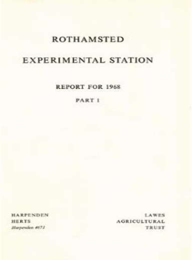
Report for 1968 - Part 1

Full Table of Content



ROTHAMSTED
EXPERIMENTAL STATION
REPORT FOR 1968
PART 1

HARPENDEN
HERTS
Harpenden 4671

LAWES
AGRICULTURAL
TRUST

Pedology Department

C. Bloomfield

C. Bloomfield (1969) *Pedology Department ;* Report For 1968 - Part 1, pp 63 - 81 **- DOI: https://doi.org/10.23637/ERADOC-1-123**

PEDOLOGY DEPARTMENT

C. BLOOMFIELD

The traditional concern of pedology is the development of the soil profile, that is the formation of more or less horizontal layers of different composition that result from inhomogeneity of the parent materials and the influence of percolating water and the various chemical, biological and physical processes that occur in the soil.

Broadly, we study the basic chemistry and mineralogy of these processes, and the nature of the specific minerals that are formed. The range of the time scales is very great—the weathering of minerals is probably measured in hundreds or thousands of years, and at the other extreme we are concerned with processes measured in days or even hours. In studying the faster processes laboratory models can often be used, but for the slower processes we are usually restricted to the study of naturally occurring samples, with all the attendant difficulties of finding suitable material, and of establishing its provenance. Providing such samples is an important secondary aspect of our work on soil mineralogy.

Soils are complex mixtures, and although much empirical knowledge of their properties has been accumulated, much more needs to be known about the form and properties of the soil constituents, and about the processes of soil dynamics. For example, deficiencies of plant nutrients, especially trace elements, are seldom attributable to an absolute deficiency of the specific element, and the availability of a plant nutrient must ultimately be governed by the physical and chemical properties of the forms in which the element occurs in the soil. Similarly, the physical properties of clay soils of similar clay content and composition can differ widely, so with these also we need to learn more about the state of the soil constituents —in this instance about the size and shape of the clay particles, and the state of their surfaces.

Mineralogy

Relation between alteration of micas and their chemical composition. The exchange of potassium at room temperature by twelve micas of widely ranging chemical composition was determined. For a given concentration and pH of the reacting solution, the equilibrium concentration of K in the solution is largely independent of the amount remaining in the mica; plotting the concentration of K in the solution against the fraction of the K that is exchanged gives sigmoid curves that are flat between 20 and 80% exchange. This exchange behaviour is a consequence of the discontinuous phase change from mica to the vermiculite-like altered mica. Cation compositions intermediate between the two species are not found, and the two phases are at equilibrium only at one solution composition, provided the temperature, pressure and initial solution concentration are specified. This solution composition differs greatly from mica to mica, and for exchange in *M* NaCl is expressed as the ratio of the concentrations of potassium to sodium between 40 and 60% exchange of the mica. This concentration ratio, or exchange parameter, denoted by R^{K}_{Na}, ranges from $1{\cdot}7 \times 10^{-5}$ for a fluorine-bearing phlogopite, to $1{\cdot}2 \times 10^{-3}$ for a reactive biotite; it is a relative measure of the free energy change when potassium mica is converted to sodium vermiculite.

Measuring the exchange parameters of different micas enabled the potassium-releasing abilities of the micas to be compared quantitatively. Fluorine is the most important single constituent influencing the exchange parameters of the 10 trioctahedral micas examined. Plotting log R^{K}_{Na} against fluorine content gave a straight line; the correlation coefficient between the two quantities was 0·945. A probable reason for this strong correlation is that the binding of potassium into the mica structure is influenced by fluorine substitution in the aluminosilicate layers. The nearest neighbours to the potassium atom are twelve oxygen atoms, six in one aluminosilicate sheet and six in the next, but the hydroxyl groups are also close enough to interact with the potassium atoms. For trioctahedral micas, in which all the octahedral sites are occupied by divalent cations, the hydroxyl groups are oriented so that the OH vector is normal to the structural layer and is directed towards the potassium atom, whereas in dioctahedral micas only two in three of the octahedral sites are occupied and the OH vector is inclined at 74° to the normal.

It has been suggested that the perpendicular orientation of the OH groups brings the hydrogen atoms close to the potassium atoms, and that repulsion between potassium and hydrogen accounts for the relative ease of potassium release from trioctahedral micas. Fluorine isomorphously replaces hydroxyl in the structure, but because there is no hydrogen combined with the fluorine there is no repulsion, and potassium is more strongly bound in the structure. The correlation between fluorine content and the exchange parameter supports this hypothesis.

Alteration of micas at higher temperatures. Micas have been reported to be readily altered by boiling with suitable electrolyte solutions, and we have started to study how temperature affects the exchange equilibria. In preliminary experiments with a phlogopite, the exchange parameter R^{K}_{Na} was increased by boiling the reaction solutions. This suggested that the ex-exchange of potassium could be much accelerated by refluxing micas with solutions of sodium and alkaline earth chlorides, and several micas were exchanged in this way. The products seem not to differ from those formed at room temperature, and they give the usual vermiculite X-ray diffraction patterns. No chloritic material or kaolinite was found in the alteration products and the mechanism of alteration seems similar to that at room temperature.

Attempts were made to exchange muscovites by boiling samples in solutions of NaCl, $CaCl_2$ and $MgCl_2$. Although initially more potassium is replaced than at room temperature, progressively smaller amounts of potassium are exchanged after each replenishment of the reaction solution, and complete exchange has not yet been achieved.

Water and hydroxyl contents of micas and their alteration products. As described in last year's Report (p. 66), the hydroxyl content of two micas increased when they were artifically altered by replacing interlayer potassium. Extension of this work to other micas has been difficult until now because the method of determining water (weighing the water taken up by an absorption tube) was insensitive and not suitable for measuring the differential evolution of water on heating. We are attempting to improve the method by using a gold barrier-layer hygrometer to determine the concentration of evolved water in a gas stream flowing over the sample; the concentration is recorded simultaneously with the temperature. Preliminary experiments indicate that the method has considerable promise once problems of calibration and base-line drift are overcome. (Newman)

Structures of micas and their alteration products

Micas. The experiments described above show that the fluorine content is strongly correlated with the ease with which potassium is released by trioctahedral micas. The greater the fluorine content, and hence the smaller the hydroxyl content, the more readily is potassium released.

