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PEDOLOGY DEPARTMENT

C. BLOOMFIELD

After a long and bravely borne illness, Dr. A. Muir died in February. Dr. Muir had been head of the Pedology Department since its formation in 1945; his personal qualities and unrivalled knowledge of world soils make his death a great loss to the department and to the world of soil science.

D. A. Osmond assumed responsibility for the administration of the department until July, when C. Bloomfield was appointed head.

G. Brown attended the Third Annual Conference on X-ray Analytical Methods at the University, Glasgow, 17–21 September, and J. H. Rayner attended an Orion programming course at the Ferranti Computing Centre, 8–26 October.

Mr. J. P. O'Callaghan of the Agricultural Institute, Johnstown Castle, Eire, spent two weeks in the department, studying X-ray diffraction methods for identifying clay minerals in soils.

Mineralogy

Ferrous sulphate hydrates. Kossenberg and Cook (*Miner. Mag.* (1961), **33**, 829–830) have published X-ray powder data for $FeSO_4.7H_2O$ and $FeSO_4.4H_2O$ which differ considerably from those in the X-ray Powder Data File, in which no serious errors have previously been detected.

To check these observations, powder patterns of $FeSO_4.7H_2O$, $FeSO_4.4H_2O$ and $FeSO_4.1H_2O$ were taken. These show that Kossenberg and Cook's data are wrong. The patterns for $-7H_2O$ and $-4H_2O$ can be indexed using the cell dimensions and space groups already published (Keating and Berry, *Amer. Min.* (1953), **38**, 501–505; Baur, *Naturwissenschaften* (1960), **47**, 467). The cell dimensions given by Midgley (*Amer. Min.* (1962), **47**, 404–409) for siderotil, $FeSO_4.4H_2O$, derived from single crystal electron diffraction and X-ray powder data are wrong. The powder pattern of szomolnokite, $FeSO_4.1H_2O$, can be indexed on the basis of a *C*-face-centred monoclinic unit cell with $a = 7{\cdot}10$ Å, $b = 7{\cdot}55$ Å, $c = 7{\cdot}61$ Å, $\beta = 116° 9'$, $a : b : c :: 0{\cdot}940 : 1 : 1{\cdot}008$, in good agreement with the axial ratios $a : b : c :: 0{\cdot}9344 : 1 : 1{\cdot}0078$, $\beta = 116° 13'$ calculated from the values obtained by Bandy (*Amer. Min.* (1938), **33**, 715) from morphological measurements.

Alunite. A sample from a mineralised zone in the Lower Pillow lavas, Paphos district, Cyprus, among some clays examined by Audrey M. Du Feu, Soil Survey, for the Geological Survey of Cyprus, gave an X-ray pattern similar to alunite, but with different spacings.

The sample was examined in detail. Chemical analysis showed its composition to be: Al_2O_3 37·2%, Fe_2O_3 1·9%, SO_3 38·2%, Na_2O 5·7%, K_2O 3·3%, H_2O 14·2%. X-ray powder diffraction indicated a hexagonal

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cell with $a = 6{\cdot}97$ Å, $c = 16{\cdot}81$ Å. The mineral is therefore an intermediate between alunite, $KAl_3(SO_4)_2(OH)_6$, and alumian (= natroalunite), $NaAl_3(SO_4)_2(OH)_6$, with a Na : K ratio approximately 3 : 1. Minerals of this composition range in the alunite group are uncommon; the material is almost pure. (Brown)

Rectorite. Work on the identity of allevardite and rectorite (*Rep. Rothamst. exp. Sta.* for 1960, p. 78) was ended. New results from X-ray diffraction measurements and chemical analysis confirm that the structure consists of pairs of dioctahedral 2 : 1 type layers, and that alternate interlayer regions absorb water (and some organic liquids), leading to swelling. This suggests a new interpretation of the structure of the interlayer region and of the swelling of the mineral.

