartz" were obtained using particle size fractions prepared from minerals isolated from rocks and sand soils.

"Mica" was the main component in fine clay. Its content was on average 31 % of the fraction. "Chlorite" comprised on average 21 % of fine clay and "amorphous material" 22 %. The content of "vermiculite" was on average 10 % and that of "smectite" 19 %.

The fine clay separated from fine textured soils showed a tendency to have high "mica", "smectite" and "vermiculite" contents whereas that separated from silt soils tended to be high in "chlorite" and "amorphous material".

In coarse clay the sum of contents of "feldspars" and "quartz" was almost one half of the total fraction. The contents of "amorphous material" and "chlorite" were about half or less of their contents in fine clay while there was no difference in the contents of "mica" between the two clay fractions.

In the silt fraction, the sum of contents of "feldspars" and "quartz" was on average nearly 80 %. Of the layer lattice minerals, "mica" was most abundant followed by "chlorite".

In the finer finesand, finesand and sand fractions, the content of "feldspars" was almost the same as in the silt fraction except for "Ca feldspar", whose maximum content occurred in the finer finesand fraction. The content of "quartz", on the other hand, increased with increasing particle size from the finer finesand to the finesand fraction and remained at that level in the sand fraction.

Minerals in the soils. The mineral composition of the soil was better assessed by calculating the mineral components using weighted average conversion factors and the results of chemical analysis on each sample than by basing the calculations on individual or average mineral compositions of fractions.

"Mica", "chlorite", "vermiculite", "smectite" and "amorphous material" made up on average about 60 % of the heavy clay soils whereas "feldspars" and "quartz" formed the major portion of coarser textured soils. Differences in mineral composition of the soils were closely dependent on the texture, and regional differences in the composition of fractions were generally small.

Correlation of mineral contents with chemical properties. Multiple regression analyses indicated that the total magnesium and iron in soils correlates closely with the contents of "mica", "chlorite" and "vermiculite". These minerals also appeared to influence the total contents of chromium, cobalt, copper, nickel, vanadium and zinc in samples.

Potassium fixation by soils in water suspension was accounted for by contents of clay, "vermiculite", pH and the level of exchangeable potassium. "Mica" was significant in explaining the amount of acid extractable potassium; "K feldspar" did not appear to have any additional effect. There were indications that "vermiculite" is a more important source of acid extractable nonexchangeable magnesium than "mica" or "chlorite", which nevertheless contributed to the amounts extracted.

Of the mineral components analyzed, "vermiculite", possibly owing to its high exchange capacity, was closest correlated with the contents of exchangeable cations. However, clay was more important than any mineral constituent in explaining variation in contents of exchangeable cations.

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SELOSTUS

Pohjamaanäytteiden mineraalikoostumuksesta ja sen suhteesta lajitekoostumukseen sekä eräisiin kemiallisiin ominaisuuksiin

Jouko Sippola

Maatalouden tutkimuskeskus

Tutkimuksen tarkoituksena on ollut selvittää eräiden suomalaisten pohjamaiden ja niistä erotettujen lajitteiden mineraalikoostumusta. Myös tutkittiin eräiden maan kemiallisten ominaisuuksien riippuvuutta mineraalikoostumuksesta. Näyteaineisto koostui 56:sta 5—80 cm:n syvyydestä otetusta pohjamaanäytteestä, jotka oli kerätty pääasiassa Etelä-Suomesta ja yleensä viljelyiltä mailta.

Lajitteiden mineraalikoostumuksen tutkimiseksi näytteistä erotettiin hieno saves (< 0.2 µm), karkea saves (0.2—2 µm), hiesu (2—20 µm), hieno hieta (20—60 µm), karkea hieta (60—200 µm) sekä hiekka (200—2 000 µm). Termistä analyysiä ja röntgenmenetelmää käytettiin mineraalilajien tunnistamiseen.

Hienosta saveksesta tunnistettiin kiille, kloriitti, vermikuliitti ja smektiitti. Kiille näytti olevan lähinnä trioktaedrista ja kloriitti savikloriittia. Smektiitti esiintyi todennäköisesti seoshilamineraalina. Karkeassa saveksessa todettiin kiilteen, kloriitin ja vermikuliitin lisäksi kali- ja plagioklaasimaasälpiä sekä kvartsia. Hiesussa ja sitä karkeammissa lajitteissa esiintyivät samat mineraalit kuin karkeassa saveksessa sekä lisäksi amfiboli- ja pyrokseniryhmien mineraaleja.

Lajitteissa runsaimmin esiintyvät mineraalit pyrittiin määrittämään kvantitatiivisesti mineraalien kemiallisiin ominaisuuksiin perustuvilla menetelmillä. Hienossa saveksessa oli ”kiille” pääkomponentti määrän ollessa keskimäärin 31 %. ”Kloriittia” oli keskimäärin 21 %, ”vermikuliittia” 10 % ja ”smektiittiä” 19 %. ”Amorfista ainesta”, joka määritettiin NaOH:lla uuttaen, oli keskimäärin 22 %. Savimaista erotetussa hienossa saveksessa vaikuttivat ”kiilteen”, ”smektiitin” ja ”vermikuliitin” määrät korkeilta verrattuina hiesumaista erotettuun hienoon savekseen, jossa vuorostaan ”kloriittia” ja ”amorfista ainesta” oli suhteellisen runsaasti.