The structures of two phlogopites with very different F contents were fully refined from X-ray diffraction measurements. Some of the structural features are compared in Table 1, which shows that some of the structural features vary with the fluorine content. The first phlogopite in the table contains no aluminium, and the last contains lithium, so that differences in the properties of the minerals are not exclusively related to their fluorine contents. Reading across the table, the layer repeat distance ($c \sin \beta$) shortens with increasing fluorine content, but the layer thickness, i.e. the distance between the centres of the outer layers of oxygen atoms, decreases much less. The layers are therefore packed more closely in structures containing more fluorine, and the movement of K ions may thus be restricted. If movement of a K ion is a first step in the alteration mechanism, alteration will become more difficult with increasing fluorine content because the layers must move further to give equal freedom of movement to the ions in a fluorine-rich structure. This is consistent with

TABLE 1

Structural features of phlogopites with different fluorine contents

	Ferriphlogopite*	P5	P6	Lithian Fluophlogopite†
Fluorine content F/(F + OH)	?0	0·25	0·67	1·0
Unit cell				
a (Å)	5·36	5·32	5·33	5·31
b (Å)	9·29	9·21	9·24	9·21
$c \sin \beta$ (Å)	10·25	10·07	10·01	9·98
Octahedral layer thickness (Å)	2·24	2·19	2·23	2·17
Twist of tetrahedra	11·0°	8·8°	7·6°	6·2°
K—O bond length (Å)	2·942	2·964	2·975	2·995
K—O spacing perpendicular to layer (Å)	1·743	1·702	1·678	1·663
Layer thickness between centres of outer oxygen atoms	6·76	6·66	6·65	6·65

* Steinfink, H. (1962) *Am. Miner.* **47**, 886–896.

† Takeda, H. & Donnay, J. D. H. (1966) *Acta Crystallogr.* **20**, 638–646.

the observed relationship of ease of alteration and F content. In the samples with more F the deeper penetration of the K atom into the trigonally distorted hexagons of O atoms, above and below it, is associated with a smaller twist of the tetrahedra, so that the closer set of six O atoms recedes and the further six O atoms approach the K atom more closely. This movement is greater than would be expected if the K atom were forced into the hexagon by the closer approach of the layers, thus forcing away the closer of the O atoms. The K atoms come closer to the silicon atoms, and to the OH,F site, although both Si and OH,F are moved slightly in the same direction in compensation.

Altered micas. In X-ray photographs of altered and partly altered crystals, produced from phlogopites showing no stacking disorder, the vermiculite-like alteration products give some streaking along c^* and so are not stacked quite regularly; the main change in the structure is an expansion of the layer spacing from 10 to 14 Å. These effects resemble those in natural vermiculites; our synthetic materials seem to be less disordered than the natural ones. (Rayner)

Clinoptilolite in English sediments and soils. A zeolite mineral, identified as clinoptilolite on the basis of its X-ray powder pattern and thermal stability (Mumpton, *Am. Miner*. (1960) **45**, 351–369), occurs in soils of the Harwell series from Halton and Ellesborough, Buckinghamshire, and in the basal Thanet Beds (Eocene) at Pegwell Bay and Upnor, Kent (*Rothamsted Report for 1964*, p. 74; *for 1965*, p. 72; *for 1967*, p. 72). We have sought this mineral in many Mesozoic and Caenozoic sediments throughout southern England, and can now report its stratigraphic and geographic distribution in detail.

The Upper Greensand is the source of clinoptilolite in the Harwell series. We found it in the malmstone facies of the Upper Greensand at many localities in Buckinghamshire, Berkshire, Hampshire and parts of Surrey near Guildford and Dorking, but it is not an ubiquitous constituent of the Upper Greensand. It also occurs in the Chalk Marl (Lower Chalk) near Cholsey, Berkshire, and in the Arngrove Stone (Corallian) near Thame, Buckinghamshire. Soils developed on these rocks, or on superficial deposits containing material derived from them, are likely to contain clinoptilolite.

Composition and structure. Specimens of the zeolite from silt fractions of the basal Thanet Beds and the malmstone were purified by flotation in a liquid of S.G. 2·3, and by electromagnetic separation. This removed quartz, felspar, mica, glauconite and other heavy minerals, but failed to separate the clinoptilolite from opaline silica in the malmstone. A chemical analysis was therefore possible only with the zeolite from the Thanet Beds, because this deposit contains no opal. The unit formula of the Thanet Beds clinoptilolite, calculated on the basis of 72 oxygen ions, is:

$$Ca_{1\cdot6}(Na_{1\cdot1},K_{0\cdot7})(Si_{29\cdot1},Al_{7\cdot2},Fe_{0\cdot3})O_{72}.23H_2O$$

The Si/Al ratio is in the range accepted for clinoptilolite, but the

Ca/Na + K ratio is between those for clinoptilolite and the closely related zeolite, heulandite.

The X-ray powder diffraction patterns of both the Thanet Beds and the malmstone zeolites are almost exactly the same as that of clinoptilolite from Patagonia described by Mason and Sand (*Am. Miner.*, (1960), **45**, 341–350). The mean refractive index of the malmstone zeolite is 1·485, but that of the Thanet Beds mineral ranges from 1·488 to 1·491; the birefringence of both is <0·004. According to Deer, Howie and Zussman (*Rock forming minerals*, London: Longmans, (1963) Vol. 4, p. 377), the refractive indices of clinoptilolite range from 1·476 to 1·489, whereas those of heulandite are greater than 1·491. Our chemical and optical results therefore suggest that most of the Thanet Beds zeolite is intermediate between clinoptilolite and heulandite.

Origin. Zeolites of the clinoptilolite–heulandite type have been reported from many sediments outside Britain, and usually occur in rocks containing weathered volcanic material. However, there is no volcanic material in any of the English sediments containing clinoptilolite, and no other evidence of local volcanic activity at the times they were deposited. The mineral was not part of the detritus, because it commonly occurs in unabraded, euhedral crystals. Further, thin sections of the malmstone show that these crystals grew within cavities in the rock, especially in the chambers of Foraminifera. We therefore suspect that the ions needed for the diagenetic crystallisation of zeolite in these sediments were derived from detrital components of non-volcanic origin. (Brown, Catt and Weir)

Origin of chalcedony in Chiltern soils. Pieces of chalcedonic silica occur in many Chiltern soils, including those of the Rothamsted Farm. They are a constituent of the coarsest material in the Clay-with-flints, and therefore commonly occur in the Batcombe series. The largest pieces are tabular, 4–5 cm across and 0·5 cm thick, but many of the smaller pieces are subspherical. Avery *et al.* (*J. Soil Sci.* (1958), **10**, 177–195) suggested that they were formed in the soil from silica derived by partial dissolution of flint. However, they are merely part of the natural insoluble residue of the Chalk, because we have obtained identical fragments of chalcedony by acid treatment of various fossil shells in the Middle and Upper Chalk at Kensworth and Totternhoe near Dunstable, at Redbourn and at Water End near Hatfield.

