SOME AMORPHOUS CONSTITUENTS
OF NEW ZEALAND SOILS

by

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ABSTRACT

Part I - Allophanes Derived from Volcanic Ash

Soils formed on weathered volcanic ash in the central and northern North Island of New Zealand contain the amorphous aluminosilicate allophane as the predominant clay mineral which is produced by the weathering of volcanic glass. Allophane has a characteristic DTA curve and I.R. spectrum which serve as a useful means of identifying the clay mineral.

Fine clays were separated from soils in the Waikato area and these showed typical allophane patterns of variable cation exchange capacity as well as DTA and I.R. spectra. Under the electron microscope these clays presented a picture of very small, ill-defined particles with indistinct edges and it was apparent that most of the properties of allophane could be explained by the presence of a colloidal system.

The colloidal properties of allophane were investigated and it was shown to be remarkable among clay minerals in having a high isoelectric point ($\sim$6). This means that allophane is positively charged under normal soil pH's (4.5 - 5.5). Synthetic aluminosilicates were prepared with varying SiO_2/Al_2O_3 ratios and it was found that with a SiO_2/Al_2O_3 ratio between 2 and 1.5 the isoelectric point was in the range 4.5 - 5.0. Increasing the ratio resulted in a lowering of the isoelectric point. If the allophane samples were deferrated using sodium dithionite and sodium citrate, then the isoelectric point of the resulting material

was below 2. The very high chemical reactivity normally associated with allophane was thus reduced, although the general properties such as the NaF/phenolphthalein test and I.R. spectra were unaffected. The results show that the ferric oxide, despite its small proportion, contributes significantly to the high isoelectric point of the allophane found in natural soils.

A definition for allophane is proposed which includes its remarkable properties of high isoelectric point, high surface area, high ion exchange capacity along with its very high phosphate retention.

The presence of imogolite was noted in New Zealand soils for the first time in one sample.

Since New Zealand has a cheap, abundant supply of this unusual material, work was initiated to find possible commercial uses for allophane. One possible use described is the removal of protein from slaughterhouse effluent. The main proteins found in slaughterhouse effluent, hemoglobin, serum albumin and gelatin, were adsorbed onto allophane and adsorption isotherms determined for each. Allophane adsorbed up to 10% by weight of protein from a solution with the protein concentration of the order 1 mg/ml, after which the clay became saturated and would adsorb no further protein. At this stage the protein-clay complex became "jelly-like" and sank to the bottom of the flask. The actual amount of uptake was dependent on the particular allophane used and the solution pH.

Allophane shows indications of having antibiotic properties. The breakdown of protein by bacterial activity was greatly inhibited by the presence of allophane in the protein solutions.

These solutions could be left open to the air for several days without any change in protein concentration measured by U.V. absorption. Also, when samples of allophane were examined under the electron microscope there were no signs of bacteria, unlike samples from non-volcanic soils in which bacteria could be readily seen. This phenomenon appears coupled with the fact that allophane from volcanic areas bears a positive charge at a pH less than about 6. The bacteria, being negatively charged, become surrounded by a coating of minute allophane particles which inhibits growth.

Part II - Synthetic Aluminosilicates

Synthetic aluminosilicates were prepared to investigate the colloidal properties of alumina and silica. Positively charged hydrated alumina will adhere to the negatively charged surface of freshly cleaved mica and will readily adsorb phosphate from a solution containing ^{32}P phosphate. Negatively charged hydrated silica was adsorbed onto the surface of alumina-treated mica. This would be expected to block the alumina to phosphate uptake, but this was not the case, the uptake being only slightly less than the alumina treated mica. If further alumina was added, little difference in phosphate uptake was again noted suggesting a uniform surface is presented to the phosphate solution. With hydrated ferric oxide and hydrated silica alternately adsorbed on the mica surface, an oscillating pattern was noted showing that layers can be built up. The experiment was repeated using ^{59}Fe to ensure that layers were built up and not being removed and then replaced. These experiments showed that amorphous hydrous silica and alumina will react in some way and it is suggested that a reaction takes place between the colloidal hydrous aluminia and silica with the formation of Al-O-Si bonds. The ferric oxide system does not however form Fe-O-Si bonds, but it is suggested the colloidal particles are held together by electrostatic bonds in a form of "colloid complex".

Fresh colloidal suspensions of hydrated alumina and silica prepared from hydrolysis of corresponding organo-derivatives, when mixed and freeze dried, provided an amorphous product with the properties of allophane. But if the solutions were allowed to age by standing for several days, mixed and then freeze dried, the DTA pattern and X-ray spectrum showed the presence of bayerite (a crystalline form of $Al(OH)_3$). Addition of acid or base to the hydrolysing solutions increased the rate of crystallisation of hydrated aluminia to either bayerite or gibbsite.

Part III - Investigation of Other "Allophane-like" Clay Minerals

An allophane-like clay mineral has been reported by the pedologists in the High Country soils of the South Island of New Zealand. These soils have been derived from greywacke. In this thesis an attempt was made to bridge the gap between the pedological and chemical descriptions of these soils.

Pedologists place great stock by the feel of a soil when it is rubbed between the fingers. When investigated it was found that it was the presence of amorphous oxides or materials less than 10^{-5}cm that produces a slippery, non-sticky feel, usually associated with the presence of allophane. These High Country soils give this characteristic test and on this basis have been thought to contain allophane. The fine clays from both these soils, and the soils derived from chlorite-schist under similar climatic conditions, were separated and investigated. The soil properties of cation exchange, phosphate retention as well as the I.R. spectra, DTA curves and chemical composition were determined.

These soils all gave a positive NaF/phenolphthalein test and up to 30% of the fine clay dissolved in boiling 0.5 M NaOH. However the DTA pattern showed a large additional exotherm and an additional endotherm which are not characteristic of allophane derived from volcanic parent material.

The electron micrographs showed the fine clays to be sharp, well-defined particles. Rocks taken from the soil and finely ground in a Tema Mill, showed similar properties. The samples were high in silica and had isoelectric points around three which means the particles bear a negative charge in soil under most field conditions. These results showed the clays to be less reactive chemically than volcanic allophanes.

A mechanism of soil formation is proposed whereby the rock is first split by ice-wedging and the pieces further ground by solifluction processes to produce very finely divided rock. The ground rock contains two X-ray amorphous components. One is micro-crystalline whose size is too small to diffract X-rays or to produce an I.R. pattern, and which can only be studied by DTA and electron microscopy. The only weathering that has taken place in this component is the oxidation of much of the iron from ferrous to ferric and a certain amount of leaching. The second component is rock whose original crystal lattice has been destroyed and so it is truly amorphous having a random structure.

It is proposed that these amorphous fractions may be a common soil constituent in alpine and polar regions. This material, which it is proposed is a variation of allophane, is given the name "Alpinite". "Alpinite" will usually weather to the more usual clay minerals. Under periglacial conditions, however, the rate of formation is high and the rate of transformation to other clay minerals is low so that a high steady state concentration is reached. So high that sample of the fine clays ($< 0.2\mu$) from soils derived at high altitudes give no X-ray pattern whatsoever.

CHAPTER 1 INTRODUCTION

1.1 BACKGROUND

New Zealand is a country very largely dependent on agriculture, and the sale of agricultural products for its economy. In the last twenty or thirty years great advances have been made in the dairying and meat producing industries. Perhaps the most important factor has not been a large increase in the land area farmed, but rather the large increase in stock-carrying capacities of the existing pastures. This increase has been due in part both to the introduction of better strains of grass seed and an increase in fertility. The most important factor has been the increase in fertility of soils due to the increased application of fertilizers.

In the mid 1920's the Waikato area became established as one of the countries most intensive areas of dairying. This was due to the introduction of phosphate topdressing on highly phosphate fixing soils - soils that were otherwise ideal in structure for high stocking rates being friable, rapid draining and not consolidated by cattle.

Early work in soil science centred largely on the discovery of trace metal deficiencies in the volcanic soils of the central North Island - but no systematic study of soil types was made until a general survey was started in the 1940s culminating in the publication of soil maps and bulletins.

The recognition that the soils of the Waikato and the other intensive dairying area, Taranaki, contained some material that appeared unique, prompted intense study and the presence of the clay allophane was discovered.

The importance of this material and its role in phosphate fixation and soil structure contribution have resulted in the desire to know more of its structure and properties. Reports of a similar material in soils of the South Island High-Country have also appeared.

The present work is concerned with a study made to determine a possible structure for allophane and to find whether the material found in the South Island is the same as that formed from volcanic ash in the North Island. The presence of large deposits of allophane in the North Island has prompted the beginning of an investigation of possible industrial uses for what is a cheap and abundant material.

1.2.1 SOILS

The term 'soil' can have several interpretations, depending on who applies the term.

To a geologist the term means the weathered regolith in which plants grow i.e. the loose material resting on bed rock.

An agronomist applies the term to the loose regolith at the surface of the earth. The soil is likely to contain horizons, and have properties not dependent on the parent rock.

Engineers consider any loose material as soil, as opposed to rock which is hard and consolidated.

The term soil used in this work is that used by the pedologists, and is material which has been so modified by chemical, physical and biological agents that it will support vegetation. This definition includes the idea of the agronomists in that there are distinct soil horizons in a soil profile.

Soil Structure

Several ideas have been put forward for the meaning of the term 'structure', but that suggested by Marshall[1] included many ideas. To quote:

> "Soil structure is the arrangement of the soil particles and of the pore space between them. It includes the size, shape, and arrangement of the aggregates formed when primary particles are clustered together into larger separable units".

Using this definition no soil is "structureless" and the structure is altered if a soil is deformed in any way.

The stability of the structure and the nature of the primary particles are closely related to the soil structure. The particular structure of a soil is dependent on the general processes of soil development discussed in the next section, but some of their influences can be discussed here.

At any stage in its development, a soil material is left with a particular kind of primary particles which can be arranged in many ways, the stability depending on their arrangement. If coarse, they are not normally clumped into aggregates and the structure is then single grained such as in sandy soils. If the primary particles include clay minerals then aggregation usually occurs and the clay form areas or 'domains' of orientated particles which give bonding to them (see section 5.5).

Soil structure affects plant growth both directly and indirectly; directly in that if the roots are unable to penetrate the soil structure a poor root system results; indirectly in that soil structure affects the retention and water availability, and aeration of the soil, which are important factors affecting plant growth.

1.2.2 WEATHERING AND SOIL FORMATION

There are several closely interdependent factors controlling weathering, the so called 'soil forming factors'.

(a) Parent material
(b) Climate
(c) Vegetation
(d) Time
(e) Topography

(a) Parent Material

The texture and chemical composition of the parent material are initially important but only as the source of the initial stage.

Soils containing entirely different clay minerals can develop from the same parent rock under a difference in the other factors[2]. The presence of alkali and alkali earth metal ions is probably the most important factor in parent material composition because rocks with little or no alkalis can only yield kaolinitic clays but igneous rocks, schists etc., usually have a plentiful supply of bases and so the three layer minerals can be formed. If the parent material is cracked then weathering can be enhanced along the cracks.

(b) Climate

Rainfall and temperature are the two main contributing features to the climatic factor. Generally weathering proceeds faster in a warm climate than a cool one, and faster in a moist climate than a dry one. The seasonal fluctuations in rainfall are important as weathering products may be fixed in the dry period.

(c) Vegetation

Climate and vegetation are closely connected since climate often determines the vegetation that will grow. Plants decay and produce organic acids which affect the rate of dissolution of inorganic products. Under trees producing acid litter, such as kauri, extensive leaching occurs and podzols are formed. Under temperate conditions with grass cover the vegetation has a much smaller effect on weathering and soil formation.

(d) Time

The weathering process is slow so that time is needed to develop soils. On the Rotomaha ash thrown out in the Tarawera eruption in 1886 very little weathering has taken place and no soil horizons are discernible, but on the Taupo pumice which is about 2,000 years old, distinct horizons have appeared and weathering is still proceeding as there is much parent material remaining.

(e) Topography

The steepness of slope controls the movement of ground water and also to a certain extent the position of the water table. If this is high, then reducing conditions are likely to be present for at least part of the year. The movement of ground water influences leaching processes, so that in soils where there is little water movement leaching is not pronounced.

1.3.1 SOIL CLAY

The result of weathering is the breakdown of products either physically or chemically. In soils the finest fraction is called clay. In general, the properties of a soil are determined largely by this fine fraction since it is the most reactive even if the percentage of clay amounts to little more than a few percent. The presence of clay is usually attributable to chemical weathering products, which involve a change in structure and composition from the parent material. The main chemical weathering agent is water and the minerals, as a result, are highly hydrated.

1.3.2 MEANING OF TERM 'CLAY'

The term 'clay' is one that has been used for a wide variety of substances from different origins and with greatly dissimilar properties. There are three major implications in the use of the term

(a) a natural material with plastic properties

(b) a composition of particles of very fine sized grains

(c) composition essentially of minerals that are hydrous aluminosilicates or occasionally hydrous magnesium silicates.

The term 'clay' has several interpretations, depending on who is using the term.

Clay is termed by geologists to be sediments or rock particles with a diameter of approximately 4μ irrespective of origin.

Ceramists emphasize the plasticity of the clay and have the following definition: "Clay is an earthy or stony mineral aggregate of hydrous alumina and silica, plastic when wetted sufficiently, rigid when dry and vitreous when fired at a sufficiently high temperature.

The definition used in this work is that used by soil scientists. In a soil, clay is the finest fraction and the most reactive part. The upper limit of particle size is set at 2μ and the lower limit is the order of molecular size.

1.4.1 EARLY CLAY COMPOSITION CONCEPTS

One of the earliest concepts of clay was that a single, pure substance existed, similar to kaolinite since this could be easily obtained in a white state, and that other clays were kaolinite with impurities. Probably the most widely held concept however was that clays were an amorphous colloidal complex without any organised structure. There were two ideas associated with the colloidal complex. One considered clays to be a mixture of hydrated silica, alumina and iron oxide. The other considered clays to be salts of ferroaluminosiliceous acids.

1.4.2 CLAY MINERAL CONCEPT

Early workers namely Le Chatlier[3], Lowenstein[4], Huckling[5] and Johnson and Blake[6] thought that clay materials were made up of extremely small particles of a limited number of crystalline materials, but it was not until the 1920's that any research tools were available to provide the experimental data to prove the theory. Two independent workers, Hadding[7] and Rinne[8] published X-ray diffraction data for clay materials. These investigators did find a very limited number of different classes of minerals in the fine fraction of a series of clays. Further work carried out by Ross and Kerr[9,10] from 1924 onwards showed the components of all clay minerals to be essentially crystalline and that there were a limited number of crystalline components to which the term clay mineral could be applied.

1.4.3 CLAY MINERAL STRUCTURE

The structure of the crystalline clay minerals has been the subject of study by many workers following the predictions of Pauling[11] who suggested a silicate layer structure.

Two units are involved in the layer structure. The first is two sheets of oxygen atoms or hydroxyl groups close packed with metal cations occupying octahedral holes in the lattice. The second is a sheet of silica tetrahedra joined at their bases to form a hexagonal network. Most clay minerals are formed by combinations of these two layers.

Two Layer Clay Minerals

This group includes the common clay minerals kaolinite and halloysite. In kaolinite an octahedral sheet containing aluminium atoms and a tetrahedral sheet with silicon atoms are combined with a common layer. The apexes of the silica tetrahedra and a layer of the alumina octahedra form this common layer of oxygen atoms. In the common layer only two thirds of the possible octahedral positions are filled by aluminium and there are three ways in which these can be filled, see fig. 1.1. The ideal formula for kaolinite is $Al_2O_3 2Si\ O_2 2H_2O$. Substitution of cations can occur in both the tetrahedral and octahedral sites and this isomorphous substitution plays an important part in the chemistry of the silicate minerals.

Halloysite differs from kaolinite in having water layers separating the kaolinite layers suggested by Hendriks and Jefferson[12], but the sheets are probably irregularly stacked since halloysite usually occurs in curved units rather than the plates of kaolinite.

Three Layer Clay Minerals

This group contains minerals which consist of an octahedral layer 'sandwiched' between two tetrahedral silica layers, the so called mica

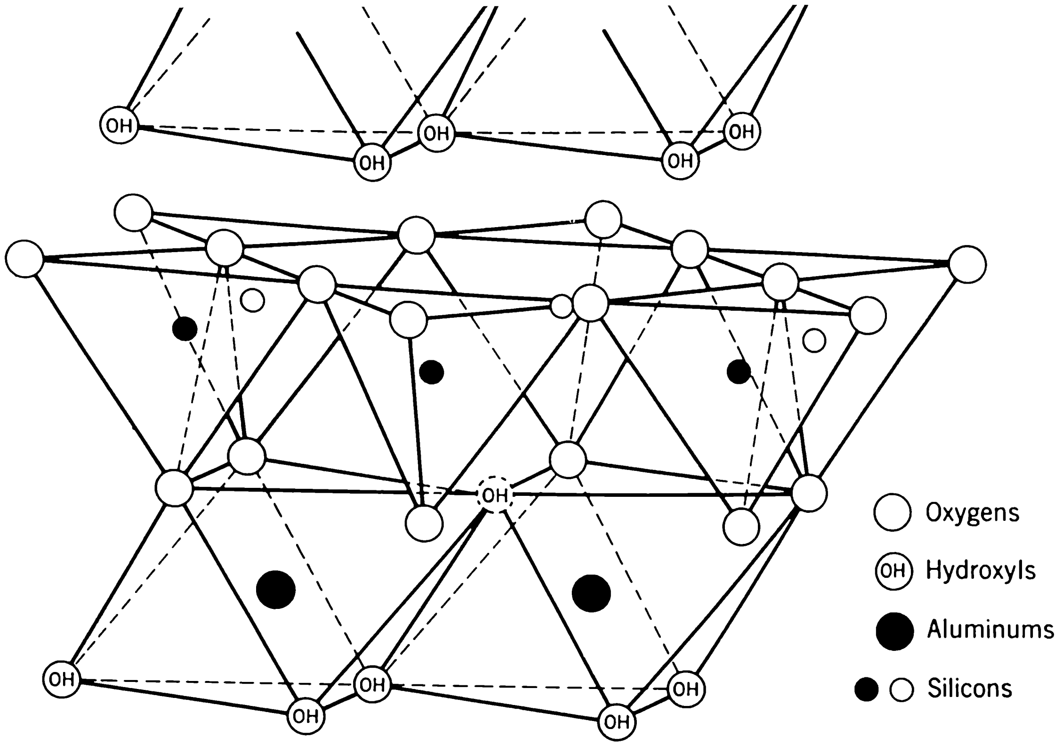


Fig 1·1 Diagrammatic sketch of the structure of the kaolinite layer.

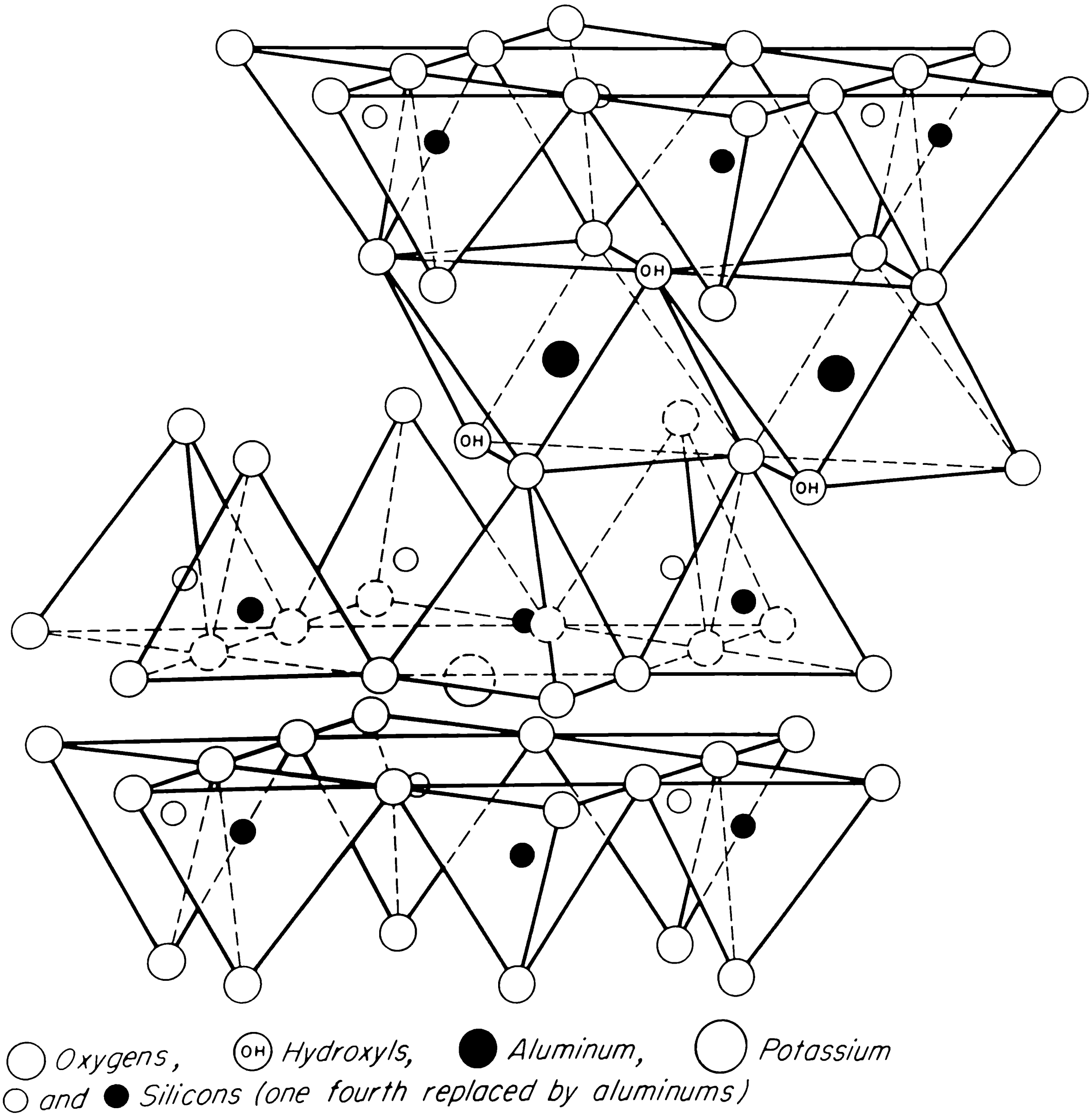


Fig 1·2 Diagrammatic sketch of the structure of muscovite.

unit as shown in the structure of muscovite (Fig. 1.2). In chlorites this layer is separated from the next three group layer by an additional octahedral layer (Fig. 1.3).

In trioctahedral minerals the octahedral positions are all filled with divalent cations such as Mg^{2+} and Fe^{2+} whereas in dioctahedral minerals only two-thirds of the octahedral cation positions are filled, usually by Al^{3+}. Considerable substitution can occur in both the tetrahedral and octahedral layers. In the octahedral layer Mg^{2+}, Fe^{2+} or Fe^{3+} can substitute for Al^{3+} and in the tetrahedral layer Al^{3+} and Fe^{2+} can substitute for Si^{4+}. Substitution of divalent ions for Al^{3+} or trivalent Al^{3+} for Si^{4+} leads to a negative charge in the crystal which is balanced by cations usually lying between the mica sheets. When the silica-alumina-silica mica units are stacked there are only weak bonds between each unit and easy cleavage between them is possible. One of the characteristics of these minerals is the ease with which water and polyalcohols can enter between the units causing expansion of the layers, the expansion dependent on the size of the molecule.

The ideal formula for montmorillonite is $Al_2O_3 4SiO_2 H_2O$ but substitution always occurs, usually in the octahedral layer where Mg^{2+} and Fe^{2+} and Fe^{3+} substitute for Al^{3+}. Substitution can vary from few to complete substitution. This substitution usually causes an imbalance in charge which is compensated in three possible ways (a) substitution elsewhere in the sheet (b) substitution of hydroxyls for oxygens in octahedral layers or (c) by exchangeable cations between the unit layers and these cations are usually hydrated.

Vermiculite is very similar to mica minerals except the unit mica sheets are separated and hydrated ions occupy the interlayer space. There is substitution by Al^{3+} for Si^{4+} in the tetrahedral layer but with a more random substitution than in mica.

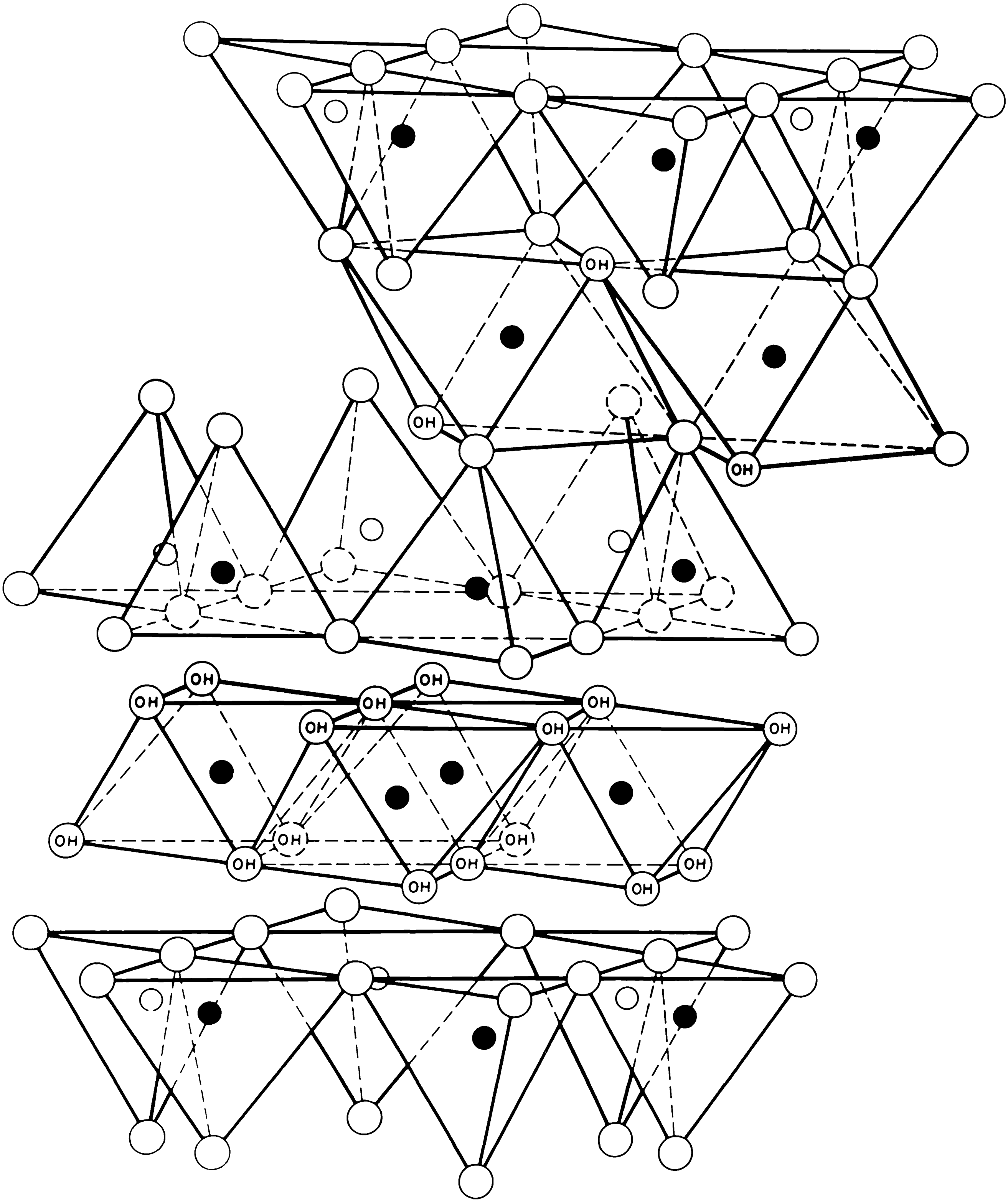


Fig 1·3 Diagrammatic sketch of the structure of chlorite.

Illites are clay minerals that lie partway between micas and montmorillonites in structure. The name was originally applied to clay sized micas but has been restricted recently to micas in which weathering has replaced many of the counter ions together with an increase in water content.

The structure of chlorite consists of a mica unit interlayered with a 'brucite' unit; an octahedral layer usually with Mg^{2+} as the octahedral ion substituted by sufficient Al^{3+} to balance the change caused by substitution in the mica unit. There are no hydrated cations in the interlayer spaces.

Mixed Layer Minerals

Clay materials are composed usually of more than one clay mineral and can be mixed in several ways. Discrete clay mineral particles with no particular orientation to one another is one common mixture. Another common way is interstratification of the layers in which the individual layers may be single or many layers thick. Mixed layers of illite and montmorillonite, and of chlorite and vermiculite is common and separation is difficult. Even the use of X-ray diffraction often fails to separate the components.

1.5 ION EXCHANGE

Clay minerals exhibit ion exchange with both cation and anion exchange capacity but cations have been studied more extensively. The exchange reaction is generally stoichiometric and does not affect the silica-alumina structure. The nature of the exchangeable ions greatly determines the properties of the clay mineral especially when divalent ions replace monovalent.

There are three causes of cation exchange capacity (CEC) in clay minerals.

(a) Broken bonds around the edge of the silicoaluminate structure give rise to unsatisfied charges, the CEC increasing as the particle size is decreased. This is the major cause of CEC in kaolinite and halloysite minerals.

(b) Substitution for Si^{4+} by Al^{3+}, Mg^{2+} and Fe^{2+} gives rise to unbalanced charges in the structure of the mineral. This accounts for 80 per cent of the CEC of vermiculite and montmorillonite.

(c) In exposed hydroxyls the hydrogen can be replaced by a metal ion but usually the hydrogens replaced come from hydroxyl groups on the broken edges of clay minerals. The CEC varies within clay minerals.

Table 1.1 Cation Exchange Capacities of Common Clay Minerals (from Grim[13])

Clay Mineral	CEC meq/100 gm
Kaolinite	3-15
Halloysite	40-50
Illite	10-40
Vermiculite	100-150
Chlorite	10-40
Allophane	25-50

The variation is due to many factors - replaceable cation and anion used, pH and the pretreatment of the clay itself. Some cations absorbed by certain clays prove very difficult to replace and are regarded as being fixed.

1.6 FORMATION OF CLAYS

Clays originate through several processes.

(a) by hydrolysis and hydration of a silicate

(b) by weathering of clay-rich sedimentary rocks

(c) by solution of a soluble rock containing relatively insoluble clay minerals which remain.

(d) by replacement in rock minerals by material from solution.
(e) by deposition from solution.
(f) by action of organic and inorganic acids on primary silicates.
(g) by chemical and physical changes after sedimentation.
(h) by laboratory synthesis.

Practically all clays can be synthesized from a mixture of oxides at moderate temperatures and pressures in the laboratory. Roy and Osborn[14] have made a detailed study of the $Al_2O_3/SiO_2/H_2O$ system in the temperature range 110°-930° and pressure range 1,000-30,000 psi and formed kaolinite, halloysite and the three layer clays. When potassium was added illite formed and when magnesium was added, montmorillonite formed. Various workers[15,16] have used less extreme conditions and have made clays at ordinary temperatures and pressures starting with silicates and aluminates. The transformation of one clay mineral to another has been studied by many workers using treatment with K^+ [17,18] or Mg^{2+} [19].

The greatest single path to clay formation however is probably that from products of weathering. There are many factors involved, as discussed above.

CHAPTER 2 LITERATURE REVIEW ON THE CLAY MINERAL ALLOPHANE

2.1 HISTORICAL

Allophane was the name applied to material first observed by Riemann in 1809 in Thuringia by Stronmeyer and Haussman[10] in 1816. The name came from two Greek words 'allos' and 'phainin' meaning 'to appear' and 'other'; apparently an allusion to the two different forms of the material due to a loss of water on standing and a change from a glassy state to an earthy one. Breithaupt[21] applied the name 'riemannite' to material in the same vicinity and Sack[22] in 1832 applied the name 'alhuyarite' to material found in veins in lignite. Dana in 1892[23] considered these were the same material as allophane. The first suggestion of allophane occurring in rocks of volcanic origin was made by Dana[24] in 1850 when he described 'samoite' as occurring in a lava cavern on the island of Upoldi in the Samoan Group but this was considered poorly crystalline montmorillonite by Ross and Kerr[9]. The name 'schrotterite' was applied by Glocker[25] to an opaline allophane described by Schrotter[26] in 1837. These names together with the term 'torniellite' seem to have been the names applied to allophane-like minerals before 1900. Ross and Kerr[9] investigated several of these compounds and found many to be either mixtures or poorly crystalline material.

The original material was colourless and translucent but various impurities have caused colour ranging from yellow-blue to pink[27,28,29,30,31,32,33].

Although most of the geological allophane reported occurred in Europe[28,34,35,36,37], there have been reports of allophane outside Europe[19,33,39].

Allophanes containing high levels of impurities have been reported and names like ferricallophane[39,40] and plumballophane[41] have been used. Other impurities common in allophane were SO_3[26,28,42] and P_2O_5 (phosphate allophane)[32,39,43] as well as varying amounts of alkali earth metals as many samples were found in limestone shales[28,31,34,44,45].

The term 'allophanoids' was widely used in Europe to describe the portion of clay soluble in dilute hydrochloric acid[46,47] but included the fine fraction of halloysitic and montmorillonitic clays.

Ross and Kerr[9] summarized the properties of allophane and considered many of the geological samples were crystalline. They proposed that the name should cover all truly amorphous aluminosilicates.

2.2 OCCURRENCE OF ALLOPHANE IN SOILS

Allophane in soil was first reported by Seki[48] in 1914 as occurring in a volcanic ash soil of Japan.

Henderson and Ongley[49] first noted allophane in New Zealand soils in a study of volcanic ash showers in the Mairoa area in 1923. Further reports of its presence in New Zealand were noted by Taylor[50] and Hutton[51].

However it was not until 1952 that any detailed study was made of its occurrence when Birrell and Fieldes[52] showed it was an important constituent of soils developed on volcanic ash. The typical characteristics of an allophanic soil were given by Gradwell and Birrell[53] and in an address, Dixon[54] summarized the important properties of allophane. Later work by Fieldes and Swindale[55] showed that allophane was an important soil constituent in New Zealand and was in fact the major portion of the clay fraction in yellow-brown loams and yellow-brown pumice soils. The presence of crystalline clays in these soils was explained by Fieldes[56] who proposed a weathering scheme from volcanic glass through to crystalline clays.

The presence of allophane was confirmed in Japanese soils in work by Sudo[57,58,59], Nozawa[60], Suzuki and Kitazaki[61] and Aomine and Yoshinaga[62]. These workers agreed with the results published by Fieldes and his coworkers that allophane was the chief constituent in soils developed from volcanic ashes.

Further reports have shown that allophane is contained in young volcanic ash soils throughout the world (especially in the Pacific Basin). In Taiwan allophane occurs together with kaolin and halloysite[63]. These were possibly formed by hydrothermal action since they were associated with fumaroles.

The young soils of Indonesia contain amorphous material which Tan[64] has described as proallophane together with vermiculite in some samples but it seems this is the allophane B described by Fieldes[56]. Lai and Swindale[65] have reported allophane in some Hawaiian soils - many of the islands' soils having been derived from volcanic ash weathered under tropical conditions. Other authors e.g. Tamura et al[66], Sherman et al[67] and Bates[68] have also reported allophanes in the latosols of Hawaii. All of these soils were moderately to strongly weathered. Patterson[69] has reported allophane and an amorphous gel in the underclays of peat beds in Kauai Island, Hawaii. The composition of the gel was 80-90% water and the remainder was high in alumina. This implied a large proportion of amorphous alumina in the gel which showed in the underclay gel DTA curve.

In Columbia[70] allophane together with a small proportion of halloysite was found in the well drained volcanic ash derived soils. However in the alluvial soils the allophane content decreased and illite and vermiculite were present, apparently derived from igneous rocks.

Allophane has also been reported in the soils of the Caribbean Islands e.g. in the British West Indies[71] and Costa Rica as well as in Chilean soils[72,73].

Fieldes[74] and Fieldes and Swindale[55] have shown that allophane develops in basalt soils and is the major constituent of the immature red and brown loams of New Zealand. It has now been recognised that allophane and gibbsite are common weathering products of basalts. Campbell[75] has shown that allophane is a major constituent of the basaltic soils around Dunedin. In general the older basaltic soils of New Zealand have weathered to form crystalline clay minerals but the younger basaltic soils contain allophane[76].

Allophane occurring in basalt soils has also been reported throughout the world. The allophane reported in Australia[77,78,79] has been derived from basalt under humid conditions which were considered by Sherman et al[67] to be necessary for the continued presence of allophane. Robertson[80] has reported the occurrence of allophane in Oregon soils on pumice tuffs. Allophane has also been reported in the lake sediments in Oregon. In the basaltic soils of Scotland allophane has been reported[81,82] together with other clay minerals. Siefferman et al[83] have reported allophane from the basaltic soils of the Cameroons in Africa.

Allophane is not restricted to warm climates. It has been reported that the ash on Mt Erebus on Ross Island in Antarctica has been partly weathered to allophane[84]. It is possible that hydrothermal conditions have formed the soils since kaolinite was present. The ground where the soil developed was warm due to the volcanic activity.

It is apparent that the occurrence of allophane is widespread throughout the world but it is only important as a major soil constituent in the young soils derived from volcanic ash.

2.3 PROPERTIES OF ALLOPHANIC SOILS

Soils high in amorphous oxides usually have a greasy feel, and the soil itself is not sticky. Birrell[85,86] has shown that drying is an irreversible reaction in that the soils fail to show plasticity when moistened again. Dispersion of the soils was difficult and drainage on the soils was good due to flocculated clays which were well aggregated. When the soil was very high in allophane (60% or more) and moist, the allophane had a waxy appearance first noted by Taylor[50].

Allophanic clays have high surface areas (ca. 200 m^2/gm) and Gradwell and Birrell[53] have shown that clays separated from soils containing allophane have a high percentage of particles with apparent diameter less than 0.2 μ. They showed that there was a strong tendency for these particles to be aggregated and that the soils were compressible. The presence of allophane in the soil gave it high plastic and liquid limits* and a high shrinkage loss when dried. Grim[87] has stated that the presence of amorphous material can both increase and decrease the plastic limit of soils. He suggested that when the limit was increased the structure of allophane approached that of montmorillonite and when decreased the structure approached that of the two layer clay minerals. Similar reasoning was also suggested for the liquid limits[87]. Field estimation of clay content was difficult if the sample had been partially dried and the feel could indicate less clay than actually present.

2.4 THERMAL PROPERTIES OF ALLOPHANE

The heating curve of allophane was first determined by Le Chatlier[88]. Ross and Kerr[9] reported the dehydration data for two samples of allophane. The curves showed that allophane lost water steadily up to 500° when the rate of loss of water started to level off. They stated that the curves were characteristic of a material in which the water was held in solution and not chemical combination, as in the kaolin minerals. This gradual loss was also shown by Nutting[89] with no prominent points of inflexion.

The data also showed that allophane contained more water than kaolinite and halloysite, most of which was lost below 200°C.

* See Glossary.

Differential thermal analysis curves have been reported by White[33]. These showed a very large endotherm due to the great loss of water between 60 to 350°C, and an exotherm above 1000°C due to the formation of mullite. These observations were borne out by work done by Fieldes[90] and Aomine and Yoshinaga[62]. Several smaller exotherms have been attributed to halloysite impurities.

On the basis of DTA data, Fieldes[56] has distinguished two different kinds of allophane, allophane A which showed an exotherm between 850 and 1000°C and allophane B which did not show the exotherm.

2.5 CHEMICAL STRUCTURE OF ALLOPHANE

Allophane has been described as clay material which appears amorphous to X-rays. This implies that there is no definite structure or chemical composition. Ross and Kerr[9] found only a diffuse band and very faint lines in the X-ray diffraction spectra of the samples they studied. They concluded:

> "allophane has no definite atomic structure or chemical composition and is a mutual solution of silica, alumina, water and minor bases and accessory acid radicles".

This mutual solution idea seemed borne out by the fact that some of the samples they studied appeared homogeneous mixtures of allophane and evansite, or allophane and chrysocolla.

Early workers[91,92] studying amorphous material considered allophane as a mixed gel of aluminium hydroxide and hydrated silica which was unstable in acid. Krasenkaya[47] considered that in allophane the alumina was free or in loose combination with silica and noted that there were no definite quantities of oxide combination, but that the allophanes were mixtures of coagulated gels. White[33] concluded from a study of two allophanes which showed diffraction bands that allophane had a more ordered structure than glass. Several other authors[93,94] have suggested an ordered phase of allophane, possibly in the transition to halloysite[93] or to gibbsite[95] from volcanic glass.

The IR spectra of allophanes have shown only a broad band around 1000 cm^{-1}. This showed that there was no regular molecular arrangement. Fieldes[96] has discussed the effects of randomness on allophane properties and stated that allophanes could be considered random structures rather than disordered or defect structures. This randomness was a property of allophanes which were considered as random-structured hydrous alumino-silicates. Differences between allophanes are thus due to their varying compositions.

Fieldes and Swindale[55] had earlier considered allophane to be an association of amorphous colloidal hydrous oxides of silicon and aluminium. Later Fieldes[56] divided the allophanes studied into two types, allophane A and allophane B with an intermediate form allophane AB distinguished by DTA patterns. The presence of two peaks in the endotherm and absence of the exotherm in the DTA curves of the allophane from young soils was interpreted by Fieldes as evidence of discrete phases of silica and alumina and designated allophane B. Allophane A was considered coprecipitated-gels and showed only a single endotherm at 120° and an exotherm at 950°C. The young volcanic ash soils contained a large amount of a mineral-organic complex which contained largely alumina bound to an organic acid. This prevented the formation of co-precipitated gels. Fieldes also attributed bands in the IR spectra to discrete amorphous silica and alumina.

Adler[97] has published IR spectra of two geological specimens of allophane which did not show bands characteristic of amorphous silica. The existence of discrete hydrous alumina and silica was questioned by Miyauchi and Aomine[98] who attributed the bands assigned by Fieldes[56] to amorphous silica, to crystalline silica or crystobalite. Fieldes and Furkert[99] reconsidered the data and concluded that amorphous silica did in fact exist although much of the effect could be attributed to domain zones of vitreous silica in the volcanic glass or hydrous silica zones in the hydrous glass.

The substitution of aluminium ions for silicon in the tetrahedral layer will give rise to a net negative charge per tetrahedron and it was suggested by Fieldes[100] that aluminium in allophane occupied tetrahedral sites because of its mode of formation from glass and feldspars in volcanic ash. This, he said, explained the unique properties of allophane. Birrell[101] examined the surface acidity of allophanes from volcanic ash and considered the allophanes closely resembled the aluminosilicate catalysts in which aluminium is held in a four-fold co-ordination. He showed that some allophanes were useful as petroleum cracking catalysts, indicative of tetrahedral aluminium affording acid sites.

Egawa[102], using X-ray fluorescence techniques has shown an apparent co-ordination number of five for aluminium which he interpreted as aluminium in both octahedral and tetrahedral sites.

Recently the presence of an ordered form of allophane called imogolite has been reported as occurring in various clays in Japan[103-107], and elsewhere[108-110]. This material has the appearance of fine threads and two theories have been put forward for its structure[111,112].

Wada[113] has proposed a chain-like structure for allophane, Fig. 2.1, but this structure did not take into account tetrahedral aluminium. He assumed two end members of a series $SiO_2Al_2O_32H_2O$ and $2SiO_2Al_2O_33H_2O$ and suggested defects to account for the discrepancy in analysis between the model and naturally occurring specimens.

Further suggestions for structural models have been made by Udagawa et al[94] and Iimura[114].

Udagawa et al[94] suggested the $SiO_2:Al_2O_3$ ratio as well as the environment of formation were the controlling factors determining the

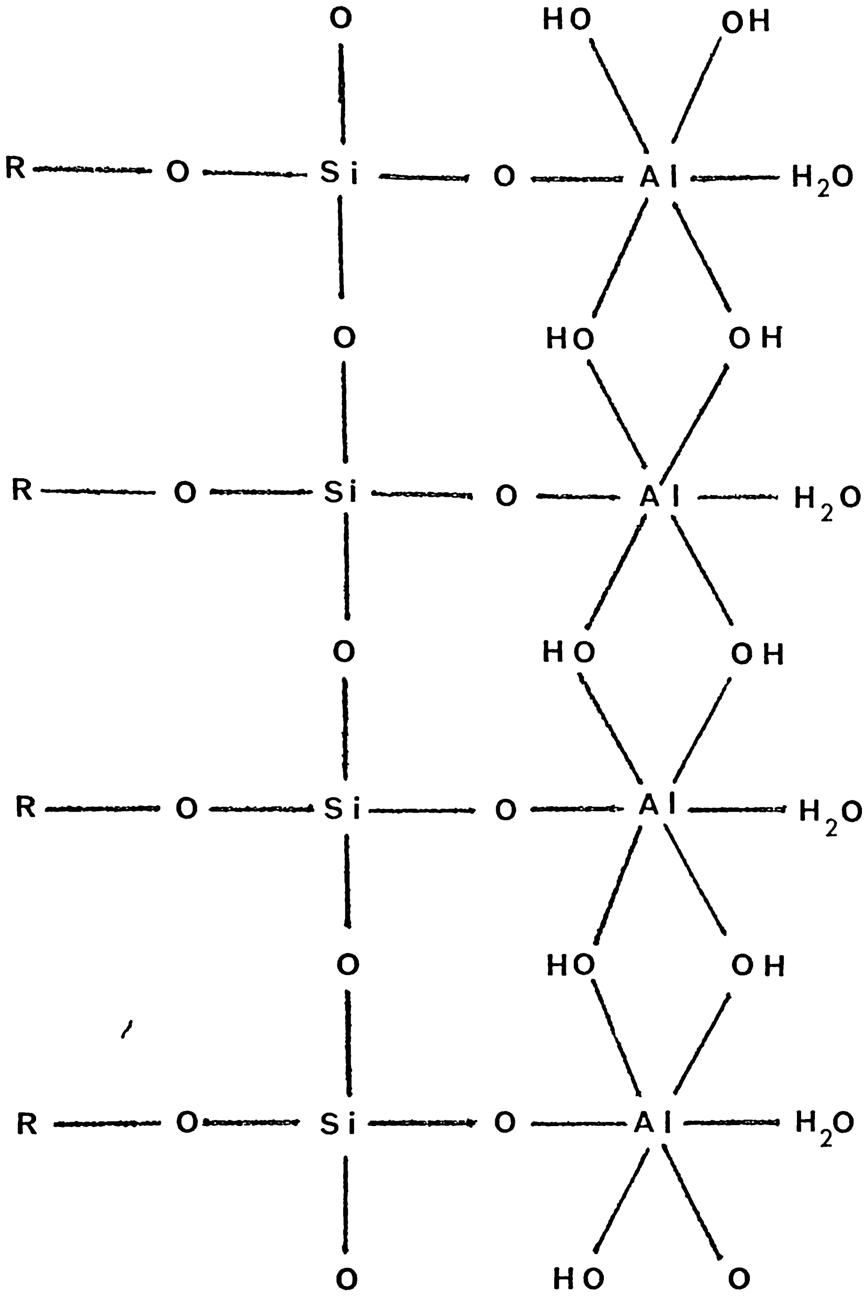


FIG 2·1 WADA'S[113] STRUCTURE FOR ALLOPHANE

R= H or $Al(OH)_5H_2O$

structure. They looked at the structure with respect to kaolinite and showed that the amount of aluminium (IV) changed from about 40% to 100% on heating from room temperature to 700°C. On heating to 1400° the amount returned to about 60%. Considering the similarity to the behaviour of kaolinite they interpreted the allophane structure to be sheet-like, similar to kaolinite rather than the chain type structure described by Wada[113]. Iimura[114] estimated the average structural formula of allophane to be:

$$(OH)_{0.86}O_{1.61}Si_{1.33}O_{1.23}Al_2(OH)_{4.77}$$

Cloos et al[115] suggested a model for amorphous aluminosilicates which they postulated would stand for allophane as well as the silico-aluminate catalysts. The basic model was that of a central core in which tetrahedral silicon was replaced by aluminium, the resulting negative charge balanced by polymeric hydroxy-alumina complexes such as $Al(OH)_2^+$ or $Al_n(OH)_m^{(3n-m)+}$ coated on the outside of the central core.

It is from this point that this thesis attempts to clarify the structure of allophane.

2.6 FORMATION OF ALLOPHANE

It appears that many of the geological samples of allophane have been formed by mutual precipitation of solutions containing silica and alumina colloids similar to that reported by McKenzie[44]. The alumina and silica have probably come from slow dissolution of crystalline minerals into slightly acid ground waters as they percolate through cracks in the overlying rocks and then precipitated out as the water evaporates or the concentration builds up sufficiently[116]. It has been suggested that impurities in the allophane give an indication of the parent rock[40,117]. Formation of allophane in hydrothermally altered rocks has also been suggested[118].

However, the majority of allophanes found have probably been formed by weathering. Fieldes and Swindale[55] have described a weathering sequence in which allophane is formed from the weathering of volcanic glass which itself is amorphous. The allophane weathered further to kaolinite. They stated it was probable feldspars went through this amorphous stage also, since they had a linked tetrahedral structure and to form layer silicates would have to pass through an amorphous stage. From further studies made by Fieldes[56] it was found that allophane was present in both weathered rhyolitic and andesitic ash and a sequence of weathering was proposed.

Allophane B ⟶ Allophane AB ⟶ Allophane A ⟶
metahalloysite ⟶ kaolinite.

Allophane B was predominent in yellow-brown pumice soils and allophane A in yellow-brown loams with metahalloysite in the brown granular clays of New Zealand. There was a trend towards more ordered clay minerals as the sequence progressed. This sequence was upheld by Aomine and Wada[119] and it has been generally accepted that allophane is the intermediate product in weathering of volcanic ash and pumice to halloysite[93].

Weakly weathered basalt gives rise to products that are recognised as allophane and Fieldes and co-workers have reported allophane on weakly weathered basalt[55,74]. Mitchell and Farmer[82] and Briner and Jackson[77] have also reported the presence of allophane on weathered basalt.
The presence of soil allophane in any soils other than those of volcanic origin is doubtful. Furkert and Fieldes[120] have reported the presence of allophane in soils on weathered sedimentary rocks and amorphous material has been reported in Egypt on alluvial soils[121]. The presence of amorphous material in soils of non-volcanic origin in New Zealand will be discussed in detail in a later chapter.

CHAPTER 3 SOILS OF NEW ZEALAND

3.1 INTRODUCTION

New Zealand has a wide range of soils due to several factors.

(a) The many kinds of mineral and organic matter present on the surface.

(b) The varied conditions of climate that occur throughout the country.

(c) The slope and drainage differences.

(d) The differing periods of soil formation.

Soils throughout the world can be classified into three broad categories. Zonal, introzonal and azonal.

(1) The zonal groups - the soil is developed on a 'normal' siliceous rock with average topography with the main differences in the soils controlled by climate and the vegetation.

(2) The intrazonal group - the soil is differentiated by the importance of a local factor such as a particular parent material or a high water table.

(3) The azonal group - the soils have characteristics modified by such causes as instability of material or the shortness of time for which the soil has developed.

In New Zealand allophane is found in soils which fall into the intrazonal and azonal groups.

3.2 ASH SHOWERS

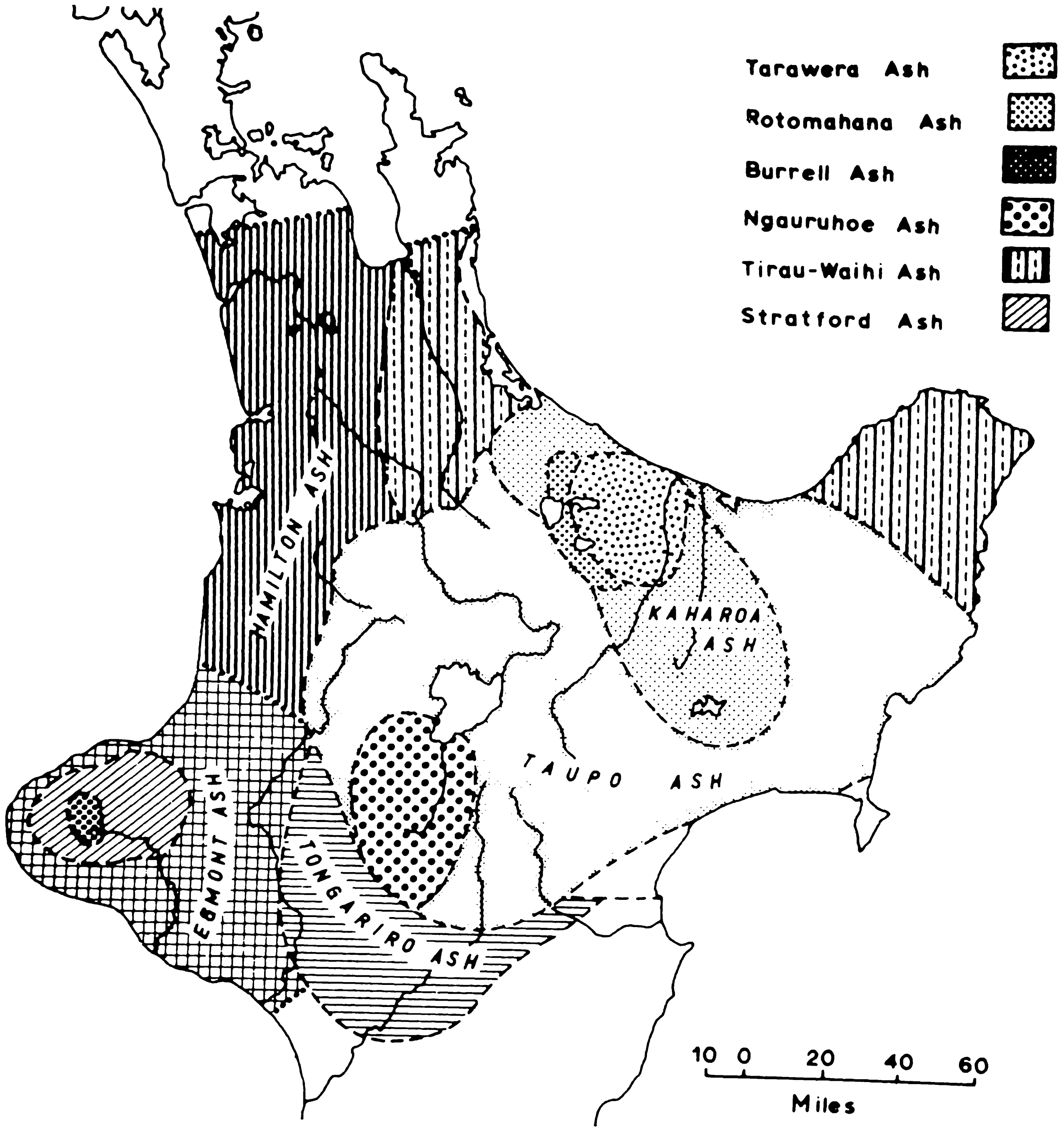
Various showers of volcanic ash and pumice have covered the greater part of the central North Island over the last fifty thousand years. The cover has been divided into several main falls by Grange[122] who commenced study on them. The major divisions are seen in Fig. 3.1.

The youngest shower is that deposited by Mt Ngauruhoe which is still depositing andesitic ash. In 1886 Mt Tarawera erupted, depositing

Fig. 3.1

Principal Soil Forming Volcanic Ash

Showers on the North Island


Tarawera Ash
Rotomahana Ash
Burrell Ash
Ngauruhoe Ash
Tirau-Waihi Ash
Stratford Ash
HAMILTON ASH
KAHAROA ASH
TAUPO ASH
EGMONT ASH
TONGARIRO ASH
10 0 20 40 60
Miles

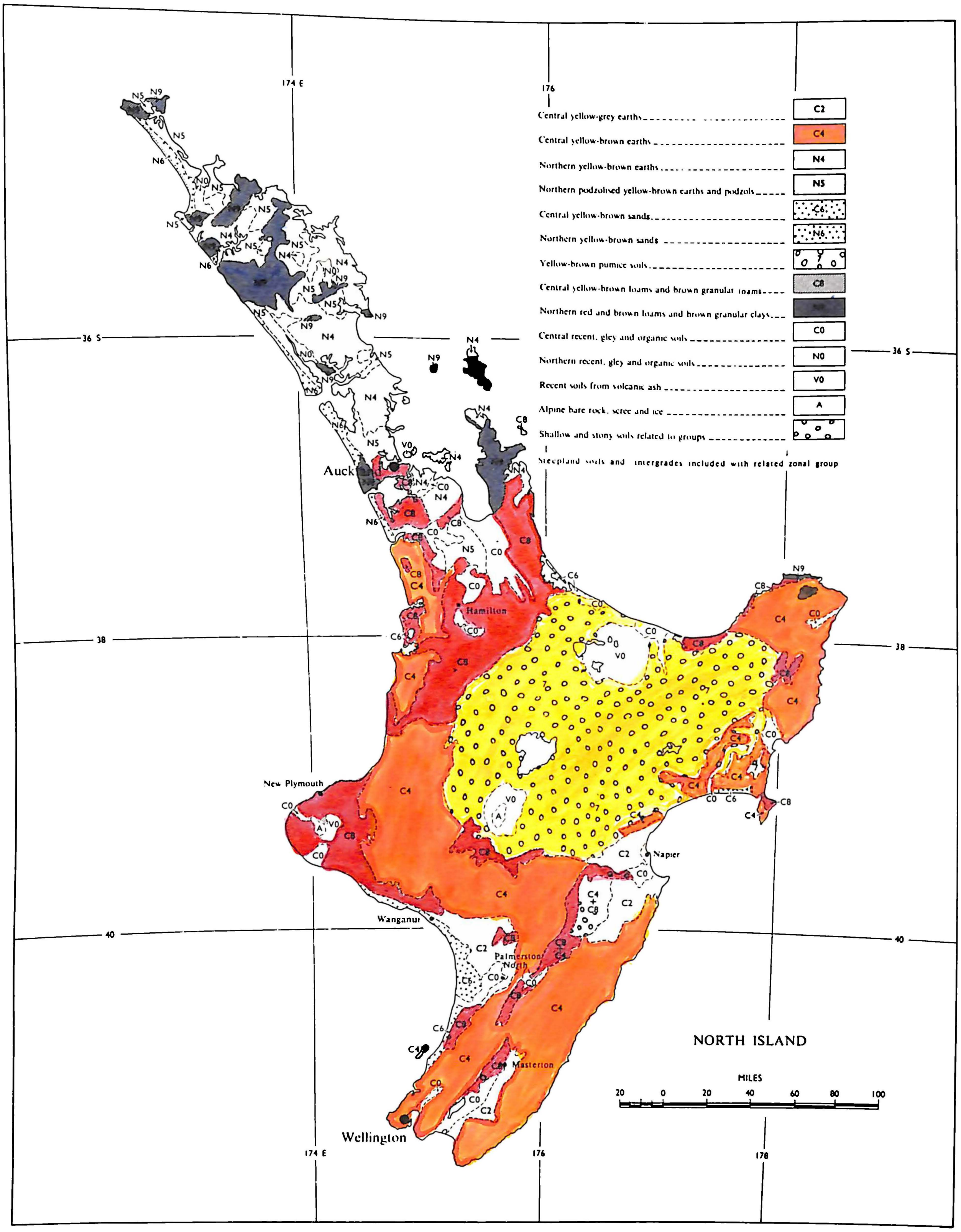


Fig. 3.2 SOILS OF NORTH ISLAND

(soils mentioned in text shown
in colour)

The vegetation growth has a very marked effect on the texture of these soils depending largely on the type of vegetation growing. The topsoil is usually very dark due to melanization.

Weathering has not progressed far in the pumice soils due to the relatively recent deposition of ash but allophane is the predominant clay mineral. Free drainage leads to severe leaching and the soils are usually deficient in bases as well as nitrate. Topdressing with superphosphate and potash as well as nitrogen combined with good management is needed to maintain pastures and prevent reversion to scrub. It was on these soils that 'bush sickness' was prevalent until the discovery of cobalt deficiencies.

(b) The Yellow-brown Loams

The parent material of these soils is typically andesitic ash although the Tirau soils have developed on an old fine rhyolitic ash. These soils have many features that are similar to the zonal yellow-brown earths that have developed on greywacke as they are in the same climatic zone. The top soils are 'fluffy' and very friable with generally a granular or crumb structure and range in colour from the brown soils on andesitic ash to yellow for those developed on rhyolitic ash.

They differ from the zonal yellow-brown earths in having as the predominant clay mineral, allophane, instead of the layered minerals of the illite group and the kaolin group. The soils when wet are slippery in contrast to the yellow-brown earths which are sticky.

The yellow-brown loams are easily worked and will grow good crops. When fertilized adequately and consolidated they will give first class pastures as is shown in the intensive dairying areas of the Waikato and Taranaki.

The parent material of fine volcanic ash was deposited intermittently and because of this gradual accumulation the vegetation was not destroyed and has played an important part in the formation of soil. The andesitic showers were the Mairoa, Egmont and Stratford showers and the rhyolitic ones, Whakatane, Tirau and Waihi. Both sorts of ashes did weather to the same product but Fieldes[56] has shown the rhyolitic ash weathered more slowly. The majority of the yellow-brown loams have formed under broadleaf forest and this has led to a slight podzolization and it is this leaching that has broken the main soil suites into various stages of development.

(c) Red-brown loams and Brown Granular Loams and Clays

The red-brown loams are confined to the Auckland district in areas where there is a high rainfall. They have been derived from basic rocks, the red loams from scoria and the brown from basaltic rocks. The soils are well developed with good structure. The soils are high in iron and alumina and besides containing amorphous constituents usually contain gibbsite. The presence of iron and alumina makes these soils highly phosphate fixing.

The brown granular loams and clays have been usually derived from andesitic rocks or from older more deeply weathered andesitic ash (e.g. Hamilton ash). They have developed uhder forest in a damp climate. The weathering has progressed beyond the amorphous stage and kaolin is the predominant clay mineral together with some halloysite. The soils have lost the friability associated with the yellow-brown loams and are dense and sticky and if they have a high clay content are very compact and difficult to work.

Azonal Soils

The recent soils derived from the ashes of Ngauruhoe and Tarawera fall into this group. The soils are generally not well developed and little weathering has taken place. However the recent ashes are important in that being basaltic, where they overlie the rhyolitic pumice beds the soils that have developed are not cobalt deficient.

CHAPTER 4 SOILS OF THE WAIKATO

4.1 INTRODUCTION

Apart from the recent peat soils most of the soils of the Waikato Basin are of the yellow-brown loam and brown granular clay types. The differences in composition are usually caused by the parent ash and local climatic factors. In the northern part of the Basin the older Hamilton ashes are the predominant parent material and the ash has weathered to clays such as kaolinite and halloysite. In the south, the Tirau and Mairoa ashes overlie the Hamilton ash and the soils developed on these contain allophane. The soils generally are well leached and where the rainfall is high, extensively leached.

The area was originally covered in mixed forest of rimu and tawa. There is evidence that kauri was an important component in the podzolized soils of the lower Waikato Basin.

The natural fertility of the soils is low and common practice is to topdress with 3-5 hundredweight of superphosphate per year per acre to keep grass production high.

4.2 DESCRIPTION OF SAMPLES

Chemical Data from Reference 126.

Ohaupo silt loam. (Soil Ref. No. 59)

Developed on Mairoa ash in rolling country under a rainfall of 50-55 inches per year.

pH of top soil	5.8	CEC	42.3 meq %	BS	26 %
sub soil	6.4		34.6		22

Representative profile 0-6" dark grey silt loam
6"- yellow-brown free silt loam on light yellow-brown silt loam.

The sample was collected from C horizon 25-30". Site N65 769341.

Otorohanga silt loam. (Soil Ref. No. 59a)

Developed on Mairoa ash in easy rolling country under a rainfall of 50-55 inches.

pH top soil 6.4 CEC 49.8 meq % BS 31 meq %

Representative profile 0-5" blackish-brown silt loam

6-10" yellow-brown free silt loam on light yellow silt loam.

The sample collected from C horizon 22-34". Site N74 669100.

Tirau sandy loam. (Soil Ref. No. 57)

Developed on Tirau ash in easy rolling country under 50-60 inches of rainfall.

	pH	CEC	BS
top soil	5.9	43.5 meq %	31 %
sub soil	5.7	11.3	17

Representative profile 0-5" brownish black sandy loam

5-8" free brown sandy loam on brown slightly compacted sandy loam.

The sample was collected from B-C horizon 20-31". Site N66 270266.

Kereone silt loam. (Soil Ref. No. 57a)

Developed on Tirau ash in easy rolling country under 45-50 inches of rainfall.

	pH	CEC	BS
top soil	6.1	43 meq %	40 %
sub soil	6.3	11	15

Representative profile 0-5" black silt loam

5-12" light brown silt loam on underlying yellow-brown sandy silt loam.

The sample was collected from 14-21". Site N66 185450.

Horotiu sandy loam. (Soil Ref. No. 48a)

Developed on mixed rhyolite alluvium and andesitic ash in flat and undulating country under 45-50 inches of rainfall.

pH top soil	5.9	CEC	41.0 me %	BS	40 %
sub soil	6.1		21.9		30

Representative profile 0-7" grey-brown sandy loam
7-15" light brown sandy loam on underlying light brown gravelly sand.

The sample was collected from B horizon. Site N65 715343.

Te Rauamoa silt loam. (Soil Ref. No. 64)

Developed on Mairoa ash under broadleaf forest with high rainfall of 80 inches or more.

pH top soil	5.6	CEC	65.0 me %	BS	13 %
sub soil	5.9		77.4		3

Representative profile 0-5" dark grey brown heavy silt loam
5- yellow-brown mottled heavy clay loam on a compact clay loam

The sample was collected from gley horizon 32-37". Site N74 565142.

Dunmore silt loam. (Soil Ref. No. 61)

Developed on Mairoa ash under tawa forest in rolling country with rainfall of 60-70 inches.

pH top soil	5.8	CEC	36.7 me %	BS	16 %
sub soil	5.7		27.2		2

Representative profile 0-4" dark brown silt loam
4- brown free silt loam moderately compacted at lower depths.

The sample was collected from the B horizon. Site N65 570650.

A sample of 'waxy' allophane was collected from a lens in the cutting on the Raglan road at a depth of 15 feet.

4.3 PREPARATION OF SAMPLES

The samples were collected from the field and kept in plastic bags to retain moisture. When required, 100 gms of the soil was broken up into a litre beaker and 200 mls of distilled water added. 10 mls of 100 volume H_2O_2 were added and allowed to stand until the sample had ceased frothing. As the samples were sub-soils there was little organic matter in the soils and no additional peroxide was needed. Once frothing had ceased the samples were heated on a water bath and then transferred to a bunsen burner and boiled for one minute. The heat was removed, 4 gms of Na_2CO_3 added and the suspension boiled for a further minute before cooling quickly. The pH was tested and if below 8.5 (close range filter paper) further Na_2CO_3 was added until the pH was about 9. The suspension was then passed through a 100 mesh sieve to remove stones and loose sand. The sieved fraction was made up to 2 litres in a measuring cylinder and allowed to settle. If the clay remained flocculated the supernatant liquid was poured off and further distilled water added, the process being repeated until dispersion was achieved (usually only once or twice being necessary). Once this occurred the samples were left undisturbed for 48 hours and then the clay suspension was siphoned off. Further distilled water was added, the suspension well shaken and then left for a further 48 hours. The separated clay suspension was centrifuged at 2500 rpm for 43 minutes to separate the fine clays. The fine clay suspension was flocculated with sodium chloride, centrifuged, washed with distilled water and ethanol, acetone being added to ensure flocculation, and then freeze dried.

Deferration was carried out with some samples by the method described by Jackson[339] after treatment with peroxide. The samples needed no further treatment for dispersion and were separated in the same way as the untreated clay.

4.4.1 DESCRIPTION OF CLAYS

Both the fine ($< 0.2\mu$) and coarse ($2-0.2\mu$) clays have the characteristic 'feel' of amorphous clay material, i.e. greasy but not sticky. All samples gave a positive 'allophane' test immediately. Apart from the Te Rauamoa and Horotiu samples the clays were all very similar in appearance. They ranged in colour from yellow-brown for the Tirau sample to orange for the Dunmore sample - all showing the characteristic colour of free ferric oxide. The Te Rauamoa sample was olive in appearance and contained 2.4% ferrous oxide since it was obtained from a gleyed horizon. The Horotiu sample contained very little iron and so was only a pale buff colour and much lighter and 'fluffier' than the other samples - very similar to the synthetic alumino-silicates prepared in chapter 7.

The deferrated samples were pale grey in appearance and 'fluffy'.

4.4.2 SODIUM HYDROXIDE DISSOLUTION

Generally when studying crystalline clay materials the amorphous material has been removed by dissolution with 0.5M sodium hydroxide. Hashimoto and Jackson[127] have used this method for estimating the percentage of allophane present. Langston and Jenne[128] showed however that poorly crystalline halloysite and kaolinite can also exhibit rapid dissolution, but usually the crystalline materials reacted over a much longer period.

Method

0.1 gm of freeze dried allophane sample was taken in a nickel crucible, 25 mls of 0.5M NaOH added and the solution boiled for 2½ mins. on a bunsen before being quenched in an ice bath. The suspension was filtered through a weighed gooch crucible, washed with distilled water, dried and the amount dissolved by the sodium hydroxide calculated. The results are shown in Table 4.1.

Table 4.1 Dissolution in 0.5M NaOH

	% Dissolved
Dunmore	94.53
Te Rauamoa (deferrated)	47.72
Tirau	81.42
Otorohanga	87.76
Taupo	76.14
Kereone	84.84
Waxy Allophane	87.76
Horotiu	83.19
Te Rauamoa	72.4

Shao[129] found about 80% of Tirau clay dissolved in boiling 0.5M NaOH. What remained undissolved was probably feldspars and a small amount of unweathered volcanic glass which was shown by Langston and Jenne[128] to dissolve slowly. The SiO_2/Al_2O_3 ratios of the dissolved portion were very similar to the actual ratios in the whole fine clay apart from the deferrated samples, which were high in silica. This is probably because alumina has been dissolved out in the dithionite-citrate treatment. The low amount of the Taupo sample that dissolved is probably due to the fact that weathering has not converted all the volcanic ash and glass into allophane.

4.4.3 CHEMICAL ANALYSIS

The fine clays were analysed by a method described by Boar and Ingram[130]. 0.2 gm of sample was taken and made up to 100 mls after fusion with lithium metaborate.

The analyses are reported in Table 4.2.

