

## Some Chemical Observations on Post-Glacial Lake Sediments

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## SOME CHEMICAL OBSERVATIONS ON POST-GLACIAL LAKE SEDIMENTS

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This paper reports the results of a somewhat exploratory investigation of the chemical composition of cores taken from the sediments of a number of lakes of the English Lake District. All the lakes studied are of glacial, and therefore presumably of synchronous, origin. The depth of post-glacial sediment varies from lake to lake but is normally between 4 and 6 m. This material, with which the paper is mainly concerned, was laid down during the biologically active phase following the end of glaciation approximately 10000 years ago. Below the organic muds of the post-glacial period, the sediment consists of glacial clays, usually varved, which pass downward into silty clays and sands the total depth of which is at present unknown.

The variation in composition of the sediments with depth and therefore with time presents a pattern of change which is observed to recur in most of the lake sediments studied. This pattern of change is most strikingly seen in the variation of carbon content with depth, but related sequences of change may be observed in the distribution of major inorganic components, for example sodium, potassium and magnesium. The observed changes in composition of the sediment can most easily be explained if the sediment is regarded as a sequence of soils derived from the drainage areas of the lakes. The composition of the residues eventually reaching the lake bed can then be accounted for in terms of the rate of erosion of the drainage basin rather than in terms of changing rates of organic productivity either on the drainage basin or in the lake waters.

The composition of the sediments does not appear to be greatly influenced by events within the lakes themselves except in the case of elements which may migrate more readily under the reducing conditions which may arise in soils and in lake muds. Examples of these are iron and manganese, and the distribution of these elements in the sediment may be used to deduce the redox conditions in the soils of the drainage basin in past times, or in the muds and hypolimnetic waters of the lakes themselves. Biological activity within the lake waters may also influence significantly the distribution in the sediments of distinctly biophile elements, of which phosphorus and sulphur are examples.

Even in the case of phosphorus, however, it seems likely that co-precipitation reactions may have more influence on deposition efficiency than does incorporation into biological tissues.

The cause of the apparently synchronous changes in erosion intensity recorded in the sediments of the various lakes remains in doubt. Some evidence derived from the halogen and boron content of the sediments is presented which may suggest at least a synchronism between major climatic changes and the variations in erosional activity.

Since halogens and perhaps boron are largely derived from oceanic air-streams, the rate of deposition of these elements may be expected to be related to the 'oceanicity' of the climate at the time of deposition of the sediment. A direct relationship is observed between the deduced intensity of erosional activity and the halogen and boron content of the sediment. The meaning of this relationship is rendered somewhat ambiguous however by consideration of possible changes in soil ionic balance attributable to progressive loss by leaching of soil-derived anions with the passage of time.

Although the gross composition of the sediment is largely dependent on conditions in the drainage system rather than in the lake waters, some deductions may be made which indicate the availability of nutrients dissolved in the waters of the lakes in past times. If material is rapidly removed from the drainage basin by erosion, nutrient elements are lost to the sediment locked in the lattice of unleached mineral particles. If however the rate of erosive removal of soil from the land surface is reduced, the mineral particles are held in the soil column in a position which allows more efficient leaching of soluble components, which then become available to the living populations of the lake.

#### INTRODUCTION

The lake basins with which this paper is concerned are contained within the area of north-west England known as the English Lake District. The lakes were formed by glaciation of a dome-shaped terrain of Ordovician and Silurian rocks. The location of the various

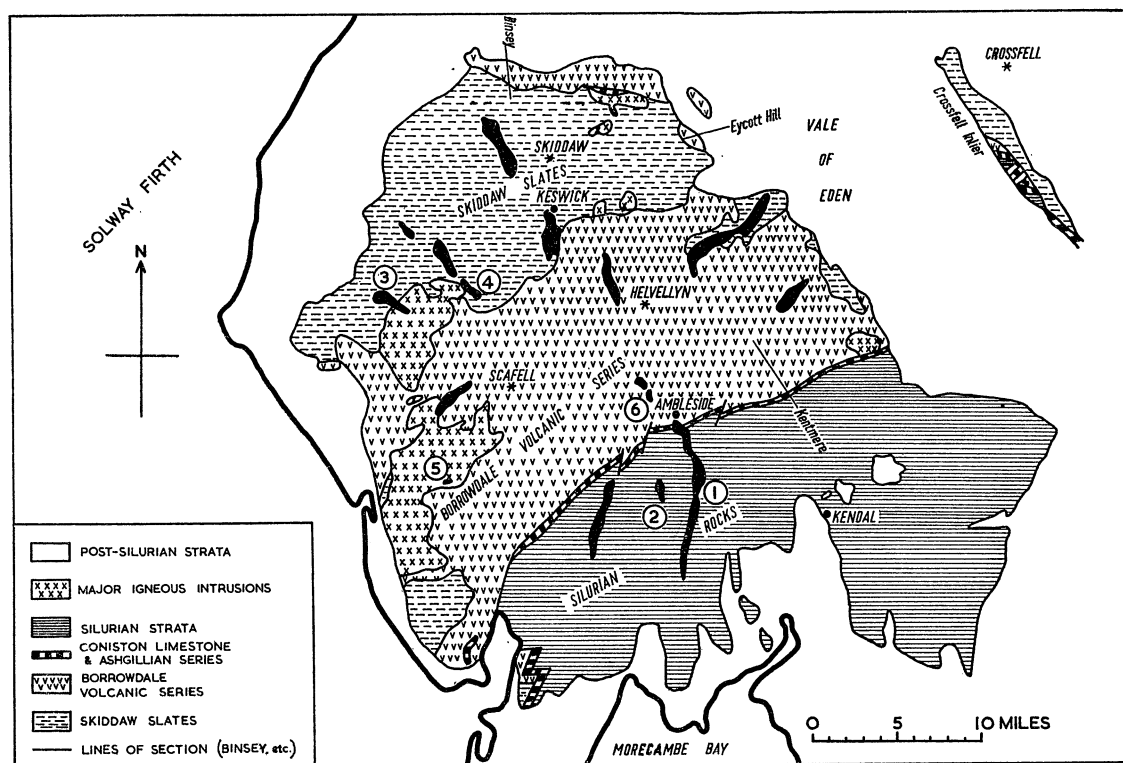


FIGURE 1. Distribution of major rocks of the English Lake District and location of the lakes discussed: (1) Windermere, (2) Esthwaite, (3) Ennerdale, (4) Buttermere, (5) Devoke Water, (6) Rydal.

lakes discussed is shown in figure 1 in relation to the geology of the area. The lakes of this area present a convenient variety of contemporary internal biological productivity ranging from the comparative poverty of Ennerdale to the richness of Esthwaite. Since much of the past work of the Freshwater Biological Association has been devoted to the study of the present-day biology and chemistry of this lake system, it seemed to be particularly advantageous to study the chemistry of the lake sediments against this background of knowledge. Mrs Tutin (Pennington), Pearsall and Franks have furthermore provided an invaluable basis for the present work from their studies on the sediments of Windermere (north basin), Rydal and Esthwaite (Pennington 1943, 1947; Pearsall & Pennington 1947; Franks 1956; Franks & Pennington 1961). These studies were largely concerned with pollen and diatom distribution, though chemical observations were made by Pearsall & Pennington (1947) on Windermere north basin and by Pearsall, Gay & Newbould (1960), on Rydal and Esthwaite. The work of Mrs Tutin (W. Pennington 1943) established an accurate chronology for the sediment of Windermere. Round (1957, 1961) has studied the distribution of diatoms in the sediments of Esthwaite and Kentmere.

#### NATURE AND SOURCE OF THE SEDIMENTARY MATERIAL

The total depth of sedimentary material accumulated in the glacially formed rock basins of the lakes studied is not at present known. There exists in the sediment however a clearly recognizable division between the mainly inorganic material laid down during active glaciation and the later more organic muds accumulated during the post-glacial biologically active phase of the drainage basin. This division between glacial clays and post-glacial organic deposits (the close of zone III) serves as a convenient reference baseline since it has been dated by Pennington (1943) at some 10 000 years B.P., a figure in good agreement with the radio-carbon date (Godwin & Willis 1959) on the zone II deposits of Windermere— $11\,878 \pm 120$  B.P. For a detailed description of the appearance and texture of the Windermere sediment reference should be made to Pennington (1943).

The thickness of the post-glacial organic deposit varies somewhat from lake to lake. For example in the north basin of Windermere and in Ennerdale the organic sediment is some 6.0 m thick while in the south basin of Windermere and in Esthwaite it is only about 4.5 m thick. The thickness of the post-glacial sediment clearly bears little relationship to the internal productivity of the lake, since Ennerdale is much less productive than Esthwaite, while the post-glacial deposit of Ennerdale is thicker than that in Esthwaite. It seems likely that the thickness of the deposits, at least within this group of lakes, is related to the rate of erosion of the drainage basins, which in turn is related to the topography of the water-sheds. From this it may be inferred that for a single lake, the major source of the sedimented material is the drainage basin of the lake rather than the material photosynthesized in its waters.

The inorganic glacial clays and silts were obviously derived from local erosion, and since 70 to 80% of the post-glacial deposit also consists of mineral matter so derived, there remains only the organic fraction which could possibly have been supplied by photosynthetic activity in the lake itself. It is probable however (Lund, Mackereth & Mortimer 1963) that the major part of the organic matter synthesized within the lake is consumed in the lake sediment rather rapidly, since the annual oxygen decrement in the hypolimnion



of the lake (at least in the north basin of Windermere) is remarkably close to that required to oxidize the annually photosynthesized material. Thus the stable organic matter which is accumulated in the lake deposit is likely to have been derived from the soils of the drainage basin rather than from production within the lake, the soil-derived organic material having already been oxidized at the soil surface to a state of considerable stability towards further oxidation. Indeed the material which finally becomes buried in the lake sediment must be very resistant to oxidation, since it must reside for a number of years at or near the sediment surface exposed to oxidizing conditions before finally becoming incorporated below the mud surface to be protected from further oxidation. One may assume then that by far the greater part of the sedimentary material of the lake muds under consideration, inorganic and organic, has been derived from erosion of soil, a view which is supported by the close similarity in chemical composition between these sediments and ordinary soils. One may then regard the sedimentary sequence of a lake deposit as a series of samples of soils eroded from the drainage basin and deposited chronologically in the lake bed.

The possibility of modification of the sedimented material must be recognized, particularly in the case of those elements whose migration rate is markedly altered by oxidation or reduction. The examples of iron and manganese are discussed in a later section. Additions to the sediment from the lake biomass must also take place since the sediments contain the remains of animals and plants of planktonic origin, but the gross chemical composition of the sediment does not appear to be greatly changed by such additions. However, the precipitation of some constituents, for example phosphorus, may be significantly influenced by incorporation of the element in the phytoplankton with subsequent deposition. It is known that *Asterionella*, a common phytoplanktonic species, is able to concentrate phosphorus into the cell from very low external concentrations (Mackereth 1952). This organism then, and presumably many others, has the capacity to precipitate phosphorus which would otherwise remain in solution and be removed from the lake basin.

If movement of material from the drainage area into the lake sediment was solely accomplished by erosional transport and subsequent deposition, the ratios of the elementary components of the sediment would remain similar to those of the lithosphere as a whole. Where however preferential removal from the soil of some component occurs by leaching, followed by migration in solution, the sediment may be either impoverished in that component where no efficient precipitation mechanism exists, or enriched when efficient subsequent deposition takes place. Examples of both types of behaviour may be found. Calcium, for example, readily enters solution in the soil, and since no efficient precipitation occurs in the lakes studied, it is carried out of the lake basin, and as time passes the sediments become increasingly impoverished in this element. On the other hand phosphorus and many heavy metal elements, may migrate in solution into the lake there to be precipitated with high efficiency by various mechanisms. The sediment then becomes relatively enriched in these elements. The final composition of the sediment is therefore influenced by a number of simultaneously active modes of transport and precipitation.

It is assumed in the present work that no large-scale diffusional movements of elements within the sediment have taken place. This is likely to be true in the case of carbon

contained in organic materials of high molecular weight, and it is certain that the greater part of the organic carbon in the sediment is so contained. One may suppose too that little migration of those elements associated with particulate mineral matter, for example potassium, will have taken place. Since the sedimentary material has, before incorporation in the sediment, spent a number of years in constant contact with the water of the lake, the elements remaining associated with the sediment will usually be present in particularly immobile forms. This must be true for those elements which are greatly enriched in the sediment as compared with the overlying water; examples of these are zinc, copper, cobalt, manganese, phosphorus and iron, for which enrichment factors between wet mud and lake water range from some  $10^4:1$  for zinc to greater than  $10^7:1$  for iron, in oxidizing conditions.

The immobility of iron and manganese is of course modified under the reducing conditions of the sediment, and there is evidence that local migration of iron into new centres of precipitation does take place within the sediment. In the lower and older sections of the sediment one often finds nodules of vivianite ( $\text{Fe}_3^{2+}[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$ ), a soft white material which becomes bright blue on exposure to the air. Such nodules, which may be as much as 1 cm in diameter, are often associated with macroscopic organic remains such as wood fragments or hazel nuts which may be filled by the mineral. Accumulations of this kind can have arisen only as secondary features brought about by migration of both iron and phosphorus into a precipitation centre, presumably initiated by the intense reducing conditions associated locally with organic matter. Such centres of reduction could conceivably have produced a local increase in ferrous iron concentration which exceeded the solubility product of vivianite. Once initiated, the precipitation of the mineral must continue by diffusion of the components from the surrounding sediment. That such a diffusional movement is slow is suggested by the apparent absence of such nodules in the younger parts of the sediment, though the greater abundance of phosphorus in the older sediment may be a contributory factor. Despite this evidence that migration of some elements does in fact take place within the sediment, it is here assumed that no large-scale alteration of the stratigraphical position of the elements studied has occurred.

Apart from the possibility of diffusional movement of the sedimentary components, one must also consider the possibility of mechanical disturbance of the stratigraphy by movements, such as slumping, which may have taken place subsequently to deposition. Many examples of slump movement in laminated glacial clays have been observed in cores taken during the present work; some of these structures have been described from the Windermere sediment by Smith (1959). Good examples of such movements are to be found in cores penetrating some 4 m into laminated clay in the south basin of Windermere at the permanent buoy of the Freshwater Biological Association. In such cores clear evidence may be observed of quite extensive post-depositional movement. For example, characteristic sequences of laminations may be repeated several times in the section with clearly distorted slip zones between the repeated sequences. These structures can only be produced by horizontal sliding of sheets of laminated clay some half a metre thick, one over the other. Other cores in the same locality show complete over-folding of the laminated clay, producing inversion and repetition of the strata (Mackereth 1965).

Although movement of laminated clay deposits is a common feature of the glacial

sediments lying in the vicinity of lake bed slopes, evidence of such movements in the post-glacial organic sediment is very uncommon. One example of a disturbed post-glacial sediment was however found in Ennerdale, where some 20 cm of post-glacial deposit immediately above the clay was found to contain numerous small discrete balls of pink glacial clay mixed into the organic material. The clay balls could only have been introduced into the post-glacial material by some post-depositional movement. In general, however, the post-glacial deposits, even when they overlie disturbed glacial clays, show no sign whatever of disturbance of the original stratigraphy. Although the post-glacial deposit is much more uniform in appearance than the laminated clay, one usually finds some visible stratification in the organic matter, often in the form of thin clay or silt bands or in the dark green laminations which were observed in the post-glacial sediments of Windermere by Pennington (1943). These visible strata usually lie horizontally and show no evidence of disturbance. One may therefore conclude that in suitable cores the chemical stratigraphy does in fact present a valid record of the post-glacial sequence of events in so far as they had influence on the composition of the sediment at the time of deposition.

### *Sampling*

Cores were taken generally in the deep areas of lakes, by means of a pneumatic coring device described by Mackereth (1958). This sampler takes continuous sections through the sediment to a depth of 6 m, which may be extended if necessary to 8 m. In the lakes examined a 6 m core was usually sufficiently deep to penetrate all the post-glacial deposits and enter the glacial laminated clays. The whole post-glacial section was therefore obtained in a single column 6 m long and 4.5 cm in diameter. Samples were taken from this column of sediment at 10 cm intervals. This was done by first carefully removing an outer layer of the core some 2 mm thick to avoid the smeared surface, disks 2 cm thick were then cut transversely, and the removed material homogenized by mixing with a spatula. The mixed material was then dried at 110 °C and ground in a mortar to a fine powder, from this powdered sample, subsamples were taken for analysis.

### ANALYTICAL METHODS

All analyses were based on the dry weight of the material.

*Organic carbon, hydrogen and ash* were determined by an empty quartz tube microcombustion procedure similar to that described by Belcher & Ingram (1950), modified only in that the absorption tubes used were constructed from polyethylene tubing which was found to be less subject to weight changes due to humidity variation than the normal glass absorption tubes. It was unnecessary to make any correction for inorganic carbonates since none are present in the organic sediments studied. The ash weight was obtained directly by reweighing the sample boat after combustion.

*Nitrogen* by micro-Kjeldahl followed either by distillation in Markham apparatus or by diffusion into boric acid.

*Sulphur*. The sample was mixed with  $\text{MnO}_2$  and ignited at 500 °C. Sulphate was then extracted into a known volume of  $\text{N}/1000$   $\text{NaOH}$  and the suspended material separated by centrifuge. Sulphate concentration in the supernatant was determined by the ion-exchange method described by Mackereth (1955).



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*Boron and halogens.* The sample (0.5 g) was mixed with 1 g of  $\text{Na}_2\text{CO}_3$  and ashed in a nickel crucible at  $500^\circ\text{C}$ ; halogens and boron were extracted into 20 ml. of hot water; aliquots were taken for analysis. Boron was determined by conversion to  $\text{BF}_3$  which was then reacted with methylene blue to form a blue complex extractable into dichlorethylene, in which solvent the colour density was measured spectrophotometrically.

Halogen was determined by a modification of Conway's method (Conway 1947) in which the halide is oxidized to halogen by acid permanganate and the halogen absorbed into potassium iodide solution. The liberated iodine was determined spectrophotometrically in ultra-violet light. It was found to be advantageous to neutralize the iodide solution with boric acid.

The remaining analyses were carried out on aliquots of a solution prepared from the sample by the following procedure: 0.5 g of sample was placed in a small polypropylene beaker (30 ml. capacity). To the sample was added 3 ml. of 40% HF solution. The sample was then heated in a fume cupboard on a hot-plate at approx.  $100^\circ\text{C}$ . Heating overnight decomposed the mineral material and removed most of the silica and excess HF. The organic residues were then transferred by means of a wash-bottle to 150 ml. quartz conical flasks, 5 ml. of  $\text{HNO}_3$  and 2 ml. of 70%  $\text{HClO}_4$  were added and the contents of the flasks evaporated on the hot-plate until the organic matter was destroyed, more  $\text{HClO}_4$  was added if necessary. The residues were then allowed to evaporate to dryness, dissolved in 2 ml. of conc. HCl and diluted to 100 ml. From this solution aliquots were taken for the following analytical procedures. All the spectrophotometric readings were made on a Unicam S.P. 500.

*Sodium and potassium.* An EEL flame-photometer was used on suitably diluted samples.

*Calcium and magnesium.* Versenate titration on well-diluted samples. Interference from heavy metals was usually avoided by high dilution (Heron & Mackereth 1955).

*Iron* by dilution with 50% HCl and direct spectrophotometry at 360 nm. The very great dilution required removed possible interferences.

*Manganese* by oxidation to permanganate measured spectrophotometrically.

