Rothamsted Report for 1966

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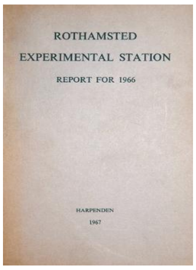

Pedology Department

C. Bloomfield

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PEDOLOGY DEPARTMENT

C. BLOOMFIELD

A. C. D. Newman attended the 2nd International Clay Conference in Jerusalem. M. A. M. A. Gad was awarded the Ph.D. degree of London University and returned to Egypt. Professor F. L. Himes returned to the United States after a stay of six months, and Professor H. E. Roberson, of the State University of New York, came to spend a year in the department.

The difficulties we have experienced in recruiting staff and the demands made on our X-ray-diffraction services this year have combined to impede the progress of some sections of our work.

Mineralogy

Alteration of trioctahedral micas. The alteration products from five trioctahedral micas (*Rothamsted Report* for 1965, p. 71) were examined in more detail and their chemical composition compared with the original micas. The structural formulae of the micas were calculated on the basis of 44 negative charges per formula unit; a simpler interpretation of the chemical composition of the alteration products were obtained by basing their formulae on the composition of the tetrahedral layer in the original mica. This approach was supported by the observation that the ratio Si/Al did not change during the process of alteration. The following examples of two such pairs of formulae show the main changes in the chemical composition:

Phlogopite:

$$K_{1\cdot78}Na_{0\cdot10}[Al_{0\cdot46}Fe^{3+}_{0\cdot11}Fe^{2+}_{0\cdot20}Mg_{5\cdot03}(Ca,Mn,Ti)_{0\cdot15}](Si_{5\cdot56}Al_{2\cdot44})O_{20}(OH,F)_4$$

$+1\cdot88$ $+12\cdot56$ $+29\cdot56$ $-44\cdot00$

Altered Phlogopite:

$$K_{0\cdot08}Na_{1\cdot64}[Al_{0\cdot46}Fe^{3+}_{0\cdot12}Fe^{2+}_{0\cdot19}Mg_{4\cdot95}(Ca,Mn,Ti)_{0\cdot14}](Si_{5\cdot56}Al_{2\cdot44})O_{20}(OH,F)_{3\cdot65}$$

$+1\cdot72$ $+12\cdot37$ $+29\cdot56$ $-43\cdot65$

Iron biotite:

$$K_{1\cdot91}Na_{0\cdot08}[Al_{0\cdot20}Fe^{3+}_{0\cdot19}Fe^{2+}_{3\cdot02}Mg_{1\cdot87}(Ca,Mn,Ti)_{0\cdot45}](Si_{5\cdot48}Al_{2\cdot52})O_{20}(OH,F)_4$$

$+1\cdot99$ $+12\cdot53$ $+29\cdot48$ $-44\cdot00$

Altered iron biotite:

$$K_{0\cdot06}Na_{1\cdot59}[Al_{0\cdot16}Fe^{3+}_{1\cdot51}Fe^{2+}_{1\cdot66}Mg_{1\cdot77}(Ca,Mn,Ti)_{0\cdot47}](Si_{5\cdot48}Al_{2\cdot52})O_{21\cdot32}(OH,F)_{1\cdot94}$$

$+1\cdot65$ $+13\cdot45$ $+29\cdot48$ $-44\cdot58$

All the micas lost some net negative charge, as measured by the sum of interlayer cations (K + Na) and by the cation exchange capacity. Micas containing more ferrous iron lost more net negative charge, but the charge that was lost was not balanced by the amount of ferrous iron that was oxidised. With phlogopite, in the formulae given above, the loss of negative charge is greater than the gain of positive charge from the oxidation of Fe^{2+}, whereas with biotite the opposite is true. It is apparent that some other reaction must be responsible for the loss of net negative charge by the micas, and we suggested that either structural hydroxyl ions were released to solution or that hydrogen ions from solution react with structural hydroxyl ions to form structural water. Atmospheric oxygen oxidises ferrous iron, without altering the net charge, by a reaction in which structural OH^- is converted to O^{2-}, with the production of water.

These reactions imply changes in the hydroxyl contents of the micas, and we are attempting to establish the hydroxyl contents of the micas before and after alteration. Infra-red spectra of the micas, obtained in collaboration with Drs. V. C. Farmer and J. D. Russell of the Macaulay Institute, indicate that changes have occurred.

Alteration of dioctahedral micas. Potassium was partly removed from three muscovites by treating them with sodium tetraphenyl boron, but the preparation of K-free materials is much more difficult than with trioctahedral micas. The partly altered materials give two sets of basal reflections, one based on the 10 Å spacing of the mica and the other based on a spacing of 9·6 Å. The latter is attributed to a collapsed sodium phase of the alteration product. This narrow spacing apparently prevents sodium being easily exchanged, so that all the sodium cannot be displaced with calcium; for instance, the exchange capacity of the calcium-saturated altered materials is only 6–13 me/100 g, even though 80–90 me Na/100 g are present in the altered mica. These observations indicate that sodium may not be the best exchanging cation to use when altering muscovite. (Brown and Newman)

Biotite and phlogopite and their alteration products. The micas being used in artificial weathering studies, and the alteration products of one of them, were examined by single-crystal X-ray diffraction. The densities of some of the crystals were measured by flotation in mixtures of organic liquids. This had two objects: to find which of the crystals were suitable for X-ray-diffraction determination of the positions of the atoms in the unit cell before and after the alteration, and to measure the unit cell molecular weight. This molecular weight is needed as a check on the structural formula derived from chemical analysis, and on such assumptions as the presence of 44 negative charges per unit cell.

