ARTIFICIAL WEATHERING OF SOME SOIL CLAYS

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ABSTRACT

An artificial weathering experiment was set up to test for reversibility within the system.

2:1 - 2:2 Al-intergrade ⟷ vermiculite ⟷ montmorillonite. Strongly chelating (0.20 M and 0.02 M citrate) and weakly chelating (0.02 M acetate) solutions buffered at pH 3.5, 4.5 and 5.5, were leached for varying periods of time up to 6 months, through B_2 horizon of Craigieburn silt loam. X-Ray diffraction of the leached soil clay fraction showed that the period of leaching was too short to cause a clay transformation from the initial 2:1 - 2:2 Al-intergrade into a 2:1 layer silicate. However, X-Ray and electron microscopy studies showed removal of some surface coatings and interlayer hydroxy Al. Analyses of the leachates showed that the citrate (chelating) buffers were more effective at removing Al and Fe from the solid phases than acetate (non-chelating) buffers. Quantities removed and rates of solution of Al and Fe increased with decreasing pH. Rapid initial loss of Al and Fe probably involved disordered gels and surface coatings. Increasing the citrate concentration above a certain limit did not increase the ability of the solution to remove Al and Fe.

Leaching with 1.5 M $AlCl_3$ solution at pH's 3.5, 4.5 and 5.5 caused rapid fixation of Al in the A_2 horizon of the Katrine silt loam. A vermiculite-montmorillonite intergrade was rapidly transformed into a 2:1 - 2:2 Al-intergrade, suggesting that an increase in pH leading to build up in Al species in the soil would result in montmorillonite being transformed into 2:1 - 2:2 Al-intergrade.

It was concluded that leaching for longer periods, using a lower concentration of chelating solution, that would more closely simulate the natural system should be attempted. Developments of the method are suggested.

CONTENTS

I REVIEW OF LITERATURE

INTRODUCTION

Recently published work has indicated that high acidity ($pH > 4.5$), and leaching by water soluble organic compounds formed under a mor forming vegetation, are important controls in the mobilisation of Fe and Al and the subsequent formation of podzols. This study investigates the relative importance of these two factors, particularly as they influence some mineralogical changes that occur during podzol pedogenesis.

Aluminium is brought into solution at low pH's and by the formation of soluble chelates with organic substances. As Al is mobilised, high alumina clay minerals become unstable and are replaced by montmorillonite and ultimately silica, which are stabilised above the podzol B horizon. A laboratory simulation of podzol weathering was studied in an attempt to isolate the pH and organic chelation factors.

FIELD RELATIONSHIPS AND THE MINERALOGY OF PODZOLS

Brydon et al. (1968) have described the mineralogy of Podzols and related Grey Brown Podzolic and Grey Wooded soils of Eastern Canada. The dominant clay mineral found in the A_2 horizon of the podzols was a well-crystalised montmorillonite with varying degrees and kinds of mica interstratifications. A further striking feature of these horizons was the complete absence of chlorite and kaolinite minerals. A sharp mineralogical change at the boundary between the A_2 and B horizons differentiated the podzols from other soils. Chlorites were present in the B horizon of podzols but not in the A_2, while montmorillonite was never found in B horizons. By contrast the clay in the A and B horizons of the Grey Brown Podzolic and Grey Wooded soils developed on similar parent materials showed a tendency for mica and chlorite to increase and for expanding clays to decrease with distance from the surface.

Several other studies have also demonstrated the presence of expanding clays in the A_2 horizons of true podzols. Gjems (1963) found intermediates between vermiculite and montmorillonite, and Brown and Jackson (1958), McKeague (1965) and Ross and Mortland (1966) identified montmorillonite. Kodama and Brydon (1968) have claimed that expanding-layer components were interstratifications of smectite, vermiculite and mica. Mills and Zwarich (1972) however claimed that in fine clays, peaks crucial to the recognition of interstratified minerals were not resolved due to broadening and that a diffractogram of a mixture of discrete minerals resembles that of an interstratified mineral. Gjems (1970) describes three podzol profiles in Yugoslavia which show a sharp increase in expanding clays in the A_2 as compared with the lower horizons. The soils were extremely acid, even in the C horizons.

Malcolm *et al.* (1969) reported similar mineralogy in a catena from the North Carolina coastal plains, where montmorillonite and swelling 2:2-2:1 Al-intergrade clays were found to be dominant clay minerals in podzol A_2 horizons. An abrupt change in mineralogy occurred in the Bh horizon where no trace of montmorillonite was found and 2:2 - 2:1 Al-intergrades were the dominant clay minerals. Associated soils in the catena were less acid and rarely showed the presence of montmorillonite in the surface horizons where 2:1 - 2:2 Al-intergrades showed their maximum development.

Campbell (1974) has reported similar observations in New Zealand. In this study an intimate relationship between contrasting podzols and non-podzols was evident. On an 18,000 - 22,300 year B.P. (Suggate and Moar, 1970) glacial outwash surface of a chronosequence of soils near Reefton, Podzolised Yellow-Brown Earths and Yellow Brown Earths form a soil complex related to the distribution of Red Beech trees (c _Nothofagus_ _fusca_) and their decaying stumps and fallen logs. Dramatic changes in chemical properties and clay mineralogy occur in surface horizons over distances up to 7 metres. Podzolised Yellow Brown Earths, in which montmorillonite forms the dominant clay mineral in the O and A horizons but is absent from the B_2 and lower horizons whixh are dominated by pedogenic chlorite, form under thick accumulations of litter adjacent to the trunks of mature trees and dead stumps. Their extent is limited however, and rapidly grade into a Yellow Brown Earth morphology.

The Yellow Brown Earths show no sharp break in the clay mineralogy between the A and B horizon. The whole profile is dominated by 2:2 - 2:1 Al - intergrades. As reported by Malcolm _et_ _al_. (1969) where montmorillonite was observed, the pH was always less than 4.5, and it was absent in horizons where the pH exceeded 4.5. In contrast to the observations of Brydon _et_ _al_. (1968) some kaolinite ($<20\%$) occurred in the horizons containing montmorillonite.

THE FORMATION OF MONTMORILLONITE IN PODZOLS

Mechanisms of montmorillonite formation in podzols have been proposed from both field and laboratory experiment.

1. THE STABILITY OF MONTMORILLONITE. - Traditional concepts.

It has long been recognised that the presence of montmorillonite in soils developed on limestone and basalt parent materials implied that a high concentration of base cation and a high pH favoured its formation. Jackson (1965) discussed other situations where montmorillonite was stabilised by the high concentration of ions such as Si^{4+}, Fe^{3+}, Fe^{2+}, Al^{3+}, Mg^{2+}, Ca^{2+} and Na^{+} in swamps, basins soil B horizons or concentrated in evaporite deposits.

Jackson (1968) examined the stability of montmorillonite in relation to pH and $Si(OH)_4$ concentration of the matrix solution and showed that montmorillonite formation was favoured by high $Si(OH)_4$ concentration and high pH. Weaver _et al_. (1971) extended this work to include Mg^{2+} concentration and demonstrated the dependence of montmorillonite stability on high levels of Mg^{2+}. A phase diagram (Fig. 1) deplaying the relative stabilities of Mg-montmorillonite, kaolite, gibbsite and amorphous silica in the system $MgO - Al_2O_3 - SiO_2 - H_2O$ was drawn summarising these conclusions.

Using previous calculation for the free energy of formation of gibbsite and kaolinite (Kittrick 1966a and 1966 b), Kittrick (1969) related montmorillonite, kaolinite and gibbsite stabilities to pH, pAl^{3+} and p $Si(OH)_4$ levels. Montmorillonite was considered purely as an aluminosilicate with

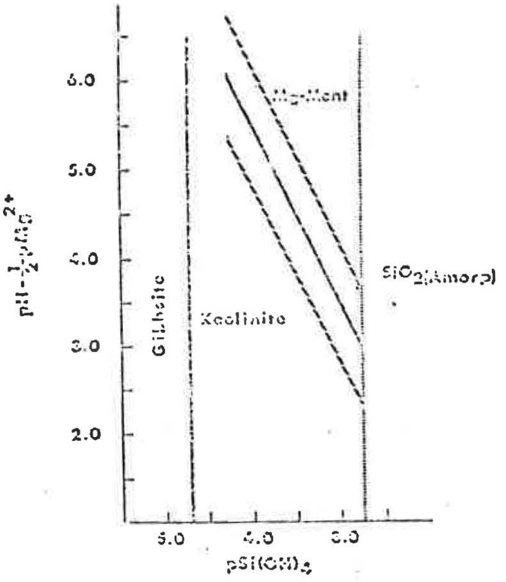


Fig. 1. Phase diagram of Mg - montmorillonite, kaolinite, gibbsite and amorphous silica in the system $MgO - Al_2O_3 - SiO_2 - H_2O$. (Weaver *et al.*, 1971).

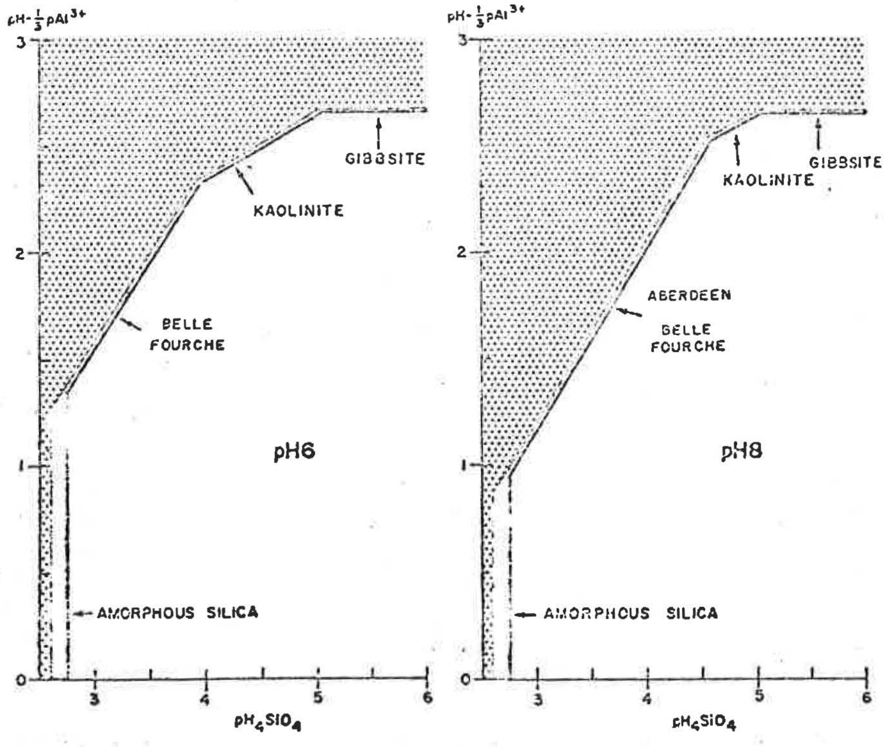


Fig. 2. Relative stabilities of montmorillonite, kaolinite and gibbsite with respect to pH, pAl^{3+} and $Si(OH)_4$ levels. (Kittrick, 1971).

other elements regarded as impurities. A composite stability diagram (Fig. 2) displayed the relative stabilities of montmorillonite, kaolinite and gibbsite. Montmorillonite was stabilised at a higher $Si(OH)_4$ activity than kaolinite and gibbsite but at a lower Al^{3+} activity. Although these results were based on a very simplified system they did agree with accepted field evidence.

Kittrick (1971) extended this work to consider the effects of elements other than Al and Si that commonly occurred in montmorillonite. Differing structural ions (Mg^{2+}, Fe^{3+}, Al^{3+} and Si^{4+}) or exchangeable ions were found to affect the relative stabilities of two montmorillonite samples. Kittrick concluded that a single most stable montmorillonite composition did not exist but that the various compositions observed in nature reflected stabilisation under a diversity of solution environments.

2. STABILITY OF MONTMORILLONITE IN PODZOLS.

Consideration of the above works suggests that it is surprising that montmorillonite should occur at all in podzols, soils that are formed in elluvial environments at low pH and base saturation. However, the formation of montmorillonite under conditions of low pH and base saturation is well documented, and in numerous examples it is the dominent clay mineral under these conditions.

Malcolm *et al*. (1969), Gjems (1970) and Campbell (1974) reported soil pH's consistently < 4.5 in the horizons where montmorillonite was the dominent clay, and it's absence from horizons with pH > 4.5. Campbell (1974) has reported montmorillonite formation at pH values as low as 3.2 in the O and 3.6 in the A_2 horizons of Podzolised Yellow Brown Earths. Malcolm et al. (1969) reported pH's as low as 3.9 in the A_2 and Gjems (1970), as low as 3.7 in the O horizons of podzols. Brydon et al. (1968) unfortunately did not give pH values for the soils they examined.

To account for the presence of montmorillonite in these 'abnormal' conditions, it is necessary to examine the podzolising environment to see what other factors could be involved in its formation and stabilisation.

3. ENVIRONMENTAL CONTROLS OF MONTMORILLONITE FORMATION IN PODZOLS.

Gjems (1970) reports a positive correlation of podzol montmorillonite with time of weathering, maximum summer temperature, the degree of drainage and acidity. Malcolm et al. (1969) considered that the most important environmental conditions for montmorillonite formation were high acidity ($pH > 4.5$) and high levels of organic matter. They claimed that as montmorillonite occurred in all positions of a catena it was unlikely that drainage was a significant factor. It was postulated that although only low pH may be sufficient for montmorillonite formation, the acidity was usually dependent on the organic matter content. Curtis (1970) however, emphasised the pH factor in podzol formation and claimed that it was unnecessary to invoke direct organic involvement to explain the essential features of podzol weathering.

As it is considered that the presence of moroid organic matter and low pH are the most significant factors, in the development of podzols and in the stabilisation of montmorillonite in such environments the present study is a preliminary attempt to investigate the relative importance of each of these factors.

4. MECHANISMS OF MONTMORILLONITE FORMATION IN PODZOLS.

Any mechanism for the formation of montmorillonite in podzols must explain:

1) Why the reported occurrences of montmorillonite are restricted to pH $\lesssim$ 4.5 and to the elluvial horizon.

2) The sharp boundary between montmorillonite in the A_2 and Al-chlorite or 2:2 - 2:1 Al-intergrade minerals of the B_2 and lower horizons.

3) The relationship between a low alumina clay material assemblage and mor forming vegetation.

Malcolm _et al_. (1969) and Gjems (1970) proposed that podzol A_2 montmorillonite formed from illite or by the dealumination of 2:1 2:1 Al-intergrades. If illite and 2:2 - 2:1 Al-intergrades occurred it is possible that montmorillonite would form both by the dealumination of the intergrade under podzolising conditions and by removal of K^+ from micaceous interlayers. Little is known of the relative rates of these reactions under conditions of low pH and base saturation.