*Zinc* by dithizone much after Sandell (1944). The dithizone was however used in xylene solution and the extraction carried out in 20 ml. screw-capped polyethylene bottles. These bottles were found to be convenient for many small-scale solvent extractions since the upper layer of solvent was readily withdrawn by opening the bottle and inserting into the neck a specially prepared pipette which closely fitted the bottle neck. Then, by gently squeezing the bottle, the upper layer was transferred to the pipette from which it was ejected directly into the spectrophotometer cell.

*Copper* was determined by extraction of the diethyldithiocarbamate complex into xylene in a similar manner to that described for zinc dithizonate.

*Cobalt* was determined using the complex formed with nitroso-R. salt as described in Sandell (1944). It was found to be unnecessary to separate copper before the cobalt determination.

*Nickel* was determined by extracting the dimethylglyoxime complex into chloroform in glass bottles. The optical density was read directly at 270 nm. Polythene bottles were found to be unsuitable for this extraction since considerable amounts of material absorbing at 270 nm were extracted by chloroform from the plastic.



*Phosphorus* was determined on a suitable dilution of the stock digest by forming the phosphomolybdate complex and reducing this to molybdenum blue with stannous chloride, the colour intensity was measured spectrophotometrically.

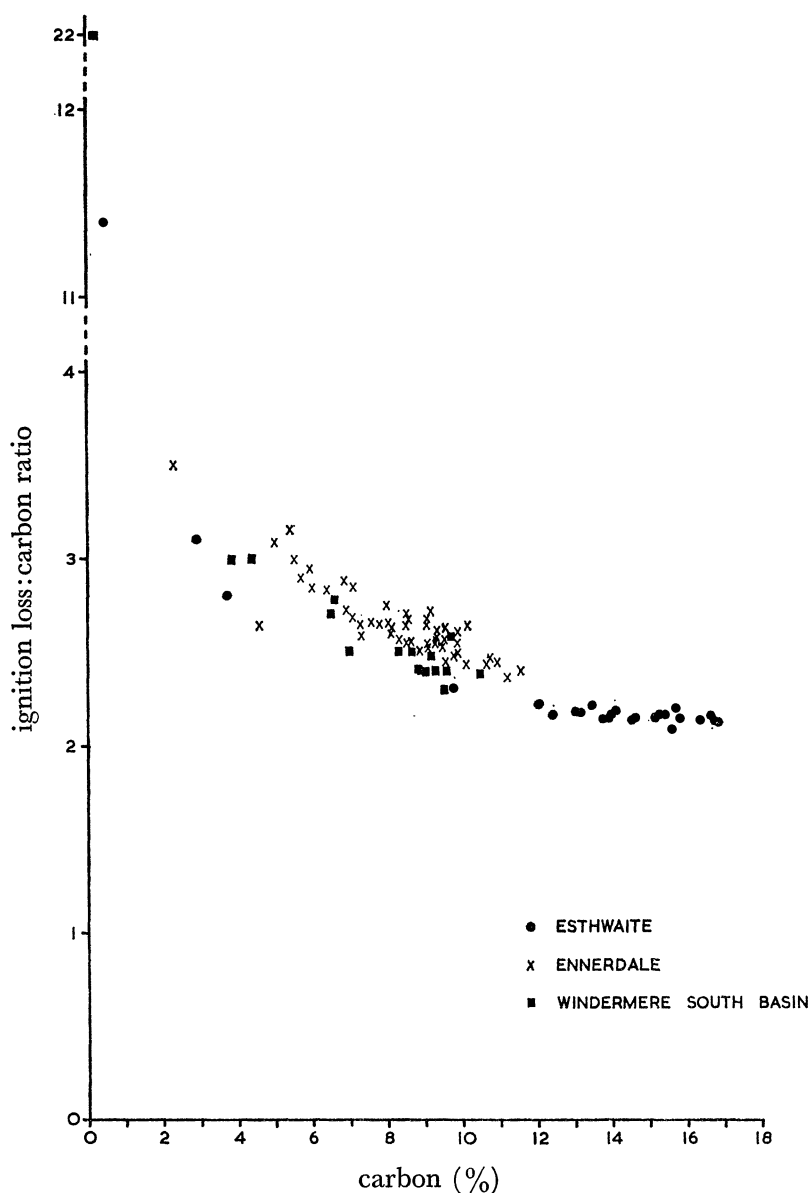


FIGURE 2. Relationship between loss on ignition and true carbon content for various lake sediment samples.

#### DISCUSSION OF ANALYTICAL RESULTS AND CONCLUSIONS

##### *Organic carbon, hydrogen and nitrogen and total mineral matter*

Ignition loss is often used to estimate organic-matter content of soil or mud samples assuming some proportionality factor. This procedure is satisfactory when applied to samples of high organic content, but leads to serious error in estimating the organic content of largely inorganic samples. This may be seen in the curve, figure 2, which relates the ratio of ignition loss to true carbon, with the true carbon content of the sample. This ratio

(ignition loss:carbon) approaches 2 as the carbon content rises, but the ratio changes markedly as the carbon content is reduced until in samples of very low carbon content it rises to as much as 22. Clearly the ignition loss in low carbon samples is due to loss of material other than organic matter. That this material is in fact water is shown by the apparently high hydrogen content of such samples. This water, which is retained at 110 °C, is associated with the clay minerals either in the lattice or by adsorption. If therefore a constant proportionality factor is applied to ignition loss data in order to convert it to 'organic carbon' the carbon content of samples containing little organic matter will be greatly overestimated. Similarly the loss of lattice or adsorbed water greatly influences the estimation of carbon to hydrogen ratios. It was supposed that the ratio of organic carbon to hydrogen might vary with the depth and age of the sediment sample and give some insight into the changes taking place over long periods of time in the composition of the buried organic material, or indeed into the differences which might exist between the organic materials deposited in lake basins of widely divergent biological type. At first sight the C/H ratio, for example, of Esthwaite sediments appeared to differ significantly from that of Ennerdale sediments, but it may be seen in figure 3, where C/H is plotted against C, that the Esthwaite and Ennerdale figures lie on the same curve. The C/H ratio diminishes progressively with decreasing carbon content because of the increasing importance of inorganic lattice hydrogen as the organic content diminishes. The large variation in C/H ratio brought about in this way masks any small variation in this ratio which may exist in the organic material of different age or origin.

The glacial clays contain also a significant quantity of nitrogen, presumably in the form of  $\text{NH}_4^+$  ions, which is released when these materials are subjected to Kjeldahl digestion. Since this also appears to be true of the clay mineral fraction of the post-glacial organic sediments, all the nitrogen found by analysis is not associated with organic material. This may lead to a spurious variation in the C/N ratio which does not reflect changes in the composition of the organic matter itself. This effect is illustrated in figure 4, where the C/N ratio of various sediments is plotted against carbon. The C/N ratio is proportional to carbon content, falling markedly at low carbon contents where the mineral  $\text{NH}_4^+$  contribution becomes increasingly significant. The proportionality of C/N with C is similar to that shown in soils (Russell 1950). The origin of the ammonia nitrogen held in the clay fraction is not indicated in the present data, nor is it clear in what form the ammonia is present. It is possible however that  $\text{NH}_4^+$  ions of radius 1.43 Å could readily replace  $\text{K}^+$  ions radius 1.33 Å in the mineral lattice (Rankama & Sahama 1949). According to the data of Lord Rayleigh (1939), igneous rocks contain only about 0.0046% of nitrogen. Kjeldahl digestion of freshly ground Borrowdale volcanic rock gave 0.007% N, whereas the glacial clays here examined contained by Kjeldahl analysis about 0.2% N, some two orders of magnitude higher. Apparently, then, the ammoniacal nitrogen contained in the clay does not originate in the source rock but is a secondary addition. No rational correction may be made for this inorganic nitrogen component since no data are available to show that the nitrogen content of the clay fraction of post-glacial sediments is constant. If however the assumption is made that this is in fact the case, an approximate correction may be made which removes the very low values of C/N ratio apparently associated with low carbon content. Misra (1938) analysed a number of surface mud

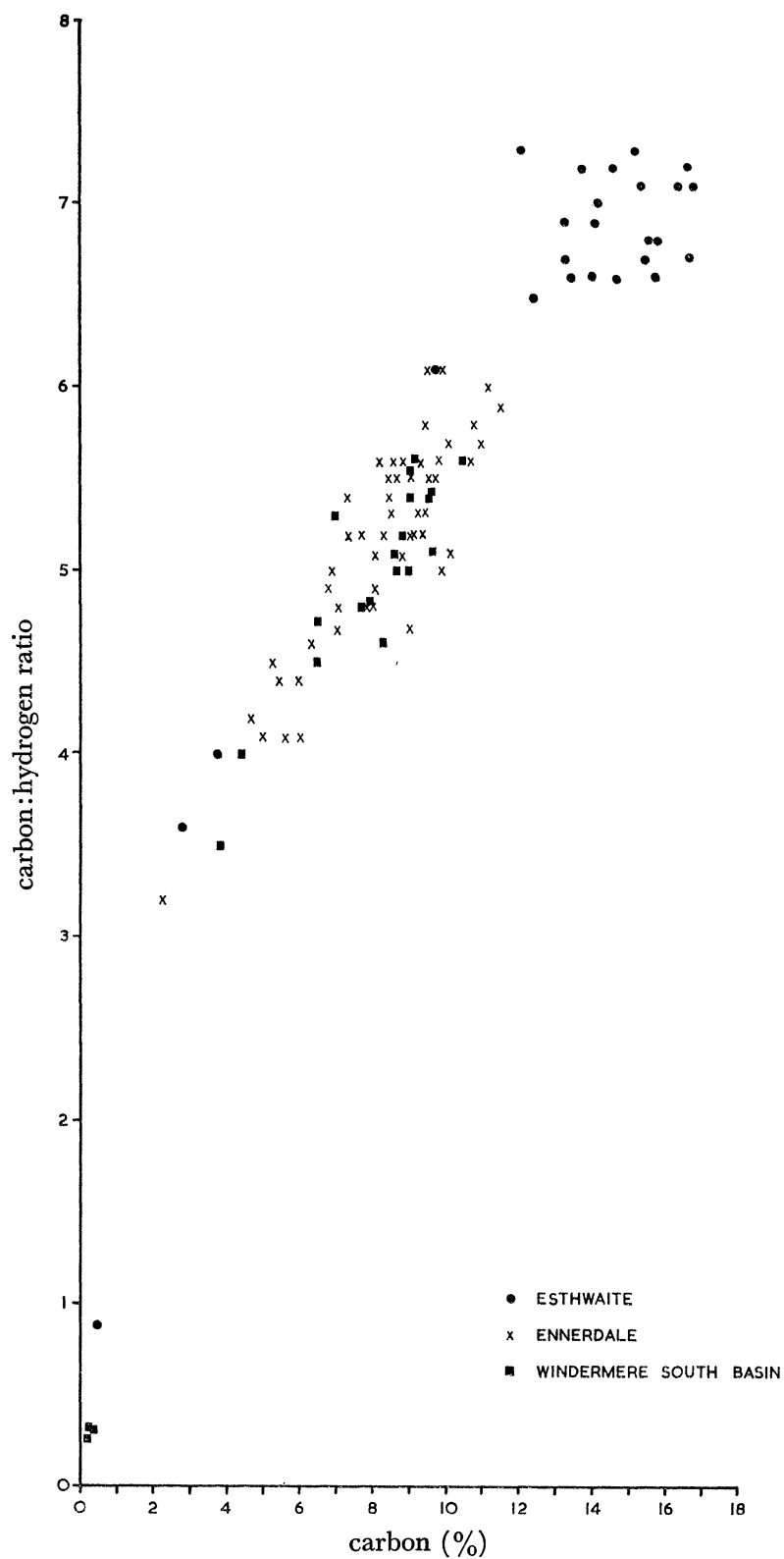


FIGURE 3. Relationship between the carbon:hydrogen ratio and the carbon content of lake sediments

samples from the lakes of the English Lake District for carbon and nitrogen. He however estimated carbon from loss on ignition with the result that all estimates of carbon in samples of low carbon content were erroneously high due to the loss of clay mineral water described above. This led to the U-shaped curve which he found by plotting apparent

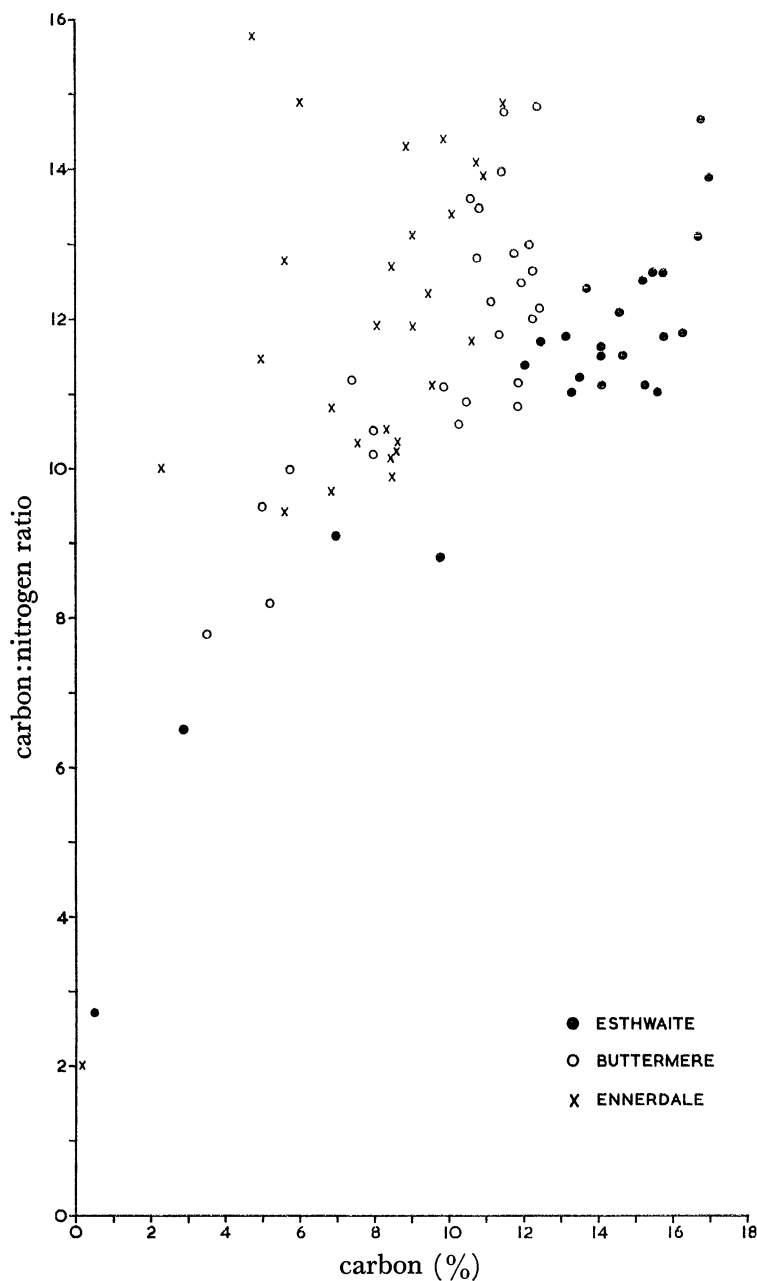


FIGURE 4. Relationship between carbon:nitrogen ratio and the carbon content of lake sediments.

C/N ratios against 'organic' matter content. The section of the curve corresponding to the more organic muds resembles that found by the present author, where loss on ignition approaches a true value for organic matter. The proportionality between C/N and organic matter then largely reflects the influence of a relatively constant contribution from inorganically held nitrogen. The part of Misra's curve which relates to samples of low



organic content shows a rise in C/N ratio with decreasing 'organic' content. This rise is entirely due to the overestimation of the organic content when loss of clay mineral water makes an important contribution to ignition loss. Misra's discussion of the significance of this curve, in terms of the changing composition of the organic fraction of the sediment, must therefore be disregarded.

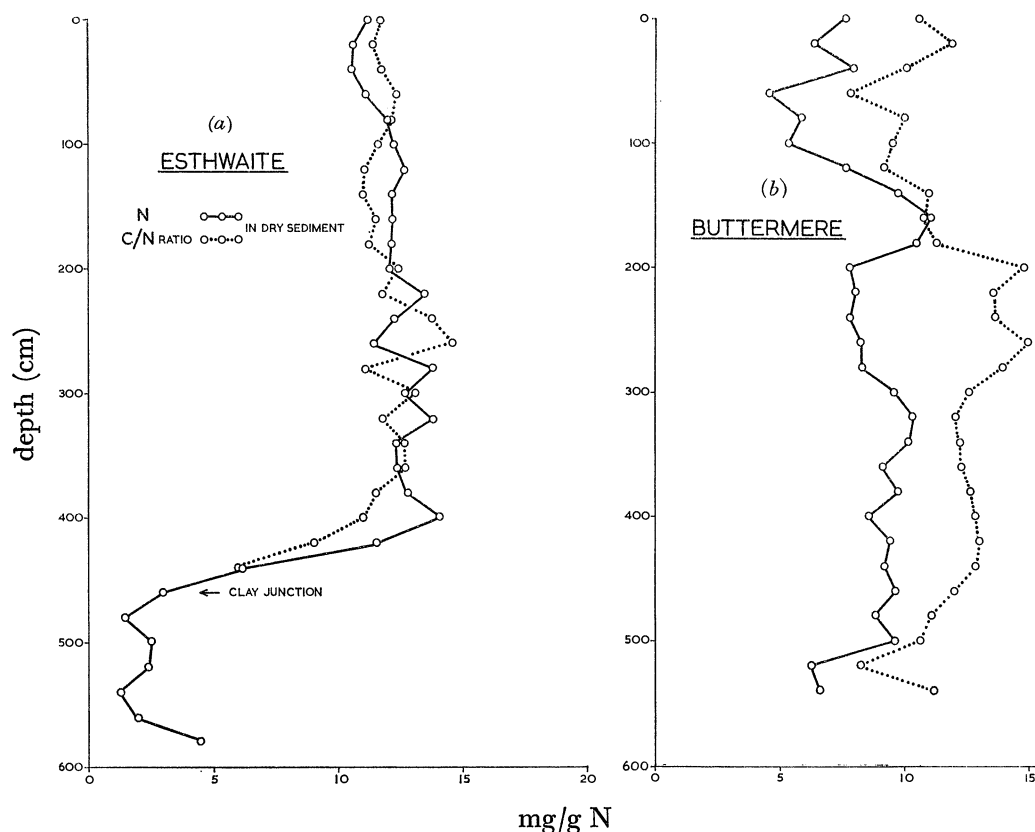


FIGURE 5. Changes in nitrogen content and carbon:nitrogen ratio with depth in the sediments of (a) Esthwaite and (b) Buttermere.

Even when some correction is made for the presence of inorganic nitrogen, considerable variation in C/N ratio remains in a sediment profile. The range of C/N ratio lies somewhat above that quoted by Russell (1950) for agricultural soils (8.5 to 11.4), it seems likely however that the C/N ratio of soils quoted is also lowered by the presence of  $\text{NH}_4^+$  associated with clay minerals in the soil, and that the C/N ratio of the organic matter of the soil would be somewhat higher and comparable with that found in lake muds. Two profiles of total nitrogen content, and of uncorrected C/N ratio are presented in figure 5.

