

CHEMICAL AND MINERALOGICAL PROPERTIES  
OF A SEQUENCE OF TERRACE SOILS NEAR  
REEFTON, NEW ZEALAND

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## ABSTRACT

Changes brought about by chemical and physical weathering were investigated in a chronosequence of terrace soils near Reefton, New Zealand. The parent materials of the soils, which ranged in age from about 1000 to over 130,000 years were outwash gravels, sands and silts derived from granite (dominant) and indurated sandstone.

Variations in pH, organic matter, particle size, cation exchange properties, total Mg, Al, Si, K, Ca, Fe and Ti, poorly-ordered and organic-complexed forms of Al and Fe, and mineralogy caused by increasing duration of weathering and by short range, short term variations in the intensity of the biotic factor were determined.

It was concluded that the younger soils represented dynamic systems in which alternative weathering cycles could replace each other as the growth, death and eventual disappearance of individual red beech trees caused localised fluctuations in pH. It was further concluded that these processes would lead ultimately to the formation of gley podzols as are now found on the two oldest surfaces, and that podzolisation preceded gleying.

Attempts were made to determine if minerals of the plumbogummite group were responsible for the high proportion of soil phosphate from these soils that, on fractionation, appeared in the residual P fraction. It was found that attempts to concentrate these minerals by prolonged digestion with HF resulted in their solution, and in precipitation of complex fluorides that yielded diffraction spacings that have been mistaken for minerals of the plumbogummite group.



SOILS OF THE REEFTON SEQUENCE. (From left: Hokitika sandy loam, Ikamatua fine sandy loam, Ahaura silt loam, Kumara silt loam and Okarito loamy sand).

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## CHAPTER ONE

### INTRODUCTION

For more than a decade the study of the soil as part of the ecosystem has been an important aspect of the research effort of the Soil Science Department of Lincoln College. The programme is based on the identification and intensive study of monosequences - soil sequences where only one of the factors influencing soil formation has varied effectively. Such sequences, although rare, are invaluable since they allow quantitative investigation of the most important trends and processes in pedogenesis. The present investigation forms a part of this overall programme. It differs from earlier studies in that it places more emphasis on mineralogical changes.

#### I. THEORETICAL CONSIDERATIONS

The first quantitative statement that a soil was a function of the interactions of various soil forming factors,

$\pi = (K, O, \gamma) B$ , where  $\pi$  = soil,  $K$  = climate,  $O$  = organisms,  $\gamma$  = geologic substratum and  $B$  = the age of the soil, is attributed to Dokuchaev (Dokuchaev, 1951). His work was developed and given a more vigorous mathematical treatment by Jenny (1941, 1946 and 1958). Jenny's fundamental equation of soil forming factors,

$s = f (cl, o, r, p, t, \dots)$ , in which  $s$  = any soil property, and the five soil forming factors, climate ( $cl$ ), the biotic factor ( $o$ ), topography ( $r$ ), parent material ( $p$ ), and time, the period of soil formation ( $t$ ) are independent variables that define the soil system, is still the major integrating theory in pedology. The incomplete nature of the function signifies that additional factors may be involved.

Jenny (1961) extended his theory to embrace the entire ecosystem and presented his general state factor equation,

$l, s, v, a = f (Lo, Px, t)$ , which states that ecosystem properties ( $l$ ), soil properties ( $s$ ), vegetation ( $v$ ) or animal properties ( $a$ ) are a function of the initial state of the system ( $Lo$  - parent material and topography), the external flux potentials ( $Px$  - climate, biotic factors, and other unspecified factors such as the application of fertilisers and returns from the atmosphere), and the age of the ecosystem ( $t$ ). When the soil is considered in isolation the state factor equation reduces to the fundamental equation of soil forming factors.

Differentiation of this latter equation, assuming all the variables to be independent gives the partial equation,

$$ds = \left( \frac{\delta s}{\delta cl} \right)_{o,r,p,t} dcl + \left( \frac{\delta s}{\delta o} \right)_{cl,r,p,t} do + \left( \frac{\delta s}{\delta r} \right)_{cl,o,p,t} dr \\ + \left( \frac{\delta s}{\delta p} \right)_{cl,o,r,t} dp + \left( \frac{\delta s}{\delta t} \right)_{cl,o,r,p} dt,$$

which indicates that the extent of any change in a particular soil property is dependent upon the sum of the changes in the soil forming factors. The magnitude of the partial derivatives indicate the relative importance of each factor. Jenny (1958) indicated that if monosequences could be found where all but one of the soil forming factors are constant or ineffectively varying it should be possible to quantitatively evaluate the effects of each of these factors. Jenny (1946) had already noted the difficulty of finding such natural situations, and had suggested that useful approximations to such conditions, within a given area, would apply when the degree of change in a specified soil property (s) conditioned by one factor, greatly exceeded the changes conditioned by the remainder.

Jenny's concepts have been discussed by Stephens (1947 and 1951), Major (1951), Crocker (1952, 1959 and 1960) and Stevens and Walker (1970). Stephens stressed that time was the only truly independent variable and objected to its inclusion in the fundamental equation, while Major and Crocker made their greatest contribution by clarifying the concept of the biotic factor. Stevens and Walker examined the theoretical considerations underlying the concept of chronosequences, and after comparing a number of the more reliable chronosequence studies concluded that chronosequences, which extended over sufficient periods of time, often showed broadly similar trends. Bidwell and Hole (1965) and Yaalon and Yaron (1966) recognised the interference of man as a factor influencing soil formation, as did Rode (1961) who also added the Earth's gravity and water to the five factors



originally established by Dokuchaev (1951).

Crocker (1952) concluded that polygenesis of soils was the rule rather than the exception, and that monosequences were likely to be both short and approximate. Jenny (1958) and Walker (1965) joined Crocker in stressing the importance of identifying and examining monosequences. Barshad (1964) considered that only comparatively young soils, those formed since the most recent glaciation, could be regarded as truly monogenetic; that is developed under constantly uniform conditions from the initiation of soil development. Barshad also stresses the need to establish the uniformity of the parent material before measuring subsequent changes due to soil formation.

## II. AIMS OF THE PRESENT STUDY

The present study was initiated with two principal objectives. The first of these was to investigate changes in soil chemical and mineralogical properties as a function of the duration of weathering in a sequence of soils developed in alluvial, outwash, and loessial deposits near Reefton, New Zealand.

Adams (1970) reported that the residual P fraction (so-called residual organic P plus residual inorganic P, by the method of Williams, Syers and Walker, 1967) contained approximately half of the total soil phosphate in two toposequences of strongly weathered and leached soils, and noted that heating to 500°C produced a substantial increase in the  $\text{NH}_4\text{F-P}$  fraction. This

increase was greater than could be accounted for by the rendering soluble of organic P. As the change in phosphate solubility was similar to that occurring in Christmas Island "c-grade" rock phosphate ore (known to contain more than 30% of crandallite) also calcined at 550°C (Doak et al. 1965), it was possible that phosphate minerals of the plumbogummite group were present in the soils.

Tan (1971) observed similar high residual P levels in the soils of the Reefton sequence. These observations led to the second aim of the study, an attempt to confirm the presence of minerals of the plumbogummite group in strongly weathered soils showing high residual P levels.

During the study it was observed that marked changes in chemical and mineralogical properties, which appeared to be related to distance from the nearest living red beech tree, decaying beech stump, or accumulation of surface organic matter, occurred in the upper horizons of the younger soils in the sequence. Since these situations represented monosequences where changes in soil properties could be attributed directly to short range, short term variations in the effectiveness or intensity of the biotic factor, the study was extended to include their investigation.

### III. THE STUDY AREA

The soils examined in the present study occur on river flats and terrace lands in the Inangahua Depression, in the south-west of the Nelson province (Figure 1). Their principal environmental and pedological features are listed in Table 1. Apart from the theoretical aspects discussed

above, the accumulation of data from soils in this area is timely in view of the proposals for the fuller utilisation of Westland beech forests (N.Z. Forest Service, 1970).

These proposals have aroused considerable interest in a populace becoming increasingly concerned with their environment.

#### IV. SOIL FORMING FACTORS

In this section the factors that have interacted and are interacting, to influence the development of the soils of the Reefton terrace sequence are considered.

##### (1) Time.

The Inangahua Depression is a tectonically controlled valley between the granitic Paparoa Range to the west and the pre-Cambrian, indurated sandstone (greywacke) foothills of the Victoria Range to the east. During the early Pleistocene the valley was filled with gravels (the "Old Man Gravels") to a depth of several thousand feet (Suggate, 1957). These gravels consist mainly of granite (dominant) and indurated sandstone, and during subsequent glacial and interglacial periods they were terraced by rivers.

As the confluence of the Buller and Inangahua Rivers formed an effective local base level, changes in the height of terraces were independent of sea level fluctuations, and were caused by variations in the supply of gravel. Although it was usually impossible to trace the various terraces upstream to moraines, Suggate (1957) considered that the major aggradational terraces were formed from outwash gravels

of successive major periods of ice advance. During the intervening interglacial periods when the supply of gravel would fall Suggate assumed that the rivers would cut down and form degradational terraces.

Bowen (1964) and Suggate (1965) recognised three late Quaternary aggradational surfaces in the Inangahua Depression that were underlain by gravels correlated with the Speargrass, Tophouse and Manuka Formations of the Upper Buller catchment. The Manuka Formation underlies a high terrace that can be followed down the Buller Valley from Murchison to Inangahua and is thought to have been deposited during the Waimaunga Glaciation (Suggate, 1965). Since the two younger formations can not with confidence be traced away from the Inangahua Valley, correlation with the Upper Buller formations is indirect. Pollen analyses have indicated that both formations were deposited during glacial periods, and a radiocarbon date of  $20,000 \pm 300$  years B.P. for the Speargrass Formation (18 km north of Reefton) indicated its correlation with the later Kumara-2 ( $K2_2$ ) advance of the Otira Glaciation (Nathan and Moar, 1973). A sample they obtained from the Tophouse Formation was beyond the range of carbon dating ( $>47,500$  years B.P.) which indicated that the Tophouse Formation was likely to be older than the later Kumara-2 advance. As the Manuka Formation had previously been correlated with the Waimaunga Glaciation, Nathan and Moar (1973) concluded that it seemed probable that the Tophouse Formation was deposited during the Waimea Glaciation. Although the earlier Kumara-2 ( $K2_1$ ) advance has not been dated, the similar degree of dissection in

deposits from both formations would seem to indicate that the earlier and later Kumara-2 advances did not differ significantly in age. The Tophouse Formation is, however, considerably more dissected than the Speargrass, and this would seem to justify the correlation proposed by Nathan and Moar.

Suggate and Moar (1970) in a revision of the chronology of the late Otira Glacial (Suggate, 1965) indicate that the later Kumara-2 advance, the greatest ice advance of the late Otira Glaciation, began prior to 22,300 years B.P. and culminated shortly after 18,600 years B.P. Pollen analyses (Suggate and Moar, 1970) indicated a barren treeless landscape and bleak conditions in the Grey Valley during this period. Conditions were not likely to be very different in the nearby Inangahua Valley. It has thus been assumed that development of the Ahaura soils, the soils formed on the outwash terrace from the later Kumara-2 advance began some 18,000 years ago.

It has been assumed that the older and the younger Ikamatua soils have formed on degradational terraces following the retreats of the earlier Kumara-3 ( $K_{3_1}$ ) and later Kumara-3 ( $K_{3_2}$ ) advances, respectively. If this assumption is correct development of these soils would have begun some 16,000 and 14,000 years B.P., respectively (Suggate and Moar, 1970). The Hokitika soils of the present flood plain have not yet developed pedogenic B horizons. Mr E.J.B. Cutler (Pedologist, Soil Science Department, Lincoln College) has estimated that the age of the soil in the area sampled is of the order of 1000 years.

Considerable difficulty is experienced in attempting to date the onset of soil formation for the soils developed on the Tophouse and Manuka Formations. Climatic variations during the past 100,000 years estimated by oxygen isotope profiles through the Greenland ice sheet at Camp Century (Dansgaard et al. 1969), by  $C^{14}$  dated pollen from Holland (Hammen et al. 1967) and by oxygen isotope profiles of deep-sea cores from the Central Caribbean (Emiliani, 1966) all show the onset of the Wisconsin (Würm) Glaciation at about 70,000 years B.P. The preceding major glaciation indicated by Emiliani commenced about 130,000 years B.P. Suggate (1965) indicates that contemporary glaciation of the northern and southern hemispheres probably occurred throughout the whole of the Pleistocene, and he thus correlates the Otira Glaciation with the Würm. Suggate (1965) also indicates that his impressions of the relative durations of the various New Zealand glaciations and interglacials (assuming unit length for the Otira Glaciation) are as follows:

Otira Glaciation (1)

Oturi Interglacial ( $\frac{1}{2}$ )

Waimea Glaciation ( $\frac{1}{2}$ )

Terangi Interglacial ( $\frac{1}{2}$ )

Waimaunga Glaciation (1)

Waiwhero Interglacial (4)

Porika Glaciation (2)

If the onset of the Otira Glaciation is assumed to have commenced about 70,000 years B.P., then the Tophouse Formation would be at least that age, and the Manuka formation at least 130,000 years. These minimum values have been used in this thesis for the ages of the Kumara and Okarito soils, respectively. It must be noted, however, that for surfaces of these ages, the assumption that the soils they carry are of comparable age may not be valid. The gravels in the C horizon of the Okarito silt loam are very strongly weathered and can be readily crushed in the fingers, which tends to suggest they were weathered in situ since deposition.

The soils of the Reefton terrace sequence may be regarded as a non-strict chronosequence as defined by Stevens and Walker (1970).

## (2) Parent Materials

The Hokitika soils on the river flats within the study area are formed from alluvium deposited by the Waitahu River, a tributary of the Inangahua. The alluvium is generally coarse textured due to the proximity of its source, and is derived from granite (dominant) and indurated sandstone. Periodic flooding adds fresh alluvium (which may, in part, be pre-weathered) to the surface of these soils from where earthworms incorporate it into the profile. Sites Ho 1-5 used in this thesis were located as far as possible from the reach of floodwaters to reduce such interruptions to the minimum.

The Ikamatua soils on the post-glacial degradational terraces are separated from the recent soils by scarps up to 6 m high, and are thus beyond the reach of flooding. As with the Ahaura, Kumara and Okarito soils on the glacial outwash terraces the parent material consists of outwash gravels, sands and silts derived from granite (dominant) and indurated sandstone.

There is some conflict as to the contribution that loess has made to the parent materials of the soils, particularly to those developed on the intermediate and high glacial outwash terraces. If loess is present in the parent materials of these soils it is likely to be of local origin. Young (1967) reported that up to six feet of massive, practically impermeable, blue-grey loess blankets terraces of the Waimaunga, Waimea and early Otira Glaciations of the West Coast of the South Island, but has not been recognised on terraces of the later Kumara-2 or the Kumara-3 advances. Although Young stated that it was not suggested that the presence of one to six feet of loess was the only, or in some cases even a major cause of the formation of gley podzols, he went on to claim that the association of thick loessial deposits with the Okarito (and Waiuta) soils of the high (outwash) terraces was clearly established, and that it seemed probable that the development of these soils had been influenced by the texture of the loess. Mew et al. (1972) have reported that only minor amounts of loess contribute to the parent material of soils on the intermediate and high glacial outwash terraces in the Inangahua Valley. Stevens (1968a) has concluded that the combination



of narrow river valleys, low wind velocity, and very high rainfall, probably precluded the formation of much loess in South Westland. He attributed the presence of gleyed loess-like material in Okarito soils in South Westland to pedogenic processes.

### (3) Topography

The relief of all the terrace surfaces is flat to gently undulating. On the low glacial outwash terrace and on the younger surfaces freely-drained soils are found on the levées and in the higher areas, and poorly-drained soils in hollows and old stream channels, and near the foot of terrace scarps. The surfaces carrying the Ikamatua and Ahaura soils tend to have a more subdued microtopography than the present river flats. Relief offers no impediment to progressive soil development in the freely-drained terrace areas.

### (4) Climate

The present climate of the West Coast of the South Island is characterised by mild temperatures and heavy, evenly-distributed rainfall. The Inangahua Depression, separated from the coast by the Paparoa Range, is less wet and has a slightly greater temperature range. Monthly temperature, precipitation and humidity data for the Reefton climatological station are summarised in Figure 2. The rainfall figures cover the period 1904-1972, but the remainder are restricted to the decade from 1960-1970.

Rainfall shows a slight spring maximum in October and November, and a late summer minimum in February. The mean annual rainfall at Reefton (69 year period) is 1919 mm, with a range from 1354-2680 mm. The mean number of days per year on which rain and snow fall are 186 and 2, respectively. Isohyet maps show that the rainfall over much of the floor of the Inangahua Depression is comparable to that at Reefton. Precipitation increases towards the north (2540 mm year<sup>-1</sup> at Inangahua Junction) and with increasing altitude up the steep sides of the Depression.

The last major retreat of the glaciers that affected the study area began some 14,000 years B.P. (Suggate, 1965). The climate of the early post-glacial period (Aranuian Stage - Suggate, 1961) is assumed to have been cool and moist, and less rigorous than the severe, but not extreme climate of the Otiran Glaciation (Gage, 1965). Moar (1966) and Walker (1966) have assumed a general rise in temperature occurred some 10,000 years ago, whereas Harris (1963), Suggate (1965) and Vucetich and Pullar (1969) have proposed a progressive warming following the retreat of the glaciers. The latter view of continued change is supported by the temperature curve derived from oxygen isotope ratios in speleothems (Hendy and Wilson, 1968). This curve indicates a steady rise of about 6°C from 20,000 to 10,000 years B.P., but short term variations may be concealed by the 1000 year means on which the curve is based. Moar (1971) found no evidence that annual precipitation has varied greatly during the past 10,000 years in North Westland, and has inferred that during this period there has been a trend towards less

equable conditions. Evidence of minor glacial advances between 8,500 B.P. and the present, has been provided by Lawrence and Lawrence (1965), Burrows and Lucas (1967) and McGregor (1967), but the phenomena were insufficient to effect any major vegetation changes (Moar 1970 and 1971).

#### (5) Vegetation

The vegetative cover of the Inangahua Valley at the time of European settlement was a mixture of beech and podocarp forest. The river flats are now almost entirely cleared for farming. Remnants of the original forest remain only in the upper reaches of the creeks and in scattered patches near the Inangahua River. These remnants show that the native vegetation was red and silver beech (scientific names of plant species are listed in Appendix I) with occasional podocarps in freely-drained areas and matai and kahikatea in the hollows. The post-glacial degradational terraces and the low glacial outwash terrace have also been largely cleared of forest. Remnants show that on freely-drained sites the forest was dominated by red beech, with some kamahi, quintinia and rimu. With increasing age matai and kahikatea on the poorly-drained areas tended to be replaced by rimu and red beech. The two highest glacial outwash terraces are now almost devoid of forest cover, and now carry either manuka scrub, or a rush, sedge, umbrella fern and sphagnum moss association. Locally drier areas have been colonised by gorse and blackberry. On the intermediate glacial outwash terrace the forest, , before burning or cutting, was of

silver pine and mountain beech, with rimu, kamahi, quintinia, toa toa and pink pine. Yellow-silver pine was found on drier sites at terrace edges. On the high glacial outwash terrace manuka, bog pine, pink pine, mountain beech and yellow-silver pine formed a stunted forest or scrub.

Present evidence, based on radiocarbon dates, suggests that following the most recent deglaciation about 14,000 years B.P. (Suggate, 1965), a period of some 4,000 years elapsed before forest became re-established in the South Island (Gregg, 1966; Godwin and Switsur, 1966; and McIntyre and McKellar, 1970). Pollen records show that Nothofagus was dominant around Tophouse about 8,000 years B.P., and that it had spread to Springs Junction, south of Reefton, some 2,000 to 3,000 years later. Before the southward spread of beech the forest was dominated by rimu and other podocarps (Moar, 1971).

Couper (1960) has shown that species of the beech and podocarp families (including red beech) were known to exist in New Zealand prior to the Pleistocene. On the basis of pollen analyses, Dr N.T. Moar (Botany Division, D.S.I.R., Lincoln, pers. comm.) has found evidence of the presence of both beech and podocarps in a sample from the Westport area, that on present geological evidence is dated prior to the Otira Glaciation. It is therefore concluded that the biotic factor involved in the genesis of the soils of the Reefton sequence has been the flora and fauna of beech-podocarp forests.

## CHAPTER TWO

### METHODS

#### I. INTRODUCTION

This section discusses the criteria applied to site selection, and the procedures used in sampling and analysing the soils.

#### II. FIELD WORK

##### (1) Existing Surveys

The soils of the Inangahua Depression were surveyed during the reconnaissance mapping of the South Island of New Zealand at a scale of 1 : 253,440 (N.Z. Soil Bureau, 1968a). No other published work exists of the soils of this area.

In 1965 Mr B.S. Kear (Soil Bureau, D.S.I.R.) prepared a report and map (1 : 63,360) of the soils in an area of some 2000 ha centred on Reefton. This survey included most of the terrace lands and some of the flanking hills and steep-lands in the lower valley of the Waitahu River. It was prepared for the N.Z. Forest Service, and was used for the characterisation of soils being considered for beech management or exotic conversion, and for the instruction of forestry students at the Reefton Ranger School. Most of the soil units used by Kear had previously been named

and described during a reconnaissance soil survey of Westland (Gibbs, Mercer and Collie, 1950), a survey that terminated 5 km south-west of Reefton.

During 1971 N.Z. Forest Service asked Soil Bureau, D.S.I.R. to provide soil data applicable to the broad planning of the former's beech forest project in Westland. As there was a need for more detailed soil data than were available further investigations were initiated. During 1972 a soil survey of approximately 44,000 ha of predominantly terrace and hill country soils in the Inangahua Valley between Reefton and Inangahua Junction was carried out at a scale of 1 : 63,360. Soil fertility studies based on the defined mapping units, which in some cases differed substantially as compared with the reconnaissance soil map (N.Z. Soil Bureau, 1968b), were also undertaken. The results of the survey, together with a broad assessment of possible nutrient deficiencies likely to be encountered on those soils that may be used for exotic forestry are contained in a report (Mew et al. 1972), the distribution of which is restricted.

## (2) Site Selection

Basic reconnaissance and selection of suitable sampling sites on the river flats and terrace lands of the Inangahua Depression was carried out in December, 1968 by Mr E.J.B. Cutler of the Soil Science Department, Lincoln College. The only more or less complete terrace sequences that have survived are located between Reefton and the Waitahu River, and south of Larry's Creek. The former

area was chosen for this study.

In order to evaluate time as a soil forming factor on these surfaces, sites were chosen with the aim of minimising possible variations in the remaining factors. The sites finally chosen were those which best fitted the following criteria.

- (i) The parent material should be uniform, and consist of river alluvium or outwash gravels, sands and silts derived from granite (dominant) and indurated sandstone. There should not have been additions of nutrients, alluvium or loess following the onset of soil development. Where variations in profile depth and texture are encountered within any soil series, profiles having the greatest depth and finest texture should be preferred.
- (ii) Where such remnants have survived the site should be located in beech dominated forest. The biotic factor dominant in the genesis of the soils should have been beech, or beech-podocarp forest and their precursors or successors.
- (iii) The area should be flat or only slightly sloping. Locally drier sites near terrace edges, and poorly-drained sites in hollows, old stream channels, or towards the back of terraces should be avoided.
- (iv) There should have been the least possible interference by man, and domestic or introduced animals.

- (v) It should be possible to determine the approximate age at the surfaces.

In a study of a chronosequence of podzols in northern Michigan, Franzmeier and Whiteside (1963) noted that variations in the intensity of podzol development occurred on materials of each age. They could not fully explain these differences, and chose, for their study, the soil from each surface that showed the maximum podzol development.

Similar variations were observed on the terraces carrying the Hokitika, Ikamatua and Ahaura soils of the present investigation. These were the only terrace surfaces in the Waitahu Valley where beech forest remnants had survived. An exploratory survey showed that the intensity of podzol development was greatest surrounding living red beech trees and decaying beech stumps, was a function of tree size, and decreased with distance from tree or stump. Differences in intensity were not discerned in profiles at distances greater than 7 m from the largest trees ( $>1$  m, diameter breast height). On these terraces an attempt was made to minimise possible effects caused by short range variations in the intensity of the biotic factor by deliberately locating sampling sites used for the chronosequence study more than 7 m from any tree, stump, fallen log, or accumulation of surface organic matter.

Because of the need to balance desirable replication against the range of soil properties that could be determined in the time available, and because of the uncertainty posed



by the biotic factor, it was decided to sample the soils of the chronosequence, initially, at a single site on each aged surface, and to make a preliminary assessment of the biotic factor by selecting two further sampling sites, one at the base of a large decaying beech stump on the main post glacial terrace, and the second in a similar position on the low glacial outwash terrace. These latter sites were 9.10 and 7.25 m, respectively, from sites sampled for the chronosequence study. As it was considered that elaboration of the relationship between the freely-drained yellow-brown earths on the younger terraces and the water-logged gley podzols on the two oldest surfaces would be aided by comparing a freely-drained yellow-brown earth with a poorly-drained soil on the same aged surface, a poorly-drained site was selected on the older post glacial terrace. The locations of the above sampling sites are shown in Figure 1.

The chosen sampling programme would give some indication of the extent of variations likely to be found in the Ikamatua and Ahaura soils and should draw attention to the possible causes of such variations. It was felt that this approach would yield more information than analysis of a number of samples chosen at random from each aged surface.

Following detailed chemical and mineralogical examination of the above soils it was concluded that further investigation of the effects of red beech on soil genesis warranted consideration ahead of replication of the chronosequence data. Seven further sampling sites were

therefore chosen along two transects on the low glacial outwash surface (Figure 3). The sites actually selected were those where distance from roots and tree buttresses made sampling possible. The transects utilised the two sites already examined on this surface. Additional grab samples, taken to check hypotheses, are discussed in the text.

The soil terminology used throughout the remainder of this thesis is illustrated by the following examples:

Ah = Ahaura silt loam.

Ah 1 = Ahaura silt loam, site 1.

Horizon designations follow Taylor and Pohlen (1962).

### (3) Sampling Procedures

Horizons of soils used to investigate the effects of red beech on soil genesis - Ah<sub>2</sub> to Ah<sub>9</sub>, and I(o) 2 - were sampled on a non-volume-weight 'grab' basis. The soils used in the chronosequence study, and the poorly-drained soil on the older post glacial terrace - I(w)- were sampled using a procedure similar to that described by Stevens (1968b). A pit with a cross section of approximately 1 m<sup>2</sup> was dug at the sampling site on each surface. The area sampled was defined by placing a square frame, 0.04 m<sup>2</sup> in area, on the surface of each horizon being sampled, with an internal edge flush with a smooth vertical side of the pit. Within this frame each horizon of the solum was removed successively, weighed, and representative subsamples taken. Contamination of one horizon by material from another was carefully avoided. All samples were stored in sealed

polythene bags. Profile descriptions (Appendices II and III) were made during, or soon after sampling.

Following analysis of the above samples additional 'grab' samples were collected at further sites on the freely-drained surfaces. These samples were used to test hypotheses developed during the investigation. Details of such sites are included in the appropriate sections.

### III. ANALYTICAL PROCEDURES

#### (1) Sample Preparation

Immediately on return from the field, half of each sample was weighed, air-dried and reweighed. Where relevant, the volume-weight was calculated. The remainder of each sample was resealed and retained in a field-moist condition.

The air-dried samples were crushed with a steel rolling-pin and sieved through a 2 mm square-holed sieve. If the quantity of mineral matter that failed to pass the sieve was insignificant ( $<1\%$  by weight) it was discarded and the  $<2$  mm fraction alone used for subsequent analyses. For the eight samples where the  $>2$  mm fraction exceeded this limit, the lowest horizon sampled from Ho 1, I(y) 1, Ah 1 and Ku 1, and the two lowest from I(o) 1 and I(w) 1, both size fractions were weighed and retained for analysis.

Part of each air-dried sample was ground to  $<53\ \mu\text{m}$  using a tungsten carbide vessel in a Tema mill. This ground material was used for elemental analyses.

## (2) Analytical Methods

With the exception of mineralogical analyses all determinations were duplicated.

(a) pH. (On  $<2$  mm air-dried soil). Soil/distilled water suspensions (1 : 2.5) were stirred, left to stand overnight, and after further stirring read on a Radiometer 26 pH meter equipped with glass-calomel electrodes. The pH of soil/molar KCl suspensions (1 : 10) were determined in a similar manner.

(b) Dry Matter and Loss-on-Ignition. Dry matter was determined by heating 10 g (approximately) samples of  $<2$  mm air-dried soil in porcelain basins overnight at  $105^{\circ}\text{C}$ . After cooling (avoiding rehydration) and reweighing, the same samples were ignited for 1 hour at  $500^{\circ}\text{C}$  and again weighed to determine loss-on-ignition (LOI).

(c) Mechanical Analysis. Air-dried soil  $<2$  mm, equivalent to 50 g oven-dried weight, was sieved and the fraction smaller than  $63\text{ }\mu\text{m}$  dispersed in 1 l of sodiumhexametaphosphate (3.5 g/l). The percentages of silt and clay were determined at  $20^{\circ}\text{C}$  by the International pipette method (Robinson and Richardson, 1933). Samples with an organic carbon content exceeding 1% (Tan, 1971) were pretreated with boiling 30%  $\text{H}_2\text{O}_2$ . These data were provided by Mr E.J.B. Cutler, Soil Science Department, Lincoln College, to whom the author is indebted.

Approximate percentages of sand (s), silt (si) and clay (cl) were also obtained by weighing the size fractions obtained by fractionation during mineralogical analyses.

Before being dispersed,  $<2$  mm air-dried soil for these analyses, was treated with boiling 30%  $\text{H}_2\text{O}_2$  to destroy organic matter and deferrated with a dithionite-citrate system buffered with  $\text{NaHCO}_3$  (Mehra and Jackson, 1960).

International size classifications were adopted: coarse sand (cs) 2 - 0.2 mm, fine sand (fs) 0.2 - 0.02 mm, silt 0.02 mm -  $2\ \mu\text{m}$ , and clay  $<2\ \mu\text{m}$ . Fine clay (f.cl) refers to material  $<0.2\ \mu\text{m}$ , and coarse clay (c.cl) to material within the size range 2 - 0.2  $\mu\text{m}$ .

(d) Total Analyses for Mg, Al, Si, K, Ca, Fe and Ti. Mixtures containing 0.400 g of ground ( $<53\ \mu\text{m}$ ), air-dried soil and 4.000 g AR  $\text{Na}_2\text{CO}_3$  were fused in platinum crucibles over a Meker burner. Melts were extracted with 1 : 1 HCl, digested on a waterbath and made to volume. Suitable aliquots were taken for the separate determination of potassium by flame emission spectrophotometry, magnesium and calcium by atomic absorption spectrophotometry (1000 ppm  $\text{SrCl}_2$  as suppressant), and iron and titanium colorimetrically using Tiron (Yoe and Armstrong, 1947). Iron was also determined colorimetrically by the Ferron method of Belyayeva (1966).

Aluminium and Silicon were determined gravimetrically as aluminium oxinate and quinoline silicomolybdate, respectively, following careful fusion of 0.500 g air-dried ( $<53\ \mu\text{m}$ ) samples with 7.000 g AR NaOH in platinum crucibles (Bennett and Reed, 1971).

(e) Cation Exchange Capacity (CEC), and Exchangeable Na, Mg, Al, K, Ca, and Fe. Samples of air-dried soil ( $<2$  mm) were leached with molar ammonium acetate (pH 7.0),

washed with 60% ethanol, distilled, and CEC determined on the ammonia absorbed in boric acid. Exchangeable Na and K (flame emission spectrophotometry) and Mg and Ca (atomic absorption spectrophotometry, using 1000 ppm  $\text{SrCl}_2$  as suppressant) were determined on suitable aliquots of the leachates.

Exchangeable Al and Fe were determined by shaking 5.000 g samples of air-dried soil ( $< 2$  mm) with 50 ml 1.0 molar KCl (unbuffered) for 2 hours, centrifuging and analysing the centrifugates for Al and Fe using the Ferron method of Belyayeva (1966).

(f) Oxalate-extractable Al and Fe. Milled ( $< 53 \mu\text{m}$ ) air-dried soils (100 - 250 mg) were shaken with 10 ml 0.2 molar ammonium oxalate (pH 3.0) in darkness, on a reciprocating shaker for 4 hours, centrifuged, and aliquots of the extracts digested (almost dry) with concentrated  $\text{HNO}_3/\text{H}_2\text{SO}_4$  to destroy organic matter and oxalate (McKeague and Day, 1966). Residues were taken up in dilute acid and Al and Fe determined colorimetrically using Ferron (Belyayeva, 1966 and Blakemore, 1968). This method gave satisfactory replication and recovery of added Al and Fe, and had the considerable advantage of enabling both elements to be determined on a single aliquot.

(g) Pyrophosphate-extractable Al and Fe. Ground ( $< 53 \mu\text{m}$ ) air-dried soils (200 mg) were shaken with 20 ml 0.1 molar sodium pyrophosphate on a reciprocating shaker for 16 hours, centrifuged and aliquots of the supernatant

digested as in (f) to destroy organic matter and hydrolyse pyrophosphate to orthophosphate (McKeague, 1967). Residues were taken up in dilute acid, but as interference by phosphate prevented the use of Ferron it was necessary to determine Al and Fe on separate aliquots. Iron was determined with 1 : 10 phenanthroline (Jackson, 1958), and Al with aluminon using the procedure of Hsu (1963) as modified by Wang and Wood (1973). Hsu had shown that pH was critical for colour development with aluminon, and that the optimum pH for systems containing HCl was between 3.7 and 4.0. Wang and Wood, however, demonstrated that sensitivity decreased rapidly below pH 4.1 in  $\text{HNO}_3/\text{H}_2\text{SO}_4$  systems, but was not affected by pH within the range 4.1 - 4.3.

(h) Phosphate Retention. Phosphate retention was assessed by measuring the percentage of added phosphate taken up in 24 hours by 5.00 g of air-dried soil (<2 mm) shaken with 25 ml of solution having an initial phosphate concentration of 0.032 molar  $\text{KH}_2\text{PO}_4$ , and buffered at pH 4.6 (Saunders, 1965). The pH of 4.6 approximates the point of maximum phosphate retention of many acid soils.

(i) Fieldes and Perrott Sodium Fluoride Test. This test (Fieldes and Perrott, 1966) was carried out on air-dried soil (<2 mm) and on water-dispersed clay (<2  $\mu\text{m}$ ) using a sample : 0.85 molar NaF ratio of 1 : 50. pH values were read after 30 minutes using a Radiometer 26 pH meter with glass-calomel electrodes. The saturated NaF used by Fieldes and Perrott was replaced by 0.85 molar,

which has been shown to give comparable results, and avoids problems associated with the use of a saturated solution (Bracewell, Campbell and Mitchell, 1970).

(j) Mineralogical Analyses. Soil samples were prepared for X-ray and thermal examinations by methods essentially similar to those described by Jackson (1956, pp. 31-188).

Organic matter was oxidised by treatments (usually 12) with 30%  $\text{H}_2\text{O}_2$ , buffered at pH 5.0 to prevent the development of low pH conditions in the soil- $\text{H}_2\text{O}$ - $\text{H}_2\text{O}_2$  slurry that could cause degradation of layer silicates (Douglas and Fiessinger, 1971; Douglas, 1971 and Lavkulich and Wiens, 1971). 'Free' iron oxides were removed by treatment with bicarbonate-buffered citrate-dithionite (Mehra and Jackson, 1960). Size fractions were separated using procedures outlined by Tanner and Jackson (1947) and Jackson (1956).

Mg- and K-saturated clay suspensions (fine,  $<0.2 \mu\text{m}$  and coarse,  $0.2 - 2.0 \mu\text{m}$ ) were prepared by four washings with 0.5 molar  $\text{MgCl}_2$  and 1.0 molar  $\text{KCl}$ , respectively, followed by repeated washing with distilled water to remove excess salts. Duplicate samples of preferentially-oriented Mg- and K-saturated clays were prepared by drying 1% suspensions on glass slides at room temperature. The amount of clay on the slides corresponded to  $3.0 \text{ mg/cm}^2$ .

Following analysis by X-ray diffraction at room temperature the Mg-saturated samples were glycerol solvated by successive light sprayings with 10% glycerol



until the specimens retained a moist appearance. As some forms of montmorillonite solvated from dry Mg-saturated clay do not expand beyond 1.4 nm (Jackson, 1956 and Fieldes, 1968) samples found to contain expanding clays were also solvated by the method described by Jackson et al. (1954).

After X-ray examination at room temperature the K-saturated samples were heated for two hours at 350°C and subsequently for one hour at 550°C. They were re-examined after each heating. To preclude resorption of water samples were stored at 150°C until X-rayed.

Several workers have shown that treatment with warm HCl facilitated the identification of kaolinite in the presence of chlorite and vermiculite (Oinuma, Kobayashi and Sudo, 1961; Sudo, Oinuma and Kobayashi, 1961; Hayashi and Oinuma, 1964; Gjems, 1967 and Wiklander and Aleksandrović, 1969). As all these minerals were likely to be encountered in the present study a batch of clay suspensions was treated with 6 molar HCl for 30 minutes at 95°C, before cation saturation and the preparation of preferentially-oriented slides.

Preferentially-oriented silt (2 - 20  $\mu$ m) specimens were prepared for X-ray analysis in a similar manner to that used for clays. Randomly-oriented specimens of silts and sands ( $>0.02$  mm) were also prepared from air-dried samples using an end-loading specimen holder similar to that described by Niskanen (1964).

Mg-saturated specimens for differential thermal analysis (DTA) were prepared by flocculating and washing

aliquots of the clay fractions, isolated by sedimentation, with 0.5 molar  $\text{MgCl}_2$ . After removal of excess  $\text{MgCl}_2$  the samples were freeze-dried, lightly ground ( $< 53 \mu\text{m}$ ) and equilibrated over saturated  $\text{Mg}(\text{NO}_3)_2$  (relative humidity, 56%) for a minimum of four days.

$\text{HF}$  digestion (Raman and Jackson, 1965; Norrish, 1968 and Sarma and Krishna Murthi, 1969/1970) was used to dissolve aluminosilicates in an attempt to concentrate resistant minerals, present in small amounts in the clay fractions, sufficiently to permit their identification by X-ray diffraction. A range of samples of other size fractions were also examined.

X-ray diffraction analyses were made on Philips equipment comprising a PW 1310 generator and PW 1050/25 goniometer, using Mn filtered  $\text{FeK}\alpha$  radiation (50 kV, 20 mA) and a proportional counter coupled to an arithmetic chart recorder using pulse height analysis. The divergence, receiving, and scatter slits were set at  $1^\circ$ , 0.1 mm and  $1^\circ$ , respectively, for clays. Wider slits were used where appropriate for silt and sand samples. A goniometer speed of  $1^\circ$ , 20/minute, a chart speed of 1 cm/minute, and a time constant of 2 seconds were used. The rate meter was varied according to the intensity of reflections from particular samples. Clays were scanned from  $2 - 40^\circ$ , 2 $\theta$  and all other samples from  $2 - 90^\circ$ .

Differential thermal analyses were carried out using an Aminco Thermoanalyser with a stainless steel sample holder. In each instance 80 mg of sample was diluted

with an equal weight of calcined kaolinite, 160 mg of which was used as the reference material, the heating rate was  $12^{\circ}\text{C}/\text{minute}$  and a flow of oxygen-free nitrogen of 20 ml/minute at a pressure of  $1.013 \times 10^5 \text{P}$  was passed through the sample.

Semi-quantitative estimates of clay mineral distribution were based upon relative peak areas of diagnostic X-ray diffraction spacings. These estimates were checked by comparison with differential thermograms.

Material within the size range 0.125 - 0.177 mm was isolated from air-dried sands (0.02 - 2 mm) by dry-sieving. The isolated fractions were further separated into magnetic and non-magnetic fractions using a Frantz isodynamic magnetic separator, operated at a current of 1.2 amp, with side and forward slopes of  $5^{\circ}$  and  $30^{\circ}$ , respectively. Three passes were made at a flow rate of 0.3 ml/minute. The two fractions were weighed and the minerals present in each identified using a polarising microscope.

### (3) Presentation of Results

In the accompanying figures and tables total chemical analyses, and oxalate- and pyrophosphate-extractable Al and Fe are expressed on the basis of the ignited weight of the sample. Mechanical analyses and cation exchange data are expressed on an oven-dry basis. Fieldes and Perrott test and phosphate retention are empirical methods and are based on air-dry soil. Data for the poorly-drained Ikamatua fine sandy loam, I(w)1, are included in tables and figures devoted to the soils

forming the chronosequence to facilitate ready comparison with the freely-drained soil of similar age. Data for the two transects on the Ahaura silt loam Ah 1, are presented separately. Data from the A<sub>2</sub> horizon at I(o) 2 are included, where relevant, with the soils of the chronosequence. Data from the 'grab' samples taken subsequent to the above analyses are not included in these tables, but are discussed in the text where appropriate.

Dashes in the tables indicate that no such sample existed, or that no meaningful value could be entered, while "n.d" indicates that the value was not determined.

Stones were present in the C horizons of the Ho 1, I(y) 1 and I(o) 1 profiles below a depth of approximately 0.40 m. The disintegrating remains of strongly weathered stones occurred below 0.62 m in the C horizon of the Ok 1 profile, but there was no evidence for the previous existence of stones at any higher level in this profile, or above 0.76 m in the Ku 1 profile. Stones were absent above 0.76 m in the I(w) 1 and Ah 1 profiles. To avoid differences caused by variations in the texture of the parent materials totals for all profiles were therefore calculated to a depth of 0.38 m, the minimum depth at which stones occurred.

Totals were also calculated to a depth of 0.76 m. As well as presenting the actual values obtained to this greater depth, an attempt was made to reduce effects resulting from variations in the depth of fine alluvium between tesseras, and thus allow more meaningful

comparisons to be made between soils. It was assumed, that for horizons containing stones,  $<2$  mm material occupied the whole volume of such horizons. The density of isolated  $<2$  mm material was determined by packing into a 50 ml measuring cylinder under gentle vibration. This approach could not, however, be applied to the Ok 1, C horizon as it was not feasible to isolate the material derived from stones. All the material from this horizon was therefore crushed to pass a 2 mm sieve. Unless otherwise stated the use of the term "estimated" in any table or figure implies that the above assumptions were used.

For profiles where horizon boundaries did not coincide with 0.38 and 0.76 m, proportionate adjustments were made.

Complete results appear in the tables with the exception of the O horizon of the I(y) 1 profile, and to a lesser extent of the I(o) 1, A horizon. The omissions do not significantly affect the results. A matrix of simple correlation coefficients was constructed using data from the soils of the chronosequence (except I(w) 1) obtained both in this study and that of Tan (1971). This is presented as Table 2.

## CHAPTER THREE

### RESULTS AND DISCUSSION

#### I. INTRODUCTION

The analytical data presented in this section are grouped, for convenience, as follows:

1. Physical Parameters. (Depth of horizons, soil pH, volume-weights, % moisture (M%), loss-on-ignition, and mechanical analyses).
2. Chemical Analyses. (Total chemical analyses and cation exchange analyses including exchangeable cations).
3. Poorly-ordered Soil Colloids. (Oxalate- and pyrophosphate-extractable Al and Fe, phosphate retention, and Fieldes and Perrott test).
4. Mineralogical Analyses. (X-ray diffraction analyses, differential thermal analyses and optical mineralogy).

