# Report for 1964

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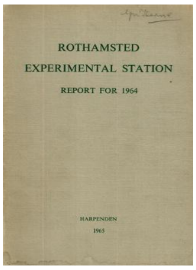

# Pedology Department

## C. Bloomfield

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# PEDOLOGY DEPARTMENT

C. BLOOMFIELD

G. Brown contributed to the first meeting of the Clay Minerals Society at The University of Wisconsin, D. S. Jenkinson and C. Bloomfield to the symposium on Experimental Pedology organised by The University of Nottingham. Bloomfield read a paper to the Nederlandse Bodemkundige Vereniging at Wageningen, and J. Catt attended the second International Working Meeting on Soil Micromorphology at Arnhem.

The subject matter of pedology is the fundamental study of the soil—its composition, properties and dynamic behaviour. The Pedology Department is therefore not necessarily concerned with topics of direct agricultural application, but rather with studies designed to increase understanding of the basic principles that determine the composition and behaviour of soils.

Because of its large surface area, the clay fraction is in many respects the most important inorganic constituent of the soil. The surface properties of a clay are ultimately determined by its structure, and we are therefore particularly concerned with the structure of clays in relation to their properties. Soil clays are usually poorly crystalline, and consequently their detailed structures are not readily determined by present-day techniques of X-ray diffraction. We are thus compelled to work on pure mineral analogues of clays, as, for example, in our current study of pyrophyllite. The layer structure of this mineral resembles that of the micas, and it also resembles 2:1 soil clays in having considerable stacking disorder. The study of pyrophyllite is thus complementary to our work on the release of potassium by micas, and to our study of soil clays, which in turn is relevant to our attempt to interpret the gross physical properties of clay soils in terms of the fundamental properties of their constituent clays.

The mineralogical composition of soils is so complex that significant facts frequently come to light during the routine examination of soils. This happened when we discovered the zeolite mineral clinoptilolite in a soil from Buckinghamshire this year—apparently the first recorded instance of its occurrence in Britain. The specificity of clinoptilolite towards the exchange of potassium suggests that the availability of cations in a soil containing this mineral will not be related in a simple fashion to the cation-exchange capacity of the soil, as this is usually determined.

The availability of nutrients to plants is determined by the form in which they occur in the soil, and the total content is of little use in assessing the availability or pedological characteristics of minor elements. We are therefore attempting to develop methods for determining the distribution of trace elements between the various soil fractions—organic matter, sesquioxides, clay and primary minerals.

By the action of its constituents and as the source of energy for microbial processes, plant material is an agent of chemical and physical change in the soil. In the context of soil profile development, we are studying the

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translocation of iron, etc., under the influence of decomposing plant residues. Polyphenols derived from tree litter seem to be involved in the development of some forest soil types, and it has been suggested that they contribute in determining the palatability of forest litter to soil fauna. The palatability of the litter would be expected to influence the extent of its activity as a soil-forming agent, and so far as palatability controls the rate of mineralisation of the litter, it is important in relation to the accumulation of organic litter and the rate at which nutrients are released and become available to plants. We are studying this in collaboration with the Entomology Department.

The amount of organic matter in a soil depends on the history of the soil, its management, the soil type and the climate. A major change in soil management will ultimately alter the organic content of the soil and thus alter the size of the nitrogen and sulphur reserves. Properties that are influenced by organic matter, e.g., structure, structural stability, and water-holding and exchange capacities, will also be affected. We are studying some of the factors governing the amount of organic matter in soil by field and laboratory experiments on the decomposition of radio-carbon-labelled plant material in soils of different pH, organic content, and mechanical and mineral compositions. Soils from the Broadbalk and Geescroft Wildernesses are being studied to obtain information on the effect of a change in soil management on the rate of accumulation of soil organic matter. These soils were allowed to revert to natural conditions about 1880, and after some 20 years A. D. Hall measured the increase in organic C and N. Samples were taken from these sites in 1964 and these, together with the 1880 and 1904 samples, are being analysed for organic C, N, S and P.

The Clay-with-flints, which is widespread on the Chalk of southern England, is an important soil parent material; its origin has been discussed for over a century. We have continued our collaboration with the Soil Survey of England and Wales in an investigation of Clay-with-flints deposits and the adjacent Reading Beds in Sussex. This area is particularly suitable for the purpose because the field evidence indicates a clear relationship between the Clay-with-flints and the exhumed sub-Eocene surface.

