

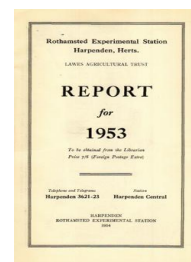
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PEDOLOGY DEPARTMENT

A. MUIR

At the invitation of the Colonial Office and the Government of Nyasaland Dr. Muir took charge of a soil survey of the Shire Valley area which was required in connection with a large development project. Prof. J. L. White of Purdue University has come for a year to work in the department of clay mineralogy. Mr. R. Greene-Kelly has been awarded the degree of Ph.D. by London University for a study of the sorption of polar molecules by clay minerals, and Mr. J. Gasser the degree of M.Sc. for his work on the behaviour of iron and other phosphates during the fermentation of plant materials under anaerobic conditions.

SOIL MINERALOGY

Kenya

During the year work has continued on the mineralogy of the "gilgai soils" of the Athi Plains, near Nairobi (see 1952 Report), and it has now been shown that these soils cannot be regarded as entirely residual from the underlying volcanic rocks (phonolites, phonolitic trachytes, etc.). This is indicated by the presence of such minerals as sillimanite, garnet, staurolite and kyanite, which are the characteristic minerals of metamorphic rocks of gneissose type, and which occur at all levels in the soil profile above that of the weathered rocks. It is very difficult, however, to make an estimate of the amount of contamination. It may well be that the soils are in the main derived from the underlying volcanic rocks, and have had a "wash" of material of foreign origin deposited on top, which has been incorporated in the soil due to the "churning-up" action resulting from their shrinking and cracking properties. (I. Stephen.)

Nyasaland

A study of the mineralogical composition of a suite of soils from the lower Shire River area has been commenced with the object of defining the types of soil parent materials, which do not appear to be all of alluvial origin. (I. Stephen.)

CLAY MINERALOGY

Soil morphology and mineralogy

It has been shown (27) that lepidocrocite of pedological origin is of widespread occurrence in British soils and that its appearance is associated with gleying. Work has been done on three gleyed soils from Lancashire in a preliminary exploration of the relation of morphology to mineralogy. The soils were those studied by Bloomfield (1952, *J. Soil Sci.*, 3, 167). Separates of closely associated brown and grey soil were used, and the clay fractions were examined by X-ray diffraction. This limited investigation suggested that the hydrated ferric oxides goethite and lepidocrocite are the pigments

of the brown mottles of gleyed soils and that rate of oxidation decides which is formed, slow oxidation favouring the formation of lepidocrocite. It also appears that the aluminosilicate clay minerals of associated brown and grey soil are identical in kind and relative amount, but variations in amount occur between different soil horizons and different profiles.

A more detailed study is being made of another gleyed profile from Lancashire in an effort to relate detailed field morphology to laboratory data. For this purpose the semi-micro method for the preparation of clays (28) was devised, and in addition an approximate method of mechanical analysis for similar small amounts of soil has given satisfactory results. (G. Brown.)

Palygorskite

The study of an occurrence of the clay mineral palygorskite (attapulgitite) has been completed and will be published shortly. The palygorskite occurs with montmorillonite in a decomposed syenite. The exchange complex of the altered rock, in agreement with the occurrence of magnesium-bearing clay minerals, is saturated dominantly with magnesium ions, and it seems clear that the alteration involved the introduction of magnesium solutions from elsewhere than the parent rock. In the field the juxtaposition of highly decomposed and essentially unweathered syenite suggests that the alteration of the rock is not due to atmospheric weathering, but to the action of hydrothermal solutions, which have permeated the rock mass.

Samples of other clays, known as pilolite (Heddle, 1879, *Min. Mag.*, 2, 206), "mountain leather" and "mountain cork" have also been examined, and these have been found to give X-ray diagrams identical with that of the Shetland palygorskite. (I. Stephen.)

Dickite and kaolinite

In collaboration with Dr. F. Smithson, University College of North Wales, examination of samples of a kaolin from British sandstones has been made in addition to those reported in *Nature* (31). In the majority of cases it has been possible to identify the mineral even when it is contaminated. The additional results are largely in accord with those published, viz., that where alteration of other minerals in the sandstone seems to have occurred, well-formed plates of the kaolin are present and have been shown to be dickite. Where no alteration is suspected well-formed plates are absent and the mineral is kaolinite. (G. Brown.)

New clay minerals

A previously unreported vermiculin, i.e., a member of the vermiculite group (cf. kaolin, kaolinite), has been encountered and shown to be the dioctahedral analogue of vermiculite. In addition, a mineral which may be analogous to the ill-defined material which some American workers call mica-intermediate has been recognized, and diagnostic criteria have been established. Both minerals occur in mixtures with other clay minerals in soil clays and pure samples have not yet been obtained.

