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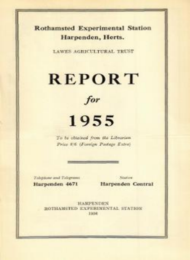
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REPORT
for
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Pedology Department

A. Muir

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PEDOLOGY DEPARTMENT

A. MUIR

A. Muir represented the Agricultural Research Council on the British Agricultural Delegation to the U.S.S.R. Dr. D. H. Ya'alon completed his clay mineralogical studies on soils formed over clay-with-flints and has returned to Israel. Mr. C. Ollier, a Colonial Office student in training with the Soil Survey, has collaborated in this particular study. Mr. D. H. Khan of Dacca University is spending two years studying soil genesis. Dr. J. H. Rayner has been appointed to the staff to work on the synthesis of clay minerals.

SOIL MINERALOGY

During the year mineralogical investigations of soils from different regions of Africa have been completed, and reports on soils from the following countries have been prepared for publication : (1) Nyasaland, (2) Kenya, (3) Tanganyika.

(1) *Nyasaland*

Mineralogical examination of the sand and clay fractions of a series of soils and parent materials from the Lower Shire Valley has confirmed the field evidence and shows that the bulk of the material forming the valley slopes is of a localized nature. In conjunction with geomorphological data it seems possible to ascribe the origin of much of the superficial deposits to a kind of pedisedimentation brought about in part by the various earth-movements associated with the Rift Valley. (A. Muir and I. Stephen.)

(2) *Kenya*

This investigation arose out of the problem of uneven growth of crops on several estates in the Athi Plain region of Kenya. Over hundreds of square miles occur roughly circular " islands " of 20–50 yards diameter at 50–100-yard intervals, on which crop growth is very much superior to that in the surrounding area. The phenomenon seems best described as an example of what has generally come to be known by the Australian word *gilgai*, and the pattern seems to be that of the normal or round gilgai.

A study of the mineralogy of the underlying rocks (soda-rich intermediate lavas including trachytes and phonolites) and the sand fractions of the soils shows that all the profiles studied have a common origin, and appear to result from the combined influence of climate and relief on the alkali-rich rocks. Under such conditions the rock weathers directly to montmorillonite, the high swelling properties of which appear to be a dominant factor in the production of gilgai relief. (A. Muir and I. Stephen.)

(3) *Tanganyika*

A series of soils from two areas (Kongwa in the Central Province and Nachingwea in the Southern Province) have been investigated. The parent rock, while in general an amphibolite, is sufficiently varied locally to cause differences in the appearance of some of the shallower soils. In the main, however, since the soils are formed on a mantle or pedisediment, there has been much mixing of the weathered products, and it is only by an examination of the resistant heavy minerals that an indication of the probable source rocks is obtained.

The clays of the red soils are characterized by a predominance of kaolinite, whereas the more poorly drained grey soils have a disordered kaolin. Other components of the clays are iron oxides and minor amounts of illite. The pallid soils contain moderate amounts of montmorillonite in the weathering zone, some of which persists into the soil. The mbuga and black soils contain montmorillonite or illite with subordinate kaolin. (A. Muir and I. Stephen.)

Rock Weathering

A study of rock weathering and soil formation on igneous soils in Shropshire has been commenced. The parent rocks are of varied composition and include rhyolite, augite-andesite, dolerite and picrite. (I. Stephen.)

Micropedology

During the year research on improving methods of preparing thin sections of soils for optical study has been carried out. The sectioning of soils in this department was started using kollolith as the impregnating medium, but temporary failure of the supply led to the search for other suitable media. Satisfactory results have been obtained using " Ceemar Embedding Resin ", enabling sections of 20–30μ in thickness to be prepared, but preparation of sections of soils of very high clay content has proved difficult, and further experimentation is proceeding on this problem.