## Mineralogy

**Clinoptilolite.** The zeolite mineral clinoptilolite was identified in the upper layers of a soil from Halton, Bucks. (a variant of the Harwell series), during the routine examination of soils on behalf of the Chemistry Department; it is an important constituent of the coarse clay and silt fractions. The lateral extent of the occurrence has yet to be established, but a previously unidentified weak reflection in X-ray patterns of the less than 2 $\mu$ clay from soils associated with Upper Greensand deposits in Buckinghamshire, Oxfordshire and Berkshire coincides with the most prominent clinoptilolite reflection.

Clinoptilolite is usually formed by the alteration of volcanic glass; as in this occurrence, it is often associated with minerals of the montmorillonite group, which suggests a similar origin.

The cation exchange capacity of the mineral is very large—about 200 me/100 g; it is an "open" zeolite, being able to accept any of the alkali or alkaline-earth metal cations. It exhibits strong cation selectivity, particularly towards caesium and potassium, so much so that it has been investigated in connection with the removal of caesium and strontium from radioactive wastes, and the extraction of potassium from mixed salt solutions. If the affinity of soil clinoptilolite for potassium is similar to that of clinoptilolite from mineral deposits, its presence is likely to affect the availability of potassium and the response of the soil to fertilisers. It is significant that Arnold and Close (*J. agric. Sci.* (1961) **57**, 295) observed an atypical release of potassium from the silt fraction of a soil of the Harwell series.

Further work is needed to establish the lateral extent of the occurrence, to locate the geological formation in which it occurs, to estimate its abundance in the soil and to investigate the effect of its unusual cation selectivity on cation availability. (Brown)

**Structure of pyrophyllite.** The structures of layer silicates are usually deduced from the structures of better crystallised analogous minerals. Of the basic model structures for clay minerals, those of talc and pyrophyllite have not been studied by modern methods. Both talc and pyrophyllite show structural disorder, and information about this, which cannot be obtained from structure determinations of fully ordered minerals, will be applicable to some extent to the disorder common in clay minerals.

The disorder in pyrophyllite is shown by an X-ray-diffraction pattern consisting of sharp and diffuse reflections. Only reflections with $k = 3n$ are sharp and these define a monoclinic sub-cell with $a = 5{\cdot}17$ Å, $b = 2{\cdot}97$ Å, $c = 9{\cdot}33$ Å, $\beta = 99{\cdot}8°$. The atomic co-ordinates in this sub-cell have been found by a least-squares refinement in the space group $C\,2/m$ (Table 1). The sub-cell structure does not correspond to any real structure. It is the ideally disordered structure and represents three interpenetrating pyrophyllite structures. From a knowledge of silicate crystal chemistry, these three inter-penetrating structures have been disentangled.

The Si–O tetrahedra in pyrophyllite are twisted 10–10½° from the ideal arrangement, leading, as in many other layer silicates, to a ditrigonal array of oxygens on the surfaces of the layers. The average Si–O bond length is 1·612 Å and the average octahedral site–O distance is 2·025 Å. The oxygens in the surfaces of the layers are not co-planar; the two crystallographically distinct oxygens are displaced 0·09 Å from the mean plane, giving a corrugated surface to the layer. Adjacent layers can come together in three ways; chains of O–O contacts between layers are either parallel to the (010) plane with contacts 2·868 Å and 3·010 Å alternately, or approximately parallel to planes at angles of ± 120° to the (010) plane with contacts 2·998 Å, 3·044 Å, 2·998 Å, 3·343 Å, 2·998 Å—sequentially. The arrangement of adjacent silicate layers in pyrophyllite differs from that in micas. In micas a ring of six oxygens on the surface of one layer is directly superposed on a similar ring on the surface of the adjacent layer, leaving a hole containing the potassium ion. In pyrophyllite the rings of six oxygens of adjacent layer surfaces, which no longer have to accommodate large cations, move until no oxygen lies directly over another. In this way the oxygens of adjacent layers can come closer together, and the surfaces of the layers interpenetrate slightly.