Data for the soils of the chronosequence (including the wetter variant of the Ikamatua silt loam) and for each of the two transects on the Ahaura silt loam, are listed in separate tables. For ease of comparison, data for Ah 1, a site that is included in the chronosequence and in both transects, are presented in all appropriate tables.

## II. PHYSICAL PARAMETERS

Data showing the depth of horizons, soil pH (in both distilled water and molar KCl), percent moisture, and loss-on-ignition are listed in Tables 3 (Chrono-sequence), 4 (Transect 1) and 5 (Transect 2). The latter two tables also list distances from the nearest living red beech or decaying stump. Horizon and tessera weights of size separates, and of organic and inorganic components are presented in Table 6, while mechanical analysis data appear in Tables 7 - 9.

### (1) Soil pH

Soil pH values throughout the chronosequence are all low to very low. Depth functions (Figure 4) show a tendency to increase slightly with depth. The I(y) 1, I(o) 1 and Ah 1 profiles all show similar values and trends. Values for these profiles are 0.3 - 0.6 units higher than at equivalent depth in the Ku 1, which, with the exception of the organic-rich B<sub>h</sub>G horizon yields values 0.1 - 0.3 units higher than the older Ok 1. The pH values of the gleyed upper horizons of I(w) 1 are lower, and those of the oxidised lower horizons, higher than the values given by the corresponding freely-drained soil, I(o) 1. The values given by the A horizons of the Ho 1 profile appear to be anomalously low for a recent soil. Trends observed along the two transects (Tables 4 and 5) (and the low value shown by the A<sub>2</sub> horizon of I(o) 2) do show, however, that considerable variations in

soil pH can occur over comparatively short distances, particularly in the upper horizons. pH values along the transects increased with distance from the nearest living red beech or decaying stump (Figures 5 and 6). The downward trends shown close to each tree in these figures probably demonstrate the localised influence of stem flow.

This influence of red beech on soil pH was confirmed using 44 additional 'grab' samples taken from the low glacial outwash terrace and younger surfaces. Half of these samples were from surface horizons taken adjacent to the stems of living trees, and all gave pH ( $H_2O$ ) values between 3.1 and 4.4. Values tended to decrease with increasing age of the soil and size of the tree. The remaining samples were surface horizons collected at least 7 m from the nearest tree, stump, fallen log, or accumulation of organic debris, and all yielded values  $> 4.5$ .

It is unlikely that the concentration of KCl-extractable aluminohydronium cations,  $Al(OH_2)_6^{3+}$ , could be high enough to explain these very low soil pH values associated with red beech trees. Concentrations of the order of  $2 \times 10^{-3}$  and 2 molar would be necessary to yield pH values of 4.0 and 3.0, respectively (Jackson, 1963a). Kaurichev, Nozdrunova and Yevseyeva (1969) have shown that the Al contents of soil solutions from gley and podzolic soils containing up to 2.7 me/100 g of exchangeable Al were  $< 2 \times 10^{-4}$  molar.



Very acid conditions arising from the oxidation of  $\text{FeS}_2$  or S could not occur at any of the sites except those on the present floodplain, where S or sulphides derived from coal mining operations, or the erosion of sulphide-bearing formations, may be deposited during flooding. The S content of rainwater in the area is unlikely to exceed 0.5 ppm, most of which would be present as sulphate (Mr A.H. Horn, Soil Science Department, Lincoln College, pers. comm.).

Chelation mechanisms are also unlikely to account for the low pH values. Huang and Keller (1970) and Hewitt (1973) have shown that dissolution of aluminosilicate minerals in chelating solutions causes a slight increase in pH.

The relationship between pH and distance from the nearest tree suggests that water-soluble organic compounds associated with the presence and growth of the trees, or with the decomposition of the organic debris that accumulates in their vicinity, are largely responsible. Kaurichev, Nozdrunova and Yevseyeva (1969) report that low molecular weight organic acids including oxalic, tartaric, citric, fumaric, malic, and glycolic accounted for 4 - 65% of the C of the water-soluble organic matter in soil solutions extracted from some gley and podzolic soils. They attributed the lower pH values of the A horizons of the forest soils they examined to the formation of carbonic acid and water-soluble compounds produced by organic matter decomposition.

Zinke (1962) has demonstrated the radial symmetry of soil properties around individual trees. Properties were shown to vary systematically with distance from the stem. Several workers have shown that for some tree species, including beech, the quantity of stemflow water is considerable, relative to the precipitation incident on the crown (Horton, 1919; Kittredge, 1948; Gilbert, 1953; and Voigt, 1960). Although stemflow enters the soil in a narrow band around the stem (Voigt, 1960) it is usually unevenly distributed around the stem (Gersper, 1970). Stemflow water has been shown to be acidic, and to contain larger amounts of C, N, Mg, P, S, Cl, K and Ca than canopy drip (Voigt, 1960; Mina, 1965; and Gersper and Holowaychuk, 1971) which in turn is more enriched than the incident rainfall (Balasubramaniam and Jayaraman, 1952; Will, 1955; Madgwick and Ovington, 1959; Voigt, 1960; and Grunert, 1964). Stemflow has also been shown to contain much greater quantities of fallout radioisotopes than the incident rainwater (Witkamp and Waller, 1963) and the depth of penetration of such isotopes has been shown to be greatest close to the stems of trees (Franklin, Gersper and Holowaychuk, 1967; and Gersper, 1970).

Anticipating that stemflow water, through the local concentration of large amounts of water, enriched in certain organic and inorganic substances from trees and from external sources, would materially influence soil formation, and could enhance the formation of podzols, Gersper and Holowaychuk (1970 a and b) examined a range

of soil properties at distances of 0, 0.5, 1.0 and 2.0 m from the stem of an American beech of 0.80 m diameter, breast height. These investigators observed similar pH trends to those found in the present study; the pH increasing from 4.5 at the stem to 6.0 at a distance of 2.0 m. As in the Ahaura transects the greatest variation occurred in the surface horizon. The rainfall affecting the site chosen by Gersper and Holowaychuk (1970 a and b) was less than half that at Reefton, and the Miami soil on which their study was located was developed from glacial till containing considerable limestone fragments. The authors did not investigate if variations continued beyond 2.0 m from the stem.

## (2) Soil Organic Matter

With the exception of the  $B_{hg}$  horizon of Ku 1, loss-on-ignition values decrease with profile depth. Considerable variations, that are related to distance from living trees or decaying stumps, occur over short distances in surface horizons (Tables 3 - 5).

Weights of organic matter (OM) (Table 6) have been calculated on the assumption that LOI = OM. Differential thermograms (discussed in Chapter 3; V, (3)) show, however, that at temperatures between 105 and 500°C some of the weight loss would be caused by loss of water from the dehydroxylation of clay minerals. To reduce such errors the use of lower ignition temperatures in the range 350 - 430°C have been suggested by Mitchell (1932), Ball (1964) and Davies (1974). Poorly-ordered hydroxy-alumina

and gibbsite, which lose some 35% of their weight around 300°C, would still be affected by these temperatures, but errors introduced from this source should not exceed 4% (maximum) of the values listed in Tables 3 - 5. Errors resulting from the dehydroxylation of phyllosilicates have not been estimated. The highly significant correlation coefficient (0.1% level) between loss-on-ignition and oxidisable carbon (oxid.C) values (Table 2) suggests, however, that the original assumption is reasonable. The mean relationship between oxid.C and LOI yields  $\text{oxid.C} = 39\%$  of LOI, or using a conversion factor from oxid.C to organic carbon (org.C) of 1.3 (Bremner and Jenkinson, 1960) gives  $\text{org.C} = 51\%$  of LOI. This approximates a conversion factor of 1.96 for org.C to OM, as compared with a commonly accepted figure of 1.74 (Hallsworth and Wilkinson, 1958).

Similar levels of organic matter (to a depth of 0.76 m) occur in Ho 1 and I(y) 1; organic matter then increasing with age of the soil to a maximum at Ah 1. This is followed by a decrease at an approximate rate of loss of  $2 \text{ kg ha}^{-1} \text{ year}^{-1}$  (Figure 7). The organic matter level at site Ah 1, deliberately located at maximum distance from the surrounding trees, is likely to be exceeded in other tesseras. Comparing sites I(o) 1 and I(w) 1 shows that restricted drainage results in a considerably increased level of organic matter accumulation.

Depth functions of organic matter accumulation are shown in Figure 8. The Hokitika and Ikamatua soils show

a decrease in organic matter levels with depth. After an initial decrease Ah 1 shows an increase in the lower horizons. Similar increases are shown by the two gley podzols. Examination of loss-on-ignition and oxidisable carbon values (Table 3, and Tan (1971), respectively) shows that the higher organic matter level of the Ah 1, B<sub>3</sub> results from the increased density of the horizon, and that of the Ku 1, B<sub>h</sub>G from a substantial increase in organic matter content that is sufficient to overcome a decrease in density, whereas that of the Ok 1, BG results from an increase in both density and organic matter content. The rather low organic matter level of the Ku 1, A horizon is related to the low density of that horizon. The proportion of the organic matter that is present in the top half of each tessera decreases with time from 90% in Ho 1 to 50% in Ku 1.

Much of the organic matter present in these soils is probably complexed with cations and with hydrous oxides of Al and Fe, and is likely to have played a significant role in the loss of Al and Fe from upper horizons during soil genesis. This conclusion is supported by the highly significant correlation coefficients (0.1% level) between loss-on-ignition and pyrophosphate-extractable Al and Fe (Table 2), and by the low values obtained throughout the sequence for the CEC of the organic fraction (Chapter 3; III, (1), (d)).

Zinke (1962) has pointed out that variations in the distribution of bark and leaf litter may cause differences

in organic carbon contents of soils with respect to distance from tree stems. Gersper and Holowaychuk (1970b) report a progressive decrease in organic carbon content of A horizons with distance from an American beech. In contrast to the present study they observed a decrease in the quantity of litter on approaching living trees. They thus attributed the observed trend in organic carbon values to carbon additions from stemflow water, and to the more anaerobic conditions existing next to the stem.

### (3) Soil Separates

Volume-weights of soil separates, and of organic and inorganic components are presented in Table 6. Similar tessera weights of soil ( $\text{kg ha}^{-1}$ ) to a depth of 0.38 m occur at the Ho 1 and I(y) 1 sites. The greater weight of material between 0.38 and 0.76 m in the former tessera results from a large increase in the quantity of stones, a depositional feature. Tessera weights of soil to both depths then decrease with age until Ah 1, and then increase substantially. The I(w) 1 tessera contains only 56% and 68% of the weight of soil present to depths of 0.38 and 0.76 m, respectively, in the comparable freely-drained I(o) 1.

Walker (1965) notes that as accumulation of organic matter causes soil volumes to increase (Dickson and Crocker, 1954; and Walker and Adams, 1958 and 1959) examination of percentage compositions could lead to the misinterpretation of soil processes. He makes a plea for sampling soils by volume when considering pedogenic processes.

In the present study the incorporation of organic matter, and the presence of large quantities of hydrous oxides of Al and Fe (Chapter 3; IV, (3)) leads to the development of loose-textured, fine granular and crumb structures. This causes a decrease in density and an upward expansion of the original soil volume. The maximum expression of this effect is seen in the I(w) 1 and Ah 1 tesseras, where the quantities of inorganic material present in each tessera show minimum values for the sequence (Figure 9).

Beyond Ah 1, loss of organic matter and of hydrous oxides has led to destruction of soil structure, and resulted in compaction and the development of dense, impermeable horizons. A consequence of this collapse in soil volume is a considerable increase in the quantity of inorganic material in a given volume; the Ok 1 tessera actually containing more than 1.5 times that present in Ah 1 (Figure 9).

If a soil is expanding upwards sampling to constant depth at each successive stage results in the exclusion of increasing quantities of material that would have been present in the original volume. Losses from the system, expressed either in absolute units, or as a percentage of the amount originally present, will tend to be overestimated. This situation exists between Ho 1 and Ah 1. Conversely, if compaction occurs sampling to constant depth would lead to inclusion in later stages of material that was below the depth of sampling at an earlier stage. Losses

from such systems may be underestimated, and elements lost at comparatively slow rates may actually appear to accumulate. To overcome these errors and determine absolute gains and losses resulting from soil development, it would be necessary to sample at each stage to the depth that the original volume then occupied, or, alternatively, to be able to deduce the original weight and composition of the material that now occupies each sampled volume. These approaches would distinguish between actual gains, and apparent gains where an element, such as Si in the present study, that is lost from the system at a slower rate than many other components, by forming an increasing percentage of an increasing total weight of inorganic material in the constant volume, appears to be accumulating. Attempts are made (Chapter 3; III, (2)) to determine actual gains and losses of total elements with time. The factors so derived could, if required, be applied to the other quantitative analyses presented in this thesis.

#### (4) Mechanical Analysis

Mechanical analysis data for the chronosequence soils are recorded in Table 7 and summarised in Figure 10. This diagram also demonstrates the effects of the differing quantities of soil in the various tesseras. Comparison of the approximate values obtained from deferrated samples used for mineralogical analyses with those obtained by the International pipette method (data supplied by Mr E.J. B. Cutler) shows that a satisfactory separation was



achieved with the former samples. The low clay percentages obtained by the pipette method for Ah 1, AB and B<sub>21</sub> horizons suggest difficulties in obtaining complete dispersion.

There is an increase in clay contents (%) with soil development to Ku 1, followed by a decline to Ok 1 (Figure 11). Clay contents decrease with depth in all soils except Ku 1, where the maximum clay percentage occurs in the B<sub>h</sub>G horizon, and Ok 1 where clay content increases with depth to reach a maximum in the B<sub>3</sub>G (Figure 12). Only 7% of the total clay occurs in the fine clay fraction ( $< 0.2 \mu\text{m}$ ) in the A horizon of Ok 1, compared with 32% and 43% in the corresponding horizon of Ku 1 and Ah 1, respectively.

If allowance is made for variations in density with depth, and depth functions of clay examined on a volume-weight basis (Figure 13) several changes become apparent. The most obvious of these is that the Ah 1 profile now resembles that of the two older gley podzols and differs from those of the remaining yellow-brown earths. Its maximum clay content now occurs in the B<sub>3</sub> horizon and not in the A. As it is generally considered that increasing clay content is associated with increasing soil development, the decline in clay content between Ku 1 and Ok 1 and the relatively low clay levels in the surface horizons of these soils and of Ah 1, require explanation. While eluviation of clay is a possible mechanism to explain the increasing clay content with

depth in the freely-drained Ah 1, clay destruction from exposure to organic chelates and low pH conditions over a considerable period is a more likely cause of the low clay levels, particularly within the fine clay fraction, now found in the surface horizons of the poorly-drained gley podzols.

Silt contents increase throughout the sequence, while with the exception of the I(o) 1 profile and the lower 0.38 m of Ok 1 there is a decline in the coarse sand fraction with time (Figure 11). Both of the anomalous values can be attributed to coarser textured parent material. The Ok 1 C horizon contains the disintegrating remains of strongly weathered stones, whereas stones are absent from the comparable depth of Ku 1. The increases in the levels of silt and clay are at the expense of the coarse sand fraction. The relative positions of the 0.38 and 0.76 m curves in Figure 14 shows the deeper penetration of soil development with time.

Although a low sand and high clay content occur in the O horizon at Ah 6, no consistent trends occur with increasing distance from either living beech tree or the decaying beech stump (Tables 8 and 9).

### III. CHEMICAL ANALYSES

The data presented in this section deal with cation exchange properties, including base saturation and the levels of the more important exchangeable cations, total elemental analyses, and oxalate- and pyrophosphate-

extractable Al, and Fe, phosphate retention and the Fieldes and Perrott test.

### (1) Cation Exchange Properties

Cation exchange data are set out initially in Tables 10-12. Data for the chronosequence, converted to a volume-weight basis appear in Table 13. The main trends apparent from these tables are illustrated in Figures 15 - 29.

(a) Cation Exchange Capacity. Cation exchange capacities of the chronosequence soils to a depth of 0.76 m (measured at pH 7.0) show an initial decline from  $6.0 \times 10^8 \text{ me ha}^{-1}$  (Ho 1, 0.76 m) to  $5.4 \times 10^8 \text{ me ha}^{-1}$  at I(y) 1, rise to a maximum value of  $1.0 \times 10^9 \text{ me ha}^{-1}$  at Ku 1, before again declining. The changes beyond Ah 1 are largely confined to the lower half of each tessera, while the initial decrease in CEC is continued as far as Ah 1 in the upper 0.38 m of the tessera. Values obtained from I(w) 1 are considerably higher than those of I(o) 1, and exceed those of Ku 1 (Figure 15). The higher organic matter content of I(w) 1 (Figure 7) and the presence of expanding 2 : 1 layer silicates in the upper part of the profile (Chapter 3; V, (3)) are responsible for the higher CEC values obtained at this poorly-drained site. Although highly significant (0.1% level) correlations occur between CEC and both loss-on-ignition and % oxidisable carbon (Table 2) the variation of CEC with time (Figure 15) does not closely resemble the accumulation of organic matter (Figure 7). The dependence of CEC on the

levels of organic matter, clay and silt will be discussed later in this section.

CEC depth functions (Figure 16) decrease with distance from the surface for Ho 1 and the several Ikamatua soils. Ah 1 and Ok 1 show increases in the subsoil after initial decreases, whereas Ku 1 shows an increase with depth to reach a maximum in the  $B_hG$  horizon. These functions closely resemble those for organic matter (Figure 8). Horizons that show anomalously high CEC values as compared with their organic matter levels (e.g. the gleyed horizons of I(w) 1, and the G and  $B_hG$  horizons of Ku 1 contain expanding 2 : 1 layer silicates (Chapter 3; V, (3)).

CEC values for both the upper and  $B_{21}$  horizons sampled along Transect 2 increase towards both living trees. Values decrease with depth, and are particularly high in the upper horizons at Ah 6, 7 and 9. Only the upper horizons show a similar trend towards the decaying stump along Transect 1. The anomalously low value shown by the  $A_2$  horizons at Ah 5 reflect their comparatively low organic matter contents.

In their study Gersper and Holowaychuk (1970 a and b) found a progressive increase in CEC towards a beech tree in the A horizon, and a progressive decrease in the  $B_2$ . They attributed the changes in the upper solum to increases in both organic matter and clay, and showed that the decrease observed in the  $B_2$  correlated with a decline in clay content.

(b) Exchangeable Na, Mg, Al, K, Ca and Fe.

Variations in the weights of exchangeable Na, Mg, Al, K, Ca and Fe per tessera throughout the sequence are illustrated in Figure 17. The levels of these exchangeable cations, excepting Fe, are highly correlated (1% level) with CEC (Table 2). The tessera weights of the four basic cations (Na, Mg, K and Ca) decline with increasing soil development to reach minimum values at Ah 1. This decline results from decreases both in CEC and in the bulk density of the soil, and from increased competition for lattice sites by Al species and  $H_3O^+$ . Subsequently, in Ku 1, an increase in bulk density, and higher clay contents in the lower solum that are dominated by expanding clays, rather than by the 2 : 1 - 2 : 2 Al-intergrades of the younger soils (Chapter 3; V, (3)) cause increases both in CEC and in the quantities of the basic cations. A fall in the amounts of organic matter and of clay to Ok 1 is responsible for the observed drop in CEC and in the quantities of the basic cations other than Na.

Exchangeable Al (Al displaced by Molar KCl) has been assumed to be present as the hydrated, trivalent monomer  $Al(-OH_2)_6^{3+}$ . Jackson (1963a) indicates that the lower concentrations of the monovalent and divalent monomers,  $[Al(OH)_2(-OH_2)_4]^+$  and  $[Al(OH)(-OH_2)_5]^{2+}$  respectively, and their greater ease of displacement from lattice sites, should limit their presence in acid soils ( $pH < 5.0$ ) to insignificant amounts. Exchangeable Fe

has been assumed to be present as the equivalent trivalent ion,  $\text{Fe}(-\text{OH}_2)_6^{3+}$ .

Exchangeable Al shows a highly significant negative correlation (1% level) with soil pH (Table 2). The decrease in exchangeable Al that occurs between I(y) 1 and Ah 1 (Figure 17) is a function of an even larger decrease in CEC (Figure 15). Throughout this period base saturation decreases (Figure 18) and exchangeable Al forms an increasing proportion of CEC. The increase in exchangeable Al to Ku 1, and the subsequent fall to Ok 1 are related to the substantial subsoil changes in CEC.

Exchangeable Fe, unlike exchangeable Al, does not correlate with soil pH. The relatively high quantities of exchangeable Fe (to 0.76 m) from I(o) 1 to Ku 1 suggests that Fe becomes mobile rather earlier than does Al.

With the exception of Fe in the lower half of the tessera, weights of the exchangeable cations are higher in I(w) 1 than in I(o) 1. This results from the higher CEC of the poorly-drained soil.

The order of abundance of the four basic cations ( $\text{me ha}^{-1}$ ) in Ho 1, the youngest soils of the sequence, is  $\text{Ca} > \text{Mg} > \text{K} > \text{Na}$ . This has altered to  $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$  by Ku 1 and to  $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$  in Ok 1. The increasing importance of Na can be explained by the higher atmospheric returns of this element, and by the abundance of the Na-rich feldspar, albite, in the parent material. The relative stability of this mineral has resulted in its survival in the coarser sand fractions of all horizons of both gley podzols.

Analyses of rainwater samples collected near the confluence of the Taipo and Taramakau Rivers, (29 km from the sea) show present-day levels in solution of 0.6, 0.08, 0.07 and 0.04 ppm for Na, Mg, K and Ca, respectively (Mr A.H. Horn, Soil Science Department, Lincoln College, pers. comm.). If the levels at Reefton, 14 km further inland, are assumed to be of a similar order atmospheric returns of 11.4, 1.52, 1.33 and 0.76 kg ha<sup>-1</sup> year<sup>-1</sup> of Na, Mg, K and Ca would occur. If returns of this order had occurred throughout the entire period of soil development they would represent additions of 5 (Ca) to 275 (Na) times the losses of exchangeable bases that occurred between I(y) 1 and Ah 1, and 44 (Ca) to  $2.5 \times 10^3$  (Na) times the actual gains from Ah 1 to Ku 1.

Depth functions for the various exchangeable cations are presented in Figures 19-24. Exchangeable Mg, K and Ca tend to decrease with depth, and, in the yellow-brown earths, with the duration and intensity of leaching. Increased subsoil levels of Mg and Ca occur in Ku 1. Exchangeable Al also decreases with depth in the freely-drained yellow-brown earths, but increases to maximum levels 0.2 - 0.5 m from the surface in the three poorly-drained soils. Exchangeable Fe, and the mobile exchangeable Na exhibit no obvious trends with depth. Levels of all six exchangeable cations correlate significantly with % oxidisable carbon and with loss-on-ignition (Table 2), but only exchangeable Na and Al correlate with % clay. Thus the variations in organic matter levels with depth are largely

responsible for the observed exchangeable cation depth functions.

Simple linear regressions between exchangeable and total Mg, Al, K, Ca and Fe yield non-significant correlations. Highly significant correlation coefficients (0.1% level) were obtained for linear regressions involving any pairings of exchangeable Na, Mg, K and Ca, while exchangeable Al correlated only with exchangeable Na (5% level). Exchangeable Fe showed no correlations with the other exchangeable cations (Table 2).

The effects of pedogenesis on the proportions of total Mg, Ca, K, Al and Fe that are present as exchangeable cations are shown in Figures 25 - 27. For each ion the proportion is always greater in the upper half of the tessera. Exchangeable Mg, K and Ca exhibit similar trends, with an initial drop from Ho 1 to I(o) 1 being followed by rises that surpass the original values. Some 4% of total K, 7% of Mg and 26% of Ca in the upper 0.38 m of the Ok 1 tessera are present as exchangeable forms. Exchangeable Al and Fe reach maximum values of 1.7 and 0.53% of the respective total elements in the upper half of the Ku 1 tessera. The proportions of total elements present as exchangeable forms in I(w) 1 exceed the values found in I(o) 1 by factors ranging from 2.7 (K) to 10 (Ca).

Levels of exchangeable Na (excepting Ah 7, 0 horizon), Mg, K and Ca (again excepting Ah 7, 0 horizon) increase towards both living trees along Transect 2 (Table 12), but show no consistent trends along Transect 1 (Table 11).



Exchangeable Al levels do not vary regularly along either transect. The observed fluctuations probably reflect variations in the returns from canopy drip, stemflow and decay of organic matter.

Gersper and Holowaychuk(1970 b and 1971) have shown that stemflow water caused exchangeable K to decrease, and exchangeable Mg and Ca to increase, with distance from trees. They surmised that the higher ratio of stemflow K to soil exchangeable K, as compared with the comparable Ca ratio accounted for their rather strange result.

(c) Base Saturation. The sum of exchangeable Na, Mg, K and Ca has been assumed to represent total exchangeable bases (TEB). Trends in TEB during soil development (Figure 15) resemble those shown by CEC, but the initial decline is greater. Variations of TEB with depth (Figure 28) show, with the exception of Ku 1, a tendency to decrease with depth. The Hokitika, Ikamatua and Ahaura soils all show the very low subsoil values characteristic of lowland yellow-brown earths (Metson and Blakemore, 1968). Comparison of the TEB values of the surface horizons of these soils indicates that decreases in TEB are associated with the duration and intensity of leaching. TEB values for the gley podzols exceed those of the younger Ah 1. The presence of expanding clays, relatively high atmospheric returns in relation to the levels present, and the restricted drainage of the gley podzols would account for these increases.

The decrease in base saturation from 50% (to 0.38 m) and 46% (to 0.76 m) at Ho 1, to 10% at Ah 1 (Figure 18) arises from a larger fall in TEB than in CEC. The subsequent increase to Ku 1 reflects a proportionately greater increase in TEB, while the further increase to Ok 1 arises from a drop in CEC of the top 0.38 m, and a proportionately greater drop in CEC in the lower half of the tessera.

The general trend shown in base saturation depth functions (Figure 29) is for an initial decrease with depth from the surface to be followed by an increase in some lower horizon. The strongly leached Ikamatua and Ahaura soils show values of 18 - 23% in the surface horizons, while the three poorly-drained soils yield values of 28 - 42%.

Base saturation values are highest in the surface horizons at all sites sampled along both Ahaura transects. Thus at each site, the horizon of lowest pH has the highest base saturation. Similar results are reported by Gersper and Holowaychuk (1970b), who also observed that there was a progressive inward decrease in base saturation towards the tree stem. No such trend was observed for the Ahaura transects, but only three of the sampling sites were located  $\leq 2.0$  m from the stem of a living tree, or decaying remains.

Several workers have examined the relationship between soil pH and base saturation (Puri, 1930; Pierre and Scarseth, 1931; Conrey and Green, 1932; and Mehlich, 1941). Some found high correlations between these two

soil properties while others did not. Jenny (1941) postulated that control of the soil-forming factors should improve correlations among soil properties, and in a later work Blosser and Jenny (1971) demonstrated very low correlations between the two properties for 80 soils collected at random over a wide area, but found very high correlations when soils from the same area were selected according to soil-forming factors.

Soil pH was not significantly correlated with base saturation for either the chronosequence ( $r = -0.130$ ) or transect ( $r = -0.148$ ) soils. Some improvement was obtained by subdividing the chronosequence samples into upper (above the B) and lower (B and below) horizons, but only the former grouping yielded a significant (5% level,  $r = -0.685$ ) correlation. Subdivision of the chronosequence samples into yellow-brown earth and gley podzol groupings also yielded higher correlation coefficients, but only the one for the latter was significant (1% level,  $r = -0.791$ ). The low correlation coefficient ( $r = 0.155$ ) shown by the upper horizons of the Ahaura transects, as compared with the significant correlation (5% level,  $r = 0.684$ ) for the B<sub>21</sub> horizons suggests that variations in soil properties that are a function of distance from the nearest red beech tree or stump may be more strongly expressed in the upper horizons.

(d) Cation Exchange Capacity as a Function of Organic Matter, Clay and Silt. It is generally recognised that the clay and organic matter fractions are responsible

for most of the CEC of soils. Several investigators have shown, however, that the silt and sand fractions of some soils can make a significant contribution (Joffe and Kunin, 1943; Coleman and Jackson, 1945; Karim and Islam, 1956; McAleese and Mitchell, 1958; LeRoux, Cady and Coleman, 1963; Tedrow, 1966; and Alexiades et al. 1973).

To fully explain cation exchange phenomena it is necessary to quantitatively assess the relative importance of the organic and inorganic soil components. Attempts to obtain this information directly involve the removal of one of the components (Baver, 1930; McGeorge, 1930; Williams, 1932; Bartlett, Ruble and Thomas, 1937; Kelley and Thomas, 1942; Davies and Davies, 1965; and Clark and Nichol, 1968) or the use of an exchange reaction specific to a single component (Addiscott, 1970).

Objections to the use of chemical extractions are that the reactions involved may be incomplete or cause degradation of the other component (Kelly, Dore and Brown, 1931; Olson and Bray, 1938; Farmer and Mitchell, 1963; and Douglas and Fiessinger, 1971). Evidence exists that the CEC values obtained may depend on the method of extraction (Mitchell, 1932). Studies by Roth et al. (1968), and Roth, Jackson and Syers (1969) have shown that the CEC's of vermiculite, nontronite, biotite and muscovite were not affected by peroxidation and prompted Syers, Campbell and Walker (1970) to suggest that the effect of  $H_2O_2$  on the CEC of clay minerals had been overestimated. The latter authors also found a high

correlation between CEC of peroxidised samples and clay content which they claimed indicated the complete removal of organic matter, or the negligible CEC of residues. Comparison of the areas of the relevant peaks on DTA thermograms both before and after 14 days treatment with hot 30%  $H_2O_2$  showed, however, that much of the original organic matter survived in some samples from the present study.

Other investigations have shown that the CEC of organic and inorganic soil fractions is not necessarily additive. The blocking of exchange sites through the formation of clay-humus complexes would yield lower whole soil CEC values than the sum of the CEC's of the two components (Meyers, 1937; and Syers, Campbell and Walker, 1970), whereas the higher whole soil values reported by Broadbent (1955) suggest degradation of one or both components during isolation.

Since the problems outlined above can only be avoided by determining the contributions of the clay and organic fractions to soil CEC on intact samples, the use of multiple regression analysis has been adopted by many investigators (Baver, 1930; Williams, 1932; Hallsworth and Wilkinson, 1958; Mohamed and Gohar, 1960; Helling, Chesters and Corey, 1964; Wilding and Rutledge, 1966; Yuan, Gammon and Leighty, 1967; Stevens, 1968b; McLean and Owen, 1969; Adams, 1970; Syers, Campbell and Walker, 1970; and Wright and Foss, 1972). Wilding and Rutledge (1966) have criticised the use, in regression analyses,

of soils that differ widely in physical, chemical and drainage characteristics. Since, by definition, all soil forming factors other than time are held constant or ineffectively varying in a chronosequence, Syers, Campbell and Walker (1970) have indicated that their examination offers a unique opportunity to study the relative contributions of organic carbon and clay to CEC. The chronosequence examined in the present study which is of greater age, and which has been more intensely leached and weathered than that investigated by Syers and his co-workers, shows, however, marked changes in both clay mineralogy and soil drainage between the younger and older members. The effect of these variations on the use of regression analyses to examine CEC as a function of organic matter and clay was examined by considering the soils of the chronosequence as a whole, and in appropriate sub-groupings. The soils of the Ahaura transects were considered separately as differences between them would be a function of the biotic factor, rather than of time.

Relevant data for the chronosequence (excluding I(w) 1), and transect samples are summarised in Tables 14 and 15, respectively. Simple regression analyses involving % oxidisable carbon (chronosequence) and loss-on-ignition (Transects) with CEC are presented in Tables 16 and 17. Highly significant correlations (0.1% level) occur between oxidisable carbon and CEC for all groupings except the gley podzols which contain higher contents of expanding 2 : 1 layer silicates (vermiculite and

montmorillonite) than the younger, freely-draining soils. Approximately 60% of the variability in CEC of the chronosequence soils (considered as a whole) could be attributed to differences in oxidisable carbon levels. As more than 90% of the variation in CEC of the transect soils could be explained from variations in loss-on-ignition (OM) it appears that fairly accurate estimates of the CEC, at least of the upper part of the profile, at different locations on the freely-drained parts of the low glacial outwash terrace, can be based on this property alone.

Highly significant correlations were also obtained between % clay and CEC for the three all soils groupings, and for the yellow-brown earths. Subdivision of the latter group resulted in lower correlation coefficients, significant only at the 5% level. The relationship was not significant for the gley podzol grouping or for the Ahaura transects. Correlation coefficients between % clay and CEC were always lower than those involving oxidisable carbon or loss-on-ignition and CEC, but use of % clay in the simple regression equation accounted for a higher proportion of the variability in the CEC of all seven chronosequence groupings (Table 18). Simple regression analysis between % oxidisable carbon or loss-on-ignition, and % clay yielded non-significant correlations with the exception of the all soils, yellow-brown earth and upper horizons yellow-brown earth groupings.

Multiple regression and correlation measure the

relationship between two or more independent variables (in this study % oxidisable carbon, or loss-on-ignition, % clay, and % silt) and a dependent variable (CEC). The multiple regression equation is of the form:

$$Y = \bar{y} + b_1(X_1 - \bar{x}_1) + b_2(X_2 - \bar{x}_2) + b_3(X_3 - \bar{x}_3),$$

where Y = the estimated CEC in me/100 g soil, and

$X_1$ ,  $X_2$  and  $X_3$  are the percentages of oxidisable carbon, (or loss-on-ignition), clay, and silt, respectively;

$\bar{y}$ ,  $\bar{x}_1$ ,  $\bar{x}_2$  and  $\bar{x}_3$  are the means of the above properties;

and  $b_1$ ,  $b_2$  and  $b_3$  are partial regression coefficients for the three variables  $X_1$ ,  $X_2$  and  $X_3$ , respectively. The equation may be written in the form:

$$Y = a + b_1X_1 + b_2X_2 + b_3X_3, \text{ where the regression constant,}$$

a, indicates the value that the CEC would have if all the independent variables equalled zero. The partial

regression coefficients,  $b_1$ ,  $b_2$  and  $b_3$ , represent CEC in terms of me g<sup>-1</sup> for oxidisable carbon, (or organic matter if loss-on-ignition used), clay and silt. The equation

assumes a linear response of CEC to each of the independent variables, and that there are no interactions between

them. These assumptions are not completely valid since

clay-organic matter complexes exist in soils (Greenland, 1971, is a recent review). Multiple regression

equations for the chronosequence samples are presented

in Tables 19 and 20, and for the transect samples in

Table 21.

Application of an F-test showed that the use of both % oxidisable carbon and % clay to predict CEC



(Table 19) gave no significant improvement over the use of % oxidisable carbon alone (Table 16) for both the upper and lower horizons of the yellow-brown earths, but was a significant improvement (5% level) for the upper horizons of the all soils grouping, and a highly significant improvement (1% level) for the remaining groups. The additional inclusion of % silt in the regression equation (Table 20) afforded a further significant improvement in the ability to predict the CEC in only two groupings, the yellow-brown earths and the upper horizons of the all soils group. A t-test was used to test the significance of the partial regression coefficients. Significant (5% level) values were obtained for the  $b_1$  coefficient for the upper horizons of both the all soils and yellow-brown earth groupings, and highly significant (1% or 0.1% levels) values for the remaining  $b_1$  coefficients. Non-significant values were obtained for more than half the  $b_2$  and for all but one of the  $b_3$  coefficients. The results of these analyses indicate that % silt should not be included in the regression equation, and that Table 19 should be preferred to Table 20. F-tests also showed that the use of multiple regression (Table 21) was not a significant improvement over the use of loss-on-ignition values alone (Table 17) in predicting the CEC of the transect soils.

The multiple coefficient of determination ( $R^2$ ) values show that all the regression equations listed in Tables 19 and 21 are highly significant (1% level), and that 87% and 94% of the variation in CEC of the

chronosequence and transect soils, respectively, may be predicted from their organic matter and clay contents.

The average relative contributions of oxidisable carbon and clay to total soil CEC are expressed by the partial regression coefficients. Thus it follows (Table 19) that each gram of oxidisable carbon contributes  $1.97 \pm 0.23$  me and each gram of clay  $0.42 \pm 0.10$  me to the CEC of the chronosequence soils. If it is assumed that oxidisable carbon forms 77% of organic carbon (Bremner and Jenkinson, 1960), and that organic carbon constitutes 58% of organic matter (Hallsworth and Wilkinson, 1958), the mean CEC of organic matter for the chronosequence soils is  $88 \pm 10$  me/100 g, a value lower than the range 100 - 400 me/100 g usually reported for soil organic matter. The low value will, in part, be caused by non-humified components, but it is likely that some of the negative charge on the organic matter is blocked or neutralised by complex formation involving hydroxy forms of Al and Fe (Walker, 1956). Clark (1964) has shown that removal of such fixed Al and Fe from exchange sites is a slow process, and that prolonged leaching with molar potassium acetate would be necessary to determine the total exchange capacity of soils containing fixed forms of these elements.

The CEC of the organic matter of the yellow-brown earths ( $110 \pm 15$  me/100 g) is higher than that of the older gley podzols ( $81 \pm 20$  me/100 g). Similarly the CEC of the organic matter from the lower horizons ( $119 \pm 28$  me/100 g) exceeds that of the upper horizons ( $71 \pm 24$  me/100 g) for

the all soils group. F-tests followed by t-tests show that the differences between the respective means are highly significant (0.1% level). Differences between the means for the CEC of organic matter from the upper and lower horizons of the yellow-brown earths ( $94 \pm 21$  and  $107 \pm 24$  me/100 g, respectively) were not significant. The lower values shown by the upper horizons and by the older soils may indicate increased complexing of organic matter with Al and Fe, and/or changes in the chemical composition of the organic matter. Tan (1971) has reported progressive increases in C/N and C/organic P ratios with increasing soil development throughout the Reefton chronosequence. The partial regression coefficients for clay are considerably lower than those for oxidisable carbon (Tables 19 and 21). A mean of  $42 \pm 10$  me/100 g is obtained for the CEC of the clay fraction of the chronosequence soils. If the yellow-brown earths and gley podzols are considered separately values of  $16 \pm 14$  and  $63 \pm 16$  me/100 g, respectively, are obtained. The higher levels of vermiculite and montmorillonite in the clay fractions of the gley podzols (Chapter 3; V, (3)) account for these differences. The regression equation for the transect soils (Table 21) indicates mean contributions to the CEC of  $127 \pm 6$  and  $8 \pm 39$  me/100 g from the organic and clay fractions, respectively. Standard errors (listed in Tables 19 and 21) indicate that for both the chronosequence and transect soils, the CEC of the organic matter fraction was less variable than that of the clay.

The relative contributions of the clay and organic fractions to the CEC of the chronosequence and transect soils were obtained using the partial regression coefficients and the mean oxidisable carbon (or loss-on-ignition) and clay percentages. The values obtained relative to the 'explained' portion of the CEC are also presented in Tables 19 and 21. The organic fraction is shown to be the major source of the CEC of the transect soils. The data for the chronosequence soils show that the organic fraction makes four times the contribution of the clay fraction to the CEC of the yellow-brown earths, but that in the gley podzols the contribution of the clay fraction has become twice that of the organic. Averaged over the sequence as a whole the two fractions make similar contributions.

Positive values of the regression constant,  $a$ , (Tables 19 and 21) represent the portion of the CEC not attributed to organic matter or clay. Some of this 'unexplained' CEC may be due to the coarser fractions, but inclusion of silt contents in the regression equations (Table 20) led to larger, not smaller values of the constant for over half the groupings listed, and yielded non-significant partial regression coefficients for % silt in all but one of the groupings. Reduction of the CEC of the clay or organic fractions through complex formation, or charge blocking, should reduce the value of the regression constant, the value of which will also be affected by any non-linearity near the origin.

The value of multiple regression equations in predicting CEC is further demonstrated in Figures 30 and 31, which illustrate the relationship between predicted and actual CEC for the transect and chronosequence soils, respectively. Four transect samples (Ah 4, A<sub>2</sub>; Ah 5, A<sub>21</sub> and A<sub>22</sub>; and Ah 6, A<sub>2</sub>) yield CEC values substantially higher than those predicted from their organic matter and clay contents. The horizons involved all contain relatively high clay contents dominated by montmorillonite. The CEC/g of clay would thus be greater than average for these samples. Since a wider range of soils is involved, the scatter diagrams for the chronosequence soils shows greater variations than that for the transects. With the exception of those Ku 1 horizons containing high expanding phyllosilicate contents, the Ahaura and older soils show lower actual CEC values than those predicted by the regression equation, while the younger soils, in general, exhibit the reverse effect. The major factor controlling this distribution pattern would seem to be a progressive decrease in the CEC of organic matter with increasing soil development. Although the number of samples involved per profile (5 - 6) is too low for too much reliance to be placed on the results, multiple correlation analyses show a progressive drop in the CEC of organic matter from 162 me/100 g in I(y) 1 to 61 me/100 g in Ok 1. McLean and Owen (1969) have also reported that the fixation of Al in non-exchangeable forms by soil organic matter is related to the extent of weathering.

(e) Effect of pH on Cation Exchange Properties.

Numerous investigators (including Bradfield, 1924; Hissink, 1924; Davis, 1945; Hanna and Reed, 1948; Coleman, Weed and McCracken, 1959; Pratt, 1961; Pratt and Blair, 1962; Helling, Chesters and Corey, 1964; Middleton, 1965; LeRoux and de Villiers, 1966; and de Villiers and Jackson, 1967b) have reported increases in soil CEC with increasing pH within the pH range 3 - 8. Observation that CEC of soils appeared to be constant at pH values  $< 5$  led Schofield (1939) to distinguish between "permanent" negative charge arising from lattice substitution and variable or "pH-dependent" negative charge which he attributed to  $\text{Si}-\text{OH}$  groups.

