Report for 1952

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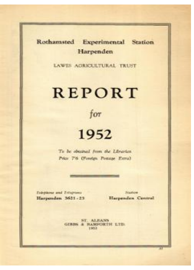

Pedology Department

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A. Muir (1953) *Pedology Department ;* Report For 1952, pp 51 - 57 **- DOI: https://doi.org/10.23637/ERADOC-1-74**

PEDOLOGY DEPARTMENT

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At the invitation of the University of California Dr. D. M. C. MacEwan attended the meeting on clays and clay technology organized by Berkeley University during the summer. Mr. K. Norrish of the Commonwealth Scientific and Industrial Research Organization completed his studies on some Australian soils derived from basalt for which, together with some other work, he was awarded the degree of Ph.D. by London University. Mr. Norrish also carried out experimental work on the swelling of montmorillonite in salt solutions which is described below. Mr. Sant Singh of the Hindu University, Benares, has begun a study of some Indian black cotton soils, and Mr. J. Gasser has started some experiments on the behaviour of phosphate in soils under water logging conditions.

MINERALOGICAL STUDIES

English soils

Little is known about the mineralogy of many of the sediments and surface deposits which give rise to the soils of this country. The opportunity has therefore been taken of examining a series of local soils in connection with a soil survey now being made in the Aylesbury district. The parent materials of the soils include Reading Beds, Clay-with-Flints, Brick-earths, and various sandy deposits (e.g. a pink sand from Ashridge and a red sandy clay from Whipsnade). The suites of minerals in all these deposits have been found to be similar, the main difference between the deposits being in the varying amounts of coarse and fine material. The chief " heavy minerals " present (in addition to iron ores) are zircon, rutile, tourmaline (brown, blue and violet varieties), kyanite, staurolite, garnet, green hornblende (rare) and andalusite (rare). The light fraction consists mainly of quartz. (I. Stephen).

African soils

The study of the soils from the Gold Coast (see 1951 Report) has been completed and will be published shortly. Further investigations have been carried out on soils from Tanganyika and the Equatorial Province of the Sudan.

In connection with a problem of poor sisal growth on an area of " gilgai " relief on the Athi Plains near Nairobi, Kenya, a number of Black Cotton Soil profiles has been examined. The general pattern of distribution of these soils, with their " island-like " relief is very like that found in Australia and elsewhere and it has been shown that the chemical and physical properties conform to the Australian results. The main soil consists of a heavy black clay, on which sisal growth is poor, with round islands of a browner and somewhat lighter-textured soil on which sisal grows well. Both kinds of soil are characterized by montmorillonite. The parent rocks of the Kenya gilgai soils are a series of incompletely differentiated volcanic rocks of Cretaceous to Recent age, among which phonolites and phonolitic trachytes are prominent. (I. Stephen, A. Muir).

CLAY MINERAL STUDIES

X-ray diffraction by inter-layer mixtures

Following on the work described in last year's report, a direct fourier-transform method has been elaborated for determining the proportions and types of components present in such mixtures, given the X-ray diffraction diagrams. This method has been tested in a few practical cases, and on the theoretical diffraction curves of Brown and MacEwan, and it appears to give reliable results, but further tests will be necessary.

The advantage of the new method is that it enables one to pass directly from the diffraction data to the composition, even in ternary and more complicated mixtures (though the more complicated the mixture, the greater is the chance of error). The "reverse" method, described in last year's report necessitates the preliminary calculation of the diffraction to be expected from a series of assumed compositions, and is thus hardly applicable to other than binary mixtures. (D. M. C. MacEwan).

Interlamellar swelling of clay minerals

A theoretical study has been made of the variation of attractive potential between charged sheets of montmorillonite, or similar lamellae, with separation, on the assumption that the following types of inter-layer force are active: (1) electrostatic attraction relayed between the negative sheets by the positive ions; (2) van der Waals' attraction; (3) "osmotic" repulsion due to the interlamellar ion clouds; (4) "adsorption" repulsion due to adsorbed layers of neutral molecules.

