Report for 1956

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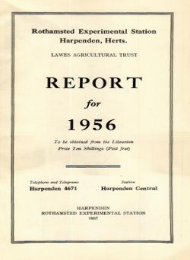

Pedology Department

A. Muir

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PEDOLOGY DEPARTMENT

A. MUIR

A. Muir and C. Bloomfield attended the 6th International Congress of Soil Science, the former being chairman of Commission V (Genesis and Cartography of Soils). During Hilary Term A. Muir gave a course of lectures on tropical soils in the Forestry Department, University of Oxford. I. Stephen has taken up a temporary post at the University of Illinois. R. R. Storrier, from Sydney, Australia, will carry out laboratory studies on the soils he has been mapping in conjunction with the Soil Survey.

MINERALOGY

Weathering and soil development of igneous rocks in Shropshire

Work on this subject has been concentrated into two main lines : (1) a detailed investigation into the products of weathering of picrite (an olivine-rich rock), and (2) a study of the development sequence of soil types found on the igneous rocks.

(1) *Picrite weathering*

In last year's Annual Report mention was made of a material which appeared to belong to the montmorillonite group which gave an excellent fibre pattern. This has led us to examine other materials in the hope that we might obtain a three-dimensionally ordered mineral of this group. A material from the same source has been found which, at least in part, consists of a montmorillonite-type mineral and which shows a degree of three-dimensional order. This new material was reminiscent of the material which has been called iddingsite, and a sample of this material is being examined. The aim of these studies is to obtain material from which X-ray-diffraction data more akin to single-crystal data can be obtained. This would allow the investigation of this mineral and many of its properties by single-crystal methods which are immensely more powerful than the powder-diffraction methods which have been used so far.

Brief notes on the preliminary examination of some of these materials are given below.

(a) *Fibro-lamellar aggregates.* In the basal soil layer fibres and lath-shaped grains of fibro-lamellar character, light yellowish-brown in colour, are fairly abundant. They appear to be derived by weathering from veins of cross-fibre greenish " serpentine " which traverses the picrite. This " serpentine mineral " has been shown by X-ray analysis to possess a chlorite-type structure.

The fibrous aggregates give fibre patterns with sharp reflexions, the repeat distance along the fibre axis is 5·3 Å. A large number of these fibres have been cursorily examined, and the variations in the diffraction patterns can be attributed to changes in humidity. The complex frequently found at normal humidities has a basal spacing of 15 Å. The zero-layer of the fibre pattern of this complex has been indexed out to a spacing of $d = 1{\cdot}45$ Å. The reflexions can all be indexed on the basis of an orthogonal net with $b = 9{\cdot}22$ Å., $c = 15{\cdot}07$ Å. In all, twenty-nine reflexions have been indexed, fourteen without ambiguity. Five unambiguously indexed reflexions are *Okl* type. Reflexions with k odd appear to be absent. The fibre beginning from a long spacing of 15 Å. can be contracted to 10 Å. by heating treatment and re-expanded again to 15 Å. by rehydration and further expanded to 18 Å. by glycerol. Throughout these changes a good fibre pattern is maintained. The fibre pattern does not change in gross features with change of long spacing, but the finer details of the pattern are altered. This may be of assistance in determining the crystal structure of the materials by allowing the use of methods similar to those used by Boyes-Watson, Davidson and Perutz (*Proc. Roy. Soc.* 1947, **A.191**, 83) in the study of the structure of horse methaemoglobin.

(b) *Lamellar montmorillonite mineral.* The X-ray characteristics and optical properties of this mineral have been established. The flakes are brown in colour with *Bxa* ⊥ 001, the plane of well-developed cleavage. A description by Arnold-Bemrose (1894, *Quart J. geol. Soc. Lond.* **50**, 63) of pseudomorphs after olivine (" Potluck pseudomorphs ") in the Carboniferous tuffs and dolerites of Derbyshire suggests their close identity with this mineral, the pseudomorphs being brown in colour and readily cleavable, the cleavage flakes showing a biaxial negative interference figure. Specimens of the " Potluck pseudomorphs " have been obtained for comparative study. An investigation of " iddingsite ", the name commonly applied to the lamellar deep reddish-brown to ruby red alteration product of olivine, has also been started in connection with the present study.