Table 4.2 Chemical Analysis of North Island Allophanes

	Kereone %	Tirau %	Waxy Allophane %	Dunmore %	Horotiu %	Taupo %
SiO_2	28.00	30.45	25.35	29.5	16.80	27.0
Al_2O_3	30.7	28.02	29.90	30.7	21.07	31.7
FeO	-	-	-	-	-	-
Fe_2O_3	4.52	4.86	3.83	4.56	0.46	6.2
MgO	0.50	nd	nd	0.28	nd	0.28
CaO	0.06	nd	nd	0.03	nd	0.03
H_2O^-	14.28	16.73	17.50	11.82	9.99	17.32
H_2O^+	16.31	31.57	17.34	16.08	43.11	13.48
Na_2O	3.72	2.84	3.39	6.2	4.03	2.78
SiO_2/Al_2O_3 (molar ratio)	1.55	1.85	1.43	1.63	1.35	1.45

The samples all contain very little other than silicon, aluminium iron and water. The sodium is probably held as exchangeable ions since the clays were flocculated with sodium chloride and therefore are sodium saturated. The only allophane sample that shows any ferrous oxide is the Te Rauamoa sample which contains 2.40% FeO.

The low occurrence of elements other than aluminium, silicon and water is similar to the analyses reported by other workers, but the samples contain more iron than the geological ones reported by Ross and Kerr[9].

4.4.4 X-RAY DATA

Powder photographs of the fine clay fractions were made using a Philips Debye camera and a Shamadzu generator with Cu Kα radiation.

The samples of fine clay are all amorphous. The coarse clay (2-0.2μ) of most samples is also amorphous. For the Dunmore sample a faint line at 4.8 Å is present which probably indicates gibbsite. For the Tirau and Ohaupo samples there are very broad halos at 4.4 and 3.3 Å which probably are lines of halloysite or kaolinite. The prolonged exposure needed to obtain these lines produces a large background caused by iron fluorescence and may have obscured any further peaks.

4.4.5 I.R. DATA

Spectra were run using a Shamadzu grating spectrophotometer. The samples were made into mulls with Nujol or hexabutadiene and run between potassium bromide plates.

The samples show the pattern usually associated with amorphous clays - i.e. a few broad featureless peaks indicating no definite structure. The centre of the bands are shown in Table 4.3 and the curves in Fig. 4.1.

Table 4.3. I.R. Peaks for Samples of Waikato Allophanes (cm^{-1})

Ohaupo	3400	1630	1015 (940sh)	460
Dunmore	3375	1630	990	460
Otorohanga				
Tirau	3350	1610	1030	450
Horotiu				
Te Rauamoa				
Taupo	3400	1630	970	460
Kereone	3200	1620	1035 (920sh)	
	3400	1635	1100,1040,970	550

The position of the major metal-oxygen peak varied and using data from chapter 7 an estimate of the silica/alumina ratio can be made.

The values estimated are shown in Table 4.4.

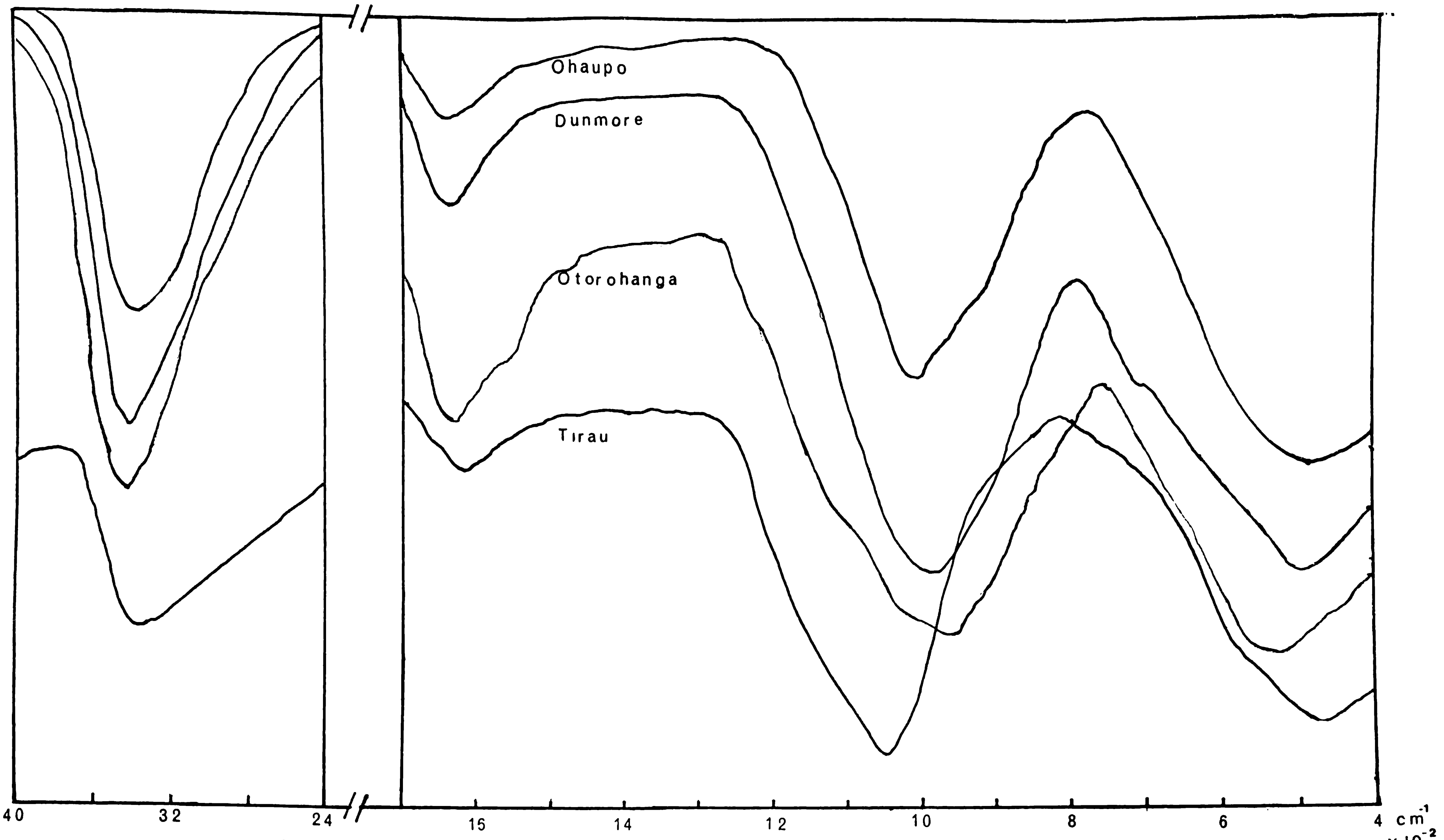


FIG 4·1 IR SPECTRA OF WAIKATO ALLOPHANES

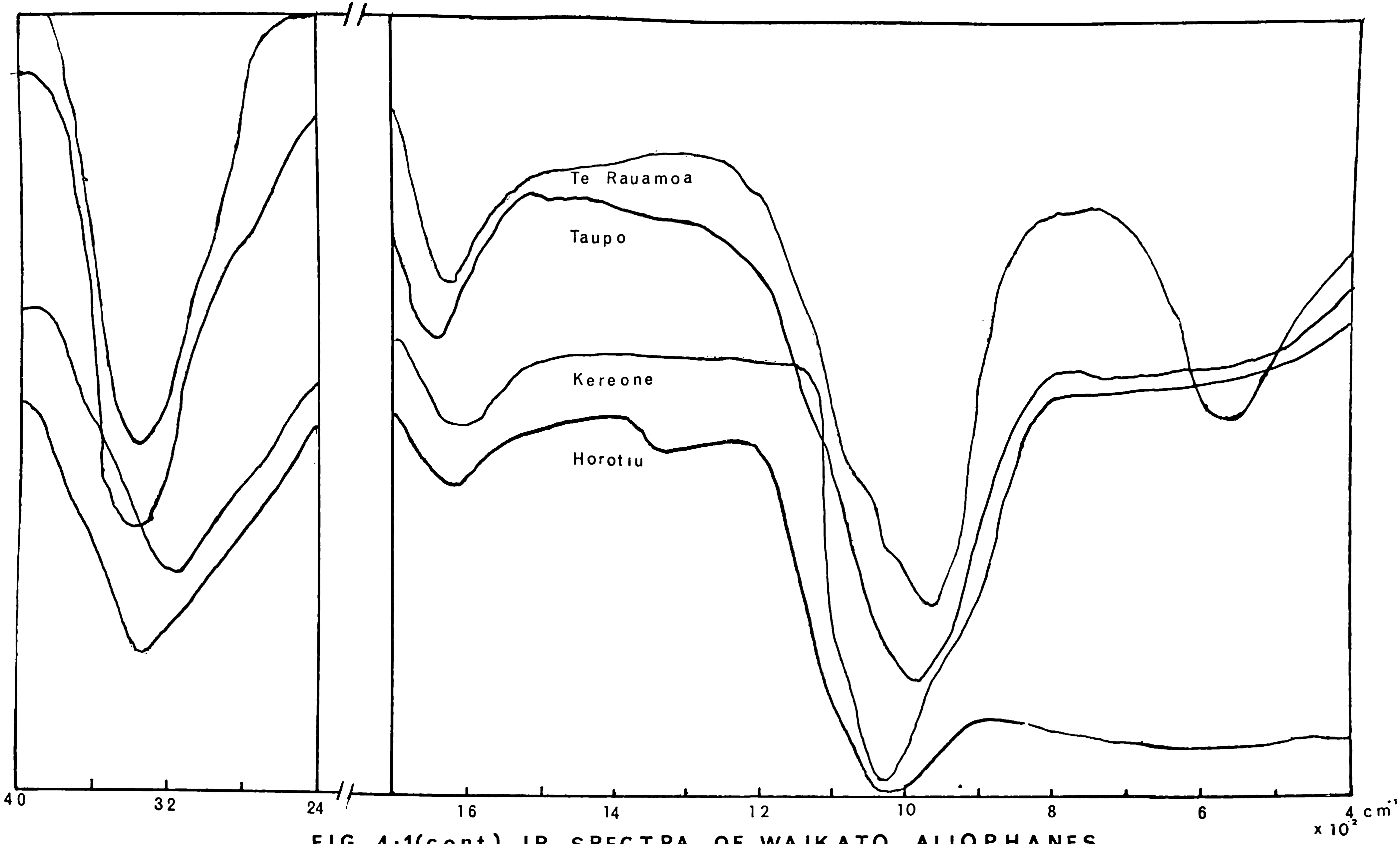


FIG 4·1(cont) IR SPECTRA OF WAIKATO ALLOPHANES

Table 4.4. Estimated and Actual SiO_2/Al_2O_3 Ratios

	SiO_2/Al_2O_3 ratio	
	Estimated	Actual
Dunmore	1.3	1.64
Tirau	2.2	1.85
Halloysite	1.80	2.0
Taupo	1.2	1.45
Kereone	2.6	1.56
Horotiu	1.3	1.36

These ratios suggest that more alumina is present in the Dunmore and Taupo samples than is actually present, and more silica in the Kereone sample. The Kereone spectrum does show a shoulder at 920 cm^{-1} suggesting there may be free alumina present, although in the DTA (see section 4.4.6) there is no splitting of the endothermic peak. There is no evidence for discrete alumina and silica phases suggested by Fieldes[56].

4.4.6 THERMAL STUDIES

The DTA curves were made using a Stone Series LB202 DTA apparatus, running the samples at 10°C/min in air.

The major peaks of the DTA patterns of the fine clays from the Waikato soils are shown in Table 4.5 and the curves in Fig. 4.2.

The TGA curves were made using a Chevenard Type TBM thermobalance at $2\frac{1}{2}$°C/min in air and are shown in Fig. 4.3.

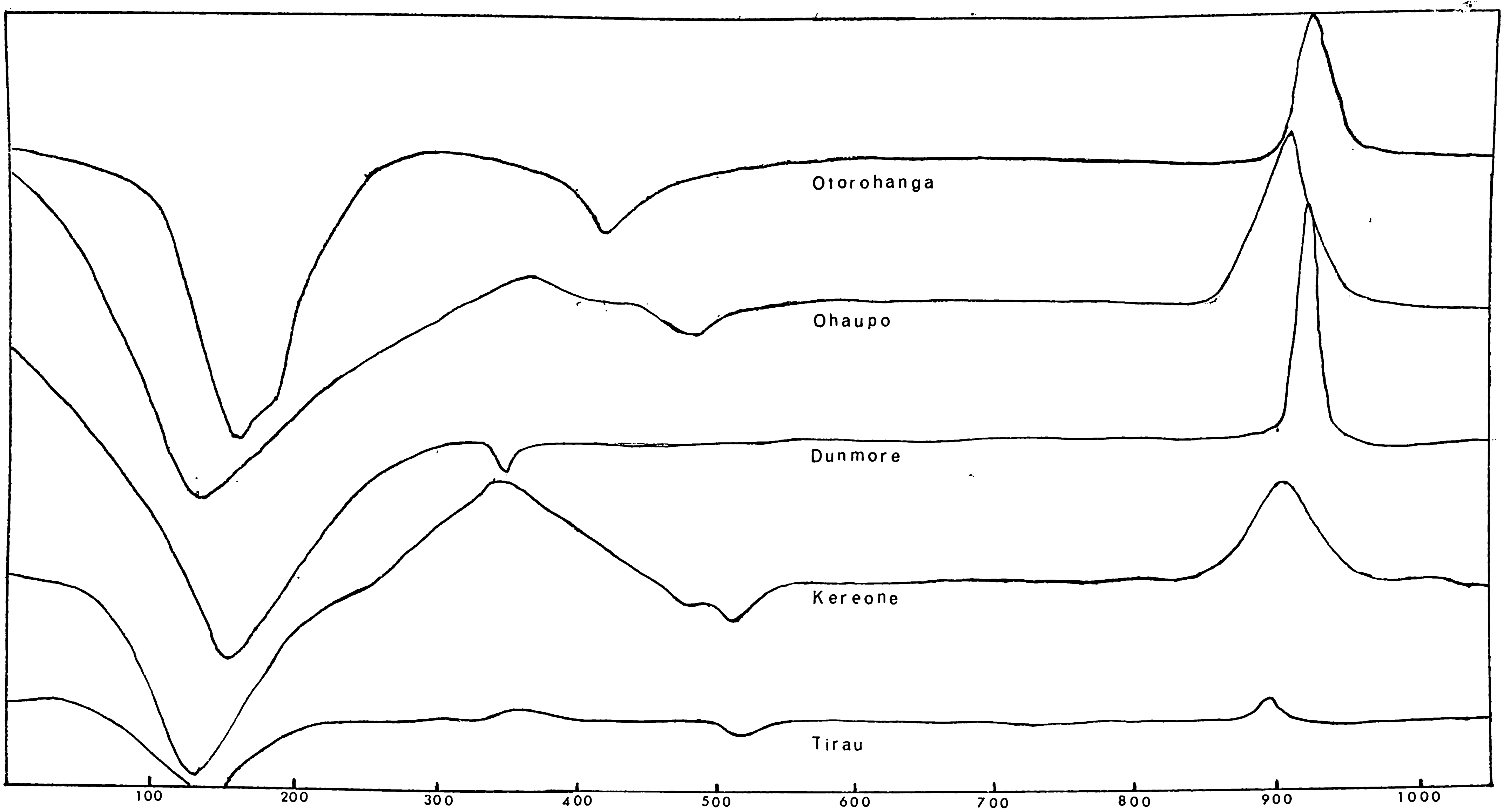


FIG 4·2 DIFFERENTIAL THERMAL ANALYSIS CURVES FOR WAIKATO ALLOPHANES

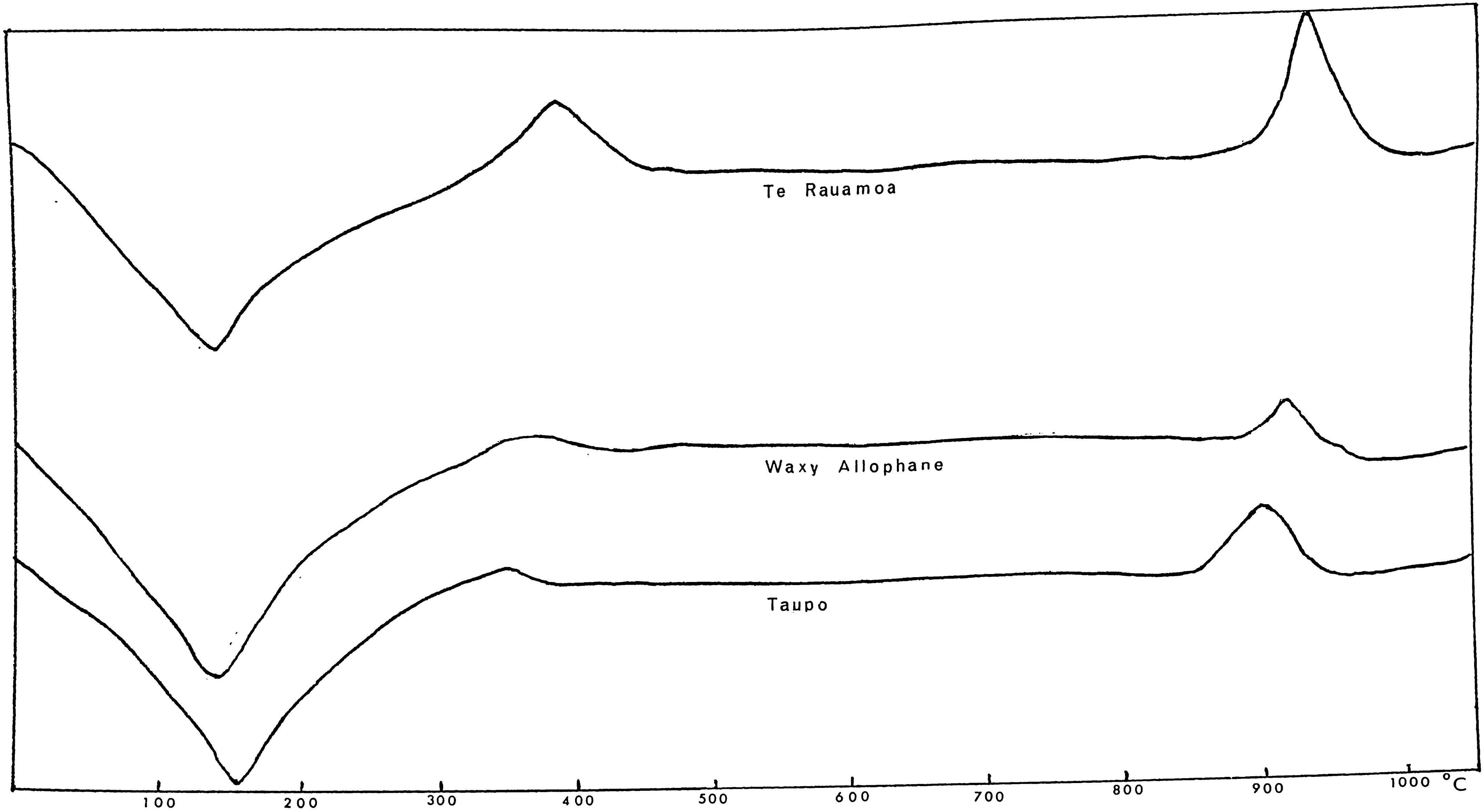


FIG 4·2(cont) DIFFERENTIAL THERMAL ANALYSIS CURVES FOR WAIKATO ALLOPHANES

Table 4.5 DTA Peaks for Waikato Allophanes

	(-)	(-)	(+)	(-)	(+)
Otorohanga	168 (180sh)	-	-	-	920
Ohaupo	130	-	-	490	905
Dunmore	155	-	-	-	920
Kereone	132	-	343	440 460	906
Tirau	139	-	-	508	895
Te Rauamoa	140	-	390	-	920
Horotiu	125	228	300	-	-
Allophane	144	-	-	-	915
Taupo sample	155	-	300	-	900
Tongariro sample	119	-	-	503	950

The TGA curves show that practically all water is lost before 600°C - largely between 50°C and 200°C. There are no large weight losses in the region 300-850°C. The main endothermic peak corresponding to water loss around 150°C is unusually large for clays and is reflected in the fact that some allophane samples contain up to 50% by weight of water. The width of the DTA peak suggests that there is a great degree of disorder since even in the dried samples, the peak extends over some two hundred degrees. The continued loss of water shown in the TGA curves after the initial loss shows that the water is not held in any particular site.

The only sample to show splitting of the endotherm is the Otorohanga sample which also shows a broad endotherm at 410°. Fieldes[56] suggested that splitting of the endotherm could indicate the presence of discrete phases of silica and alumina in young soils but the Otorohanga soil is considered semi-mature[126] and unlikely to contain discrete phases. It is possible that the peak is due to the presence of a small amount of free hydrated alumina and that the peak at 410°C is due to gibbsite although it seems too high.

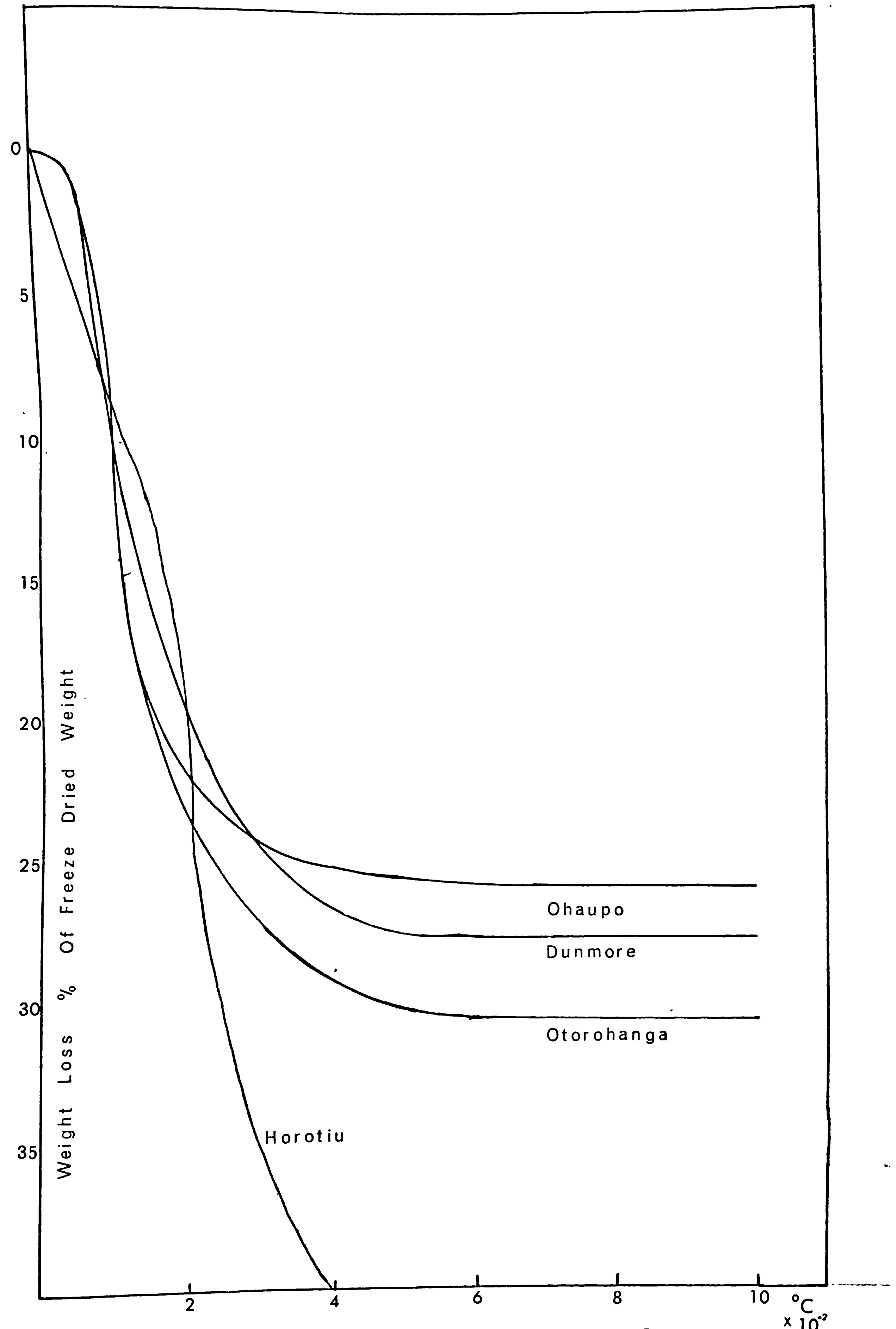


FIG 4·3 TGA CURVES FOR WAIKATO ALLOPHANE

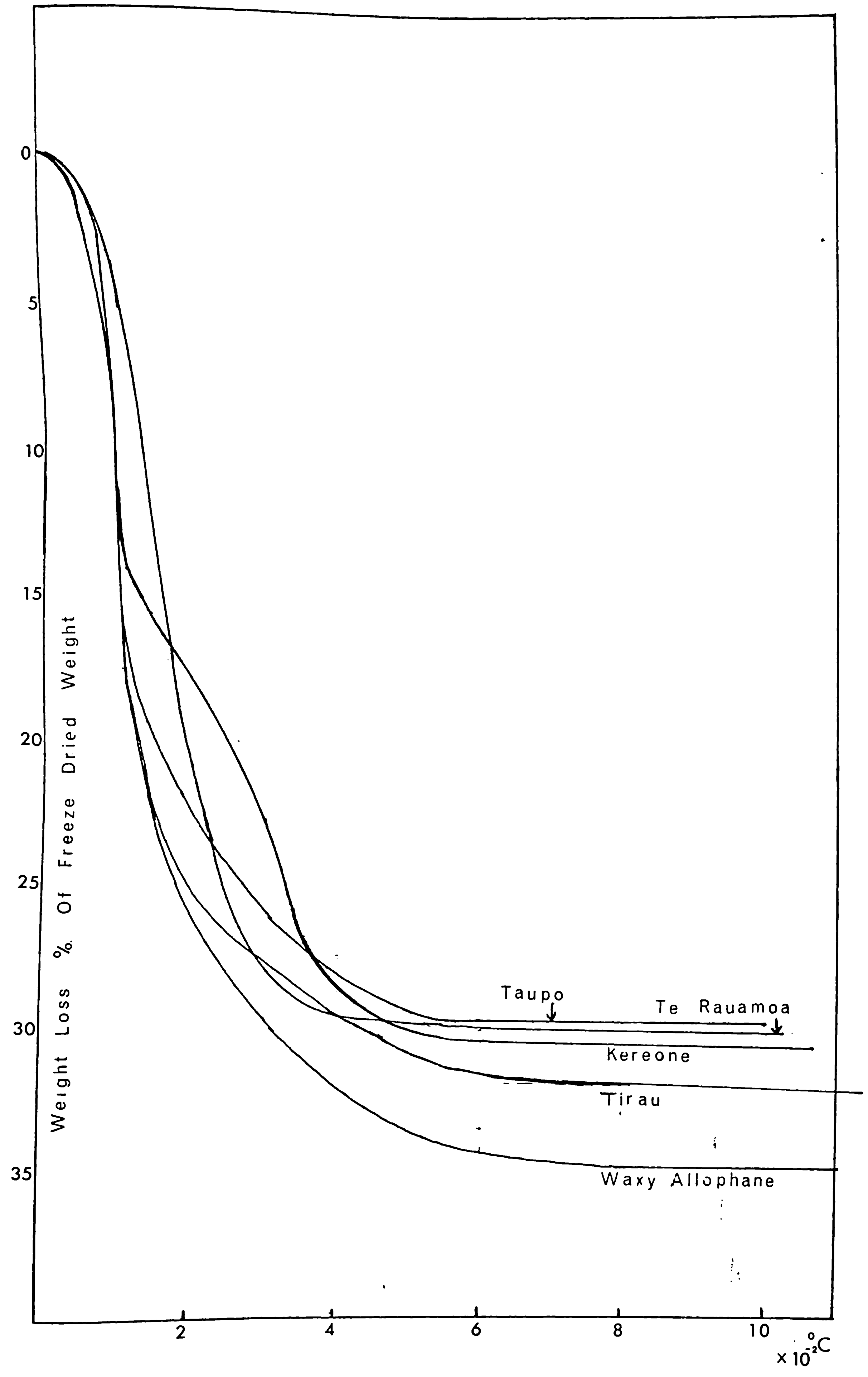


FIG 4·3(cont) TGA CURVES FOR WAIKATO ALLOPHANES

The generalised DTA pattern of allophane used by most authors is that of a straight line between the endotherm around 150°C and the exotherm at 900°C. The curves shown by Fieldes[56] and those shown in Fig. 4.2 usually show small broad peaks in the region 300-800°C. The Ohaupo sample shows a small endotherm at 410°C and the Otorohanga sample a medium endotherm at 410°C. There is another group of samples with peaks about 80°C higher. The Tirau and Otorohanga samples show small peaks at 506°C and Ohaupo and Kereone show large peaks at 480°C and 506°C respectively. These peaks lie higher than expected for gibbsite or bayerite which have been shown by Mackenzie and Berggren[340] to have peaks in the region 300-350°C. Kaolin gives an endotherm at 580° which was not found by Fieldes[56] in the samples he studied. It is also higher than the peaks found for the Waikato samples. The peaks are possibly due to small amounts of poorly crystalline layer silicates forming.

The complete absence of any peaks in the region 350-800°C is shown by the sample from a waxy pan described by Taylor[50], Dunmore, the young Taupo sample and Horotiu. The Dunmore sample is considered one of the oldest in the weathering sequence of those studied[126] so that the peaks in the younger samples are possibly due to impurities.

The Dunmore sample shows a small sharp endotherm at 330°C which may be due to crystalline aluminium hydroxide.

Apart from small exotherms between 300-350°C due to small traces of organic matter the only sample to show a low temperature exotherm is the Te Rauamoa sample which has a medium exotherm at 380°. This sample contains 2.4% FeO and the soil sample was taken from a gleyed horizon just beneath an old buried A horizon. Even though it has been treated with hydrogen peroxide it is probable that some organic material is contributing to the peak although the exothermic rise on the other samples is usually at a lower temperature, approximately 300°C.

In contrast to the main endotherm the exotherm at approximately 920°C is sharp. This peak is due to the transition to mullite. In the young Taupo sample the peak is small but in the Dunmore sample, the oldest studied, the peak is very sharp and intense. Fieldes[56] found young soils gave no indication of an exothermic peak but the Taupo sample in this case does. The only sample which does not show an exotherm is the Horotiu sample which is developed on mixed rhyolite-andesite alluvium and therefore young. The lack of a peak was attributed by Fieldes[56] to discrete hydrous silica and alumina.

The samples remained X-ray amorphous until after the exothermic peak when the mullite pattern was noted.

4.4.7a CATION EXCHANGE

The cation exchange capacity (CEC) of allophanic clays has been shown to differ widely and to be extremely dependent on the concentration of leaching solutions and washing solutions (see next chapter). Aomine and Jackson[131] used a Δ CEC value to estimate the amount of allophane present in soils. The procedure described by these authors was followed but the final CEC measurement was made using the micromethod described by Mackenzie[132]. Iron was not removed before the determination but several values were determined for some dithionite-citrate treated samples.

Method

30-50 mg of clay were weighed into six 12 ml centrifuge tubes, three of which were treated at pH 3.5 in an acetate buffer and three at 10.5 in a carbonate buffer according to the method of Aomine and Jackson[131] and allowed to stand for 24 hours. The next afternoon the samples were washed twice with ammonium acetate solution (pH 7) and allowed to stand overnight in 1M ammonium acetate. The procedure of Mackenzie[132] was then followed. The samples were transferred to a Markham distillation flask, 10 ml of saturated NaOH added and the ammonia distilled into 0.1M boric acid. This was back titrated with 10^{-2}M HCl from a 10ml burette using a mixture of methylred and xylene cyanol FF indicators to detect the end point.

The results are shown in Table 4.6.

Table 4.6 Cation Exchange Values for Waikato Allophanes

	CEC (meq/%)		
	pH 3.5	pH 10.5	Δ CEC
Kereone	32.0	97.3	65.3
Dunmore	51.0	145.8	94.8
deferrated	48.0	150.4	102.4
Otorohanga	29.1	86.4	57.3
Ohaupo	23.7	97.0	73.3
deferrated	31.8	80.7	48.9
Horotiu	24.8	64.5	39.7
Te Rauamoa	58.8	134.3	75.5
deferrated	41.8	130.4	88.6
Tirau	45.0[a]		
deferrated	38.7	77.0	38.3
A horizon	69.2	119.4	125.0
Taupo sample	31.7	74.3	42.6
'Allophane'	28.6	84.8	56.2
Kaolinite	5.93	6.02	-

[a] Value at pH 7 from ref. 126.

The samples show the variation noted by Aomine and Jackson[131] although in many samples it is not as marked. The samples with the lowest Δ CEC are those of Horotiu and Taupo which have a low SiO_2/Al_2O_3 ratio, with an Al_2O_3 percentage of 55.8% somewhat higher than samples such as Tirau which has a percentage of 48.0% and Dunmore with 51%. The low CEC values show there are fewer exchange sites available.

The deferrated samples show both increases and decreases in CEC. The well-developed more mature allophanes, Dunmore and Te Rauamoa, show an increase in Δ CEC probably due to an unblocking of the ion exchange sites with the removal of iron oxide and a small amount of alumina. This also was noted by Kawai[338]. The Tirau and Ohaupo samples however show a decrease in CEC and Δ CEC possibly due to attack of the alumina sites on the surface. Fridland et al[133] showed that amorphous iron oxides could contribute to a large amount of the CEC of soils with kaolinite as the main clay mineral. They showed that amorphous hydrated ferric oxide had a marked CEC unlike the crystalline oxides. It is then possible that the removal of iron oxide from these samples, which tend to show a little more order will remove a large part of the high CEC material.

The A horizon of the Tirau soil shows a high CEC as well as a high Δ CEC (71.00 meq/%) which was the figure quoted as being an average value for the allophanes studied by Aomine and Jackson[131]. The difference is due to the presence of organic material which has a high CEC.

4.4.7b PHOSPHATE RETENTION

Phosphate retention is the rapid removal of phosphate from solution prior to phosphate fixation which is a slow process, and results in the retained phosphate becoming unavailable to plants. The method used was an adaptation of that outlined by Saunders[134].

Reagents

P-retention solution. 4.40 gm of KH_2PO_4 and 16.4 gm anhydrous CH_3COONa were dissolved in water and 12.5 ml glacial acetic acid added. The solution was cooled and made up to 1 l.

Vanomolybdic acid reagent. 0.7 gm ammonium vanadate were dissolved in 120 ml boiling water, cooled and 5 ml nitric acid added and the solution diluted to 250 ml. 12.5 gm of ammonium molybdate were dissolved in water and made up to 250 ml. The vanadate solution was then added to 250 ml of 1 + 2 nitric acid followed by the molybdate solution and thoroughly mixed.

Method

50 mg of clay was weighed into a 12 ml centrifuge tube and 2 ml of the buffered phosphate solution (pH 4.6 and 1 mg P/ml) added. The tube was stoppered and shaken overnight. In the morning 2 ml of distilled water was added, the tube briefly shaken and then centrifuged. 2 ml of solution was withdrawn and run into a 10 ml volumetric flask, 5 ml of the vanomolybdic acid reagent added and the flask made up to the mark with distilled water. The optical density was read at 470 nm with a 0.06 mm slit and the density compared with that of standards.

Instead of the normal % P-retention the results are expressed as mg P retained/gm allophane in Table 4.7.

Table 4.7 Phosphate Retention in Waikato Fine Clays

	mg retained/gm clay
Tirau	27.28
Tirau (deferrated)	20.74
Tirau A horizon	21.60
Kereone	25.90
Ohaupo	27.38
Ohaupo (deferrated)	16.63
Otorohanga	31.8
Dunmore	27.50
Dunmore (deferrated)	23.78
Taupo	34.50
Kaolinite (Std sample) from Lamar Pit, Sth Carolina	4.20

Although these results cannot be compared directly with results obtained by Saunders[134] they can be compared with each other.

It is clear that deferration of allophane leads to a reduction in the P-retention value showing that iron contributes to a large value. The sample with the highest value is the Taupo sample and this contains the highest iron content. As this is the youngest sample it probably has not had time for a large amount of ordering to take place and so has more free amorphous oxides present. The phosphate retention has been attributed to iron and aluminium at soil pH's (~ 6.5) and it would appear that the increase in iron content contributes to the increase in P-retention. The other allophanes are generally older and contain less iron probably due to leaching with humic acids since the A horizons are extensively developed.

4.4.8 SURFACE AREA AND WATER ADSORPTION

All of the allophane samples contain a high proportion of water. Some of this is lost when the sample is heated to 105°C. Most of the water lost is regained by allowing the sample to stand over a saturated potassium nitrate solution.

Shao[129] used a technique which involved the measurement of water adsorption isotherms and from this was able to obtain an estimate of the surface area. He emphasised that this adaption of the method devised by Brunauer et al[135] was only approximate since only limited data was available for the low pressure region.

The simplest form of the BET adsorption equation is for a monolayer of molecules adsorbed on a free surface and is represented by the equation

$$\frac{p/p_o}{W(1-p/p_o)} = \frac{C-1}{W_m C} \times p/p_o + \frac{1}{W_m C}$$

where p/p_o = relative partial pressure

W = weight water adsorbed for 1 gm of sample

W_m (the surface index) = mass of water to cover the surface completely as a monolayer

C (the index of the average net heat of adsorption of the first layer) = $e^{(E_1-E_L)}$ RT

E_1 = heat adsorption per mole of the first layer

E_L = heat of liquifaction per mole

By plotting p/p_o $(W(1-p/p_o))$ against p/p_o a straight line should be obtained with a

Slope = $\frac{C-1}{W_m C}$ and an intercept = $\frac{1}{W_m C}$

And by solving these equations values for W_m and C can be obtained. The surface area S_o can then be calculated

$$S_o = \frac{(\text{No. of } H_2O \text{ molecules}) \times \text{cross section of } H_2O \text{ molecules}}{\text{Wt. sample in gms}}$$

The best value for water cross sectional area appears to be that reported by Livingston[136] of 10.5A^2.

$$S_o = \frac{W_m \times 6.02 \times 10^{22}}{18} \times \frac{10.5}{10^{20}}$$

$$= W_m \times 3.51 \times 10^3 \text{ m}^2/\text{gm}$$

Solving the simultaneous equations

$$m = \frac{C-1}{W_m C} \qquad \text{... (1) where intercept = s}$$

$$s = \frac{1}{W_m C} \qquad \text{... (2)} \qquad \text{slope = m}$$

$$C = \frac{1}{W_m s}$$

$$\therefore \; m = \frac{1/W_m s - 1}{W_m \times 1/W_m s}$$

$$= \frac{1 - W_m s}{W_m s} \times s$$

$$= \frac{1 - W_m s}{W_m}$$

$$W_m m = 1 - W_m s$$

$$\therefore \; W_m = \frac{1}{m+s}$$

The dried samples were weighed into preweighed containers and allowed to equilibrate with water vapour over saturated salt solutions in an incubator at 25°C. The samples were taken out every two days and weighed until constant weight was obtained.

The results are given in Table 4.8.

Table 4.8 Water Uptake and Surface Areas for Allophane

	p/p_o	% Wt uptake	$W(1-p/p_o)$	$\frac{p/p_o}{W(1-p/p_o)}$
Dunmore	0.96	38.00	1.52×10^{-2}	63.2
	0.75	30.70	7.67×10^{-2}	9.77
	0.51	27.5	13.49×10^{-2}	3.78
	0.327	23.1	15.46×10^{-2}	2.10
	0.113	13.6	12.08×10^{-2}	0.988
	0.083	12.9	11.82×10^{-2}	0.666
		$s = 0.25$	$m = 5.92$	
		$W_m = 0.162$ gm		
		$S_o = 569$ m^2/gm		
			$\times10^2$	
Otorohanga	0.96	36.0	1.44	78.4
	0.75	31.0	7.75	9.68
	0.51	22.4	11.1	4.65
	0.327	19.4	13.05	2.50
	0.113	12.7	11.26	1.00
	0.083	7.9	7.24	1.15
		$s = 0.21$	$m = 7$	
		$W_m = 0.139$ gm		
		$S_o = 486$ m^2/gm		
Ohaupo	0.96	26.7	1.06	89.9
	0.75	21.2	5.30	14.2
	0.51	16.5	8.06	6.31
	0.327	13.7	9.22	3.55
	0.113	8.0	7.10	1.59
	0.083	7.3	6.69	1.24
		$s = 0.49$	$m = 7.48$	
		$W_m = 0.1001$		
		$S_o = 352$ m^2/gm		

Kereone	0.96	36.2	1.45	66.3
	0.75	25.2	6.30	11.90
	0.51	17.7	8.67	5.28
	0.327	15.3	10.30	3.18
	0.113	8.90	7.89	1.43
	0.083	8.40	7.70	0.96

$s = 0.47$ $m = 8.14$

$W_m = 0.116$

$S_o = 407\ m^2/gm$

Allophane (waxy pan)	0.96	36.7	1.46	65.4
	0.75	34.0	8.5	8.82
	0.51	30.8	15.09	3.38
	0.327	24.9	16.76	1.95
	0.113	19.6	17.38	0.65
	0.083	13.7	12.56	0.66

$s = -0.01$ $m = 6.02$

$W_m = 0.166$

$S_o = 583\ m^2/gm$

Te Rauamoa	0.96	23.0		104
	0.75	21.3		14.08
	0.51	19.8		5.26
	0.327	18.2		2.67
	0.113	16.0		0.80
	0.083	12.9		0.70

$s = 0.15$ $m = 6.17$

$W_m = 0.158$

$S_o = 555\ m^2/gm$

Te Rauamoa deferrated		19.6		122
		18.6		16.13
		17.0		6.12
		15.7		3.09
		12.5		1.02
		11.6		0.78

$s = 0.05$ $m = 9.30$

$W_m = 0.108$

$S_o = 379\ m^2/gm$

Otorohanga deferrated	0.96	25.6	93
	0.75	18.3	17.4
	0.51	14.1	16.4
	0.327	11.9	4.08
	0.113	6.3	2.02
	0.083	5.3	1.81

$s = 0.95$ $m = 9.18$

$W_m = 0.0996$

$S_o = 351\ m^2/gm$

The values obtained are higher than those described by Gradwell and Birrell[53] who used nitrogen to determine the surface areas and obtained values ranging between 172 and 205 m^2/gm with lesser values for clays containing kaolinite or halloysite. Birrell and Fieldes[86] quoted values for the Tirau clay of 330 m^2/gm and 350 m^2/gm for samples dispersed at pHs 12 and 3.8 respectively but these values were for the whole clay fraction.

Shao[129] obtained a value of 855 m^2/gm but his adsorption figures were higher than those recorded here. At high relative humidities there was considerable adsorption by the glass vials being used and water tended to condense on small dust particles in the empty vials run for blanks. Shao did point out however that the BET equation only holds for the low relative humidities so that this error will not be included in the final figure for surface area.

Orchiston[137] studied surface areas by water uptake and obtained a 16.5% uptake at a relative humidity of 43% somewhat lower than the uptakes in this study and certainly lower than measured by Shao.

The surface area of allophanes has been measured by several other methods; by stearic acid, ethylene glycol monoethyl ether EGME[138], glycerol and cetyl pyridinium bromide CPB[139], triethyl ammonium chloride[140], orthophenanthroline[138]. These all suffer from difficulties although Aomine and Otsuka[138] used EGME and glycerol to obtain values similar to those obtained by water. Kinter and Diamond[140] found no triethylammoniumchloride was adsorbed by allophane and attributed this to the positive charge of the allophane. Greenland and Quirk[139] used CPB but found allophane would not adsorb a monolayer, which they attributed to the fact that much of the surface is in stable pores, inaccessible to a double layer of the long molecule. Later[141] they found CPB was adsorbed at pH 4 and only a small amount at pH 7.8 which they attributed to the positive charge on the allophane.

The surface areas of clays have been divided into two types, external and internal. The external surface is accessible to all species including nitrogen but the internal sites are accessible only to polar molecules. In a study of soil allophanes Aomine and Otsuka[138] found the external surface area of allophane measured by N_2 adsorption averaged about 130 m^2/gm whereas the total surface area measured using water was of the order of 500 m^2/gm. The external area of other clays measured by nitrogen is given in Table 4.9.

Table 4.9 Surface Areas of Clay Minerals

Mineral	S_o (N_2)	S_o(Glycerol)	Ref.
Kaolinite	15.5		142
	35.6	30	140,142
Illite	97.1	62.0	140
Montmorillonite	15.5	80.3	140,142
Halloysite	43.2		142

Wada[143] concluded after studies of deuterium exchange on allophane that all the structural OH groups were located at the surface and this was also suggested by Fripiat[144].

The areas measured in this study lie in the range quoted by Aomine and Otsuka[138]. The highest values are for the Dunmore and Te Rauamoa samples, in both of which deferration caused an increase in Δ CEC. The Taupo sample shows a high surface area despite the age of the sample but it is possible that as the allophane samples age then the surface area decreases as more order is formed in the sample.

The deferrated samples are both lower in surface area than the undeferrated samples. Greenland and Quirk[141] considered the amorphous oxides of iron and aluminium had low surface charge densities and their removal would not affect the surface area, but they were using cetylpyridinium bromide which has been shown to give false readings with allophanes.

4.4.9 ELECTRON MICROGRAPHS

The samples were suspended in water and a drop placed on a collodian film and viewed by electron transmission.

The three micrographs (plates 4·1 - 4) shown, Dunmore, Te Rauamoa and waxy allophane have the characteristic pattern seen in the micrographs published by Fieldes and his coworkers[56,145]. These are very small particles which are often aggregated into clumps with no definite structure. Under high power the particles have a fuzzy edge.

The surface area of the clay is of the order of 500 m^2/gm which means the particles must have a diameter of the order of 60 Å.

A modification of allophane called imogolite has been reported by the Japanese. This was first reported by Yoshinaga and Aomine[103] and differentiated from allophane by its fibrous nature and possession of an X-ray diffraction pattern. Further work by other Japanese workers[104,105,106] have shown that imogolite has a chain like structure with a lattice spacing of approximately 13 Å. Aomine and Miyauchi[105] have further differentiated imogolite into A and B forms with different thermal behaviour and lattice spacings.

Imogolite has not previously been reported in New Zealand although Claridge (reported by Fieldes and Furkert[120]) suggested it could occur in New Zealand soils.

Plate 4.1

Electron Micrograph of Dunmore Allophane

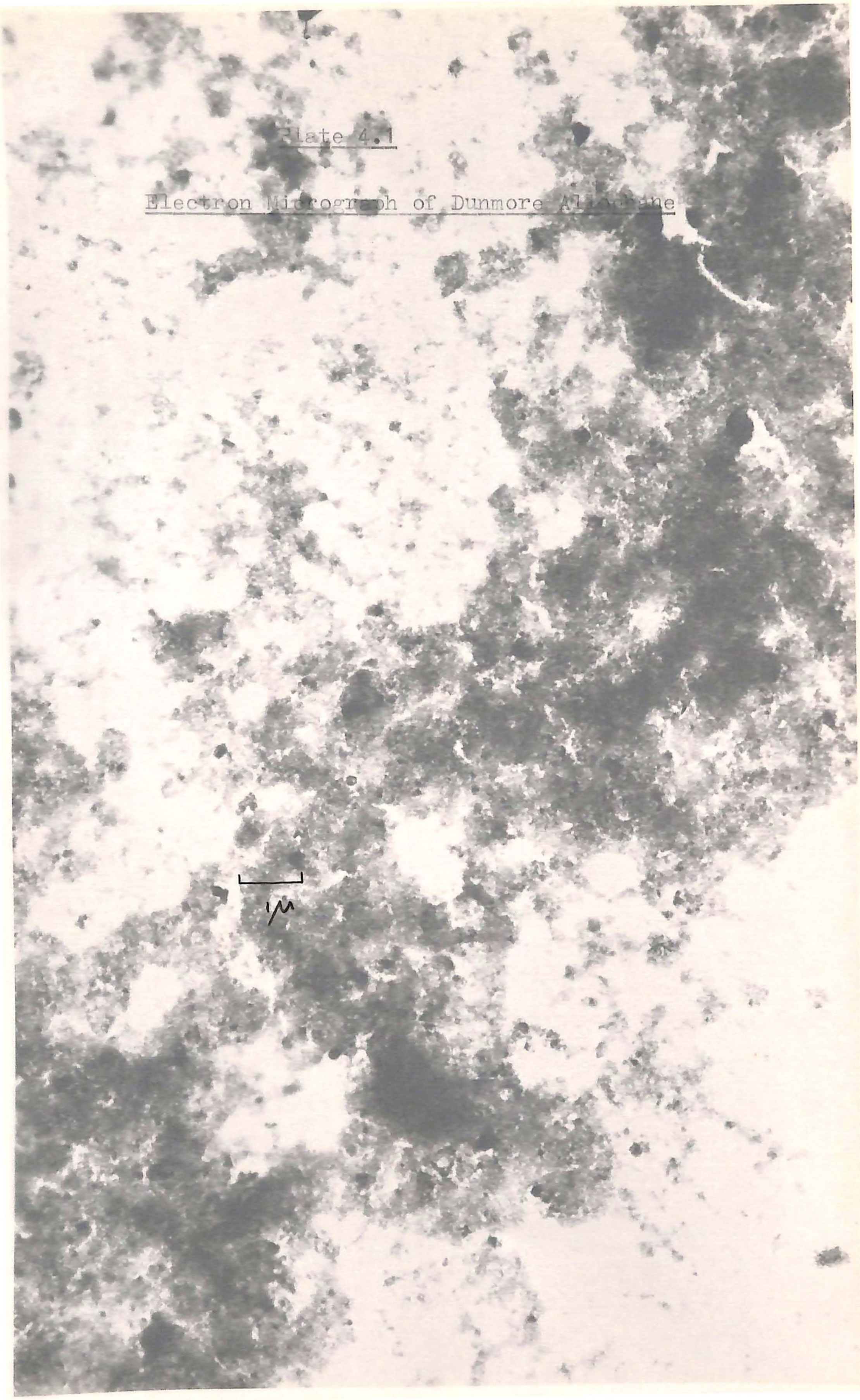
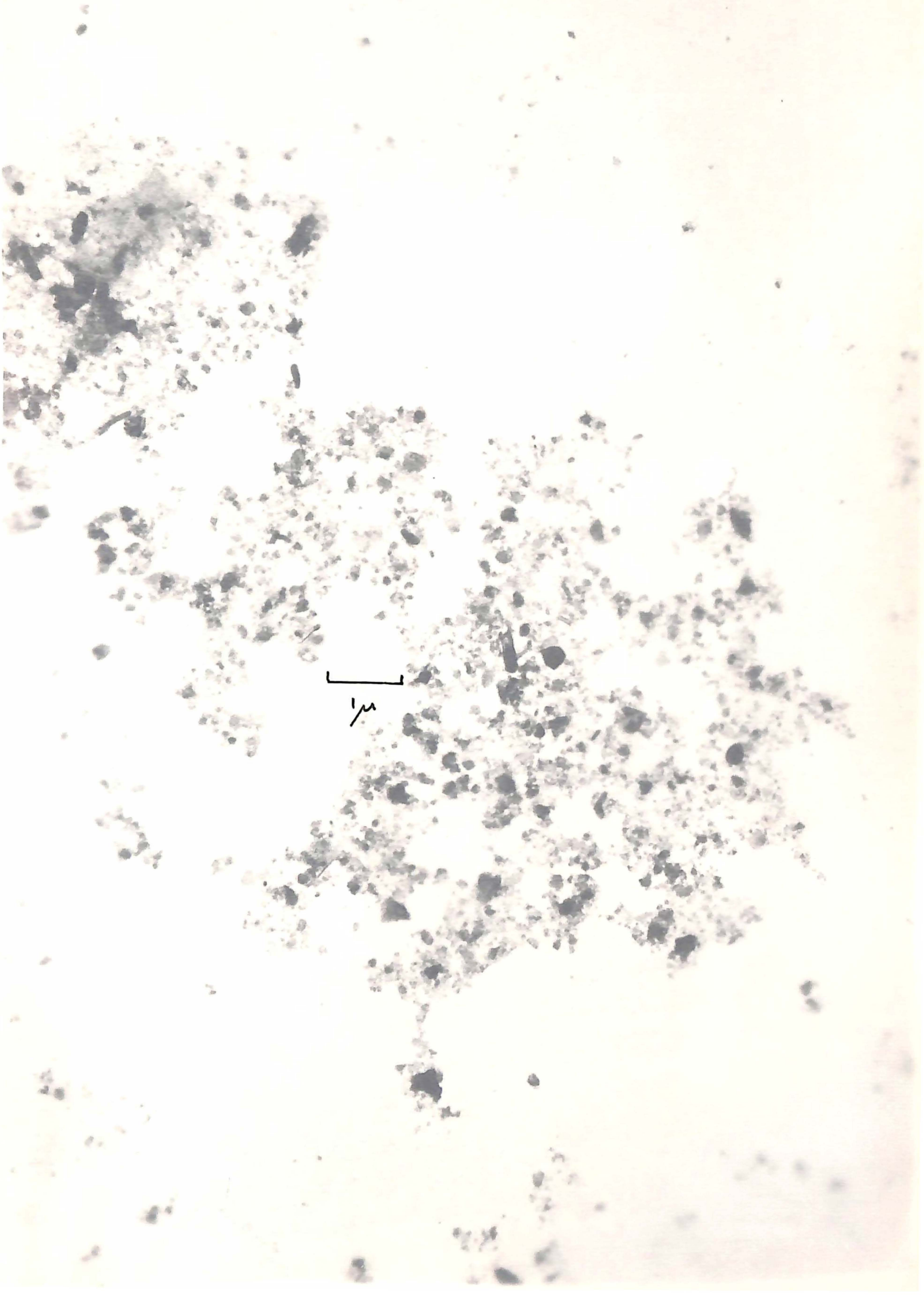


Plate 4.2

Electron Micrograph of Te Rauamoa Allophane



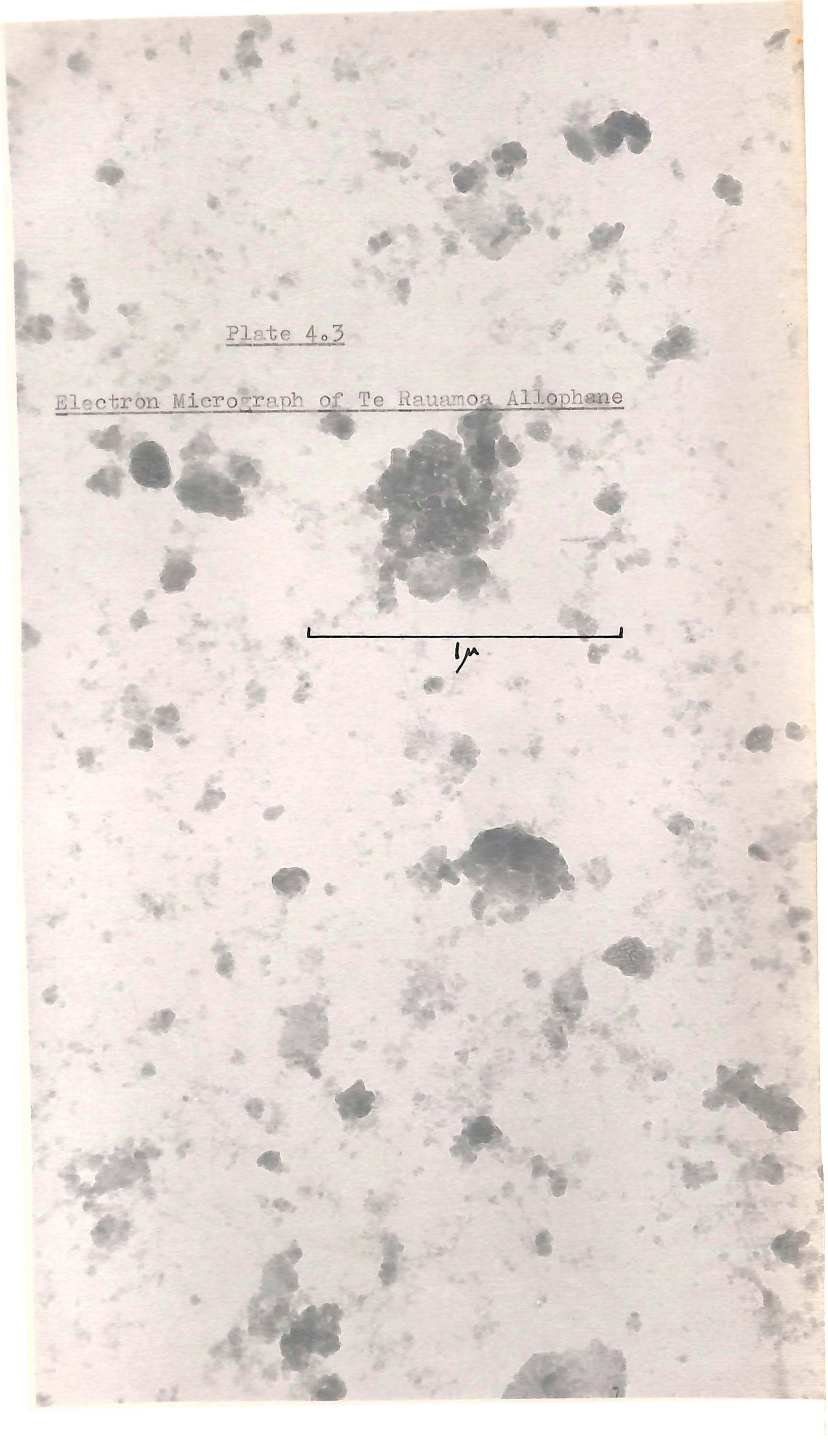


Plate 4.3

Electron Micrograph of Te Rauamoa Allophane

Plate 4.4

Electron Micrograph of Waxy Allophane

7

The sample from the waxy lens of allophane, similar to that described by Taylor[50], contains material that has the same appearance under the electron microscope as imogolite. No special treatment to concentrate imogolite was made and the suspension was very dilute but there are several clumps of the tangled fibres. The X-ray analysis of the 'waxy' allophane sample does not show any peaks in the region suggested for imogolite and the DTA curve also does not indicate imogolite so that it is probably present only in small amounts.

4.5 DISCUSSION

The wide range of chemical composition noted by other workers is present.

There must be some form of order present in the structure of some of the allophanes, because of the presence of small endotherms, usually attributed to layer silicates. They occur at a lower temperature than expected however. The sharpness and intensity of the exothermic peak in some samples also points to order. The formation of halloysite and kaolinite in the weathering scheme proposed by Fieldes[56] means that some orientation of the silica tetrahedra must take place before crystallization can occur. This is partially in line with the sheet-like structure suggested by Udagawa et al[94] but does not imply the whole structure is sheet-like. Lack of crystallinity until after the exothermic peak was noted by Udagawa et al[94] but this contradicts their sheet model. They found that a spinel phase, stable over a small temperature range, was formed preceding the mullite formation. However the allophane they studied was relatively free from impurities as also was the synthetic allophane studied and only in these was the spinel phase formed.

The higher iron concentrations present in the Waikato allophanes must catalyse mullite formation since Udagawa et al[94] quoted temperatures in excess of 1000°C for the transformation to the spinel phase and the samples studied here all show transformations to mullite at temperatures below 950°C.

Fieldes[56] described allophane A and allophane B on the basis that allophane B did not show an exothermic peak. Probably what he was seeing was a degree of ordering in the weathering sequence since there appeared an abrupt change to crystalline materials in the curves shown. The X-ray traces show no evidence for discrete crystalline clay minerals (although if they were present in amounts below 3% then they would be unlikely to be recorded). But if there are small centres where the silica and alumina are aligned, the centres themselves being randomly arranged, then it could be expected that these would appear in the DTA traces although undetected by X-ray or I.R.

Treatment of allophanes with citrate-dithionite has altered the chemical properties although the basic structure remains unchanged since there is no change in the I.R. spectra or DTA curves. This shows that the properties of allophane are largely determined by its surface characteristics and not its basic structure. The surface areas are much higher than those for the clays shown in Table 4.9 and the particles have very small diameters. These partially explain the highly reactive nature of allophane compared to other clay minerals.

4.6 CONCLUSION

The allophanes found in the volcanic ash soils of the Waikato have characteristics of allophanes separated from soils developed on volcanic ash elsewhere in New Zealand and throughout the world.

The DTA evidence suggests there are centres of structure in the older samples of allophane which are not detected by any other means. There is no evidence for discrete silica or alumina so the evidence points to random areas of order. These areas must be of short range but orientation of these areas leads to crystallization of halloysite.

Treatment of allophane with sodium dithionite and citrate in some cases increases the cation exchange capacity. However, the surface area and phosphate retention are decreased and there is no change in DTA or I.R. curves showing that only the surface is affected, the basic structure not being altered.

A micrograph is presented showing the presence of imogolite in New Zealand soils.

CHAPTER 5 COLLOIDAL PROPERTIES OF ALLOPHANE AND ITS CONTRIBUTION TO SOIL STRUCTURE

5.1 INTRODUCTION

Good structure is important for soils to give a high yield of plant growth by allowing the access of air to the roots. Good structure is also important in areas where high stocking rates are common since a soil with poor structure will not recover after trampling by stock.

Allophanic soils have good structure and recover rapidly after trampling. From the previous chapter it can be seen that the properties of allophanic soils can be considered as properties of a soil colloid. It was felt worthwhile to investigate the colloidal properties of allophane in an effort to answer the questions of why allophanic soils have good structure and why they recover rapidly after heavy stock movement.

5.2 VARIABLE CATION EXCHANGE CAPACITY

Birrell and Fieldes[52] noted that the volcanic ash soils containing allophane had a high exchange capacity for NH_4^+, K^+, Na^+ and Ba^{++} and these ions could be easily leached with water.

Birrell[152] noted that the apparent cation exchange capacity (CEC) of allophane varied with differing concentrations of ammonium acetate solutions and was also affected by the alcohol washings in the standard method of CEC determination developed by Metson[333]. He suggested there must be some acid functional groups present which accounted for the strong retention of some cations at high pH, cations which were only released on treatment with dilute acids.

The negative charge in clay minerals arises from several factors (see section 1.4). Schofield[334] distinguished between permanent charge, due to structural substitution and a charge which varied with pH, which he attributed to Si-OH groups. The negative charge due to isomorphous substitution is neutralized by a countercharged ion usually Na^+ or K^+ in natural samples. These countercharged ions can be fixed, such as the K^+ ions in mica, or readily replaceable. This means that the terms 'negative charge' and 'cation exchange capacity' are not synonomous. 'Cation exchange capacity' usually indicates only the part of the total structural negative charge that is measurable by cation exchange using a standard method.

Bolt[146] has shown that in the crystalline 1:1 and 1:2 silicates there is no appreciable cation exchange capacity that is pH dependent and that any such pH dependent charge induced on the clay edges from silanol dissociation ($\text{Si-OH} \rightarrow \text{Si-O}^- + \text{H}^+$) is completely reversed by unbuffered washings.

The great variability in CEC due to pretreatment of the allophane was noted by Aomine and Jackson[131] and used as a basis for estimation of allophane percentage in soil clays. This work was followed by a paper by Volk and Jackson[147] in which the authors attributed the pH dependent charge to hydroxy aluminium species, a suggestion already made by Fieldes and Schofield[148]. This was further amplified by de Villiers and Jackson[149] who suggested the following equation to account for the pH dependence of CEC at the edges of fixed interlayer hydroxy aluminium units

$$- (\tfrac{1}{2}\text{OH})_4\text{Al}(\text{OH}_2)_2{}^+\text{X}^- + \text{nKOH}$$

$$\longrightarrow \quad -(\tfrac{1}{2}\text{OH})_{(4+2n)}\text{Al}(\text{OH}_2)_{(2-n)}^{(1-n)+}\,\text{X}^-_{(1-n)}$$

$$+ \text{nK}^+\text{X}^- + \text{nH}_2\text{O}$$

in which X^- represents the negatively charged silicate lattice with isomorphous substitution and n is generally less than 1. The reaction is a deprotonation of the $-\text{AlOH}_2$ group by KOH and leads to an adsorption of exchangeable cations in this case K^+. This gives rise to the buffering capacity of allophane noted by Fieldes and Schofield[148].

Wada and Ataka[150] have modified a method devised by Schofield[151] for measuring charge to eliminate alcohol washings. They suggested that there were two effects taking place in the ion adsorption on allophane. Firstly, the Coulombic attraction mainly dependent on pH and secondly, salt adsorption which was dependent not on pH but on concentration. This effect has also been noted by Birrell[152].

The cation exchange capacity of kaolin and illite[153] and montmorillonite[154] were found to be largely independent of salt concentrations. This can be interpreted as a measure of the definite electric charge carried by the clay minerals at a given pH and may arise from isomorphous substitution in the crystal lattice, from broken bonds or from the dissociation of H^+ from the hydroxy groups at the crystal edges. The attraction then is largely electrostatic in origin.

Allophane is remarkable in that it possesses both positive and negative charge sites in the low pH region and so will physically adsorb salts depending on concentration. This variable adsorption has been noted by Fieldes and Schofield[148].

5.3 ISOELECTRIC POINT*

In their initial studies Birrell and Fieldes[52] noted that allophanes could be dispersed at two widely spaced pH's. They suggested, on the basis of flocculation data, that two colloid systems with different isoelectric points were present which could mutually coagulate. They suggested the isoelectric point of allophane lay on the acid side of neutral pH. This was in the range suggested by Mattson[155] for isoelectrically prepared aluminosilicates. Japanese workers also recognised that some of the unique properties of allophanic soils were due to the colloidal particles having isoelectric points at pH's less

* For definition see 5.5.

than seven. (Refs. quoted by Aomine and Egashira[156]).

In a later paper Fieldes and Schofield[148] used a method devised by Schofield[151] and measured the electric charge on allophane. From the net charge due to absorbed Na^+ and Cl^- ions from solution, the authors found allophane had a variable negative charge over the pH range pH6-8. The samples were equilibrated with sodium chloride solution, leached with ammonium nitrate and the amount of Na^+ and Cl^- ions in the NH_4NO_3 solution determined, taking into account entrained NaCl solution.

Birrell and Gradwell[154] have devised an equilibrium method to overcome the large correction needed in the estimation of entrained salt solution inherent in Schofield's method and have also eliminated the need for washing which caused changes in the pH of the leaching solutions and any alcohol washings. They gave figures for equal anion and cation uptakes of Tirau allophane which differed by as much as 1.2pH units depending on the anions and cations used.

Iimura[157] used Schofield's method and obtained a pH value of 6 for equal anion and cation uptake. Aomine and Egashira[156] used a method which involved flocculation to estimate the charge on clays and concluded that in the field, for Ando soils at least, the clay was positively charged.

5.4 ION SELECTIVITY

Birrell and Gradwell[154] found that for the same cation the uptake of anions varied. This was studied further by Birrell[158] who showed that the amount of cation adsorbed depended on the solvated size of the cation. For the potassium ion a very pronounced selectivity has been noted by During[159] for New Zealand allophanic soils. In a study of the response to potash topdressing on Horotiu soils, Hogg[160] noted that a deficiency in magnesium could result, due to the pronounced fixation of potassium and subsequent replacement of magnesium which was lost by leaching. Fixation of potassium in aluminosilicates has also been noted by van Reeuwijk and de Villiers[161] and in New Zealand soils, by Saunders and Metson[162]. The fixation noted by Saunders and Metson was preceded by Ca and Mg losses by leaching.

Selectivity of large cations with low hydration energies by other clay minerals has been noted by several workers and a comprehensive review has been given by Sawhney[163]. The cations such as K^+, NH_4^+, Rb^+ and Cs^+ which can produce interlayer dehydration and subsequent layer collapse, are fixed, whereas cations such as Ca^{2+}, Mg^{2+} and Sr^{2+} which have high hydration energies and produce interlayer expansion, are not fixed, and can be replaced by the ions such as K^+.

In using a measurement of ion exchange to obtain a value for isoelectric point of allophane, consideration must be made of the ion selectivity. The discrepancies noted by Birrell[158] have been described above and Birrell and Gradwell[154] have shown that physical adsorption of ammonium ions can lead to an error in CEC values determined for allophane. The strict control of conditions necessary, together with the variability in determination of CEC, led to a search for a more direct method of determining the charge on allophane particles.

5.5 PARTICLE CHARGE

If two phases of different chemical composition are in contact then an electrical potential difference will develop between the two phases. This potential difference is accompanied by a charge separation, one side of the interface positive, the other negative. Two structures are possible if one phase is a solid and the other a solution.

If the solid surface is charged and the electrolyte solution has the opposite charge several possibilities arise.

The first is a model proposed by Helmholtz in 1879 in which the opposite charge is a plane of charge held at a distance δ , this phenomenon constituting the Helmholtz double layer. The potential falls away abruptly from the surface to zero at the plane of fixed charge (Fig. 5.1(a)).

A second possibility involves the proposal by Gauy of a diffuse double layer but developed further by Stern to include a plane of fixed charge at a distance δ and a diffuse layer extending outwards. This plane of charge can be insufficient to balance the surface charge and gives the situation shown in Fig. 5.1(b) or can be greater than the surface charge causing charge reversal as in Fig. 5.1(c). These phenomena give rise to Stern double layers.

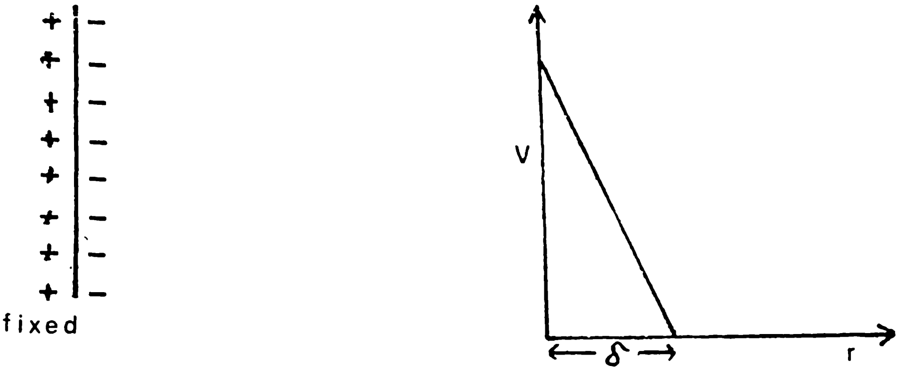
The interaction of surface and solution ions determines the structure of the double layer in any given situation. If negative ions are not adsorbed onto a positive solid surface then the layer will be entirely a diffuse Gouy layer. If there is a slight adsorption at approximately the molecular diameter distance, then there will be a layer of counter ions and a small diffuse Gouy layer.