Brydon _et al_. (1968) discounted trioctahedral chlorite as a parent to montmorillonite, in the East Canadian podzols they examined, as they concluded it was more likely to alter to amorphous alumino-silicates than to montmorillonite. They suggested that the A_2 montmorillonite could have originated by one or more of three mechanisms:

1) Inheritance
2) Synthesis from solution, after Jackson (1965)
3) Direct alteration from mica.

It is important that these authors did not state the pH values for the horizons concerned. If the pH of the horizons where montmorillonite was observed were < 4.5 as has been reported for montmorillonite formation by other authors, it would be difficult to believe that formation occurred through precipitation from solution. Jackson (1965) postulated a mechanism for the nucleation of montmorillonite from solution involving $Si(OH)_4$ adsorption, in a cation rich environment, on to sesquioxic layers at pH values between five and nine. The pH and cation environmental conditions rule against such a mechanism for explaining montmorillonite formation in podzols.

5. DEALUMINATION OF 2:2 - 2:1 A1-INTERGRADE TO FORM MONTMORILLONITE.

The formation of montmorillonite from 2:2 -2:1 A1-intergrade or pedogenic chlorite involved the removal of inter-layer hydroxy - A1 polymers (Dixson and Jackson, 1962). Two factors were considered important

1) Dissolvation of A1 in solution of low pH (< 4.5)
2) Formation of soluble organo -A1 complexes or chelates.

We shall consider this factor first.

(a) The Organic Factor.

Previous work has confirmed that an organic factor is involved in podzol pedogenesis and in the stabilisation of montmorillonite. Although a moist cool climate is one of the main factors dominating the distribution of podzols, an important factor dependent on climate is the presence of a coniferous vegetation forming an acid mor litter. Wilklander and Aleksandrovic' (1969) found that podzols were common under needle forests and brown earths or transition between brown earths and podzols form under deciduous forest in Sweden. Rozhnova and Kasatkina (1970) however, described weakly podzolised soils in which montmorillonite had formed under oak and spruce-oak forests in Russia.

Work by Bloomfield (1953-1955) and others has shown that extracts of leaves and bark from rimu, kauri, scotts pine, larch and aspen mobilised Fe and Al from soils over a wide pH range, under aerobic and anerobic conditions. The most likely mechanisms for mobilisation involved the formation of soluble metal-organic complexes and/or the formation of chelates with some portion of the organic matter providing the ligand.

A review of the evidence for organo-metalic chelate formation in soils was given by Schnitzer and Khan (1973). Although it was difficult to prove the presence of chelating agents and chelation complexes in soils (Mortenson, 1963), the circumstantial evidence in favour of cheluviation was strong.

Opinions vary as to the identity of the organic species that provide chelating ligands. Coulson et al. (1960) agreed with Bloomfield (1957) on the importance of polyphenols and polysaccharides; Bloomfield finding that the power to mobilise was directly related to the polyphenols content of organic matter extracts.

Fulvic acids were characteristic of, and formed a major proportion of the organic matter extractable from podzols (Schnitzer, 1970). They were also more effective for chelating metals than humic acids (Ponomareva, 1964; Schnitzer and Khan, 1972). Schnitzer and Ogner (1970); and Wright and Schnitzer (1963) considered that fulvic acids were able to form water-soluble and water insoluble complexes with metal ions and hydrous oxides as a result of a high content of oxygen containing functional groups, especially carboryl and phenolic hydroxyl groups. Bloomfield (1955) found that they can also interacted with clay minerals and promote clay illuviation.

It should not be thought, however, that large colloidal fulvic acid molecules are the main sesquioxide transporting agents. There is general agreement that smaller organic molecules are more important as chelating agents than are larger more complex substances. A number of very low molecular weight compounds such as amino acids, aliphatic acids, organo phosphates and phenols which are known to chelate metal, have been separated from soil organic matter. Bloomfield (1955) demonstrated that the relatively simple organic compounds present in unhumified plant debris were much more important than colloidal humus in causing migration of Fe and A1 and promoting the illuviation of clay. Although it is usual for podzols to be associated with accumulation of moroid humified litter, this is not necessarily the major source of organic chelating agents. Coulson (1960) contended that an acid humus layer was not an essential prerequisite for podzolisation but was a concurrent feature and not the main cause. Beech (<u>Fagus sylvatica</u>) growing on base-deficient sites were found to supply a greater range and quantity of polyphenols, which were less liable to be converted to more complex substances at the soil surface, than the beech growing on base-rich sites. The humus under beech was relatively free of simple compounds and apart from tannin stripping of moroid humus, a major source of polyphenols available for leaching came directly from the leaves and bark, dialised by rainfall with maximum flushes in spring and early summer.

Malcolm and McCracken (1968) have shown that substantial amounts of water soluble organic matter can be added to the soil by canopy drip. Active compounds responsible for Fe and Al mobilisation in this canopy drip were identified as polyphenols, reducing sugars and organic acids.

(b) The Dissolution of Al at Low pH.

Aluminium has tended to be regarded as an immobile ion, but work by Huang and Keller (1971) and (1972), Huang and Kiang(1972) and Curtis (1970) has shown that Al has a definite solubility in solution of low pH and high complexing ability.

Curtis (1970) considered the dissolution of Al from gibbsite and kaolinite (Fig. 3) and inferred that environments should lose Al at a greater rate than Si (dealumination) when the pH dropped below 4.5. Clay minerals with a high proportion of Si in their structure (montmorillonite and quartz) could then become stable (as already stated Curtis tended to discount the importance of organic chelates in the formation of podzols). Above pH 4.5 he considered desilication was the dominent process and clay minerals with high Al contents eg: pedogenic chlorite, 2:1 - 2:2 Al-intergrades, kaolinite, gibbsite and allophane were stabilised. Curtis did state that organic chelates, which

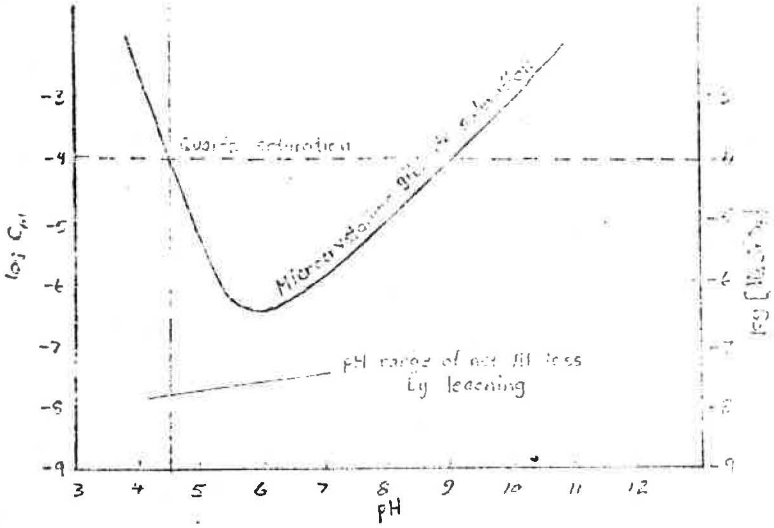


Figure 3. The dependance of quartz and microcrystaline gibbsite solubility on pH (Curtis, 1970).

increased the solubility of gibbsite by complexing Al, could raise the pH at which gibbsite solubility exceeds that of quartz but that it was not necessary to involve direct organic involvement.

A desilication environment would move towards a lateritic end point and conversely dealumination would move towards a podzol endpoint of soil pedogenesis.

With a modification of Jackson's (1963) scheme and differing from Fieldes (1968), Campbell (1973) has devised a clay mineral weathering diagram which shows the influence of these two weathering environments.

On a glacial outwash surface (18,000-22,300 years B.P.) Campbell (1974) postulated that a primary desilication cycle of weathering has occurred, with pH values > 4.5, lower levels of organic matter and the development of a 2:2 - 2:1 Al-intergrade-kaolinite-allophane-gibbsite mineralogy. However around living beech trees and decaying stumps, where the pH had

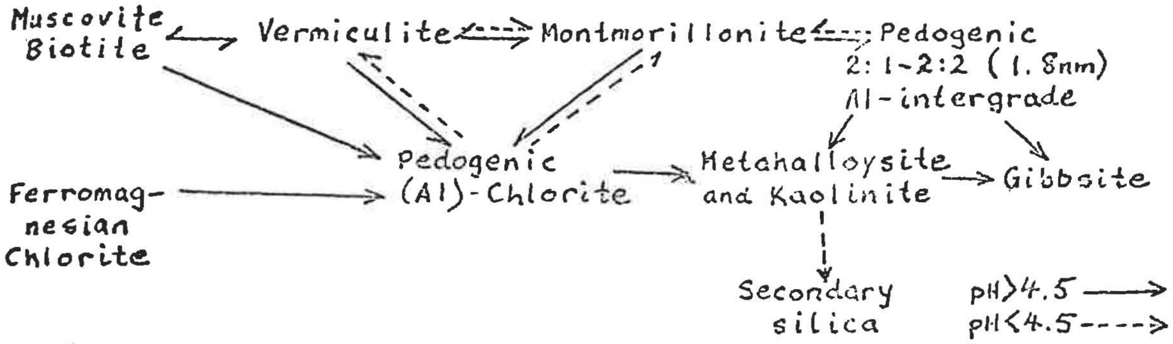


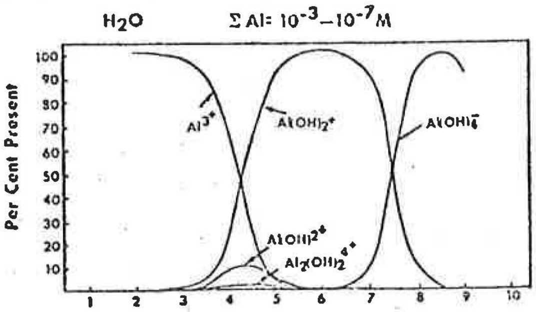
Figure 4. Clay mineral genesis under two weathering environments ($pH > 4.5$ and $pH < 4.5$) (Campbell, 1973).

dropped below 4.5 and organic matter levels had increased, a second cycle of weathering occurred. Dealumination processes had dissolved allophane and gibbsite and transformed the intergrade to vermiculite and montmorillonite above the B_2 horizons, thus forming a Podzolised Yellow Brown Earth morphology. This second cycle of weathering has also been proposed by Gjems (1970). As an alternative to this, Campbell (pers. comm.) postulated that at low pH even the intergrade may dissolve so that mica would become the montmorillonite parent.

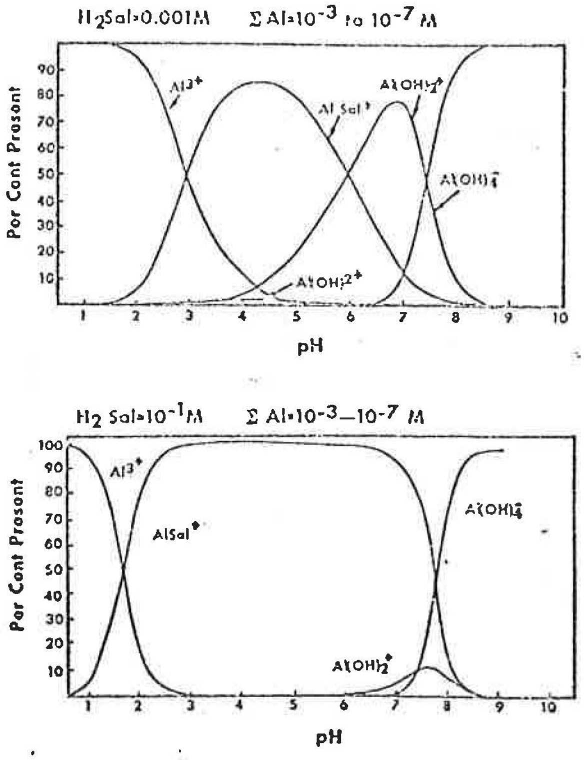
At the opposite extreme of Curtis (1970) the Russian school of thought (Poromareva, 1964) however stressed the importance of organic chelates as supplied by plant residues in effecting the solubility of aluminium. Where temperatures were low enough to retard the microbial population, biocycling was slow and humus accumulated at the surface. This was then leached under humid conditions and mobile organic compounds complexed Al and removed it from the A_2 horizon. The organic cycle rather than the pH was emphasised as the prime Al mobilising factor.

(c) Experimental Dissolution of Aluminosilicates.

Huang and Keller (1972) determined Al species in solution under differing pH conditions in water and acetic, as partic, salicylic and citric acids. The following Al species Al^{3+}, $Al(OH)_2^{+}$, $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^{-}$ were present in aqueous solution and in a salicylic acid solution an Al(salicylate)$^+$ ion existed. The relative solubilities that they found of these ions, at various pH's and in pure aqueous and organic acid solutions, are shown in Figure 5.



~~Fig.~~ 1. Distribution of Al ionic species (all hydrated) in an aqueous solution of Al-hydrate mineral as a function of pH. $\Sigma Al = 10^{-3}$–10^{-7} M.



~~Fig.~~ 2. Distribution of Al ionic species (all hydrated) from an Al-hydrate mineral in (a) 0·1M and (b) 0·001M solutions of salicylic acid. $\Sigma Al = 10^{-3} - 10^{-7}$M. $\Sigma H_2Sal = [H_2Sal] + [H_2Sal^-] + Sal^{2-} + Al\,Sal^+$.

Figure 5. Huang and Keller (1972).

After 12 to 14 days Si dissolved faster than Al but in organic acid solutions the order was reversed. The ability of the organic acids to dissolve Al increased in the order: acetic < aspartic < salicylic < citric. The order is not that of the acid dissociation constants (pK values) but of the complexing capacities of the acids.

The concentration of the acids used, 0.01M is likely to be greater than the concentration of complexing organic acids in nature. Care must be taken in extrapolating from laboratory results, at a higher concentration, to field conditions.

The citrate ion is highly stabilised by complexing a metal ion and forming two chelate ring structures (one 5-membered and one 6-membered).

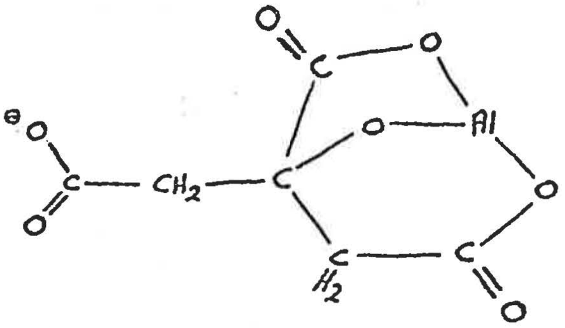


Figure 6. Al - citrate chelation complex.

In 0.01M citric acid with albite and anorthite, Al was dissolved 15 to 8260 times as fast with citric acid than with water. The weaker complexing, acetic acid removed Al 10 to 970 times more rapidly than water. The faster dissolution from anorthite was attributed to complex attack on tetrahedral Al sites.