Photographs of four phlogopites and two biotites, taken in rotation and Weissenberg cameras, show a wide range of order–disorder; the most ordered has all sharp spots and no streaks, whereas the least ordered has sharp spots only for reflections with $k = 3n$. The disorder is even greater for the one sample of altered material that has been examined. The reflections with $k = 3n$ are sharpest; other reflections occur mainly as streaks. Reflections are spread in a way that shows disorientation between different parts of the crystal, perhaps caused by bending, as is postulated for talc. (Brown and Rayner)

Solution chemistry of mica alteration. The release of mica-K to aqueous solutions is influenced by the environment; a study of the factors influencing mica alteration was started. Preliminary experiments showed that of the cations Na^+, Ca^{2+} and Mg^{2+}, Na^+ is the most effective in releasing K; barium may also be very effective, but analytical grade barium salts contain enough K to inhibit its release from micas. Other comparative experiments showed that acetates are less effective than chlorides.

In the main group of experiments different micas were extracted exhaustively with NaCl solutions adjusted to pH values between 3 and 9 with HCl or Na_2CO_3. The solutions were unbuffered, so that the hydrogen ions taking part in the reactions could be estimated from the change in pH. The first extracts contained most K, between 1 and 25 ppm K, depending on the mica. In subsequent extracts the rate at which K was removed soon slowed and became constant at a level characteristic for a particular mica, over a wide range of exchange, before falling to zero when all the K had been removed. The pH of the solutions increased when they were initially more acid than pH 7·4, and decreased when they were more alkaline; this suggests that pH 7·4 is an equilibrium pH for solution in contact with micas. The rate K was extracted increased with acidity, and considerable quantities of hydrogen ions were sorbed from the most acid solutions. The influence of pH on biotites was greater than on phlogopites or muscovites. Hydrogen-ion sorption was not directly related to K release, similar amounts being sorbed by micas that had released very different quantities of K. Hydrogen ions may react with the micas to form non-vermiculite products, but no evidence of this was found by X-ray examination. The products formed at different acidities are being examined further. (Newman)

Potassium-supplying power of soil minerals. Experiments were begun with grass grown in pots to determine the potassium-supplying power of different size-fractions of a soil from the Harwell Series, Halton, Bucks. This soil was chosen because the separation of fractions at 0·3 μ e.s.d. gives a fine fraction that is predominantly montmorillonite, and a coarser fraction, 5–0·3 μ e.s.d., that contains predominantly mica and clinoptilolite (*Rothamsted Report* for 1965, p. 72).

A thousand grams of surface soil was treated with hydrogen peroxide to remove organic matter and dispersed with sodium hexametaphosphate solution; the fine clay was removed completely by centrifuging and decanting, and the coarser fraction by settling and decanting. (This operation was on a larger scale than usual for us and involved the transport and use of more than a thousand litres of de-ionised water.) A separate sample of soil was pre-treated with hydrogen peroxide and sodium hexametaphosphate and sieved through a B.S. No. 300 mesh to obtain the fraction of particle size less than 53 μ. The fractions were divided into two equal portions, one of which was saturated with calcium ions from normal calcium nitrate solution and the other with calcium and potassium ions from a normal solution of calcium and potassium nitrates at a ratio of equivalent weights of 5:1. The samples were then washed with one-tenth dilutions of these solutions and dried from ethanol. Coarsely sieved, but otherwise untreated, soil and Kieselguhr were included as controls. The various fractions were diluted with Kieselguhr to give the proportions of each that were present in the original soil, and each mixture used to fill three 3-in. pots. The pots were sown with Perennial Ryegrass S 23 in March and given a basic dressing of N, P and trace elements. The grass was cut monthly at 2 cm above soil level; the cuttings were dried and weighed and their sodium and potassium contents determined. In the preliminary results there are quite large differences in the yields of dry matter and in potassium uptake from the different fractions; potassium is removed quickly from the montmorillonite contained in the fine clay fraction during the early stages of growth. (Weir, with Talibudeen, Chemistry Department)

The clay mineralogy of soils from Colombia, South America. Eight surface soils from Colombia, which were used by Dr. Mario Blasco Lamenca of London University in work for a Ph.D. degree, were examined mineralogically.

The soils are representative of agricultural soils in the Cauca Valley in south-west Columbia. The Buenaventura soil is situated in marine-terrace deposits between the Western Andes and the Pacific Ocean, and the others occur in terrace deposits flanking the Cauca River between the Central and Western Andes, at an altitude of about 3,000 ft above sea-level. Mean annual rainfall is 40 in. and mean annual temperature 24° C in the Valley, but in the area covered by the Cerritos and Risaralda soils the rainfall and temperature are 50–60 in. and 22° C respectively. The area covered by Buenaventura soils has a mean annual rainfall of 300 in. and a mean annual temperature of 28° C.