Finally if there is strong adsorption charge reversal occurs and the Gouy layer is of the same charge as the surface.

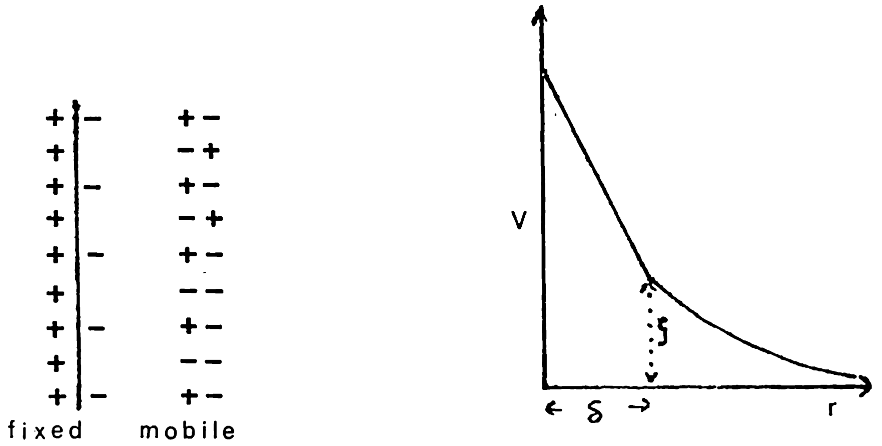
The existence of the double layer gives rise to several electrokinetic effects, all dependent on the fact that part of the double layer is only loosely attached and therefore mobile.

The magnitude of the electrokinetic effect depends on how much of the electric charge remains in the mobile part of the double layer. The potential at the dividing line between the fixed and mobile portions is the zeta potential (ζ - potential or electrokinetic potential). It is commonly assumed that the whole diffuse portion is mobile and so the ζ -potential is the potential value at the distance δ of the fixed charge.

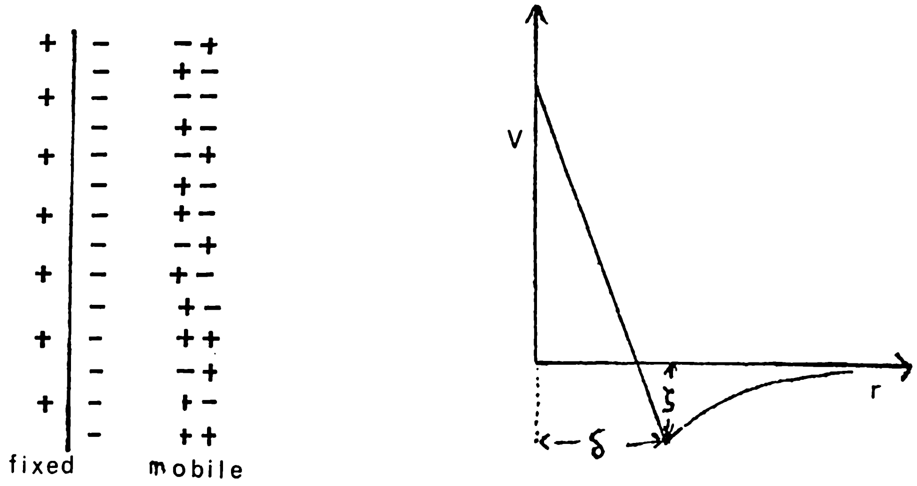
The zeta potential can be expressed mathematically but cannot be



(a) Helmholtz model



(b) Stern model I



(c) Stern model II

FIG 5·1 MODELS FOR ELECTRICAL DOUBLE LAYER AND ZETA POTENTIAL measured directly. By appropriate use of the electrokinetic phenomena which can be measured, the zeta potential can be calculated. The distance over which particles repel each other and the force of the repulsion is related to the zeta potential and is a surface phenomenon.

When a charged particle is placed in an electric field, the negative particles are attracted to the positive electrode and the counter ions to the negative. This movement is due to the surface charge. In colloid chemistry the isoelectric point is the pH when the net surface charge on the colloid is zero and this is determined by zero movement in an electric field.

By measuring the sign of the zeta potential a more direct method of obtaining the sign of surface charge can be made. The methods used by Fieldes and Schofield[148] and Birrell and Gradwell[154] measured the net charge on a particle, not the surface charge, and while for allophane with its high surface area this may be close to the surface charge, it need not necessarily be so. A small adsorption of material such as humic acid, which with its high CEC would have a drastic effect on the measured net charge, need only have a small effect on surface charge.

In order to measure the charge on particles several commercial zeta-meters have been constructed[164]. These consist essentially of two electrodes across which an electric potential is placed and a means by which particle movement can be seen.

In this work a simple zeta-meter was constructed to allow measurement of the sign of the particle charge of allophane colloids.

5.6 EXPERIMENTAL - DETERMINATION OF SIGN OF PARTICLE CHARGE

As clay particles are very small, of the order of 2μ or less, they are barely visible even under the most powerful optical microscope so that when working with fine clay ($< 0.2\mu$) it was only possible to observe aggregations under the optical microscope.

A simple apparatus consisting of a microscope slide and long cover slip separated by two thin strips of platinum foil, which also served as electrodes, was used (see Fig. 5.2). Brass drawing pins set in a small box were used as contacts for the platinum strips which were bent up to make contact. Alligator clips connected to the shaft of the pins were connected to a 300 volt dry battery to provide the potential. The whole apparatus, a simple electrophoresis cell, was mounted on a microscope stage.

A fine clay slurry was placed on a clean microscope slide, the electrodes placed in the suspension with the aid of tweezers and a long cover slip carefully placed on top covering both electrodes. The box with the contacts was carefully positioned with the foil and brass pins touching and the cell left for a minute or so to allow particle movement to settle. The microscope was then focussed and the potential switched on. The direction in which the particles moved was noted. No attempt was made to find how fast the particles moved, only the direction in which they moved.

Clays that had been dispersed at both pH 3.5 and pH 10.5 were used. Freeze-dried clays were dispersed in water and left to equilibrate and the pH measured with a pH meter using a glass electrode and calomel reference electrode. To change the pH small amounts of HCl or NaOH were added and the solution left to equilibrate and the pH measured again.

Samples of deferrated clays were used without drying and several fresh samples (not flocculated or dried) of allophane were also used.

5.7 RESULTS

The initial pH at which the clays were dispersed made no difference to the final pH at which there was no detectable movement. The pH range over which measurement could be measured was limited to 3 on the acid side and 10 on the alkali, since beyond these points, the concentration of electrolytes was such that hydrolysis became too great and the bubbles of

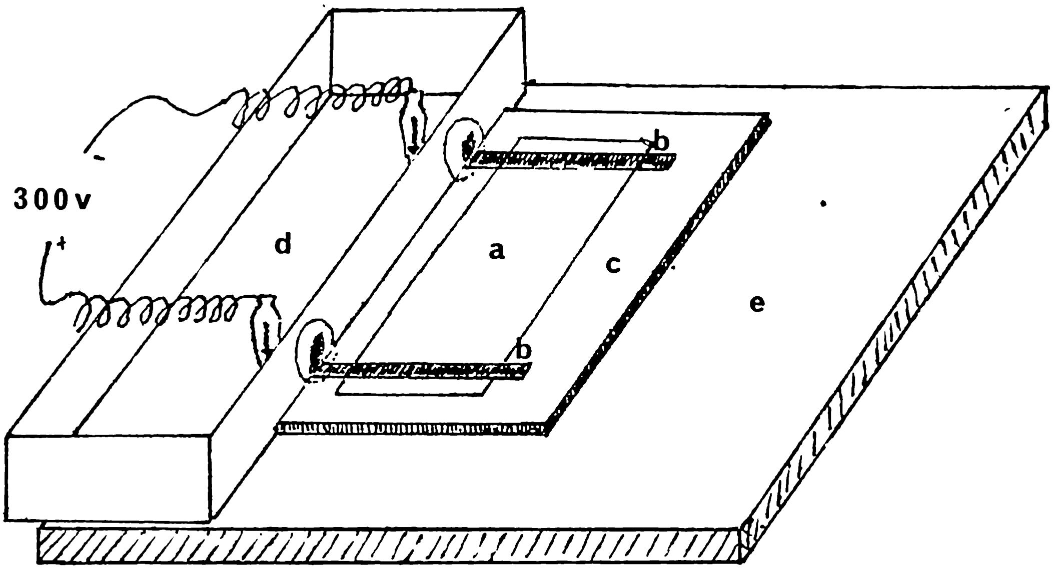


FIG 5·2 SIMPLE ZETA METER

a cover slip
b platinum foil
c microscope slide
d box with contacts
e microscope stage

gas produced swept the particles across the field of vision. Even with the pH in the middle of the range, prolonged viewing was not possible as small bubbles caused by hydrolysis finally coalesced and swept the particles aside as they escaped from under the coverslip.

The isoelectric points are recorded in table 5.1. With fresh suspensions of the clay, the individual particles could not be seen but by using a large resistor in series, the potential was lowered and the current allowed to flow for several minutes. The area around one electrode could be seen to be clear and the area around the opposite electrode denser in colour. This effect was visible to the naked eye.

Table 5.1 Isoelectric Points of Natural Allophane Samples

	Isoelectric Point	SiO_2/Al_2O_3	Fe_2O_3
Tirau	6.0	1.85	4.86
Horotiu	4.6	1.35	0.46
Dunmore	6.0	1.63	4.56
Te Rauamoa	5.6		
Te Rauamoa (deferrated)	< 3		
Kereone	6.4	1.55	4.52
Waxy Pan Allophane	5.8	1.43	3.38
Ohaupo	5.6		
Otorohanga	6.0		
Otorohanga (deferrated)	< 3		
Taupo	4.6	1.45	6.2
Tirau (thioglycolic acid treatment)	4.8		
Tirau (salicilic acid treatment)	4.6		
Tirau (citrate dithionite treatment)	< 3		

Samples of deferrated clays were also tested but the isoelectric point could not be measured since it lay below 3. In the suspension of deferrated clays the individual particles could not be seen but after passing the current for 30 seconds or so, clumps of flocculated particles could be seen under the microscope clustered around and on the positive electrode while the negative electrode remained clean.

The isoelectric points do lie in the range suggested by Birrell and Fieldes[52] and Fieldes and Schofield[148] but tend to be somewhat higher for some samples. Since the isoelectric points of the deferrated samples are so low they could not be measured by this method,it appears possible that the presence of iron oxide plays an important part.

Experiments on Deferrating Allophane

Treatment of allophane with a 1% solution of thioglycollic acid or salicylic acid resulted in most of the iron being removed from the sample. The isoelectric point of the treated samples was lowered. In order to ensure there was no contamination from adsorbed organic anions, the samples were treated with hydrogen peroxide and the isoelectric points taken again. No change was noted.

The isoelectric points of the synthetic aluminosilicates, discussed in Chapter 7 were measured using the same technique described above. These lay one pH unit or more, less than those for the natural allophanes discussed in this chapter.

5.8 DISCUSSION

Allophane appears unique among clays in having a high isoelectric point. Fieldes and Swindale[148] considered that the presence of iron oxide played no part in the variable negative charge found. Wada[101] also considered iron to be insignificant and usually removed amorphous oxides with Na-citrate and dithionite treatment. Work by several authors on allophanes and aluminosilicates in general (see Chapter 7) has confirmed that the variable negative charge is connected with the aluminium in tetrahedral sites. However study of the influence of iron on allophane properties has been neglected since much of the work on allophanes has been with deferrated samples.

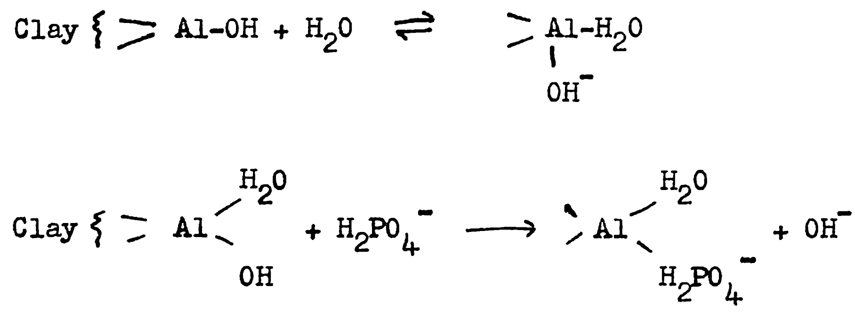
There has been no explanation for the positive charge on allophane which is present despite the low base saturation in the field.

Positive charges in kaolinite

Positive charge sites in kaolinite have been suggested as forming on the edges of crystals by proton transfer[151,156]. Flocculation has been attributed to attraction between the positive edges and the negative cleavage faces[165] and is affected by pH. OH^- ions neutralize the H^+ ions on the crystal edges and so the number of positive charges is decreased allowing dispersion. This is not salt flocculation where physical adsorption of salts gives rise to charge sites.

These positive sites are probably the sites for phosphate adsorption which has been considered by Muljadi et al[166] to be an exchange between phosphate ions and the OH^- counter ions.

e.g.



$$\text{Clay}\,\{ > \text{Al-OH} + H_2O \rightleftharpoons\ > \underset{\substack{|\\ OH^-}}{\text{Al}}\text{-}H_2O$$

$$\text{Clay}\,\{ > \text{Al}\begin{smallmatrix} H_2O \\ OH \end{smallmatrix} + H_2PO_4^- \longrightarrow\ > \text{Al}\begin{smallmatrix} H_2O \\ H_2PO_4^- \end{smallmatrix} + OH^-$$

These are probably also the sites for Cl^- ion adsorption, since Cl^- uptake was much reduced on pretreatment with KH_2PO_4[166]. Using cetyltrimethyl ammonium bromide, Cashen[167] was able to block some of the negative sites on kaolinite but the net charge always remained negative. The work on aluminosilicates in Chapter 7 makes it unlikely the surface charge can be attributed entirely to hydroxy aluminium complexes. The isoelectric points for the pure aluminosilicates lie at least a full pH unit lower than those for allophane but the alumina may possibly contribute in part since the aluminosilicates have higher isoelectric points than samples of the deferrated allophanes.

In allophane there are considerably more positive charge sites than can be accounted for by edge charges since the phosphate uptake is considerably more than that of kaolin or other crystalline clays. The phosphate retention has been attributed by other workers[168-170] to hydrolysed alumina complexes.

Effect of Iron in Clays and Soils

Sumner[171] found that by artificially precipitating ferric oxide onto kaolinite he was able to raise the isoelectric point of the clay-ferric oxide complex to as high as 4. The oxides studied were goethite and lepidocrocite which were shown by Parks[172] to have a lower isoelectric point than that of amorphous hydrous ferric oxide. The kaolinite-iron oxide complexes had considerable variable negative charge which Sumner attributed to ferric oxides. Further work by Follett[246] and Greenland and Oades[337] have shown that iron hydroxide colloid would associate with kaolinite.

In a study on soil stability in iron poor soils, aggregation has been noted by Schahabi and Schwertman[173] when amorphous iron oxide was added. They found only 2% amorphous oxide was sufficient to cause maximum aggregation. Any additional oxide had no effect. Dion[174] has shown that removal of iron oxides greatly facilitates dispersion and it was found that allophanic soils when treated with citrate-dithionite did not need any additional dispersing treatment. Dion[174] has also shown that there is an increase in base exchange probably due, in the light of present studies, to a large increase in the permanent negative charge. Quirk[175] and Schofield and Sampson[165] have further noted that kaolinite with a small amount of iron oxide impurity ($< 2\%$) has proved difficult to disperse and has abnormal chloride adsorption.

The deferrated allophanes lose their positive charge. Watkinson[176] observed that dithionite-citrate treatment often removed aluminium and has suggested that dithionite treatment without sodium citrate might remove less aluminium. This suggestion was followed when only a small amount of aluminium was detected in the dithionite extract but the isoelectric point is still too low to be measured.

The treatment with thioglycolic acid and salicyclic acid did not remove all the iron but nevertheless reduced the isoelectric point.

Thus the iron seems an integral part of soil allophane. The variable amount found in soils led Fieldes and Swindale[148] to consider it unimportant in charge structure but this is probably because only a small proportion is required to have a pronounced effect.

Iron oxide will be electrostatically bonded to the surface of allophane (see Chapters 8 and 9) and so a large percentage will not be essential to give a positive charge to the surface.

5.9 INFLUENCE OF ALLOPHANE ON SOIL STRUCTURE

The agriculturalists' 'ideal' soil is loam that is deep and friable with a good crumb structure, sufficiently strong to stand up against wind, downpours and stock movement, and yet readily worked by implements.

The soil condition necessary for healthy plant growth is due largely to the presence of aggregates of particles in the soil rather than single particles. These aggregates are called crumbs. The formation of crumbs causes pores to be formed. Agriculturalists refer to the best soils as loams and these contain about 35-40% of pore space as opposed to sands which have less than 34% and 'clays' which have more than 40% of pore space. The sands are very easy to work but hold little water reserve whereas the 'clays' are difficult to work and have high water reserves. The loams lie midway between both extremes.

The presence of pores in soil allows a plentiful access of air to plant roots and ensures good respiration of roots and germinating seeds. It also ensures that soil micro-organisms are able to function aerobically.

The pore space also allows free draining provided the soil structure is not broken down in heavy downpours.

Allophanic soils have a much larger percentage of pores than alluvial soils and yet have been shown by Birrell[178] to have high compressive strengths despite the large pore space. Gradwell and Birrell[53] have shown that once breakdown has been achieved then the soils are highly compressible. These authors noted as well, that despite the fine size of the allophane particles when fully dispersed (in one clay 40% of the soil particles lay below 0.2μ average diameter), the permeability of the soils was not low and that allophane had a tendency to form aggregates.

Russell[179] suggested an hypothesis that crumb structure formed at low moisture content was due to cohesion by orientated molecules of water between positive ions and negative clay particles which broke down when the suspension was diluted (see Fig. 5.3). This explains the salt coagulation of clays in which orientation of the water molecules is brought about by ions.

Difficulty in dispersing allophanic soils has been noted by Davies[180] and was attributed by Birrell[178] to the presence of sesquioxides causing flocculation. In the course of this study it has been noted that although the samples of ground rock from the South Island soils (see Chapters 10 and 11) can be dispersed with distilled water, treatment with sodium carbonate is necessary to disperse the allophanic subsoils. These soils are low in organic matter and were treated with boiling 6% H_2O_2 as a precaution so that it is unlikely organic acids are responsible for the aggregation. It is then obvious that for allophanic soils at least, Russell's theory is not the solution.

Emerson[181] suggested a model to display how clay may be arranged within an aggregate. Clay units have been shown to pack together into orientated domains which behave as units. These units or packs themselves

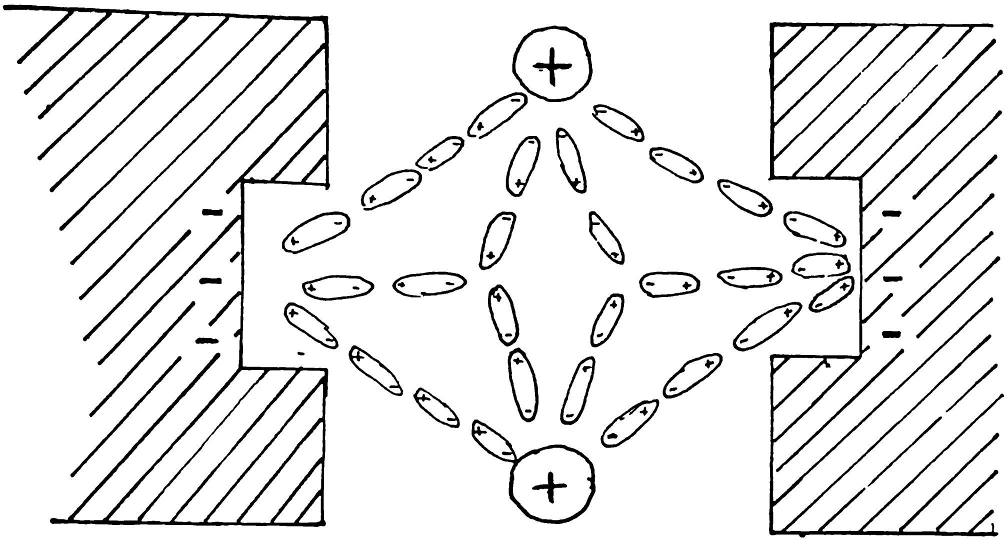


FIG 5·3 CRUMB STRUCTURE SUGGESTED BY RUSSELL[179]

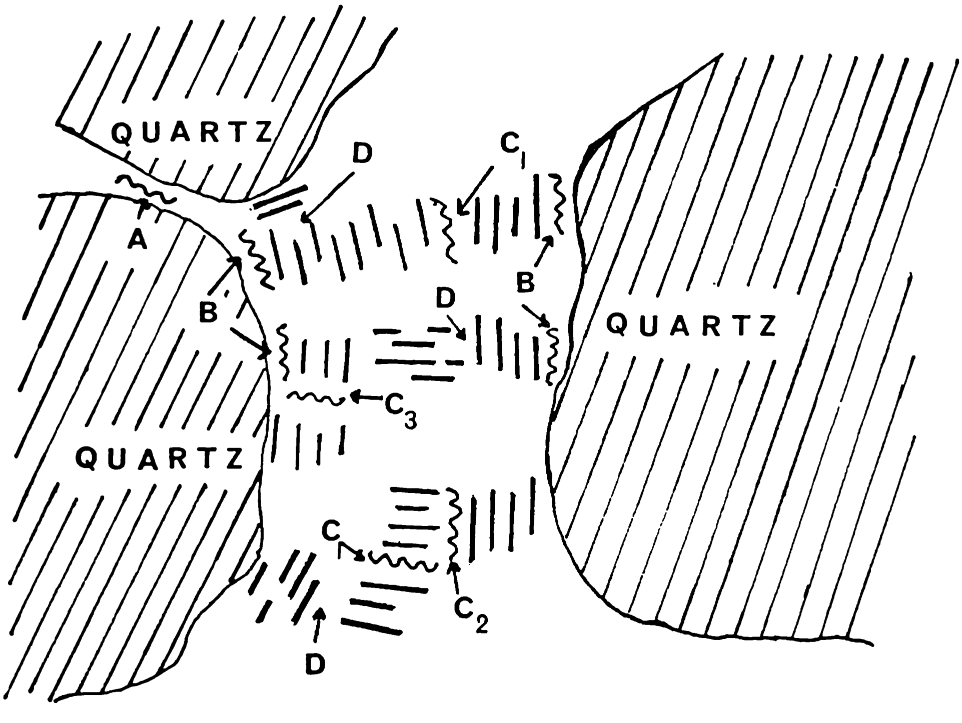


FIG 5·4 POSSIBLE ARRANGEMENTS OF QUARTZ, CLAY DOMAINS AND ORGANIC MATTER IN AN AGGREGATE (EMERSON[181])

Type of bond	A	Quartz–Organic Matter–Quartz
	B	Quartz–Organic Matter–Domain
	C	Domain–Organic Matter -Domain (C_1 face-face C_2 edge-face C_3 edge-edge)
	D	Domain edge–Domain face

can form bonds as shown in Fig. 5.4 with organic matter, or with cementing agents and so form soil crumbs. The cementing agent is often free iron oxide in many soils as well as alumina. The cementing action of ferric oxide is shown in the formation of iron pans. In arid soils, partially soluble salts can function as cementing agents and if these and other cementing agents are deposited progressively then nodules or pans may form.

Allophane, by virtue of its irregular shape, will not form domains as do the layered minerals and so is unlikely to form domain orientated bonds common with the other clays. Allophanic soils have good structure and are easily worked. Being porous they drain readily and are not compacted by heavy stock movement. Because the minerals from which the soils are derived are usually deficient in essential elements, the soils themselves are deficient in elements such as potassium, possibly magnesium[162] and cobalt (lack of this causes bush sickness). Allophane has been shown to be highly phosphate fixing and also fixes molybdate, both in forms unavailable to plants.

Despite the fact that allophanic soils are relatively infertile, most of the intensive dairying in New Zealand is carried out on pastures grown on allophanic soils. This is accomplished by heavy applications of artificial fertilizers. The advent of aerial topdressing of superphosphate has seen a rapid increase in the stock carrying capacities of the Taranaki and Waikato pastures. Despite the high cost of fertilization it is economical for two reasons. The first is a favourable climate and the second and probably more important reason, is the suitability of the pasture for very intensive grazing, something not possible on the zonal yellow-brown earths.

Allophane has a net positive charge at soil pH's and hence coats the quartz, feldspar and glass particles in the soil and acts as a cementing agent. If the model proposed by Russell[179] is considered and the positively charged ions with their orientated water molecules replaced by allophane particles, then a structure results in which the crumb is held together by electrostatic attraction. It will not break down on dilution as does the model proposed by Russell[179].

The range of composition shown by allophanes from different soils is also likely to be reflected in the individual particles of any one soil. Thus two adjacent particles need not necessarily have the same isoelectric point or the same spacial distribution of charge. In topsoils the presence of organic acids adsorbed on allophane particles can cause a lowering of the isoelectric point.

The slight differences in isoelectric point of particles will, under the slight pH cycling in the field caused by changes in rainfall and plant growth, result in the particles carrying opposite charges at some intermediate pH. The particles will then associate and allow the soil structure to recover after tillage or stock trampling. The aggregates of particles formed will be firmly held together by electrostatic forces as well as hydrogen bonds since the aluminosilicates have been shown to have free hydroxyl groups on the surface (see section 7.2). Work by Perrott et al[341] has shown that when a positively charged colloidal particle is adsorbed on a negatively charged surface it will not be desorbed when the charge is reversed. Therefore once the allophane particles are attached they would be expected to remain so until physically disrupted when they might break in another place. This strong bond causes the soil to behave as though there were less clay present than is actually contained and this is one way pedologists 'feel' allophanic soils.

On the edges of the volcanic ash showers the allophane is mixed with layered clay minerals such as montmorillonite, vermiculite and illite. These clays are negatively charged at soil pHs and so form a strong electrostatic bond with the positively charged allophane. The soil derived from this mixture has good structure maintaining the open network characteristic of pure allophanic soils. Because the underlying rock forms part of the parent material and weathers to clay minerals with reserves of potassium and other ions, the natural fertility of these soils are not as low as the pure allophanic soils and these soils lie among the best, agriculturally speaking, in the country.

5.10 INFLUENCE OF ALLOPHANE ON PLANT GROWTH

The high isoelectric point of allophane has a serious effect on plant growth. There are few positively charged colloids in nature and even fewer in the soil, among them being hydrous oxides of aluminium and iron. These represent a small proportion of the soil which, as a whole is still negatively charged. The hydrous oxides act as a cement between the negatively charged clay particles. However in some New Zealand subsoils the amount of allophane present is sufficient so that the soil itself is positively charged at pH's below 6. This pH is higher than that which is maintained by a saturated solution of carbon dioxide in equilibrium with the air so that without any addition of humic acids, which will tend to lower the pH still further, the subsoils will be in an environment which renders the soil positive. This creates a problem for biological systems since they have developed in soils that are negatively charged. The non-occurrence of bacteria in any of the electron micrographs is particularly noticeable. They are present in all samples of the South Island high country soils which are negatively charged at the same pH (see Chapters 10 and 11).

The development of plants on freshly exposed cuttings in volcanic ash soils is very slow and the cuttings stay bare for years or until higher plants have established sufficient footing to produce plant acids to neutralize the charge.

The difficulty in establishing pastures in young volcanic ash soils has been noted[182] and attributed to elemental deficiency of phosphorus but Jackman[183] showed that carbon deficiency limited microbial activity which led to a large amount of necessary minerals remaining in the organic layer. He has also shown that treatment with calcium hydroxide results in a release of plant nutrients by an increase in microbial activity. This is due to a subsequent increase in pH and thus a reversal of charge on the allophane.

The activity of various enzymes has been shown to be reduced by monolayer adsorption on clays[184] but with the very small size of allophane particles monolayer adsorption on the particles seems unlikely. What is more probable is an adsorption of the small positive allophane particles onto the negative organic surface rendering it inaccessible to microbes. Any rise in pH, due to liming will render the allophane negative and so it will no longer be attracted to the organic materials.

The bacterium-clay complex has been reported for montmorillonite[185,186] where the interaction gives the bacteria a protection against desiccation and high temperatures[187]. Both the montmorillonite and bacteria have a net negative charge on their surfaces and the bond is via cations or between positive charges on the edges of the montmorillonite platelets.

The attraction between bacteria and allophane will be much stronger as the allophane surface has a net positive charge and attraction will not be via cations or induced edge charges. Thus the bacteria will be surrounded by a positive charge envelope of allophane particles from which enzymes are unable to penetrate as they are adsorbed. This decrease in bacterial activity will account for the buildup of an organic layer in the A horizon and eventually result in charge reversal in the topsoil. The reversal allows the establishment of good pastures in soil which remain high in organic material.

Liming will have a further effect apart from ensuring that the allophane will become negatively charged. Fieldes and Schofield[148] have shown that allophane has a buffering capacity on raising the pH and attributed this to a return to equilibrium due to the slow reaction of inaccessible tetrahedral aluminium sites.

With the small size of allophane particles the number of inaccessible sites would be expected to be small and the phenomenon can be explained by slow crystallization of amorphous aluminium hydroxide - a phenomenon found in Chapter 7 where crystalline bayerite and subsequently gibbsite are found in the synthetic aluminosilicates prepared under alkaline conditions. The formation of crystalline hydroxides will lower the phosphate fixing potential of the soil so making more phosphate available to plants.

5.11 CONCLUSION

Allophane has a high isoelectric point, in the range 4.6-6.4. This is sufficiently high so that in the field the soils will be positively charged. The positive charge is due to the presence of a small amount of iron electrostatically adsorbed on to the surface of the aluminosilicate core.

The positive charge on the allophane particles contributes to the good structure found in allophane soils as electrostatic bonds can be formed between the allophane particles, sand and silt.

The positive charge inhibits the activity of micro-organisms which are negatively charged. This leads to a build up of humus in the A horizon of the soil, further aiding the soil structure.

CHAPTER 6

POSSIBLE INDUSTRIAL USES FOR ALLOPHANE

6.1 INTRODUCTION

The unique property of high isoelectric point for allophane which gives the allophane positive charge at near neutral pH's as well as high cation and anion exchange capacities suggest that allophane must have uses in industry. The high cation and anion exchange capacities are similar to the synthetic zeolites and so allophane could prove useful as a water purifier.

The cost of obtaining pure allophane would be small as there are abundant deposits in New Zealand. Many of the soils of the Waikato, Rotorua and Taranaki areas contain up to 35% allophane with pockets of up to 80% allophane and there are sites where the allophane layer is 20 ft deep. Montmorillonite has been found in deposits suitable for commercial use and it is possible that allophane with its higher reactivity could also be found to be a useful commercial product. The time available for this work has allowed only one possible use to be investigated.

One of the greatest problems facing New Zealand is the pollution of the environment especially her natural waterways. The growth of weed in lakes and rivers of the North Island especially, has caused great concern and an awareness that waste water emptied into the rivers and lakes must be purified. The discharge into rivers of effluent from slaughter-house floor washings has caused great concern as the waste is largely protein and cannot be filtered out. A process has been developed at the Meat Research Institute in Hamilton where the pH of the wash solution is dropped to 4, coagulating about 70% of the protein which can be scimmed off after air flotation.

Several schemes have been devised to remove the organic material which is readily broken down by microbial activity into plant nutrients. Chemical treatment of waters is commonly used to precipitate unwanted salts and chlorine is added to kill the microbial activity in domestic water. Alum is added to remove phosphates but it has been shown that the phosphate level in New Zealand waters is low.

Lignosulphonic acids have been used as a method of reducing the amount of protein in waste water.

The use of ion exchange resins has been developed at the Physics and Engineering Laboratory, D.S.I.R.[188]. Protein is adsorbed onto the resin and then back washed and concentrated. In the light of recent advances in organo-clay complexes and the effect of clays on the activity of certain enzymes it is suggested that allophane could be used as an absorbant of protein, especially that found in slaughter house effluent since this causes pollution. The proteins, bovine serum albumin, hemoglobin and gelatin are common constituents of the effluent. Their adsorption, together with that of egg albumin, on allophane was studied at various pH's and an estimate of the time of adsorption made.

6.2 LITERATURE REVIEW

6.2.1 Organo-Clay Complexes

The interaction of clays with organic molecules has been known for some time. Demolin and Barbier[189] have shown clays are capable of fixing proteins and humic acids and Mattson[190] showed the cation exchange capacity was reduced by complexing the clay with protein.

Most of the work has involved the adsorption of aliphatic and aromatic amines which behave similarly to inorganic cations[191] and similar cation exchange capacities were obtained. Smith[192] was able to show that a definite chemical equivalent of organic bases existed where saturation was reached and that when saturation was reached or approached, flocculation occurred. The amount of organic ion adsorbed varied with its ability to orientate to the clay mineral surface as well as its size. The organic molecules can orientate themselves between the layers, and several authors[191,193] have shown that several arrangements of the molecules are possible in the interlayer positions. Hendricks[191] showed that the organic cation was held at the surface of the silicate layers and caused expansion of the 001 spacing, the expansion depending on the size of the organic cation.

The range of organo-clay complexes that have been prepared is very wide; complexes being known of organic base-clay, polyalcohol-clay and n-paraffin-clay usually with montmorillonite as the clay, and discussion of these is beyond the scope of this work. Grim[13] has given a comprehensive cover of the different types formed and this study will confine itself to the protein complexes that form.

Ensminger and Geiseking[194] found montmorillonite adsorbed protein and Mortland and Geiseking[195] found later that some enzymes were inactivated when adsorbed on clays. Amino acids, peptides and protein have been intercalated into mica type silicates in much the same way as aliphatic quaternary ammonium salts[193]. Talibudeen[196] found that the energy of adsorption due to electrostatic attraction was sufficient so that some proteins would uncoil. It was possible to prepare a monolayer complex at low protein concentrations with the monolayer being strongly adsorbed on the clay sheet, analogous to adsorption of glycol. On treatment with further protein the 'crinkled' protein would uncoil and a double layer complex would form. For low pH's the protein could be exchanged almost quantitatively but as the pH was raised towards the isoelectric point of the protein, the interaction decreased[305] due to the diminishing number of cationic sites on the protein. Albumins are able to penetrate the layers[197] and so form intercalation compounds but globular proteins appear able to only penetrate a short distance into the lattice. McLaren and Peterson[198] have shown that the protein adsorption follows a Langmuir isotherm but is initially steeper. Mills and Creamer[199] studied the adsorption of casein onto halloysite and obtained adsorption of 4% by weight of clay. Allophane has many more charge sites than halloysite and so would be expected to adsorb more protein.

6.2.2 INTERACTION OF ALLOPHANE WITH ORGANIC MATERIAL

The effect of allophane on enzyme activity was first noticed by the Japanese who found that volcanic ash soils in Japan had very high humus contents irrespective of their climate, situation or vegetation. They were led to believe that organic material would be readily retained in allophanic soils and somehow protected from bacterial attacks. Aomine and Kabayashi[200,201] have shown that the activity of the enzymes protease, α- and β-amylase, and cellulase were reduced by the presence of allophane clay. They found that allophane was able to absorb proteins at both the positive and negative sites whereas the other clays studied - montmorillonite and halloysite largely adsorbed the enzymes as cations. In the later paper[201] they found that protease could be partially released from the clay by treatment with sodium acetate buffer at pH 5.0, the pH used for the experiments to ensure the enzyme was positively charged. Still later[202] they showed that starch could be protected from enzyme action by allophanic clays as well as montmorillonite.

The high stability of organo-allophane complexes has been noted by Fieldes[56] who was not able to remove all organic matter from young soils with hydrogen peroxide. Mattson[190] believed that proteins adsorbed onto clay might be more resistant to microbiological breakdown than unadsorbed proteins. The decay has been studied on montmorillonitic and kaolinitic soils which were found to slightly retard breakdown.

Broadbent et al[203] in a study of pumice soils of New Zealand, suggested that enhanced organic matter stability was somewhat illusionary and subject to the units considered. Taking into account the low bulk density of the soils they have shown that C and N are mineralized at a comparable rate to non-allophanic soils and suggested the quantity of allophane present is insufficient to exert any marked effect. Walker et al[204] have found that although the amount of organic material is higher in allophanic soils, the rate of decomposition of organic material is similar to that in illite soils. However it is clear from their studies that soils with high allophane content have a slower mineralization of carbon and nitrogen. The quantities of organic matter retained is extremely large in old pastures. Jackman[183] has discounted nutrient deficiencies, apart from carbon, as causing a low microbial population and found that liming of the allophanic soil has a small decrease in amount of organic material retained.

A stable clay-organic matter complex is present which forms only slowly and Broadbent et al[203] suggested that aluminium was the cause. They reasoned that the surface of the organic material combines with aluminium to give a poor fit for enzymes which degrade the rotting plant material. Kosaka and Honda[205] have also noted that humus accumulates in the volcanic soils of Japan which they also attributed to the formation of aluminium salts of humic acids. However Schnitzer and Skinner[206] have found that both iron and aluminium form stable amorphous organo-complexes.

The high humic acid content (500 tons humus/hectare) of soils developed on andesite aglomerate tuffs in Czechoslovakia was attributed by Saly and Mihalik[207] to accumulation of humus by allophane. Allophane has been shown to retain large amounts of humified clover extract[350,351] and Inoue and Wada[351] have suggested that iron content has little effect on the adsorption although this work was carried out in alkaline conditions to avoid the positive charge of allophane.

Little work has been carried out to study the extent of uptake of protein and this study measures the uptake of several proteins.

6.4 EXPERIMENTAL

The proteins bovine serum albumin (BSA) bovine hemoglobin, gelatin and egg albumin were selected for study as being a representative set of proteins. The first three are common constituents of slaughterhouse effluent.

Initially a series of runs was carried out in conical flasks into which a weighed amount of allophane was placed. The allophane was suspended in water and dilute hydrochloric acid added dropwise until the required pH was obtained. The suspension was allowed to stir overnight on a magnetic stirrer and the pH checked with a close range indicator paper and a few drops of dilute acid again added if necessary. The use of complex buffers was avoided since in the near neutral range the normal buffers are phosphate buffers which react chemically with allophane. Once the required pH was obtained and the clay had equilibrated with the pH for at least 12 hours the suspension was then centrifuged, the acid solution decanted, and the clay resuspended in 200 ml of distilled water and stirred slowly with a glass encapsulated magnetic follower in a conical flask.

A small volume of concentrated protein at the same pH was added from a pipette, allowed to mix and 10 ml of solution removed, centrifuged and the adsorbance of the solution measured at 210nm using a Hilger and Watts Uvispek spectrophotometer. Measurements were repeated until nearly constant when a final reading was made after 24 or 36 hours. After each reading the clay left in the bottom of the 15 ml centrifuge tube was carefully washed back into the flask with the protein solution and the flask covered with plastic film. A very small quantity of distilled water was needed for a final rinse of the tube but this did not affect the final adsorbance reading by more than 2%.

The concentration of protein in solution was calculated using a calibration curve constructed by measuring the optical density of solutions whose concentrations had been determined by micro Kjeldahl digestion and subsequent ammonia distillation. The concentration of the strong protein solution was also determined by Kjeldahl.

After 24 hours a further addition of protein was made to the suspension and the readings repeated. This process required many additions of concentrated solution in order to reach saturation levels and time stretched to three weeks on one occasion. Decomposition of protein occurred with gelatin and egg albumin after three days and solutions became cloudy even in dilute solutions and with the addition of a few drops of redistilled toluene. To counteract this rapid breakdown which was not noted with hemoglobin or BSA until after a fortnight or so another method was developed.

In this method 50 mg of clay were weighed into several 15 ml centrifuge tubes, and then treated with dilute hydrochloric acid until they were equilibrated at the required pH. The tubes were then centrifuged and the liquid decanted off.

12 ml of various strength protein solutions, adjusted to the same pH as the clays, were then added to each tube with a glass ball for stirring. The tubes were sealed and mounted on a circular frame which rotated at 3 rpm and left for twenty-four hours. The gelatin samples had to be left in a cool room.

After 24 hours the tubes were centrifuged and their optical densities measured and the protein strength calculated.

6.5 RESULTS

(a) Bovine Serum Albumin (BSA)

The adsorption data for BSA on Tirau and Dunmore at pH 6 and 7 is shown in Tables 6.1 and 6.2, curves are in Figs. 6.1 and 6.2. By plotting the amounts taken up against the equilibrium concentrations of protein the curves shown in Figs. 6.3 and 6.4 were obtained. The adsorption follows a Langmuir isotherm until moderate protein concentrations were reached when the curve climbs away from the expected value. This is due to decomposition of the protein. For the last few additions the runs had been in progress for about a fortnight and the solutions appeared slightly cloudy but on centrifuging a clear solution was obtained. There appeared little smell from the protein solution until after the last addition when an offensive smell was noticed. A control solution without allophane started decomposing after three days, when left covered at room temperature, and became cloudy. By the end of the week it began to smell.

Additions 1 and 13 of the Tirau run at pH 6 were taken, the final optical density subtracted from the initial one and the results plotted on semi-log paper (Fig. 6.5). This enables an estimate to be made for the half-time for the reaction. This was also done for the Dunmore sample at additions 2 and 12.

From these it is seen that the half-time for protein adsorption increases as the allophane becomes nearly saturated from one hour to several hours although it is possible that what is being observed for the final samples is a slow breakdown of protein by microbial activity.

Table 6.1 Adsorption of Bovine Serum Albumin on Tirau Allophane

Addtn No.	Time (hrs)	O.D.	Protein conc. (mg/ml)	Uptake (mg/g)	Total Uptake mg/g
(a) pH 6.					
1	0	0.113	0.071		
	1	0.090			
	5	0.075			
	15	0.070			
	24	0.070	0.041	6	6
2	0	0.140			
	1	0.136			
	2	0.120			
	5	0.107			
	24	0.098	0.061	5.6	11.6
3	0	0.152			
	15	0.132			
	24	0.130	0.082	4.4	16.0
4	0	0.180	0.18		
	0.5	0.180			
	1	0.170			
	2	0.165			
	5	0.164			
	24	0.160	0.14	2.8	18.8
5	0	0.223	0.25		
	1	0.200			
	5	0.193			
	24	0.190	0.20	10	28.8
6	0	0.279	0.31		
	2	0.253			
	5	0.253			
	15	0.242			
	24	0.237	0.26	10	38.8
7	0	0.330	0.37		
	2	0.325			
	24	0.305	0.34	6	45
8	0	0.520	0.58		
	1	0.514			
	2	0.514			
	24	0.483	0.54	8	53

Table 6.1 (cont.)

Addtn No.	Time (hrs)	O.D.	Protein conc. (mg/ml)	Uptake (mg/g)	Total Uptake mg/g
9	0	0.562	0.63		
	1	0.563			
	2	0.555			
	5	0.550			
	24	0.528	0.59	8	61
10	0	0.613	0.68		
	1	0.613			
	24	0.600	0.67	2	63
11	0	0.958	1.08		
	5	0.942			
	15	0.908			
	36	0.899	1.02	8	71
12	0	1.181	1.49		
	5	1.154			
	15	1.125			
	36	1.080	1.31	22	93
13	0	1.483	2.10		
	2	1.463			
	10	1.378			
	15	1.342			
	36	1.304	1.74	72	165
(b) pH 7					
1	0	0.159			
	2	0.086			
	5	0.053			
	15	0.039			
	24	0.036	0.017	14.4	14.4
2	0	0.078			
	1	0.061			
	5	0.045			
	15	0.047			
	24	0.045	0.025	3.4	17.8
3	0	0.080			
	5	0.058			
	24	0.054	0.031	2.2	20.0
4	0	0.106			
	2	0.099			
	5	0.093			
	24	0.088	0.054	1.4	21.4

Table 6.1 (cont.)

Addtn No.	Time (hrs)	O.D.	Protein conc. (mg/ml)	Uptake (mg)	Total Uptake (mg/g)
5	0	0.115			
	1	0.112			
	24	0.093	0.057	1.8	23.2
6	0	0.141			
	2	0.123			
	5	0.116			
	24	0.105	0.065	3.8	27.0
7	0	0.156			
	2	0.148			
	5	0.140			
	24	0.125	0.079	3.0	30.0
8	0	0.175			
	2	0.165			
	5	0.157			
	24	0.149	0.095	2.4	32.4
9	0	0.253			
	1	0.244			
	5	0.234			
	24	0.227	0.26	2.2	34.6
10	0	0.330			
	1	0.325			
	5	0.315			
	24	0.310	0.36	1.6	36.2
11	0	0.520	0.58		
	5	0.492			
	24	0.484	0.54	8	44.2
12	0	0.731	0.82		
	5	0.714			
	13	0.694			
	36	0.690	0.78	8.0	52.2
13	0	0.921	1.05		
	1	0.912			
	5	0.907			
	10	0.861			
	36	0.839	0.94	22	74.2
14	0	1.428	2.00		
	1	1.418			
	10	1.316			
	36	1.305	1.74	52	126
15	0	2.084	3.41		
	36	1.615	2.39	100	226

Table 6.2 Adsorption of Bovine Serum Albumin on Dunmore Allophane

Addtn No.	Time (hrs)	O.D.	Protein conc. (mg/ml)	Protein Uptake mg/g
(a) pH 6				
1	0	0.028		
	0.5	0.025		
	1	0.020		
	5	0.020		
	24	0.019	0.006	0.66
2	0	0.048		
	1	0.046		
	4	0.028		
	5	0.039		
	15	0.030		
	24	0.029	0.012	2.06
3	0.2	0.057		
	0.75	0.054		
	10	0.047		
	24	0.038	0.021	3.46
4	0.2	0.065		
	1.25	0.064		
	1.75	0.057		
	3	0.055		
	5	0.043		
	20	0.050		
	36	0.048		
	48	0.043	0.026	5.26
5	0.25	0.105		
	1	0.099		
	2	0.099		
	3	0.097		
	5	0.096		
	9	0.095		
	25	0.093	0.049	7.06
6	0.5	0.160		
	1	0.144		
	4	0.133		
	24	0.131	0.083	9.66
7	0.2	0.189		
	1	0.176		
	4	0.163		
	24	0.161	0.103	13.86

Table 6.2 cont.

Addtn No.	Time (hrs)	O.D.	Protein conc. (mg/ml)	Total Uptake mg/g
8	0.2	0.219		
	2	0.212		
	4	0.204		
	10	0.199		
	24	0.187	0.122	15.86
9	0	0.245	0.34	
	2	0.241		
	10	0.233		
	15	0.226		
	24	0.224		
	36	0.224	0.250	33.9
10	0	0.282	0.365	
	10	0.272		
	24	0.247	0.280	50.9
11	0	0.296	0.370	
	8	0.286		
	15	0.279		
	24	0.263	0.30	64.86
12	0	0.514	0.58	
	2	0.509		
	10	0.504		
	15	0.486		
	36	0.472	0.53	74.86
13	0	0.972	1.14	
	5	0.964		
	15	0.958		
	36	0.932	1.07	88.9
14	0	1.437	2.02	
	1	1.432		
	5	1.418		
	15	1.409		
	36	1.362	1.84	124
15	0	1.895	2.84	
	8	1.755		
	36	1.743	2.76	160

Table 5.2 (cont.)

Addtn No.	Time (hrs)	O.D.	Protein conc. (mg/ml)	Total Uptake mg/g
(b) pH 7				
1	0	0.020		
	1	0.018		
	5	0.017		
	24	0.015	0.005	0.40
2	0	0.044		
	1	0.037		
	2	0.037		
	6	0.036		
	24	0.024	0.011	2.00
3	0	0.053		
	1	0.056		
	2	0.053		
	10	0.042		
	24	0.040	0.021	2.40
4	0	0.070		
	4	0.059		
	5	0.058		
	15	0.048		
	24	0.047	0.026	4.40
5	0	0.075		
	5	0.069		
	15	0.067		
	24	0.065	0.038	5.00
6	0	0.123		
	2	0.111		
	4	0.091		
	5	0.104		
	10	0.102		
	15	0.099		
	24	0.096	0.059	7.6
7	0.2	0.155		
	1	0.149		
	15	0.117		
	24	0.116	0.073	11.8
8	0	0.175		
	1	0.169		
	2	0.166		
	5	0.166		
	24	0.151	0.097	13.8

Table 6.2(cont.)

Addtn No.	Time (hrs)	O.D.	Protein conc. (mg/ml)	Total Uptake mg/g
9	0	0.206		
	1	0.203		
	5	0.198		
	10	0.197		
	24	0.191	0.200	15.6
10	0	0.246	0.280	
	2	0.213		
	24	0.195	0.22	27.6
11	0.2	0.253	0.28	
	1	0.250		
	2	0.248		
	10	0.233		
	24	0.223	0.25	33.6
12	0	0.270	0.30	
	10	0.245		
	24	0.240	0.28	37.6
13	0.2	0.509	0.58	
	1	0.496		
	2	0.494		
	10	0.470		
	24	0.468	0.53	47.6
14	0	0.974	1.14	
	5	0.966	1.11	
	15	0.958		
	36	0.916	1.05	69.6
15	0	1.412	1.96	
	1	1.393		
	5	1.333		
	15	1.321		
	36	1.280	1.70	122
16	0	1.810	2.90	
	36	1.725	2.70	162

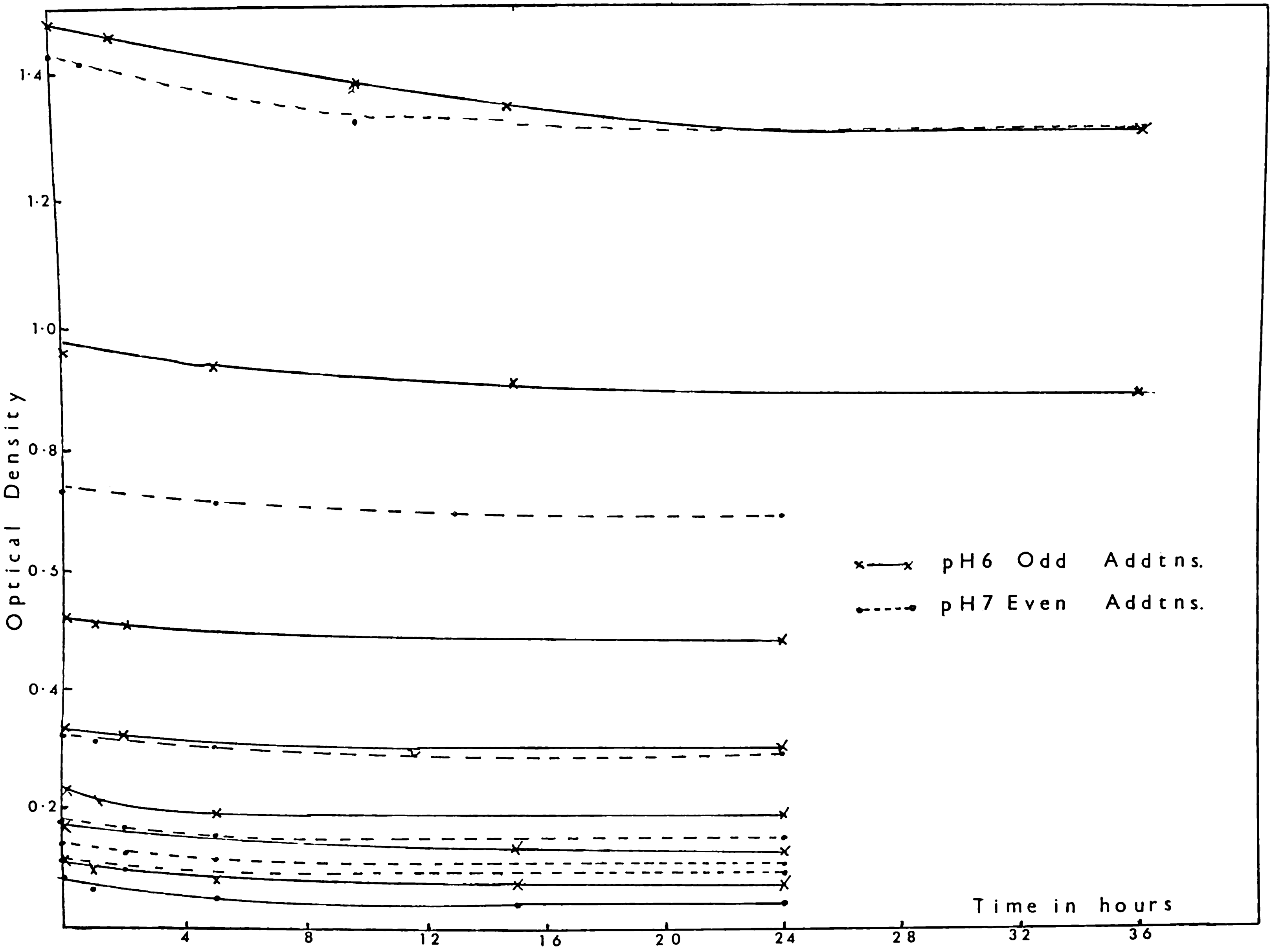


FIG 6·1 ADSORPTION OF BSA WITH TIME ON TIRAU ALLOPHANE

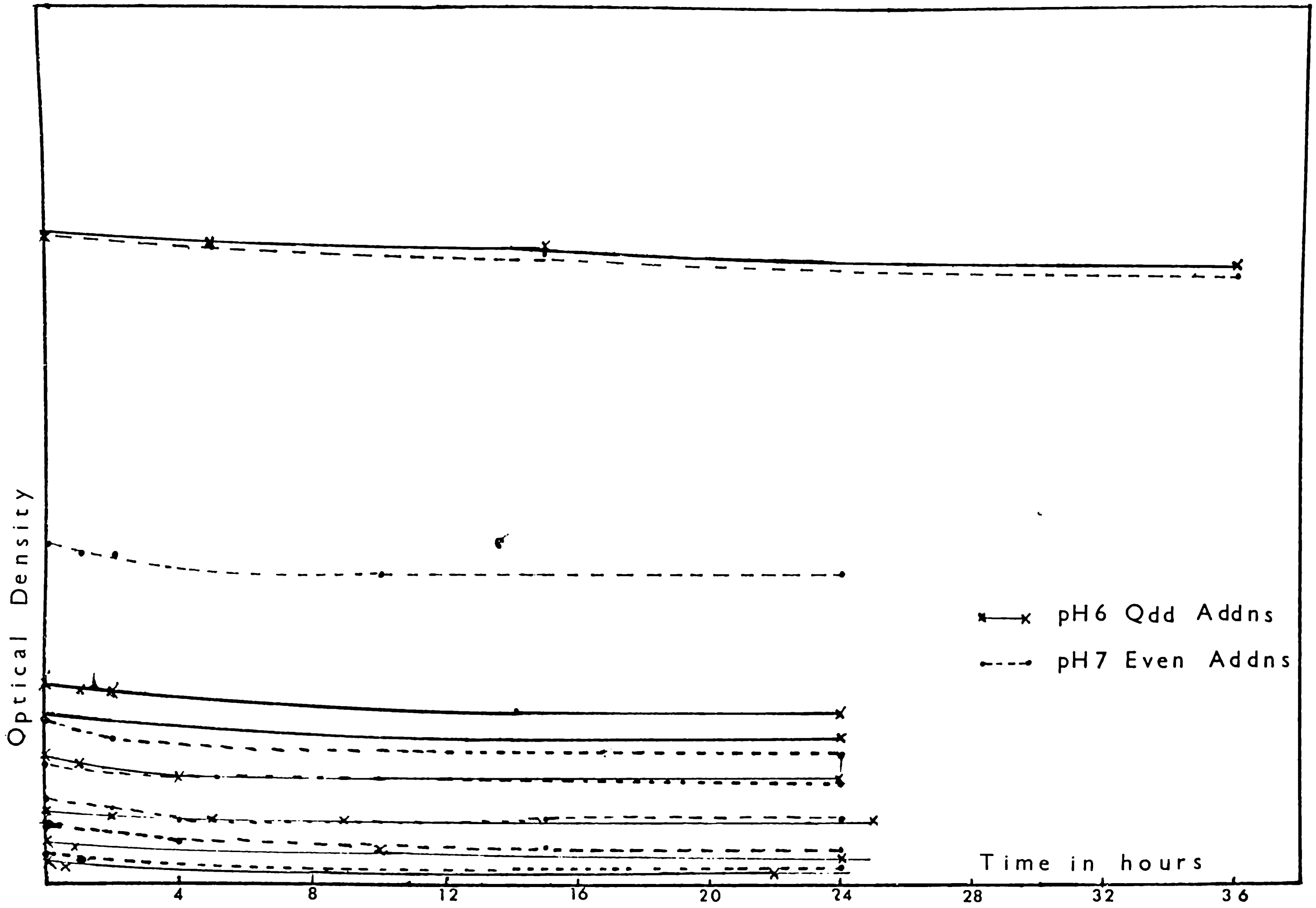


FIG 6·2 ADSORPTION OF BSA WITH TIME ON DUNMORE ALLOPHANE

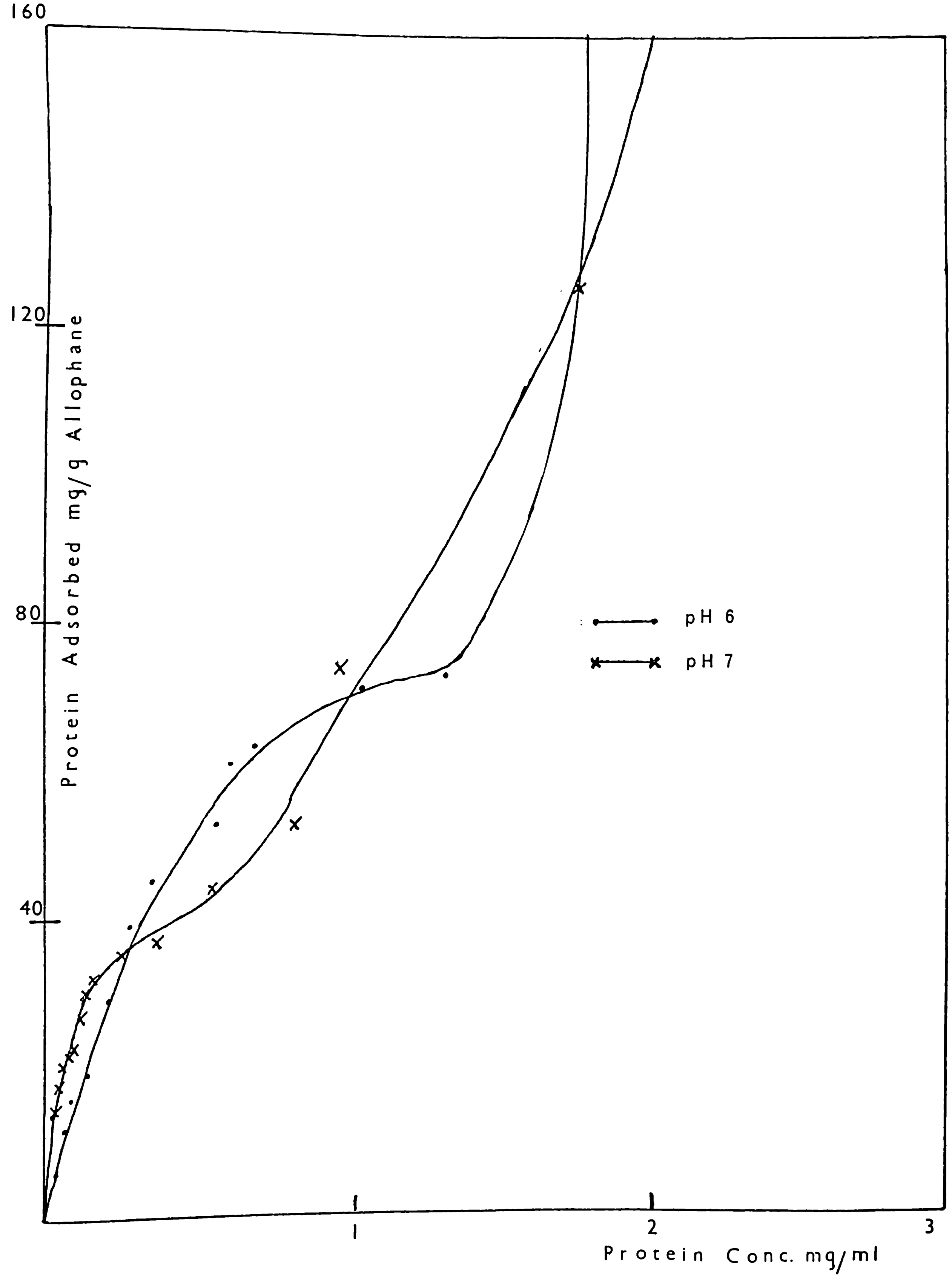


FIG 6·3 ADSORPTION OF BSA ON TIRAU ALLOPHANE

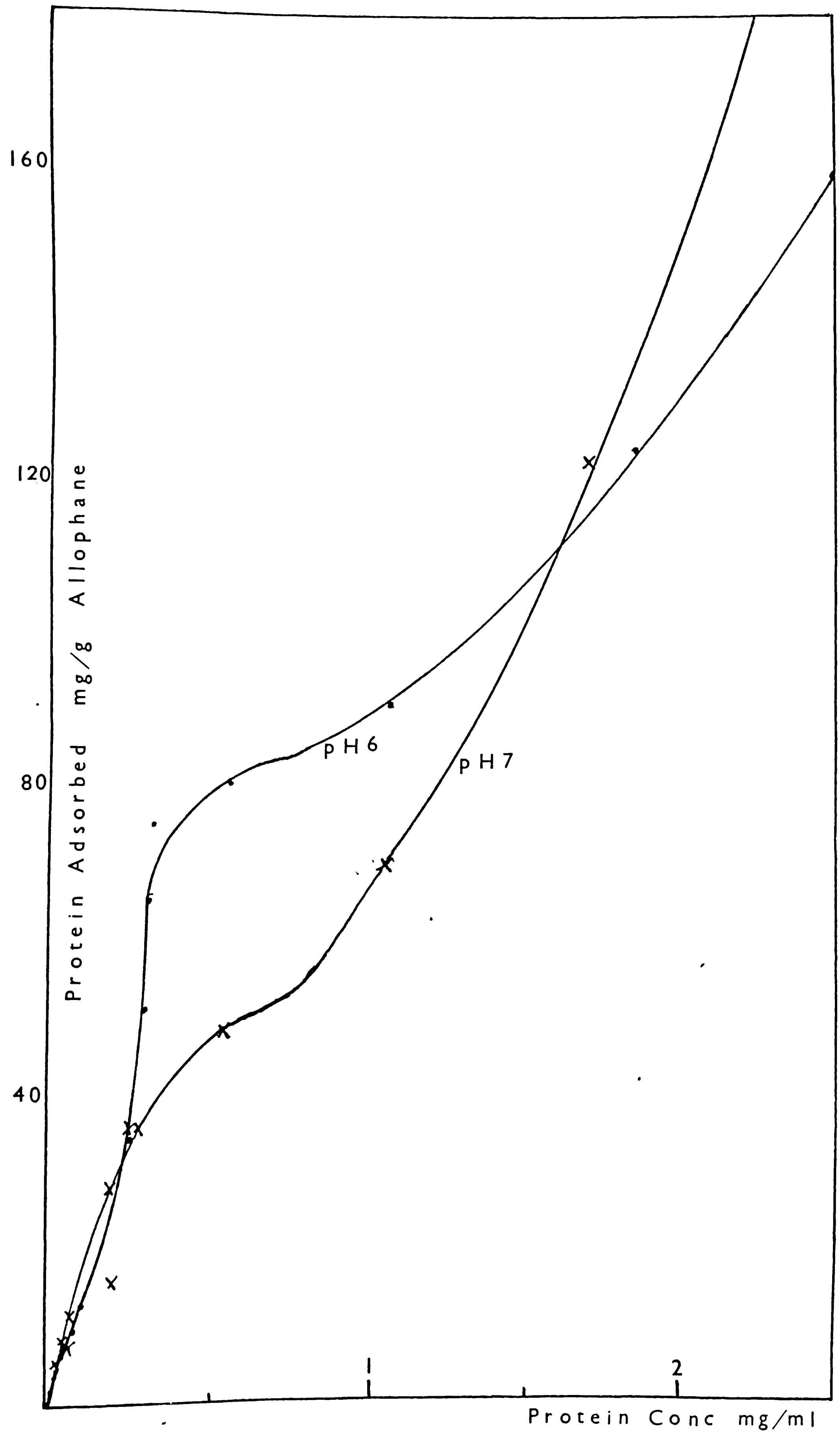


FIG 6·4 ADSORPTION OF BSA ON DUNMORE ALLOPHANE

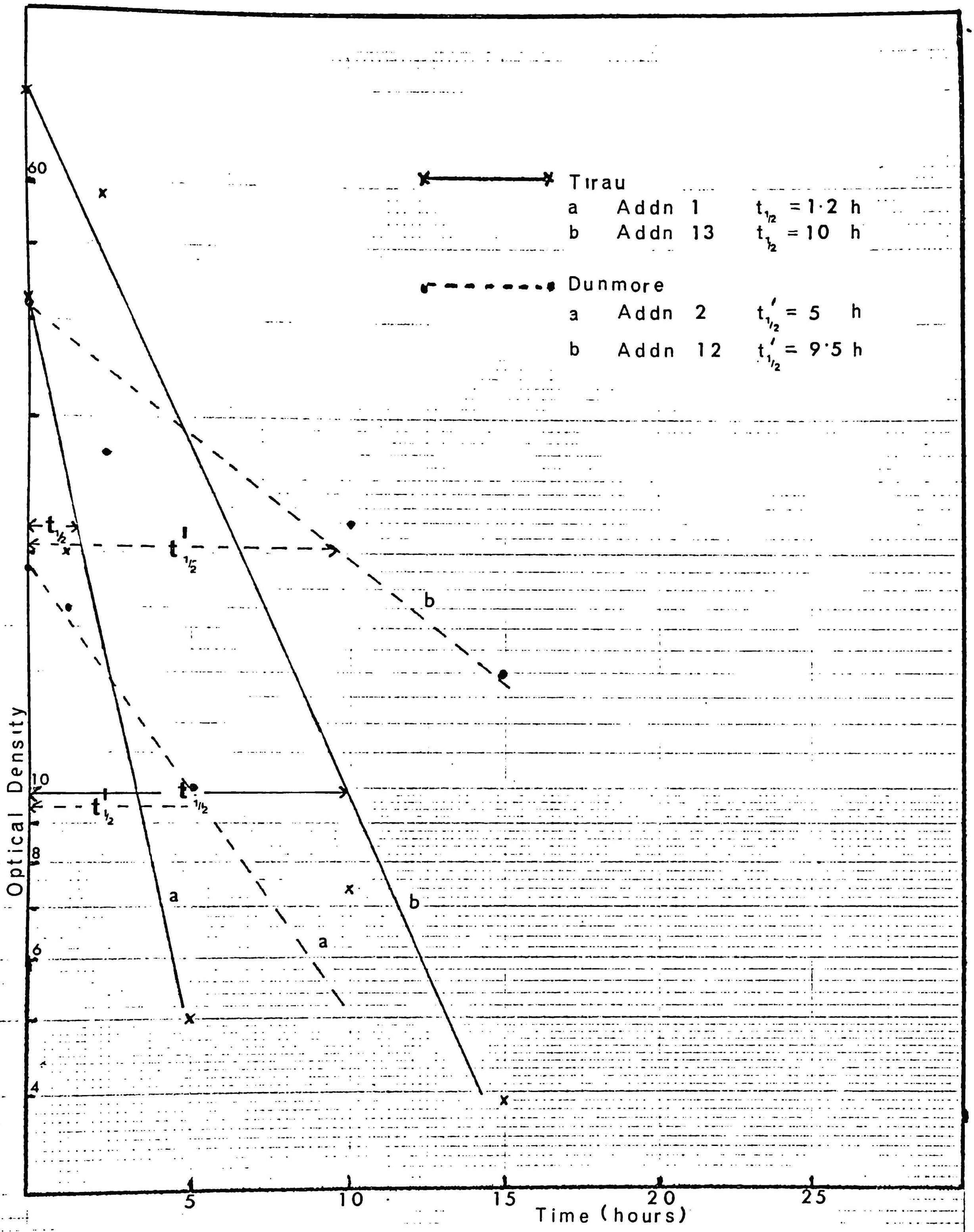


FIG 6·5 HALF TIME FOR ADSORPTION OF BSA ON ALLOPHANES

Table 6.3(a) Adsorption of BSA on Dunmore Allophane

	Initial conc. mg/ml	Final conc. mg/ml	Wt Allophane gm	Protein Uptake mg/gm
pH 4.5	0.165	0.10	0.0489	13.3
	0.423	0.12	0.0527	55.0
	0.825	-	0.0532	-
	1.65	1.195	0.0495	80.2
	2.47	1.95	0.0509	102.0
	4.13	3.47	0.0429	155.0
pH 5.0	0.165	0.02	0.0489	28.6
	0.413	0.12	0.0520	56.0
	0.825	0.56	0.0473	67.8
	1.65	1.10	0.0611	90.0
	2.47	2.00	0.0599	79.0
	4.13	3.40	0.0683	107.0
pH 8.2	0.165	0.2	0.0430	-
	0.413	0.270	0.0620	16.2
	0.825	0.600	0.0550	28.5
	1.65	1.40	0.0570	30.6
	2.47	2.26	0.0450	37.0
	4.13	3.60	0.0513	64.0

Table 6.3(b) Adsorption of BSA on Tirau Allophane

	Initial conc. mg/ml	Final conc. mg/ml	Wt Allophane gm	Protein Uptake mg/gm
pH 4.5	0.165	0.008	0.0457	17.1
	0.413	0.140	0.0472	46.2
	0.825	0.480	0.0547	63.0
	1.65	1.22	0.0481	89.5
	2.47	1.52	0.0593	160.0
	4.13	3.02	0.0566	196.0
pH 5	0.14	0.025	0.0561	10.1
	0.30	0.23	0.0430	28.7
	0.60	0.24	0.0517	29.8
	0.90	0.64	0.0505	54.8
	1.20	0.88	0.0488	72.2
	2.40	2.00	0.0437	95.3
	3.32	2.84	0.0405	120
pH 7.8	0.165	0.2	0.0452	-
	0.413	0.40	0.0443	2.94
	0.825	0.72	0.0492	21.4
	1.65	1.44	0.0456	46.0
	2.47	2.20	0.0507	53.4
	4.13	3.80	0.0443	74.6

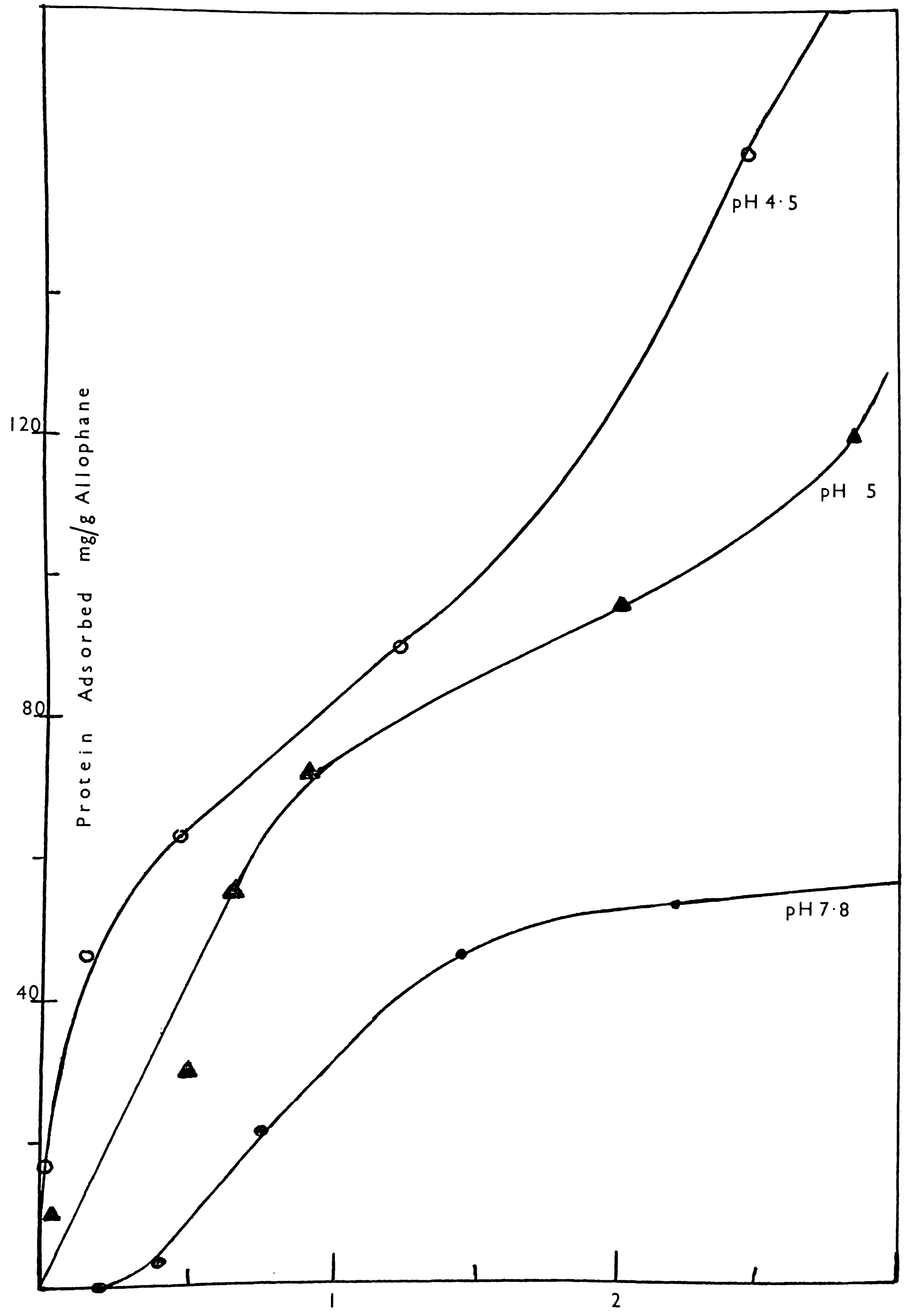


FIG 6·6 ADSORPTION OF BSA ON TIRAU ALLOPHANE

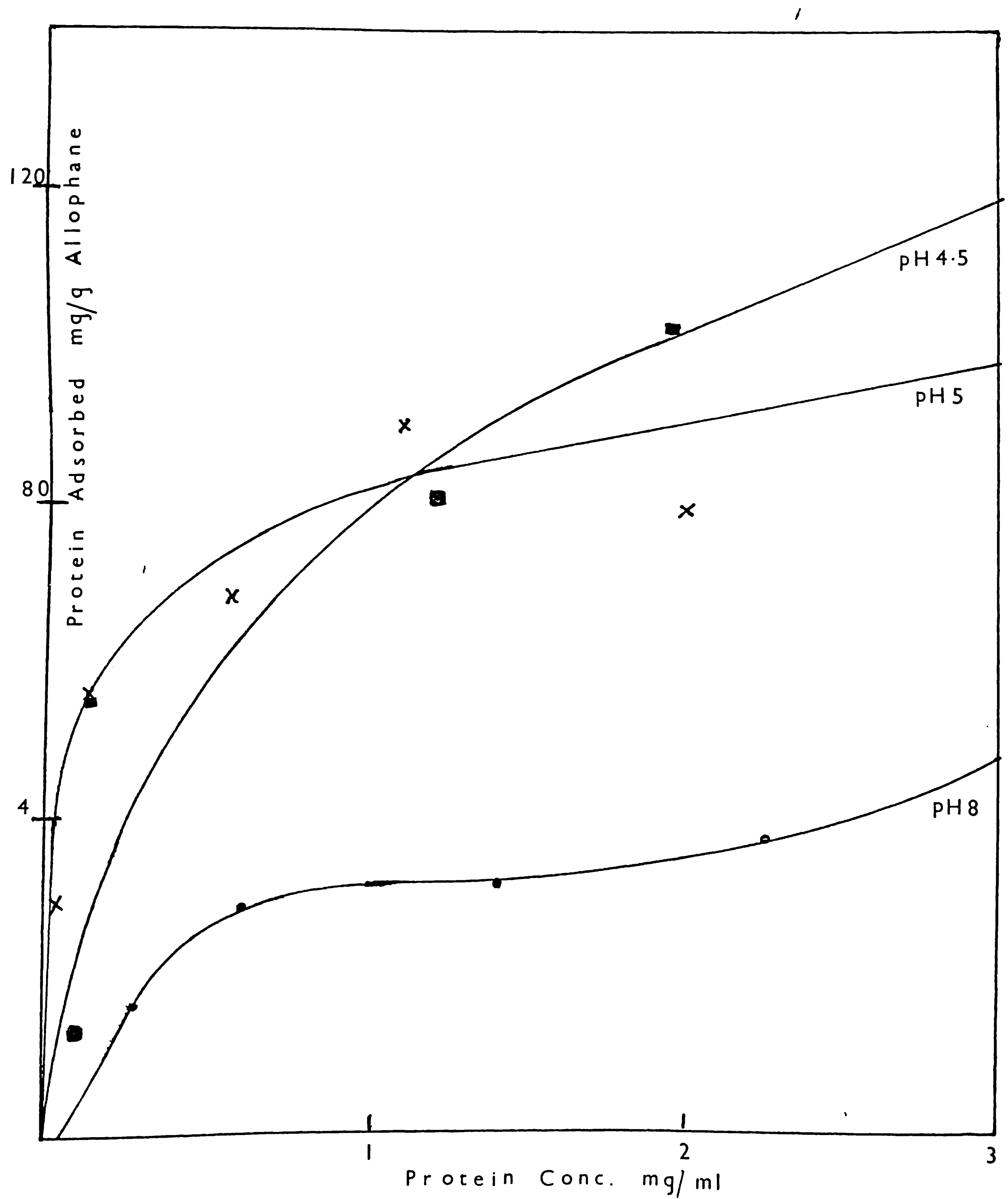


FIG 6·7 ADSORPTION OF BSA ON
DUNMORE ALLOPHANE

When the protein was saturated or nearly saturated it sank to the bottom in a 'jelly-like' mass. It was difficult to keep this moving and the magnetic stirrer speed was increased.

