

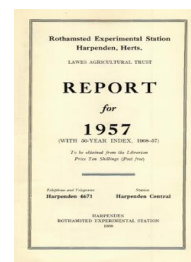
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Pedology Department

A. Muir

A. Muir (1958) *Pedology Department ; Report For 1957*, pp 65 - 75 - DOI:
<https://doi.org/10.23637/ERADOC-1-90>

PEDOLOGY DEPARTMENT

A. MUIR

D. M. C. MacEwan returned from his secondment to the University of Granada, and has since resigned to take up a post in University College, Dundee. I. Stephen returned from the University of Illinois, where he spent nine months in the Agronomy Department teaching and supervising post-graduate research work. Messrs. R. R. Storrier and J. Loveday have been carrying out laboratory studies on soils they have been mapping in conjunction with the Soil Survey. Mr. D. H. Khan of Dacca University completed his research work on soils derived from calcareous rocks for which he was awarded the degree of Ph.D. of London University. R. Greene-Kelly was selected to study in Moscow under the Royal Society Exchange Scheme.

MINERALOGY

Picrite weathering (Shropshire)

The work has been confined to a more detailed study of two of the weathering products mentioned in last year's report—fibrous montmorillonite and iddingsite. The specimen of the latter used for this study is from an Australian source.

(a) *Fibrous montmorillonite mineral*

X-ray fibre patterns of air dry material have been measured and a cell $a = 5.3 \text{ \AA}$. (fibre axis), $b = 9.2 \text{ \AA}$., $c = 15.0 \text{ \AA}$., $\beta = 96-98^\circ$ fits the observed reflexions. The indexing is based on zero, first and second layers. Reflexions of the type $00l$, $0kl$ and hkl have been unambiguously indexed in terms of the above cell. The occurrence of hkl reflexions shows without any assumptions that the material is ordered in three dimensions. More reflexions and more precise measurements will be needed to index the pattern more fully; the difficulties are that the cell is large and also the reflexions, being somewhat broad, cannot be measured precisely.

A cation-exchange capacity of 96 m.e./100 g. air-dry material has been obtained by saturating with calcium nitrate and replacing with magnesium nitrate solutions. (G. Brown.)

(b) *Iddingsite*

X-ray work on the iddingsite mentioned in last year's report has continued in order to establish the nature of the material and to find its relation to the original olivine. Because the crystals give weak diffuse spots and streaks, it was necessary to use oscillation photographs to establish the nature of the reciprocal lattice. Complete sets of oscillation photographs have been obtained about three axes, and a preliminary analysis of these shows that the crystals consist of three phases, unaltered olivine, a goethite-like material

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and a material which is probably a 2 : 1 layer lattice silicate. The olivine was identified by comparison with a rotation photograph of known olivine in the same orientation. The goethite-like material is in parallel alinement to the olivine with the 10 Å., 6 Å. and 4.7 Å. olivine axes parallel to the 10 Å., 3 Å. and 4.6 Å. axes of the goethite-like material. The layer lattice mineral is also in parallel alinement with the 10 Å., 6 Å. and 4.7 Å. olivine axes parallel to 5 Å., 9 Å. and 15 Å. axes of the layer lattice material.

The olivine phase gives sharp spots and appears to be a single crystal or a few small fragments of a single crystal, probably a relic of the original olivine. The goethite-like phase gives diffuse spots which show that this phase is in the form of a large number of very small crystals in parallel alinement. The layer lattice mineral shows broad 00 l spots and a hexagonal array of hk streaks which show that it is composed of small crystals in parallel alinement and also that there is lack of order in the stacking of the layers. In addition to these phases there are a number of spots which appear to be superlattice reflexions from the goethite-like phase, possibly due to disorder of the cations.