The soils are briefly described below:

1. Chernozem-like (Palmira soil). Well-drained slightly acid to neutral silt loam, developed in Quaternary alluvial terrace deposits; ecological type tropical dry forest.
2. Latosol (Villarrica soil). Well-drained very acid clay developed in dissected Pleistocene terrace deposits; ecological type tropical dry forest.
3. Latosol (Jamundi soil). Moderately well-drained to well-drained very acid silt loam, developed in deltaic deposits; ecological type tropical dry forest.
4. Ando soil (Cerritos soil). Moderately well-drained to well-drained acid fine sandy loam, developed in volcanic ash; ecological type sub-tropical moist forest.
5. Halomorphic soil (Saline Palmaseca soil). Poorly drained saline clay, developed in Quaternary alluvial terrace deposits; ecological type tropical dry forest.
6. Halomorphic soil (Saline-sodic Palmaseca soil). Poorly-drained

saline clay, developed in Quaternary alluvial terrace deposits; ecological type tropical dry forest.

7. Recent Alluvial soil (Risaralda soil). Moderately well-drained acid sandy loam, developed in alluvial and volcanic materials; ecological type sub-tropical moist forest.

8. Highly leached latosol (Buenaventura soil). Well-drained acid sandy loam, developed in Tertiary dissected marine terrace deposits; ecological type tropical wet forest.

Clay-size fractions ($<2\ \mu$ e.s.d.) of the soils were examined by X-ray diffraction, electron microscopy and some of the selective chemical tests described below; the results are given in Table 1.

TABLE 1

Percentage composition of the clay fractions of some Columbian soils

Sample	1	2	3	4	5	6	7	8
Amorphous $SiO_2 + Al_2O_3$	10	15 (Gi)	15	20	10	10	15 (Gi)	15 (Gi)
Soluble Fe_2O_3	5 (Go)	4 (Go)	5 (Go)	3	2·5	2·5	4 (Go)	5 (Go)
Mica	25	1	2	4	29	22	9	5
Kaolinite/halloysite	—	50	40	35	—	—	20	50
Mixed-layer minerals	20	—	—	—	5	—	—	—
Montmorillonite	—	10	10	—	35	40	35	5
Vermiculite	25	—	10	25	—	—	15	—
Chlorite	20	10	—	—	10	15	—	15
Quartz	tr.	10	15	5	tr.	5	5	10
Felspar/Cristobalite	—	—	—	10 (Cr)	5 (Fe)	5 (Fe)	—	—
Exchange capacity m-eq/100 g	54	36	49	54	48	56	55	43

Gi = gibbsite, Go = goethite, Cr = cristobalite, Fe = felspar, tr. = trace

All the clays contained appreciable amounts of soluble silica, alumina and iron oxide. Only part of the soluble iron occurs as goethite where this is reported, the remainder being amorphous to X-rays. Gibbsite, which is only partly represented as soluble Al_2O_3, was observed in samples 2, 7 and 8. In samples 2, 3, 4 and 8 the ratio of amorphous SiO_2:amorphous Al_2O_3 is sufficiently close to 2 to indicate the presence of allophane; samples 1, 5, 6 and 7 contain no allophane.

Samples 2, 3, 4, 7 and 8 contain kaolin minerals. Sample 4 contains a partially dehydrated tubular halloysite with a basal spacing of 7·3 Å. A few very similar tubular particles were observed in electron micrographs of samples 7 and 8. The kaolin mineral in sample 2 is also tubular, but as its basal spacing is 7·1 Å, it is either metahalloysite or rolled kaolinite. The kaolinites in samples 3, 7 and 8 are predominantly platy, but they have none of the characteristic euhedral particles of primary kaolins, and they seem to be considerably weathered. The kaolinite in sample 8 gives a sharp basal reflection, but those of the other two are broad.

Mica is most abundant where kaolinite is absent (numbers 1, 5 and 6). Much of the chlorite, vermiculite and montmorillonite in the samples, including those that contain little mica, were probably derived from mica by weathering. The montmorillonite in sample 5 is the only one that contains small particles seemingly unrelated to the large mica flakes. The chlorites and vermiculites are mostly well crystallised and give sharp basal reflections. Two mixed-layer minerals occur in sample 1: one is a non-expanding interstratified mica-chlorite with a basal spacing of 12 Å, and the other an expanding interstratified montmorillonite–vermiculite. All the samples contain quartz, and in addition sample 4 contains cristobalite, samples 5 and 6 felspar and sample 7 a small amount of amphibole.

The two halomorphic soils (samples 5 and 6) contain very similar suites of clay minerals, the others differ in various ways, but can be broadly grouped into those that contain allophane and kaolin minerals and those that do not. The soils were largely derived from alluvial terrace deposits; as only surface samples were available, no conclusions can be made concerning the weathering changes that produced the various suites of clay minerals. (Weir and Ormerod)

Methods of clay mineral analysis. Primarily to test new methods of analysis, detailed mineralogical analyses were made of some British sedimentary clays that are important soil parent materials. The $<1\ \mu$ e.s.d. fractions of London Clay, Weald Clay and Gault Clay were compared by X-ray diffraction and selective chemical methods with similar fractions of a fireclay and a pure kaolinite. In the selective chemical tests (Alexiades, C. A. & Jackson, M. L., *Proc. Soil Sci. Soc. Am.* (1965), **29**, 522–527), amorphous material and kaolinite are determined by extraction with alkali, mica from the non-exchangeable potassium content of the clay, montmorillonite and vermiculite from two values of the exchange capacity, and chlorite from the amount of water lost between 300° and 950° C, allowance being made for the water content of other minerals present.