This material occurs as brown lamellae with optical properties which suggest three-dimensional order. At least part of the material in an optically continuous specimen belongs to the montmorillonite group, for a basal spacing of about 15 Å. can be increased to about 18 Å. when treated with glycerol. Oscillation photographs about the normal to the optic axial plane show a pattern of spots superposed on powder rings, and from the spots an axial repeat distance of 9·2 Å. is obtained. In a perpendicular direction in the plane of the flake the repeat distance is 5·3 Å. The nature of the spots and rings suggests that we are dealing with a disordered crystal along with a microcrystalline substance which shows preferred orientation with respect to the crystal. A more detailed examination will be required to find out if the crystal and the powder are the same material in different forms or if one material, e.g., the powder, is derived from the other, i.e., the crystal, by alteration processes.

(c) *Iddingsite.* A specimen of iddingsite selected from its optical properties has been examined by oscillation methods. The specimen was set to rotate about the normal to the optic axial plane. These photographs show definite layer lines of rather diffuse spots. The identity period is 10·1 Å. for strong layer lines, but weak intermediate layer lines show that the true repeat distance is 20·2 Å. Also on the photograph is a layer line with a period of 5·3 Å., which may represent the parallel growth of a material similar to the lamellar material mentioned above. This specimen is now being examined by moving-film methods. It appears from this specimen that a diffraction pattern distinct from olivine and from montmorillonite-type minerals is obtained from at least one specimen which would be called iddingsite. (G. Brown and I. Stephen.)

(2) It has proved possible to recognize a development sequence of soils in Llanfawr, a small ridge of augite–andesite rising to about 1,325 ft. The first member of the sequence is represented by a protoranker (an AC-soil) developed under moss and bilberry found on the highest, most exposed part of the ridge where rock outcrops. Lower down the slopes transition stages between rankers and braunerde-like soils are developed, and the final stage is that of a typical braunerde showing A, (B) and C horizons. Similar development sequences have also been noted on other outcrops of igneous rocks in Shropshire, and on the " Ivyscar-rock " (a quartz microdiorite) on the Malvern Hills, and details of the transition are being investigated. (I. Stephen and D. A. Osmond.)

(3) *Chiltern soils*

Mineralogical investigations of the fine sands and coarse silts of three profiles, representative of the Winchester, Batcombe and Charity series, as mapped by the Soil Survey, have been completed.

The " heavy mineral " studies indicate non-uniformity of parent material in the Batcombe, and, to a smaller degree, in the Winchester profile. In the Batcombe (excluding the A horizons) and in the Winchester, the main non-opaque heavy minerals are zircon, tourmaline, rutile, staurolite and kyanite, with garnet and green hornblende rare. The evidence for non-uniformity of parent material is strongest in the Batcombe, and is based on the fact that in the A horizons, garnet, and to a lesser extent, epidote and chlorite are conspicuous heavy minerals, while in the lower layers they are present only in minor amounts. The same trend is shown in the A_1 horizon of the Winchester profile. In the Charity profile there is no mineralogical evidence for profile non-uniformity, and garnet is a common constituent of the residues in all horizons. The association of the garnet–epidote–chlorite assemblage with the horizons rich in coarse silt suggests that these deposits may be of loessial origin.

Quartz is the dominant " light mineral " throughout the Batcombe and Charity profiles, and in the upper 2 feet of the Winchester, but in the lower layers of the latter profile the dominance of flint and the presence of collophane supports the view that these basal layers are largely Chalk-derived. (I. Stephen.)

Silica. Unusual forms of chalcedonic silica occur in the sand fractions of clay-with-flints soils. Three types of grain have been recognized : those which consist of bundles of parallel rods, those which have a honeycomb appearance and more rarely botryoidal grains. Optical examination showed that the grains consist of chalcedonic silica. X-ray examination of powders showed the quartz pattern. Oscillation photographs of single rods and cell walls show that the quartz crystallites are arranged with their *c*-axes in sub-parallel alignment perpendicular to the rod axis. There is also a strong tendency for the *a*-axes to lie along the rod axis.

Optical examination of single rods and thin sections of grains cut in different directions confirm these findings and also show that the grains are often optically continuous over considerable areas. Chemical analysis of air-dry material gave SiO_2 99·16 per cent, H_2O 0·84 per cent. The fragile nature of the grains shows that they have been formed more or less *in situ*. The grains are thought to be of inorganic origin, and a possible mode of formation has been proposed. This work is now being prepared for publication. (G. Brown and C. D. Ollier.)

CLAY MINERALOGY

(a) *Limestone residues*. This work extends the work on Chalk residues mentioned in last year's report. This year samples from Lower Chalk, Oolitic Limestone, Magnesian Limestone and Carboniferous Limestone have been examined.