The complexing power of organic acids in removing framework cations from the clay minerals, kaolinite, illite and montmorillonite was also investigated (Huang and Keller, 1971). Unfortunately 2:1 - 2:2 Al-intergrade minerals were not examined. The organic acid solutions were found to remove Al up to 500 times more readily than water. Al dissolved faster in organic acids than Si from kaolinites and illites, but the montmorillonite lost Si to solution faster than the Al even in the strongly complexing citrate solution. Illites have a higher Al to sI ratio and may therefore yield Al more readily. The degree of lattice order was not thought to be an over-riding control.

THE HIGH ACIDITY OF PODZOL A HORIZONS.

Jackson (1963) stated that soils with pH values of less than 4.2 were not of major agricultural importance and were of theoretical interest in the laboratory only. He attributed lower pH values to mineral colloidal electrolytes or free H_2SO_4, from FeS_2 or S. As already stated, Malcolm et al. (1969), Gjems (1970) and Campbell (1974) have reported pH's as low as 3.9, 3.7 and 3.2 respectively in the O and A horizons of podzols, where there is little possibility of the production of free H_2SO_4 from FeS_2 or S oxidation. Such low pH's are surprising and difficult to explain. Campbell (1974) postulated that the establishment of beech eventually reduced upper horizon pH values below 4.5 but suggested no mechanism.

Jackson (1963) claimed that the monomeric aluminohexahydronium ion ($Al(OH_2)_6^{3+}$) was the dominant proton donor in very acid soils and organic matter only became a dominant proton donor in weakly acid soils.

However, the presence of high chelate supplying vegetation that can be correlated with low pH ($\leqslant 4.5$) in podzols seems to suggest two possible sources of the acidity.

1) That Al hydrolysis is involved.

(a) of the aluminohexahydronium ion

$$[Al(^{-}OH_2)_6]^{3+} + H_2O \rightleftharpoons [Al(OH)(OH_2)_5]^{2+} + H_3O^+$$

(b) of aluminosilicates

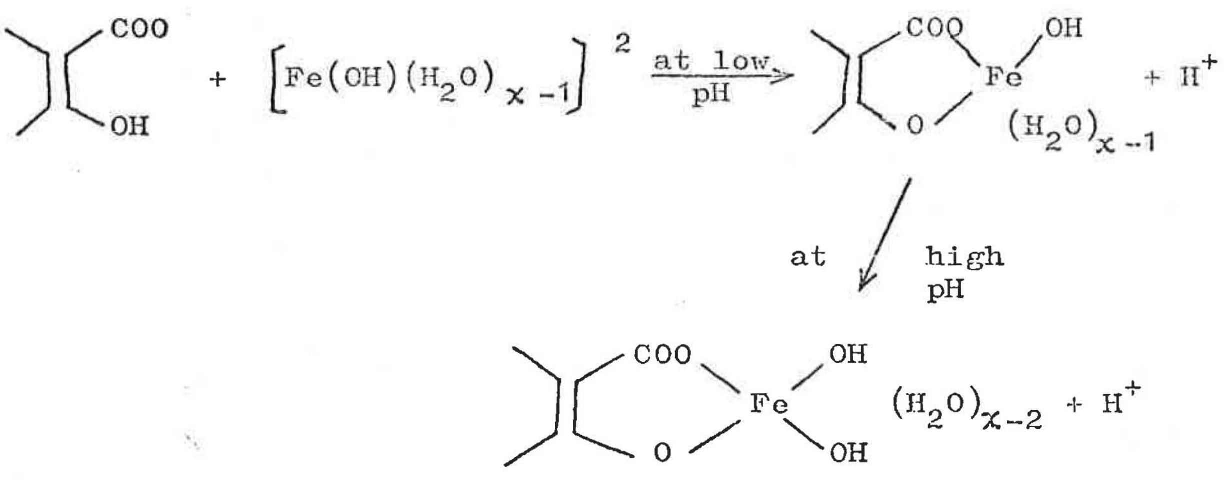
$$-Al-O-Na + H_2O \rightleftharpoons -Al-O-H + Na^+ + OH^-$$

Jackson (1963) quoted p $[Al(OH_2)_6]^{3+}$ values at - 0.3 at pH3, and 2.7 at pH4; i.e. if $[Al(OH_2)_6]^{3+}$ hydrolysis was involved in the high acidity, a concentration of 2×10^{-3}M would be required to produce a pH of 4 and a concentration of 2M, to produce a pH of 3. The $[Al(OH_2)_6]^{3+}$ concentration needed to produce the reported pH's are most unlikely to occur in nature.

Hydrolysis of aluminosilicate cations is not likely to contribute to high acidity as the activity of OH^- ions is increased.

2) That the organic matter is involved. There is probably a sufficient concentration of simple organic compounds in the podzol soil solution to produce a high acidity. The concentration of citrate needed in the soil to give a pH of 4 is 10^{-5} M.

A low pH may also be produced by chelation. If on chelation of Al and Fe, H^+ ions are displaced from the donor ligand, the pH of the soil solution should drop. It is well documented that the complexing of metal ions to humic and fulvic acids in aqueous solution produced a titratable pH drop as the metal ions displaced H^+ (Schnitzer and Khan, 1972; Ponomareva, 1964). Van Dijk (1971) presented a scheme for Fe which could be analagous to the complexing of Al from a crystaline state.



From Van Dijk (1971).

<u>Test of the possibility of chelation involvement.</u> It was decided to test this hypothesis by shaking samples of the B_2 horizon of the craigieburn silt loam (the clay mineralogy being predominently 2:1 - 2:2 Al-intergrade) in solutions of complexing organic acids.

0.2M and 0.02M solutions of Na citrate (strong chelating agent), Na acetate (weak chelating agent) and distilled water were prepared in duplicate and 100 mls placed in a 750 ml polythene bottle with 50 gm of soil. The mixture was shaken (rotatory shaker) continuously and the pH's checked daily for for the first week and thereafter weekly for a further nine weeks.

The results were inconclusive and no marked drop in pH was observed. Instead pH values tended to rise slightly.

It was concluded that buffering by the soil was too strong for any noticeable pH drop to occur.

This experiment does not necessarily prove that the release of H^+ ions through chelation is not significant in nature but merely that it was not significant under the experimental conditions.

Work by Ponomareva (1964), and Kawaguchi and Matuso (1960) has shown the importance of a low ratio of amount of soil to complexing solution and low concentration of complexing solution for maximum chelation of Fe and Al. Ponomareva (1964) found that by decreasing the Al_2O_3/fulvic acid ratio and fulvic acid concentration, a point was reached where the system became mobile (Al_2O_s concentration, 70 mg/l; Al_2O_3/fulvic acid = 0.25).

It is suggested that the same experimental procedure be carried out using a natural leaf extract at a low solution to soil ratio. An inhibatory substance should be added to prevent microbial growths.

THE REFORMATION OF 2:1 - 2:2 Al-INTERGRADE FROM MONTMORILLONITE

On the low glacial outwash terrace surface of the Reefton Chronosequence (Ahaura soils), no montmorillonite was found at distances greater than 7 m from existing trees, stumps or fallen logs. The beech trees have either always influenced the same position over some 20,000 years of soil formation, or there have been generations of trees growing somewhat randomly over the area (Campbell, 1974). The latter alternative seems far more likely. As the soil distribution implies that montmorillonite was formed in the life time of each tree, it can be concluded that most sites on this surface must have suffered a series of desilication and dealumination weathering cycles. It is suggested that following the death, and eventual decay of an individual tree, the pH in the vicinity could rise to > 4.5 and the supply of chelates fall, unless the site is influenced by other nearby trees (Campbell, 1974). A desilication environment would return with the re-establishment of a vermiculite ⟷ 2:1 - 2:2 Al-intergrade mineralogy.

The reformation of 2:1 - 2:2 Al-intergrade under a desilication weathering environment (Figure 4) involved the precipitation of Al in the montmorillonite interlayers. The deposition of Al in 2:1 layer silicates has been widely studied as reviewed by Gupta and Marlik (1969). They prepared an $Al(OH)_3$ - montmorillonite complex by washing montmorillonite with $AlCl_3$ in neutral solution. Al-hydroxide with an Al/OH ratio = 0.33, was precipitated in the clay interlayers after 17 hours. The resultant clay had the properties of Al-chlorite and showed no aging effects.

Turner (1967) investigated the effects of experimental conditions on the forms of Al deposited in the interlayer spaces and demonstrated the presence of positively charged exchangeable polymeric Al ions.

Vermiculite and montmorillonite showed little difference in their uptake of Al ions under experimental conditions (Sawhney, 1968). Montmorillonite tended to fix only Al hydroxide in it's interlayers which became stabilised with time, whereas vermiculite fixed Al ions as well as Al-hydroxy ions, and it's stability remained static with time. This was explained by the greater expanability of montmorillonite which allowed the organisation of hydroxy-Al ions into a gibbsite structure where as the restricted expansion in vermiculite prevented it.

As Al precipitated to form Al diamers and polymers, there was a lowering of pH which implied that the OH^- ions were supplied by water hydrolysis (Jackson, 1963). Jackson postulates that the resulting polymer had the form;

$$Al_2(OH)_{12}\ (OH_2\ldots\ldots OH)_5(OH^{0.5+})_2$$

and Richburg and Adams (1970) presented evidence for the presence of $Al_6(OH)_{15}^{3+}$ as the dominant form of Al in solution. This hexaluminohydroxyhydronium ion was thought to be small enough to fit into montmorillonite interlayer spaces. With time it rearranged to give a more stable gibbsite structure.

II EXPERIMENTAL PROCEDURE.

An attempt was made under open system conditions to distinguish between the effects of pH and complexing ability of leaching solutions, on the dissolution of Al from 2:1 - 2:2 Al-intergrade. Soil samples containg 2:1 - 2:2 Al-intergrade clay were leached with solutions of varying pH and chelating ability. Several batches were prepared and analysed for clay transformation into vermiculite or montmorillonite by X-Ray diffraction after varying lengths of time. It was hoped also to obtain some quantitative measure of the rate of removal of Al from intergrade interlayers under natural conditions.

To attempt to determine if montmorillonite was able to be converted into a pedogenic chlorite structure, the fixation of Al at various pH's of leaching solution was also followed.

EXPERIMENTAL DESIGN.

Because the experiment had to be completed within 6-months, time was scaled down. To accomplish this the strength of the chelating agents were increased to levels higher than would be expected in nature. The experiment was designed as a pilot scheme, which if successful in producing clay transformation, would warrant the setting up of a long-term experiment using complexing strengths more realistic of conditions found in nature.

THE LEACHING OF ALUMINIUM

METHOD

Less than 2 mm B horizon material from a Craigieburn silt loam in which 2:1 - 2:2 Al-intergrade was the dominant clay mineral was used as the starting material. This soil, a high country yellow brown earth, was chosen as representative of the starting material from which natural podzols have developed.

A mixture of 3 parts of acid washed quartz sand (shown to be free of impurities by X-Ray diffraction analysis) to 1 part of soil by weight, was weighed and placed in leaching tubes with a minimum of packing. The soil was supported in the tubes on glass wool and covered by about 1 cm of acid washed quartz sand (Figure 7). The tubes were set up in racks and inverted 500 ml polythene bottles with bases removed were used as reservoirs. To ensure that the soils were not brought under gleying conditions, the leaching rate was governed by controlling the flow from the reservoir, to prevent water collecting at the soil surface. The flow rate thus had to be less than or equal to the natural leaching rate of the soil in the tube.

Nine leaching solutions were prepared - combinations of 3 levels of pH (3.5, 4.5 and 5.5 buffers)* and 3 levels of complexing ability (0.02M sodium acetate/acetic acid buffer (Ac); and 0.2M, and 0.02M sodium citrate/citric acid buffer (Cit)). Each solution was used to leach one sample of soil

* pH's were chosen to straddle pH 4.5.

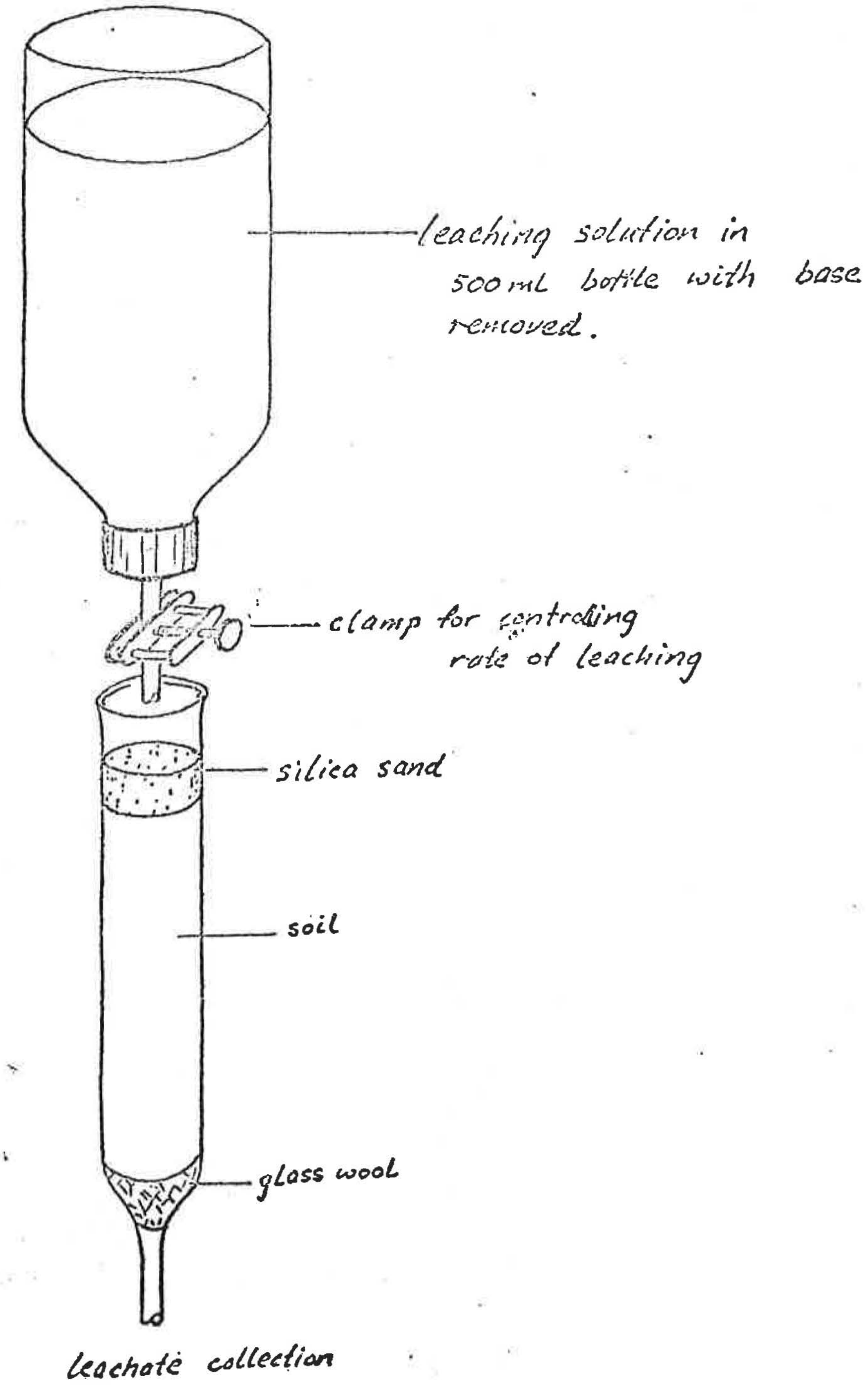


fig 7. Leaching assembly with solution reservior and tube containing the soil. The leachate was collected in a 500 ml polythene bottle.