Pratt and Blair (1962) and Helling, Chesters and Corey (1964) showed that pH-dependent CEC was related to both organic matter and clay. Investigations by Martin and Reeve (1960), Turner and Nicol (1962) and Snitzer and Gupta (1964) noted that Al and Fe complexes with organic matter exhibited weak acid properties and could contribute to pH-dependent CEC. Clark (1964) suggested that the pH-dependence of the positive charge of hydroxyalumina species held by weakly acidic (negative) organic functional groups could be responsible for the variable CEC associated with Al-organic complexes. Bhumbra and McLean (1965) observed that organic matter correlated with increases in CEC between pH 7.0 - 8.2, and that extraction of Al with KCl decreased pH-dependent CEC. They concluded that pH-dependent CEC was related to hydroxyalumina as well as

to organic matter. In a subsequent study McLean, Reicosky and Lakshmanan (1965) showed that the pH-dependent CEC of the surface horizons of seven Ohio soils was primarily associated with organic matter. The high correlation they found between organic matter and Al extracted by ammonium acetate at pH 4.8 led them to conclude that the rise in CEC at higher pH was caused by the freeing of exchange sites on organic matter as complexed hydroxyalumina species were displaced and precipitated as  $\text{Al}(\text{OH})_3$ . Although conceding that these conclusions could be correct Sawhney, Frink and Hill (1970) indicated that direct evidence to support the hypothesis was needed, since deprotonation of hydroxyalumina species, or of organic functional groups, would yield the same pH-dependent CEC. In a comprehensive review, Coleman and Thomas (1967) indicated that pH-dependent CEC had two components, the weakly dissociated functional groups of soil organic matter and the hydroxyalumina and Fe coatings and interlayers associated with clay minerals. Sawhney, Frink and Hill (1970) proposed a method for determining the relative contributions of each of these components. They considered that any increases in CEC developed by the unblocking of exchange sites as hydroxyalumina and Fe coatings and interlayers were precipitated, as hydroxides would be permanent, whereas increases in CEC associated with deprotonation of organic functional groups would be reversible. In a later study Sawhney and Norrish (1971) demonstrated that kaolinite, halloysite, imogolite and allophane could

contribute to the reversible component of pH-dependent CEC, whereas the pH-dependent charge on crystalline Al- and Fe- hydrous oxides was small. De Villiers and Jackson (1967a and b) had previously demonstrated, however, that the pH-dependent CEC of both synthetic and organic-free (30%  $H_2O_2$ ) naturally occurring aluminous chlorites was reversible. Their use of synthetic materials in the latter work precluded the possibility of the effect being influenced by incomplete oxidation of soil organic matter.

Several other workers have reported that volcanic ash soils containing allophane possessed pH-dependent charge (Wada and Ataka, 1958; Aomine and Jackson, 1959; Fieldes and Schofield, 1960; Jackson, 1965; and Hendricks, Whittig and Jackson, 1967), while Van Reeuwijk and de Villiers (1968 and 1970) have reported similar behaviour by co-precipitated, amorphous, aluminosilicate gels. In their later paper these investigations postulated a structural model for allophane in which a permanent negative charge, arising from isomorphous substitution of Al for Si within a tetrahedral framework, was partially blocked by positively charged hydroxyalumina species. It is unfortunate that Van Reeuwijk and de Villiers (1968 and 1970) did not determine if the pH-dependent CEC of their gel systems was reversible. Being free of interference from organic matter such systems should provide an ideal opportunity to confirm whether or not the pH-dependent CEC associated with hydroxyalumina is reversible over the



pH range 4.8 - 8.2.

Organic matter has been shown to make a substantial contribution to the CEC of the yellow-brown earth members of the chronosequence. The high phosphate retention and oxalate-extractable Al values, and the results obtained by the Fieldes and Perrott test, indicate that these soils also contain high levels of hydroxyalumina. Consequently these soils should possess considerable pH-dependent CEC. As the CEC determinations obtained in this study (Tables 10 - 12) were made at pH 7.0, the values obtained will be considerably higher than those existing at the field pH of the soils. As a consequence of this the base saturation values obtained are likely to be considerably lower than those actually existing in the field. In retrospect, it is concluded that in future studies, cation exchange data would be more meaningful if measured at the field pH of the soils, rather than at the arbitrary value of 7.0.

## (2) Total Elemental Analyses

Total elemental analyses for the chronosequence and transect samples are listed initially (as % of ignition residue) in Tables 22 - 25. Data for individual horizons of the chronosequence soils, converted to a volume-weight basis, are then presented in Tables 26 and 27, and the tessera totals to depths of 0.38 and 0.76 m in Tables 28 and 29, respectively. Profile depth functions, and the main trends occurring with time are illustrated in Figures 32 - 50. In these diagrams both actual and estimated (assuming entire volume of tessera occupied by

< 2 mm material) values are presented.

Levels (%) of total Mg, Al, K, Ca and Fe decline with increasing age of the soil (Tables 22 and 23), and with the exception of Al and Fe increase with depth from the surface. Aluminium levels tend to be highest in B horizons, but those of Fe show no consistent trends. Total Si levels increase with the age of the soil, and decrease with profile depth. Maximum Ti levels would appear to occur between Ah 1 and Ku 1. Analyses of the > 2 mm material (Table 23) indicate that, in general, this fraction contains higher levels of Mg, K and Ca, and lower levels of Al, Si and Fe than are found in the finer fraction.

Lack of volume-weight data limits the value of the total elemental analyses along the Ahaura transects. The most significant feature observed in the transect data (Tables 24 and 25) is the very low Fe levels in the A<sub>2</sub> horizons at Ah 5. These values indicate that the loss of Fe from the upper part of the profile has been greater at the base of the decaying beech stump than at any other point along either transect. A low Fe level (2.89%) was also obtained from the A<sub>2</sub> horizon at I(o) 2, also sited at the base of a large decaying beech stump.

The values ( $\text{kg ha}^{-1} \text{cm horizon}^{-1}$ ) shown in the various depth functions (Figures 32 - 38) are controlled by variations in elemental composition (Tables 22 and 23) and in bulk-density. The latter controls the weight of inorganic material in unit soil volume (Figure 39). The depth functions for total Mg, Al, K, Ca and Fe increase

with profile depth, and decrease with increasing age of the soil. The high values shown by the total Si and Ti depth functions are caused by the relative 'accumulation' of these elements. Values for  $I(w)$  1 are always less than for the comparable, but freely-drained  $I(b)$  1. Part of this discrepancy is explained by the lower bulk-densities of the former profile, but the greatest difference, which occurs with Fe, is also a result of the mobility of this element under poorly-drained conditions.

With the exception of the period from Ho 1 to  $I(y)$  1, tessera weights of total Mg, Al, K, Ca and Fe fall with increasing duration of weathering and leaching (Figures 40 - 44, respectively). The comparable values shown by all elements other than Ca, in the upper 0.38 m of both Ho 1 and  $I(y)$  1 suggests that some of the material in the A horizon of the former soil may be pre-weathered, and have eroded from older surfaces. Parent material variation, or serious underestimation of the age of Ho 1, are less likely explanations. Mineralogical analyses (Chapter 3; V) suggest the parent materials are similar, while the AC profile morphology of Ho 1 indicates that its age could not approach that of  $I(y)$  1. The fall in tessera weights of Si and Ti (Figures 45 and 46, respectively) between  $I(y)$  1 and Ah 1 is caused by the steadily decreasing tessera weights of inorganic material, which overcomes, particularly for Si, the effect of increasing elemental levels (%). The subsequent increase in tessera weights of these elements beyond Ah 1 results

from increases in the elemental levels and in the bulk-density of the soils. Tessera weights of all seven elements are lower in I(w) 1 than in I(o) 1. With the exception of Fe, most of the variation results from the former soil containing only 73% (to 0.38 m) by weight of the inorganic material present in the latter.

Simple linear regressions between the various total element levels (Table 2) yield highly significant correlations (1% level) for all possible pairings except Ti v Al (non-significant) and Ti v Si and Ti v K (significant only at the 5% level). Correlation coefficients are negative for all pairings involving either of the two 'accumulating' elements, Si and Ti, except for the pairing of Si v Ti.

The quantity of any element present in a soil volume at a particular time is the resultant of the quantity inherited from the parent material, plus gains from the atmosphere and returns from living and decaying organisms, minus losses to growing organisms, to leaching and to mechanical means. Local variations in parent material, and in the soil volumes actually explored by the root systems of individual trees, and the localised gains and leaching losses associated with stem flow, ensure that some variations in elemental levels can be expected within any given area.

Table 30 lists the measured annual losses of seven elements ( $\text{kg ha}^{-1}$ ) to the constant depth of 0.38 m during various periods of soil development. To allow comparison of relative rates of loss these absolute values are also

expressed, in the same table as percentages of the quantities of each element present, at the beginning of each period considered. Since pre-weathered material may be present in the Ho 1 profile, this soil has been excluded from the table. As a further check on relative rates of loss, elemental ratios are listed in Table 31. The use of the relatively shallow depth of 0.38 m in Table 30 avoids problems that would arise in allowing for the presence of stones in the lower parts of some sola. As weathering usually decreases in intensity with depth from the surface, changes are likely to be more marked if a relatively shallow depth is considered as this avoids 'dilution' with comparatively unaltered material. Relative rates of elemental loss may also be inferred from Figure 47 which illustrates the changes in elemental percentage composition with time; also to a depth of 0.38 m.

During the period I(y) 1 to I(o) 1 annual rates of loss of the elements examined are of the order, Mg > K > Ca > Al > Fe > Si > Ti, whereas the order for the period I(y) 1 to I(w) 1 is Fe > Mg > K > Ca > Al > Si > Ti. This again demonstrates the much greater mobility of Fe under reducing conditions. If the period I(y) 1 to Ok 1 is considered as a whole, rates of loss follow the order, Mg > K = Fe > Ca > Al. When calculations are based on a constant sampled volume of soil material, Si and Ti show apparent gains, not losses, when periods extending beyond Ah 1 are considered. If it were possible to have isolated a given volume of soil material at time zero and examined

it throughout the entire period of soil development that has occurred, the quantities of all seven elements examined here could be expected to have decreased with time. It is of interest to note that the estimated annual additions of Mg, K and Ca from rainfall of 1.52, 1.33 and 0.76 kg ha<sup>-1</sup>, respectively, exceed the annual losses of those elements from the parent material in the period beyond Ah 1.

To enable data to be presented on a percentage-remaining basis it was necessary to decide what should be taken as being representative of the parent material at time zero. Since stones were absent from the top 0.38 m of all the sola, sand from the nearby Waitahu River, and the <2  $\mu$ m fraction from the C horizon of Ho 1, were considered to be the most suitable materials available. The densities of the two materials were similar (1.58 and 1.57 g cm<sup>-3</sup>, respectively) and variations in elemental percentage compositions were < 5% of the amounts present, with the exception of Ca (8% higher in Ho 1, C). In the calculations and figures discussed in the remainder of this section the < 2  $\mu$ m fraction from the C horizon at Ho 1 has been assumed to be representative of the parent material of the various soils.

The curves shown on the left hand side of Figures 48 - 50 show percentage remaining data calculated on the basis of a constant sampled volume. The curves for Mg, Al, K, Ca and Fe all show a rapid initial loss which decreases as steady state conditions are approached. The reasons for the increases shown by Si and Ti have already been discussed.

Elemental ratios (Table 31) suggest that Si is lost at a faster rate than Ti between Ho 1 and Ah 1, and that this trend is reversed beyond Ah 1. It is considered that annual loss, and percentage-remaining values more closely approaching those from an 'isolated' initial volume, as already defined, could be obtained if the values listed in Table 28 were 'corrected' to show no loss of Si between Ah 1 and Ok 1, and no loss of Ti between the parent material and Ah 1. When such adjustments are made the total element values obtained for the Ahaura and younger soils become up to three times those listed in Table 28, thus confirming that the material now present in unit volume of the two gley podzols is the residue from the continued weathering and leaching of a much greater initial volume. As losses of Si and Ti would have occurred from any isolated volume during pedogenesis, however, it is likely that the applied 'corrections' are insufficient and that the degree of error becomes greater, the younger the soil. To assist comparison with the data in Table 28 the 'corrected' values, Section A of Table 32, have been reduced proportionally such that the 'corrected' and 'constant volume' values for Ho 1 are similar. The effect of these adjustments is to compare increasing soil volumes between Ho 1 and Ah 1, with decreased soil volumes beyond Ah 1, thus correcting for an initial expansion and subsequent contraction of the soil volume.

Since a 'corrected' annual loss of Ti between Ah 1 and Ok 1 ( $0.038 \text{ kg ha}^{-1}$ ) can be obtained from Section A of Table 32, a further refinement can be made to the data in that section if it is further assumed that a constant loss of Ti occurred throughout pedogenesis. The values so obtained, again reduced proportionally to give similar values for Ho 1 to those listed in Table 28, are presented in Section B of Table 32. These data were used to construct the percentage-remaining diagrams shown on the right hand side of Figures 48 - 50 and to calculate the 'corrected' annual losses listed in Table 33. The 'corrected' values yield lower annual losses in the earlier stages of soil development, and higher values in the later stages than those shown in Table 30. In addition Si and Ti are shown as being lost throughout pedogenesis. In general, the rate of loss of the various elements examined tended to decrease with time.

The reliability of the data in Tables 30 and 32, and in Figures 48 - 50 is influenced by the uncertainty in the ages of the different land surfaces, particularly of the two oldest, and by the lack of information on the relationship between the age of the surfaces and the age of the soils that have developed on them. The data also suffered from a lack of replication. However, the work of Blosser and Jenny (1971), and the variations observed along the Ahaura transects, have indicated that a considerable number of random samples would probably have been required to effect any noticeable improvement, and



that it was, therefore, advantageous to specifically select sites by soil forming factor ordination, the approach that was attempted in the present study.

The portions of the 'corrected' percentage-remaining curves (Figures 48 and 49) that occur before the onset of steady state conditions tend to follow a first-order rate law, and yield the following values for the respective first-order rate constants:

Mg	$8.3 \times 10^{-5}$	year <sup>-1</sup>
Ca	$6.7 \times 10^{-5}$	"
K	$4.8 \times 10^{-5}$	"
Fe	$3.9 \times 10^{-5}$	"
Al	$2.0 \times 10^{-5}$	"

These values indicate that Fe is lost at a faster relative rate than Al in the earlier stages of soil development.

Stevens (1968b) reports annual losses of Mg and K of 2 and 9 kg ha<sup>-1</sup>, respectively, and on a percentage-remaining basis of  $9 \times 10^{-4}$  and  $21 \times 10^{-4}\%$ , over 22,000 years in a chronosequence of soil near the Franz Josef glacier, New Zealand. These values can not be compared directly with those in Table 30 because of the differing sampling depths involved. Losses to a depth of 0.76 m, which can be compared with Stevens's values can, however, be calculated from the data in Table 29. If the period I(y) to Ok is considered (since the end member of both sequences is an Okarito soil) the comparable losses are

0.7 and 1.1 kg ha<sup>-1</sup>, and  $8 \times 10^{-4}$  and  $7 \times 10^{-4}\%$ , respectively. The variation in the rate of loss of K relative to Mg may result from differences in composition, and thus stability of the micas and feldspars present in the respective soils, or from the considerable difference in precipitation between the two areas.

Marshall (1941) proposed the use of index minerals (those that are resistant to weathering and immobile) for evaluating changes that occurred during soil formation. He recommended zircon, tourmaline, garnet, anatase and rutile as suitable index minerals. Barshad (1964) added quartz, albite and microcline to this list. Raeside (1959) has indicated, however, that quartz, garnet and possibly zircon should not be used as index minerals in soils that have existed for long periods under high rainfall. If an index mineral contains an element that is present only in that mineral, such as zirconium in zircon, that element may be determined chemically in preference to making a mineralogical analysis.

An attempt was made to quantitatively evaluate clay formation, the destruction or migration of clay, and volume change in the soils of the Reefton sequence with the method described by Barshad (1964) using the weight of Ti in the soil as the index. Mineralogical analyses had confirmed the presence of both anatase and rutile, but no attempt was made to differentiate between oxide titanium, and titanium isomorphously substituted into aluminosilicate minerals (Dolcater, Syers and Jackson, 1970). The results are presented in Table 34. Since

Ti was not completely immobile throughout the development of the soils, the reliability of these data would decrease with increasing age of the soil. The largest increases in volume are shown by the surface horizons of the I(o) 1, I(w) 1 and Ah 1 soils, while the greatest compaction occurs in the subsoils of the two gley podzols. The high relative gains of clay in the topsoils, however, is unexpected and requires explanation. As pH is low, and rainfall high, clay in the surface horizons was likely to have been destroyed or transported down the profile. The likely explanation for the values obtained is that weathering and leaching have caused the downward translocation of Ti. This would result in the calculations showing clay gains in the upper sola, and loss of clay in the subsoils.

The calculations involved in Table 34 also yield the weights of parent material from which the present soil volumes were derived. Thus present day soil volumes that contained equal weights of parent material can be estimated, and used to calculate the percentage of elements initially present in a chosen weight of parent material that remain at various stages of soil development. Such values, based on the top 0.38 m of the Ho 1 profile, to allow comparison with Figures 48 - 50, are listed in Table 35. The values from Table 35 are similar to the 'constant volume' values (left hand side of Figures 48 - 50) for the Ku 1 and Ok 1 profiles, but greater than the 'corrected values' (right hand side of Figures 48 - 50) for the younger soils.

#### IV. POORLY-ORDERED SOIL COLLOIDS

Poorly-ordered, clay-sized aluminosilicates (allophanes) have a marked effect on soil properties and soil productivity. This is a function of their large surface area and high chemical reactivity. Their ability to adsorb phosphate ions may render a large part of added fertilizers unavailable to plants, they are capable of adsorbing pollutants from both water and the atmosphere, while the high permeability of volcanic soils containing appreciable quantities of these colloids has caused problems associated with excessive drainage in rice-growing areas.

Naturally occurring, poorly-ordered aluminosilicates and hydrous oxides have proved difficult to isolate from soils because of their close association with both crystalline clay minerals and organic matter. Considerable doubt thus exists as to their structure and composition range, and the problem of their quantitative determination remains to be solved.

##### (1) The Nature of Poorly-ordered Aluminosilicates

Historically the term 'allophane' has been used to designate naturally occurring amorphous (to X-rays), hydrous aluminosilicates of widely varying chemical composition, or even more generally to include any amorphous substances of indefinite composition present in soil clays (Mitchell, Farmer and McHardy, 1964). Lai and Swindale (1969) have defined allophane as a hydrated

aluminosilicate mineral, that has no ordered structure and is amorphous to X-rays. Minerals are usually defined by a fairly narrow composition range, or by their structural characteristics. As the range of chemical compositions reported for allophanes exceeds that usually permitted for a single mineral, they may be members of a mineral series. If this is the case their properties should be a function of composition, and it should be possible to recognise the end members of the series. At an international seminar on amorphous clay minerals held in Fukuoka, Japan in 1969, the following tentative definition was proposed:

"Allophanes are members of a series of naturally occurring minerals which are hydrous aluminium silicates of widely varying chemical composition, characterized by short range order, by the presence of Si-O-Al bonds, and by a differential thermal analysis curve displaying a low temperature endotherm and a high temperature exotherm with no intermediate endotherm."

(van Olphen, 1971)

This definition fails to define the end members, although the report does indicate that they could not be alumina and silica as these lacked Al-O-Si bonds. The definition is also unsatisfactory in that it fails to provide any basis for quantitative estimation. The size, position, and shape of the high temperature exothermic peak used in the definition can be altered appreciably by techniques used in obtaining the clay fraction from soils (Campbell, Mitchell and Bracewell, 1968) and by the nature of the

exchangeable cation (Miyauchi and Aomine, 1966).

Poorly-ordered aluminosilicates are difficult to isolate from soils because of their close association with both crystalline clay minerals and organic matter. Their high chemical reactivity, as compared with more crystalline aluminosilicates, may result in their alteration or partial destruction and solution during isolation of the clay fraction of soils. Farmer and Mitchell (1963) have also shown that Al and Fe oxalates can be formed during the oxidation of organic matter with peroxide. The difficulty in extracting 'pure' species must lead to doubts about the reliability of published chemical data for allophanes.

Poorly-ordered aluminosilicates show little characteristic response to such established instrumental techniques as X-ray diffraction, infrared absorption spectroscopy and electron microscopy (Bracewell, Campbell and Mitchell, 1970). With the exception of the partially ordered mineral, imogolite, (Yoshinaga and Aomine, 1962; Wada, 1967; Yoshinaga, Yotsumoto and Ibe, 1968; Russell, McHardy and Fraser, 1969; Wada and Yoshinaga, 1969; Wada et al., 1972; and Eswaran, 1972) they are amorphous to both X-rays and electrons, and when visible on electron micrographs are diffuse and shapeless. Infrared spectroscopy shows only diffuse bands that tend to be obscured when small quantities of amorphous materials occur in association with crystalline clays. Differential thermal analysis and infrared absorption spectroscopy can, however,

be used to characterise the clay fractions of so-called allophanic soils derived from volcanic ash.

Allophane was first reported as a soil constituent by Seki (1913), who from chemical and petrological evidence, deduced its presence in Japanese volcanic ash soils. Its presence in similar soils in New Zealand was first noted by Henderson and Ongley (1923), who deduced its presence from silicate analyses, and later by Taylor (1933). The first comprehensive investigation of the chemical and physical properties of allophane was carried out by Ross and Kerr (1934) who examined a geological allophane by X-ray, thermal, and chemical methods.

In the 1950's and the first half of the following decade extensive investigations were carried out on the volcanic ash soils of New Zealand and Japan using the techniques applied by Ross and Kerr (1934) augmented by infrared spectroscopy, electron microscopy, and measurement of surface properties. In New Zealand, Birrell and Fieldes (1952) and Fieldes (1953, 1955 and 1957) reported that the clay fractions of both the yellow-brown pumice soils (from rhyolitic ash) and the yellow-brown loams (from rhyolitic and from andesitic ash) were composed predominantly of allophane. Aomine and Yoshinaga (1955) showed that the clay fractions of certain 'ando soils' from volcanic ash were likewise composed largely of allophane. Allophanes were also reported as being a dominant clay constituent of some weakly-developed New Zealand red loams and brown loams formed on basalt

(Fieldes, 1953; and Fieldes and Swindale, 1954) and of soils formed from ultrabasic rocks (Fieldes, 1966; and Furkert and Fieldes, 1968).

By the mid 1960's it had become increasingly evident that poorly-ordered inorganic compounds, be they referred to as allophanes, aluminosilicate gels, or simply as amorphous materials, were of widespread occurrence in soils. As well as being important constituents of the clay fractions of soils derived from volcanic ash and some basalts from numerous locations, including Australia (Hosking, Nielson and Carthew, 1957; Simonett and Bauleke, 1963; Briner and Jackson, 1969; and Hamblin and Greenland, 1972), Canada (Pettapiece and Pawluk, 1972), Cameroon (Sieffermann and Millot, 1968; and Sieffermann, Jehl and Millot, 1968), Colombia (Mejia, Kohnke and White, 1968; Cortes and Franzmeier, 1972; and Calhoun, Carlisle and Luna, 1972), Hawaii (Tamura, Jackson and Sherman, 1953; Patterson, 1964; Lai and Swindale, 1969; and Wada et al. 1972), Indonesia (Kitagawa, Kyuam and Kawaguchi, 1973), Oregon (Tidball, 1965; and Chichester, Youngberg and Harward, 1969), Papua New Guinea (Haantjens, 1964; Greenland, Wada and Hamblin, 1969; Parfitt, 1972 and 1974), and the Phillipines (Kitagawa, Kyuma and Kawaguchi, 1973), these materials have also been shown to occur, as early weathering products of plagioclase in granodiorite (Snetsinger, 1967), from the weathering of kaolinite and halloysite (Jackson, 1956), in cambic and/or spodic horizons (Furkert and Fieldes, 1968; Brydon,



Kodama and Ross, 1968; Yuan, 1969; Raman and Mortland, 1969/1970; Bracewell, Campbell and Mitchell, 1970; Brydon and Day, 1970; Brydon and Shimoda, 1972; and Campbell, 1974), and as coatings on the surfaces of other minerals (Follett et al. 1965a; and Jones and Uehara, 1973).

The Commission on New Mineral names of the International Mineralogical Association (Fleischer, 1963) concluded that the data then available (1963) were clearly inadequate to justify a new name for the fibrous aluminosilicate of low crystallinity designated 'imogolite' by Yoshinaga and Aomine (1962). That much of the difficulty experienced in characterising imogolite was probably caused by its contamination with other poorly-ordered aluminosilicates with which it invariably occurred was shown by Wada (1966), when he succeeded in isolating a relatively pure form of the fibrous material, and demonstrated that its infrared absorption spectra indicated a unique structure. Wada (1967) proposed a structural scheme for soil allophanes, which he claimed ranged in composition from  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  to  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ . Wada considered that imogolite formed from the end-member with the lower  $\text{SiO}_2 : \text{Al}_2\text{O}_3$  ratio. Hashimoto and Jackson (1960) and Briner and Jackson (1969) have, however, reported allophanes with  $\text{SiO}_2 : \text{Al}_2\text{O}_3$  ratios exceeding 2.4. The latter authors suggested that these materials be called "siliceous allophane". The structure proposed for imogolite by Wada (1967) and extended by Wada and Yoshinaga (1969) was based on a repeat distance of 0.84 nm parallel

to the fibre axes and an interfibre distance of 1.72 nm. A careful electron diffraction study by Russell, McHardy and Fraser (1969) showed the interfibre distance to be 2.3 nm and thus demonstrated that the structure proposed by Wada and his co-worker was untenable. Russell and his associates proposed a structure which did meet the observed unit cell parameters. This consisted of continuous distorted chains of Al-O octahedra linked by isolated  $\text{Si}_2\text{O}_7$  groups. The presence of the bridging  $\text{Si}_2\text{O}_7$  groups was indicated by an infrared absorption band near  $930\text{ cm}^{-1}$ , and confirmed in a subsequent study (Cradwick et al. 1972).

Faced with an increasing weight of evidence that imogolite was indeed a unique aluminosilicate the International Mineralogical Association referred the matter to the Nomenclature Committee of the Association International Pour L'etude Des Argilles for advice. The latter body decided (Pedro, 1970) to approve the name 'imogolite' for the hydrous aluminosilicate having a fine thread-like morphology and the diffraction characteristics described by Wada and Yoshinaga (1969) and by others.

Since imogolite was first described by Yoshinaga and Aomine (1962) its occurrence in weathered volcanic ash has been reported from Japan (Aomine and Miyauchi, 1965; Kawasaki and Aomine, 1966; Kanno, Onikura and Higashi, 1968; Yoshinaga and Yamaguchi, 1970; Aomine and Mizota, 1972; and Wada and Tokoshiki, 1972), New Zealand (Yoshinaga, Tait and Soong, 1973; and Kirkman, 1974), Chile (Besoain, 1968/1969; and Aomine, Inoue

and Mizota, 1972), Indonesia (Kitagawa, Kyuma and Kawaguchi, 1973), New Hebrides (Quantin, 1972), Papua New Guinea (Greenland, Wada and Hamblin, 1969; Parfitt, 1974; Bleeker and Parfitt, 1974; and Parfitt and McHardy, 1974), the Phillipines (Kitagawa, Kyuma and Kawaguchi, 1973) and West Germany (Jaritz, 1967). Imogolite gels have also been observed in pumice beds (Miyauchi and Aomine, 1966; Yoshinaga, 1968; Yoshinaga and Yamaguchi, 1970; and Tazaki, 1971). Imogolite thus occurs widely in weathered pyroclastic materials. Its presence in soils derived from basaltic rocks has also been reported (Siefferman and Millot, 1968; and Wada et al. 1972).

Although the mechanisms of its formation have yet to be determined, imogolite is obviously a widely occurring mineral, and future reports of its presence in cambic and spodic horizons of soils, other than those developed from volcanic materials, are likely once sufficient care is taken to isolate relatively pure specimens. The two subspecies of imogolite postulated by Aomine and Miyauchi (1965), and the intermediate phase between imogolite and allophane proposed by Kanno, Onikura and Higashi (1968) are probably, as suggested by Russell, McHardy and Fraser (1969) simply the results of incomplete separation of imogolite from other poorly-ordered aluminosilicates.

From his investigation of a sequence of New Zealand soils derived from volcanic ash of increasing age (yellow-brown pumice soils, through yellow-brown loams to brown

granular clays) Fieldes (1955) postulated that the mineral weathering sequence found in the clay ( $< 2 \mu\text{m}$ ) fraction was: volcanic glass  $\rightarrow$  allophane B  $\rightarrow$  allophane AB  $\rightarrow$  allophane A  $\rightarrow$  metahalloysite  $\rightarrow$  kaolinite. The main differences found between allophane A and B were reported to be that the latter contained a higher proportion of very fine particles, and showed infrared absorption at  $800 \text{ cm}^{-1}$  (characteristic of discrete silica) that was absent from allophane A. Allophane A, but not allophane B, gave a sharp DTA exotherm about  $900^{\circ}\text{C}$ , caused by the formation of mullite. (A similar reaction occurs with 1 : 1-Type phyllosilicates). Fieldes (1955) considered allophane AB to be an intermediate between allophane B and allophane A. The above evidence led Fieldes to conclude that Al and Si were closely linked in allophane A, but that alumina and silica were discrete in allophane B.

Following these observations of Fieldes several workers reported the presence of material having the properties of allophane B, allophane AB, or of amorphous silica in the clay fractions of volcanic ash soils from Japan (Kanno, 1959; Matsui, 1959; Egawa and Sato, 1960; Ishii and Kondo, 1962; and Shinagawa, 1962), Chile (Besoain, 1964) and Papua New Guinea (Bleeker and Parfitt, 1974). Miyauchi and Aomine (1964) questioned, however, the existence of allophane B in Japanese ash soils for they observed that the finest particles separated from such soils ( $< 0.2 \mu\text{m}$ ) had properties characteristic of allophane A, not of allophane B. They concluded that the exothermic

DTA reaction of the whole clay fraction ( $<2\ \mu\text{m}$ ) depended largely on its fine clay ( $<0.2\ \mu\text{m}$ ) content, while the infrared absorption at  $800\ \text{cm}^{-1}$  was caused by the presence of cristobalite in the coarse clay ( $0.2 - 2.0\ \mu\text{m}$ ).

Fieldes and Furkert (1966) re-examined the New Zealand soil sequence this time applying the methods used by Miyauchi and Aomine (1964). Rather surprisingly, since the high temperature DTA exotherm was one of the criteria that had been used to distinguish allophane A from allophane B, the fine and coarse clay fractions of the soils were not subjected to DTA. On the basis of infrared evidence alone they admitted the presence of allophane A in the fine clay fraction of the New Zealand soils, but claimed that there was insufficient cristobalite in the coarse clay fractions to account for the observed variations in the infrared spectra at  $800\ \text{cm}^{-1}$ . They concluded that the weathering sequence, as earlier proposed by Fieldes, remained a satisfactory framework for studying differences between allophanic materials in volcanic ash soils. Birrell and Fieldes (1968) and Furkert and Fieldes (1968) merely reiterate the material presented in earlier works.

Shoji and Masui (1969 a and b) have shown that the clay fractions of recent volcanic ash soils in Hokkaido contained abundant discrete siliceous amorphous materials. These were more siliceous in the A horizon than in the C, and tended to become more siliceous with increasing particle size. As they found no evidence of discrete amorphous silica in any of the volcanic glasses present

in the soils, or in the fresh ash and pumice used for comparison, that found in the clay could not be derived from these sources as suggested by Fieldes and Furkert (1966). Electron optical examination of the material isolated from the soils led them to conclude that opaline silica, probably of pedogenic origin, was the dominant form of discrete amorphous silica present. Although plant opal was present in small quantities in the soils, it was absent from the clay fractions.

The progression from feldspar or glass  $\rightarrow$  allophane  $\rightarrow$  halloysite is frequently described as a typical weathering sequence for volcanic ash soils (Sudo, 1954; Sudo and Takahashi, 1955; Aomine, 1957; Tsuchiya and Kurabayashi, 1958; Kanno, 1959; Aomine and Wada, 1962; Wada, 1967; Mejia, Kohnke and White, 1968; Yoshinaga and Yamaguchi, 1970; Bleeker and Parfitt, 1974; and Kirkman, 1974). Parfitt (1974) has suggested that under tropical conditions volcanic glass weathers rapidly and can form allophane or imogolite. He concludes that the silica present in solution is initially adsorbed by plants and may form biogenetic opal. Under the prevailing humid conditions the opal redissolves and is either leached from the soil or precipitated with alumina to form allophane. Halloysite is said to form directly from feldspar, or from allophane, depending on the conditions present in the soil.

Wada and Matsubara (1968) have also demonstrated the parallel formation of allophane and imogolite from pumice, and the lack of a sequential relationship between

the two or with gibbsite. They concluded that the actual products formed depended on the composition of the microenvironment and on the heterogeneous nature of the parent material. Yoshinaga and Yamaguchi (1970) have suggested that imogolite is a product of high leaching (desilication) and that it is absent from environments where resilication prevails. A scanning electron microscope study of seven volcanic ash soils (Eswaran, 1972) found no evidence of alteration following the reported sequence: allophane  $\rightarrow$  imogolite  $\rightarrow$  halloysite (Yoshinaga and Aomine, 1962; Wada, 1967; and Wada et al. 1972). From their morphology, and random distribution in the matrix Eswaran (1972) concluded that both allophane and imogolite could be formed by precipitation from soil solution. Imogolite was also observed (one sample) as a direct alteration product of volcanic glass. Halloysite was observed to form directly from feldspar, confirming earlier observations by Park<sup>nv</sup>am (1969) and Eswaran and de Coninck (1971). Like Wada and Matsubara (1968), Eswaran (1972) stresses the need to examine the microenvironment.

Grim (1953) suggested that allophanes possessed a random arrangement of silica tetrahedra, alumina octahedra with occasional other units. Wada (1967) proposed a structure for allophane in which tetrahedralsilica chains were linked through shared corner oxygen atoms to, depending on composition, either one or two octahedral alumina chains. Udugawa, Nakada and Nakahira (1969),

however, have proposed a sheet-like structure for the material. By comparing surface area determinations using polar liquids with those obtained from low temperature nitrogen adsorption and application of the BET equation Aomine and Otsuka (1968) concluded that allophanes possessed both internal and external surfaces, the former being inaccessible to nitrogen. Kitagawa (1973) has suggested that ferric ions may substitute for Al in allophane.

The CEC of allophane, including its pH-dependence, has been explained as arising from the dissociation of hydrogen ions from exposed Si-OH and Al-OH groups (White, 1953; Wada and Ataka, 1958; Fieldes and Schofield, 1960; and Yoshinaga and Aomine, 1962). De Villiers and Jackson (1967a and b) suggested that the pH dependence of the CEC of allophane was analogous to that of pedogenic chlorite (a 2 : 1 - 2 : 2 hydroxyalumina intergrade between vermiculite and chlorite, formed by the pedogenic accumulation and polymerisation of alumina in the interlayers of vermiculite). Their proposal necessitated a 'core' carrying a permanent negative charge arising from the occupation of tetrahedral Si lattice sites by Al, that was partially surrounded by positively charged hydroxy-alumina species.

Since a direct study of natural soil allophanes is hampered by the apparent inability to isolate 'pure' and unaltered specimens several investigators have turned their attention to synthetic aluminosilicate gel systems



in their efforts to establish the nature of allophane. Two groups investigating such systems have independently proposed a similar structural model for allophane that successfully explains the CEC behaviour, differential thermograms, and phosphate adsorption and availability observed with natural systems. Since this work represents a significant advance in our understanding of these poorly-ordered systems, and because it is intended to discuss some of the results of the present study in relation to the proposed model, the relevant papers are reviewed below in some detail.

Van Reeuwijk and de Villiers (1970) set out to test the earlier hypothesis of de Villiers and Jackson (1967a and b) using a series of aluminosilicate gels ranging in composition between pure alumina and silica end members. The gels were prepared by mixing appropriate quantities of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  at pH 6.0, as previously described by van Reeuwijk and de Villiers (1968). On DTA all the gels, except the alumina end member, recorded an endothermic peak between 100 and 200°C caused by loss of hydration water. Only those gels with compositions between 45 and 80%  $\text{Al}_2\text{O}_3$  gave, in addition, a high temperature exothermic peak near 980°C. The pure alumina end member, and the 80%  $\text{Al}_2\text{O}_3$  gel also displayed endotherms about 300°C, which X-ray diffraction analyses indicated were due to bayerite. X-ray and electron-optical examination failed to detect crystalline components in any of the remaining gels. Crystallisation of bayerite

from freshly-precipitated alumina has also been reported by Gastuche (1964), Hsu and Bates (1964) and Hsu (1968). The presence of silica thus appears to hinder the crystallisation of bayerite from amorphous alumina.

The silica end member prepared by van Reeuwijk and de Villiers (1968) showed an increase in negative charge between pH 4 and 10. Addition of alumina into the gel system caused a linear increase in negative charge, and a decrease in the extent of the pH-dependence of CEC, until a composition of 22%  $\text{Al}_2\text{O}_3$  was reached. These observations indicated that the two components of the gels had interacted to give a product with permanent negative charge. The composition yielding the maximum CEC corresponded to a substitution of 1 Al : 3 Si, which has been shown by Milliken, Mills and Oblad (1950) and Leonard et al. (1964) to be the maximum substitution permissible in a stable structure. A one-in-four substitution would yield a theoretical CEC of 318 me/100 g, a value in close agreement with those obtained experimentally by van Reeuwijk and de Villiers (1968 and 1970).

A linear fall in CEC, at pH 10, as the  $\text{Al}_2\text{O}_3$  content was increased above 22% showed that alumina in excess of that value could not be accommodated in tetrahedral sites. Since the excess alumina would carry zero charge at pH 10, it would act simply as an inert diluent. The behaviour of CEC-composition functions at lower pH values indicated that alumina above 22% composition was positively charged, and that this charge was pH-dependent. At low pH and

high  $\text{Al}_2\text{O}_3$  content, net positive charge was developed. Since an alumina content above 80% led to the formation of bayerite, and because of deviations from linearity of the pH-composition functions at pH 4 and 7, van Reeuwijk and de Villiers (1970) concluded that the negative charge on the 'tetrahedral core' was capable of exerting a restrictive influence on the polymerisation reactions that controlled the size and charge of polynuclear hydroxyalumina. As the  $\text{Al}_2\text{O}_3$  content increased the complexity of the polymer coatings increased, and the charge per Al atom decreased. Such a control of the polymerisation of Al species by crystalline phyllosilicates had previously been discussed by Jackson (1960, 1963a and 1963b) and Hsu (1968).

Cloos, Herbillon and Echeverria (1968) and Cloos et al. (1969) working with aluminosilicate gels prepared by the slow hydrolysis of mixtures of aluminium isopropoxide and ethyl silicate, a method developed by Leonard et al. (1964), deduced a similar structural model for allophane. Their conclusions were based on the observation that CEC values (ammonium acetate at pH 7) of the gels were lower than the potential values calculated from the relative amounts of Al present in four-fold coordination as determined by an X-ray fluorescence technique (White, McKinstry and Bates, 1958; de Kimpe, Gastuche and Brindley, 1961 and 1964; Gastuche and Herbillon, 1962; Gastuche et al. 1963; Day, 1963; and Leonard et al. 1964). This technique utilised shifts in wavelength or in peak position

of  $\text{AlK}\alpha$  radiation as a result of changes in the coordination number of the aluminium ions present. Since these changes were small results were often expressed in the form

$\Delta 2\theta$ , where:

$\Delta 2\theta = 2\theta(\text{Al metal}) - 2\theta(\text{Al in sample})$ , where  $2\theta$  represents the deflection angle for the particular analysing crystal employed. Wardle and Brindley (1971) have discussed the dangers of using this technique for estimating  $\text{Al(IV)} : \text{Al(VI)}$  ratios, and demonstrated that the procedure is acceptable only if the Al-O bond lengths in the substances used as standards approximate those in the unknowns. White and Gibbs (1969) have shown that much larger shifts in peak position occur if  $\text{AlK}\beta$  emission is used, and concluded that correlations can be made between  $\Delta \text{AlK}\beta$  and both the coordination number and Al-O bond lengths in unknown materials irrespective of their degree of crystallinity.

The major difference between the allophane models proposed by the two independent groups is that Cloos and his co-workers have reported the presence of considerable six-fold coordinated aluminium in gels of low alumina content. De Villiers (1971) has indicated that the reason for this difference is that cations other than protons and aluminium ions are absent from gel systems prepared from organic components. Some aluminium ions are thus needed to balance the negative charges developed in the core. In the gels prepared from simple inorganic salts sufficient sodium ions would be available for that purpose.

The recognition of four distinct phases in these

model systems (amorphous silica, negatively charged aluminosilicate, positively charged polymeric hydroxy-alumina and crystalline alumina) must lead to a better understanding of the nature of poorly-ordered materials in natural systems, and provide a basis for evaluating different qualitative tests or quantitative determinations. The ease with which van Reeuwijk and de Villiers (1968) were able to prepare gels by precipitation from inorganic materials suggests that such reactions could occur widely in nature. If co-precipitation is a method by which these gels are formed during pedogenesis the presence of a disordered parent material should not be an essential requirement. Gels should form as readily from (say) weathering granite, as from disordered volcanic materials of similar composition. The dominance of volcanic ash soils in studies on soil allophanes probably merely reflects the difficulty of identifying poorly-ordered components in soils where they occur in association with crystalline materials. The work initiated by de Villiers, Cloos and their associates should be extended to determine

- (i) the pH and concentration limits that define the stability limits of the gel systems,
- (ii) what substitution by Fe and other cations is possible
- (iii) how and in what forms organic matter can be adsorbed by the gels, or incorporated during their formation, and
- (iv) what initiates or inhibits their crystallisation.

Some of this information may be available in the much earlier works of Mattson. It is perhaps timely that his works should be reviewed in the light of our present knowledge.

(2) Problems Associated with Quantitative  
Determination of Poorly-ordered Materials

Although a number of procedures have been used to estimate the quantities of poorly-ordered aluminosilicates present in soils, none is capable of providing a rigorous quantitative determination of these materials. At the present time, and despite its theoretical limitations and empiricism, selective dissolution by chemical reagents is the most satisfactory method available for estimating the allophane content of soils. Its use was recommended by the International seminar on amorphous clay minerals held at Fukuoka, Japan in 1969 (van Olphen, 1971). Of the modern instrumental techniques becoming available, the seminar favoured the use of neutron activation analysis, and microprobe analysis.

Classically, alkaline reagents have been favoured for the dissolution of poorly-ordered aluminosilicates, but free alumina and silica, and all of the commonly occurring phyllosilicates are soluble to varying degrees in alkaline solutions. Selective dissolution techniques exploit the knowledge that rates of solution are controlled by specific surface area, structural order and bond strength, and are thus higher for poorly-ordered than for crystalline aluminosilicates. However, in soil clays

a continuum from nearly perfect crystallinity to almost complete disorder is likely to exist. Where in such a system can a dividing line be placed satisfactorily?

In the method developed by Hashimoto and Jackson (1960) a 100 mg sample is placed in a nickel beaker, 100 ml of 0.5 molar NaOH added and the suspension brought rapidly to the boil. After boiling for exactly 2.5 minutes the contents of the beaker are rapidly cooled to room temperature and the supernatant solution removed for analysis. The method is simple and easy to apply, but has the disadvantage that small variations in heating and cooling rates could result in samples spending different periods at elevated temperatures. Since the actual heating time is so short, this could lead to results from different laboratories not being strictly comparable.

An alternative procedure, developed at the Macaulay Institute for Soil Research, Aberdeen, Scotland, (Follett et al. 1965a and b), involves shaking 100 mg samples with 80 ml of cold 5%  $\text{Na}_2\text{CO}_3$  for 16 hours, after which the supernatant liquid is removed for analysis. The leaching is repeated with further additions of carbonate until the quantities of alumina and silica extracted are minimal. The residue is then subjected to successive two hour digestions at  $100^\circ\text{C}$  with 80 ml of 5%  $\text{Na}_2\text{CO}_3$  until the extracted alumina and silica are again minimal. This method is far more time consuming than that developed by Hashimoto and Jackson (1960).