**TABLE 1**

*Atomic co-ordinates in pyrophyllite*

| | x | y | z |
|---|---|---|---|
| Al | 0 | 0 | 0 |
| Si | 0·275 | 0·500 | 0·292 |
| O(1) | 0·208 | 0·500 | 0·116 |
| O(2) | 0·070 | 0·172 | 0·358 |
| O(3) | 0·241 | 0 | 0·339 |

Work is now in progress seeking a combination of the possible pyrophyllite structures, which can be derived from the fully-disordered sub-cell structure, that will account for the intensities of the reflections with $k \neq 3n$. (Brown and Rayner)

**Potassium fixation in montmorillonites.** The relative importance of the interlayer charge and the type of lattice substitution ($Al^{3+}$ for $Si^{4+}$ ions in the tetrahedral layer, or $Mg^{2+}$ or $Fe^{2+}$ for $Fe^{3+}$ or $Al^{3+}$ ions in the octahedral layer) in determining the extent of potassium fixation by expanding layer-lattice silicate minerals is uncertain because pure minerals of suitable composition are very scarce, and previous tests have always been made on minerals of a limited range of composition. Six montmorillonite–beidellites were recently acquired in which the interlayer charge ranged from 0·72 $M^+/Si_8O_{22}$ to 1·00 $M^+/Si_8O_{22}$, and the tetrahedral substitution of Al for Si from 0·14 $M^+/Si_8O_{22}$ to 0·93 $M^+/Si_8O_{22}$. The extent to which these minerals fixed potassium against exchange by ammonium was determined. With increasing interlayer charge the fixation of potassium increased almost linearly from 2 to 40 milli-equivalents per 100 g; there was no correlation between the tetrahedral charge and the amount of fixed potassium. For these specimens, therefore, the size of the interlayer charge is the dominant factor in determining the extent of potassium fixation. (Weir)

**Computer programmes.** Programmes for crystallographic calculations were not available for the Orion computer. Programmes were written for the calculation of structure factors and Fourier syntheses, the refinement of atomic parameters by a full matrix least squares, the calculation of interplanar spacing from cell dimensions and of inter-atomic distances and angles from atomic co-ordinates. The programmes were written in Extended Mercury Autocode because this was easier than machine code, and because this autocode can also be used on Atlas computers. Most established groups doing computer crystallographic calculations are now in the process of changing to second-generation computers, and some exchange of programmes should be possible. Programmes written here were sent to Nottingham University and to Imperial College, both users of Atlas computers, and programmes have recently been received from Imperial College.

As well as crystallographic calculations, additions have been made to programmes written in the Statistics Department so that they can be used in soil classification, and a programme was written for the calculation of structural formulae of minerals from their chemical analyses. (Rayner)

## Physical Chemistry

**Structure and properties of clay soils.** The technical difficulty of measuring accurately the volume of a soil pat has hindered our study of the shrinking of clay soils for a long time; the mercury pyknometer made last year (*Rothamsted Report* for 1963, p. 65) was too insensitive for the purpose. A mercury displacement balance, accurate to 0·001 cm$^3$, has been developed and used to study the residual shrinkage of clay soils, i.e., the anomalous shrinkage in which the decrease in volume of the soil-water system is less than the volume of the water removed by evaporation. With the greater accuracy of the new instrument it has been established that residual shrinkage often proceeds irregularly, showing that the stresses generated during the removal of water are not relieved evenly. The effect is small and within the limits of accuracy of the techniques hitherto available for its measurement. Residual shrinkage begins surprisingly early; some samples even reach this point at their plastic limit.

The influence of soil shrinkage on the volume of trapped air bubbles was investigated.

We now have a pressure-membrane apparatus for five samples that extends the available suction range to pF 4.

**The orientation of clay aggregates.** Clay aggregates formed by drying suspensions on solid surfaces show a preferred orientation of the clay mineral crystals so that the flakes tend to lie parallel to the surface. Such aggregates show biaxial interference figures when viewed perpendicularly to their plane. This weak secondary orientation has been assumed to be caused by further orientation of the clay crystals in the plane of the aggregate, so as to align their other axes; this process is presumably easier for lath-like crystals.

We have shown that a clay mineral aggregate containing lath-like crystals produces biaxial interference figures only when the surfaces of the aggregate are distorted into folds. Thus the secondary orientation is probably caused by the distortion of primary orientation in the region of folds, and is an artifact of poor preparative technique. (Greene-Kelly and Gallavan)

**Release of potassium from micas.** The release of potassium from mica minerals of a wide range of composition has been investigated, using sodium tetraphenyl boron to extract potassium. All the trioctahedral micas examined released potassium, but the rate differed between minerals. After 3 weeks the potassium content of a biotite decreased from 9·5% to 3·0% $K_2O$, whereas in the same time the $K_2O$ content of a phlogopite decreased from 10·5 to 7·5%. A fine-grained dioctahedral muscovite seemed to lose little or no potassium when treated in the same way.