In previous years reference has been made to an unidentified 14 Å. mineral which resembled vermiculite in collapsing to give a 10 Å. spacing after heating to 300° C., but which did not collapse to 10–11 Å. spacing after boiling for short periods with ammonium salt solutions. It has been shown that prolonged treatment, 10-hour boiling with ammonium or potassium salt solutions, collapses the mineral, giving a 10–11 Å. spacing, and that the collapse can be reversed by treatment with Mg-salt solutions. It is thought that these experiments show that the mineral is a vermiculin with a difficultly exchangeable cation, and it is suggested that this cation may be partly organic. In addition, the mineral has an (060) spacing of 1.50 Å., and hence is probably the dioctahedral analogue of vermiculite.

The name "degrading illite" has been given provisionally to a material which gives a band with a high angle edge at 10 Å. and which "tails off" towards lower angles. In some cases the low angle edge of the band is at 14 Å., but generally the band is not so broad. The width of the band depends in part on the exchangeable cation. The band disappears after treatment of the clay with glycerol and, if vermiculin is absent, a sharp line at 14 Å. appears. It has not yet been possible to decide whether all the layers responsible for the band expand to 14 Å. with glycerol treatment, or whether the band is resolved into lines at 10 Å. and 14 Å., as the mineral is always associated with much illite with a strong line at 10 Å. It is hoped that comparative photometry will lead to a decision on this point. When the clay is heated to 300° C. for 12 hours the band disappears along with the 14 Å. vermiculin line, and the intensity of the 10 Å. is enhanced by the collapse. (G. Brown.)

Lancashire soil parent materials

Further work has been done on these to explore the usefulness of clay mineralogy for differentiating surface deposits, commonly known as drifts, which form the parent materials of many British soils. Previously C. J. Tapp, of the Soil Survey of England and Wales, had been able to differentiate the Carboniferous and Triassic drifts according to the rate at which they release potassium to strong acids, the latter having a higher rate of potassium release than the former, and his work suggested that the cause of the difference lay in the clay fractions. Careful examination of the clays from a number of soils shows that their mineralogy is never simple. The clay minerals found are kaolin, illite, "degrading illite", vermiculin and chlorite. All are often present, and no clay has been found with fewer than three of them. In addition, all clays derived from Triassic deposits contain a small amount of a mineral similar to that from the Keuper Marl which Honeyborne (*Clay Minerals Bulletin* 1, 150) described. As well as the clay minerals, lepidocrocite, goethite, quartz and anatase are common constituents, the last two in small amounts.

An attempt is being made to unravel these complex suites, giving particular attention to the hydrous micas, by careful photometry of X-ray patterns of clays which have had different diagnostic treatments. A measure of success is promised not only in correlating and in a few cases correcting field classification of drifts but also in relating the potassium release figures to the illite content of the

clays. In addition, our knowledge of the clay mineralogy of these drifts has been increased. (G. Brown.)

Broadbalk soils

A start has been made in a detailed study of the Broadbalk soils in an area including Plots 2-13 and the Wilderness. The objects of this work are two-fold. First, to correlate differences in clay properties with comparatively recent changes in vegetational cover and fertilizer treatment. Secondly, to assess the relative value of different methods of studying the clay fraction. The results already obtained have shown that the differences between the surface soils of the arable plots and those of the Wilderness are superficial, and are not reflected by changes in the clay mineral content. The exchange capacities vary, but this has been satisfactorily correlated with the amounts of organic matter present in the soil. Profiles examined in the Wilderness show poor development; although there is an increase of clay content going down the profile, little or no change in clay composition occurs. This is explained by the results of detailed study of the clay fraction of the C horizon. Here the composition of the clay is nearly independent of size fraction, and it can be concluded that these soil clays would not be altered in composition during the process of being washed down the profile. These studies have also emphasized the ease with which the Broadbalk soil clay is deflocculated in the absence of organic matter. Considerable improvement in stability was observed with surface soils from the Wilderness, which are higher in organic matter than those from the arable plots. The total exchange capacity of different size fractions from the C horizon increases with decreasing particle size, but the changes are much less than might be expected if the exchange capacity is proportional to surface area. The composition of the clay fraction has been found to be illite, kaolinite, with small quantities of chlorite and goethite. The quantitative estimation of the composition of the clay fraction has not proved feasible by X-ray methods, but differential thermal analysis has been successfully employed to estimate the amount of kaolinite. A value of 20 per cent, nearly independent of particle size, was found. This figure does not appear to be compatible with the results of silicate analysis of the clay fractions if it is assumed that the clay consists predominantly of kaolinite and illite. Much higher values were obtained for the sesquioxides than would be expected from the mineralogical composition. The occurrence of amorphous aluminium and iron oxide appears probable. (R. Greene-Kelly.)