Although much of the work so far has been concerned with perfecting techniques, a series of sections of red soils (terra rossa, rotlehm, etc.) from Cyprus have been prepared for future study, and a start has been made in sectioning local soils developed on chalk, clay-with-flints, etc. In the soils developed on clay-with-flints and allied deposits, preliminary studies of the sections show a marked micromorphological change in the profiles, the dense " braunlehm-like " character of the lower horizons being replaced in the surface layers by a fabric characterised by the flocculated structure elements of a braunerde, this fabric alteration apparently being related to weathering under present-day conditions. (I. Stephen and D. A. Osmond.)

CLAY MINERALOGY

Soil Morphology and Mineralogy

No work has been done on this during the year. A microfocus X-ray tube is being constructed with which it is hoped X-ray examination (radiographic and diffraction) of soil sections may be made in the manner of petrofabric analysis. (G. Brown and G. C. Dibley.)

Dickite

The mineralogical work on dickite is now completed and has been prepared for publication. (G. Brown.)

Pyrite

X-ray identifications of pyrite and pyrite pseudomorphs have been made for Dr. F. Smithson. The pseudomorphs were shown to be mixtures of goethite and haematite, the proportions of these influencing the colour. The very dark brown pseudomorphs contained more haematite than the light brown. A single pseudomorph was examined by single crystal methods and the goethite and haematite was shown to be polycrystalline, with no preferred orientation with respect to the pyrite. This work has been written up and will be published in Dr. Smithson's paper. (G. Brown.)

As a corollary to this work a number of pyrite pseudomorphs of different habit and from different environments are being investigated by single-crystal methods to find the effect of habit and environment on the oxidation. (G. Brown and G. C. Dibley.)

Collophane

Examination of the insoluble sand fraction of the Upper and Middle Chalk has revealed the presence of collophane apparently derived from fish. The properties of this occurrence have been investigated by optical and X-ray methods, and this work has been accepted for publication by the *Mineralogical Magazine*. (G. Brown and C. D. Ollier.)

Clay-with-flints

The phase of the work mentioned in last year's annual report has been completed. Mineralogical examinations of clay, silt and sand fractions and detailed mechanical analyses have been carried out for five complete profiles. The results show that four of the profiles are polygenetic. Changes in particle-size distribution curves are accompanied by mineralogical changes. The chief pedological change in the clay minerals appears to be an increase in the proportion of dioctahedral vermiculite at the expense of dioctahedral mica in the surface horizons. (G. Brown and D. H. Ya'alon.)

Quantitative analysis

A method for the estimation of free iron oxides in clays by X-ray methods is being investigated. The basis of the method is the formation of haematite from iron oxides on heating to moderate temperatures in air. The proportion of haematite can then be estimated by an internal standard method. With mechanical mixtures of iron oxides and clays heating gives sharp haematite reflections, and for concentrations in the range 5–10 per cent, haematite can be estimated with an accuracy of ±10 per cent in the presence of mica, kaolinite or montmorillonite minerals by comparing peak intensities. However, when the iron oxide is precipitated on the clay, heating gives broad haematite reflections, and estimations based on peak intensities give low results. An attempt to overcome this difficulty by using integrated intensities is being made. (G. Brown and R. Farrow.)

Chalk residue

The insoluble clay fraction of the Upper and Middle Chalk samples investigated in connection with collophane have been examined.

The bulk of the clay consists of a mixture of a mica and a montmorillonite mineral. The mica seems to be concentrated in the coarser clay. (G. Grown and R. Farrow.)

Techniques

A simple vapour-pressure method of adding glycerol to clay specimens has been tested and adopted for routine identifications. An extrusion device for banded powder specimens using hypodermic needles has been developed. A 9·0-cm. powder camera has been modified so that it can record spacings up to 100 Å. (G. Brown, G. C. Dibley and R. Farrow.)

Anglesey

The X-ray patterns of a number of soil clays taken in previous years have been interpreted. The results will be included in the memoir to the Anglesey sheet of the Soil Survey. (G. Brown.)

Shropshire

X-ray diffraction has been used to identify the finely crystalline materials encountered in the rock-weathering study which is being carried out by I. Stephen. A mineral which gives excellent fibre patterns, fibre period about 5·3 Å., has been identified as a mineral of the montmorillonite group, and structural work on this and closely related minerals is being carried out. (G. Brown.)