The replacement of shell carbonate by chalcedony is most common in fossil lamellibranchs, especially *Inoceramus* spp., but also occurs in brachiopods (Terebratulidae and Rhynchonellidae) and echinoids (*Echinocorys scutatus* and *Micraster* spp.). Most of the tabular fragments in the soils are derived from *Inoceramus* shells, because these are much more common than any other fossil in the Upper Chalk of Hertfordshire. The silicification of all the fossils is partial, and varies greatly in extent; some *Inoceramus* fragments retain their original form almost completely, whereas other lamellibranchs and some of the brachiopods and echinoids contain only small, isolated patches of chalcedony.

The silica was emplaced after burial of the shells in the chalk sediment on the sea floor. An *Inoceramus* preserved partly in flint and partly in chalk showed no chalcedonic replacement in the flint but was extensively replaced where it had been covered by chalk. The flint, which was probably formed from silica deposited as a gel on the sea floor, had thus protected part of the shell from post-depositional silicification. The silica replacing shell carbonate was therefore derived from interpore solutions in the partly consolidated chalk.

In *Inoceramus* the chalcedony occurs mainly in rods that grow between the calcite columns of the shell. Each rod is composed of fibrous quartz crystals elongated parallel to the *c* crystallographic axis and arranged in a crude radial pattern perpendicular to the rod axis. The *a* crystallographic axes are also ordered so that one of them is parallel to the rod axis. The only crystalline component is α-quartz, but the mean refractive index of the chalcedony (1·535) suggests that it contains a little opaline silica, or possibly water. Surfaces of the chalcedony corresponding approximately to the original surfaces of the shell often have a macroscopic pattern of raised concentric circles, which interfere to give complex patterns. Similar patterns occur in a form of silica known as beekite, which replaces the calcite of fossil corals and brachiopods in the Carboniferous Limestone. (Brown and Catt)

Radiocarbon dating

Loess. An organic horizon resting on loess and overlain by Neolithic hillwash at Pegwell Bay, near Ramsgate, Kent, gave an age of 6120 ± 250 years B.P. (Sample No. I-3538). The sample was decalcified before analysis and modern roots were removed by repeated centrifugation in distilled water. This date indicates that the organic horizon accumulated during the Post-glacial Zone VIIb (the Atlantic period), and that the loess, which is the parent material of many Kentish soils, is therefore older than this.

Glacial deposits. Fossil moss separated from silts overlain by the Drab, Purple and Hessle Tills at Dimlington, Holderness, East Yorkshire, gave an age of 18500 ± 400 years B.P. (Sample No. I-3372). A second sample of moss from the same horizon was analysed in a different laboratory by a slightly different method, yet gave almost the same age, 18240 ± 250 years B.P. (Sample No. Birm. 108). As the Hessle Till or its correlatives are overlain at several localities in northern England by deposits of Late-glacial Zone I, the Drab, Purple and Hessle Tills must all have been deposited in the comparatively short period between 18000 and approximately 13000 years B.P. The Hessle Till is the parent material of soils over large areas of Lincolnshire, eastern Yorkshire and parts of Co. Durham and Northumberland. (Catt, Madgett and Weir)

Iron oxides. A previously unreported form, resembling lepidocrocite (γ-FeOOH), was found in natural and laboratory-prepared hydrous ferric oxides. The X-ray powder pattern has broad lines that correspond to the strongest reflections of lepidocrocite, but the reflection of largest spacing has $d \simeq 6{\cdot}7$–$6{\cdot}8$ Å, compared with $d = 6{\cdot}27$ Å for lepidocrocite. This displacement resembles those reported for pseudo-boehmite, the hydrous alumina precipitated from aluminium salts by alkali. Boehmite, γ-A10.OH, is isostructural with lepidocrocite and it has been suggested that the pseudoboehmite pattern is caused by the entrainment of water and foreign ions between elementary boehmite-like micelles.

The natural material was formed in tile drains in a restored open-cast coal site, apparently by the action of ferrous iron oxidising bacteria. (*Rothamsted Report for 1966*, p. 23). A similar material was formed in the laboratory as a thin surface film when an anaerobic fermentation solution of lucerne with ferric oxide was exposed to the atmosphere. In both of these all the reflections were broad, but the reflection corresponding to the 6·27 Å lepidocrocite reflection was much broader than the others. Similar material was encountered in work on the synthesis of iron oxides. The reddish-brown precipitate formed by aerating a mixed solution of sodium malonate and ferrous sulphate gave an X-ray pattern similar to those described. It differed from them in that more reflections were observed, all of which were narrower than the corresponding reflections of the natural materials, but again the reflection of spacing was displaced to $d \simeq 6{\cdot}7$ Å. By contrast, lepidocrocite prepared by atmospheric oxidation of ferrous bicarbonate or formate solutions gave broadened reflections, denoting small crystal size, but with the usual spacing, $d = 6{\cdot}25$ Å for the 020 reflection. The material precipitated from the malonate solutions contained 11·3, 10·6, 12·4 and 13·6% carbon for four different preparations. It seems therefore that the displacement of the 020 reflection in the synthetic malonate-derived material may be caused by retention of malonate ions, probably between some of the iron hydroxide layers that make up the lepidocrocite structure. The similar natural materials may also have absorbed organic material but this cannot be established by analysis because of the possible presence of plant debris that cannot be separated from the iron oxide. (Bloomfield and Brown)

Clay physics

Pore structure of clay aggregates. The pore sizes under investigation were extended to the range 3 to 4000 $\times 10^{-10}$ m and these can be conveniently divided into three groups according to the method of measurement used. The volume of micropores 3–15 $\times 10^{-10}$ m is measured by comparing the shape of the nitrogen sorption isotherm at $-196°$ C with that of a closely similar but non-porous adsorbent. Appreciable micropore volume is shown by a positive deviation in the isotherm at low pressures when comparison is made at the same relative pressures. Micropore volumes are also estimated by using different-sized molecules as adsorbates. The volume of micropores in clay aggregates can be as much as 20% of the volume of all the pores smaller than 4000 $\times 10^{-10}$ m. The volumes of pores 15–200 $\times 10^{-10}$ m (pores that show capillary condensation) are estimated from the higher pressure region of the nitrogen sorption isotherm, and the volumes of pores 200–4000 $\times 10^{-10}$ m are measured by carbon tetrachloride sorption over carbon tetrachloride–hexadecane solutions of known vapour pressures. Both these methods depend on the validity of Kelvin's equation. The methods are being applied to the study of aggregate formation by montmorillonites and illites as a function of particle size, cation saturation and solvent treatment. The effect of removing solvent by evaporation above its critical temperature, which avoids shrinkage from surface tensional forces, was studied; clay aerogels of small bulk density and freely permeable to gases were prepared from pentane.

