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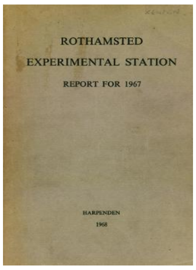
Full Table of Content



Pedology Department

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PEDOLOGY DEPARTMENT

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The Pedology Department's concern is the study of the fundamental properties of soil—its genesis and composition, and its static and dynamic behaviour. Our effort is divided between the study of the mineralogical and chemical composition of soils, clay mineralogy, the weathering of soil minerals, the physical properties of soil in relation to its composition, the dynamics of soil organic matter and the role of organic matter as an agent of soil-forming processes.

Mineralogy

Alteration of trioctahedral micas. Changes in the chemical composition of micas caused by the removal of potassium implied that their structural hydrogen content changed (*Rothamsted Report* for 1966, p. 63). Because this conclusion is important in interpreting the chemical composition and properties of alumino-silicate clays it was necessary that it should be confirmed, if possible by direct analysis, and much time was spent developing a procedure to determine structural hydrogen as rigorously as possible.

As hydrated cations are introduced into mica during its alteration, the analytical procedure must distinguish between structural hydrogen (that is, hydrogen present as hydroxyl groups in the alumino-silicate layers) and hydrogen present as water between the layers; for many years this has been a fundamental difficulty in clay mineral analysis. Usually the two forms of hydrogen are distinguished by thermal analysis: hydration water is often evolved at much lower temperatures than water formed during dehydroxylation. In principle, this provides a method for determining both forms of hydrogen; in practice, the lowest temperature at which all hydration water is removed varies greatly, depending on chemical composition, particle size and the experimental conditions. Also, because water is produced from both thermal dehydration and thermal dehydroxylation, without further evidence it is impossible to say from which reaction the water originates. These problems are particularly acute with new materials, like altered micas, for which independent evidence is lacking. In the procedure we have developed this evidence is obtained by infra-red analysis.

The angular deformation of the water molecule, a vibration mode of two hydrogen atoms bonded to an oxygen atom, absorbs in the region of 1600–1650 cm^{-1}, so that absorption in this region is a specific indication that the matrix contains water, as distinct from hydroxyl. With Drs. V. C. Farmer and J. D. Russell of the Macaulay Institute, the infra-red spectra of self-supporting films of altered micas were recorded after heating *in vacuo* at temperatures up to 750° C. The temperature at which the absorption at 1650 cm^{-1} decreased to background was the point at which all hydration water was driven off.

Two phlogopites were altered with sodium tetraphenylboron until 95% of the potassium was removed, and the products analysed for major elements by the usual methods. Infra-red evidence shows that the alteration product of one mica must be heated to 400° C before all the hydration water is released; the corresponding temperature for the other product is 700° C. The released water was weighed after absorption on magnesium perchlorate; water evolved between the above determined temperature and 1000° C was calculated as structural hydrogen. To complete the analysis, the alteration products were analysed for fluorine: the usual Willard–Winter distillation method gave low recoveries, and a pyrohydrolytic method was developed to obtain adequate accuracy (see below).

Structural formulae of the two altered phlogopites were calculated assuming only that the structural unit contained 24(O + F). The ideal formulae for the unaltered micas contain $O_{20}(OH,F)_4$, but the formulae of their alteration products contain fewer O atoms and more than 4(OH,F), showing that the structural hydrogen contents of the micas increased during alteration. This is evidence that the alumino-silicate layers in phlogopites lose charge by protonation of structural oxygen anions, forming new hydroxyl groups. The structural formulae also showed that Al-for-Si substitution within the tetrahedral layer remains unchanged when micas are altered with tetraphenylboron, confirming a hypothesis used to calculate structural formulae when structural hydrogen analyses were not available (Newman and Brown, *Clay Min.* (1966), **6**, 297–310). (Newman)

Alteration of dioctahedral micas. Because barium is often an efficient exchanger for potassium, attempts were made to alter two muscovites using a solution containing barium tetraphenylboron and $BaCl_2$. After 18 extractions lasting about 3 weeks the muscovites were washed, examined wet by X-ray diffraction and analysed for barium. The degree of alteration was measured by the increase in barium content: the muscovites were about 6 and 11% altered, respectively. X-ray diffractometer traces of wet and dry oriented films showed only basal reflections from a 10-Å layer spacing; reflections from expanded layers were not found, even though these should have been readily observed if present at 6–11% concentration. A mixture of altered and unaltered micas gave an identical diffraction pattern, and there was no discernible splitting of the maxima.

These observations show that the structure of micas is little changed when barium exchanges for potassium, so that diffusion between the layers is hindered and alteration cannot proceed beyond the superficial regions. Barium is therefore not a useful cation for altering dioctahedral micas.

We thank P. D. Salt of the Chemistry Department for determining Ba by flame emission. (Brown and Newman)

Solution chemistry of mica alteration. Mild acidity (pH 3) increases the rate potassium is released from some micas, and work on this "pH effect" was extended to micas of widely differing composition. A wholly satisfactory explanation of all the observations cannot yet be given; no simple correlation with chemical composition or structure has yet been found, and the earlier report that biotites show a larger pH effect than phlogopites

(*Rothamsted Report* for 1966, p. 65) is now known not to be invariably true. However, micas of large pH effect often alter more easily. The mica was altered at several pH values and the products analysed chemically; neither the chemical composition nor the exchange capacity of the products depended on the pH at which the mica was altered. (Newman)

Structures of layer silicates. The complete X-ray-diffraction patterns needed to examine the three-dimensional structure were collected for two of the phlogopites being studied in the mica alteration project. For one phlogopite the data was collected by Weissenberg X-ray photography for the zero and three higher levels about two axes through the crystal. Similar photographs were taken for talc, for which a preliminary examination has been reported. The intensities of the reflections were estimated visually by comparison with a scale of spots. Averaging reflections that should be the same by symmetry gave 511 independent reflections for phlogopite and 668 for talc. The second phlogopite, with different alteration characteristics, was examined and data collected for the zero and 12 higher layers from a crystal rotated about its *b* axis, using the linear diffractometer in the Chemistry Department of Nottingham University (by the kindness of Dr. S. C. Wallwork). Two measurements were made of each of 823 independent reflections, but symmetry related reflections were not measured.