(there were no duplicates). Five batches were prepared, (Figure 8) each running for a different length of time ranging from one to six months. Toluene was added to prevent the growth of microorganisms.

CONDUCT OF EXPERIMENT

475 mls of solution was placed in each reservoir and allowed to drip into the leaching tube at a rate controlled by clamping the reservoir outlet. When the 475 mls of solution had leached it was returned to the reservoir and re-leached. This process was repeated six or seven times and then the leachate was replaced by a fresh solution. Fe and Al in the leachates were analysed after each run from batch 2, the second longest leaching run.

The total Al and Fe for the Craigieburn silt loam was determined by A.W. Young (pers. comm.). Fe was determined by the O-phenanthroline method and Al by the NaOH fusion, quinoline pnecipitate, gravimetric method.

For the leaching to have maximum effect it was necessary to change the solution frequently to prevent Al in solution reaching equilibrium with the solid phases. A change of solution after each six leachings was a compromise between this and the time factor in preparing fresh solutions.

The layer of acid washed silica sand placed over the soil prevented packing of the top layer of soil by the dripping action of the solution and helped to disperse the solution throughout the soil.

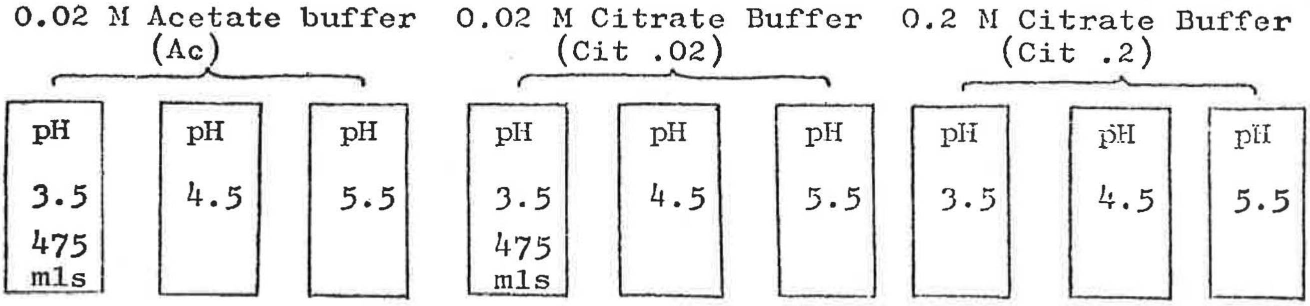


Fig. 8. Each batch of 9 tubes (5 batches = 45 tubes) was set up in this manner. The boxes representing the leaching solutions in the reservoirs. Each reservoir leached a tube containing a mixture of Craigieburn silt loam and quartz sand.

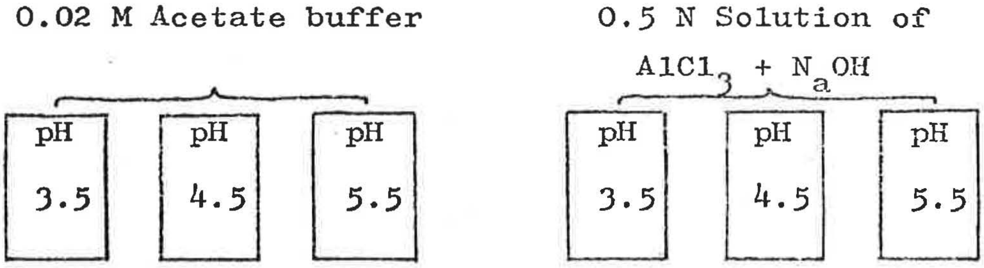


Fig. 9. Each batch of 6 tubes (5 batches = 30 tubes) was set up in this manner. The boxes representing the leaching solutions in the leaching assembly (Fig. 7) reservoirs. Each solution leached a solution containing a mixture of Katrine A_2 soil and quartz sand.

PROBLEMS ENCOUNTERED.

Initially soil samples were leached without the use of sand. Although the solution initially leached through the soil rapidly (about 4 hours) it decreased, until after about 10 leachings, the rate had all but stopped. After comparing polythene pellets and silica sand, a mixture of 3 parts of sand to 1 part of soil by weight was found to be the best method of increasing and maintaining the permeability of the system. In time even with this mixture the permeability decreased until about 48 hours was required to leach 475 mls. At this extremely low rate of leaching difficulty was experienced in controlling the flow rate. It was common for some clay sized particles to get into the reservoir on recycling the liquid, and to block the rate control. The dripping rate varied with the head of liquid in the reservoir, thus requiring close supervision of the tubes to prevent saturation and overflow of the solution from the top of the leaching tubes (an average of about 1½ hours per day was spent checking the tubes throughout the run of the experiment).

The decrease in the permeability with time corresponds to the progressive breakdown of the initial peds, and a change in soil colour from the initial reddich yellow (7.5 YR 6/8) to a light grey colour (10 YR 6/1). Thus as Fe was leached from the soil, structure deteriorated and pores were blocked. If the rate of leaching became too slow in any tubes, the soil was removed from the tube and allowed to dry at room temperature. Peds reformed on drying and the soil was replaced in the tube with the addition of extra silica sand. The permeability was increased for a number of days by this treatment.

The procedure was not resorted to on more than two occasions for any one tube.

FIXATION OF Al IN MONTMORILLONITE

The same experimental procedure was used as for the leaching of Al from 2:1 - 2:2 Al-intergrade.

Soil samples from the A_2 horizon of the katrine podzol were collected, treated as for the craigieburn soil, and placed in leaching tubes. This soil is predominantly montmorillonitic, and is assumed to have formed from a pedogenic chlorite or 2:1 - 2:2 Al-intergrade under the influence of leaching beneath mor forming beech forest.

To simulate the reversion of a podzol to yellow-brown earth mineralogy, six solutions were prepared - combination of three levels of pH (3.5, 4.5 and 5.5 buffers) and two levels of Al activity (0.01M Acetate buffer and .5N $AlCl_3$ solution). The $AlCl_3$ solution was prepared and brought to the required pH with addition of NaOH, following the method of Sawhney (1968).

In the case of Al fixation it was the time of contact with the Al solution rather than the rate of leaching that was the important time factor. Five batches were made up (Figure 8) however and run concurrently with the Craigieburn soils changing the solution after a period of six to eight leachings.

Similar practical difficulties with leaching were experienced with this soil. The initial soil had a complete lack of structure and permeability problems were experienced from the outset. If the soil was allowed to dry out it became strongly hydrophobic. This may have been caused by the presence of waxes in the organic matter.

III RESULTS

X-RAY DIFFRACTION ANALYSIS OF THE INITIAL SOILS

X-Ray diffraction analysis was carried out in order to:

1) Characterise the initial clay mineralogy so that transformation that may occur on leaching would be recognised.

2) Evaluate clay pre-treatment methods prior to X-Ray diffraction analysis of the leached soils.

Katrine A_2 and Craigieburn B_2 horizon soils were given the following pre-treatments (Figure 10).

Soil	Pre-treatment	Clay fraction separated	Sample code
Katrine	untreated	whole clay $< 2.0\mu$	K whole
		coarse clay $2.0\mu - 0.2\mu$	K coarse
		fine clay $< 2.0\mu$	K fine
Craigieburn	"	whole clay	C whole
		coarse clay	C coarse
		fine clay	C fine
Katrine	Organic matter (O.M.) removed -30% boiling peroxide	coarse clay	Kp coarse
		fine clay	Kp fine
Craigieburn	"	coarse clay	Cp coarse
		fine clay	Cp fine
Katrine	O.M. removed + deferration*	coarse clay	Kp-Fe coarse
		fine clay	Kp-Fe fine
Craigieburn	"	coarse clay	Cp-Fe coarse
		fine clay	Cp-Fe fine.

Figure 10. Pre-treatments, clay fractions separated and samples analysed from the initial Katrine A_2 and Craigieburn B_2 horizons.

* Dithionite-citrate-bicarbonate extraction of Fe (Mehra and Jackson, 1960).

Clay particles were first separated by centrifugation and organic matter (O.M.) removed by boiling with 30% H_2O_2. Deferration was accomplished using the dithionite-citrate-bicarbonate method of Mehra and Jackson (1960).

0.5% clay suspension were prepared and saturated with either Mg^{2+} or K^+ using molar salt salotuions of $MgCl_2$ and KCl respectively. Orientated specimens were prepared by pipetting clay on to glass slides and drying at room temperature. X-Ray diffraction was carried out using a Philips X-Ray diffractometer at a scanning speed of 1° per minute. Samples were irradiated with Fe filtered, Fe K radiation and detection was by a proportional counter. Pulse height analysis was used. The diffractograms obtained are reproduced in Figures 11 and 12.

CRAIGIEBURN B_2

Absence of expansion of the 1.46 nm peak with Mg^{2+}/glycerol and absence of complete collapse to 1.0 nm of K^+ saturated clay on heating to 350°C indicated the presence of a 2:1 - 2:2 Al-intergrade. Broadening of the 1.4 nm peak towards 1.0 nm on heating indicates closure or partial closure of some interlayer spaces as hydroxy-Al is gradually dehydrated by heating at successively higher temperatures.

It is noticeable that there is little difference between fine clay ($< 0.2\mu$) and coarse clay ($0.2\mu - 2.0\mu$) mineralogy and little difference in the peaks of the untreated and the clay from which organic matter had been removed.

However differences are apparent in the diffractograms

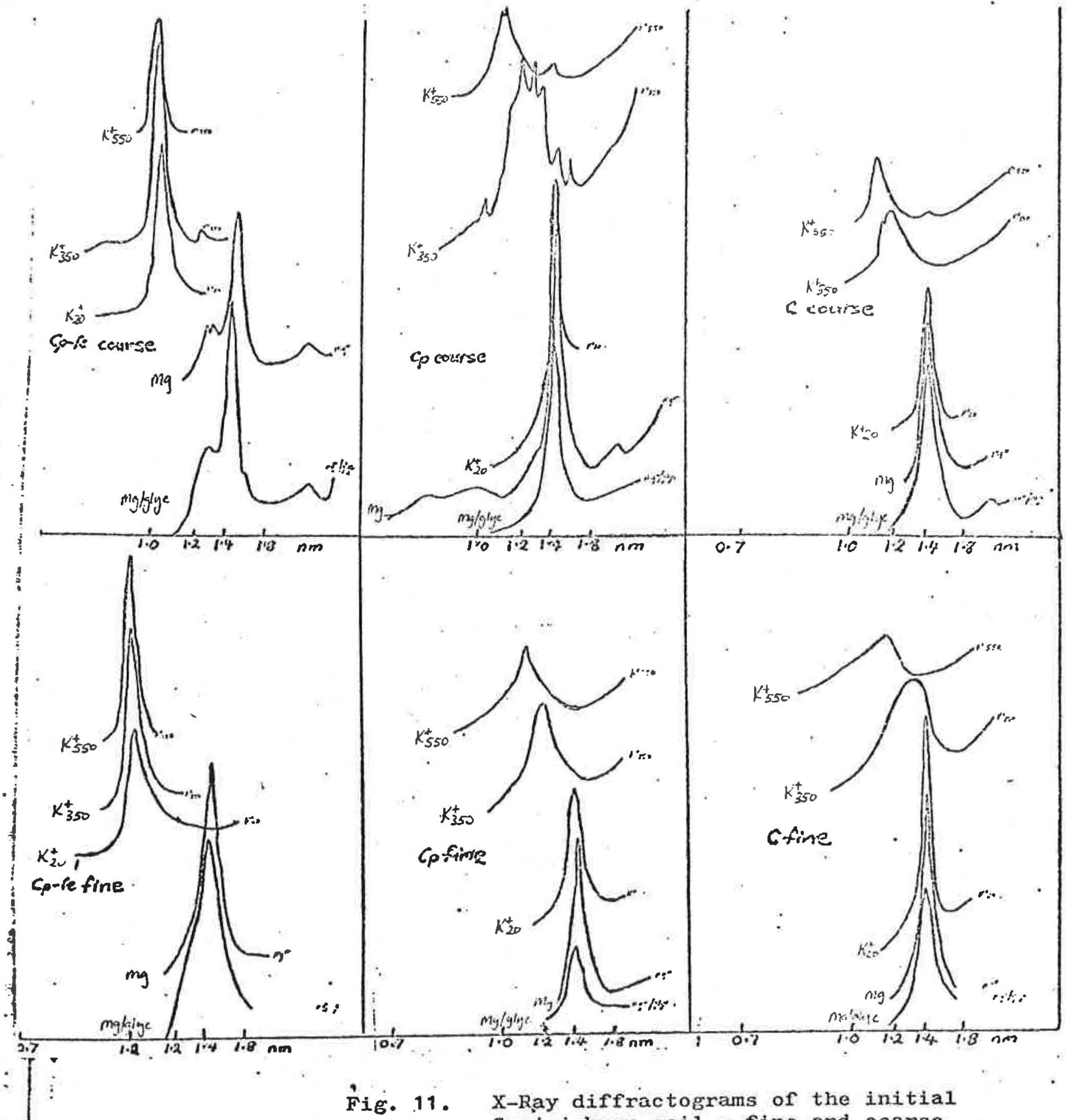


Fig. 11. X-Ray diffractograms of the initial Craigieburn soil - fine and coarse fractions. C-untreated, Cp-peroxidised i.e. organic matter removed, Cp-Fe-peroxidised and deferrated