Comparison of the results of complete mineralogical analyses of the five clays by chemical methods with semi-quantitative estimates from X-ray diffraction showed that kaolinite is under-estimated by the chemical method when much of this mineral is present, and that the least reliable of the chemical methods is that for estimating chlorite, as this incorporates the accumulated errors of the other determinations.

The chemical methods are based on the properties of pure minerals, and because of the variability of the compositions of clay minerals in soils and sediments the results are subject to error. This is also true of X-ray-diffraction analysis, but in conjunction the two methods enable the composition of the mixture to be assessed more accurately than by either method alone. (Ormerod and Weir)

Computer programmes for crystallography. Programmes written in this department were used to find the structures of crystals from X-ray-diffraction measurements. An A.R.C. unit of structural chemistry (attached to University College, London) was set up in October, and many of its calculations in crystallography will be sent to Rothamsted. To meet this extra work our set of programmes was extended by adding others used on Atlas and adapting them all to deal with as many different space-group symmetries as possible. The programmes have been successfully used for our layer silicate measurements and for the structures being studied by the A.R.C. Unit.

The programmes are described in outline in "Programmes and Programming Facilities Available on the Rothamsted Orion" issued to users as item Orion/56. At present they all read their data each time from paper tape. It is intended that the data will soon be written on magnetic tape at the beginning of a crystal structure refinement, and when needed they will be read from the tape by the different programmes. The incremental plotter recently acquired by the Statistics Department, and the Fortran compiler now available on the Orion, should make it possible to use programmes written in America to draw stereoscopic diagrams of atomic arrangements in molecules or in parts of crystal structures, and to draw contoured electron density maps from a table of electron densities calculated, but not printed, by the computer. (Rayner)

Clay physics

Shrinkage of cohesive soils. The factors that control the shrinkage of cohesive soils were further studied. The amount of shrinkage that a cohesive soil undergoes from pF 2 to 6 depends on the initial treatment of the soil. To evaluate the effect of remoulding on the pore structure another series of measurements was made on samples that were pre-dried to pF 6 and then rewetted to pF 2. (Our earlier measurements were made on remoulded soils.) This treatment decreases the void ratio and changes the pore-size distribution. We have also measured ethylene glycol retentions, exchange capacities, exchangeable sodium and the moisture contents of the air-dry soils. The results, although not yet complete, show that with pre-dried soils the external specific surface area, as measured by nitrogen adsorption, correlates less well with shrinkage between pF 4 and 6 than with remoulded soils; this suggests that pre-drying forms aggregates between which most of the shrinkage occurs, and hence the effective external surface is less than that measured by nitrogen adsorption. It was noted previously that the montmorillonite content, as determined by X-ray diffraction, is inadequate as an index of the extent of shrinkage (*Rothamsted Report* for 1965, p. 75). However, some interesting relationships appear when the montmorillonite content is redefined in terms of the amount of interlamellar ethylene glycol retained under standard desorption conditions. The interlamellar ethylene glycol, calculated by subtracting the amount required to form a monolayer on the external surface from the total amount of glycol retained by a soil, is not directly related to the montmorillonite content, as determined by X-ray diffraction, because it includes the expanding characteristics of all the clay minerals in the soil. The interlamellar glycol contents correlated well with the shrinkage between pF 4 and 6 for both remoulded and pre-dried soils. This, in part, is explained by the observed change in the interlamellar spacing of montmorillonite-type interlayers in this range. It is interesting that the air-dry moisture contents correlate well with total ethylene glycol contents, which suggests that for routine purposes the latter determination, with its added complication, may not be necessary. It is also of interest that when the external specific surface area of the clay fraction of a soil is small the interlamellar glycol content is also usually small, which implies that the coarser clay particles are less likely to have expanding interlayers. However, when the specific surface area of the clay is large the interlamellar ethylene glycol content can vary considerably. (Greene-Kelly and Gallavan)

Geochemistry

Geochemistry of the Yorkshire Lias. Work on the Lower and Middle Lias was completed, concluding our geochemical survey of the Yorkshire Lias sediments. The Lower Lias is divided into 13 palaeontological zones; the uppermost eight of these (totalling approximately 520 ft of sediment) are exposed in Robin Hood's Bay, and parts of two lower zones (*angulatum* and *bucklandi*) are exposed on the foreshore at Redcar. The Middle Lias is approximately 140 ft thick and comprises two zones, both of which are fully exposed in cliff sections near Staithes.

There is little geochemical or mineralogical evidence of the provenance of the Lower Lias sediments. However, the shales contain less Si, Ca, Mg, K and Na, but more Al and Ti, than the average amounts in shales, which suggests that the detritus was intensely weathered and possibly derived from pre-existing sediments. This suggestion is supported by the occurrence of mainly resistant detrital minerals (rutile, zircon and tourmaline) in the heavy sand and silt fractions. In some zones the sediments are more calcareous than in others, so that the pH of the water near the sediment interface was probably rather variable during deposition of the Lower Lias. Mildly reducing conditions were maintained throughout most of the Lower Lias, though there is some evidence for slightly more reducing conditions in the *jamesoni*, *ibex* and *davoei* zones. Si, Al, Ti, Mg, Na, K, Ga, Cr, Zr, Ba and some of the Fe, V, Co and Ni in the shales occur in the detrital minerals; Ca, Mn, Sr and some of the Fe were precipitated from the sea-water as carbonates, whereas the remainder of the Fe, Co, Ni and V were precipitated as sulphides. Organic matter was less important in concentrating minor elements in the Lower than in the Upper Lias; variable amounts of Pb, Mn, Cu, Ni and Co occur in pieces of fossil wood from the *oxynotum*, *jamesoni*, *ibex* and *davoei* zones, but only very small amounts of Mn and Ni are associated with the organic matter disseminated throughout the shales.