Crystal structures have been calculated from all these data, and those for the talc have been fully refined. For phlogopite the agreement between the observed and calculated intensities can be improved by allowing for absorption of X-rays in the crystals and for differences in the amount of atomic vibration in different directions, but the results should not be much altered, as the *R* factors obtained from photographic and diffractometer data were small—13·3 and 12·0% respectively. Distortion of the very soft crystals made the talc intensity data a little less accurate, but the disagreement factor, *R*, is decreased to 13·5% by using a model with anisotropic vibration parameters.

The twist of the tetrahedra in talc is 3·4°. The mean Si–O distance in the tetrahedra is 1·616, compared with a mean of 1·616 Å for all layer silicates with tetrahedra with no substitution of Al or Fe for Si. In the electron density map a density corresponding to a hydrogen atom is visible above the O of the expected OH group, in a direction perpendicular to the sheets. This is the position expected in a trioctahedral mineral. There are only a few substitutions at the trioctahedral and tetrahedral sites in this talc. Substitution alters the infra-red OH frequencies. The electron density at the expected H site in the other minerals will be examined to see if it is altered by substitution.

The first phlogopite (P6) is much harder to alter than the other (P5), and chemical analysis shows that P6 contains more fluorine, enough for $\frac{2}{3}$ occupancy of the OH/F site, whereas P5 has only enough for $\frac{1}{4}$ F. The twists of the tetrahedra are about 7·6° for P6, 8·8° for P5 and 11·0° for the ferriphlogopite (with Fe rather than Al replacing some Si in the tetrahedra) studied by Steinfink, (*Am. Miner.* (1962), **47**, 886–896). The tetrahedra site-to-oxygen distances are 1·650 for P6, 1·659 for P5 and 1·681 Å for ferriphlogopite. The potassium atoms in micas have twelve neighbours, but, as the tetrahedra twist, these are divided into six closer and six farther neighbours, the difference between the two groups increasing the greater the twist. The means of the six shorter K–O distances for these phlogopites are in the order expected from the twists: 2·974 Å for P6, 2·964 Å for P5 and 2·942 Å for Steinfink's ferriphlogopite. (Rayner)

Mixed magnesium–aluminium hydroxides. Octahedrally co-ordinated layers containing mainly aluminium and magnesium seem to play an important role in the formation of natural and synthetic clay minerals. We have therefore studied the mechanisms involved in the production of hydroxides containing octahedrally co-ordinated layers.

When solutions containing aluminium or magnesium are made alkaline gelatinous aluminium or magnesium hydroxides are precipitated; at first these are poorly crystalline, but on aging they transform into crystalline materials in which the Al or Mg ions are octahedrally co-ordinated between sheets of hydroxyls. Crystal growth seems to be inhibited by impurities trapped in the gel-like precipitates, and dialysis promotes crystallisation.

In many clays the octahedral layer contains both aluminium and magnesium ions. With Mlle M. C. Gastuche, Institut Agronomique, University of Louvain, and Professor M. M. Mortland, Department of Soil Science, Michigan State University, we have studied the effect of dialysis on precipitates formed from mixed magnesium–aluminium solutions to see whether mixed Mg–Al octahedral layers could be synthesised, and if so, the conditions controlling their formation.

Solutions prepared by mixing magnesium and aluminium chloride solutions in various proportions were brought to pH 10 with sodium hydroxide and the resultant precipitates dialysed for 1 month. Pure magnesium solutions gave brucite, and pure aluminium solutions gave a mixture of aluminium hydroxide species, bayerite with gibbsite and some nordstrandite. From mixed solutions new compounds were formed, together with brucite when the initial solution contained much magnesium, and with bayerite from aluminium-rich solutions. From initial solutions with $Mg/Mg + Al = 0·83$ to $Mg/Mg + Al = 0·67$ hydroxides were formed that contained both Mg and Al, without detectable amounts of other phases.

Two different forms of the Mg–Al hydroxides were found. They have similar but distinct X-ray powder-diffraction patterns, which resemble those reported by Feitknecht and Gerber (*Helv. chim. Acta* (1942), **25**, 131) for mixed Mg–Al hydroxides and by Roy, Roy and Osborn (*Am. J. Sci.* (1953), **251**, 337) for natural and synthetic hydrotalcite (a mixed magnesium–aluminium hydroxycarbonate). The two forms are characterised by their basal spacings, 7·92 Å for the compound obtained from solutions with $Mg/(Mg + Al)$ about 0·80, and 7·60 Å from solutions with $Mg/Mg + Al$ about 0·70; solutions of intermediate composition produced mixtures. Chemical analysis of the two forms showed that both contained essential CO_2, and that the 7·92 Å material contained more magnesium and less aluminium than the 7·60 Å material.

The X-ray powder patterns have both sharp and diffuse reflections. The basal spacings are all sharp. The presence of both sharp and diffuse non-basal reflections indicate a partially disordered layer structure. The features of the X-ray patterns can be explained if the structure consists of two-dimensionally regular hexagonal unit layers, with $a = 3{\cdot}048$ Å, and layer thickness = 7·60 Å for the aluminium-rich compound, and $a = 3{\cdot}072$ Å, layer thickness = 7·92 Å for the aluminium-poor compound. These unit layers are superimposed with considerable stacking disorder but with a tendency to form two-layer and three-layer sequences.

The contents of the unit layer were calculated from its dimensions, and the chemical analysis, assuming a density of 2·00 for both forms. The results indicate: (i) that the unit layer contains one metal cation, i.e. $Mg + Al = 1$; (ii) that the unit layer contains 3 oxygen atoms; and (iii) that the difference in the Mg:Al ratio is caused by replacement of Mg by Al and that this compositional change is accompanied by changes in the dimensions of the unit layer.

These observations allow a structure to be proposed for the compounds. The unit layer consists of three sheets of oxygens (or hydroxyls). Two of these sheets are held together by the cations and form trioctahedral layers similar to those in brucite, but having some Mg replaced by Al. This substitution leads to a positive charge on the brucite-like layer, which is balanced by a 3-Å-thick interlayer sheet containing CO_3 groups that lie parallel to the hydroxyl sheets. In addition to CO_3, water molecules, which are easily removed by heating, are taken into the interlayer sheets, ideally enough to fill the sites left vacant, although in practice this sheet may not be entirely filled.