The samples at pH's 4.5, 5 and 8 were run using centrifuge tubes. The results are tabulated in table 6.3 and plotted in Figs. 6.6 and 6.7.

There is little difference in the amount adsorbed onto the different allophanes. At pH 5-6 both Tirau and Dunmore allophanes will adsorb 10% of their weight of protein at an equilibrium concentration of 2 mg/ml. Above this concentration coagulation takes place at pH 5 whereas at pH 4.5 coagulation takes place above 1 mg/ml.

(b) Gelatin

Gelatin adsorption was limited to an equilibrium concentration of approximately 0.5 mg/ml - this resulted from the addition of a saturated solution to the tubes. The concentrated solution would keep only 24 hours before it went cloudy, even with the addition of toluene and being kept in a cold room.

At pH 4 no equilibrium was reached as the protein was coagulated by the acid clay although only for the highest initial concentration was any coagulent seen (unlike egg albumin). The data is shown in Table 6.4 and plotted in Fig. 6.8.

(c) Egg Albumin

Only weak solutions could be used since any agitation was sufficient to coagulate the protein in the concentrated solutions. The tubes on the disc, after revolving slowly overnight, showed a coagulated mass of white protein at all pH's for strong solutions. Allophane at pH 4.5 immediately coagulated the protein at all concentrations and no significant absorption in the UV was noted. The results are recorded in the following table (Table 6.5) and plotted in Fig. 6.9.

Table 6.4 Gelatin adsorbed on to Tirau allophane

	Initial Conc. (mg/ml)	Final Conc. (mg/ml)	Wt Allophane (gm)	Protein Uptake (mg/gm)
pH 4	0.100	0.398x10^{-1}	0.0535	48.8
	0.190	0.380x10^{-1}	0.0579	23.8
	0.348	0.325	0.0482	11.62
	0.486	0.172	0.0503	95.7
	0.600	0.080	0.0520	50.1
pH 5	0.033	0.001	0.0547	5.5
	0.083	0.053	0.0544	5.6
	0.165	0.083	0.0513	8.0
	0.250	0.692x10^{-1}	0.0574	27.6
	0.412	0.165	0.0673	36.8
	0.502	0.302	0.0500	40.0
pH 6.3	0.100	0.102	0.301	-
(15 ml samples)	0.190	0.175	0.0201	14.5
	0.348	0.312	0.0200	27.3
	0.486	0.445	0.205x10^{-1}	29.9
	0.600	0.512	0.0440	30.0
	(the amount of clay sample was reduced)			
pH 7	0.033	0.035	0.0500	-
	0.083	0.065	0.048	3.6
	0.165	0.090	0.0483	15.3
	0.250	0.130	0.0491	24.8
	0.412	0.280	0.0426	26.9
	0.502	0.335	0.0532	30.2

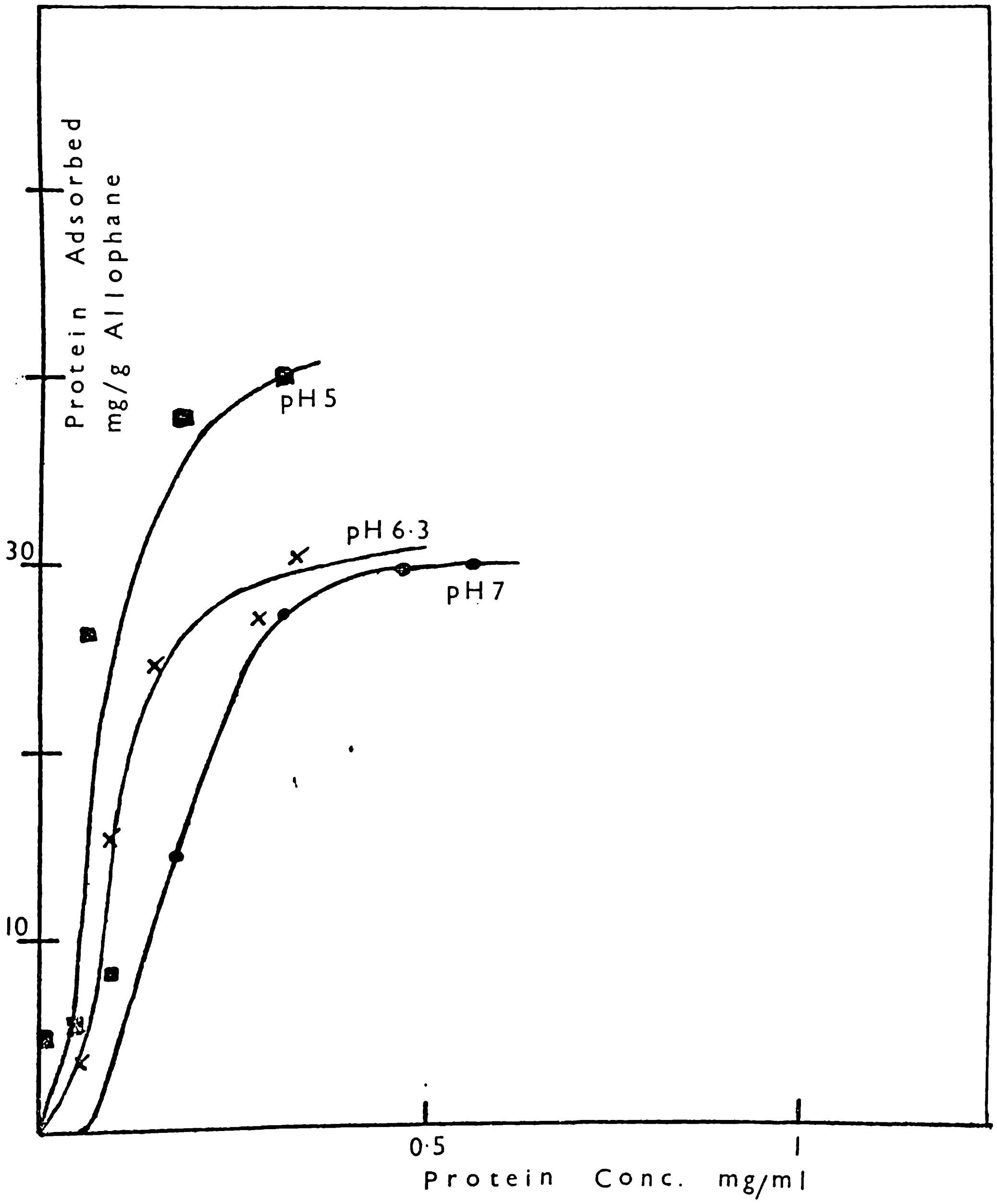


FIG 6·8 ADSORPTION OF GELATIN ON TIRAU ALLOPHANE

Table 6.5 Egg albumin adsorption on Tirau Allophane

	Initial Conc. mg/ml	Final Conc. mg/ml	Allophane gm	Adsorption mg/gm
pH 4.5		Immediate coagulation		
pH 6	0.025	0.020	0.0501	10.9
	0.114	0.042	0.0584	12.3
	0.151	0.084	0.0521	12.8
	0.228	0.120	0.0501	21.2
	0.35	coagulation		
pH 7	0.075	0.050	0.0510	4.9
	0.114	0.052	0.0509	12.2
	0.151	0.091	0.0491	12.2
	0.228	0.142	0.0489	17.6
	0.35	coagulation		

(d) Hemoglobin

The hemoglobin samples were coagulated with the constant stirring needed in the flasks for an adsorption against time so that the tube method was developed. Even so it appears that either a second layer of protein is deposited or else coagulation takes place. From experience with the other proteins the rise in curves at pH of 4.5 and 5 can be attributed to coagulation by the acid environment but this is not expected with pHs of 6 and 7. Both curves do show signs of levelling out around concentration of 1.2 mg/ml of protein but then curve sharply upwards. As the method involved measuring the loss in optical density in solution the protein could be deposited on the tube walls, on the allophane or even suspended in solution and precipitated by centrifuging.

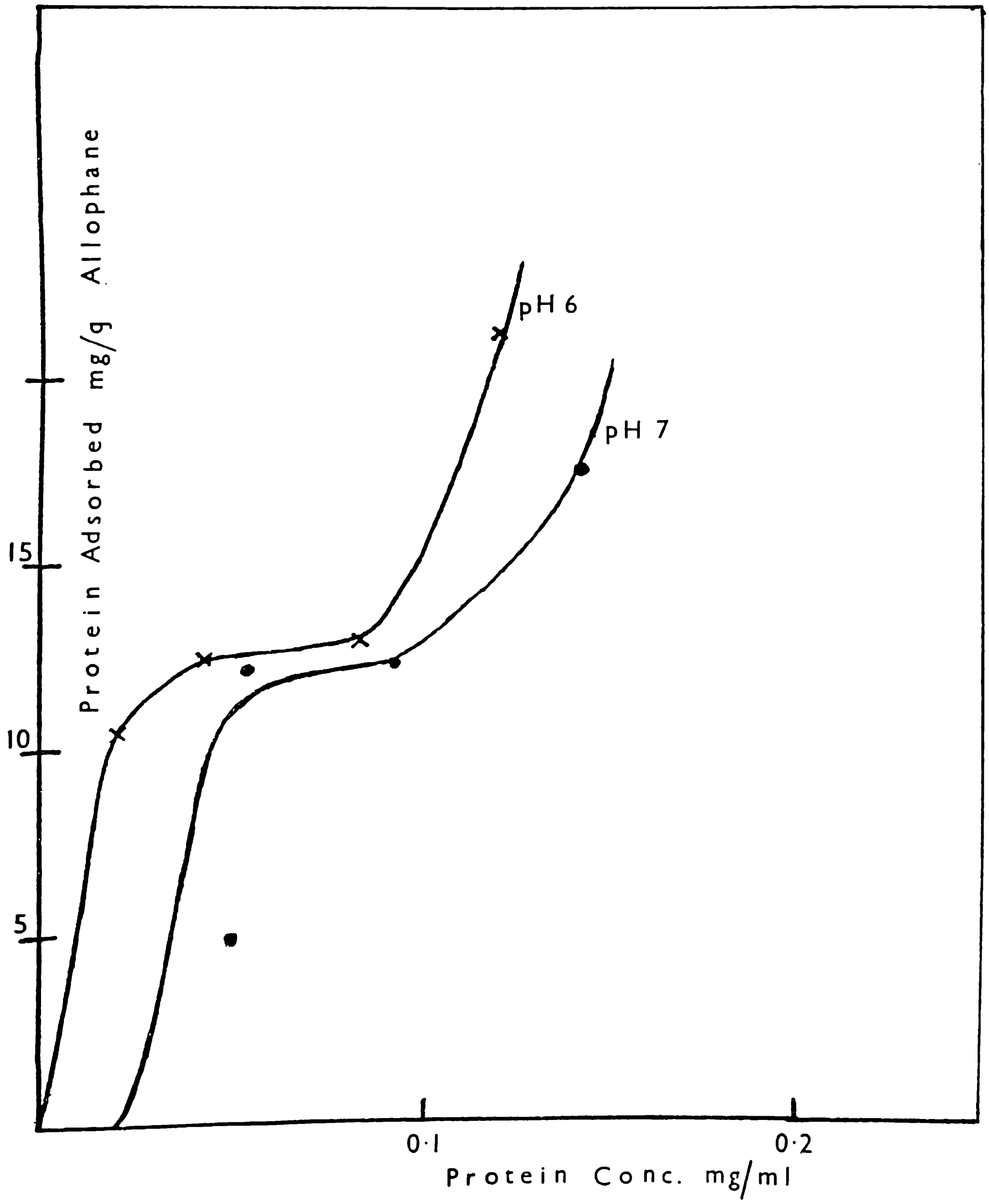


FIG 6·9 ADSORPTION OF EGG ALBUMIN ON TIRAU ALLOPHANE

Any of these possibilities will not be detected.

At pH 5 (measured with close range pH paper) a sample could be maintained with only slight loss on being turned end over end for 24 hours but at pH 4.5 the loss was greater, although cloudiness was not noted in the sample. It would seem then that agitation does cause a loss of hemoglobin due to coagulation. A sample of hemoglobin at pH 4.5 after standing for 24 hours showed a slight decrease in absorbance, but after agitation this loss increased to about 15%. The results are shown in Table 6.6 and plotted in Fig. 6.10.

6.6 DISCUSSION

The rather slow half-time for protein adsorption, about 1½ hours or more as the allophane becomes nearly saturated may mean the proteins have to undergo conformational changes before they can be adsorbed onto the allophane. This may also account for the added stability of protein-allophane complexes since natural enzymes that break down the proteins will not have a 'good fit' with the denatured protein.

No ready way of removing the protein from the allophane was found, possibly due to the altered nature of the protein. The Grant process[188] involved backwashing with strong sodium hydroxide solution. Certainly a strong solution of sodium hydroxide would dissolve part of the allophane and probably release the protein in a coagulated form suitable for air flotation.

The isoelectric points of the proteins studied are listed below.

Table 6.7 Isoelectric Points of Proteins

(values from Ref. 208)

Egg albumin	4.6
Gelatin	4.9
Serum albumin	4.7
Hemoglobin	6.8

Table 6.6 Adsorption of Hemoglobin on Dunmore Allophane

	Initial Conc. mg/ml	Final Conc. mg/ml	Wt Allophane gm	Protein Uptake mg/gm
pH 4.5	0.131	0.015	0.0540	21.5
	0.262	0.150	0.382	29.3
	0.655	0.463	0.0460	41.7
	1.31	0.985	0.0554	58.7
	1.97	1.515	0.0486	94.5
	3.28	2.525	0.0486	150.5
pH 5	0.131	0.038	0.0552	16.85
	0.262	0.146	0.0509	22.0
	0.655	0.460	0.0553	35.3
	1.31	1.040	0.0541	49.8
	1.97	1.515	0.0533	85.5
	3.28	2.640	0.0484	133
pH 6	0.57	0.26	0.0546	56.1
	0.95	0.53	0.0536	79.2
	1.31	0.82	0.0528	93.5
	1.58	1.11	0.0494	94.5
	1.72	1.24	0.0493	98.0
	2.36	1.68	0.0516	131.1
	4.20	3.40	0.0471	187.5
pH 8.2	0.131	0.115	0.0480	3.33
	0.262	0.242	0.0487	4.11
	0.655	0.328	0.0424	7.73
	1.31	1.100	0.0567	37.0
	1.97	1.660	0.0602	51.8
	3.28	2.940	0.0621	54.8

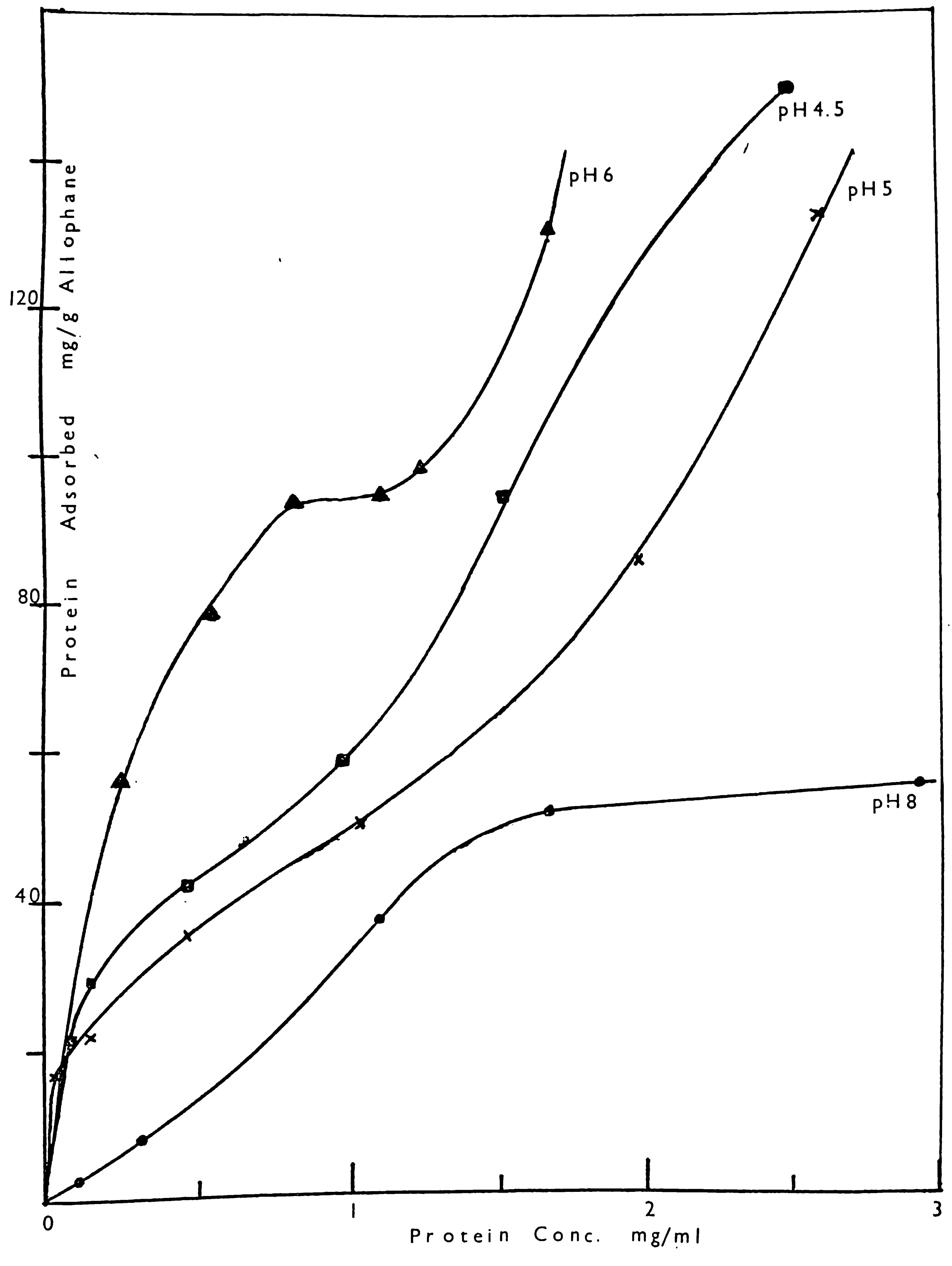


FIG 6.10 ADSORPTION OF HEMOGLOBIN ON DUNMORE ALLOPHANE

At or near the isoelectric point proteins are less soluble and more easily coagulated than on either side of the isoelectric point. This probably contributes to the coagulation of the proteins at pH 4.5 by allophane since blanks at this pH are stable provided they are not violently agitated. This also probably accounts for the departure of hemoglobin adsorption from the expected curve at pHs 6 and 7 since the isoelectric point of this protein lies much higher than the others. The isoelectric points of the two clays are 6.

The adsorption for BSA, gelatin and egg albumin has a maximum between pH 5 and 6 discounting any loss due to coagulation. This corresponds to the point where allophane is positively charged or neutral and the protein is negatively charged.

When the charges on the protein and allophane particles are both negative the adsorption decreases. The point when both are positive cannot be easily studied since at low pHs the proteins are coagulated.

For hemoglobin the maximum adsorption is at pH 6 when the protein will be positively charged and the allophane negative. This occurs at a concentration of 1 mg/ml. Any increase in concentration beyond this results in coagulation.

6.7 CONCLUSION

Allophane is able to absorb the types of protein studied. The greatest uptake with albumins occurs when the protein is negatively charged and allophane is positively charged. This occurs at pH 5 when Dunmore allophane will adsorb 100 mg of BSA/gm (10% by weight) of allophane at a protein concentration of 2 mg/ml. Tirau allophane adsorbs slightly less about 85 mg/gm at the same pH. At pH 5 Tirau allophane will adsorb 40 mg of gelatin at a protein concentration of 0.3 mg/ml.

The greatest adsorption of hemoglobin occurs when the allophane is neutral and the hemoglobin positively charged. This occurs at pH 6 when 98 mg/ml are adsorbed at a protein concentration of 1.2 mg/ml.

The adsorption curves for BSA and gelatin are much steeper than for hemoglobin, more than half the saturation value being adsorbed before the equilibrium protein concentration reaches 0.1 mg/gm whereas for hemoglobin the half-saturation point is not reached until 0.3 mg/gm.

6.8 SUGGESTIONS FOR FURTHER WORK

The pilot scheme designed by the Meat Research Institute involves lowering the pH of the waste water to 4. At pH 4.5 BSA and egg albumin showed signs of coagulation so it is possible that allophane may act as a coagulating agent for proteins. Since it is impractical to use test tubes for these low pHs a series of experiments using columns of soil allophane equilibrated at various pHs could be conducted. The half time for the adsorption reaction increases as the amount of protein adsorbed increases so the use of a column should enable the optimum flow of polluted water to be evaluated.

This work has been carried out with pure proteins on separated allophane. Separation of clays is tedious and on the industrial scale expensive so that experiments carried out on whole sub-soils high in allophane could determine the practicality of using allophane to adsorb protein on an industrial scale.

Slaughterhouse effluent contains material other than protein which may block adsorption on allophane and experiments must be carried out using actual effluent at varying pHs to ensure that the adsorption figures obtained in the laboratory scale tests here apply when large scale conditions apply.

PART II. A SYNTHETIC APPROACH

BACKGROUND

The work in Part I has shown that allophane has a variable composition. In the volcanic soils it has a positive charge associated with the presence of iron. Because the methods required to remove 'free' iron oxide alter the chemical properties of allophane, an alternative method is needed to prepare iron-free allophane.

This section of work deals with the preparation and properties of some synthetic aluminosilicates prepared by two methods.

A structure and definition for allophane are also discussed.

CHAPTER 7. AMORPHOUS ALUMINOSILICATES AND IRON SILICATES

7.1 INTRODUCTION

The similarity of allophane to aluminosilicates has been discussed above. Birrell[101] showed that allophane had a marked surface acidity like the aluminosilicate catalysts and Fieldes and Schofield[148] pointed out the similarities with ion exchange.

It is perhaps pertinent at this point to very briefly review what is known of the aluminosilicates and their importance as cracking catalysts.

Thomas[209] in 1949 reviewed what was known of the cracking catalysts and considered them to be acids of composition $(HAlSiO_4)_x$ where the active unit is an acidic hydrogen associated with a tetrahedral aluminium. The maximum activity was at an Al/Si ratio of 1:1. The acidity of these centres has been measured by several workers[211,212,213] using various organic indicators and the general conclusion was that the sites were partially of a Bronsted type since they responded to trace amounts of water.

Tamele[214] has noted in his review, that the cracking catalysts are amorphous and lose their activity when converted into crystalline materials. He showed that on mixing fresh neutral silica sol with fresh neutral alumina sol, a strong acid reaction developed. When coprecipitated with sodium hydroxide the sodium ions held by the precipitate were readily replaceable by NH_4^+ ions. It was found that in the presence of silica no free aluminium hydroxide was precipitated when sodium hydroxide was added to a solution of $AlCl_3$. Millikan et al[215] measured the base exchange of the silicoaluminates and found a maximum at 33% alumina. They also found if the samples were dried out they lost their activity which they considered was associated with hydroxy groups.

The charge on the surface of aluminosilicates is usually negative and averages 1.4 electrons per $m\mu^2$ [144]. Provided the aluminium content remains low enough to allow distribution in the tetrahedral state then the surface charge increases with alumina content.

Fripiat[144] considered that the presence of a tetrahedral aluminium would activate a neighbouring proton on a silica group which would then react to give a measure of the tetrahedral aluminium.

In a series of papers Léonard and his coworkers[216-218] have studied the structure and properties of amorphous aluminosilicates prepared by cohydrolysis of organic derivatives of Al and Si. In the first paper[216] X-ray fluorescence techniques were used together with I.R. spectroscopy. They showed that aluminium could occupy tetrahedral sites up to a ratio of 33% Al_2O_3. When the alumina content was increased the percentage of tetrahedral aluminium dropped till at 100% Al_2O_3 the aluminium was all octahedrally coordinated. On heating, tetrahedral aluminium was stabilized, but in a different form, this probably corresponding to the metakaolinite form. They reasoned that as the aluminium content was increased there would be a stage when there was insufficient silica to completely surround the tetrahedral alumina and the alumina would then become octahedral (see Fig. 7.1).

The aluminosilicates when prepared by cohydrolysis were X-ray amorphous up to an Al/(Al+Si) ratio of 0.8 when crystalline phases of alumina appeared in X-ray analysis. Several structural models have been proposed, some of which have been discussed above under allophane structure. In the preparation of aluminosilicates by hydrolysis of organo derivatives, the only cations that can be present are protons or probably H_3O^+ ions or hydroxy-aluminium species of which there can be quite a variety. The effect of other ions in solution has been investigated by Siffert[219] who found clay materials were formed and this has also been found by several authors[15,16].

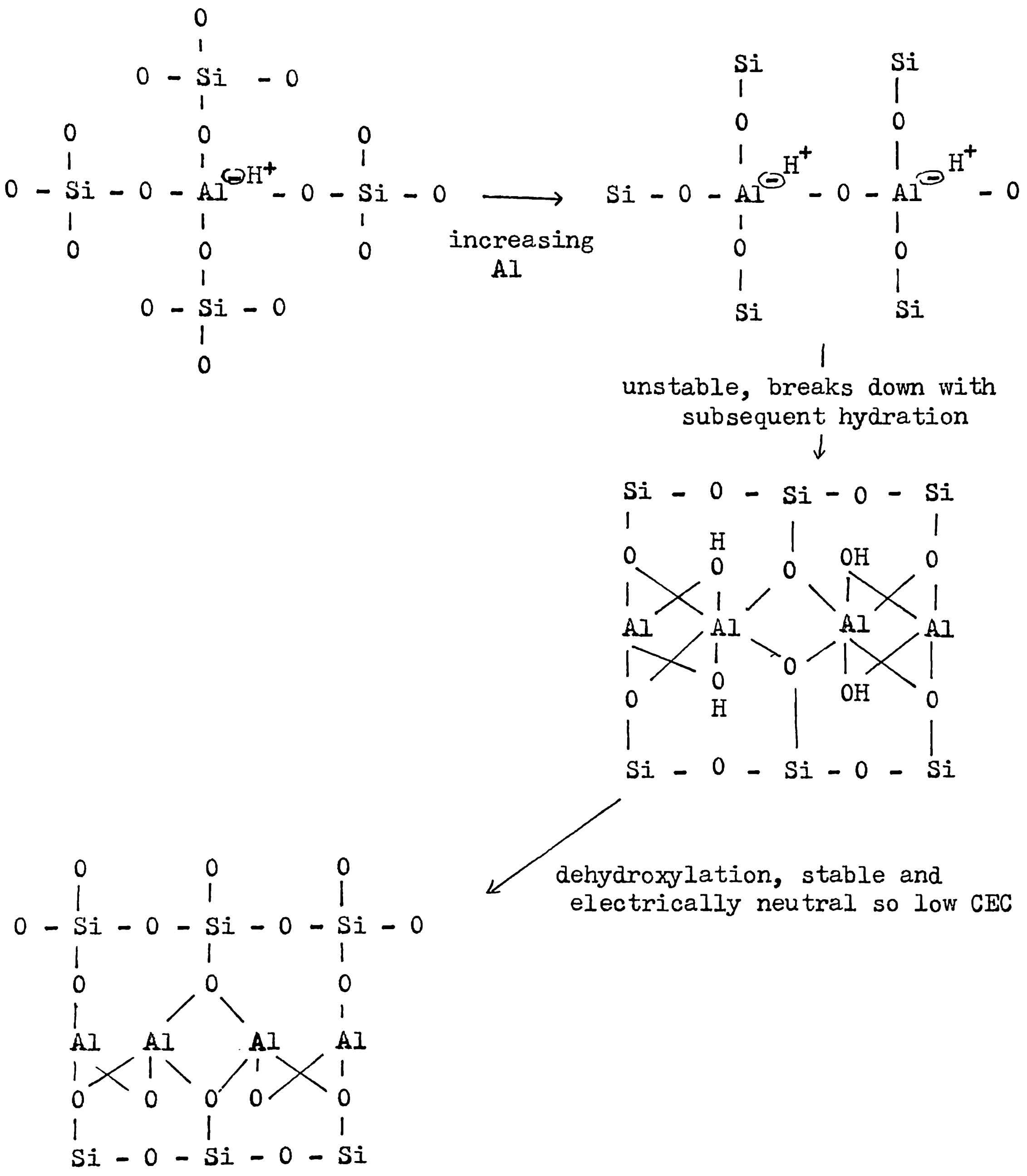
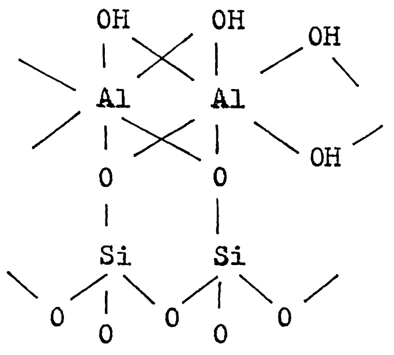


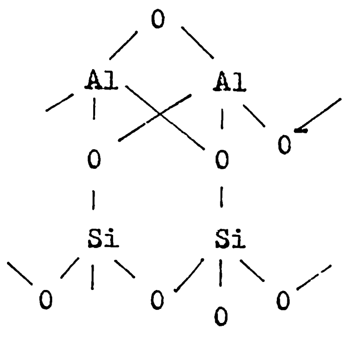
Fig. 7.1 Schematic Structural Relationships in Aluminosilicates (from Léonard et al[216]).

The active sites were investigated in a second paper by Léonard and coworkers[218] using ammonia and they found the CEC at a maximum when Al/(Si+Al) ratio was 0.33. They concluded that the Bronsted acid sites originated from isomorphous substitution of the alumina into silicon tetrahedral sites and that Lewis sites in the high silica samples were due to silicon atoms.

On dehydration, however, the Bronsted site was usually considered a Lewis type since it is associated with a hydroxyl deficiency at the surface.



clean surface



dehydroxylated

The formation of these sites has been supported by studies on the dehydroxylation of kaolinite where aluminium is considered four coordinated in the little known metakaolinite[332] since there are too few hydroxyl groups for the aluminium to remain six coordinated.

The aluminosilic acid gels have been found to be ion-selective in cation adsorption, this being especially so for potassium[161]. This has been noted for allophanic soils in New Zealand[159].

The method of preparation described by Léonard et al[216] gives a way of preparing aluminosilicates which have no impurities whatsoever whereas the aluminosilicates prepared by Mattson[155] have sodium and chloride ions as contaminants.

In this study investigations were made to determine isoelectric points on pure samples and samples treated with iron hydroxide as well as a brief investigation of iron silicates.

7.2 EXPERIMENTAL

Reagents

Aluminium isopropoxide was prepared by dissolving amalgamated aluminium in isopropanol, refluxing off the excess isopropanol and vacuum distilling the aluminium isopropoxide. Ethyl orthosilicate was distilled from BDH supplied tetraethylorthosilicate. Ferric chloride solutions were prepared by dilution from BDH AnalaR ferric chloride solution.

Samples

Five different series of amorphous aluminosilicates were prepared.

Series A. Aluminium isopropoxide and tetraethyl orthosilicate were hydrolysed together in polythene beakers. The samples were allowed to age for 3 days and then freeze-dried.

Series B. Samples were prepared as above but with the addition of sodium hydroxide to the hydrolysing solution to bring the pH up to 9, and freeze dried with the small amount of sodium hydroxide retained.

Series C. Samples were prepared as in series A but with HCl added to adjust the pH to 3.5 and freeze dried.

Series D. Rankin[221] was able to prepare a form of silica gel by passing a solution of sodium silicate through an ion exchange column. A solution of 10^{-4}M aluminium chloride was passed through a Deacidite FF column in the hydroxy-form and a solution of sodium silicate (10^{-4}M) passed through an Amberlite I.R. 120 column in the acid form. The two solutions were combined and dried on a rotary evaporator.

Series E. Samples of aluminium isopropoxide and ethyl orthosilicate were hydrolysed separately in polythene containers and then mixed and freeze dried after 1 day (samples E1), 3 days (E3) and one week (E7) of being added to the hydrolysing liquid. The samples were aged for 1 day before freeze drying.

Samples of ferric oxide/silica gels were prepared by several methods.

Sample FA. Tetraethyl orthosilicate was hydrolysed in a 1M solution of ferric chloride, aged for three days and then freeze dried. The mass was ground, thoroughly washed with distilled water and allowed to air dry.

Sample FD. A 10^{-4}M solution of $FeCl_3$ (freshly prepared) was passed through a De Acidite FF column in the hydroxy form and added to a solution of sodium silicate passed through an Amberlite IR120 column in the hydrogen form and the combined mixture dried on a rotary evaporator.

Two samples of a hydrous ferric oxide/alumina/silica gel were prepared.

Sample MA. A 1:1 mixture of ethylsilicate and aluminium isopropoxide was hydrolysed in a 1M solution of ferric chloride, with a small amount of sodium hydroxide added to raise the pH to 5. The sample was freeze dried, then ground and washed with distilled water and allowed to air dry.

Sample MB. An aluminosilicate with SiO_2/Al_2O_3 ratio of 1 prepared by the method for series A was suspended in a 10^{-2}M solution of aged ferric chloride. (The solution had become a colloidal suspension of ferric hydroxide.) The suspension was centrifuged and the supernatant liquid poured off. The solid remaining was freeze dried.

Two further methods were used to prepare aluminosilicates. Tetraethyl-orthosilicate was added to a suspension of gibbsite in water and the mixture left for three months with periodic shaking. A corresponding mixture of fine silica gel and aluminium isopropoxide in water was also made and left for three months with periodic shaking. After this time these two samples were dried on a rotary evaporator.

The molar ratios of the samples are shown in Table 7.1.

Table 7.1 Molar Ratios of Aluminosilicates

		SiO_2/Al_2O_3	% Al_2O_3
Series A	Sample A1	1.24	57.9
	A2	1.46	53.6
	A3	2.18	43.8
	A4	3.04	35.9
	A5	7.03	18.8
Series B	B1	1.00	
	B2	1.5	
	B3	2.0	
Series C	C1	1.5	
	C2	2.0	
Series D	D1	1.0	
	D2	1.5	
	D3	2.0	
Series E	E1A	0.5	
	E1B	1.0	
	E1C	1.50	
	E3A	0.5	
	E3B	1.0	
	E3C	1.5	
	E7A	0.5	
	E7B	1.0	
Sample	FA	SiO_2/Fe_2O_3	1:0.2
	FD	SiO_2/Fe_2O_3	1.0
	MA	$SiO_2/Al_2O_3/Fe_2O_3$	1:0.5:0.1
	MB	$SiO_2/Al_2O_3/Fe_2O_3$	1:1:$<$ 0.01

7.3 RESULTS

7.3.1 X-RAY DATA

Powder photographs were made using a Philips Debye camera and a Rigaku X-ray generator.

The samples in series A, D, E1 and E3 were X-ray amorphous.

In series B, bayerite is present in all samples. The peaks are small and broad in the low alumina samples but sharp in the high alumina samples with small peaks due to gibbsite in the highest alumina sample.

In series C two broad lines appear in the X-ray diffraction patterns of the samples. The lines do not correspond to any well-formed crystalline oxide or hydroxide of aluminium but show broad bands at 6.7Å and 2.4Å which are close to the strongest peaks of boehmite. Papee et al[220] have described a precipitated boehmite with peaks in this range which they considered poorly crystalline and termed 'pseudoboehmite'. This compound also had broad weak peaks and it appears probable that pseudoboehmite has been formed in the samples.

The high alumina sample of series E3 and all the samples of series E7 show gibbsite in the X-ray diffraction traces. A sample of hydrolysed aluminium isopropoxide left in the hydrolysing solution for 7 days was freeze dried and also shows gibbsite in the powder camera photograph. A sample freeze dried after 1 day is X-ray amorphous.

Samples FA, MA and MB are all X-ray amorphous. FD shows lines that correspond to NaCl showing the component ions had not been removed by the ion exchange columns.

The gibbsite/ethylsilicate sample shows no diminuation of the gibbsite peaks. This indicates that no major reaction has occurred between the crystalline hydroxide and the hydrous silica. The silica gel/aluminium isopropoxide sample was amorphous.

7.3.2 THERMAL DATA

The samples were run on a Deltatherm apparatus at 10°C/min in air.

Series A and E1 show typical allophane-like traces (Fig. 7.1). A broad endotherm due to water loss occurs around 140° but varies with the SiO_2/Al_2O_3 ratio. The only other peak is an exotherm above 900°C, the exact position dependent on the SiO_2/Al_2O_3 ratio (see Table 7.2). The peak temperature increases as the ratio increases and has virtually disappeared when the ratio reaches 7.03.

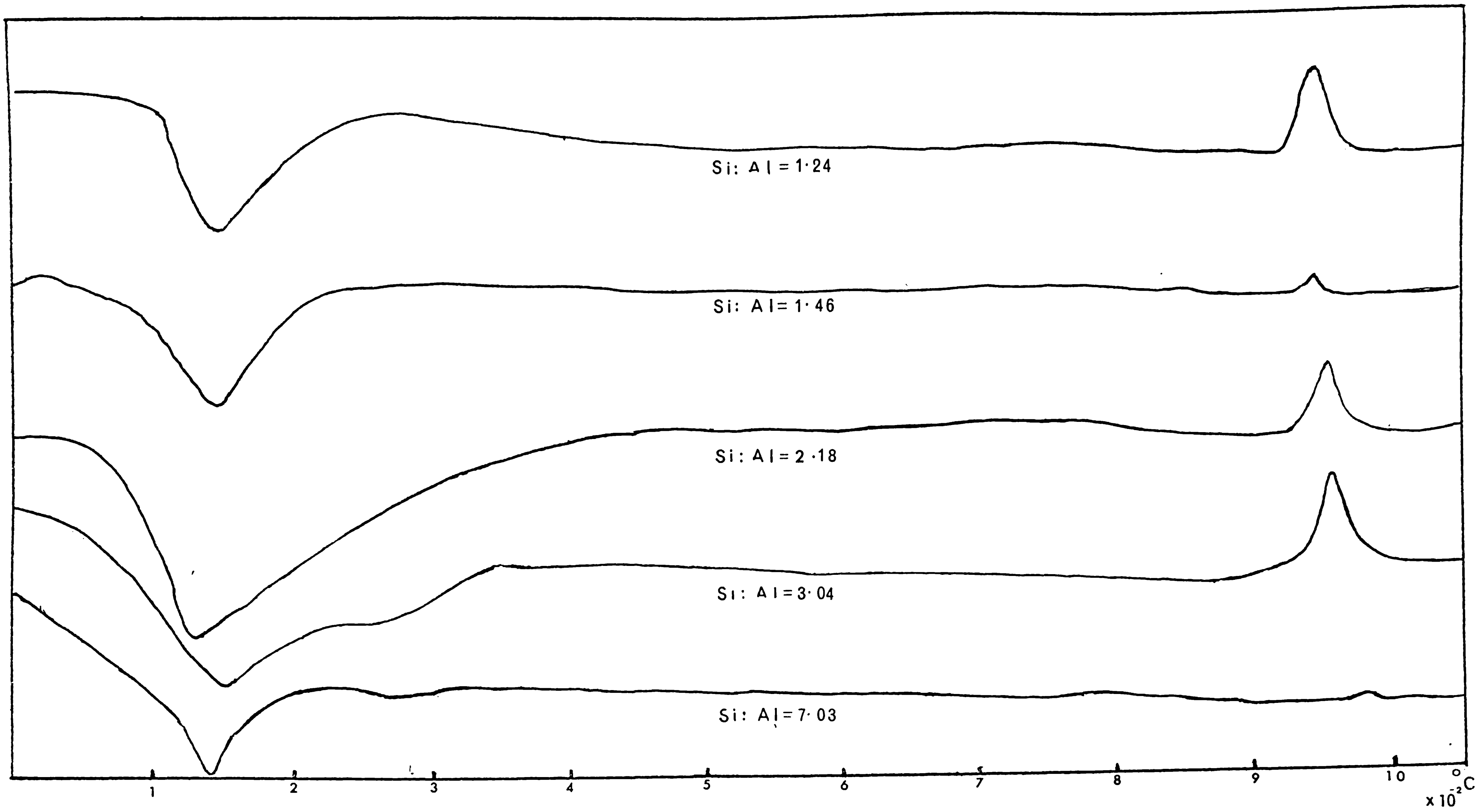


FIG 7·1 DTA CURVES OF SYNTHETIC ALUMINOSILICATES

Table 7.2 Major DTA Peaks for Aluminosilicates

		SiO_2/Al_2O_3	endotherm	exotherm
Series A and E1		1.24	157	940
		1.46	146	946
		2.18	128	956
		3.04	161	963
		7.03	146	988
Series B		2.0	145,295	975
Series C		2.0	130,285	
Series D		2.0	120	360, -
Series E	E3C	1.5	132,288	950
	E7B	1.0	140,290	-
Sample FA			130	-
FD			135	350

Series B and C samples show similar curves but with the addition of an endotherm due to crystalline aluminium hydroxide at approximately 300°C (Fig. 7.2a,b). This endotherm is pronounced in the low silica samples and the exotherm at 930°C is very small and broad. In all cases it is very much smaller than for the A and E1 samples but does show some silica and alumina have reacted.

The series D samples have no exotherm above 900°C but have a broad exotherm between 300 and 400°C, Fig. 2(c). This is probably due to burnoff of organic matter that has leaked from the ion exchange columns. The presence of this organic material has prevented formation of Al-O-Si bonds since mullite does not form.

The size of the endotherm at approximately 300°C in the series E3 and E7 samples is very large and shows that a great deal of the hydrous alumina has crystallized to gibbsite. The absence of any exothermic peak means that little silica and alumina have reacted.

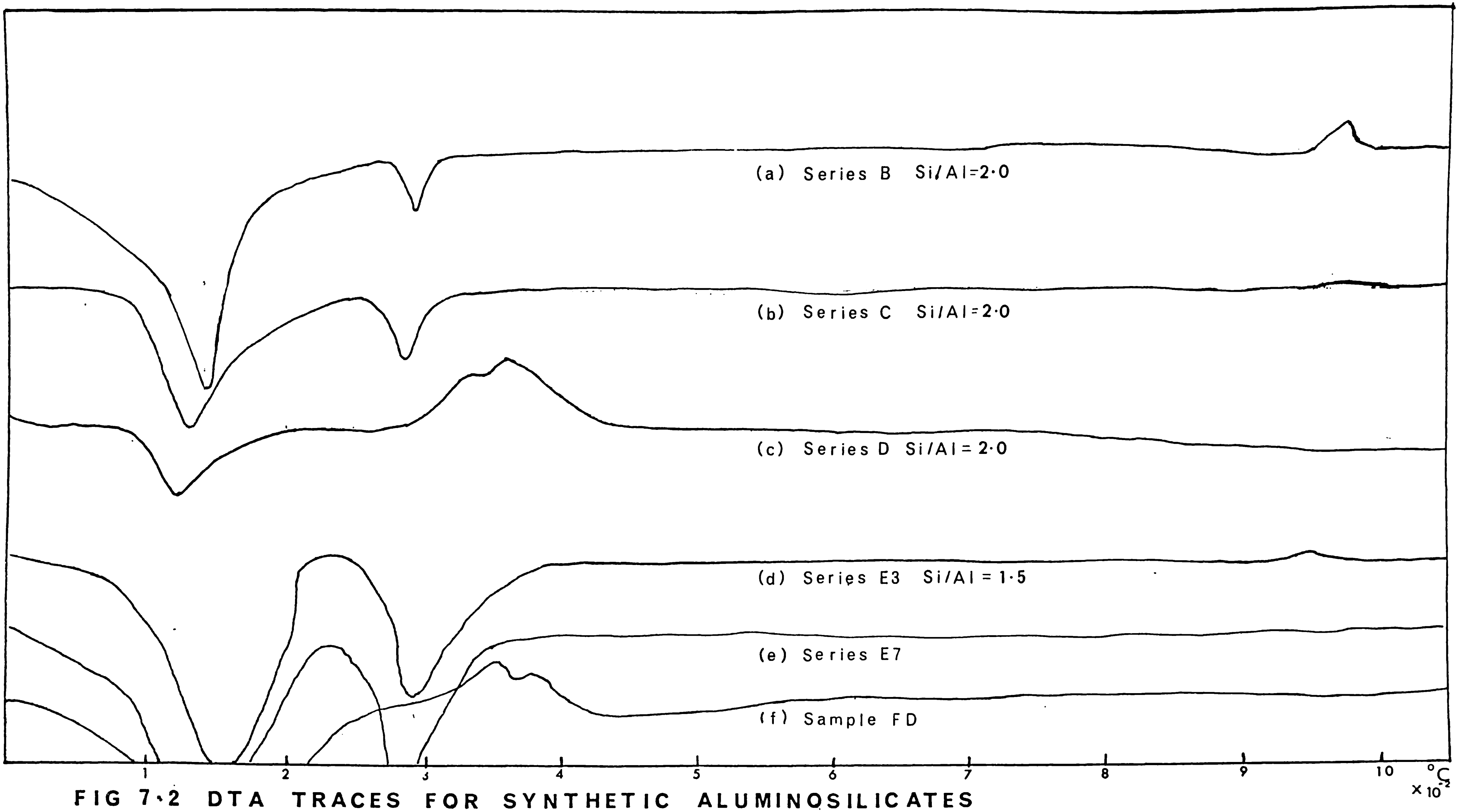


FIG 7·2 DTA TRACES FOR SYNTHETIC ALUMINOSILICATES

The samples FA and FD show similar patterns with only a broad endotherm in the region 120-200°C and possibly, in the case of FD, an exotherm following although this may be a shift in the baseline.

The gibbsite/hydrolysed ethyl silicate shows two endothermic peaks, one at 120°C due to hydrous silica and the other at 310°C due to gibbsite.

The silica gel/hydrolysed aluminium isopropoxide mixture shows two endotherms at 120° and 140°, and a very small exotherm at 980°C. This indicates that silica and alumina have reacted but that there is some discrete oxides present.

7.3.3 INFRA-RED DATA

I.R. spectra were run using Nujol and HCBD mulls between KBr plates.

The only samples to show the spectra characteristic of amorphous aluminosilicates are the samples from series A and E1 and the silica gel/hydrolysed aluminium isopropoxide mixture. In these samples the position of the band around 1000 cm^{-1} varies depending on the SiO_2/Al_2O_3 ratio. There appears very little difference in peak position for the different sample preparations (see Table 7.3 and Fig. 7.3).

Table 7.3 Peak position with SiO_2/Al_2O_3 ratio

SiO_2/Al_2O_3 ratio	peak position cm^{-1}
0 ($Al(OH)_3$)	1020 and 970
1.24	965
1.46	1000
2.18	1030
3.04	1040
7.03	1045
∞ (SiO_2)	1080

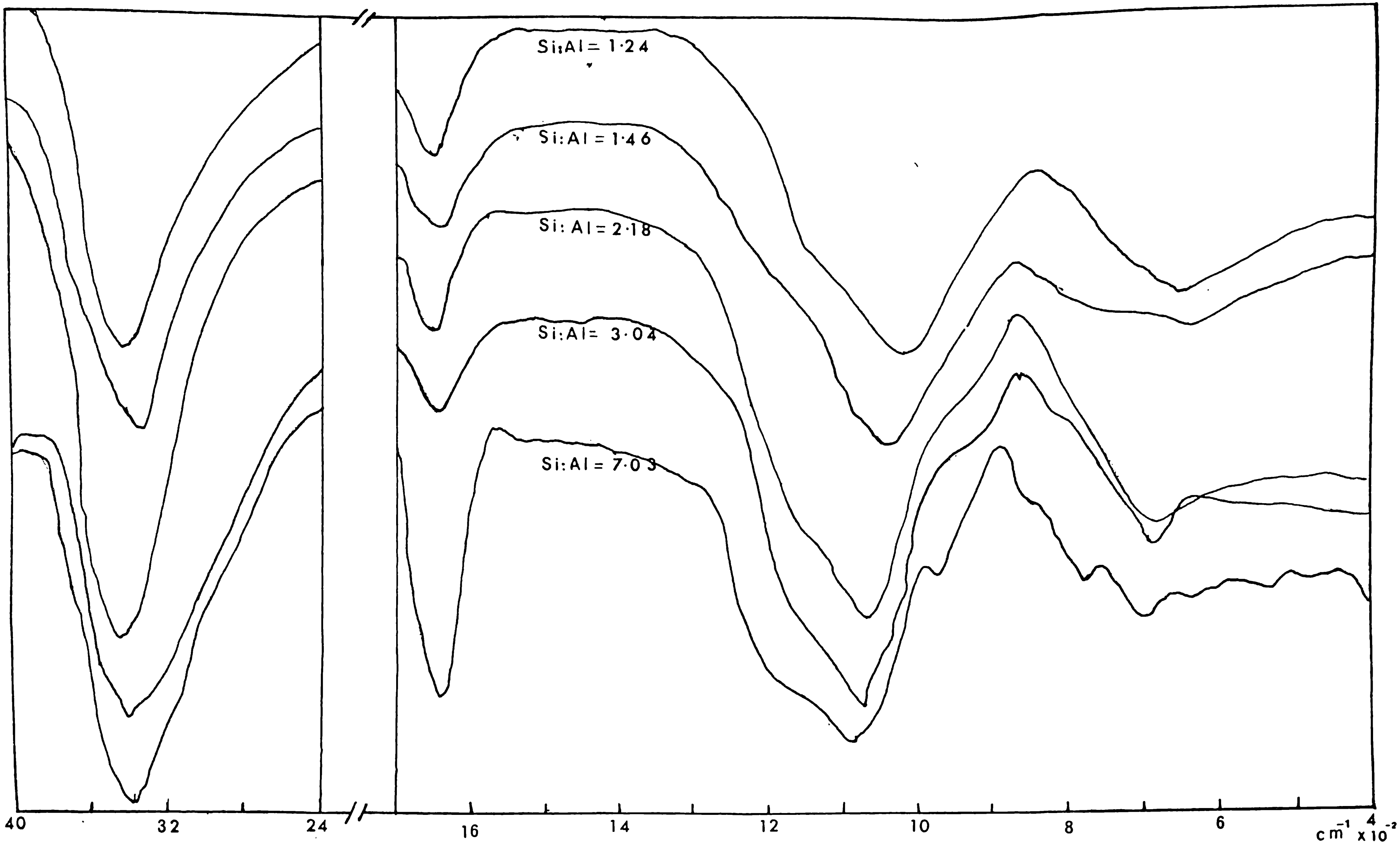


FIG7·3 IR SPECTRA OF AMORPHOUS ALUMINOSILICATES

Amorphous silica shows a series of bands at 955 cm^{-1}, 790 cm^{-1} and 720 cm^{-1} apart from the main band at 1080 cm^{-1} and a shoulder at 1150 cm^{-1}. These peaks are not present in the series A and E1 showing there is no free silica in these samples (Fig. 7.4). For the silica gel/hydrolysed aluminium isopropoxide mixture there is a band at 790 cm^{-1} but no other band characteristic of silica. The small exotherm at 980°C in DTA means some reaction has taken place but sufficient to remove the silica gel structure. In series D there is a distinct shoulder at 950 cm^{-1} which is possibly due to silica that has not reacted with alumina but there are no other peaks that could be attributed to silica.

Amorphous hydrous alumina has bands at 780 cm^{-1} and 720 cm^{-1} as well as the intense band that is split with peaks at 1020 and 970 cm^{-1}. These bands are sharp in the crystalline hydroxide gibbsite with an additional band at 910 cm^{-1} (see Fig. 7.5).

In series E3 and E7 there are bands around 720 cm^{-1} and 780 cm^{-1} which are broad in E3 but sharpen up in the E7 sample (see Fig. 7.5).

In series B there are sharp peaks in the region 800-700 cm^{-1} due to bayerite and in series C several sharp peaks about 800 cm^{-1} probably due to boehmite (see Fig. 7.5).

The samples of ferric silicate mixed gels give spectra which seem a mixture of hydrous ferric oxide and silica gels with a series of peaks due to both (see Fig. 7.6).

7.3.4 CATION EXCHANGE

The cation exchange capacities of the aluminosilicates were determined using the methods described in section 4.4.5 except for a cracking catalyst, ion exchange resin and samples FA and FD which were determined at pH 7. The results are shown in Table 7.4.

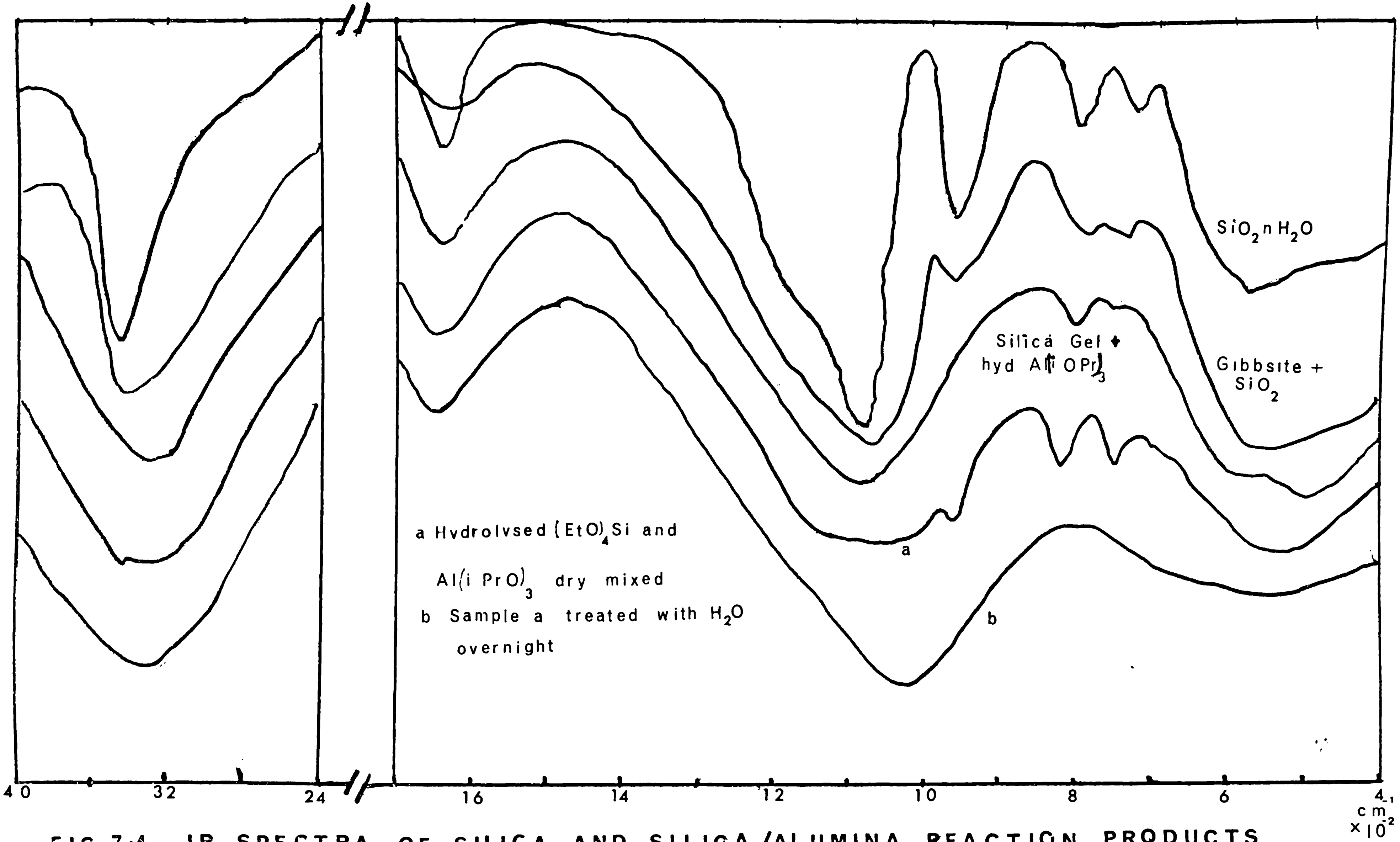


FIG 7·4 IR SPECTRA OF SILICA AND SILICA/ALUMINA REACTION PRODUCTS

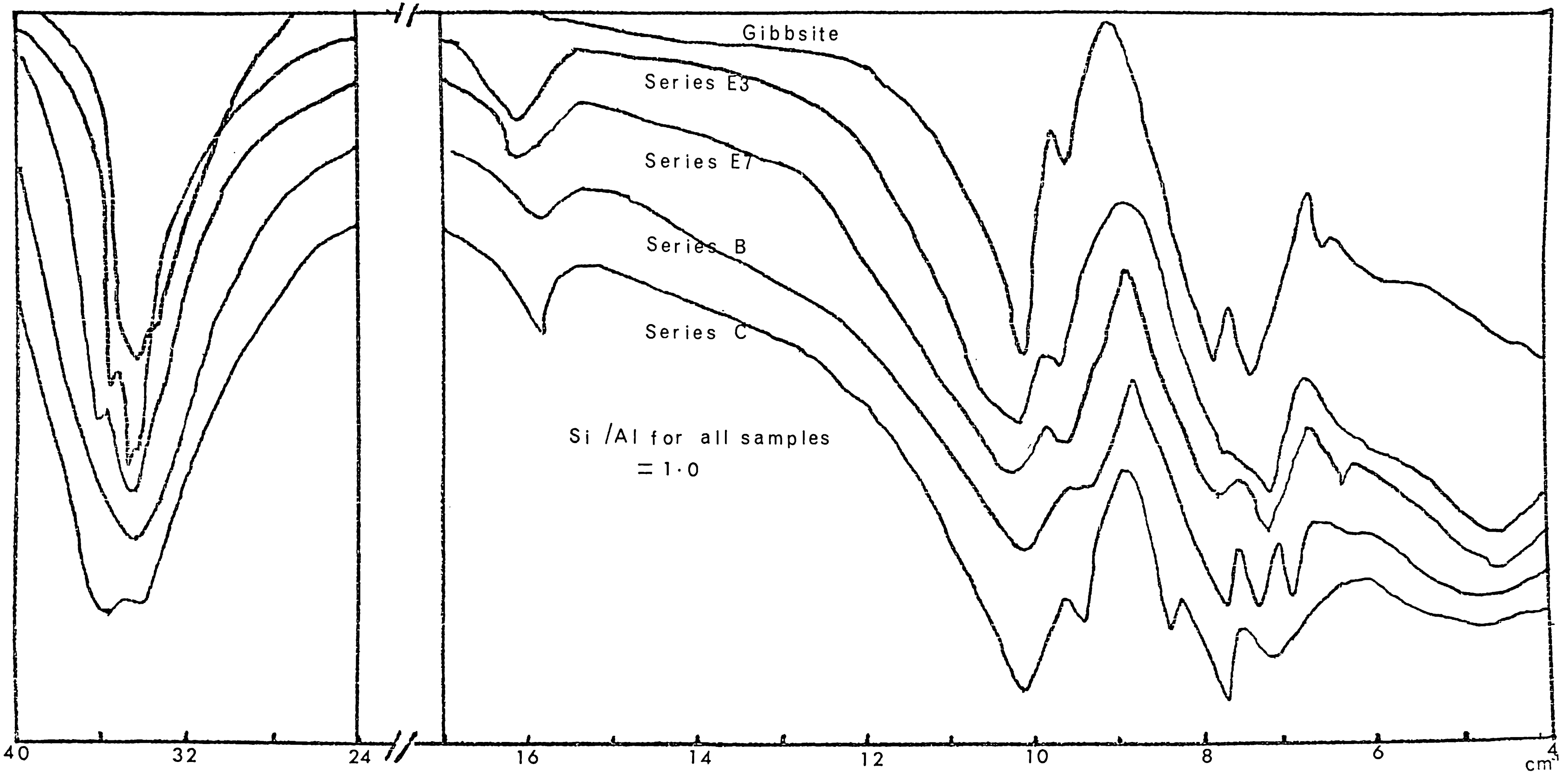


FIG 7·5 IR SPECTRA OF GIBBSITE AND ALUMINA/SILICA REACTION PRODUCTS

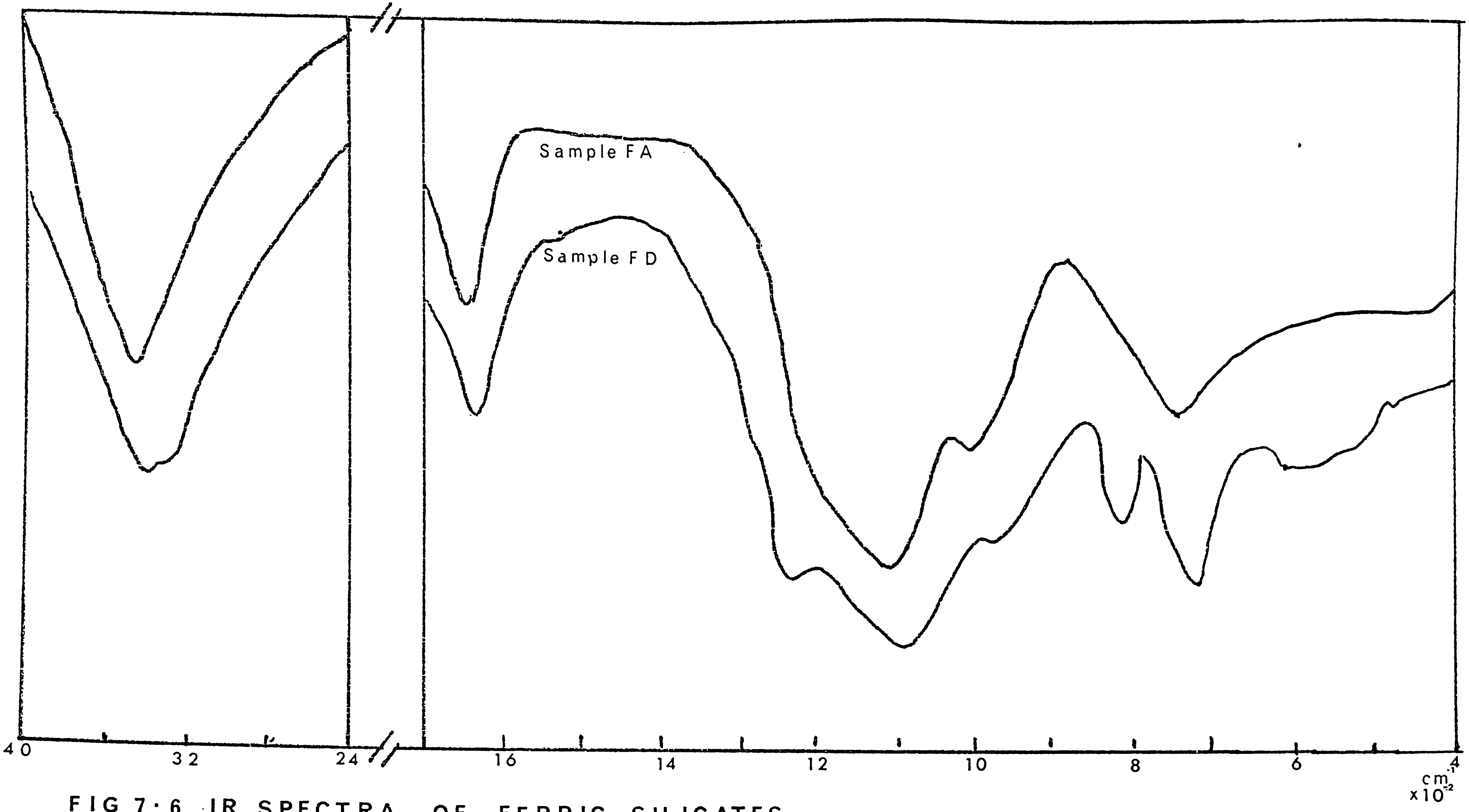


FIG 7·6 IR SPECTRA OF FERRIC SILICATES

Table 7.4 Cation Exchange Capacities of Aluminosilicates

(meq/gm)

		%Al_2O_3	pH 3.5	pH 7	pH 10.5	Δ CEC
$Al(OH)_3$ (amorphous)			0.17		0.19	0.02
SiO_2/Al_2O_3 =	1.24	57.9	1.00		1.48	0.48
	1.46	53.6	1.02		1.62	0.60
	2.18	43.8	1.09		1.80	0.71
	3.04	35.9	1.46		2.20	0.74
	7.03	18.8	1.07		1.79	0.72
Cracking Catalyst SiO_2/Al_2O_3 = 5				1.13		
Delcalso FF Ion Exchange Resin				2.98		
SiO_2nH_2O (amorphous)			0.08		0.08	
Sample FA				0.31		
FD				0.38		

The aluminosilicate samples were all completely soluble in boiling 0.5M NaOH. Treatment with boiling Na_2CO_3 dissolved most of the samples although they were not very soluble in the cold solution. Therefore the CEC value obtained at pH 10.5 is likely to be low since some of the sample will have dissolved.