Miscellaneous

In addition to materials already mentioned, soil clays from Aden, Cyprus, Kenya, Tanganyika, Nyasaland, Israel and St. Helena have been examined. In England soils and clays from Lincolnshire, Buckinghamshire, Hertfordshire and Kent have been examined. (G. Brown and R. Farrow.)

The sorption of water by clay minerals

The studies on the crystalline swelling of montmorillonite minerals have been continued. The influence of different monovalent cations and composition of the substrate on the amount of adsorbed water required to give different sheet separations has been investigated. The chief obstacle to accurate evaluation of the internally held water is the correction for that held externally, but this has now been satisfactorily overcome by the use of lithium-treated montmorillonites (see earlier Reports). The very slow approach to equilibrium of these systems has meant that comparatively few results could be obtained on one apparatus, but during the year a multiple sorption apparatus incorporating six quartz spiral balances and a manifold to which six detachable X-ray samples could be sealed has been constructed and has greatly improved matters. A paper describing the work carried out during the last four years is in preparation.

The calorimeter described in last year's Report has been used to measure the heat capacity of sodium montmorillonite–water systems as a function of the water content and the temperature. Up to 20 per cent water the heat capacity at room temperature varies roughly linearly, but is slightly greater than would be expected if the heat capacities of the dehydrated mineral and liquid water were additive. Superimposed on this relation were significant fluctuations which appeared to be correlated with the crystalline swelling of the mineral. At lower temperatures the calorimeter behaved less satisfactorily, due to lead conductance, and it became necessary to modify the design. A new calorimeter of greatly increased precision has been designed for low-temperature work and for the further investigation of the small fluctuations already mentioned. A large part of the construction has been completed. (R. Greene-Kelly.)

Microcalorimeter

As foreshadowed in last year's Report, a microcalorimeter has been designed and constructed for the measurement of small heat effects occurring in clay systems. Since many heat changes occur over comparatively long periods, it has been necessary to aim at very constant conditions in and around the calorimeter. Since large clay mineral samples involve lengthy preparation and are difficult to disperse in heats-of-immersion studies, it has been necessary to develop sensitive methods of temperature measurement. The use of a thermistor as a temperature-sensitive element was investigated in detail and found to be satisfactory if its power sensitivity was arranged to be low. A Wheatstone-bridge circuit was used to measure the resistance of the thermistor, particular attention being paid to the elimination of parasitic potentials. The out-of-balance current was measured, using a linear galvanometer, this giving a sensitivity of about $3{\cdot}0 \times 10^{-5}$° C./mm. Alternatively a d.c. amplifier and recorder could be used. The thermistor was directly calibrated in joules with an electrical heater in the calorimeter at the time of the experiment. The calorimeter itself was a 300-ml. vacuum flask which was closed by a Perspex lid through which the stirrer, sample breaker and leads passed, and the whole was enclosed in a brass box which was itself immersed in a double thermostat. The evacuated samples, for heats-of-immersion studies, were enclosed in 2-cm.-diameter sealed glass bulbs and were broken under the selected liquid by screwing down a rod from outside the calorimeter. The results have shown that the precision of measurement of heat of immersion depended on the reproducibility of the blank heat of bulb breakage, which at present may vary by as much as 0·1 joule. Recently suitable bulbs have been obtained (from a glass-works), and in view of their reproducible size and wall thickness they are expected to be more satisfactory. The calorimeter has been tested by measurement of heats of solution of potassium chloride, and has been used to measure the heats of wetting of kaolinite and montmorillonite in water and salt solutions. Kaolinite evacuated at room temperature showed a heat of wetting in water which is roughly proportional to its surface area, 0·3 joule being evolved for every square metre wetted. Sodium montmorillonite showed a larger heat of wetting in water which was accompanied by slow heat evolution for several hours. If the expansion was limited to crystalline swelling, the thermal drift was found to disappear, and it therefore seemed that it was due to continued expansion and eventual breakdown of the clay crystals. A detailed investigation of the heat effects accompanying swelling phenomena in clays is in progress, in conjunction with X-ray and negative-ion adsorption measurements. It is also hoped to utilize the calorimeter in the study of heats of solution of minerals. (R. C. Gallavan and R. Greene-Kelly.)