(b) *Aylesbury Sheet (238)*. In connection with the soil survey of this sheet a large number of soil clays and clays from the underlying geological formations have been examined. Fifty samples from Gault Clay, Upper Greensand, Chalk Marl, Lower Chalk and Kimmeridge Clay have now been studied. In addition, the clays from twenty-three complete soil profiles have also been examined from soils occurring in the area. (R. Farrow and A. M. Du Feu.)

Quantitative analysis

Iron oxides. The work mentioned in last year's report has been continued. Co-precipitated iron oxides on kaolinite give broad haematite reflexions when heated at 700° C., and this results in low values for Fe_2O_3 when the estimations are based on standard curves obtained using well-crystallized haematite and peak intensities. Attempts to use integrated intensities measured photographically have failed due to the experimental difficulty in measuring peak areas accurately enough.

It has been found that the breadth of haematite reflexions obtained from co-precipitated iron oxide on kaolinite is related to the proportion of iron oxide present in the mixture. This suggests that the iron oxide in contact with the clay mineral surface forms smaller haematite crystals than the iron oxide which is further from the clay surface. This in turn suggests that a proportion of the iron oxide is more strongly held on the surface of the clay. It may therefore be possible to investigate the active surface of clay minerals for sorption of iron oxide by X-ray methods when suitable methods are used for the quantitative analysis of the haematite formed on heating. It is hoped that the X-ray diffractometer will assist in this work by giving accurate estimations of integrated intensities, as well as peak heights of haematite reflexions from well-crystallized ("standard") haematite and also from the less well-crystallized haematite obtained when co-precipitated iron oxide is heated. (R. Farrow and G. Brown.)

X-ray structure analysis

The 1953 Annual Report mentioned the need for faster methods of performing crystallographic calculations and described the work being done on an electromagnetic Fourier synthesis machine of the Bevers–McEwan type. The presence of the Elliott 401 electronic computer at Rothamsted has made much faster calculation possible. In collaboration with J. C. Gower of the Statistics Department, programmes have been written for the calculation of structure factors and two-dimensional Fourier syntheses. For a structure with N atoms in each unit cell a structure factor can be calculated in $7N/80 + 3$ seconds, which shows the speed achieved. (J. H. Rayner.)

Electron microscopy of montmorillonite minerals

We have been co-operating this year with H. L. Nixon in studying the morphology of montmorillonite minerals, and the results obtained have shown a considerable improvement on previously published work.

The mineral investigated most fully is the Unter-Rupsroth montmorillonite from the Rhon-gebirge, Germany. When sodium- or lithium-saturated samples of this mineral are completely dispersed in water they show a flat lath or plate-shaped habit. The particle size is large for a montmorillonite, dimensions of $3 \times 4\ \mu$ being quite common. Sections of the plate edges are frequently straight and joined by steps at angles of 120° to the edges. It is unusual to find a complete hexagonal plate, as in the kaolin minerals, but these small 120°-angle steps are common and reflect the pseudo-hexagonal symmetry of the mica layer in the same way.

The plates or laths are extremely thin, and estimates of the thickness are liable to be inaccurate owing to the low shadowing angle and thickness of metal that have to be employed. However, it seems fairly certain that a completely dispersed montmorillonite has a flake thickness of 10 Å. or one mica layer.

Wyoming bentonite has also been investigated. The flakes are mostly plate-shaped with irregular outlines, although one or two with crystallographic regularity have been seen. The range of particle size in the latter and in the montmorillonite from Redhill, Surrey, is very considerable, and it is hoped to make an estimate of this by comparison of micrographs and settling velocities when a suitable centrifuge is available.

Preliminary attempts to use the spray-droplet technique with montmorillonite suspensions were successful and showed that some droplets contained only a single flake 10 Å. thick. The droplets had to be sprayed without albumen on account of the thinness of the sheets, so that unfortunately the droplet outline could not be seen and had to be inferred. It is hoped to continue this work in the future, and put the results on a quantitative basis.

Black Jack Mine Beidellite

A full investigation of the nature and properties of the mineral has been undertaken. It is found as a gangue with lead and silver ores, and is particularly pure, with minor amounts of quartz as the only recognized impurity.

The naturally occurring mineral contains 73 m. eq. Ca, 25 Mg, 2 Na and 2 K per 100 g., as exchangeable cations, and yet only

0·16 per cent MgO enters the lattice in the octahedral positions. 0·3–0·4 per cent K_2O is not exchangeable, and the Fe_2O_3 content is 0·5–0·7 per cent. X-ray powder patterns give typical 17·7 Å. (001) series and (*hk*) bands with glycerol-treated flakes.