In figure 6 the variations of carbon content and of total ash content with depth in a number of lake sediment profiles are shown. Since the sediments consist essentially of variable mixtures of organic and mineral components, the ash content (dashed line) approximates to a mirror image of the organic carbon content. The most striking feature which is presented by these diagrams is the remarkable similarity which exists between the carbon profiles of lakes of very different biological and geographical character. Thus, a significant relationship may be seen between the carbon profiles from the sediments of

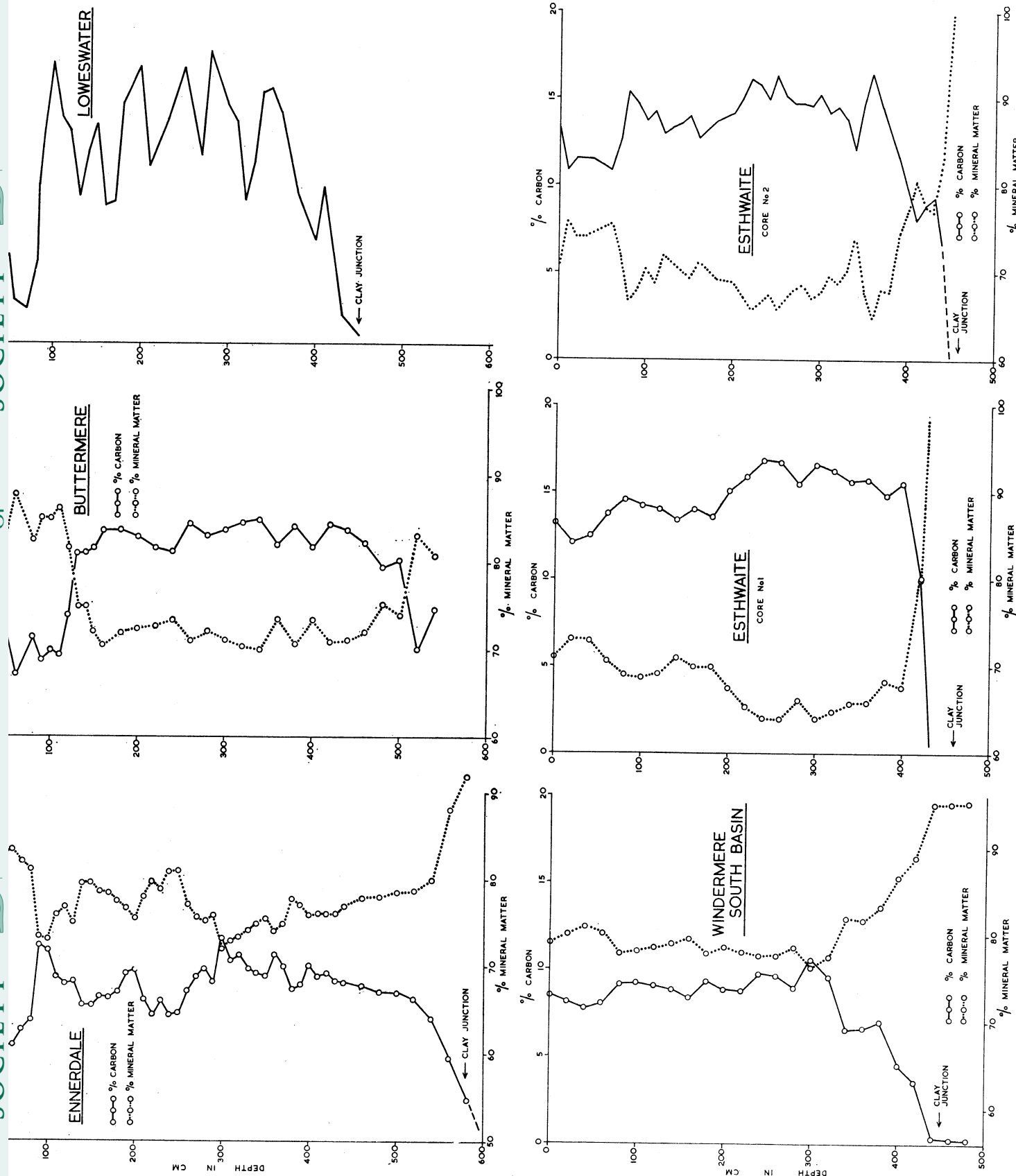


FIGURE 6. Variation of carbon content and total mineral content with depth in the sediment, in the lakes named on the diagram. The arrow marks on the diagrams the depth of the close of late-Glacial zone III in each case.

Ennerdale and of Esthwaite, two lakes representing the extremes in the present series of lakes, of biological poverty and richness. This again suggests that the decisive factors influencing lake sediment composition are active outside the lake rather than within it. The similarity of the various sediment carbon profiles becomes more apparent when the vertical depth scale is converted approximately to a time-scale to allow for the various overall rates of deposition in the various lakes. In figure 7 profiles from the sediments of

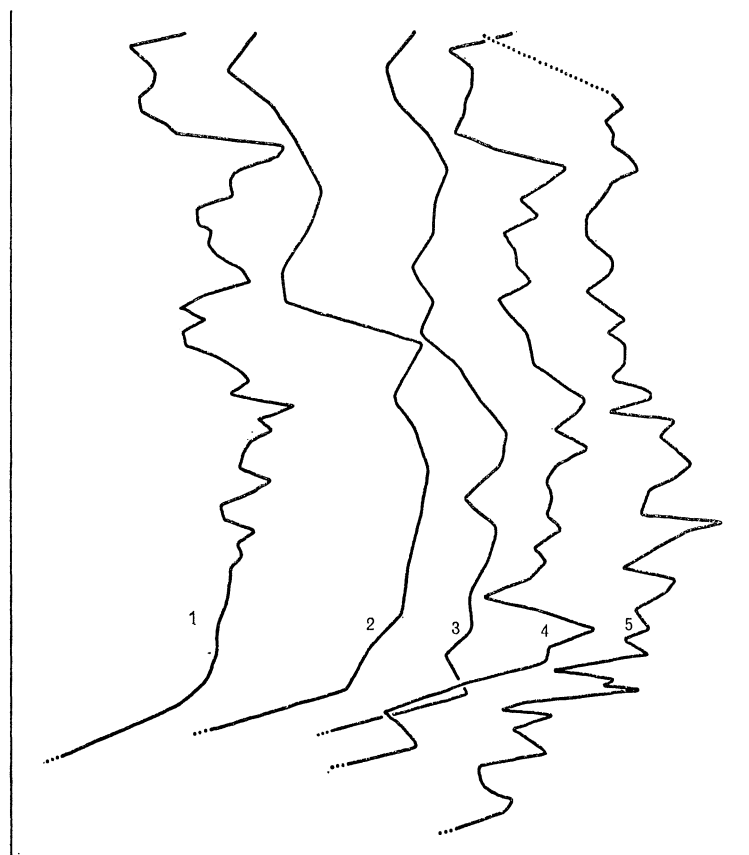


FIGURE 7. Carbon content plotted against an approximate time-scale (vertical axis) for a number of lake sediment columns. The lower end of the diagram corresponds to an age of roughly 10000 years. The sedimentary carbon profiles are from (1) Ennerdale, (2) Rydal, (3) and (4) Esthwaite, and (5) Linsley Pond.

three different drainage systems are shown (plotting variations in C against a vertical time-scale). These are (1) Ennerdale, (2) Rydal (from the data of Pearsall *et al.* 1960), (3) and (4) two cores from Esthwaite, and (5) the profile from Linsley Pond (U.S.A.) taken from the data of Vallentine & Swabey (1955) (which is similar to the earlier analysis of Hutchinson & Wollack (1940) though in greater detail). In this diagram the vertical scale of each profile has merely been expanded or contracted to bring the junction of post-glacial to glacial sediments into approximate coincidence. It is assumed that this junction does in fact represent a synchronous point not only in the sediments of Lake District lakes but also in Linsley Pond. Figure 8 shows a composite profile of carbon content against time made by superimposing plots of percentage carbon on suitably adjusted

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vertical scales arranged as before to bring the clay junction to the same depth. The carbon content figures from the sediments of Esthwaite (2 cores), Ennerdale, Rydal and Buttermere are here represented and the solid line represents the time/carbon profile from Linsley Pond. Here again a degree of concordance between the profiles is seen which can hardly be ascribed to coincidence. Any attempt at explanation of the carbon profiles of lake sediments must therefore be capable of accounting for this similarity of carbon variation with depth in the sediment not merely on a regional basis but perhaps also on a

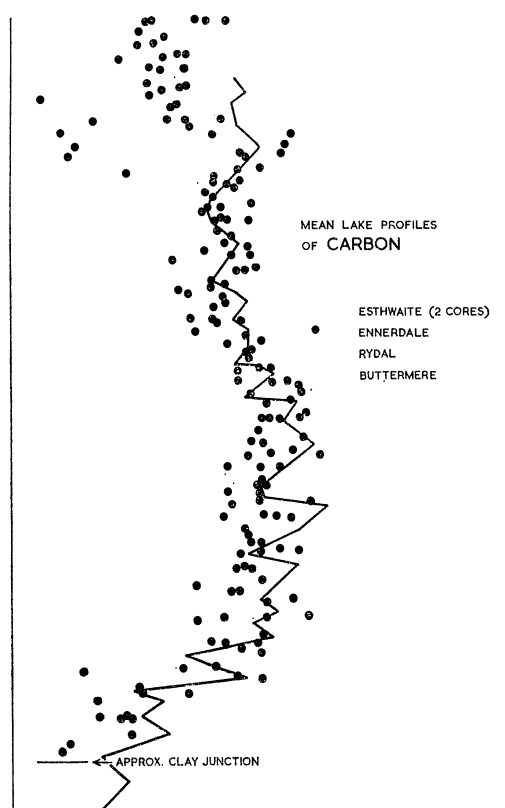


FIGURE 8. Composite diagram made by superimposing carbon data from various sediment columns. The vertical scale approximates to time. The various sediment depths have been adjusted to bring the junction between glacial and post-glacial into coincidence. The solid line represents data from Linsley Pond. Clay junction at approximately 10000 years B.P.

wider scale. More data are however required from widely separated localities before the remaining possibility that the similarity between the sediments of Linsley Pond and those of the English Lake District is coincidental can be completely dismissed.

The influences which bring about gross changes in composition of the sediments of the English Lake District lakes should be sought in the drainage systems of the lakes. Three factors which might alter the ratio of organic material to mineral material in the sediment appear to be possible. These are (1) variation in the rate of deposition of organic matter, conceivably brought about by changes in the organic productivity of the drainage system or in the nature of the organic matter produced; (2) variation in the rate of deposition of mineral matter which would reflect variation in the intensity of erosion of the drainage system; (3) variation in the rate of destruction of organic matter at the sediment surface



by bacterial decomposition. The final result could of course be reached by the simultaneous variation of all three influences.

The data on variation in relative concentration of organic and inorganic material presented above offer no means of distinguishing between these various possibilities. It is apparent that the organic matter which becomes incorporated in the sediment has already reached a state of considerable stability towards further oxidation, so that variation in the rate of bacterial oxidation of this material does not seem likely to be an important factor in determining the residual concentration of organic carbon. The most likely choice must therefore lie between variation in the rate of organic production and variation in the intensity of erosion in the drainage system.

One may perhaps consider two types of change that soils undergo. These are (1) maturation by leaching, in which some components of the soil mineral material are removed in solution, thus leaving the residue *in situ* impoverished in the leached components, and (2) erosive removal of the soil from the site of leaching and subsequent deposition of the eroded material in the lake sediment where it is effectively protected from further leaching. These two processes are in a sense opposed. Intense erosion would remove the soil material before the processes of chemical attack had time to be fully effective. One may then suppose that the composition of the debris removed from the land surface would give some indication of the length of time the material had been exposed to leaching before its final removal and 'fossilization' in the lake sediment. The final concentration of sensitive components remaining in the sediment would then reflect the position of a steady state existing between the processes of maturation and erosion.

Elements which one would expect to be sensitive to leaching attack include the alkali metals, and of these sodium and potassium are the most abundant and readily determined. Both sodium and potassium are associated with the mineral fraction of the sediment rather than with the organic material. This may be deduced from figure 9, where the sodium and potassium content of various sediment samples is plotted against percentage mineral content. The samples plotted are taken from the sediment of Esthwaite and Ennerdale, representing two geologically different basins. Esthwaite derives much of its drainage from sedimentary rocks while Ennerdale derives its drainage from igneous rocks. Both sediments however demonstrate the near linearity of the relationship between the mineral content of the sediment and the sodium-potassium concentration. The content of potassium in glacial-clays (represented by 100% mineral content) somewhat exceeds the lithospheric average content of potassium (25.9 mg/g, Rankama & Sahama 1949), while the sodium content (plotted  $\times 2$  in the figure) is only about half the lithospheric average (28.3 mg/g, Rankama & Sahama 1949). Some leaching of sodium has therefore taken place even in the intensely erosive conditions existing during the deposition of the glacial clay.

If one now assumes that the variation in mineral content of the sediment was brought about by variation in the intensity of erosion of the soils of the drainage system, there should, on the grounds discussed above, exist a direct relationship between the mineral content of the sediment (representing erosion intensity) and the sodium and potassium content of the mineral matter. That this relationship does exist is shown in figure 10, where the sodium and potassium content of the mineral material from various sediment samples

is plotted against the percentage mineral content of the sediment. The concentration of alkali metal elements in the mineral matter diminishes progressively with diminishing total mineral content of the sediment. One may reasonably conclude therefore that the mineral content of the sediment is related directly to the intensity of erosion. The variations in gross composition of the lake sediments with time must then be related primarily to variation in time of the intensity of erosion in the drainage system rather than to

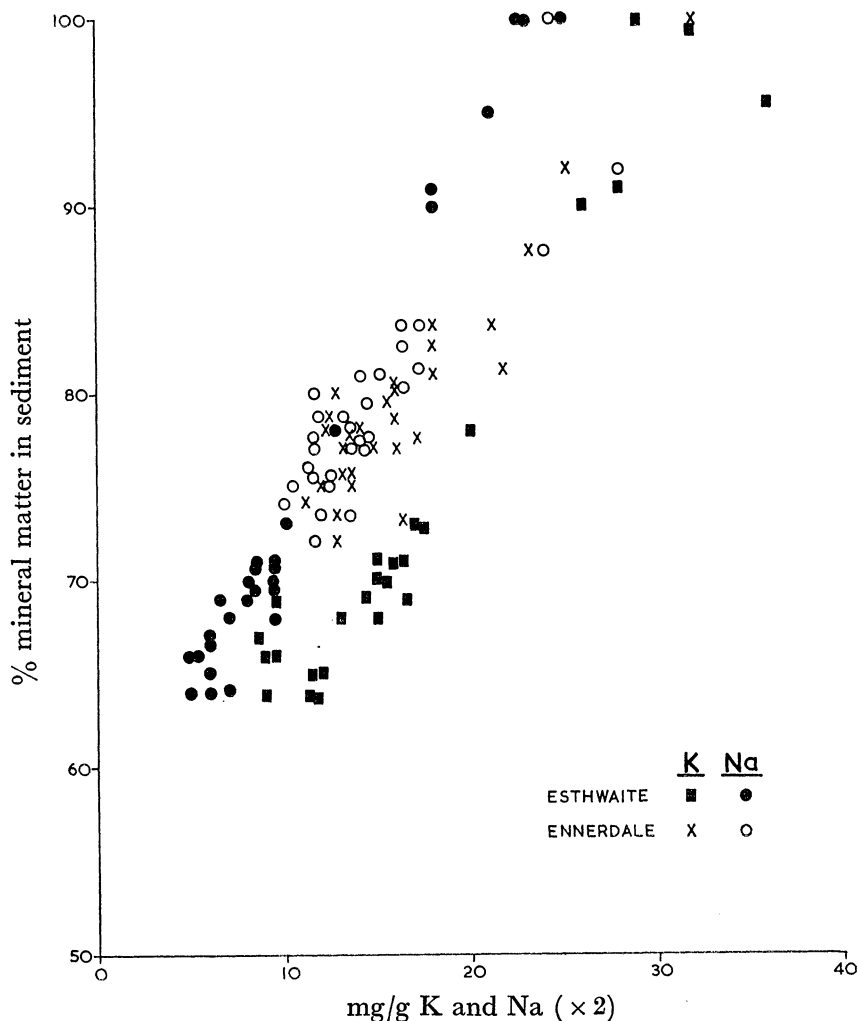


FIGURE 9. Relationship between total mineral content and the concentration of sodium and potassium in the dry sediments of Ennerdale and Esthwaite.

variation in the rate of production and deposition of organic material, since a variable rate of organic deposition (or indeed of bacterial decomposition), could not be expected to produce the observed relationship between gross composition of the sediment and alkali metal content of the contained mineral material.

The concentration of potassium and sodium (and other associated elements) in the sediment may then be regarded as being directly proportional to the intensity of erosion to which the drainage system was exposed at the time the sediment was laid down. High sedimentary potassium must indicate more intense erosion with relatively ineffective

leaching of the soil. Low potassium content must indicate more effective leaching of the soil attributable to less intensive erosion which allows a longer period of residence of the soil on the drainage system exposed to conditions in which leaching could proceed. Since the supply of nutrient elements to the lake environment itself is closely associated with the formation of soils in the drainage area and the effectiveness with which such soils are leached, the relative importance of erosion and leaching in the soils must have a bearing

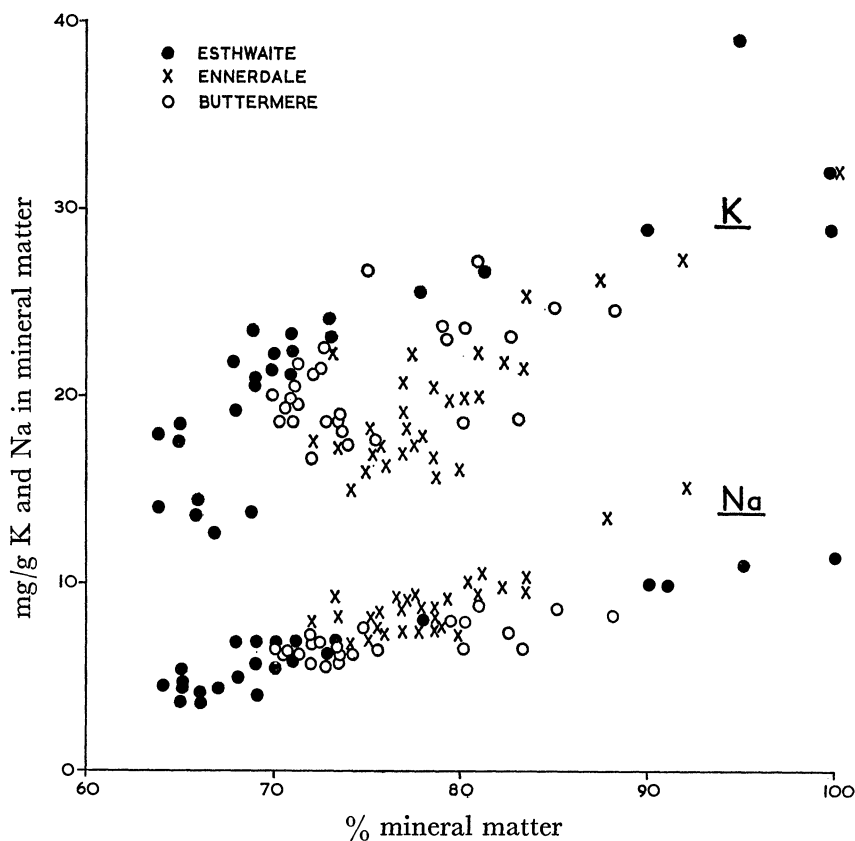


FIGURE 10. Relationship between the sodium and potassium content of the mineral matter, and the total mineral content in the sediments of Esthwaite, Ennerdale and Buttermere.

on the potential productivity of the lake at any given time. Thus intense erosion will prevent the accumulation of soils and will remove the nutrient elements still locked in the lattice of mineral particles to be deposited in the sediment and removed effectively from the biosphere. On the other hand a regime of less intense erosion will allow soil to accumulate in which mineral particles are held in a suitable spatial position to allow leaching to bring the various nutrient elements into solution in a form which is available to the living populations of the lake. Periods of more intense erosion would then seem to be unfavourable to high internal productivity in the lake, while periods of lower erosion intensity may be expected to be periods of higher internal lake productivity. The direct effect of erosion rate on the composition of the lake sediments may therefore be reinforced by the variable contribution of internally produced organic material. The final composition of the sediment may then be expected to be the result of both the direct and indirect influence of the intensity of erosion. Therefore under given climatic conditions,

the potential internal productivity of a lake basin is determined at least in part by the topography of the drainage system which sets the erosion rate characteristic of that basin and determines the position of the equilibrium between soil formation and leaching on the one hand and erosion and soil removal on the other. Although the sediments of Esthwaite and Ennerdale have varied in unison in composition in time, at any given time the erosion rate in the Ennerdale basin has been greater than that in the Esthwaite basin as evidenced by the greater mineral content of the Ennerdale sediments. One might then expect that less soil will have accumulated on the Ennerdale drainage area than on that of Esthwaite, and that Ennerdale will have had a lesser internal productivity than Esthwaite throughout the history of the two basins. Such a conclusion is supported by the present relative richness of Esthwaite and poverty of Ennerdale. To take a more general view, it is at least possible that the striking relationship between lake productivity and mean depth described by Rawson (1955) in Canadian lakes may find a basis in the association of deep and unproductive lakes with areas of severe relief where the erosion rate might be expected to be high.