The proposed structure differs from those accepted for compounds of this kind. Previously the trivalent cations were thought to be located in a disordered interlayer sheet and the brucite-like layer to contain divalent cations only. This structure is unsatisfactory. For example, positions are not given for the trivalent cations, and it is difficult to suggest structurally reasonable sites for them; also differences in structural dimensions in synthetic materials with different Mg:Al ratios, and between similar natural materials, are not explained. The structure we propose resolves these difficulties and is likely to apply to other synthetic and natural materials. These include the minerals of the pyroaurite group, for which no structure has been given before; the compound that has been given the ideal formula $4CaO.Al_2O_3.13H_2O$ and the related mineral hydrocalumite; a recently described nickeliferous magnesium hydroxide mineral and many synthetic hydroxides that contain both di- and trivalent cations. (G. Brown with Mlle M. C. Gastuche and Professor M. M. Mortland)

The morphology of Na-montmorillonite particles. Work on montmorillonites previously done independently by Professor H. E. Roberson in the United States, and by Weir in this department, was extended by making an electron-microscopic study of montmorillonite particles from four bentonites. Two samples from Wyoming, one from Chambers, Arizona, and one from Fayette County, Texas, were saturated with Na-ions and divided into four different size-fractions (0·5–1·0 μ, 0·1–0·5 μ, 0·05–0·1 μ and

$<0{\cdot}05\ \mu$ e.s.d.) by repeated dispersion and centrifugation. Electron microscopy showed that the finest fractions consist predominantly of very thin separate flakes, whereas all the coarser fractions, totalling 80% or more of the samples, are composed of groups of flakes termed micro-aggregates. Although these micro-aggregates swell to give large interlayer spacings, they are stable in dilute suspension, and can be disrupted into separate flakes only by ultrasonic agitation. The chemical compositions of different fractions of the same sample are very similar; thus differences in dispersion behaviour between separate flakes and those in micro-aggregates cannot be attributed to differences in interlayer charge or ionic substitution. The stability of micro-aggregates is thought to result from the interleaving of their component flakes during crystal growth, and unless the flakes themselves are ruptured by ultrasonic vibration, this prevents their complete separation in dilute suspensions. (Weir and Roberson)

The clay mineralogy of Broadbalk soils. As part of a study of the mineralogy of Broadbalk soils, the clay fractions of twelve samples of surface soils (0–9 in.), taken by the Chemistry Department in 1965 from sections Ia, II, III and IV of Plots 3 (Nil), 10 (N) and 13 (NPK), were examined chemically and by X-ray diffraction. Ten-gram sub-samples were treated to remove calcium carbonate and organic matter, then dispersed and separated into coarse sand, fine sand, silt and clay. The mineralogical composition of the clay fractions was determined by X-ray diffractometry of Mg-saturated samples and the amounts of non-exchangeable K_2O in the clay fractions by flame photometry.

TABLE 1

Particle-size distribution of Broadbalk soils

(% weights of fractions on a carbonate- and organic matter-free, air dry basis)

	Section			
	Ia	II	III	IV
Plot 3				
Coarse sand >250 μ	5·2	4·2	4·9	6·1
Fine sand 250–50 μ	14·5	12·7	15·1	16·5
Silt 50–2 μ	53·4	61·0	57·4	54·8
Clay <2 μ	26·8	22·0	22·5	22·6
Plot 10				
Coarse sand >250 μ	4·0	3·7	4·7	5·6
Fine sand 250–50 μ	14·9	15·5	14·8	14·0
Silt 50–2 μ	48·1	57·6	54·1	52·7
Clay <2 μ	33·0	23·3	27·4	27·7
Plot 13				
Coarse sand >250 μ	4·5	5·1	6·1	6·0
Fine sand 250–50 μ	17·4	16·7	14·7	14·4
Silt 50–2 μ	48·5	55·6	55·2	51·4
Clay <2 μ	29·6	22·7	24·0	28·3

The clay fractions contain approximately 45% expanding minerals, 25% mica, 20% kaolinite, and small amounts of chlorite, quartz, felspar, lepidocrocite and goethite. The expanding minerals consist of various proportions of vermiculite and montmorillonite; they are typical of expanding minerals found in many soil clays in that they expand less regularly with ethylene glycol, and collapse less completely on heating, than do well-crystallised specimens of montmorillonite and vermiculite.

Table 2 gives the percentage clay in the soil and percentage non-exchangeable K_2O in the clay for each of the analysed plot sections, together with plot and section means.

TABLE 2

% clay in the soil and % non-exchangeable K_2O in the clay fraction of Broadbalk soils

	Section								Plot means	
	Ia		II		III		IV			
	Clay	K_2O	Clay	K_2O	Clay	K_2O	Clay	K_2O	Clay	K_2O
Plot 3	26·8	1·74	22·0	2·02	22·5	1·94	22·6	1·81	23·5	1·88
Plot 10	33·0	1·68	23·3	1·97	27·4	1·78	27·7	1·53	27·9	1·74
Plot 13	29·6	1·77	22·7	1·92	24·0	1·91	28·3	1·86	26·2	1·87
Section means	29·8	1·73	22·7	1·97	24·6	1·88	26·2	1·73	25·9	1·83

The differences in clay contents between plots and between sections are significantly larger at the 5% testing level than the residual variation. For the non-exchangeable K content of the clay, the difference between sections is significantly larger than the residual difference at the 5% level, whereas the variation between plots is not. The composition of the surface soils of Broadbalk is thus very variable. This variability shows in the K content of the clay and masks any effect that different K fertiliser treatments may have had on the mineralogy of the soils. Such effects may be looked for by comparing samples taken from the same part of particular plots in 1965 with those taken very much earlier. Samples from 1865, 1880 and 1893 exist, and if the areas sampled then correspond closely with the present plot sections, samples taken in 1965 from selected plots will be compared with earlier samplings. (Weir and Ormerod)

Mineralogy of the Eocene deposits of North-east Kent. In soil profiles developed in layered composite parent materials the mineralogical changes caused by weathering and other pedological processes are often obscured by differences in the original composition of the various deposits involved. Changes in mineral composition and particle-size distribution caused by weathering and eluviation are therefore evaluated most easily in profiles developed in homogeneous parent materials. Petrographic studies of many profiles in South-east England, such as those containing Clay-with-flints horizons (*Rothamsted Report* for 1964, p. 84), show that far-travelled wind-blown silt (loess) is a common constituent of surface soil horizons. The weathering of loess is therefore probably an important process by which some nutrients in these soils (e.g. K) become available to plants. Many of the "brickearth" soils in Kent are developed in thick deposits of loess-like material, and should be suitable for studying the effects of weathering on this important soil parent material. South-east England lay within the large European area of late Quaternary loess deposition, but not all the Kentish brickearths are composed exclusively of far-travelled silt. In particular, many of them are thought to contain variable amounts of sediment carried by wind or water from local Eocene deposits. The search for a soil profile developed in uncontaminated loess therefore involves recognising derived Eocene material. Consequently, we have studied the mineralogical composition of samples from all the major sub-divisions of the Eocene beds exposed in North-east Kent.

