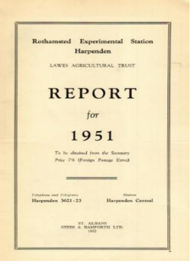
Rothamsted Report for 1951



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PEDOLOGY DEPARTMENT

By A. Muir

MINERALOGICAL STUDIES

African soils

The study of the soils of the Kongwa groundnut area has been extended to cover the sand fractions and some work has been done on a group of soils from the Equatoria Province of the Sudan. The minerals found in the Kongwa soils are those normally developed in metamorphic rocks of the gneissose type. Species noted included the following:

amphibole, iron ores, garnet, kyanite, sillimanite, zircon, rutile, epidote, staurolite, tourmaline, biotite, quartz, feldspar.

The Sudan soils are representative of various stages in three of the four catenary groups that have been recognized by Dr. H. Greene. All appear to be derived from high-grade paragneisses or schists of the basement-complex, as all contain the mineral sillimanite.

A comparative study of two profiles from acid schist and hornblende—garnet-gneiss of the Archaean complex near Accra, Gold Coast, is in progress. The basic gneiss weathers to give a sandy clay soil characterized mineralogically by a quartz-garnet-montmorillonite assemblage, while the acid schist gives a sandy quartzose soil with smaller amounts of clay comprising both montmorillonite and kaolin.

CLAY MINERAL STUDIES

Techniques

During the year a four-window X-ray set for crystallography, based on the self-rectifying gas tube, has been completed by Mr. Dibley, mechanic to the department. This is a completely self-contained unit of low initial cost having an X-ray output corresponding to about 10-15 ma at 30-40 kv. Provision is made for very rapid interchange of targets. The tube normally gives a point focus by means of a hollow spherical aluminium cathode, but experiments have been carried out to determine the best shape of cathode for obtaining a true linear focus, should this be wanted.

This set was exhibited at the Conference of the X-ray Analysis Group of the Institute of Physics, held in Leamington Spa in April. Two similar sets are to be built for use in the Pedology Department and the Soil Survey.

Mention was made in last year's report of efforts that were being made to reduce X-ray exposure times. Further work on the problem has shown that there is a lower limit to the angle at which the powder camera axis may be set with respect to the target face, due to absorption of radiation in the target material itself. This is because the depth at which the X-rays are produced is appreciable—of the order of a few microns. The phenomenon is of importance only when a narrow beam is used. The observation is in fact a rediscovery of an early result, but it seems to have been lost from sight in recent years.

Electron diffraction

The electron diffraction patterns of montmorillonite obtained by Professor Finch have been indexed and calculations have been made of the intensity of diffractions to be expected from a normal beam photograph of a flake of montmorillonite. The atomic coordinates used were those conditioned by a muscovite superposition of half-layers and the three possible arrangements of the octahedral aluminium ions were tried. All three arrangements gave fairly good agreement with the experimentally observed intensities. Other methods of super-position of the half-layers were used in subsequent calculations but agreement was not as good as with the muscovite super-position.

Calculations were also made of the distributions of intensity across several (hk) bands, again based on the atomic coordinates of muscovite. These bands were (11, 02) and (33, 06) and (19, 53, 46) and although the calculated band shapes agree very well with the observed shapes the positions of the maxima are displaced.

Quantitative determination of clay minerals

The theory of X-ray reflections given by oriented aggregates, which was mentioned in last year's report under this heading, and which has been developed further, was communicated to the 2nd International Congress of Crystallography in Stockholm, by K. Norrish and D. M. C. MacEwan. A detailed theory of the absorption of X-rays in powder specimens of different shapes has also been worked out. It is hoped to apply these theories to the quantitative determination of clay minerals in mixtures, using oriented specimens. This will be an advantage over the usual procedure of trying to obtain a completely unoriented specimen—always difficult of achievement, even if it were desirable. The results could also be applied to the determination of the degree of orientation of fibrous or flaky minerals in aggregates.

