# Report for 1949

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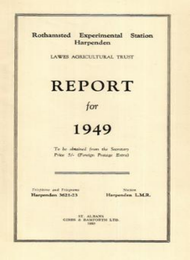

## Pedology Department

### A. Muir

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# PEDOLOGY DEPARTMENT

By A. Muir

## WEATHERING OF ROCKS AND MINERALS

During the year work was continued on the rocks and soils of the Malvern Hills. In the case of the soil derived from biotitite it has been shown that the clay mineral present represents a mixed chlorite-vermiculite structure. This is the first report of such a mineral type forming an essential part of the colloid fraction of a soil, although the existence of such a structure had been suggested, and later verified for larger crystals by Barshad in California. In the Malvern soil (of low pH) the predominantly chloritic material of the weathered rock passes into a vericulitic material in the soil, the transition taking place both in the coarse flakes of weathered biotite and in the clay, although the process does not seem to be quite the same for the two types of material. An interesting point is that even in the upper soil horizon there was very little true vermiculite present, most of it existing in mixed-layer minerals. On the basis of these observations it is suggested that there is a complete range of intermediate minerals between chlorite and vermiculite and an explanation of the possible means of transition can be given.

## CLAY MINERAL STUDIES

A start has been made in a survey of the clay mineralogy of a large number of sedimentary rocks from various parts of England and Wales. In particular, several samples of Keuper Marl deposits have been examined, and the general presence of the chloritic components mentioned in last year's report has been confirmed. (See abstracts under Stephen and MacEwan, 1950). Analyses have also been made of soil clays from the Middle East and East Africa.

In connection with the expansion of X-ray diffraction work in the department, an experimental design for a gas X-ray set suitable for mineralogical work has been evolved and this is now being constructed.

Work on surface and interlamellar absorption by clay minerals and related substances, from solution, has been commenced by Mr. R. Greene-Kelly under a special A.R.C. grant.

### *Absorption complexes of α-zinc hydroxide*

In extending the work on this subject it has been found that replacement of absorbed Naphthol Yellow anions can be effected by inorganic and aromatic anions. The kinetics of such exchange is specific for each anion. For halide anions, the rate of replacement follows the series $F^- > Cl^- >> Br^-$. The rate of replacement with I– is imperceptible (if there is any) even at elevated temperatures (70°C). Only the chloride exchange experiment resulted in the conversion of the primary dye complex into a flake of structure similar to the α–form of $Zn(OH)_2$ from $ZnCl_2$ solutions.

Anion exchange with *other* dyestuffs proved of greater interest. Three dyestuffs, of which two could not be induced to form primary complexes with α–$Zn(OH)_2$ due to low solubility or high molecular weight, were interacted with a flake of the primary complex. In all cases, the change in the basal spacings was consistent with a replacement of naphthol yellow anions; in two cases the observed spacings could be quantitatively predicted from a calculation of the areas of the dyestuffs molecules. This is, so far, the only proof (indirect as it is) of the uptake of dyestuff in layers. All attempts to induce preferred orientation in the primary naphthol yellow complex (including pressure treatment of some hundred atmospheres) were unsuccessful, and direct proof of layer absorption of dyestuffs by X-ray methods could not be obtained.

The conditions necessary for the production of the expanding type of the naphthol yellow primary complex mentioned in the Annual Report for 1948 were investigated; dyestuff concentration during precipitation and the extent of washing were found to be the critical factors.

Subsequently, a host of complexes has been prepared with different organic anions with a view to ascertaining what particular structural characteristics in the absorbed organic anions encourage the formation of stable well-oriented primary complexes. The occurrence of substituent nitro- or nitroso- groups, preferably in ortho- or para- configuration with -OH groups, seems to be conducive to their formation, suggesting a modified chelate bonding on the zinc hydroxide surfaces. Highly oriented and crystalline precipitates can be formed in this way, the effect being heightened by precipitation at higher temperatures. The temperature effect is less marked on complexes with larger organic anions or molecules containing a greater number of $NO_2$ groups.

Analyses of X-ray powder diagrams and uni-dimensional Fourier analyses of (001) reflections in oriented flake diagrams of some of these complexes reveals the uptake of the organic anions in layers. The Fourier analyses suggest the formation of $Zn(OH)_2$ layers with three sheets of (OH) groups in each layer rather than two as in the brucite structure.

### *Location of adsorbed ions and molecules on montmorillonite*

This work has now been completed, and the resultant Fourier curves show two interesting points. Firstly, the exchangeable cations in the montmorillonite-glycerol complex take up a position midway between the inorganic layers of the mineral. Secondly, the structure of the inorganic layers of montmorillonite is in accordance with that proposed by Hofmann rather than that suggested by Edelman.