There are many uncertainties in any such calculations, particularly in the values assumed for the van der Waals' constant A, and the dielectric constant of the medium; but two conclusions emerge clearly from the calculations: (1) the electrostatic force can, in principle, be much more important than the van der Waals' force, if the cations are assumed to be "floating" between the sheets; (2) the electrostatic force will die away very rapidly with distance (approximately exponentially), so that at large separations (say > 100 Å) it is likely to be negligible. (D. M. C. MacEwan).

The water sorption work described in the last Annual Report has been supplemented by X-ray work. The results have shown that interlamellar sorption of water on Na-montmorillonite occurs only if the resultant water concentration is greater than 3-4 H_2O/Na^+. This explains why Na-montmorillonite gives a single D.T.A. low temperature endothermic peak, whereas Li-montmorillonite gives a double peak. In the former case the water of hydration is squeezed out rapidly along with the remaining interlamellar water, whereas in the latter case differences of water mobility are allowed to develop. It has also been found that the results when combined with indirect heat data are best explained on the basis of a predominant electrostatic interaction between the silicate sheets and the interlayer ions. It can be concluded that the maximum interlayer ion concentration consistent with expanding properties of the mineral depends on the nature of the exchange ions and with Na^+ is about 160 m.e. per 100 g. This explains why Na-vermiculite with about 140 m.e. Na expands with water whilst paragonite with 270 m.e. does not. It seems likely that the occurrence of considerable potassium fixation in soils is connected with this dependence of water sorption on the nature of the interlayer cation. The replacement of cations by K+ might be expected to lead to a more complete exclusion of interlamellar water owing to its lower hydration energy. This water exclusion would tend to make cation exchange slower and lead to apparent fixation.

The sorption of pyridine and other similar ring compounds on montmorillonite has been studied by one-dimensional Fourier syntheses and spacing measurements. It has been found that these molecules are most commonly orientated with the plane of their rings perpendicular to the plane of the silicate sheets. This observation has enabled many different types of sorbed ring compounds to be distinguished merely by using spacing measurements. The possibility of utilizing montmorillonite both as concentrating agent for traces of organic compounds and as a method of identifying them *in situ* is under investigation. (R. Greene-Kelly).

Using a curved-quartz X-ray monochromator, a study has been made of the variation of *c*-axis spacing with salt concentration in a series of montmorillonite-water-salt systems. It has been possible to trace a definite *c*-axis spacing up to a value of rather above 100 Å. For the Na-montmorillonite+NaCl system, to take a typical example, the spacing increases up to about 20 Å as the concentration of salt is decreased; on further decreasing the concentration, a region of mixed spacings then occurs, followed by a markedly larger spacing, in the region of 35Å, which increases steadily to 100 Å (and perhaps further) on still further dilution. The whole process is reversible.

The spacing variation has been studied in more detail by the calculation of fourier transforms from microphotometer records of the X-ray diagrams. A considerable number of calculations have also been made on the effects to be expected from curvature, waviness, and lack of parallelism of the layers. The general conclusions which are as yet tentative, are that, in the high-spacing (> 30Å) complexes, (1) the layers are almost completely parallel; (2) the separation between them is very variable, the " spacing " determined from the X-ray data being an average effect; (3) the layers may be wavy, provided the angular deviations are small.

Polyvalent ions, Ca++ being typical, do not give the large spacings. H+-clay in suspension in HCl solution shows an interesting effect, large spacings similar to those obtained with Na+-NaCl systems being initially obtained, but reverting on standing to small spacings similar to those given by polyvalent ions. The tentative explanation of this is that it is due to the gradual release of Al+++, or other polyvalent ions, from the clay at low pH values. (K. Norrish, D. M. C. MacEwan).

The results of dehydration tests on expanding minerals have confirmed the Hofmann and Klemen hypothesis (1950) that exchange ions of small radius, e.g. less than 0·8 Å, move into vacant octahedral sites on heating. Recent work has shown that it is also necessary that the charge on the silicate sheet originates from octahedral substitutions, otherwise no movement takes place. In

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effect this means that montmorillonite is the only common mineral of the montmorillonoid group that shows this property. This work has been made the basis of a specific test for montmorillonite (23). The test has been applied to many of the clays previously investigated, and found to contain a dioctahedral montmorillonoid mineral, with the view of classifying them as montmorillonites or beidellites (nontronites). Several new problems concerning the weathering of soil parent materials to clays have arisen from this work and are under investigation. (R. Greene-Kelly).