It appears that in the alteration of the olivine the original lattice of close-packed oxygens has not been greatly disturbed and that the changes have occurred by the movement of cations within small regions to form microcrystals of the alteration products. The parallel alinement of the major components of our iddingsite explains why it behaves optically as a single crystal. The same explanation probably holds for all iddingsites which show coherent optical properties. In certain aspects this work does not agree with the results of the recent study of iddingsite by Ming Shan-Sun (*Amer. Min.* 1957, **42**, 525-533), who states on the basis of examination of iddingsites from New Mexico that goethite is the only crystalline phase and that the other substances shown by chemical analysis are largely amorphous. (G. Brown.)

Glaucinite in Lower Greensand

Optical examination of some samples of this formation and also of associated soils in Bedfordshire and Buckinghamshire has shown that glauconite (and its alteration products) occurs only in small amounts in the fine sands examined. Dilute acid extraction, which probably decomposes only the glauconite present, showed an average of about 20 p.p.m. K, with a maximum value of about 40 p.p.m., confirming the paucity of the mineral in the sands of the materials examined. (I. Stephen and C. L. Bascomb.)

Jarosite

A pale-yellow fine-grained powder which occurs in cracks and veins in soil from Bow Brickhill has been identified by X-ray powder diffraction as jarosite, a basic potassium iron sulphate. Optical and chemical tests confirm this identification. Previously unidentified lines on X-ray patterns of clays of some soils from Romney Marsh were subsequently identified as jarosite lines, and examination of the soils showed small amounts of pale-yellow powdery material. Both the iron and sulphur are probably derived from pyrite, and the alkali from other minerals, possibly clays, by acid attack. Dilution

and leaching of such solutions could precipitate jarosite which, once precipitated, is not readily redissolved in water. This appears to be the first time that jarosite has been identified in soils, although its occurrence is not surprising. (G. Brown.)

CLAY MINERALOGY

Soil clays

Soil samples examined by X-ray methods in the past year included several from abroad—from Iraq, Borneo, Kenya and Somaliland.

The Iraq soils and some of Somaliland profiles contained appreciable quantities of palygorskite, the X-ray results in some cases being checked by electron-micrography. The Iraq soils confirm the impression that this mineral is widespread in the Middle East, having been found in the Syrian desert (Muir, *J. Soil Sci.* 1951, **2**, 169) and in soils of the Karun delta and the foothill region of South-West Persia. The relationship to rock formation (i.e., Tertiary) pointed out earlier would seem to be in part confirmed by the Somaliland soils, which are associated to a considerable extent with Eocene rocks.

Of a number of forest soils from Borneo, some were interesting in showing a moderate to high content of gibbsite in their clay fraction, particularly a peaty mountain soil on granite, the subsoil clay of which consisted largely of that mineral. The Kenya soils were the upper horizons of a profile which included parent rock of trachytic affinity and weathered material above this. The main clay minerals proved to be kaolin and mica, with some haematite. Several thin sections of the rock and its weathered counterparts have been made.

In addition to these—samples of clay balls of unknown origin containing plant remains were received from the Rhodes-Livingstone Museum, Rhodesia, and were examined for clay mineral content and other things with a view to determining their origin.

British samples examined include a number from Buckinghamshire, Hertfordshire, Worcester, Kent and Shropshire, sent in by soil surveyors. A survey of the clay minerals of clays and limestones at all levels of the geological column in England and Wales has been undertaken. The Geological Survey and Museum has supplied a number of specimens, seventeen of which have already been examined for clay mineral content. It is also hoped to examine the heavy minerals of some of these materials. (A. M. Du Feu.)

X-ray structure analysis

The programmes for crystallographic calculations using the Elliot 401 computer written in collaboration with J. C. Gower (Statistics) were described at an Institute of Physics X-Ray Analysis Group meeting (*Brit. J. appl. Phys.* **9**, 1, 1958). Work on the structure of muscovite using these programmes has for the moment been set aside, since it has been found that very similar work is already being done by E. W. Radoslovich at the Waite Institute. The programmes have proved very useful in completing two pieces of work done elsewhere and now prepared for publication—"The crystal

structure of a hydrated nickel cyanide ammonia complex", by J. H. Rayner and H. M. Powell, and "The crystal structure of sodium formaldehyde bisulphite", by J. H. Rayner. (J. H. Rayner.)