Removal of potassium from a flake of mica is accompanied by the appearance of a line parallel to the edge of the flake, which is visible under the microscope and which moves inwards as more potassium is extracted. The appearance of the area between this line and the edge of the flake is quite different from that of the unaltered mica, the most obvious feature being the presence of wrinkles normal to the edge. The mean refractive index ($\beta \simeq \gamma$) of the outer zone is approximately 0·02 less than that of the unchanged mica. This line is thought to mark the expansion of the mica layers from 10 Å and to be close to the phase boundary between changed and unchanged mica.

Small samples of fully changed mica were saturated with magnesium and examined on an X-ray diffractometer. The products from a biotite gave basal reflections similar to those of vermiculite, and there were no reflections that could be attributed to unchanged mica. The products from a phlogopite gave a vermiculite pattern of reflections and also a weak diffuse pattern, which apparently originated from small regions of occluded mica, a few hundred Å thick.

The X-ray-diffraction pattern of oriented flakes of partly altered mica showed strong vermiculite basal reflections and weaker basal reflections of unaltered mica. Grinding increased the intensity of the mica reflections relative to those of vermiculite. This suggests that alteration proceeds not only by penetration of ions from the edges of the flakes but also by penetration through cracks in the basal surfaces, possibly with subsequent movement parallel to the basal surfaces.

We are preparing enough of the fully altered micas to permit the study of any major changes in the composition of the silicate layers that accompany the removal of potassium. Crystals large enough for single crystal studies are being used for this, as we intend to study the relation between the crystal structures of the mica and the alteration products. (Newman)

## Spectrochemistry

Work on the use of exchange resins to isolate and concentrate Mo, Pb and Zn from soils was continued (*Rothamsted Report* for 1963, p. 66). Quantitative recoveries were obtained from soils dissolved by digestion with $HF/H_2SO_4$. The solution is made 1·5 normal to HC1 and passed through a column of an anion-exchange resin (Amberlite CG 400, chloride form); metals forming chloro complexes that are stable at this acid concentration are exchanged, whereas iron and aluminium are washed through. The resin, containing the Mo, Pb and Zn, is ashed in the presence of $Al_2O_3$ and the residue analysed spectroscopically. For 1 g of soil the limits of detection are: Mo 0·2, Pb 1, Zn 50 ppm. The method is particularly suitable for small samples, e.g., with soil fractions. (Le Riche)

**Geochemical prospecting.** Samples of alluvium, plants and underground water from dry valleys draining uneconomic ore deposits of Cu–Pb–Zn in the south-eastern Egyptian desert, are being examined spectrographically to assess the applicability of this method to geochemical prospecting in arid regions.

In the 500 samples of alluvium so far examined the concentrations of

Pb and Zn are below the limits of detection, but Cu anomalies were detected as far as 1½ km from an 800 × 10 m mineralised ore body. For a mineralised ore body measuring 180 × 6 m, the limit at which a Cu anomaly could be detected was 200 m, and only 50 m from a body of 50 × 3 m. Lead anomalies were detected in the alluvium no more than 50 m from the ore body. A residual soil above an oxidised ore body contained 813 ppm Pb, but 150 m from the deposit the Pb content of the alluvium was only 30 ppm. It seems therefore that Pb cannot be detected by analysing dry valley alluvium, and that the method is satisfactory for Cu only with big deposits. The slight mobility of Cu in this arid desert environment is to be expected from the alkalinity of the soil, which is high in relation to the pH at which $Cu^{2+}$ is precipitated—8·6 compared with 5·3.

Thirty-three plant samples were analysed; very little Cu, Pb and Zn is taken up compared with the amounts accumulated by plants of humid regions. The Pb, Cu and Zn contents range from $<$0·01 to 0·4, 1 to 6 and 1 to 96 ppm respectively.

Cu, Pb and Zn could not be detected in the water from the only two wells found along the shear zone in which mineralisation has occurred. This is not surprising as the waters were alkaline, pH 8·7 and 8·5, and the water table was well below the oxidised zone of the ore bodies. (Gad)

## Soil Chemistry

**Partial sterilisation of soil.** Partial sterilisation briefly accelerates the decomposition of soil organic matter and so accelerates mineralisation of carbon and nitrogen. The results of work on this process, begun 4 years ago in the Chemistry Department (*Rothamsted Report* for 1961, p. 43; for 1962, p. 44), are summarised below.