The porosities of clay films prepared by evaporation of aqueous suspensions through cellophane membranes were estimated by density measurements. The apparent densities can be measured by a flotation method, and true densities by precision pycnometry of aqueous suspensions, using specially designed pycnometers for viscous suspensions. Although the films were always less porous than corresponding cores prepared under high pressures, the porosities of films from different materials varied surprisingly (0·04 to 0·27), indicating that the packing of lamellar crystals is critically dependent on particle size and morphology. (Gallavan and Greene-Kelly)

Optical studies on clays and clay soils. Clay orientation is commonly observed in soil sections and is used as a diagnostic feature in soil classification. However, it is often uncertain whether the clay orientation was produced by shearing stresses on the soil fabric (for example during differential earth movements), by wetting and drying, or by transport of the finer soil as a suspension, and its subsequent deposition along fissures (clay illuviation). We are investigating how shearing stresses, and wetting and drying, influence clay orientation in a soil of the Ragdale series. Small initial uniaxial stresses of 5–10 lb in^{-2} (3·5–7·0 N m^{-2}) imposed clay orientation in remoulded samples and this was not appreciably altered by subsequent drying and re-wetting, however this was done. The possibility that artifacts were introduced by the drying and impregnation of the samples with embedding resin was investigated, and it was established that our procedure does not significantly alter the clay orientation.

Although nearly all clay soils show some orientation effects, these vary considerably in their intensity and form. Obviously this depends on the way they arise, but there is evidence that under the same conditions some clays orient more easily than others. Mineralogical constitution has been suggested as an important factor in this connection and that illites, for example, orient more easily than montmorillonites. Our preliminary studies show that particle size has an effect that can be more important. (Greene-Kelly and Mackney)

Spectroscopy

The heavy metal-contamination of the soil, and of plants grown on plots given sewage sludge in the Woburn market-garden experiment, was described in the *Rothamsted Report for 1960*, p. 81. Acetic acid extractable Cr, Cu, Ni, Pb and Zn were significantly enhanced in the treated soils and also in the leek, globe beet and potato crops grown on them in 1960–61, although crop yields were unaffected. The treated plots received annual applications from 1942 to 1961, totalling 568 tons/acre, of West Middlesex sewage sludge, after which no more was applied. Examination of soil from the same plots in 1967 showed that the treated plots still contained significantly more of these elements than untreated plots, and carrots grown on them contained more Cr, Ni and Zn. Evidently foreign metals can be retained in soil for several years; this illustrates the danger of their accumulating when manures containing metal-polluted organic material are applied repeatedly. To lessen the risk of contamination, the sludge used at Woburn was deliberately chosen from a mainly residental area.

We are collaborating with the Soil Association in field trials at Haughley. Preliminary results show that the concentrations of Co, Cr, Cu, Fe, Mo, Ni, Pb, Sn, V and Zn in some of the sludge composts being used are much greater than in the soils to which they are being applied. (Le Riche)

Soil chemistry

Fumigation with methyl bromide. Soils from the fumigated strip on Broadbalk were analysed for bromine (*Rothamsted Report for 1967*, p. 81), mineral and mineralisable nitrogen. In an experiment done by Corbett (Nematology Department) a strip 3 m wide running across the field from plot 2A to plot 20 was fumigated with methyl bromide in October 1967. Soil samples were taken immediately afterwards from the fumigated part of each plot, together with samples from the adjacent unfumigated part. Soil from the treated part of the plots contained from 3 to 6 ppm more ammonium nitrogen than soil from the untreated part, and more nitrogen was mineralised on incubation (21 days at 25° C) by the treated than the untreated soils. These effects of soil fumigation on mineralisation of nitrogen are well known; the unexpected feature of the results was that methyl bromide failed to suppress nitrification. Ammonium nitrogen concentrations in the fumigated and unfumigated soils were uniformly small (less than 2 ppm) after incubation. The reason became apparent in the June after fumigation, when zones a metre or so in diameter of wheat in the fumigated strip became scorched. These zones corresponded to the methyl bromide injection sites, suggesting that, contrary to earlier conclusions (*Rothamsted Report for 1967*, p. 81), the application of methyl bromide was uneven. As twelve soil cores were taken per sample, each sample probably contained cores from both heavily and lightly fumigated zones. Presumably the ammonium released during incubation by soil from heavily fumigated zones was nitrified by nitrifying organisms derived from soil from the lightly fumigated areas, in which they survived. (Jenkinson)

Bromine in the above-ground parts of wheat plants from the experiment was measured by X-ray fluorescence spectroscopy. Much bromine was taken up by the wheat plants in fumigated plots, especially in the scorched zones. For example, there were two scorched zones in the fumigated part of plot 3 (unmanured) and wheat plants taken in mid-July from the centre of one zone contained 4200 ppm bromine, from the other 2400 ppm. Wheat from an unscorched but fumigated part of this plot contained 98 ppm bromine, whereas wheat from the untreated part of plot 3 contained only 2 ppm. A semi-quantitative comparison of the plants from one of the scorched zones on plot 3 and from the untreated part of the same plot showed that roughly similar amounts of iron, manganese, calcium, potassium, magnesium, phosphorus, chlorine and sulphur were present in both; the ratios of the contents of these elements in the scorched and unscorched plants ranged from 1·25 to 0·71, whereas with bromine this ratio was approximately 2000. Voelcker demonstrated that bromide depresses wheat yields (*Jl R. agric. Soc.* (1900), *3rd ser.* **11**, 553), and, as we did, found that the damage is not apparent until late in the growing season. (Brown and Jenkinson)

Residual effects of formaldehyde on the mineralisation soil organic matter. Soil samples were taken in March 1968 from a field experiment (Pastures, sponsored by Widdowson and Salt) on the residual and cumulative effects of formaldehyde on the growth of wheat.