Gedroits (1963) has suggested dissolution in KOH to

remove amorphous constituents, while Alexiades and Paxinos (1965), compared dissolution by KOH with some earlier work using NaOH, and concluded that the former was less destructive of poorly crystalline clays.

However, the amount of comparative work that has been done on the relative merits of the various alkaline reagents is small. De Villiers (1971) considered that the data then available (four samples compared by Follett *et al.* 1965a) indicated that the method of Hashimoto and Jackson (1960) was less destructive of crystalline clays, and more efficient in dissolving allophane than that of Follett and his co-workers. Three reference clay minerals, and one soil clay, a Tirau sandy loam from New Zealand known to contain kaolinite as well as allophane (Fieldes, 1955) are, in the opinion of this author, insufficient to draw any such conclusions. Since it is presumably the hydroxyl ion concentration that controls the rate of solution, it would seem more logical to expect that the method more efficient at dissolving allophane was also more destructive of crystalline aluminosilicates, unless the concentration of some other ion present could be shown to exert some destructive or protective effect.

A more recent comparison by Briner and Jackson (1969) showed that boiling 0.5 molar KOH for 2.5 minutes extracted 13.78% of the  $\text{SiO}_2$  and 8.48% of the  $\text{Al}_2\text{O}_3$  from a basaltic soil clay, compared with a total of 11.24%  $\text{SiO}_2$  and 7.13 %  $\text{Al}_2\text{O}_3$  from two 'cold' and five 'hot' extractions with 5%  $\text{Na}_2\text{CO}_3$ . The molar  $\text{SiO}_2 : \text{Al}_2\text{O}_3$



ratios of the material extracted by the two methods were 2.8 and 2.7, respectively. These results would seem to indicate that both methods had extracted the same component or components, and that the former was the more drastic.

The reaction between hydroxyalumina and fluoride ions (Hensley and Barney, 1958; Yuan and Fiskell, 1959; Egawa, Sato and Nishimura, 1960; and Huang and Jackson, 1965) was used by Fieldes and Perrott (1966) as the basis of a test for allophanic material in soils that could be used in the field. A quantitative application of this test was devised by Bracewell, Campbell and Mitchell (1970). Brydon and Day (1970) claimed that as allophane, amorphous  $\text{Al}(\text{OH})_3$ , synthetic dioctahedral chlorite, podzol B horizons yielding oxalate — extractable Al values  $> 1\%$ , and ground gibbsite, all gave positive results with the Fieldes and Perrott NaF test, it should not be considered specific for allophane but merely indicative of the presence of hydroxyalumina.

The present author has observed that any crushed aluminosilicate minerals (but not quartz) yield positive Fieldes and Perrott test values. Since crushed albite and obsidian give positive results it is reasonable to expect a similar response from the Al-substituted, tetrahedral allophanic core proposed by de Villiers and Cloos and their respective associates, except for systems with very low  $\text{Al}_2\text{O}_3$  content. Mitchell et al. (1968) have shown that after 1.9% of the  $\text{SiO}_2$  and 2.7% of the

$\text{Al}_2\text{O}_3$  in a soil clay had been extracted by cold 5%  $\text{Na}_2\text{CO}_3$ , the residue gave little evolution of hydroxyl ions when treated with 1.0 molar  $\text{NaF}$ . A second sample of residue, however, yielded a further 13.6% of  $\text{SiO}_2$  and 15.0% of  $\text{Al}_2\text{O}_3$  when treated with hot 5%  $\text{Na}_2\text{CO}_3$ . The molar  $\text{SiO}_2$  :  $\text{Al}_2\text{O}_3$  ratios of the original soil clay, and the material extracted by cold and by hot 5%  $\text{Na}_2\text{CO}_3$  were 3.1, 2.6 and 2.9, respectively. Mitchell and his co-workers concluded that the material extracted by cold 5%  $\text{Na}_2\text{CO}_3$  was related to that responsible for positive responses to the Fieldes and Perrott test. Their work indicates that the use of an alkaline dissolution treatment more drastic than cold 5%  $\text{Na}_2\text{CO}_3$  should be avoided. The higher  $\text{Al}_2\text{O}_3$  content of the material extracted by cold 5%  $\text{Na}_2\text{CO}_3$  as compared with that subsequently extracted by the heated reagent has also been reported by Follett et al. (1965a) and by Briner and Jackson (1969).

Complexing reagents such as acid ammonium oxalate (Tamm, 1922), pyrophosphate (Aleksandrova, 1960) and citrate (Mitchell, Farmer and McHardy, 1964) remove, from soils, poorly-ordered forms of Fe, as well as those of Al and Si. Several workers (Deb, 1950; Schwertmann, 1959 and 1964; Gorbunov, Dzyadevich and Tunik, 1961; McKeague and Day, 1966; McKeague, 1967; Dudas and Harward, 1971; and McKeague, Brydon and Miles, 1971) have demonstrated that acid ammonium oxalate can be used as a measure of the quantity, or activity of the amorphous forms of Al and Fe in soils. The Al extracted by this reagent has

been correlated with phosphate retention by soils (Williams, Scott and McDonald, 1958; Franklin and Reisenauer, 1960; Bromfield, 1965; Saunders 1965; and Sree Ramulu, Pratt and Page, 1967). Tandon (1970) has reported a similar correlation for fluoride — extractable Al. As the positively charged polymeric hydroxyalumina species surrounding allophanic cores appear to be involved in phosphate adsorption (Cloos, Herbillon and Echeverria, 1968; and Cloos et al. 1969) it may be concluded that they are soluble in both oxalate and fluoride reagents. Although polymeric hydroxyalumina species associated with 2 : 1 Type phyllosilicates and other soil components may not be as accessible to the reagents as those of allophanic gel systems, they too must be regarded as soluble to some extent.

As early as 1934, Lundblad urged that Tamm's reagent be used cautiously in the presence of easily soluble unweathered minerals. LaJoie and de Long (1945) have reported that Tamm's reagent was unsuitable as a criterion for differentiation of podzols and podzolic soils. McKeague, Brydon and Miles (1971) showed that although magnetite was attacked by acid oxalate, goethite and hematite, which are more common in soils, were relatively unaffected. Arshad, St Arnaud and Huang (1972) have claimed that the use of acid oxalate as an extractant for amorphous forms of Al and Fe may have limitations for soils containing trioctahedral phyllosilicates, and suggest that extraction with potassium pyrophosphate may

be more suitable. Schwertmann (1973), however, criticised their work on the grounds that freshly-ground trioctahedral minerals were unsuitable for testing a method to be used with soils, and suggested that pyrophosphate was unsuitable for measuring pedogenic iron since it essentially determined only organic-bound forms.

Aleksandrova (1960) reported that 0.1 molar sodium pyrophosphate extracted humus, and its Al and Fe salts from soils. Bascomb (1968) showed that 0.1 molar potassium pyrophosphate extracted Fe from organic complexes and amorphous gels, but not from aged amorphous hydrous oxides. McKeague (1967) presented evidence that 0.1 molar sodium pyrophosphate was reasonably specific for organic-complexed Al and Fe in soils, and in association with Brydon and Miles (1971) demonstrated that organic-bound Al and Fe, amorphous forms of Al and Fe, and crystalline Fe oxides could be estimated approximately by pyrophosphate, acid oxalate and citrate-bicarbonate-dithionite extractions, respectively. These workers claimed that their results, together with the earlier works of Bascomb (1968) and McKeague (1967 and 1968), indicated that pyrophosphate-extractable Al and Fe (and possibly C) could be used as the basis of a chemical criterion for spodic horizons. They claimed that for this purpose pyrophosphate was more specific than the pyrophosphate — dithionite treatment proposed by Franzmeier, Hayek and Simonson (1965), and that unlike acid oxalate it did not attack magnetite or other easily weathered Fe-bearing minerals such as olivine or montmorillonite.

As with other selective dissolution methods the use of acid oxalate or pyrophosphate must be largely empirical. Such methods can not differentiate sharply between different forms of Al and Fe, because in natural soil systems these elements are present in various continua. It should also be remembered that an empirical method that is developed and shown to be suitable in one environment may be quite unsuitable in others. Segalen et al. (1971) consider that some highly weathered tropical soils, from which acid oxalate extracts very low quantities of Fe, contain, nevertheless, appreciable quantities of amorphous Fe oxides, and consequently have used a more drastic extractant to determine them.

Dilute acids have been used by Rich and Obenshain (1955), Kirsanov (1958) and Deshpande, Greenland and Quirk (1964) to remove poorly-ordered forms of Al and Fe from soils, while Tweneboah, Greenland and Oades (1967) have shown that treatment of soil clays with 0.5 molar  $\text{CaCl}_2$  at pH 1.5 extracts Al, but little Si or Fe. Since this latter treatment substantially reduced the positive charge developed at low pH it was concluded that in the range of soils examined this property was largely due to "active" hydroxyalumina species.

De Villiers (1971) has suggested that the quantitative determination of allophane in soils may have to be based on a specified selective dissolution procedure. Before such a solution is adopted rigorous comparative studies involving both synthetic aluminosilicate gels and a wide

range of soil clays are required. The use of the comparatively simple synthetic gel systems, where the relative proportions of Al in four-fold and six-fold coordination could be determined, would allow monitoring of the effects of different reagents on the various identifiable phases present.

A major weakness in many of the attempts to quantitatively determine amorphous components by selective dissolution already documented is their use of highly crystalline reference clay minerals and oxides (often of geologic, rather than pedogenic origin) as standards for testing the effects of reagents on crystalline soil components. Such reference materials are likely to be more resistant to attack than those formed by pedogenic processes. Ideally, the crystalline aluminosilicates and oxides present in the actual soil clays under investigation should be used for these essential comparative studies. Wada and Greenland (1970) have demonstrated that this can satisfactorily be accomplished by using treated and untreated samples in the reference and sample positions of a double beam infrared spectrophotometer. The difference pattern then recorded is used to characterise the material actually removed by the dissolution treatment employed. As they have indicated, differential DTA could be used in a similar manner. Their work has shown that the material extracted by the citrate-bicarbonate-dithionite method of Mehra and Jackson (1960), by 2%  $\text{Na}_2\text{CO}_3$  (Jackson, 1956) and by 0.5 molar NaOH (Hashimoto

and Jackson, 1960), used successively, depended primarily on the initial mineral assemblage of the sample.

Phyllosilicates, including disordered kaolinites were dissolved from clays in which they were major constituents. They further demonstrated that the method of Hashimoto and Jackson appeared to remove material that was more ordered than that removed by 2%  $\text{Na}_2\text{CO}_3$ , but that heating at  $90^\circ\text{C}$  for 15 minutes with 2%  $\text{Na}_2\text{CO}_3$  did not completely remove allophane.

### (3) Amorphous and Organic-complexed Forms of Al and Fe in Soils of the Reefton Sequence

A preliminary survey was carried out to determine the nature of the materials extracted from samples of the  $<2\ \mu\text{m}$  fraction (isolated by sedimentation from distilled water only) from the  $\text{B}_{22}$  horizon of I(o) 1, the  $\text{B}_3$  and  $\text{C}_{12}$  horizons of Ah 1, and the G horizon of Ok 1, by three selective dissolution procedures. The treatments examined were those of Hashimoto and Jackson (1960), Follett et al. (1965a), and shaking for 2 and for 60 minutes with 0.85 molar NaF (pH 7) using a soil : solution ratio of 1 : 50. After extraction the samples were washed with distilled water, Mg-saturated by washing (four times) with 1.0 molar  $\text{MgCl}_2$ , freed of excess  $\text{MgCl}_2$  by successive washings with distilled water (twice), ethanol-water (1 : 1), acetone-water (1 : 1) and acetone, air-dried at  $20^\circ\text{C}$ , weighed, and then stored at a relative humidity of 56%. Duplicate 80 mg samples were subjected to all those operations performed on the treated samples except the

initial extraction. Care was taken to ensure that physical losses of material during treatments was minimal.

The material extracted by each of the dissolution procedures was characterised by differential DTA. The dissolution residue and the untreated duplicate, both made to 160 mg with calcined kaolinite were used as the reference and sample, respectively. Examples of the difference thermograms obtained are shown in Figure 51. These tests showed that all three procedures extracted gibbsite and phyllosilicates as well as amorphous aluminosilicates, particularly from the younger soils. They confirm the desirability of testing so called selective dissolution reagents for inactivity against other components on the actual soils involved, rather than against standard reference clay minerals that are often of geologic rather than pedogenic origin, and which may well be more ordered, and more resistant to attack than the minerals actually present in the samples. The results may also question the suitability of alkalis and fluorides in P fractionation schemes such as those proposed by Chang and Jackson (1958), or Williams and Walker (1969). (A rigorous evaluation of selective dissolution techniques is being undertaken by Mr A.W. Young, of the Soil Science Department, Lincoln College. His initial results show that oxalate and citrate also attack the crystalline components present in younger soils of the Reefton chronosequence).

Despite these shortcomings it was decided to use Tamm's acid ammonium oxalate procedure as modified by



McKeague and Day (1966) and 0.1 molar sodium pyrophosphate (McKeague, 1967) as the means of obtaining approximate values for the amorphous and organic-complexed forms of Al and Fe in the soils of the present study. Application of these methods does at least allow comparison with the data published by McKeague and his associates for a range of Canadian soils that appear to have chemical and mineralogical similarities with those of the Reefton sequence, and with the criteria set out in 'Soil Taxonomy', a publication by the Soil Conservation Service, U.S. Department of Agriculture, Washington (1970). Phosphate retention (Saunders, 1965) and hydroxyl release by fluoride ions (Fieldes and Perrott, 1966) were also determined to obtain an index of the chemical reactivity of the various hydroxyalumina components. Data from the above analyses, and the main trends exhibited are presented in Tables 36 - 43 and Figures 52 - 65.

For comparative purposes whole soil, and water-dispersed size separates from the B (0.15-0.28 m) and C (0.51-0.64 m) horizons of a Taupo sandy silt collected from the New Zealand Soil Bureau's reference site at Wharepaina - N85/793738- (N.Z. Soil Bureau Bulletin, 1968a p. 74-75), and water-dispersed  $< 2 \mu\text{m}$  material from Ah 1, B<sub>21</sub> and C<sub>12</sub>, and Ok 1, G were subjected to similar analyses. The results of these and other relevant analyses performed on these samples are presented in Tables 44 - 46 and in Figure 66. Taupo sandy silt is reported by the N.Z. Soil Bureau to contain only

allophane in the  $< 2 \mu\text{m}$  fraction. (The author is grateful to Mr W.A. Pullar for providing the samples).

Poorly-ordered forms of Al and Fe as determined by oxalate-extractable Al and Fe levels (% of ignited weight) increased with age of the soil from Ho 1 to Ah 1, then declined markedly (Table 36). This trend shown by oxalate-extractable Al is in agreement with that found by Mokma et al. (1973) in a chronosequence of soils developed from alluvial and morainic deposits from the Franz Josef Glacier. Their sequence also culminated in the Okarito soil. The levels extracted from the A and  $A_{2g}$  horizons of the weakly gleyed I(w) 1 are much lower than those extracted from comparable depths in the free-draining I(o) 1 (Table 36). The quantities of Al and Fe ( $\text{kg ha}^{-1}$ ) extracted to constant depth (Figure 52) reach maximum values by I(o) 1 or Ah 1, then fall. Although the variations in volume-weight of the soils (Figure 9) act to reduce this effect, it should be noted that differential DTA analyses (Figure 51) suggest the possibility that crystalline components in the Ikamatua and Ahaura soils may have been more soluble in oxalate than those from the older soils.

Oxalate-extractable Al and Fe values for the upper 0.38 m of I(w) 1 are considerably lower than those for I(o) 1, but are comparable to a depth of 0.78 m. This suggests that destruction of poorly-ordered forms of Al and Fe, or their downward translocation occurs under poorly-drained conditions.

The percentages of total soil Al extracted by oxalate to constant profile depth reach maxima of 17 and 15% to 0.38 and 0.76 m, respectively, at Ah 1, while the corresponding maxima for Fe, also reached at Ah 1 are 45% and 37% (Figure 53). The percentage of total Al and Fe extracted by oxalate from the upper 0.38 m of each tessera exceeds that from the lower half for the free-draining soils of the sequence, but the reverse occurs in the poorly-drained members, with the exception of the comparable Al values from Ok 1. The shapes of these curves (Figure 53) are generally similar to those of Figure 52.

The continued accumulation of poorly-ordered forms of Al and Fe from Ho 1 to Ah 1, and the greatly reduced quantities in the two older gley podzols are also clearly demonstrated by the depth functions ( $\text{kg ha}^{-1} \text{cm horizon}^{-1}$ ) presented in Figures 54 and 55. Maximum accumulations occur in the B horizons of the younger, freely-drained soils, whereas depth functions for both gley podzols show an increase with depth from the surface (Al) or little variation (Fe). Maximum accumulation occurs at greater depth in I(w) 1 than in I(o) 1. Loss of poorly-ordered forms of Fe is very evident in the upper horizons of I(w) 1. Because bulk density increases with depth, depth functions expressed on a volume-weight basis ( $\text{kg ha}^{-1} \text{cm horizon}^{-1}$ ) may show maxima lower in the profile than would occur if percentage of ignited weight was the basis used. Depth functions illustrating the

percentage of total soil Al extracted by oxalate (Figure 56) decrease with depth for Ho 1, I(y) 1 and I(o) 1, reach maxima in B horizons for I(w) 1 and Ah 1, and increase with depth for the two gley podzols. The comparable functions for Fe (Figure 57) decrease with depth for all four free-draining soils, pass through a minimum for Ku 1, increase with depth for Ok 1, and reach a maximum in the B<sub>22</sub> horizon of I(w) 1.

Oxalate-extractable Al and Fe in the surface horizon along the Ahaura transects tend to increase with distance from the living trees and decaying stump. The percentages of the total elements extracted show a similar trend. Those are the only consistent trends observed (Tables 37 and 38). Oxalate-extractable Al and Fe levels are very low in the A<sub>21</sub> horizon at Ah 5, and are comparable with those found in the older gley podzols. Simple regression analyses involving only the transect samples show no correlation between pH or organic matter (as indicated by loss-on-ignition values) and oxalate-extractable Fe. Correlation between pH and oxalate-extractable Al is significant only at the 5% level. Increased stem-flow effects (no other transect site is within 1 m of any tree stem), operating over a longer period of time, are considered to be responsible for the very low values found in the A<sub>21</sub> horizon at Ah 5.

The trend shown by organic-complexed forms of Al and Fe, as determined by extraction with sodium pyrophosphate often closely matched those described for oxalate

extraction. It can be seen from Table 2 that simple regression analyses involving any pair of these four variables are highly significant (0.1% level).

The quantities of Al and Fe extracted by pyrophosphate (% of ignited weight) are greater in Ah 1 than in the younger or older soils. The amounts extracted from the gleyed upper horizons at I(w) 1 were considerably lower than from the free draining I(o) 1 (Table 39). The quantities extracted to constant profile depth (Figure 58) also reach maxima at Ah 1, and both the shape of the curves and the actual quantities involved closely resemble the oxalate-extractable data presented in Figure 52. Volume-weight variations again act to depress the maxima. Oxalate extracts more Al and Fe than pyrophosphate from the lower half of the Ikamatua (all) and Ah 1 profiles, but the reverse occurs in Ok 1 and on the lower half of the Ku 1 tessera. The major differences between the percentages of total soil Al and Fe extracted by pyrophosphate (Figure 59) and oxalate (Figure 53) are the higher proportion of Al in Ok 1, and Fe in both gley podzols extracted by the former reagent.

Depth functions ( $\text{kg ha}^{-1} \text{ cm horizon}^{-1}$ ) for pyrophosphate-extractable Fe for the younger freely-drained soils show maximum values near the surface and then decrease with depth, whereas the three poorly-drained soils all have much lower values in the upper half of the profile and reach their maximum levels below 0.4 m (Figure 60). Depth functions for Al (Figure 61)

are generally similar to those described for Fe, but the maximum values for I(o) 1 and Ah 1 occur lower in the profile, and high values are shown by the lower horizons of Ah 1, Ku 1 and Ok 1. The percentage values listed in Table 39 show that the general increase with depth shown by both gley podzols results from increased levels of extraction as well as from variations in bulk density. The depth functions (Figures 60 and 61) also show the continued accumulation of organic-complexed forms of Al and Fe from Ho 1 to Ah 1.

Depth functions showing the percentage of total Al in organic-complexed forms (Figure 62) decrease with depth for the free draining soils, show maxima in the  $A_{2g}$  and  $B_2G$  horizons of I(w) 1 and Ok 1, respectively, while that for Ku 1 increases with depth. The decrease with depth shown by the free draining members of the sequence is more pronounced in the depth functions showing the percentage of total Fe that is extractable by pyrophosphate (Figure 63). The function for Fe obtained for Ku 1 is more complex than that for Al. Values decrease with depth to the G horizon, rise in the organic rich  $B_hG$ , then fall to zero in the  $B_2G$  before again rising steeply in the  $B_3G$ . The A horizon value of Ok 1 is the highest obtained in the sequence, and subsoil values remain high in this profile. The relatively high percentages of total Al and Fe extracted by pyrophosphate from the two gley podzols is a consequence of the low contents of total Al and Fe in these soils,

and not of any accumulation of organic-complexed forms.

There is some tendency for the levels of organic-complexed forms of Al and Fe in the surface horizon to decrease with distance from a living beech tree or decaying stump (Tables 40 and 41). The lowest values along either transect are again found in the  $A_{21}$  horizon at Ah 5. Simple regression analyses show that along the transects pyrophosphate-extractable Fe correlates at the 0.1% level with pH and at the 1% level with loss-on-ignition, but that Al shows no such correlation.

Depth functions expressing phosphate retention (Figure 64) and Fieldes and Perrott test values (Figure 65) show that an increase in the reactivity of the poorly-ordered hydroxyalumina gel phase, at constant profile depth, occurs with time for the freely-drained members of the sequence. This increase, and the extension of a high reactivity to greater profile depth, also as age increases, result from both higher clay contents (Table 7) and an increase in the proportion of total soil Al occurring in gel form (Figures 53 and 56). That the reactivity is largely a function of the clay fraction can also be seen by comparing the values obtained on applying the Fieldes and Perrott test to water-dispersed clay with those obtained from the  $< 2$  mm fraction (Figure 65), or by comparing the oxalate-extractable Al and Fe, phosphate retention, and Fieldes and Perrott values obtained with the water-dispersed  $< 2$   $\mu$ m fraction of the  $B_{21}$  and  $C_{12}$  horizons of Ah 1 (Table 46) with the

corresponding values obtained from the  $< 2$  mm fraction (Table 36, and Figures 64 and 65).

A considerable reduction in activity of the gel phase is evident in the upper horizons of the poorly-drained soils. Comparison of the phosphate retention depth functions of  $I(w)$  1 and  $I(o)$  1 (Figure 64) suggests that some translocation to the  $A_{2g}$  and lower horizons may have occurred in the former soil. The water-dispersed  $< 2 \mu$ m fraction from the G horizon of Ok 1 is notably inactive (Table 46).

Simple regression analyses (Table 2) indicate significant (1% level) or highly significant (0.1% level) correlations between all possible pairings of phosphate retention, Fieldes and Perrott test (soil), oxalate-extractable Al and Fe, pyrophosphate-extractable Al and Fe, and loss-on-ignition values for the chronosequence samples except loss-on-ignition v Fieldes and Perrott test (not significant), loss-on-ignition v oxalate-extractable Al (5% level only) and pyrophosphate-extractable Fe v Fieldes and Perrott test (5% level only). Soil pH correlated only with oxalate-extractable Al and Fieldes and Perrott test (1% level) and with phosphate retention and loss-on-ignition (5% level). These correlations indicate that complexing by water soluble chelates may be more significant than increased solution of alumina under lower pH conditions in explaining the loss of reactive gel material from the upper horizons of the poorly-drained soils.



Oxalate-extractable Al, phosphate retention and Fieldes and Perrott test values are highly correlated (0.1% level) with both  $\text{NH}_4\text{F-P}$  and non-occluded P, and there is a significant negative correlation (1% level) between these phosphate fractions and montmorillonite content. Oxalate-extractable Al and phosphate retention, but not Fieldes and Perrott test, also correlated (0.1% or 1% levels) with occluded inorganic P and residual P. No correlation occurred with acid-extractable P (Table 2).

Phosphate retention values for the surface horizon increase with distance from the decaying beech stump, or from the living trees along both Ahaura transects. Values are very high (>90%) in all  $\text{B}_{21}$  horizons. Fieldes and Perrott test values, particularly those of the water-dispersed  $\leq 2 \mu\text{m}$  fraction confirm these trends (Tables 42 and 43). Destruction of reactive hydroxyalumina gel phases, or their movement down the profile thus appear to be associated with those processes that are more intense near the stems of existing or decaying trees.

The phosphate retention and Fieldes and Perrott test values for the  $\leq 2 \text{ mm}$  fraction at Ah 1 exceed those shown by the Taupo sandy silt (Tables 44 and 45). The latter soil, however, contains  $\leq 2\%$  of clay. The amounts of Al (%) extracted from both soils by oxalate are comparable, but more Fe is extracted from the Ahaura B horizons than from the Taupo B. Pyrophosphate extracts considerably more Al and Fe from the Ahaura. These results would seem to indicate that both the Ahaura and

Taupo soils contain comparable quantities of 'allophanic' gel species, and that the former soil contains, in addition, greater amounts of poorly-ordered, hydrous iron oxides and of organic-complexed amorphous forms of Al and Fe. These conclusions are supported by the results of DTA (Chapter 3; V, (3)). It should be noted, however, that neither oxalate nor pyrophosphate is likely to be specific. That some overlap does occur between them is demonstrated by the sum of oxalate- and pyrophosphate-extractable Fe from the A and AB horizons of Ah 1 exceeding total soil Al. A similar result is obtained for the sum of the Al extracted by the reagents from the  $< 0.2 \mu\text{m}$  fraction of the Taupo B horizon. Schnitzer and Skinner (1964) have claimed that oxalate extracts Al and Fe organic complexes from soils.

Schwertmann (1964) defined the ratio of oxalate- to dithionite-extractable Fe as the "active" Fe ratio. McKeague and Day (1966) have shown that podzol B horizons have distinct accumulations of oxalate-extractable Fe, and consequently a high "active" Fe ratio. The National Soil Survey Committee of Canada has defined an 'f' horizon tentatively as one enriched with hydrated iron, and having a chroma of  $\geq 3$  and redder than the horizon above or below. McKeague and Day argued that as all the podzol B horizons that they had studied also contained distinct accumulations of oxalate-extractable Al, this element too should be included in any definition of a B<sub>f</sub> horizon. They tentatively proposed that horizons in

which the percentage of oxalate-extractable (Al + Fe) exceeded that of the C horizon by  $\geq 0.8\%$ , or horizons in which the percentage of dithionite-extractable (Al + Fe) exceeded that of the C horizon by  $\geq 1.0\%$  be designated as  $B_f$  horizons. By this definition, the A and AB horizons at I(y) 1, the A,  $B_{21}$  and  $B_{22}$  horizons of I(o) 1, the  $B_{21}$  and  $B_{22}$  horizons of I(w) 1 and the A, AB,  $B_{21}$ , and  $B_{22}$  horizons of Ah 1 could be classified as  $B_f$  horizons (Table 36).

Stonehouse and St Arnaud (1971) have used the "active" Fe ratio to separate well-drained and poorly-drained soils. They reported that reducing conditions kept the iron oxides in the upper horizons in a readily extractable form. For the range of soils studied (Chernozemic, Solonetzic, Gray Wooded and Gleysolic) the well-drained members had "active" Fe ratios  $< 0.35$  in the upper horizons, whereas in the poorly-drained soils the ratio exceeded 0.35. In the freely-drained Ah 1 profile of the present study, 44% of the total Fe in the A horizon and 51% in the AB are oxalate-extractable (Figure 56). These horizons, then, must yield "active" Fe ratios in excess of 0.35, and it is likely that the upper horizons of I(o) 1 would yield a similar result. Thus the value proposed by Stonehouse and St Arnaud (1971) is likely to be applicable only to a restricted range of soils.

Alexander (1974) has investigated if "active" iron ratios showed any definite age trend, and demonstrated,

that for a sequence of eight well-drained Xerolls on adjacent terraces above the Truckee River in Nevada, under a subhumid climate, the ratio increased to 0.37 during the first several thousands of years of soil development, and then decreased to a practically constant value of 0.18 during several hundred thousand years. He concluded that although the ratio values were not sufficiently unequivocal to be used alone for placing associated Quaternary deposits in sequence, they could prove a useful supplement to other criteria. A similar age trend is also shown by the percentage of total Al and Fe removed by oxalate in the present study (Figures 53, 56 and 57). Here the decline after some 18,000 years is associated with the solution of allophanic gels by water-soluble organic chelates at low pH. The presence of amorphous, organically-complexed forms of Al and Fe in the older gley podzols prevents such a definite trend being observed for the percentage of total Al and Fe extracted by pyrophosphate (Figures 59, 62 and 63). Since doubt exists as to just what components are being extracted from differing systems by chemical reagents there may be some advantage in using one absolute term in so called "active" iron ratios. Such an approach was used by Ellis (1969) when he used the ratio of dithionite-extractable Fe to total Fe as an index of the degree of weathering under aerobic conditions.

McKeague, Brydon and Miles (1971) have stated that fractionation of the amorphous iron content of soils is necessary to distinguish between amorphous iron in

spodic horizons that is usually associated with organic matter, and that present in soils developed on volcanic ash and in some prominently mottled cambic horizons. Attempts to effect a similar fractionation are reported by the United States Department of Agriculture (1970). The latter work claims that pyrophosphate at pH 10 seems to remove Al and Fe from amorphous organic complexes more readily than from other amorphous species, whereas other extractants, such as oxalate, pyrophosphate at low pH and citrate-dithionite, are less selective of the amorphous compounds that are typical of spodic horizons. McKeague and his co-workers claimed, however, that although pyrophosphate is reasonably specific for organic-complexed forms of Fe, it is less specific for these forms of Al. Much of the available research on these reagents has involved extractions of synthetic organic complexes with Al and Fe, and of both synthetic and natural oxides and hydrous oxides. It is clearly desirable that the reagents should be tested on a wide range of soils, and that differential techniques such as those described in this section be applied in an effort to determine the components extracted by each reagent from actual soils.

Furkert and Fieldes (1968) have claimed that the amorphous component in spodic B horizons is allophanic, and Brydon and Shimoda (1972) have demonstrated that the major portion of the clay fraction of the B horizon of a podzol from Nova Scotia contained an amorphous component that had many properties similar to those reported for

allophane. Although they also found a substantial 'free' iron content (45% oxalate-extractable, 10% pyrophosphate-extractable) they were unable to determine its precise nature. They found no evidence that it was structurally bound to the allophane as has been proposed by Jackson (1965) and concluded by Raman and Mortland (1969/1970). In the present study considerable quantities of Al and Fe are extracted from the water-dispersed  $<2 \mu\text{m}$  fraction of the  $B_{21}$  and  $C_{12}$  horizons of Ah 1 (Table 46). These fractions also gave very high values for phosphate retention and for the Fieldes and Perrott test. It is likely that they too contain allophanic gels.

Morphologically the Ikamatua and Ahaura B horizons resemble cambic horizons. They contain high contents of both oxalate- and pyrophosphate-extractable Al and Fe species. Ratios of pyrophosphate-extractable Al + Fe to clay content, and the index of accumulation of amorphous material in spodic horizons:  $(\text{CEC} - 0.5\% \text{ clay})$  multiplied by horizon depth (United States Department of Agriculture, 1970) were calculated to see if these horizons could qualify as spodic horizons on the basis of their amorphous content. These data together with oxalate-extractable Al and Fe to clay ratios are presented in Tables 47 - 49. The horizons that meet the criteria of an index value  $> 90$ , and a ratio of % pyrophosphate-extractable  $(\text{Al} + \text{Fe}) / \% \text{ Clay} > 0.2$  are the A horizon of I(o) 1, the AB horizon of Ah 1, Ah 2 and Ah 3, the  $A_2$  horizon of Ah 4, the  $B_{21}$  horizon of Ah 5, and Ah 6, the  $B_1$  horizon of Ah 8 and the AB horizon of Ah 9.

The general tendency for % oxalate-extractable Al (and Fe) / % clay values of the well-drained members of the sequence to be greater in the B and C than in the A horizons ( Table 47) indicates that amorphous inorganic gels are accumulating faster than clay in the lower horizons. Possible explanations for this observed trend would include inhibition of gel formation in upper horizons, downward translocation of gels in colloid form, formation of gels at a faster rate than clay in lower horizons and destruction of gels in the upper horizons. The ratios of oxalate-extractable to pyrophosphate-extractable Al and Fe to constant profile depth (Table 50) indicate an increasing relative importance of inorganic, amorphous Al to I(o) 1, followed by a decline in its importance relative to amorphous organic-complexed forms in the older soils. Amorphous, inorganic Fe declines in importance in soils older than Ah 1. These results can be interpreted as indicating the eventual solution of inorganic, amorphous gels by water-soluble chelates, and the conversion of Al and Fe to organic-complexed amorphous species. The lower ratios obtained for the Fe extractions may result from differences in the stability constants of the respective Al and Fe organic complexes. Those of Fe complexes increase as pH falls, whereas those of Al fall (Townsend and Aguilar, 1971).

The analyses performed on the Taupo sandy silt warrant further comment even although this soil did not form part of the Reefton chronosequence. The Taupo soil,

unlike the chronosequence soils, is formed on pyroclastic materials. The United States Department of Agriculture in the publication 'Soil Taxonomy' (1970) considers that the amorphous materials present in spodic horizons (organic-complexed forms of Al and Fe, extracted by pyrophosphate at pH 10) differ from the inorganic, allophanic gels (oxalate-extractable) formed in pyroclastic materials. The ratios of oxalate- to pyrophosphate-extractable Al (and Fe) are certainly higher for the Taupo soil, than for any of the chronosequence samples, but it should be considered that factors other than parent material could contribute to such differences. The rainfall at the Taupo site (1270 mm) is considerably lower, the pH (6.2 - 6.6) much higher, and the age of the soil is but 1700 years. The present vegetation at the Taupo site is tussock, cocksfoot, and bracken fern, but the area carried podocarp forest prior to Polynesian fires (N.Z. Soil Bureau, 1968b).

The most striking feature evident from the analyses performed on the Taupo samples (Tables 44 and 45) is the marked differences in chemical properties between the clay fractions and the coarser material. The Al and Fe extracted from the soil by oxalate and by pyrophosphate came essentially from the clay fractions, and these form less than 2% of the material that could be dispersed by repeated sedimentation in distilled water, or by mechanical analysis following dispersion with Calgon. Phosphate retention and Fieldes and Perrott test values were also



determined by the reactivity of the clay fractions. Total Al and Fe increased considerably with reduction in particle size, while total Si and K decreased. The fine clay fractions thus yielded molar  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios between 1 and 2 while those of the 2 - 53  $\mu\text{m}$  fraction exceeded 8.

When considered in conjunction with these chemical parameters the DTA's (Figure 66) provide further evidence in support of the soil allophane model proposed by van Reeuwijk and de Villiers (1970). Only the two fine clay fractions, with  $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3 + \text{SiO}_2$  ratios of 56% (B horizon) and 47% (C horizon) yield any appreciable high temperature exothermic reaction. The 2 - 53  $\mu\text{m}$  fraction of both horizons, and even the 0.2 - 2.0  $\mu\text{m}$  fraction from the C horizon, do not show this reaction. These samples all have  $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3 + \text{SiO}_2$  ratios  $< 22\%$ . The 0.2 - 2.0  $\mu\text{m}$  fraction from the B horizon (ratio of 33%) shows a considerably reduced reaction. Van Reeuwijk and de Villiers (1970) have demonstrated that the reaction is given by co-precipitated aluminosilicate gels with  $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3 + \text{SiO}_2$  ratios of 45, 60 and 80%, but not by gels with ratios  $\leq 30\%$ . These results indicate that a composition somewhere between 30 and 45%  $\text{Al}_2\text{O}_3$  is necessary before the reaction is initiated. As it is likely that isolation of the various size fractions of the Taupo soil was incomplete, the 0.2 - 2.0  $\mu\text{m}$  fraction from the B horizon could well contain  $< 0.2 \mu\text{m}$  material with a higher  $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3 + \text{SiO}_2$  ratio.

The high loss-on-ignition values from the  $<0.2 \mu\text{m}$  fractions indicate a close association between the inorganic and organic components. The suppression of the exothermic reaction when DTA's are carried out in a dynamic  $\text{N}_2$  atmosphere also suggests a strong link exists between allophane and organic matter. Such bonding could also result in finer, more aluminous gels being incorporated into a larger size fraction. Both Miyauchi and Aomine (1964) and Campbell, Mitchell and Bracewell (1968) have demonstrated an increase in the intensity of this exotherm with decreasing particle size, but unfortunately neither group determined the chemical compositions of their size separates. The exothermic reaction, which leads to the formation of mullite, spinels and  $\gamma$ -alumina thus occurs with both co-precipitated aluminosilicate gels, and with natural allophanic soils. Wahl, Grim and Graf (1961) have shown that the formation of mullite from synthetic mixtures depends on the structures of the components rather than on the chemical composition of the mixture. It has been demonstrated (Mr A.W. Young, Soil Science Department, Lincoln College, pers. comm.) that a co-precipitated aluminosilicate gel containing 45%  $\text{Al}_2\text{O}_3$  yields mullite between 900 and 1000°C, whereas mixtures containing the same quantities of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  as discrete amorphous phases do not. This implies that some structural association must exist between Al and Si before nucleation of mullite occurs at these

temperatures, and that this relationship exists in both synthetic aluminosilicate gels and in soil allophanes.

The DTA pattern for the  $< 0.2 \mu\text{m}$  fraction, and to a lesser extent of the  $0.2 - 2.0 \mu\text{m}$  fraction of the Taupo B horizon show an unexpected suppression of the high temperature exotherm, and a strong endothermic reaction between  $800$  and  $1000^{\circ}\text{C}$  when run in a dynamic  $\text{N}_2$  atmosphere (Figure 66). When the sample was heated in air or  $\text{O}_2$  to  $600^{\circ}\text{C}$ , cooled to room temperature,  $10 \text{ mg}$  of activated charcoal added, and re-run in a  $\text{N}_2$  atmosphere a strong exothermic reaction was observed. The original sample run in an air or  $\text{O}_2$  atmosphere gave a much lower reaction, a feature previously noted by Campbell, Mitchell and Bracewell (1968). This earlier work had also shown that charcoal appeared to have a catalytic effect on the formation of mullite. The only explanations that can be offered for the suppression of the exotherm in the  $< 0.2 \mu\text{m}$  fraction from the B horizon of the Taupo soil when run in  $\text{N}_2$  are that either unexpectedly strong bonds exist between the allophanic gel and organic matter, which heating to  $900^{\circ}\text{C}$  has not completely disrupted, or that the organic matter content was so high, and so intimately distributed throughout the sample, that the charcoal formed on heating in the  $\text{N}_2$  atmosphere coated the aluminosilicate particles to such an extent that nucleation of mullite was prevented.

Mr Young (pers. comm.) has also found that the broad infrared absorption band near  $1000 \text{ cm}^{-1}$  decreased in frequency with decreasing particle size for the size

separates from the Taupo B and C horizons. This indicates an increase in Al-O-Si bonding relative to Si-O-Si with decreasing particle size. For the same samples Mr L.G. Livingstone (Soil Science Department, Lincoln College, pers. comm.) has demonstrated shifts in the wavelength of  $AlK\beta$  radiation with decreasing particle size. This suggests that the proportion of the Al that is in six-fold co-ordination increases with decreasing particle size, and consequently with an increase in the  $Al_2O_3$  content.

It is concluded from the above data that the finest material present in the B and C horizons of the Taupo sandy silt is a chemically-precipitated aluminosilicate gel, not merely comminuted parent material. This conclusion is supported by the variations in total K with decreasing particle size and could be further tested by determining trace element levels of the various size separates, a technique that has been applied by Borchardt, Harward and Knox (1971).

The chemical properties of precipitated gels would depend largely on their alumina content. This in turn would be a function of parent material and other soil forming factors. Such gels, particularly if they contained appreciable amounts of Al as six-fold coordinated hydroxyalumina, may well be more reactive than comminution products or weathering residues of similar particle size, where the Al would largely remain in four-fold co-ordination. Both precipitated gels and comminuted materials could exist in the same soil. As a

precipitated weathering product, the gel should be in equilibrium with its environment and tend to persist providing there were no drastic changes within the system. Comminution products and weathering residues, however, are likely to be unstable and be reacting with the same environment. Their rate of reaction should increase as their particle size decreases, unless they are stabilised by surface coatings of hydrous oxides or by forming complexes with organic matter. Thus in environments favouring their formation, precipitated gels should tend to dominate in the finest fractions.

The infrared absorption patterns for the  $< 0.2 \mu\text{m}$  fractions of a sequence of volcanic ash soils of increasing age (Fieldes and Furkert, 1966) show changes in frequency with increasing age. This trend is consistent with an increase in the  $\text{Al}_2\text{O}_3$  content of precipitated gel systems, and implies higher Al levels in the matrix solutions with increasing soil age. As the solubility of alumina increases relative to silica at lower pH (Curtis, 1970) a decrease in pH as weathering progressed could provide these conditions.

Thus soils having the properties of allophane B may contain in addition to comminuted parent materials, silica gels and co-precipitated aluminosilicate gels, where Al was present largely within a tetrahedral silica framework. Soils with the properties of allophane A, on the other hand, would need to contain aluminosilicate gels with a polymeric hydroxyalumina phase. In an effort to fully

explain the differences observed in New Zealand volcanic ash soils of increasing age work with both synthetic and natural systems should be undertaken to establish what reactions take place if more siliceous gels are introduced into matrix solutions that would be in equilibrium with gels having a higher alumina content. The limits of gel formation in terms of Al and Si concentrations at pH values  $<6$  should also be established.

Bracewell, Campbell and Mitchell (1970) have shown that the  $\text{Al}_2\text{O}_3$  content of the water-dispersed  $<1.4 \mu\text{m}$  fractions of the three youngest soils of the sequence examined by Fieldes and Furkert (1966) increased with the age of the soil. They also obtained a high temperature exothermic reaction from all three soils on DTA examination of the  $<1.4 \mu\text{m}$  fraction in a  $\text{N}_2$  atmosphere, although that given by the youngest soils was slight: Fieldes and Furkert (1966) did not present DTA data, but the soils were so examined by Fieldes (1955), who failed to obtain a reaction from the two youngest members of the sequence. The samples used by Fieldes were peroxidised and then dispersed at a pH of 10.5. Campbell, Mitchell and Bracewell (1968) have shown that both of these treatments tend to reduce the height of the exothermic peak.

Further studies should be undertaken to determine if an age sequence of volcanic ash soils contains gel systems of increasing  $\text{Al}_2\text{O}_3$  content. In addition to chemical and physical examination of a range of size separates the pH and Al and Si contents of the matrix solutions should be determined.

## V. MINERALOGICAL ANALYSES

In this section the mineralogy of the sand ( $> 20 \mu\text{m}$ ), silt ( $20 - 2 \mu\text{m}$ ), coarse clay ( $2 - 0.2 \mu\text{m}$ ) and fine clay ( $< 0.2 \mu\text{m}$ ) fractions is discussed. Unless otherwise stated organic matter and free iron oxides and hydrous oxides were removed by the methods described by Jackson (1956) prior to size fractionation.