1. Very different methods of partial sterilisation, e.g. irradiation with $\gamma$-rays, exposure to chloroform or methyl bromide vapours, oven drying or exposure to moist heat, all cause mineralisation flushes of comparable magnitude and specific activity in non-uniformly labelled soils. It does not seem possible that the different physical changes caused by such different treatments could all operate to essentially the same extent on the same fraction of the soil organic matter, so that the accelerated mineralisation is apparently not caused by such physical changes as the exposure of fresh surfaces to microbial attack or the removal of a protective film of wax.

2. Incubation of unsterilised soil with partially sterilised soil does not alter the size of the flush. This suggests that partial sterilisation does not affect mineralisation by destroying toxic substances that inhibit microbial growth, or by disturbing a host–predator balance in the unsterilised soil.

3. The flush probably occurs primarily from the decomposition of killed or damaged organisms by surviving or recolonising organisms. The amount of easily soluble organic matter is increased by $\gamma$-ray irradiation or by exposure to chloroform vapour; this is probably due to leakage of cell contents. However, the much larger increase in soluble organic matter caused by heat treatment cannot be fully explained in this way. Heat apparently increases the solubility of the humified organic matter, and some

of the soluble material provides a substrate for surviving or recolonising organisms, additional to that provided by the killed organisms.

4. The biomass can be divided into two parts—a part derived from recently added plant residues, which has a half life of very approximately 2 years, and a part that is independent of recent additions of plant material, and which is unchanged in quantity over the 4 years' duration of our experiments. This division is reminiscent of Winogradsky's division of the soil population into a zymogenic and an autochthonous part.

5. The size of the soil biomass can be roughly estimated from the size of the flush caused by treatments not involving heat, e.g., by exposure to chloroform vapour.

**Hydrolysis of soil organic matter.** Soils were incubated 1–4 years in the field with uniformly $^{14}C$ labelled plant material before the organic matter was fractionated by hydrolysis with 6*N*-HCl for 12 hours under reflux. Three fractions were obtained: "uronic" carbon, evolved as carbon dioxide during hydrolysis, and carbon soluble and insoluble in HCl. The relative proportions of these fractions were about the same after incubation for 1 or 4 years: about 5% uronic carbon, 42% HCl-soluble and 52% HCl-insoluble carbon. Similarly, the relative proportions of labelled carbon in the three fractions did not alter on incubation; of the labelled carbon in the soil about 5% was "uronic", about 63% soluble and 30% insoluble in HCl after 1 or 4 years' incubation with the labelled plant material. Similar results were obtained when the carbon was separated into fractions soluble and insoluble in cold 72% $H_2SO_4$.

These results could be interpreted as showing that these fractions of the soil organic matter all decompose at the same rate, but this is not in accord with the results of the experiments on partial sterilisation, which showed that these soils contained a small heavily labelled fraction that decomposes rapidly. The boundaries between fractions separated by chemical hydrolysis are not those between fractions of different biological stability. Nevertheless, the HCl-insoluble organic carbon is the most lightly labelled fraction yet found in these soils, and is almost certainly the oldest. (Jenkinson)

**The accumulation of organic matter in uncultivated soils.** In 1882 a portion of Broadbalk, on which wheat had been grown without manure for 40 years, was not harvested. Part was left untouched thereafter and reverted to woodland, and part has been stubbed at intervals to exclude trees and bushes. In 1904 A. D. Hall determined the accumulation of carbon and nitrogen during the first years of the experiment (*J. agric. Sci.* (1905) **1**, 241–249). We resampled the sites in October 1964 to measure changes in organic content since 1904: the samples taken in 1964 and 1904, together with those taken in 1881 from the adjacent unmanured plot on Broadbalk, provide a unique chronosequence for measuring net rates of accumulation of organic carbon, nitrogen, phosphorus and sulphur in uncultivated land.