Twenty-three samples were separated into sand ($<50\ \mu$), silt (50–20 μ, 20–5 μ and 5–2 μ) and clay ($<2\ \mu$) fractions. The sands and coarse and medium silts were divided into light and heavy fractions with bromoform and analysed with a petrological microscope. The clay, fine silt and medium silt fractions were analysed by X-ray diffractometry and supplementary chemical determinations.

The Thanet Beds, which are the lowest major subdivision of the Eocene deposits in Kent, are 60–110 ft thick and very variable in colour and texture. They are separated from the underlying Chalk by the Bullhead Bed (2–4 in.), which contains flint nodules in a glauconitic sandy clay matrix. The lowest 1–2 ft of the Thanet Beds are also strongly glauconitic, and at some localities (Pegwell Bay near Ramsgate and Upper Upnor near Rochester) the fine and medium silt fractions from this horizon contain abundant clinoptilolite. This mineral also occurs in the Bullhead Bed at Upnor, but not in comparable horizons at Mockbeggar near Faversham, approximately half-way between Upnor and Pegwell Bay. The detrital sand and coarse silt fractions from all horizons of the Thanet Beds are composed mainly of quartz, flint fragments and alkali felspar. Heavy mineral suites from these size fractions contain mainly iron ores, zircon, garnet, epidote, tourmaline, staurolite, kyanite, rutile and biotite. The clay fractions contain 50–90% montmorillonite and small amounts of mica, but no kaolinite. Vermiculite and interstratified mica/chlorite occur in the clay from the Bullhead Bed at Mockbeggar, and chlorite in clay from a blue-grey horizon approximately 40 ft below the top of the Thanet Beds at Bishopstone Point near Herne Bay. The fine silt fractions from the Bullhead Bed at Upper Upnor, the basal Thanet Beds at Mockbeggar and the topmost Thanet Beds at Lower Upnor all contain jarosite.

The Woolwich Beds overlie the Thanet Beds, and in East Kent comprise 25–40 ft of marine sands, which are mineralogically similar to the Thanet Beds. In north-west Kent the succession is thicker and essentially non-marine; for example, at Lower Upnor the Woolwich Beds consist of 54 ft of mainly estuarine sediments. The sand and coarse silt fractions from these contain a more restricted heavy mineral suite than the equivalent fractions from the Woolwich Beds in East Kent. This suite resembles that of the Reading Beds, which are the lateral equivalent of the Woolwich Beds in areas west of London. Clay fractions from the Woolwich Beds at Upnor also resemble clays from the Reading Beds in that they contain much well-crystallised kaolinite.

The succeeding Oldhaven Beds consist of 14–24 ft of marine sands with beds of black flint pebbles near the base. Their detrital sand fractions are mineralogically similar to those of the Thanet Beds, but the coarse silts are characterised by an unusual abundance (9%) of zircon. The clay fractions are composed of montmorillonite with small amounts of mica and kaolinite.

The London Clay is approximately 450 ft thick, and consists of blue-grey and brown silty clays that lack appreciable quantities of sand except in the lowest 1–2 ft (the London Clay Basement Bed) and the highest 20–30 ft. The detrital sand and coarse silt minerals in the lower parts are similar to those of the underlying Oldhaven and Thanet Beds, except for the addition of chlorite, muscovite and deep-green biotite. However, in the higher beds of the London Clay the heavy mineral assemblages are like those in the overlying Claygate and Bagshot Beds; there is less zircon, kyanite, staurolite and tourmaline than in the lower parts, but much more garnet, epidote and amphiboles. The main non-detrital sand and silt minerals are calcite, pyrites and, at some horizons, siderite. The Basement Bed and the Oldhaven Beds have similar clay fractions, but clays from all other parts of the London Clay succession contain 40–60% montmorillonite, 20–30% mica, 10–15% kaolinite and 5–10% chlorite.

The mineralogical effects of weathering can often be traced to unusually great depths in the London Clay. Most of this weathering probably occurred during late Tertiary or early Quaternary times, because such weathering profiles occur as commonly beneath thick covers of Quaternary deposits as at the surface. The main weathering processes were oxidation of pyrites and leaching of the clay by sulphuric acid produced during this oxidation. The alteration of pyrites to iron oxides changed the colour from dark blue-grey to brown throughout the weathered parts of the deposit. Reaction between the sulphuric acid and carbonate in the clay produced gypsum, which forms large euhedral crystals both within the clay and locally in the sands of the underlying Oldhaven Beds. The deep-green biotite in the sand and coarse silt fractions is also altered in weathered parts of the London Clay. The weathered biotite is pale yellow-brown, and the basal sections shown by cleavage flakes are slightly more pleochroic and more birefringent than those of the unaltered mica. The optic axial angle is also slightly greater in the weathered biotite than the unweathered. Most of the altered flakes are almost uniformly yellow-brown throughout, but some are only partly weathered and show either irregular brown patches or well-marked brown birefringent margins around green unaltered cores. (Catt and Weir)

Clay physics

Specific surface areas of clays. The technique for preparing clay samples for external specific surface-area measurements was studied in more detail. Clays prepared by solvent washing rapidly adsorb nitrogen at —196° C, and specific surface areas calculated from the isotherms represent the area of the individual crystals, determined only by the size of the ultimate particles. The method showed that, contrary to the results of some workers, the external specific surface area of montmorillonites is determined only by the particle size of the fraction, and that it is not affected by later treatment, provided that care is taken to avoid comminution. It is particularly interesting that the specific surface areas of Na-saturated montmorillonites were unchanged when dried after expanding and dispersing in water, despite considerable differences in procedure. This suggests that the clay crystals preserve their identity when swollen.

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Pore-size distribution in clays and cohesive soils. Measurements of pore-size distribution provide useful information on the structure of clay aggregates. We have therefore adapted our Sartorius vacuum balance to measure nitrogen adsorption up to high relative pressures. We use thermocouples and a nitrogen-vapour-pressure thermometer to measure the temperature of the liquid nitrogen bath, and have established the conditions under which the sample bucket actually reaches the bath temperature. The gravimetric method is more accurate than volumetric methods at high relative pressures, and needs only a very small sample. The adsorption must be measured under conditions of constant pressure because porous adsorbents exhibit hysteresis; the large ballast volume first used was not entirely adequate, and a sensitive manostat of new design was developed, which has proved very satisfactory. Nitrogen isotherms measured on clays dried from various solvents show that the pore-size distribution depends greatly on the solvent used. Moreover, clay aggregates can be prepared that do not exhibit isotherm hysteresis, and so must be nearly monodisperse. Hysteresis reappears when these aggregates are compressed because small pores form that empty and fill by capillary condensation at different relative pressures. Excessive compression can cause an apparent loss of surface area because the nitrogen molecules at low temperatures have too little energy to penetrate the smallest pores. A similar phenomenon has been reported with carbons.