The lower parts of the Middle Lias *margaritatus* zone consist mainly of sandy sediments with intercalated sandy shales and calcareous or sideritic nodule bands, but the high parts of this zone, and almost all the overlying (*spinatum*) zone, are dominated by ferruginous shales containing seams of sideritic and chamositic ironstones. The lowest parts of the *margaritatus* zone are strongly calcareous and were probably deposited in mildly alkaline water (pH greater than 7·8), but the pH during deposition of the remaining parts of the Middle Lias was probably near neutral. Mildly reducing conditions of deposition probably persisted throughout most of the Middle Lias, but in the highest parts of the *spinatum* zone there is evidence of more strongly reducing conditions. This later phase was the beginning of a long period of stagnant sea-bottom conditions that persisted throughout the early part of the Upper Lias, i.e. the Whitbian.

In the non-ferruginous Middle Lias sediments the amounts of most elements were determined by the composition of the detritus, but Fe, Ca, Co, Ni, Cu and Mo were precipitated from the sea-water as sulphides or carbonates. Cu, Ni and Mo are also associated in part with organic matter. In contrast, the ferruginous shales and ironstones contain large amounts of non-detrital material. Some of the Si and Al in these rocks was extracted from the sea-water by formation of chamosite; large amounts of V, Cr, Ni, Co and Pb are associated with this mineral, possibly because it was deposited as a negatively charged gel to which the cations were attracted. Most of the Fe not incorporated in chamosite was precipitated as the carbonate, siderite. The only minor element concentrated in the siderite is Mn, which was either co-precipitated with the $FeCO_3$ as $MnCO_3$, or proxies for Fe^{2+} in the siderite structure. (Catt and Gad)

Differentiation between detrital and non-detrital material in sediments. In the work described in the previous section we needed to distinguish detrital material, i.e. that deposited in solid form, from that deposited from solution. This distinction has a wider significance, as elements contained in detrital minerals are in general less easily affected by pedological processes, and consequently are less readily available to plants than those of non-detrital origin.

Dilute acetic acid has been used to dissolve non-detrital material in assessing the distribution of trace elements between detrital and non-detrital material in carbonate rocks, but as this reagent has no effect on pyrite, which is a major non-detrital constituent of Lias shales, an alternative treatment was developed. The finely powdered rock is treated with hydrogen peroxide, which dissolves sulphides and some of the organic matter. The sample is then treated with acid ammonium oxalate solution under ultra-violet light.

Three methods of treatment were compared: (i) acetic acid; (ii) oxalate alone; and (iii) peroxide followed by oxalate. More iron and aluminium were extracted from shales by oxalate than by acetic acid; some of the extra amount may derive from organic matter. Peroxide/oxalate dissolved more iron and trace elements than the other two treatments; these extra amounts derived mainly from the sulphide and, possibly, also from organic matter that was unaffected by oxalate alone. Up to 50% of the total Co, Cu, Mo, Ni and Pb were extracted by peroxide/oxalate treatment, but very much smaller proportions of the total Cr, Ga, Ti and V were dissolved, indicating that these elements are predominantly associated with detrital minerals. (Gad and Le Riche)

Soil chemistry

The determination of total sulphur in soil. A new method was developed for routine use. The soil is refluxed with $K_2Cr_2O_7$ and H_3PO_4 to oxidise sulphur compounds to sulphate, cooled and then heated with activated charcoal; sulphate is thus quantitatively reduced to SO_2. The evolved SO_2 is trapped in H_2O_2, treated with a measured excess of $Ba(ClO_4)_2$ solution and the excess Ba^{2+} titrated with standard K_2SO_4 solution using Sulphonazo III (Budesinsky, *Anal. Chem.* (1965), **37**, 1159) as indicator. The whole procedure takes about 30 minutes. No interference is caused by addition of 1,000 ppm of Fe^{3+}, Pb^{2+}, Al^{3+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Sn^{2+}, Sr^{2+}, Zn^{2+}, Mg^{2+}, Ba^{2+}, NH_4^+, K^+, Na^+, SeO_4^{2-}, F^-, Cl^-, Br^-, $B_4O_7^{2-}$, NO_3^- or NO_2^- to the soil. The recovery of sulphur from sulphamic acid, S-benzylthiuronium chloride, sulphanilic acid, methionine and cystine was within ±2% of the theoretical value. Acceptable results were obtained for the sulphur contents of previously analysed samples of anthracite, Portland cement and basic slag. Results on soils were comparable with those obtained by the vanadium pentoxide method (Bloomfield, *Analyst*, *Lond.* (1962), **87**, 586): for example, a sample from plot 3 of Broadbalk was found to contain 197 ppm sulphur by the new method compared with 184 ppm by vanadium pentoxide method. For a sample from plot 2B of Broadbalk the corresponding figures were 501 and 483 ppm.