In addition to the clays reported above, samples from Northumberland, Yorkshire, Cambridgeshire, Bedfordshire, Buckinghamshire, Hertfordshire, Sudan, Gold Coast, Kenya and Persia have been examined. (G. Brown.)

Potash fixation

A number of surface soils from Eire was examined in an attempt to relate clay mineralogy to potash fixation which had been established by field experiments. It was found that "degrading illite" was the only distinguishing clay mineral between soils which fixed potassium and those which did not. No potassium fixation could be

attributed to illite or vermiculin. It has been possible to foretell which soils are potassium fixers by X-ray-diffraction tests. However, this work has been done on a limited number of soils, and it is hoped to extend it. (G. Brown.)

Ion exchange studies

The dioctahedral montmorillonite minerals can now be identified with precision by means of a diagram which relates their composition to their expanding properties after lithium saturation and heating. Over fifty montmorillonite minerals from soils and deposits have been classified by this technique. It has been concluded that dioctahedral soil montmorillonite minerals generally belong to the intermediate class where the exchange capacity originates about equally from tetrahedral and octahedral substitution. A study of montmorillonite minerals derived from different parent materials has emphasized the need for a more exact knowledge of the relation between the magnesium content of the parent material and the type of clay mineral derived from it. Although it is generally true that under basic conditions magnesium-bearing parent materials give rise to montmorillonite whereas those low in magnesium give beidellite, several exceptions to this rule have been found.

The exchange capacity of lithium-saturated montmorillonite after drying has been found to give reliable values for the external surface area of the crystallites. This method is superior to gas-adsorption methods for studying the micro-structure of montmorillonite aggregates. The results, using this new method, of a study of the effect of the method of preparation of the montmorillonite on its external area has shown that, in contradiction to what was previously believed, the external surface is unaltered by different methods of preparation, despite the fact that the macro properties of the mineral are very different. The same technique has been used to study the variation of external area between montmorillonites of different morphology as revealed by the electron microscope. Surprisingly little variation has been found.

The distribution of exchange cations in the mixed lithium-sodium montmorillonite system has been investigated using the lithium-fixation method. If the lithium ions are distributed uniformly in the mixed systems, their fixation would lead to the trapping of sodium ions. If there is no miscibility the availability of the sodium ions should be unaffected by lithium fixation. In the case of Redhill montmorillonite it has been concluded that only limited miscibility occurs between the two cations.

The effect of dehydration on the availability of exchange cations on kaolin minerals has received detailed study. It has been found that after drying only lithium ions are fixed by kaolin minerals, and in contrast to montmorillonite the exchange capacity is hardly changed, structural cation exchange having taken place. This interesting effect is being further studied. (R. Greene-Kelly.)

Adsorption on clay minerals

The X-ray work on the montmorillonite complexes with simple organic molecules has been considerably extended. About a

hundred different compounds have been investigated, and in practically all cases it has been possible to interpret the results in terms of the shape and the orientation of the sorbed molecule. The techniques used for this work have been applied to the problem of the stereoisomerism of piperidine and its derivatives. Although the energy of interaction between organic molecules and montmorillonite can only be roughly estimated by X-ray methods, it is clear from the results obtained that strong interaction is more likely to occur if the organic molecule is capable of electron donation to the clay mineral. This tendency emphasizes the importance of organically combined nitrogen in promoting strong interactions between clays and soil organic matter. (R. Greene-Kelly.)

Techniques and methods

In addition to techniques previously mentioned, exploratory work has been done in the use of X-ray diffraction to establish orientation in sedimentary deposits such as lacustrine clays, and the method seems satisfactory.

The Wiessenberg goniometer has been modified for clay mineral work, and its use for the determination of orientation in oriented aggregates, which is required for quantitative clay mineral analysis, is being explored. (G. Brown.)

Powder camera

An improved form of our 9-cm. powder camera has been designed, and one of these cameras has been made for us. This camera has adjustable tantalum slits, adjustable screening plates and a screw adjustment for the film-locating peg. The specimen holder carries a pointer moving over a gradual scale of angles. The specimen can be rotated or oscillated by means of an external motor, coupled to the camera by a flexible drive. (D. M. C. MacEwan.)