Black Jack Mine Beidellite

Work has continued on this mineral to establish it as a true end member of the montmorillonite-beidellite series and to investigate its properties fully.

Optical work. A thin section of the naturally occurring material has been made and examined with the petrological microscope. Typical lath-shaped flakes occur in small spherulites with their long axes radially arranged and the expanding *c*-axis as the other most frequently seen. When the material is converted to the sodium form without dispersion the spherulites break down into smaller units having the appearance of small closed fans of material. If these fans are treated with successively more dilute sodium chloride solutions they swell in the manner of montmorillonites beyond the limits of crystalline swelling and the laths rotate as the "fan" opens. Examples of these expanded fans have been obtained with the electron microscope.

The values of the higher of the two refractive indices determined on K, Na and Ca oriented aggregates which had been heated to 280° C. to expel interlayer water were 1.557, 1.545 and 1.525 respectively and the birefringence 0.035 in each case. X-ray examination showed that appreciable lattice penetration of the 1-bromo-naphthalene and paraffin oil mixture had taken place, giving rise to 14 Å., 14.4 Å. and 16.5 Å. basal spacings. A controlled expansion was tried using a glycerol, water and potassium mercuric iodide mixture. However, the oils changed refractive index rapidly in air and, as the material reached equilibrium slowly in each oil, the method was difficult to use.

X-ray work. The small fans of material seen in the light microscope are too small to be used directly in the X-ray cameras, and oriented aggregates have to be used instead. If a small amount of water is added to the sodium beidellite and the resulting gel dried on to a glass surface a high degree of orientation is achieved without complete dispersion of the fans. The resulting X-ray pattern, the best results are given with the single-crystal camera, shows discrete *hkl* reflexions instead of the usual montmorillonite bands. Assuming an orthorhombic unit cell for the ethylene glycol saturated Na-flake, the geometry of these reflexions has been calculated and shown to fit the pictures obtained. If the aggregates are made from better-dispersed material the reflexions merge and become band-like. It is not yet clear whether powder patterns from the naturally occurring undispersed clay show a symmetry other than orthorhombic.

The new diffractometer was used with an oriented aggregate of Na-beidellite expanded with ethylene glycol. The relative intensities of twenty 00 l reflexions with a basal spacing of 16.9 Å. were measured. Previously only fourteen orders had been obtained using 9-cm. powder cameras. Structure factors were calculated for an assumed structure and Fourier syntheses made on the computer using a programme by J. C. Gower. The refined structure had an "R factor" of about 16 per cent and showed that the distribution

of ethylene glycol, as seen in a one-dimensional projection, is more likely to be in a flat-topped peak for each layer of molecules than in two equal well-defined peaks for each layer, as suggested by Brindley in his work on alleverdite. It is hoped to repeat this work using molybdenum radiation to give greater resolution.

Electron microscopy of clay minerals.

Work has continued with H. L. Nixon on the beidellite and other problems of clay mineral microscopy. The coming of the Siemens microscope has shown that with a machine capable of high resolution and contrast, the greatest clarity of detail even for the 10 Å. or 20 Å. flakes of montmorillonite is given with unshadowed mounts.

A new method of mounting has been used in which a minute amount of Na-beidellite was placed on a collodion grid and sprayed with water to cause partial dispersion. This has resulted in a characteristic and quantitative sample of the whole being obtained, and shows the existence of an amount of very small particle-size material together with the fans of large laths previously described. The nature of this small material is not yet known, but will be investigated.

A new technique has been worked out to measure particle thicknesses of 10 Å. or 20 Å. Montmorillonite flake edges of 60–200 Å. in height are photographed before and after shadowing. The step height, which is great enough to be measured accurately at a magnification of 35,000, is obtained from the shadowed picture, and the unshadowed one photometered to relate the density of the flake whose shadow has been measured to that of the smallest density change obtainable. Results on the few photographs of beidellite measured show that flakes 10 Å. thick are found and are quite visible but seem to be produced in quantity only with very careful dispersion.