The accumulation of sulphur in uncultivated soils. Work on the accumulation of nitrogen, carbon and organic phosphorus in Broadbalk and Geescroft wilderness (*Rothamsted Report* for 1965, p. 77) was extended to sulphur, using the new method for determining the total sulphur. Soluble and absorbed sulphate was determined by Williams and Steinberg's method (*Pl. Soil* (1962), **17**, 279); the difference between the sulphur thus determined and the total sulphur was called organic sulphur. In 1883, when last cultivated, Geescroft contained 90 lb of sulphate sulphur and 830 lb of "organic" sulphur per acre in the top 27 in. In 1881 the Broadbalk site contained 120 lb of sulphate sulphur and 890 lb of "organic" sulphur. By 1964 the wooded section of Broadbalk wilderness had gained 50 lb of sulphate sulphur and 790 lb of organic sulphur. The corresponding gains by 1965 for Geescroft wilderness, now wooded, were 410 and 540 lb. These differences between the Broadbalk and Geescroft sites are almost certainly caused by the difference between the pH values of the two soils; the sites are so close that it is unlikely that there is any great difference in the annual income of sulphur from the atmosphere. Calcareous Broadbalk retained relatively little sulphate, either in the 1880s or now. In 1883 the pH values of the 0–9-in., 9–18-in. and 18–27-in. layers of Geescroft were 6·1, 6·9 and 7·1, values insufficiently acid to permit much sulphate to be retained. By 1965 the pH at these depths had fallen to 4·5, 5·5 and 6·2 respectively, so that now they are sufficiently acid for sulphate to be retained. Over the 80 odd years of the experiment Geescroft wilderness gained about 5 lb of sulphate sulphur per acre per annum, but Broadbalk gained only 0·5 lb. In contrast, the development of acidity restricted accumulation of organic sulphur, just as it restricted accumulation of organic nitrogen, carbon and phosphorus.

The determination of carbonised material in soil. As part of the current programme of work on the measurement of natural and bomb-derived radio-carbon in soil, it is necessary to know how much coal or charcoal is present. A method, based on Greenland and Ford's procedure for separating light material from soil, was developed. The dry soils are dispersed ultrasonically in a mixture of bromoform and xylene of S.G. 2, and the light fraction removed by centrifuging. Plant material contained in the light fraction is removed by treatment with warm NaOCl solution (10% available Cl_2), followed by cold 72% H_2SO_4, and the residual carbonised material weighed. Recoveries of added bituminous coal and charcoal ranged from 95 to 98%. Soils from the top 9 in. of the Park Grass

Permanent Grass experiment contain up to 0·27% of carbonised material. (Jenkinson)

Mechanism of podzolisation. The experiment reported last year (*Rothamsted Report* for 1965, p. 78) on how aging of fallen oak, beech and larch leaves affects the iron-mobilising properties of their water extracts was repeated with picked and fallen leaves, and with γ-ray irradiated picked oak and fallen larch leaves. The picked and fallen leaves behaved similarly, except that the picked ones were slightly more active. Aging had the same qualitative effect on both picked and fallen leaves as previously described, although the oak and larch leaves collected in 1965 were rather less active than those of 1964. Irradiated oak leaves were rather less active than unirradiated ones, but the pattern of changing activity during aging was exactly the same. The only effect of irradiation on the iron-mobilising properties of the fallen larch needles was to retard the decline of their activity slightly. Thus microbial action seems not to be an important factor in this aspect of the aging process. (Bloomfield, King and Pruden)

Formation of ochre deposits in field drains. At the request of Mr. R. H. Miers, Ministry of Agriculture, we examined samples of ochre from drains in restored open-cast coal sites, near Nottingham. At one site (Spanker) the drainage water was very acid, pH 3·2, and contained 145 mg SO_4^{2-} per 100 ml. After an initial lag period ferrous iron was rapidly oxidised and precipitated as hydrous ferric oxide when an inorganic medium containing ferrous iron was inoculated with the ochre; by subculturing, the lag phase was shortened to less than 24 hours. It is claimed that ochre formation can sometimes be prevented by threading the tiles with copper wire, but in our experiments the oxidation and precipitation of iron was unaffected by copper. After several passages through the ferrous iron medium the culture was transferred to a medium containing elemental sulphur. Sulphur was oxidised after a few days' incubation, so organisms of the Thiobacillus group are probably the agents responsible for the formation of ochre at this site.

Oxidation of pyrite is the likely first stage in the sequence of reactions leading to these deposits, and iron is probably reduced at lower levels where the soil is waterlogged. Very large amounts of sulphide were produced when a lactate–sulphate medium was inoculated with the ochre. It is difficult to explain the presence of such active sulphate reducers in the ochre, as in the waterlogged region the soil is much too acid to permit their growth.