Organic complexes of montmorillonite

The structures of montmorillonite complexes and saturated organic compounds have been investigated. The orientations of ring compounds in saturated and aromatic complexes have been found to be similar (see last year's Report). The influence of di-substitution on any one ring atom in piperidyl rings has shown that there must be appreciable distortion of the tetrahedral bond angles in a similar way to that reported by Hassel for the chloro*cyclo*hexanes. Chain complexes have been found to show a puzzling variation in spacing with chain length, the most likely explanation being that it is due to C–C single-bond oscillations. The consequence of assuming this effect has led to the generalization that C–H—O (silicate) distances are always reduced from normal Van der Waal's distances in montmorillonite complexes.

The crystalline swelling of montmorillonite saturated with organic cations is shown to occur in certain organic liquids. The resultant interlamellar separation is determined entirely by either one or other of the molecules and not by combinations of them. This swelling clearly would interfere with the use of organic cation montmorillonites as molecular sieves, as has been suggested by Barrer and co-workers.

The competition for exchange sites on montmorillonite between ethylamine and inorganic cations has also been investigated. Whilst ethylamine ions are strongly sorbed in the absence of external concentrations of inorganic cations, the presence of a comparable inorganic cation concentration can reduce the sorption considerably. If ethylamine montmorillonite is washed with dilute sodium choride or even calcium bicarbonate solutions the nitrogen is rapidly and quantitatively removed. It seems therefore that such low-molecular-weight amines derived from plant and animal remains could not be retained for long in clay soils. This is in agreement with the " normal " swelling behaviour of montmorillonites found in soils. (R. Greene-Kelly.)

A thermal balance for clay mineral work

The d.t.a. method does not give quantitative data on water loss in clay minerals, as it measures temperature differences. It is sensitive to packing, conductivity and thermal reactions involving the generation or absorption of heat. The role of a thermal balance is to provide information on weight loss in minerals under the conditions existing in the d.t.a. apparatus, and it must have a comparable sensitivity. In addition, the sample size should be as small as possible, and in practice 100-mg. samples are used.

The balance consists of a silica coil spring suspended in a glass tube, which is separated from the furnace by two water-cooled collars with sliding vanes to shield the spring from radiation from the furnace. The sample is placed in a platinum bucket 1 cm. in diameter and 4 mm. in depth, which is attached to the spring by a thin platinum wire. The furnace is controlled by a chromel–alumel thermocouple suspended in the furnace space by the bucket, and attached to a Kent recorder which operates a powered variac.

Movement of the spring is followed manually with a cathetometer which can be read to 0·02 mm. and represents a change in weight of 0·05 mg. or 0·5 per cent of a 10 per cent weight loss on a 100-mg. sample. When working for the greatest accuracy, as in the 0–300° C. region on montmorillonite, the cathetometer is set at successive positions 0·010 cm. apart and the time of each reading recorded and correlated with the temperature. As the sample is so small, there are no packing effects, and the temperature in the sample is uniform.

The data of weight loss with time or temperature are converted to rate of weight loss with temperature to compare with d.t.a. curves. This operation has been programmed by J. Gower in the Statistics Department and is performed on the electronic calculator. Using different cams on the Kent recorder, the rate of heating can be varied from 20° per minute to 5° per minute, and when manually controlled the rate can be maintained at 2° per minute, so that intermediate stages between d.t.a. curves at 10° per minute and equilibrium-weight-loss curves can be obtained. Accuracy of setting and reading the cathetometer increases when the rate of heating is decreased.

Curves have been made for several kaolinites and dickite, halloysite, vermiculite and various montmorillonite samples. Work on clays from Broadbalk shows that the method gives a reliable value for kaolin content and is unaffected by particle size and organic matter in the soil.