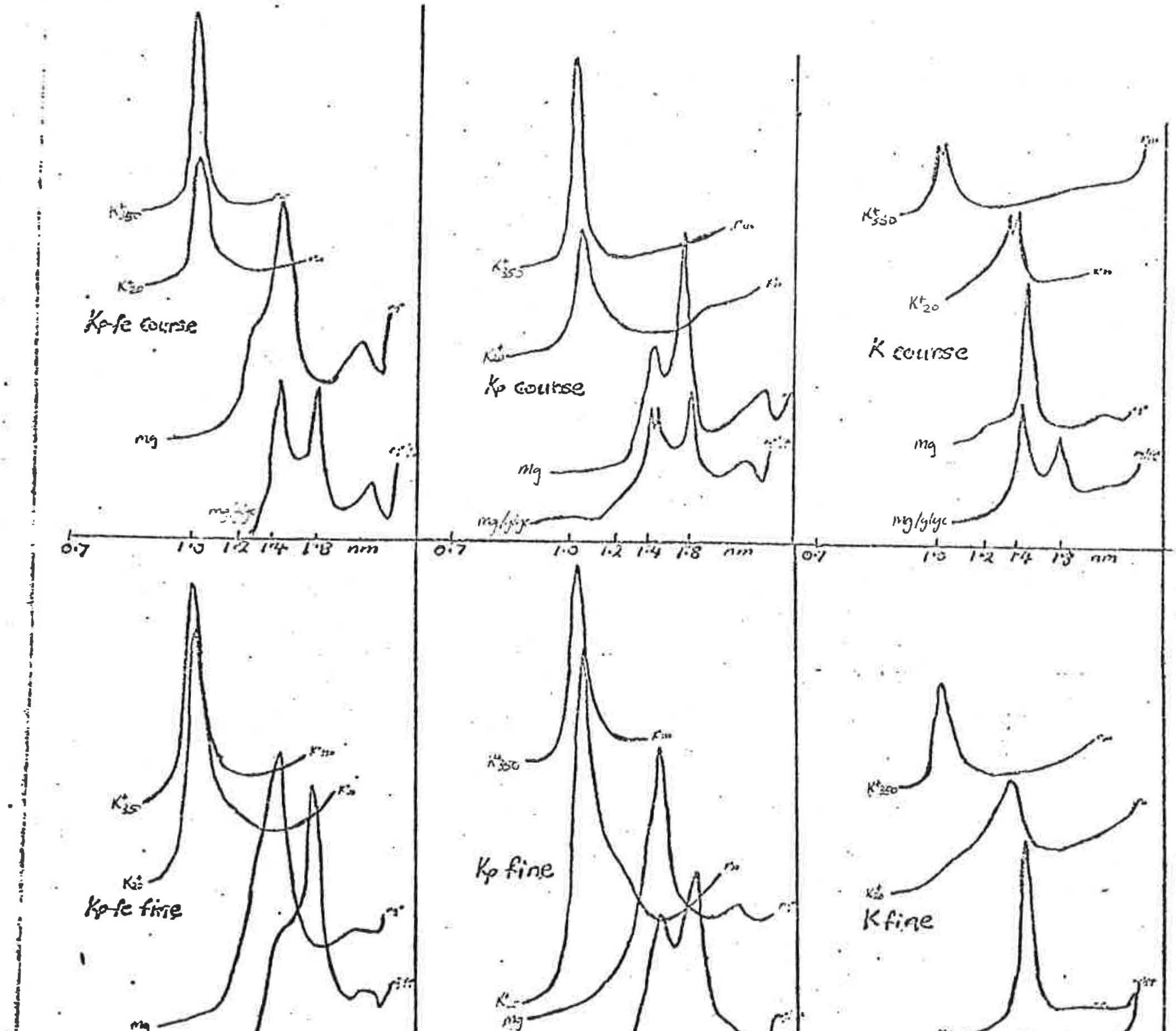


Fig. 12. 'X-Ray diffractograms of the initial Katrine A_2 soil, fine and coarse fractions. K-untreated, Kp-peroxidised, i.e. organic matter removed, Kp-Fe-peroxidised and deferrated.'

of the deferrated clays, where complete collapse of the 1.4 nm peak to 1.0 nm occurred on heating. This implies that the interlayer material was removed during the deferration procedure, with the formation of vermiculite. Mehra and Jackson's (1960) deferration procedure is therefore considered too severe for treatment of the Craigieburn clays. Dudas and Harwood (1971) showed how alkaline dissolution and Fe removal treatmenys affected clay minerals. Treatment with NaOH-dithionite-citrate-bicarbonite was shown to be capable of removing interlayered compounds, and it was concluded that KOH-acid ammonium oxalate should be used for clay pre-treatment where alteration of crystaline components is to be minimised.

In the analysis of the leached clays it was important to determine the clay transformation caused by leaching without the possibility of transformations caused by pre-treatments. It was therefore decided, that the leached clay analyses be performed without pre-treatment, and that they should be compared to untreated initial soils.

Removal of the interlayers by deferration showed that the hydroxy-Al interlayers were lightly held in the 2:1 - 2:2 Al-intergrade clay from the Craigieburn B_2. Thus leaching of these clays by complexing solutions at low pH should have the capability of removing the interlayer with the formation of vermiculite or montmorillonite.

KATRINE A_2

A 2:1 layer silicate clay mineral was indicated by complete collapse to 1.0 nm on heating to 350°C. This mineral is shown to be a mixture of vermiculite and montmorillonite by the splitting of the 1.4 nm peak into 1.42 nm and 1.8 nm components on Mg^{2+}/glycerol solution. A low intensity peak at about 2.2 nm implies some interstratifications.

There is little difference in mineralogy between the fine and coarse clay. The untreated peaks were sharp and peroxidation increased their intensity. Peroxidation followed by deferration tended to decrease the vermiculite components in the fine clay.

ANALYSIS OF LEACHED SOIL CLAYS

After leaching for the required time the soil clays were examined to determine whether any clay transformation had occurred. The soils were removed from the leaching tubes and the clays separated by sedimentation. X-Ray diffractograms were made and compared to the diffractograms of the initial soils.

METHOD

No pre-treatments were made in order to reduce the possibility of producing artificial transformations.

From the Katrine A_2 soils the whole clay fraction ($< 2.0\mu$) was separated. Clay suspension (of 1%) were prepared and saturated with K^+ (1M KCl) and 2 mls of suspension dryed on glass slides at room temperature.

From the Craigieburn soils whole clay ($< 2.0\mu$) and fine clay ($< 0.2\mu$) fractions were separated. Two clay suspensions (of 1%) were prepared, for each sample, one saturated with Mg^{2+}

($1M\ MgCl_2$) and the other with K^+ ($1M\ KCl$).

X-Ray diffractograms were made of the Mg^{2+} saturated clays, which were then sprayed with 10% glycerol, dryed and X-Rayed again. Diffractograms were prepared of the K^+ saturated clays after drying at room temperature and again after heating for two hours at 350°C in an oven.

The batch 3 soils were not analysed after negative results were obtained for batchs 2 and 4.

DISCUSSION.

The results are presented as clay d-spacings in Tables I, II and III.

Craigieburn Soils.

No transformation to montmorillonite was found in any of the soil clays (Table I and II) as the Mg^{2+} saturated clay lattices did not expand on glycerol solvation. From this result it was decided to concentrate on the analysis of batch 1, which experienced the longest period of leaching (75 leachings).

The K^+ saturation of batch 1 (Table II), also showed that a transformation to vermiculite did not occur. Vermiculite would have been indicated by lack of expansion of the Mg^{2+} peak and the complete collapse of the K^+_{350} peak to 1.0 nm. The lack of complete collapse to 1.0 nm and lack of expansion showed that 2:1 - 2:2 Al-intergrade was still present in the Craigieburn soil.

However there was some suggestion that extra collapse on heating of the intergrade had occurred in the batch 1 soil clays compared to the initial Craigieburn soil clays. In the whole

Table I d- spacings of whole clay fractions from leached Craigieburn and Katrine A_2 soils

	d (001) spacings (nm) whole clay (< 2.0 μ)								
SOILS	BATCH 5 (15 leachings)			BATCH 4 (30 leachings)			BATCH 2 (60 leachings)		
Craigieburn	d Mg^{2+}	d Mg^{2+}/glyc	Expansion	d Mg^{2+}	d Mg^{2+}/glyc	Expansion	d Mg^{2+}	d Mg^{2+}/glyc	Expansion
0.2 M Cit									
pH 3.5	1.44 s*	1.44 s	none	1.46 s	1.45 s	none	1.45 s	1.46 s	none
4.5	1.44 s	1.44 s	"	1.46 s	1.45 s	"	1.44 s	1.43 s	"
5.5	1.44 s	1.43 s	"	1.46 s	1.45 s	"	1.44 s	1.43 s	"
0.02 M Cit									
pH 3.5	1.44 s	1.43 s	"	1.47 s	1.46 s	"	1.46 s	1.45 s	"
4.5	1.44 s	1.44 s	"	1.46 s	1.46 s	"	1.46 s	1.45 s	"
5.5	1.44 s	1.43 s	"	1.46 s	1.45 s	"	1.44 s	1.44 s	"
0.02 M Ac									
pH 3.5	1.43 s	1.41 s	"	1.46 s	1.44 s	"	1.44 s	1.42 s	"
4.5	1.42 s	1.43 s	"	1.46 s	1.46 s	"	1.46 s	1.43 s	"
5.5	1.43 s	1.44 s	"	1.46 s	1.46 s	"	1.42 s	1.46 s	"
Katrine	d K^+20	d K^+350	Collapse	d K^+20	d K^+350	Collapse	d K^+20	d K^+350	Collapse
Al pH 3.5	1.42 s	1.10 vb	3.2	1.46 b*	1.12 s	0.34	1.46 s	1.15 s	0.30
4.5	1.46 s	1.12 vb	3.4	1.47 b	1.13 s	0.35	1.45 s	1.12 s	0.33
5.5	1.44 s	1.25 vb	1.9	1.44 b	1.11 s	0.33	1.41 s	1.10 s	0.31
Ac pH 3.5	1.20 vb*	1.02 s	1.8	1.27 b	1.03 s	0.25	1.27 b	1.02 s	0.24
4.5	1.33 vb	1.02 s	3.1	1.29 b	1.04 s	0.25	1.28 b	1.02 s	0.26
5.5	1.34 vb	1.03 s	3.1	1.30 b	1.04 s	0.26	1.30 vb	1.03 s	0.25

* s = sharp peak, b = broad peak, vb = very broad peak.

Table II. d- spacings of whole clay fractions from leached batch 1 soils.

SOILS	d (001) - Spacings <u>whole clay</u> fraction ($<2.0\mu$) BATCH 1 (75 leachings)						
Craigieburn	d Mg^{2+}	d Mg^{2+}/glyc	Expansion	d K^{+}20	d K^{+}350	Collapse	d K^{+}550
0.2 M Cit.							
pH 3.5	1.49 s	1.47 s	None	1.45 s	1.20vb	0.25	1.11 s
4.5	1.46 s	1.46 s	"	1.45 s	1.18 b	0.27	1.12 s
5.5	1.48 s	1.46 s	"	1.45 s	1.18 b	0.27	1.11 s
0.02 M Cit.							
pH 3.5	1.48 s	1.46 s	"	1.44 s	1.20 s	0.24	1.10 s
4.5	1.47 s	1.46 s	"	1.44 s	1.20 s	0.24	1.12 s
5.5	1.47 s	1.46 s	"	1.44 s	1.20 s	0.24	1.12 s
0.02 Ac							
pH 3.5	1.46 s	1.45 s	"	1.44 s	1.23 s	0.22	1.15 s
4.5	1.47 s	1.46 s	"	1.44 s	1.20 s	0.24	1.11 s
5.5	1.46 s	1.45 s	"	1.44 s	1.20 s	0.24	1.12 s
Craigieburn initial soil				1.46 s	1.26 s	0.20	

Katrine	d K^{+}20	d K^{+}350	Collapse
A1 pH 3.5	1.47 s	1.12 s	3.5
4.5	1.46 s	1.13 s	3.3
5.5	1.46 s	1.13 s	3.4
0.02 Ac pH 3.5	1.28 b	1.02 s	2.6
4.5	1.29 b	1.03 s	2.6
5.5	1.29 b	1.03 s	2.6

Table III. D-spacings of fine clay fraction from leached batch 1 soils.

	d (001)- Spacings fine clay fraction ($< 0.2\mu$)						
SOIL	BATCH 1 (75 leachings)						
Craigieburn	d Mg^{2+}	d Mg/glyc	Expansion	d K^{+}20	d K^{+}35b	Collapse	d K^{+}550
0.2 M Cit.							
pH 3.5	1.47 s	1.46 s	none	1.44 s	1.18 b	0.26	1.11 s
4.5	1.47 s	1.46 s	"	1.44 s	1.18 b	0.26	1.13 s
5.5	1.47 s	1.46 s	"	1.43 s	1.20 b	0.23	1.17 s
0.02 M Cit.							
pH 3.5	1.43 s	1.44 s	"	1.43 s	1.20 b	0.23	1.16 s
4.5	1.46 s	1.46 s	"	1.44 s	1.20 b	0.24	1.15 s
5.5	1.45 s	1.44 s	"	1.44 s	1.20 b	0.24	-
0.02 M Ac							
pH 3.5	1.43 s	1.44 s	"	without deferration-insufficient fine clay			
Craigieburn initial soil	14.6 s	14.4 s	"	1.44 s	1.35 b	0.10	

clay fraction the initial soil collapsed by 0.2 nm but the leached clays of batch 1 collapsed by up to 0.27 nm. Little confidence cna be placed on this however as the clay leached with the 0.02 M acetate buffers collapsed by the same amount as the clays leached by the 0.02M citrate buffers. Analyses of the leachates showed that little Al was leached from the acetate leached soils, so these clays should have shown little change from the initial soil mineralogy. It must be mentioned that difficulties were experienced in obtaining an X-Ray diffractogram of the initial whole clay fraction of the Craigieburn soil. A high intensity peak, on heating the K^+ saturated clay to 350°C, was difficult to obtain and was very broad.

In the fine clay fraction (Table III) increased collapse on leaching compared to the initial soil was more definite. The fine clay fraction of the initial soil collapsed by about 0.10 nm whereas the leached clays collapsed by up to 0.26 nm. This implies that some hydroxy-Al interlayer material was removed from the intergrade interlayer by leaching. In making this interpretation it should be noted that insufficient fine clay for analysis could be separated from the soils leached by the 0.02M acetate buffers. During leaching very little Fe was removed and the peds had not broken down sufficiently to allow separation of the fine clay fraction without deferration. Deferration could not be attempted as the procedure was shown to be capable of promoting increased collapse.

Katrine Soils.

For the Katrine soils a transformation from the montmorillonite-vermiculite assemblage into 2:1 - 2:2 Al-intergrade occurred as expected.

The results (Tables I and II) show a marked difference between the clays leached with Al solution and the control clays leached with acetate buffers. In batch 5 (the soils leached only 15 times in about 30 days) the Al and acetate buffer leached soils show a difference in behaviour. The acetate leached soil clays collapsed from a very broad peak centered on about 0.13 nm to a sharp 1.0 nm peak on heating to 350°C. The Al leached soil clays however collapsed from a sharp peak at about 1.44 nm to a broad peak centered on about 1.10 nm. With increased time of leaching these peaks became sharper. In batch 1 the soil clays leached with acetate buffer are still clearly expandable 2:1 layer silicates with 1.29 nm K_{20}^{+} peaks which collapse to sharp peaks at about 1.0 nm on heating to 350°C. Clays leached with Al however show incomplete collapse from 1.46 nm to 1.13 nm. Al has therefore precipitated in the interlayer spaces with the formation of 2:1 - 2:2 Al-intergrade minerals.

3. LEACHATE ANALYSES

B_2 HORIZON OF CRAIGIEBURN SILT LOAM.

EXPERIMENTAL.