Preliminary electron micrographs show very large lath-shaped flakes, 25 µ long, 8 µ broad and 40–50 Å. thick in one instance (fine sand in one direction, silt in another and very small clay in the third!). The particles have good crystallographic outlines, and frequently successive laths are superposed with parallel or slightly fanned edges.

Comparison of the derivative of the thermal-balance curve and the d.t.a. trace shows close similarity. The Ca-clay shows the typical two-component low-temperature exothermic peak corresponding to loss of hygroscopic moisture, and calculation of the water associated with the high-temperature component of this peak gives 3·5 per cent water, or slightly more if the asymmetry of the peak is allowed for. This is considerably less than the 5·4 per cent required if each Ca ion is to be 6 co-ordinated with water molecules.

There is a loss of water, forming a small peak and not exceeding 1 per cent between 290° and 400° C. This may be due to an impurity, and needs further investigation. The total loss of structural water occurs between 200° and 900° C., and is equal to 7·2 per cent. (A. H. Weir.)

Apparatus

A microfocus four-window X-ray tube of the Ehrenberg–Spear type has been constructed and has been in use for about six months. The size and shape of the focal spot can be varied within wide limits. A point focus of about 40 µ diameter can be obtained for applications requiring a fine focus. For routine diffraction studies a focal spot 1 × 0·1 mm. is used. Other sizes and shapes of focal spots can be obtained if required. (G. C. Dibley.)

MICROPEDOLOGY

Work has continued on the morphology of soils and sediments (mainly from Cyprus and the Chiltern area) by means of the thin-section technique.

Chiltern soils

Excellent samples of highly oriented clay layers have been noted where a clay drift overlies " brickearth ". The latter is seamed with narrow more or less vertical fissures, several feet long, practically filled with red-brown clay that contrasts strongly with the yellow-brown brickearth. The clay deposit is often layered, and optical examination of sections cut normal to the layering shows mass extinction and positive elongation, indicating a high degree of optical continuity. The layered nature of the clay aggregates in the joints suggests that they are derived from the overlying clay drift by a process of repeated cyclic sedimentation.

Thin-section studies of horizons of the Batcombe and Charity profiles suggests that clay migration has been an operative process in the development of at least a part of the profiles. This work is being continued, and it is hoped that a study of the distinctive patterns of clay morphology that exist in soils will yield information about the conditions of deposition of the parent material, and the genesis and development of the soils themselves.

Cyprus soils

The micromorphology and mineralogy of terra rossas and rotlehms associated with calcareous sediments and igneous rocks respectively have been studied. The investigation confirms differences observed in the field, and assists in the differentiation and classification of the soils. A report on this work has been submitted for publication. (I. Stephen and D. A. Osmond.)

PHYSICAL CHEMISTRY OF SOIL MINERALS

The mechanism of aggregate formation in soils

A calorimetric method has been devised for determining the area of the liquid–vapour interface in systems of solid particles wetted with a liquid. A theoretical relation between this area and the suction applied to the liquid has been derived and is being experimentally verified. By the use of this method it is possible to obtain new information concerning the plastic changes which occur as solids wet and the effect that the solid has on the surface energy of the liquid film. It is anticipated that in conjunction with the low-temperature, gas-adsorption methods in use the process of aggregate formation in soils can be followed and methods of control investigated. (R. Greene-Kelly and R. C. Gallavan.)

Heats of wetting of soils

Whilst the total heat of wetting of a soil is dependent on the clay content, the heat of wetting per unit area of wettable surface is markedly dependent on the work of structural adjustment necessary to accommodate the water film. It has been found that for soils a convenient measure of the exchangeable cation environment may be made by measuring the heat of wetting per milli-equivalent of exchangeable cations. The results have suggested that most exchangeable cations in soils (low in organic matter and iron oxides) originate from sterically restricted positions probably located inside the clay mineral crystals. The only exceptions so far found are soils very high in kaolins. It seems that the ionic environment of exchangeable cations in illites is fundamentally identical to that in montmorillonites and vermiculites, in that the ions originate from deep in the crystals and not merely from their frayed edges. Further investigations on illites and vermiculites, with special reference to potassium fixation, are planned. (R. Greene-Kelly.)