The adsorption of carbon tetrachloride was used with success for routine measurements of pore volumes of cohesive soils. Compressing soil progressively diminishes the pore volume of large pores, but not of pores smaller than 300 Å; this shows that the pore volume of the smaller pores is a function of clay packing, and that it is not readily influenced by superficial factors. Pore volumes thus measured on different soils of about the same clay content differ considerably, and the differences are not related to either their specific surface area or the type of the predominant clay mineral. Simple considerations suggest that the pore volumes are determined by such factors as the degree of mutual orientation of clay crystals, and thus they could provide a useful index of the development of structure in cohesive soils.

Interfacial studies. Soil-water potential can be expressed as the sum of three components—the gravitational, osmotic and capillary potentials. The gravitional potential can be readily calculated, but the osmotic and capillary potentials are difficult to separate. The capillary potential was measured experimentally by replacing the air–water interface on saturated soil samples by an interface of water with a suitable immiscible liquid, so that the interfacial tension is very small (less than 3 dynes/cm). As expected, the water potential of saturated glass beads is predominantly determined by capillary effects, whereas the water potential of a saturated montmorillonitic clay soil is predominantly determined by osmotic effects. Micaceous clay soils of small specific surface area showed intermediate behaviour.

In unsaturated systems of small osmotic water potentials the interfacial area can be calculated from the suction–moisture content curve and can also be directly measured from the heats of immersion in water. With non-expanding materials the calculated and observed areas agreed substantially down to a relative vapour pressure of 0·5. Below 0·5 the observed areas were progressively less than the calculated values, presumably because osmotic effects became increasingly important. (Greene-Kelly and Gallavan)

Geochemistry

Geochemistry of Lias shales. The technique described in the *Rothamsted Report* for 1965 (p. 75) for concentrating trace elements on an anion-exchange resin was applied to the determination of total Ag, Mo, Pb, Sn and Zn in Upper Lias shales from Yorkshire (*Rothamsted Report* for 1966, p. 70), in which the concentrations of these elements are usually less than the spectrochemical detection limits. The particular advantage of the technique is that it permits these elements to be separated from the preponderating quantities of Al_2O_3, Fe_2O_3 and SiO_2, and under the conditions used gives an enrichment of about fifty-fold. With 1-g samples the detection limits are: Ag, 0·01; Mo, 0·1; Pb and Sn, 0·5; Zn, 20 ppm.

Ag (range 0·01–0·38 ppm) is strongly correlated with organic C and with Cu in excess of 20–30 ppm, which itself seems to be organically accumulated.

Mo (range 0·13–20 ppm) is much less enriched than in the lower Lias of southern England, where amounts up to 250 ppm are associated with organic matter (*Rothamsted Report* for 1957, p. 72). A weaker correlation with organic C in the Yorkshire shales results from less enrichment of Mo by organic matter, so that most of the Mo is associated with other components of the shales.

Pb (range 11–140 ppm) is weakly correlated with Fe_2O_3, S and organic C; up to 30% of the Pb in some shales was extracted by H_2O_2/ammonium oxalate (*Rothamsted Report* for 1966, p. 71), indicating that about 30% of the Pb is in non-detrital form and 70% probably in detrital minerals.

Sn (range 1·7–4·2 ppm) is positively correlated with Al_2O_3 and K and negatively correlated with Fe_2O_3, S and organic C, showing it to be present mainly in detrital minerals.

Zn (range 52–250 ppm). Carbonate-free shales contain about 80 ppm Zn, and amounts in excess of this are related to the $CaCO_3$ and organic C contents. About 50–80 ppm of the Zn therefore probably resides in detrital minerals, the remainder being largely non-detrital. (Le Riche)

Soil chemistry

Chemical tests for potentially available nitrogen in soil. Some new tests for mineralisable nitrogen in soils were compared with the $Ba(OH)_2$ test described in the *Rothamsted Report* for 1963 (p. 55). All tests were done on a heterogeneous group of 14 soils of known nitrogen-releasing capacity (Gasser, J. K. R., *J. Sci. Fd Agric.* (1961), **12**, 562). Table 3 shows the results. The best correlation with nitrogen-releasing capacity was given by $NaHCO_3$-extractable "glucose", i.e. the extracted material that reacted with anthrone, expressed as the glucose equivalent. The next best correlations were with Ba(OH)$_2$-extractable "glucose" and hot-water-extractable "glucose". These "glucose" determinations are suitable for automated analyses and merit more extensive testing. No chemical test gave as close a correlation with uptake of nitrogen by plants as did the nitrogen mineralised on incubating 21 days at 25° C (Δ mineral N).

TABLE 3

Correlation coefficients between some chemical measurements and release of nitrogen by soil, as measured either by uptake of nitrogen by ryegrass in pot experiments, or by Δ mineral nitrogen

Chemical measurement	Δ mineral N	Uptake of N by ryegrass
% N	0·46	0·34
Δ mineral N	—	0·84
Ba(OH)$_2$ extracted non-NO$_3$ N	0·57	0·47
Ba(OH)$_2$ extracted "glucose"	0·78	0·70
Boiling water extracted N (*a*)	0·62	0·65
Boiling water extracted "glucose"	0·70	0·70
NaHCO$_3$ extracted N (*b*)	0·79	0·70
NaHCO$_3$ extracted "glucose"	0·84	0·77
NH$_4$ N released by KMnO$_4$ (*c*)	0·52	0·28
NH$_4$ N released by Ca(OH)$_2$ (*d*)	0·76	0·67

(*a*) Keeney, D. R. & Bremner, J. M. (1966) *Agron. J.* **58**, 498.
(*b*) McLean, A. A. (1964) *Nature, Lond.*, **203**, 1307.
(*c*) Subbiah, B. V. & Asija G. L. (1956) *Curr. Sci.* **25**, 259.
(*d*) Prasad, R. (1965) *Pl. Soil* **23**, 261.

The effects were measured of prolonged air-dry storage on Δ mineral N and on "glucose" extracted by Ba(OH)$_2$. When four air-dry soils were stored for 3½ years the largest increase in Δ mineral N was 80%, the smallest 20%. Changes in extractable "glucose" during this period were not measurable, suggesting that for the purpose of this test air-dry soils can safely be stored before testing.