X-ray diffraction by inter-layer mixtures

Many clay minerals are composed of minute lamellae interstratified on a molecular scale, and they then give rise to diffuse X-ray reflections, and non-integral orders of reflection. It is of interest to have an X-ray technique for determining what components are present in such a case, and what their relative proportions are. This problem can be attacked by calculating a series of curves, using various assumed mixtures, which may be compared with the photographs actually obtained. Suitable curves for some commonly occurring mixtures have been published by G. Brown and D. MacEwan (see this Report for 1949, pp.152-153), and their usefulness was acknowledged at the International Congress of Soil Science (Clay Minerals Section) in Amsterdam last year, when it was suggested that they should be augmented by calculating a number of further cases.

A direct comparison of these theoretical curves with experimentally determined intensities in the case of a random montmorillonite-glycerol mixture has recently been made. It has been found that heating lithium montmorillonite to a comparatively low temperature reduced its sorption of organic liquids. Preliminary

X-ray photographs of previously heated lithium montmorillonite showed that the rate of sorption of glycerol was slow and could be controlled by heating. In this way samples with increasing amounts of sorbed glycerol could be obtained. The photographs also suggested that the glycerol was sorbed was the two-layer complex even at low sorption values and that these layers were randomly distributed. The Hendricks and Teller formula was applied to this case and X-ray diffraction patterns were obtained of samples which contained different amounts of sorbed glycerol. Comparison of the observed diffraction patterns and the intensity distributions obtained by calculations showed good agreement.

Sorption of organic molecules by montmorillonite

A study of the effect of intensive drying on the sorption of acetonitrile, nitrobenzene and pyridine was carried out. The results confirmed Glaeser's conclusion that the formation of " Normal " complexes can be inhibited. The results of later work suggested that the effect was in some cases due to a depression of the rate of interlaminar penetration.

The pyridine complexes of Li-, Na-, K-, montmorillonite were examined by differential thermal analysis, and it was found that the Li and Na clays gave complex low temperature peaks whereas K clay gave a simple peak. This was interpreted as indicating marked ion-pyridine interactions in the former case. Nitro-benzene gave a similar peak with Na- montmorillonite. In view of these complex peaks it was decided that a more detailed study of the work of Hendricks, Nelson and Alexander on the hydrates of montmorillonite was desirable. Detailed isobaric dehydration and hydration curves of Li-, Na-, Ca-, Mg-, montmorillonite and Li-hectorite were carried out. Great care was taken to establish equilibrium at each point, some points taking several days. The conclusions from this work were that differential thermal curves show differences in diffusion coefficient rather than changes in solvation energies and that definite hydrates are not formed in montmorillonite. Two further items of interest resulted. First, it was found that the apparent amount of structural water left after the mineral had apparently lost all of its sorbed water depended on the hydration energy of the exchange cation. K- montmorillonite gave 5·0 per cent hydroxyl water in agreement with the Hofmann structure. Secondly, hysteresis effects were observed on rehydration, being most marked with Li- montmorillonite. The unusual properties of Li- montmorillonite have been discussed in a note to the Clay Minerals Bulletin (in the press).

Owing to the desirability of obtaining less ambiguous information than was obtained in liquid studies (Rothamsted Annual Report, 1950), and some quantitative data on the energy changes on sorption, work was commenced on vapour phase measurements. The results confirmed that hysteresis is always present at room temperature when interlaminar sorption takes place. Rates of sorption studies on adsorption and desorption have been carried out in which the effect of varying the temperature, pressure, and coverage, on the rate coefficients was determined. The results suggest that the desorption isotherm is probably the best measure of the free surface energy lowering of the sorbate, and that the main causes of hysteresis arise from the fact that work must be done to provide sorption sites in the mineral.

The desorption isotherm of water from Na- and K- montmorillonite has been measured in detail. Heats of desorption have been deduced using the Clausius-Clapeyron type equation and their variation with amount sorbed determined. The heats are less than those observed by workers on the zeolites and reach a maximum on the external surface.