The limiting factors in the accuracy of the method include the furnace-control system, the accuracy of setting the cathetometer and oscillation in the spring due to radiation effects in the furnace. Further work will be concerned with these points and in making the balance self-recording. (R. Greene-Kelly and A. H. Weir.)

Soil clays

The detailed investigation of the kaolinite–illite clays separated from the C horizon of the Broadbalk soils on clay-with-flint material has been continued. Confirmation of the estimation of kaolinite by differential thermal analysis has been obtained by the use of the new quartz-spiral thermal balance developed in conjunction with A. Weir. The difficulty of correcting the differential thermal curves for the presence of traces of organic matter is to a large extent avoided in the thermal balance, since the thermal effects detected by d.t.a. obtained from the oxidation of traces of carbon tend to magnify out of all proportion the amounts causing the effect. Simple X-ray comparison methods have been applied to the different size fractions, and whilst for the coarser fractions the amounts of kaolinite determined compared favourably with thermal methods, the finer fractions, which showed appreciable line broadening, gave useless results, at least when peak heights are compared. The possiblity that peak areas may provide a better method of comparison is being investigated, but clearly there is much to be said for thermal methods in such cases, for they are not so dependent on particle-size variation.

The study of the surface properties of the Broadbalk clays as a function of particle size has shown that the adsorption of water and polar organic compounds from the vapour phase at low pressures is more a function of the cation-exchange capacity than the extent of the external surface. This suggests that crystalline swelling had occurred. It was estimated that the internal area was of the order of 300 sq. m./g., and allowing for the amount of non-expanding minerals, this showed that about one in three sheets expanded in this soil illite. This was not greatly effected by particle size. Thermal and ion-exchange studies are also in progress. (R. Greene-Kelly.)

SPECTROGRAPHY

Methods

The use of the Lundegårdh flame method for the determination of exchangeable bases in soils has now been discontinued. A considerable saving of time has been achieved by the use of a flame photometer for the determination of potassium and sodium and of the versenate method for calcium. Magnesium is determined spectrographically by the porous-cup method.

A spark spectrogaphic method for aluminium

In connection with Dr. Rayner's work on mineral synthesis, a solution spark method has been worked out for the medium spectrograph. The method is required to be rapid, to work with 0·1 g. of sample, and in the first instance only for determinations of Si, Al and Mg. The spectrographic technique is tedious when a single element is required, and only becomes competitive with colorimetric methods when several elements are to be determined.

The sample is taken into solution by fusion with sodium hydroxide or digestion with hydrofluoric and sulphuric acids. A nickel solution is used at 1,000 p.p.m. as internal standard and the line Ni 2981 Å. read against Al 3092 and 3082 Å. The plate is callibrated, using an iron arc and step sector, and single-step burns are used with four replications of each solution. Using Kodak B.10 plates, the greatest linearity of calibration is found when a density scale of $\frac{i_0}{i} - 0{\cdot}9$ is used. This gives a straight line between 1·1 and $\bar{1}{\cdot}7$. On the advice of Mr. Ballanger, National Agricultural Advisory Service, Bristol, all the cup electrodes are now heated to 500° C. before use to prevent boiling in the cups. This method is susceptible to changes in the sodium concentration of the solution. An accuracy of 3–4 per cent is obtainable. (A. H. Weir and J. Beckett.)

Geochemistry of lias shales

Investigations into the molybdenum content of the calcareous shales of the Lower Lias have shown that, where the whole extent of the formation has been examined, high concentrations are confined to the lower zones. The shales with high concentrations always contain between about 10 and 50 per cent calcium carbonate, and a correlation has been found between the content of molybdenum, nickel, copper and vanadium, on the one hand, and of organic carbon in excess of 2 per cent, on the other. When the organic carbon content is below about 2 per cent the shales contain fairly constant levels of these elements : Mo $<$ 5 p.p.m., Ni and Cu about 50 p.p.m. and V about 150 p.p.m. These levels increase with organic carbon in excess of 2 per cent in such a way as to suggest that their content is proportional to the shale's present or past content of some organic constituent which does not normally occur in the basic 2 per cent. The amount of cobalt appears to be independent and is relatively constant at between 10 and 30 p.p.m. (H. H. Le Riche.)