The distribution of sodium and potassium in the dry sediment and in the mineral fraction in lake sediment cores, shown for various lakes of the English Lake District in figures 11 and 12, may now be regarded as being indicative of the way in which the relative intensities of erosion and leaching have varied in the area in post-glacial time. In every case the total sodium and potassium content of the sediment was at a maximum (as was the sodium and potassium content of the mineral material) during the closing stages of actual glaciation (this section is missing in the Buttermere core which did not enter the glacial clay). At this time, the sediments laid down were almost wholly inorganic; this reasonably represents the stage of maximum erosion intensity in the profiles studied. The beginning of deposition of organic post-glacial sediments is in every case associated with a marked fall both in total sodium and potassium content of the sediment and in sodium and potassium content of the mineral fraction. This stage presumably represents the marked reduction in erosion intensity at the end of active glaciation, when soils were being formed and held together by vegetation. The period of declining alkali metal content in the sediment is followed by a substantial period of minimum total sodium and potassium content and minimum sodium and potassium content in the mineral matter of the sediment. This phase must represent a period of minimum erosion and maximum leaching efficiency which should correspond to a period of maximum internal productivity of the lakes themselves. This period of minimum sodium and potassium content was followed in each case by a phase of steadily increasing concentration of sodium and potassium in the sediment extending to the present surface with minor fluctuations. This period on the hypotheses already discussed must be one of steadily increasing erosion rate and diminishing efficiency of leaching, and presumably of steadily declining lake productivity. The observations presented do not therefore support a concept of lake evolution from relative poverty towards richness, but suggest rather that a phase of relative mineral richness occurred quite early in the post-glacial history of the lakes.

The approximate dating of these phases may be deduced from a consideration of the Esthwaite sediments, where the distribution of pollen has been studied by Franks & Pennington (1961). The pollen zonation provides approximate depth-time relationships.



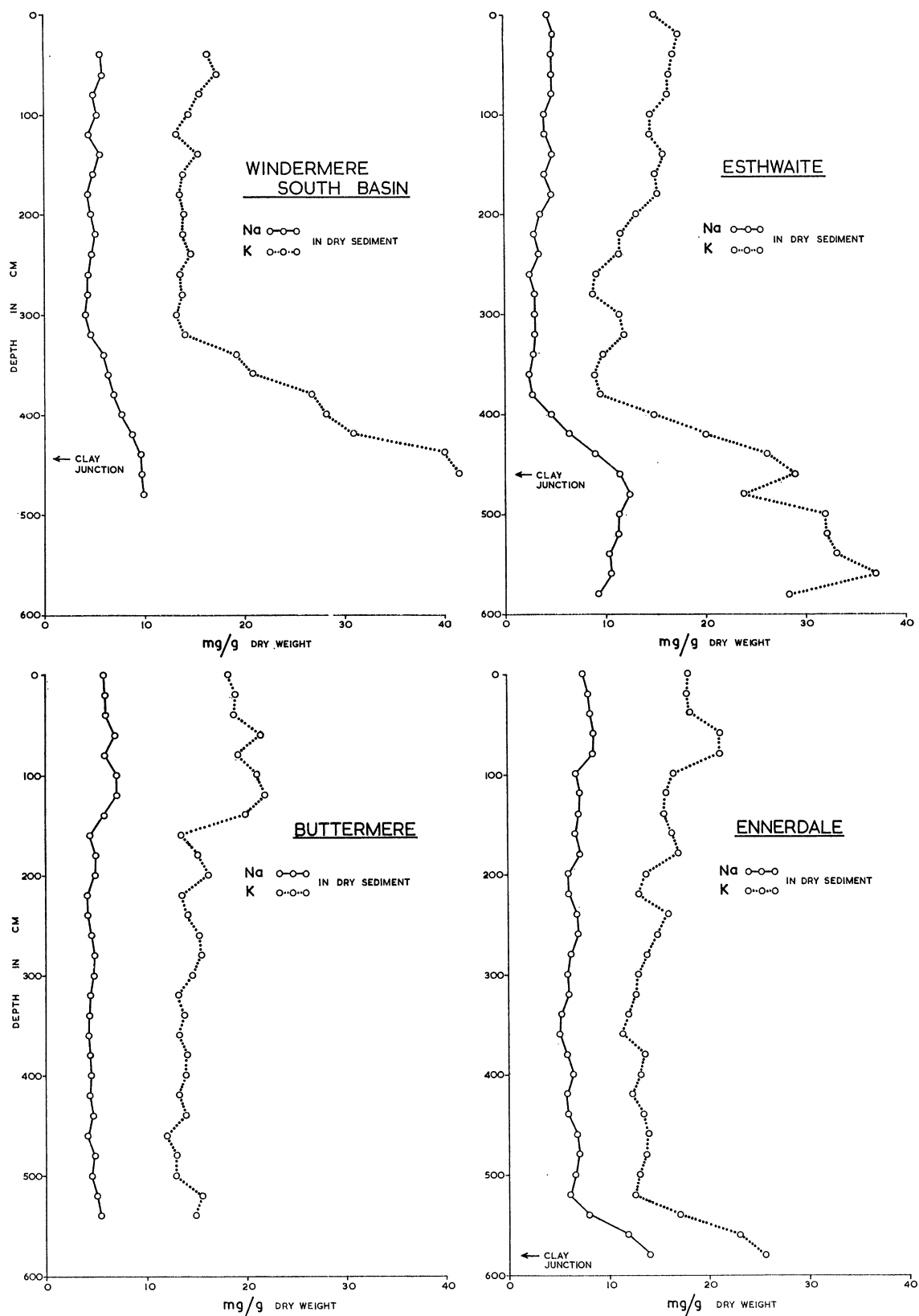


FIGURE 11. Distribution in depth of the concentration of sodium and potassium in the dry sediments of Windermere (South basin), Esthwaite, Buttermere and Ennerdale.

OBSERVATIONS ON POST-GLACIAL LAKE SEDIMENTS

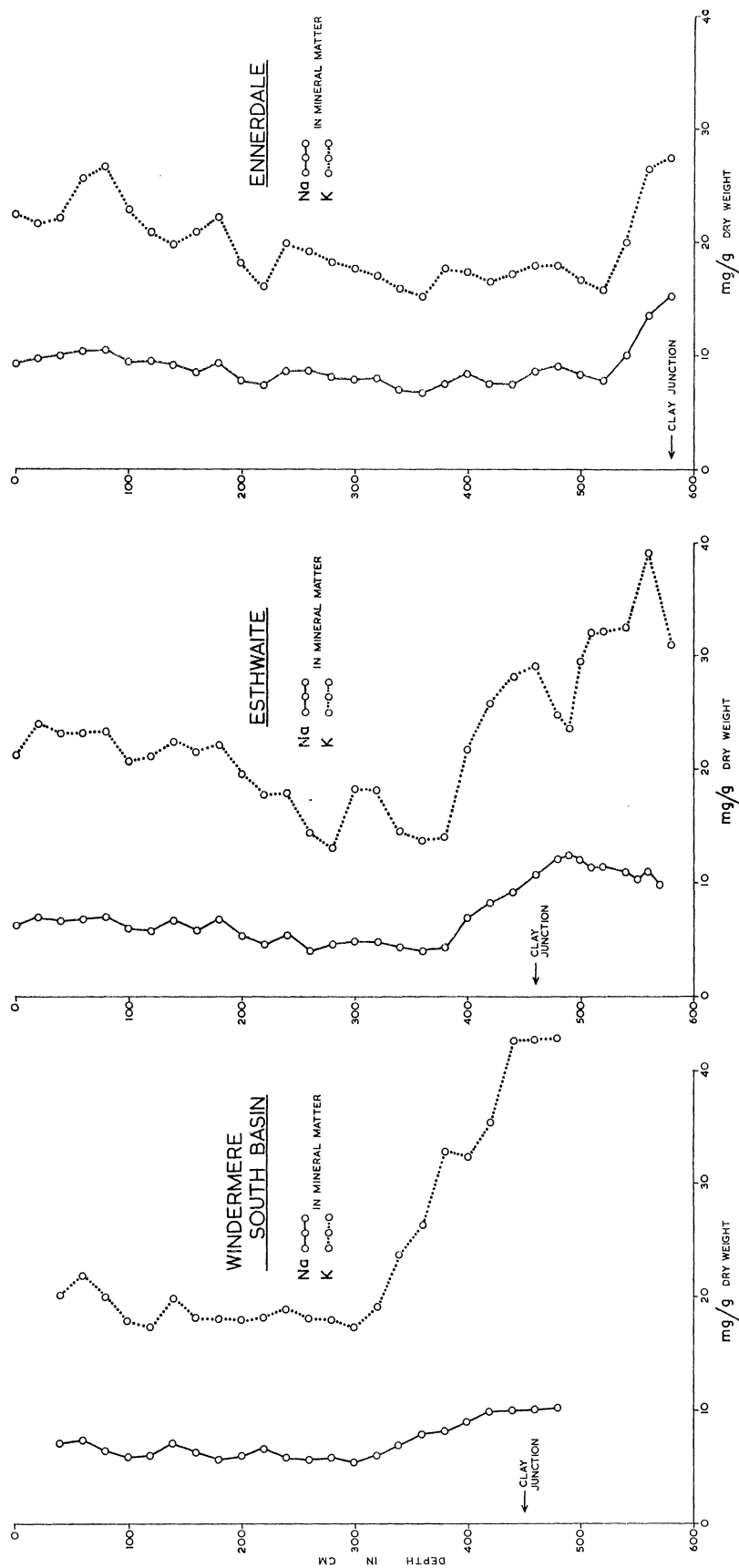


FIGURE 12. Distribution in depth of the concentration of sodium and potassium in the mineral matter of the sediments of Windermere (south basin), Esthwaite and Ennerdale.

The phase of rapidly diminishing potassium concentration, occurring at about 440 cm depth in Esthwaite, representing the termination of active glaciation, may then be dated at some 10500 years B.P. The phase of minimum erosion intensity from approx. 380 to 260 cm depth covers a period lasting from about 9000 to 5000 B.P., and the phase of steadily increasing erosion rate occupies a period from about 5000 B.P. to the present day. It seems reasonable to suppose that the similar changes occurring in other lake sediments

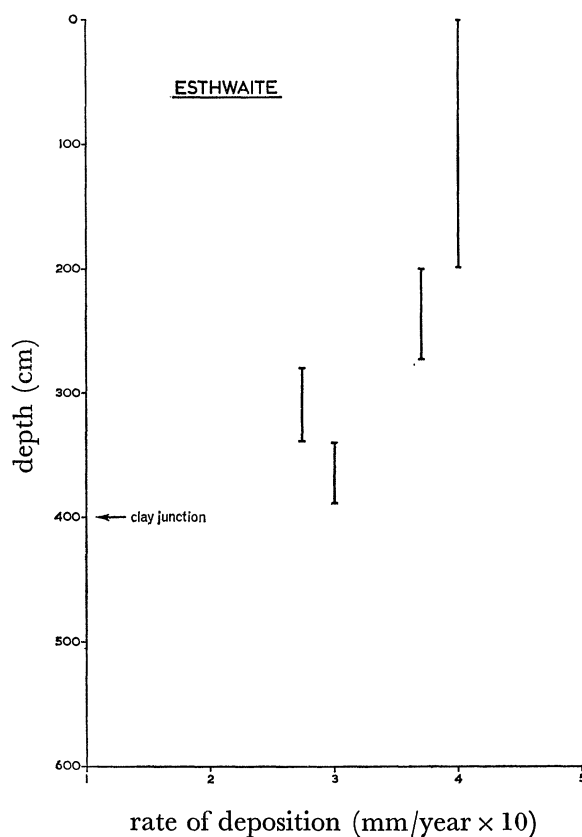


FIGURE 13. Approximate rates of sedimentation in various depth zones in the sediment of Esthwaite derived from the pollen data of Franks (1956).

were essentially synchronous with those in Esthwaite. Using the pollen zonation of Franks, an approximation may be made to the rate of sedimentation in these depth zones. This has been done in figure 13 for one Esthwaite core (somewhat shorter than the ones analysed by the present author). From this diagram it may be seen that the deposition rate in the post-glacial sediment reached a minimum about 300 cm down and later increased towards the sediment surface. Below 300 cm the rate of deposition again increases with increasing depth and presumably rises sharply during the late-glacial, for which there are no pollen data. If one supposes that the glacial clay represented a period of rapid deposition, then this rough figure of changing deposition rate with time shows a marked resemblance to that for the distribution of potassium and the deduced rate of erosion. It is likely then that the rate of deposition was controlled by the rate of supply of mineral material, the deposition of carbon remaining roughly constant. That the deposition of carbon may have been substantially similar also in different lake basins is

suggested by the close similarity in the total mass of carbon deposited on unit area in deep areas of lakes as widely different as Esthwaite and Ennerdale. The greater depth of deposit in Ennerdale and its lower carbon concentration is substantially accounted for by the greater weight of mineral material deposited on unit area.

If one concludes that the dominant factor controlling the rate of deposition and the gross composition of the sediment at any given time was the intensity of erosion, it is of interest to attempt to discover why the intensity of erosion changed.

From the pollen diagram of Franks (1956) relating to a core from Esthwaite, it is clear from the plot of tree to non-tree pollen ratio against sediment depth that increasing erosion is associated with a reduction in this ratio, presumably corresponding with a diminishing tree cover in the drainage basin. Such a relationship could indicate either that the increased intensity of erosion was brought about by diminishing tree cover, or alternatively that external factors increased the rate of erosion and reduced the suitability of the habitat for tree growth.

Pearsall & Pennington (1947), in considering their data on the changing organic content of the sediments of Windermere north basin, produced substantial arguments favouring the role of early human communities in effecting far-reaching changes in the ecological regime of the drainage basin of that lake. Though not denying the possibility of climatic change as a factor, they concluded that the forest clearance probably to be associated first with a megalithic society and later with Norse settlements could account for the observed changes in composition of the sediments. There can be no doubt in view of this evidence that a close association in time occurs between the existence of populations of early peoples and the changing composition of the lake sediments associated with their habitats. That this relationship is the only causal one remains however less certain, since the hypothesis must explain the widespread occurrence of such changes. It is for example conceivable that the changing levels of human activity were associated with climatic change which was itself the decisive influence both on human population and on erosion intensity. Some purely chemical indication of climatic variation was therefore sought which would be independent of the interpretation of pollen distribution data.

Most of the halogen occurring in solution in the waters of the English Lake District is derived from rain. The halogen is introduced into the rain from the ocean in fine particles of spray. Furthermore the amount of halogen carried in ocean-derived rain depends on the storminess of the ocean. Gorham (1958) showed in Lake District rain the great dependence of chloride concentration on wind speed and direction, and temperature. High concentration of rain chloride is directly related to high wind speed and low temperature. The rate of precipitation of halogen on to the drainage system should then be a direct measure of the frequency of oceanic storms both now and in the past. If then the halogen retained in a lake sediment depends on the rate of supply of halogen from the rain, the variation with depth of sedimentary halogen could be expected to record the influence of the ocean on climate at the time of deposition of the sediment. The work of Gast & Thompson (1959) on the volatility of boric acid at the surface of the ocean suggests also that the boron in rain is acquired during passage of the air-stream, from which the rain was precipitated, over the ocean surface. Therefore the rate of precipitation of boron on a land surface should also be influenced by the oceanicity of the prevailing air stream.

In view of these possibilities a core from Esthwaite was analysed for its content of halogen (largely Cl and Br) and boron. The results of these analyses are plotted in figures 14 and 15. The distribution of halogen in the sediment shows that an association exists between the organic material and the retained halogen. This is indicated by the marked rise in halogen

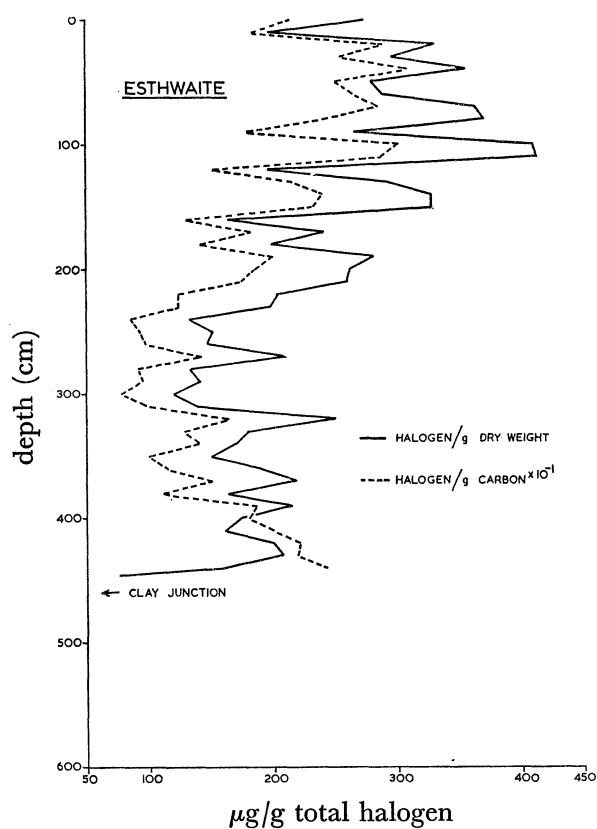


FIGURE 14

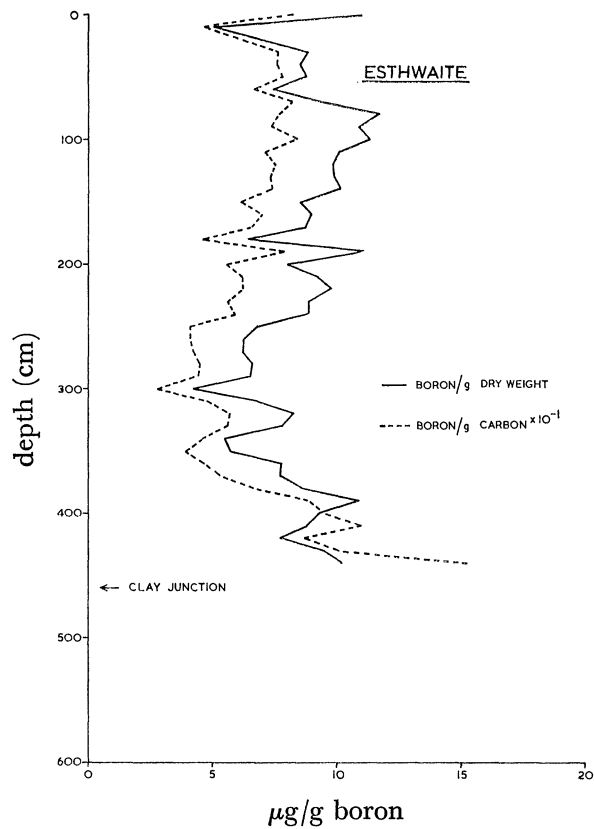


FIGURE 15

FIGURE 14. Distribution in depth of the halogen content in the dry sediment of Esthwaite (solid line) and the relationship between halogen and carbon (dashed line).