### (1) Mineralogy of the Sand Fraction

In an attempt to assess the uniformity of the parent material throughout the chronosequence, the mineralogical compositions of a narrow size range ( $177 - 125 \mu\text{m}$ ) from the C horizon of each soil, and from the A horizon of each gley podzol, was determined using a polarising microscope. To facilitate identification of minerals other than quartz and feldspar, samples were further subdivided into magnetic and non-magnetic fractions using a Frantz isodynamic magnetic separator operating at a current of 1.2 amp, and set with side slope of  $5^\circ$  and forward slope of  $30^\circ$ . Slides for mineralogical determination were prepared by immersing the separated grains in clove oil. A minimum of 250 grains from each slide were examined. The results of these analyses presented as weighted means, are listed in Table 51.

The mineral grains showed increasing alteration with time. This made positive identification difficult and some two-thirds of the grains from the A horizon of the oldest soil (Ok 1) were listed as unidentified. The

proportion of minerals appearing in the magnetic fraction, and the levels of mica and chlorite are much lower for the gley podzols than for the younger soils. The quartz/feldspar ratios for the C horizons (excepting I(o) 1) showed a general increase with time, while those for the A horizon of the Ku 1 and Ok 1 soils were considerably higher than the values from the corresponding C horizons. These results are consistent with the increased weathering of a parent material of similar mineralogical composition, and indicate that the surface horizons of both gley podzols have undergone more intensive weathering and leaching than the underlying C horizons. The discrepancy shown by I(o) 1 may be caused by a variation in the particle size distribution of the parent material. It is difficult to explain the comparatively high value for the proportion of magnetic minerals in the A horizon of Ok 1. With the exception of small numbers of biotite and garnet all the grains in this fraction were too altered to permit identification. Despite deferration and a very low total Fe content these weathered residues may have retained sufficient Fe to render them paramagnetic.

Biotite was the dominant mica identified in the size range examined. This was partly a consequence of its greater ease of identification when partly altered. Optical examination of coarser sand fractions showed that muscovite was the dominant mica mineral, and that its dominance was greatest in the gley podzols - the two oldest soils. Some of the grains listed as unidentified



in Table 51 are probably sericitic residues. The dominant feldspar was sodic plagioclase. Smaller amounts of potassium feldspar were present in all samples.

Visual and optical examination of weathered gravels from the C horizons of the younger soils showed that the feldspar appeared to be weathering at a faster rate than muscovite. This is consistent with the observed weathering sequence proposed by Goldich (1938), but differs from the order of weathering stability based on bond energies calculated by Keller (1954). The significance of this greater stability of muscovite on clay mineral genesis is discussed in Chapter 3; V, (3), (c).

## (2) Mineralogy of the Silt Fraction

Semi-quantitative analysis of the 20 - 2  $\mu$ m fraction was based on the intensity of diagnostic X-ray diffraction spacings from randomly-oriented specimens. Phyllosilicates present in minor amounts in the finer part of the size range were detected by the use of preferentially-oriented specimens. These were prepared by air-drying aqueous suspensions on 38 x 25 mm glass slides. The oriented specimens were prepared using the same cation and glycerol saturation procedures required for the analysis of the clay fractions.

The dominant minerals present in the silt fraction were quartz, sodic plagioclase, mica and chlorite. Smaller amounts of potassium feldspar, vermiculite, interstratified mica-vermiculite, kaolite, gibbsite and hornblende were also observed.

The quartz content increased with increasing age of the soil, and decreased with depth from the surface. In both gley podzols the silt fraction of all horizons (except Ku 1, C) was composed mainly of quartz. The feldspar content of the silt fraction increased during the first 18,000 years of soil development, but was very low in the Kumara and Okarito profiles. As with quartz, feldspar levels decreased with profile depth, but the variations were not as marked. Quartz/feldspar ratios, as indicated by the intensity of the quartz (100) spacing divided by that of the plagioclase (002) (Table 52) are comparable for soils younger than 18,000 years, but become much greater in the older gley podzols. The trends described here are similar to those observed by Mokma et al. (1973) for a chronosequence of soils in South Westland. The earlier fall in silt feldspar contents in this latter sequence is probably a function of the much higher rainfall in South Westland.

The mica content of the silt fraction decreased progressively with time, and increased with profile depth. Vermiculite (detected by a decrease in the intensity of the 1.4 nm spacing, and the enhancement of the 1.0 nm spacing following  $K^+$  saturation and heating at  $350^{\circ}C$ ), and interstratified mica-vermiculite (2.4 and 1.2 nm spacings on  $Mg^{2+}$  saturation) were present in all samples containing mica. Chlorite showed a similar trend to that described for mica, but was depleted more rapidly. Strong reflections from the first four orders of the basal

spacing (after allowing for any kaolinite present), and an increase in intensity of the 1.4 nm reflection on heating at 550°C indicate the presence of a well-ordered ferro-magnesian chlorite. This mineral would be largely responsible for the trioctahedral (060) spacings such as that illustrated in Figure 67. Chlorite was not found in the A horizon of Ah 1, or above the B<sub>3</sub>G horizons of Ku 1 and Ok 1. Resolution of its second order spacing from the fourth order spacings of chlorite and vermiculite showed the presence of small quantities of kaolinite in the A and B horizons of all soils. Small amounts of hornblende were found in all horizons of the Ahaura and younger soils. Examination of the (060) spacings (Figure 67) of the silt fraction from the assumed parent material (C horizon of Ho 1) showed that dioctahedral phyllosilicates were more abundant than trioctahedral.

Gibbsite was identified on the basis of the (002) spacing at 0.483 nm, the strongest reflection, which was destroyed on heating at 350°C. It was observed only in preferentially-oriented specimens and was not sufficiently abundant to enable other reflections to be detected for confirmation. Gibbsite was not detected in the Ho 1 and Ok 1 profiles, found only in the B<sub>2</sub> horizons of the three Ikamatua soils and in the C horizon of Ku 1, but was present in the B<sub>21</sub> and all lower horizons of Ah 1. The strongest reflection was given by the B<sub>3</sub> horizon of Ah 1. The occurrence of gibbsite in these soils is discussed in Chapter 3; V, (3), (c).

The only difference observed between I(w) 1 and I(o)1 was the lower mica and chlorite levels in the gleyed horizons of the former soil as compared with comparable depths in I(o) 1. No obvious trends occurred along the two Ahaura transects.

The considerable changes in mineralogy of the silt fraction with time are the resultant of gains from the physical breakdown of the minerals remaining in the coarser fractions, and losses by chemical weathering to the clay fraction. Such changes are influenced by the varying resistance to physical and chemical weathering of the different mineral species. The gradual dominance of both the sand and silt fractions by quartz indicates its greater comparable stability. The higher contents of mica and chlorite in the silt fraction of the younger soils of the sequences, as compared with the 177 - 125  $\mu\text{m}$  fraction, result from their susceptibility to mechanical comminution, whereas the decrease in their contents towards the soil surface is consistent with an increasing intensity of chemical weathering.

### (3) Mineralogy of the Clay Fraction

Clay fractions (coarse, 2 - 0.2  $\mu\text{m}$ ; fine, <0.2  $\mu\text{m}$ ) of the chronosequence and transect samples were separated from the soil (<2 mm) following peroxidation and deferration (Jackson, 1956). All samples were examined by X-ray diffraction and by DTA. To check if the minerals present were affected by the above chemical treatments, water-dispersed clay (<2  $\mu\text{m}$ ) from selected samples was

also examined. Concentration of resistant minerals, present in minor amounts, was attempted by digestion of 1 g samples of the water-dispersed clay with 20 and 48% HF for periods of up to 24 hours.

(a) Diagnostic Criteria for Clay Mineral

Identification. Identification of the crystalline mineral species present was based primarily on X-ray diffractometry. The diagnostic criteria applied are discussed below. Unless otherwise stated they refer to preferentially-oriented specimens. Where DTA was required to confirm a diagnosis, the criteria used are discussed in context.

(i) Micaceous clay minerals: These are recognised by a 1.0 nm basal spacing, and its integral series of higher order reflections, that do not shift on varying the exchangeable cation, with glycerol solvation, or upon heating at 550°C (MacEwan, 1946). Illite, originally defined by Grim, Bray and Bradley (1937), has tended to become widely used as a general name for micaceous minerals in the clay fraction of soils. However, the proposed classification scheme for phyllosilicates of the Nomenclature Committee of the AIPEA (Association International pour l'Etude des Argiles) (Bailey et al. 1971) has left open the status of illite (and of hydromica and sericite). The committee stated that

"it is not yet clear whether or at what level they would enter the (classification) table; many materials so designated may be interstratified".

Dioctahedral and trioctahedral species may be distinguished from each other by the position of the (060) reflection (0.149 to 0.152 nm for the former, and 0.152 to 0.1535 nm for the latter) and by the relative intensities of the first and second order basal reflections - the latter is almost absent in trioctahedral species (Brown, 1955).

(ii) Vermiculite: A 1.4 nm basal spacing on glycerol solvation of  $Mg^{2+}$  saturated clay, which collapses to give a sharp 1.0 nm spacing on  $K^+$  saturation and heating to 350°C, is used to indicate the presence of vermiculite. In contrast to chlorite, vermiculite has a very weak 0.7 nm reflection.

(iii) Montmorillonite: The presence of montmorillonite is indicated by a basal spacing of 1.8 nm in glycerol solvated,  $Mg^{2+}$  saturated clays. As with vermiculite this spacing collapses to 1.0 nm on  $K^+$  saturation and heating at 350°C. In this study glycerol solvation was carried out by lightly spraying air-dried specimens with a 10% aqueous solution of glycerol and allowing them to dry at room temperature. This procedure was repeated until the dried samples appeared translucent. Since it has been reported that some montmorillonite spacings do not expand beyond 1.4 nm if dried prior to the addition of glycerol (Jackson, 1956; and Fieldes, 1968), A horizon samples yielding 1.4 nm spacings were also examined using the solvation technique recommended by Jackson et al. (1954). Both techniques gave comparable results.

(iv) Chlorite: This group of minerals is recognised by an intergral series of peaks associated with a basal spacing of 1.4 nm, that show no expansion on glycerol solvation, or collapse when heated at 550°C. Heating at 550°C sharpens the first order spacing and increases its intensity, whereas the intensities of the higher order spacings decrease. The first and third order spacings of iron-rich chlorites are relatively weak compared with those of magnesium-rich species (Brown, 1955; and Brindley and Gillery, 1956), but this does not necessarily apply to chlorites occurring in the clay fraction of soils since defects produced by weathering may also influence the relative intensities of the individual reflections (Bradley, 1954).

(v) Kaolinite group minerals: Kaolinite is characterised by strong first and second order basal reflections at 0.715 and 0.36 nm, respectively, that show no expansion on glycerol solvation, but disappear on heating at 550°C, since at this temperature, the crystal structures of minerals of the kaolinite group are destroyed. Metahalloysite shows a broad basal spacing ranging from 0.72 - 0.75 nm, which is sharpened and reduced to 0.72 nm on heating at 350°C. Some halloysites show strong reflections at 1.0 nm. with no second order peak and a third order of about 0.34 nm. If dried at 110°C they show collapse to about 0.72 nm.

In the presence of chlorite, identification of kaolinite by X-ray diffraction may prove difficult, since

the second and fourth order reflections of the former tend to overlap the first and second order kaolinite spacings. When this occurs the presence of kaolinite is best confirmed by the use of infrared absorption spectroscopy, DTA, by the formation of intersalation complexes with potassium acetate (Andrew, Jackson and Wada, 1960), hydrazine (Wada and Yamada, 1968) or dimethyl-sulphoxide (Garcia and Camazano, 1968) which cause expansion of the kaolinite lattice but do not affect chlorite, or by digestion with 6 molar HCl for 30 minutes at 95°C (Hayashi and Oinuma, 1964), which eliminates chlorite, 2 : 1 - 2 : 2 Al-intergrades and vermiculite, but only partially dissolves kaolinite.

In the present study kaolinite second order reflections occurred at 0.358 nm. In all coarse clay, and in some fine clay specimens this peak was resolved from the fourth order reflections of 1.4 nm species which tended to occur at about 0.534 nm (Figure 68). Often, too, the first order kaolinite spacing at 0.76 nm was resolved from their second order reflections. The presence of kaolinite was, however, always confirmed by DTA, and with selected samples, by HCl digestion (e.g. Figure 68).

(vi) Interstratified minerals: Differential weathering of individual layers of the various phyllosilicate minerals described above leads to the formation of interstratified clay minerals. These intergrades contain



layers of two or more different components. If these occur with a fixed periodicity a regularly interstratified mineral occurs. Such minerals show first order basal spacings corresponding to the sum of the basal spacings of the individual components, and yield an integral series of higher order reflections. The intensities of these reflections tend to be strongest near the basal reflections of the component layers. In contrast the first order spacing of randomly - interstratified minerals is intermediate between those of the individual components and the higher order reflections form non-integral series (MacEwan, Ruiz Amil and Brown, 1961). In theory, all transitions between regularly-and randomly-interstratified minerals are possible. The diagnostic criteria of the mixed-layer minerals observed in this study are as follows:

2 : 1 - 2 : 2 Al-intergrade (or pedogenic chlorite or chloritised vermiculite): These intergrades are characterised by a sharp, high intensity, 1.4 nm reflection that gradually collapses towards 1.0 nm on heating to progressively higher temperatures (Dixon and Jackson, 1962). Complete collapse to a sharp 1.0 nm spacing does not occur on heating, nor does the 1.4 nm reflection intensify. The properties of the intergrade are therefore intermediate between those of vermiculite and chlorite, and its resistance to collapse on heating results from the presence of hydroxyalumina polymers in the interlayer spaces.

The New Zealand Soil Bureau recognises two forms of vermiculite in soils, vermiculite (2) which collapses to 1.0 nm at room temperature on  $K^+$  saturation, and vermiculite (1) which collapses

to 1.0 nm only on heating at 550°C (Fieldes, 1968). Unfortunately Fieldes does not indicate whether the collapse of vermiculite (1) yields a sharp 1.0 nm spacing, or merely a broad low intensity band approaching 1.0 nm, but it appears likely that vermiculite (1) is a 2 : 1 - 2 : 2 Al-intergrade.

A similar intergrade with properties intermediate between those of montmorillonite and chlorite also occurs.

Mica-vermiculite: This type of interstratification is characterised by a reflection between 1.0 and 1.4 nm on  $Mg^{2+}$  saturation and glycerol solvation, which collapses to give a sharp 1.0 nm spacing on  $K^+$  saturation and heating at 350°C. The presence of a reflection about 2.4 nm on glycerol solvation indicates some regularity in the interstratification.

Mica-chlorite: These intergrades show a spacing between 1.0 and 1.4 nm that is not affected by glycerol solvation, or by heating at 550°C.

Interstratified montmorillonite: Peak migration curves for random interstratifications of 1.0 and 1.75 nm layers (MacEwan, Ruiz Amil and Brown, 1961; and Ruiz Amil, Garcia and MacEwan, 1967) indicate that changes in the relative proportions of the two components do not significantly alter the position of the 1.8 nm spacing. The major variation is in the intensity of the peak. This means that the 1.8 nm spacing in a diffractogram could be due to an interstratified montmorillonite-mica.

Estimating the degree of interstratification (if any) is usually based on the position of the 001 (1.0 nm)/002 (1.8 nm) peak which migrates between 0.885 and 1.00 nm as the mica content increases. Other higher order peaks may also be used, but these are often of lower intensity and/or overlapped by peaks from other components.

Mills and Zwarich (1972) postulate, however, that as overlapping peaks are not resolved if the spacing between them is less than the width at half peak height of the individual peaks, fine clay fractions containing discrete mica and montmorillonite could be wrongly interpreted as containing an interstratified mineral. They suggest that the apparent position of the broad peak caused by the unresolved first order mica and second order montmorillonite peaks in mixtures of the discrete minerals would also vary with changes in the relative concentrations of the two components, and thus cause the diffractograms to resemble those of interstratified minerals. They conclude that in the absence of definite evidence of interstratification it is advisable to consider the sample as a mixture of two discrete species.

The presence of a 2.8 nm spacing in  $\text{Mg}^{2+}$  saturated, glycerol solvated specimens from the  $A_2$  horizons of some soils from the present study does, however, indicate an interstratified mica-montmorillonite. Examples of interstratified montmorillonite-vermiculite were observed in other surface horizons. These samples showed expansion to between 1.4 and 1.8 nm on  $\text{Mg}^{2+}$  saturation and glycerol solvation, while  $\text{K}^+$  saturated specimens yielded a sharp 1.0 nm peak on heating at  $350^\circ\text{C}$ . Other samples, which gave a broad, low intensity band with one or two maxima in the range 1.0 to 1.4 nm for  $\text{K}^+$  saturated specimens, collapsed to a strong sharp 1.0 nm spacing when heated at  $350^\circ\text{C}$ , and showed expansion to

larger spacings and the appearance of a 1.0 nm peak on  $Mg^{2+}$  saturation and glycerol solvation, probably contained three component, mica-vermiculite-montmorillonite, interstratified clays.

(vii) Quartz: Identification of quartz in X-ray diffractograms of soil clays is usually based on the (100) spacing at 0.426 nm, since the more intense (101) reflection at 0.3343 nm nearly coincides with the strong third order reflection of micaceous minerals.

(viii) Gibbsite: Crystalline gibbsite is recognised by the presence of the (100) spacing at 0.485 nm. In the present study no other spacings could be obtained for confirmation and its presence was always checked by DTA. The 0.485 nm spacing was destroyed on heating at 350°C.

(ix) Feldspars: Small quantities of plagioclase and potassium feldspars in soil clays are usually recognised by spacings between 0.318 and 0.324 nm (Jackson, 1956 and 1964).

(x) Amphiboles: Most amphiboles have a (110) plane that coincides with their perfect cleavage plane. This yields a reflection between 0.840 and 0.848 nm that can be used to indicate the presence of amphiboles in preferentially-oriented specimens (Jackson, 1956 and 1964).

(xi) Titanium oxides: These minerals were identified in randomly-oriented specimens following HF digestion. The presence of rutile was indicated by reflections at 0.326 (110), 0.249 (101), 0.230 (200), 0.219 (111),

0.205 (210), and 0.1687 nm (211), and anatase by spacings at 0.351 (101), 0.238 (004), 0.189 (200), 0.170 (105) and 0.1665 nm (211).

(xii) Plumbogummite minerals: Minerals of this group show spacings near 0.574, 0.352, 0.296, 0.270, 0.252, 0.221, 0.218, 0.190 and 0.175 nm. The identification of these minerals in HF digestion residues using the method proposed by Sarma and Krishna Murti (1969/1970) encountered difficulties associated with the solution of the minerals and the precipitation of complex fluorides having X-ray diffraction patterns that could be confused with those of the phosphates. This aspect of the results is discussed in detail in Chapter 3; V, (4).

(xiii) Goethite: Crystalline goethite is recognised by spacings at 0.497, 0.418, 0.270, 0.258 and 0.244 nm.

(b) Quantitative Analysis of Soil Clays. In the qualitative identification of clay minerals by X-ray diffraction the positions of the various basal reflections and their alteration or otherwise under different treatments is evaluated. For this purpose preferred orientation along the basal planes is desired. For the quantitative analysis of mixtures, however, the (hkl) reflections from randomly-oriented samples should be measured. If mixtures for analysis contain essentially monomineralic components, and these pure components are also available for calibration purposes it is possible to obtain a high

degree of accuracy by this method (Hofmann, 1956; Mitchell, 1960; and MacKenzie, 1961). The clay minerals found in soils show variations in particle size and in their degree of crystallinity, changes in chemical composition within individual mineral groups, interstratification, and contamination with organic matter and amorphous substances. Quantitative analysis by X-ray diffraction becomes rather uncertain for such systems as it is not possible to refer the (hkl) reflections to known standards (Grim, Bradley and White, 1957; and Weaver, 1958) and it has become customary to utilise the intensities of the basal spacings for both semi-quantitative and qualitative determinations.

The intensities of the characteristic X-ray diffraction spacings of minerals can not be used directly as indicative of their concentrations because of variations between diffractograms caused by instrumental (e.g. width of divergence, receiving, and scatter slits) and sample (e.g. thickness, and degree of preferred orientation) parameters. In addition, different minerals, different planes of atoms within a mineral, and different samples of the same mineral, may vary in the intensity with which they diffract X-rays. Iron-rich chlorites for example, give less intense 1.4 nm reflections than magnesium-rich varieties (Brown, 1955; and Brindley and Gillery, 1956). The intensities of chlorite spacings thus depend on mineral composition as well as concentration.

Useful comparisons and indications of trends may be obtained, however, by utilising intensity ratios based

on diagnostic peak areas. Since these ratios yield information on only two of the minerals in a sample, and because any observed variations may be caused by changes in the concentration of one or of both components, it is desirable that the concentration of each mineral be expressed as a part of the total mineral concentration. This has been achieved in the present study using an approach similar to that of Johns, Grim and Bradley (1954), in which the "percentage" of each phyllosilicate component is obtained from weighted intensities. To obtain such "percentages" it is necessary to assume that the properties of each mineral do not vary between samples, that the weighting factor for each mineral applies equally to all particles of that mineral in all the samples compared, and that the sum of the weighted (peak-area) intensities represents the total composition of the sample.

The diagnostic peak areas considered were:

- (i) Illite (mica):- area of the 1.0nm reflection ( $\text{Mg}^{2+}$  saturated, glycerol solvated slide).
- (ii) Montmorillonite:- area of the 1.8 nm reflection ( $\text{Mg}^{2+}$ /glycerol).
- (iii) Chlorite:- area of the 1.4 nm reflection ( $\text{K}^+$ /550°C).
- (iv) Vermiculite:- area of the 1.4 nm reflection ( $\text{Mg}^{2+}$ /glycerol) minus the area of the same reflection following  $\text{K}^+$  saturation at 20°C.
- (v) Kaolinite:- area of the 0.7 nm reflection ( $\text{K}^+$ /350°C) multiplied by the proportion of kaolinite in the resolved 0.35 nm

kaolinite second order/chlorite fourth order doublet. The justification for this has been demonstrated by Biscaye (1964).

- (vi) Pedogenic chlorite:- area of the 1.4 nm reflection ( $K^+$ /20°C) minus the area of the same reflection after heating at 550°C.
- (vii) Interstratified Illite-Vermiculite:- area of the 1.2 nm reflection ( $Mg^{2+}$ /glycerol) minus the area of the same reflection after  $K^+$  saturation.
- (viii) Interstratified Illite-Chlorite:- area of the 1.2 nm reflection ( $K^+$ /550°C).

Peak areas were obtained by the technique described by Schultz (1964). Some difficulty was encountered in estimating the intensity of kaolinite in fine clay specimens containing both kaolinite and chlorite in which the 0.35 nm doublet was unresolved. In these instances the chlorite contribution to the 0.7 nm spacing was estimated on the assumption that the chlorite first order: second order peak area ratio was similar for both the fine and coarse clay fractions. Some samples containing interstratified minerals yielded very broad, low intensity bands between 1.0 and 1.8 nm, that collapsed to sharp 1.0 nm peaks on  $K^+$  saturation followed by heating at 350°C. The concentration of these minerals was determined from the area of the 1.0 nm peak at 350°C. If a discrete 2 : 1 - Type phyllosilicate was also present it was assumed that the contributions of that mineral and of the



intergrade to the 1.0 nm peak were additive and linear.

The measured intensities were weighted because diffraction intensity is dependent on the angle of reflection. Since reflections at lower angles of incidence give stronger peaks of greater intensity than reflections at higher angles, application of factors which compensate for this should make direct comparison of peak areas more reasonable. Although this type of analysis is crude by comparison with situations able to utilise random specimens and reliable standards, it is reasonably sound in its approach, and for poorly-crystalline materials Brindley (1961) considers that it is probably the best that can be devised. It must be stressed that the weighted peak-area "percentages" obtained are constructions and should be considered as unverifiable approximations of actual percentages. The factors used to weight the measured peak-areas are discussed below.

Johns, Grim and Bradley (1954) have shown that at 1.7 nm the reflected intensity of an expanding 2 : 1- Type phyllosilicate is four times that exhibited by the same mineral at 1.0 nm, while Bradley (1953) has further indicated that the reflections at 1.4 and 1.2 nm also exceed those at 1.0 nm, by factors of three and two, respectively. The measured intensity of illite was, therefore, used as reference, and those of montmorillonite, vermiculite and interstratified illite-vermiculite reduced accordingly. The 1.4 nm chlorite reflection in

ignited specimens has been shown to be comparable to the illite 1.0 nm reflection (Weaver, 1958). The measured intensities of chlorite and interstratified illite-chlorite were, therefore, not adjusted. Schultz (1958) has shown that the peak-area ratio of the 0.7 nm kaolinite reflection and the 1.0 nm reflection of collapsed 2 : 1 - Type phyllosilicates ranges from 1 : 1 for poorly-crystalline kaolinite, to 2 : 1 for highly-crystalline varieties. An indication of the degree of crystallinity of kaolinite can be obtained from the area : height ratio of the 0.7 nm spacing (Schultz, 1958), but the presence of chlorite interferes. Digestion with HCl to remove chlorite was not attempted as this could possibly attack any poorly-ordered kaolinite present, and an intermediate value for the ratio of 1.5 : 1.0 was used for weighting purposes. Pedogenic chlorite can vary in composition from approaching vermiculite to that of a dioctahedral Al-chlorite. This mineral has been weighted as a vermiculite in all samples. Consequently its "percentage" will tend to be underestimated in samples where the degree of hydroxyalumina interlayering is extensive.

Weighted peak area "percentages" for the phyllosilicates present in the clay fractions of the chronosequence and transect soils are listed in Tables 53 to 58. Also indicated in these tables are the relative intensities of the quartz (100) spacing and the presence of feldspars and hornblende. Quartz intensities are

expressed as percentages of the highest value measured, that of the coarse clay fraction of the A horizon of the Okarito soil.

Differential thermal analysis is recognised as a highly quantitative and reproducible technique for the estimation of gibbsite (de Villiers, 1969; and Davis and Holdridge, 1969). It was used in the present study to determine gibbsite levels in the clay fractions isolated from the chronosequence soils (Figures 69 - 76). The gibbsite used as reference came from nodules found in the subsoil of the Waiotu friable clay. These were ground to pass a 53  $\mu\text{m}$  sieve and air-dried at 105°C before weighing. X-ray, differential thermal and infrared analyses failed to detect any contamination. As the main gibbsite exotherm is not appreciably affected by particle size variation (MacKenzie, 1957) a single reference plot of peak area v concentration (Figure 77) was used for all size fractions. The results obtained are included in Tables 53 - 58.

An alternative approach to quantitative mineralogical analysis of soil clays has been devised by Alexiades and Jackson (1966b). Their system combines selective dissolution methods developed earlier for the determination of mica, quartz and feldspar (Kiely and Jackson, 1965), amorphous aluminosilicates, gibbsite and 1 : 1 -Type phyllosilicates (Hashimoto and Jackson, 1960), anatase and rutile (Raman and Jackson, 1965), cation exchange capacity measurements for the determination of vermiculite

and montmorillonite (Alexiades and Jackson, 1965) and thermal analyses to determine chlorite (Alexiades and Jackson, 1966a) into a single unified scheme. Their scheme has found application outside the authors' laboratories (e.g. Le Roux, 1973; and Murali, Sarma and Krishna Murti, 1974), but has yet to achieve widespread routine application.

It was considered that satisfactory application of the scheme to the present study was hampered by a number of factors which could affect its accuracy. The differential DTA techniques, already discussed in Chapter 3; IV, (3)., showed that treatment with boiling 0.5 molar NaOH (Hashimoto and Jackson, 1960) removed crystalline gibbsite and phyllosilicates from the yellow-brown earths. Use of this reagent would thus lead to the levels of the dissolved minerals being underestimated, and the quantities of amorphous aluminosilicates grossly overestimated.

Niederbudde (1973) has reported significant positive correlations between the amount of potassium fixed and the quantity of beidellitic smectite, as estimated from the intensity of the 1.8 nm spacing, for a range of soils and sediments from loessial districts in Central Germany and Lower Bavaria. No significant relationship existed between fixed potassium and vermiculite contents. An estimation of vermiculite content, based on potassium fixation, of these soils would include the smectite. With muscovite the dominant mica in the present study area,

the possibility of the montmorillonite mineral formed by pedogenesis belonging to the montmorillonite-beidellite series must be considered. Ross and Mortland (1966) have shown that beidellite was formed in the  $A_2$  horizons of spodosols, by the removal, through weathering, of the interlayer material in a 2 : 1 - 2 : 2 Al-intergrade. Smectites with layer charge arising predominantly from tetrahedral substitution of Al for Si have their main dehydroxylation peak in the  $500^{\circ}\text{C}$  region when examined by DTA, whereas that of montmorillonite itself usually occurs about  $700^{\circ}\text{C}$  (Greene - Kelly, 1957). Differential thermograms (Figures 71 - 75) for clay fractions that contain appreciable smectite (Tables 53 - 58) show dehydroxylation peaks in the  $500 - 550^{\circ}\text{C}$  region, but no peaks about  $700^{\circ}\text{C}$ . The presence of structural defects can, however, cause a reduction in the dehydroxylation peak temperature of well-defined montmorillonites (Grim and Bradley, 1948; and Greene-Kelly, 1957).

The presence in the A and upper B horizons of the yellow-brown earth members of the sequence of considerable organic matter (as characterised by intense DTA exotherms stretching from 200 to  $700^{\circ}\text{C}$  — peak temperatures  $300 - 350^{\circ}\text{C}$  — when run in an oxidising atmosphere) that is not removed by exhaustive digestion with  $\text{H}_2\text{O}_2$  could also interfere with mineral determinations based on CEC measurements. Other criticisms of the method are that it assumes a fixed value for the CEC of all vermiculites, and that hydroxy-Al interlayers in pedogenic chlorite may

prevent potassium fixation by preventing interlayer collapse or by denying access to ions.

Because of possible errors caused by the above factors it was decided not to apply the scheme in the present study, and to rely on the use of the weighted peak—area "percentages" to determine trends in clay mineralogical composition.

(c) The Ahaura Transects. The clay mineralogy of the transect soils is considered first, since it gives a particularly clear insight into the competing processes that control the clay mineralogy of the soils of the sequence.

(i) At site Ah 1: At Ah 1, the maximum sampled distance from either of the two living beech trees, or the decaying beech stump, the dominant minerals present in both the fine (Table 53) and coarse (Table 54) clay fractions are mica, chlorite, vermiculite, pedogenic chlorite and kaolinite. Minor amounts of gibbsite (determined quantitatively by DTA), quartz, feldspar and an amphibole were present in the coarse clay fraction; but only the first named was observed in the fine clay.

Kaolinite levels in the clay fractions, as determined by weighted peak-area "percentages", showed little variation with profile depth. This was confirmed by DTA (Figure 73). Comparison of the peak areas for kaolinite dehydroxylation from these thermograms with standard curves containing known additions of kaolinite showed agreement with the 10-20% levels obtained by the X-ray

technique. It should be remembered, however, that the amounts of the various clay minerals present in individual soil horizons also depend on the clay contents of those horizons. An attempt to show absolute trends, with both profile depth and increasing soil age, is shown in Table 55. To construct this table the weighted peak-area "percentages" presented in Tables 53 and 54 are multiplied by the relevant clay contents (Table 7) and summed. These values show comparable amounts of kaolinite in the Ahaura A and B horizons, with lesser amounts in the coarser textured C horizons. Table 55 makes no allowance for the presence of "clay" minerals in the silt fraction.

The exothermic peak between 900 and 1000°C shown by the fine clays (Figure 73) is too large to be explained solely in terms of the kaolinite content, but the coarse clay fractions show little evidence of this peak. Its loss is unlikely to be related to particle size, or to the degree of order of the kaolinite. Although the presence of a high level of organic matter has been shown to suppress the equivalent reaction in an allophanic material (Figure 66), and the Ahaura clay fractions do retain peroxide-resistant organic matter even in the lower horizons, this is not likely to be responsible, since the fine clay fraction retains the higher amount and the organic matter is more likely to be associated with components other than kaolinite. Saunders and Giedroyc (1950) have shown that iron compounds may completely suppress the peak, but the samples used were deferrated.

Mica is found only in the lower horizons, vermiculite increases both in concentration and amount towards the surface, whereas chlorite and pedogenic chlorite are most abundant in the upper part of the B horizon. The method used to differentiate between primary and pedogenic forms of chlorite in this study would tend to overestimate the former at the expense of the latter, if the hydroxyalumina interlayers developed during pedogenesis contributed to the intensity of the 1.4 nm spacing at 550°C. The horizons with the highest content of pedogenic chlorite, the B<sub>21</sub> and B<sub>22</sub>, are also the horizons where the highest percentage of total soil Al is oxalate-extractable (Figure 56). The increase in vermiculite towards the surface, the particularly high levels in both size fractions from the A and AB horizons, and its persistence to greater depth in the coarser clay fraction are confirmed by variations in the low-temperature endothermic peak system of the differential thermograms (Figure 73).

Since weathering intensity decreases with depth the maximum accumulation of the intergrade, pedogenic chlorite, might be expected to occur at the surface as reported by Rich (1968). However, the combination of low pH and high organic matter content of the A horizon may have prevented or inhibited intergrade formation, or may have caused the dealumination of an intergrade formed at an earlier stage of soil development. Studies by Heller-Kallai, Yariv and Riemer (1973) have suggested



that sorption of organic materials by clays rather than impeding chloritisation may under certain circumstances actually cause it. The mere sorption and desorption of amines or aminoacids has led to the fixation of hydroxy-alumina by montmorillonite. An increasing accumulation of hydroxyalumina interlayers with depth is shown by an increasing resistance of  $K^+$  saturated clays to collapse on heating. The fine and coarse clays from the A horizon collapse to sharp 1.03 nm peaks at  $350^{\circ}\text{C}$ , but those from the  $B_{21}$  yield broader spacings at 1.13 nm that collapse further to form asymmetric peaks at 1.05 nm if heated at  $550^{\circ}\text{C}$  (Figure 78).

Harward and Theisen (1962), and Harward, Theisen and Evans (1962) have shown that the identification of clay minerals in soils is influenced by sample preparation. They found that the tendency to identify minerals of the montmorillonite group increased with increasing intensity of the treatments used to remove "free" iron or effect dispersion. Use of water-dispersed  $< 2 \mu\text{m}$  clay from the Ahaura A and B horizons as a reference confirmed that although the deferrated clays used in this study did collapse more readily on heating, vermiculite and not pedogenic chlorite was the dominant species present in the A and AB horizons. The endothermic peaks between 400 and  $430^{\circ}\text{C}$  (Figure 73) are probably associated with hydroxyalumina species. These peaks are more strongly expressed in the deferrated fine and coarse clay samples, than in the water-dispersed  $< 2 \mu\text{m}$  fraction.

The results obtained for this profile are consistent with the weathering of mica and primary chlorite to vermiculite and pedogenic (aluminous) chlorite. The kaolinite present may well have formed through chemical weathering of feldspars.

(ii) Effect of red beech on clay mineral genesis: The mineralogical composition of the clay fractions from the B<sub>21</sub> horizons showed little variation along either transect, but some striking changes were observed in the upper horizons (Tables 56 - 59). In all topsoil horizons where pH values were < 4.5 both clay fractions were dominated by a mineral that expanded to 1.8 nm on Mg<sup>2+</sup> saturation and glycerol solvation. The 1.8 nm spacing was sharpest, most intense and found to greatest profile depth at Ah 5 and Ah 6; that is nearest the stems of the decaying beech stump and the larger living beech (Figure 78). The fine clay fraction from the A<sub>21</sub> horizon at Ah 5 gave reflections at 2.8, 1.79, 0.925, 0.601, 0.453 and 0.301 nm as well as those from kaolinite at 0.716 and 0.358 nm. The intense 1.8 nm spacing and the fairly rational series of higher orders suggest a dominance of montmorillonite (the fifth order of which would also contribute to the 0.358 nm spacing), but the presence of a 2.8 nm spacing indicates some interstratification with mica. The 0.925 nm peak would indicate a mica layer contribution of 50% when fitted to the peak migration curves of MacEwan, Ruiz Amil and Brown (1961), but the higher order peaks

at 0.453 and 0.301 nm indicate a lower mica content of 40%. Mills and Zwarich (1972) discussed the difficulties encountered in the recognition of interstratified mica-montmorillonite clays, and note that when particle size is small, failure to resolve the montmorillonite (002) and mica (001) spacings causes diffractograms from samples containing discrete minerals to resemble those of interstratified clays. Mills and Zwarich also note that consideration should be given to the possibility that dispersion of montmorillonite into single flakes one layer (1.0 nm) thick during dispersion and their subsequent flocculation during slide preparation, may cause interstratified species to be created, destroyed or altered.

With increasing distance from Ah 5 or Ah 6 (e.g. from Ah 5 to Ah 2) the 1.8 nm spacing from the fine clay fraction decreased in intensity and broadened towards 1.0 nm. The 0.9 - 1.0 nm reflection also broadened and moved towards 1.0 nm until at Ah 2 it had become a 1.0 nm shoulder on a broad 1.8 nm peak. Migration of the 0.9 - 1.0 nm peak indicates an increasing mica content (MacEwan, Ruiz Amil and Brown, 1961), while the loss in intensity and broadening of the 1.8 nm spacing indicates a loss of crystal order. All clays that expanded to 1.8 nm collapsed to sharp 1.0 nm reflections following  $K^+$  saturation and heating.

The coarse clay fraction at Ah 5 also gave an intense 1.8 nm spacing, and it showed a broad peak at 0.96 nm, which although asymmetric, was not resolved

into 0.9 and 1.0 nm spacings. With increasing distance from the living trees or the decaying stump the intensity of the 1.8 nm reflections showed the same changes as described for the fine clay specimens. Spacings at 2.8 nm were also given by the coarse clay fractions. Montmorillonite was also a major component of both clay fractions from the  $A_2$  horizon at I(o) 2, and the OA horizon at I(w) 1 (Tables 53 - 55).

It can not be stated with certainty whether the clay fractions from these very acid surface horizons contain largely discrete montmorillonite and mica, or whether there is considerable interstratification of these two components and possibly of vermiculite as well. The very intense 1.8 nm spacings given by some of the samples (e.g. at Ah 5) would seem to indicate a montmorillonite content greater than that predicted by the peak migration curves of MacEwan, Ruiz Amil and Brown (1961). This uncertainty, and the obvious changes that take place along the transects, cause problems in recording these minerals in Tables 56 - 59. Similar problems have been encountered by Schultz (1964), Biscaye (1965) and Brydon, Kodama and Ross (1968).

Biscaye (1965) used the ratio of the height of the 1.8 nm peak above background (p) to the depth of the "valley" on its low-angle side (v) as a measure of the crystal order of montmorillonite. Because of the low-angle position of the montmorillonite peak (about  $6^{\circ}2\theta$ ), the depth of the "valley" is a function of where the low-

angle side of the 1.8 nm montmorillonite peak intercepts, and adds to the general background radiation, which rises exponentially at low angles. A well-ordered montmorillonite would have a v/p ratio approaching one, and decreasing crystal order would be indicated by lower values for the ratio. Since the v/p ratio makes no direct assessment of peak width it may not be completely independent of montmorillonite concentration, and thus may be suspect as a true measure of crystallinity. Because of the very low 2 $\theta$  angle involved Biscaye (1965) considers it to afford a good approximation. The ratios obtained for samples from the present study containing appreciable amounts of montmorillonite are listed in Table 60. This table also includes a number of samples not previously identified. Their significance is discussed later in this section.

On the basis of the calculated v/p ratios, a purely arbitrary value of 0.7 was used to separate the smectite components in Tables 53 - 59, and in Table 61. The better-ordered members were designated as montmorillonite, and the less-ordered as interstratified minerals. It must be stressed, however, that there appears to be some interstratified montmorillonite-mica in all samples, and that there appears to be a regular decrease in smectite content with distance from living beech trees or decaying stumps. As these changes can not be determined quantitatively the arbitrary approach has been adopted in order that the tables can indicate that differences do occur. The only alternatives would be to designate

all the materials as montmorillonite, or as interstratified smectites.

A small quantity of kaolinite was present in all horizons containing montmorillonite, but chlorite, pedogenic chlorite, and gibbsite were not identifiable in the diffractograms. Differential thermograms of both the fine and coarse clay fractions from the  $A_2$  horizons at I(o) 2 and Ah 5 do not show the low temperature, multiple endothermic peak system associated with  $Mg^{2+}$  saturated vermiculite, or the 400 - 430°C endotherm associated with pedogenic chlorite (Figure 74). Less gibbsite is present in these samples than at comparable profile depth at Ah 1 (Figure 73). Gibbsite is thus destroyed during the processes that lead to montmorillonite formation. The water-dispersed  $<2 \mu m$  clay fractions at I(o) 2 and Ah 5 do show multiple low temperature endotherms, but these may be associated with the higher organic matter content of the samples. The greater gibbsite content shown by these samples, as compared with the fine and coarse clay fractions which had undergone peroxidation and deferration, indicates that some gibbsite was lost during preparation of the latter samples. The presence of a sharp endothermic reaction at 573°C indicates the presence of quartz in the coarse clay fractions of the  $A_2$  horizon at Ah 5, but it is not observed in the clay from the  $B_{21}$  horizon at this site (Figure 74). This indication of a higher quartz content in the  $A_2$  horizon is supported by the diffraction data (Table 57).

At Ah 5, 6 and 7 the clay fractions of all horizons above the B<sub>21</sub> contained montmorillonite as a major component. Further from the stump, or from the larger living beech, at Ah 2, 3, 4 and 9 montmorillonite occurred only in the surface horizon. At these sites, with increasing depth from the surface, montmorillonite tended to be replaced first by vermiculite and then by pedogenic chlorite. Furthest from the influences of the living trees and the decaying stump, at Ah 1 and Ah 8, montmorillonite gave way to vermiculite in the surface horizon (Tables 56 - 59).

A thin humus-iron pan occurred between the A<sub>22</sub> and B<sub>21</sub> horizons at Ah 5, but it did not extend as far as Ah 4. The material isolated from the pan gave a loss-on-ignition value of 63%, and 52% and 51% of its iron content was extractable by oxalate and pyrophosphate, respectively. It was largely amorphous to X-rays, only a small quantity of quartz being detected. Differential thermograms confirmed the presence of quartz and indicated a small amount of gibbsite (Figure 74). The endothermic peak at 95°C represents water held by organic matter and/or poorly-ordered gels. The endotherm at 708°C is puzzling - it does not appear in the clay fractions from the horizons above and below the pan, nor can it belong to any crystalline phyllosilicate. Its temperature is rather high for poorly-ordered forms of Al and Fe. The only explanation that can be offered for the presence of this peak is that it may be associated with the decomposition of iron-humic complexes in an inert atmosphere.

To check if high concentrations of montmorillonite were always present in the surface horizons close to the stems of living beech trees and decaying beech stumps, and if the presence of montmorillonite was restricted to localised areas surrounding these trees and stumps, 35 additional "grab" samples were obtained. Four of the samples were collected on the Hokitika sandy loam, and the remainder from the Ahaura silt loam. In all instances the O horizons which ranged from 0 - 0.15 m in depth were ignored, and the underlying A or A<sub>2</sub> horizons sampled. Clay mineralogical data from some of these samples are included in Table 60 and 61, and pertinent site characteristics are discussed in the text.