A similar study is now being made with hectorite, a trioctahedral montmorillonoid. This is not yet complete, but the Fourier curves confirm the Hofmann structure for the montmorillonoids.

### *Interstratified clay minerals*

Work in the department and elsewhere has shown that randomly interstratified clay minerals are fairly common in soil clays. To facilitate their identification the intensity and distribution of scattered X-radiation from a number of types has been calculated using the formula derived by Hendricks and Teller (J. Chem. Phys., 1942, **10**, 147). The types chosen were those most likely to be encountered in practice and the results will prove of great value.

## SPECTROGRAPHIC WORK

Work has begun on the investigation of the Mo content of soils, and working curves for its determination have been derived. It is already well known that certain soils derived from the lower Lias have abnormally high Mo contents and it is hoped that some information will be obtained on the general distribution of Mo in different types of soil. The Mo content of most soils appears to be of the order of a few parts per million only, which is near the spectroscopic limit of detection.

Some analyses for Mo have been done for the Botany Department on samples of lettuce from water culture experiments.

The routine analysis by the Lundegardh method has been going satisfactorily. Some 400 samples, mainly soils sent in by the soil surveyors, have been analysed for the exchangeable ions, K, Na, Ca, Mg, Sr and Mn. Some determinations of Mn have also been carried out on wild oat samples for the Botany Department.

## Gleying in Soils

The study of artificially produced gleying on incubating soil material in sugar media has been continued. Determinations have been made of the residual sugar and ferrous iron contents of the fermentation solutions, as measures of the rate of microbial growth and of the gleying reaction respectively. In such experiments not only the sugar, but also the iron curves, are of sigmoid form, suggesting a microbial process as the rate-determining factor in the process of gleying.

Experiments have been made using grass or leaves in place of dextrose as the source of energy, thereby simulating soil conditions more closely. It has been found that under these conditions the results are comparable with those obtained in sugar fermentations, both in the extent and rapidity of the process.

The aliphatic acids produced in the sugar fermentations form complexes with ferric iron. As the published data on the composition of these complexes do not agree in certain instances, a number of redeterminations have been attempted by potentiometric and conductrimetric titrations—the methods used in general, by previous investigators. As a solution of a ferric salt is strongly hydrolyzed and consequently highly acid, it has generally been found necessary to employ solutions of the sodium salts of the organic acids in order to obtain a pH value sufficiently high to allow complex formation to occur. Thus during titration, the pH varies between wide limits, often by as much as 4 or 5 units. In addition to the direct effect of the pH on the quantity being measured, the relationship between the pH and the stability of the particular complex must be considered. Thus if during the titration of the sodium salt with a ferric solution, the pH falls to a value at which appreciable dissociation of the complex commences, the concentration of $Fe^{\cdot\cdot\cdot}$ in the solution will increase, regardless of any consideration of the stoichiometric end-point of the complex formation. Hence the ratio $Fe^{\cdot\cdot\cdot}$/organic acid, as determined by the point of inflection in the experimental titration curve, will be a function of the initial pH of the solution titrated, the pH of the titrant, and the dissociation of the complex as a function of pH, as well as of the theoretical composition of the complex. Should the complex be stable at low pH values, only the last factor will be operative. This is the probable explanation for the agreement of different workers on some systems, while the preceding factors, no doubt, are the cause of the non-accordance of results for other, less stable systems.

### BIO-GEOCHEMISTRY OF ALUMINIUM

Aluminium accumulators were found to be far more widespread than was hitherto known. Vast areas of tropical rain-forests and secondary growth contain a large proportion—often pure stands—of Al-accumulating trees and shrubs. The effect of a continuous fall of leaves rich in aluminium on tropical soil formation is being studied. A preliminary analysis of 40 leaf samples from the Caucasus which were supposed to be aluminium rich did not reveal abnormal amounts of this element. Only a small part of the comparatively high total of the aluminium content of topsoils in this region can therefore be ascribed to present-day vegetation.

Since the tea-bush is the best known aluminium plant it was chosen for detailed study. From the analyses of over 300 samples from Ceylon and East Africa, the following points have emerged :—

1. The Al content is very low in the growing parts but increases continuously with age, rising to more than 17,000 p.p.m. from less than 100 p.p.m.
2. Phosphorus uptake is normal in a healthy tea-bush and its mobility is unaffected by the aluminium.
3. The tea-bush probably holds the record for high Mn content without toxicity symptoms ; healthy leaves may contain as much as 10,000 p.p,m. Mn. It is conceivable that the presence of similar amounts of Al protect the leaf tissue from Mn damage which would certainly occur in plants which are not aluminium-accumulators.