FIGURE 15. Distribution in depth of the boron content in the dry sediment of Esthwaite (solid line) and the relationship between boron and carbon (dashed line).

content of the sediment on passing from the inorganic glacial clays to the beginning of the organic post-glacial sediments. This observation agrees with those of Selivanov (1940) who found that halogens in soils are associated with the organic matter rather than with the mineral fraction. Despite this association, the distribution of halogen does not resemble that of organic carbon in the post-glacial muds, but follows more closely the changing proportion of inorganic material. The distribution of halogens in the profile resembles that of potassium. The distribution of halogen is not however related directly to the deposition of inorganic material as is that of potassium, but is nevertheless associated with the intensity of erosion. One hypothesis to account for this association between halogen and erosion intensity is that originally envisaged, that the rate of deposition of halogen is related to gross climatic conditions at the time the sediment was laid down. This would imply a direct relationship between sedimentary halogen and the 'oceanicity' of the climate. A



further implication would be that increasing 'oceanicity' was associated with increasing erosion of the drainage basin. If one accepted this hypothesis, the post-glacial period could be divided into three climatic phases: (1) an immediate post-glacial phase of decreasing 'oceanicity', (2) a period of minimum 'oceanicity', and (3) a period of increasing 'oceanicity', reaching a maximum at some 1.0 m depth in the Esthwaite sediment but remaining at a high level up to the present.

Since halogen is associated with the organic material of the deposit, it is perhaps more reasonable to consider the distribution of halogen in relation to unit weight of carbon, so that variations brought about simply by the varying organic content can be eliminated. The dashed line in figure 14 represents the variation with depth of halogen in relation to organic carbon ( $\mu\text{g halogen} \times 10^{-1}/\text{g C}$ ); it will be seen that this quantity varies with depth in much the same way as total halogen content. Although the marked maximum at about 1.0 m is reduced, the main feature remains—a division into three zones.

The distribution of boron in the Esthwaite sediment follows that of halogen with remarkable closeness, and the distribution of the ratio of boron/g. organic carbon (dashed line, figure 15) is similar to the corresponding distribution of the halogen/carbon ratio. The boron distribution again can be divided into three zones: (1) a zone of decreasing boron content immediately following the close of glaciation, (2) a period of minimum boron deposition, and (3) a period of increasing boron deposition.

The boron content of the sediment is considerably higher on average than the average content of this element in igneous rocks ( $3 \mu\text{g/g}$ , Rankama & Sahama 1949). Considerable enrichment of presumed biological origin has therefore taken place. Despite the fact therefore that boron, like halogen follows a distribution somewhat similar to potassium, the boron content unlike that of potassium cannot merely be a function of the total content of the mineral products of erosion. It is then difficult to see any reason for the association of boron and halogen in the sediment other than that both elements were supplied in the rain falling upon the drainage system. Though the data discussed above suggest the influence of a climatically controlled and variable rain composition, they cannot be taken as proof of such a climatic variation. At least one other interpretation of the observations is possible. One may suppose that in the soil there exists a substantially constant ion-exchange capacity. If then the soil particles are in equilibrium with a solution of electrolytes in the soil interstices, the proportions of the ionic species remaining associated with the soil exchange centres will depend on the relative proportions of the various ionic species in solution in the soil water. The electrolytes dissolved in the interstitial water of the soil are derived from two sources: (1) electrolytes supplied in solution in the rain falling upon the soil; (2) electrolytes derived by leaching of the soil. While the major anion derived from the soil is bicarbonate ion, the relevant rain-derived anions are chloride and borate. The proportions of the ionic species present in the soil interstitial water may then be changed either by changing the rain-derived contribution of chloride and borate, or by changing the content of bicarbonate derived from the soil. If we now suppose that since early post-glacial times progressive leaching of the soil has led to a progressive decline in the concentration in the soil of electrolytes derived from leaching, then, even though the supply of rain-derived electrolytes had remained substantially constant, a progressive change in the proportions of the various anions in the soil interstitial water would have

taken place. This change in ionic proportions would have led to a progressive increase in the ionic proportion of chloride and borate, so that in the competition to occupy soil ion exchange centres, the chloride and borate ions might be expected to become increasingly dominant as leaching of the soil progressed. The increasing concentration of chlorine and boron in the Esthwaite sediment above some 300 cm depth could then be interpreted as reflecting the increasing dominance of chloride and borate derived from a substantially constant rain contribution falling upon a soil which supplied a diminishing concentration of mineral-derived electrolytes. On similar grounds the observed distribution of halogen and boron in the sediment could be brought about merely by increasing the rainfall without altering its composition. Increased rainfall even of constant composition would dilute the products of leaching in the interstitial water of the soil while maintaining the concentration of chloride and borate, to produce a change in ionic proportions which would be reflected in the final concentration of chlorine and boron remaining associated with the soil particles.

The concentration of chlorine and boron in the sediment of Esthwaite may then on the one hand be climatically controlled either by alteration in the concentration of the rain solutes, or by an alteration in the total rainfall, or both. Or on the other hand the sedimentary concentration of these elements may reflect a progressive fall in concentration in the soil of mineral-derived electrolytes, which could be attributed to progressive impoverishment of the soil by leaching.

Since the concentrations of halogen and boron in the sediment appear to be related to erosion intensity, one must suppose that the intensity of erosion may be controlled by one of two factors (apart from possible human interference with the system). These are (1) increasing oceanic influence on the climate expressed possibly in increased rainfall and (2) progressive impoverishment of the soil by leaching.

#### *Distribution of calcium and magnesium*

The distribution of these two elements in depth, shown for the sediments of three lake basins in figure 16, presents features which may be interpreted in the light of the foregoing conclusions on the changing intensity of erosion in post-glacial time. Magnesium has a distribution similar to that of the alkali metals. Magnesium, like potassium, is clearly associated with the mineral products of erosion. In the glacial clays the magnesium content closely approaches the average lithospheric concentration of this element (20.9 mg/g, Rankama & Sahama 1949). This concentration falls steeply in each case on passing from the clays into the post-glacial organic deposits. Thereafter the concentration falls to a minimum then again rises irregularly towards the sediment surface in much the same way as does the potassium concentration. Calcium on the other hand is not so clearly associated with the mineral erosion products and is evidently more easily leached from the soil than is magnesium. Calcium is abundantly precipitated into these sediments only at times of very intense erosion when the rate of precipitation of clastic material is high enough to prevent the removal by leaching of much of the calcium. This effect is clearly seen in the sediments of Esthwaite, the very high peak of calcium at 480 cm is contained in a zone of coarsely laminated glacial clays which are sufficiently calcareous to effervesce on acidification. At this time the rate of erosion of the somewhat calcareous country rocks was

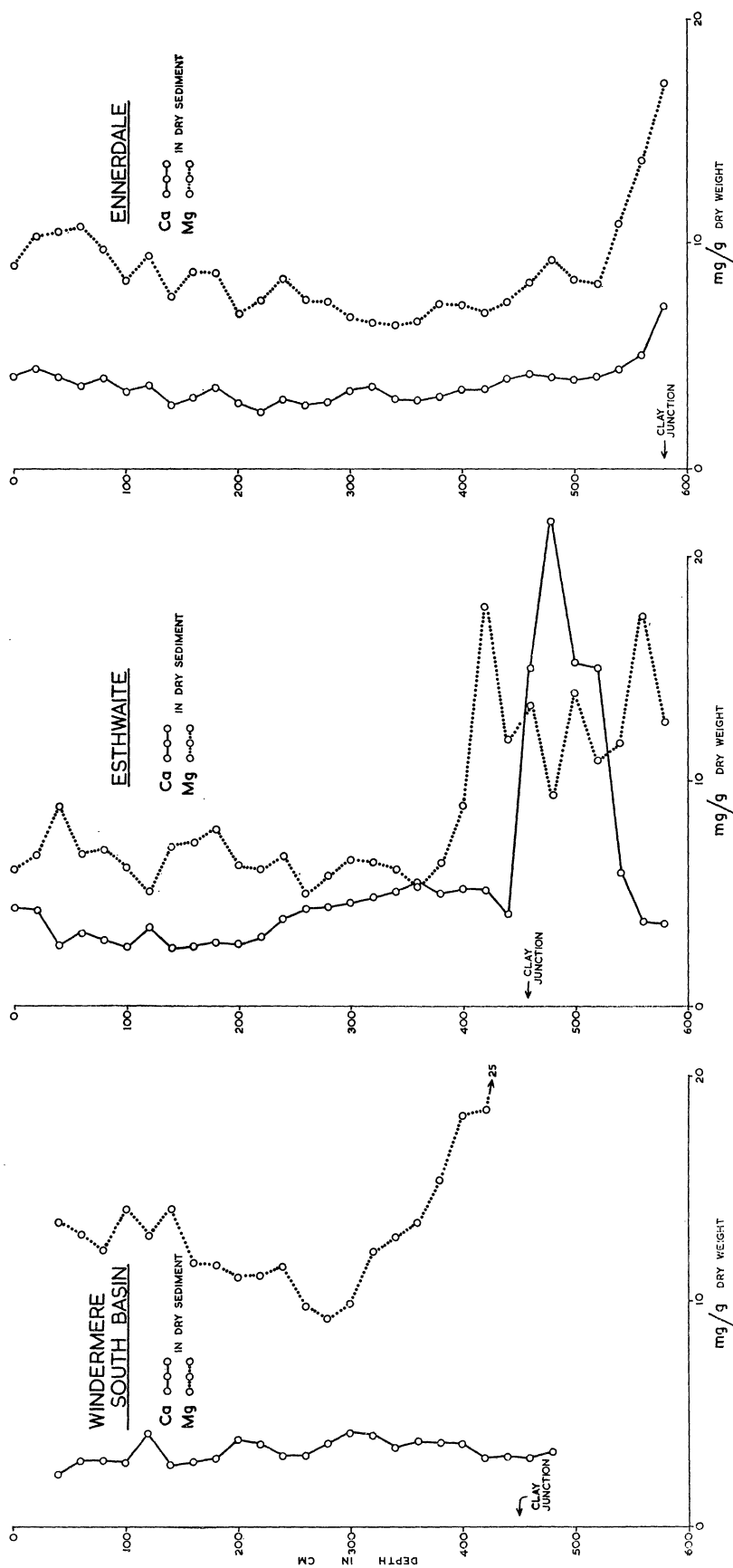


FIGURE 16. Distribution of the concentration of calcium and magnesium in the sediment columns of Windermere south basin, Esthwaite and Ennerdale.

evidently so high that leaching was insufficient to remove and carry away the calcium in solution. This condition does not recur at any time in the post-glacial sediments, which are generally poor in calcium. One must conclude that the early waters of Esthwaite, derived from the drainage of newly glaciated terrain, must have been very much more calcareous than at present, and it seems likely that this is true of all the lakes of this area. This conclusion is in accord with the findings of Round (1957, 1961), who concluded that the early diatoms from Lake District lake deposits are characteristic of much more calcareous conditions than those prevailing today in the now calcium-poor waters of the area. In the post-glacial sediments of Esthwaite, calcium does not show a clear relationship with erosion products but is more closely associated with organic matter. One may then conclude that in these conditions of geology calcium is only associated clearly with erosion intensity in periods of exceptionally active erosion which occurred here only during actual glaciation. Similar conclusions could be derived from a study of the calcium content of the sediments of the south basin of Windermere, where again, although magnesium directly follows the deduced erosion rate, calcium does not. (In this section from Windermere, although the core studied enters the glacial clay it does not contain the coarsely laminated and more calcareous material, which here lies deeper in the clay than in Esthwaite.) In Ennerdale on the other hand the distribution of calcium is similar to that of magnesium. One may conclude that in this basin, which lies largely in igneous rocks, the calcium is at least in part contained in more stable minerals than the calcite of the Silurian sedimentary rocks, and is therefore less easily removed from the mineral particles. From this it follows that less calcium will be carried in solution in the drainage waters of the Ennerdale basin than in those of either Esthwaite or the south basin of Windermere, and this is in fact the case at the present day.

#### *Iron and manganese*

The migration of the elements so far considered takes place either by bodily removal of the sedimentary material by erosion or by direct solution from the soils, followed either by precipitation into the lake sediments or, if no precipitation occurs, removal to the ocean. Direct solution under oxidizing conditions does not appear to play an important part in the mobility of iron and manganese; this is to be expected in view of the very low solubility of the oxidized forms of both elements. Under reducing conditions however both elements may be expected to become mobilized and to pass into solution, manganese more easily than iron. The rate of transport of these two elements may then be expected to be influenced by the intensity of erosional activity on the one hand and by the redox conditions prevailing in the drainage system on the other hand. Erosional transport would not be expected to bring about any separation of the two elements, so that under purely erosional conditions the concentration ratio of iron:manganese should remain that of the lithosphere. When transport by reduction to the mobile manganous and ferrous forms occurs, considerable separation of the elements may be expected, since manganese is more easily reduced than is iron. The influence of these factors is illustrated in the distribution of manganese and iron in the sediments of Esthwaite, Windermere south basin and Ennerdale, three basins that represent a gradation in organic productivity in order of decreasing richness.



The distribution in depth of the concentration of manganese and iron in the three lake sediments is shown in figure 17. In the case of the Ennerdale sediments it will be seen that at the lower end of the core, where the sample enters the glacial clays, the concentration of both iron and manganese approaches the average lithospheric concentration of these elements (1.0 mg/g Mn and 50 mg/g Fe, Rankama & Sahama 1949) though manganese is somewhat above the average. On passing upwards into post-glacial deposits, the concentration of both elements falls in response to dilution of the products of erosion by organic additions. The profiles of iron and manganese follow that of potassium throughout the post-glacial column, indicating a purely erosional mode of transport of both elements. That little or no reductive separation of iron and manganese has taken place in the drainage system is shown by the near constancy of the iron:manganese ratio throughout the profile, the ratio lying a little below the lithospheric average. One may then conclude that in this drainage basin, since no disturbance of the iron:manganese ratio has taken place, the redox conditions in the soils have never been such as to facilitate the transport of these elements in ionic form.

In the sediment of Windermere south basin, the fine pink glacial clay below 430 cm depth has a higher iron and manganese content than the lithospheric average. This enrichment may have been brought about by mechanical separation of finely particulate material resulting in a rather iron-rich clay. The ratio of manganese to iron in the clay is however similar to that of the lithosphere as a whole, indicating purely erosional transport of both elements. On passing upwards from the clay into the organic post-glacial deposits, a steep rise in manganese occurs while the iron concentration falls. In this sediment, the iron concentration changes with depth in a similar way to that seen in Ennerdale, and follows the distribution of potassium; iron, then, is assumed here also to have moved largely by erosional transport, a view supported by the closeness of the sedimentary iron content to that of the lithosphere. The behaviour of manganese on the other hand is quite different from that shown by this element in the Ennerdale sediment. Whereas, in Ennerdale, the manganese concentration remains proportional to that of iron, maintaining the ratio of the elements roughly similar to that in the lithosphere, in the Windermere sediment, soon after the end of glaciation, the manganese content rose steeply to reach in the lower sediments an average concentration some 5 times as high as in igneous rocks, and reaching a maximum about 1 m down in the sediment of 13 mg/g. The iron:manganese ratio then, diverged very greatly from that of the lithosphere soon after the cessation of the deposition of the glacial clays (figure 18). These observations are interpreted as follows. The enrichment of manganese in the sediment of Windermere with respect to iron can only be brought about by preferential removal of manganese from the soils of the drainage system with its subsequent deposition in the lake sediment. This preferential migration must be brought about by onset of reducing conditions in the soils of sufficient intensity to produce manganous ion but not intense enough to effect large-scale reduction of iron to ferrous ions. Manganese carried in solution into the lake basin (which never becomes anaerobic) is there oxidized and eventually resides in the sediment as manganese dioxide. That this precipitation is going on at the present time is shown by the black coating of manganese dioxide which covers deep-water rocks and any object which has lain undisturbed for some tens of years on the lake bed. Examples are found in pieces of broken



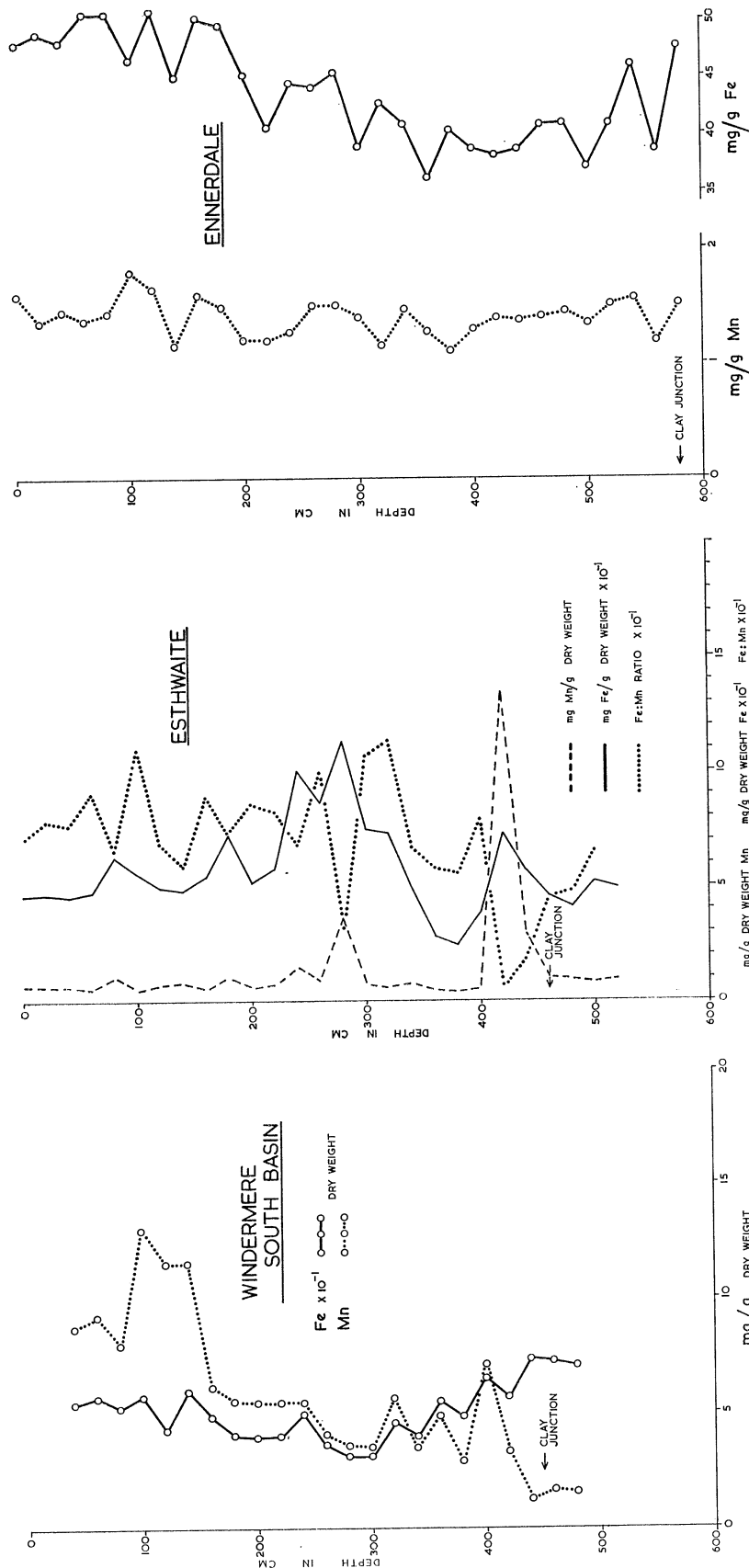


FIGURE 17. Distribution in depth of the concentration of iron and manganese in the dry sediment of Windermere south basin, Esthwaite and Ennerdale.