Table 2 shows the oxygen consumed, carbon dioxide evolved, and nitrogen mineralised by these soils on incubation with and without an 18-hour exposure to chloroform vapour. Incubation was for 10 days at 25° C; all soils were inoculated with fresh soil before incubation, whether exposed to chloroform vapour or not. Oxygen uptake, carbon dioxide evolution and nitrogen mineralisation were all increased by exposure to chloroform vapour. These increases were smaller in soils that had previously been treated with formaldehyde. Presumably a section of the soil biomass was eliminated by the formaldehyde; in samples not receiving formaldehyde this part of the biomass remained to be killed by chloroform, and thus contributed to the observed flush of decomposition. The results in Table 2 were obtained with soils from plots where the wheat received 63 kg/ha nitrogen; similar results were obtained with soils from plots where the wheat received 125 kg/ha. For the soils not treated with chloroform, metabolism was slightly faster in soil that had been repeatedly treated with formaldehyde than in untreated soil; this suggests that the flush of decomposition after fumigation had not completely subsided at the time of sampling, 6 months after formaldehyde was last applied.

TABLE 2

Effects of fumigation on the mineralisation of soil organic matter

Field treatment	Laboratory treatment	O_2 consumed, ml O_2 at S.T.P./ 100 g soil	CO_2 evolved, mg CO_2–C/ 100 g soil	Increase in mineral N, mg mineral N/ 100 g soil
None	None	22	9	0·8
	$CHCl_3$ vapour	57	25	4·5
Formaldehyde in 1965, 1966, 1967	None	23	11	1·2
	$CHCl_3$ vapour	37	17	2·8
Standard error		±2·0	±1·5	±0·14

The release of less mineral nitrogen after the second fumigation may explain, in part at least, the decreasing effectiveness of repeated formaldehyde treatments in increasing crop yield. For an example of this effect, see *Rothamsted Report for 1965*, p. 49. (Jenkinson and Powlson)

Radio-carbon dating of soil organic matter. Table 3 gives some preliminary results from our work on the measurement of natural and bomb-derived radio-carbon in soil. The main conclusions so far are:

(1) The soil organic carbon in arable topsoil is much older than suggested by earlier calculations, based on measurements of the rate organic matter accumulates in soil.

(2) The ages of the organic carbon in soils sampled in the 1880s, from two arable fields less than a kilometre apart on the same soil series, were similar all the way down the profiles. This suggests that the age of the organic matter in these soils is characteristic of the soil, rather than of some adventitious event in its history.

(3) The age of the organic carbon increases with depth down the profile.

(4) In contrast to the Broadbalk and Geescroft samples, which contain little or no coal or charcoal, both samples from Park Grass contain coal, in similar amounts. The Park Grass 1886 and 1966 samples contain 0·16% and 0·13% coal carbon respectively. Assuming that the coal contains no radioactive carbon, and knowing the total and coal-carbon contents of the soil, the age of the coal-free soil carbon can be calculated. For the 1886 sample the corrected equivalent age is 600 years, compared with 50 years for the 1966 sample.

(5) Samples taken in 1966 from both Park Grass and Broadbalk give much more recent dates than the corresponding samples taken in the 1880s. This difference is attributed to the entry of radiocarbon from thermonuclear explosions into the soil organic matter. Knowing the amount of thermonuclear radiocarbon in the atmosphere over the last decade (Nydal, R., *J. Geophys. Res.* (1968) **73**, 3617), the amount of organic matter entering the soil each year can be calculated from the difference between the pre- and post-bomb results. For Broadbalk plot 3 this amounts to 1000 kg organic carbon per hectare per year, and for Park Grass plot 3 from 2500 to 2000 kg, the exact figure depending on assumptions about the life span of grass roots. For comparison, the amount of organic carbon harvested each year from Broadbalk (plot 3) is 1400 kg per hectare (grain + straw), from Park Grass (plot 3) 700 kg per hectare (two hay crops). (Jenkinson)

TABLE 3

Radiocarbon dating of organic matter in Rothamsted soils

Field	Plot	Cropping	Sampling depth, in.	Sampling date	% C	% N	pH	Equivalent age, years*
Broadbalk	3 (unmanured)	Continuous wheat	0–9	1881	0·94	0·104	8·0	1385 ± 140†
			9–18	1881	0·58	0·076	7·6	1950 ± 130
			18–27	1881	0·44	0·065	7·1	3670 ± 130
			0–9	1966	0·96	0·107	8·0	875 ± 120†
Geescroft	3 + 4 (P + K but no N)	Continuous beans	0–9	1883	1·04	0·118	7·1	1280 ± 125
			9–18	1883	0·58	0·084	7·1	1870 ± 130
			18–27	1883	0·49	0·071	7·1	3180 ± 135
Park grass	3, unmanured, unlimed	Permanent grass	0–9	1886	3·14	0·270	5·7	1040 ± 125‡
			0–9	1966	3·09	0·256	5·4	390 ± 120‡

* i.e. the age of a homogenous sample with the same value of δC-14 as that of the (heterogeneous) sample analysed.

† Decalcified with dilute hydrochloric acid before dating. ‡ Contains coal and charcoal.

Sulphate reduction in waterlogged soils. The physiological disease of rice caused by the formation of free H_2S in the soil occurs widely. When immobilised as FeS, S^{2-} formed by microbial reduction of SO_4 seems not to harm the rice plant, and so the factors that influence the distribution of S^{2-} between FeS and H_2S in flooded soils are of economic importance. The proportion of the reduced sulphur that occurs as H_2S is influenced by the reactivity of the ferric oxide contained in the soil, and the term 'active ferric oxides' was introduced by Japanese workers to denote the fraction of the total ferric oxide content that can form FeS. Our laboratory studies show that this simple concept is not adequate. With a given soil the proportion of free H_2S is decreased by increasing the proportion of soil, i.e. of 'active ferric oxide', in the reaction mixture, but the relationship between the iron content of the reaction mixture and the amount of FeS formed during incubation is not linear; the proportion of free H_2S formed decreases asymptotically with increasing Fe_2O_3 content.