Although much analytical work remains to be done, the following points have emerged:

1. The bulk density of the soil has decreased: in 1881 the weight per acre of dry soil (including stones) down to a depth of 27 in. was 9·11 million lb. To obtain this weight of soil in 1964 it would have been necessary to sample the stubbed section to a depth of 29·8 in. and the wooded section to 30·7 in. Most of the decrease in bulk density occurred in the top 9 in.
2. Over the period 1881–1964, the net gain of nitrogen by the soil in the wooded site was 3,870 lb/acre, and 3,950 lb in the stubbed site, both figures calculated on the weight of soil down to 27 in. in 1881 and corrected for subsequent expansion of the soil. Over the first 23 years the annual gain for the stubbed site was 100 lb/acre, over the next 60 years 27 lb of nitrogen per acre per year. Eighty-five per cent of the accumulated nitrogen is in the top 9 in. of soil.

It is not clear how this nitrogen has accumulated. It is unlikely to be from symbiotic fixation, because the stubbed and wooded sections gained almost the same amount of nitrogen over the past 60 years, despite the very different vegetation of the two sites. Enhanced fixation of nitrogen may not be the sole cause of the accumulation; part may be due to decreased annual losses of soil nitrogen, particularly during the early years of the experiment. (Jenkinson and Bloomfield)

**Mechanism of podzolisation.** Continuing work on the reaction between aqueous leaf extracts and ferric oxide (*Rothamsted Report* for 1962, p. 75), the net change in the composition of leaf extracts was studied after the solution and sorption processes have gone to completion. Leaf extracts of oak, beech and Scots pine were reacted with ferric oxide, aseptically and aerobically, and then passed through columns of ferric oxide supported on acid-washed "Celite". Under these conditions there is very little net solution of iron. Analysis of the original extract and the combined column effluent and washings showed that for oak about 95% of the polyphenolic material was retained in the column; 40–60% of the sugars, total nitrogen and $\alpha$-amino acids were also retained. Carboxylic acids seem to be retained to some extent.

Sugars and amino acids were not affected when pure solutions were passed through columns of ferric oxide, but both were retained from mixed solutions. (King, Pruden and Bloomfield)

**Palatability of leaf litter.** Previous results indicated that soft thin leaves are consumed more readily by soil fauna than leaves that are thick and tough. This was tested by exposing oak leaf discs of the two types in an oak-dominant woodland. The leaves were placed on the surface of the soil, in December 1962, and covered with freshly fallen litter; worms were excluded by a nylon mesh. Samples were taken throughout 1963 and the extent of attack assessed before the residues were analysed for ash, polyphenols, total nitrogen, etc. As determined by photometric measurement of the area of the discs, the thin soft leaves were attacked very much more readily than the thick leaves—after 11 months the thin leaves had almost completely disappeared, whereas 60% of the thick leaves still remained.

This difference was not correlated with differences in the polyphenol or wax contents of the original leaf material of the two series (Table 2). The experiment is being repeated in an attempt to avoid the gross soil contamination that vitiated the analysis of the exposed leaf discs. (King, Pruden and Bloomfield, with Heath, Entomology Department)

TABLE 2

*Percent oven dry matter*

| | Ash | Total N | Petroleum ether soluble | 50% methanol soluble | Lignin | Polyphenols (arbitrary units) |
|---|---|---|---|---|---|---|
| Unpalatable | 6·7 | 2·95 | 2·12 | 4·90 | 45·8 | 94 |
| Palatable | 6·7 | 1·77 | 2·72 | 5·58 | 36·3 | 100 |

**Oxidation of elemental sulphur in the presence of phosphate fertilisers.** We have studied the oxidation of elemental sulphur in triple superphosphate- and diammonium phosphate-based fertilisers. The fertilisers, supplied by The Sulphur Institute, had the following approximate percentage compositions: (*a*) triple superphosphate 80, S 20; (*b*) diammonium phosphate 80, S 20; (*c*) diammonium phosphate 82, S 14, paraffin wax 4; (*a*) and (*b*) were powders, passing 36 mesh, and (*c*) consisted of pellets 2–3 mm in diameter.

The fertilisers were incubated at 27° C with an acid (pH 4·4) clay loam, at 40% of the water-holding capacity with and without 2% calcium carbonate; the initial sulphur content of the reaction mixtures was 0·1%.