Soil clay mineralogy

Lancashire boulder clays. Twenty samples from the lowest layers of soil profiles overlying drifts of Triassic, Carboniferous and mixed Trias-Carboniferous origin have been examined by X-ray diffraction. It is thought that the degree of disorder of the layers of the hydrous mica mineral commonly occurring in them may be a useful method of differentiating the Triassic from the Carboniferous drifts as soil parent materials. It seems that the hydrous micas in the Triassic drifts are less disordered than in the Carboniferous drifts, but the work is not complete. (G. Brown).

Soils from Cornwall. A study of the weathering of igneous and metamorphic rocks in the Lizard area, Cornwall, has been completed. Kaolin, illite and chlorite occurred in the clay ($<\cdot002$ mm.) separated from the weathered product immediately overlying granite (and derived from its biotite), and montmorillonoid and talc from that overlying the serpentine. (J. R. Butler).

An unidentified 14 *A mineral occurring in British soil clays.* In many of the soil clays from Britain which have been examined a mineral occurs which resembles chlorite in some respects and vermiculite in others, and may consist of interstratified chloritic and vermiculitic layers. It has not yet been possible to obtain the mineral in a pure state but careful work on its reaction to heat will probably establish its identity. (G. Brown).

Tropical soils. Many soil clays from Kenya, West Africa and India have been examined. It has been found that a 14 Å mineral resembling the unidentified mineral reported above occurs along with a montmorillonoid, kaolin and mica in some examples of black cotton soil from India. (A. Muir, G. Brown).

Australian soils. The results of a study of a series of black and red soils on basalt from the Lismore district suggest that the trend in each soil is towards the formation of minerals low in silica and it seems probable that the red soils may represent a more advanced stage of weathering than the black. Nontronite occurs in the parent rock and may be an important factor in maintaining the black soil stage where the direct change from rock to lateritic material would have been expected. (K. Norrish).

Grey wooded soils. An examination of the clay mineralogy of some grey wooded soils from Alberta and Saskatchewan showed that montmorillonoids, a 14 Å mineral, hydrous mica, kaolin, quartz and calcite occur. Interesting features about these soils are that there is an apparent synthesis of a 14Å mineral in the B horizon and that the montmorillonoid of the parent material differs from the montmorillonoid in the surface layers. This suggests recrystallization of the clay material.

Lepidocrocite. This mineral has been shown to occur in gleyed soils in Anglesey and Lancashire, and it is probably the pigment responsible for the orange mottling which occurs in these soils. An account of this work will appear in a forthcoming number of the Journal of Soil Science. Arising out of this work an attempt at the quantitative estimation of the lepidocrocite present is being made.

During the year techniques have been devised which enable X-ray examination of the clay from amounts of soil considerably less than 0·5 grams and if the need arose the amount required could easily be reduced ten-fold. This enables the clay from separate small segregations to be readily examined. (G. Brown).

GEOCHEMISTRY

Distribution of trace elements in rocks and soils

A general survey of the distribution of trace elements in soils of England and Wales has started with a study of several Lancashire soil profiles. The four parent materials derived from Carboniferous and Triassic rock materials carrying soils with drainage conditions ranging from free to very poor have similar concentrations of Ba, Cr, Ga, Li, Ni, Rb, Sr and V but significantly different concentrations of Mn and Zr. From the parent material to the surface soil the concentration of most elements (based on the oven-dry weight) decreases irrespective of drainage conditions, e.g. Cr, Li and Rb; the concentration of Mn varies irregularly in the profiles and those of Pb and Sn increase markedly towards the surface, for example, reaching 160 p.p.m. Pb and 40 p.p.m. Sn compared with 25 p.p.m. and 4 p.p.m. respectively at depth. (J. R. Butler).

The association of the Teart pastures of Somerset with certain beds of the Lower Lias formation is now well-known, and *a priori* it would be expected that other dark clays and shales would be high in molybdenum. Investigations are proceeding on the distribution of certain trace elements in sedimentary rocks, with particular reference to the Lower Lias deposits, as a step towards an understanding of their distribution in soils derived from these formations. This work has been much facilitated by the co-operation of the Geological Survey who have kindly supplied samples from a deep boring at Northleach. The Lias deposits are also being studied at their outcrop on the Dorset coast.