Sites Ho 2 and Ho 3 were located between two living red beech trees with diameters (breast height) of 0.72 and 0.75 m, standing 7.20 m apart. The sites were 1.2 and 3.5 m, respectively, from the larger tree. The pH values of the sampled A horizons were 4.4 and 4.5. The fine clay fraction at Ho 2 gave a broad peak at 1.50 nm on Mg<sup>2+</sup> saturation and glycerol solvation, that collapsed to 1.0 nm following K<sup>+</sup> saturation and heating. This fraction contains an interstratified mineral that possesses both vermiculite and montmorillonite layers. No montmorillonite, or interstratified minerals containing montmorillonite were detected in the coarse clay fraction at this site, or in either clay fraction from Ho 3.



Sites Ho 4 and 5 were at the base of decaying stumps. As at sites I(o) 2 and Ah 5 the trees had fallen, but the stems had shattered and stumps remained in the soil. Both A<sub>2</sub> horizons gave pH values of 4.2, and both clay fractions from each site contained montmorillonite. The 1.8 nm peaks were, however, asymmetric with pronounced tails on the high-angle side, indicating either interstratification with vermiculite or the presence of discrete vermiculite.

Sites Ah 10, 12 and 16 were located at the base of decaying stumps on the Ahaura silt loam, while Ah 11 and 13 were 2.0 m from Ah 10 and Ah 12, respectively. Ah 14 was located 4.5 m east of Ah 5, at a point where the remains of a decaying log made contact with the soil. The log is the remains of the tree that fell leaving its stump at Ah 5. Ah 15 was the same distance from the base as the stump as Ah 14, but was 2.0 m further from the fallen tree remains. The bleached A<sub>2</sub> horizon material from site Ah 17 was collected beside an uprooted stump. Site Ah 18 was located at the base of a red beech tree that had reached a diameter (breast height) of 1.02 m before being killed by fire. Site Ah 19 was 2.0 m from the stem of this tree, while site Ah 20 was 0.5 m from the base of the largest living red beech (2.36 m diameter, breast height) in the bush remnant where all the Ahaura samples described in this thesis were taken. Soil pH values for all the sampled horizons with the exception of the A horizon at Ah 19 (4.6) were <4.0.

The clay fractions from Ah 19 gave broad peaks at 1.54 nm (fine) and 1.52 nm (coarse). The remaining samples all showed the presence of well-ordered montmorillonite (Tables 60 and 61). Both clay fractions from Ah 19 are dominated by an interstratified mineral containing both montmorillonite and vermiculite layers.

Sites Ah 21 to Ah 40 were all located at least 7 m from any living tree, decaying stump, fallen log or other accumulation of decaying organic matter. Hollows, slightly raised areas, and the edge of the forest remnant were also avoided. These samples all gave pH values within the range 4.6 - 5.0, and none of them contained a clay mineral that showed expansion beyond 1.4 nm. Vermiculite was the major component in these samples.

(iii) A dynamic system - Podzolisation versus laterisation:

From the results of these analyses it is concluded that at distances greater than about 7 m from existing, mature red beech trees or large decaying beech stumps, where soil pH values exceed 4.5 and organic matter levels are (comparably) lower, the stable weathering products formed from the mica, chlorite and feldspar of the parent material are pedogenic chlorite, kaolinite, allophane and gibbsite; all products that contain (or can contain) a high level of Al relative to Si. Gibbsite is included in this list as it is considered that the available data (Tables 53, 54 and 62, and Figures 79 and 80) suggest the pedogenic formation of gibbsite, rather than the accumulation of a

mineral inherited from the parent material. The quantity of clay-sized gibbsite in constant soil volume increases with the age of the soil to reach a maximum in Ah 1, then declines. The proportion of total soil Al present as gibbsite in the Ikamatua and Ahaura soils is at a maximum in the B horizons (Table 62). Depth functions (Table 62 and Figure 80) show that the maximum accumulation of gibbsite occurs in these horizons. These results are unlikely to be materially affected by failure to determine the gibbsite content of the silt fraction, since X-ray diffractograms indicated that it was detected in the silt fractions of only those horizons that contained high gibbsite levels in the clay fractions. Downward translocation of gibbsite from the A to the B horizon would also explain the observed depth functions, but could not account for the marked accumulation of gibbsite in the Ahaura profile. Possible parent material variations can, however, not be completely ignored in alluvial soils. Gibbsite is highly correlated (1% level) with pH, phosphate retention, oxalate-extractable Al, and Fieldes and Perrott test values (Table 2), thus it tends to occur in those horizons containing the highest levels of poorly-ordered aluminosilicate gels. Miyazawa (1966) considers allophane is desilicated by organic materials, with subsequent crystallisation of gibbsite, but the evidence obtained in this study suggests that Al not Si is mobilised in the presence of organic matter. Precipitation of alumina in the interlayer spaces of expansible layer silicates tends

to prevent the solubility product of  $\text{Al}(\text{OH})_3$  being exceeded in soils containing actively weathering micas (Jackson, 1960 and 1963b). Jackson (1963a) indicates, however, that cyclic fluctuations in pH could result in small gibbsite units becoming negatively charged at pH values above 4.8 and thus being repelled by the negative surfaces of montmorillonite and nucleating a free gibbsite phase.

Gardner (1970) presented thermodynamic data to show that gibbsite should not precipitate in soils containing both quartz and kaolinite unless the quartz was coated with impermeable films, but Lodding (1972) argues that the presence of feldspar may radically alter the limits set by Gardner.

It is postulated that the presence of gibbsite in these soils may have arisen from the rapid hydrolysis of feldspars, causing the release of alumina at a faster rate than it could be assimilated in the interlayer spaces of the slower weathering micas. This could result in the solubility of  $\text{Al}(\text{OH})_3$  being exceeded, particularly in lower horizons where the pH was higher, and during periods when the soil solution became concentrated through the partial drying of the soil. Van Reeuwijk and de Villiers (1970) have shown that poorly-ordered  $\text{Al}(\text{OH})_3$ , that yielded crystalline  $\text{Al}(\text{OH})_3$  (bayerite) on dialysis, was precipitated in addition to aluminosilicate gels from solutions rich in Al relative to Si. MacKenzie (1957) notes that aging of alumina gels is much more rapid than

with iron oxide gels, and indicates that amorphous alumina hydrates would have a very transient existence in nature. Segalen (1971) indicates that at pH values  $< 4.2$  Al is liable to move over short distances, but will precipitate when pH exceeds 4.2 giving an often amorphous product. If the product remains surrounded by anions crystallisation is inhibited, but if drainage is good and anions are leached gibbsite crystallises and may even precipitate directly. In medium drainage environments Segalen considers Al recombines with silica to form 1 : 1-Type clays if Si concentration is low and 2 : 1 -Type phyllosilicates if it is high.

An abundance of aluminous weathering residues might also result in mica weathering rapidly, or even directly to a 2 : 1 - 2 : 2 Al-intergrade and could help to explain the differing mica weathering sequences proposed by Jackson (1963b) and Fieldes (1962 and 1968). Whereas Jackson proposes the sequence:

Mica  $\longleftrightarrow$  Vermiculite  $\longleftrightarrow$  2 : 1 - 2 : 2 Al-intergrade, Fieldes shows an intergrade as the precursor of vermiculite:

Mica  $\longrightarrow$  Illite  $\longrightarrow$  Vermiculite (1)  $\longrightarrow$  Vermiculite (2), where vermiculite (1) is defined as the component with higher hydroxyalumina interlayering and higher interlayer change. A partial explanation for this rather unexpected order proposed by Fieldes may be found in Table 6.3.7 on Page 34, in Fieldes (1968), which shows

maximum vermiculite (1) contents, and no vermiculite (2), in the central and southern yellow-brown earths, and high vermiculite (2) levels in the northern, weakly leached yellow-brown earths, and northern podzolised yellow-brown earths. The remaining data in the table scarcely support Fieldes's order, and it is considered that the vermiculite (2) found in the more strongly weathered soils has been formed by the dealumination of vermiculite (1) during a second cycle of weathering at low pH. This mechanism will be elaborated later in this section. It is perhaps pertinent to note that Fieldes (1958, 1962 and 1968) shows silica as the final stage in the weathering of mica. No mention is made of gibbsite. Jackson (1963b and 1964) on the other hand makes no reference to silica in his sequence and shows gibbsite as the final stage. Fieldes has stressed reactions leading ultimately to a podzol, whereas the end member in Jackson's sequence would be a laterite. Pedogenic chlorites are probably stable intermediates in soils when pH exceeds 4.5, but should suffer dealumination if pH values drop below 4.5.

From the results obtained in the present study it is concluded that in the yellow-brown earth soil environment where  $\text{pH} > 4.5$ , Al and Fe are tending to accumulate relative to Si, and the soil is moving, albeit slowly, towards a lateritic end product. Under these conditions pedogenic chlorite appears to accumulate, and there is no direct evidence of its alteration to kaolinite. Since

kaolinite levels do not rise during the first 18,000 years, losses of kaolinite from the clay fraction would have to match possible kaolinite formation from the intergrade.

It is further concluded that the onset of a combination of low pH conditions ( $\leq 4.4$ ) and high organic matter levels, associated with the growth of individual red beech trees, initiates a second weathering cycle in which Al and Fe are readily lost from the upper horizons, resulting in the disappearance of allophane, gibbsite and ferromagnesian chlorites, and in the dealumination of pedogenic intergrades, which are transformed first into vermiculite, and eventually to montmorillonite. The direction of weathering has now changed, and the soil is altering towards a podzol. The maximum expression of this cycle would be observed in the upper horizon close to the stems of the larger living trees and decaying stumps, where stem flow effects were greatest, and had operated for the longest duration. This pattern was observed on the Ahaura transects where montmorillonite graded outward to vermiculite, and with depth to vermiculite and then to pedogenic chlorite. The occurrence of montmorillonite at lower pH conditions than vermiculite may be related to a decrease in layer charge allowing a greater expansion, or to the more complete removal of interlayer material.

The results obtained in this study thus verify the conclusions of Malcolm, Nettleton and McCracken (1969), Gjems (1970) and Kapoor (1973). In these three studies

(and in the present one) high organic matter levels, and soil pH values of 4.4 - 4.5 or less, appeared to be critical for dealumination of the intergrade and formation of montmorillonite. Although, in theory, low pH ( $< 4.5$ ), however obtained, should cause dealumination of 2 : 1 - 2 : 2 hydroxyalumina intergrades, such low pH values are unlikely to occur in soils without the dominant influence of organic matter. Gjems (1970) also considered that under low pH conditions montmorillonite would also form directly from illite. From differences in expansion with glycol following treatment with 0.5 - 1.0 molar HCl to remove interlayers Kapoor (1972) concluded that interlayered smectites were present in the  $A_2$  horizons of soils when pH values exceeded 4.4, but that the intergrades found in the  $B_2$  horizons of soils with more acid  $A_2$  horizons containing montmorillonite were interlayered vermiculites.

The presence of interstratifications involving combinations of mica, vermiculite, montmorillonite and pedogenic chlorite layers supports a conclusion that the latter three components were derived from mica. The weathering sequence proposed by Jackson et al. (1952) indicated reversibility between vermiculite and montmorillonite, while reversibility between vermiculite and pedogenic chlorite was indicated in a later publication (Jackson, 1963b). Frink (1969) has reported the dealumination of a chloritised vermiculite from an acid upland soil after it was transported to a neutral lake



bottom environment. The high charge vermiculite initially formed was subsequently transformed to illite.

Kodama and Schnitzer (1973) have shown that two chloritic minerals, leuchtenbergite (magnesium-rich) and thuringite (iron-rich) were decomposed in 0.2% aqueous fulvic acid solutions at pH 2.5 - the iron species more readily than the magnesium. It could be argued from this result and the known solubility of ferromagnesian chlorites in inorganic acids (Brindley and Youell, 1951; and Ross, 1969) that pedogenic chlorite should be largely dissolved in the low pH environment of the surface horizons near living red beech trees, and that the montmorillonite concentrated in those horizons formed as a direct alteration product of mica. It is unfortunate that Kodama and Schnitzer (1973) did not include a naturally occurring pedogenic chlorite in their investigation.

The mineralogical changes associated with tree growth observed along the Ahaura transects are consistent with current concepts of podzolisation - the mobilisation of Al and Fe from the A horizon by chelation and their subsequent immobilisation in the B horizon (Muir, 1961; Rode, 1964; and McKeague, 1965). Bloomfield (1953-1955), DeLong and Schnitzer (1955), Schnitzer and DeLong (1955), Lossaint (1959), Coulson, Davies and Lewis (1960b), Muir, et al. (1964), Muir, Bown and Logan (1964) and Malcolm and McCracken (1968) have shown that rainfall leachates and/or aqueous extracts of leaves from a range of tree species could form water-soluble complexes with

Fe and Al over a wide pH range under both aerobic and anaerobic conditions. DeLong and Schnitzer (1955) suggested that Fe moved as a ferric hydroxide complex protected by organic matter. Acidic polysaccharides (Schnitzer and DeLong, 1955), and polyphenols and organic acids (Bloomfield, 1957) were considered to be the active species involved in mobilisation. Bloomfield (1953) noted that the extract reduced ferric iron to ferrous. Coulson, Davies and Lewis isolated polyphenols from leaves (1960a) and from the B horizons of podzol soils (1960b). Schnitzer and DeLong (1959) showed that the capacities of leachates to mobilise Fe ranged from 2 - 18 mg Fe/g of organic matter, and that variation depended both upon tree species and time of sampling. Muir, Logan and Bown (1964) showed that citric, malic and quinic acids from a Scots Pine extract were the major components responsible for the mobilisation of Fe. Seven aminoacids were identified in the extracts but they were largely ineffective in maintaining Fe in solution above pH 4.5. As noted by Martin and Reeve (1957) much of the early work tended to ignore the role of Al in podzolisation, but McKeague (1967 and 1968) and McKeague and Day (1969) have stressed its significance. Romans (1970) considers that a podzol begins with the accumulation of a surface humus mat that gradually breaks down into colloidal humus with a high C/N ratio (usually 20 - 30). Constituents of the humus are then thought to attack the uppermost

mineral horizons forming soluble complexes that are leached into the B horizon where they are deposited as a result of microbial and fungal breakdown of the organic ligands. It is pertinent to note that in the present study there is a high positive correlation (0.1% level) between montmorillonite content and the C/N ratio (Table 2). Ross and McNeilly (1973) have demonstrated the presence of polyphenol-oxidising enzymes in litter and in soil under hard beech forest. The enzymes appeared to have originated mainly from micro-organisms, with particular fungi possibly involved, and not from hard beech leaves.

The presence of montmorillonite in the  $A_2$  horizons of podzols from other areas has been reported by Whittig and Jackson (1955), Brown and Jackson (1958), Gjems (1960, 1963, 1967 and 1970), Franzmeier, Whiteside and Mortland (1963), Brown and Tedrow (1964), Ross and Mortland (1966), Brydon, Kodama and Ross (1968), Kodama and Brydon (1968), Wiklander and Aleksandrović (1969), Malcolm, Nettleton and McCracken (1969), Rozhnova and Kasatkina (1970), McKeague and Brydon (1970) and Sokolova, Targul'yan and Smirnova (1971).

Mokma et al. (1973) report the absence of distinct 1.8 nm peaks in clays from the  $A_2$  horizons of the older soils in a chronosequence. Determination of montmorillonite content by a cation exchange technique (Alexiades and Jackson, 1965 and 1966b) showed 10 - 20% of that mineral in the A and B horizons of soils older than 250 years, but showed no concentration of it in the  $A_2$

horizons of the podzolised soils. This failure to observe high montmorillonite levels in the podzolised members may be explained, in part, by the siting of their sampling pits. Stevens (1963 and 1968b) indicates that these were located as far as possible from the existing trees, and that profiles were excavated, by horizon, over an area of either 0,436 or 1,000 m<sup>2</sup>. The age of the Okarito soil, the oldest of the sequence, was given as comparable to that of the Ahaura silt loam of the present study, but the Franz Josef sequence is in an area of much higher rainfall than at Reefton, and there are differences in parent material. If montmorillonite levels were also related to the tree distribution pattern in the area investigated by Mokma and his co-workers, the location of the sampling pits would tend to be in areas where lower montmorillonite levels, or its absence, could be expected.

Little information is available on the life-span of red beech in the area, but Dr C.J. Burrows (Botany Department, University of Canterbury, pers. comm.) has measured (elsewhere) growth rates of 0.25 - 0.50 m (dbh) in 100 years and estimates that trees may live to between 500 and 700 years, and remain on the ground in excess of 100 years. As red beech tends to form even-aged stands the duration of each generation would approach the age limits of the trees.

It can be inferred from the above, and the likely presence of beech and podocarps in the study area for some 6,000 and 14,000 years, respectively, that several

generations of these species will have affected the Ahaura (and Ikamatua) soils, and thus it is necessary to postulate that sites such as Ah 1, Ah 8 and Ah 21 - 40 have never been close enough to be influenced by any living beech during the past 6000 years, or that each successive generation of trees occupied the same sites, or that following the death, decay and eventual disappearance of any particular tree, montmorillonite can revert towards a pedogenic intergrade, provided the particular area is not affected by other nearby trees. Of the three alternatives the latter is the most plausible. Surface horizon pH values at the base of decaying stumps (3.5 - 3.9) are higher than those near the stems of the larger living trees (3.1 - 3.5). The A horizon pH value of the older Kumara silt loam, where the native forest has been destroyed following European settlement of the area, is even higher (4.5). Should pH values rise locally following the complete disappearance of particular trees, increasing layer charge, and the accumulation of some interlayer alumina, could prevent expansion of clay minerals beyond 1.4 nm.

It is therefore concluded that transformation of the pedogenic intergrade to montmorillonite in these soils is dynamic and reversible. Lietzke and Mortland (1973) have demonstrated the dynamic character of a naturally chloritised vermiculite in the laboratory, and postulated that chloritisation and dechloritisation probably occurred readily in the field as well. The

conclusion is supported by the presence of an inter-stratified montmorillonite-vermiculite (which may also contain mica layers) in the A horizon at Ah 19. Before being destroyed by fire the tree 2 m away had reached a diameter of 1.02 m (breast height) as compared with diameters of 1.11 and 0.68 m for the two living trees at the extremities of Transect 2. This intergrade represents an intermediate step in the sequence:

Montmorillonite  $\longleftrightarrow$  Vermiculite  $\longleftrightarrow$  Pedogenic chlorite, but it is necessary to show that the reaction is moving in the forward direction. As the tree involved was only slightly smaller than the larger living beech from Transect 2, it seems reasonable to assume it had reached a comparable age before it was killed. As montmorillonite is now found at Ah 7, 4 m from the living beech, it is likely that it was once present in the surface horizon at Ah 19 in sufficient concentration to cause expansion to 1.8 nm.

(iv) Development of gley podzols: During weathering beyond 18,000 years there has been a continuing loss of Al and Fe relative to Si (Table 31 and Figure 81). It can be seen from Figure 81 that the changes that are taking place near living trees and decaying stumps are altering the Al, Fe and Si levels towards those now found at Ku 1. This alteration has been greatest in the upper half of the A<sub>2</sub> horizon at Ah 5, and least in the A horizon at Ah 1. The comparable positions

occupied by the Hokitika, Ikamatua and Ahaura soils in Figure 81 support the contention expressed by Rode (1949), Stobbe and Wright (1959) and Franzmeier, Whiteside and Mortland (1963) that a conditioning process of base removal was necessary before podzolisation was initiated. In the present context 'conditioning' represents the time necessary for the pH of the surface horizons to drop below 4.5. It is the period during which laterisation, not podzolisation is operating.

It is considered that given sufficient time the dynamic processes now operating on the Ahaura silt loam would ultimately produce the soil properties now observed at Ku 1. The absence of any visual mineralogical or chemical signs of podzolisation in the younger soils, other than in the vicinity of existing trees and stumps, indicates that lateral movement of Al and Fe must occur in the yellow-brown earths. The friable crumb and granular structures of the soils, the high rainfall, the dispersion of stem-flow water, and the slight slope on the terraces, indicate that lateral movement of water is at least possible. Analysis of water dispersed  $< 2 \mu\text{m}$  clay from the A and AB horizons at Ah 1 shows that  $> 50\%$  of the iron content of these horizons is present in the clay fraction.

As Al and Fe are depleted through the effects of successive generations of beech, the ability of the soil to recover from the localised podzolisation around individual trees would be reduced, and "egg-cup" podzols

indicating the positions of trees from previous generations would persist. Eventually these would coalesce to form a uniformly podzolised surface. Loss of Al from the upper horizons would coincide with the disappearance of allophane, gibbsite and pedogenic chlorite, and lead to the persistence of expanding 2 : 1 -Type phyllosilicates. Mica reduced to clay size by physical weathering, would alter further towards montmorillonite. Montmorillonite content showed a high positive correlation (0.1% level) with total Si, and a high negative correlation (0.1% level) with pH, total Al and total Fe (Table 2). The mineral phase stability diagram for the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  developed by Weaver, Jackson and Syers (1971) indicates that at low pH a high concentration of  $\text{Si(OH)}_4$  in the matrix solution is necessary for montmorillonite stability. Loss of the poorly-ordered forms of Al and Fe, and a reduction in organic matter content would lead to a collapse of soil structure. The presence of expanding clays, particularly if occasional drying of the soil occurred, and an increase in silt content at the expense of coarse sand, would assist in the formation of the massive, relatively impermeable horizons now found in the Kumara silt loam. It is considered that such soils would become poorly-drained even in the absence of iron pans. Young (1967) reports instances of poorly-drained Okarito soils in which no iron pans can be recognised. It is therefore concluded that the



Kumara and Okarito soils represent more advanced stages of weathering than the Ahaura silt loam, and that podzolisation has preceded gleying.

(v) Practical implications: Much of the free-draining terrace land and river flats carrying the Hokitika, Ikamatua and Ahaura soils is now devoted to agriculture. Lietze and Mortland (1973) raise a question of practical importance when they ask if the continued liming of acid soils containing pedogenic chlorite will eventually result in dealumination of the chlorite and the subsequent fixation of  $K^+$  and  $NH_4^+$ . The results obtained in this study would indicate that the maximum fixation of these ions would occur under the conditions that led to the formation of vermiculite and possibly of montmorillonite. The high vermiculite levels found in the A horizons of the older Ikamatua and Ahaura soils indicates that these soils should now fix  $K^+$  and  $NH_4^+$ . Raising the pH of these soils should create conditions more favourable for the existence of pedogenic chlorite, and aluminosilicate gels. Microcrystalline gibbsite shows minimum solubility in water at pH values between 5.5 and 6.5 (Robertson and Hem, 1969). It is likely, therefore, that pedogenic chlorite and allophanic gels would be most stable within this pH range. Raising the pH of these soils towards the levels desired for agricultural practice would also decrease the anion retention capacity of allophanic gels.

(d) The Chronosequence Soils. Quartz was detected in the fine clay fraction in the C horizon of the Hokitika sandy loam, and from the A to B<sub>2</sub>G horizons (inclusive) of the Okarito loamy sand (Table 53). It was present in all soil horizons in the coarse clay fraction (Table 54). The increase in intensity of the quartz (100) spacing (Table 54), and the presence of the sharp endothermic peak caused by the quartz  $\alpha \longleftrightarrow \beta$  inversion at 573°C in the thermograms from the coarse clay fractions of the Kumara and Okarito soils (Figures 75 and 76), indicate much higher quartz contents in the older, gley podzols. Inversion reactions are accompanied by comparatively small energy charges, thus the peak indicating the  $\alpha \longleftrightarrow \beta$  quartz inversion is small in relation to the various chemical charges that may occur when clay minerals are heated. The very strong quartz spacings, the weak reflections from other minerals, and the low clay content, particularly in the fine clay range (Table 7), in the A and AG horizons of the Okarito loamy sand, indicate that this soil has undergone weathering that was more intense, and/or of longer duration than have the younger soils.

The presence of high levels of quartz in the sand, silt and clay fractions of the upper horizons of this soil also support the view of Mew et al. (1972) that loess has made but a minor contribution to the parent material of the soils on the intermediate and high glacial outwash terraces. Loess deposited at (or since) the time the

low glacial outwash terrace was formed could not have altered to this extent. The most probable cause of the marked increase in quartz (and total Si) content between Ah 1 and Ku 1, and again between Ku 1 and Ok 1, is weathering for a considerable period at low pH. Under these conditions quartz accumulation can be explained in terms of its greater resistance to weathering and the relative constancy of its solubility over the pH range involved (Robertson and Hem, 1969), and by the increased solubility of Al and Fe in the presence of OM at low pH.

Feldspars were rarely observed in the fine clay fractions, but were almost always present in the coarser fraction. Small quantities of an amphibole (presumably hornblende, which was identified in the sand fraction) were present in the coarse clay fraction of the Ahaura and younger soils. Its absence from the older soils is consistent with its relative instability to weathering.

The initial accumulation of gibbsite and its decline in soils older than the Ahaura silt loam was discussed in the previous section. The presence of poorly-ordered aluminosilicates can be inferred from the high oxalate-extractable Al, P retention, and Fieldes and Perrott test values, but caution must be used in such interpretation since it has been demonstrated that crystalline compounds from the Ikamatua and Ahaura soils are attacked by both oxalate and NaF. Additional evidence for the presence of allophanic gels is shown by increases in the peak heights of the low temperature

(120 - 150°C) endothermic and the high temperature (>900°C) exothermic reactions shown by the fine clay fractions from subsoil horizons of I(o) 1, I(w) 1 and Ah 1 (Figures 71 - 73). The increases concerned can not be explained in terms of increasing amounts of organic matter or phyllosilicates. The highest oxalate-extractable Al value obtained (5.1% - Table 36) was from the B<sub>21</sub> horizon of the Ahaura silt loam. If it is assumed that

- (i) all the extracted Al came from allophanic gels, and
- (ii) that the molar SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the gel was of the order of 1.92 (equivalent to the <0.2 μm fraction from the C horizon of the Taupo sandy silt - Table 45), this would indicate an allophane content (ignited weight basis) of some 6%.

Since a considerable part of the extracted Al came from other sources the actual allophane content will be considerably less than this maximum value.

Trioctahedral chlorite is virtually absent from the gley podzols, but occurs in both clay fractions of the younger soils. Difficulties in distinguishing between the 1.4 nm peak intensity due to trioctahedral chlorite and that from pedogenic Al-chlorites has probably led to the values shown for the former being overestimated in Tables 53 - 59), and this is probably why the maximum chlorite levels appear in the B horizon. Like mica, the chlorite levels will be controlled by the relative rates of addition from the coarser fractions, and losses by chemical weathering.

The factors controlling the weathering of mica have been adequately discussed in the previous section, and these explain the major trends observed in the chronosequence soils: the increase in vermiculite towards the surface in the yellow-brown earth profiles, and the occurrence of maximum pedogenic chlorite levels in the B horizons, and its absence from the upper horizons of the gley podzols. Little montmorillonite occurred in the free-draining yellow-brown earths, as sampling sites were located away from any living tree, or decaying remains, but interstratifications involving mica, vermiculite and montmorillonite did occur in the gley podzols. These had higher mica contents than the intergrades associated with living beech trees and decaying stumps on the Ahaura silt loam. This could be explained by one or more of the following mechanisms: weathering of silt and sand-sized feldspar in a poorly-drained environment; fixation of K from incident rainfall, or released from the weathering of coarser materials; the further weathering to illite and interstratified illite-vermiculite of mica freshly reduced to clay size; loss by destruction of vermiculite and montmorillonite; or by additions from the atmosphere.

Interstratified minerals containing a considerable montmorillonite component occur in the OA horizon at I(w) 1; the interstratified clay in the comparable horizon of the freely-drained I(o) 1 is illite-vermiculite. These observations are consistent with the pH values of the respective soils (Table 3).

Kaolinite percentages show little variation with depth or increasing soil age from Ho 1 to Ah 1, but higher levels occur in the gley podzols (Tables 53 and 54). The low values shown for Ho 1 in Table 55, reflect a lower clay content, as do the values of Ok 1 as compared to those in Ku 1.

The comparable kaolinite levels in Ho 1 and the yellow-brown earths, despite the much lower pedogenic chlorite levels in the former soil (Tables 53 and 54), may indicate that kaolinite formed from the rapid hydrolysis of feldspar, rather than from the weathering of mica. Possible external additions can not be ignored, however, for a soil situated on the present flood plain. At pH values  $< 4.5$  dealumination of pedogenic chlorite appears to lead to vermiculite, thus precluding kaolinite formation. Brydon, Kodama and Ross (1968), and Mokma et al. (1973) have reported lack of kaolinite formation in podzol soils.

X-ray diffraction analysis of a range of samples following HF digestion (see Chapter 3; V, (4)) indicated that small quantities of anatase and rutile were present in all the soils.

The differences in mineralogy (Tables 51 - 54, and Figure 81) and in total elemental analyses (Table 22) between Ah 1 and Ku 1, and between Ku 1 and Ok 1 represent major advances in soil development that could indicate warmer environments than those occurring during the past 18,000 years and/or that the Kumara silt loam is much

older than the Ahaura silt loam, and the Okarito loamy sand is much older than the Kumara silt loam. The results tend to support the correlation of the Tophouse formation with the Waimea glaciation (Nathan and Moar, 1973) and the Manuka with the Waimaunga (Suggate, 1965), and if anything would perhaps indicate that both soils could be older than the minimum ages used in this thesis.

#### (4) Problems Encountered in the Identification of Plumbogummite Minerals

Minerals of the plumbogummite group are hydrated alumino-phosphates with formula  $XAl_3(PO_4)_2(OH)_5 \cdot H_2O$ . The various end members include plumbogummite itself (where X = Pb), crandallite (Ca), goyazite (Sr), gorceixite (Ba), and florencite (Ce and other rare earths).

##### (a) Concentration Attempts using HF Digestion.

The investigations of Norrish (1968) and Sarma and Krishna Murti (1969/1970) have suggested that these minerals are a common form of soil phosphate, and that they represent an end product in the weathering of inorganic soil phosphorus. Both investigations used HF digestion in attempts to concentrate the phosphate sufficiently to allow identification by X-ray diffraction. Norrish (1968) showed that, given favourable circumstances, a considerable concentration could be obtained by treating 2 g of soil clay with 160 ml of 20% HF for 2 minutes. Using this technique, Sarma and Krishna Murti (1969/1970) failed to detect plumbogummite minerals in HF residues from soils containing considerable quantities of micaceous

minerals and quartz. They attributed this to the failure of the two-minute digestion to dissolve sufficient silicate mineral matter to achieve the plumbogummite concentration necessary for its detection by X-ray diffraction, and consequently adopted a more drastic HF digestion, originally used by Raman and Jackson (1965) in the determination of anatase and rutile in soils and sediments. This involved treating 1 g samples with 30 ml of 48% HF for 24 hours. Water-dispersed clays ( $< 2 \mu\text{m}$ ) from selected soil horizons (Ho 1, A<sub>12</sub> and C; I(y) 1, A and AB; I(o) 1, A and B<sub>21</sub>; Ah 1, A; Ah 5, B<sub>21</sub>; Ku 1, all horizons; and Ok 1, all horizons) were analysed. Sand ( $> 20 \mu\text{m}$ ) and silt ( $20 - 2 \mu\text{m}$ ) from a number of these horizons (Ho 1, A<sub>12</sub> and C; I(y) 1, A; I(o) 1, A; Ah 1, A; Ku 1, B<sub>1</sub>G; and Ok 1, B<sub>3</sub>G) and sand collected from the Waitahu river near the Ho 1 site were also examined. As all these samples were known to contain micaceous clay minerals and quartz, clay ( $< 2 \mu\text{m}$ ) from the B horizon of a Kaiteiteri hill soil (a strongly-leached soil developed on pre-argillised granite that contained mainly kaolinite in the clay fraction - Adams, 1970), and a sample of ground ( $< 53 \mu\text{m}$ ) Christmas Island 'C-grade' rock phosphate ore (that contained in excess of 30% of crandallite), were included for comparative purposes. These two samples were provided by Dr J.A. Adams (New Zealand Soil Bureau, D.S.I.R.).

Because of the appreciable quantities of micaceous clay minerals and quartz in the chronosequence samples



the more drastic HF digestion favoured by Sarma and Krishna Murti (1969/1970) was initially chosen as the most suitable means of concentrating any plumbogummite minerals present. Following digestion, residues were washed with 50 ml portions of hot 3 molar HCl (twice), distilled water (twice), 96% ethanol (twice) and benzene before being dried at 110°C. Phosphorus contents of the samples and their digestion residues were determined, following carbonate fusion, by the method of Alexander and Robertson (1968) by Mr D.T. Howarth (Lecturer in Chemistry, Lincoln College) to whom the author is indebted. The digestion residues from all the chronosequence samples, and from the river sand and the Kaiterteri hill soil gave similar X-ray diffraction spacings. A typical example of these data is included in Table 63. The d-spacings and intensities obtained were in agreement with those reported by Sarma and Krishna Murti (1969/1970) as belonging to minerals of the plumbogummite group. However, the intensities of the spacings obtained from the residues from the chronosequence samples decreased with increasing age of the soil, and with decreasing particle size. The spacings were not given at all by the residue from the Christmas Island rock phosphate, which was largely dissolved by the treatment. These observations suggested that the diffraction spacings were not caused by a mineral of the plumbogummite group, and that they were associated, not with a weathering end product, but with some species that was being depleted as

weathering progressed.

To check this possibility, a range of 16 unweathered rock samples (including granite, obsidian, pumice, andesite, basalt, gneiss, siltstone and greywacke) and two samples of muscovite were ground to  $< 53 \mu\text{m}$  and then subjected to a similar HF digestion. A representative selection of the X-ray data obtained appears in Table 63. Every residue gave spacings that corresponded to those obtained from the soil samples. Apart from  $\text{Na}_2\text{SiF}_6$  (from obsidian),  $\text{K}_2\text{SiF}_6$  (from muscovite), rutile and zircon, no other spacings were observed in any of these diffractograms. The weights of residue produced from 1 g rock samples ranged from  $< 30$  mg for the granite, obsidian, pumice and greywacke samples to 450 mg for one of the basalts. In general, the more basic the rock, the greater the weight of residue produced.

The P content of the residues ranged from 0.008% (basalt) to 0.014% (muscovite). If it is assumed that the P content of plumbogummite minerals is of the order of 10 - 15%, all of these residues would contain plumbogummite concentrations of  $< 0.2\%$ . Sarma and Krishna Murti (1969/1970) reported values ranging from 80 to 1060  $\mu\text{g/g}$  for the P content of their HF residues. These values would correspond to maximum plumbogummite mineral contents ranging from 0.1 to 1.6%. It is inconceivable that the low contents of plumbogummite minerals that could be present in the rock or muscovite residues of the present work, or in the samples of Sarma

and Krishna Murti, could be responsible for the strong diffraction patterns obtained.

As plumbogummite minerals are unstable above  $400^{\circ}\text{C}$  (Norrish, 1957; Blanchard, 1971; and Trueman, 1971) it is unlikely that they would be present in a range of igneous rocks. No changes were produced in the X-ray diffraction patterns obtained from the residues by heating the soil, ground rock or muscovite samples at  $600^{\circ}\text{C}$  for one hour prior to HF digestion. Sarma and Krishna Murti (1969/1970) also reported that the spacings they attributed to plumbogummite minerals were removed by treatment with NaOH, but unfortunately the conditions of this treatment were not specified. Treatment of 1 g samples of soil, ground rock, and muscovite with 50 ml of boiling 2 molar NaOH for 5 minutes prior to digestion with HF had no effect on the diffractograms obtained from the residues. When a 1 g sample of Christmas Island rock phosphate ore was boiled for 2.5 minutes in 50 ml of 0.5 molar NaOH, all the crandallite it contained dissolved.

It was concluded from the evidence so far obtained that the products obtained from a 24 hour digestion in 48% HF were not plumbogummite minerals, but artefacts produced by the interaction of HF with the samples.

(b) Synthesis of Complex Fluorides. Norrish (1968) reported that  $\text{NH}_4\text{MgAlF}_6$  which gave similar diffraction reflections to those of plumbogummite minerals could precipitate during HF attack on soil samples containing Mg, but that it could be removed by

warm 2 molar HCl. Since the residues obtained in the present study were insoluble in hot acid it is unlikely that they were this particular fluoride. An X-ray spectrographic scan of one of the residues indicated that Al, Ca, K, Mg and Fe were the major components. No magnesium, aluminium fluorides in which  $\text{NH}_4^+$  might be replaced by other cations of similar size were listed in the Powder Diffraction File published by the Joint Committee on Powder Diffraction Standard (1973 Edition). Consequently  $\text{NaMgAlF}_6$ ,  $\text{KMgAlF}_6$  and  $\text{Ca}_{0.5}\text{MgAlF}_6$  were precipitated by addition of HF to appropriate quantities of NaCl, KCl,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and  $\text{AlCl}_3$  dissolved in distilled water, and the mixture allowed to stand for 24 hours. Fluorides with compositions between those of the end members were also prepared. All the prepared fluorides yielded X-ray diffraction spacings similar to those of  $\text{NH}_4\text{MgAlF}_6$  indicating that  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  could replace  $\text{NH}_4^+$  in that structure. Diffraction data for the three end members, and for crandallite and gorceixite (the two members of the plumbogummite group most frequently reported in soils) are compared in Table 64. No spacings other than those listed in this table were obtained from any of the fluoride precipitates, and the yield of each product approximated that calculated from the assumed chemical formula.

Significant differences, both in the positions of the spacings and in their relative intensities, occur between the data from the complex fluorides and those for

the two plumbogummite minerals. Comparison of the data listed in Table 64 with those in Table 63, and with the values reported by Sarma and Krishna Murti (1969/1970), shows that digestion of rock and soil samples for 24 hours in 48% HF has resulted in the precipitation of complex fluorides, and not in the concentration of minerals of the plumbogummite group.

Differential thermograms of the rock and soil residues resembled those obtained from the complex fluorides (Figure 82) and were quite different from published curves for plumbogummite minerals (Norrish, 1957; Blanchard, 1971; and Trueman, 1971).

The precipitated complex fluorides were all unaffected by a 15 minute boil in 6 molar HCl (0.25 g solid : 50 ml acid). Thus, unlike  $\text{NH}_4\text{MgAlF}_6$ , these fluorides would not be removed from digestion residues by washing with warm HCl. No explanation can be offered for this considerable difference in solubility.

The diffraction spacings given by the complex fluorides disappeared if 100 mg of fluorides were boiled with 50 ml of 0.5 molar NaOH for 2.5 minutes. In all cases they were replaced by spacings at 0.778, 0.388, 0.259, 0.230, 0.196, 0.153 and 0.150 nm. It has not been possible to identify these spacings.  $\text{CaF}_2$  was also produced from fluorides containing Ca. These spacings were also obtained following similar NaOH treatments of the residues from the soil, rock, and muscovite samples that had been treated with 48% HF for

24 hours. The complex fluorides decomposed when heated at 600°C for one hour. The products of this heating included  $\text{Na}_2\text{MgAlF}_7$  (weberite),  $\alpha\text{-CaAlF}_5$ ,  $\text{KMgF}_3$  and  $\text{CaF}_2$ . Residues from soil, rock and muscovite samples that had been digested for 24 hours with 48% HF also yielded these products when heated to 600°C. These thermal and chemical observations confirm that the digestion residues contained complex fluorides.

(c) Optimising the Conditions for HF Digestion

In order to establish at what point during a 24-hour digestion fluorides were first precipitated, 1 g samples of powdered ( $< 53\ \mu\text{m}$ ) granite were treated with 30 ml of 48% HF for periods ranging from 2 minutes to 24 hours. The dominant minerals in the granite were feldspar, quartz and muscovite. Most of the feldspar dissolved in the first 5 minutes, and it was not detected in the residues after 4 hours. Although the initial rate of solution of quartz was slower, it too had dissolved within 4 hours. Some 90% by weight of the sample dissolved in the first hour. As it dissolved more slowly than the quartz and feldspar, the relative amount of muscovite in the digestion residue increased during the first 3 hours. Fluorides were first detected in the residue after 2 hours. Between 2 and 14 hours the intensities of the fluoride diffraction spacings increased, while those of muscovite declined. After 14 hours muscovite was no longer identifiable in the residue, and the intensities of the fluoride spacings remained constant. It is concluded

from these observations that Mg concentration was the limiting factor in the precipitation of the fluoride. Although the rapid initial solution of the feldspar would have provided the necessary concentrations of the remaining ions, it appeared that the solubility product of the fluoride was not exceeded until solution of the muscovite had provided a sufficient Mg concentration. This explanation would also account for the tendency of residue weights to increase as rocks became more basic. Whether Fe could substitute for Mg and/or Al in the fluorides was not investigated.

It is likely that the various minerals present in soil samples have different rates of solution in HF. Norrish (1968) has reported that prolonging HF attack to dissolve other resistant minerals such as illite, could cause solution of plumbogummite minerals, and the present investigation has shown that the crandallite in Christmas Island rock phosphates was soluble in HF. For soil samples that do contain HF-resistant minerals, the digestion conditions that would give the maximum chance of identifying any plumbogummite minerals that were present, would be those that resulted in the highest possible concentration of them in the residue. In an attempt to define these conditions 1 g samples of water-dispersed  $< 2 \mu\text{m}$  clay from the following chronosequence soil horizons; Ho 1, A<sub>12</sub> and C; I(y) 1, A; I(o)1, A; Ah 1, A and B<sub>21</sub>; Ku 1, A and B<sub>h</sub>G; and Ok 1, A and B<sub>3</sub>G, and from the B horizon of the Kaiteriteri hill soil, were digested for

periods of 2 minutes, and 2, 15 and 24 hours with 80 ml of 20% HF, and for 24 hours with 30 ml of 48% HF. X-ray diffraction data and P contents were obtained for all residues. (The P analyses were again carried out by Mr D.T. Howarth).

The chemical data obtained from the Kaiteriteri hill soil are summarised in Table 65, and the X-ray data in Table 66. With this soil, which contained mainly kaolinite in the clay fraction, the mildest treatment used (20% HF for 2 minutes) produced a residue that contained 0.82% P. If this P were present in minerals of the plumbogummite group they would account for about 8 - 12% by weight of the residue. The X-ray diffraction data for this residue show the presence of plumbogummite minerals, phyllosilicate clays, quartz and goethite, but no fluorides. An even higher P content (1.54%) occurred in the residue from the two-hour digestion. X-ray diffraction again showed the presence of plumbogummite minerals, but no quartz, fluorides or goethite could be identified. Prolonging the digestion beyond 2 hours led to precipitation of complex fluorides, a reduction in the P content of the residue, and to a reduction in the percentage of the total P in the clay that was recovered in the residue. Plumbogummite minerals could still be identified in the digestion residue after 24 hours when the HF concentration was 20%, but not when it was increased to 48%. If all the P recovered in the residue following this latter treatment were assigned to plumbogummite



minerals, they would form  $<1.7\%$  of the weight of the residue. It is doubtful if X-ray diffraction would detect this low concentration. These data also confirm the solubility of (soil) plumbogummite minerals in HF.