Decomposition of plant material in the field. An experiment was started in 1962 on the decomposition of ryegrass, uniformly labelled with carbon-14, in soils of differing pH values, organic-matter content and clay content (*Rothamsted Report* for 1963, p. 67). Table 4 gives the amounts of plant carbon retained in the soil after exposure in the field for up to 5 years. The main conclusions are as follows:

TABLE 4

Decomposition of labelled ryegrass in soil

					% ryegrass carbon retained after			
Soil No	pH	% clay	Plant addition*	Treatment	0·5 year	1 year†	2 years	5 years
1	8·1	18	Tops	Bare	33·0	31·0	23·4	17·2
2	7·8	18	,,	,,	32·6	32·4	25·8	18·3
3	6·9	20	,,	,,	32·6	31·3	24·6	18·7
4	4·8	21	,,	,,	32·3	31·3	25·9	20·0
5	3·7	21	,,	,,	45·7	42·4	30·1	20·1
6	6·2	8	,,	,,	28·0	26·7	21·2	15·1
7	3·7	5	,,	,,	41·4	35·7	25·8	16·8
8	7·1	19	Roots	,,	31·8	27·9	24·4	20·8
8	7·1	19	,,	Under grass	40·5	38·5	—	30·7

* 0·125% plant carbon (labelled) added to each soil. † L.S.D. (5%) = 2·8.

1. Although in the early stages decomposition was slower in the very acid soils 5 and 7, after 5 years there was little difference between the extent of decomposition in these and more nearly neutral soils of similar clay content.

2. Compared with soil 6 (8% clay), slightly less labelled carbon was lost from soils 1, 2 and 3, all of which contained nearly 20% clay. The acid sandy soil 7 (5% clay) also retained slightly less plant carbon than the acid soil 5 (21% clay). These differences persisted throughout the experiment.

3. Throughout the whole of the experiment, significantly more labelled plant carbon was retained in soil growing grass than in soil kept bare. In some way, growing grass restricts decomposition of the labelled plant residues that were initially incorporated in the soil.

Radio-carbon dating of soil organic matter. Initial measurements of natural and bomb-derived radio-carbon in soil show that the mean age of the organic matter in soil from the unmanured plot of the Broadbalk continuous wheat experiment is 1385 ± 140 years. The soil sample was taken in 1881, to a depth of 9 in., and contained no coal or charcoal. This soil therefore contains organic matter at least 10 times older than the mean ages previously calculated from measurements of the annual CO_2 flux or from measurements of the rate of accumulation of organic matter in the soil. In both these calculations it was assumed that all fractions of the soil organic matter are equally resistant to mineralisation, an assumption that is now shown to be untenable. Many more radio-carbon measurements are required before reaching final conclusions, but it now seems likely that even in temperate climates, and where decomposition is not restricted by adverse conditions of aeration, pH or by deficiency in microbial nutrients, soils can contain very resistant organic fractions. (Jenkinson)

Release of nitrogen by partially sterilised soil. A light sandy soil (0·089% N) from a site under continuous cereals (Lansome field) was exposed to either a sterilizing dose of gamma-rays (2·5 megarads), to methyl bromide (1000 ppm for 72 hours), to formaldehyde (1000 ppm for 72 hours) or left untreated. Nitrogen was mineralised two to three times faster in the treated than in the untreated soil. Spring wheat and ryegrass were grown in the soils after methyl bromide and formaldehyde had been allowed to escape: Table 5 gives the dry-matter production and nitrogen uptake. The irradiated soil produced most dry matter, whether or not fertiliser nitrogen was given. Without fertiliser nitrogen, the methyl bromide and formaldehyde treatments increased production of dry matter by wheat and ryegrass to almost the same extent. However, with the largest application of fertiliser nitrogen given, neither methyl bromide nor formaldehyde increased the amount of dry matter produced by ryegrass above that of the control: with wheat these treatments decreased dry-matter production. Nitrogen uptake was almost the same for both ryegrass and wheat, and was linear over the whole range of fertiliser dressings. In this experiment the increase in yield from partial sterilisation was caused by the additional soil nitrogen mineralised: neither with wheat nor with ryegrass was there any indication that the additional growth following partial sterilisation was the result of control of soil-borne pathogens. Inoculation of the treated soil with untreated soil did not alter either dry-matter production or uptake of nitrogen.

TABLE 5

Production of dry matter and uptake of nitrogen by wheat and ryegrass grown in partially sterilised soil

Treatment	Dry matter in roots and tops (g/pot)			Nitrogen in roots and tops (g/pot)		
	No*	N_1†	N_2‡	No	N_1	N_2
			Ryegrass			
None	3·0	13·8	17·6	0·031	0·186	0·337
Methyl bromide	5·2	14·8	17·9	0·059	0·212	0·369
Formaldehyde	5·0	14·8	17·0	0·053	0·218	0·390
Irradiation	7·1	16·5	20·2	0·075	0·221	0·393
L.S.D. (5%)		0·88			0·015	
			Wheat			
None	3·0	10·2	14·0	0·034	0·174	0·323
Methyl bromide	3·9	9·7	11·8	0·065	0·223	0·365
Formaldehyde	4·4	11·2	12·7	0·061	0·217	0·372
Irradiation	5·5	13·1	14·7	0·079	0·239	0·388
L.S.D. (5%)		1·23			0·013	

* No fertiliser nitrogen.
† 0·177 g nitrogen applied (as $Ca(NO_3)_2$) per pot.
‡ 0·354 g nitrogen applied (as $Ca(NO_3)_2$) per pot.