When saturated with tetramethyl ammonium cations all the samples have a basal spacing of 23·5 Å, i.e., 4·2 Å more than the 19·3 Å basal spacing of the collapsed lattice; this cannot be confused with any of the hydrates. This value can be compared with that of 13·5 Å (= 9·5 + 4 Å) for tetramethyl ammonium montmorillonites. Further, different spacings are given by sodium- or magnesium-saturated air-dry material. These results show that the nature of the exchangeable cation affects the swelling and that the exchangeable cations lie in the expanding interlayer region. The amount of swelling is very similar to that of montmorillonite. Thus, the amount of swelling of glycerol-saturated rectorite (= allevardite) is 27·4–19·3 = 8·1 Å, compared with 14·3–9·5 = 4·8 Å for vermiculites and 17·6–9·5 = 8·1 Å for montmorillonites.

Chemical analysis substantiates this interpretation. The cation-exchange capacity, about 50 m.e. per 100 g ignited material, is what would be expected if alternate interlayers are montmorillonite-like. A structural formula for a 44-oxygen unit, derived from the analysis of the sample from Baluchistan, Pakistan, the alkali cations being divided between exchangeable and non-exchangeable positions according to the measured exchange capacity, gives the following structural formula:

$$(Na_{0{\cdot}72})\ (Na_{1{\cdot}72}K_{0{\cdot}04})\ (Mg_{0{\cdot}04}Al_{8{\cdot}20})\ (Si_{12{\cdot}80}Al_{3{\cdot}20})O_{44}$$

The exchangeable cation charge, +0·72, is very similar to the charge in a montmorillonite interlayer region of area 9 Å × 5 Å, and the charge in the other interlayer, +1·76 per 9 Å × 5 Å, approaches that of micas.

To summarise, rectorite (= allevardite) is a double-layer mineral made up of pairs of 2 : 1 type alumino-silicate layers. Alternate interlayers are mica-like (large charge and non-swelling) and montmorillonite-like (small charge and swelling). The cations of the mica-like interlayers are fixed; those of the montmorillonite-like interlayers are exchangeable. Swelling takes place as in montmorillonite by the hydration (or solvation) of the exchangeable cations, and the amount of swelling is controlled by them. (Brown and Weir)

Pyrophyllite. X-ray diffraction patterns cannot be obtained from single clay particles, as these are too small to be handled. The mineral pyrophyllite can be obtained in pieces big enough to give X-ray patterns and

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as it is structurally related to 2 : 1 minerals such as montmorillonite and beidellite, its structure is being studied.

X-ray diffraction photographs of a small piece of pyrophyllite from Graves Mount, Georgia, show a pattern less simple than that of a single crystal. This seems to be typical of pyrophyllite whatever the origin of the sample. Some spots on the film are sharp, but others are more diffuse and joined together by weak streaks; a third series of reflections is so streaked that the spots run together. The positions of all the spots show the unit cell to be $a = 5{\cdot}16$, $b = 8{\cdot}90$, $c = 18{\cdot}64$ Å, $\beta = 100° 45'$; the sharp spots alone give a sub-cell $a = 5{\cdot}16$, $b = 2{\cdot}97$, $c = 9{\cdot}32$ Å, $\beta = 100° 45'$. Even the sharp spots are spread a little along Debye–Scherrer arcs, as they would be for a stack of crystallites growing out fan-wise from a point.

Hendricks (*Z. Kristallogr.* (1938), **99**, 264–274) showed that the intensities of the sharp spots on his very similar photographs of pyrophyllite agreed roughly with those calculated from a structure proposed by Gruner; however, the intensities of the second set of more diffuse spots were not at all those expected for this model, and Hendricks concluded that there must therefore be random displacements of whole sheets of the structure by sixths of the cell edge along the *b* axis.

In Gruner's structure an edge of the tetrahedron of the oxygen atoms around a silicon atom is parallel to the *a* axis of the crystal. Crystal structures of other layer silicates, determined since 1954, have shown that in these minerals the tetrahedra are twisted about the *c* axis until the edge is at an angle of 7–14° to the *a* axis. The intensities of the sharp spots on our photographs, measured with a Joyce, Loebl photometer, were compared with those calculated for parallel and twisted tetrahedra. The agreement is better for the twisted model. Electron density maps, calculated from the intensities of the sharp spots, show that, within the sub-cell of symmetry $C2/m$, there are two sites of equal probability for each of the atoms known to be present.