Variations have been found in the molybdenum content of these deposits ranging from well below 10 to over 100 p.p.m. The evidence so far suggests that the high Mo concentrations are confined to the shaly deposits in the lower zones of the Lower Lias, there being little in the limestone bands or the higher zones. It is intended also to study the Mo distribution in shaly deposits from other formations to see whether, in fact, these high concentrations are peculiar to the Lower Lias, or are of more general occurrence. (H. H. LeRiche).

In connection with the study of the Cornwall soils reported above it was found that the trace element content of the rocks differed considerably as would be expected from their different mineralogical compositions, and on weathering to clay there is evidence for a slight loss of gallium with respect to aluminium; similarly the ratio K/Rb changes in favour of K, the larger ionic radius of rubidium facilitating its preferential removal since it cannot be held tightly by the clay minerals. (J. R. Butler).

SPECTROGRAPHIC WORK

The high dispersion glass spectrograph (constructed by Professor Mannkopff of Göttingen, whilst at Rothamsted) has proved highly suitable for studying the complex arc spectra of the rare earths. The relatively common members of the group, Sc, Yt, La, Ce, Pr, Nd, Gd, and Dy, can be estimated in a natural mixture of the rare earth oxides by using the very stable line pairs given by most of the possible pairs of elements. Samarium (a fairly common rare earth) volatilizes in the arc conspicuously before the other elements mentioned above and preliminary tests indicate that barium may be a suitable internal standard.

The determination of Ba, Li, Rb and Sr in soils and other solid specimens is now on a routine basis by using Cr, Sm and Cs as internal standards for Sr, Ba and the alkalis respectively. The minimum number of spectrograms (resulting from separate burns of the specimens) required to estimate the elements Ba, Be, B, Cs, Cr, Co, Cu, F, Ga, Ge, In, La, Rb, Li, Mo, Mn, Ni, Rb, Ag, Sr, Tl, Sn, V, Yt, and Zr, is now five. (J. R. Butler).

GLEYING OF SOILS

Continuing the investigation of the movement of sesquioxides in the soil, attention has been concentrated on the properties of the debris of various species of conifers with respect to the mobilization of iron and aluminium in forest soils. It has been found that, for some ten different species, sterile water extracts of the undecomposed leaves or needles will dissolve ferric and aluminium oxides, with reduction of the former to the ferrous state. The effect has been investigated over the pH range of 4-7·5, and it has been found that both solution and reduction take place even under conditions at once alkaline and aerobic. While the extent of the solution and reduction is decreased by aeration or by raising the pH, the degree to which these factors influence the reaction varies considerably for the different species.

In the case of Scots pine it has been possible to show that the ferrous compounds formed by reaction with ferric oxide are organic complexes which possess great stability under oxidizing and alkaline conditions. The dissolved aluminium appears to be present in the form of an organic complex of comparatively low stability.

A number of deciduous and other types has also been investigated. In this group it has been found that, while the same type of solution-reduction reaction takes place, the variation between species is much greater than in the case of the conifers. Thus heather is active in mobilizing iron at pH values in the region of 4·5, i.e. the untreated water extract, both under aerobic and anaerobic conditions; if, however, the pH of the extract is previously raised to 7, the activity falls to a comparatively negligible value. In contrast, a water extract of aspen leaves is very active in mobilizing the sesquioxides under anaerobic conditions, even at the high pH values, although its activity is markedly decreased by the presence of air. This latter observation is of interest in connection with the " Bluff Podzols " and grey wooded soils of central Canada and similar soils in the Soviet Union which occur in part under aspen. Thsee soils are podzolic in character, but may have pH values up to or above 7. Thus far, the laboratory findings have been in keeping with the field evidence. In the case of autumn-fallen ash leaves, however, the aqueous extract is a fairly efficient mobilizer of iron, and, although its effectiveness is considerably reduced by raising the pH of the reaction mixture, the residual effect is still appreciable. Since the ash is not known to be a podzol-forming species, it is apparent that an additional factor must be involved. Possibly the soil micro-fauna are responsible for counteracting the leaching action of the ash and similar non-podzolizing species. (C. Bloomfield).