Twenty to fifty per cent of the sulphur was oxidised after 10 weeks' incubation, more rapidly in the presence of calcium carbonate. Both the phosphates promoted the oxidation of sulphur, particularly in the presence of carbonate; without carbonate, more sulphate was produced in the presence of triple superphosphate, but when carbonate was present this difference decreased with time. The sulphur was surprisingly reactive in the pelleted composition—in the presence of carbonate it was only slightly less active than in the finely divided triple superphosphate mixture. (Bloomfield and Pruden)

## Soil Genesis

**Clay-with-flints.** The Clay-with-flints, a heavy red-brown clay containing unworn flint nodules, is a widespread superficial deposit on the Chalk of southern England. Avery *et al.* (*J. Soil Sci.* (1959) **10**, 177–195) and Loveday (*Proc. Geol. Ass.* (1962), **73**, 83–102) showed that in the Chilterns the Clay-with-flints is overlain by the Plateau Drift, and rests on a high-level surface cut in the Chalk. The flint fraction of the Clay-with-flints is derived from the Upper Chalk, but the ratio of clay to flints is too high for the whole deposit to be merely an insoluble residue of the Chalk, and it is generally considered that most of the clay is derived from Eocene sediments. In the area between the Arun and Adur gaps, in Sussex, the Clay-with-flints rests on remnants of the sub-Eocene surface and forms the subsoil of the Winchester Series. The basal Eocene deposit—the Reading Beds Clay—forms a small escarpment at the foot of this surface. Hodgson

(*Rep. Soil Surv.* (1964), no. 16, 18) suggested that the Patching Series, which occurs on the same surface but lower than the Winchester Series, is derived in part from remnants of the Reading Beds left as outlying masses during the recession of the escarpment. Mechanical and mineralogical analyses of samples from the Winchester and Patching Series, the unweathered Reading Beds Clay and the Swanmore Series (a surface water gley soil on the Reading Beds) were made to determine the origin of the Clay-with-Flints in this part of Sussex.

The Reading Beds are characterised by a heavy mineral assemblage containing magnetite, ilmenite, leucoxene, tourmaline, zircon, rutile, kyanite and staurolite. In the Swanmore Series the only additional minerals occur in the topsoil, where felspar, hornblende, garnet and apatite have been introduced as part of a silt admixture. Both the Winchester and Patching Series contain the typical Reading Beds suite of minerals in all horizons, but there are also some chalk-derived flint, collophane and limonite pseudomorphs after pyrites. In the Winchester series the chalk-derived material is dominant only in the lowest horizon, immediately above the irregular chalk surface at a depth of approximately 50 in. The topsoils of the Winchester, Patching and Swanmore Series contain the same silty material.

The clay fractions of samples from the unweathered Reading Beds and a Winchester profile, which included an apparently unaltered remnant of Reading Beds in the subsoil, were analysed by chemical, X-ray-diffraction and electron-microscopic methods. Each clay fraction was divided into coarse (0·5–2·0 $\mu$ e.s.d.), medium (0·1–0·5 $\mu$ e.s.d.) and fine ($<$ 0·1 $\mu$ e.s.d.) portions. The clays from the Winchester profile and the Reading Beds Clay differ in several ways. Unweathered Reading Beds Clay contains less fine clay, less amorphous material and more mica than the clay fractions of the Winchester series, and electron micrographs show that it is better crystallised. The Winchester samples contain more non-exchangeable potassium than can be accounted for by the size of the 10-Å mica diffraction peak; this excess of potassium probably occurs in 10-Å layers randomly distributed in expanding minerals. In the Reading Beds Clay the amounts of non-exchangeable potassium indicate the same proportion of mica as that estimated from the size of the 10-Å diffraction peak. The Reading Beds remnant enclosed within the Winchester subsoil has approximately the same clay mineral composition as the surrounding Winchester clay. The differences between unweathered Reading Beds Clay and the remnant of Reading Beds Clay in the Winchester subsoil can be attributed to a long period of weathering in the Winchester profile.

It is impossible to distinguish Chalk-derived clay in the samples of Winchester subsoil that contain Chalk-derived sand, but as insoluble chalk residues always contain some clay, this probably indicates the insensitivity of the analytical methods.

To summarise, the sand fractions of the Winchester and Patching soils contain minerals identical to those of the Reading Beds, and the only additional minerals are those derived from the chalk or introduced by silty additions to the topsoil. The bulk of the clay in the Clay-with-Flints forming the Winchester subsoil is therefore derived from the Reading

Beds, remnants of which were left on the sub-Eocene surface. Clay mineral analyses confirm that this clay has been strongly weathered. This clay probably became intimately mixed with chalk-derived flint by periglacial activity during the Pleistocene period. The silty addition to the topsoil of all the profiles studied is mineralogically similar to material in the surface horizons of drift soils of the Chilterns (Avery *et al.*, 1959), and is probably of windblown origin. (Catt and Weir)