The positions of the atoms are being refined by difference Fourier syntheses, and it is hoped to distribute each atom over the 12 possible sites in the full cell in a way that explains the presence of the other spots and streaks in the X-ray diffraction pattern. (Brown and Rayner)

Physical Chemistry

Clay soils. Further studies on the properties of clay soils (see *Rep. Rothamst. exp. Sta.* for 1961) were concerned with soil-water curves. We have shown that the properties of remoulded soils depend more on the clay content than on any other factor, although natural soils of similar clay content may differ greatly. The soil suction curve expresses this difference as the additional quantity of water retained at a certain pF when a soil is remoulded. When cycled between pF 1 and 3 a remoulded soil slowly recovers its original suction curve. Soils may be thus compared under closely controlled conditions by pretreating the soil (e.g., by sieving) and remoulding, and then cycling on a tension plate.

Clay minerals. When large organic cations (e.g., dodecylammonium) are introduced into montmorillonite the mineral swells considerably in a

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range of organic liquids. The swelling in nitrobenzene, pyridine and quinoline was studied by low-angle X-ray scattering and birefringence measurements. In nitrobenzene the scattering approximated to that from single 10-Å layers, and ordered complexes were formed in pyridine and quinoline. Birefringence measurements showed that in nitrobenzene and pyridine the interlayer liquid was anisotropic; the former system is of interest, as it has common features with the swelling of Na-montmorillonite in water.

The specific heats of the montmorillonite–water system are being determined to gain more insight into the nature of interstitial water. (Greene-Kelly)

Spectrochemistry

Work continued on the location of trace elements in soils, using extraction with acid ammonium oxalate in ultra-violet light to remove free oxides before fractionating the soil into sand, silt and clay. The influence of pH on the process was studied, using two brown earths. At pH 3·3, the value normally employed, nearly all the extractable material was removed in one treatment, and the extract contained little silica. Less material was extracted at pH 7·0, but the composition of the extract was similar to that obtained at pH 3·3. Oxalic acid of the same molarity (pH 1·25) extracted more material and a much higher proportion of silica. It seems, therefore, that the bulk of the free oxides, with which large proportions of some of the trace elements are associated, are removed at pH 3·3 without causing serious attack on silicates.

Under these conditions the extracted material consisted of about two-thirds Fe_2O_3 and one-third Al_2O_3. This amount of aluminium is too great to have come only from exchange sites, and as less than 1% of the silica in the soil was dissolved, it is unlikely that the aluminium came from the silicate minerals. Gibbsite and boehmite were almost insoluble in the oxalate reagent, and so it is unlikely that solution of free alumina could account for the high proportion of aluminium extracted. Norrish and Taylor (*J. Soil Sci.* (1961), **12**, 294–306) showed that soil goethites contain aluminium isomorphously replacing iron. It therefore seems probable that the aluminium and some of the trace elements extracted by oxalate are incorporated with ferric oxide in the soil.

Comparison of surface and subsoil horizons showed that in the more highly organic surface soils the clay fractions and extracted material were richer in Co, Cu, Mn and Pb. This suggests that appreciable proportions of these elements were associated with organic matter. (Le Riche and Weir)

Potatoes and red beet from the plots receiving sewage sludge in the Woburn Market Garden Experiment were analysed for the Field Experiments Section, in connection with their study of the residual effects of the large amounts of Cr, Cu, Ni and Zn contained in sewage sludge.

Eighteen soils were analysed for "available" B, Cu, Mn, Mo and Zn at the request of the Malkerns Research Station, Swaziland. Crop responses to Mo and Zn had been obtained on some of these soils, and B and Cu

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deficiencies were suspected on others. It seems possible that the high Mn content of some of the soils may inhibit uptake of other elements.