The FeS : H_2S ratio is also influenced by the nature of the plant material used as the source of energy. The samples of dried lucerne and rice blade used in our experiments dissolved nearly identical amounts of iron when incubated anaerobically with soil without added sulphate, but in sulphate reduction experiments with lucerne and rice blade respectively, about 40 and 20% of the reduced sulphate was recovered as H_2S, although the pH values of the two systems were almost the same.

In the sulphate reduction experiments the amounts of Fe equivalent to the FeS formed during the incubation greatly exceed the amounts of Fe dissolved by anaerobic incubation without added sulphate. This suggests that the greater part of the FeS is formed by direct reaction between S^{2-} and undissolved Fe_2O_3. However, on this assumption it is difficult to explain the apparently greater ability of rice blade than of lucerne to increase the reactivity of the Fe_2O_3 with respect to H_2S, when without added sulphate the two plant materials dissolve identical amounts of the oxide.

In these experiments the system becomes very alkaline when Na_2SO_4 is used as the source of sulphate, and comparison of the with- and without-Na_2SO_4 systems, in which the final pH values are around 8·0–8·5 and 6·5–7·0 respectively, is of doubtful validity. However, the pH of the system remains very close to that of the sulphur-free system when elemental S is substituted for Na_2SO_4, but the relationship between the FeS : H_2S ratios obtained with lucerne and rice blade persists. Relatively more FeS is formed under the less alkaline conditions that develop when S is substituted for Na_2SO_4, although the fact that the solubility of FeS increases with decreasing pH would suggest the opposite effect; the amount of iron dissolved increases with decreasing pH in the sulphur-free system, which supports the view that reaction between dissolved iron and S^{2-} is more important than direct reaction of the latter with Fe_2O_3. (Bloomfield and Pruden)

Soil organic matter–trace element reactions. Continuing our study of the reactions between soil organic matter and trace elements (*Rothamsted Report for 1967*, p. 78), we find that the oxides of Cu, Pb, Zn, Ni, Co, Mn and Fe are dissolved by aerobically decomposing lucerne or wheat straw. As judged by their concentrations in water extracts of the reaction mixtures, and in contrast to their behaviour under anaerobic conditions, Fe and Mn are the least mobile of the elements studied. Relatively large amounts of all the elements combine with the insoluble organic residue. After removing untreated oxide by sedimentation in water, the concentrations of metal in the lucerne residues ranged from 1·5 mg Pb to 5·8 mg Mn per g dry matter. With straw the values were considerably smaller. Extraction with N/10 acid decreased the metal contents of the residues to values closely comparable with those reported in last year's *Report* (p. 79) for acid-extracted lucerne–metal carbonate composted products.

Quite small proportions of the water-extractable metals are removed by dialysis against water through Visking cellulose, although the greater part is dialysable against dilute acid. This constitutes another difference between the aerobic and anaerobic systems, the products of the latter being in true solution. (Bloomfield, Kelso, Maria Piotrowska and Pruden)

Water extracts of aerobically incubated lucerne are dark brown and much more intensely coloured than those from wheat straw. The extracts are slightly alkaline, and almost all the coloured material is precipitated when the solution is acidified to about pH 3. The mobilised humified material is thus essentially humic, as opposed to fulvic, acid. Residual coloured material was removed from the acidified extract by treatment with polyamide powder and small amounts of polysaccharide were precipitated by adding ethanol.

Material sorbed by clay from the original extract has a profound effect on the surface properties of the clay—after treatment with a composted lucerne extract and washing with water, a sample of kaolinite flocculated–deflocculated at about pH 3, compared with about pH 9 for the untreated clay. (Bloomfield and King)

Mechanism of podsolisation. Earlier work on the reaction between aqueous leaf extracts and ferric oxide led to the postulate that iron was dissolved in true solution (*Rothamsted Report for 1952*, p. 56). Later workers found the mobilised iron to be in colloidal suspension and so regarded the process as one of peptisation. Our evidence also led us to presume that ferric iron was reduced to the ferrous form, and this view, too, has been contested. Although it must be admitted that the evidence is not conclusive, reduction of the iron still seems the most likely possibility, and on this assumption an explanation can be suggested for the discrepancies between our results and those of later investigators, who seem to have confined their studies to fully aerobic systems. If iron is reduced in the process of dissolution, reoxidation of the ferrous compounds could result in the formation of colloidal material. To test this hypothesis hydrous ferric oxide was treated with an aqueous leaf extract, in a Visking dialysis tube immersed in leaf extract of the same concentration. Air was replaced by nitrogen and the apparatus sealed with oxygen traps containing granulated zinc and acidified Cr^{2+} solution. After about 3 weeks the concentration of dissolved iron in the dialysate and in the dialysed reaction mixture were determined; 96 and 98% respectively of the iron dissolved by Scots

https://doi.org/10.23637/ERADOC-1-123

Pine and larch needle extracts was in true solution. The remainder could be colloidal, but more probably resulted from slight disequilibrium of the solution and dialysis processes. With an oak leaf extract, 71% of the dissolved iron was in true solution.

Much of the dissolved iron contained in the larch and oak leaf dialysates was precipitated after exposure to atmospheric oxidation for 4–5 days. Exhaustive dialysis of the aerated dialysates against water removed only 13 and 9% respectively of the originally dialysable iron from the larch and oak leaf solutions.

It therefore seems that the initial stage in the mobilisation of iron by aqueous leaf extracts is essentially a process of solution rather than of peptisation. The formation of colloidal iron compounds in the aerated dialysates supports the view that the iron is reduced in the solution process. (Bloomfield)

Isolation of polyphenols from aqueous extracts of fallen oak leaves. The oak extract was chosen to examine whether a fraction of large molecular weight containing only polyphenols could be isolated, using Sephadex G-25. Dialysing the extract through Visking tubing for 14 days, with frequent changes of water, removed all but negligible amounts of potassium and sodium. The dialysate constituted 9·6% of the dry weight of the starting material and contained gallic, protocatechuic, vanillic and ellagic acids; the last was deposited from solution after a few days.