crockery removed from the lake bed by Mr B. Walker while diving in the lake; such articles are usually covered on the upper surface by a thin black layer rich in manganese. The sharp rise in manganese content in the Windermere sediments occurring soon after the commencement of deposition of organic sediments is, then, considered to represent the development in the drainage system of reducing soils. Since Esthwaite drains into the south basin of Windermere a contribution to the manganese input into Windermere

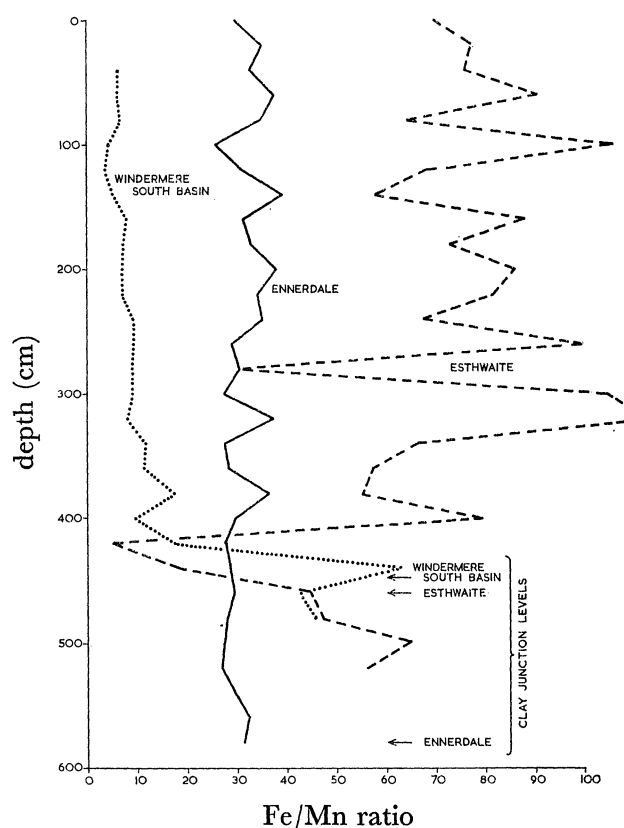


FIGURE 18. Variation with sediment depth of the ratio of iron to manganese in the sediments of Windermere south basin, Ennerdale and Esthwaite.

obviously derives from Esthwaite. However, in this context the drainage basin and sediments of Esthwaite should be regarded merely as a part of the drainage basin of Windermere south basin.

In Esthwaite the glacial clays below 460 cm again have iron and manganese content closely similar to the average for the lithosphere. On passing upwards into the organic deposits a very marked rise in manganese content occurs similar to that described in the sediments of the south basin of Windermere. A smaller rise also occurs in the iron concentration. The large rise in manganese concentration is soon followed however by an equally marked fall to a manganese content only about half that occurring in the glacial clays. The manganese in the sediment remains thereafter at a low level (apart from the relatively minor maxima at 280, 240 and 80 cm which are discussed later) up to the sediment surface. Iron also behaves in a manner not seen in either Ennerdale or Windermere, rising after the initial minimum at 380 cm to reach a maximum at 280 cm with an iron

content double that of the average lithosphere. It is considered that the distribution of iron and manganese in this sediment is related not only to the development of reducing soil in the drainage area, but also to the development of a periodically anaerobic hypolimnion in the lake itself. In the case of manganese, the early phase of increasing deposition is postulated to represent the first development of reducing soils, facilitating transport of manganese and some iron into the lake basin where it was oxidized and precipitated in the manner proposed in Windermere. In Esthwaite however it is postulated that this phase was rapidly followed by the development of reducing conditions in the lake basin of such intensity as to produce during summer stratification an anaerobic hypolimnion which did not (and does not today) occur in the south basin of Windermere or in Ennerdale. It is then further postulated that the development of periodically anaerobic conditions led to the reduction of manganese in the lake sediment itself and to its further migration out of the lake with resultant impoverishment of the sediment in this element.

That such a migration did occur and indeed occurs today is established by a study of the distribution of manganese in the water of Esthwaite throughout the year for which I am indebted to Mr J. Heron. Figure 19 shows that manganese is in fact released from the sediments of Esthwaite during thermal stratification and carried into the epilimnion at the overturn to be removed in the effluent from the lake basin. No such mobilization of manganese occurs in the thermally stratified south basin of Windermere.

The distribution of manganese in the sediments of Ennerdale, Windermere south basin, and Esthwaite is summarized in figure 20 and compared with the distribution of manganese in Linsley Pond (from Hutchinson & Wollack 1940). The dotted curve which represents Linsley Pond has been shortened to suit the diagram, but the depth-time relationship is such that the lower end of the Linsley Pond profile, representing the junction between the glacial clay and the post-glacial sediments, corresponds in time with the 460 cm level of the Esthwaite profile. The distribution of manganese in the Linsley Pond sediment bears a striking resemblance to that in the Esthwaite sediment. This would be expected on the hypothesis outlined above, since Linsley Pond is a similarly productive lake and would therefore be expected to lose manganese from its sediments during periods of anaerobiosis. It is then postulated that the position of the marked fall in manganese concentration in the early deposits of both Esthwaite and Linsley Pond represents the time of the first formation of an anaerobic hypolimnion, and that therefore these lakes assumed this character of eutrophic water bodies at an early stage in their histories. In the figure the manganese profile of Ennerdale has been moved to the left for the sake of clarity.

The distribution of iron in the Esthwaite sediment, which is quite unlike that observed in either Ennerdale or the south basin of Windermere (figure 17), is postulated to have been produced by similar mechanisms to those proposed in the interpretation of the Esthwaite manganese profile. It is suggested that the early iron maximum at 420 cm resulted from the migration of ferrous iron from the drainage system with its subsequent precipitation in the oxidizing conditions of the early lake basin. The subsequent fall in concentration to a minimum at 380 cm then represents the development of sufficiently reducing conditions in the lake basin to facilitate further migration of iron from the lake with resulting impoverishment of the sediment in this element. The iron maxima at 280,

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240, 180 and 80 cm depth would then represent the return of relatively oxidizing conditions in the lake which prevented or reduced the migration of iron out of the lake basin.

In the above interpretation of the variation in depth of iron and manganese concentration in the deposits of Esthwaite one has assumed that the observed changes have been

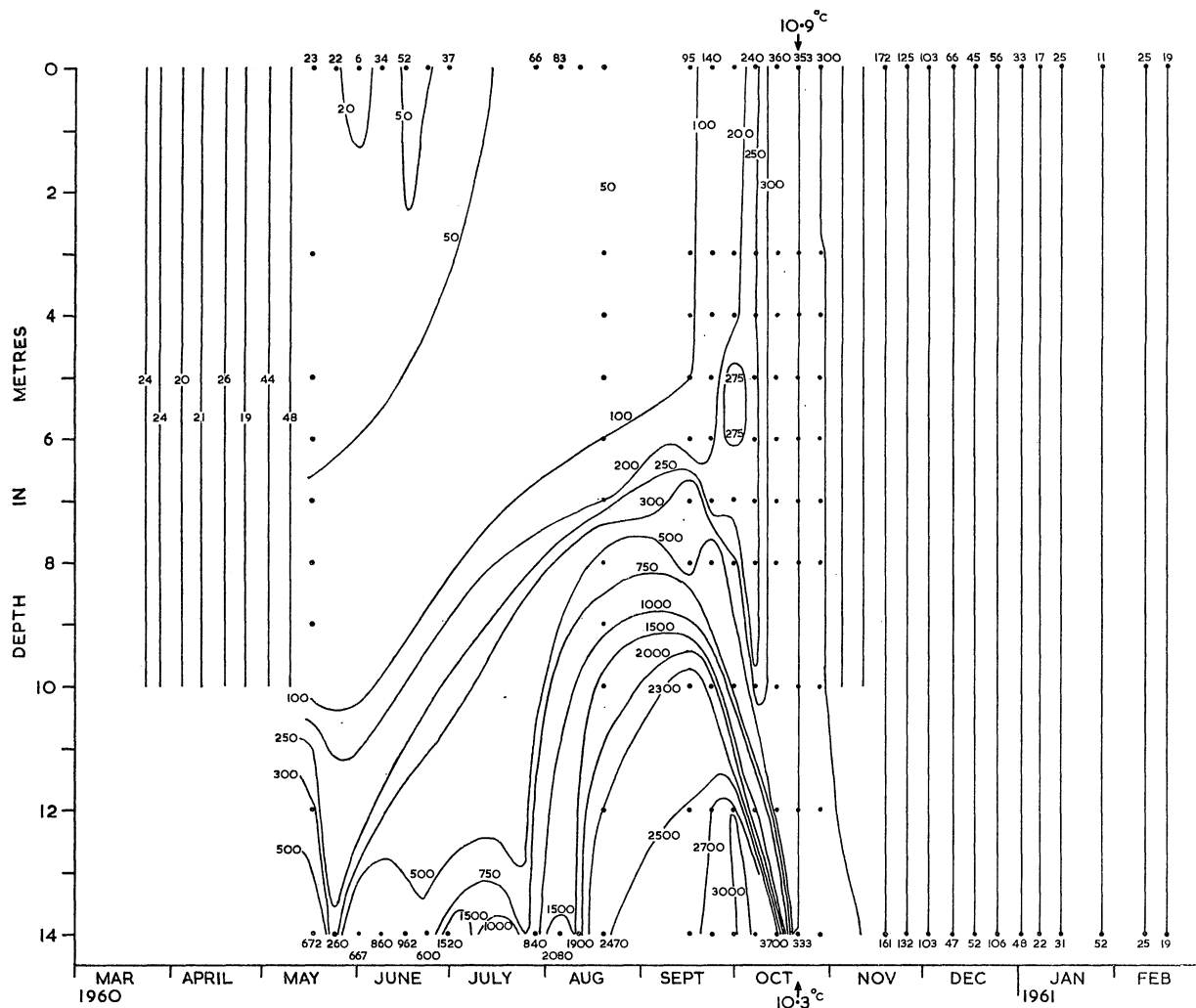


FIGURE 19. Concentration of total manganese ( $\mu\text{g}/\text{l}$ ) in the waters of Esthwaite throughout the year. Release of manganese from the sediment in an anaerobic hypolimnium may be observed, followed by distribution of this element throughout the water column at the breakdown of thermal stratification.

brought about by the influence of a changing lake redox situation on a more or less constant rate of input of iron and manganese from the drainage system. It could well be objected that a similar distribution of these elements may have been produced not by changes in the redox conditions of the lake basin but by changes in the rate of supply of iron and manganese to the lake.

Consider that two limiting cases are possible: (a) that the rate of supply of both elements was substantially constant throughout the post-glacial period and the variations in sedimentary concentration were brought about solely by variation in lake redox conditions,

and (b) that the redox conditions in the lake were constant and the variation in sedimentary concentration was produced by variation in the rate of supply of these elements from the drainage system. In case (a) the redox conditions in the lake may vary in such a way that the efficiency of precipitation and retention of iron and manganese is increasing or decreasing as the conditions become more or less oxidizing. In a phase of increasing oxidation, the efficiency of retention of iron will be increased before the precipitation of manganese is increased. Increasing oxidative efficiency will therefore increase the iron

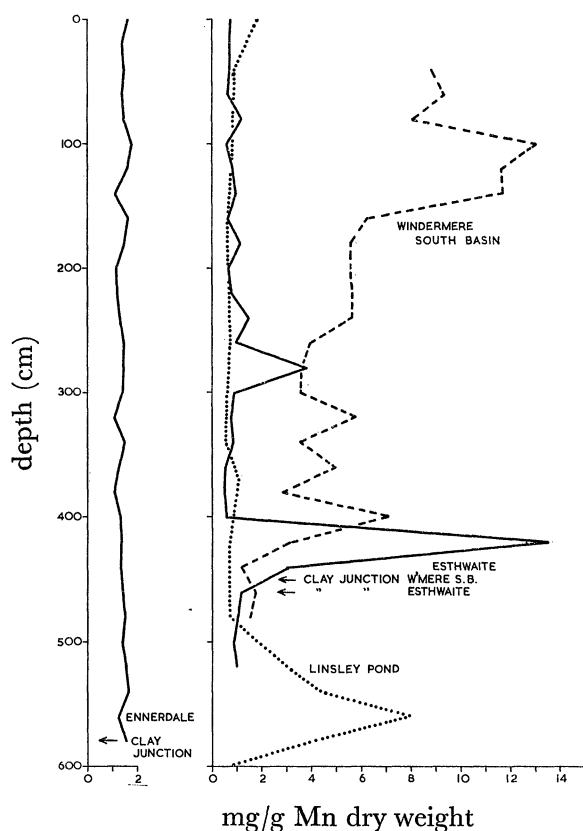


FIGURE 20. The distribution in depth of manganese in the dry sediment of Ennerdale, Esthwaite and Windermere south basin (Ennerdale and Esthwaite solid lines, Windermere dashed) compared with the manganese content of the sediment of Linsley Pond (dotted line). The Linsley Pond profile has been shortened to suit the diagram, but the lower end of the profile approximates in age to the position of the clay junction on the other profiles.

concentration relative to that of manganese in the sediment, leading to a rise in the sedimentary iron:manganese ratio. As the intensity of oxidation is further increased, precipitation of manganese will take place as well as iron and the iron:manganese ratio will fall. Reversal of this process towards a renewal of more reducing conditions will first reduce the rate of precipitation of manganese, again increasing the iron:manganese ratio, followed by a fall in this ratio as the precipitation and retention of iron is again diminished by increasingly reducing conditions. In such a situation then a maximum in the iron:manganese ratio might be expected to occur in the sedimentary profile both before and after



the period of maximum oxidation. If the periods of maximum oxidation in the Esthwaite profile are taken to be the maxima in the iron distribution profile, each maximum in iron concentration should be preceded and followed by a maximum in the iron:manganese ratio. The maxima in the iron distribution curve should correspond with minima in the profile of iron:manganese ratio. In figure 17 relating iron, manganese and the iron:manganese ratio (dotted) to depth in the sediment of Esthwaite, this expectation may be seen to be in close accord with the observed situation.

If on the other hand case (*b*) is postulated, then the maxima in the distribution profile of iron must correspond to increased migration of ferrous iron from the drainage system. Before large-scale reduction of iron to the ferrous state occurs in the soil it must be assumed that reduction of manganese is already maximal. Increased reductive efficiency then will lead to increased migration and supply of iron but to little change in the rate of supply of manganese. The increased rate of supply of iron must then lead to an increase in the iron:manganese ratio of the precipitated material. If case (*b*) was applicable, then, to the situation in Esthwaite, the maxima in the iron profile should correspond with the maxima in the ratio of iron:manganese, precisely the opposite to the observed result. One may then conclude that the major influence on the distribution of iron and manganese in the sediment of Esthwaite has been the variation in oxidative and reductive intensity in the lake basin itself. Obviously one cannot assume that variation in the rate of supply has had no influence whatever, but each maximum in the iron and manganese profile in the Esthwaite sediment probably corresponds to a period of increased oxidative intensity in the lake from whatever cause.

The variation in iron:manganese ratio with depth in the three lake sediments here discussed (Ennerdale, Windermere south basin and Esthwaite) is summarized in figure 18. The profile of iron:manganese ratio in Ennerdale lies somewhat lower than the igneous rock average (50), but since the glacial clays of Ennerdale have a lower than average ratio this probably reflects a property of the local country rocks. The essential differences between the different lakes and drainage areas represented by these three sediments are clearly seen in this figure. Ennerdale represents a relatively impoverished biological regime both in the soil and in the lake itself where the iron:manganese ratio remains substantially constant and close to that of igneous rocks. Windermere south basin represents a system in which more reducing soils drain into a constantly oxidizing lake basin, producing a very low iron:manganese ratio. Esthwaite represents a relatively rich biological system both in the drainage system and the lake itself, producing a high iron:manganese ratio in the sediment which is sensitive to fluctuations in the redox conditions of the lake basin, which produce corresponding fluctuations in depth-time in the iron:manganese ratio. One might predict the existence of a fourth system not represented in the lakes here studied, in which a reducing soil drains into a more eutrophic lake basin than Esthwaite, in which an anaerobic hypolimnion has been a constant feature of the lake. The sediment of such a lake would be expected to have a constant low manganese content throughout the period of eutrophy, associated with a constant and high iron:manganese ratio. The manganese data of Hutchinson & Wollack on Linsley Pond suggest that the latter lake may represent such a system.

*Phosphorus*

Because of the very low solubility of phosphorus in the presence of precipitating oxidized forms of both iron and manganese one might expect to find an association in the lake sediments between phosphorus and iron and manganese. On the other hand the pronouncedly biophile character of phosphorus must also have an important influence on the migration and precipitation of this element. That the incorporation of phosphorus into algal cells, which may take place from exceedingly dilute solutions, must play an important part in the precipitation of phosphorus into the sediment is demonstrated by the marked seasonal variation in phosphate concentration in lake waters. This variation is correlated with the seasonal fluctuations of algal growth. The efficiency of this mode of removal of phosphate from solution in Windermere, for example, is demonstrated by Heron (1961), who shows that phosphorus is annually reduced in concentration in the waters of this lake to less than 1 part in  $10^{10}$ . There can be no doubt that this reduction in concentration is largely brought about by incorporation of the element into planktonic algae. One must conclude then that much of the phosphorus entering the lake eventually reaches the sediment either in association with iron or manganese or incorporated into biological material. The concentration of phosphorus finally residing in the sediment of the lake will then depend on four factors: (1) the rate of supply of phosphorus to the lake basin; (2) the efficiency of the precipitating mechanism; (3) the rate of accumulation of the sediment as a whole; (4) the rate of loss of phosphorus from the recently sedimented material. Some insight into the relative importance of these factors in the sedimentation of phosphorus in three different lake basins may be gained from a study of the phosphorus distribution in the sediments of Ennerdale, Windermere south basin and Esthwaite. The variation of phosphorus concentration with depth in the sediment in these three lakes is presented in figure 21; the solid line in each case represents concentration ( $\mu\text{g P/g}$ ) on a dry-weight basis. The lower end of the curves pass into glacial clay; in Ennerdale at 580 cm, Windermere south basin at 440 cm, Esthwaite at 460 cm. The concentration of phosphorus in the clays resembles the average concentration of this element in igneous rocks ( $1180 \mu\text{g/g}$ , Rankama & Sahama 1949), though the concentration in the Ennerdale clay is significantly lower than the average, presumably reflecting a local deviation of the country rock composition.