The cation exchange capacities are higher at pH 3.5 than those of natural allophanes. This may be due to the short aging period which has left many active groups which, under natural weathering conditions, would combine giving a reduced activity.

The cracking catalyst was supplied by Nalco Chemical Co., U.S.A. and has a SiO_2/Al_2O_3 ratio of 5, and an $Al_2O_3/Al_2O_3 + SiO_2$ ratio of 25%. The maximum that has been noted by other authors is apparent since the last sample has a lower cation exchange capacity than the previous two. The cracking catalyst would appear to fill the gap between ratios 3.04 and 7.03. They all lie very much lower than the ion exchange resin which is based on a zeolite structure.

The ferric silicates both have lower cation exchange capacities than the aluminosilicates showing that little substitution has occurred.

7.3.4 P-RETENTION

A modified form of the method described by Saunders was used for series A samples (see section 4.4.6). The results are shown in Table 7.5.

Table 7.5 Phosphate Retention of Aluminosilicates

mole ratio SiO_2/Al_2O_3	% Al_2O_3	mg PO_4^{3-} ret/gm sample
0	100	v.v.high
1.24	57.9	30.82
1.46	53.6	28.03
2.18	43.8	34.02
3.04	35.9	33.46
7.03	18.8	26.88
∞	0	0
F.A.		22.19
F.D.		31.18

There is a minimum of phosphate retention at a SiO_2/Al_2O_3 ratio of 1.46. This ratio corresponds to a minimum for surface area (section 7.3.6). If the phosphate retention mechanism is an exchange with hydroxyl groups as suggested in Chapter 5, then this ratio could correspond to a minimum number of Al-OH groups available for phosphate retention. Saunders[134] stated that changes in phosphate retention of soils followed the amount of Tamm-soluble Fe and Al, i.e. amorphous oxides, within the soil profile. Fieldes[256] suggested that the tetrahedral sites could retain phosphate but this would appear unlikely since these sites have a negative charge associated with them. The very high retention of amorphous aluminium hydroxide shows that octahedral hydroxyaluminium on the aluminosilicate particles is capable of causing the phosphate retention without the need to invoke tetrahedral sites.

The phosphate retention for the aluminosilicates is greater than for the natural allophane samples. This is probably because the samples were not aged and contain more free Al-OH groups than allophane.

There are also no extraneous ions to block the sites as in allophane, the balancing ions being hydroxyaluminium which also will retain phosphate.

7.3.5 ISOELECTRIC POINT

The isoelectric points of the aluminosilicates were determined using the method outlined in section 5.5.

The results are shown in Table 7.6.

Table 7.6 Isoelectric Point of Synthetic Aluminosilicates

		Isoelectric Point
Amorphous hydrated SiO_2 ($(EtO)_4Si$ hydrolysis)		3
" " ($SiCl_4$ hydrolysis)		<3
Amorphous $Al(OH)_3$		7.8
$Al(OH)_3$ (freeze dried after aging 3 days)		6.2
Aluminosilicate SiO_2/Al_2O_3 =	1.24	5.2
	1.46	5.0
	2.18	4.8
	3.04	4.8
	7.03	4.2
Series D sample treated with $Fe(OH)_3$	1.0	3.7
	1.24	5.3
	1.46	5.0
	2.18	5.6

The isoelectric point of amorphous silica prepared from ethylorthosilicate hydrolysis is pH 3 or slightly less. It was difficult to estimate because of the hydrolysis of the acid solution. For silica prepared from silicon tetrachloride the value is well below 3, the limit of the apparatus.

For amorphous hydrous alumina from hydrolysed aluminium isopropoxide, the isoelectric point decreases as the hydroxide ages.

For the aluminosilicates, as the SiO_2/Al_2O_3 ratio increases the isoelectric point decreases ranging from 5.2 to 4.2. They are about one pH unit less than the allophane samples studied in Chapter 5 with the corresponding SiO_2/Al_2O_3 ratios. When treated with a suspension of ferric hydroxide (prepared by making a 10^{-2}M $FeCl_3$ solution and allowing to stand for 1 month) the isoelectric point is raised into the range of the natural allophanes.

The series D sample has a much lower isoelectric point than expected from its SiO_2/Al_2O_3 ratio showing the influence of organic matter that has leaked from the ion exchange columns.

Because the aluminosilicates do not have isoelectric points as high as the natural allophanes it would appear that iron plays a large part in determining the surface charge. Free alumina does raise the pH as seen with the low SiO_2/Al_2O_3 ratios, but any further Al_2O_3 added is likely to crystallize and lower the isoelectric point as seen with the two $Al(OH)_3$ samples.

7.3.6 SURFACE AREA

The surface areas of series A were determined using the method outlined in section 4.4.8. The results are tabulated in Table 7.7.

Table 7.7 Surface Areas of Amorphous Aluminosilicates

	p/p_o	W gm/gm	$\frac{p/p_o}{W(1-p/p_o)}$
$SiO_2(nH_2O)$	0.96	0.2249	106
	0.75	0.2137	14.04
	0.51	0.1948	5.34
	0.327	0.0952	5.10
	0.113	0.0360	3.54

Intercept 3.0 Slope 5.0

so $W_m = 0.125$ gm

$S_o = 439\ m^2/gm$

amorphous $Al(OH)_3$	0.96	0.617	38.9
	0.75	0.3411	8.80
	0.51	0.2887	3.61
	0.327	0.2297	2.11
	0.113	0.1587	1.13
	0.083	0.0798	0.80

Intercept 0.11 Slope 6.16

so $W_m = 0.1595$

$S_o = 560\ m^2/gm$

$SiO_2/Al_2O_3 = 1.24$	0.96	0.1874	1.28×10^2
	0.75	0.1863	16.1
	0.51	0.1719	6.05
	0.327	0.1700	2.85
	0.113	0.1323	0.966
	0.083	0.0170	

Intercept 0.24 Slope 6.53

so $W_m = 0.148$

$S_o = 520\ m^2/gm$

$SiO_2/Al_2O_3 = 1.46$	0.96	0.228	105
	0.75	0.216	13.89
	0.51	0.204	5.10
	0.327	0.196	2.52
	0.113	0.160	0.80

Intercept -0.36 Slope 7.71

so $W_m = 0.130$

$S_o = 455\ m^2/gm$

Table 3.7 cont.

	p/p_o	W gm/gm	$\frac{p/p_o}{W(1-p/p_o)}$
SiO_2/Al_2O_2 = 2.18	0.96	0.2461	97.8
	0.75	0.2442	12.3
	0.51	0.2191	4.75
	0.327	0.2103	2.32
	0.113	0.1427	0.894
	0.083	0.0282	0.300

Intercept 0.2 Slope 6.72

so W_m = 0.1445

S_o = 507 m^2/gm

SiO_2/Al_2O_3 = 3.04	0.96	0.495	48.5
	0.75	0.288	10.42
	0.51	0.241	4.32
	0.327	0.209	2.32
	0.113	0.146	0.87
	0.083	0.041	-

Intercept 0.09 Slope 6.83

so W_m = 0.1445

S_o = 507 m^2/gm

SiO_2/Al_2O_3 = 7.03	0.96	0.6043	39.8
	0.75	0.4990	6.03
	0.51	0.2820	3.69
	0.327	0.2062	2.35
	0.113	0.1260	1.01
	0.083	0.0210	0.44

Intercept 0.32 Slope 6.22

so W_m = 0.153

S_o = 537 m^2/gm

The surface areas are of the same order as the natural allophanes. There is a minimum at SiO_2/Al_2O_3 = 1.46. This also corresponds to the minimum of P-retention and may indicate that a change in structure is occurring.

7.4 DISCUSSION

Generally the co-hydrolysed aluminosilicates behave in the same way as natural allophanes. They have the same DTA patterns, IR spectra and CEC behaviour although the actual CEC is higher possibly due to the fact that the gels were not aged for more than three days. The other likely reason is that for the natural allophanes some of the negative charge will be neutralized by iron and so reduce the cation exchange capacity measured.

In practically all samples there has been a chemical reaction between the hydrated alumina and silica to form Al-O-Si bonds, presumably with the elimination of water. For the noncrystalline products there is no evidence for discrete hydrated alumina or silica which means that there can be no definite composition for an amorphous aluminosilicate. This interaction of colloidal hydrous alumina and silica has been noted before[155,222] and attributed by Eitel[222] to attraction of opposite charges on the colloids but he did not suggest any chemical bond formation. Iler[223] has noted that there is a marked increase in viscosity of the mixture if coagulation takes place but that if either colloid is present in excess then there is no coagulation because of a complete reversal of charge. He further noted that the absorption of colloidal alumina was less on pure silica than one with impurities since most silicous surfaces contaminated with trace amounts of alumina are negative to pH 3 or 4. The compounds from the references quoted by Eitel[222] suggested a mixed gel with the approximate composition of $Al_2O_3 2SiO_2 2H_2O$ which was termed 'prokaolin' and which remained amorphous for several years.

Jones and Handreck[226] investigated the effects of ferric and aluminium salts on silica adsorption at varying pHs and found the best range for adsorption was between pH 4 and 10. This is in accordance with what is known of the oxides. At pH's much greater than 8 the charge on hydrated alumina and ferric oxides becomes increasingly more negative and so repels the silica particles which themselves will start dissolving at the high pH. As the pH approaches the lower limit the metal oxides will tend to dissolve and the charge of the hydrous silica will decrease, eventually becoming positive.

The samples showing discrete alumina in the IR have crystalline aluminium hydroxide present. These samples are usually the series in which the hydrated alumina had been aged before being added to the silica suspension. Mackenzie et al[224] suggested that there was no true amorphous aluminium hydroxide formed after aging. The non-appearance of any characteristics of the aluminium hydroxides or oxyhydroxides in the aluminosilicates formed by co-hydrolysis under neutral conditions suggests silica is able to stabilize the amorphous form of alumina, or at least inhibit crystallization. Certainly in allophane samples crystallization has taken thousands of years to form clay minerals such as halloysite under natural weathering conditions.

The isoelectric point of the samples was at least one pH unit lower than those for the allophanes studied in Chapter 5. The values for the isoelectric point of amorphous hydrous alumina have been reviewed by Parkes[172] and could be as high as 9 but the value for the crystalline forms are much lower. If the high isoelectric point of allophanes is due in some way to aluminium species it would be expected to be noticed in the synthetic aluminosilicates which have not been weathered and contain only silica and alumina and no contaminating species. The observation by Mackenzie et al[224] that amorphous aluminium hydroxide crystallized on aging would possibly mean that on further aging the isoelectric point of the aluminosilicates would be lowered still further due to crystallization to gibbsite of the octahedrally coordinated aluminium. Gibbsite has been noted in the older allophane samples and it is apparent that if the weathering scheme proposed by Fieldes[56] is followed aluminium must be lost from all of the natural samples, some of this probably crystallizing as gibbsite.

The immediate rise in isoelectric point noted when ferric hydroxide is added to the samples shows that iron is important in the surface charge of allophane and aluminosilicates.

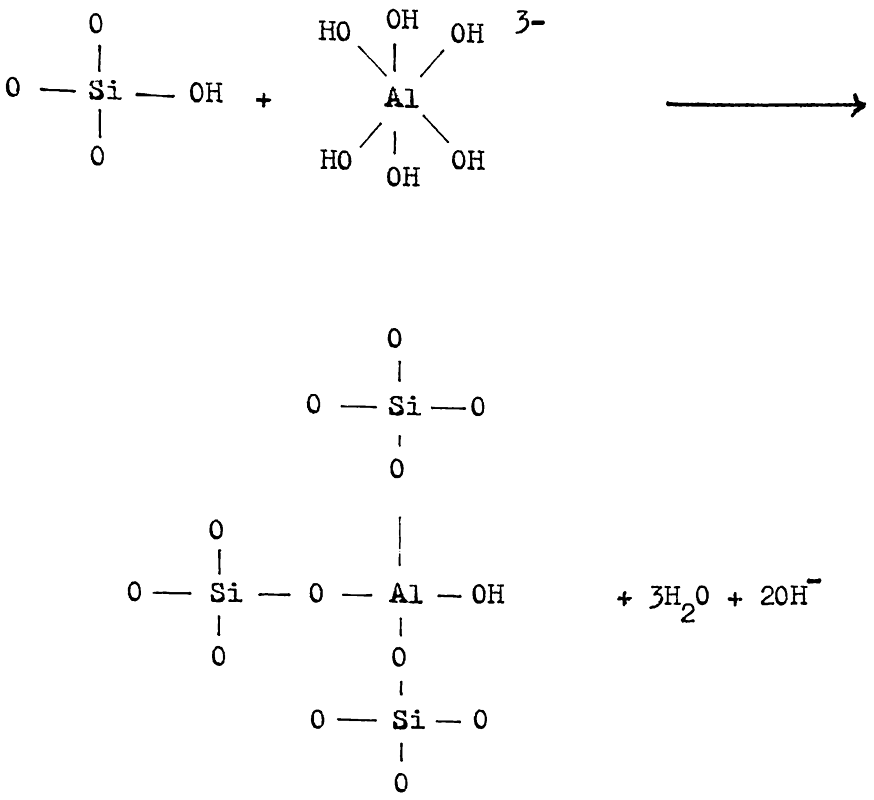
Hydrous ferric oxide is also able to form mixed gels with hydrous silica. The IR spectra show peaks due to discrete hydrous silica and ferric oxide so there is no chemical bond formed.

Iler[227] has suggested that a bond of the type

$$\mathrm{Fe(OH)_2^{2+}} + \equiv\mathrm{Si{-}OH} \longrightarrow \equiv\mathrm{Si{-}O{-}Fe(OH)_2} + \mathrm{H^+}$$

is formed since work by Hazel et al[228] has shown that there is some release of protons on interaction of hydrous silica and ferric oxide and suggested a moderately strong ferrisilicic acid was formed. But work by Trichet[225] and Herbillon and Tran Vinh An[229] led these authors to conclude that SiO_2 was chemisorbed onto the hydrous ferric oxide and that further silica polymerization took place on the chemisorbed silica.

An acid does appear to be formed with the hydrous alumina-silica reaction since Tamele[214] has found that four equivalents of base were needed to neutralise aluminium chloride in the presence of silica, three for the chloride and one for the alumino-silicic acid formed by the reaction:



Dry mixtures of aluminium hydroxide (gibbsite) and silica gel do show characteristics of a discrete mixture of alumina and silica, even after wetting. If the aluminium hydroxide and silica, products from freeze drying of the hydrolysis products from organoderivatives are mixed, they too show characteristic bands in the I.R. spectra but on moistening and leaving for 12 hours, most of the bands disappear to be replaced by the single band of amorphous aluminosilicate showing that interaction has taken place. This confirms the ideas of Hazel et al[228] that chemical bonds are formed. Thus it appears impossible to prepare a mixed gel of hydrous alumina and silica where discrete centres of alumina and silica are present, sufficient to show properties characteristic of the individual oxides.

Since the hydrous alumina gels readily formed crystalline products of bayerite and boehmite on aging it is probable that in the gel the aluminium is six-coordinated. To form an aluminosilicate with the characteristics of allophane, the aluminium must change its coordination number from 6 to 4 so there must be some movement of Al^{3+} ions into the framework of silica tetrahedra.

It has been suggested that the octahedral hydroxide patterned the formation of the lattice layers by orientating the SiO_4^{4-} tetrahedra and this was confirmed by De Kimpe and Gastuche[230].

The similar ionic radii of aluminium and silicon, 0.50 and 0.41Å respectively, means substitution can take place and aluminium can be isomorphously substituted in the formation of aluminosilicate gels without any appreciable strain. In this case however the aluminium hydroxide does not seem to be dictating the formation pattern. Ethyl silicate does not hydrolyse as rapidly as aluminium isopropoxide and yet a crystalline product is not obtained. It is possible the alcohol inhibits crystallization. In the next chapter the presence of large amounts of alcohol does not have any effect on Al uptake on a freshly cleaved mica surface which is negative so is unlikely to cause any effect on the formation of aluminosilicate bonds. This is unlike organic acids which can complex aluminium. This was shown to occur with series D which have atypical properties.

7.5 CONCLUSION

Fresh solutions of hydrous silica and amorphous hydrous alumina will react forming Al-O-Si bonds. The aluminosilicates have isoelectric points below 5.2. They are able to attract hydrous ferric oxide forming an electrostatic complex raising the isoelectric point into the range of the natural allophanes. Addition of further alumina is unlikely to raise the isoelectric point because of crystallization of aluminium hydroxide on aging. Organic acids can partially prevent the formation of Al-O-Si bonds and neutralize the surface charge lowering the isoelectric point.

Hydrous ferric oxide and silica will form a mixed gel but no Fe-O-Si bonds are formed. The gel is held together with electrostatic bonds.

CHAPTER 8. ALTERNATIVE SYNTHETIC APPROACH - REACTIONS OF COLLOIDAL PARTICLES WITH EACH OTHER AND WITH SURFACES

8.1 INTRODUCTION

The results in Chapter 5 showed the importance of colloidal properties in a study of allophane and the need to study the interaction of colloidal particles with each other. In allophanic soils the surfaces of sand and silt particles will be coated with colloidal allophane.

To confirm that colloidal hydrous alumina and silica would react and also to see if colloidal hydrous ferric oxide and silica would react the interactions of the colloidal particles were studied.

The difficulty of studying the reactions of colloidal particles has been overcome by adsorbing the positively charged colloids onto the 001 surface of freshly cleaved muscovite mica. Mica is very good for this purpose since it is inert, negatively charged, and can be readily cleaved providing a clean smooth surface of known structure similar to that of several clay minerals.

8.2 LITERATURE SURVEY

Iler[231] has been able to sorb alternate layers of positively and negatively charged alumina and silica colloids onto the surface of glass. The colloids used were a crystalline hydrous alumina, boehmite, and silica of approximately 100 $m\mu$ diameter. No chemical reaction was noted between the layers and several layers could be deposited, sufficient so that the layers could be seen by interference. However, the colloidal particles were large and the alumina crystalline. From the previous section it has been shown that little reaction between crystalline aluminium hydroxide and silica occurs over a period of several months.

Matijevic et al[232] have shown that coagulation in sols is caused by polymerized hydroxy-aluminium species and not simple Al^{3+} ions. Iler[231] found that aluminium was not adsorbed onto glass and so could not adsorb silica unless the aluminium sample had sufficient alkalis added to correspond to a ratio Al^{3+}:OH of 2.5 which rendered the hydroxy-aluminium complex positive.

Workers at Victoria University of Wellington[234-239] have studied the adsorption and retention of anions on the freshly-cleaved surface of treated muscovite in an attempt to gain insight into the mechanism of phosphate retention and fixation. The results of these studies led Hoare[240] to conclude that phosphate was absorbed into small spherical particles deposited on the mica surface. The particles formed from treatment with $AlCl_3$ and were probably hydrolysed aluminium particles. The presence of hydrolysed species on the surface was confirmed by Langdon[241] and Perrott[242]. Perrott[242] studied the effects of phosphate adsorption on mica treated with many cations and found P32 phosphate was adsorbed by mica only after it had been treated with hydrolysed samples of Fe^{3+}, Al^{3+}, Cr^{3+}, Th^{4+} and Zr^{3+}.

This method gives a controlled way of placing a known ion on the surface of mica. The negative charge density is somewhat higher than that for glass and so allows for a higher ion uptake.

The work at Victoria University has confirmed that hydrolysed cations or hydroxy complexes can be adsorbed onto the surface of mica and experiments have shown that the particles are not easily removed by desorption or washing treatments.

The minute quantities of material adsorbed (mica has one cation exchange site for every 50Å) means that concentrations of the order of 10^{-10} moles/cm^2 must be detected and the only satisfactory way found was using radio isotopes.

Unfortunately there is no suitable Al isotope to study the movement of Al in any system. But by limiting the number of possible cations in a system it has been possible to deduce the presence of aluminium using the reaction with radiophosphate as an indicator. However this means the surface has then been modified and so cannot be studied further but by using a series of experiments, one at each stage, the development can be followed.

The lack of any suitable Al radioisotope led workers at Victoria University to study the reactions of the iron analogue since two suitable iron isotopes are available, Fe-55 and Fe-59. The uptake of P-32 on iron treated mica surfaces has also been studied and shown to proceed in the same way as the uptake on alumina-treated mica.

8.3 EXPERIMENTAL PROCEDURES

Previous workers had great difficulty with contamination due to insufficient washing and cleanliness. The presence of small amounts of dust and oil contaminated the mica surface and caused uneven adsorption of phosphate. A detailed description of how the clean technique was devised has been reported by Perrott[242] and the history will not be gone into here. Only the necessary details for this work are discussed.

Pyrex glass apparatus was used since this was easier to clean and has been shown by Rees[265] to cause no more contamination than polythene. Some of the volumetric-ware used was soda glass but this did not appear to have a detrimental effect on results. Glassware was cleaned in a mixture of approx. 1:6 $HNO_3:H_2SO_4$. This was kept in a 2 l beaker standing in an aluminium pot partly filled with sand and heated by a hot plate controlled by a simmerstat to 110°. Stainless steel implements were cleaned in this bath and rendered passive by the addition of a fresh amount of nitric acid each time the bath was used. Hard plastic tops were used for volumetric-ware and these were soaked in a cold 1:1 nitric:sulphuric acid mixture for 24 hours.

All apparatus was removed with stainless steel tongs, washed first under running hot water to remove any acid, and then with distilled water at least three times and stored in a box in cleaned test tubes held in p olyurethane holders. These were kept as dust free as possible by a clear sheet plastic cover (see plate 8.1). When necessary the apparatus was dried under an infrared lamp.

The apparatus was handled with clean disposable plastic gloves.

Previous workers have used several methods for observing uptake on mica surfaces and modifications of these were used.

Mica sheets were cut into convenient sizes and used in the "dust-free box". A piece was taken by clean forceps, split with a sharp needle, trimmed with clean scissors on three sides and hung on a chromatography clip. A clean pair of forceps was used to handle the freshly cut edges of mica which was trimmed with a further pair of scissors which cut only fresh mica and then placed on the spotting device or in a beaker (see later section).

Perrott[242] used a technique where he added sodium hydroxide to a solution of aluminium chloride in the mole ratio 2:1, added 10^{-5}M KH_2PO_4 and 1 drop of high specific activity P-32 solution. Adsorption was studied using a so-called spotting technique devised by Langdon[241] (apparatus shown in plate 8.2). This allowed a fresh solution to come in contact with a clean surface of mica. When the time of treatment had elapsed the mica piece was wetted to avoid uptake of radioactive solution by the edges, and then rinsed with distilled water from a wash bottle and the mica dried under an infrared lamp.

This method was used to study any effects ethanol or isopropanol had on the uptake of hydrous alumina complexes as it was proposed to use

Plate 8.1

Clean Box for Protection Against Dust

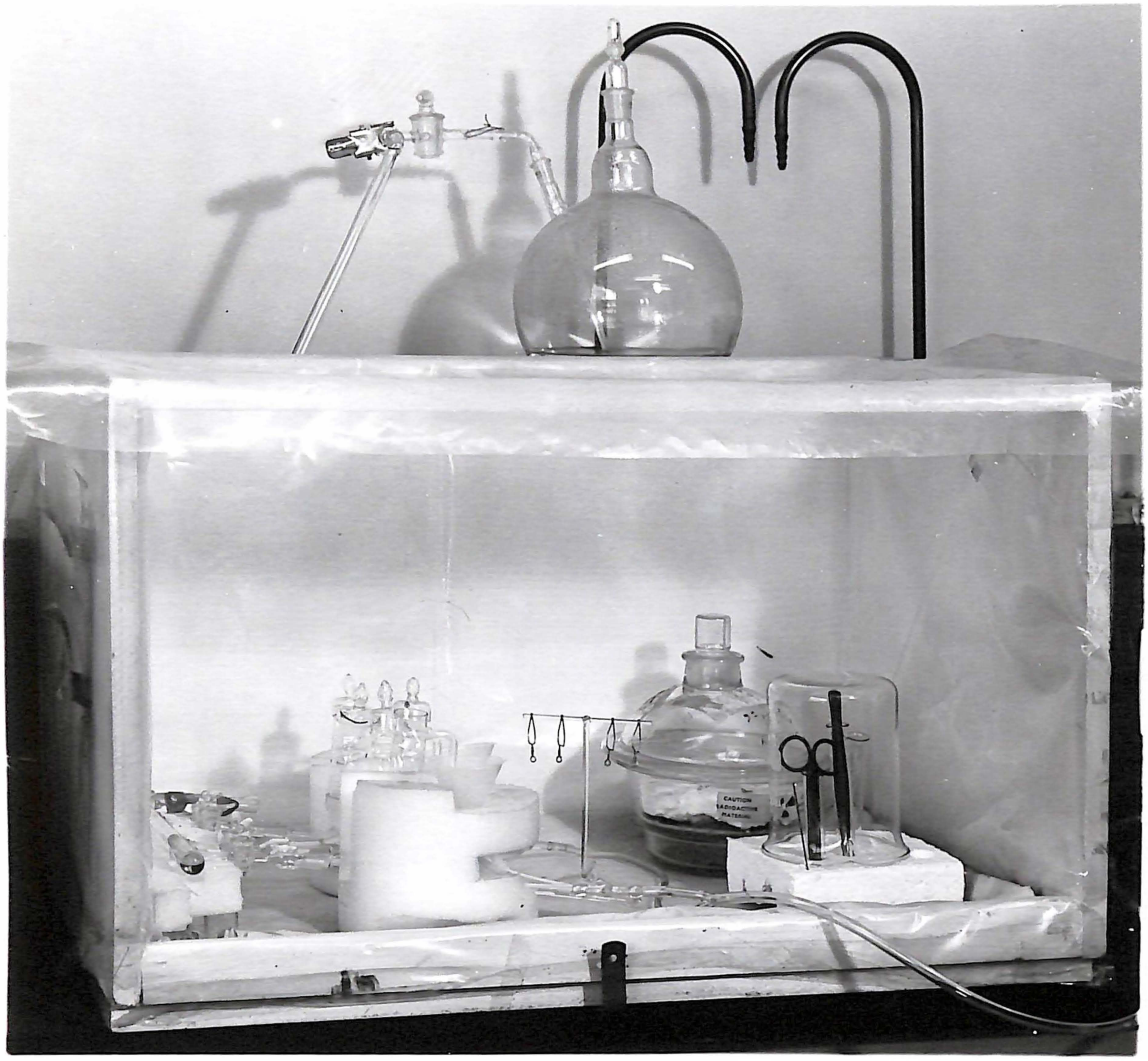
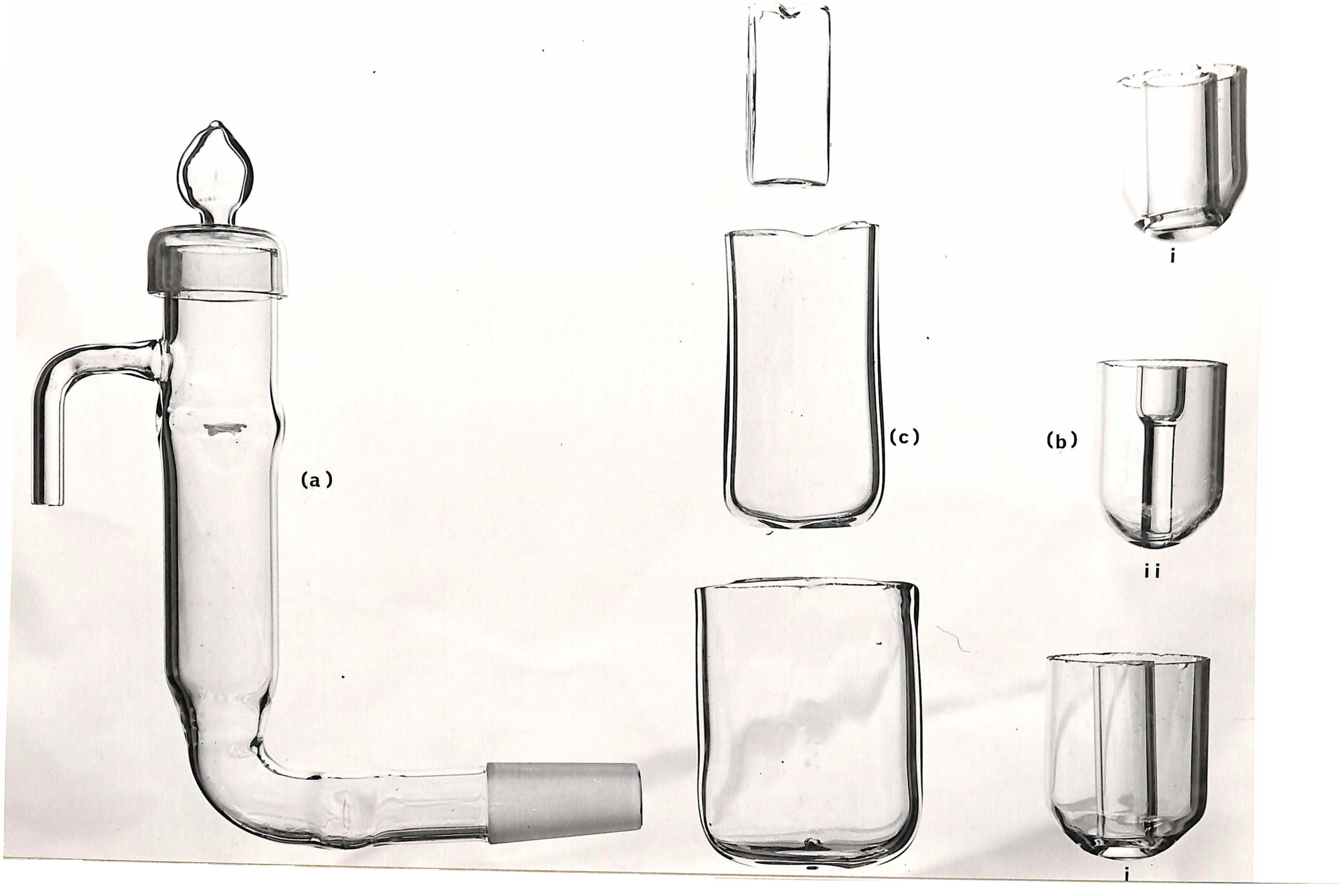

CAUTION
RADIOACTIVE
MATERIAL

Plate 8.2

(a) Washing device

(b) Spotting devices
  (i) for P32 solutions
  (ii) for Fe59 solutions

(c) Mini and maxi beakers


(a)
(c)
(b)
i
ii
i

organo derivatives to obtain hydrous Al_2O_3 and SiO_2 colloids free from other ions.

Perrott found that the greatest amount of phosphate adsorbed on pretreatment with $AlCl_3$ was at concentration of 10^{-3}M $AlCl_3$ but found streaking occurred as hydrolysis took place. To overcome this, runs were made using 10^{-3}M $AlCl_3$ with sufficient sodium hydroxide added to make up to 2×10^{-3}M OH^-. This ensured formation of a hydrolysed aluminium species. A fresh solution was made up each time.

The procedure followed was to make up a series of 10 ml volumetric flasks containing 10^{-3}M $AlCl_3$, 2×10^{-3}M NaOH, 10^{-6}M KH_2PO_4 plus 3 drops of carrier free P-32 solution and the required concentration of alcohol. Two spotting devices were then filled and overflowed with a clean dropper, and a freshly cleaved piece of mica placed over each and left for 100 mins when the mica was removed, rinsed with distilled water from a washbottle and then dried under an I.R. lamp. One drop of the solution was placed on a weighed aluminium planchet, reweighed to determine the volume of solution (density assumed equal to 1) and dried under an I.R. lamp. The pieces of mica were then autoradiographed. When the autoradiographs had been developed, a suitable area was selected and a punch taken of the mica sample (either 0.322 sq.cm or 0.200 sq.cm depending on uniformity of surface). This was placed on an Al planchet and counted in the counting set-up described below. The planchet with the corresponding solution was counted between the two samples. The half-life of P32 (14.3 days) is long enough not to have to allow for decay provided the samples are counted within several hours of each other. In order to provide reasonably short counting times the activity of the solution needed to be high $\sim 10^5$ cts/min/ml. This gives about 3000 cts/min for 1 drop which is about 0.03 ml. The activity on the surface varied but usually ranged from about 100 cts/min/cm^2 to 1000 cts/min/cm^2 depending on the adsorption coefficient.

When working with organoderivatives sufficient aluminium isopropoxide in a saturated dry ethanol solution was added to 250 mls of water to make up a 10^{-2}M solution of Al and the solution shaken overnight and used the next day. For working runs 1 ml of the hydrolysed solution was taken and made up to 10 ml to give solutions 10^{-3}M in Al. The solutions were kept no longer than 1 day since the work from the previous chapter showed that crystallization takes place rapidly after the initial hydrolysis.

Ethyl silicate was dissolved in dry ethanol and made up to 10^{-1}M. Then 25 mls were taken and made up to 250 mls in a polythene flask and shaken for three days. Hydrolysis of ethyl silicate is slow but the characteristic smell of ethyl silicate has gone after two days of continuous shaking, and a freeze dried sample of the hydrolysate, dried at 60° shows no evidence for CH bands which would be expected if incompletely hydrolysed ethyl silicate was present.

The 10^{-2}M solution of hydrous silica was kept in the dark and diluted to 10^{-3}M for a working solution. The stock solution was kept for one week only to avoid any build up of highly polymerized silica.

The treatment of mica was modified to accommodate a succession of treatments. The strip technique described by Perrott[242] and Langdon[241] was the second method used.

A hydrous alumina solution was placed in a beaker (plate 8.1) and a long, freshly cleaved piece of mica placed in it. After 100 mins this was removed and washed in a washing device described by Perrott[242] (plate 8.2). It was then either placed on a spotting device to determine phosphate uptake or placed in another beaker containing hydrous silica solution and left for 100 mins before being removed, washed and placed on a spotting device containing phosphate. Further pieces of hydrous alumina and silica treated mica were placed alternately in hydrous alumina and silica solutions and then phosphate adsorptions studied.

Samples were run leaving the mica in $Al(OH)_3$ solutions overnight before phosphate treatment and silica treatment.

Attempts were made to prepare an organo-iron derivative as described by Bradley et al[243] but without success. Since Lamb and Jacques[244] showed that little Cl^- ion was adsorbed in the formation of ferric hydroxide and in clay minerals phosphate adsorption blocks Cl^- adsorption, solutions of partially hydrolysed $FeCl_3$ were used. To prevent any chlorocomplexes from forming, a fresh solution of 10^{-2}M $FeCl_3$ was made up each day from BDH AnalaR ferric chloride solution and for working solutions diluted to 10^{-3}M solution to which was added 2×10^{-3}M NaOH.

Mica was also treated successively with ferric hydroxide solution and silica solution and the surface studied with phosphate uptake.

To test the possibility that the ferric hydroxide layer was being removed by silica treatment the experiments were repeated using Fe-59 as a tracer in the $FeCl_3$ solution, being added before the sodium hydroxide solution.

Because it was difficult to obtain carrier free iron as Fe-59 and because the efficiency of the end window counters was low for the high energy gammas this meant that high concentration of iron tracer was needed and specially designed spotting devices were used with a solid core and a small cup on the end (Plate 8.2).

Reagents

The reagents used were AnalaR grade wherever possible. The aluminium foil for making aluminium isopropoxide was laboratory grade, as was the ethyl silicate which was redistilled. The P-32 was supplied as high specific activity carrier free orthophosphate and the Fe-59 as high activity $FeCl_3$ from Amershams, England.

Counting Gear

The counting gear used was Philips described in detail by Hoare[240]. The errors involved in radioactive counting can be reduced by increasing the number of counts made. This can be done either by using long counting times or having high specific activity. A high activity was aimed for with samples from solutions having count ranges about 5000 counts per minute. With high count rates coincidence corrections are needed and a table of coincidence corrections was compiled using the formula

$$\text{True count rate} = \frac{\text{observed count rate}}{1 - \tau \times \text{observed count rate}}$$

where τ is the dead time of the counter.

τ was set to 600μ secs using an electronic quench calibrated by an oscilloscope. The treatment of errors is discussed by Perrott[242], Langdon[241] and Hoare[240]. For high adsorption of phosphate Perrott suggested a total variation ~ 12% or less which seems reasonable since the error in counting is likely to be less than 5%, provided the total number of counts recorded are more than 5000 counts.

8.4 RESULTS

The results are expressed as either an adsorption coefficient k

$$k = \frac{A_l}{A_s}$$

where A_l is activity of liquid in cts/min/ml

A_s is activity of surface in cts/min/cm^2.

The units of k are cm.

or as the number of ions adsorbed per sq.cm using the formula derived by Hoare[240].

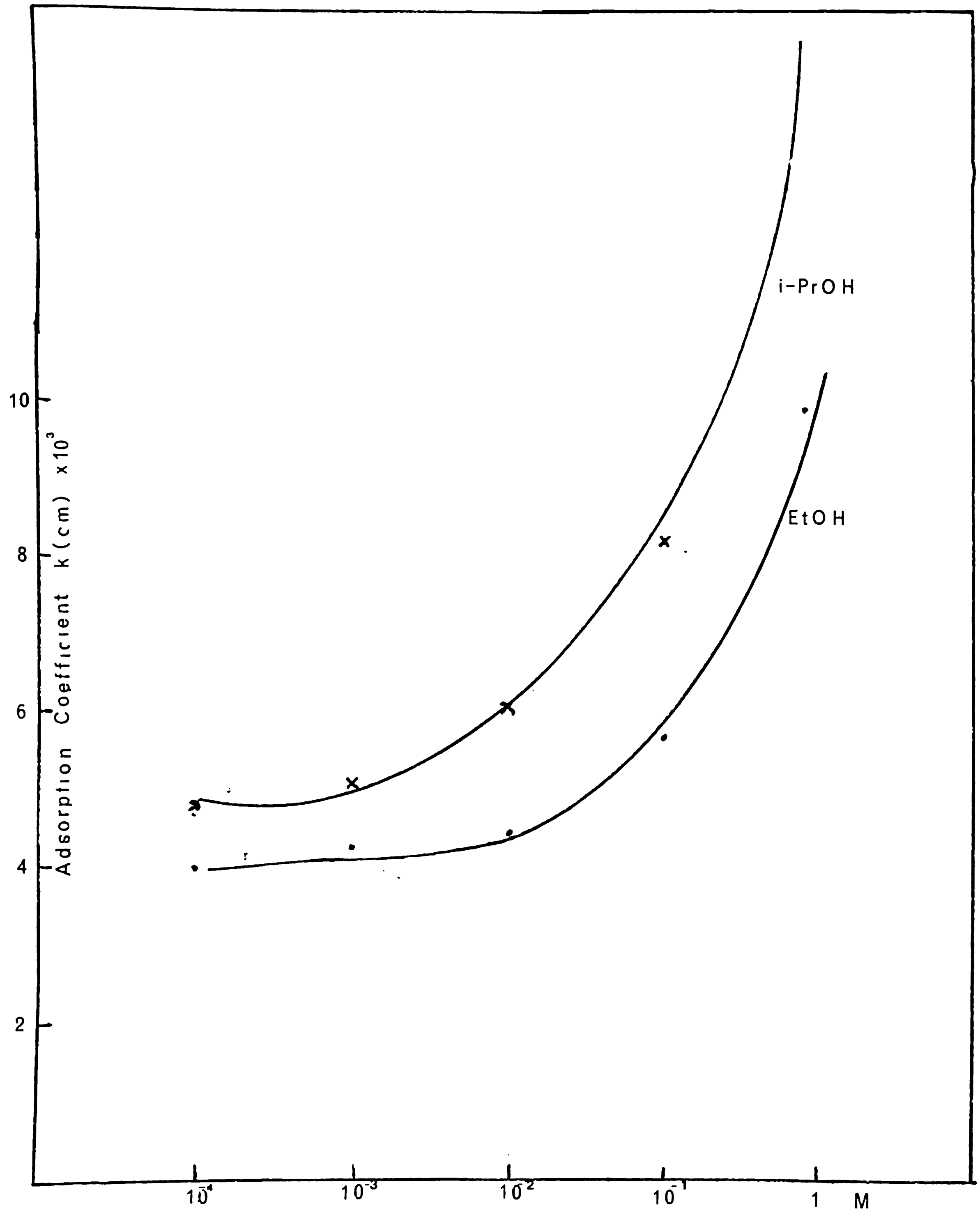


FIG 8·1 - ADSORPTION COEFFICIENT FOR P^{32} UPTAKE ON MICA TREATED WITH Al^{3+} AND ALCOHOLS

Table 8.2 and Fig. 8.2 show the results of using alcohols with progressively longer alkyl chains. As the alkyl chain is increased in length then the molecules become more hydrophobic and force the positively charged hydroxyaluminium complex with its associated phosphate out of solution onto the negative mica surface.

Table 8.2 Adsorption coefficients with alcohols

Conc.	BuOH kx10^3	i BuOH kx10^3	t BuOH kx10^2	OcOH kx10^2
10^{-4}M				0.429
10^{-3}M	7.50	4.15	4.04	5.37
2x10^{-3}M	19.1	5.83	4.92	-
10^{-2}M	41.1	22.4	7.70	

The straight chain carboxylic acids give a different pattern as shown in Table 8.3 and Fig. 8.3.

Table 8.3 Adsorption coefficients for P-32 uptake on treatment of 10^{-3}M Al^{3+} with organic acids

k x 10^3 (cm)

	CH_3COOH	C_2H_5COOH	C_3H_7COOH	$C_5H_{11}COOH$	$C_7H_{15}COOH$
10^{-1}M	2.63	3.01	3.80	3.82	-
10^{-2}M	2.81	3.52	3.91	3.98	4.89
10^{-3}M	3.45	3.86	4.04	4.01	4.67
10^{-4}M	3.61	3.89	4.03	4.04	4.54
10^{-5}M	3.84	3.94	4.00	4.24	3.88
Std	4.03				

Values are mean of three results.

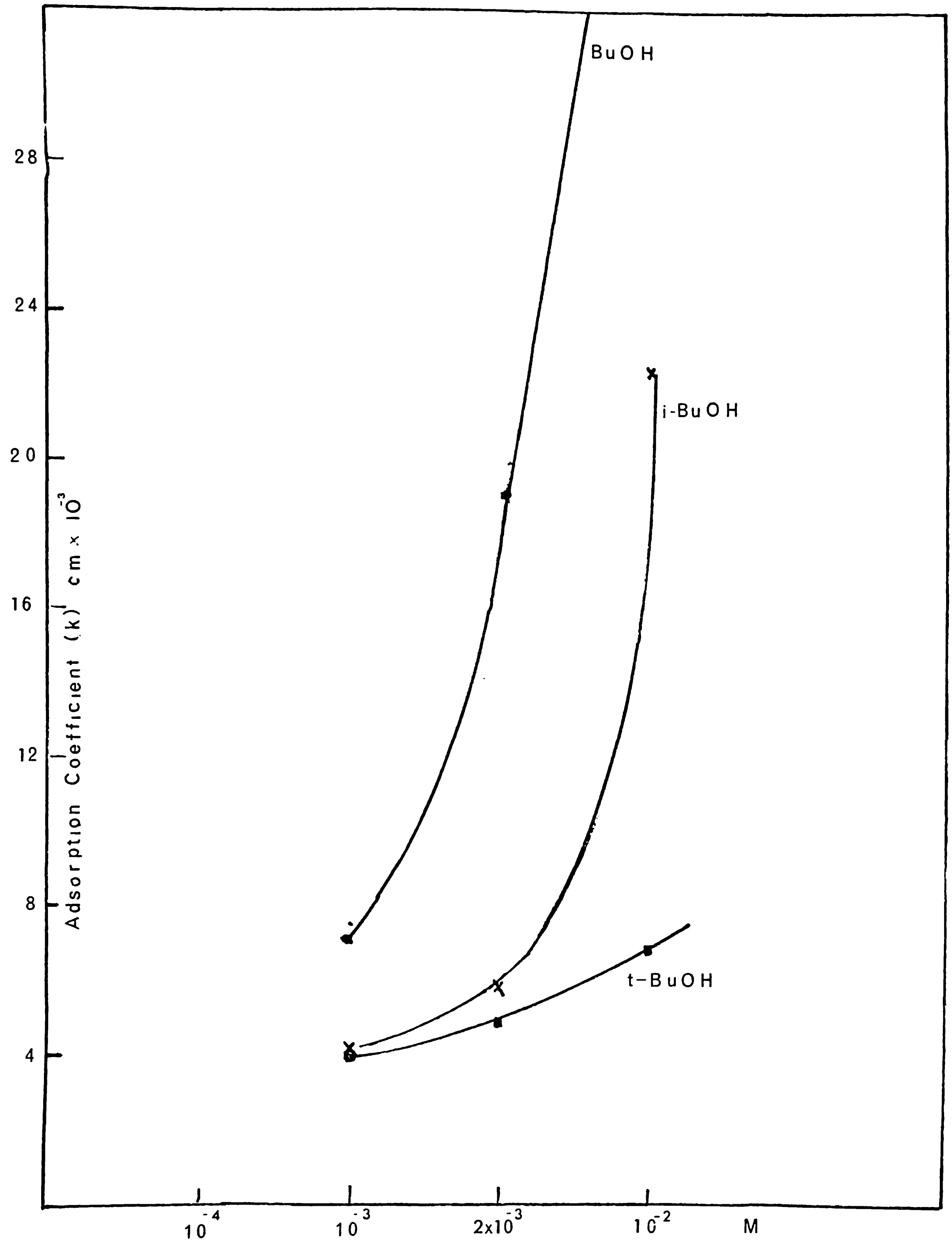


FIG 8·2 ADSORPTION COEFFICIENT FOR P^{32} UPTAKE ON MICA WITH TREATMENT Al^{3+} AND ALCOHOLS

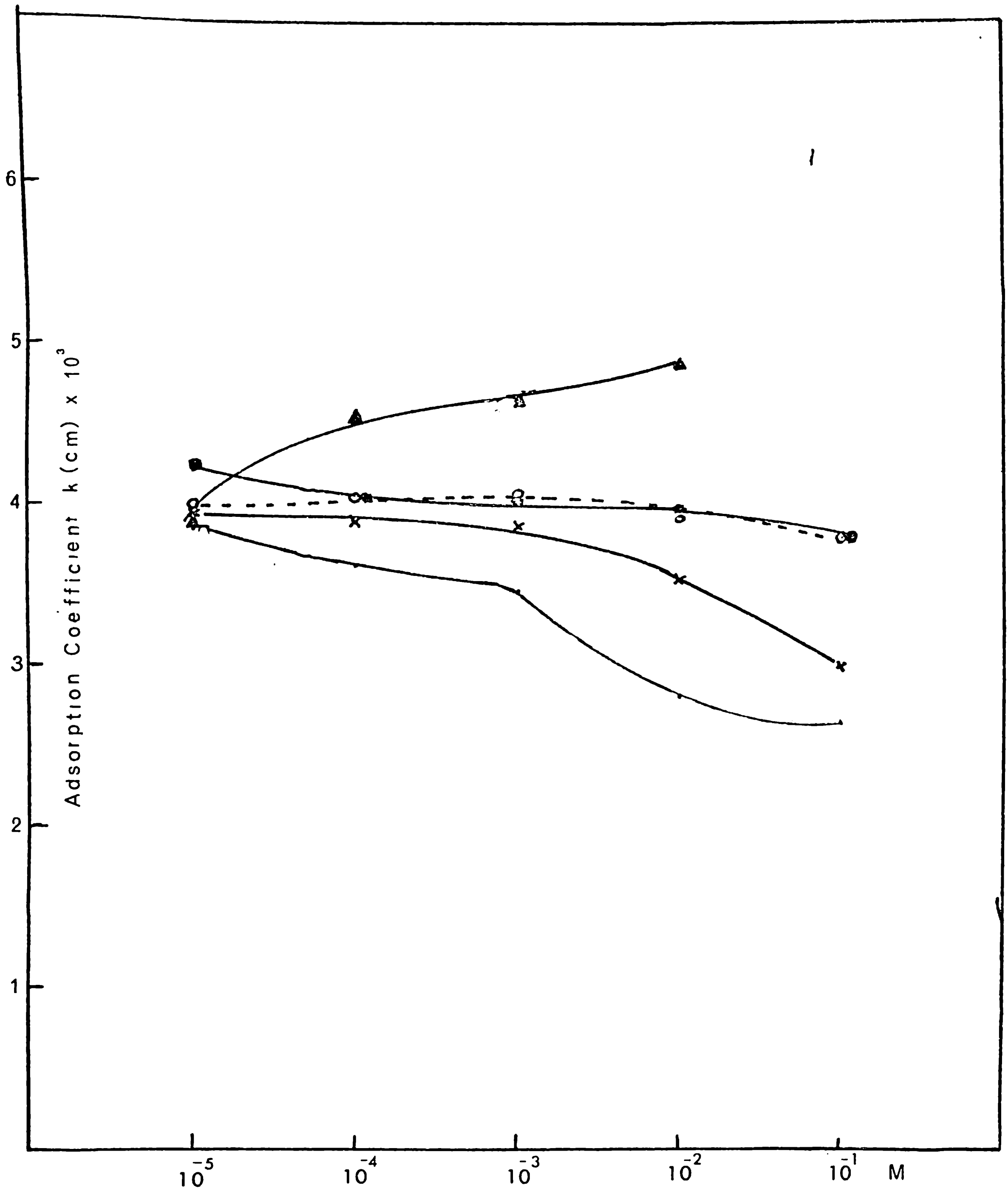


FIG 8·3 ADSORPTION COEFFICIENTS FOR P^{32} UPTAKE ON MICA WITH TREATMENT WITH 10^{-3}M Al^{3+} AND ORGANIC ACIDS

●——● acetic
×——× propionic
○——○ butyric
■——■ hexanoic
▲——▲ octanoic

The more soluble acids, acetic and propionic, show less uptake whereas as the chain length is increased an increased uptake is noted. This is probably due to precipitation of aluminium alkylate which because of the greater concentration of aluminium species is positively charged and so adheres to the mica surface. A sharp change is noted between 10^{-3}M and 10^{-2}M concentration for acetic and propionic acid when the aluminium is neutralized and then assumes a negative charge due to adsorbed alkylate ion and so adsorption on mica is reduced.

The lesser adsorption for the lower acids is probably due to complex species which remain in solution until neutralization occurs. With organic acids with stronger complexing groups such as the humic acids the phosphate uptake on mica would be likely to be greatly reduced as most of the aluminium would be complexed. This would explain the apparent non-interaction of silica and alumina in the series D sample in the previous chapter since the reactive groups have complexed with organic groups and are unavailable for silica interaction. The results of phosphate uptake after alternate treatment with hydrous silica and alumina are shown in Table 8.4 and Fig. 8.4.

Table 8.4 Absorption coefficients for P32 uptake for alternating treatment with hydrous alumina and silica

	hyd $(i\text{-OPr})_3Al$		10^{-3}M Al^{3+} + 2×10^{-3}M OH^-		10^{-2}M Al^{3+} + 2×10^{-2}M OH^-	
	ions/cm^2	k(cm)x10^2 *	ions/cm^2	k(cm)x10^3 *	ions/cm^2	kx10^2(cm) *
Al layer	1.47×10^{13}	2.45	5.47×10^{12}	9.13	3.09×10^{13}	5.12
Si layer	0.54×10^{13}	0.898	0.874×10^{12}	1.45	1.80×10^{13}	3.00
Al layer	6.13×10^{12}	1.02	1.95×10^{12}	3.23	2.64×10^{13}	4.38
Si layer	4.10×10^{12}	0.681	1.14×10^{12}	1.89	1.74×10^{13}	2.89
Al layer	5.55×10^{12}	0.921	1.74×10^{12}	2.88	2.13×10^{13}	3.71
Si layer	4.83×10^{12}	0.802	1.23×10^{12}	2.04	2.47×10^{13}	4.11

* Figures are average of at least three determinations.
Error less than 1% for average.

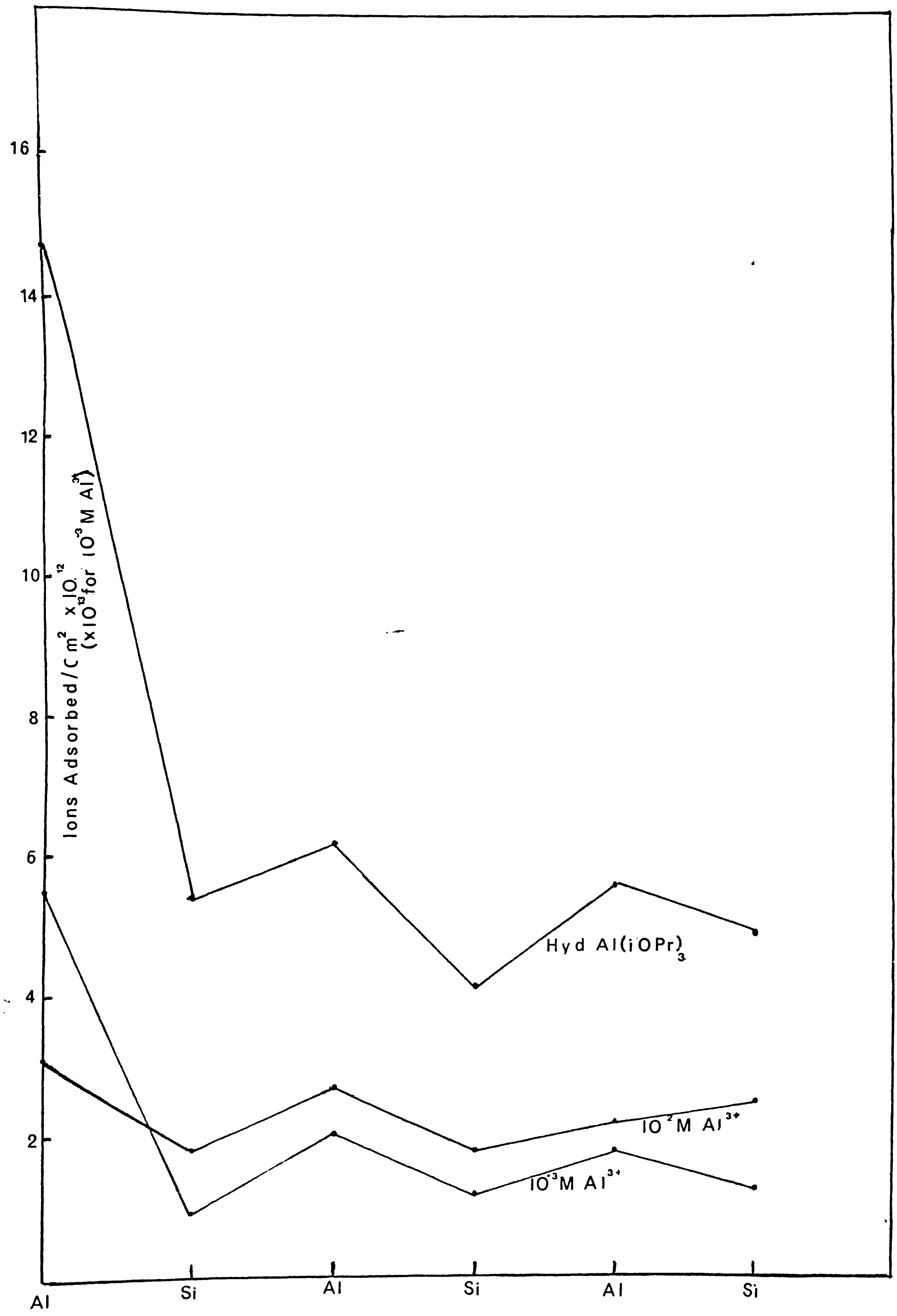


FIG 8·4 P^{32} UPTAKE FOR ALTERNATING TREATMENT WITH HYDROUS ALUMINA AND SILICA

The uptake by hydrolysed $Al(i\text{-}OPr)_3$ is greater than for the corresponding hydrolysed Al^{3+} solution showing that adsorbed ions possibly do play a small part in the surface charge of the hydroxyaluminium complexes. There is an expected periodicity but it is much less marked than that for the ferric oxide treatment shown in Table 8.5 and Fig. 8.5. From this it can be inferred that an almost uniform layer is being presented to the phosphate by the alumina/silica system.

The P32 uptake for alternating treatment with hydrolysed ferric chloride and silica (Table 8.5 and Fig. 8.5) shows pronounced periodicity.

The results of alternate mica treatment with Fe-59 in the hydrolysed ferric chloride and silica are given in Table 8.6. From these it can be seen that successive layers of iron are being deposited and not being removed. The slight decrease in the number of ions/cm^2 after each SiO_2 treatment of the ferric oxide surface of mica is due to the slow desorption of iron colloid noted by other workers.

The results of Fe-59 uptake on hydroxyaluminium treated mica are shown in Table 8.7. There is an increase of uptake which is discussed in the next section.

8.5 DISCUSSION

The lack of pronounced periodicity of phosphate uptake after hydrous alumina and silica treatments means either the silica is not being adsorbed, although there was an initial decrease in P uptake, or some form of chemical reaction is occurring between the adsorbed silica and alumina. The results of the Fe-59 uptake show that the silica is present but has reacted in some way since there is more iron taken up than on an untreated clean mica surface. This can only be the case if there are more cation exchange sites available. These must be generated by the reaction of the hydrous alumina and silica, the aluminium being forced into tetrahedral coordination and so producing further negative sites available for cation exchange.

for

Table 8.5 Absorption coefficients for P32 uptake/alternating treatment with hydrous ferric oxide and silica

	10^{-1}M $FeCl_3$	10^{-2}M $FeCl_3$		10^{-2}M $FeCl_3$ + $2x10^{-2}$M OH^-		10^{-3}M $FeCl_3$		10^{-3}M Fe^{3+} + $2x10^{-3}$M OH^-	
	k(cm)*	k(cm)* x 10^2	ions/cm^2 x 10^{12}	k(cm)* x 10^1	ions/cm^2 x 10^{13}	k(cm)* x 10	ions/cm x 10^{13}	k(cm)* x 10	ions/cm^2 x 10^{13}
Fe layer	$6.68x10^{-2}$	8.72	5.25	1.71	10.3	1.11	6.69	1.33	7.98
Si layer	$7.60x10^{-3}$	1.24	0.746	0.138	0.830	0.629	0.379	0.182	1.09
Fe layer	$1.21x10^{-1}$	7.04	4.24	2.40	14.4	2.47	14.9	1.08	6.50
Si layer	-	0.42	0.253	0.812	4.94	0.836	0.505	0.133	0.801
Fe layer	-	3.20	1.92	1.71	10.3	1.40	8.43	0.866	5.21
Si layer	-	0.14	0.0843	0.227	1.37	0.698	0.420	0.131	0.789

* Figures average for at least three determinations

Error less than 1% for the average

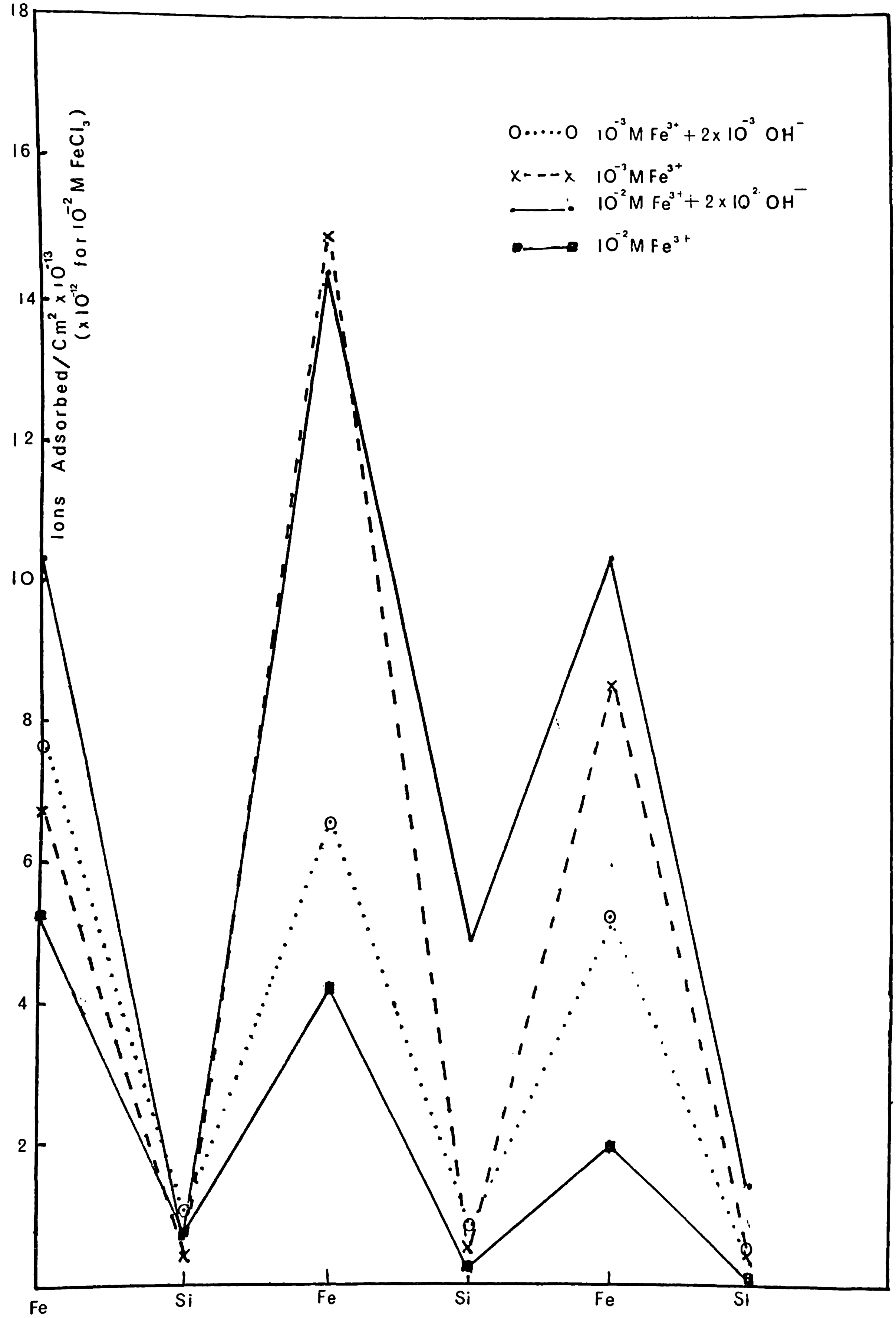


FIG 8·5 P^{32} UPTAKE FOR ALTERNATING TREATMENT WITH HYDROUS FERRIC OXIDE AND SILICA

Table 8.6 Absorption coefficients for alternating treatment of mica with Fe-59 solutions

	$10^{-3}M + 2x10^{-3}M\ OH^-$		$10^{-2}M + 2x10^{-2}M\ OH^-$	
	ions/cm^2 $x10^{13}$	k(cm) x 10^4	ions/cm^2 $x10^{15}$	k(cm) x 10^3
Std	6.24	1.04	7.02	1.17
Treatment with $10^{-3}M\ SiO_2nH_2O$	4.78	0.799	5.05	0.842
Treatment with further Fe-59 colloid	12.82	2.14	11.60	1.93
2nd treatment with $10^{-3}M$ SiO_2nH_2O	12.50	2.08	11.20	1.86

Table 8.7 Absorption coefficients for alternating Fe-59 treatment of hydrous alumina and silica treated mica

	ions/cm^2 x 10^{14}	k(cm) x 10^5
Al pretreatment (hyd. $Al(iOPr)_3$ 100 min) then 60 min Fe-59 treatment ($10^{-3}M$ Fe + $2x10^{-3}M\ OH^-$)	0.0477	0.795
120 mins Fe-59 treatment	0.0666	1.11
Al + SiO_2 treatment (both 100 min)		
Fe treatment 60 min	1.23	20.5
Fe treatment 120 min	1.26	21.0

The amount of aluminium adsorbed on the mica surface is difficult to estimate. There are 6.24×10^{13} ions/cm^2 of hydrous ferric oxide adsorbed which is less than that required to give a monolayer coverage as stated by Langdon[241] as 4×10^{14} ions/cm^2. The solubility products of $AlPO_4 2H_2O$ and $FePO_4 2H_2O$ are 3.16×10^{-31} and 5×10^{-35} respectively[347]. The amount of phosphate adsorbed for Al treatment and Fe treatment is 5.47×10^{13} and 7.98×10^{13} ions/cm^2 respectively at 10^{-3}M concentration. As the solubility product of $AlPO_4$ is greater than that for $FePO_4$ it is likely that there will be at least as much alumina as ferric oxide adsorbed. The amount of ferric oxide adsorbed onto the aluminosilicate is 1.23×10^{14} ions/cm^2, twice as much as for pure mica (623×10^{13} ions/cm^2) so there must be twice the number of exchange sites available. If it is assumed that iron colloid fills all the available sites then the number of additional sites will be the difference, i.e. 6.1×10^{13} sites. There is a small amount of iron lost on silica treatment, presumably due to desorption and the establishing of an equilibrium rather than charge reversal by the silica. But the adsorption of ferric oxide onto a silica layer deposited on mica is greater than for pure mica i.e. $12.82-4.78 = 8.04 \times 10^{13}$ ions/cm^2 instead of 6.24×10^{13} ions/cm^2. Even if this adsorption is allowed for an increased adsorption is found when iron-59 colloid is adsorbed onto a silica layer deposited on hydrous alumina. The increase is $12.3-8.04 = 4.3 \times 10^{13}$ ions/cm^2.

This then is the number of additional sites on the surface after one treatment of alumina and silica.

The calculations are approximate but nevertheless serve as a guide. The additional sites could be produced by additional silica uptake but there is no reason to suspect this. What is more probable is that aluminium has entered the tetrahedral lattice of the silica network creating a negative site which will be a cation exchange site.

The initial drop in P uptake is probably due to loss of the aluminium into tetrahedral sites, additional alumina being adsorbed to balance this extra negative charge on the next treatment and so on - a constant or nearly constant amount of octahedral alumina remaining to adsorb phosphate.

Langdon[241] showed that the adsorption of the iron colloid onto mica was rapid - the reaction being almost complete after 3 minutes, so that the difference in adsorption figures for the two adsorption times of Fe-59 on alumina treated mica is due to replacement of alumina by iron oxide. Hemwall[170] considered that aluminium was responsible for phosphate fixation as insoluble aluminium phosphate. He suggested small amounts of soluble aluminium were released by clay minerals. This probably occurs for the aluminosilicate formed on the mica surface although the difference in adsorption of Fe-59 with time lies within experimental error. There was unfortunately no ready way of detecting any alumina loss.

The iron oxide-silica treatment confirms the result found in the previous chapter. Iron and silica do not react but are held solely by electrostatic forces in what is proposed as a 'colloid complex'; 'colloid' to emphasize the colloidal nature of the particles and 'complex' since the particles are held firmly together by electrostatic bonds. The actual structure will depend on the particle size and numbers of individual particles present.

Iron oxide readily forms aggregates. Langdon[241] showed that these aggregates could be adsorbed on mica and in turn absorb phosphate and were not desorbed. This is not the case with Fe^{3+} ions which were shown to be exchangeable and would not adsorb phosphate. Aggregates are adsorbed for treatment with 10^{-2}M $FeCl_3$ + $2x10^{-2}$M OH^- since $7.02x10^{15}$ ions/cm^2 are adsorbed, at least a factor of 10 too high for monolayer coverage.

The ferric oxide layer adsorbed is not fully neutralized by the silica layer although approximately 90% of the sites are blocked compared to the alumina-silica case where less than 45% of the sites are blocked to phosphate uptake. This shows that aggregates are adsorbed which are inaccessible to silica colloid but are accessible to the dihydrogen phosphate ion.

Iron analogue of allophane

Tamura and Jackson[342] have suggested that an iron(III) analogue of allophane will not exist but their reasoning seems a little vague. However the reactions of colloidal hydrous ferric oxide and silica in forming only a 'colloid complex' bears out their prediction. They suggested a ferrous iron analogue of allophane. Attempts to prepare this have been unsuccessful. Ethylsilicate was hydrolysed in a solution of ferrous chloride through which nitrogen was bubbled. However the product obtained after freeze drying and washing was rust coloured showing that oxidation had occurred and the ferrous analogue was unstable.

'Colloid complexes' in clays

Clays have been described by Mickherjee and Mitra[245] as electrolytic colloids, the colloidal particles surrounded by a double layer. Ions able to reverse this double layer can flocculate clays by either blocking this charge as in the case of polyphosphates or by bridging the negative charges as with hydrous ferric oxide, neutralizing the charge and providing positive sites for attraction. A small addition of aged 10^{-3}M solution of ferric chloride immediately coagulated a stable suspension of high country soil clays (see Chapter 9) or synthetic aluminosilicate, both of which are negatively charged above pH 5. Follett[246] has shown that amorphous ferric oxide is adsorbed onto the negative faces of kaolinite flakes and causes reversal of charge.

This is affected only by pretreatment with cetyl pyridinium bromide and not by other ions including Al^{3+}. This shows that if hydroxy aluminium complexes are adsorbed onto clay surfaces they can be replaced by hydrous ferric oxide. This is probably because Fe(III) in solution exists as a fully hydrolysed species except at very low pH's whereas Al(III) is only partially hydrolysed at pH's up to 5 and so is easily replaced by hydroxy iron 'colloid complexes' which are fixed.