Samples from another site (Biggin Hill) contained 2–11 mg SO_4^{2-} per 100 ml and were only slightly acid—pH 6·5–6·7. This material had no effect when incubated in the ferrous iron medium. Under the microscope the material appeared as masses of tangled filaments impregnated with ferric oxide, quite unlike the Spanker sample and resembling descriptions of filamentous iron bacteria. There was no concentration of trace elements in the Spanker ochre, but manganese was 10 times more abundant in the Biggin Hill sample than in the adjacent soil (Le Riche); this is significant, as it has been claimed that the filamentous iron bacteria can oxidise manganous as well as ferrous ions. An ochre sample from an organic soil near Spilsby, Lincs., resembled the Biggin Hill material. We have succeeded in growing the Biggin Hill and Spilsby filamentous bacteria in the laboratory, using an aqueous extract of dried lucerne to maintain ferrous iron in solution at the required near-neutral pH values. In this medium precipitation of iron was inhibited for several days by the presence of a piece of copper wire. The subsequent precipitation of iron in the presence of copper may have been caused by other micro-organisms, as the microscopic appearance of the precipitates were different. In the light of our previous observation that cupric oxide is readily dissolved by aqueous plant extracts (Ng & Bloomfield, *Geochim. cosmochim. Acta* (1961), **24**, 206–225), it is not surprising that enough metallic copper dissolved to give the considerable concentration of 7 mg/l. It seems unlikely that such a concentration could be achieved in field drains. (Bloomfield and Pruden)

Acid sulphate soils. Several million acres of coastal soils in tropical countries are reported to have large accumulations of sulphides of marine origin. Although these soils are often otherwise well suited for intensive agriculture, the acidity that develops when they are reclaimed is detrimental to most crops. Samples from fields of oil palms, where yields were less than half the average, were collected during a visit to Malaya to advise on the use of such soils. The samples included soils from a 30-ft cross-section between two drains that were dug in 1961 to study the effect of intensive draining on the development of acidity. Far from ameliorating the condition of the soil, the intensive leaching has intensified acidification, presumably by promoting oxidation of sulphur compounds. At 35–40 in. depth, i.e. the depth of the drains, the pH of the soil is about 2·7, approaching that of long-exposed soils, in which the pH seems to be stabilised around 2·5. This suggests that the soils contain reserves of oxidisable sulphur compounds, oxidation of which has kept pace with the leaching of sulphate. To test this supposition we determined sulphate before and after treating the soil with H_2O_2. Pyrite, and presumably part of the organically combined sulphur, is oxidised by H_2O_2, so that the oxidisable sulphur can be estimated by difference. That these soils still have considerable reserves of oxidisable sulphur is shown by the 2–10-fold increase in the sulphate content after treatment with peroxide. They cannot therefore be reclaimed by even the intensive leaching to which they have been subjected.

When sampled the wet soils were forced into wide-necked jars and covered with molten paraffin wax, but pockets of air were inadvertently trapped in several of the jars. After about 3 months these pockets were surrounded by zones of soil of different appearance from the bulk. The most noticeable change was the appearance of a yellow-brown incrustation that resembled material found last year in mangrove swamp soils from Guinea (*Rothamsted Report* for 1965, p. 74) and that was shown by X-ray diffraction also to be jarosite, $KFe_3(SO_4)_2(OH)_6$. (Pyrite and marcasite were also identified by G. Brown.)

After a very short lag period ferrous iron and elemental sulphur were oxidised when the appropriate media were inoculated with the newly formed jarosite. The shortness of the lag phase suggests that organisms of the Thiobacillus group are active in the soils, and that they are responsible for the characteristic rapid oxidation and development of acidity when the soils are exposed.

The total sulphur contents of the soils we have examined are between 0·4 and 4%, but much larger values have been reported. Sulphate contents vary 100-fold within one profile, and it is difficult to devise a method of determination that is both flexible enough to accommodate this wide variation and suitable for routine survey purposes. Twelve total sulphur determinations a day can be made by heating the sample with V_2O_5, collecting sulphur oxides in dilute H_2O_2 and titrating the resulting sulphuric acid with standard alkali, but we have yet to find a suitable routine method for determining sulphate. (Bloomfield, with J. K. Coulter and R. Kanaris-Sotiriou, Ministry of Overseas Development)

Fractionation of copper-containing compounds extracted from peat. Earlier we reported the extraction of copper from an organic soil by benzene : methanol. Roughly half the total copper, which amounted to 0·2%, was so extracted (*Rothamsted Report* for 1961, p. 71). Four other peat soils, previously saturated with copper by treatment with a solution of copper sulphate, behaved similarly. The extracted materials have been fractionated by solubility methods. The quantities of copper and organic matter extracted from the benzene : methanol-soluble material, and the proportion of copper in the extract, increase with increasing polarity of the solvent, so a range of copper compounds is probably involved. One fraction of the Wisbech soil extract yielded a white precipitate shown to be an ester $CH_3(CH_2)x{\cdot}OOC(CH_2)yCH_3$. In the major component x is 29 and y 16. Minor components have $x = 27, 25$ and $y = 14, 12$. Another fraction from the Wisbech soil contained copper pheophytin *a*, but this seemed to be an artefact formed during the extraction. (Bloomfield and Himes)

The occurrence of wax in West Indian soils. What seems to be a plant wax was isolated from the surface horizon of an allophanoid latosolic from Dominica. The soil occurs in a region of "elfin woodland" where the annual rainfall is 200 or more inches and the relative humidity often 100%. The white wax-like material constitutes approximately 3% by weight of the air-dried soil. Other West Indian soils have yielded up to 2% of colourless, transparent waxy materials. The wax in the Dominican soil hinders wetting and dispersion of the soil, and may also affect its cation-exchange capacity and field properties. (Ormerod)

Apparatus and techniques

Purification of Titan Yellow as a reagent for magnesium. The extreme variability of Titan Yellow is a serious disadvantage in what would otherwise be a very useful reagent for determining magnesium. We have developed a method by means of which enough of the magnesium-reactive constituent for several hundred determinations can be separated from the commercial dyestuff. The reactivity of this component is such that it can be used at a concentration as small as 0·008%; it accounted for 28·5% of our original sample (Eastman Kodak).