PHYSICAL CHEMISTRY OF SOIL MINERALS

The mechanism of aggregate formation in soils

Last year's work has been continued. One case of the theoretical relation between water-vapour interfacial area and the suction has been verified. Further examples are under investigation.

The calorimetric technique has been applied to the study of the behaviour of adsorbed liquid films at very high relative pressure, with the result that apparent discontinuities in film formation have been detected. These are being studied in greater detail.

An investigation has been made of the micro-structure of montmorillonite and kaolin powders by measuring the low-temperature nitrogen-adsorption isotherms on samples of different water contents. With montmorillonite the surface area is very sensitive to small additions of water, indicating that the exposed surface consists predominantly of cracks of the order of 3–10 Å. in width. These would be expected if irregular silicate sheets of 10 Å. thickness were laid one over another. Monolayer interlamellar expansion leads to no sudden change in structure either permanent or temporary, indicating that the aggregates have considerable rigidity at low

contents. Kaolinite showed, as was expected, much less dependence of surface area on water content.

The effect on the surface areas of wetting and drying sodium saturated powders of clay minerals has been studied. Montmorillonite forms coherent aggregates of very low surface area with cracking predominantly parallel to the (001) planes, the bigger cracks being easily visible under a microscope. There is no evidence that such a dried aggregate has a unique surface area dependent only on "particle size"; the surface area increases rapidly on disturbance, due probably to further extension of cracks and exposure of slits formed by imperfect packing of the silicate sheets. By contrast, dried illitic and kaolinitic aggregates have surface areas independent of previous treatment suggesting that the crystallites are comparatively loosely packed together. Further study on soil-derived materials of different particle sizes is planned.

Heats of wetting of clay minerals

A detailed study is being completed of the heats of wetting of clay and related minerals. The importance of the kind of exchange cation has been emphasized in earlier work, and in last year's Report the work of swelling was mentioned as another important factor. Further study has revealed that the charge density is also of importance. Of particular interest is the observation that when the relation for non-expanding minerals between the heat of wetting per unit area and the charge density is extrapolated to zero charge density, the heat per unit area is found to be equal to that of samples of quartz examined in the department. This suggests that these quartz samples are of low charge density whilst quartz samples mentioned in the literature as giving higher heats may well have higher charge densities.

Water adsorption by clay minerals

Studies on the water adsorption by members of the montmorillonite group have been continued. Preliminary correlation of the stability of the water layers with charge density has been made and has further emphasized the importance of this quantity in determining clay properties. Dehydration isobars of montmorillonite have been measured and compared with isotherms and d.t.a. curves, and this has now enabled a detailed interpretation of the latter to be made. Calorimetric studies are also in progress both of heats of adsorption of water and heats of solution of clay minerals (see last year's Report). (R. Greene-Kelly and R. G. Gallavan.)

Laboratory synthesis of clay minerals

The apparatus for the high-pressure synthesis of clay minerals has now all been received and is being set up in a high-pressure cubicle, giving the operator protection in the case of the sudden escape of steam. It should now be possible to extend the work on clay mineral synthesis begun last year using apparatus at the Imperial Chemical Industries Plastics Division at Welwyn Garden City. (J. H. Rayner.)

APPARATUS

X-ray diffractometer

During the year a counter diffractometer has been installed. The new equipment comprises a Newton Victor Raymax 60 demountable X-ray generator, a Hilger Y.115 X-ray diffractometer and associated counting equipment supplied by Labgear. A demountable X-ray set was chosen to give maximum flexibility in choice of target materials.