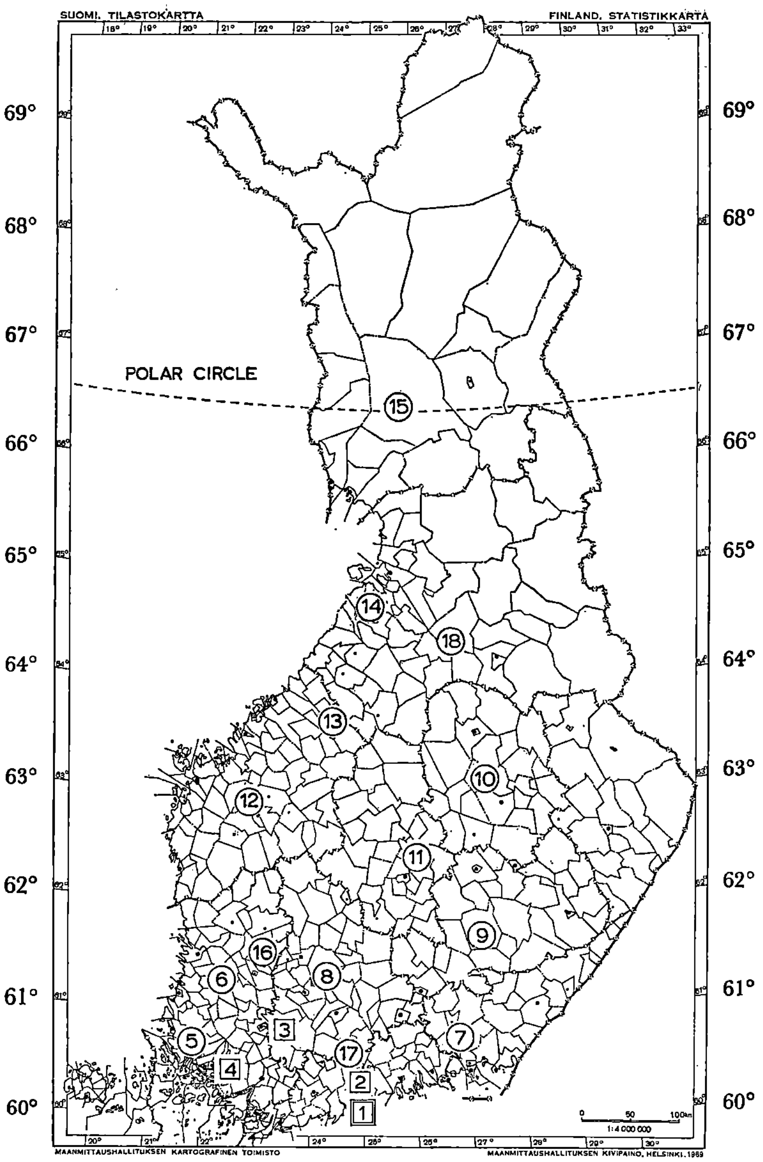
Karkean saveksen ”maasälpien” ja ”kvartsin” yhteismäärä oli lähes puolet koko lajitteesta. ”Amorfisen aineksen” ja ”kloriitin” pitoisuudet olivat karkeassa saveksessa suunnilleen puolet niiden pitoisuudesta hienossa saveksessa. Savilajitteiden kiillepitoisuudessa ei sen sijaan ollut merkitsevää eroa.

Hiesulajitteessa ”maasälpien” ja ”kvartsin” summa oli keskimäärin lähes 80 %. ”Kiille” oli hiesun runsain kerroshilamineraali. Hienossa ja karkeassa hiedassa sekä hiekassa olivat ”kali-” ja ”natriummaasälpien” pitoisuudet melkein samat kuin hiesussa. ”Kalsiummaasälpää” oli suhteellisen runsaasti hienossa hiedassa. Lajitteiden ”kvartsi”pitoisuus lisääntyi hiukkaskoon kasvaessa.

Maan mineraalikoostumus osoittautui olevan paremmin määritettävissä käyttäen muuntokertoimia ja kunkin näytteen kemiallisten analyysien tuloksia kuin perustaen laskelmat lajitteiden keskimääräiseen tai näytekohtaiseen mineraalikoostumukseen.

”Kiille”, ”kloriitti”, ”vermikuliitti”, ”smektiitti” ja ”amorfinen aines” muodostivat noin 60 % aitosavien aineksesta, kun taas karkeamman lajitekoostumuksen omaavissa maissa ”maasälvät” ja ”kvartsi” olivat vallitsevina. Maalajien mineraalikoostumuksien erot riippuivat kiinteästi lajitekoostumuksesta. Alueelliset erot lajitteiden mineraalikoostumuksessa olivat vähäiset.

Suoritettujen regressioanalyysien tulokset viittasivat siihen, että maiden kokonaismagnesiumin ja -raudan määrät riippuivat lähinnä ”kiilteen”, ”kloriitin” ja ”vermikuliitin” pitoisuuksista. Mainitut mineraalit näyttivät vaikuttavan myös kromin, koboltin, kuparin, nikkelin, sinkin ja vanadiinin kokonaismääriin. Kaliumin pidättyminen vesisuspensiossa näytti riippuvan ”vermikuliitin” pitoisuuden lisäksi näytteen saveksen ja vaihtuvan kaliumin pitoisuuksista sekä pH:sta. ”Kiille” selitti merkitsevästi 1 *N* suolahappoon uuttuvan vaihtumattoman kaliumin määrien vaihteluja, eikä ”kalimaasälvällä” ollut merkitsevää lisävaikutusta. ”Vermikuliitti”, luultavasti suuresta vaihtokapasiteetista johtuen, selitti suuremman osan vaihtuvien kationien määrien vaihtelusta kuin muut mineraalikomponentit.



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