After extraction with acetone the dye is dissolved in water and poured on to a column of the dextran gel "Sephadex G-10", which is then eluted with water to remove sodium chloride (a major contaminant) and a yellow compound that gives a fugitive colour with magnesium. The active fraction is eluted from the column with 50% aqueous acetone. (King and Pruden)

Light-scattering photometer. A light-scattering photometer was made to study the particle aggregation of clays in suspension, in relation to the structure of clay aggregates. The photometer is more adaptable than commercial models, is sensitive and stable, and gives satisfactory scattering envelopes with pure liquids such as benzene. (Greene-Kelly and Dibley)

Measurement of surface areas by nitrogen adsorption. The nitrogen-adsorption apparatus was modified to speed determinations and economise in the use of liquid nitrogen. The modifications include the use of constant-volume sample tubes and of sample inserts that can be changed rapidly without the need to clean the enclosing tubes. The inserts are filled with adsorbent beforehand and degassed in a separate apparatus; they can then be transferred to the measuring apparatus without appreciable gain in moisture content. With the modified apparatus, 60 determinations can be made in a week. (Greene-Kelly and Gallavan)

Method of drying clay specimens. The preparation of clays and cohesive soils for their study in the dry state is important in the study of shrinkage. These materials are not rigid, so the large stresses imposed by surface-tensional forces considerably compress the structure. Samples of clay prepared by drying from water are dense and usually impermeable to gases, and in consequence specific surface areas measured on material prepared in this way are not the external surfaces of individual crystals, but those of aggregates of crystals; the measured areas thus depend on the degree of grinding that the sample has received, rather than on any more fundamental property. The structure of clays can be improved by displacing the water with a liquid of smaller surface tension before the clay is isolated, but complete displacement of water is difficult to achieve and the clay is still compressed. A method that has proved very successful is to displace the water by alcohol, followed by benzene, and then to allow the residual water and alcohol to partition between the clay and synthetic Linde zeolite 5A, which adsorbs water and alcohol but not benzene. After some days the clay exhibits no apparent volume change when the benzene is removed, and forms a fluffy porous and unoriented powder. The product resembles a freeze-dried clay, but differs in having a large external specific surface area and exhibiting no signs of aggregation. Extensions of this method are being used to study the change in soil pore structure during shrinkage and to investigate the fundamental particle size of montmorillonite. (Greene-Kelly)

U.S. Geological Survey analysed rock samples. Six new rock samples have been prepared by the U.S. Geological Survey, to be issued as primary standards in place of the earlier samples G-1 and W-1. As before, the samples will be analysed in various centres to establish the most probable values for the various constituents; we are collaborating in this project. Table 2 gives the results of our analyses for the major constituents. Magnesium was determined with Titan Yellow, purified as described above, and the other elements by the rapid methods commonly used in the department. (Pruden)

TABLE 2

U.S. Geological Survey standard rock samples

Per cent

	Granite G-1	Granite G-2 Split 76 Position 10	Andesite AGV-1 Split 8 Position 18	Granodiorite GSP-1 Split 19 Position 32	Basalt BCR-1 Split 61 Position 31	Peridotite PCC-1 Split 36 Position 6	Dunite DTS-1 Split 21 Position 29	Diabase W-1
SiO_2	72·41	69·91	59·39	67·51	55·52	42·61	41·65	52·52
Al_2O_3	14·12	15·09	16·79	14·65	13·22	0·21	0·15	14·76
TiO_2	0·28	0·57	1·25	0·77	2·45	<0·01	<0·01	1·09
FeO	0·93	1·32	2·14	2·36	8·78	4·39	6·51	8·57
Fe_2O_3	0·87	1·30	4·37	2·06	4·07	3·33	1·20	1·52
CaO	1·38	2·02	4·44	2·05	6·14	0·42	0·14	10·84
MgO	0·38	0·75	1·52	0·94	3·46	43·63	49·19	6·63
MnO	0·02	0·03	0·09	0·08	0·23	0·17	0·18	0·18
P_2O5	0·09	0·16	0·53	0·31	0·34	<0·01	<0·01	0·16
K_2O	5·45	4·49	2·91	5·47	1·80	0·02	0·03	0·65
Na_2O	3·33	4·06	4·11	2·74	3·20	0·01	0·01	2·08
H_2O^-	0·05	0·26	0·94	0·28	0·39	0·28	0·00	0·12
H_2O^+	0·42	0·55	1·16	0·43	1·07	4·54	0·60	0·55

X-ray diffractometry service

The demand for X-ray-diffraction service work, with the necessary ancillary chemical analyses, continues to increase. In the past year the Soil Survey of England and Wales and the Ministry of Overseas Development have been the main users of the service. We have been able to satisfy all the requests that have been made, but only at the expense of our own work.

We have examined 66 soil clays for other people, and a little less than half the working time of the diffractometer, which is working to capacity, was devoted to work other than our own. (Brown, Ormerod, Pruden and Weir)

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