Having chosen a demountable tube, it was necessary to use a monitoring system rather than attempt to stabilize the X-ray output, as slight changes in operating conditions can give rise to variations in output. We therefore use two counting channels, one to measure the diffracted X-ray intensity, while the other continuously measures the primary X-ray beam. The relative intensities at different settings are then given by the ratios of counts in test and monitor channels. The counting equipment is two Geiger tubes followed by two quench probes, feeding either the Labgear triple-gate ratio counter or two ratemeters which are followed by a chart recorder adapted for ratio recording. The chart recorder is used for routine work, but where more detail is required the line profiles are plotted point by point using the ratio counter.

The diffractometer originally operated with a two-slit system to define the effective source and the divergence of the beam. Using a vertical 6×0.6 -mm. focus in the X-ray tube in place of the first slit, we have been able to obtain high resolution with high intensities without using Soller slits. For example, in chart recording we are able to resolve the $\alpha_1\alpha_2$ doublet at $2\theta = 35 - 40^\circ$ at a scan speed of $\frac{1}{4}^\circ 2\theta$ per minute. This performance is similar to that given by commercial units with Soller slit systems. We have also made and fitted a separate angle marker pen on the margin of the chart to the chart recorder which correlates chart translation counter-arm rotation. In this way the whole chart width is available for recording. (G. Brown and R. Farrow.)

Preliminary work on the adjustment and testing of the diffractometer indicated the necessity for a pulse generator, and a suitable instrument has been developed. It is capable of giving rectangular pulses of positive and negative polarity, and of variable amplitude and duration, at six switched pulse rates, ranging from 5–5,000 p.p.s. With this instrument it is now a simple procedure rapidly to check the operation of the count-rate indicating and scaling circuits of the diffractometer. (R. Farrow.)

Micro-focus X-ray tube, etc.

The micro-focus X-ray tube described in the Annual Report for 1956 has been in operation for most of the year, having been used in conjunction with a single crystal camera, an ordinary 9-cm. powder camera and two new cameras made during the year. These new cameras are a low-angle camera and a focusing camera of the Bragg-Brentano type. The low-angle camera has been designed to be adjustable in all directions with the minimum of trouble; variations in slit width, and distances between slits and specimen can be set up with ease. When used with the micro-focus set only two slit systems are necessary, though for special applications a third slit

can be used. All slits can be adjusted for width and independently for position. It has been found that the process of positioning the whole camera in relationship to the X-ray beam is not as difficult as was expected, providing the right sequence is followed; the same thing is true of the adjustment of the various parts of the camera itself. Spacings in the order of 500–600 Å. can be obtained with a specimen-to-film distance of up to 25 cm.

The focusing camera is of a conventional design, using a flat specimen and giving for any one setting only one side of the X-ray pattern. Variations in length of exposure and slit width enable varying degrees of resolution to be obtained, though there are limitations in the range over which the best resolution can be got; this is a normal feature of this type of camera and one of its main disadvantages, a disadvantage which is, however, offset by the short exposure time required. This is in the region of 15 minutes.

In the early part of the year some exploratory work was done on X-ray micro-radiography using the micro-focus tube. The best results were obtained with a fine-resolution emulsion and the contact method with the specimen in close contact with the film. Further work on this subject was not possible, as the fine-focus set was required for diffraction purposes with a larger-size focus than is suitable for micro-radiography.

Some preliminary attempt was made to obtain silicon radiation using one of the gas-sets. This was not successful owing to the considerable amount of ionization which took place inside the camera which had to be made a part of the X-ray set, in order that the losses of the very long wavelength radiation in window material should not occur.

It is hoped that further work on X-ray micro-radiography and on the use of silicon radiation will be possible by using an old electron microscope. With some modification this instrument will be used as an X-ray set for experimental purposes. (G. C. Dibley.)

High-frequency titrimeter

At the request of C. Bloomfield, a high-frequency titrimeter has been built. This instrument is based on the design of Stelzner and Kelly, and operates on a frequency of 250 Mc/s. It is a single-valve oscillator using a type 955 "acorn" triode with a resonant line-tank circuit. The titration cell, of 50 ml. capacity, is placed between the lines and the oscillator response to the changing electrical characteristics of the solution being titrated is followed by observing changes in grid current, after the manner of a grid-dip oscillator.