8.6 CONCLUSION

Hydrous alumina colloid can be adsorbed onto the 001 face of freshly cleaved mica. Hydrous silica when adsorbed over the alumina-treated mica reacts with the alumina to form Al-O-Si bonds. This reaction generates more cation exchange sites than were originally present on the mica surface.

Hydrous ferric oxide and silica form a 'colloid complex' where the colloidal particles are held together by electrostatic bonds. Alternate layers of ferric oxide and silica can be adsorbed on to the 001 face of mica. The ferric oxide analogue of allophane is unlikely to exist.

The presence of organic acids affects the adsorption of hydrous alumina onto the surface of cleaved mica, and has an effect on the reaction of hydrous alumina and silica.

CHAPTER 9 STRUCTURE OF ALLOPHANE

9.1 INTRODUCTION

Early workers suggested that allophane was a simple mixture of amorphous hydrous alumina and silica but I.R. work by Adler[97] has shown a simple mixture is not the case since only a broad peak about 1000 cm^{-1} is obtained. This does not show the characteristic peaks of discrete silica.

Several authors have suggested structures for allophane. Fieldes[56] postulated the presence of discrete alumina and silica when he described allophane B as the precursor to allophane A which behaved in a similar way to geological allophane. The presence of the free oxides was questioned by Miyauchi and Aomine[98], who suggested that Fieldes' evidence could be ascribed to the presence of crystobalite in the coarse clay fraction. Fieldes and Furkert[120] reconsidered the evidence and proposed the term allophane B should be retained and extended to cover hydrous material that had many of the characteristics of allophane.

Cloos et al[247] suggested a structure for aluminosilicates that consisted of a negatively charged aluminosilicate held together by positively-charged hydroxy aluminium species. This structure was superseded by another model proposed by Cloos and his coworkers[115] and similar to that suggested by de Villiers and Jackson[149] in which a central core containing tetrahedral aluminium randomly arranged, is surrounded by hydroxy-aluminium species balancing the charge.

Wada[113] has proposed the chain structure described above (section 2.5) but this model contains no tetrahedral aluminium and has order. Iimura[114] has suggested a sheet-like structure but this also suffers from the disadvantage that order is present and would be expected in the DTA curves and IR spectra.

9.2 INTERACTION OF SILICA AND ALUMINA

The occurrence of discrete amorphous alumina and silica together in the fine clay of sub-soil seems extremely unlikely when the data in Chapter 7 is considered. The attempts to prepare an unreacted mixture of the amorphous oxides were successful only in the dry state. Once the dry samples were made and wetted the characteristic peaks of silica disappeared. Only if crystalline aluminium hydroxide was present were the alumina peaks retained. It would appear, however, from the experiment using ion exchange resins, that if organic material interacts with colloidal alumina before it comes in contact with colloidal silica then the reaction does not occur as there is no exothermic peak in the DTA.

In Chapter 8 organic acids affected the phosphate uptake of hydrous alumina particles on mica probably by forming a complex and reversing the charge of the alumina particles. This strong interaction of organic material and colloidal hydrous alumina would possibly cause the model first proposed by Cloos et al[247] to fall apart by removal of the hydroxyaluminium species. The reaction of organic acids with alumina probably explains the presence of silica that is recorded in some allophanic topsoils.

In the weathering of volcanic ash and glass small colloidal particles of hydrous SiO_2, Al_2O_3, TiO_2 and Fe_2O_3 will be formed. The silica and TiO_2 will be negatively charged whereas ferric oxide and alumina will be positively charged. The dimensions of the particles will be small - probably not much bigger than molecular size and they will be attracted together electrostatically, like the ions in a crystal lattice. This gives rise to the phenomenon of a 'colloid complex' first described in Chapter 8. Generally there will be little organic material present since volcanic glass does not provide a suitable medium for plant growth and so the particle interaction will not be modified by the presence of organic acids.

The lattice will not be regular as the particles will be of different sizes and may have regions that are mainly silica and alumina depending on the size of the particles. The colloid complex will only have a transitory appearance in the case of hydrous alumina and silica as the components react rapidly to form amorphous aluminosilicates. The iron however will, in the case of hydrous ferric oxide, form a 'colloid complex' with silica.

9.3 STRUCTURE OF AMORPHOUS ALUMINOSILICATES

The main band in the IR spectra of synthetic aluminosilicates is a combination of Al-OH, Si-OH, Si-O-Si and Al-O-Si bands and is dependent on several factors such as SiO_2/Al_2O_3 ratio, preparation, time of aging, and pH of solution for formation. The synthetic aluminosilicates show a shift towards lower energies as the SiO_2/Al_2O_3 ratio decreases. The energies of the peak maxima lie in the range suggested by Launer[248] for layer and framework silicates. This reflects a change in degree of polymerization of silica. Isolated SiO_4 tetrahedra were shown by Launer to exhibit absorption in the range 1020-820cm^{-1}. The samples with low SiO_2/Al_2O_3 ratios have peak maxima in this range although the peaks are broad. Thus for low SiO_2/Al_2O_3 ratios there are isolated silica tetrahedra. Increase in silica tetrahedra polymerization as the SiO_2/Al_2O_3 ratio increases causes an increase in the maxima up to that for silica gel at 1080cm^{-1}.

The natural allophane samples have peak maxima ranging from 970cm^{-1} for the Taupo sample to 1030cm^{-1} for the Tirau sample. This may represent some difference in degree of polymerization of silica tetrahedra in the various samples and the peak maxima cannot be obtained by knowing the SiO_2/Al_2O_3 ratio. This difference in degree of polymerization is expected in the weathering scheme glass allophane kaolinite, i.e. from a disordered glass to an ordered crystalline aluminosilicate. The Taupo sample has the lowest peak maxima energy and is the youngest sample studied and so would be expected to have the least amount of polymerization if formed from the colloidal oxides from the weathered glass. As the allophane samples age then polymerization of the silica network will occur as the structure order proceeds towards the crystalline aluminosilicates halloysite and kaolinite. The peak maxima for the Tirau sample lies in the range suggested by Launer for layer silicates showing that considerable polymerization has occurred.

It was pointed out by Lai and Swindale[65] that there was reason to doubt the use of synthetic aluminosilicate gels to depict the structure of allophanes and this would appear the case since as shown in Chapter 4 the peak position of the major band in the IR does not determine the SiO_2/Al_2O_3 ratio. The only ions that are present in the aluminosilicates for balancing the charge due to isomorphous substitution are protons, aluminium and hydroxy-aluminium species. H-clays have been shown by Cashen[343] to be unstable and convert to Al-clays so it is probable that aluminium or more likely hydroxyaluminium species are the counter charges. This is unlike the natural allophanes where other ions, especially hydrated Fe^{3+}, can neutralize the charge caused by substitution. Thus only for low SiO_2/Al_2O_3 ratios is there considerable tetrahedral substitution as there is then sufficient Al present to neutralize the charge caused by tetrahedral coordination. The structure then is likely to be a framework since there is only limited tetrahedral substitution of Al.

The isoelectric point will be lower than natural allophanes since there is limited charge remaining on the surface. The limiting factor for substitution will be the amount of Al present. As the concentration of hydroxyaluminium increases then crystallization of aluminium hydroxide occurs. Cloos et al[115] suggested a SiO_2/Al_2O_3 ratio of 0.13 for the first appearance of crystalline hydroxide but pseudo-crystalline material is probably present before this.

The major difference, however, between the synthetic alumino-silicates and natural allophanes is the occurrence of elements other than Al, Si, O and H, in particular Fe, in the natural allophanes.

9.4 IMPORTANCE OF IRON

Kopp[249] considered that the importance of tetrahedral iron was neglected and cited minerals in which iron is present in the tetrahedral sites. Ossaka et al[250] have prepared artificial aluminosilicates which they claim contain up to 5% of incorporated iron oxide, any additional oxide appearing as hydrated ferric oxide. They did not give the coordination state or the form of this incorporated oxide.

The difference in ionic size of Fe^{3+} (0.64Å) and Al^{3+} (0.50Å) compared to that of Si^{4+} (0.41Å) suggest that iron is unlikely to substitute to any great extent for silicon in the tetrahedral layer. The replacement for iron by aluminium in oxides is common and accompanied by a reduction in cell size[251] but the increase necessary to accommodate iron in the tetrahedral sites of a silica lattice is likely to render the structure unstable.

In the natural allophane samples studied the amount of iron does not exceed 5% and can be removed readily without any apparent structural alteration since the DTAs and IR spectra remain unchanged. The Mössbauer spectrum of allophane suggests there is free ferric oxide present and it is not incorporated in the structure as suggested by Ossaka et al[250].

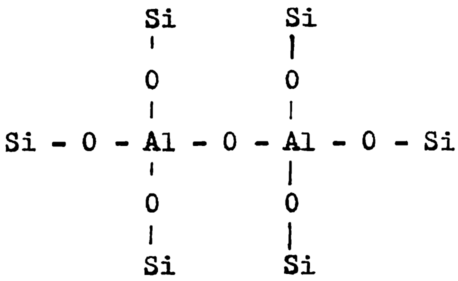
Treatment of the aluminosilicates with hydrous ferric oxide raised the isoelectric point. It is unlikely that the iron will be incorporated into the aluminosilicate structure but what is more likely is that the iron oxide will be electrostatically attached to the aluminosilicate surface giving it an overall positive charge. In other words iron forms a 'colloid complex' with the aluminosilicate particles which in the case of allophane will be sufficient to hold the structure together.

9.5 DEFINITION AND STRUCTURE OF SOIL ALLOPHANE

The definition of allophane has varied since it was first proposed for a particular mineral in 1816 by Stronmeyer and Haussman[20]. However essentially it has been taken to mean an amorphous hydrated aluminosilicate with indefinite structure present in clays. Recently a working definition was proposed[344]:

"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."

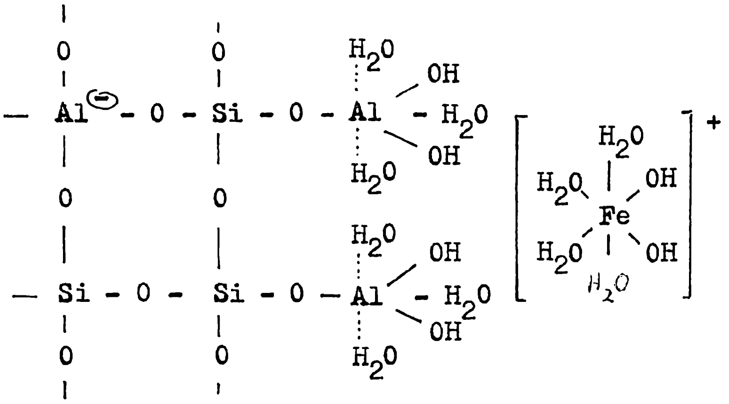
This definition does not include the properties of high chemical activity and high isoelectric point characteristic of the allophanes of the Waikato Basin studied in Chapters 4 and 5. Generally the presence of iron in any definition of allophane has been ignored. However the change in chemical properties of allophanes treated with agents to remove the 'free' ferric oxide means that iron is an integral part of the structure and constitution of allophanes found in soils derived from volcanic ash. The following model is proposed for allophane. The basic assumption is that aluminium is tetrahedrally coordinated in a central core. Lai and Swindale[65] have suggested there may be centres of type



$$\begin{array}{ccccccc} & & \mathrm{Si} & & \mathrm{Si} & & \\ & & | & & | & & \\ & & \mathrm{O} & & \mathrm{O} & & \\ & & | & & | & & \\ \mathrm{Si} - & \mathrm{O} - & \mathrm{Al} & - \mathrm{O} - & \mathrm{Al} & - \mathrm{O} - & \mathrm{Si} \\ & & | & & | & & \\ & & \mathrm{O} & & \mathrm{O} & & \\ & & | & & | & & \\ & & \mathrm{Si} & & \mathrm{Si} & & \end{array}$$

despite the conclusion of Leonard et al[216] that such centres would be unstable. Such centres may be unstable in aluminosilicates but could be stabilized by charges such as hydroxy iron species in natural allophanes. The large number of tetrahedral sites would lead to a negative charge on the core which is balanced by hydroxyaluminium and hydroxy iron species. This model is similar to that proposed by Cloos et al[115] but includes the presence of iron.

The high reactivity of hydrous alumina and silica probably will mean that the hydroxy aluminium species are bonded to silica units but remain in octahedral coordination.



The combination shown above will mean that there will be few Si-OH groups on the surface although treatment with some reagents (e.g. dithionite-citrate) will remove some of the hydroxy-aluminium leaving the Si-OH surface which is less reactive. The surface octahedral hydroxyaluminium will give pH dependent cation exchange capacity and also the deuterium exchange noted by Wada[143].

Small centres of hydrous silica and alumina may give rise to the small endothermic peaks noted in the DTAs of the Waikato allophanes. These centres as well as the tetrahedral aluminium centres are randomly arranged so that the IR spectrum is an average of many individual bands.

The positive charge is caused by the presence of iron which is electrostatically attached to the aluminosilicate core. Deferration does not normally remove all iron and that which is remaining is possibly balancing the charge caused by adjacent tetrahedral aluminium atoms and is trapped in the core. The iron can be considered as forming a 'colloid complex' with the aluminosilicate core.

On the basis of this model the following modified definition of allophane is proposed.

Allophane is a 'colloid complex' of an amorphous hydrous aluminosilicate of widely varying composition, having a short range ordered structure of Al-O-Si bonds and a small amount of amorphous hydrous ferric oxide.

9.6 CONCLUSION

Allophane, as a naturally occurring constituent in volcanic soils, is a 'colloid complex' of an amorphous aluminosilicate and amorphous hydrous ferric oxide of indefinite composition. It contains Al-O-Si bonds with some aluminium occurring in tetrahedral sites. The iron oxide is electrostatically bonded to the negative charge on the aluminosilicate and confers on allophane a positive charge in the soil.

PART III

SOILS OF THE SOUTH ISLAND HIGH COUNTRY

CHAPTER 10 AMORPHOUS CONSTITUENTS OF SOILS DERIVED FROM SEDIMENTARY ROCKS

10.1 INTRODUCTION

Since the studies made by Hendriks and Fry[252] and Kelley et al[253] the inorganic amorphous materials in soils have been dismissed as unimportant and it was thought that only crystalline clays played any part in the chemical properties of soils. This was despite the fact that Hendriks and Fry[252] indicated that X-ray diffraction would not identify any amorphous matter present, apart from a general blackening of the photographic film.

Before the availability of X-ray diffraction apparatus Mellor[254] considered clays to be made up of two parts, one crystalline and the other amorphous. Only one or two workers persisted with the idea that amorphous material was present. The foremost of these was Mattson[190] who postulated a colloidal complex of crystalline core surrounded by an amorphous coating.

But in general soil chemists have ignored amorphous material. As recently as 1968 Grim[13] in his comprehensive treatise on clay stated "It is the author's opinion that allophane is rather uncommon in soils and clays and that it is rarely an important factor in accounting for the physical properties of such clay materials". This view was not expressed, however, by Mitchell et al[255] in 1964 who considered a more balanced view of the effect of amorphous material was now being accepted. Since 1952, New Zealand pedologists have been very aware of the important role the amorphous clay mineral has on the properties of the soils derived from volcanic ash in the North Island. The characteristic feel of allophanic type soils, i.e. the clay is slippery but not sticky, has been noted by pedologists to occur in the high country soils of the South Island, in particular the high country yellow-brown earths. The presence of allophane has also been suggested as occurring in the soils of the central yellow-brown earths in the lower North Island. These soils have developed on the sedimentary mountains forming the Tararua ranges of the North Island.

The presence of allophane in these soils could not readily be explained since there is little evidence of volcanic ash being deposited. This is especially so in the South Island, where the parent material of the high country yellow-brown earths is either schist or greywacke.

The large amount of pedological and chemical evidence, some of which is discussed in the next section, has not been well documented but suggests that amorphous clays are present in soils derived from non-volcanic material in the high country soils of New Zealand. The purpose of this work was to investigate the fine clays of South Island high country soils to see if they are allophane.

As the high country soils are derived from two main parent materials, chlorite-schist and greywacke, soils derived from them were examined and subjected to the same chemical investigations as the volcanic allophane described in chapters 4 and 5.

10.1.2 "ALLOPHANE-LIKE" AMORPHOUS MATERIAL IN N.Z. SOILS DERIVED FROM NON-VOLCANIC PARENT MATERIAL

The presence of amorphous material in soils derived from sedimentary rocks in New Zealand was reported by Fieldes[256] in 1962 as occurring in the zonal brown-grey earths, yellow-grey earths and yellow-brown earths. He suggested that the small percentage of allophane present cemented the soil particles of yellow-brown earths together, accounting for their good structure.

Fieldes and Furkert[99] studied the significance of grinding on a crystalline feldspar and showed that after 48 hours grinding in a Spex mill, a sample of albite gave no X-ray diffraction pattern and had an I.R. pattern and DTA curve similar to that of allophane. They also showed that the grinding of volcanic glass (obsidian) gave an I.R. pattern and DTA curve similar to that of allophane. Fieldes[96] suggested the occurrence of allophane is associated with conditions that favour formation of random-structured aluminosilicates.

An 'allophane test' has been developed by Fieldes and Perrott[257]. The method uses sodium fluoride and phenolphthalein, where the fluoride ion replaces OH groups on the hydroxy-aluminium species causing a rise in pH turning phenolphthalein paper pink. Using this test the authors have reported the presence of allophane-like material in Puketeraki soil - a South Island high country yellow-brown earth developed on greywacke - as well as Belmont soil, a central yellow-brown earth developed on greywacke in the North Island. The presence of further amorphous material has been reported by Furkert and Fieldes[120] in soils derived from greywacke, the yellow-grey to yellow-brown earths of the southern North Island as well as soils derived from loess and sand. The proportion of allophane was determined by the dissolution method of Hashimoto and Jackson[127] and did not exceed more than 10% of the total soil. The predominant clay in all cases was either illite or hydrous mica derivatives. They stated that allophane developed in the high country soils under high rainfall and low temperatures.

Later Birrell and Fieldes[86] reported the occurrence of allophane in soils of the yellow-grey earth type which have micaeous minerals as the predominant clay. Some of the soils have been considered as forming on a mixture of weathered greywacke and volcanic ash. The proportion of the amorphous material in these samples, estimated by NaOH dissolution, was usually less than 10%.

10.1.3 NON-SOIL AMORPHOUS MATERIAL

The original allophane reported by Stronmeyer and Hausmann[20] occurred in fissures in marl. Further naturally occurring non-soil allophanes have been reported by White[33], McKenzie[44] and Snetsinger[345] which appear to come from much the same origins as the original samples. The allophane reported by McKenzie was found in limestone and is formed by solutions percolating through overlying shale and precipitating out as encrustations on the roof of the limestone caverns.

Snetsinger has reported material found in the centre of plagioclase crystals and suggested it was the first stage of weathering of the rock.

A further amorphous gel has been reported by Robertson and Twedily[346] as occurring in Skye diatomite. They suggested the gel was an uncrystallized alumina-ferric oxide-silica gel formed by the living diatoms as they extracted SiO_2 from the water.

10.1.4 OCCURRENCE OF ALLOPHANE-LIKE AMORPHOUS MATERIAL IN SOILS OUTSIDE NEW ZEALAND

The presence of amorphous oxides in clays has long been known, and various chemical methods have been suggested[258,259] for their removal prior to investigation of the crystalline clays. However it has been redognised that the treatment often removes the very material that gives the soil some of its more important properties. The removal of 'free iron oxides' usually removed a large amount of aluminium as well[258].

The presence of amorphous material has been reported by De Mumbrum and Bruce[260] as occurring in the fine clay of the Mississippi alluvial terraces. The predominant clay was montmorillonite with smaller amounts of mica, kaolinite and quartz. They were not able to state the origin of the parent material of the soil as it had been deposited by the river.

De Mumbrum[261] described amorphous aluminous material which coated the predominant vermiculite clay in the poorly drained soils of the Mississippi coastal terrace and it has been reported that alluvial soils in Egypt contain amorphous material[121]. The amorphous material is not the major constituent but was considered to play an important part in its properties. De Mumbrum[261] showed the material extracted had a SiO_2/Al_2O_3 ratio ranging from 0.25 to 1.75 even though the soils as a whole were highly siliceous.

Kirkman et al[81] reported the presence of amorphous material in soils developed on dune sands in Scotland and Mitchell and Farmer[82] also reported amorphous material in Scottish soils which were highly siliceous and they suggested that the amorphous material might be associated with an organic cycle of weathering. There have been other reports of alluvial deposits containing amorphous constituents[262,263].

Using the 'allophane test' devised by Fieldes and Perrott[251] Bradley and Vimpany[78] have reported allophane in the zonal yellow earths and yellow podzolic soils of Australia, developed on sandstone and shale respectively.

10.1.5 FORMATION OF AMORPHOUS MATERIAL

In their scheme of weathering of primary rock-forming minerals, Fieldes and Swindale[55] suggested the formation of amorphous hydrous oxides from materials such as olivine, hornblende and augite which weather through to kaolinite.

Jackson et al[264], in a study of the weathering of the layer silicate minerals, suggested that a decrease in intensity of the basal spacing could possibly be due to an increase in the content of amorphous material and gave a mechanism by which X-ray amorphous zones could arise in weathering. This was also suggested by other authors. Brindley and Youell[265] used hydrochloric acid to remove magnesium and octahedral aluminium from the layer silicate penninite and a magnesium chlorite. They were able to readily extract 47% of the aluminium and the amorphous product which remained, retained the flaky appearance of chlorite. Mering[266] has been able to reconstitute a montmorillonite-like product using the appropriate ions from an HCl extracted montmorillonite. Brindley and Youell[265] were able to form a mica-like product from their amorphous material on treatment with magnesium ions.

Dyal[267] reported the presence of mica leptyls, which were small, weak and very thin, skeletal remains of mica in Florida soils.

The presence of amorphous material has been reported in the so-called 'soils' of Antarctica[268,269]. Chemical weathering is limited in this region but Claridge[268] found examples of surface weathering and consequent oxidation of iron as well as release of salts. He suggested that some of the clay minerals, especially the poorly crystalline and amorphous fractions, were probably derived from rock fragments weathering in the soil. Generally, the clays were formed from the slow hydration of micas but in many places were ground rock particles. The amorphous material was suggested to have come from feldspars and under the cold conditions had not had time to crystallize.

The similarity of the soils in the Antarctic to those in Central Otago has been noted by Claridge[268,270], and for this reason soils derived from the chlorite schists were investigated. Comparisons are made with the high country yellow-brown earths developed on greywacke.

10.2 ZONAL SOILS

Amorphous products of weathering have been reported in the central yellow-brown earth soils in the hills north of Wellington as well as the South Island high country soils, and a brief review follows of the zonal soils which contain amorphous material.

Central Yellow-brown Earths (see Fig. 10.2)

These are zonal soils and have developed on the greywacke mountain backbone of the southern North Island and northern South Island. Usually all stages of weathering appear in these soils. Clay minerals representing the various stages of degradation of micaeous minerals occur so that the platy and layered minerals are common in the clay fraction as well as the final weathering stage of kaolinite. The structure of most yellow-brown earths is good and it was suggested by Fieldes[256] that this could be attributed to the presence of fine particles of feldspar resembling allophane. As these soils have developed under moderate rainfall, leaching is high and the soils are unsuitable for cropping but with top-dressing of superphosphate, are suitable for farming and are in fact used for most of the sheep farming in the country.

High-Country Yellow-brown Earths

These soils have developed, as their name implies, in the high country of the South Island. The major difference between this type and the yellow-brown earths considered above, is the altitude at which they develop. The high country soils are considered to have developed over 3,000 ft (1000m) in altitude and consequently stretch most of the length of the South Island. Soils have developed on greywacke in the north and chlorite-schist in the south (see Fig. 10.1). The climate is moist but cold, so that weathering has not progressed far and the soils are shallow and full of stones. This coarse texture can be partly attributed to the short time since the last glacial period when the hills were scraped down to bare rock. Usually the clay content is low and micaeous clay minerals are predominant but amorphous constituents have been reported present. Because of the altitude the vegetation is limited to tussock and scrub, and erosion is widespread once the vegetation cover is broken.

As the high country yellow-brown earths cover a large amount of the South Island and are used for extensive sheep farming, they are very

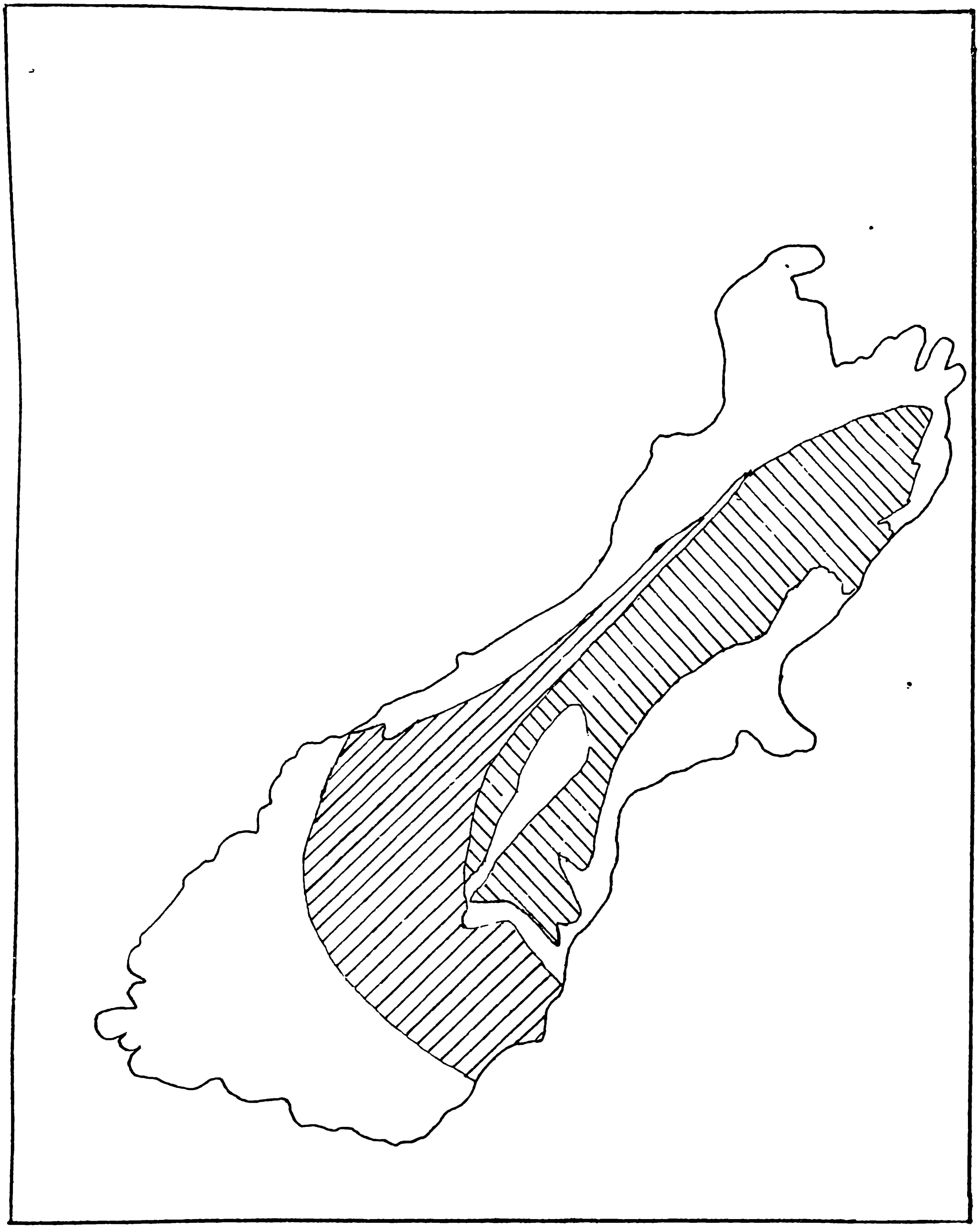


FIG 10·1 CHLORITE–SCHISTS AND GREYWACKE IN THE SOUTH ISLAND

▨ Clorite-schist

▧ Greywacke

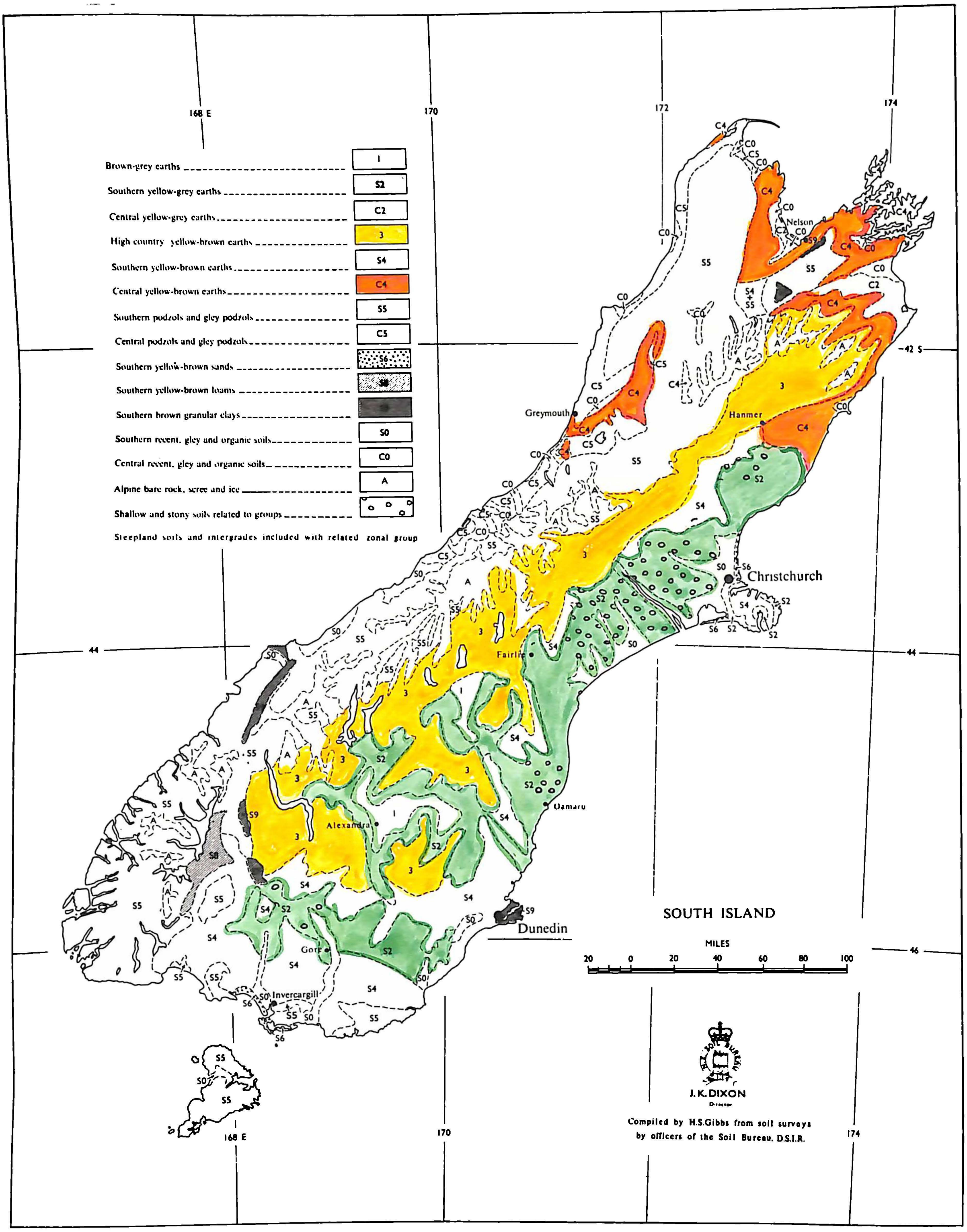


Fig. 10.2 SOILS OF SOUTH ISLAND

(Soils mentioned in text shown
in colour)

important. A large proportion of the fine grade New Zealand wool comes from the large stations situated on the foothills of the mountains relying on the high country tussock for summer feed pastures. Because the land lies above 3000 feet a great deal is under snow during the winter months and so is unsuitable for intensive farming. Burnoff and overstocking has created loss of vegetation and the wind has removed the soil in many places and left bare rock. Little is known of the response of the soils to fertilizers, as the soils are naturally poor in nutrients but it is generally considered that with good management and grassing, the carrying capacity of the more gentle slopes can be increased allowing the steeper slopes to recover. Planting of trees on the steeper slopes to prevent scouring by surface runoff is being carried out in many areas.

Yellow-Grey Earths

Yellow-grey earths are found in the south of the South Island in areas with less rainfall than the yellow-brown earths. Generally they have formed on loess deposits from schist but also on slopes of rock waste. Soil moisture is generally low and so weathering has not progressed far.

The clay content is low and mainly consists of hydrated micas and illites. The phosphate retention is low as weathering has not produced large amounts of strongly phosphate-fixing amorphous oxides.

Use of these soils is limited as drought conditions often prevail but they can be used for sheep grazing as well as cereal growing where the rainfall is adequate.

Chemical Properties

	pH	CEC meq %	Base Sat. %	Cit. Sol. P (mg %)
A horizon	4.7	16.4	5	1
B horizon	4.9	13.3	3	1
C horizon	4.8	8.5	0	1

Representative profile	A. very friable dark brown peaty sand loam
	B. dark brown crumbs of sandy-loam which is friable
	C. yellow-brown gritty fine sand loam with some stones

Carrick silt or stony loams (Soil Set No. 55c).

These soils have developed on schist solifluction detrius. The sample was collected at 4,000 ft. The native vegetation is snow or fescue tussock. The rainfall varies from 40-50 inches per annum.

Chemical Properties

	pH	CEC meq %	Base Sat. %	Cit.Sol. P (mg %)
A horizon	4.9	16.5	10	1
B horizon	5.0	13.7	5	1
C horizon	5.0	11.2	3	1

Representative profile	A. dark-brown friable silty loam with crumb structure
	B. same as above
	C. yellow-brown nutty fine sandy loam with fragmented rock.

Blackstone silt or sandy loams (Soil Set No. 9).

These soils have developed on schist. The sample was collected from 3,000 ft. The native vegetation is fescue and blue tussock. The rainfall varies from 25-50 inches.

Chemical Properties

	pH	CEC meq %	Base Sat. %	Cit. Sol. P (mg %)
A horizon	5.5	18.6	40	9
B horizon	5.6	12.4	24	4
C horizon	6.8	10.8	22	4

Representative profile A. very dark brown nutty/crumb sandy loam that is friable

B. olive brown blocky/nutty sandy loam that is friable

C. olive heavy sandy loam on schist.

Dunstan steepland soils - silt to stony silt loams (Soil set No. 57d).

The soils have developed on schist and local schist loess. The native vegetation is snow tussock. The sample was collected from 5,000 ft. The annual rainfall varies from 25-50 inches.

Chemical properties

	pH	CEC meq %	Base Sat. %	Cit. Sol. P (mg %)
A horizon	5.3	17.6	29	16
B horizon	5.2	15.7	8	7

Representative profile A. dark grey brown nutty/crumbed silt loam which is friable

B. yellow brown blocky stony silt loam which is firm to friable on fragmented schistose greywacke.

11.3 PREPARATION OF SAMPLES

The low amount of clay in each sample made it necessary to handle large quantities of soil. 500 gm of soil was dry sieved through a 30 mesh sieve to remove the stones and larger sand particles which were washed with distilled water into a litre beaker and then discarded. The sieved fraction was added to the litre beaker and distilled water added to make up about 500 mls. The water was boiled for one minute and the sample set aside to see if dispersion occurred. Only for the Carrick soil was any dispersion noted and then a very small amount was dispersed. The water was again brought to the boil, the heat removed and 10 gm of sodium carbonate added and the suspension boiled for one minute. When cool, the supernatant liquid, if any, was poured off. The soil was then wet sieved through a 100 mesh sieve (to remove sand) into a two litre beaker or measuring cylinder, the sieve being washed until the water was clear. The sample in the two litre cylinder or beaker was allowed to stand. If the suspension of soil was still flocculated it was allowed to settle, the supernatant liquid decanted and distilled water added. This process was repeated until the clay dispersed. The sample was then thoroughly shaken and allowed to settle for 3 hrs 50 mins for each inch of fall[279]. Typically the samples were left undisturbed for 48 hours and the suspension containing all particles below 2μ decanted off and retained for centrifuging. Further distilled water was added and the sample thoroughly shaken and allowed to settle for 48 hours again, the process being repeated until the liquid after 48 hours standing was clear.

The clay suspension was centrifuged in 100 ml centrifuge tubes in a Multex centrifuge at 2500 rpm for 43 min to separate the coarse and fine clays. The times were evaluated using the nomograph and formula of Tanner and Jackson[280]. The fine clay fraction was poured into a two litre beaker and flocculated with sodium chloride. This process was repeated until the liquid from the centrifuge tube was clear. The flocculated fine clay was centrifuged and washed with water and then ethanol until a sample of the washing liquid gave no precipitate with silver nitrate. The fine clay was then freeze dried. The coarse clay was allowed to air dry in the bottom of the centrifuge tube at room temperature and then ground.

No precautions were made to exclude bacterial contamination in any operation, the cylinders and flasks being covered with a watch glass at night.

Two samples of unweathered chlorite-schist were broken up and ground in Tema mill. The clay sized particles were separated by dispersion in distilled water and centrifuging. The particle size $< 0.2\mu$ was flocculated with sodium chloride and then washed with distilled water and freeze dried.

11.4 DESCRIPTION OF CLAYS

The sieved soils when wetted have the feeling of a soil with little clay, i.e. greasy but not sticky, characteristic of soils that are high in amorphous oxides. When the fine clay fraction ($< 0.2\mu$) is separated, this retains the non-sticky feel but the coarse fraction ($2-0.2\mu$) has a sticky feel associated with crystalline clays such as illite and vermiculite. The fine particles of ground chlorite-schist ($< 0.2\mu$) do not have the non-sticky feel but feel greasy and slightly gritty.*

The fine clays are pale olive-yellow in colour when moistened but on heating acquire the characteristic rust colour of ferric oxide which suggests that there is ferrous iron present in the sample. The ground chlorite schist is grey in colour showing a high percentage of iron present in the ferrous state. On heating this, iron oxidized and a rust colour is obtained.

All samples, including the ground chlorite-schist, give the 'allophane test' suggested by Fieldes and Perrott[257].

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* The author wishes to acknowledge the help of Mr H. S. Gibbs in ascertaining the pedological 'feel' of a soil.

11.5 DISSOLUTION IN SODIUM HYDROXIDE

The amount of amorphous material was estimated by using the method described by Hashimoto and Jackson[127]. This was the method used by Birrell and Fieldes[86] to estimate the proportions of allophane in a range of soil groups. The results are shown in table 11.1.

Table 11.1 Dissolution of High Country Yellow Brown Earth Fine Clays in 0.5M NaOH

	Total dry wt. dissolved	SiO_2/Al_2O_3 in extract
Obelisk	12.2%	3.20
Carrick	37.86%	2.59
Blackstone	10.5%	1.39
Dunstan	16.43%	2.10
Ground-chlorite schist $< 0.2\mu$	8.5%	10.5

The figures show that only for the Carrick sample is there an appreciable amount of material soluble in boiling NaOH. The low percentage obtained for the other samples shows that conditions in which the Carrick sample was found are suitable for retention of amorphous material. The samples all show high SiO_2/Al_2O_3 ratios in the extracted portions, especially for the ground chlorite schist. The value for the Blackstone sample actually is in the range found for the volcanic samples but the other samples are all more siliceous.

11.6 CHEMICAL ANALYSIS

The fine clays were subjected to analysis by the method described in section 4.4.4 and the results are tabulated in table 11.2.

The outstanding difference between these clays and the volcanic samples is the large amount of total iron, much of which is present in the ferrous form. In order to be present in the ferrous form the iron

Table 11.2 Chemical Analysis of Fine Clays from High Country Yellow-Brown Earths derived from Chlorite-Schists

	Obelisk %	Carrick %	Blackstone %	Dunstan %
SiO_2	29.5	30.0	41.5	32.99
Al_2O_3	20.1	23.6	25.1	21.46
FeO	5.88	1.54	2.30	6.29
Fe_2O_3	8.00	10.03	8.71	8.04
TiO_2	0.57	0.50	0.17	nd
CaO	0.06	0.34	0.11	nd
MgO	1.39	4.32	3.27	nd
H_2O^-	5.19	3.90	2.87	5.43
H_2O^+	20.21	10.02	16.78	16.03

	SiO_2/Al_2O_3 (mole ratio)	$SiO_2/(Al_2O_3 + Fe_2O_3)$ (mole ratio)
Obelisk	2.50	1.82
Carrick	2.17	1.71
Blackstone	2.82	2.31
Dunstan	2.62	2.12

must be contained in a crystalline lattice since ferrous iron is subject to oxidation if occurring free. The samples also contain appreciable amounts of alkaline earth elements showing that complete leaching has not taken place. These elements are unlikely to be present simply as exchangeable ions since the soils have been reported low in exchangeable bases with total base saturation less than 5% for the subsoils and the exchangeable Ca and Mg levels less than 0.5 meq % [278]. These ions must be fixed in the lattice of the minerals, a further evidence for little chemical weathering. Mica and some chlorite are present and these probably contain the alkaline earth metals. The samples are high in silica, more than can be accounted for by the clay minerals. There is no evidence for quartz in the clay samples (from DTA and IR data as well as X-ray of the coarse clay fraction) so it is possible that amorphous silica is present since the sodium hydroxide extractions were also high in silica.

11.7 X-RAY STUDIES

X-ray powder diffraction patterns were run initially with a Philips Debye camera on a Rigaku generator using Cu Kα radiation. Later samples were run using a Philips generatcr and diffractometer with Cu Kα radiation. The high iron content of the samples meant a high background and several samples were run using Fe Kα radiation but no advantage was noted.

The only fine clays to show any diffraction patterns are Blackstone and Dunstan. The peaks are small and very broad (Fig. 11.1). Both samples show the presence of poorly crystalline illite or hydromica (see table 11.3).

Table 11.3 X-ray Peaks for Fine Clays from High Country Yellow-Brown Earths Derived from Chlorite-Schist

Blackstone	Dunstan
4.48	4.48
3.5	3.51
3.34	
2.57	2.58

There is a suggestion of quartz in the Blackstone sample shown by a small sharp peak at 3.34Å but the peak at 4.26Å is not present. Neither show evidence of chlorite but there is a suggestion of residual feldspars in the Dunstan sample. The peaks are small and broad for all samples and are not sharpened after treatment with sodium hydroxide to remove the amorphous constituents.

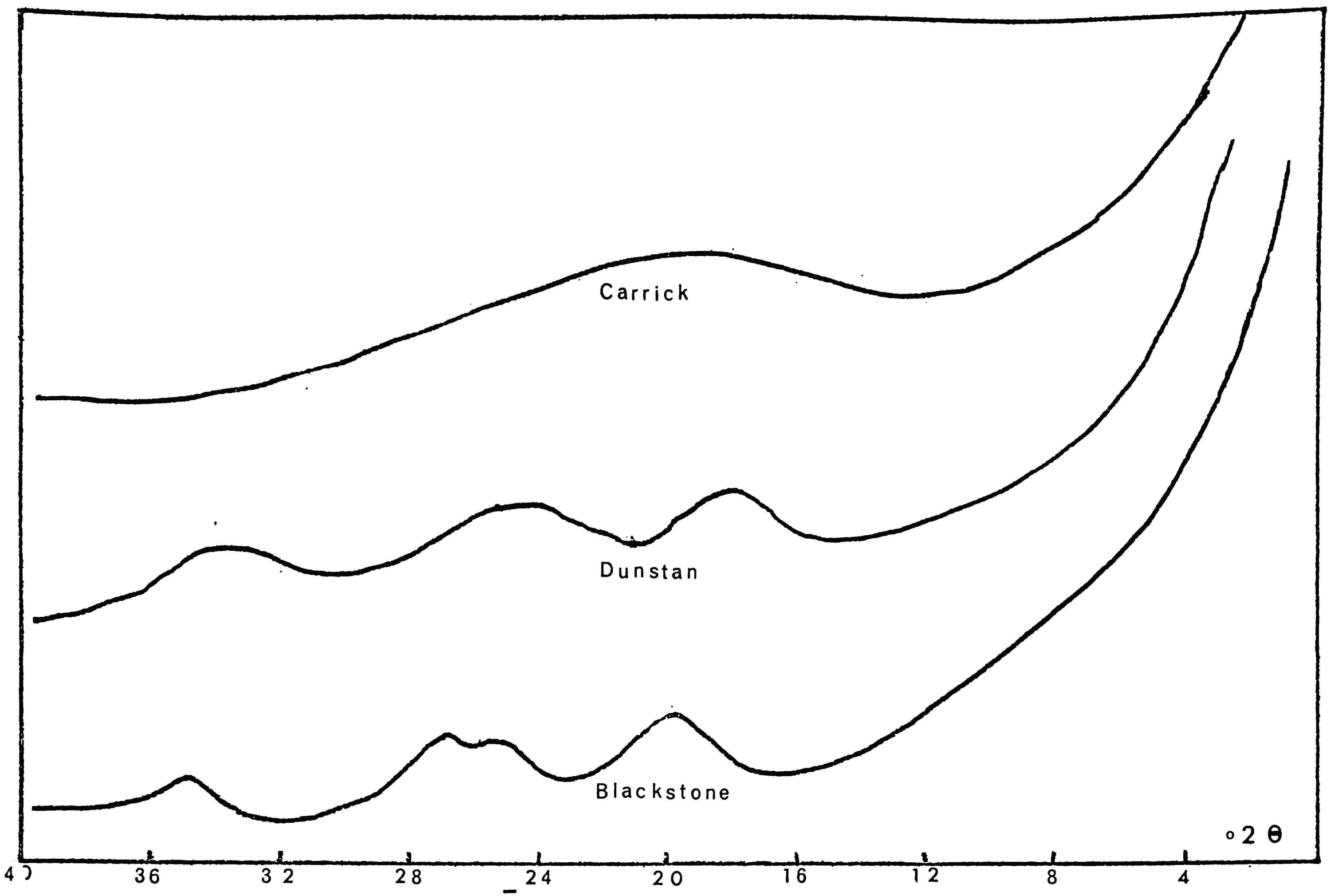


FIG 11·1 SMOOTHED X-RAY DIFFRACTION PATTERNS FOR FINE CLAYS FROM HIGH COUNTRY YELLOW-BROWN EARTHS

The coarse clays of all samples show diffraction patterns indicative of illite, muscovite and an illite-chlorite mixture (see table 11.4) but generally no chlorite. The peaks are broad. There is a peak at 14.04Å in the Carrick sample and a corresponding peak at 7.0Å but these are small and it could be that vermiculite is present although the peak at 7.0Å is stronger than the one at 14Å indicating chlorite. There was no change on K saturation and heating showing that if there is any vermiculite present it is there only in small quantities.

The silt and fine sand fractions of the four soils give similar patterns (see Table 11.5).

They all show the expected composition of New Zealand schist rocks with muscovite, chlorite and feldspar minerals present together with quartz.

When the samples of coarse clay were heated to 500° the only effect was a sharpening of the illite peaks. When heated to 1000°C, peaks due to hematite and spinel were present. When the ground rock samples were heated to 500°C the peaks due to chlorite disappeared and left only the spectra of quartz mica and feldspar. This disappearance has also been reported by Warshaw et al[285] who suggested an amorphous phase was formed for a sedimentary iron chlorite after 270°C. This is in contrast to evidence presented by Brindley and Ali[286] who stated that the chlorite structure was maintained to 760°C.

Discussion

The non-appearance of feldspars in the clay fraction is not surprising since these minerals are known to weather rapidly. Study of the weathering has been made and there is speculation as to how the layer silicates can form from feldspars.

Fieldes and Swindale[55] suggested a micaeous intermediate between feldspar and kaolinite and montmorillonite has also been suggested as an

Table 11.4 d-Spacings for Coarse Clays of High-Country Soils Developed on Chlorite-Schist

	Chlorite 4	Chlorite 2	Obelisk	Carrick	Blackstone
ch	14.27 vw	14.27 w	14.02 w	14.04 w	
	12.45 w				
			11.8 s	11.8 s	
m,i	9.93 m	10.05 s	10.04 m	9.93 m	10.00 s
ch	7.08 vs	7.08 vs	7.08 m	7.08 m	-
f	6.37 w				
m,i	4.97 w	4.98 m	4.93 m	4.91 s	
ch	4.71 w	4.71 w			
m	4.46 w	4.48 w	4.48 s	4.46 w	4.48 vs
q	4.25 s	4.26 w			
			4.15 vw		
f	4.025	4.03 w			
					3.90 w
f	3.77 s	3.79 w			
m		3.74 w			3.75 w
f	3.66 m	3.67 w			
ch	3.54 m	3.54 s	3.53 w		
			3.48 w	3.50 w	3.50 m
qi	3.34 vvs	3.35 vs	3.35 s	3.34 s	3.35 s
f.m,i	3.19 vvs	3.19 s	3.20 m	3.19 w	3.21 m
m	2.99 w	2.99 m	3.00 w	2.98 w	2.99 m
f	2.96 w				
f	2.92 w				
ch i	2.86 w	2.86 w			2.86 m
		2.80 w			
	2.60 w	2.61 w			2.59 w
ch	2.56 m	2.59 m	2.58 m	2.55 m	2.57 vs
q	2.46 w	2.46 w			
m	2.39 w	2.39 w	2.39	2.37 w	2.39 w
q	2.28 w				
	2.13 w				2.14 w
ch	1.98 w	1.99 m	1.99 w	1.99 m	1.99 m
	1.89 w				

cont...

Table 11.4 cont.

	Chlorite 4	Chlorite 2	Obelisk	Carrick	Blackstone
q	1.82 m	1.82 w			
	1.79 w				
	1.72 w				
ch	1.54 w	1.54 w			
	1.51 w	1.51 w	1.51 w		1.51 w

Key
ch = chlorite
m = muscovite
i = illite
f = feldspar
q = quartz

vvs = very, very strong
vs = very strong
s = strong
m = medium
w = weak

Table 11.5 X-ray Data for Sand Fraction of High Country Yellow-Brown Earths

	Obelisk	Carrick	Blackstone	Dunstan
ch	14.29 w	14.2 w	14.27 w	14.25 w
	11.79 w			11.95 } b.ms
	11.06			11.62 }
m	9.82 vs	9.97 s	10.04 vs	10.04 w
ch	7.08 s	7.08 m	7.08 s	7.08 s
f	6.37 vs	6.37 m	6.42 w	6.42 w
m	4.97 s	4.95 ms	4.98 s	4.95 s
ch	4.72 w			4.71 ms
m	4.48 w		4.48 w	4.48 ms
q	4.27 vs	4.25 s		
			4.27 s	4.25 s
f	4.04 s	4.02 w	4.03 s	4.03 ms
m	3.86 w	3.86 m	3.86 vw	
	3.79 s	3.78 m	3.77 m	3.79 ms
f	3.68 m	3.66 m	3.68 w	3.66 w
ch	3.54 m	3.50 bm	3.53 m	3.54 s
	3.51 m		3.51 s	3.50 vw
qm	3.34 vvs	3.3x vvs	3.34 vvs	3.34 vs
f	3.19 vvs	3.19 vvs	3.20 vs	3.19 vs

cont....

Table 11.5 cont.

	Obelisk	Carrick	Blackstone	Dunstan
f		2.99	2.99	3.02 w
f	2.93 m	2.96 w	2.97 m	2.97
		2.93		
m	2.87 w	2.87 m	2.87 w	2.83(b) w
m	2.79 w	2.79 w	2.80 w	
f	2.64 w			
f	2.56 w		2.57 w	2.60 w
	2.48 w		2.50 vw	
q,f	2.46 m	2.46 m	2.46 m	2.45 w
				2.40 w
			2.32 vw	
q	2.28 w	2.28 m	2.28 vw	
	2.26 w	2.24 w	2.24 vw	
	2.19 w			
q	2.13 m	2.13 w	2.13 w	2.13 w
ch	1.99 m	1.99 w	1.99 s	1.99 w
	1.89 m		1.89 vw	1.89 w
q	1.82 s	1.82 m	1.82 m	1.82 ms
	1.80 w		1.80 w	
	1.78 w	1.79 w	1.79 m	
	1.76 w			
q	1.67 w	1.67 w		1.68 w
	1.60 w			
q	1.54 m	1.54 m	1.54 m	1.54 m
		1.46 w	1.46 vw	
	1.42 w		1.43 vw	
q	1.38 w	1.38 w	1.38 vw	
q	1.37 m	1.37 w		

intermediate[281]. Mackenzie et al[282] noted the weathering of feldspar to illite rather than montmorillonite, the illite being an intermediate product. There is no evidence in the X-ray for montmorillonite but illite is present. Fieldes and Swindale[55] recognized that feldspars must go through an amorphous stage in weathering before a layered structure could be formed since feldspars have a framework structure. The amorphous material present in the fine clay has probably come from feldspar weathering and this is the material that is truly amorphous and soluble in NaOH.

Jackson et al[283] have classified chlorites in Stage 4 of their weathering scheme together with biotite, and state that chlorites would be expected to occur in large amounts only in youthful soils but could be present in sedimentary deposits. Bayliss and Loughnan[284], in a study of weathering of clay-slates in New South Wales found chlorite particularly unstable and readily altered to kaolinite. They noted that the primary weathering product was a thermally unstable vermiculite with a basal spacing of 14Å, and that any montmorillonite formed was degraded in the upper soil layers to leave illite which is relatively stable to chemical attack.

There is no evidence for kaolinite or montmorillonite in the samples. The Obelisk and Dunstan samples show peaks at 11.8Å which are possibly an illite-chlorite interlayer but the peaks are small. The absence of chlorite in the clays is due to its relatively rapid breakdown compared to the other minerals present. Even in the ground rock samples the peaks due to chlorite are not strong. The instability of the chlorite is due to the brucite layer which can be readily leached under the high rainfall that is found for the soils of the high country.

The loss of magnesium will result in a lattice which is easily expanded and highly charged and this will be easily attacked.

11.8 INFRARED STUDIES

The infra-red spectra were made using Nujol and HCBD mulls between potassium bromide or potassium chloride plates on a Shamadzu infrared spectrometer with a grating monochromator.

The curves from all samples including those of ground rock show broad peaks characteristic of amorphous material; see Fig. 11.2. The samples of fine clay all display peaks due to hydroxyl stretching in the 3400-3600 cm^{-1} region as well as bending modes in the 1630-1650 cm^{-1} region as shown in table 11.6. The ν OH bands are broad and unsymmetrical, usually centred at 3400 cm^{-1}. The only sample to show actual splitting is Blackstone.

Table 11.6 Infrared Bands due to Hydroxyl Groups in Fine Clays from South Island High Country

	ν OH cm^{-1}	δ H_2O cm^{-1}
Obelisk	3400 (broad)	1640
Carrick	3700sh 3600sh 3400	1625
Blackstone	3600 3720sh 3460	1635
Dunstan	3400	1630 (wk)

Buswell et al[287] and later Buswell and Dudenbostel[288] found that in montmorillonite the band at 3600 cm^{-1} was also split into two peaks, one at 3635 cm^{-1} which they attributed to unbonded hydroxyl and the other at 3390 cm^{-1} attributed to H-bonded hydroxyl and which was greatly affected on drying. Roy and Roy[289] noted that the peak at 3460 cm^{-1} could not be attributed to absorbed water only since it was present in samples heated to 225°C. The doublet occurring in kaolinite at 2.7μ (3700 cm^{-1}) has been attributed to 'inner' and 'outer' hydroxyl groups in the structure[290,291]. The 'inner' hydroxyls are intralattice hydroxyl groups whereas the 'outer' hydroxyls are those on the basal plane providing the bonds between unit layers of the clay mineral. Roy and Roy[289] have shown that this could not be the case, in a study of deuteration of kaolinite.

The size of the particles in the fine clay samples ($< 0.2\mu$) studied means there will be a large proportion of the so-called 'outer' hydroxyls

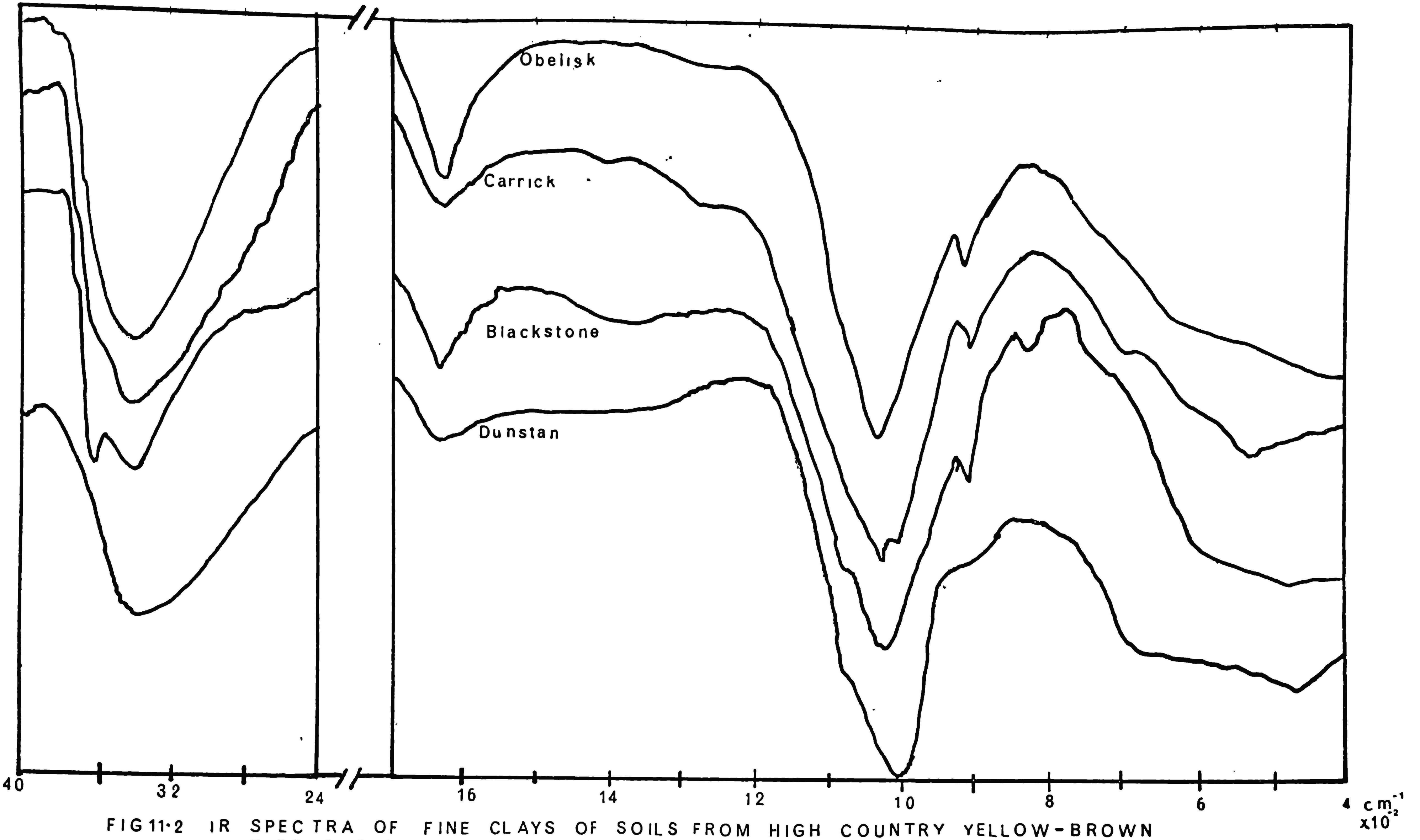


FIG 11·2 IR SPECTRA OF FINE CLAYS OF SOILS FROM HIGH COUNTRY YELLOW-BROWN EARTHS DEVELOPED ON CHLORITE-SCHIST

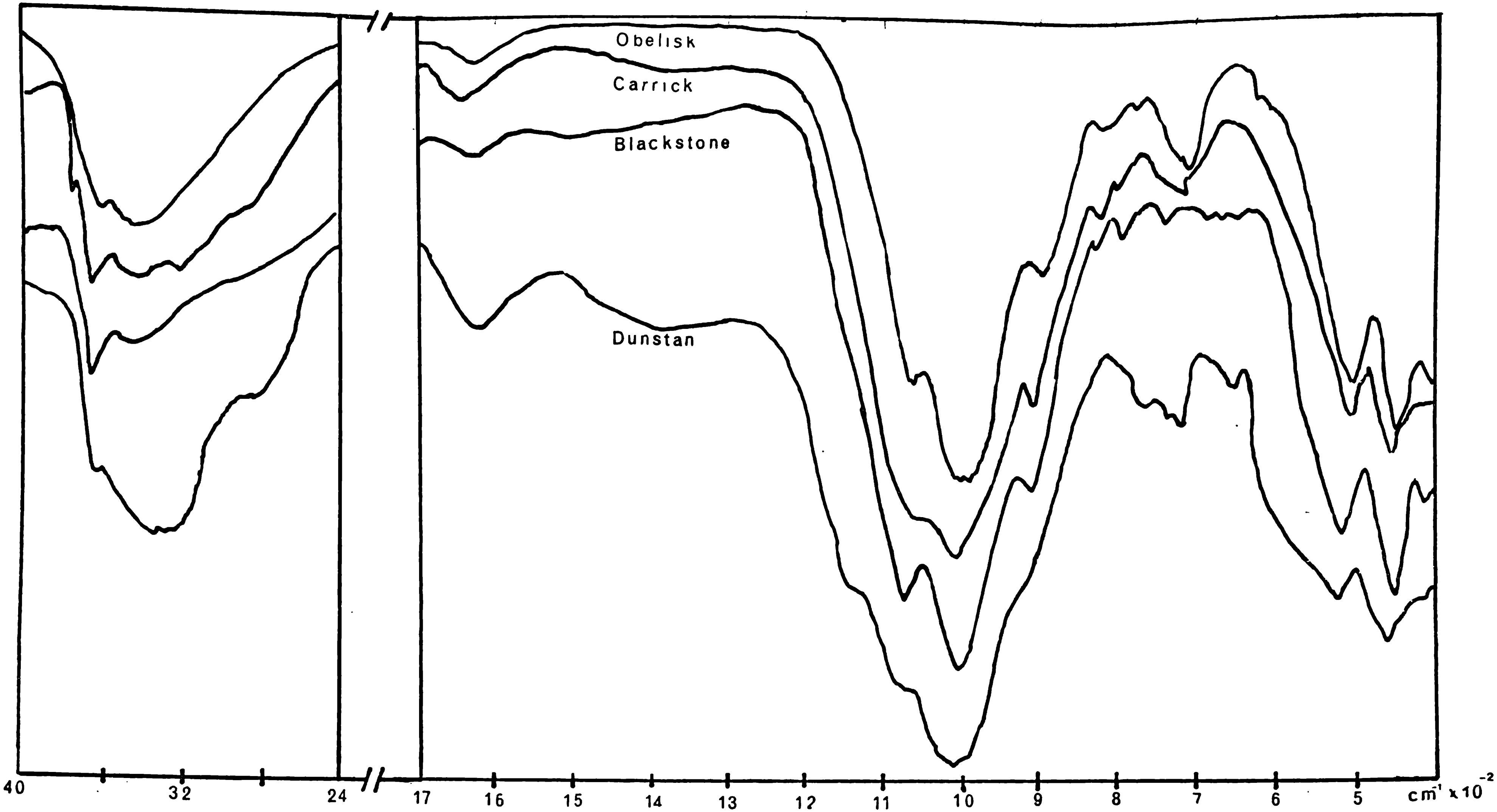


FIG 11·3 IR SPECTRA OF COARSE CLAYS FROM HIGH COUNTRY YELLOW-BROWN EARTHS DEVELOPED ON CHLORITE-SCHIST

Keeling[292] stated that as clays became more disordered then peaks at 920 cm^{-1} and 1120 cm^{-1} became weaker leaving the main peak at 1030 cm^{-1}, and the peaks at 700, 760 and 800 cm^{-1} also weakened. This is observed with the South Island clays.

With ground chlorite schist the same pattern is repeated (Fig. 11.4). The samples of ground rock particles 2-0.2μ in size show a splitting of the hydroxyl band with peaks at 3600 cm^{-1} and 3400 cm^{-1} but this collapsed to a single broad peak at 3425 cm^{-1} and 3450 cm^{-1} for chlorite-2 and chlorite-4 respectively. The peaks in the coarse samples of ground rock are sharp in the region 1150-400 cm^{-1} with many peaks for both samples. But in the fine particle size ($< 0.2\mu$) the bands merged together and only broad bands result in this range (see Table 11.9).

Table 11.9 Major Infrared Bands of Ground Chlorite Schist

			cm^{-1}			
Chlorite-2	($< 0.2\mu$)	1070sh	1020	1140sh	910sh	720,520,470,
	(2-0.2μ)	1060sh	1000	1140	900sh	780,760,740,710,690, 640,515,450
Chlorite-4	($< 0.2\mu$)	1090sh	1015	1140	910sh	720,585,515,460
	(2-0.2μ)	1080sh	1000	1140	-	770,750,730,710,680, 640,600sh,570,500sh, 440

The assigning of the various bands in the metal-oxygen stretching region is difficult but trends have been noticed by several authors[248,290,293-296].

The band around 1000 cm^{-1} has usually been attributed to Si-O stretching[291,293] and was within the range stated by Launer[178] for layer silicates. Miller[291] has assigned bands in kaolinite at 1029 cm^{-1} and 1006 cm^{-1} to Si-O stretching and bands at 787 cm^{-1} and 692 cm^{-1} to Si-O bending. He has also attributed bands at 1105 cm^{-1} and 1093 cm^{-1} to Al-OH stretching modes and 931 cm^{-1} and 910 cm^{-1} to Al-OH bending modes. A peak at 750 cm^{-1} was also attributed to Al-OH since it disappeared during dehydroxylation. Stubican and Roy[293] have attributed a further peak at

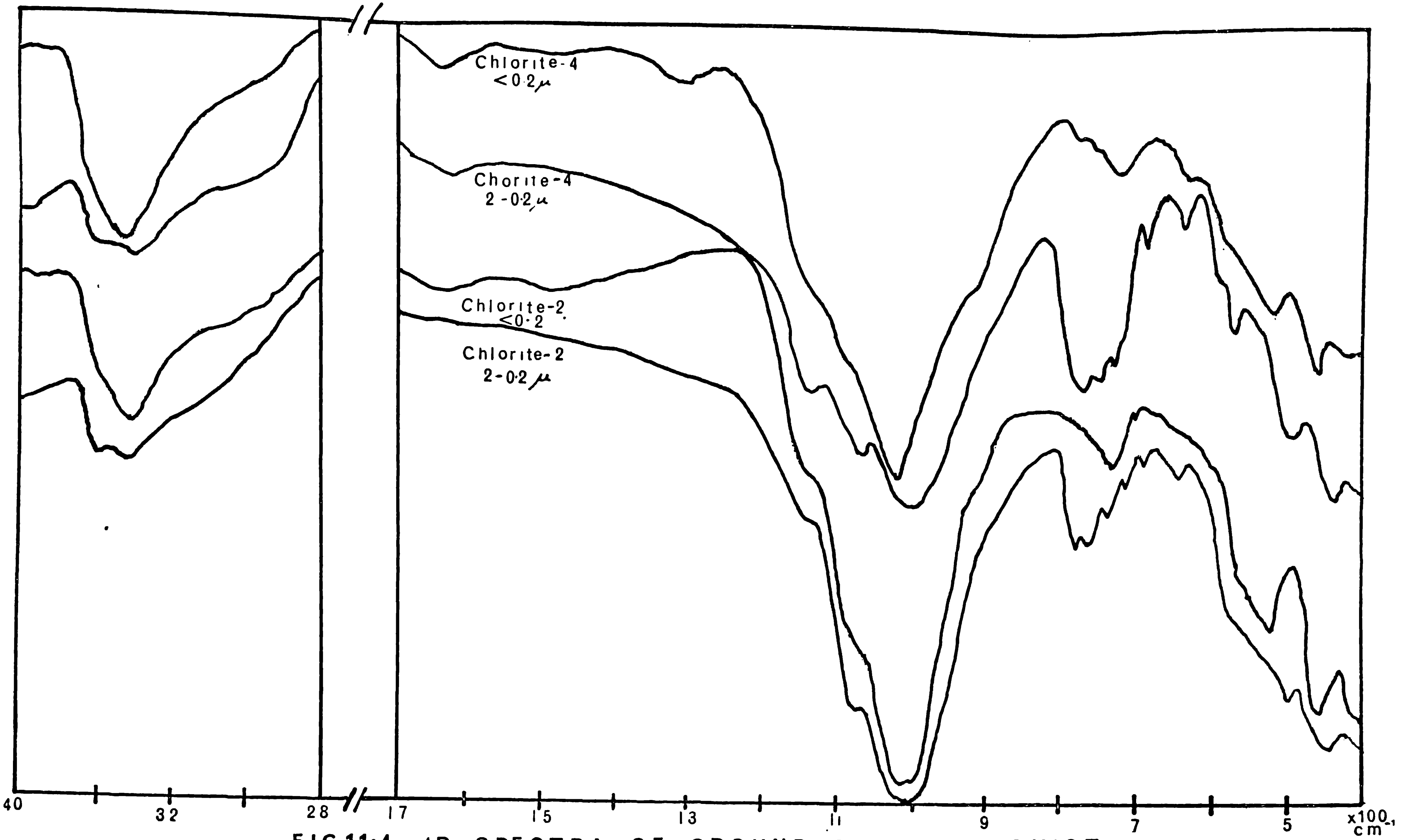


FIG 11·4 IR SPECTRA OF GROUND CHLORITE SCHIST

430-460 cm^{-1} to Si-O bending and further stated that there is unlikely to be any pure Me^{3+}-O or Me^{2+}-O absorption bands and attributed those bands between 500 and 800 cm^{-1} to SiO-Me^{3+}. The position of bands is dependent largely on substitution in both octahedral and tetrahedral sites and this was recognized by many authors.

The infrared absorption of chlorites has been studied by several workers[293,297,298]. The spectra all have shown a multiplicity of peaks in the metal-oxygen stretching region but Stubican and Roy[293] and Hayashi and Oinuma[298] assigned most of them.

With artificially prepared chlorites Stubican and Roy[297] showed that 14Å chlorites had a simple spectrum with three major peaks and small shoulders, the peaks attributed to Si-O and shoulders to Al-OH and Mg-OH bands. The septachlorites showed Al-OH bands at 910 cm^{-1} which were not present in the 14Å chlorite spectra.