During the year, analyses have been carried out for the Botany Department in connection with studies of the uptake of iron, vanadium and molybdenum in water-culture experiments. Trace-element analyses have also been done for the Grassland Research Station, Hurley, and for the Botany Department of the University of Southampton on crops where failure was suspected of being associated with trace-element deficiencies. (H. H. Le Riche.)

Trace elements in wheat shoots

Broadbalk was sampled in the last week of May 1954 for a small pilot experiment on the effect of fertilizer treatment on the trace-element content of wheat shoots. Plots Nos. 2, 3, 5, 8, 10, 13, 17 and 18 were selected as likely to show the greatest differences, and the top two-fifths of the field were sampled for shoots and soil (0–8 inches).

The analyses were done spectrographically, using the method of Farmer for copper, manganese and iron and the concentration method for the traces, cobalt, vanadium and molybdenum. Results on the total soils showed very small variation from plot to plot in the elements concerned. Iron was present at 5 per cent, copper 10 p.p.m. and manganese 0·1 per cent, cobalt 25 p.p.m., vanadium 60 p.p.m., molybdenum < 10 p.p.m. The pH value of the soils is approximately 7·5 for all the plots except No. 8, where continued application of ammonium sulphate had resulted in pH values down to 5·5 in the lower part of section 1 of the plot. This in the bulk sample from the plot showed in the molybdenum uptake for the shoots, which was as low as 0·09 p.p.m.

Iron and manganese uptake in the shoots showed a ratio varying from 1·3 to 0·8, with the amount of iron varying from 100 p.p.m. in plots 3 and 18 to 60 p.p.m. in plots 2 and 17. Molybdenum shows a minimum of 0·09 p.p.m. in plot 8 and a maximum of 0·4 p.p.m. in plot 18. Cobalt, vanadium and copper show very little variation from plot to plot, the plants containing 6 p.p.m. copper, 0·05 p.p.m. cobalt and 0·15 p.p.m. vanadium.

There is a slight tendency for the amount (in p.p.m.) of the elements to increase in the plots with a low yield and a low weight per shoot, which leads to difficulty in the presentation of data. The variations shown in the elements between plots are not very large, and there is no deficiency in the soil. In plot 3, which has had no treatment since 1839, 30 γ of Mn and Fe, 2 γ of Cu, 0·08 γ of Mo, 0·05 γ V and 0·03 γ Co are removed per shoot from the soil reservoir, and no difference is found in the total trace-element contents of the soil from this plot compared with the others.

Plots 12 and 13 on Park Grass were sampled for Cocksfoot (*Dactylis glomerata*) in June 1955 just before the first cut when the plants were in flower. Whole plants were cut an inch above the ground and the samples divided and analysed in three parts, the flower, the woody stems and non-flowering stems. Plot 12 had no treatment and has a pH of 5·2 (1935). The unlimed part of plot 13 had alternate dung and guano and a pH of 4·6, and the limed part a pH of 6·4. The plots were sampled in the fourth year after liming.

The opportunity was taken to try a composite scheme of analysis, 20 g. of dried material were wet-ashed, made up to 200 ml. and two small aliquots taken, one for sodium and potassium on the flame photometer and calcium by Lundegårdh technique, and the other for porous-cup determinations on phosphorus, manganese, magnesium, iron, copper and zinc; the remainder was concentrated for trace elements in the normal way.