The adsorption of pyridine and water on Na- montmorillonite has given data on the probable part played by the external surface during sorption. Good correspondence has been obtained between Escard's surface area by nitrogen adsorption on Na- montmorillonite and the amounts of adsorbate covering the external surface as deduced from isotherms.

Isotherms obtained with Na- montmorillonite flakes were similar to those obtained with alcohol flocculated powders except that the former seem to have a smaller external area.

The study of the interaction of amino-acids and proteins on montmorillonite has been concluded. Fixation of these molecules by the proton transfer mechanism previously described (Rothamsted Annual Report, 1950) was found to prevent the expansion of montmorillonite by the uptake of water or glycerol; even the smallest amino-acid showed this effect. Changes in the X-ray pattern of these complexes, as the size of the adsorbed molecule was increased from glycine to salmine (a large basic molecule of mol. wt. *ca.* 8,000), coupled with chemical determinations for N, showed the effect of the progressive filling up of the interlamellar space.

Two other mechamisms operate in the fixation of these amino-acid molecules in which the presence of the nitrogen compound does not prevent the expansion of the clay sheets with glycerol. Firstly, adsorption at the iso-electric point of the acid due to the dipole character of the molecule; and secondly, coordination with copper when this is the base exchange cation. These complexes are very labile.

The fixation of proteins, which form insoluble salts with base exchange cations e.g. Ca-edestin, Zn-insulin, showed characteristics which suggest that precipitation of these salts occurs at the edges of the interlammelar space rendering the clay inert to water and glycerol expansion. For stability, this compares favourably with the first type of complex.

Clay mineralogy of rocks and soils

Palygorskite. A specimen of a white to yellowish white fibrous material found in pockets in weathered granite in the Shetland Isles has been found to consist of the mineral palygorskite associated with minor amounts of montmorillonite. Further work on this material and on palygorskites from other British occurrences is in progress.

Glauconite. Work was commenced during the year on the weathering of the mineral glauconite, and soil profiles overlying highly glauconitic materials of the Upper Greensand and Bracklesham Beds were collected. Owing to the resignation of Mr. I. L· Freeman from the Soil Survey this work has been suspended.

Lepidocrocite. In several soils from the north of England investigated during the past year, lepidocrocite γ-hydrous ferric oxide, has been found associated with the orange mottling which is prominent in gleyed soils. An attempt is being made to separate the red iron oxide which occurs in what seems to be a pure condition from the dead root channels of a gleyed horizon with a view to characterizing it by X-ray diffraction.

Lancashire boulder clays. An investigation of several different types of boulder clays has been made with a view to differentiating the drifts which form the parent material of many of the soils in England. There were no striking differences between the samples studied, the main constituents being illite, kaolin and chlorite. It is possible that a detailed examination of each type may enable the drifts to be identified by the minerals present in minor amounts.

Black cotton soils. The clays from a group of soils of this type from India, Nigeria, Gold Coast and Southern Rhodesia, examined on behalf of the Road Research Laboratory, proved without exception to contain a montmorillonoid as the dominant clay mineral, with minor amounts of kaolin and illite. In the case of a dark valley soil from Kongwa little or no montmorillonoid is present in the clay, the main constituents being illite and kaolin. It is possible that this soil may be derived from a recent limestone.

SPECTROGRAPHIC WORK

The investigation of the trace element content of soils continues with particular reference to those derived from the Lower Lias. It would appear that the bulk of the Mo, V, Co, Ni and Cr in these soils resides in the clay fraction, though not in the alumino-silicate clay minerals. Further investigations are proceeding with a view to establishing what factors involved in controlling the distribution of trace elements in such soils derived from sedimentary deposits.

Investigations are being carried out on rice samples from Malaya, where it is thought that low yields may be due to trace element malnutrition and also on spruce trees for the Forestry Commission, where similar trouble is suspected.