It is hoped that by means of this method titrations can be performed in the presence of strong concentrations of electrolyte, the instrument oscillating quite readily when the cell is loaded with 50 ml. of 1.2N-NaCl. A full investigation of the capabilities of this titrimeter is being carried out. (R. Farrow.)

SPECTROCHEMISTRY

Geochemistry of Lias shales

Previous work on numerous specimens of Lower Lias shale from several sites has shown that a relationship exists between the

amounts of the trace elements molybdenum, vanadium, copper and nickel and of organic carbon. It has also been found that both the trace element and organic-carbon contents are related to that of calcium carbonate, rising to a maximum with 20–40 per cent CaCO_3 . The evidence suggests that the latter relationship is primarily one between calcium carbonate and the organic matter with which the trace elements are associated. This in turn would seem to imply that the organic matter in the depositing material influenced the deposition of calcium carbonate.

The high levels of molybdenum in Lower Lias shales which are responsible for the teart disease on soils derived from them in central Somerset, have been shown also to occur in this same formation as far away as the Stowell Park borehole at Northleach (Glos.) and in the outcrop at Lyme Regis.

The fact that no confirmed cases of teart have been reported in the latter area can probably be ascribed to two causes; namely that the steep slopes here promote good drainage, so facilitating the removal of excessive molybdenum and at the same time result in no large areas of soil being derived from any one shale band particularly rich in it.

The zones of the Lower Lias, which in these localities are rich in molybdenum, also occur in the Vale of Glamorgan and give rise to soils over a wide area. Shales examined from this area, however, were found not to contain abnormal amounts, except at Lavernock Point near Cardiff. The absence of teart in Glamorgan therefore apparently results from the absence of excessive amounts of molybdenum in the formation here. This is probably due to the proximity of the contemporary coastline having caused conditions unfavourable to the deposition of the type of organic material which accumulated molybdenum.

Trace element survey of Broadbalk

The preliminary work on the trace-element content of Broadbalk (plots 2, 3, 5, 8, 10, 13, 17) reported by A. H. Weir and J. Beckett (*Rep. Rothamst. exp. Sta. for 1955*) has been extended by the quantitative spectrographic determination of a number of elements in these plots. The results show a remarkable uniformity in the total amounts of these elements over the field, as is indicated by the following figures giving the maximum and minimum amounts found (in p.p.m.):

Co ...	...	{ 17.3 $\pm$ 1.3 (plot 2)	to	21.5 $\pm$ 2.6 (plot 8)
		{ 17.3 $\pm$ 0.5 (plot 3)		21.5 $\pm$ 1.7 (plot 17)
Ni ...	...	23.0 $\pm$ 1.8 (plot 3)	to	31.2 $\pm$ 1.5 (plot 17)
Cu ...	...	20.5 $\pm$ 1.7 (plot 5)	to	27.8 $\pm$ 3.3 (plot 2)
Mn ...	...	623 $\pm$ 71 (plot 18)	to	686 $\pm$ 62 (plot 13)
Cr ...	...	45.8 $\pm$ 2.4 (plot 3)	to	63.5 $\pm$ 12.3 (plot 17)
Ga ...	...	17.0 $\pm$ 2.3 (plot 5)	to	22.3 $\pm$ 4.2 (plot 17)
V ...	...	55.0 $\pm$ 3.5 (plot 3)	to	73.3 $\pm$ 7.6 (plot 17)

While these figures indicate the general levels, interpretation of the differences would be dangerous in the absence of analytical data to show how much has been added with the fertilizers during the field's

history, but in this connection it may be significant that plot 3 (no manure since 1839) is lowest in several elements. (H. H. Le Riche and S. Burnett.)