The adverse effect of methyl bromide or formaldehyde on wheat given the largest amount of fertiliser nitrogen was almost certainly caused by non-volatile degradation products of these chemicals remaining in the treated soil. The soil that had been treated with methyl bromide contained 121 ppm bromine, determined by X-ray fluorescence spectroscopy (see below); all the residual bromine was removed by leaching with N-K_2SO_4 solution, and so was presumably retained in the soil as Br^-. (Jenkinson, with Nowakowski and Mitchell, Chemistry Department)

Sulphate reduction in waterlogged soil. Despite the presence of considerable excess iron, only part of the H_2S formed by reduction of sulphate is fixed as FeS when top and subsoil from the Rothamsted farm are incubated anaerobically with plant material and sodium sulphate. The $FeS:H_2S$ ratio is increased by raising the pH of the system, and by increasing the proportion of soil in the reaction mixture, i.e. by increasing the $Fe_2O_3:SO_4$ ratio, but under the most favourable of these conditions considerable H_2S is still lost. Very little H_2S escapes if the sulphate is added as $FeSO_4$, or if a reactive form of Fe_2O_3 is added. With the Rothamsted soil loss of H_2S from the system is reduced very considerably by aerating the supernatant liquid to simulate a lowland rice soil profile. (Bloomfield and Pruden)

Fixation of trace elements by soil organic matter. In studying interactions between soil organic matter and trace elements, plant material was composted aerobically with the carbonates, or basic carbonates, of Mn, Cu, Ni, Co, Zn and Pb under conditions permitting soluble matter to diffuse out of the system. Samples taken after incubating for 7 and 17 months at 25° C were extracted with 0·1*N*-HCl (HNO_3 for $PbCO_3$) to remove unreacted carbonate, before determining the residual metal contents. The amounts of the various elements that were fixed in 17 months under these conditions ranged from 0·1 mg Pb to 1·1 mg Cu per g dry matter. The same plant material, composted alone for the same period, fixed 0·04 mg Pb to 0·5 mg Cu per g when shaken with 0·1*N* acid solutions of the carbonates under the same conditions as those of the extraction process. (Bloomfield and Pruden)

The occurrence of wax in West Indian soils. We previously reported the presence of about 3% wax in a surface soil from Dominica (*Rothamsted Report* for 1966, p. 75). We could not obtain more of the original soil, and supposedly similar material from a different site in Dominica contained only 0·04–0·24% wax. Examination of the original wax by thin-layer chromatography, NMR and gas chromatography showed it to consist mainly of straight-chain C_{22}, C_{23} and C_{24} hydrocarbons, with small amounts of branched-chain C_{18} to C_{22} hydrocarbons. The wax closely resembled a commercial paraffin wax, and the possibility that it is adventitious cannot be excluded. (King)

Apparatus and techniques

Determination of fluorine in silicates. At present cerium Alizarin Fluorine Blue (CAFB) seems to provide the best colorimetric method for determining fluorine, but a preliminary separation is necessary to eliminate interference by other elements present in silicates. Steam distillation of fluorine from concentrated sulphuric, perchloric or phosphoric acids at 140–150° C (Willard–Winter distillation; Ingamells, C.O., *Talanta* (1962), **9**, 507–516) is the standard procedure, but this is slow and needs careful control of the temperature. Recovery is incomplete if the temperature is too low, and if it is too high small amounts of acid are carried over into the distillation. In preliminary experiments with CAFB, sulphate caused negative interference whereas phosphate enhanced the colour. If the temperature was kept low enough to prevent distillation of acid recoveries of F from NaF and CaF_2 were only 80–90% complete, whereas at higher temperatures apparently complete recoveries from phosphoric acid distillations could be caused by incomplete distillation combined with positive interference from phosphate in the distillate; recoveries from sulphuric acid at higher temperatures were smaller, because of interference by sulphate. No combination of conditions could be found that gave satisfactory results with the apparatus available.

High-temperature hydrolysis has occasionally been used to separate fluorine, but the only known application to silicate analysis uses very complex silica apparatus. This method was tested with a much simpler apparatus that proved entirely adequate. Air, saturated with water vapour by bubbling through water at 90° C, is passed through a silica tube in which the sample, mixed with V_2O_5, is heated by an electric furnace. The outlet of the silica tube, which is narrower than the main tube, is bent downward through a right-angle and is cooled by a detachable water jacket. The condensate, containing only water and HF, is absorbed in NaOH solution contained in a small polyethylene bottle; the end of the silica tube must dip below the surface of the alkali. Fluorine was recovered completely after heating at 660° C for 15 minutes, but the pyrohydrolysis was continued for a further 15 minutes to ensure complete recovery. With samples containing more than 1% F the distillates were titrated with $Th(NO_3)_4$ using Alizarin Red S indicator; for less than 1% F the colorimetric reagent CAFB was used.

The method is quick, and recoveries from added NaF or CaF_2 are 96–99% F, with a relative precision of ±1–2%. Preliminary fusion of micas with Na_2O_2 and precipitation of Al and Si are not necessary; the fluorine content of micas determined by this method are substantially (10–30%) greater than those found after Willard–Winter distillation. (Newman)

X-ray fluorescence analysis. A Philips PW 1540 Vacuum Spectrometer was installed in March; after 2–3 months initial "teething" troubles its performance has exceeded our expectations.

Zinc determinations in shales. Zinc was determined in over 100 Lias shales containing 10–700 ppm Zn, in connection with the geochemical studies of M. A. Gad, H. H. Le Riche and J. A. Catt. The method of analysis was basically that of Reynolds (*Am. Miner.* (1963), **48**, 1133–1143) modified for use with a gold anode X-ray tube. The intensity of Compton-scattered Au $L\beta$ radiation was used to estimate relative mass-absorption coefficients of different samples for Zn $K\alpha$ radiation. Artificial "shale" standards were used for calibration. The lower limit of detection was about 1 ppm and the total analysis time per sample about 300 seconds.

Total sulphur in acid sulphate soils. A rapid method of assessing the total sulphur content of acid sulphate and potentially acid sulphate soils would be valuable in allowing many soils to be examined quickly for survey purposes. X-ray fluorescence analysis seemed likely to provide such a method, and we have therefore compared the S $K\alpha$ count rate, obtained directly from ground soils, with the sulphur content (0·1–5·0% sulphur) as given by a single chemical determination, of 31 soils from Banting, Malaya.

An acceptable straight-line relationship was obtained for mineral soils (defined as soils having a loss on ignition of less than 25%) with a maximum relative deviation of ±15% of the chemically determined S content, using the S $K\alpha$ count rate directly. With organic soils (defined here as those with loss on ignition greater than 25%) for which the uncorrected S $K\alpha$ count rate deviates greatly from the straight-line relationship obtained with mineral soils, the observed count rates can be readily corrected to the same straight line as the mineral soils by using an empirical correction factor derived from the percentage weight loss on ignition at 450° C. Again the maximum relative deviation is ±15% of the sulphur content. The average relative deviation for mineral soils, using uncorrected count rates, and for all soils using the correction factor, is about ±7% of the sulphur content.

The X-ray fluorescent determination has a lower limit of detection of less than 10 ppm sulphur, using a chromium anode X-ray tube and a 2-μ-thick polycarbonate flow counter window, for a total counting time of 200 seconds per sample. The amount of sulphur in the Malayan soils we examined is such that shorter counting times give sufficient precision, and we estimate that less than 1 minute instrument time would be required for each sample.