The dialysed fraction represented 3·6% of the dry weight of the starting material, and paper chromatography showed it contained a small amount of ellagic acid, some of which precipitated on standing. The main bulk of the dialysed fraction consisted of material unresolved on two-way paper chromatograms (6% acetic acid) and *sec.*-butanol/acetic acid/water (14/1/5)) and seen as a streak from the origin in the direction of the first solvent. Some resolution was obtained by passing a 50% aqueous acetone solution through a column of Sephadex G-25, with 50% aqueous acetone as eluent. Two bands were resolved, the first, dark-brown and well-defined, emerged at the void volume of the column. On paper chromatograms with the above solvents this product gave a streak from the origin to R_f 0·8 (in 6% acetic acid). The pH of an aqueous solution of the fraction was 4·2; with aqueous ferric chloride it gave a green colour.

The second band was light brown and tailed considerably. It gave a streak of R_f 0·0–0·9 (in 6% acetic acid), densest between R_f 0·2 and 0·7. The pH of an aqueous solution was 3·8, and the colour with aqueous ferric chloride yellow-green.

The ratio of the weights of the fractions was: Band 1/Band 2 = 1/1·6.

The molecular weight of compounds excluded by Sephadex G-25 at the void volume decreases when the eluent is changed from water to an organic solvent. With water as eluent the exclusion M.W. should be about 5000, but using 50% aqueous acetone may have decreased the value to less than 2000.

Because polysaccharides and polyphenols behave similarly with Sephadex, polysaccharides were isolated by precipitation with ethanol, dissolved in water, passed through a column of polyamide powder and eluted with water. The small polyphenolic contaminant was held at the top of the polyamide column and the pure polysaccharides were isolated from the effluent in the usual way.

Hydrolysis of oak-leaf polyphenols. The two fractions from the Sephadex column, after removing polysaccharides, were hydrolysed with boiling 2N HCl for 1 hour. Phenolic-hydrolysis products were isolated by extracting the hydrolysate with ethyl acetate. When chromatographed Band 1 showed strong spots of gallic, protacatechuic and ellagic acids, also a considerable amount of a new spot, R_f 0·0 in acetic acid, and running just ahead of ellagic acid in *sec*.-butanol/acetic acid/water. A faint streak of material, unresolved in the first direction, remained. Band 2 yielded only small amounts of gallic and ellagic acids and retained much of the original unresolved material.

Different phenolic fractions can thus be resolved on Sephadex G-25. These fractions contain hydrolysable components; it is known that oak wood and oak bark tannins are of mixed hydrolysable and condensed types, but this is the first time that hydrolysable tannins have been isolated from the larger molecular weight fraction of oak leaf polyphenols. (King)

Apparatus and techniques

X-ray fluorescence analysis

Silicate analysis for major elements. To minimise matrix effects, fusion of the silicate into a glass with lithium tetraborate-lanthanum oxide flux (Norrish *et al.* (1967) *Methods in determinative mineralogy*, Chapter 4, Edited by J. Zussman, London: Academic Press) was adopted and applied with our equipment. Instrumental conditions were established and procedures for calculating element percentages from observed X-ray intensities developed. This required writing a programme to correct for dead time counting losses, and to calculate nominal percentages by comparing the corrected count rates with those obtained from standards. The nominal percentages are then corrected for residual matrix effects, using a programme originally developed by Norrish, which has been adapted for the Rothamsted computer.

Rocks and soils can be analysed for Fe, Mn, Ti, Ca, K, P, Si, Al, Mg and Na. Ten samples can be analysed per day; about half the time is spent in preparing the samples and half in measuring the intensities. At present the output from the X-ray spectrometer is produced on a printer and has to be punched on tape for computing. By linking a tape punch to the spectrometer it will be possible to use the computer to produce corrected results directly from the tape output. (Brown and Kanaris-Sotiriou)

Total sulphur in soils. The method described in last year's Report (p. 80) was applied successfully to soils containing 50–500 ppm total sulphur, the usual range for agricultural soils; for these relatively small concentrations it is necessary to avoid contamination of the sample in the spectrometer. Absorption of sulphur compounds from back-streamed oil vapour causes appreciable error; even when an uninhibited mineral oil of small sulphur content is used in the rotary pump used to evacuate the spectrometer, the apparent sulphur content increased at about 4 ppm per minute. This contamination was decreased to less than 0·2 ppm sulphur per minute, which is acceptable, by covering the surface of the specimen that is exposed to X-rays with a 2 micron film of 'Makrofol KG', a polycarbonate. With these conditions, less than 10 ppm of S in soil can be detected. (Brown and Kanaris-Sotiriou)

Thin windows for flow proportional counters. Thin windows are required in determining light elements by X-ray spectrometry. Various materials have been used: mylar film, 6μ, and recently 3·5μ thick, 2μ polycarbonate films, and 1μ polypropylene film. The last is prepared in the laboratory by stretching thicker polypropylene, but the others can be bought.

Some users have found that polycarbonate films rupture after they have been used for a short time. We find that, when polycarbonate films are carefully fitted, they last for more than six months. For long life it is essential to fit the polycarbonate film so that its direction of easy splitting is transverse to the collimator blades that support the film when the spectrometer is evacuated. It is also essential to ensure that the ends of the collimator blades are quite smooth.

Because of the long life of the correctly fitted polycarbonate film we have measured the transmission of commercially available thin films for some light elements and compared these with the transmission expected from polypropylene films stretched to 1 micron thickness (Table 4).

TABLE 4

Percentage transmission of thin films

Radiation Film	S$K\alpha$	Si$K\alpha$	Al$K\alpha$	Mg$K\alpha$	Na$K\alpha$
12μ mylar	59	32	16	6	3
6μ mylar	77	58	43	26	13
3·5μ mylar	88	76	66	53	37
2μ polycarbonate	90	81	73	63	50
1μ polypropylene	99	97	95	92	88

The measured values are for films coated with a layer of aluminium to make them conducting; the values calculated for 1 micron polypropylene are therefore larger than those that would be obtained in practice.

Of the commercially available films, 2μ polycarbonate is best; the advantage of the extra transmission obtained from 1μ polypropylene films must be weighed against the effort and practice needed to make them. (Brown and Kanaris-Sotiriou)

Determination of dead time of counting equipment. When measuring X-ray intensities it is essential to know the time that the counting system is inoperative after detecting each photon, the 'dead time'. A method was devised that allows the dead time to be calculated directly from measured intensities. Using a single foil method, the times taken to accumulate a fixed number of counts (N) before and after a thin foil is inserted in the beam, T_1 and T_2, respectively, is measured for a range of count rates. A value of t must be found for which $(T_1 - Nt)/(T_2 - Nt)$ is constant and independent of count rate. The dead time is then t (Norrish *et al.* (1967) *Methods in determinative mineralogy*, Chapter 4, Edited by J. Zussman, London: Academic Press). To avoid time-consuming trial and error, a least squares method was adopted to calculate the 'best' value of t directly.