The probable assignments of some bands of the clay fractions are included in Tables 11.7 and 11.8.

The peak at 910 cm^{-1} is reasonably well resolved in the fine clays suggesting that the 14Å chlorite structure has broken down by weathering, as the peak is barely discernible on the $< 0.2\mu$ fraction of ground chlorite-schist rock and not at all in the coarse fraction (2-0.2μ) and is not present to any great extent in the coarse clays.

There are few bands in the region of 800-600 cm^{-1} for the fine clays with perhaps only a shoulder around 720 cm^{-1} which is probably due to a Si-O band attributed to a Si-O bending mode by Hayashi and Oinuma[298] and Miller[291]. There is no fine detail in the lower range with only a broad band at 470 cm^{-1} due to a combination of the bands from Si-O and Si-O-M.

In the ground chlorite-schist samples the peaks at 720 cm^{-1} are probably due to Fe-O-Si and those at 585 cm^{-1} and 515 cm^{-1} to Al-O-Si. Hayashi and Oinuma[298] have considered the position of the Al-O-Si band with substitution and from their evidence the high position of the band at

585 cm^{-1} would point to most of the aluminium in the samples occupying octahedral sites together with the iron and magnesium. This is unlike allophane where some of the aluminium is in tetrahedral sites.

In a study of mixed layer clays Oinuma and Hayashi found that illites had the same pattern as occurs for the fine clays studied here. There are few well defined peaks in the range 900-400 cm^{-1}. The patterns published by them showed only two bands 820 cm^{-1} and 750 cm^{-1} as well as the low energy band around 500 cm^{-1}.

In the coarse clays (2-0.2μ) there are a number of very small peaks in the region 850-700 cm^{-1} and the band around 500 cm^{-1} is resolved into two, one at 510 cm^{-1} and the other 460 cm^{-1}. The lack of strong bands in the region 850-700 cm^{-1} suggests that the Si-O-Al and Si-O-Fe linkages, even in the coarse clay, are highly disordered although there are plenty of Al-OH linkages as the bands at 908 cm^{-1} and 1075 cm^{-1} due to Al-OH are present as shoulders on the main Si-O band. This is in contrast to the ground chlorite-schist rock which shows well defined bands in this region which can be assigned to specific M-O-Si modes.

The IR spectra of the heated samples show a less complex pattern with weaker bands around 1035 cm^{-1} and shoulders at 1135 cm^{-1} and 1200 cm^{-1} (see Table 11.10).

Table 11.10 Major Peaks in I.R. Spectra of Fine Clays Heated to 600°C

	cm^{-1}			
Obelisk	1070(sh)	1000	720	460
Carrick	1135	1035	720	-
Blackstone	-	1015	720	475
Dunstan	1140(sh)	1008	-	480
Chlorite-4 (<0.2μ)	1135(sh)	1020	-	-

11.9 THERMAL STUDIES

DTA curves were run on a Stone series 202 DTA apparatus and TGA samples on a Chevanard Type TBM thermobalance.

The curves are shown in Fig. 11.9 and major peaks listed in Table 11.11.

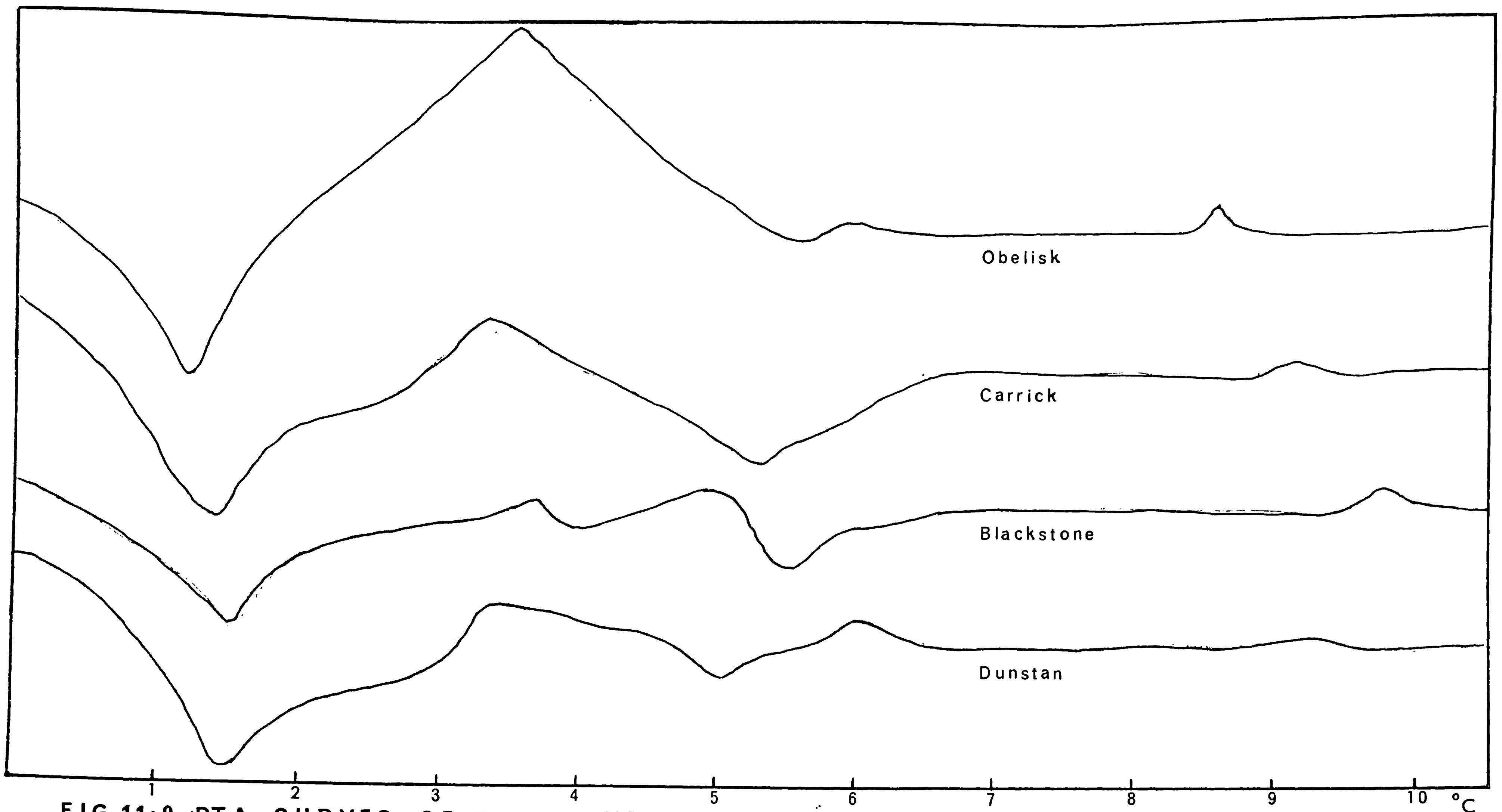


FIG 11·9 DTA CURVES OF FINE CLAYS FROM HIGH COUNTRY YELLOW-BROWN EARTHS DEVELOPED ON CHLORITE-SCHIST

Table 11.11 Major Peaks in DTA of some South Island High Country Clays

Obelisk		Carrick		Blackstone		Dunstan		C4		C2	
exo	endo	exo	endo	exo	endo	exo	endo	exo	endo	exo	endo
	135		120		122		125		100		113
						255					
355		345		330		325		345		350	
									422		430
								610		590	
	600		533		535		532		690		-
860		912		985		-		880		855	

The chemical analysis has shown a high proportion of iron both in ferric and ferrous forms and it is probable that the exothermic peak between 300 and 400° in the DTA is largely due to the iron oxide transformations. The exotherm is unusual in its size. Even under an argon atmosphere, some samples produce the very large peak so it is unlikely to be associated with any readily oxidizable material such as organic matter carried over from the washing. Also an exothermic peak appears in the samples of ground chlorite-schist rock which did not have organic solvents used in the washing.

Oxides and oxyhydroxides of iron often show exothermic effects in the region 200-600°C due to two effects, the oxidation of ferrous iron to ferric and a transformation of γFe_2O_3 formed from dehydration of FeO(OH) to αFe_2O_3 or hematite which occurs in the temperature range 590°C to 600°C. Many workers have studied the effects of thermal treatment of both synthetic and naturally occurring iron oxides and oxyhydroxides[299-303]. With synthetic ferric oxide gels the position of the exothermic peak has been shown to depend on pH and time of aging[299,300,302].

Mackenzie and Meldau[299] found that goethite was formed from synthetic amorphous gels on aging but did not greatly affect the exothermic peaks. Towe and Bradley[301], have shown that the synthesized ferric oxide gels are related in structure to hematite and in fact on aging form crystallites of hematite. Despite these crystallites Towe and Bradley[301] published a DTA curve with an exotherm at 425°C and formation of hematite was observed by X-ray. Mackenzie[304] showed in samples of β FeOOH, that before the exotherm around 450, a mixture of α Fe_2O_3, γ Fe_2O_3 and β FeOOH was present, while hematite was the only phase present after the peak at 500°C. Gheith[300] showed that the peak occurring at 310°C was the crystallization of amorphous Fe_2O_3, resulting from dehydration of hydrous Fe_2O_3, to hematite. Naturally occurring hydrous ferric oxides have been investigated by Kulp and Trites[302] who found the large exotherm associated with synthetic gels was largely absent or certainly small and that the predominant feature was an endotherm around 390°C for goethite and somewhat lower for lepidocrocite. Mackenzie[303] published curves for two soil clays rich in iron which closely resemble those obtained for the South Island soils and showed this effect could not be due to goethite.

Samples of the fine clays heated to 1000°C showed the presence of hematite which was not present at 500°C, so that it is likely that the exothermic peak present in the fine clays can be attributed to the oxidation of ferrous iron in a crystalline lattice and crystallization of amorphous iron oxide.

Addison et al[305] and Addison and Sharp[306] in a study of oxidation of ferrous iron in crocidolite, an amphibole,* showed the process followed the equation

$$4Fe^{2+} + 4OH^{-} + O_2 \longrightarrow 4Fe^{3+} + 4O^{2-} + 2H_2O \qquad (1)$$

rather than the simpler process expressed by the equation

$$4Fe^{2+} + O_2 \longrightarrow Fe^{3+} + 2O^{2-} \qquad (2)$$

* see Appendix.

The oxidation was accompanied by a slight loss in weight due to the evolution of water. For each gram of ferrous iron present in the sample 18 mg of weight was lost in the oxidation step.

However the TGA curves (Fig. 11.10) shows that the loss over the temperature 200-499° is too great to be attributed to oxidation of ferrous iron and must be due to water loss as well.

It has been suggested by Fieldes and Taylor[307] that free ferric oxide can be detected by its colour, but the fine clays from the high country soils are grey or yellow-olive in colour rather than red or yellow. When heated the soils turn red as hematite is formed so it is probable the proportion of free iron oxide is small. A Mössbauer spectrum (see Fig. 11.11) shows the iron is held in a lattice position so it is probable that little ferric oxide is present in the free state.

Most of the water appears bound as hydroxyl groups rather than simply as absorbed water. The low temperature endotherm is due to the loss of the absorbed water and the end of the peak corresponds to the change in slope on the TGA curve. Compared to the amorphous fraction from volcanic clays the amount of water lost is small. This is to be expected due to the low amount of water exchanged over saturated salt solutions (see section 11.14).

The second endotherm is due to dehydroxylation of layer silicate relics. Several of the TGA curves show no inflexion in the weight loss curves. This is not characteristic of illite and montmorillonite clays. It is strange that the peak at 530° which is usually large is not associated with any increase in the rate of loss of weight. It can only be that the peak also reflects a change in structure of the sample.

The samples of ground chlorite-schist were separated into fine and coarse clay-sized particles. The DTA of the two fine samples shows a similar pattern to the clays but with the dehydroxylation peak at 420-430°C, about 100°C lower than for the soil clays (see Fig. 11.12). The peak position is also lower in temperature than that associated with normal

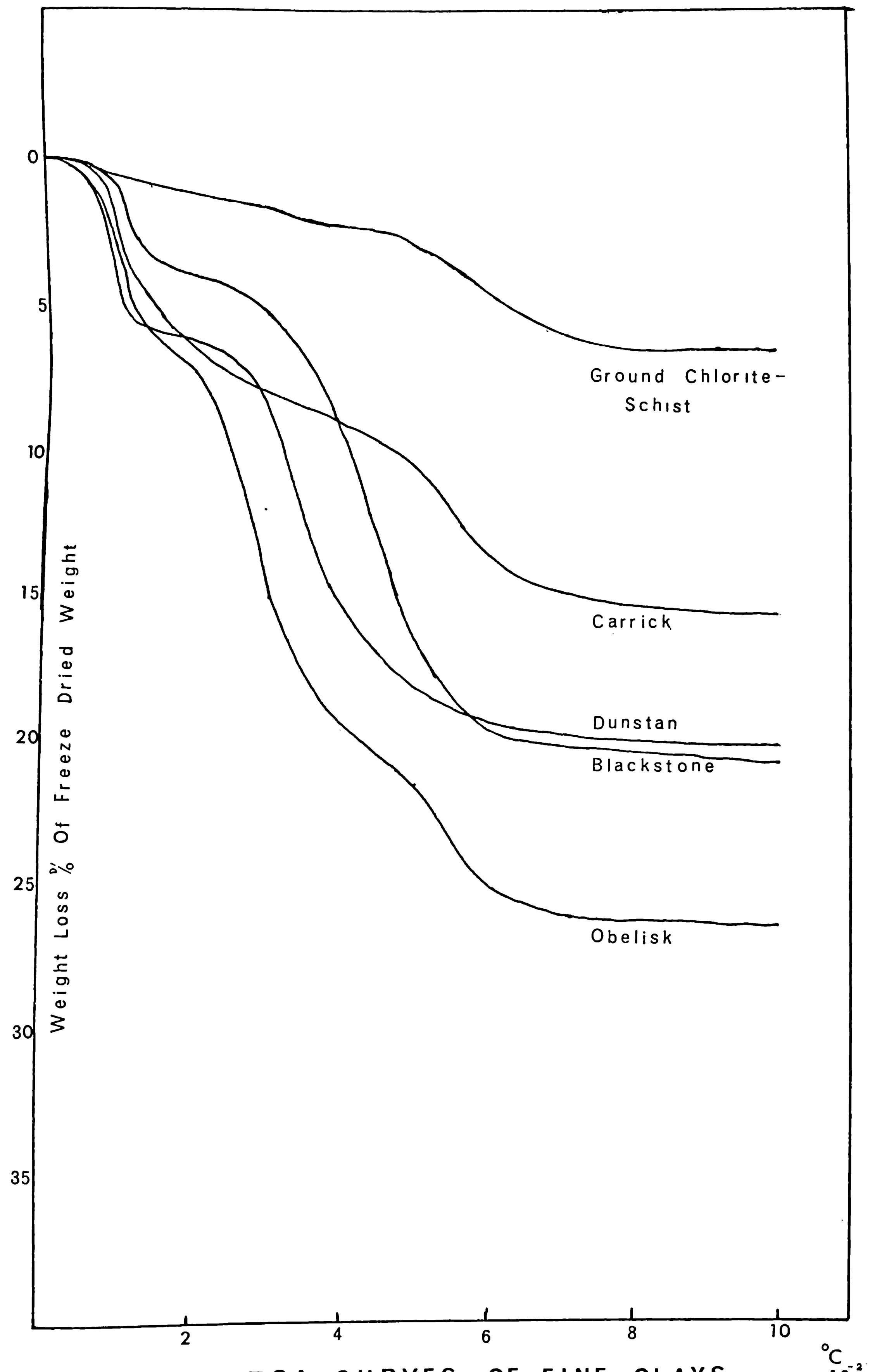


FIG 11·10 TGA CURVES OF FINE CLAYS SEPARATED FROM HIGH COUNTRY YELLOW-BROWN EARTHS DEVELOPED ON CHLORITE SCHIST

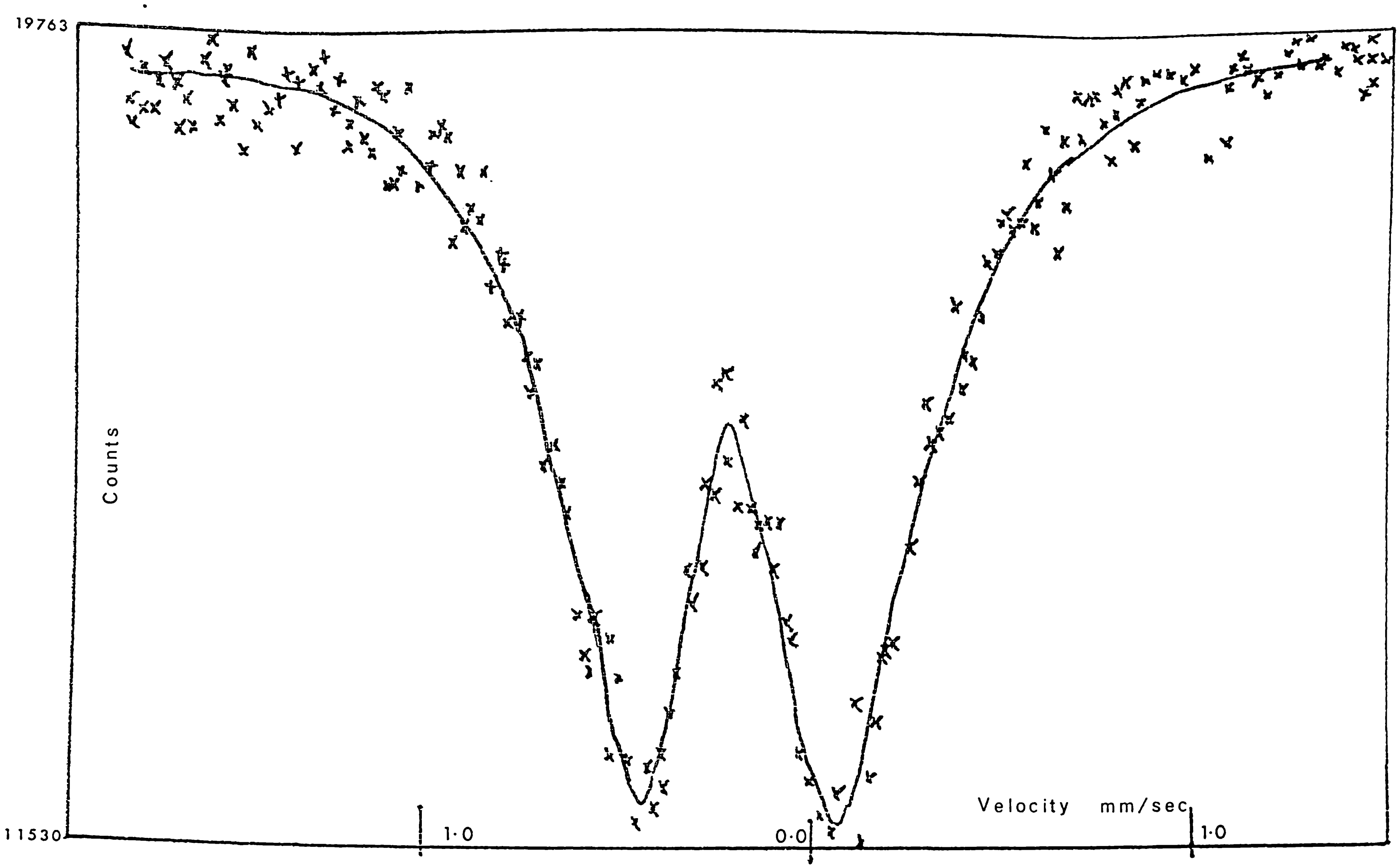


FIG 11·11 MOSSBAUER SPECTRUM OF CARRICK FINE CLAY

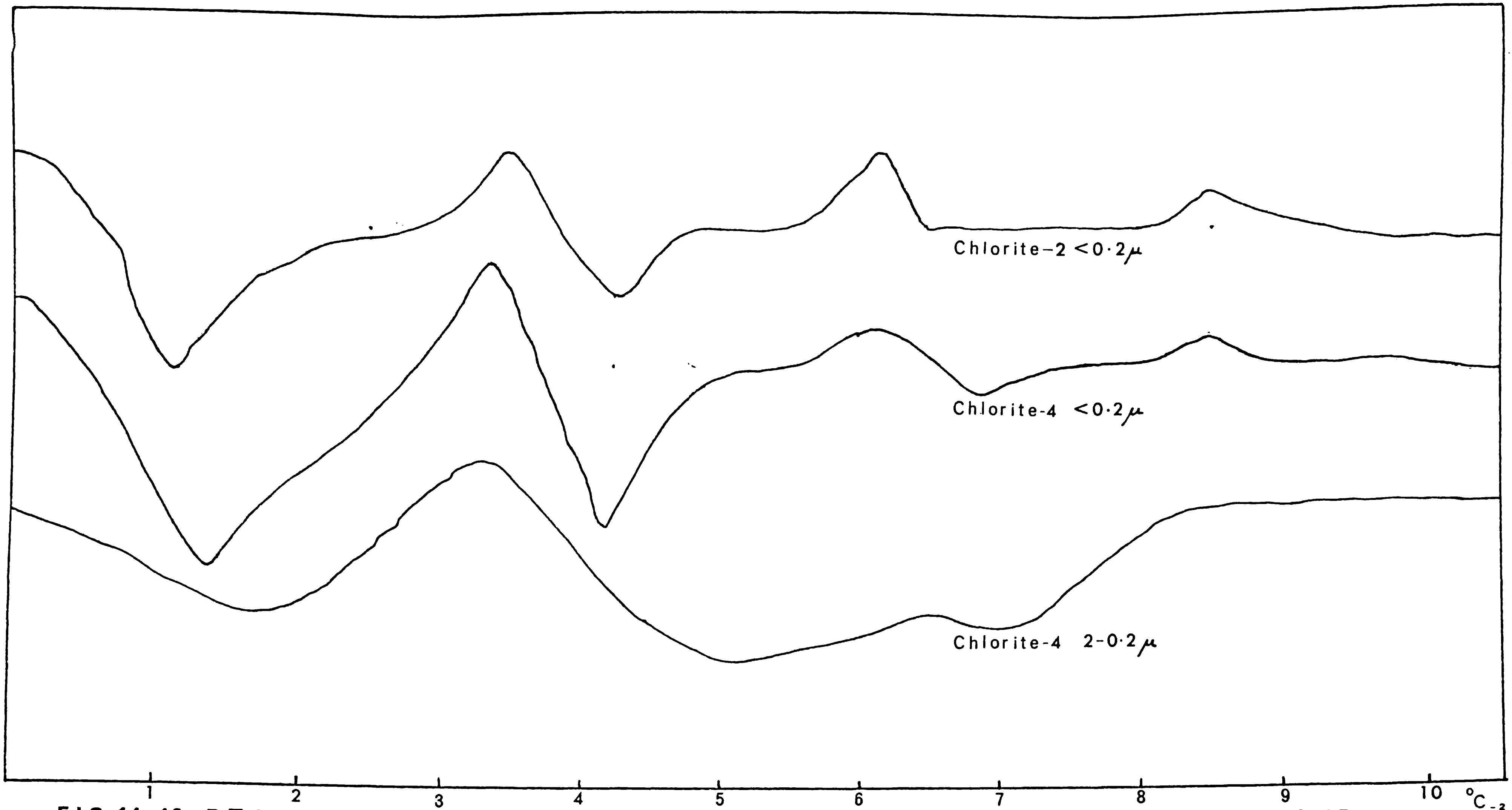


FIG 11·12 DTA CURVES OF GROUND CHLORITE-SCHIST FROM THE SOUTH ISLAND chlorite samples described by Caillère and Henin[308] which did not show a large exothermic peak. Sabatier[309] showed that particle size could have a large effect on thermal curves especially of chlorites and tended to give low temperatures for reactions as well as a sharpening of peaks. The DTA for the 2-0.2 μ fraction of ground chlorite schist are not as distinct as those for the finer fraction bearing out Sabatier's observation. What probably happens is that the structure of the chlorite has been so disorganized that most of the hydroxyl groups are on the edges of particles and so are more easily lost. Also the inner hydroxyl groups have not far to migrate to the surface of a small particle. The dehydroxylation peaks that were reported by Kirkman et al[81] were at 503-518°C which again was lower than that usually associated with the layer clays. Fieldes and Furkert[99] have shown that grinding can disorder the structure of a feldspar so it could give a non-characteristic DTA pattern.

All the samples except Dunstan show a small exotherm about 850-900°C. This is not crystallization of mullite but rather the formation of spinel. No mullite is found in the samples heated to 1200°C. There is also no evidence for any crystalline form of silica on heating. Samples were only taken to 1200°C and hematite and a spinel the only phases present in the X-ray patterns of the heated samples.

11.10 CATION EXCHANGE

The cation-exchange capacities of the fine clays were measured by the adaption of the method described by Mackenzie[132] and described in section 4.4.7a.

Table 11.12 Cation Exchange Capacities of some South Island High Country Fine Clays

	pH 3.5 (meq/%)	pH 10.5 (meq/%)	ΔCEC (meq/%)
Obelisk	28	32	4
Carrick	22	25	3
Blackstone	20	24	4
Chlorite-2 ($<0.2\mu$)	21	22	1
Chlorite-4 ($<0.2\mu$)	18.2	23	5
Waxy Allophane	28.6	84.8	56.2

The samples do not show the large CEC values characteristic of the volcanic allophanes in Chapter 4 but have values in the range suggested by Grim[13] for illites. The ΔCEC is also low suggesting that little truly amorphous material is present. The total exchangeable bases for the soils are in the low to very low range[278] despite the high figures for Mg^{2+} in the analyses. This means that considerable leaching has taken place so that the vegetation is limited by both nutrient supply and climate to tussock grasses. The low values for CEC indicate that little vermiculite is present since this has values in excess of 100 meq/% [13].

11.11 PHOSPHATE RETENTION

The adaption of Saunder's method described in section 4.4.7b was used. The values obtained for the fine clays are shown in Table 11.13.

Table 11.13 P-retention of Some South Island High Country Fine Clays

	mg/gm P retained
Obelisk	3.86
Carrick	6.99
Blackstone	6.75
Dunstan	17.46
Chlorite-2 ($<0.2\mu$)	19.5
Chlorite-4 ($<0.2\mu$)	19.2
Waxy Allophane	27.3

The phosphate retention is approximately 25% of the value for the volcanic allophanes (see waxy allophane value). The ground rock samples have a higher value than the soils derived from them. This is probably because a large amount of the free aluminium and iron responsible for P-retention at the pH used has been leached from the clay. The fine clays themselves are highly siliceous suggesting that mica relics such as those found by Dyal[267] are present which will be likely to have little cationic or anionic activity, like the amorphous silica in section 7.3.5.

The phosphate extracted by citric acid for these soils is very low[278] and suggests that the plant nutrient level is very low.

11.12 ISOELECTRIC POINT

The isoelectric point of the fine clays were determined using the method outlined in section 5.5. The results are tabulated in Table 11.14.

Table 11.14 Isoelectric Points of some South Island Fine Clays

	pH at isoelectric point
Obelisk	< 3
Carrick	3.6
Blackstone	3.3
Dunstan	< 3
Ground chlorite-schist	< 3
Illite	< 3

These figures show that the amorphous material does not behave in the same way as the volcanic allophanes.

There is some correlation with the amount of ferric oxide present. Both the Dunstan and Obelisk fine clays contain more than 5% FeO and the isoelectric points are too low to be measured. The Carrick and Blackstone samples have little FeO and more Fe_2O_3 and show isoelectric points sufficiently high to be measured although not as high as would be expected for the amount of iron present. This is further evidence that the iron is not present as 'free' ferric oxide and shows that the amorphous fraction of the South Island soils is not the same as that of the volcanic soils of the North Island.

11.13 ELECTRON MICROSCOPY

The fine clay suspensions were dropped on a copper grid coated with a collodian film and dried in a desiccator overnight over silica gel in covered petri dishes. The particles were then viewed by transmission mode.

The particles when viewed are very much bigger than those of volcanic allophane with individual particles up to 0.2μ in diameter, unlike the volcanic allophanes where particles this size were clearly seen to be aggregates. The particles have sharp edges and show striations (see Plates 11.1-11.7). These closely resemble those seen by Dyal[267] and Gal and Rich[310]. The striations are termed moiré patterns and were related by movement of the mica laminae. The striations moved when the beam was intensified and gave the appearance of water boiling off.

The particles are obviously thin as the beam can readily penetrate them. Stereo pictures showed the particles to have very little depth and possess sharp edges.

The larger particles are irregularly shaped and they reflect the weathering conditions under which they were formed, i.e. frost riving and grinding.

Besides the coarser particles in the micrographs of Carrick and Blackstone there is a small amount of much finer material which appears similar to that of allophane and also bears close resemblance to that in the micrographs published by Claridge[268] of the Antarctic 'soils'.

Also present in the micrographs are bacteria which are absent in the volcanic samples. This shows that despite the low bacterial count in

Plate 11.1

Electron Micrograph of Obelisk Clay

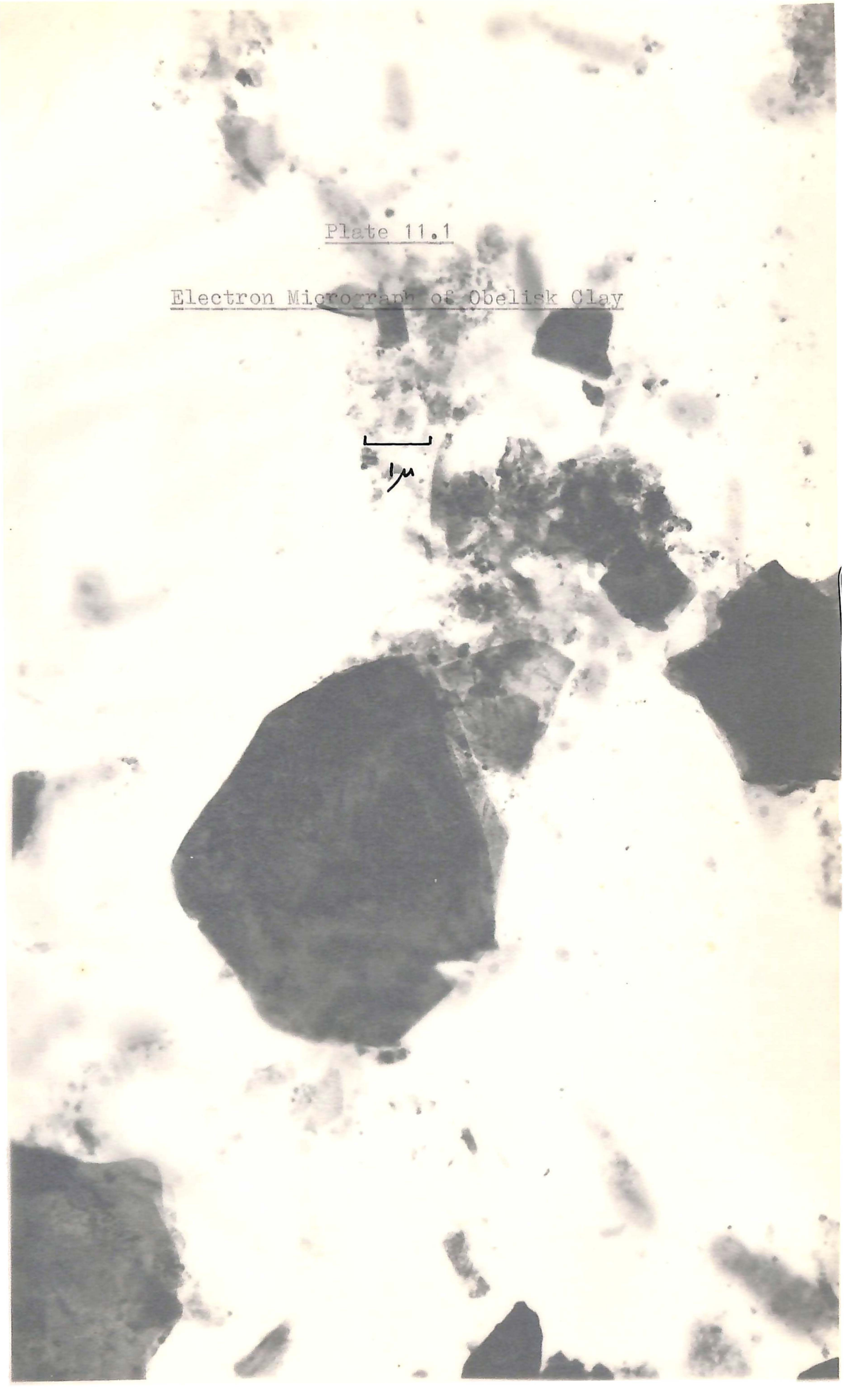


Plate 11.2

Electron Micrograph of Carrick Fine Clay

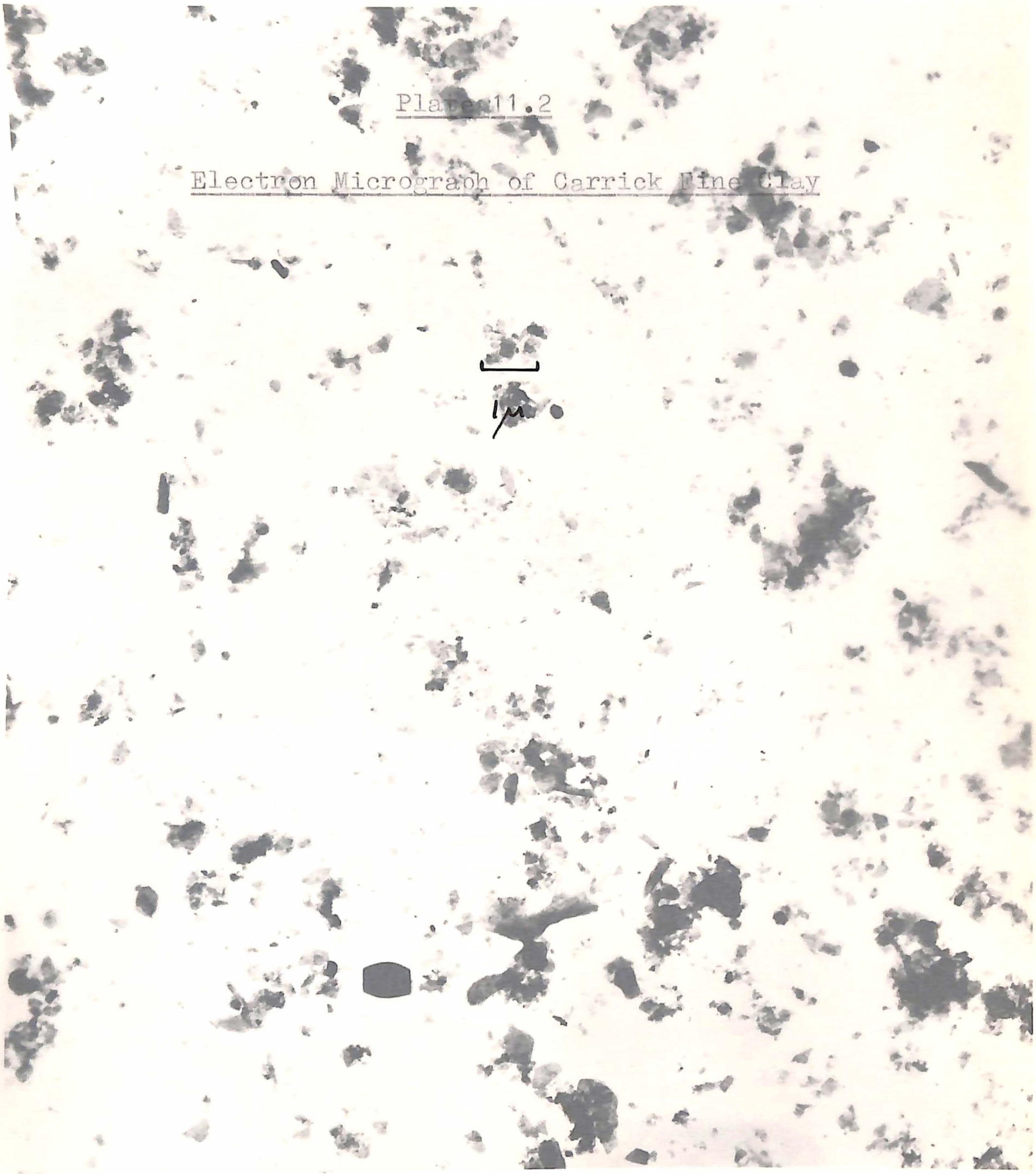


Plate 11.3

Electron Micrograph of Blackstone Fine Clay

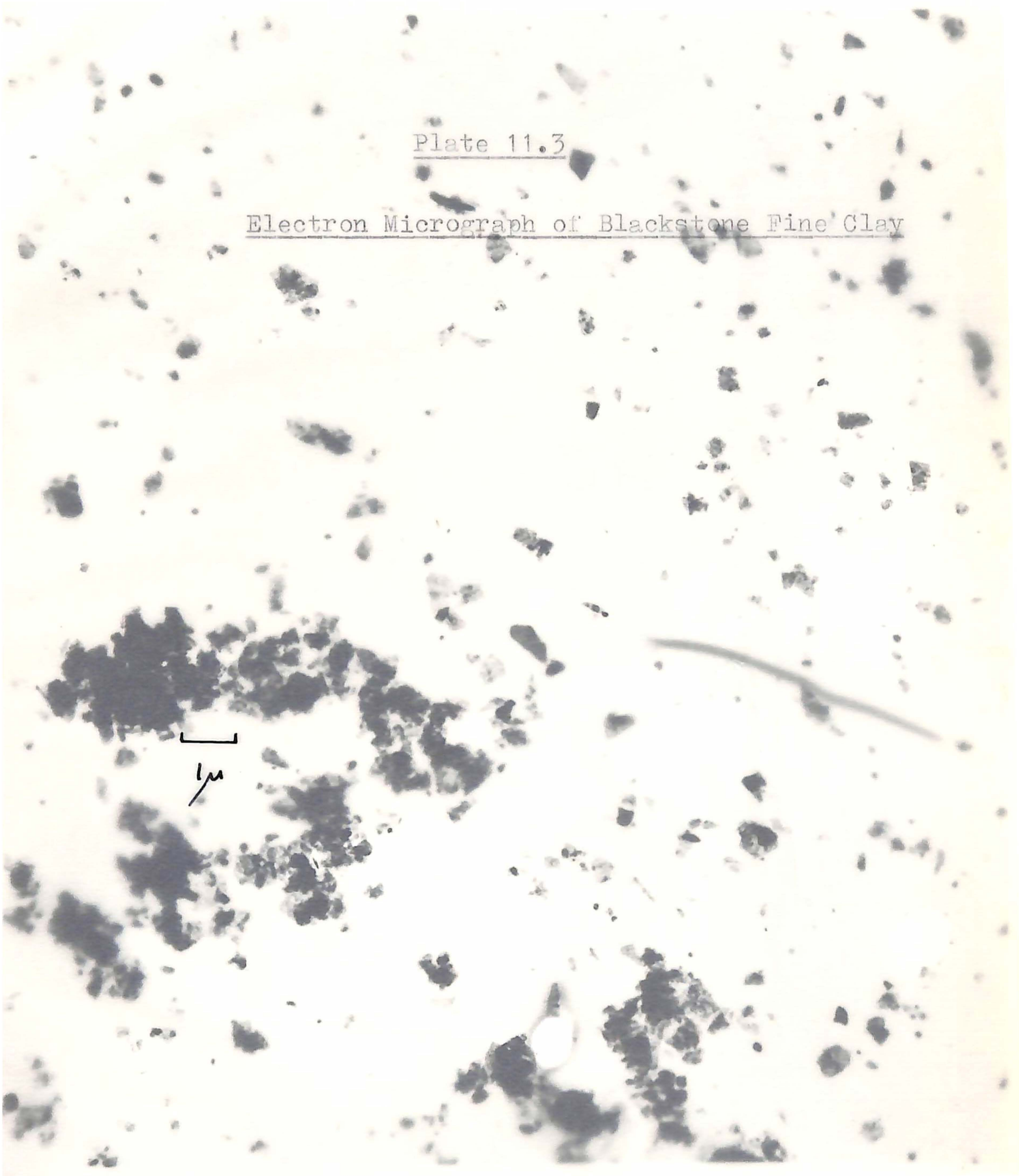


Plate 11.4

Electron Micrograph of Blackstone Fine Clay

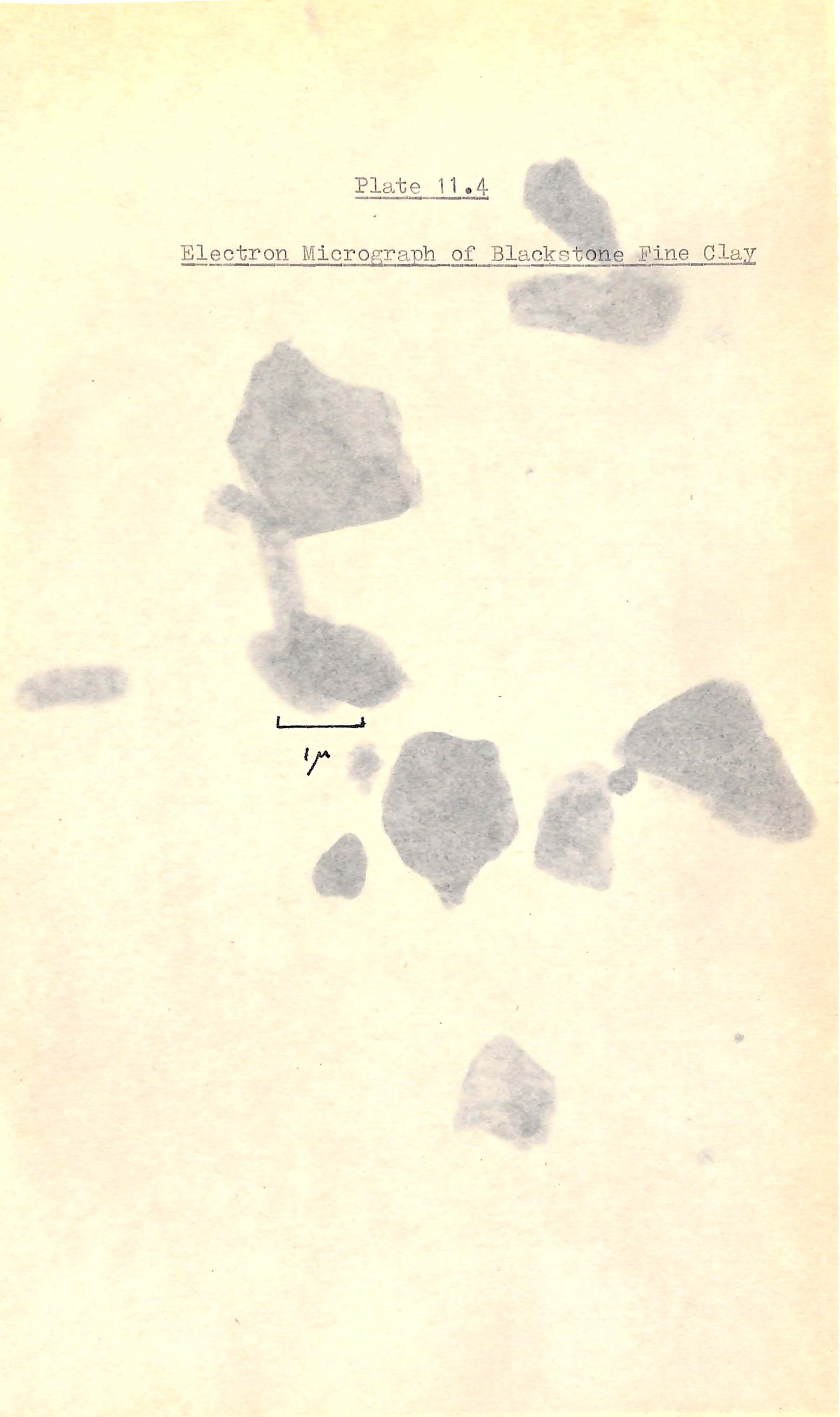


Plate 11.5

Electron Micrograph of Ground Chlorite - 2 Schist

(Clay sized fraction)

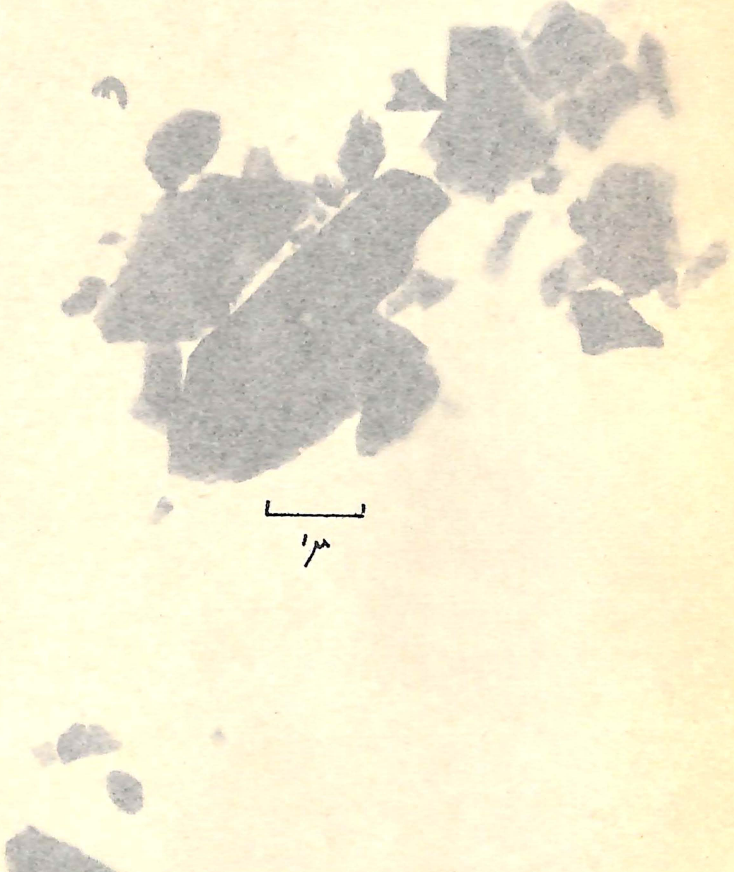


Plate 11.6

Electron Micrograph of Ground Chlorite-4 Schist

(Clay sized fraction)

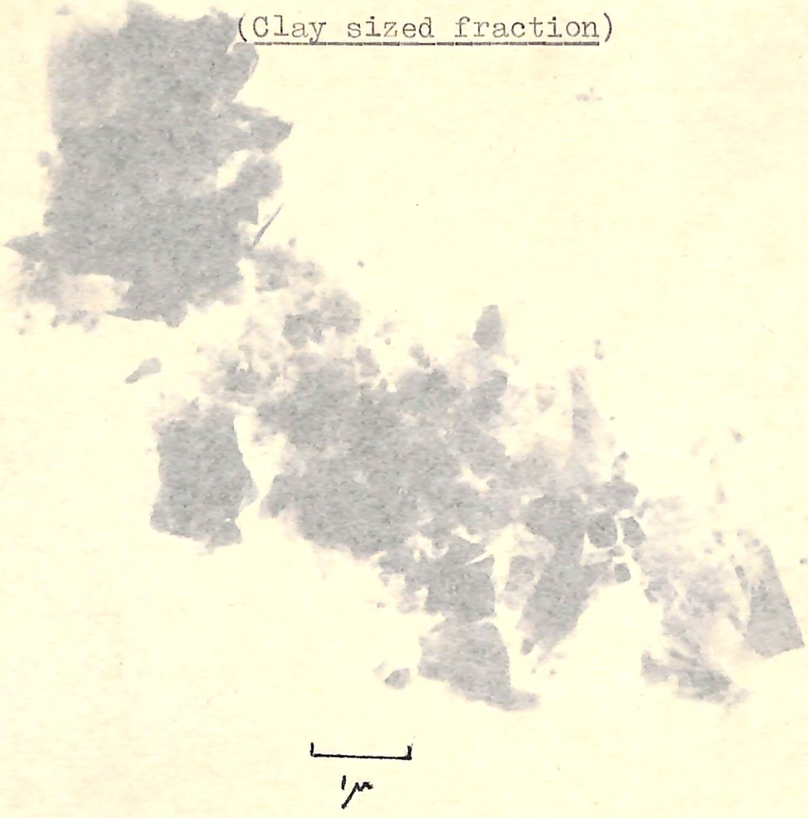
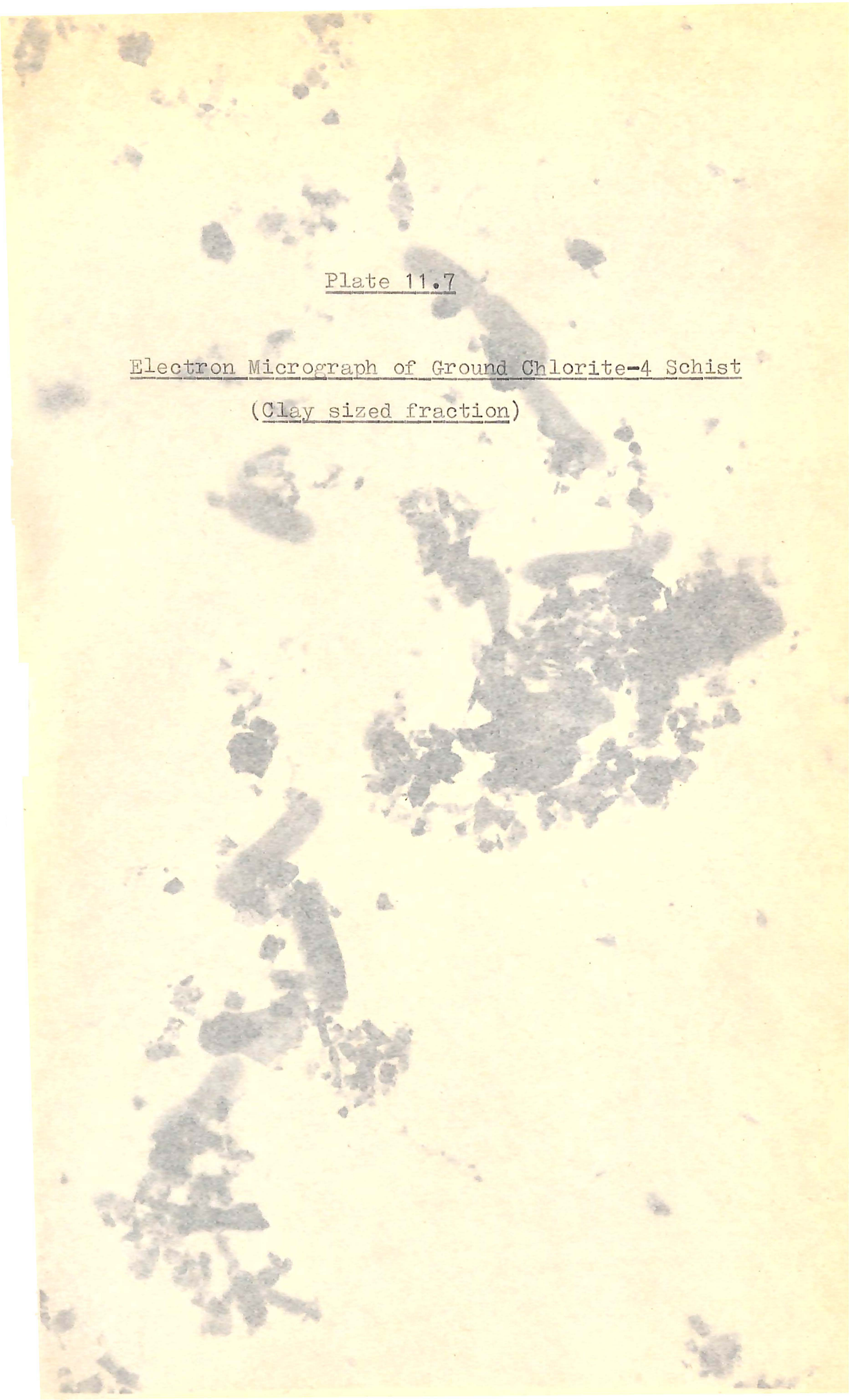


Plate 11.7

Electron Micrograph of Ground Chlorite-4 Schist

(Clay sized fraction)



the soils, bacteria can flourish once the conditions are favourable.

11.14 SURFACE AREA AND WATER ADSORPTION

Measurement of water uptake over saturated salt solutions was made and surface areas evaluated by the method outlined in section 4.4.8. The values obtained for uptake are tabulated in table 11.15.

Table 11.15 Water Adsorption and Surface Areas for High Country South Island Soils

	p/p_0	W gm/gm	$\frac{p/p}{W(1-p/p_0)}$	
Obelisk	0.96	0.123	195	When plotted
	0.751	0.063	47.6	Intercept = 1.9
	0.51	0.044	23.7	
	0.327	0.040	12.15	Slope = 31.2
	0.113	0.024	5.30	so W_m = 0.032 gm
	0.083	0.004	2.26	S_o = 123 m^2/gm
Carrick	0.96	0.134	179	When plotted
	0.751	0.076	39.5	Intercept = 0.85
	0.51	0.051	20.4	
	0.327	0.042	11.57	Slope = 22.8
	0.113	0.037	3.44	so W_m = 0.042 gm
	0.083	0.033	2.74	S_o = 147 m^2/gm
Blackstone	0.96	0.129	186	When plotted
	0.751	0.058	51.7	Intercept = 1.40
	0.51	0.032	32.52	
	0.327	0.024	20.25	Slope = 38.8
	0.113	6.022	5.79	so W_m = 0.025 gm
	0.083	0.010	0.91	S_o = 87.7 m^2/gm
Chlorite-4	0.96	0.0732	327	When plotted
	0.751	0.0371	80.9	Intercept = 2.30
	0.51	0.0245	42.5	
	0.327	0.043	22.8	Slope = 61.5
	0.113	0.0440	9.10	so W_m = 0.0156
	0.083	0.003	-	S_o = 54.7 m^2/gm

Compared with the surface area of the order of 400 m^2/gm for volcanic allophanes these figures show the particles are not as fine as volcanic allophane with much less surface area. The water adsorbed is less than the volcanic allophanes and is in the region for illite given by Nelson and Hendricks[311].

The clays show a higher value for S_o than the ground chlorite schist of the same nominal diameter and indicate there must either be smaller particles or more irregular shapes. From the previous section it was seen that the particles are much the same shape but there is a small proportion of fine material which appears structureless.

11.15 DISCUSSION

The soil series Obelisk, Carrick and Blackstone were collected from the same parent material on the slopes of the Old Man Range in Central Otago and show influences of climate due almost solely to height.

If the chemical properties of these three are considered first, Obelisk retains less phosphate than either Carrick or Blackstone. This is probably a combination of two effects. Stout[312] and Schoen[313] have shown that a decrease in the size of kaolinite particles results in an increase in phosphate fixation which follows retention. It can be clearly seen from the electron micrographs that the particles of Obelisk fine clay are larger than those of Carrick and Blackstone and so probably will retain less phosphate.

The other possible effect is due to the low number of potential retention sites. Obelisk soils have weathered less due to the lower temperatures encountered at the higher altitude than Carrick and Blackstone. The rate of formation of P-retaining material is then low but removal is high under the high rainfall.

A further evidence of less weathering occurring in the Obelisk sample can be seen in the DTA curves. The Obelisk fine clay retains a peak at 600°C which is also present in the ground chlorite-schist, absent in the Blackstone and Carrick samples but present in the Dunstan sample collected also at 5000 ft. The Dunstan sample shows signs of further weathering than the Obelisk sample but as it was collected from a different site this may only be due to a change in the parent material.

Further weathering has taken place in the development of the Blackstone sample. It has been placed in the yellow-grey earth classification[278] and nutrient levels have been considered high probably because a great deal of leaching has not taken place. The Blackstone soil is one of the samples which is not X-ray amorphous. The pattern shows the presence of poorly crystalline illite, showing again that although oxidation of iron has taken place the mica has not weathered beyond the first stage suggested by Fieldes and Taylor[307]. If the amount of ferrous iron is considered as an index of weathering then Obelisk would be the least weathered with Blackstone next and Carrick last. Certainly the Blackstone soils are unlikely to be strongly leached under the lower (18-25") rainfall than found for the Obelisk soils (40-70") so that although the average temperature is warmer, little more chemical weathering will take place. The Carrick soils have developed under a moderate rainfall (40-50") and because they have developed at a lower altitude than the Obelisk soils have progressed further along the weathering cycle. The Carrick fine clays are X-ray amorphous and less siliceous than any of the other samples and also have the highest phosphate retention which suggests that more amorphous sesquioxides are present. The large percentage of fine clay that dissolved in boiling 0.5M NaOH confirms that this sample has the highest amount of truly amorphous material. However, the P-retention values are much lower than expected with the amount dissolved in NaOH. Follett et al[259] have shown that crystalline material is little attacked by boiling NaOH so it is likely that much of what dissolves is amorphous silica and unable to fix phosphate.

The large amount of material remaining which, in the case of Obelisk and Carrick fine clays, is amorphous suggests there must be at least pseudo-crystalline material present.

Hutton[314] has published analysis figures for some schists of the South Island. These were all high in silica and contained quartz as a major constituent. The analyses he reported were high in bases such as Ca and Mg as well as FeO. A large amount of these elements is lost on clay formation and iron is oxidized to the ferric state and analysis figures for the fine clays show that iron and aluminium are retained. Ball[315] has published figures for clay chlorites which contain appreciable amounts of magnesium which is not present in the fine clays studied here. The clay with the most Mg (Carrick) contains only 4.32% Mg as opposed to clays with 19.06% found by Ball and 16.23% in the chlorites reported by Hutton. This suggests that in fact there is little chlorite in the fine clay fraction.

For the Dunstan sample collected on Coronet Peak, a comparison with the parent rock is possible. Hutton[314] published an analysis for the rock (see A Table 11.16) and also for chlorite (B table 11.16) found in the same vicinity.

Table 11.16 Analysis of South Island Rock[314]

	A %	B %
SiO_2	43.39	26.69
Al_2O_3	15.05	19.57
Fe_2O_3	4.53	3.49
FeO	5.43	21.80
MgO	4.02	16.23
CaO	14.23	0.17
H_2O^-	2.26	11.17
H_2O^+		0.12
TiO_2	1.39	2.30

From these figures it is clear that a concentration of non-siliceous material occurs in the fine clay probably due to the non-break up and weathering of quartz grains. The low FeO/Fe_2O_3 ratio compared with that in the parent rock means considerable oxidation must have taken place. This could be achieved by mechanical breakup of the rocks and subsequent oxidation.

The initial weathering product of muscovite is usually illite or hydromica. Butler[316] has shown that on weathered muscovite schist in Norway, the only recognizable clay mineral is illite, the analysis suggesting a material very similar to potassium deficient muscovite with some of the ferrous iron lost. In weathering, Anderson and Hawkes[317] suggested that the first ions to be lost are the bases followed by silica and finally iron and aluminium, and this appears to be the case with the clays in the high country yellow-brown earths.

Chlorite can weather to a vermiculite product but there appears little evidence for vermiculite in any of the samples studied, suggesting that the observation of Bayliss[318] that illite is more resistant to weathering is correct, and that if vermiculite has formed it has readily weathered further.

There is little chlorite in the coarse clays shown only by very small peaks in the X-ray which means that either fractionation has occurred or that the chlorite rapidly weathers once it reaches small clay size. Since it is layered it is unlikely to form structureless material on weathering.

Biotite has been shown to weather to an aluminous vermiculite-chlorite interlayer[319], with a 14Å basal spacing which does not collapse on heating unlike vermiculite[320]. Walker[321] has shown breakdown of soil biotite into vermiculite with an increase of basal spacing from 10Å to 14Å with a consequent loss of Mg^{2+} and oxidation of Fe^{2+}. There was no trace of chlorite formation.

Thus the small amount of amorphous structureless material seen in the electron microscope is not formed from micas or chlorite, so the probable source is feldspars. These have a framework structure and in order to form kaolinite, Fieldes and Taylor[307] have postulated the formation of amorphous oxides in the weathering sequence. Fieldes and Furkert[99] and Furkert and Fieldes[120] suggested that amorphous hydrous feldspars be included in the definition of allophane B. The term 'hydrous feldspars' has been used by Fieldes[100] to describe amorphous material not soluble in boiling NaOH.

It is apparent however from the course of these studies that if the classification made by Fieldes and Furkert[120] for allophane B is used, amorphous hydrous mica must further be included in the definition as this also is not soluble in boiling NaOH. An exothermic peak on which the distinction between allophane A and allophane B was made is, however, present in the Blackstone, Obelisk and probably the Dunstan sample as well as the ($< 0.2\mu$) ground chlorite-schist but not the Carrick sample. The peaks are smaller and broader than for the volcanic allophanes but on X-ray analysis of the product mullite is not found. Rather, the product is hematite and a spinel, no doubt reflecting the lower aluminium content and high iron content. There is no evidence for silica but it is possible that at 1000°C transition to cristobalite is occurring and the silica is going through an amorphous stage.

The Carrick fine clay has a dehydroxylation peak around 535°C, as does the Blackstone fine clay, unlike that normally accepted for allophane. Thus it must be considered that there is order in the sample due to the mica structure, despite the IR spectra and also the pedological feel of the fine clays.

A comparison of the electron micrographs of the fine clays and ground chlorite-schist shows little difference. The ground rock particles are perhaps a little sharper, denser and more uniform in size but very closely resemble the coarse particles of the fine clays. The main difference in the micrographs is the very fine material that is present in the fine clay samples.

This fraction is probably truly amorphous and derived from weathering of feldspars in the manner as described by Fieldes and Taylor[307] and the cold conditions prevailing have prevented its further crystallization into layered silicates. This is probably the fraction that dissolves in NaOH. The low amount of amorphous material present in the Blackstone sample shows that crystallization has taken place under the warmer conditions prevailing at the lower altitude at which the soil has developed. The fraction remaining after sodium hydroxide treatment is still largely amorphous to X-rays but has considerable order.

Weathering

The problem arises as to how chlorite-schist can be rendered amorphous. Ground chlorite-schist is crystalline with sharp peaks even for the $< 0.2\mu$ fraction although many of the smaller peaks have merged with the background. Under the electron microscope the particles of the ground rock are almost uniform with very sharp edges. The fine clays from the soils however have a range of particle size as well as a small amount of very fine material. Some of this material is coating the edges of the largest particles. From the chemical properties it is obvious that weathering has progressed beyond the simple grinding stage and that chemical weathering has taken place. The ground rock has high P-retention values due to unleached cations but comparable CEC since this is due to structural substitution which will be much the same in relatively unaltered material.

A further discussion of how breakup to the small size occurs will be made after the next chapter.

In order to distinguish the amorphous material of the high country from allophane found in the soils of the North Island derived from volcanic ash it is proposed to call this material 'alpinite'. This does not necessarily imply the material is a new mineral but gives a distinction as to the mode of formation. 'Alpinite' is formed mainly by a process of mechanical weathering as proposed in Chapter 13 whereas allophane has formed by chemical weathering, usually from volcanic glass and its distinguishing features are noted in Chapter 13.

11.16 CONCLUSION

The fine clays of the South Island high country soils developed on chlorite-schist contain X-ray amorphous material that has some physical characteristics of allophane. Only a small proportion of the fine clay is soluble in boiling 0.5M NaOH and therefore truly amorphous.

The chemical properties of the amorphous material show it does not have the high reactivity associated with allophane and has many properties common with the finely ground parent material.

It is proposed this material be called 'Alpinite' to distinguish it from allophane derived from volcanic ash.

CHAPTER 12 CLAYS FROM SOILS DERIVED FROM GREYWACKE

12.1 INTRODUCTION

The occurrence of amorphous material in the soils derived from chlorite schist prompted investigation of soils derived from greywacke and lying in the yellow-brown earth group, especially those of the high country sub-group. The Puketeraki sample has already been suggested as containing amorphous material and this was studied together with another soil derived from the same parent material on the Craigeburn range of the South Island (see Fig. 12.1). The suggestion that soils of the ranges of the North Island also contained amorphous material[322] led to a study of a sample from the Akatarawa ranges, north of Wellington.

12.2 DESCRIPTION OF SAMPLES[278]

Puketeraki. Silt or sandy loams developed on greywacke detrius (solifluction deposits and local loess) collected at 3000 ft. The native vegetation is snow tussock with light scrub. Rainfall is 40-80".

CEC	A = 28 meq/%	Total Exchangeable bases	21%
	B = 17.2		8%
	C = 9.5		

Representative Profile

A horizon.	dark grey brown crumbly loam which is very friable.
B	Yellow-brown crumbly loam that is friable.
C	pale olive brown loamy sand on stony sand.

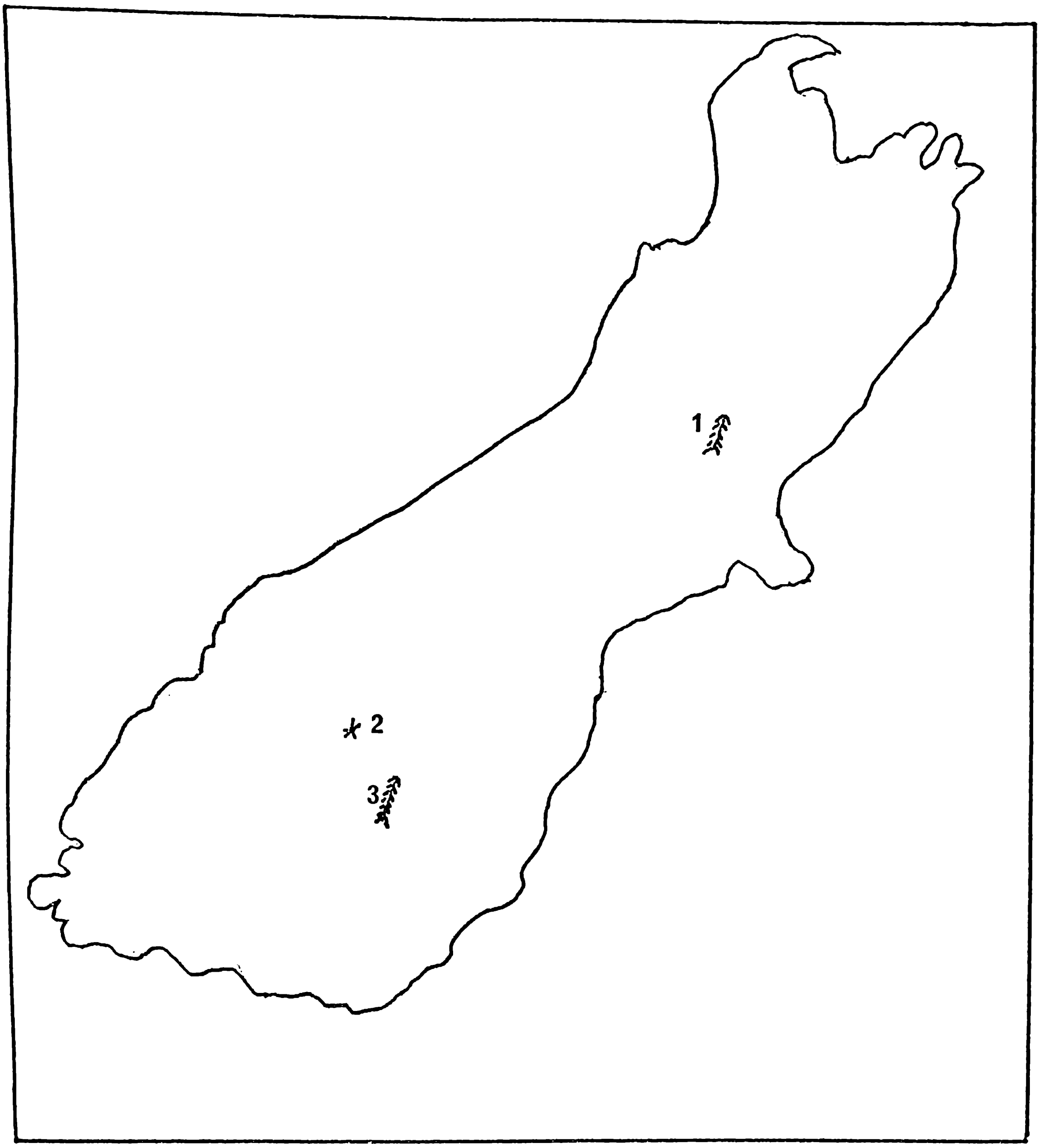


FIG 12·1 SAMPLE SITES IN THE SOUTH ISLAND

1 Craigieburn Range
2 Coronet Peak
3 Old Man Range

Cass Silt to stony loams developed on greywacke loess over glacial moraines and greywacke gravels. The sample collected at 3300 ft. The native vegetation is snow tussock and fescue tussock. Rainfall is 40-60".

CEC	A 19.8 meq/%	pH 5.9	Total Exchangeable bases	35%
	B 14.6	5.8		8%
	C 7.7	6.2		9%

Representative Profiles

A very dark grey-brown crumbly silt loam which is friable.

B yellow-brown crumb to nutty silt loam which is firm.

C pale olive-brown gravelly sand.

Spenser Loams tending to stony loams developed on argillite and solifluction detrius under sub-alpine grassland. Sample collected at 5700 ft above sea level. Rainfall is 80-160".

CEC	A 21.1 meq/%	pH 4.5	Total Exchangeable bases	0.6%
	BC 11.2	5.1		0.3%

Representative profile

A dark-brown crumb to granular friable silty loam.

B grey flecked with red firm yellow-brown blocky silt loam

BC pale olive nutty structure, friable stony loam tending to stony greywacke matrix.

The Akatara sample was collected from site N165 635629 and general characteristics are included under the Rimutaka stony loam and characteristics for this are given[278].

The soils are developed on greywacke, usually under forest, in the case of Akatarawa an exotic pine forest now stands. The rainfall is moderate to high (50 in. p.a.).

Representative Profile

A dark-grey stony loam

B greyish yellow stony silt loam with yellow mottling

C greywacke.

12.3 EXPERIMENTAL

The soils were treated in the same manner as those in the previous chapter. Rocks from Puketeraki and Spenser soils were ground in a Tema mill and then sedimented in distilled water and tested, along with the corresponding soils.

The chemical and physical tests were carried out by the same techniques as those in the previous chapter.

12.4 DESCRIPTION OF CLAYS

The Puketeraki sample is yellow-brown in colour and the Akatarawa sample similar. The ground rock from this soil has practically the same colour showing free ferric oxide present. The Spenser sample is olive-grey in colour and the ground rock grey, showing little ferric iron in the sample. The Cass sample lies intermediate between these two with a brown-olive colour.