The leachates (60 samples) were collected from soils after each run of 6 to 8 leachings. Al and Fe were determined in the leachates (Table IV) and the values plotted against time in Figures 13, 14, 15 and 16.

The citrate or acetate in solution was destroyed with a HCl/HNO_3 mixture (Blakemore, 1968), with the addition of 15 mls fig 13. Cumulative plot of Al leached from Craigieburn soil with time.

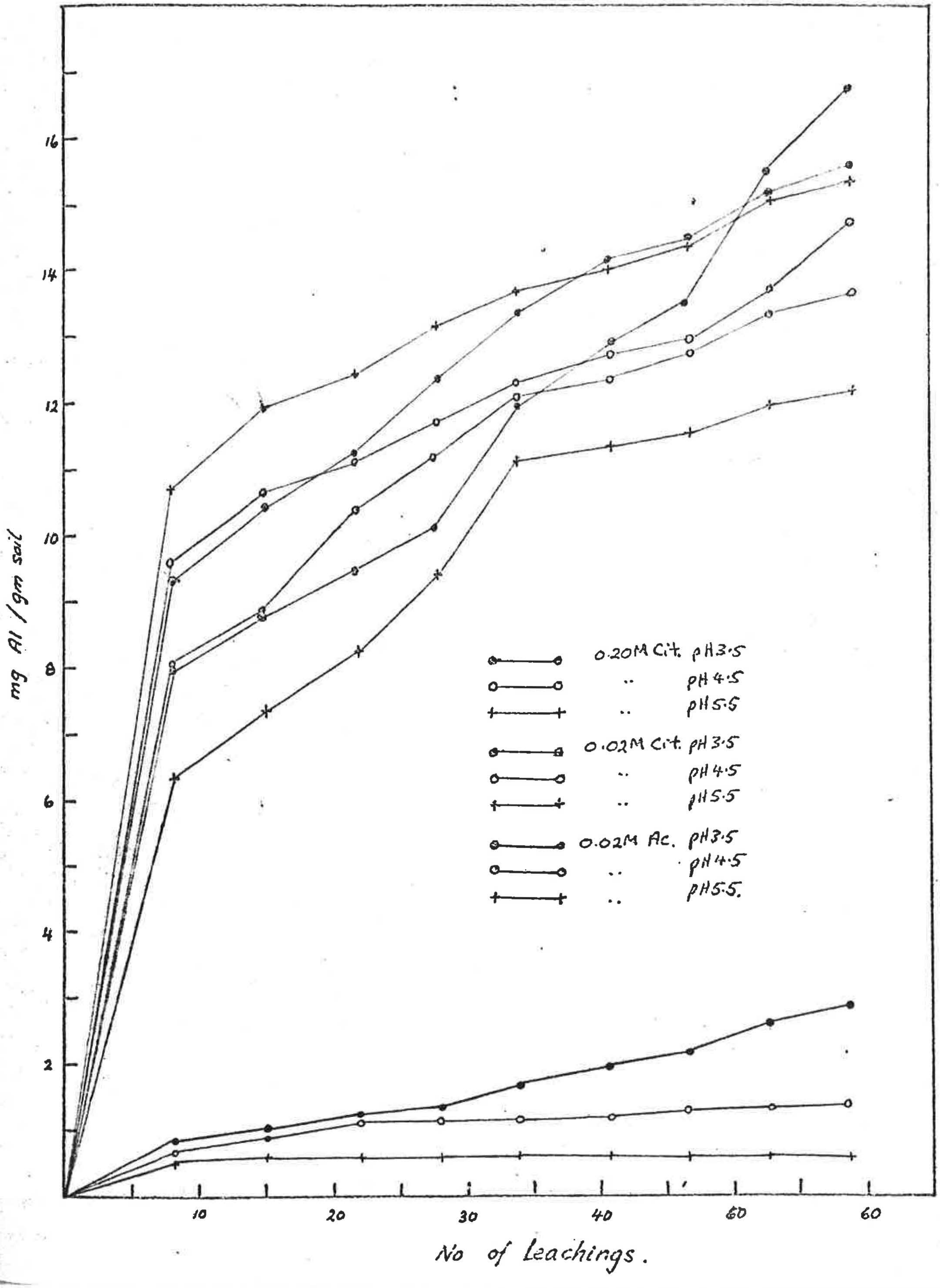


fig 14. Al leached from Craigieburn silt loam with time

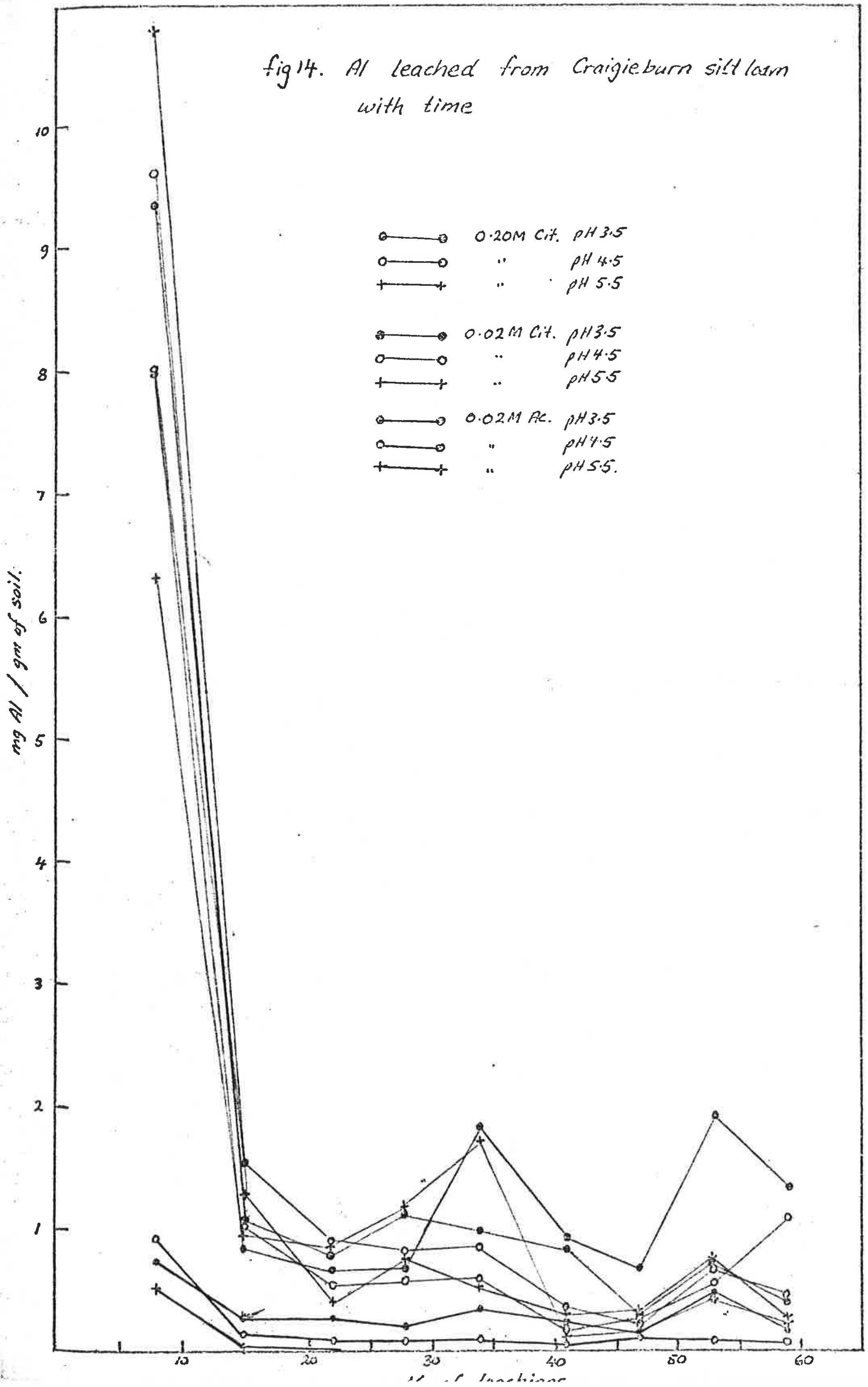


fig 15 Cumulative plot of Fe leached from Craigieburn silt loam against time.

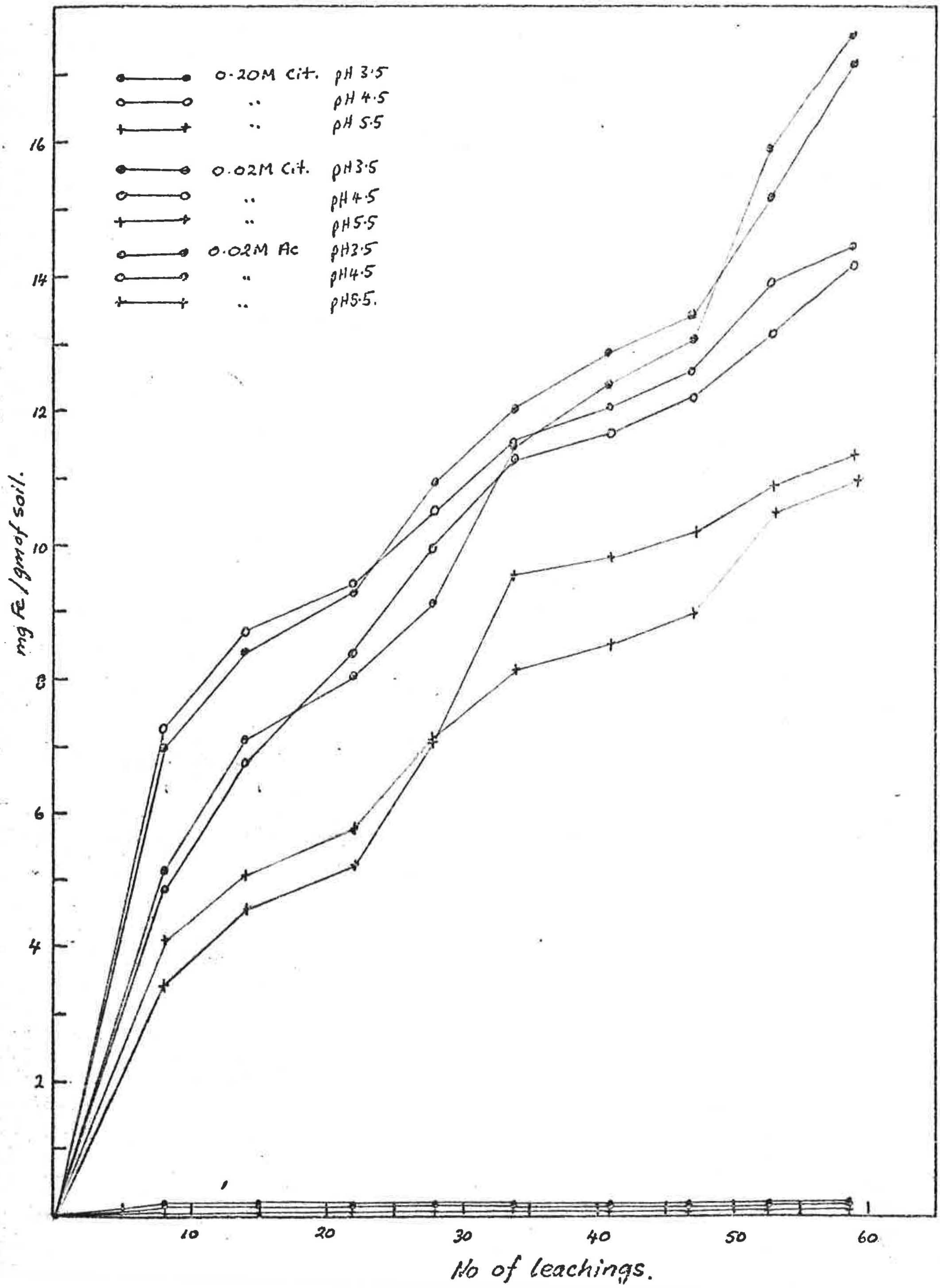
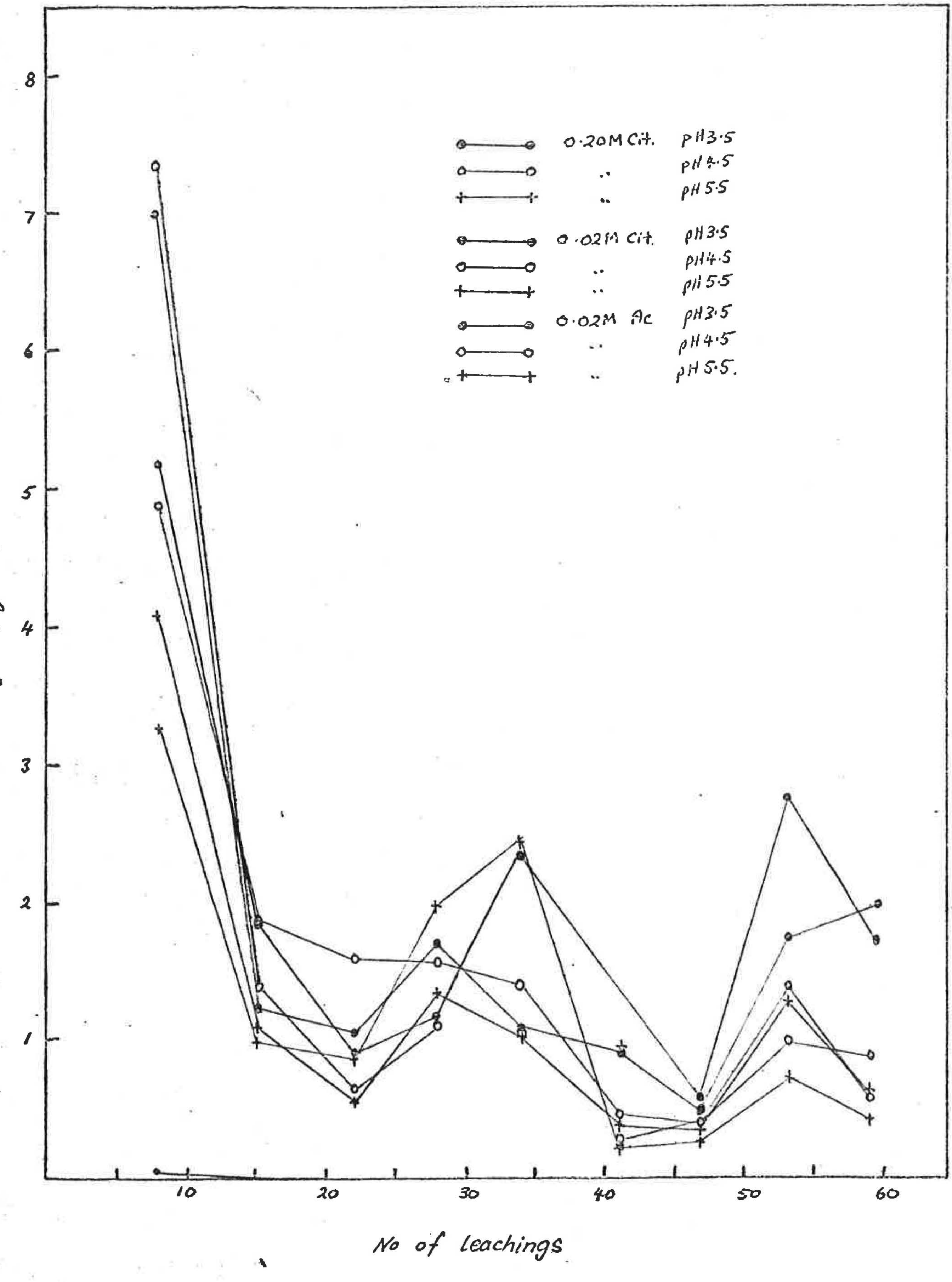


fig 16 Fe leached from Craigieburn silt loam against time.



of perchloric acid (A.H. Horn, Pers. comm.). The perchloric acid was added because interference occurred during the elemental determination. The HCl/HNO_3 mixture by itself did not completely destroy the organic matter present in the samples. Al and Fe were determined by the ferron method of Belyayeva (1966).