Iron oxides

It has been observed that ferruginous soils give exothermic peaks during differential thermal analysis. Although this has been attributed to iron oxides, the reason for the effect is not known. By a combination of differential thermal analysis, weight loss analysis and X-ray methods it has been established that goethites of increasing particle size show a diminished exothermic peak and a progressive difference in temperature at which adsorbed and structural water are lost. The final product is always haematite of relatively large crystal size, and it seems likely therefore that the exothermic reaction is due to the difference in total surface energy between goethite and its firing product. If the crystallization of the haematite is inhibited, for example, by epitaxial growth of the iron oxide on kaolinite, then the exothermic peak is greatly reduced. (R. Greene-Kelly and J. B. McGarry.)

Water adsorption by clay minerals

Fundamental studies on water adsorption by members of the montmorillonite group have been continued. Much new data have been accumulated; for example, it has been shown that little or no difference in the water-sorption characteristics was found between members of the group provided the charge density remained constant, although the regularity of the hydrated crystal varied considerably. This would suggest that the way the sheet charge is generated in the montmorillonite group is of little importance in determining the water-film thickness, and hence the ionic mobility in the crystals. (R. Greene-Kelly.)

Potassium fixation and crystal energy

There have been two suggestions to explain why potassium ions are fixed by clay minerals. The first is that the potassium ion is of such a size that it satisfies special co-ordination requirements and the second that the ionic mobility is a function only of the hydration possible in the crystal, and this in turn depends on the hydration energy of the interlamellar cations and their charge density. An attempt is being made to decide between these two factors by the direct measurement of the crystal-energy changes due to various interlamellar cations. This is being accomplished by the accurate determination of the heats of solution, and so far the results suggest that the crystal energy is little affected by the presence of potassium ions. This would be in accord with the hydration theory of potassium fixation. Heats of solution measurements are also being applied to quantitative investigation of the energy associated with " mistakes " in clay minerals, and thus supplement the qualitative results from X-ray analysis. (R. Greene-Kelly.)

Miscellaneous investigations

Differential thermal and weight-loss analyses and determination of surface areas by the use of nitrogen or carbon dioxide adsorption at low temperatures have been carried out on a variety of materials in connection with other studies. In addition, an investigation of the surface energy of quartz powders as a function of particle size has been carried out for the Ministry of Fuel and Power (Safety in Mines) in conjunction with studies on the origin of pneumonokoniosis. (R. Greene-Kelly, R. C. Gallavan and J. B. McGarry.)

The laboratory synthesis of clay minerals

A programme of laboratory synthesis of clay minerals has been begun in an effort to provide fundamental information on the formation of clay minerals in soils.

At pressures and temperatures well above those found in soils (say at 300° C. and 300 atmospheres) clay minerals can be synthesized in a few hours from silica–alumina gels. A number of syntheses of this kind have been carried out using apparatus kindly put at our disposal by the I.C.I. Plastics Division at Welwyn Garden City. The products have been characterized by methods already developed in this department. X-ray diffraction and differential thermal analysis show that a substantial part of the gel has been converted to clay minerals. Both kaolin and beidellite have been found. X-ray diffraction showed that the kaolin mineral was kaolinite rather than halloysite. The d.t.a. curves showed marked asymmetry in the kaolinite peaks at 540–590° C. This shape of peak has been associated with halloysite in contrast with the symmetrical peak usually found for kaolinite. In this case it is most probably due to the fine particle size of kaolin. This is also suggested by an electron-microscope examination of one of the samples.

These high-temperature experiments will now be continued at Rothamsted, and a high-pressure laboratory is being set up. The apparatus should make possible measurement of the kinetics of clay mineral formation. The change of ion-exchange properties accompanying it will also be followed. The apparatus may later be used to study clay mineral formation by breakdown of crystalline alumino-silicates—probably the main source of clay-mineral deposits in nature.

Attempts to prepare clay minerals at temperatures closer to those found in soils have not so far been successful. X-ray and d.t.a. examination of silica–alumina gel samples boiled for a month at ordinary pressure show some changes from the unboiled material, but no well-crystallized clay minerals. For comparison, experiments using much more dilute solutions such as were used by Hénin (e.g., Hénin and Robichet, *Clay Minerals Bulletin* **2**, 110 (1954)), will be tried. (J. H. Rayner.)

SPECTROCHEMISTRY

Further work has been done on the study of trace-element distribution in Lower Lias shales, the parent materials of the teart soils of Somerset. A point of particular interest is the apparent rarity of this trouble on soils derived from similar bituminous shales. This raises the question as to whether the high concentrations of molybdenum which give rise to teart are in fact very rare or whether it is due to an unusual combination of predisposing factors of which a high level of soil molybdenum is only one.