All samples including the ground rocks give the allophane test described by Fieldes and Perrott[257].

The sieved soils (shingle and coarse sand removed) when moistened and rubbed between the fingers, felt greasy but not sticky but the coarse clays when separated had the stickiness associated with platy-clay minerals. The fine clays of Puketeraki and Spenser have the feel of clays with some amorphous material but were slightly sticky whereas the Cass sample did feel completely amorphous. The ground rock samples at all sizes felt sticky indicating little amorphous material.*

---

* The author thanks Mr H. S. Gibbs, for assistance in ascertaining the pedological 'feel' of a soil.

The Akatarawa fine clay samples are very similar in appearance to the volcanic allophanes further north, the soils having a similar texture and much the same colour. It has been suggested that these soils have been derived from a mixture of volcanic ash overlying greywacke. However the coarse clays have the sticky feel of platy clays such as vermiculite although the fine clays have a characteristic amorphous feel. The soil has the characteristic buff colour of free ferric oxide and contains very little ferrous iron.

12.5 DISSOLUTION IN SODIUM HYDROXIDE

The samples were treated in the same way as described in section 11.5 and results shown in Table 12.1.

Table 12.1 Dissolution in Sodium Hydroxide

	% dissolved	SiO_2/Al_2O_3 of extract
Puketeraki	21.66	3.02
Spenser	27.72	2.75
Cass		
Ground Puketeraki Rock	14.32	6.78
Ground Spenser Rock	9.10	8.32
Akatarawa	35.03	2.51
Carrick	34	

From these figures the fine clays of the greywacke derived soils can be seen to contain less amorphous material than the schist derived soils. The Akatarawa sample contains more amorphous material than the South Island samples - possibly because of the more extensive weathering that has taken place.

12.6 CHEMICAL ANALYSIS

The samples were fused with sodium carbonate and boric acid and dissolved in hydrochloric acid. The silica was determined gravimetrically, aluminium by DCTA and iron by o-phenanthroline. The ferrous iron was determined by the method described by Wilson[349]. The results are shown in Table 12.2.

Table 12.2 Chemical Analysis of Fine Clays from H.C. Yellow-brown Earths on Greywacke

	Spenser %	Puketeraki %
SiO_2	28.72	31.33
Al_2O_3	22.32	17.56
Fe_2O_3	0.35	3.19
FeO	6.15	3.38
H_2O^-	7.92	5.62
H_2O^+	31.12	36.36
SiO_2/Al_2O_3	2.18	3.12

Alkali and alkaline earth metals were not determined.

The chemical analyses confirm the visual estimates of weathering. The Spenser sample contains very high amounts of ferrous iron which must be contained in a crystal lattice and also the SiO_2/Al_2O_3 ratio is low showing little aluminium has been lost. The rainfall is considerably higher than that for Puketeraki soils so leaching would be expected to be higher. The base saturation for Spenser is less than a third that of Puketeraki showing this to be the case.

12.7 X-RAY STUDIES

From the X-ray studies a similar pattern is found to that with the chlorite schists although the South Island samples are not actually X-ray amorphous (see Table 12.3 and 12.4).

The parent material when ground contains large amounts of quartz and feldspars (probably albite) and small amounts of the micas muscovite and sericite as well as a chlorite (probably penninite) (see Table 12.5).

Table 12.3 X-ray Peaks of Fine Clays from High Country Yellow-Brown Earths Derived from Greywacke

	Puketeraki	Spenser	Cass	Akatarawa
i	9.92 w		amorphous	amorphous
		7.13 m		
	6.45 w			
	5.84 s			
	4.85 m			
ill	4.46 m	4.50 m		
g	4.20 m			
		3.55 w		
ill	3.33 w	3.35 vw		
	2.90 m			
g	2.69 w			
ill	2.54 w	2.57 w		
	2.15 w			
	1.99 w			

ill = illite
g = goethite

s	strong
m	medium
w	weak
vw	very weak
vb	very broad

The Spenser rocks contain more chlorite and micas than does the Puketeraki sample.

The sand fraction of the soils contain predominantly the same materials as the ground rock but usually with smaller amounts of feldspars and often a concentration of quartz relative to muscovite and chlorite.

The fine ground rock fractions($< 0.2\mu$) show similar spectra to the coarser fraction but with the basal spacing peaks very much reduced in intensity compared to the other spacings, showing that in grinding to this size fraction, long range order is partially broken up.

Table 12.4 X-ray Peaks of Coarse Clays from High Country Yellow-Brown Earths Derived from Greywacke

	Puketeraki	Spenser	Cass	Akatarawa
verm ch	14.15 m	14.26 w	14.19 w	
			11.06 m	
			10.00 m	
verm ch	7.05 w	7.02 m	7.08 s	
			4.95 m	
	4.82 w			
ch			4.72 w	
	4.46 w	4.48 w	4.48 w	4.44 w
q	4.25 w	4.25 w	4.25 w	
		4.18 w		
f		4.04 w		
f		3.86 w		
f		3.79 w		
f		3.67 w		
ch	3.52 w	3.54 m	3.54 m	
q	3.34 s	3.34 vs	3.35 s	3.34 w
f m	3.18 w	3.19 vs	3.19 m	
	3.04 w	3.07 m		
m	2.98 w	2.99 m	2.99 m	
			2.87 w	
		2.80 w	2.79 w	
		2.60 w	2.60 w	
	2.56 w	2.57 w	2.57 m	2.57 w
		2.50 w		
q		2.45 m		
		2.39 w	2.39 vw	
			2.13 vw	
			1.99 w	
			1.89 vw	
q			1.82 vw	

q = quartz
f = feldspar
m = muscovite
ch = chlorite

s = strong
m = medium
w = weak

Table 12.5 X-ray Peaks of Sand Fractions and Ground Rocks of High Country Yellow-Brown Earths Derived from Greywacke

	Puketeraki Sand	Spenser Sand	Cass Sand	Gnd Puketeraki Rock	Gnd Spenser Rock
ch	14.32 w	15.25 w	14.51 vw		14.25 w
				13.8 w	
m	9.8 vw	9.93 w	10.04 m	10.04 w	9.92 m
ch	7.02 w	7.08 m	7.14 m	7.13 w	7.08 w
f	6.37 w	6.37 w	6.46 w	6.42 w	6.37 w
m		4.98 w	4.98 m		4.95 w
ch		4.75 w	4.75 m		4.72 w
ch	4.48 w	4.50 s	4.50 w		4.47 w
q	4.25 s	4.27 m	4.27 s	4.25 vs	4.25 s
f	4.02 m	4.04 w	4.03 m	4.04 w	4.02 m
f			3.86 w	3.86 w	3.86 w
f	3.77 w	3.79 w	3.78 w	3.78 w	3.77 w
f	3.66 w	3.68 w	3.68 w	3.67 w	3.66 w
		3.54 w	3.55 w		3.53 w
f,ch	3.49 w	3.49 w	3.49 w	3.48 w	
q	3.36 vvs	3.35 vvs	3.35 vvs	3.35 vvs	3.35 vvs
		3.24 w		3.24 w	3.23 m
m,f	3.19 s	3.19 vs	3.20 vs	3.19 w	3.19 vs
	2.99 vw	2.99 w	2.99 w	2.98 w	
f	2.93 w	2.93 w	2.94 w	2.94 w	
		2.86 w	2.87 w	2.86 w	
	2.56 w		2.59 w	2.57 w	2.59 w
ch		2.50 w			
q	2.46 m	2.46 w	2.46 m	2.46 s	2.44 w

and other quartz lines

ch = chlorite
f = feldspar
m = muscovite
q = quartz

The coarse clay fractions show evidence of weathering. There is usually little quartz present and little evidence for feldspars. The muscovite peaks have broadened and probably represent hydrous micas or illites since the fine structure has largely disappeared.

The Puketeraki sample shows no basal spacing for illite but the peak at 4.46Å is pronounced.

There is an increase in intensity of the peak at 14.3Å in the Puketeraki sample and a splitting of the peak at 7Å suggesting the presence of chlorite and vermiculite. On K saturating and heating to 500°C the peak lessened in intensity but did not entirely disappear which confirms the presence of vermiculite and also chlorite. The fine Puketeraki clay shows little indication of quartz and only small broad peaks indicating hydrous micas but there are additional peaks suggesting the presence of goethite. The sample is yellow in colour - close to the colour of the yellow-brown earths of the lower North Island indicating there is free ferric oxide present this being in the form of goethite. This is unlike the Spenser sample which is greyish-yellow and from the analysis contains much ferrous iron. The very small broad peaks show that most of the sample is X-ray amorphous.

The Spenser clay contains chlorite and hydrous mica as the main constituents. The 14Å peak did not collapse on K saturation and heating showing no vermiculite. There is no feldspar present in the clay fraction and very little quartz. The fine clay fraction has three very broad and small peaks in the X-ray pattern which can be attributed to illite. There are also peaks at 7.13Å and one at 3.35Å probably due to chlorite and quartz respectively.

The Cass fine clay is X-ray amorphous. The coarse clay shows the same characteristics as the fine clays of the previous two, i.e. small broad peaks due to illite showing that the clay has very little long range order in the structure. However there is an additional peak at 11Å possibly due to a chlorite-illite interlayer.

All samples show a high background due to iron fluorescence.

On heating to 500° the pattern is simplified by the loss of most of the smaller peaks but the peaks are no sharper and represent only the strongest lines of micaeous clays usually without the basal spacing around 9.9Å.

The Akatarawa samples, from the North Island, show no diffraction pattern for the fine clays and only three broad lines corresponding to illite for the coarse clays.

12.8 I.R. STUDIES

Generally the fine clays show an amorphous pattern although the exception is the Puketeraki sample which shows detail in the range 920-700 cm^{-1} (Fig. 12.2 and Table 12.6).

The coarse clays show an increase in the peak resolution similar to the pattern found with the soils with chlorite schist as parent material (Fig. 12.3 and Table 12.7).

Vermiculite has a small sharp band at 870 cm^{-1} and there is a band in the Puketeraki sample at 880 cm^{-1} suggesting that vermiculite is present in the fine clay. This band is absent in all the other samples.

The hydroxyl band in muscovite is very sharp at 3650 cm^{-1} indicating tightly bound water. In the Cass, Puketeraki, and Akatarawa samples the water peak is split so it is probable that this is due to muscovite mica since the other clay minerals show this peak at a lower energy.

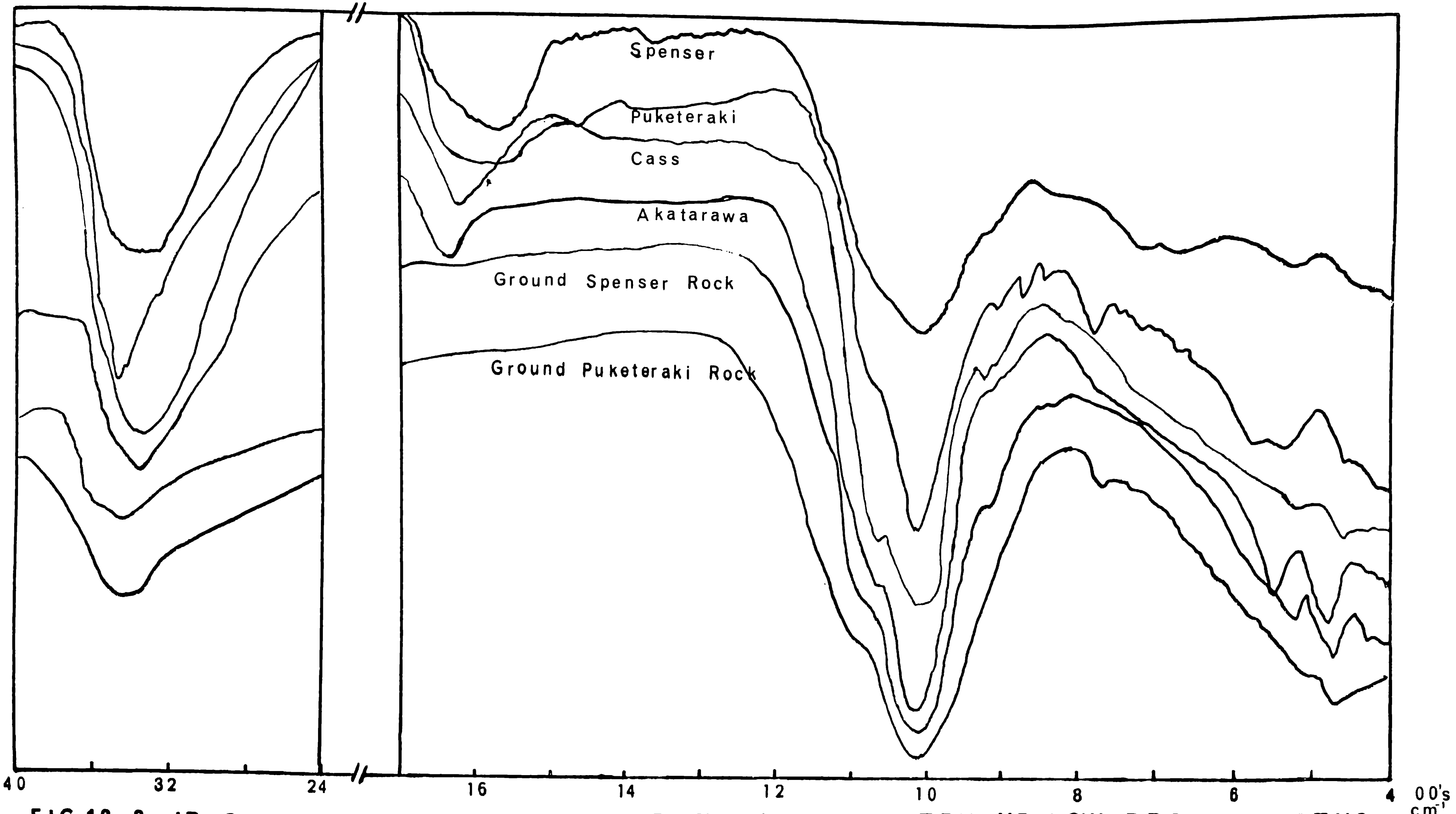


FIG 12·2 IR SPECTRA OF FINE CLAYS FROM HIGH COUNTRY YELLOW-BROWN EARTHS DEVELOPED ON GREYWACKE

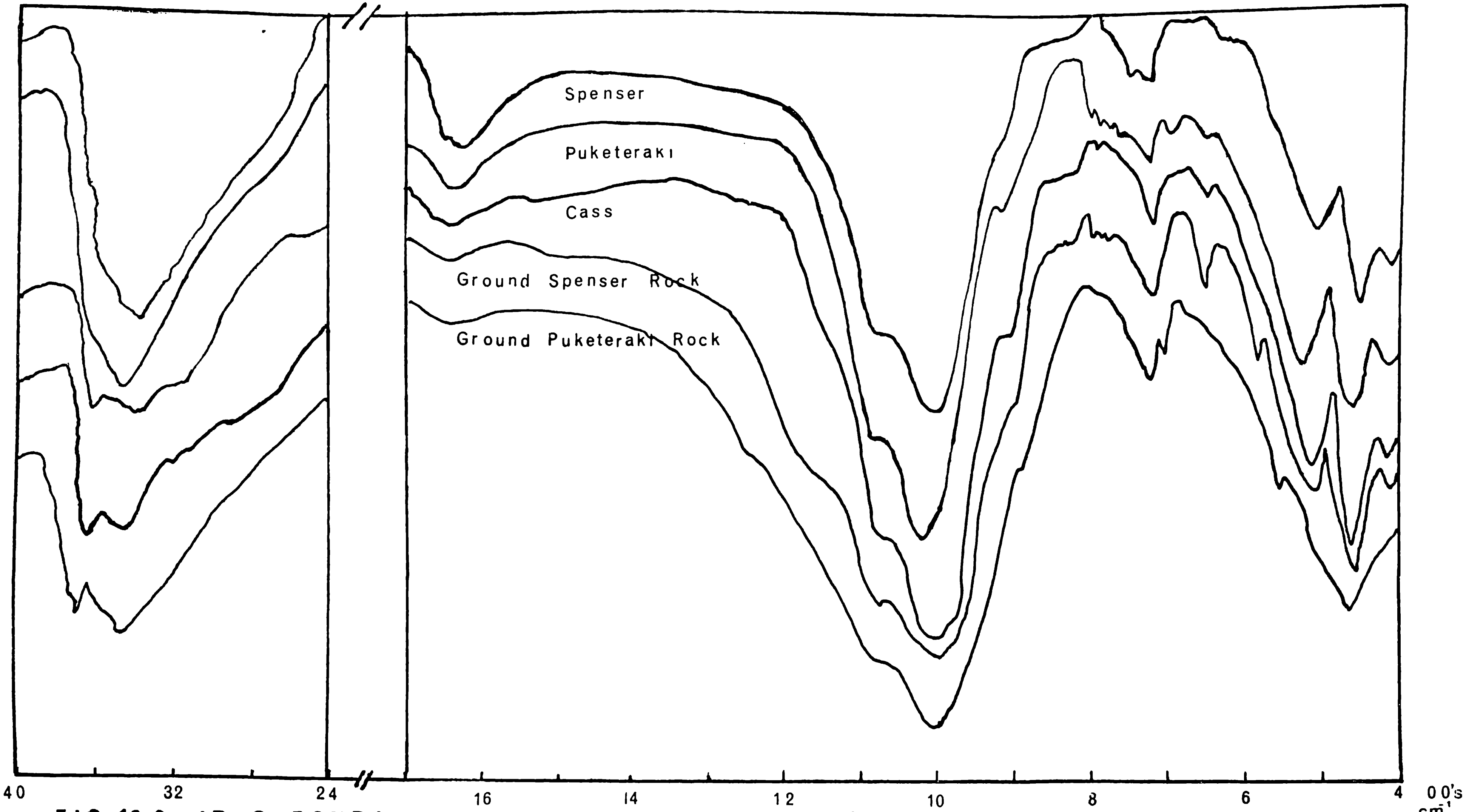


FIG 12·3 IR SPECTRA OF COARSE CLAYS FROM HIGH COUNTRY YELLOW-BROWN EARTHS DEVELOPED ON GREYWACKE

Table 12.6 Major Bands in I.R. spectra of Fine Clays from High Country Soils Derived from Greywacke

	ν OH	δ H_2O	Al-OH	Si-O	Al-OH			
Spenser	3350	1570		1010			460	
Puketeraki	3450	1630	1080(sh)	1020	910sh	790	550	
Cass	3350	1630	1060(sh)	1008	910			
Akatarawa (5ft)	3600-3450	1630	1080(sh)	1015	910sh		520	460
Ground Spenser Rock	3450	-	1080	1020	903		510,	450
Ground Puketeraki Rock	3400	-	1080sh	1010		720		460

Table 12.7 Major Bands in I.R. Spectra of Coarse (2-0.2μ) Clays from High Country Soils Derived from Greywacke

	ν OH	δ OH	SiO and Al-OH	Unassigned
Spenser	3600(sh) 3400	1635	1135sh 1080sh 1005 910sh	820sh 755 635 510 460
Puketeraki	3650(sh) 3500	1635	1085 1015 910	770 715 520 460
Cass	3650 3425	1635	1080(sh) 1000 910	825 720 515 465
Akatarawa (5 ft)	3725 3650 3450	1630	1100sh 1030 910	790 680 520 460
Ground Spenser Rock	3650 3450	1640	1160sh 1080 1000 910	790 715 580
Ground Puketeraki Rock	3600 3400	1620	1100sh 1000 910sh	790 770 505 450

12.9 THERMAL STUDIES

The DTA curves are shown in Fig. 12.4 and the major peaks tabulated in Table 12.8.

The greywacke-derived fine clays show similar peaks to those of the fine clays from schist parent material with an exotherm centred around

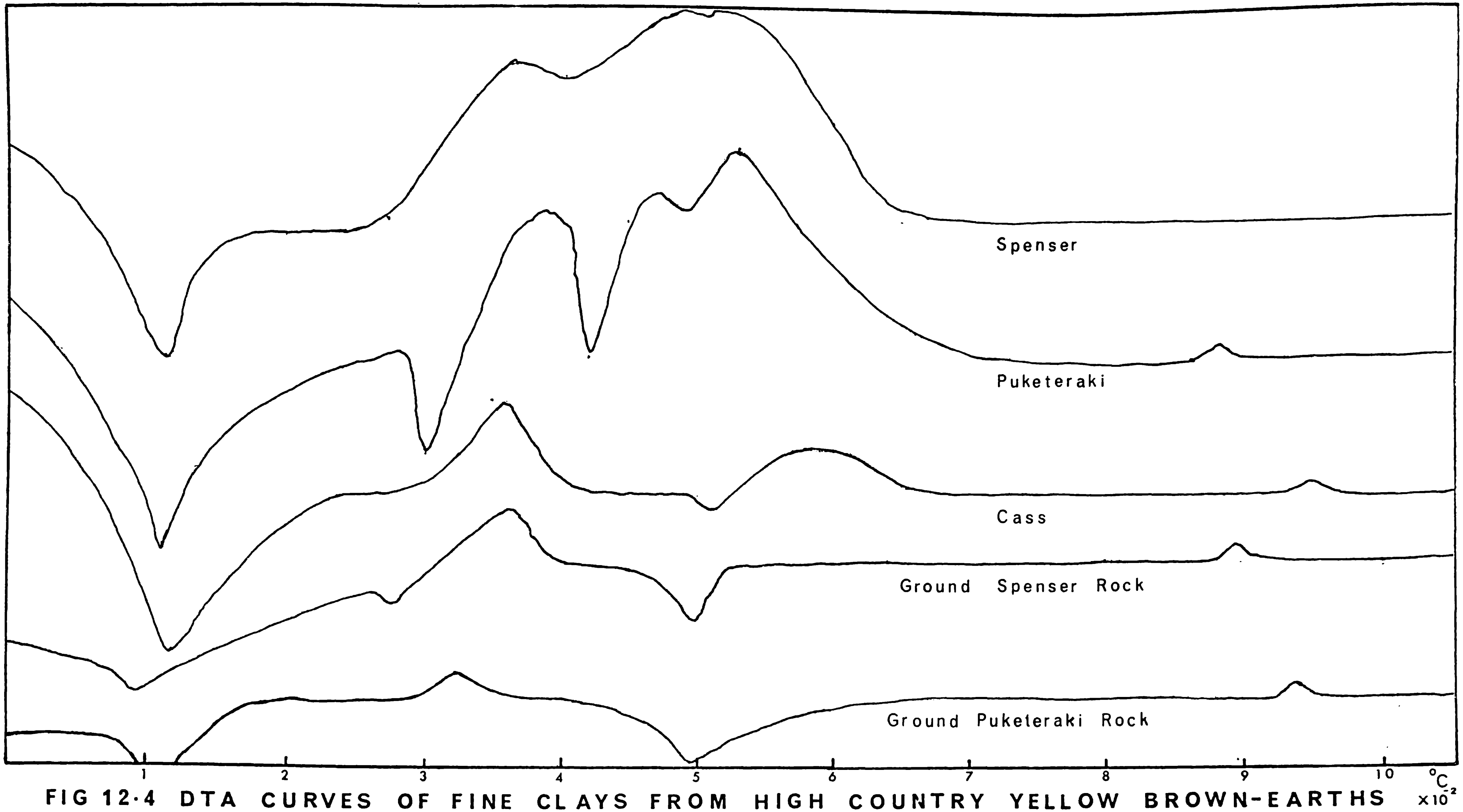


FIG 12·4 DTA CURVES OF FINE CLAYS FROM HIGH COUNTRY YELLOW BROWN-EARTHS DEVELOPED ON GREYWACKE

300°C. This is followed by an endotherm at 500°C. However this is not present in the Spenser sample, possibly being masked by the large broad exotherm although there is a dip in the curve at 405°C. The endotherm is also present in the Puketeraki sample but to a larger extent. As neither of these reach the baseline it is possible that there are actually two exotherms in the curves, one due to iron oxidation, the other to organic burnoff but since the Puketeraki sample contains little ferrous iron this doublet is unlikely and is probably a dehydroxylation.

The TGA curve of the fine clays are shown in Fig. 12.5. The Puketeraki sample shows a general weight loss but there are two regions where there is an increase in the rate of loss. The one from 210-290°C corresponds to vermiculite and one from 375-430° shows on the DTA curve as an endotherm so is a dehydroxylation. This endotherm is in the same position as that in the ground chlorite schist so is probably due to unweathered chlorite or micas.

The endotherm in the Puketeraki sample at 300° is probably due to vermiculite which was detected in the coarse clay fraction.

The dehydroxylation peaks in both the ground rock samples occur somewhat higher than that for the schist samples suggesting that the fine fraction contains a more ordered phase. It is clear that some separation occurs on grinding since the quartz inversion peak occurs with the coarser fraction of ground rock but not the fine.

The difference between the spectra of the Spenser and Puketeraki and their corresponding rocks is marked and would suggest that a considerable amount of weathering has taken place. This is certainly so in the case of the Puketeraki sample since it contains vermiculite which is a product of weathering.

The Spenser sample shows a steady weight loss after 210°. As this corresponds in general to an exotherm it seems possible that there must be some burnoff of organic matter that is not attacked by peroxide.

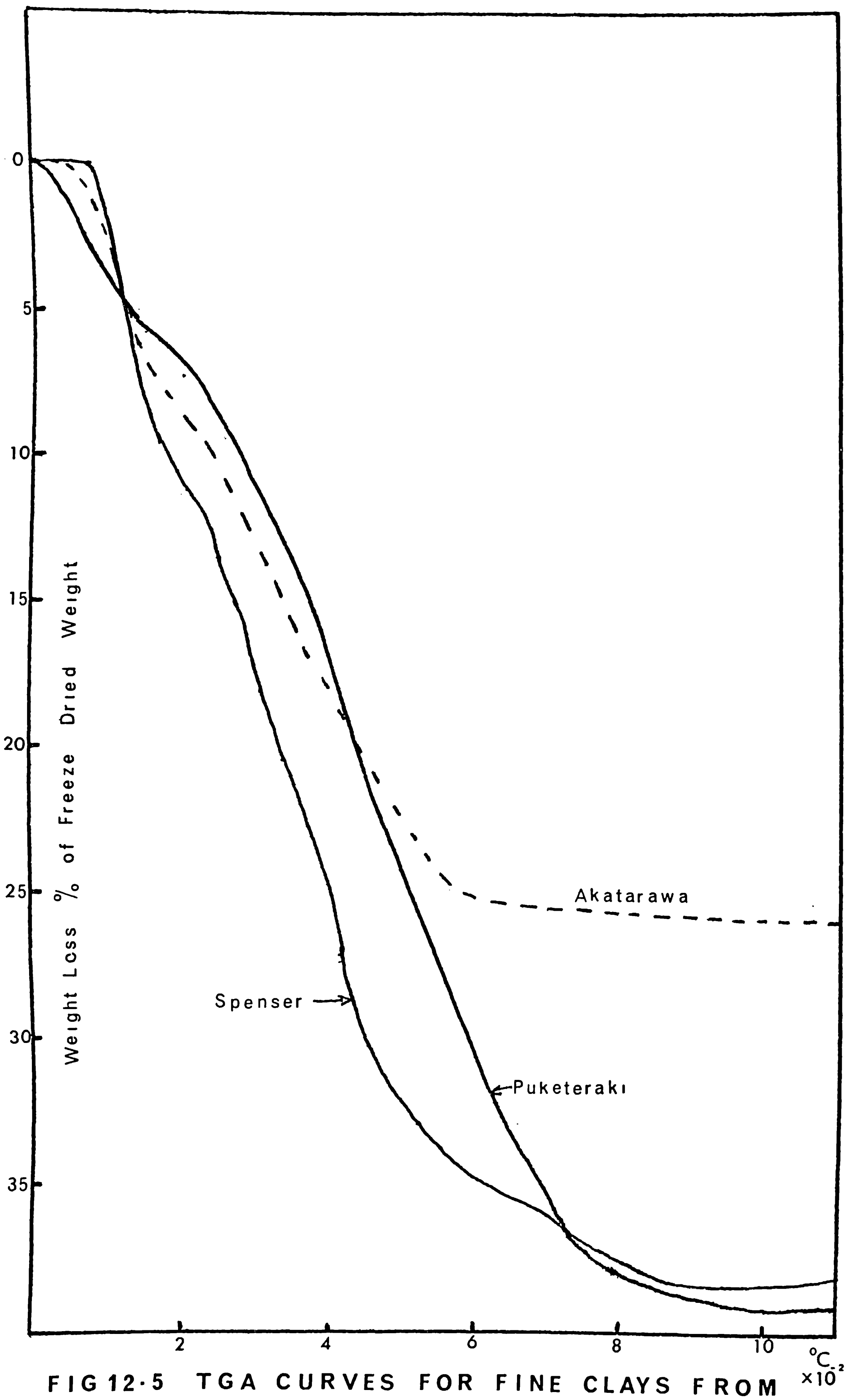


FIG 12·5 TGA CURVES FOR FINE CLAYS FROM HIGH COUNTRY YELLOW BROWN EARTHS DEVELOPED ON GREYWACKE

The Akatarawa sample shows a trace very similar to the Cass sample, both of these being very close to the ground greywacke rock which would suggest little weathering. Since the Akatarawa sample was obtained from a lower altitude than the South Island samples this is unexpected since weathering is likely to have progressed further in the warmer climate.

The thermal weight loss curve shows no sharp losses in weight after the initial loss before 150°, only a gradual loss which is complete by 600°C showing that there is considerable disorder in the sample despite the dehydroxylation peak at 518°C in the DTA.

None of the fine clay samples show a large exotherm aboue 800°C. This is shown by the ground rock samples although the peaks are broad.

The fine clays when heated to 1000°C were largely amorphous. At 600°C the characteristic X-ray peaks of a collapsed micaeous material are present but these disappear on raising the temperature. In the chlorite schist samples a spinel phase and hematite were formed but in the greywacke samples these are not apparent. Forsterite is formed at 1100°C together with some spinel but this disappears on heating to 1200°C when only forsterite is present which shows there is considerable magnesium in the sample. At 1200°C most of the iron appears incorporated into the forsterite lattice and is present as ferrous iron since the colour has changed back to the grey-brown colour from the reddish colour found at 600°C.

12.9a Electron Microscopy

Samples of fine clay were suspended in water and sprayed onto a collodian film and viewed by transmission mode in the electron microscope. The resulting micrographs are shown in Plates 12.1-12.3. The samples show similar characteristics to the fine clays discussed in the previous chapter. However the particles are smaller and less well defined than the fine clays derived from chlorite schist. The Spenser sample has less very fine material than either the Puketeraki sample or Akatarawa sample showing that less weathering has taken place. The Akatarawa *

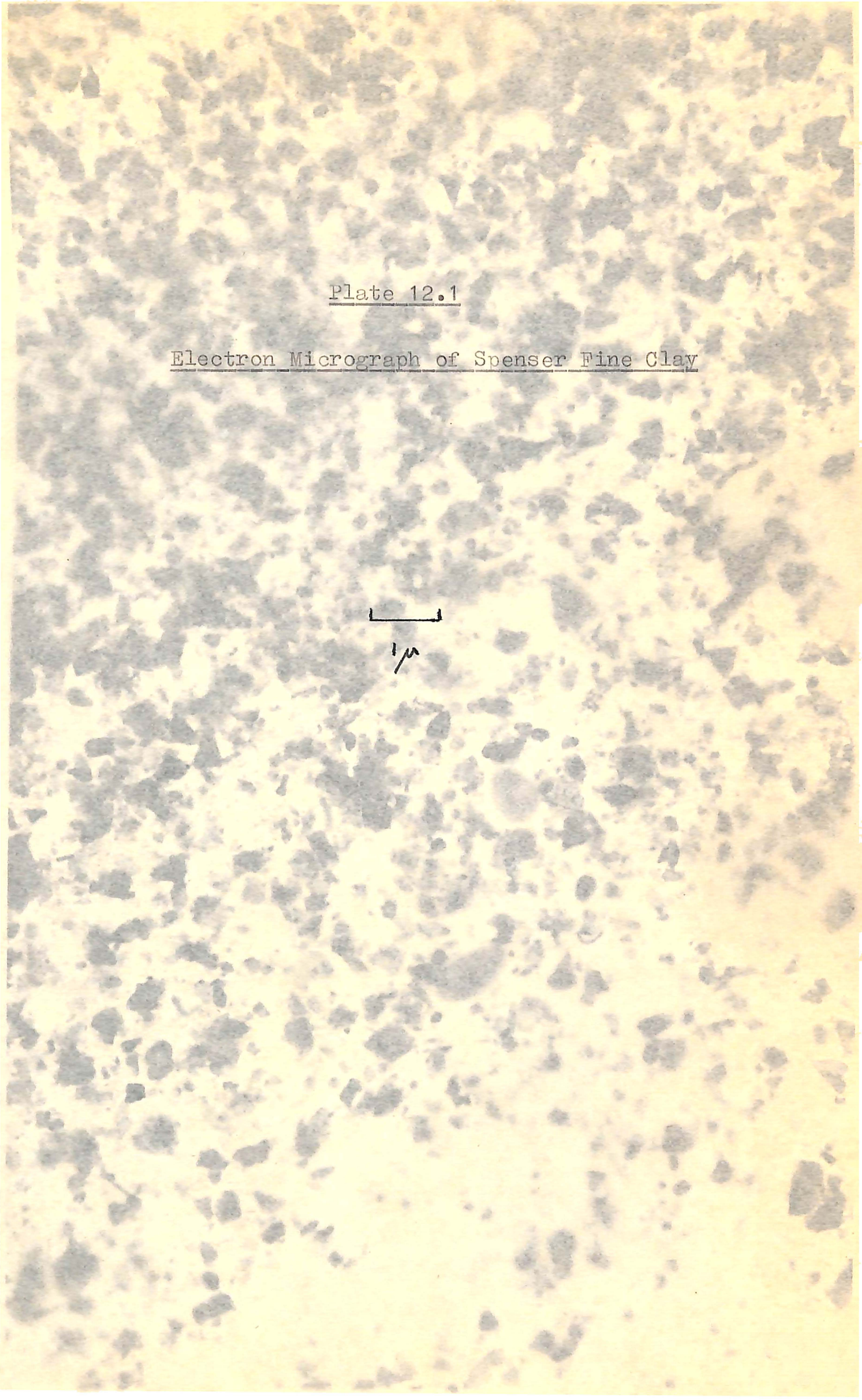
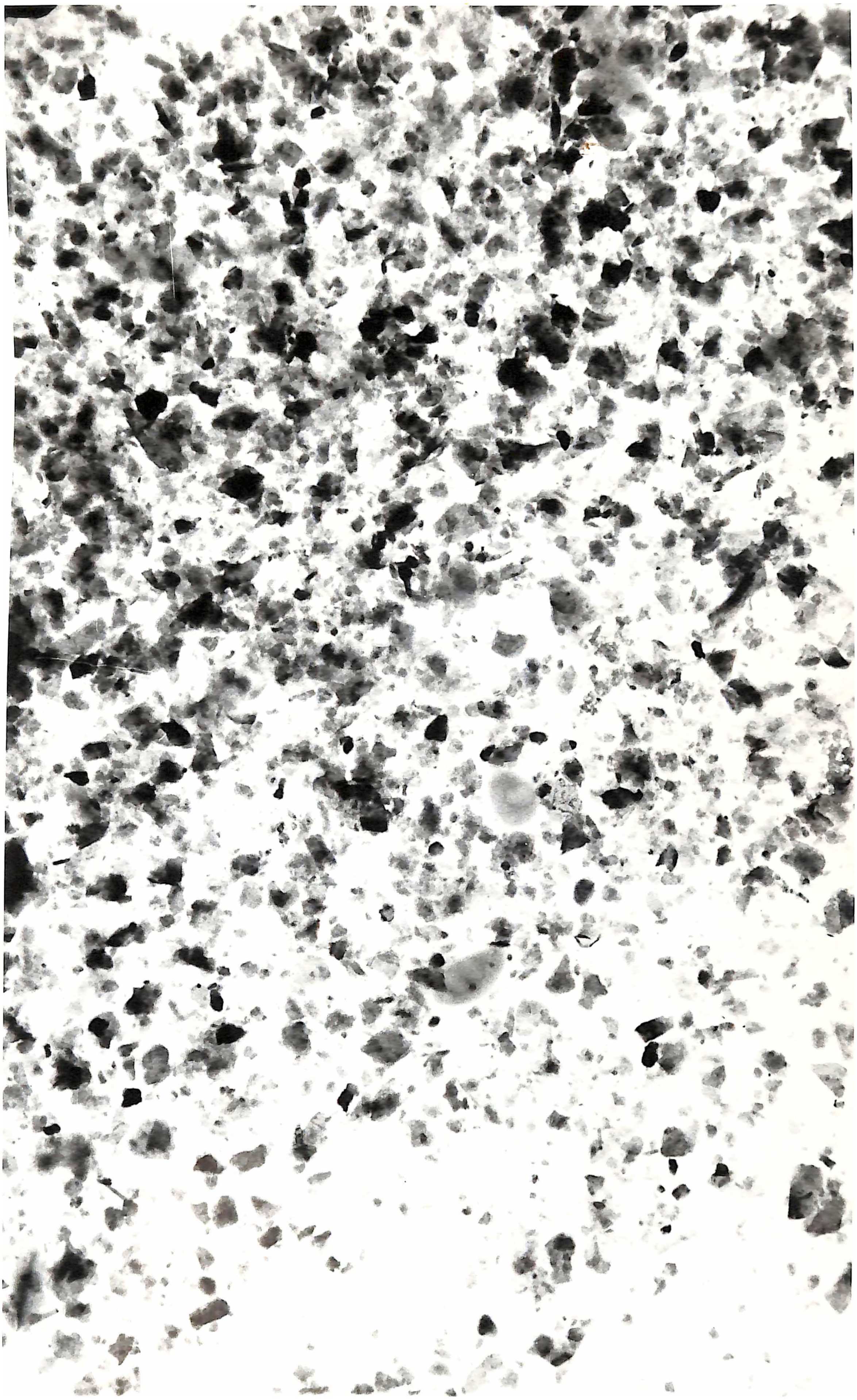


Plate 12.1

Electron Micrograph of Spenser Fine Clay



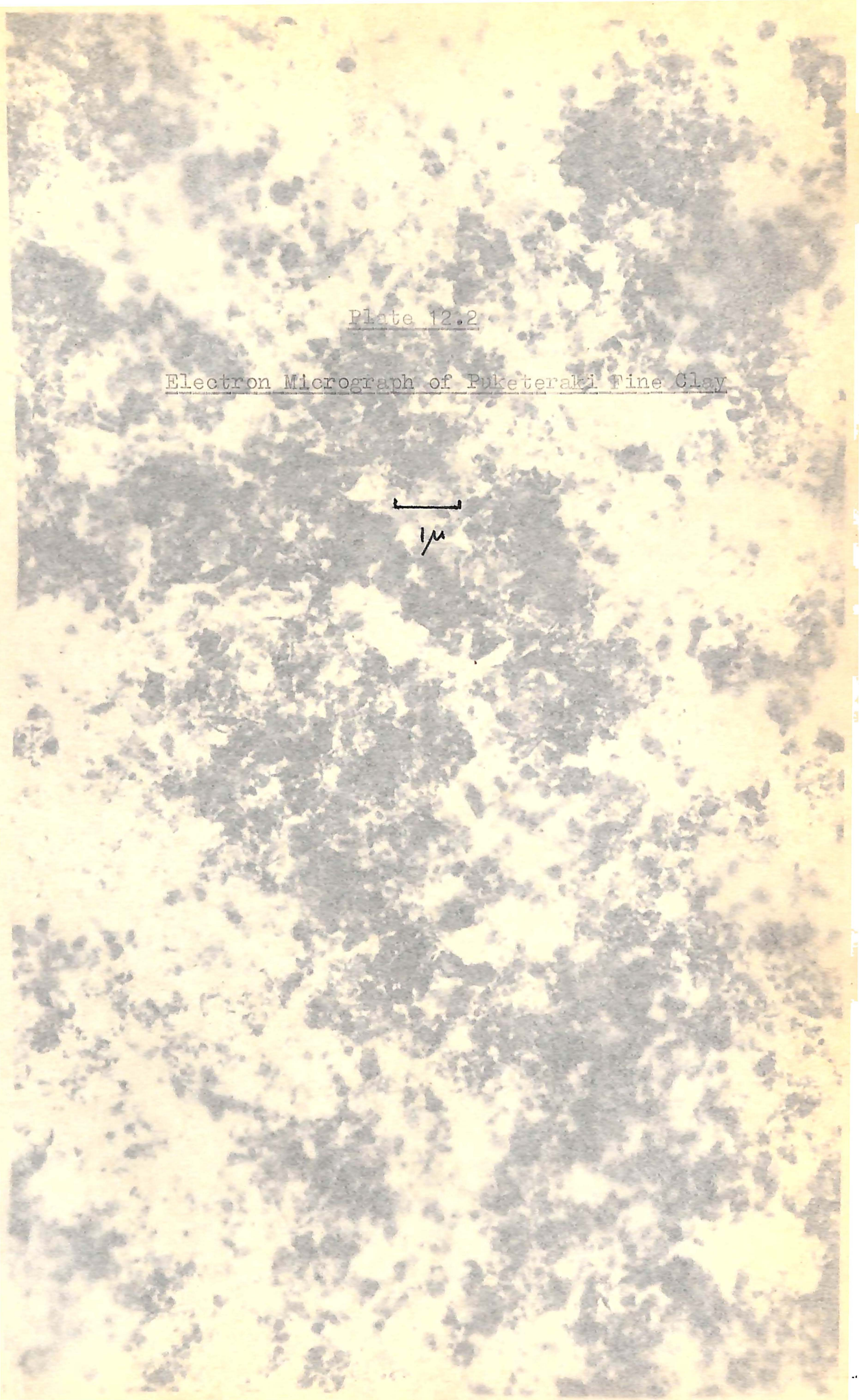


Plate 12:2

Electron Micrograph of Puketeraki Fine Clay

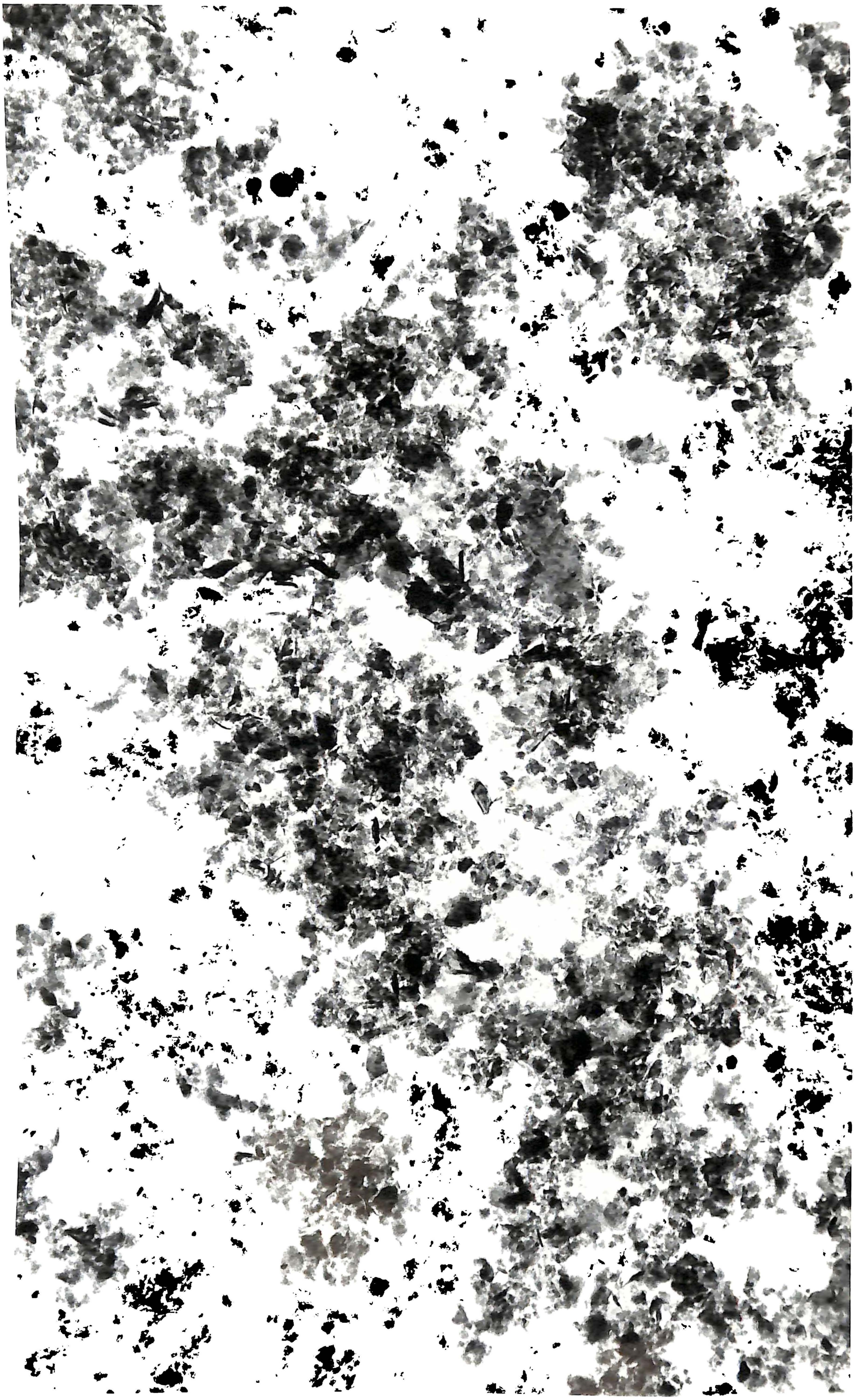


Plate 12.3

Electron Micrograph of Akatarawa Fine Clay

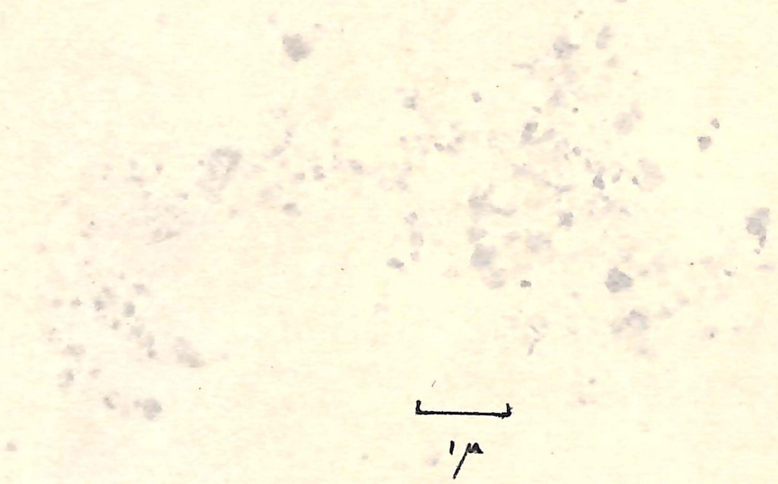


Table 12.8 Major Peaks in the Fine Clays of Soils Derived from Greywacke

Spenser		Puketer-aki		Cass		Gnd Rock (Puketeraki)		Gnd Rock (Spenser)		Akatarawa 4'		Akatarawa 7'	
endo	exo	endo	exo	endo	exo	endo	exo	endo	exo	endo	exo	endo	exo
112		105		95		90		105		115		130	
			275										
		300											
	375		360		360		360		370		365		337
		425											
405				520		500		544		518		520	
	500		470										
	-		885		945		935		940		855		890

12.10 CATION EXCHANGE

The cation exchange capacity (CEC) was determined using the method outlined in section 4.4.7a.

The values obtained are tabulated in the following table.

Table 12.9 CEC Values for Some Fine Clays of High Country and Central Yellow-brown Earths Derived from Greywacke

Sample	CEC meq/% pH 3.5	pH 10.5	Δ CEC
Spenser	13.3	34.9	21.6
Puketeraki	17.6	23.9	14.3
Akatarawa 7'	18.1	23.1	5.0
5'	33.1	48.7	15.6
Waxy Allophane	28.6	84.8	56.2
Carrick	22.0	25	3.0
Vermiculite	100-150		

---

* sample contains little coarse material and looks similar to the micrographs of volcanic allophane in Chapter 4. This suggests that much of the Akatarawa sample is allophane derived from volcanic ash rather than greywacke which the soil overlies. The Akatarawa fine clay was X-ray amorphou confirming the large proportion of very fine material that is seen in the electron micrograph.

The CEC values are lower than the typical allophane values and the Δ CEC very much lower. However the Δ CEC values are higher than those for the schist-derived soils and is probably reflected in the fact that the clays contain more vermiculite than the schist-derived soils. The amount of vermiculite must be relatively small since the very high CEC normally associated with vermiculite is not present.

The Akatarawa sample from 5 ft has a value rather higher than the others. This is possibly because as it has weathered under a warmer climate there is more vermiculite in the clay.

Vermiculite is a weathering product of chlorite and mica and because the clays have not developed the high CEC expected of vermiculite (above 100 meq/%) means that there must be a large amount of relatively unweathered material present in the clay fraction.

12.11 PHOSPHATE RETENTION

The P-retention of the soils was obtained using the method described in section 4.4.7b and the results are shown in the following table.

Table 12.10 P-retention Values for Fine Clays of Yellow-Brown Earths Derived from Greywacke

	mg P retained/gm fine clay
Spenser	19.03
Puketeraki	20.14
Cass	19.3
Akatarawa 2'	14.9
4'	30.3
5'	14.8
7'	12.7
Waxy Allophane	27.3
Carrick	6.99

The P-retention values confirm the higher reactivity of the greywacke soils over the schist soils retaining about twice to three times as much phosphate although not as much as the volcanic allophanes.

The Akatarawa samples were collected from beneath a pine tree where accumulation of plant humus had caused separation of distinct layers in the subsoil. The 4 ft sample was taken from an iron rich layer immediately preceeding a pale layer. It is apparent from this range of samples that free iron oxide is responsible for a large amount of P-retention.

It is difficult to ascertain whether the soil is derived exclusively from sedimentary rock as it has been suggested that some volcanic ash could be part of the parent material[322] and certainly ash has been reported in the Manawatu area[323]. Unfortunately time did not permit a further examination of the correlation of iron content and isoelectric points of similar soils.

12.12 ISOELECTRIC POINT

The isoelectric points of the fine clays were determined using the method outlined in section 5.5 and the results are shown in the following table.

Table 12.11 Isoelectric Point for Fine Clays of Soils Derived from Greywacke

Spenser	< 3
Puketeraki	3.6
Cass	< 3
Akatarawa 4'	4.6
7'	4.2

The results reflect largely the trend found with the soils derived from chlorite schist. The very weakly weathered Spenser fine clay has an isoelectric point too low to be measured as does the Cass sample.

The Puketeraki sample is at the same value as the Carrick sample, higher than expected for the amount of ferrous iron present, but this may be reflected in the overall nature of the amorphous material from greywacke. The Akatarawa sample shows a higher value than found for any of the clays from sedimentary parent material but this is probably a result of more extensive weathering and a concentration of iron developed under the acid litter. The sample from 4 ft has a higher isoelectric point than expected because of the concentration of iron found.

12.13 DISCUSSION

Many of the characteristics of the high country yellow-brown earths derived from chlorite-schist are found with the high country yellow-brown earths derived from greywacke. The parent greywacke contains more feldspars than the schist and consequently less chlorite and muscovite. The fine clays from the greywacke-derived soils contain ill-defined illite and vermiculite whereas the schist-derived soils contain less vermiculite and are, on the whole, more amorphous. The greywacke-derived fine clays are more reactive with higher CEC and P-retention figures. This is probably due to the higher proportion of feldspars in the greywacke which weather more quickly. There is little truly amorphous material present shown by the small percentage that dissolves in boiling 0.5M NaOH. The weathering of feldspars to illite has been suggested by Mackenzie et al[282] and it would appear that poorly crystalline illite or vermiculite is the weathering product. Vermiculite could be expected to give the higher CEC found in the greywacke-derived clays than the schist-derived ones.

Despite the higher reactivity it is clear that chemical weathering nevertheless, has been limited. The Spenser fine clay contains 6% FeO, oxidation of which is likely to be one of the first chemical changes the rock minerals will undergo. The weathering of feldspars has probably released most of the ferrous iron which is oxidized to the ferric iron found in the clays. In the case of Spenser this weathering has been severely limited since the amount of ferric iron that has been released is insufficient to give the soil the characteristic yellow-brown colour of yellow-brown earths.

The close similarity of the properties of the greywacke-derived fine clays to those derived from schist suggest they should also be considered to contain 'Alpinite' despite the fact that some are not X-ray amorphous. The samples after NaOH treatment show no sharpening of X-ray lines of illite. This means the bulk of the sample is disordered or at best has only short range order.

The Akatarawa fine clay also contains a large proportion of X-ray amorphous material. Unfortunately time did not permit a closer examination of this sample but it indicates that the conditions under which 'Alpinite' is formed are not confined to the South Island but occur in the mountain soils of the North Island as well.

12.14 CONCLUSION

South Island high country soils developed on greywacke contain amorphous material which has similar properties to the amorphous material found in the fine clays from soils derived from chlorite schist. The fine clays contain some poorly crystalline vermiculite as well as the amorphous material 'Alpinite' which give them more reactivity than the fine clays developed from chlorite-schist. A fine clay from a North Island sample shows similar properties indicating that the presence of amorphous material is not confined to the South Island high country.

CHAPTER 13. DISCUSSION OF THE FORMATION OF ALPINITE

13.1 INTRODUCTION

The yellow-brown earths of New Zealand have developed on sedimentary rocks in a climatic region where there is a high rainfall and so the soils are generally well leached. The major clays found in the soils range from illites for the soils developed on schists to vermiculite for those developed on greywacke.

In the more temperate regions, i.e. for soils in the central and southern yellow-brown earth types, the normal weathering processes give rise to easily recognized clay minerals which are highly crystalline and readily identified.

In the high country sub group (soils lying over 3000 ft) the soils are frozen for a large proportion of the year and normal weathering processes will not take place. However, the soils contain a small but significant amount of clay, some of which has been shown to be X-ray amorphous.

The problem arises as to how the rock can be rendered amorphous and yet still retain the appearance and many of the properties of the original parent material. This chapter deals with several processes and puts forward a theory for soil formation in periglacial soils.

13.2 FORMATION OF CLAY-SIZED PARTICLES

The presence of amorphous material in the so-called soils of Antarctica has been mentioned above (see section 10.1.4). Little chemical weathering takes place in the extreme climate and some other form of weathering must be responsible for fine particle formation.

Chemical weathering in the dry inland valleys of Central Otago has been shown to be slow[324] and mechanical breakup of rocks by frost action has been prevalent. With the low rainfall in these areas, salt has accumulated and it has been suggested that salt fretting* contributes to the breakup of rocks[324].

Frost action can cause vigorous movement of rocks and soil, and plants have been shown to be lifted bodily from the ground[325]. This movement causes the shattered rocks to grind against each other[326] and in hilly country sorting of soil occurs by frost action causing striations to be developed, directed down the line of greatest slope. Where the ground is horizontal a network of polygons is formed; the patterned ground that has been described by Gradwell[327]. Penner[328] has shown that the pressure developed in frost heaving increases as the average particle size decreases.

During the summer months the ground dries out and cracks appear. Fine material can be blown into these cracks or be moved by stock and during winter is subjected to increased frost heaving and grinding, so breaking down the fine particles still further. Greenland[335] has noted that in the freeze and thaw of Cass soils, only the surface freezes and that the mass movement of the soil can be correlated to the number of freeze and thaw cycles.

The other process by which soil can be moved bodily, and in which there is considerable grinding action of rocks is solifluction. This is the slow flow of water saturated waste under the influence of gravity. The characteristic feature of the material is sharp angular blocks in an even matrix. The fine material is a product of frost riving or congelifraction as the process of breakup by frost action has been called and chemical weathering is at a minimum. Solifluction occurs in the South Island high country and has occurred in the southern part of the North Island in the Tararua ranges[329].

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* see Glossary.

A combination of the above two processes break the rocks down to fine sand size and it is the sand fraction that is the major proportion of the soils studied. Breakdown of particles by frost riving and solifluction does not appear to progress much beyond the 6μ limit suggested by Dylik and Klatk (quoted by McDowall[330]).

McDowall[330] carried out a series of experiments of repeated cycles of freezing and thawing or multigelation, and investigated the effect on particle size distribution of the various clay minerals. He found that generally there was an increase in the percentage of fine fraction formed after a large number of cycles. The breakdown of layered clay minerals such as illite and vermiculite was less pronounced than for clays such as kaolinite. He also showed that for some samples it was the $1-5\mu$ fraction that was most affected and this gave an increase in the number of particles of fine clay size ($< 0.2\mu$).

Certainly the areas of the high country of the South Island undergo many cycles of repeated freezing and thawing with as many as 200 frosts per year[331] having been reported. For at least two months of the year the soils are saturated and frozen to a depth of 8 inches[331].

These processes then give a mechanism by which rocks can be ground to particles that lie in the fine clay ($< 0.2\mu$) range.

13.3 CHEMICAL WEATHERING

If the above mechanism was the only process involved in clay formation in the high country yellow-brown earths, then the soils would be expected to be grey in colour like the ground chlorite-schist and greywacke of the Spenser soil due to FeO. Although the fine clays do contain some ferrous iron, the proportion is very much lower than expected from ground rock, showing that oxidation is one of the first steps in chemical weathering. This was also noted by Claridge[268] in the Antarctic where the rocks had a reddish colour on the outside due to a ferric oxide layer. The phosphate retention for the ground rock is higher than that for the fine clays showing there are less sites for retention in the clay. This will be due to leaching under the high rainfall. There is also a loss in magnesium and calcium, probably from the feldspars, since they weather rapidly and are not present in the coarse clay. The weathered products will produce the truly amorphous random-structured material that appears in the electron microscope as fine structureless particles.

Jackson et al[264] have suggested a scheme where in the layered silicates preferential weathering occurs along the layers. This can give rise to amorphous structure and cause the appearance of basal spacings intermediate between 10 and 14Å. The Carrick and Obelisk samples show weak spacings in this range for the coarse clay so it is apparent that this type of weathering has occurred to some extent. That these samples show these intermediate spacings is significant. The Blackstone sample has weathered at a lower altitude to more crystalline illite and the amorphous fraction is not retained.

Klug and Alexander[348] have stated that for well crystallized material sharp lines are obtained if the particle size is greater than 0.1μ. As the size drops below this limit the lines become very broad and diffuse. The ground chlorite-schist of $< 0.2\mu$ particle size gives good powder diffraction patterns showing a well crystallized sample. However the chemical weathering has partially altered the ordered structure so that it has defects. Weathering has also produced some very small material which probably has a particle size several orders of magnitude smaller than 0.1μ. These two effects give rise to a diffraction pattern that is featureless except for very broad peaks in the position of the strongest lines.

13.4 POSSIBLE APPLICABILITY TO OTHER PERIGLACIAL SOILS

The conditions under which 'alpinite' is formed are not exclusive to New Zealand. Neither does the formation depend on the parent material since both greywacke and chlorite-schist give 'alpinite' with similar properties. They could be considered general in any region where the climate is such that chemical weathering is at a minimum and undergoes sufficient extremes so that frequent freeze and thaw cycles will be common. These conditions would be expected to be found today in Alaska and the North American mountain chain, and probably much of Europe during the last glacial period.

The influence the parent material will have on properties of 'alpinite' will be one of degree rather any major difference. The similarity of the central yellow-brown earths derived from the weathering of greywacke to those of the South Island has been discussed above with the Akatarawa sample although it was difficult to isolate a clay that was free from volcanic ash.

Very recently Wells and Furkert[350] have published a paper in which they mentioned the occurrence of an allophane with properties less than those expected from volcanic allophanes. This clay was found at an altitude of nearly 4000 ft (1250 m) on the slopes of Mt Ruapehu and it seems possible this material could be ground rock corresponding to 'alpinite' derived from andesite.

The Horotiu allophane discussed in Chapter 4 makes up less than 10% of the total soil and has several singular properties. The soil is an alluvial one deposited by the Waikato River from deposits washed down from the mountains of the central North Island and this clay might be a result of the grinding of material during the last glaciation.

13.5 DIFFERENCES BETWEEN ALLOPHANE AND 'ALPINITE'

The distinct differences in properties between the fine clays of the high country and those of soils derived from the weathering of volcanic ash has led to the proposal of the term 'alpinite' to make these clear.

The mode of formation is different. Allophane is formed by chemical weathering of volcanic glass whereas 'alpinite' is formed from the mechanical breakdown of rock under factors controlled by climate. The physical properties of the soils containing allophane and 'alpinite' are much the same but usually the soils containing 'alpinite' have only a few percent of the material present whereas some of the allophanic soils contain more than 30% allophane.

The major differences of allophane and alpinite are shown in Table 13.1.

13.6 SOIL STRUCTURE AND POSSIBLE USE OF HIGH COUNTRY YELLOW-BROWN EARTHS

The lack of large amounts of free iron oxide in the samples means that the structure will not be as good as that found in the allophanic soils of the North Island. The isoelectric points of the fine clays lie below that normally encountered in field conditions and so the particles will not be positively charged in the soils.

However, in the A horizon the pH is usually lower, e.g. for Carrick it is 4.9 so there is likely to be regions where it is considerably lower than this, possibly low enough to render the nearby particles positive giving rise to the crumb structure noted. The nutrient status of the soils is very low and for any use to be made of the soils, fertilizers will need to be applied. In this respect the soils are similar to the pumice soils of the central North Island where little weathering has also taken place and nutrient levels are low. The cooler climate limits growth to tussock although there is evidence[336] that forests once grew on some of the soils.

Table 13.1 Major Differences between Allophane and Alpinite

Property	Volcanic Allophane	'Alpinite'
Observations		
colour	red or orange	grey-olive to yellow-brown
feel	greasy but not sticky	fine clay: greasy but not sticky coarse clay: usually sticky
Physical properties		
X-ray	amorphous	fine clay amorphous coarse clay may show broad lines due to illite
I.R.	typical amorphous pattern	typical amorphous pattern
DTA	endotherm ~ 120°C exotherm ~ 900°C	dependent on parent material but usually additional endotherm ~ 560°C
Electron microscope	very small 'fluffy' particles with no distinct edges	wide distribution of angular particles down to limit of resolution
Surface Area (H_2O)	high ~ 500 m^2/gm	medium ~ 100 m^2/gm
Chemical properties		
SiO_2/Al_2O_3	1.5- 2.4	variable but usually > 2
FeO/Fe_2O_3	usually 0	1-5
CEC	high ~ 100 meq/100gm variable with pH	medium ~ 20-40 meq/100gm variation with pH not great
P-retention	very high ~ 80%	medium to low ~ 10-30%

The steepness of the hills on which many of the high country yellow-brown earths have developed and the thinness of the soils means conventional farming is impossible. Probably the best use of the land would be forestry with trees adapted to the climate, which would provide cover and allow the soils to develop without being eroded and also provide a useful forestry industry.

13.7 CONCLUSION

The South Island high country soils are subjected to climatic conditions that result in the development of fine particles from frost action. The cold climate slows the rate of weathering to more crystalline products, so that the rate of formation of amorphous material is high and the rate of loss low so that a high steady state concentration occurs. A mechanism exists for the formation of fine clay-sized particles that are amorphous to X-rays. These particles retain a degree of order from the parent material. The amorphous material has certain properties in common with allophane but is distinguished by having properties common with the parent material. It is given the name 'alpinite' to differentiate it from volcanic allophane.

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GLOSSARY OF SOIL SCIENCE TERMS

A horizon	The surface horizon containing the maximum organic matter accumulation and maximum biological activity. Soluble salts have been leached from this zone.
albite	a mineral of the plagioclase group.
alluvial and alluvium	a general term for deposits laid down by rivers usually associated with recent geological time.
amphibole	a mineral group with the general formula $A_{2-3}B_5(SiAl_4)O_{11}(OH)_2$ where $A = Mg^{2+}$, Fe^{2+}, Ca^{2+} or Na^+ and $B = Mg^{2+}$, Fe^{2+}, Al^{3+} and Fe^{3+}
andesite	a basic volcanic rock.
argillite	a sedimentary rock derived from siltstone or claystone which has undergone a further process of hardening.
augite	a mineral of the pyroxene group.
azonal soil	a soil without a distinct profile.
B horizon	the horizon below A with an accumulation of silicate clays together with iron and aluminium oxides.
base saturation percentage	the extent to which the soil is saturated with exchangeable cations other than Al^{3+} or H^+. It is expressed as the percentage of total cation exchange capacity.
blocky	a term used to describe soil structure - where the aggregates are in the form of blocks.
C horizon	the horizon little affected by biological activity and often containing parent material.
chrysocolla	a copper silicate $CuSiO_3 2H_2O$.
crumb	a term used to describe structure where the aggregate is soft porous and rounded and less than 5mm in diameter.
citrate soluble P	phosphate that is extracted from 10g of soil by 100ml of 1% citric acid in 24 hours. The values give an approximate index to the amount of phosphorus 'available' to plants.
clay	(i) soil particles $< 2\mu$ equivalent diameter. (ii) soil containing more than 40% clay sized particles (see diagram at end of glossary.)
dioctahedral	refers to clay minerals with only two-thirds of the possible aluminium octahedral sites filled by other cations.

evansite	a basic aluminium phosphate $Al_3(PO_4)(OH)_6$.
feldspars	a group of rock forming minerals.
forsterite	Mg_2SiO_4 which usually contains Fe^{2+} as an impurity.
friable	term applied to soils that can be crumbled easily.
gley soil	soil that has developed under conditions of poor drainage which results in the reduction of iron and the development of a grey colour and mottling.
goethite	a form of FeO (OH).
granular	a term used to describe structure where the aggregates are in the form of granules.
greywacke	a type of sedimentary rock making up the backbone of the North Island and the northern South Island.
horizon	a soil layer with distinct characteristics produced by soil forming processes.
hornblende	a member of the amphibole group of minerals.
igneous rocks	rocks formed by cooling from a molten state.
illite	hydrous mica that is clay sized and partly weathered.
intrazonal soils	soils with well developed characteristics reflecting the dominance of some local factor.
latosol	a zonal soil characterised by a low SiO_2/M_2O_3 ratio, low CEC and low content of soluble constituents, viz., laterites.
lepidocrocite	a form of FeO(OH).
liquid limit	the moisture content of the soil expressed as a percentage by weight of oven-dried soil at which the soil will just flow when jarred.
loam	a soil texture term (see diagram at end of glossary).
loess	material transported and deposited by wind usually being silt-sized particles.
marl	soft calcium carbonate.
olivine	a mineral series of solid solutions of forsterite and fayalite Fe_2SiO_4.
plagiclose	a mineral group with formula $(Na,Ca)(Al,Si)Si_2O_8$.
plastic limit	is the lowest moisture content at which the soil can be rolled to form a thread without breaking into pieces, expressed as a percentage of oven dried weight.

podzols	soils of the zonal group formed in temperate and humid climates under acid litter producing trees and characterized by a highly leached A_2.
profile horizon	a vertical section through a soil through all its horizons and including parent material.
regolith	the unconsolidated layer of weathered rock and soil on the earths surface.
rhyolite	a volcanic rock in which the constituents are too small to be distinguished by the naked eye.
salt fretting	the slow surface breakup of rocks by the action of soluble salts penetrating surface cracks and crystallizing particularly common in arid regions.
sandstone	a compacted sedimentary rock formed from sand grains.
sedimentary rock	rock formed by accumulation of sediment.
shale	laminated sediments of which the particles are clay sized.
silt	(i) particles between 50 and 2μ. (ii) a soil texture class (see diagram).
solifluction	slow flow of water-saturated waste under the influence of gravity.
spinel	a mineral with formula AB_2O_4 but often applied to $MgAl_2O_4$.
structure	the combination of primary soil particles into secondary units.
texture	the relative proportions of sand, silt and clay in a soil (see diagram at end of glossary).
trioctahedral	refers to clay minerals with all possible octahedral aluminium sites occupied by other cations.

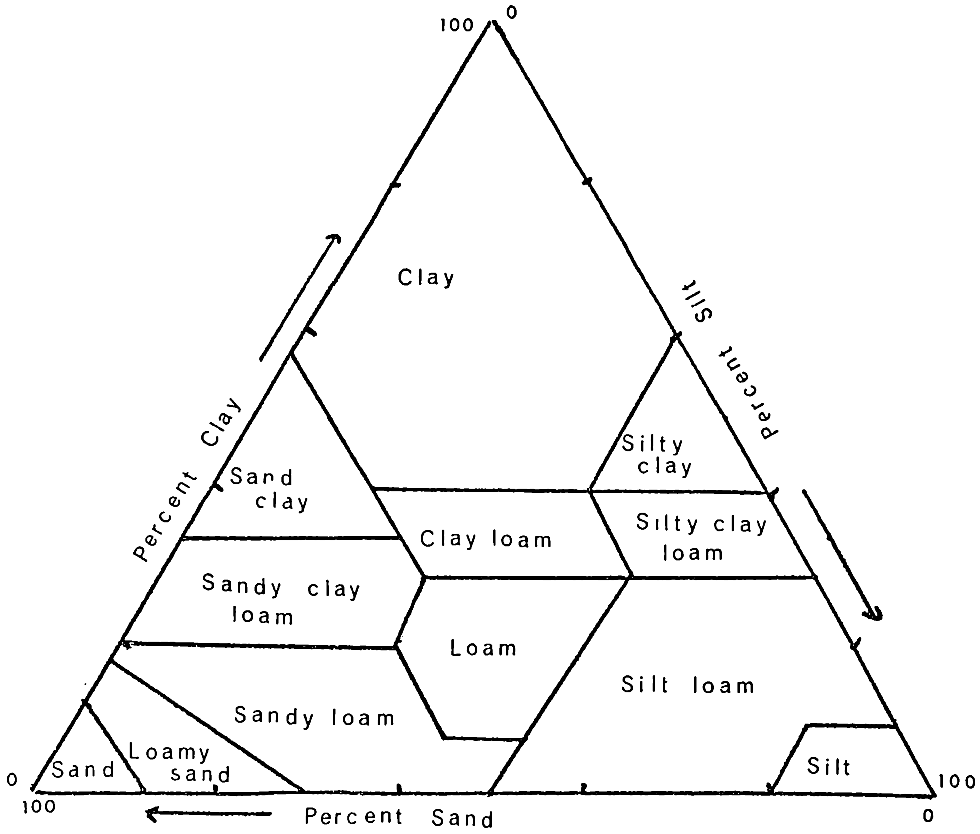

DIAGRAM FOR DETERMINING TEXTURAL NAME OF A SOIL

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