RESULTS AND DISCUSSION.

1) Under the experimental conditions used the chelating strength of solution was the major factor controlling the amount of Al and Fe dissolved (Figs. 13 and 15). The 0.20 M and 0.02 M citrate buffers, at the three pH values used, all leached Al and Fe more rapidly than any of the 0.02 M acetate buffers (Figures 13,14,15 and 16).

2) The Effect of pH is most clearly shown in the dissolution of Al by the 0.02 M acetate buffers (Figures 13 and 15). Al was dissolved most rapidly by the pH 3.5 buffer and least rapidly by the pH 5.5 buffer. Al dissolution by the 0.20 M and 0.02 M citrate buffers do not show such a simple pattern. After 35 leachings in the 0.02 M citrate buffers the quantity of Al removed decreased with increasing pH (Figure 13). In the 0.20 M citrate buffers, however, the quantity of Al removed at pH 5.5 eceeded that at pH 4.5 (Fig. 13). Also at pH 3.5 the quantity of Al removed in the 0.02 M citrate buffer was greater than that removed in the 0.20 M citrate buffer.

The reason(s) for these irregularities was not determined. The analyses were reproduceable. The results may have been effected by drying out the soil to increase it's permeability. The 3.5, 4.5 and 5.5 pH 0.02 M citrate buffer leached soils were dried after 34 leachings and the pH 3.5 0.02 M citrate buffer leached soil, after 53 leachings. During weekends the tubes drained and often started to dry-out, and such fluctuations in moisture content were not uniform between all samples. Drying may have caused the rate of Al release to increase and raises the question of the role of wetting and drying in dealumination weathering processes in the soil. Temperature variation or other environmental factors could only be responsible for changes that effected the dissolution in all solutions.

3) The rate of Fe dissolution and quantity increased with decreasing pH (Fig. 15).

4) The cumulative leaching curve for Fe (Fig. 15) shows the importance of chelation in the solution of Fe. Considerably more Fe was dissolved by the citrate buffers than was dissolved by any acetate buffer. Increasing the strength of the acetate buffers from 0.02 M to 0.20 M, however, did not cause any appreciable increase in the solution of Fe. pH of the buffer rather than the strength of the citrate, appeared to be more important; the amount of Fe leached, tending to increase with decreasing pH. The irregularities that occur in these curves (especially for the 0.20 M citrate buffer at pH 3.5) may be caused by the drying of the samples as discussed above.

5) The abrupt initial change in slope observed in Figures 13, 14, 15 and 16 may represent the end of a rapid initial

attack on the most disordered gels and surface coatings.

6) Care must be taken in extrapolating these results to natural systems. The chelating power of the 0.02 M and 0.20 M citrate buffers is likely to be much greater than the chelating power of natural soil solutions. The results do show, however, that both pH and chelating ability are important factors influencing the rate and amounts of Al and Fe leaching from the B_2 horizon of Craigieburn silt loam.

7) Although the 0.20 M and 0.02 M citrate buffer solutions differed in concentration by a factor of 10, the difference in the rate of leaching of Al and Fe was not great. Therefore at some level of chelating ability between that of 0.02 M acetate and 0.02 M citrate, there appears to be a limiting level above which there is no appreciable increase in the rate of Al or Fe chelated for an increase in the chelating ability of the solution.

8) The dissolution of Al and Fe from gel or crystaline surfaces would involve attack by either H_3O^+ or by the chelating ion. The similar rates of solution of Al and Fe in 0.20 M and 0.02 M citrate solutions indicates that the reaction mechanism does not involve only a simple attack by the chelating ion. At these concentrations of citrate a reaction involving H_3O^+ is probably the rate determing step.

0.02 M citrate however dissolved Al and Fe more rapidly than did acetate (at pH values between 3.5 and 5.5). This suggests that below a certain level the concentration of the chelating groups may be involved in the rate determing step.

Similarities in the dissolution properties indicate that the majority of Al and Fe came from the same phases and that solution was by similar mechanisms.

9) An attempt was made to characterise the leached phases by examining the initial and leached soils by scanning electron microscopy.

Plates 1 and 2 show the initial Craigieburn soil (H_2O dispersed, $< 2\mu$ fraction). The larger clay particles are covered with clusters of very fine particles. The clusters were unstable and disaggregated under focus of the electron beam. Plates 3 and 4 show the influence of leaching. The fine particles present in the original soil were less conspicuous and particles showed cleaner more angular and planar surfaces. Plates 5 and 6 show a comparison between relatively weak and strong leaching. The fine clay particles leached 30 times with pH 3.5 acetate buffer are rounded and roughly textured, but the fine clay particles leached with pH 3.5 0.20 M citrate are more angular and plate-like in appearance.

10) In the natural soil system all degrees of order from random to approaching complete order may exist. The Al and Fe supplying phases in the soil may be placed in categories of increasing order

(a) Aluminosilicate gel systems* Poorly ordered oxides and hydrous oxides of Al and Fe Hydroxy-Al coatings on layer silicates*

(b) Hydroxy-Al interlayers in 2:1 - 2:2 Al-intergrade minerals*

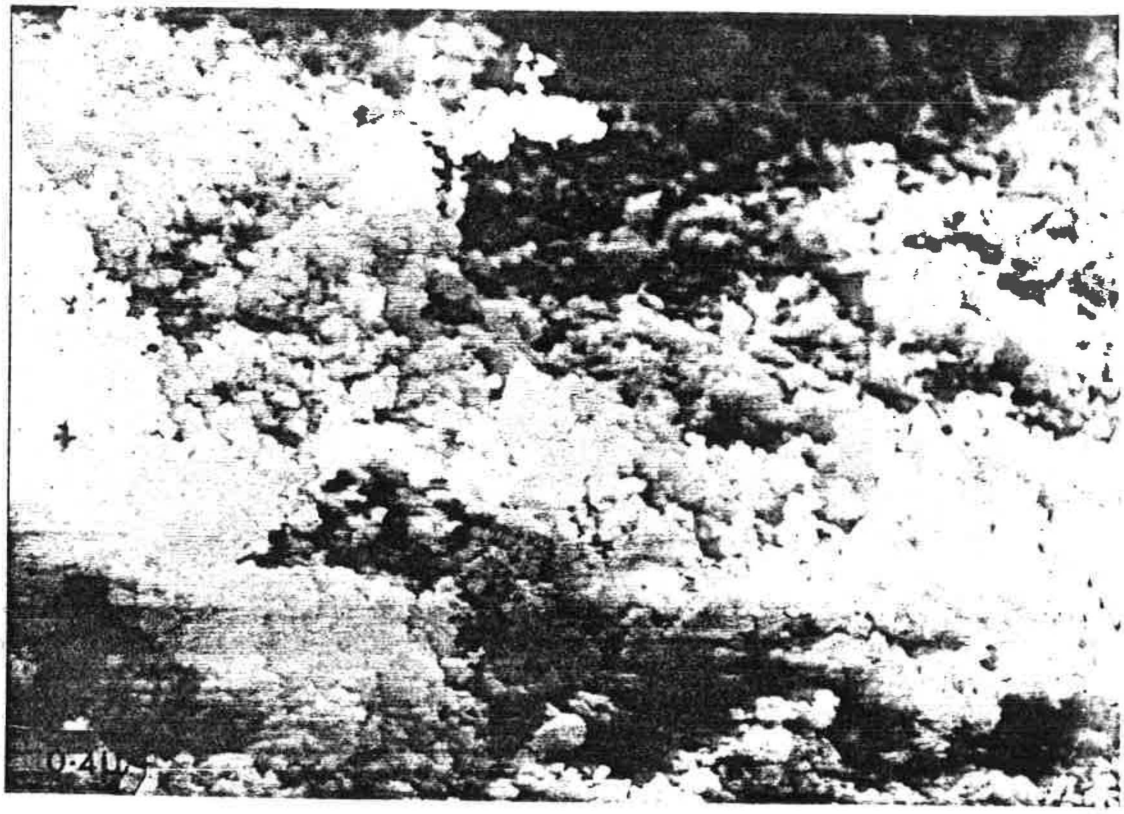


Plate 1. Whole clay fraction of initial Craigieburn soil. Largest particles are less than 2μ

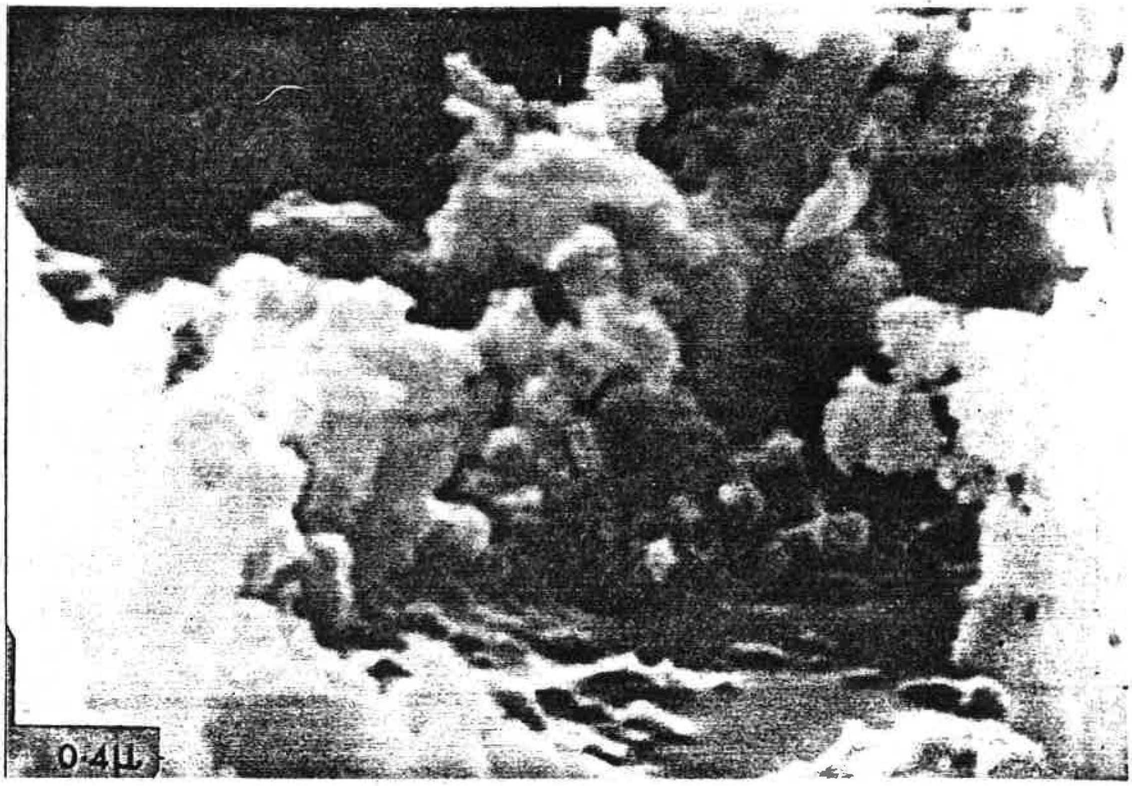


Plate 2. Whole clay fraction of initial soil micrograph. Enlargement of Part of above.

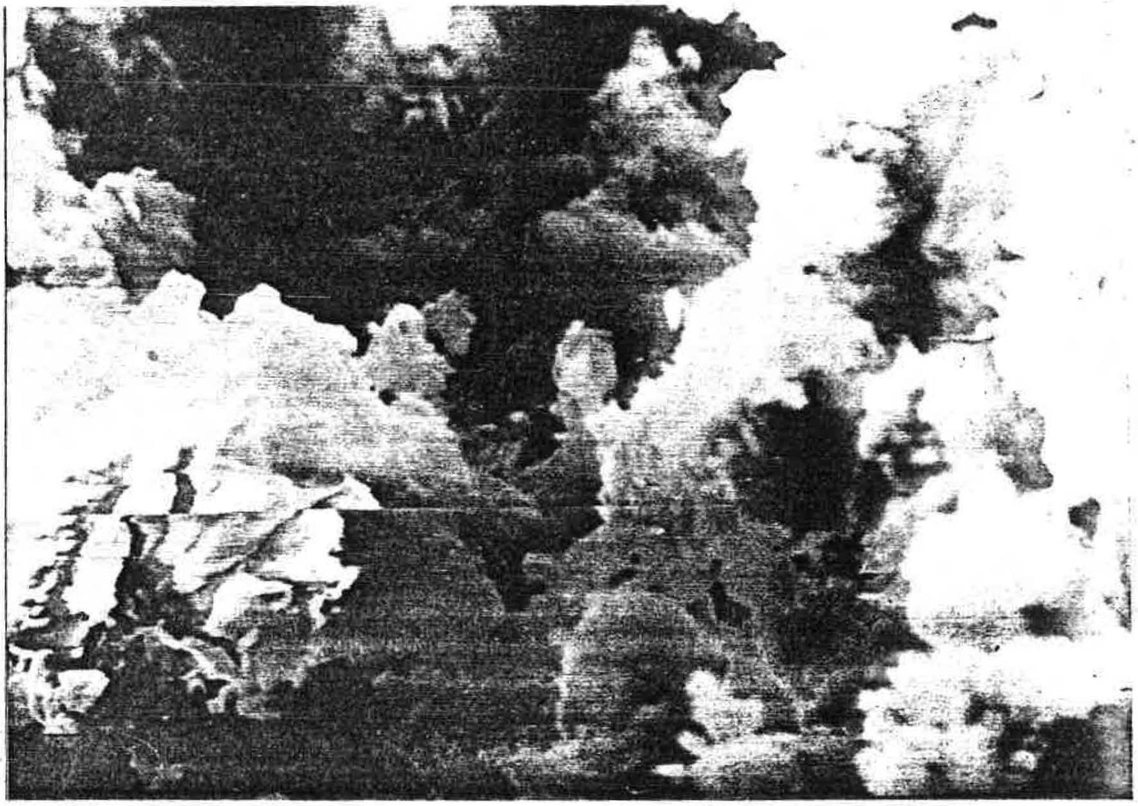


Plate 3. Craigieburn soil leached with pH 5.5 0.2 M Citrate buffer. (60 leachings) whole clay fraction.