At the time of deposition of the glacial clay, the migration and precipitation of phosphorus was evidently accomplished by direct erosive removal and deposition of fine rock particles practically unchanged in the process with respect to phosphorus content. A marked change in the mode of movement of phosphorus was brought about by the cessation of active glacial erosion and the formation of relatively stable soils in the drainage areas of the three basins. In each case passage upwards from the clay into the post-glacial organic deposits is marked by a great increase in the concentration of phosphorus in the sediment, to reach maxima, deep in the post-glacial sediments, with concentrations some 3 to 5 times as great as the concentration found in the glacial clay. The concentration of phosphorus in the sediments of Ennerdale and Esthwaite falls in a more or less irregular manner as the sediment surface is approached. The marked change in concentration of phosphorus on transition from clay to post-glacial sediment can only be brought about

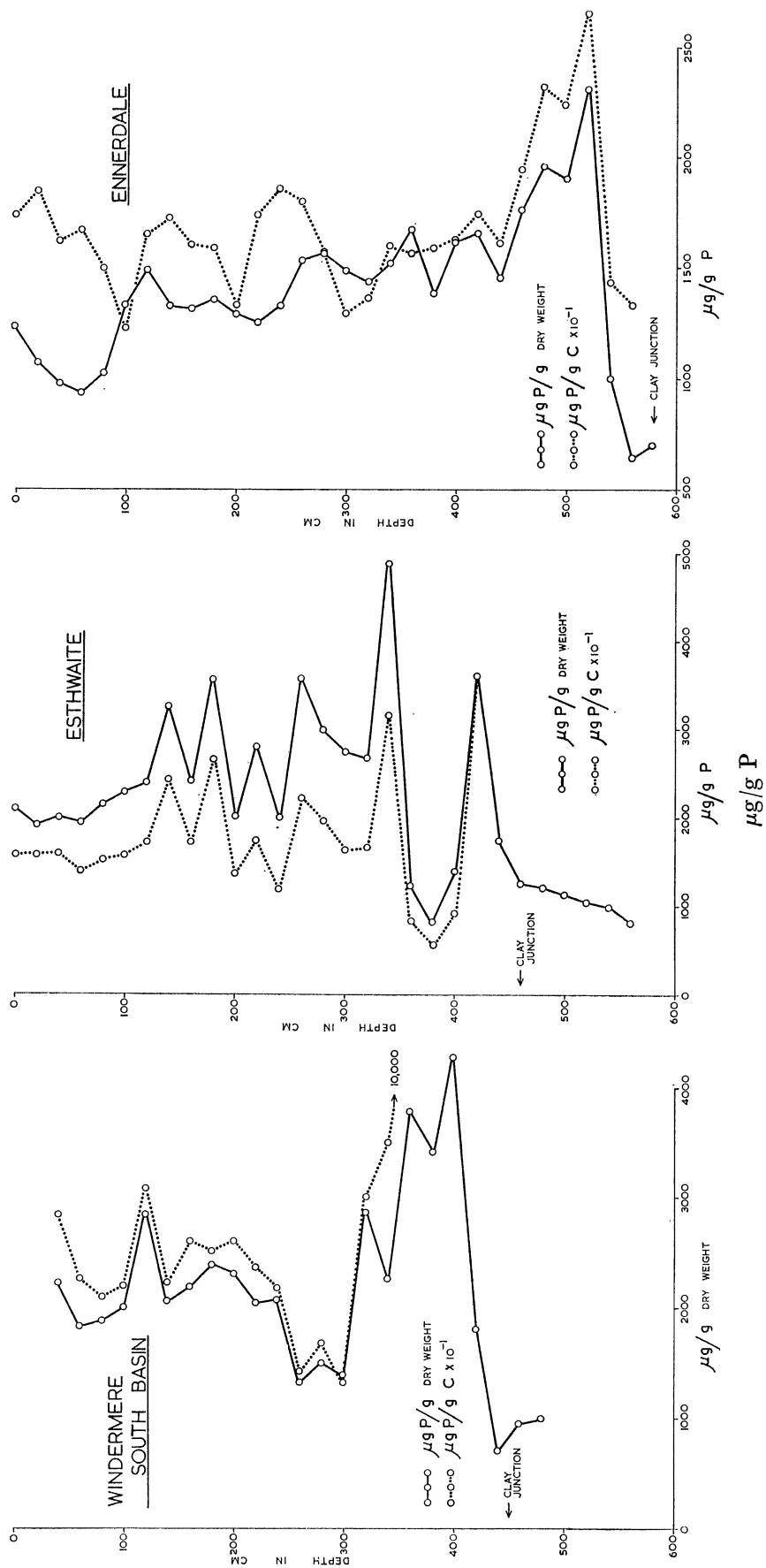


FIGURE 21. Distribution in depth of the concentration of phosphorus in the dry sediments of Windermere south basin, Esthwaite and Ennerdale (solid line), and of the relationship between carbon and phosphorus (dotted line).

by a profound change in the mechanism of transportation and precipitation of the element in response to the formation of a stable soil system. The great enrichment of the sediment in phosphorus relative to the igneous rock composition must result from preferential removal of phosphorus (as phosphate) in solution by leaching, followed by a more or less efficient precipitation of the element in the lake basin itself. Since mineral erosion continues throughout the post-glacial period, the solution-precipitation mechanism must be superimposed on a continuing deposition of eroded particle-bound phosphorus. The marked change in sedimentary concentration of phosphorus at the clay/post-glacial interface suggests that solution followed by precipitation of phosphorus is the more important transport mechanism in post-glacial times.

In order to simplify the potential complexities of simultaneous variation in relative importance of the four factors which could have bearing on the sedimentary phosphorus concentration, some preliminary assumptions may be made. First we may consider the Ennerdale sediment which appears to present the least complicated case. It is considered that losses of phosphorus from the sediment surface can only become significant in the case of a lake whose hypolimnion becomes periodically anaerobic. (This statement will be discussed later with reference to the Esthwaite sediment). It is here assumed then that in the case of Ennerdale, which never approaches anaerobiosis, loss of sedimented phosphorus is and has been negligible. It was earlier suggested that two processes were involved in the sedimentation of phosphorus in the non-calcareous systems here discussed. These were (1) co-precipitation of phosphorus with iron and manganese, these metals having been carried in solution initially in the reduced form, to be oxidized and precipitated into the lake sediment; (2) precipitation of phosphorus incorporated into the organic material synthesized in the lake largely by phytoplankton. In the discussion of the iron-manganese distribution in Ennerdale the conclusion was reached that transportation of these elements had occurred largely by erosional removal of the minerals containing them. Little opportunity would therefore here exist for co-precipitation of phosphorus. One would then expect to find little relationship between the iron-manganese concentration of this sediment and the phosphorus concentration. This expectation is supported by the distribution profiles of phosphorus and iron in the Ennerdale sediment, which, at least above 400 cm depth, change in opposite senses as the sediment surface is approached, iron rising steadily in concentration, while phosphorus falls. One may assume then that the precipitation efficiency for phosphorus in the Ennerdale basin has not been influenced by variations in the iron-manganese cycle, and that the precipitation of phosphorus was here largely biological and relatively constant. If then the rate of supply of phosphorus had been constant throughout the post-glacial period, the concentration of phosphorus at any depth would merely be inversely related to the rate of deposition of the sediment as a whole at that depth. It was earlier shown that the carbon content of the lake sediments here discussed is inversely related to deposition rate, so that if all the assumptions made above approach any validity, one should discover in Ennerdale an approximately constant relationship between carbon and phosphorus, both elements merely reflecting the changing rate of deposition. The carbon and phosphorus profiles in Ennerdale do in fact show a great similarity if one disregards the large phosphorus maximum at 520 cm. This relationship is more clearly seen in figure 22 where the relationship between carbon and



phosphorus in Ennerdale and Esthwaite is plotted. In figure 21 a mean ratio of phosphorus to carbon of some 16 mg P/g C may be discerned for Ennerdale. The very marked deviation from this mean occurring between 440 and 540 cm, where the phosphorus/carbon ratio rises to a maximum at 520 cm of some 27 mg P/g C, must then be related either to an increased efficiency of the precipitation mechanism or to an increased rate of supply of phosphorus. There is no apparent means of distinguishing between these two possibilities. One may reasonably suppose however, that in the early post-glacial period, the soils were in fact richer in readily leachable phosphorus and that the rate of supply was

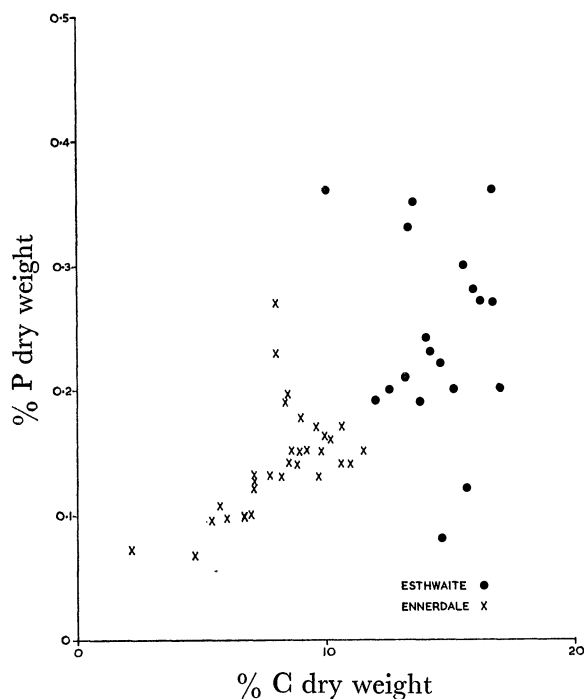


FIGURE 22. Relationship between carbon and phosphorus in sediment samples from Esthwaite and Ennerdale.

greater at that time than it was later, after some thousands of years of elution. The distribution of phosphorus in depth in the Ennerdale sediment may result then from the interplay of two variables (as a first approximation)—a rather steadily diminishing rate of supply of phosphorus, and a fluctuating rate of deposition of the sediment as a whole. Superimposed upon this system is a relatively constant contribution of phosphorus retained in the lattice of the mineral fraction of the sediment. Since the mineral fraction of the Ennerdale sediment averages some 80% of the dry weight, phosphorus retained in the lattice would contribute a significant part of the whole. For this reason, relating the whole of the phosphorus in the sediment to carbon would result in an erroneously high estimate of phosphorus related to unit weight of carbon. The mean apparent relationship of some 16 mg P/g C quoted above is therefore much too high and is indeed higher than the mean figure for freshwater algae of the area—some 7 mg P/gC. If, however, it is assumed that the post-glacial mineral fraction of the sediment retains phosphorus to the extent of some 700  $\mu\text{g/g}$  (the glacial clay content), then a correction for the mineral contribution to



phosphorus content of the post-glacial sediment would reduce the phosphorus presumed to be associated with organic material to 8 mg P/g C, which is close to the average relationship for algae.

In the sediment of the south basin of Windermere the mechanism of deposition must be different from that postulated in Ennerdale. In the Windermere sediment between some 300 cm depth and the clay junction at 440 cm the phosphorus content is very high. The apparent phosphorus:carbon ratios are here about 100 mg P/g C, which even on correction for possible mineral lattice phosphorus content reduce only to some 60 to 70 mg P/g C. This is an order of magnitude greater than the phosphorus:carbon ratio found in algae or in plant material in general. Inspection of the phosphorus distribution in the Windermere sediment in comparison with the iron–manganese distribution reveals a direct relationship between these elements. In view of the fact that phosphate is very strongly co-precipitated when manganese is precipitated in oxidizing conditions (unpublished result), and in view of the conclusion previously discussed that large-scale precipitation of manganese must have taken place in the Windermere basin, it appears reasonable to suppose that the close relationship between iron and particularly manganese and phosphorus in the Windermere sediment is brought about by co-precipitation of phosphorus with precipitating manganese and iron compounds. The very high phosphorus content of this sediment below 300 cm must then be accounted for by the high efficiency of this co-precipitation mechanism. The sedimentary concentration of phosphorus would be further enhanced by the relatively high early input rate of phosphorus resulting from an early soil availability of phosphorus similar to that proposed in the Ennerdale basin. The later tendency for phosphorus concentration to rise in this sediment from a minimum at about 280 cm towards the surface is then probably related to the rising input of manganese which occurs synchronously. One assumes that in Windermere as in Ennerdale losses of phosphorus from the sediment have played little part in producing the observed distribution.

In the sediment of Esthwaite the concentration of phosphorus again is apparently associated with that of iron and manganese, showing little relationship to carbon figure 22. The phosphorus maximum at 410 cm almost certainly results from co-precipitation with iron or more probably manganese at that level, and the marked minimum occurring between 360 and 400 cm depth is synchronous with the minimum in iron and manganese content. This iron–manganese minimum was earlier attributed to loss of both iron and manganese from the Esthwaite sediment at a time when the sediment was particularly reducing. One is led then to the conclusion that the phosphorus minimum at 380 cm resulted directly from the loss of iron from the lake basin at that time. Since the precipitation of both iron and manganese results in the co-precipitation of phosphorus, loss of manganese (which has occurred in the Esthwaite basin throughout most of post-glacial time) does not incur loss of phosphorus, since phosphorus is held by the retained iron. If, however, a substantial loss of iron also occurs, then loss of phosphorus associated with the iron may be expected. In connexion with the postulated loss of phosphorus at about 380 cm in the Esthwaite sediments, it is interesting to examine the analyses of Livingstone & Boykin (1962) of the phosphorus content of the sediments of Linsley Pond. The distribution of phosphorus in Linsley Pond shows a marked resemblance to that found in the

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English lakes here discussed. Very high concentrations of phosphorus occur in the early post-glacial deposits, followed by a striking fall in concentration at about 850 cm (the depth of the glacial clay interface is 1100 cm), to reach a minimum at about 600 cm, rising thereafter as the surface is approached to a concentration some three times as great as that at the minimum. From the data of Hutchinson & Wollack (1940), the iron concentration in Linsley Pond appears to follow a similar profile, reaching a minimum in their core (L10) at about 700 cm, but since according to Livingstone & Boykin the L10 core was probably about 1 m deeper than that studied by themselves, it may be presumed that the iron minimum in Livingstone & Boykin's core lay in fact at about 600 cm to correspond with their phosphorus minimum. Since the concentration of iron in the L10 core at the minimum—some 23 mg Fe/g dry weight—closely resembles that in Esthwaite at the minimum (380 cm)—25 mg Fe/g dry weight—it seems reasonable to suppose that conditions in the two lakes, in so far as possible iron losses are concerned, were very similar at the time the respective minima in iron and phosphorus were produced. Then if the phosphorus minimum in Esthwaite is explicable on the presumption of loss of iron with its associated phosphorus, it is reasonable to suppose that the same mechanism produced the striking fall in the Linsley Pond sediment phosphorus, and that the continuing relatively low phosphorus concentration in the latter sediment was brought about by a more prolonged period of significant iron loss than occurred in Esthwaite.

In summary one may imagine a series of lake systems in which the various processes discussed above influence the sedimentary phosphorus concentration with varying importance. Purely biological precipitation, because it is operative for part of the year only, might be expected to be relatively inefficient compared with a more continuous process of co-precipitation with oxidizing iron and manganese. Where co-precipitation is superimposed upon biological precipitation, high total efficiency of sedimentation might be expected to lead to relatively greater concentrations of phosphorus in the sediment, as for example in the early deposits of Esthwaite and Windermere south basin and presumably of Linsley Pond. Since further migration of iron out of the lake basin is apparently correlated with significant loss of phosphorus from the sediment it must be presumed that a very important part is played by both manganese and iron, not only in precipitation of phosphorus to the sediment but also in its retention therein. It is likely that the form of the association between, for example, phosphorus and iron changes after the incorporation of the elements into the sediment. In oxidizing systems adsorption of phosphate on to ferric hydroxide is probably of major importance. According to Gaarder (1930) hydrolysis of ferric phosphate is extensive above about pH 3 to 4, whereas the addition of a large excess of ferric hydroxide removed practically all phosphate from solution until the pH rose above 8. Once incorporated into the sediment, however, much of the iron must be reduced to the ferrous state and phosphorus present is at least partly held as the hydrated ferrous phosphate (vivianite) which, as has been already mentioned, is present in visible masses in the older layers of the sediment. The finding of Livingstone & Boykin (1962) that a part of the phosphorus of Linsley Pond sediment is extractable by water (which would be curious if the phosphorus was still in the form in which it was precipitated) may be explicable if phosphorus is more soluble in the form of vivianite than it is when adsorbed on to ferric hydroxide.

*Sulphur*

The results of determination of total sulphur in the deposits of Ennerdale and Esthwaite are presented in figure 23. The concentration of sulphur in the glacial clays (about 1 mg/g) is somewhat higher than that given for the average lithosphere by Clarke & Washington (1924) ( $520 \text{ parts}/10^6$ ). In the post-glacial organic sediments, the sulphur concentration is markedly higher than that of the average lithosphere, rising in Esthwaite to a maximum

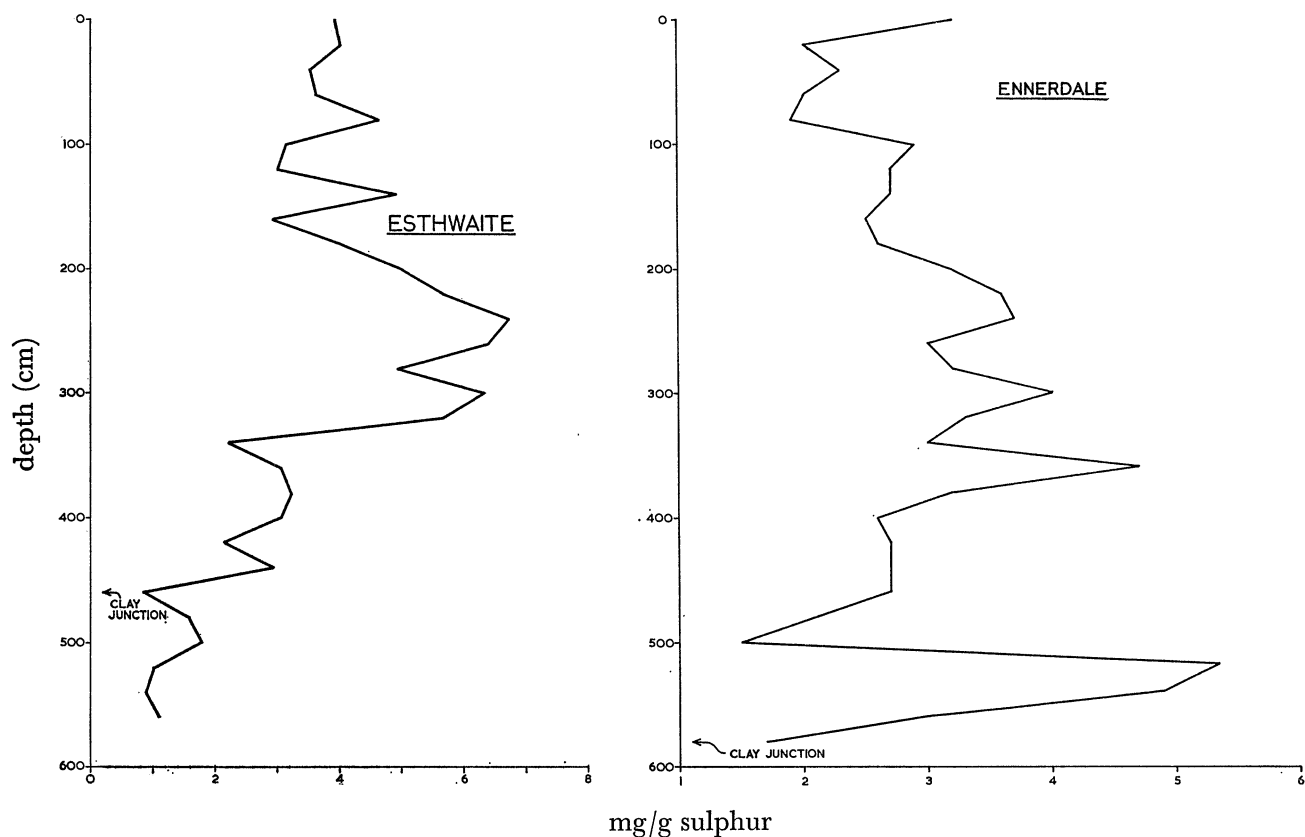


FIGURE 23. Variation with depth of the sulphur content in the dry sediments of Esthwaite and Ennerdale.

of almost 7 mg/g, more than ten times the lithospheric average, but of the same order of magnitude as that given for shales (Clarke 1924, from analyses of H. N. Stokes), of  $2600 \text{ parts}/10^6$ .