Similar trouble due to molybdenum/copper unbalance has been reported from New Zealand, California, Eire and elsewhere, but in none of these cases has it been shown to be due to high concentrations of molybdenum in the parent rock. In this connection it has been found that the relatively small amount of copper in the Lias shales (<100 p.p.m.) is much more firmly bound than is the molybdenum. Prolonged leaching of the shale with water was found to remove about half of the molybdenum. Treatment with an HF/HCl mixture removed most of it, leaving only a small residue attributable to the pyrite incorporated in the shale. These treatments removed very little of the copper and suggest that it is mostly organically bound, since little occurred in the pyrite.

When such a material, containing also calcium carbonate, is subjected to soil-forming processes, it is to be expected that most of the molybdenum will become soluble and be slowly removed from the soil at a rate dependent upon the drainage conditions. The copper, being more firmly bound, is largely unavailable, and therefore unable to counteract the toxic effects of the molybdenum.

As previously reported, a relationship has been found between the amounts of molybdenum, vanadium, copper and nickel in these shales, which suggests a common cause for their accumulation, such as adsorption by organic matter. It is well known that vanadium is accumulated by certain marine creatures and that it is sometimes heavily concentrated in oils; but the other elements mentioned are not known to be appreciably accumulated in this manner, which suggests that this mechanism is probably not a major factor in the Lias shales.

It seems likely that such high concentrations of molybdenum are not necessarily rare, but in order to produce teart soil several other factors are involved, e.g., presence of calcium carbonate, relatively low or unavailable copper and imperfect drainage. (H. H. Le Riche.)

SOIL CHEMISTRY

It was reported last year (*Rep. Rothamst. exp. Sta. for* **1955**, 65) that the solution of ferric oxide by aqueous leaf extracts appears to be largely the result of the joint action of carboxylic acids and reducing compounds. It now seems that the reducing compounds involved are polyphenols. After having been stored for some time, a rimu leaf sample was found to have lost the greater part of its ability to dissolve ferric oxide. A comparison of this material with an active sample has been undertaken, as this seems to be a promising approach to the problem of classifying the constituents responsible for the action of the leaf extracts.

Qualitative tests with triphenyltetrazolium chloride showed that a water extract of the active leaf had a much greater reducing capacity than a similar extract prepared from the inactive sample, and the difference could not be ascribed to differences in the reducing sugar contents of the two samples. Although the satisfactory use of triphenyltetrazolium chloride has been reported for the determination of reducing sugars, it has not been possible to use this reagent for a quantitative determination of reducing capacities of aqueous leaf extracts. However, by means of hypoiodite oxidation before and after clearing with lead acetate, it was found that the non-sugar-reducing capacity of the active rimu was some three times greater than that of the inactive material. The greater extent of oxygen absorption by an extract of the active leaves under alkaline conditions was an indication that the reducing compounds responsible for the difference are polyphenols.

Polyphenols have been separated by precipitation with chloroform from methanol extracts of the leaves after prior extraction of the latter with light petroleum ether. Ultra-violet absorption spectroscopy of the chloroform precipitates obtained from the two rimu samples indicates that the polyphenol content of the active leaf, in agreement with the reducing capacity determination, is approximately three times as large as that of the inactive rimu.

Some difficulty has been experienced in securing complete removal of carboxylic acids from the chloroform precipitated polyphenols, but nevertheless it has been found that for the active rimu, while neither the polyphenols nor the acids alone have very much action on ferric oxide, the two together give a solution/reduction effect that approaches that of the untreated extract in magnitude. Further, addition of polyphenols from the active rimu to a water extract of the inactive leaves leads to a very considerable increase in the extent of solution of ferric oxide, the increase being greater than would be expected if the effect were purely additive.

In view of the history of the inactive rimu it seems probable that its deterioration resulted from an insufficiently rigorous initial drying, so that enzymic oxidation of the polyphenols took place, probably following the absorption of atmospheric moisture. The effects of such enzymic action on the properties of leaf extracts is therefore being studied.

It seems probable that the acid constituent of aspen-leaf extracts, to which reference was made in connection with the deflocculation of kaolinite (*Rep. Rothamst. exp. Sta. for* **1955**, 65), is a polyphenol oxidation product. While both this substance and the polysaccharide constituent alone cause deflocculation of kaolinite, at moderate concentrations the two together give appreciable reflocculation of the clay. (C. Bloomfield.)