Centrifuge separation of clays

A small-scale method for fractionating clays according to grain size, based on Marshall's two-layer method, has been in use here for some time (see ref. 34, Report for 1949). Although the method is useful, it has been found to be subject to certain defects, due to "streamer" formation, and it is being re-examined to see if it can be improved, by using a graded viscosity distribution in the centrifuge tubes instead of a viscous layer (glycerol solution) sharply passing into a layer of low viscosity. (D. M. C. MacEwan.)

Gas X-ray tube

A gas X-ray tube, of our own design, has been in use here for a considerable period and, in view of the simplicity of this type of X-ray generator, we wished to study its performance with various electrode positions and sizes. For this purpose an experimental gas tube has been constructed, with removable sections, allowing various dimensions to be made. This work has shown that, in ordinary operation, a considerable proportion of the total current passes to the tube wall and not to the target, a condition which is not easily remedied. Pure aluminium is the best cathode metal found; a flat cathode with a central hole of suitable depth is found to give improvement both in focus and intensity.

This work has been mainly empirical in nature; lack of time has precluded a highly systematic approach to the problem.

It is now proposed to stabilize the conditions of operation of the tube, and use it as a source of X-rays. (G. Dibley.)

Scales for measuring X-ray photographs

Direct-reading Ångström scales have been made for $\text{CuK}\alpha$ radiation. These are very rapid in use, and much more accurate than any direct-reading scales with which we are acquainted, since they have finely-spaced divisions, and full compensation for changes in film dimensions. (D. M. C. MacEwan.)

Fourier synthesis

A rapid method of fourier synthesis is desirable, both for studies on montmorillonite and for possible future work on micas, etc. A Beevers-MacEwan type machine has therefore been obtained on loan from the Dewar Crystallographic Laboratory, Edinburgh, and a counting unit is now being made for it. One experimental counter has been assembled, using ex-R.A.F. "impulse motors". These are very inexpensive, and will count readily at 20/sec., and probably faster. They will not count negatively: consequently separate counters are used for negative and positive counting, and a subtraction unit has been made, by which automatic subtraction is performed. The use of stepwise charging of a condenser for counting is also being experimented with; this method should be very rapid, but will not be accurate. (D. M. C. MacEwan.)

Fourier transforms

This method for analysing interlayer mixtures, mentioned in last year's report, has been further studied. A slide-rule-type scale has been made which enables the necessary calculations to be very rapidly carried out. (D. M. C. MacEwan.)

GEOCHEMISTRY

Investigations are being continued into the trace element content of sedimentary rocks of the Lower Lias formation. Analyses have been carried out on samples from a boring at Northleach and from the Dorset coast, and certain correlations have been found between their contents of molybdenum, vanadium, nickel and copper. Abnormally high contents of Mo (i.e., > 20 p.p.m.) have been found only in the lower zones, from *Jamesoni* downwards, and here only in the less highly calcareous strata.

The content of these elements appears, in turn, to be closely related to that of material oxidizable by the dichromate wet-oxidation method, this consisting of organic matter with more or less pyrite. The pyrite, which is presumed to be of secondary origin, has been found to contain a relatively large amount of Mo, but no detectable V, whereas the separated clay fraction contains the bulk of the V and little Mo. These findings suggest that both elements were originally laid down with the organic material, but have subsequently been differently segregated.

It has not been possible so far to separate the organic matter completely from the clay, but it is hoped that further experiment will

make it possible to demonstrate whether, in fact, these elements are directly associated with the organic matter. (H. H. Le Riche.)

The general minor-element survey of English soils has been extended, and a number of Cu- and Zn-deficient samples from Wales are being studied. The results of the study of minor-element distribution in some Lancashire soils have been published (33).

A spectrographic method for determining Sm, Yb and Eu in a mixture of rare earth oxides has been used; eleven of the sixteen rare earths are now determinable.

The problem of the estimation of niobium in rocks and soils has been approached spectrographically; using the internal standard method Nb has been estimated in pyrochlore-rich soils, but the results compare unfavourably with those obtained by the much longer chemical or absorptiometric methods.

A semi-quantitative spectrographic method for estimating Pb in twig samples has been used for twigs collected from areas where variable amounts of Pb occur in the soils. The time for each determination is 4 minutes in batches of twenty or more. The method should be of some use in geochemical prospecting. (J. R. Butler.)