Calcium in non-flowering shoots showed very little variation between plots, 0·34 per cent for plot 12, 0·31 per cent for unlimed plot 13, and 0·36 per cent for limed 13; for the stems and flowers the results were 0·15–0·2 per cent. Copper uptake followed the pH of the plots, and was the only investigated element to do so; unlimed 13 contained 6·5–70 p.p.m., 12, 4·5–6·0 p.p.m. and limed 13, 3·5–5·0 p.p.m. Molybdenum occurred at 0·05–0·09 p.p.m. in plot 12 and increased to 0·15–0·25 p.p.m. in unlimed 13, and 0·3–0·4 p.p.m. in limed 13. Vanadium is lowest in the latter, 0·04–0·08 p.p.m. and highest in plot 12, 0·06–2·0 p.p.m. Cobalt is very low in all three: unlimed 13, 0·07–0·18 p.p.m., plot 12, 0·04–0·08 p.p.m. and limed 13, 0·03–0·07 p.p.m. The figures quoted for molybdenum, vanadium and cobalt on plot 12 are very low for grasses, and so are the vanadium and cobalt figures on the limed half of plot 13. (A. H. Weir and J. Beckett.)

SOIL CHEMISTRY

A study of leaf leachates

Further work on the properties of leaf extracts has provided additional evidence for the presence of substances that inhibit the solution/reduction of hydrous ferric oxide. This has been demonstrated by comparing the extent of solution of ferric oxide caused by an untreated extract, a dialysed extract and a mixture of the untreated and the dialysed solutions. The dialysed extract is considerably less active than the untreated material, but nevertheless its activity is appreciable. Addition of the dialysed solution to the untreated extract causes a marked decrease in the mean extent of solution/reduction.

On the basis of earlier work, it has been difficult to reconcile laboratory results with field observations on the podzolizing properties of the two New Zealand species rimu and kauri (*Rep. Rothamst. exp. Sta. for 1953*, 61). Both these species shed their bark, and water extracts of the two barks possess approximately the same moderate activity. Comparison of the properties of leaf and bark extracts with a mixture of the two reveals a considerable difference between the two species; for the kauri, the mixed leaf and bark extract has virtually the same solution capacity per unit weight of plant material as the leaf extract alone, but with rimu, in the presence of the bark extract, the extent of solution of ferric oxide is decreased to less than half its original value. It is therefore apparent that compared with kauri bark, a rimu-bark extract has a much greater inhibiting effect on the reaction.

Using ion-exchange resins in conjunction with paper chromatography, it has been shown that for several tree species a large part of the solution/reduction activity is due to the action of simple carboxylic acids and reducing agents present in the leaf extracts; the joint action of the two groups of compounds is appreciably greater than the sum of their individual effects.

Some success has been achieved in producing podzolization in columns of quartz coated with ferric oxide. In these experiments the sand columns were treated intermittently with dilute leaf extracts of a wide variety of species. In all cases considerable amounts of iron were lost from the columns. After standing for a few weeks the columns all showed clearly visible B horizons. So far as can be said at present, it seems that the formation of the B horizon is caused by drying out and consequent aeration of the upper layers of the column, but this question needs further study.

The study of the deflocculation of kaolinite suspensions by leaf extracts has been continued. It has been found that the initial dispersion caused by low concentrations of the extracts is caused by an irreversible sorption of organic compounds on the clay surfaces; the reflocculation produced at higher concentrations of leaf extract is reversible and may be counteracted by dilution. The effect of the irreversible sorption of the pH of flocculation is very marked; untreated kaolin, which is flocculated at pH values below 9, approximately, remains dispersed down to about pH 3 after treatment with a leaf extract. Both the deflocculation and flocculation stages are caused by large-molecular-weight compounds, since dialysis of the extracts has virtually no effect on the process.

While the action of kauri- and rimu-bark extracts on kaolinite seems to be due simply to the presence of polyphenols, the action of an aspen-leaf extract is much more complex. In the latter case several anionic species are present in the extract, and any one of these alone causes dispersion of the clay; one such substance that has been isolated is an acid which appears to be present in the extract as the salt of a weak base. It has been found that this compound, which is strongly sorbed on kaolinite, causes deflocculation of the clay, even when added in high concentrations; it is a comparatively major constituent of the extract, forming approximately 1 per cent of the dry leaf. Aspen-leaf extracts also contain small amounts of a polyuronide, and this, too, is a powerful deflocculating agent. The evidence suggests that other deflocculating agents are also present in aspen leaves. (C. Bloomfield.)