Plumbogummite minerals could not be positively identified in any of the digestion residues from the chronosequence samples. The highest P content obtained from any of these residues was  $0.21\%$  from the B<sub>3</sub>G horizon of the Okarito silt loam following a two-hour digestion with  $20\%$  HF. This amount of P corresponds to a maximum plumbogummite mineral content of  $2-3\%$ . The diffractogram obtained from the residue after the two-hour digestion does show a small peak at  $0.296$  nm, sandwiched between two fluoride spacings at  $0.302$  and  $0.289$  nm (Figure 83). It is possible that the  $0.296$  nm spacing is derived from a mineral of the plumbogummite group, but no additional spacings of these minerals were observed. The  $0.296$  nm spacing was absent in samples subjected to more drastic HF digestion.

Figure 83 also shows that the ratio of the intensity of the (101) spacing of anatase to that of the (110) spacing of rutile decreased from  $2.89$  after the two-hour digestion to  $0.83$  following 24-hour treatment with  $48\%$  HF. These results indicate that anatase is dissolved by digestion with HF, and that rutile is either less soluble than anatase or insoluble. The other chronosequence samples examined gave comparable results. The  $<2$   $\mu\text{m}$  clays were then subdivided into fine and coarse fractions and separate treatment of these by two-hour

digestion with 20% HF showed that anatase tended to be concentrated in the finer fraction and rutile in the coarser. The finer particle size of anatase may account for its greater solubility in HF.

Although the soils of the Reefton chronosequence, and the Kaiteriteri hill soil, were known to contain high so-called 'residual' P fractions, plumbogummite minerals could be positively identified only in the latter soil. The P—containing compounds in the chronosequence soils could not be concentrated sufficiently by HF digestion to permit their identification by X-ray diffraction. It is unlikely that identification of plumbogummite minerals in soils containing appreciable quantities of mica, quartz or other minerals, that do not dissolve rapidly in HF, can be achieved by increasing the duration or intensity of the digestion, as plumbogummite minerals appear to be soluble in HF, and prolonged digestion leads to the precipitation of complex fluorides. Similarities between the X-ray diffraction spacings of such fluoride precipitates and those of plumbogummite minerals have led to the precipitates being mistaken for minerals of the plumbogummite group. Techniques that can remove micaceous minerals and quartz without loss of P, or chemical methods that compare changes in inorganic phosphate fractions before and after calcination (Adams, Howarth and Campbell, 1973) are suggested as possible areas for further investigation.

## CHAPTER FOUR

## SUMMARY

1. A chronosequence of soils ranging in age from about 1000 to at least 130,000 years, developed on a series of glacial outwash terraces near Reefton, New Zealand, was recognised, described and studied.
2. Changes in soil chemical and mineralogical properties as a function of the duration of weathering were investigated.
3. The effects of impeded drainage and of short term, short range variations in the intensity of the biotic factor were examined.
4. Attempts were made to determine if minerals of the plumbogummite group were responsible for the high proportion of soil phosphate from some strongly weathered soils that, on fractionation, appeared in the residual P fraction.
5. Literature pertaining to the factors influencing soil formation in the study area, the analytical procedures used, the nature of poorly-ordered soil colloids, the qualitative and quantitative determination of crystalline and non-crystalline clay minerals, and the genesis of clay minerals were reviewed.

6. The parent materials, relief, climate and vegetation found in the area were described. Soil morphogenesis was illustrated by detailed profile descriptions and by a colour plate.
7. The sampling methods and analytical techniques used in the study were described.
8. Soil pH values throughout the sequence were low to very low, and nowhere  $> 5.4$ . Depth functions showed slight increases. The pH of the surface horizon was related to distance from the nearest living red beech, or decaying beech stump, and variations of up to 1.4 units were observed over distances  $< 6$  m.
9. The total weight of soil in a tessera initially declined, but following the collapse of soil structure and the development of gley podzols considerable increases occurred. The resulting variations in the weight of inorganic material in constant soil volume made it difficult to determine the actual gains and losses caused by pedogenesis.
10. Multiple regression analyses showed that about 90% of the variation in CEC of the soils could be predicted from their clay and organic matter contents. The mean CEC's of clay and organic matter were  $42 \pm 10$  and  $88 \pm 10$  me  $100\text{g}^{-1}$ , respectively. The organic fraction made four

times the contribution of the clay fraction to the CEC of the yellow-brown earths, but in the gley podzols the clay contribution was twice that of the organic fraction. A progressive drop in the CEC of organic matter with increasing soil development, and the presence of expanding 2 : 1-Type phyllosilicates in the older soils, were responsible for these differences.

11. Total Mg, Al, K, Ca and Fe decreased asymptotically with increasing soil development. Because they formed an increasing percentage of a greater total weight of inorganic material, total Si and Ti increased beyond 18,000 years, when data were compared on a volume-weight basis. Alternative methods of analysing the data were considered.
12. Application of a differential DTA technique showed that recognised methods of allophane determination by selective dissolution analyses dissolved appreciable gibbsite and crystalline phyllosilicates from the yellow-brown earth members of the sequence. It is essential that materials of pedologic rather than geologic origin are used to check the inactivity of soil clays in selective dissolution reagents. Differential DTA and infrared techniques make it possible to test actual components in any given range of samples.

13. Poorly-ordered and organic-complexed forms of Al and Fe accumulated during the first 18,000 years of soil development. The former were reduced to low levels in the two gley podzols.
14. On the Ahaura silt loam, the oldest yellow-brown earth in the sequence, growth of individual red beech trees concentrated rainfall, caused a reduction in pH and increased the supply of water soluble chelates. This led to localised depletion of Al and Fe in relation to Si in the upper horizons, and levels of these elements were altered towards those now found in the gley podzols. The magnitude of the change increased with the size and age of the tree and decreased with distance from it.
15. Differences in the mineralogical compositions of the sand, silt and clay fractions between soils of increasing age were consistent with the further weathering of a parent material of similar mineralogical composition.
16. It was concluded that in yellow-brown earth environments where  $\text{pH} > 4.5$ , Al and Fe were accumulated relative to Si, and the soil was moving (slowly) towards a lateritic end product. Under these conditions the stable weathering products of mica, ferromagnesian chlorite and feldspar from the parent material were pedogenic

chlorite, kaolinite, gibbsite and allophane. It was further concluded that the combination of low pH ( $< 4.5$ ) and high organic matter levels associated with the growth of individual beech trees initiated a second weathering cycle in which Al and Fe were lost from the upper horizons resulting in the destruction of allophane, gibbsite and ferromagnesian chlorite and in dealumination of pedogenic intergrades first to vermiculite and then to montmorillonite. The direction of weathering was thus altered towards a podzolic end product. The maximum expression of the second cycle was observed in the upper horizons close to the stems of the larger living beech trees and decaying stumps where stemflow effects were greatest and had operated for the longest duration. The yellow-brown earth environment was considered to represent a dynamic system in which both cycles could alternate.

17. It was concluded that the gley podzols represented more advanced weathering stages than the yellow-brown earths, and that podzolisation preceded gleying. The presence of loess of low permeability was not considered to be a necessary prerequisite for the formation of gley podzols.
18. Prolonged digestion with HF dissolved minerals of the plumbogummite group, and precipitated complex fluorides that gave X-ray diffraction spacings

that have been confused with those of plumbogummite minerals.

19. The identification of plumbogummite minerals in HF—digestion residues depended upon the degree of concentration of the phosphate that could be obtained. They were identified in a clay fraction with a high content of kaolinite, but not in samples that contained appreciable mica and quartz.
20. The considerable variations in chemical and mineralogical properties that could occur over very short distances in the yellow-brown earth members of the sequence indicated that considerable care is necessary when sampling such soils. The samples taken from these soils for the chronosequence part of the study should be regarded as indicative of sites showing minimum podzolisation.



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## REFERENCES

- ADAMS, J.A. 1970. A study of soil sequences in relation to the growth of Pinus radiata in Nelson. Thesis, Ph. D., Lincoln College, University of Canterbury, N.Z. 376 p.
- ADAMS, J.A., HOWARTH, D.T., & CAMPBELL, A.S. 1973. Plumbogummite minerals in a strongly weathered New Zealand soil. J. Soil. Sci. 24: 224-231.
- ADDISCOTT, T.M. 1970. A note on resolving soil cation exchange capacity into 'mineral' and 'organic' fractions. J. agric. Sci., Camb. 75: 365-367.
- ALEKSANDROVA, L.N. 1960. The use of sodium pyrophosphate for isolating free humic substances and their organic-mineral compounds from soil. Soviet Soil Sci. 2: 190-197.
- ALEXANDER, E.B. 1974. Extractable iron in relation to soil age on terraces along the Truckee River, Nevada. Proc. Soil. Sci. Soc. Am. 38: 121-124.
- ALEXANDER, T.G., & ROBERTSON, J.A. 1968. Ascorbic acid as a reductant for total phosphorus determination in soils. Can. J. Soil Sci. 48: 217-218.
- ALEXIADES, C.A., & JACKSON, M.L. 1965. Quantitative determination of vermiculite in soils. Proc. Soil Sci. Soc. Am. 29: 522-527.

- ALEXIADES, C.A., & JACKSON, M.L. 1966a. Chlorite determination in clays of soils and mineral deposits. *Am. Miner.* 52: 1855-1873.
- ALEXIADES, C.A., & JACKSON, M.L. 1966b. Quantitative clay mineralogical analysis of soils and sediments. *Proc. natn. Conf. Clays* 14: 35-52.
- ALEXIADES, C.A., & PAXINOS, S.A. 1965. A method for determination of allophane in soil clays. *Agric. Annls Aristotelian Univ., Thessaloniki* 1965: 275-301.
- ALEXIADES, C.A. et al. 1973. High trioctahedral vermiculite content in the sand, silt and clay fractions of a gray brown podzolic soil in Greece. *Soil Sci.* 116: 363-375.
- ANDREW, R.W., JACKSON, M.L., & WADA, K. 1960. Intersalation as a technique for differentiation of kaolinite from chloritic minerals by X-ray diffraction. *Proc. Soil Sci Soc. Am.* 24: 422-423.
- AOMINE, S. 1957. Potassium economy of Japanese volcanic ash soils. *Jap. Potassium Symp. int. Potash Inst., Berne*: 88-102.
- AOMINE, S., INOUE, A., & MIZOTA, C. 1972. Imogolite of Chilean volcanic ash soils. *Clay Sci.* 4: 95-103.
- AOMINE, S., & JACKSON, M.L. 1959. Allophane determination in Ando soils by cation-exchange capacity delta value. *Proc. Soil Sci. Soc. Am.* 23: 210-214.

- AOMINE, S., & MIYAUCHI, N. 1965. Imogolite of imogolayers in Kyushu. Soil Sci. Pl. Nutr. 11: 212-219.
- AOMINE, S., & MIZOTA, C. 1972. Distribution and genesis of imogolite in volcanic ash soils of northern Kanto, Japan. (Abst.). 1972 Int. Clay Conf., Madrid, p. 103-104.
- AOMINE, S., & OTSUKA, H. 1968. Surface of soil allophanic clays. Trans. 9th int. Congr. Soil Sci., Adelaide, I: 731-737.
- AOMINE, S., & WADA, K. 1962. Differential weathering of volcanic ash and pumice, resulting in formation of hydrated halloysite. Am. Miner. 47: 1024-1048.
- AOMINE, S., & YOSHINAGA, N. 1955. Clay minerals of some well-drained volcanic ash soils in Japan. Soil Sci. 79: 349-358.
- ARSHAD, M.A., ST. ARNAUD, R.J., & HUANG, P.M. 1972. Dissolution of trioctahedral layer silicates by ammonium oxalate, sodium dithionite-citrate-bicarbonate, and potassium pyrophosphate. Can. J. Soil Sci. 52: 19-26.
- BAILEY, S.W. et al. 1971. Summary of national and international recommendations on clay mineral nomenclature. Clays Clay Miner. 19: 129-131.
- BALASUBRAMANIAM, C., & JAYARAMAN, M.V. 1952. Review of literature on rainfall as fertilizer. Madras agric. J. 39: 519-520.

- BALL, D.F. 1964. Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils. J. Soil Sci. 15: 84-92.
- BARSHAD, I. 1964. Chemistry of soil development, p. 1-70. In Bear, F.E., ed. Chemistry of the soil. 2d ed. Reinhold, New York. (A.C.S. Monograph No. 160). 515 p.
- BARTLETT, J.D., RUBLE, R.W., & THOMAS, R.P. 1937. The influence of hydrogen peroxide treatments on the exchange capacity of Maryland soils. Soil Sci. 44: 123-138.
- BASCOMB, C.L. 1968. Distribution of pyrophosphate-extractable iron and organic carbon in soils of various groups. J. Soil Sci. 19: 251-268.
- BAVER, L.D. 1930. The effect of organic matter upon several physical properties of soils. J. Am. Soc. Agron. 22: 703-708.
- BELYAYEVA, N.I. 1966. Determination of aluminium in the presence of iron: spectrophotometric method using the reagent Ferron. Soviet Soil Sci. 2: 218-220.
- BENNETT, H., & REED, R.A. 1971. Chemical methods of silicate analyses - A handbook, p. 75-78. Academic Press, London.
- BESOAIN, E.M. 1964. Clay formation in some Chilean soils derived from volcanic materials. N.Z. Jl. Sci. 7: 79-86.

- BESOAIN, E.M. 1968/1969. Imogolite in volcanic soils of Chile. *Geoderma* 2: 151-169.
- BHUMBLA, D.R., & McLEAN, E.O. 1965. Aluminium in soils : VI. *Proc. Soil Sci. Soc. Am.* 29: 370-374.
- BIDWELL, O.W., & HOLE, F.D. 1965. Man as a factor of soil formation. *Soil Sci.* 99: 65-72.
- BIRRELL, K.S., & FIELDES, M. 1952. Allophane in volcanic ash soils. *J. Soil Sci.* 3: 156-166.
- BIRRELL, K.S., & FIELDES, M. 1968. Amorphous constituents. *Soil Bur. Bull. N.Z.* 26 (2): 39-48.
- BISCAYE, P.E. 1964. Distinction between kaolinite and chlorite in recent sediments by X-ray diffraction. *Am. Miner.* 49: 1281-1289.
- BISCAYE, P.E. 1965. Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans. *Geol. Soc. Am. Bull.* 76: 803-832.
- BLAKEMORE, L.C. 1968. Determination of iron and aluminium in Tamm's soil extracts. *N.Z. J1 agric. Res.* 11: 515-520.
- BLANCHARD, F.N. 1971. Thermal analysis of crandallite. *Q. J1 Fla Acad. Sci.* 34(1): 1-9.
- BLEEKER, P., & PARFITT, R.L. 1974. Volcanic ash and its clay mineralogy at Cape Hoskins, New Britain, Papua New Guinea. *Geoderma* 11: 123-135.

BLOOMFIELD, C. 1953-1955. A study of podzolization.  
I-VI.  
J. Soil Sci 4: 5-16, 17-23.  
Ibid. 5: 39-45, 46-49, 50-56.  
Ibid. 6: 284-292.

BLOOMFIELD, C. 1957. The possible significance of  
polyphenols in soil formation. J. Soil  
Sci. 8: 389-392.

BLOSSER, D.L., & JENNY, H. 1971. Correlations of  
soil pH and percent base saturation as  
influenced by soil-forming factors.  
Proc. Soil Sci. Soc. Am. 35: 1017-1018.

BORCHARDT, G.A., HARWARD, M.E., & KNOX, E.G. 1971.  
Trace element concentration in amorphous  
clays of volcanic ash soils in Oregon.  
Clays Clay Miner. 19: 375-382.

BOWEN, F.E. 1964. Geological map of New Zealand  
1:250,000. Sheet 15, Buller. N.Z.  
Geological Survey, D.S.I.R., Wellington.

BRACEWELL, J.M., CAMPBELL, A.S., & MITCHELL, B.D. 1970.  
An assessment of some thermal and chemical  
techniques used in the study of the poorly-  
ordered aluminosilicates in soil clays.  
Clay Miner. 8: 325-335.

BRADFELD, R. 1924. The importance of hydrogen ion  
concentration in physico-chemical studies  
of heavy soils. Soil Sci. 17: 411-422.



- BRADLEY, W.F. 1953. Analysis of mixed-layer clay mineral structures. *Analyt. Chem.* 25: 727-730.
- BRADLEY, W.F. 1954. X-ray diffraction criteria for the characterization of chlorite material in sediments. *Proc. natn. Conf. Clays* 2: 324-334.
- BREMNER, J.M., & JENKINSON, D.S. 1960. Determination of organic carbon in soil. Oxidation by dichromate of organic matter in soil and plant materials. *J. Soil Sci.* 11: 394-402.
- BRINDLEY, G.W. 1961. Quantitative analysis of clay mixtures, p. 489-516. In Brown, G., ed. *The X-ray identification and crystal structures of clay minerals*. 2d ed. Mineralogical Society, London. 544p.
- BRINDLEY, G.W., & GILLERY, F.H. 1956. X-ray identification of chlorite species. *Am. Miner.* 41: 169-186.
- BRINDLEY, G.W., & YOEELL, R.F. 1951. A chemical determination of "tetrahedral" and "octahedral" aluminium ions in a silicate. *Acta Crystallogr.* 4: 495-496.
- BRINER, G.P., & JACKSON, M.L. 1969. Allophanic material in Australian soils derived from Pleistocene basalt. *Aust. J. Soil Res.* 7: 163-169.

- BROADBENT, F.E. 1955. Basic problems in organic matter transformations. Soil Sci. 79: 107-114.
- BROMFIELD, S.M. 1965. Studies on the relative importance of iron and aluminium in the sorption of phosphate by some Australian soils. Aust. J. Soil Res. 3: 31-44.
- BROWN, B.E., & JACKSON, M.L. 1958. Clay mineral distribution in the Hiawatha sandy soils of northern Wisconsin. Proc. natn. Conf. Clays 5: 213-226.
- BROWN, G. 1955. The effects of isomorphous substitution on the intensities of the 001 reflections of mica-and chlorite-type structures. Mineralog. Mag. 30: 657-665.
- BROWN, J., & TEDROW, J.C.F. 1964. Soils of the Northern Brooks Range, Alaska: 4. Well drained soils of the glaciated valleys. Soil Sci. 97: 187-195.
- BRYDON, J.E., & DAY, J.H. 1970. Use of the Fieldes and Perrott sodium fluoride test to distinguish the B horizons of podzols in the field. Can. J. Soil Sci. 50: 35-41.
- BRYDON, J.E., KODAMA, H., & ROSS, G.J. 1968. Mineralogy and weathering of the clays in orthic podzols and other podzolic soils in Canada. Trans. 9th int. Congr. Soil Sci., Adelaide, II: 41-51.
- BRYDON, J.E., & SHIMODA, S. 1972. Allophane and other amorphous constituents in a podzol from Nova Scotia. Can. J. Soil Sci. 52: 465-475.

- BURROWS, C.J., & LUCAS, J. 1967. Variations in two New Zealand glaciers during the past 800 years. *Nature* 216: 467-468.
- CALHOUN, F.G., CARLISLE, V.W., & LUNA Z. 1972. Properties and genesis of selected Colombian andosols. *Proc. Soil Sci. Soc. Am.* 36: 480-485.
- CAMPBELL, A.S. 1974. The influence of red beech (Nothofagus fusca) on clay mineral genesis. *Trans. 10th int. Congr. Soil Sci., Moscow*, VI: 60-67.
- CAMPBELL, A.S., MITCHELL, B.D., & BRACEWELL, J.M. 1968. Effects of particle size, pH and organic matter on the thermal analysis of allophane. *Clay Miner.* 7: 451-454.
- CHANG, S.C., & JACKSON, M.L. 1958. Soil phosphorus fractions in some representative soils. *J. Soil Sci.* 9: 109-119.
- CHICHESTER, F.W., YOUNGBERG, C.T., & HARWARD, M.E. 1969. Clay mineralogy of soils formed on Mazama pumice. *Proc. Soil Sci. Soc. Am.* 33: 115-120.
- CLARK, J.S. 1964. Aluminium and iron fixation in relation to exchangeable hydrogen in soils. *Soil Sci.* 98: 302-306.
- CLARK, J.S., & NICHOL, W.E. 1968. Estimation of the inorganic and organic pH-dependent cation exchange capacity of the B horizons of podzolic and brunisolic soils. *Can. J. Soil Sci.* 48: 53-64.

CLOOS, P., HERBILLON, A., & ECHEVERRIA, J. 1968.

Allophane-like synthetic silico-aluminas.

Phosphate adsorption and availability.

Trans. 9th int. Congr. Soil Sci., Adelaide,  
II: 733-743.

CLOOS, P. et al. 1969. Structural organization in  
amorphous silico-aluminas. Clays Clay  
Miner. 17: 279-287.

COLEMAN, N.T., & THOMAS, G.W. 1967. The basic chemistry  
of soil acidity, p. 1-41. In Pearson, R.W.,  
& Adams, F., eds. Agronomy 12. American  
Society of Agronomy, Madison, Wisconsin.  
274 p.

COLEMAN, N.T., WEED, S.B., & McCracken, R.J. 1959.  
Cation-exchange capacity and exchangeable  
cations in Piedmont soils of North Carolina.  
Proc. Soil Sci. Soc. Am. 23: 146-149.

COLEMAN, R., & JACKSON, M.L. 1945. Mineral composition  
of the clay fraction of several Coastal  
Plain soils of Southeastern United States.  
Proc. Soil Sci. Soc. Am. 10: 381-391.

CONREY, G.W., & GREEN, T.C. 1932. Relation of state of  
development of soils to their degree of base  
saturation. Am. Soil Surv. Ass. Bull.  
13: 111-124.

CORTES, A., & FRANZMEIER, D.P. 1972. Climosequence of  
ash-derived soils in the Central Cordillera  
of Colombia. Proc. Soil Sci. Soc. Am. 36:  
653-659.

COULSON, C.B., DAVIES, R.I., & LEWIS, D.A. 1960a.  
Polyphenols in plant, humus and soil. I.  
Polyphenols of leaves, litter and superficial  
humus from mull and mor sites. J. Soil Sci.  
11: 20-29.

- COULSON, C.B., DAVIES, R.I., & LEWIS, D.A. 1960b.  
Polyphenols in plant, humus and soil.  
II. Reduction and transport by polyphenols  
of iron in model soil columns. J. Soil  
Sci. 11: 30-44.
- COUPER, R.A. 1960. New Zealand Mesozoic and Cainozoic  
plant microfossils. N.Z. geol. Surv. Paleont.  
Bull. 32: 1-87.
- CRADWICK, P.D.C. et al. 1972. Imogolite, a hydrated  
aluminium silicate of tubular structure.  
Nature phys. Sci. 240: 187-189.
- CROCKER, R.L. 1952. Soil genesis and the pedogenic  
factors. Q. Rev. Biol. 27: 139-168.
- CROCKER, R.L. 1959. The plant factor in soil formation.  
Aust. J. Sci. 21: 180-193.
- CROCKER, R.L. 1960. The plant factor in soil formation.  
Proc. IX Pacif. Sci. Congr. 18: 84-90.
- CURTIS, C.D. 1970. Differences between lateritic  
and podzolic weathering. Geochim.  
Cosmochim. Acta. 34: 1351-1353.
- DANSGAARD, W. et al. 1969. One thousand centuries of  
climatic record from Camp Century on the  
Greenland ice sheet. Science, N.Y. 166:  
377-381.
- DAVIES, B.E. 1974. Loss-on-ignition as an estimate of  
soil organic matter. Proc. Soil Sci. Soc.  
Am. 38: 150-151.

- DAVIES, B.E., & DAVIES, R.I. 1965. Changes in exchangeable cations and exchange capacity of soil consequent on oxidation of its organic matter. J. agric. Sci., Camb. 65: 241-243.
- DAVIS, C.E., & HOLDRIDGE, D.A. 1969. Quantitative estimation of clay minerals by D.T.A. Clay Miner. 8: 193-200.
- DAVIS, F.L. 1945. Retention of phosphates by soil: II. Effect of drying of certain cations and anions on the cation-exchange capacity of soils. Soil Sci. 59: 175-190.
- DAY, D.E. 1963. Determining the co-ordination number of aluminium ions by X-ray emission spectroscopy. Nature 200: 649-651.
- DEB, B.C. 1950. The estimation of free iron oxides in soils and clays and their removal. J. Soil Sci. 1: 212-220.
- DE KIMPE, C., GASTUCHE, M.C., & BRINDLEY, G.W. 1961. Ionic coordination in alumino-silicic gels in relation to clay mineral formation. Am. Miner. 46: 1370-1381.
- DE KIMPE, C., GASTUCHE, M.C., & BRINDLEY, G.W. 1964. Low temperature synthesis of kaolin minerals. Am. Miner. 49: 1-16.
- DE LONG, W.A., & SCHNITZER, M. 1955. Investigations on the mobilization and transport of iron in forested soils. I. The capacities of leaf extracts and leachates to react with iron. Proc. Soil Sci. Soc. Am. 19: 360-363.

- DESHPANDE, T.L., GREENLAND, D.J., & QUIRK, J.P. 1964.  
Charges on iron and aluminium oxides in soils.  
Trans. 8th int. Congr. Soil Sci., Bucharest,  
III: 1213-1225.
- DE VILLIERS, J.M. 1969. Pedosolquioxides - composition  
and colloidal interactions in soil genesis  
during the Quaternary. Soil Sci. 107:  
454-461.
- DE VILLIERS, J.M. 1971. The problem of quantitative  
determination of allophane in soil.  
Soil Sci. 112: 2-7.
- DE VILLIERS, J.M., & JACKSON, M.L. 1967a. Cation  
exchange capacity variations with pH in  
soil clays. Proc. Soil Sci. Soc. Am. 31:  
473-476.
- DE VILLIERS, J.M., & JACKSON, M.L. 1967b. Aluminous  
chlorite origin of pH-dependent cation  
exchange capacity variations.  
Proc. Soil Sci. Soc. Am. 31: 614-619.
- DICKSON, B.A., & CROCKER, R.L. 1954. A chronosequence  
of soils and vegetation near Mt. Shasta,  
California. III. J. Soil Sci. 5: 173-191.
- DIXON, J.B., & JACKSON, M.L. 1962. Properties of inter-  
gradient chlorite-expansible layer silicates  
of soils. Proc. Soil Sci. Soc. Am. 26:  
358-362.
- DOAK, B.W. et al. 1965. Low-temperature calcination  
of 'C'-grade phosphate from Christmas  
Island. N.Z. Jl agric. Res. 8: 15-29.

- DOKUCHAEV, V.V. 1951. Writings. Vol 6, p. 381.  
Akademia Nauk, Moscow.
- DOLCATER, D.L., SYERS, J.K., & JACKSON, M.L. 1970.  
Titanium as free oxide and substituted  
forms in kaolinites and other soil minerals.  
Clays Clay Miner., 18: 71-79.
- DOUGLAS, L.A. 1971. Hydrogen peroxide-organic matter-  
pH interactions. Proc. Soil Sci. Soc.  
Am. 35: 514.
- DOUGLAS, L.A., & FIESSINGER, F. 1971. Degradation of  
clay minerals by  $H_2O_2$  treatments to oxidize  
organic matter. Clays Clay Miner. 19:  
67-68.
- DUDAS, M.J., & HARWARD, M.E. 1971. Effect of  
dissolution treatment on standard and soil  
clays. Proc. Soil Sci. Soc. Am. 35: 134-139.
- EGAWA, T., & SATO, A. 1960. A study on D.T.A. curves  
of the allophanic clays separated from  
volcanic ash soils in Japan. Adv. Clay  
Sci. 2: 385-393.
- EGAWA, T., SATO, A., & NISHIMURA, T. 1960. Release of  
OH ions from clay minerals treated with  
various anions, with special reference to  
the structure and chemistry of allophane.  
Adv. Clay Sci. 2: 252-262.
- ELLIS, R.C. 1969. Mineral losses during soil  
formation in granitic material.  
Aust. J. Soil Res. 7: 317-323.
- EMILIANI, C. 1966. Isotopic paleotemperatures.  
Science, N.Y. 154: 851-856.



- ESWARAN, H. 1972. Morphology of allophane, imogolite and halloysite. *Clay Miner.* 9: 281-285.
- ESWARAN, H., & DE CONINCK, F. 1971. Clay mineral formations and transformations in basaltic soils in tropical environments. *Pédologie* 21 : 181-201.
- FARMER, V.C., & MITCHELL, B.D. 1963. Occurrence of oxalates in soil clays following hydrogen peroxide treatment. *Soil Sci.* 96: 221-229.
- FIELDES, M. 1953. The formulation of secondary minerals in soils in relation to parent material, silicate structure and degree of weathering. *Proc. Aust. Conf. Soil Sci., Adelaide*, 2: 6.29.1 - 6.29.6.
- FIELDES, M. 1955. Clay mineralogy of New Zealand soils. Part 2: Allophane and related mineral colloids. *N.Z. J1 Sci. Technol.* B37: 336-350.
- FIELDES, M. 1957. Clay mineralogy of New Zealand Soils. Part 4: Differential thermal analysis. *N.Z. J1 Sci. Technol.* B38: 533-570.
- FIELDES, M. 1958. The role of clays in soil fertility. *Proc. N.Z. Inst. agric. Sci.* 4: 84-102.
- FIELDES, M. 1962. The nature of the active fraction of soils. *Trans. Commns IV & V, int. Soc. Soil Sci. (Conf. New Zealand, 1962)*: 62-78.
- FIELDES, M. 1966. The nature of allophane in soils. Part 1: Significance of structural randomness in pedogenesis. *N.Z. J1 Sci.* 9: 599-607.

- FIELDES, M. 1968. Clay mineralogy.  
Soil Bur. Bull. N.Z. 26 (2): 22-39.
- FIELDES, M., & FURKERT, R.J. 1966. The nature of  
allophane in soils. Part 2: Differences in  
composition. N.Z. J1 Sci. 9: 608-622.
- FIELDES, M., & PERROTT, K.W. 1966. The nature of  
allophane in soils. Part 3: Rapid field  
and laboratory test for allophane.  
N.Z. J1 Sci. 9: 623-629.
- FIELDES, M., & SCHOFIELD, R.K. 1960. Mechanisms of  
ion adsorption by inorganic soil colloids.  
N.Z. J1 Sci. 3: 563-579.
- FIELDES, M., & SWINDALE, L.D. 1954. Chemical weathering  
of silicates in soil formation.  
N.Z. J1 Sci. Technol. B36: 140-154.
- FLEISCHER, M. 1963. New mineral names.  
Am. Miner. 48: 434.
- FOLLETT, E.A.C. et al. 1965a. Chemical dissolution  
techniques in the study of soil clays:  
Part 1. Clay Miner. 6: 23-34.
- FOLLETT, E.A.C. et al. 1965b. Chemical dissolution  
techniques in the study of soil clays:  
Part 2. Clay Miner. 6: 35-43.
- FRANKLIN, R.E., GERSPER, P.L., & HOLOWAYCHUK, N. 1967.  
Analysis of gamma-ray spectra from soils  
and plants. II. Effects of trees on the  
distribution of fallout. Proc. Soil Sci.  
Soc. Am. 31: 43-45.

- FRANKLIN, W.T., & REISENAUER, H.M. 1960. Chemical characteristics of soils related to phosphate fixation and availability. Soil Sci. 90: 192-200.
- FRANZMEIER, D.P., HAJEK, B.F., & SIMONSON, C.H. 1965. Use of amorphous material to identify spodic horizons. Proc. Soil Sci. Soc. Am. 29: 737-743.
- FRANZMEIER, D.P., & WHITESIDE, E.P. 1963. A chronosequence of podzols in Northern Michigan. I. Ecology and description of pedons. Q. Bull. Mich. St. Univ. agric. Exp. Stn 46: 2-20.
- FRANZMEIER, D.P., WHITESIDE, E.P., & MORTLAND, M.M. 1963. A chronosequence of podzols in northern Michigan. III. Mineralogy, micromorphology, and net changes occurring during soil formation. Q. Bull. Mich. St. Univ. agric. Exp. Stn 46: 37-57.
- FRINK, C.R. 1969. Chemical and mineralogical characteristics of eutrophic lake sediments. Proc. Soil Sci. Soc. Am. 33: 369-372.
- FURKERT, R.J., & FIELDS, M. 1968. Allophane in New Zealand soils. Trans. 9th int. Congr. Soil Sci., Adelaide, III: 133-141.
- GAGE, M. 1965. Some characteristics of Pleistocene cold climates in New Zealand. Trans. R. Soc. N.Z. 3: 11-21.

- GARCÍA, S.G., & CAMAZANO, M.S. 1968. Differentiation of kaolinite from chlorite by treatment with dimethyl-sulphoxide. Clay Miner. 7: 447-450.
- GARDNER, L.R. 1970. A chemical model for the origin of gibbsite from kaolinite. Am. Miner. 55: 1380-1389.
- GASTUCHE, M.C. 1964. The octahedral layer. Proc. natn. Conf. Clays 12: 471-493.
- GASTUCHE, M.C., & HERBILLON, A. 1962. Etude des gels d'alumine: cristallisation en milieu désionisé. Bull. Soc. chim. Fr. 1404-1412.
- GASTUCHE, M.C. et al. 1963. Study of intermediate stages in the kaolin-metakaolin transformation. Clay Miner. Bull. 5: 227-236.
- GEDROITS, K.K. 1963. Chemical analysis of soils, p. 248 - 251. Translated from the Russian. Israel Programme for Scientific Translations, Jerusalem. 608 p.
- GERSPER, P.L. 1970. Effect of American beech trees on the gamma radioactivity of soils. Proc. Soil Sci. Soc. Am. 34: 318-323.
- GERSPER, P.L., & HOLOWAYCHUK, N. 1970a. Effects of stemflow water on a Miami soil under a beech tree: I. Morphological and physical properties. Proc. Soil Sci. Soc. Am. 34: 779-786.

- GERSPER, P.L., & HOLOWAYCHUK, N. 1970b. Effect of stemflow water on a Miami soil under a beech tree: II. Chemical properties. Proc. Soil Sci. Soc. Am. 34: 786-794.
- GERSPER, P.L., & HOLOWAYCHUK, N. 1971. Some effects of stemflow from forest canopy trees on chemical properties of soils. Ecology 52: 691-702.
- GIBBS, H.S., MERCER, A.D., & COLLIE, T.W. 1950. Soils and agriculture of Westland, N.Z. Soil Bur. Bull. N.Z. 2:1-24.
- GILBERT, G.E. 1953. Rainfall interception by relatively undisturbed deciduous forest in central Ohio. Thesis, Ph.D., The Ohio State University, U.S.A.
- GJEMS, O. 1960. Some notes on clay minerals in podzol profiles in Fennoscandia. Clay Miner. Bull 4: 208-211.
- GJEMS, O. 1963. A swelling dioctahedral clay mineral of vermiculite-smectite type in the weathering horizons of podzols. Clay Miner. Bull. 5: 183-193.
- GJEMS, O. 1967. Studies on clay minerals and clay-mineral formation in soil profiles in Scandinavia. Saertr. Meddr norske Skogsfors Ves. nr 81: 299-415.
- GJEMS, O. 1970. Mineralogical composition and pedogenic weathering of the clay fraction in podzol soil profiles in Zalesine, Yugoslavia. Soil Sci. 110: 237-243.

- GODWIN, H., & SWITSUR, V.R. 1966. Cambridge University natural radiocarbon measurements, VIII. Radiocarbon 8: 390-400.
- GOLDICH, S.S. 1938. A study of rock weathering. J. Geol. 46: 17-58.
- GORBUNOV, N.J., DZYADEVICH, G.S., & TUNIK, B.N. 1961. Methods of determining non-silicate amorphous and crystalline sesquioxides in soils and clays. Soviet Soil Sci. 2: 1252-1259.
- GREENE-KELLY, R. 1957. The montmorillonite minerals (smectites), p. 140-164. In MacKenzie, R.C., ed. The differential thermal investigation of clays. Mineralogical Society, London. 456 p.
- GREENLAND, D.J. 1971. Interactions between humic and fulvic acids and clays. Soil Sci. 111: 34-41.
- GREENLAND, D.J., WADA, K., & HAMBLIN A. 1969. Imogolite in a volcanic ash soil from Papua. Aust. J. Sci. 32: 56-57.
- GREGG, D.R. 1966. Age of Pyramid Valley Moas. A. Rep., Canterbury Mus., Christchurch, N.Z., 1965-1966. p. 34.
- GRIM, R.E. 1953. Clay mineralogy. McGraw-Hill, New York, 384 p.
- GRIM, R.E., & BRADLEY, W.F. 1948. Rehydration and dehydration of the clay minerals. Am. Miner. 33: 50-59.

- GRIM, R.E., BRADLEY, W.F., & WHITE, W.A. 1957.  
Petrology of the Paleozoic shales of  
Illinois. Ill. Geol. Surv. Rep. Invest.  
203: 35 p.
- GRIM, R.E., BRAY, R.H., & BRADLEY, W.F. 1937.  
Mica in argillaceous sediments.  
Am. Miner. 22: 813-829.
- GRUNERT, F. 1964. The biological nutrient cycle in  
mixed stands of pine and beech and in  
stands of pine. Albrecht-Thaer-Arch.  
8: 435-452.
- HAANTJENS, H.A. 1964. Lands of the Buna-Kokoda area,  
Papua New Guinea.  
C.S.I.R.O. Aust. Land Res. Surv. No 10: 83.
- HALLSWORTH, E.G., & WILKINSON, G.K. 1958. The  
contribution of clay and organic matter to  
the cation exchange capacity of the soil.  
J. agric. Sci., Camb. 51: 1-3.
- HAMBLIN, A.P., & GREENLAND, D.J. 1972. Mineralogy of  
soils from the Holocene volcanic area of  
southern Australia. Aust. J. Soil Res.  
10: 61-79.
- HAMMEN, T.V.D. et al. 1967. Stratigraphy, climatic  
succession and radiocarbon dating of the  
last glacial in the Netherlands.  
Geologie Mijnb. 46: 79-95.
- HANNA, W.G., & REED, J.F. 1948. A comparison of  
ammonium acetate, barium acetate, and  
buffered barium chloride methods of  
determining cation-exchange properties  
of limed soils. Soil Sci. 66: 447-458.

- HARRIS, W.F. 1963. Paleo-ecological evidence from pollen and spores. *Proc. N.Z. ecol. Soc.* 10: 38-44.
- HARWARD, M.E., & THEISEN, A.A. 1962. Problems in clay mineral identification by X-ray diffraction. *Proc. Soil Sci. Soc. Am.* 26: 335-341.
- HARWARD, M.E., THEISEN, A.A., & EVANS, D.D. 1962. Effect of iron removal and dispersion methods on clay mineral identification by X-ray diffraction. *Proc. Soil Sci. Soc. Am.* 26: 535-541.
- HASHIMOTO, I., & JACKSON, M.L. 1960. Rapid dissolution of allophane and kaolinite-halloysite after dehydration. *Proc. natn. Conf. Clays* 7: 102-113.
- HAYASHI, H., & OINUMA, K. 1964. Behaviours of clay minerals in treatment with hydrochloric acid, formamide and hydrogen peroxide. *Clay Sci.* 2: 75-91.
- HELLER-KALLAI, L., YARIV, S., & RIEMER, M. 1973. The formation of hydroxy interlayers in smectites under the influence of organic bases. *Clay Miner.* 10: 35-40.
- HELLING, C.S., CHESTERS, G., & COREY, R.B. 1964. Contribution of organic matter and clay to soil cation-exchange capacity as affected by the pH of the saturating solution. *Proc. Soil Sci. Soc. Am.* 28: 517-520.



- HENDERSON, J., & ONGLEY, M. 1923. The geology of the Mokau subdivision with an account of the adjoining areas and of the Te Kuiti district, Pirongia and Taranaki, divisions. Bull. geol. Surv. N.Z. 24(n.s.): 1-83.
- HENDRICKS, D.M., WHITTIG, L.D., & JACKSON, M.L. 1967. Clay mineralogy of andesite saprolite. Proc. natn. Conf. Clays 15: 395-407.
- HENDY, C.H., & WILSON, A.T. 1968. Paleoclimatic data from speleothems. Nature 219: 48-51.
- HENSLEY, A.L., & BARNEY, J.E. 1958. Reaction of silica-alumina catalysts with sodium fluoride. J. phys. Chem., Wash. 62: 1560-1563.
- HEWITT, A.E. 1973. Artificial weathering of some soil clays. Dissertation, Dip. Agr. Sci., Lincoln College, University of Canterbury, N.Z. 66 p.
- HISSINK, D.J. 1924. Base exchange in soils. Trans. Faraday Soc. 20: 551-556.
- HOFMANN, U. 1956. Clay mineral studies in Germany, 1954 and 1955. Proc. natn. Conf. Clays 4: 161-165.
- HORTON, R.E. 1919. Rainfall interception. Mon. Weath. Rev. 47: 603-623.

- HOSKING, J.S., NEILSON, M.E., & CARTHEW, A.R. 1957.  
A study of clay mineralogy and particle size. Aust. J. agric. Res. 8: 45-74.
- HSU, PA HO. 1963. Effects of initial pH, phosphate and silicate on the determination of aluminium with aluminon.  
Soil Sci. 96: 230-238.
- HSU, PA HO. 1968. Heterogeneity of montmorillonite surface and its effect on the nature of hydroxy-aluminium interlayers.  
Clays Clay Miner. 16: 303-311.
- HSU, PA HO, & BATES, T.F. 1964. Formation of X-ray amorphous and crystalline aluminium hydroxides. Mineralog. Mag. 33: 749-768.
- HUANG, P.M., & JACKSON, M.L. 1965. Mechanism of reaction of neutral fluoride solution with layer silicates and oxides of soils.  
Proc. Soil Sci. Soc. Am. 29: 662-665.
- HUANG, W.H., & KELLER, W.D. 1970. Dissolution of rock-forming silicate minerals in organic acids. Am. Miner. 55: 2076-2094.
- ISHII, J., & KONDO, Y. 1962. Clay minerals of Quaternary volcanic ash and pumice deposits in Hokkaido. Earth Sci. 62: 29-45.
- JACKSON, M.L. 1956. Soil Chemical Analysis - Advanced Course. Published by the Author, Department of Soil Science, University of Wisconsin, Madison, WI 53706. 991 p.

- JACKSON, M.L. 1958. Soil Chemical Analysis.  
Prentice-Hall, Englewood Cliffs,  
New Jersey, 498 p.
- JACKSON, M.L. 1960. Structural role of hydronium in  
layer silicates during soil genesis.  
Trans. 7th int. Congr. Soil Sci., Madison,  
II: 445-455.
- JACKSON, M.L. 1963a. Aluminium bonding in soils:  
a unifying principle in soil science.  
Proc. Soil Sci. Soc. Am. 27: 1-10.
- JACKSON, M.L. 1963b. Interlayering of expansible layer  
silicates in soils by chemical weathering.  
Proc. natn. Conf. Clays 11: 29-46.
- JACKSON, M.L. 1964. Soil clay mineralogical analysis,  
p.245-294. In Rich C.I., & Kunze, G.W.,  
eds. Soil clay mineralogy. The University  
of North Carolina Press, Chapel Hill.  
330 p.
- JACKSON, M.L. 1965. Free oxides, hydroxides, and  
amorphous aluminosilicates, p. 578-603.  
In Black, C.A., et al., eds. Agronomy  
9(1): American Society of Agronomy,  
Madison, Wisconsin. 770 p.
- JACKSON, M.L. et al. 1952. Weathering sequence of  
clay size minerals in soils and sediments:  
II. Chemical weathering of layer silicates.  
Proc. Soil Sci. Soc. Am. 16: 3-6.
- JACKSON, M.L. et al. 1954. Some analyses of soil  
montmorin, vermiculite, mica, chlorite,  
and interstratified layer silicates.  
Proc. natn. Conf. Clays 2: 218-240.