SOIL CHEMISTRY

Activity of leaf extracts

Fractionation of aqueous leaf extracts by dialysis shows that, while the greater part of the activity in mobilizing iron resides in the dialysable fraction, the residual activity of the heavier molecular weight fraction is appreciable, and the sum of the amounts of iron dissolved at equivalent concentrations by the two fractions is, for several species, greater than the amount dissolved by the original extract. This effect cannot be due to the presence of artefacts, since a reconstituted extract prepared from the two fractions has quantitatively the same activity as the untreated extract.

Paper chromatographic examination shows that dialysis removes those polyphenolic constituents that are of sufficiently small molecular weight to permit their separation into discrete spots on the chromatogram; the polyphenols remaining in the dialysed extract are too complex to do more than produce a streak in the aqueous acetic acid used as the irrigating solvent in the first direction.

Changes taking place in the leaf after it falls from the tree lead to an increase in the more complex polyphenols at the expense of the low-molecular-weight species. In all the species tested the bulk of the polyphenols present in aqueous extracts of fallen leaves are of this condensed type; storage of the undried leaves leads ultimately to a marked decrease in the activity of the water extracts, and this decrease is accompanied by a decrease in the polyphenol content of the extract. Presumably continued enzymic oxidation ultimately leads to such a degree of condensation of the polyphenols that these are rendered largely insoluble in water.

If a leaf extract is allowed to percolate down a column of ferric oxide, and the rate of addition of the extract is not too great, the intensely coloured reaction products are retained in the column and a virtually iron-free and colourless effluent may be obtained for column loadings equivalent to several times the bed volume. The pH of a rimu leaf extract rose from 4.1 to 7.0 after passage through a column; no polyphenols could be detected in the effluent, and the amino acid content had been decreased very considerably. (C. Bloomfield.)

Effect of soil waterlogging

In the previous studies on waterlogged soils, the experimental conditions chosen were such that tendencies towards mobilization effects would be enhanced, and, conversely, any tendencies towards immobilization would be minimized. These investigations have now been extended to deal with systems more nearly approaching actual soil conditions, and with elements other than iron, to which most attention had previously been given.

Incubation of top-soil from an arable field (a heavy clay loam derived from London Clay) at moisture contents slightly above its water-holding capacity, converts iron and manganese oxides to

water soluble compounds. Addition of organic matter in the form of dried grass (either roots or aerial parts) increases the extent of mobilization. Leaching the incubated soil with molar ammonium acetate solution (pH 7) removes greater quantities of these elements than does water extraction, and for iron and manganese this disparity is considerable. A large proportion of the iron and manganese reaction products are thus sorbed on the soil colloids sufficiently strongly to resist leaching by water. An interesting feature of the water and ammonium acetate extraction curves is that while the former shows a fairly rapid initial rise, followed by a slow increase which continues throughout the rest of the incubation (*c.* 30 days), the ammonium acetate curve rises more steeply at first, and quickly reaches a constant value. In other words, the quantity of "fixed" iron or manganese is greatest in the early stages of the incubation, and decreases with time. This suggests that the initial solution/reduction of the iron and manganese compounds is quite rapid, since this point is presumably indicated by the point at which the ammonium acetate extraction curve becomes horizontal, but that further slower changes take place which result in decreased sorption of the reaction products.

For calcium and potassium, as would be expected, ammonium acetate extraction of the soil incubated without additional organic matter gives constant values from zero time throughout the incubation. Addition of grass, however, causes a decrease in the amount of calcium recovered by ammonium acetate extraction. Owing to the relatively small amount of calcium present in the soil, it will be necessary to repeat these experiments under conditions in which the effect of experimental error in the calcium determinations will be less important.

The effects of aeration and of drying on the incubated soil have also been studied. Both treatments cause rapid immobilization of the iron; the amount of manganese extracted by ammonium acetate is scarcely affected by aeration, but water-soluble manganese disappears after a time. In general, drying is more effective than aeration in causing immobilization. (J. W. O. Jeffery and C. Bloomfield.)