For the routine determination of exchangeable cations in soils by the Lundegardh flame technique a method has been adopted whereby the ammonium acetate is allowed to percolate through the soil automatically. This gives results in good agreement with the standard filtration method and has the advantage that the exchange capacity is readily determined afterwards on the same sample.

GLEYING IN SOILS

It has previously been reported that soil material may be gleyed in the laboratory by the action of anaerobically fermenting plant material. It has been found that despite the extensive reduction of the ferric oxide, the fermentation extract is capable of reducing further ferric iron provided this is in soluble form. In addition, the rate and extent of the gleying is decreased considerably if the ferric oxide is previously subjected to moderate heating. This suggests that the overall rate of the process of gleying is determined by the rate of the initial solution of the ferric oxide. By comparing the progress of gleying and the production of acid and reducing compounds during the fermentation of different plant species it is hoped to obtain further information on this aspect of the problem. It has been found that the ferrous solutions obtained by fermentation of different plant species may vary considerably in their ease of oxidation. The extracts of some species, notably oak leaves, oxidize so readily that the preparation of samples for analysis is difficult. The choice of grass for the initial experiments was therefore a fortunate one.

It is known that the kauri (*Agathis Australis*) is exceedingly active in podzol formation, and its debris is said to give a very acid litter. Samples of kauri leaves and bark have recently been received from New Zealand and it is hoped that they will afford an easier approach to the problem of the initial solution of ferric oxide in the fermentation process.

Published accounts of the iron content of gley soils show that in certain cases gleying does not result in appreciable diminution of the iron content of the soil and it is difficult to reconcile these results with those of the fermentation experiments since in the latter there is an almost complete removal of the ferric oxide. It seems probable, however, that the previous workers examined the mottled type of gley soil, and that the analyses were made on bulk samples. The effect of small scale migration of iron would thus be obscured. In an attempt to resolve this contradiction, two types of gley soils have been examined:—

(1) a uniformly dark grey soil covered by 12 inches of acid peat and containing no roots;

(2) a soil showing extensive orange-red mottling on a pale grey background.

For (1) it was found that the iron content of the bulk samples increased slowly over the first twelve inches of the mineral soil—(from 0·5-0·8 per cent, expressed as Fe_2O_3), thereafter increasing more rapidly from 1·6 per cent at 16 inches to 3 per cent at 24 inches. In the case of (2) the total iron content of the bulk samples decreased fairly regularly with depth, falling from 10-13 per cent at the surface to 4-6 per cent at 3 feet. Analysis of hand picked samples of the grey and brown material showed that while the total iron content of the grey material remained essentially constant at 2-3 per cent, that of the brown mottles decreased slightly irregularly with depth from 17 to 8 per cent at about 3 feet. The free ferric oxide was in general roughly 2 per cent less than the total iron on both the grey and brown separates. It is significant that while root channels were absent from the soil under peat, which was not mottled, in (2) the iron-stained patches were always located around old root channels.

On the basis of these results it is suggested that soil (1) and the grey material from (2) represent the true end products of gleying, and correspond to the soil residues from the fermentation experiments. The iron staining in (2) represents an opposing tendency which is associated, in this case at least, with some such factor as aeration or enhanced bacterial activity, which is in turn associated with the root channels. The essential constancy of the iron content of the grey material from (2) is surprising, since it might be expected that with increasing intensity of gleying a continuous decrease in the iron content would be produced in the gleyed soil.

Some, as yet unconfirmed, results obtained in fermentation experiments suggest that the grey colour of gley soils is caused by sorption of ferrous-organic compounds on the clay and it seems likely, therefore, that the 2-3 per cent " ferric oxide " of the grey separates represents the saturation value of this sorption complex.

A further result of this work is that the distribution of free alumina has been found to follow that of the free ferric oxide, i.e. the free alumina content of the brown patches is higher than that of the grey fraction.