The mechanism of precipitation of sulphur into lake sediments is probably largely biological. The sulphur content of planktonic algae is rather constant. *Anabaena* from Windermere contains about 12 mg/g in the dry material and the diatom *Asterionella* about 6 mg/g. Since about half the dry weight of *Asterionella* is silica, these figures suggest that the sulphur content of the organic material of these algae is very similar. Other algae examined showed contents varying about 10 mg/g on the dry material. Precipitated algal material may then be expected to carry into the sediment a significant amount of sulphur presumably derived originally from sulphate ion in the epilimnion of the lake. Bacteria situated at the mud/water interface have the capacity to reduce the sulphate of the overlying water to sulphide (Mortimer 1941-2), in which form sulphur would be expected to

be held in the sediment as ferrous sulphide. Since the iron content of the sediment is very much greater than would be required to hold all the sulphur present as FeS, only a small part of the total iron of the sediment can be present as FeS, though a significant proportion of the sedimentary sulphur may be so contained. No attempt, however, was made to determine the distribution of the sedimentary sulphur between the possible chemical forms. The supply of sulphur to the lake basin in the form of sulphate is at the present time much greater than would be required for any potential algal growth ( $10 \times 10^6$  cells/l. of

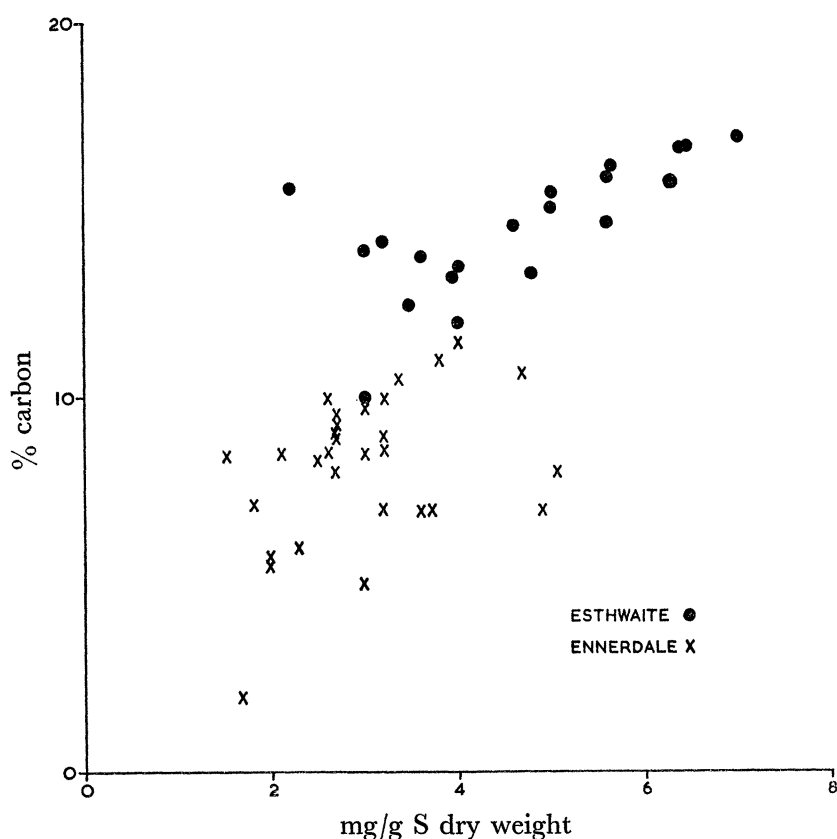


FIGURE 24. Relationship between carbon and sulphur content in the sediments of Esthwaite and Ennerdale.

*Asterionella* require  $9 \mu\text{g/l. S}$ , while the water contains some  $2000 \mu\text{g/l. S}$  as sulphate). The rate of precipitation of sulphur into the sediment may then be expected to be substantially independent of variations in the concentration of sulphate in the lake water, and dependent largely upon the biological regime of the lake and its drainage basin.

Despite the fact that the iron content of the sediment is everywhere greatly in excess of the quantity required to contain all the sulphur as ferrous sulphide, a distinct positive relationship appears to exist in the sediment of Esthwaite, for example between the iron and sulphur concentrations at any level; this is a puzzling feature for which no adequate explanation occurs to the author. In view of the probable biological basis of all precipitation and fixation mechanisms for sulphur, it is not surprising to find the positive relationship between sulphur and carbon content in the sediment, which is demonstrated in figure 24. Since the rate of sedimentation of sulphur is probably not controlled by the



rate of supply as sulphate in solution, it is presumed that the distribution of sulphur has little bearing on the rate of supply. If this is the case, one would not expect to discover any indication of a recent increase in the rate of sulphur deposition related to addition of sulphate to atmospheric precipitation from industrial coal combustion. There is evidence from rain composition studies (Gorham 1958) that much of the present dissolved sulphate of the surface waters of the area may well be derived from atmospheric pollution, but no indication that recent sediment is richer in this element from this cause is to be found. Indeed the maximum rate of sedimentation of sulphur into the sediments occurs in Esthwaite between 240 and 320 cm down in the sediment. It is likely then that atmospheric additions of sulphur from industrial pollution has little biological significance at least as a source of sulphur; the evidence suggests that this element has been in relative abundance throughout post-glacial times.

*Zinc, copper, cobalt, nickel*

The distribution in depth of these elements in the post-glacial sediments of Ennerdale, Windermere south basin and Esthwaite is shown in figures 25 and 26. The concentration of zinc, copper, cobalt and nickel and other heavy metal elements in the sediments is vastly greater than that occurring in the lake waters which at some time have been in contact with them. It seems clear therefore that the heavy metal elements are firmly bound to the solid particles of the sediment and are contained to an insignificant extent in the interstitial waters of the sediments. Thus the mean content of zinc, copper, cobalt and nickel in the sediments of the three lake basins studied are given in table 1, together with mean lithospheric content from Rankama & Sahama (1949).

TABLE 1

	parts/10 <sup>6</sup>			
	Co	Ni	Cu	Zn
south basin, Windermere	20	55	32	200
Esthwaite	35	50	30	200
Ennerdale	18	18	16	140
Lithospheric average	23	80	70	132

The mean concentrations of Zn, Cu and Co occurring in the practically unpolluted waters of Windermere are approximately as follows in parts/10<sup>9</sup>: Zn 5, Cu 0.5, Co 0.02. The ratio of concentration between sediment particles and water for these three elements is 40 000:1 for Zn, 64 000:1 for Cu, and 1 000 000:1 for Co. The nickel concentration in Windermere water is not known, but is likely to be of the same order of magnitude as that of copper. It will be observed that the concentration of zinc, copper and nickel is appreciably lower in the sediments of Ennerdale than in those of either Esthwaite or the south basin of Windermere.

The mechanisms of precipitation of these elements into the sediment may be various. It is likely that the metals incorporated into algal material and thereby conveyed from solution into the sediment would be held there as insoluble sulphides in the reducing conditions of the mud. An examination of the profiles of concentration of these elements in the sediment cores however, suggests that co-precipitation with manganese and iron may



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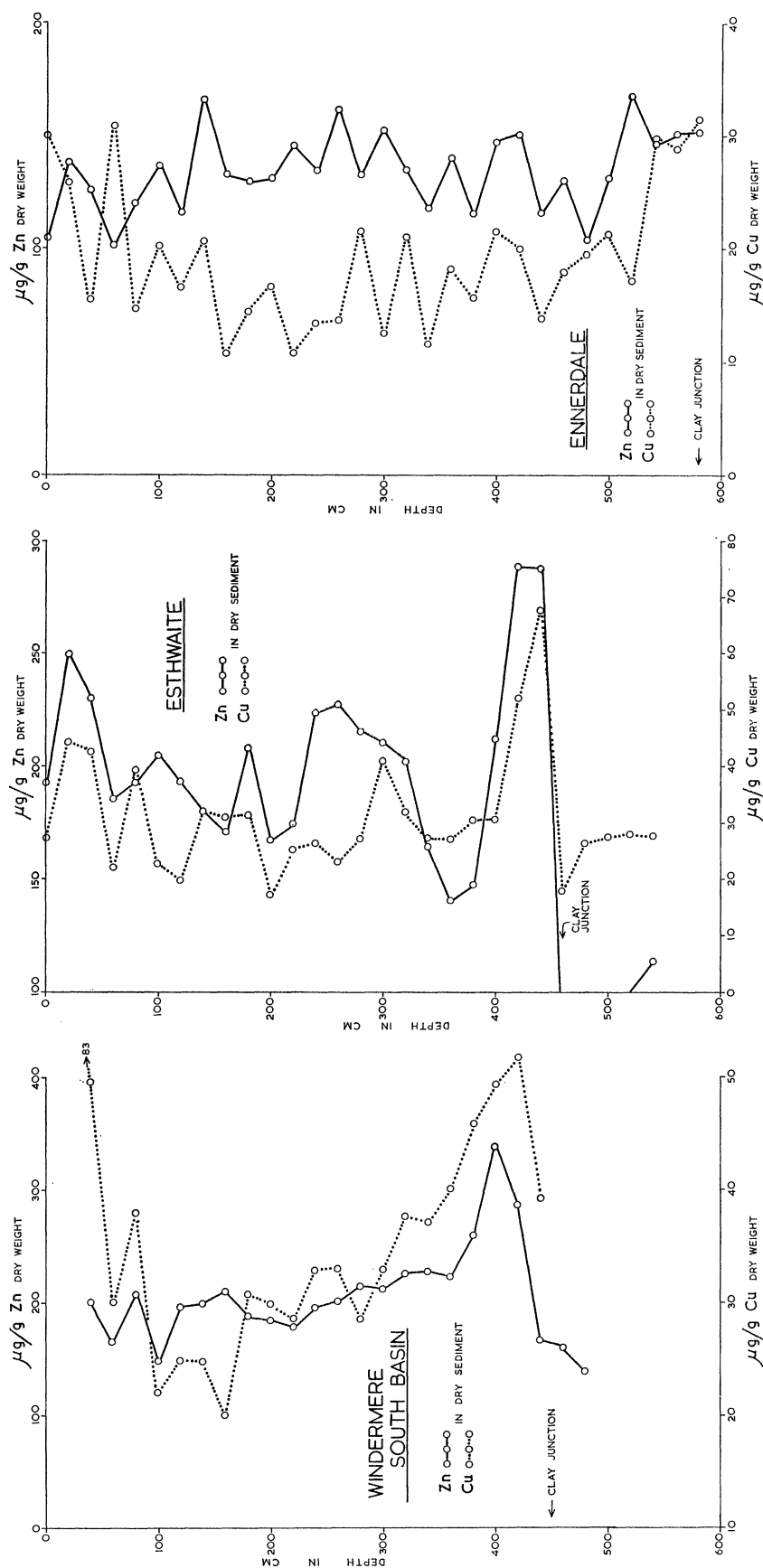


FIGURE 25. Distribution of copper (dotted line) and zinc (solid line) concentrations in the sediment columns of Windermere south basin, Esthwaite and Ennerdale.

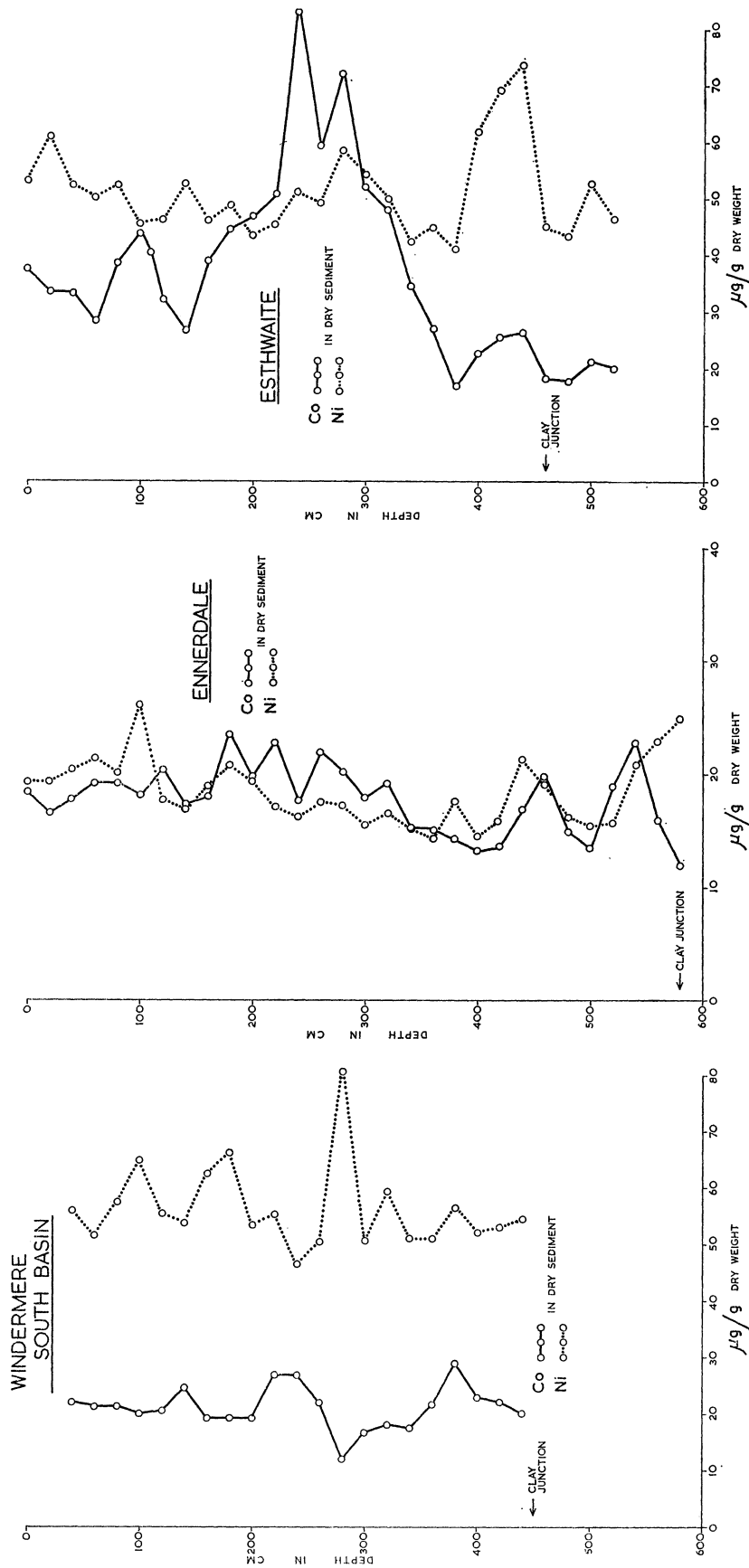


FIGURE 26. Distribution of nickel (dotted line) and cobalt (solid line) concentrations in the sediment columns of Windermere south basin, Esthwaite and Ennerdale.

perhaps play a dominant part in removing the heavy metals from the water into the sediment. In Esthwaite, for example, a striking relationship may be seen between the concentration profiles of iron and manganese and those of cobalt and nickel. The large maximum in manganese concentration at 420 cm is clearly associated with the maximum in nickel concentration in this zone, and also with the smaller maximum in cobalt between 420 and 440 cm. The preferential association of cobalt with iron rather than with manganese is, however, clearly seen in the pronounced cobalt maxima at 280 and 240 cm, corresponding in this profile exactly with the large iron maxima at the same levels. The much feebler association between nickel and iron at these levels is noteworthy. The nickel maximum at 280 cm corresponds more strongly with the manganese maximum at that level. Notable maxima in the concentration profiles of copper and zinc in the Esthwaite sediment also occur between 420 and 440 cm in depth, corresponding closely with the maxima in Co, Ni, Mn and Fe at this level discussed above. An association between the zinc concentration and that of iron is also apparent between 320 and 240 cm and at 180 cm, although above 180 cm no clear relationship between zinc and iron appears to exist. In particular the maxima occurring in the profiles of zinc, copper and nickel at some 20 cm depth in the sediment seems to have no relationship with the distribution of either iron or manganese.

It was suggested in the section dealing with the transport of iron and manganese into lake sediments that the Esthwaite and Ennerdale basins behaved differently in this respect. The iron-manganese transport in Esthwaite was brought about largely by reductive separation of these elements in the drainage system and transport, at least initially, of the elements in solution. In Ennerdale, however, no evidence of preferential separation of iron and manganese could be seen and in this case transport of iron and manganese appeared to take place largely by erosional removal of the soil. This difference between the two basins may now be used to account for the rather wide differences in distribution of zinc, copper, cobalt and nickel in the two sediments. The distribution profiles of these elements (Zn, Cu, Ni, Co) show that the variations in concentration with depth in the Esthwaite sediment is much greater than that in Ennerdale; in particular the large maxima in Esthwaite just above the glacial clay between 420 and 440 cm and at 280 and 240 cm are not present in the Ennerdale sediment. These maxima in the Esthwaite sediment appear to be related to the iron-manganese maxima and may be attributed to co-precipitation with these elements. In Ennerdale, however, since iron and manganese have not been transported to any significant extent in solution, the possibility of co-precipitation in the manner found in Esthwaite does not arise. One would then expect the distribution of heavy metals in the sediments of these two lake basins to differ in a manner similar to that actually observed.

The distribution of zinc, copper, cobalt and nickel in the south basin of Windermere sediment resembles that of Esthwaite rather than Ennerdale. A marked maximum in the concentration of zinc, copper and cobalt is observed just above the clay/organic interface. There is however no very clear relationship between iron-manganese on the one hand and the other heavy metals discussed on the other.

In the above discussion of the distribution of heavy metals in the sediments and also in the earlier consideration of the distribution of iron and manganese it has been assumed

that these elements were added to the sediment directly by contemporary addition of material. One might argue, however, that the maxima in concentration of these elements existing just above the glacial clay/organic sediment interface could be of secondary origin brought about by diffusion from the underlying clay into a position favouring precipitation. They could have been added to the sediment from below rather than from above. This possibility, however, does not seem likely in the case of manganese for example. In the Esthwaite sediment, the manganese concentration just above the clay interface is an order of magnitude higher than that present in the clay. This manganese could scarcely have been derived from the clay without producing a marked impoverishment in this element in the clay itself. In fact the manganese concentration in the clay remains close to that of the lithosphere as a whole. A hypothesis suggesting diffusion from below is also difficult to support in view of the absence of such interfacial maxima in the Ennerdale sediment which would presumably be expected to behave in a similar way to the Esthwaite and Windermere south basin sediments if diffusion from below had been an important mechanism.

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