The method can probably also be used to determine sulphate, i.e. acid-extractable sulphur compounds, by determining total sulphur before and after extraction with dilute hydrochloric acid. This would eliminate time-consuming chemical procedures for determining dissolved sulphate. The method can be extended to determine total sulphur in the 50–500 ppm range of agricultural soils.

Bromine in soils. Bromine residues are retained by the soil after fumigation with methyl bromide. In D. S. Jenkinson's experiments on partial sterilisation, soils were treated with 1000 ppm methyl bromide. They were later analysed for total bromine by X-ray fluorescence spectrometry, using the untreated soils with known amounts of added sodium bromide as standards. The treated soils contained about 120 ppm more bromine than the original soils. Leaching the treated soils with N potassium sulphate solution removed all the added bromine.

Because of these results, we analysed soils from D. C. M. Corbett's (Nematology Department) fumigation experiment on Broadbalk by the same method. Samples were taken across the field from treated and adjacent untreated areas of plots 20, 3, 10 and 2B. The amounts of bromine added by the methyl bromide treatment, obtained by comparison of treated and untreated samples, were plot 20, 6 ppm; plot 10, 6 ppm; plot 3, 6 ppm; plot 2B, 14 ppm. The amount of bromine in the untreated soil was small, and the method is estimated to be precise to ±1 ppm bromine. The methyl bromide had therefore been applied uniformly, and much more is retained by plot 2B, the FYM plot, than by the others. (Brown and Kanaris-Sotiriou)

Structure and synthesis of Titan yellow as a reagent for magnesium

The study of Titan yellow (*Rothamsted Report* for 1966, p. 75) was concluded. When reduced with $SnCl_2$ and HCl commercial Titan yellow formed 2-(*p*-aminophenyl) 6-methyl benzthiazole 7-sulphonic acid, which was purified as its crystalline ammonium salt; the ammonium salt was identical to the salt made from the authentic 7-sulphonic acid. Nuclear magnetic resonance spectra confirmed that the sodium sulphonate group of Titan yellow is in the 7-position.

We previously described the separation of the Mg-reactive fraction from commercial Titan yellow; unfortunately only a few hundred milligrams of the reagent can be isolated at a time by this method. We have now synthesised pure Titan yellow in 20 g batches, enough for many thousands of magnesium determinations. 2-(*p*-Aminophenyl) 6-methyl benzthiazole 7-sulphonic acid is coupled with an equimolecular quantity of its diazonium chloride. The synthesis is unusual, in that the diazonium chloride is a solid, and can therefore be washed free from acid and inorganic salt before the coupling reaction. The final product (Titan yellow) thus contains a negligible amount of the inorganic impurities that are major constituents of the commercial reagent. (King and Pruden)

Purification of commercial Alizarin Red S for use as a reagent for aluminium. Several samples of Alizarin Red S gave very different responses when used for the absorptiometric determination of Al. Analyses showed the samples to consist of differing proportions of Na and K Alizarin sulphonate, together with the free sulphonate and large amounts of inorganic Na and K salts. The inorganic salts were readily removed from a column of Sephadex G-10 with water, and continued elution with water removed the dyestuff. As the K sulphonate is sparingly soluble in water, we used samples containing predominantly the Na salt so that a reasonably concentrated solution could be applied to the column. With 2 g of the commercial compound in 10 ml water, and 75 g Sephadex G-10, sufficient purified material for several hundred determinations can be prepared. Free Alizarin sulphonic acid in the product is converted to the Na salt by titrating with NaOH to pH 4. (King and Pruden)

Miscellaneous

United States Geological Survey analysed rock samples. These new rock samples for which we have reported major element analyses (*Rothamsted Report* for 1966, p. 77) were analysed spectrochemically for minor elements. Ag, Mo, Pb, Sn and Zn were determined by the method described above and the remainder by direct arcing of the ignited material.

TABLE 6

United States Geological Survey standard rock samples (*ppm*)

	Granite G-2	Andesite AGV-1	Basalt BCR-1	Dunite DTS-1	Granodiorite GSP-1	Peridotite PCC-1
Split	76	8	61	21	19	36
position	10	18	31	29	32	6
Ag	0·03	0·06	0·02	0·01	0·03	0·01
Ba	3000	2700	820	<10	2000	<10
Co	<3	15	40	150	<3	130
Cr	13	10	12	3500	17	2700
Cu	16	67	27	6·8	37	8·9
Ga	19	17	19	<5	17	<5
Mn	180	630	1300	1100	290	1100
Mo	<0·1	1·7	1·2	<0·1	0·3	<0·1
Ni	4·3	15	8·5	1900	11	1700
Pb	23	25	10	6·1	39	5·3
Sn	1·3	3·7	1·5	1·1	5·5	1·3
Sr	490	800	490	<10	230	<10
Ti	3500	8900	27000	<<100	5700	<<100
Zn	85	77	130	56	110	39
Zr	370	240	150	<30	690	<30

(Le Riche)

Phenolic esters of dwarf bean (*Phaseolus vulgaris*) leaves. Esters of caffeic acid, ferulic acid and *p*-coumaric acid were isolated from dwarf-bean leaves. Chromatography and spectrophotometry showed that the phenolic nuclei are linked through their carboxyl groups to an aliphatic hydroxy acid, common to each. The esters can convert tryptophan to auxins *in vitro*; the caffeoyl ester, which is present in the largest amount, is the most active. (King, with Wheeler, Botany Department)

X-ray diffractometry and spectrographic services. Demands for clay mineral analyses were fewer than in 1966, but more than 100 soil and sedimentary clays were analysed for workers outside Rothamsted, including soil clays from Malaysia, the Canary Islands and from N.A.A.S. Experimental Husbandry Farms. (Weir and Ormerod)

Heavy metal toxicity in Central African soils. Soils in which heavy-metal toxicity was suspected as a cause of crop failures were analysed for trace elements on behalf of the Agricultural Research Council of Central Africa. In one instance Ni–Cr toxicity was revealed in an area where it had not previously been recognised, 20 miles from the nearest rocks known to be rich in these elements. (Le Riche)

Staff and visiting workers

A. C. D. Newman attended the joint meeting of the Clay Minerals Group of the Mineralogical Society and the Groupe Belge des Argiles, held in Brussels in June; C. Bloomfield visited Malaya for six weeks, under the Colombo Plan.

Professor H. E. Roberson returned to the United States after spending a year in the department.