For accurate intensity measurements, t must be known to better than 10% relative. This requires that $N \simeq 10^6$ and to avoid errors caused by instrumental drift the counts are best accumulated by alternating between measurements without and with foil for periods of $T_1/10$ and $T_2/10$ respectively. (Brown, Kanaris-Sotiriou and Rayner)

Determination of fluorine in silicates. The important influence of constituent fluorine on the exchange properties of micas emphasises the need for a reliable method for determining fluorine. The method briefly described in last year's Report (p. 79) was refined to measure the fluorine contents of micas quickly and accurately. Attention was especially directed towards improving the reproducibility of the conditions for pyrohydrolytic separation of fluorine; a gas-heated reaction tube allows better control than the electrical heater previously described. Based on the results of many replicate analyses, the method has a relative precision of ±2% and one person can complete eight analyses in a day. (Newman)

Determination of sulphur dioxide with rosaniline dyes. In seeking ways to improve the colorimetric finish to the determination of sulphur dioxide in the determination of total sulphur in soils, we reinvestigated the relative merits of pararosaniline hydrochloride and rosaniline hydrochloride (fuchsin) as colorimetric reagents in the sulphite–hydrochloric acid–formaldehyde reaction. The purity of the dye samples can be assessed by paper chromatography and spectrophotometry. When pure, each is suitable for determining sulphur dioxide, but pararosaniline hydrochloride is preferred because of the smaller optical density of the reagent blank.

The commercial samples at our disposal were very impure, and sometimes incorrectly labelled by the manufacturers—the 'pararosaniline hydrochloride' used by Bloomfield (*Rothamsted Report for 1961*, p. 70) was actually fuchsin. Samples are conveniently purified by precipitating the base from a filtered solution of the hydrochloride with sodium hydroxide and recrystallising from aqueous methanol. The base, which can be stored as such, is reconverted to the hydrochloride in preparing the reagent.

The chief defect of the unpurified reagent is the lack of reproducibility between successive batches prepared from the same sample. The purified reagent does not suffer from this defect; it is also very much more sensitive and gives a linear response up to 80 μg SO_2 per 50 ml, compared with a maximum linear response of about 20 μg SO_2 per 50 ml with the old reagent. (Bloomfield, King and Pruden)

Colorimetric determination of calcium in silicate minerals. Calcium in silicate minerals is usually determined by flame photometry or by titrating with EDTA. The flame photometric determination is subject to interference from aluminium, sodium and potassium, and the end-point of the EDTA titration is often difficult to see.

We find that glyoxal bis (2-hydroxy anil), (GBHA), in alkaline solution, is suitable for determining calcium in silicate minerals. Co-precipitation of calcium with magnesium and iron under the alkaline conditions of the reaction is prevented by adding mannitol to the test solution; aluminium remains in solution as sodium aluminate. The red calcium/GBHA complex is extracted into a mixture of chloroform and isoamyl alcohol before measuring its optical density at 531 nm.

Fifty micrograms of calcium can be determined in the presence of 3000 μg of magnesium and 2000 μg of iron. The calibration is linear between 0 and 80 μg of calcium per 20 ml. (King and Pruden)

The effect of organic matter on the determination of ferrous iron in soils and rocks. Organic matter interferes in the final determination of Fe^{2+} in the analysis of soils and rocks (Hillebrand *et al.* (1953), *Applied inorganic analysis*, New York: Wiley) and numerous methods have been proposed to overcome errors from this source. Equally serious errors, which are often overlooked, are caused by the reduction of ferric iron by organic matter during the initial acid attack—an effect demonstrated as long ago as 1914 (Morison, C. G. T. Doyne, H. C., *J. agric. Sci.* **6**, 97–101). We find that adding ferric oxide to a humose soil or to an organic shale causes a several-fold increase of the apparent ferrous content, as determined colorimetrically in hydrofluoric acid digests. The apparent ferrous content increases to a maximum with increasing proportions of ferric oxide, and the total iron content of the digest only appreciably exceeds the ferrous content once this maximum is attained, i.e. once the reducing capacity of the organic matter is exceeded. As determined in the presence of organic matter, values for the ferrous iron contents of silicate materials obtained by present-day chemical methods do not have even qualitative significance. The same strictures apply to the acid extractants commonly used to determine labile ferrous iron in waterlogged soils, e.g. aqueous aluminium chloride, sodium acetate, etc. (Bloomfield and Pruden)

The determination of ferrous sulphide in soil in the presence of ferric oxide. In studying the course of the reduction of sulphate in waterlogged soil, ferrous sulphide had to be determined in the presence of unreduced ferric oxide. Using mixtures of calcium sulphide and ferric oxide we found that considerable proportions of the sulphide were oxidised by Fe^{3+} when the mixtures were acidified to release H_2S. Adding metallic zinc or tin to the mixture before acidification did little to limit the extent of the interference, but the loss of sulphide was largely overcome by adding stannous chloride to the acid used to liberate H_2S. The stannous chloride reagent gave 97·5% recovery of S^{2-}, with a 30-fold excess (weight for weight) of Fe_2O_3 over S^{2-}.

Although this method was satisfactory in our work with laboratory-incubated soils, its use with natural soils should be regarded with caution. Pyrite is an important constituent of many sulphidic soils, and with the stannous chloride reagent this could cause positive error. The distribution of FeS in gley soils is usually very sporadic, and the need to avoid oxidation precludes prior mixing and subdivision of the sample; a representative sample would thus probably need to be impossibly large. To this difficulty must be added those of determining the dry weight of the sample and of avoiding errors caused by the presence of pyrite and/or ferric oxide, so that to attempt to determine ferrous sulphide in a natural soil by existing methods seems hardly worth while. (Bloomfield and Pruden)

Staff and visiting workers

Mrs. Maria Piotrowska, of the Pulawy Institute of Soil Science and Plant Cultivation, Poland, arrived in October to spend a year in the department. J. H. Rayner acted as conference secretary for the Institute of Physics X-ray Analysis Group Conference on Accuracy and Automation in X-ray Analysis. The department was visited by members of the joint conference of the Groupe Belge des Argiles and the Clay Minerals Group of the Mineralogical Society.

https://doi.org/10.23637/ERADOC-1-123