SOIL CHEMISTRY

Effects of leaf extracts on soil constituents

Further work on the solution of soil sesquioxides by leaf leachates has shown that both the iron and aluminium compounds formed in this process are strongly sorbed by soil colloids. It is suggested that this process is responsible for the immobilization of the sesquioxides which leads to the formation of the B horizon in podzolized soils. The sorption is particularly pronounced in the case of the New Zealand rimu, and consequently attention has been concentrated on this species.

Although it is very difficult to achieve a strictly valid comparison of the extent of sorption from the leachate of different species, on the basis of the measurements made thus far it is possible to suggest an explanation of such anomalies between the laboratory and field observations as were mentioned in the previous report (1952, p. 57). Thus, while the kauri is a more effective podzol former than the rimu, it has been found in the laboratory that of the two, rimu leaf extracts give rise to much more extensive solution of ferric oxide. On the other hand, sorption from rimu solutions is also more pronounced, so that under field conditions the kauri would give rise to greater net loss of ferric oxide from the A horizon. The same argument may be applied in the case of such broad-leaved species as ash, which, although they apparently do not give rise to any detectable movement of sesquioxides in soils, nevertheless give appreciable solution effects in the laboratory. No doubt faunal activity under broad-leaved cover also contributes in counteracting the leaching process.

A feature of grey wooded soils which are formed under a predominantly aspen cover, is that although the A₂ horizon is leached of sesquioxides, this horizon commonly has a high percentage base saturation. This apparent paradox may be readily explained by the fact that aspen leaves have been found to contain a relatively high proportion of water-soluble calcium compounds.

Although podzolized soils, *sensu stricto*, are predominantly formed on sandy materials in which clay movement would not be apparent, cases are known in which a strong textural profile is developed, and three widespread groups of soils, the grey wooded and grey brown podzolic soils of North America, and the grey forest soils of the U.S.S.R., always show this textural profile. It has been found that at low concentrations, aqueous extracts of the leaves of several tree species are capable of deflocculating clay suspensions, which would account for the removal of clay from the A₂ horizon. At higher concentrations of the leaf extracts a tendency towards reflocculation develops. Experiments on the bark of kauri and rimu, both of which shed their bark, have shown that weight for weight, the bark has a greater deflocculating action than the leaves, and furthermore does not appear to give rise to reflocculation at higher concentrations. Further study of these processes will, it is hoped, be of value in connection with the podzol group as a whole. (C. Bloomfield.)

Mobilization of phosphate under anaerobic conditions

The effect of anaerobically fermented plant material (dried grass) on the mobilization of phosphates of aluminium, calcium and iron and of phosphated clays has been tested. No conclusive evidence for any mobilization of either aluminium or phosphate from aluminium phosphate was obtained. With various calcium phosphates the calcium and phosphate were readily mobilized due to the lowering of the pH during fermentation. In the case of a crystalline basic ferric phosphate and a non-crystalline ferric hydroxyphosphate the fermented grass caused a mobilization of both iron and phosphate. The basic ferric phosphate exhibited re-adsorption of the phosphate, presumably by "free" iron oxide. In the case of the ferric hydroxyphosphate, particle size affected the amount mobilized.

Both kaolin and montmorillonite removed phosphate from the fermenting grass solution. With phosphated clays fermented grass mobilized phosphate previously fixed by treatment of the clays with KH_2PO_4 . In the case of kaolin about half the amount fixed was released, and with montmorillonite the amount remaining fixed was about equal to the amount taken up from the fermenting solution by the untreated clay. It is thought that the adsorption of inorganic P by montmorillonite occurs mainly through amorphous sesquioxides on the surface. Kaolin may also sorb phosphate in this way and also through hydroxyl replacement on the edge aluminium atoms of the crystals.

Oxidation of extracts containing iron phosphate gave a precipitate of basic ferric phosphate with organic matter, a small but significant amount of iron and phosphorus remaining in solution. It seems that this stability of iron phosphate may account for the movement of phosphorus in association with iron within the soil profile. (J. K. R. Gasser.)

The coloration of black tropical soils

A study of some black soils from India (Regur, Kabar and Karail) suggests that their dark coloration is mainly due to their clay organic complex. Using a variety of clays, formation of similar

complexes has been studied in the laboratory under anaerobic and partially aerobic conditions. Among the factors which seem to be associated with the dark clay-humus complex are : (a) clays of high base exchange capacity, especially when in a dispersed state due to the presence of sodium; (b) conditions favouring reduction of iron; (c) acid reaction, even as low as pH 3, and (d) certain types of nitrogenous plant residues somewhat resistant to decomposition and usually base saturated. A comparative study of the black soils with their neighbouring red soils suggests that the organic matter of the black soils is more easily oxidizable but less easily hydrolysable. (Sant Singh.)