Plate 4. Craigieburn soil leached 60 times with pH 5.5 0.2 M Citrate buffer. Largest particles are less than 2μ

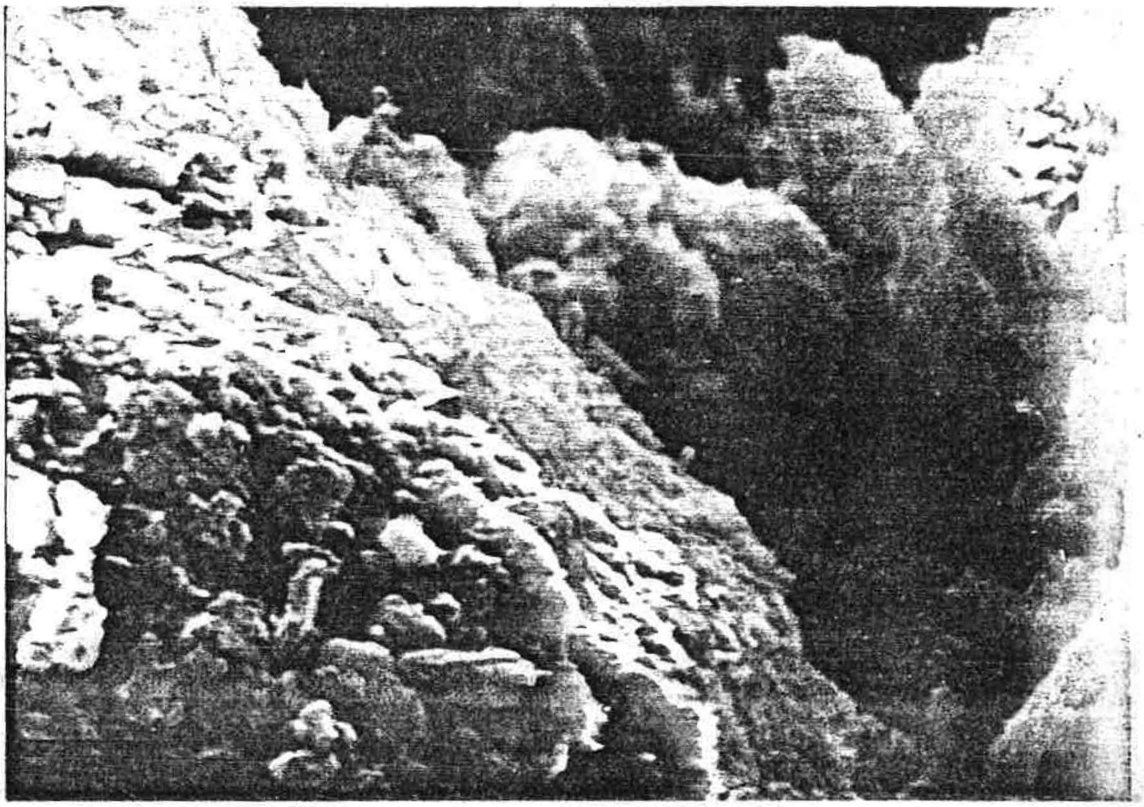


Plate 5. Craigieburn soil leached with pH 3.5 Acetate buffer (30 leachings). Large particle, less than 2μ, is covered with fine clay material.

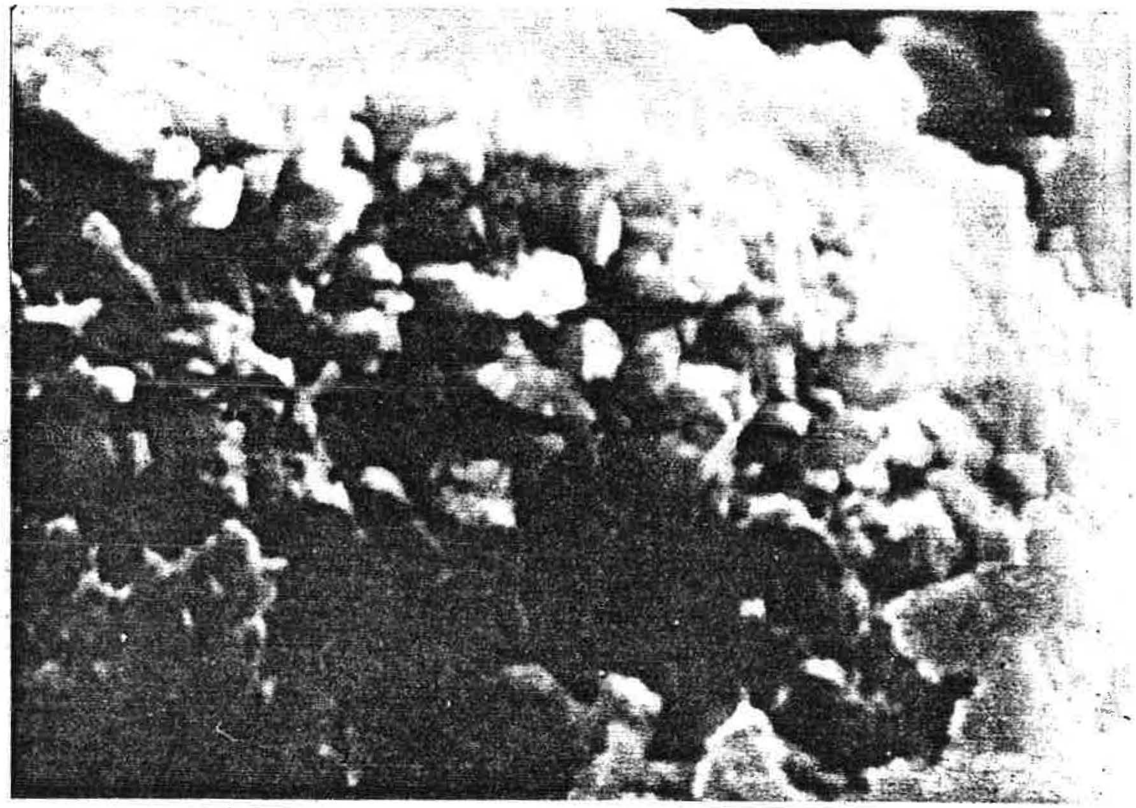


Plate 6. Craigieburn soil leached 60 times with pH 3.5 0.2 M Citrate buffer. Large particle covered with disordered material.

(c) Al and Fe in crystaline minerals.

(* In these systems some Fe may subsitute for Al).

The rates of Al and Fe dissolution should decrease with increasing order. The rapid decrease in rate of Al and Fe dissolution after the first 8 leachings (Fig. 14 and 16) therefore, probably corresponds to the destruction of the most randomly ordered phases and the initiation of attack on more highly ordered phases.

11) 15.6 mg Al/gm of soil, or 8.7% of the total Al, was removed after 60 leachings with 3.5 pH 0.20 M citrate buffer. 8.1 mgAl more than the oxalate extractable (by the method of McKeague and Day, 1966), per gram of soil, was removed by leaching (Table 4). McKeague and Day claimed that oxalate extraction removed much of the Al and Fe from amorphous soil colloids and little from crystaline oxides and aluminosilicates. Therefore, it is probable that after 60 leachings some of the hydroxy-Al interlayers were attacked. This is confirmed by the X-Ray diffraction analyses of the clays (Table III) which shows that enough Al was leached to allow some collapse of the intergrade. A longer period of leaching at low pH would appear to be required to remove all of the hydroxy-Al interlayers and stabilise vermiculite. An even longer period probably involving protonation is presumably needed to reduce the interlayer change on the 2:1 type layers and yield montmorillonite.

17.2 mgFe/gm of soil, or 43.2% of the total Fe, was removed after 60 leachings which was almost equivalent to the oxalate extractable Fe (Table IV).

The composition of the material extracted by oxalate contained twice the amount of Fe relative to Al as was removed by citrate leaching. The most probable explanation for this is the increased solubility of Fe in oxalate, a stronger reducing solution than citrate.

Table IV. Comparison of Al and Fe leaching (Batch 2-60 leachings) with total and oxalate extractable Al_2O_3 and Fe_2O_3 from Craigieburn soil.

	Al	Fe
Total Al_2O_3 and Fe_2O_3 in Craigieburn soil*	17.6 mg /gm soil	39.7 mg /gm soil
Al and Fe removed after 60 leachings with 3.5 pH 0.20 M citrate buffer	15.6 mg /gm soil	17.2 mg /gm soil
% of total Al and Fe removed by leaching	8.7% of Total Al	43.2% of Total Fe
Oxalate extractable Al_2O_3 and Fe_2O_3*	8.1 mg /gm soil	17.1 mg /gm soil
% of total Al and Fe removed by oxalate	45.7% of Total Al	43.0% of Total Fe
Amount of Fe and Al leaching has removed relative to oxalate extractable	Leaching removed 7.5 mg / gm soil <u>more</u> Al than oxalate	Leaching removed 0.1 mg / gm soil <u>less</u> Fe than oxalate
Molar ratio of Fe to Al removed after 60 leachings with 3.5 pH 0.20 M citrate	0.70 : 1	
Molar ratio of oxalate extractable Fe to Al	1.35 : 1	

* A.W.Young (pers. comm.).

4. EXPERIMENTAL LEACHING AND THE NATURAL LEACHING RATE

To derive any quantitative measure of the natural leaching rate of Al from the experimental data some relevant questions should be considered.

1) What is the relationship of the experimental to the natural rate of solution movement through the soil?
2) How does the chelating ability of the experimental leaching solution compare with that of natural soil solutions?

As transformation of a 2:1 - 2:2 Al-intergrade was not fully achieved by the experimental leaching of the B_2 horizon of the Craigieburn silt loam, no quantitative data, on the amount of Al that must be removed, for stabilisation of vermiculite or montmorillonite is available.

The Reefton study area (of Campbell, 1974) can be considered as a suitable system for comparison with the experimental data.

As the cross sectional area of the leaching tubes was 3.14 cm^2, the 475 cm^3 of solution passed through the tube at each leaching was equivalent to 1510 mm of rainfall. The annual rainfall at Reefton is 1919 mm (1904-1972), and assuming no runoff, the passage of 475 cm^3 of solution through a leaching tube is equivalent to 1.27 years of natural leaching. The 75 leachings of batch 1 were therefore equivalent to 95 years of natural leaching, and the 60 leachings of batch 2, to 76 years of natural leaching, in terms of solution movement. The laboratory solutions were, however, in actual contact with the solid phases for a considerably shorter time than would occur in the field, and their effectiveness would thus be less than suggested by the above figures.

There seems to be no available information on the chelating strength of soil solutions. No educated guesses can be made of the concentration factor of the citrate buffer's chelating ability relative to the chelating ability of the soil solutions.

It is possible to compare the complexing ability of citric acid with that of fulvic acid. If it is assumed that all COOH and acidic OH groups on fulvic acid are involved in chelation, the number of chelating groups per gram of fulvic acid can be calculated. Stevenson and Butler (1969) show that the average acidity of COOH and acidic OH in fulvic is 1190 meq/100 gm. The citrate molecule has three acid groups that are involved in chelation. One mole of citric acid contains 3eq of chelating groups. Citric acid therefore has an acidity of approximately $\left(\frac{3}{\text{mw}} \right) = 1000$ meq/100 gm. Therefore the number of chelating groups supplied by 100 gm of citric acid is approximately equal to the number of chelating groups supplied by 100 gm of fulvic acid. Similar calculations may be carried out with other natural organic chelating products.

To use this information to compare the experimental and natural concentration factors in solution it is necessary to know the mean concentration of fulvic acid (etc) in the natural soil solution (i.e. under red beech with an annual rainfall of 1919 mm), and the rate at which natural chelating groups move through the soil profile. Although Tate (1970) has determined the concentration of polyphenols in litter under red beech at Taita, Lower Hutt, he does not give data on rates of movements through the soil.

The contact time required to remove hydroxy-Al interlayers and transform a 2:1 - 2:2 Al-intergrade to montmorillonite is in excess of that achieved in batch 1. Although formation of montmorillonite, as reported by authors including Malcolm _et al_. (1969), Gjems (1970) and Campbell (1974), was not achieved, the results obtained were consistant with the mechanism proposed by Campbell, 2:1 - 2:2 Al-intergrade vermiculite, prior to montmorillonite formation. A longer contact time is required to check if complete removal of interlayers, followed by protonation results in montmorillonite formation. To allow meaningfull comparison with natural systems lysymeter studies of natural soil solutions should also be undertaken. Such observations were outside the scope of the present study.

IV SUMMARY AND CONCLUSIONS

1) The period of leaching was too short to cause complete transformation of the 2:1 - 2:2 Al-intergrade to vermiculite. X-Ray and electron microscope evidence suggested that surface coatings and some interlayer hydroxy-Al was removed and that the clay was becoming more vermiculitic.

2) Citrate (chelating) buffers were more effective at removing Al and Fe from solid phases than acetate (non-chelating) buffers. Quantities removed and rates of solution of Al and Fe increased with decreasing pH.

3) Rapid initial loss of Al and Fe probably involved disordered gels and surface coatings.

4) Increasing citrate concentration above a certain limit does not increase the ability of the solution to remove Al and Fe.

5) It is considered that observed irregularities in the dissolution of Al and Fe were caused by non-uniform wetting and drying.

6) Fixation of Al occurred rapidly in the A_2 horizon of the katrine silt loam. A vermiculite-montmorillonite intergrade was rapidly transferred into a 2:1 - 2:2 Al-intergrade. This suggests that an increase in pH and a build up of Al species in soil solution would result in montmorillonite being transformed into a 2:1 - 2:2 Al-intergrade.

7) The experiment should be repeated using a lower concentration of chelating solution and continued for a longer period. Extracts from the leaves and bark of mor forming vegetation should be included amongst the chelates investigated.

8) The leaching method used in this study is not suited for long term studies. The method is laborious and difficulties occur associated with permeability.

P.J. Tonkin (pers. comm.) has suggested that these limitations could be overcome by leaching < 2 μm material (separated by H_2O dispersion), contained on porous ceramic tiles. Leaching solutions could be drawn through the tile under gentle vacuum allowing ready control of wetting and drying. Temperature could be controlled in a thermostatically controlled room. After desired periods of leaching the tile could be removed from the leaching apparatus, x-rayed and returned for further leaching. This method would result in a considerable saving in both time and solutions. Time scaling could be achieved by having a high leaching rate rather than by increasing the concentration of the solutions, as was used in the present study. Although, scaling time by increasing the leaching rate is not recommended by Crawford (1968).

9) The results obtained in this study are consistant with the explanations given by Campbell (1974) to account for the effects of red beech on clay mineralogy.

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