- JARITZ, G. 1967. Ein Vorkommen von Imogolit in Bimsböden Westdeutschlands. Z. Pfl-Ernähr. Düng. Bodenk. 117: 65-77.
- JENNY, H. 1941. Factors of soil formation. McGraw-Hill, New York, 281 p.
- JENNY, H. 1946. Arrangement of soil series and types according to functions of soil-forming factors. Soil Sci. 61: 375-391.
- JENNY, H. 1958. Role of the plant factor in the pedogenic functions. Ecology 39: 5-16.
- JENNY, H. 1961. Derivation of state factor equations of soils and ecosystems. Proc. Soil Sci. Soc. Am. 25: 385-388.
- JOFFE, J.S., & KUNIN, R. 1943. Mechanical separates and their fractions in the soil profile: II. The cation exchange properties and pedogenic implications. Proc. Soil Sci. Soc. Am. 8: 384-387.
- JOHNS, W.D., GRIM, R.E., & BRADLEY, W.F. 1954. Quantitative estimations of clay minerals by diffraction methods. J. sedim. Petrol. 24: 242-251.
- JOINT COMMITTEE ON POWDER DIFFRACTION STANDARDS. 1973. Powder diffraction file.
- JONES, R.C., & UEHARA, G. 1973. Amorphous coatings on mineral surfaces. Proc. Soil Sci. Am. 37: 792-798.

- KANNO, I. 1959. Clay minerals of volcanic-ash soils and pumices from Japan. Adv. Clay Sci. 1: 213-233.
- KANNO, I., ONIKURA, Y., & HIGASHI, T. 1968. Weathering and clay mineralogical characteristics of volcanic ashes and pumices in Japan. Trans. 9th int. Congr. Soil Sci., Adelaide, III: 111-122.
- KAPOOR, B.S. 1972. Weathering of micaceous clays in some Norwegian podzols. Clay Miner. 9: 383-394.
- KAPOOR, B.S. 1973. The formation of 2:1 - 2:2 intergrade clays in some Norwegian podzols. Clay Miner. 10: 79-86.
- KARIM, A., & ISLAM, A. 1956. A study of ion-exchange properties of silt. Soil Sci. 82: 433-436.
- KAURICHEV, I.S., NOZDRUNOVA, YE., M., & YEVSEYEVA, R.P. 1969. Content and forms of water-soluble aluminium compounds in soil solutions. Pochvovedenie 9: 68-78.
- KAWASAKI, H., & AOMINE, S. 1966. So-called 14 Å clay minerals in some Ando soils. Soil Sci. Pl. Nutr. 12: 144-150.
- KEAR, B.S. 1965. Soils of the Reefton District. N.Z. Soil Bureau Report (Restricted distribution). 16 p.
- KELLER, W.D. 1954. Bonding energies of some silicate minerals. Am. Miner. 39: 783-793.

- KELLEY, C.W., & THOMAS, R.P. 1942. A method of estimating the organic exchange complex of a soil. Proc. Soil Sci. Soc. Am. 7: 201-206.
- KELLEY, W.P., DORE, W.H., & BROWN, S.M. 1931. The nature of the base exchange material of bentonite, soils, and zeolites as revealed by chemical investigations and X-ray analysis. Soil Sci. 31: 25-56.
- KIELY, P.V., & JACKSON, M.L. 1965. Quartz, feldspar and mica determination for soils by sodium pyrophosphate fusion. Proc. Soil Sci. Soc. Am. 29: 159-163.
- KIRKMAN, J.H. 1974. Clay mineralogy of some ash beds of Rotorua area, North Island, New Zealand. Clay Miner. (In press).
- KIRSANOV, A.T. 1958. Methods for the agrochemical analysis of soils. Publ. House Acad. Sci. U.S.S.R.
- KITAGAWA, Y. 1973. Substitution of aluminium by iron in allophane. Clay Sci. 4: 151-154.
- KITAGAWA, Y., KYUAMA, K., & KAWAGUCHI, K. 1973. Clay mineral composition of some volcanogenous soils in Indonesia and the Philipines. Soil Sci. Pl. Nutr. 19: 147-159.
- KITTREDGE, J. 1948. Forest influences. McGraw-Hill, New York. 394 p.

- KODAMA, H., & BRYDON, J.E. 1968. A study of clay minerals in podzol soils in New Brunswick, Eastern Canada. Clay Miner. 7: 295-309.
- KODAMA, H., & SCHNITZER, M. 1973. Dissolution of chlorite minerals by fulvic acid. Can. J. Soil Sci. 53: 240-243.
- LAI, S., & SWINDALE, L.D. 1969. Chemical properties of allophane from Hawaiian and Japanese soils. Proc. Soil Sci. Soc. Am. 33: 804-808.
- LA JOIE, P.G., & DE LONG, W.A. 1945. The acid-oxalate extracts of podzol and podzolic soils. Scient. Agric. 25: 215-220.
- LAVKULICH, L.M., & WIENS, J.H. 1971. Hydrogen peroxide-organic matter-pH interactions. Proc. Soil Sci. Soc. Am. 35: 514.
- LAWRENCE, D.B., & LAWRENCE, E.G. 1965. Glacier studies in New Zealand. Mazama 47: 17-27.
- LÉONARD, A. et al. 1964. Structure and properties of amorphous silicoaluminas. I. Structure from X-ray fluorescence spectroscopy and infrared spectroscopy. J. phys. Chem., Wash. 68: 2608-2617.

- LE ROUX, F.H., CADY, J.G., & COLEMAN, N.T. 1963. Mineralogy of soil separates and alkali-ion exchange-sorption. Proc. Soil Sci. Soc. Am. 27: 534-538.
- LE ROUX, J. 1973. Quantitative clay mineralogical analysis of Natal oxisols. Soil Sci. 115: 137-144.
- LE ROUX, J., & DE VILLIERS, J.M. 1966. Cation exchange capacity and degree of saturation with metal cations of highly weathered soils. S. Afr. J. agric. Sci. 9: 31-42.
- LIETZKE, D.A., & MORTLAND, M.M. 1973. The dynamic character of a chloritized vermiculite soil clay. Proc. Soil Sci. Soc. Am. 37: 651-656.
- LODDING, W. 1972. Conditions for direct formation of gibbsite from K-feldspar - Discussion. Am. Miner. 57: 292-294.
- LOSSAINT, P. 1959. Étude expérimentale de la mobilisation du fer des sols sous l'influence des litières forestières. II. Annls agron. 10: 493-542.
- LUNDBLAD, K. 1934. Studies of podzols and brown forest soils. Soil Sci. 37: 137-155.
- MACEWAN, D.M.C. 1946. Identification and estimation of montmorillonite group. J. Soc. chem. Ind., Lond. 65: 298-304.



- MACEWAN, D.M.C., RUIZ AMIL, A., & BROWN, G. 1961.  
Interstratified clay minerals, p. 393-445.  
In Brown, G., ed. The X-ray identification  
and crystal structures of clay minerals.  
2d ed. Mineralogical Society, London. 544 p.
- MACKENZIE, R.C. 1957. The oxides of iron, aluminium  
and manganese, p. 299-328. In The  
differential thermal investigation of clays.  
Mineralogical Society, London. 456 p.
- MACKENZIE, R.C. 1961. The quantitative determination  
of minerals in clays. Acta Univ. Carol.  
Geol. Suppl. 1: 11-21.
- McALEESE, D.M., & MITCHELL, W.A. 1958. Studies on the  
basaltic soils of Northern Ireland: V.  
Cation-exchange capacities and mineralogy  
of the silt separates (2 - 20  $\mu$ ).  
J. Soil Sci. 9: 81-88.
- McGEORGE, W.T. 1930. The base exchange property of  
organic matter in soils. Ariz. agric.  
Exp. Stn Tech. Bull. 30: 181-213.
- McGREGOR, V.R. 1967. Holocene moraines and rock  
glaciers in central Ben Ohau Range,  
South Canterbury, New Zealand.  
J. Glaciol. 6: 737-748.
- McINTYRE, D.J., & McKELLAR, I.C. 1970. A radiocarbon  
dated post-glacial pollen profile from  
Swampy Hill, Dunedin, New Zealand.  
N.Z. Jl Geol. Geophys. 13: 346-349.

- McKEAGUE, J.A. 1965. Properties and genesis of three members of the Uplands catena. Can. J. Soil Sci. 45: 63-77.
- McKEAGUE, J.A. 1967. An evaluation of 0.1 M pyrophosphate and pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in podzols and some other soils. Can. J. Soil Sci. 47: 95-99.
- McKEAGUE, J.A. 1968. Humic-fulvic acid ratio, Al, Fe, and C in pyrophosphate extracts as criteria of A and B horizons. Can. J. Soil Sci. 48: 27-35.
- McKEAGUE, J.A., & BRYDON, J.E. 1970. Mineralogical properties of ten reddish brown soils from the Atlantic provinces in relation to parent materials and pedogenesis. Can. J. Soil Sci. 50: 47-55.
- McKEAGUE, J.A., BRYDON, J.E., & MILES, N.M. 1971. Differentiation of forms of extractable iron and aluminium in soils. Proc. Soil Sci. Soc. Am. 35: 33-38.
- McKEAGUE, J.A., & DAY, J.H. 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46: 13-22.
- McKEAGUE, J.A., & DAY, J.H. 1969. Oxalate-extractable Al as a criterion for identifying podzol B horizons. Can. J. Soil Sci. 49: 161-163.

- McLEAN, E.O., & OWEN, E.J. 1969. Effects of pH on the contributions of organic matter and clay to soil cation exchange capacities. Proc. Soil Sci. Soc. Am. 33: 855-858.
- McLEAN, E.O., REICOSKY, D.C., & LAKSHMANAN, C. 1965. Aluminium in soils : 7. Proc. Soil Sci. Soc. Am. 29: 374-378.
- MADGWICK, H.A.I., & OVINGTON, J.D. 1959. The chemical composition of precipitation in adjacent forests and open plots. Forestry 32: 14-22.
- MAJOR, J. 1951. A functional, factorial approach to plant ecology. Ecology 32: 392-412.
- MALCOLM, R.L., & McCracken, R.J. 1968. Canopy drip: A source of mobile soil organic matter for mobilization of iron and aluminium. Proc. Soil Sci. Soc. Am. 32: 834-838.
- MALCOLM, R.L., NETTLETON, W.D., & McCracken, R.J. 1969. Pedogenic formation of montmorillonite from a 2:1 - 2:2 intergrade clay mineral. Clays Clay Miner. 16: 405-414.
- MARSHALL, C.E. 1941. A petrographic method for the study of soil formation processes. Proc. Soil Sci. Soc. Am. 5: 100-103.
- MARTIN, A.E., & REEVE, R. 1957. Chemical studies of podzolic illuvial horizons: II. The use of acetylacetone as extractant of translocated organic matter. J. Soil Sci. 8: 279-286.

- MARTIN, A.E., & REEVE, R. 1960. Chemical studies of podzolic illuvial horizons. IV. The flocculation of humus by aluminium. J. Soil Sci. 11: 369-381.
- MATSUI, T. 1959. Some characteristics of Japanese soil clays. Adv. Clay Sci. 1: 244-259.
- MEHLICH, A. 1941. Base unsaturation and pH in relation to soil type. Proc. Soil Sci. Soc. Am. 6: 150-155.
- MEHRA, O.P., & JACKSON, M.L. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays Clay Miner. 7: 317-327.
- MEJIA, G., KOHNKE, H., & WHITE, J.L. 1968. Clay mineralogy of certain soils of Colombia. Proc. Soil Sci. Soc. Am. 32: 665-670.
- METSON, A.J., & BLAKEMORE, L.C. 1968. Cation exchange properties. Soil Bur. Bull. N.Z. 26 (2): 67-72.
- MEW, G. et al. 1972. Soils of the Inangahua Depression, South Island. N.Z. Soil Bureau Report. (Restricted distribution). 151 p.
- MEYERS, H.E. 1937. Physiochemical reactions between organic and inorganic soil colloids as related to aggregate formation. Soil Sci. 44: 331-357.

- MIDDLETON, K.R. 1965. Determination of aluminium and iron, and the relation of aluminium to clay in certain tropical soils. Soil Sci. 100: 361-367.
- MILLIKEN, T.H., MILLS, G.A., & OBLAD, A.G. 1950. The chemical characteristics and structure of cracking catalysts. Discuss. Faraday Soc. 8: 279-290.
- MILLS, J.G., & ZWARICH, M.A. 1972. Recognition of interstratified clays. Clays Clay Miner. 20: 169-174.
- MINA, V.N. 1965. Leaching of certain substances by precipitation from woody plants and its importance in the biological cycle. Soviet Soil Sci. 6: 609-617.
- MITCHELL, B.D., FARMER, V.C., & MCHARDY, W.J. 1964. Amorphous inorganic material in soils. Adv. Agron. 16: 327-383.
- MITCHELL, B.D. et al. 1968. Mineralogical and chemical characteristics of a gley soil from North-east Scotland. Trans. 9th int. Congr. Soil Sci., Adelaide, III: 67-77.
- MITCHELL, J. 1932. The origin, nature and importance of soil organic constituents having base exchange properties. J. Am. Soc. Agron. 24: 256-275.
- MITCHELL, W.A. 1960. A method for quantitative mineralogical analysis by X-ray powder diffraction. Mineralog. Mag. 32: 492-499.

- MIYAUCHI, N., & AOMINE, S. 1964. Does "allophane B" exist in Japanese volcanic ash soils? Soil Sci. Pl. Nutr. 10: 199-203.
- MIYAUCHI, N., & AOMINE, S. 1966. Effects of exchangeable cations on the high temperature exothermic peak of allophane. Soil Sci. Pl. Nutr. 12: 13-17.
- MIYAZAWA, K. 1966. Clay-mineral composition of andosols in Japan with reference to their classification. Bull. natn. Inst. agric. Sci., Tokyo B17: 1-100.
- MOAR, N.T. 1966. Post-glacial vegetation and climate in New Zealand. Royal Meteorological Society. Proc. int. Symp. Wld Climate 8000 to 0 B.C: 155-156.
- MOAR, N.T. 1970. A new pollen diagram from Pyramid Valley swamp. Rec. Canterbury Mus. 8: 455-461.
- MOAR, N.T. 1971. Contributions to the Quaternary history of the New Zealand flora, 6. Aranuiian pollen diagrams from Canterbury, Nelson, and North Westland, South Island. N.Z. Jl Botany 9: 80-145.
- MOHAMED, M.K., & GOHAR, A.A.I. 1960. Contribution of clay, silt and organic matter to the potential fertility of Egyptian soils as measured by their cation exchange capacities. U.A.R. Minist. Agric. Publ., 42 p. (Abstr. in Soils Fertil. 24:7. 1961).

- MOKMA, D.L. et al. 1973. Mineralogy of a chronosequence of soils from greywacke and mica-schist alluvium, Westland, New Zealand. N.Z. J. Sci. 16: 769-797.
- MUIR, A. 1961. The podzol and podzolic soils. Adv. Agron. 13: 1-56.
- MUIR, J.W., LOGAN, J., & BOWN, C.J. 1964. The mobilization of iron by aqueous extracts of plants. II. Capacities of the amino-acid and organic-acid fractions of a pine needle extract to maintain iron in solution. J. Soil Sci. 15: 226-237.
- MUIR, J.W., et al. 1964. The mobilization of iron by aqueous extracts of plants. I. Composition of the amino-acid and organic-acid fractions of an aqueous extract of pine needles. J. Soil Sci. 15: 220-225.
- MUNSELL COLOR COMPANY INC. 1954. Munsell soil color charts. Munsell Color Company Inc., Baltimore, Maryland.
- MURALI, V., SARMA, V.A.K., & KRISHNA MURTI, G.S.R. 1974. Mineralogy of two red soil (alfisol) profiles of Mysore State, India. Geoderma 11: 147-155.
- NATHAN, S., & MOAR, N.T. 1973. Age and correlation of Late Quaternary terraces in the Lower Inangahua Valley, West Coast, South Island, New Zealand. J.R. Soc. N.Z. 3: 409-414.
- NEW ZEALAND FOREST SERVICE. 1970. Rep. N.Z. St. Forest Serv. 63 p.

- NEW ZEALAND SOIL BUREAU. 1968a. Soils of New Zealand. Soil Bur. Bull. N.Z. 26(3): 1-127.
- NEW ZEALAND SOIL BUREAU. 1968b. General Survey of the Soils of South Island, New Zealand. Soil Bur. Bull. N.Z. 27: 1-404.
- NIEDERBUDDE, E.A., 1973. Beziehungen zwischen K-Fixierungsvermögen und Dreischicht-Tonmineralen in Bodenprofilen aus Löß. Z. Pfl-Ernähr. Düng. Bodenk. 135: 196-208.
- NISKANEN, E. 1964. Reduction of orientation effects in the quantitative X-ray diffraction analysis of kaolin minerals. Am. Miner. 49: 705-714.
- NORRISH, K. 1957. Some phosphate minerals of soils. Proc. 2nd Aust. Conf. Soil Sci. 1(1): 17/1-15.
- NORRISH, K. 1968. Some phosphate minerals of soils. Trans. 9th int. Congr. Soil Sci., Adelaide, II: 713-723.
- OINUMA, K., KOBAYASHI, K., & SUDO, T. 1961. Procedure of clay mineral analysis. Clay Sci. 1: 23-28.
- OLSON, L.C., & BRAY, R.H. 1938. The determination of the organic base-exchange capacity of soils. Soil Sci. 45: 483-496.
- PARFITT, R.L. 1972. Amorphous material in some Papua New Guinea soils. Proc. Soil Sci. Soc. Am. 36: 683-686.



- PARFITT, R.L. 1973. Clay minerals in recent volcanic ash soils of Papua New Guinea.  
Proc. 9th Congr. Inqua, Christchurch: 278.
- PARFITT, R.L., & McHARDY, W.J. 1974. Imogolite from New Guinea. Clays and Clay Miner.  
(In press).
- PARHAM, W.E. 1969. Formation of halloysite from feldspar: low temperature artificial weathering versus natural weathering.  
Clays Clay Miner. 17: 13-22.
- PATTERSON, S.H. 1964. Halloysitic underclay and amorphous inorganic matter in Hawaii.  
Clays Clay Miner. 12: 153-172.
- PEDRO, G. 1970. Report of the AIPEA Nomenclature Committee. AIPEA News1. No 4: 3-4.
- PETTAPIECE, W.W., & PAWLUK, S. 1972. Clay mineralogy of soils developed partially from volcanic ash. Proc. Soil Sci. Soc. Am. 36:  
515-519.
- PIERRE, W.H., & SCARSETH, G.D. 1931. Determination of the percent base saturation and its value in different soils at definite pH values.  
Soil Sci. 31: 99-112.
- PRATT, P.F. 1961. Effect of pH on the cation-exchange capacity of surface soils.  
Proc. Soil Sci. Soc. Am. 25: 96-98.
- PRATT, P.F., & BLAIR, F.L. 1962. Cation-exchange properties of some acid soils of California.  
Hilgardia 33: 689-706.

- PURI, A.N. 1930. The relation between pH value and state of saturation in soils. Soil Res. 2: 181-184.
- QUANTIN, P. 1972. The nature and fertility of soils on volcanic ash from recent eruptions in the New Hebrides Archipelago, I and II. Cah. ORSTOM, Sér. Pédologie 10: 123-151.
- RAESIDE, J.D. 1959. Stability of index minerals in soils with particular reference to quartz, zircon and garnet. J. sedim. Petrol. 29: 493-502.
- RAMAN, K.V., & JACKSON, M.L. 1965. Rutile and anatase determination in soils and sediments. Am. Miner. 50: 1086-1092.
- RAMAN, K.V., & MORTLAND, M.M. 1969/1970. Amorphous materials in a spodosol: Some mineralogical and chemical properties. Geoderma 3: 37-43.
- RICH, C.I. 1968. Hydroxy interlayers in expansible layer silicates. Clays Clay Miner. 16: 15-30.
- RICH, C.I., & OBENSHAIN, S.S. 1955. Chemical and mineralogical properties of a red-yellow podsollic soil derived from muscovite. Proc. Soil Sci. Soc. Am. 19: 334-339.
- ROBERTSON, C.E., & HEM, J.D. 1969. Solubility of aluminium in the presence of hydroxide, fluoride and sulphate. U.S. Geol. Surv. Wat. - Supply Pap. 1827-C. 37 p.

- ROBINSON, G.W., & RICHARDSON, M. 1933. The dispersion of soils in mechanical analysis. Tech. Commun. imp. Bur. Soil Sci. 26.
- RODE, A.A. 1949. p. 350. In Joffe, J.S. Pedology. 2d ed. Pedology Publications, New Brunswick. 662 p.
- RODE, A.A. 1961. The soil forming process and soil evolution. Translated from the Russian. Israel Programme for Scientific Translations, Jerusalem. 100 p.
- RODE, A.A. 1964. Podzolisation and lessivage. Pochvovedenie 7: 9-23.
- ROMANS, J.C.C. 1970. Podzolisation in a zonal and altitudinal context in Scotland. Rep. Welsh Soils Discuss. Grp. No 11: 88-101.
- ROSS, C.S., & KERR, P.F. 1934. Halloysite and allophane. U.S. Geol. Surv. prof. Pap. 185-G: 135-148.
- ROSS, D.J., & McNEILLY, B.A. 1973. Biochemical activities in a soil profile under hard beech forest. 3. Some factors influencing the activities of polyphenol-oxidising enzymes. N.Z. J1 Sci. 16: 241-257.
- ROSS, G.J. 1969. Acid dissolution of chlorites: release of magnesium, iron and aluminium and mode of attack. Clays Clay Miner. 17: 347-354.
- ROSS, G.J., & MORTLAND, M.M. 1966. A soil beidellite. Proc. Soil Sci. Soc. Am. 30: 337-343.

- ROTH, C.B., JACKSON, M.L., & SYERS, J.K. 1969.  
Deferration effect on structural ferrous-  
ferric iron ratio and CEC of vermiculites  
and soils. *Clays Clay Miner.* 17: 253-264.
- ROTH, C.B. et al. 1968. Ferrous-ferric ratio and  
CEC changes on deferration of weathered  
micaceous vermiculite. *Israel J. Chem.*  
6: 261-273.
- ROZHNOVA, T.A., & KASATKINA, T.V. 1970. Soils forming  
under oak forests in the northwest.  
*Pochvovedenie* 9: 10-19.
- RUIZ AMIL, A., GARCÍA, A.R., & MACEWAN, D.M.C. 1967.  
X-ray diffraction curves for the analysis  
of interstratified structures.  
Volturna Press, Edinburgh. 180 p.
- RUSSELL, J.D., McHARDY, W.J., & FRASER, A.R. 1969.  
Imogolite: A unique aluminosilicate.  
*Clay Miner.* 8: 87-99.
- SARMA, V.A.K., & KRISHNA MURTI, G.S.R. 1969/1970.  
Plumbogummite minerals in Indian soils.  
*Geoderma* 3: 321-327.
- SAUNDERS, H.L., & GIEDROYC, V. 1950. Controlled  
atmosphere d.t.a. *Trans. Br. Ceram. Soc.*  
49: 365-374.
- SAUNDERS, W.M.H. 1965. Phosphate retention by New  
Zealand soils and its relationship to free  
sesquioxides, organic matter, and other  
soil properties. *N.Z. Jl agric. Res.* 8:  
30-57.

SAWHNEY, B.L., FRINK, C.R., & HILL, D.E. 1970.

Components of pH dependent cation exchange capacity. Soil Sci. 109: 272-278.

SAWHNEY, B.L., & NORRISH, K. 1971. pH dependent cation exchange capacity: Minerals and soils of tropical regions. Soil Sci. 112: 213-215.

SCHNITZER, M., & DE LONG, W.A. 1955. Investigations on the mobilization and transport of iron in forested soils. II. The nature of the reaction of leaf extracts and leachates with iron. Proc. Soil Sci. Soc. Am. 19: 363-368.

SCHNITZER, M., & DE LONG, W.A. 1959. Interaction of iron with rainfall leachates. J. Soil Sci. 10: 300-308.

SCHNITZER, M., & GUPTA, V.C. 1964. Chemical characteristics of the organic matter extracted from the O and B<sub>2</sub> horizons of a Gray Wooded soil. Proc. Soil Sci. Soc. Am. 28: 374-377.

SCHNITZER, M., & SKINNER, S.I.M. 1964. Organo-metallic interactions in soils: 3. Properties of iron- and aluminium-organic matter complexes, prepared in the laboratory, and extracted from a soil. Soil Sci. 98: 197-203.

SCHOFIELD, R.K. 1939. The electrical charges on clay particles. Soils Fertil. 2: 1-5.

SCHULTZ, L.G. 1958. Quantitative X-ray determination of some aluminous clay minerals in rocks. Proc. natn. Conf. Clays 7: 216-224.

- SCHULTZ, L.G. 1964. Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. U.S. Geol. Surv. prof. Pap. 391-C. 31 p.
- SCHWERTMANN, U. 1959. Die fraktionierte Extraktion der freien Eisenoxide in Boden, ihre mineralogischen Formen und ihre Entstehungsweisen. Z. Pfl-Ernähr. Düng. Bodenk. 84: 194-204.
- SCHWERTMANN, U. 1964. Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. Z. Pfl-Ernähr. Düng. Bodenk. 105: 194-202.
- SCHWERTMANN, U. 1973. Use of oxalate for Fe extraction from soils. Can. J. Soil Sci. 53: 244-246.
- SEGALEN, P. 1971. Metallic oxides and hydroxides in soils of the warm and humid areas of the world: formation, identification and evolution. p. 25-39. In Proceedings Bandung Symposium "Soils and Tropical Weathering." Unesco, Paris. (Nat. Resour. Res. Ser. 11). 149 p.
- SEGALEN, P. et al. 1971. La détermination du fer libre dans les sols a sesquioxydes. Cah. ORSTOM, Sér. Pédologie 9: 3-27.
- SEKI, T. 1913. Two volcanic loams of Japan. Landw. VersStn. 79/80: 871-890.

- SHINAGAWA, A. 1962. Further accumulation of humus on the volcanic ash soils originated from Volcano Sakurajima's ashes. Bull. Fac. Agric. Kagoshima Univ. 11: 155-205.
- SHOJI, S., & MASUI, J. 1969a. Amorphous clay minerals of recent volcanic ash soils in Hokkaido (I). Soil Sci. Pl. Nutr. 15: 161-168.
- SHOJI, S., & MASUI, J. 1969b. Amorphous clay minerals of recent volcanic ash soils in Hokkaido (II). Soil Sci. Pl. Nutr. 15: 191-201.
- SIEFFERMANN, G., JEHL, G., & MILLOT, G. 1968. Allophanes and clay minerals in the weathered products of basalts from Mount Cameroon. Bull. Grpe fr. Argiles 20: 109-129.
- SIEFFERMANN, G., & MILLOT, G. 1968. Equatorial and tropical weathering of recent basalts from Cameroon: allophanes, halloysite, metahalloysite, kaolinite and gibbsite. Proc. int. Clay Conf., Paris, 1: 417-430.
- SIMONETT, D.S., & BAULEKE, M.P. 1963. Mineralogy of soils on basalt in N. Queensland. Proc. Soil Sci. Soc. Am. 27: 205-212.
- SNETSINGER, K.G. 1967. High-alumina allophane as a weathering product of plagioclase. Am. Miner. 52: 254-262.
- SOKOLOVA, T.A., TARGUL'YAN, V.O., & SMIRNOVA, G. YA. 1971. Clay minerals in Al-Fe humus podzolic soils and their role in the formation of the soil profile. Pochvovedenie 5: 103-114.

- SREE RAMULU, PRATT, U.S., & PAGE, A.L. 1967. Phosphorus fixation by soils in relation to extractable iron oxides and mineralogical composition. *Proc. Soil Sci. Soc. Am.* 31: 193-196.
- STEPHENS, C.G. 1947. Functional synthesis in pedogenesis. *Trans. R. Soc. S. Aust.* 7: 168-181.
- STEPHENS, C.G. 1951. The present state of soil science. *Aust. Inst. agric. Sci.* 17: 126-131.
- STEVENS, P.R. 1963. A chronosequence of soils and vegetation near the Franz Josef Glacier. Thesis, M. Agr. ~~Sci.~~, Lincoln College, University of Canterbury, N.Z. 160 p.
- STEVENS, P.R. 1968a. Loess deposits and gleyed horizons in Okarito soils of North and South Westland. *N.Z. Jl Geol. Geophys.* 11: 1271-1273.
- STEVENS, P.R. 1968b. A Chronosequence of Soils near the Franz Josef Glacier. Thesis, Ph. D., Lincoln College, University of Canterbury, N.Z. 389 p.
- STEVENS, P.R., & WALKER, T.W. 1970. The chronosequence concept and soil formation. *Q. Rev. Biol.* 45: 333-350.
- STOBBE, P.C., & WRIGHT, J.R. 1959. Modern concepts of the genesis of podzols. *Proc. Soil Sci. Soc. Am.* 23: 161-164.
- STONEHOUSE, H.B., & ST. ARNAUD, R.J. 1971. Distribution of iron, clay and extractable iron and aluminium in some Saskatchewan soils. *Can. J. Soil Sci.* 51: 283-292.



- SUDO, T. 1954. Clay mineralogical aspects of the alteration of volcanic glass in Japan. Clay Miner. Bull. 2: 96-106.
- SUDO, T., OINUMA, K., & KOBAYASHI, K. 1961. Mineralogical problems concerning rapid clay mineral analysis of sedimentary rocks. Acta Univ. Carol. Geol. Suppl. 1: 189-219.
- SUDO, T., & TAKAHASHI, H. 1955. Shapes of halloysite particles in Japanese soils. Proc. natn. Conf. Clays 4: 67-79.
- SUGGATE, R.P. 1957. The geology of Reefton subdivision. Bull. geol. Surv. N.Z. (n.s.) 56: 1-146.
- SUGGATE, R.P. 1961. The upper boundary of the Hawera series. Trans. R. Soc. N.Z. (Geol.) 1: 11-16.
- SUGGATE, R.P. 1965. Late Pleistocene geology of the northern part of the South Island, New Zealand. Bull. geol. Surv. N.Z. (n.s.) 77: 1-91.
- SUGGATE, R.P., & MOAR, N.T. 1970. Revision of the chronology of the late Otira Glacial. N.Z. J1 Geol. Geophys. 13: 742-746.
- SYERS, J.K., CAMPBELL, A.S., & WALKER, T.W. 1970. Contribution of organic carbon and clay to cation exchange capacity in a chronosequence of sandy soils. Pl. Soil 33: 104-112.

- TAMM, O. 1922. Eine Method zur bestimmung der anorganischen Komponente des Gelkomplexes im Boden. Meddn St. SkogsförsAnst. 19: 387-404.
- TAMURA, T., JACKSON, M.L., & SHERMAN, G.D. 1953. Mineral content of low humic and hydrol humic latosols of Hawaii. Proc. Soil Sci. Soc. Am. 17: 343-346.
- TAN, T.O. 1971. Studies on a chronosequence of terrace soils near Reefton. Thesis, M. Agr. Sci., Lincoln College, University of Canterbury, N.Z. 77 p.
- TANDON, H.L.S. 1970. Fluoride-extractable aluminium in soils. 2: As an index of phosphate retention by soils. Soil Sci. 109: 13-18.
- TANNER, C.B., & JACKSON, M.L. 1947. Nomographs of sedimentation times for soil particles under gravity or centrifugal acceleration. Proc. Soil Sci. Soc. Am. 12: 60-65.
- TAYLOR, N.H. 1933. Soil processes in volcanic ash-beds. N.Z. Jl Sci. Technol. 14: 338-352.
- TAYLOR, N.H., & POHLEN, I.J. 1962. Soil Survey Method. Soil Bur. Bull. N.Z. 25: 1-242.
- TAZAKI, K. 1971. Imogolite in the Daisen loam and the Sanbesan loam. J. geol. Soc. Japan 77: 407-414.
- TEDROW, J.C.F. 1966. Properties of sand and silt fractions in New Jersey soils. Soil Sci. 101: 24-30.

- TIDBALL, R.R. 1965. A study of soil development on dated pumice deposits from Mount Mazama, Oregon. Thesis, Ph.D., University of California, Berkeley, U.S.A.
- TOWNSEND, W.N., & AGUILAR, J. 1971. Contribution to the study of the podsolisation process. *Commun. Soil Sci. Pl. Anal.* 2: 383-388.
- TRUEMAN, N.A. 1971. Minerals for agriculture. *Aust. Inst. Min. Metall. Annual Conf. Symp. Pap. No. 2*: 1-20.
- TSUCHIYA, T., & KURABAYASHI, S. 1958. On the clay minerals of the Kanto loam. *J. geol. Soc. Japan* 64: 605-615.
- TURNER, R.C., & NICOL, W.E. 1962. A study of the lime potential: I. *Soil Sci.* 93: 374-382.
- TWENEBOAH, C.K., GREENLAND, D.J., & OADES, J.M. 1967. Changes in charge characteristics of soils after treatment with 0.5M calcium chloride at pH 1.5. *Aust. J. Soil Res.* 5: 247-261.
- UDAGAWA, S., NAKADA, T., & NAKAHIRA, M. 1969. Molecular structure of allophane as revealed by its thermal transformation. *Proc. int. Clay Conf., Tokyo* 1: 151-159.
- UNITED STATES DEPARTMENT OF AGRICULTURE, SOIL CONSERVATION SERVICE. 1970. Selected chapters from the unedited text of the Soil Taxonomy of The National Cooperative Soil Survey. U.S. Department of Agriculture, Washington, D.C.

- VAN OLPHEN, H. 1971. Amorphous clay materials.  
Science, N.Y. 171: 91-92.
- VAN REEUWIJK, L.P. & DE VILLIERS, J.M. 1968. Potassium fixation by amorphous aluminosilica gels.  
Proc. Soil Sci. Soc. Am. 32: 238-240.
- VAN REEUWIJK, L.P., & DE VILLIERS, J.M. 1970. A model system for allophane.  
Agrochemophysica 2: 77-82.
- VOIGT, G.K., 1960. Distribution of rainfall under forest stands. Forest Sci. 6: 2-10.
- VUCETICH, C.G., & POLLAR, W.A. 1969. Stratigraphy and chronology of Late Pleistocene volcanic ash beds in central North Island, New Zealand. N.Z. Jl Geol. Geophys. 12: 784-837.
- WADA, K. 1966. Deuterium exchange of hydroxyl groups in allophane. Soil Sci. Pl. Nutr. 12: 176-182.
- WADA, K. 1967. A structural scheme of soil allophane. Am. Miner. 52: 690-708.
- WADA, K., & ATAKA, H. 1958. The ion uptake mechanism of allophane. Soil Pl. Fd, Tokyo 4: 12-18.
- WADA, K., & GREENLAND, D.J. 1970. Selective dissolution and differential infrared spectroscopy for characterization of 'amorphous' constituents in soil clays. Clay Miner. 8: 241-254.

- WADA, K., & MATSUBARA, I. 1968. Differential formation of allophane, "imogolite" and gibbsite in the Kitakami pumice bed. Trans 9th int. Congr. Soil Sci., Adelaide, III: 123-131.
- WADA, K., & TOKASHIKI, Y. 1972. Selective dissolution and difference infrared spectroscopy in quantitative mineralogical analysis of volcanic-ash soil clays. Geoderma 7: 199-213.
- WADA, K., & YAMADA, H. 1968. Hydrazine intercalation-intersalation for differentiation of kaolin minerals from chlorites. Am. Miner. 53: 334-339.
- WADA, K., & YOSHINAGA, N. 1969. The structure of "Imogolite". Am. Miner. 54: 50-71.
- WADA, K. et al. 1972. Imogolite and allophane formed in saprolite of basalt on Maui, Hawaii. Clays Clay Miner. 20: 375-380.
- WAHL, F.M., GRIM, R.E., & GRAF, R.B. 1961. Phase transformations in silica-alumina mixtures as examined by continuous X-ray diffraction. Am. Miner. 46: 1064-1076.
- WALKER, D. 1966. A commentary on botanical data from New Guinea, Australia and New Zealand, p. 149. In Sawyer, J.S. ed. World Climate from 8000 to 0 B.C. Royal Meteorological Society, London. 229 p.
- WALKER, T.W. 1956. The accumulation of organic matter in grassland soils. Trans 6th int. Congr. Soil Sci., Paris, II: 409-416.

- WALKER, T.W. 1965. The significance of phosphorus in pedogenesis, p. 295-316. In Hallsworth, E.G., & Crawford, D.V. eds. Experimental pedology. Butterworths, London. 414 p.
- WALKER, T.W., & ADAMS, A.F.R. 1958. Studies on soil organic matter. I. Soil Sci. 85: 307-318.
- WALKER, T.W., & ADAMS, A.F.R. 1959. Studies on soil organic matter. II. Soil Sci. 87: 1-10.
- WANG, C., & WOOD, F.A. 1973. A modified aluminon reagent for the determination of aluminium after  $\text{HNO}_3 - \text{H}_2\text{SO}_4$  digestion. Can. J. Soil Sci. 53: 237-239.
- WARDLE, R., & BRINDLEY, G.W. 1971. The dependence of the wavelength of  $\text{AlK}\alpha$  radiation from alumina-silicates on the Al-O distance. Am. Miner. 56: 2123-2128.
- WEAVER, C.E. 1958. Geologic interpretation of argillaceous sediments. Part 1. Origin and significance of clay minerals in sedimentary rocks. Bull. Am. Ass. Petrol. Geol. 42: 254-271.
- WEAVER, R.M., JACKSON, M.L., & SYERS, J.K. 1971. Magnesium and silicon activities in matrix solutions of montmorillonite-containing soils in relation to clay mineral stability. Proc. Soil Sci. Soc. Am. 35: 823-830.
- WHITE, E.W., & GIBBS, G.V. 1969. Structural and chemical effects on the  $\text{AlK}\alpha$  X-ray emission band among aluminium containing silicates and aluminium oxides. Am. Miner. 54: 931-936.

- WHITE, E.W., McKINSTRY, H.A., & BATES, T.F. 1958.  
Crystal chemical studies by X-ray fluorescence.  
7th Ann. Conf. X-ray Analysis, Denver, 2:  
239-245.
- WHITE, W.A. 1953. Allophanes from Lawrence County,  
Indiana. *Am. Miner.* 38: 634-642.
- WHITTIG, L.D., & JACKSON, M.L. 1955. Interstratified  
layer silicates in some soils of northern  
Wisconsin. *Proc. natn. Conf. Clays* 3:  
322-336.
- WIKLANDER, L., & ALEKSANDROVIĆ, D. 1969. Mineral  
analysis of Swedish soils. I. Brown earths  
and podzols. *Lantbr Högsk. Annlr* 35:  
895-919.
- WILDING, L.P., & RUTLEDGE, E.M. 1966. Cation-exchange  
capacity as a function of organic matter,  
total clay, and various clay fractions in  
a soil toposequence. *Proc. Soil Sci.  
Soc. Am.* 30: 782-785.
- WILL, G.M. 1955. Removal of mineral nutrients from tree  
crowns by rains. *Nature* 176: 1180.
- WILLIAMS, E.G., SCOTT, N.M., & McDONALD, M.J. 1958.  
Soil properties and phosphate sorption.  
*J. Sci. Fd Agric.* 9: 551-559.
- WILLIAMS, J.D.H., SYERS, J.K., & WALKER, T.W. 1967.  
Fractionation of soil inorganic phosphate  
by a modification of Chang and Jackson's  
procedure. *Proc. Soil Sci. Soc. Am.* 31:  
736-739.

- WILLIAMS, J.D.H., & WALKER, T.W. 1969. Fractionation of phosphate in a maturity sequence of New Zealand basaltic profiles: 2. Soil Sci. 107: 213-219.
- WILLIAMS, R. 1932. The contribution of clay and organic matter to the base exchange capacity of soils. J. agric. Sci., Camb. 22: 845-851.
- WITKAMP, M., & WALLER, H.D. 1963. Landscape studies using radioactive tracers: II. Behaviour of Cs-137 on the floor of a tulip poplar forest. Abstr. in Bull. ecol. Soc. Am. 44(3): 73-74.
- WRIGHT, W.R., & FOSS, J.E. 1972. Contributions of clay and organic matter to the cation exchange capacity of Maryland soils. Proc. Soil Sci. Soc. Am. 36: 115-118.
- YAALON, D.H., & YARON, B. 1966. Framework for man-made soil changes - an outline of metapedogenesis. Soil Sci. 102: 272-277.
- YARIV, S., & HELLER, L. 1970. Sorption of cyclohexylamine by montmorillonites. Israel J. Chem. 8: 935-945.
- YOE, J.H., & ARMSTRONG, A.R. 1947. Colorimetric determination of titanium with disodium-1, 2-dihydroxybenzene-3, 5-disulphonate. Analyt. Chem. 19: 100-102.
- YOSHINAGA, N. 1968. Identification of imogolite in the filmy gel materials in the Imaichi and Shichihonzakura pumice beds. Soil Sci. Pl. Nutr. 14: 238-246.



- YOSHINAGA, N., & AOMINE, S. 1962. Imogolite in some Ando soils. Soil Sci. Pl. Nutr. 8: 114-121.
- YOSHINAGA, N., TAIT, J.M., & SOONG, R. 1973. Occurrence of imogolite in some volcanic ash soils of New Zealand. Clay Miner. 10: 127-130.
- YOSHINAGA, N., & YAMAGUCHI, M. 1970. Occurrence of imogolite as gel film in the pumice and scoria beds of Western and Central Honshu and Hokkaido. Soil Sci. Pl. Nutr. 16: 215-223.
- YOSHINAGA, N., YOTSUMOTO, H., & IBE, K. 1968. An electron microscopic study of soil allophane with an ordered structure. Am. Miner. 53: 319-323.
- YOUNG, D.J. 1967. Loess deposits of the West Coast of the South Island, New Zealand. N.Z. J1 Geol. Geophys. 10: 647-658.
- YUAN, T.L. 1969. Composition of the amorphous material in the clay fraction of some entisols, inceptisols and spodosols. Soil Sci. 107: 242-248.
- YUAN, T.L., & FISKELL, J.G.A. 1959. Aluminium studies. II: The extraction of aluminium from some Florida soils. Proc. Soil Sci. Soc. Am. 23: 202-205.

YUAN, T.L., GAMMON, N. (Jr.), & LEIGHTY, R.G. 1967.

Relative contribution of organic and clay fractions to cation-exchange capacity of sandy soils from several soil groups.

Soil Sci. 104: 123-128.

ZINKE, P.J. 1962. The pattern of influence of individual forest trees on soil properties.

Ecology 43: 130-133.