Three soil profiles were analysed, for 12 elements, to provide information on monoliths sent to the exhibition of world soils at the International Soil Science Conference in New Zealand, 1962.

Suspected Pb toxicity in sitka spruce from Tarenig Forest (Forestry Commission) was not confirmed.

Thirty to forty other samples, including many different types of material, were examined for workers at Rothamsted and elsewhere. (Burnett)

Soil Chemistry

Mechanism of podzolisation. The simulation of podzolisation by the action of sterile aqueous extracts of various tree leaves on columns of ferruginous sand was reported in *Rep. Rothamst. exp. Sta.* for 1955. This work was taken up again in an attempt to learn more about the nature of the organic compounds involved. When a leaf extract is added sufficiently slowly to a ferruginous column most of the colouring matter is removed from the extract. With several species about 99% of the polyphenols were retained in the column, and the pH of the extracts increased from about 5 to above 8. Because of the alkaline reaction of the effluents volatile basic nitrogen compounds are lost, and it remains to be seen whether this effect is solely responsible for the decreased total nitrogen contents of the effluents.

Such experiments are time-consuming, taking 2–3 months for the preparation of 100 ml or so of effluent. More can be obtained in a few weeks if the extract is first allowed to react with ferric oxide for several days; the blue-black, iron-rich solution thus obtained can then be passed comparatively quickly (*c.* 1 litre in 24 hours) through a column of ferric oxide-coated kieselguhr to give a pale yellow and almost iron-free solution. In a typical experiment the iron content of the reaction solution was decreased from 65 to 4 mg/litre.

Coloured material is retained in the upper part of the column, blackening the ferric oxide, and cannot be removed by washing with water. It seems reasonable to suppose that it is this sorption of iron and organic matter on ferric oxide that is responsible for the redeposition of iron and organic matter in the B horizon of a podzol. (Bloomfield)

Waterlogged soils. The reduction of sulphate and the formation of ferrous sulphide in waterlogged soils are of considerable importance, and failure to recognise that these processes are common but not invariable features of gley soils has led to considerable confusion in the literature of these soils.

Sulphate reduction is being studied as part of the department's work on waterlogged soils. Initial difficulties in obtaining reproducible sulphate reduction in the laboratory have been overcome by the use of enrichment cultures prepared from sulphide-containing soils. Sulphate disappears rapidly after flooding, and although considerable quantities of dissolved iron are invariably present, the ferrous sulphide formed usually accounts for only half the sulphate reduced, the remaining sulphur being lost from

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the system as hydrogen sulphide. The proportion of the total sulphur immobilised as ferrous sulphide increases rapidly with increasing pH. It has been observed in Japan, and elsewhere, that the roots of rice plants growing in degraded soils containing little iron are often damaged by hydrogen sulphide, and this has been ascribed to insufficient iron to immobilise the sulphide. Our observations that relatively large amounts of hydrogen sulphide can exist in a flooded soil in the presence of excess iron suggests that this explanation may not be correct. (Bloomfield and Pruden)

Numerical Soil Classification

In collaboration with the Soil Survey of England and Wales, the numerical method used in taxonomy by Sneath (*J. gen. Microbiol.* **17**, 201–226) was applied to soils. Data from soil surveyors' descriptions and laboratory measurements of 91 horizons in 23 Glamorganshire soils were given numerical values and the similarity between every pair of horizons calculated by an electronic computer. Two paths were then followed; the horizons were either sorted into groups linked by a minimum degree of similarity or the degree of similarity of two soils was assessed from the similarities of their horizons, and the soils themselves were then sorted into groups. Sorting into groups at several levels of similarity makes it possible to draw a "family tree". The family trees for horizons and for soils are much alike, and both resemble the soil surveyor's classification in picking out the two groups called by the surveyors red-brown calcareous soils and brown earths. The numerical method used does not show which properties have contributed to the similarity. There is also some tendency to bring soils of the same soil series together, but this is less clear. (Rayner and Gower, Statistics Department)

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